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AN EXPERIMENTAL AND THEORETICAL STUDY OF THE SECONDARY DEUTERIUM ISOPOE EFFECTS ON THE IONIZATION IN THE BENZOIC, o-TOLUIC, MESITOIC, AND PHENYLACETIC ACID SYSTEMS.

by

ADRIAN DEMAYO

A thesis submitted to the Faculty of Graduate Studies in partial fulfilment of the requirements for the degree of Doctor of Philosophy

Carleton University
Ottawa, Ontario
January, 1969

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The undersigned hereby recommend to the Faculty of Graduate Studies acceptance of this thesis, submitted by Adrian Demayo, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Preface.

Secondary deuterium isotope effects on equilibria and reaction rates have been studied for a long period of time.\textsuperscript{1,3} The problem of their true origin, however, has not been completely solved, though considerable progress has been made especially in the last several years in explaining the isotope effects from a more fundamental point of view.\textsuperscript{4-8} Different steric requirements of deuterium or carbon-deuterium bonds as compared with hydrogen or carbon-hydrogen bonds,\textsuperscript{9-11} zero-point energy differences,\textsuperscript{12} different inductive effects,\textsuperscript{13,14} hyperconjugation,\textsuperscript{11,15,16} and changes in force constants in going from reactants to products\textsuperscript{8} are some of the concepts which have been used to explain secondary deuterium isotope effects.

The present work was carried out with the intention of contributing to the solution of the problems of the origins of secondary deuterium isotope effects. With this in mind, the system of benzoic acid and methyl-substituted benzoic acids presented interesting possibilities.

It is widely accepted that the difference in the dissociation constant of o-toluic acid and benzoic acid is due to the steric interaction between the methyl and the carboxyl groups in the former acid.\textsuperscript{17,18} Consequently, if we compare the dissociation constant of o-toluic acid with that of methyl-deuterated o-toluic acid we should be able to obtain information about the steric requirements of the -CD\textsubscript{3} group as compared with those of the -CH\textsubscript{3} group. This steric effect, if present, should be magnified in deuterated 2,3-dimethylbenzoic, 2,6-dimethylbenzoic and mesitoic acids. If there is any difference in the inductive effects of the -CH\textsubscript{3} group as compared with those of the -CD\textsubscript{3} group, it should become apparent in the dissociation constants.
of the p-toluic and mesitoic acids. Similar considerations are valid
for ring deuterium-substituted benzoic acids. For these reasons we
have studied some of the most representative pairs of isotopic acids
in this system: o-toluic and o-toluic-d7, mesitoic and mesitoic-d9
and benzoic, benzoic-2-d and benzoic-d5 acids.

The thesis is divided into two major self-standing parts.
Part A is devoted to the experimental determination of the dissociation
constants and the thermodynamic quantities of ionization (free
energy, enthalpy, entropy and specific heat) of the acids mentioned
above in solvent water and over a range of temperatures. One of the
objectives of our work was to determine the dissociation constants
very accurately since it was predictable that the isotope effects
we were seeking were going to be very small. As it is well known,
accurate results require a great experimental effort. That is why
in the first sections (1 to 6) we analyse in detail the conductance
method as it is used for the determination of the dissociation constants
of weak acids in aqueous solution. We believe that such a detailed
description of the experimental method used in this work is necessary
for the understanding of the significance of the results presented in
the next sections. The determination of the dissociation constants
and the calculation of the thermodynamic functions of ionization is given
in a separate section for each of the isotopic pairs of acids.

To obtain a more complete picture of the system with which we
were working, in addition to the acids mentioned above we determined
the dissociation constants and the thermodynamic functions of
ionization of m-toluic and p-toluic acids. These results are given
in section 12.
Finally in section 9 are given the results obtained for the dissociation constants and the thermodynamic functions of ionization of phenylacetic and phenylacetic-α-d₂ acids. The dissociation constants of these two acids in aqueous solution, at 25°C, were determined before by two different groups and different results were obtained. Our work, besides trying to settle this difference, expanded the previous work by determining the dissociation constants and the thermodynamic functions of ionization over a range of temperatures (20 to 40°C).

In the last two sections (13 and 14) of part A we discuss the meaning of the thermodynamic functions of ionization in relation to the molecular structure of the acids. The interpretation of our results for ΔG, ΔH, ΔS and ΔC_p has been based on the theories and arguments presented in these sections.

The second major part of this thesis, part B, deals with the actual secondary deuterium isotope effects. Some of their history and some of the theories proposed to explain them are reviewed in section 15. In the remaining sections (16 to 20) we try to rationalize the results obtained in part A for the ratio K_H/K_D by semi-theoretical calculations of the Bigeleisen-Wolfsberg-Stern type. Since these calculations required all the vibrational frequencies of the molecules and ions involved in the equilibria studied here, an approximate vibrational analysis of benzoic, o-toluic, and phenylacetic deuterated and undeuterated acids and of their anions is given in the same sections.

Finally an explanation about the appendices. The computer was used to a large extent throughout this thesis. As a result the volume of the computer output pertinent to this thesis is large. We decided to include the computer programs in appendices. For a rapid reference to them the appendices are not numbered sequentially. Their
numbers have the following form: xx.xx.xx, e.g. 13.9.11. The first two numbers, e.g. 13.9, represent the subsection of the thesis to which the respective appendix belongs. The last number, e.g. 11, is a sequential number within the subsection. The computer output which contains the detailed calculations have been deposited with the Department of Chemistry of Carleton University. These "Detailed calculations" are indexed by the same method as that used for appendices inquiries regarding the "Detailed calculations" should be directed to Dr. P.M. Laughton, Department of Chemistry, Carleton University, Ottawa.
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1. INTRODUCTION

Several methods are available for the determination of dissociation constants of acids. These methods are discussed in most electrochemistry textbooks.22

A review of these methods, also, has been published in "Tables of dissociation constants of organic acids in aqueous solution" published by IUPAC.23

The factors we had to consider in choosing a method for our work were:

1. The results had to be very accurate. We were aware that the differences in the dissociation constants of deuterated and undeuterated species of a given acid were going to be extremely small (if any at all!). Since we wanted to calculate the thermodynamic quantities ΔH, ΔG, ΔS and eventually ΔG_p, the accuracy of the results was the most critical factor.

2. The method should be applicable to a wide range of acids. Although we planned to determine the dissociation constants for a specific group of acids (benzoic acids) we looked for a method that could be used to study other acids as well.

3. Simplicity.

The predominating factor was, undoubtedly, the first one. Estimates of the precision of the two widely used methods for determining dissociation constants give 0.01% for the conductance method24 and 0.2% for the EMF method.25 Invariably the literature shows that the conductance method has been the method able to give more accurate results. The fact
that, as we now believe, the accuracy of the method is somewhat overestimated is another matter which will be discussed later.

Regarding point 2, the conductance method presented considerable advantages: it could be used for any acid provided that the acid was stable in aqueous solution (this is a limitation of any of the methods) and also practically unmodified setups could be used for equilibria and kinetic studies.

The third factor, i.e. simplicity, represented, in our opinion, the weak point of the conductance method. We were only familiar with the experimental details of the conductance method. It could be said with certainty that the conductance method was not a simple method with which to work. Though its principle was a very simple one, i.e. the measurement of the electrical resistance across two electrodes immersed in a solution, when the ultimate accuracy is sought there is a large number of details which to be cared for. These finer details, which are discussed in sections 2 to 6, experimentally complicate the conductance measurements.

Since, as was mentioned above, the precision of the results was the determining factor, we have chosen the conductance method for the determination of the dissociation constants.

Four elements form the experimental basis of the conductance method. They are:

a. the bridge
b. the cell
c. the temperature control
d. the preparation of the solution
Each of these elements is examined next with the exception of the last one which is treated separately when presenting the determination of the cell constant (section 6).

A fifth important element, the method of calculation, is examined in detail in subsection 8.6.
2. THE BRIDGE

2.1. Generalities

The resistance of the solution (or any resistance for that matter) can be measured with a Wheatstone bridge. In its simplest form such a bridge has the following design:

![A simple diagram of a Wheatstone bridge.](image)

Current from the source S goes to A where the circuit divides: one part goes through the unknown resistance $R_x$ and the known adjustable resistance $R_2$; the other part of the current passes through two known, fixed resistances $R_3$ and $R_4$. Some form of a balance detector I is connected between B and D.

The source of the current can be a dc source. In this case when the indicator indicates no current the following relation holds:

$$\frac{R_x}{R_3} = \frac{R_2}{R_4} \quad (2.1.1)$$

As is well known, any current going from an electrode to another electrode, passing through an electrolyte, causes a chemical reaction. Thus a dc current passing through an aqueous solution will
cause the formation of oxygen and an acid at one electrode and of hydrogen and a base at the other. The term "polarization" is used to describe concentration and chemical changes due to electrolysis and also the potentials at the electrodes which result from these changes. To overcome the difficulties due to polarization, the most usual procedure is to make use of alternating current (ac) in the measurement of the resistance of a solution. The simplest explanation for the use of ac current is that the electrolysis produced by the current flow for an instant in the positive direction tends to be immediately reversed by the passage of the current in the negative direction and vice versa.

The use of the alternating current introduces several complications in the measurement of conductivity (conductivity is the inverse of resistance). The most important complication is that the equilibrium condition for the bridge becomes:

\[ \frac{Z_X}{Z_3} = \frac{Z_2}{Z_4} \]  \hspace{1cm} (2.1.2)

where \( Z \)'s are complex impedances.

A complex impedance can be written in the following form:

\[ Z = R + jX \]  \hspace{1cm} (2.1.3)

where \( R \) is the real part of the impedance or the resistance and \( jX \) is the imaginary part of the impedance or the reactance.
An angle $\theta$ can be defined:

$$\theta = \tan^{-1} \frac{X}{R}$$ \hspace{1cm} (2.1.4)

which is called the phase-angle difference and is the angle by which the voltage leads the current. Now the equilibrium condition of the bridge depends on the exact composition of each of the arms in terms of $R$, $C$ and $L$ ($C = \text{capacitance}$ and $L = \text{inductance}$).

A large number of papers published over a wide period of time present various bridge designs. Classical papers on the subject are those by Jones and Josephs, Jones and Bollinger, Shedlovsky and, more recent, those by Ives and Pryor and Janz and McIntyre.

Today, increasingly sophisticated bridges are available on the market from different manufacturers: General Radio, ESI, Wayne and Kerr, etc.

In most of the bridges, arms number 3 and 4 are of equal value and of identical construction. In terms of impedance this leads to:

$$Z_3 = Z_4$$ \hspace{1cm} (2.1.5)

Thus the equilibrium conditions becomes:

$$Z_x = Z_2$$ \hspace{1cm} (2.1.6)

that is, the impedance of the unknown arm should be equal to the impedance of the measuring (or standard) arm.

The logical thing to do at this point would be to discuss the elements of the unknown and standard arms. The equivalent circuit
of the unknown arm has a direct relationship with the cell design and for this reason is dealt with in subsection 3.3.

2.2. The Standard Arm

The usual construction for the standard arm is a variable standard resistor in parallel with a variable standard capacitor.

![Fig. 2.2.1](image)

A schematic representation for the standard arm of a Wheatstone bridge.

By adjusting the two parameters $C_s$ and $R_s$ the null indicator $I$ is brought to balance. If the unknown arm has the same type of circuit as the standard arm, then $C_s$ will be equal to $C_x$ and $R_s$ to $R_x$. Unfortunately, as we are going to see further on, in most of the cases these equalities do not hold.

Different types of bridges are available. Any one of the elements of the unknown arm can be measured directly by using the appropriate type. Thus a capacitance bridge will measure $C_x$, a resistance bridge will measure $R_x$, an impedance bridge will measure $Z_x$ and so on. The problem is to determine which parameter will give the most significant experimental data for a given study.

Regarding the precision the best bridges in the market claim 0.01% precision. This means five significant figures in the quantity being measured. The new GR-1605-AH bridge claims an accuracy of 0.003% on impedance difference measurements. However, when measuring an unknown resistance or capacitance the limiting factor is the
precision of the variable standard resistor or capacitor. The best variable ac resistors in the market claim an initial accuracy of only 0.01% (by ESI). The electrical standard section of the National Research Council (A. Dunn, private communication) point out that even these values are determined by calculation using dc measurements on the resistors and estimates of their other electrical parameters.

2.3. **Our Bridge**

The basic design of the bridge used in our work is that described by Janz and McIntyre.\(^29\)

The diagram of the bridge is given in fig. 2.3.1.

**Bridge parts.**

**Impedance comparator:** GR type 1605-A

**Switch:** three poles rotary selector switch by Leeds and Northrup (cat. no. 31-3-0-3). The switch has a low contact resistance (0.001\(\Omega\)) and low capacitance between points (<0.5\(\mu\)F).

**Capacitors:** Johnson Differential No. 167-31 with capacity per section of max. 11pF and min. 2.8pF in parallel with a "dual section" capacitor (Johnson Capacitor No. 167-53), with a maximum capacity per section of 99pF, modified to a differential capacitor.

**Wiring:** RG-59 AU - with low capacitance per unit length (20pF/foot).

**Connectors** (at the end of the leads): BNC coaxial connectors, cable plugs, Amphenol part No. 86475.

**Standard resistors:** Two types of high precision resistors were used without any appreciable difference between them. The resistors were:
a. type GR-510. Six decades from 0.1 Ω/step to 10,000 Ω/step were connected in series. The decades had an accuracy of 0.05% for the 10 Ω/step decade and 0.025% for the higher valued decade. Later these decades were changed to a

b. DECABOX Model DB 62 made by ESI. The box consisted of six decades connected in series. The smallest of the decades was of a value of 0.1 Ω/step. The claimed accuracy of the box was 0.01%.

The reason for the change was the better accuracy of the ESI box.

Type GR-510 decade resistors claim no frequency dependence in the range of frequencies we were using (up to 5,000 Hz). ESI do not give frequency characteristics for their decades.

The temperature coefficients of both types of resistors were small enough to be considered negligible in our work. 31, 32

**Standard capacitors:** Provisions were made in the wiring of the bridge to connect a variable standard capacitor in parallel with the variable standard resistor. As a variable capacitor we had a GR Type 1419-B Polystyrene Decade Capacitor. Because most of our measurements did not require the use of this variable capacitor for the balance of the phase angle difference, it was kept disconnected most of the time.

Before every set of measurements, the bridge was checked against a decade resistance box inserted in the unknown arm. For this purpose we used a GR Type 1432-M or Type 1432-L Decade Resistor. The results obtained in checking the bridge against these Decade
Resistors are shown in subsection 2.4.

The impedance comparator circuit: An amplitude-stabilized, R-C oscillator provides four test frequencies. The comparator comes equipped with 1, 2, 5 and 20 kHz frequencies. We changed the 20 kHz frequency for a 3 kHz one because frequency anomalies became apparent at 20 kHz. The oscillator is coupled to the bridge through a special bridge transformer, which also provides the inductively coupled unity ratio-arms. The construction of the transformer is in such a way that the two arms are balanced to within one part in $10^6$. The impedance difference at 1 kHz is less than 50 mΩ and the coefficient of coupling is greater than 0.9997.

The standard and the unknown impedances form the other two arms.

The unbalance voltage from the bridge is amplified, and the push-pull output attenuated with two separate range switches to provide independent magnitude and phase-difference ranges.

Separate phase-sensitive detectors are used to measure the in phase and quadrature voltage components. The two orthogonal components are fed to differential amplifiers which drive the output meters.

The instrument is calibrated by injecting a 1% unbalance voltage and setting the oscillator level to give the correct reading.

The guard circuit: This is a feature of the Impedance comparator which makes possible measurements of large impedances located at some distance from the instrument itself.

The guard circuit extends the high impedance range for remote measurements by effectively reducing the stray capacity to
ground that would be added by cable shields.

Two wires are necessary to attach the unknown component to the instrument (fig. 2.3.2). The lead from the transformer side can be shielded without introducing any significant error because an impedance placed across one side of the transformer to ground \((Z_b, \text{fig. 2.3.2})\) has little effect on the bridge balance due to tight coupling of the transformer and its low resistance. Moreover this lead, because of its low impedance, is relatively insensitive to pickup. The capacity to ground of the other lead \((Z_a, \text{fig. 2.3.2})\) which is connected to the amplifier input produces attenuation and phase shift of the signal voltage if the measured component \((Z_x, \text{fig. 2.3.2})\) is of high impedance. This capacitance is especially large if the lead is shielded to prevent pickup and to remove the capacity between the two leads, which would otherwise shunt the unknown.

In order to reduce this effect a guard voltage is brought out which can be used to drive the amplifier input shield. Since the guard voltage is approximately 0.97 of the amplifier input the capacitance to the shield is effectively reduced by a factor of 30. Note that if the detector is nulled (both meters reading zero) by the variation of standard, \(Z_b\) (fig. 2.3.2), the guarded position has no effect on the balance conditions. The value of the unknown at null is equal to that of the standard and can be measured in terms of impedance. This will be shown in more detail when the bridge equations are discussed.

2.4 Bridge Equations \(^{35}\)

The basic bridge circuit is shown in fig. 2.4.1.
FIG. 2.3.2.
DIRECT IMPEDANCE MEASUREMENT USING A VARIABLE STANDARD

FIG. 2.4.1.
THE BASIC BRIDGE CIRCUIT
\[
\frac{E_o}{E_{in}} = \frac{Z_X - Z_S}{Z_X + Z_S} \tag{2.4.1}
\]

The real part of this is:

\[
\text{Re} \left( \frac{E_o}{E_{in}} \right) = \frac{|Z_X| - |Z_S|}{|Z_X| + |Z_S|} \frac{1 + \cos(\theta_X - \theta_S) - 1}{1 + \frac{|Z_X|}{2|Z_S|} + \frac{|Z_S|}{2|Z_X|}} \tag{2.4.2}
\]

and the imaginary part is:

\[
\text{Im} \left( \frac{E_o}{E_{in}} \right) = \frac{\sin(\theta_X - \theta_S)}{\cos(\theta_X - \theta_S) + \frac{|Z_X|}{2|Z_S|} + \frac{|Z_S|}{2|Z_X|}} \tag{2.4.3}
\]

When both meters indicate zero:

\[
\Delta Z = \text{Re} \left( \frac{E_o}{E_{in}} \right) = 0 \tag{2.4.4}
\]

\[
\Delta \theta = \text{Im} \left( \frac{E_o}{E_{in}} \right) = 0 \tag{2.4.5}
\]

then

\[
Z_X = Z_S
\]

\[
\theta_X = \theta_S
\]

The "Impedance difference" meter (\(\Delta Z\) meter) reads:

\[
\frac{|Z_X| - |Z_S|}{|Z_X| + |Z_S|} \tag{2.4.6}
\]
The "Phase angle" meter (Δθ meter) reads:

\[(\theta_x - \theta_s)\]  
in radians. \hspace{1cm} (2.4.7)

If point A (refer to fig. 2.3.2) is grounded the reading of the ΔZ meter is:34

\[
\frac{Z_x - Z_s}{Z_x + Z_s} \frac{2}{1 + \frac{Z_s}{2Z_b}}
\]  
(2.4.8)

If the guard circuit is used the reading is approximately:34

\[
\frac{Z_x - Z_s}{Z_x + Z_s} + \frac{Z_0Z_s}{Z_aZ_b} \frac{2}{1 + \frac{Z_s(1-K)}{2Z_b} + \frac{Z_0Z_s}{2Z_aZ_b}}
\]  
(2.4.9)

where \(Z_0\) is the output impedance of the guard circuit. It consists of 20Ω in series with 1.0μf. \(K\) is the guard circuit gain (0.97).

In the case of relation (2.4.8) it is obvious that if the reading is zero

\[Z_x = Z_s\]  
(2.4.10)

In the case of (2.4.9) this equality is not so obvious.

If the reading is zero (ΔZ = 0) from (2.4.9):

\[Z_x(2Z_aZ_b + Z_0Z_s) = Z_s(2Z_aZ_b - Z_0Z_s)\]  
(2.4.11)

From (2.4.11) \(|Z_x| = |Z_s|\) only if
\[ 2Z_aZ_b \gg Z_oZ_s \]

or

\[ Z_oZ_s \gg 2Z_aZ_b \]  \hspace{1cm} (2.4.12)

The first of these inequalities is the one which occurs most frequently. This becomes more evident if we substitute some values:

\[ Z_a = Z_b = 1,000 \text{ k}\Omega \] (this corresponds to a capacitance of 160 pF at a frequency of 1,000 Hz)

\[ Z_o = 200 \text{ \Omega} \]

\[ Z_s = 100 \text{ k}\Omega \]

Then:

\[ Z_aZ_b = 10^{12} \gg Z_oZ_s = 2 \times 10^7 \]

The wiring of the standard and unknown arms of our bridge is more complicated than that shown in fig. 2.6.2 and than that implied by Janz and McIntyre's paper.\textsuperscript{29}

A diagram of the circuit of the bridge is shown in fig. 2.4.2. A detailed diagram of the wiring of the standard and unknown arms is given in fig. 2.4.3 and 2.4.4 for two of the four possible switch positions, assuming negligible inductances.

**The equations of the standard arm.**

Consider only a part of the circuit given in fig. 2.4.3:
$Z_S$: Variable standard impedance

$Z_X$: Unknown impedance

$R_{x1}, R_{x2},$ and $R_{y1}$: Leads resistances

**FIG. 2.4.2.**

THE WIRING OF THE BRIDGE. SWITCH IN POSITION 1
NETWORK FOR THE STANDARD ARM

\[ R_{s}^{(1)} \] - Standard resistance
\[ C_{S} \] - Capacitance of the decade resistor
\[ C_{d1} \] - The first part of the differential capacitor
\[ R_{x1}, R_{x2} \] - Resistance of the leads to the cell
\[ C_{x1}, C_{x2} \] - Capacitance of the leads to the ground

NETWORK FOR THE UNKNOWN ARM

\[ R_{x} \] - Unknown resistance
\[ C_{x} \] - Capacitance associated with \( R_{x} \)
\[ C_{d2}^{(1)} \] - The second part of the differential capacitor
The superscript \((1)\) refers to the position of the switch

FIG. 2.4.3.
SWITCH - POSITION 1
NETWORK FOR THE STANDARD ARM

\[ R_s^{(2)} \] - Standard resistance
\[ C_s \] - Capacitance of the decade resistor
\[ C_{d1}^{(2)} \] - The first part of the differential capacitor
\[ R_{y1}, R_{y2} \] - Resistance of the leads to the cell
\[ C_{y1}, C_{y2} \] - Capacitance of the leads to the ground

NETWORK FOR THE UNKNOWN ARM

\[ R_x \] - Unknown resistance
\[ C_x \] - Capacitance associated with \( R_x \)
\[ C_{d2} \] - The second part of the differential capacitor

The superscript \((2)\) refers to the positions of the switch.

FIG. 2.4.4.

SWITCH - POSITION 2
**NETWORK FOR THE STANDARD ARM**

- $R_s^{(2)}$ - Standard resistance
- $C_s$ - Capacitance of the decade resistor
- $C_{d1}^{(2)}$ - The first part of the differential capacitor
- $R_{y1}, R_{y2}$ - Resistance of the leads to the cell
- $C_{y1}, C_{y2}$ - Capacitance of the leads to the ground

**NETWORK FOR THE UNKNOWN ARM**

- $R_x$ - Unknown resistance
- $C_x$ - Capacitance associated with $R_x$
- $C_{d2}$ - The second part of the differential capacitor

The superscript (2) refers to the positions of the switch.

**FIG. 2.4.4.**

**SWITCH - POSITION 2**
The impedance of this part is obtained from:

\[ \frac{1}{Z} = \frac{1}{R_{X1} + R_{X2}} - \frac{\frac{1}{\omega C_{X1}}}{\frac{1}{\omega C_{X2}}} \]  \hspace{1cm} (2.4.13)

This leads to:

\[ \text{Re}(Z) = \frac{(R_{X1} + R_{X2}) (C_{X1} + C_{X2})^2}{(C_{X1} + C_{X2})^2 + \left[ C_{X1} C_{X2} (R_{X1} + R_{X2}) \right]^2} \] \hspace{1cm} (2.4.14)

\[ \text{Im}(Z) = -\frac{\omega C_{X1} C_{X2} (R_{X1} + R_{X2})^2 (C_{X1} + C_{X2})}{(C_{X1} + C_{X2})^2 + \left[ \omega C_{X1} C_{X2} (R_{X1} + R_{X2}) \right]^2} \] \hspace{1cm} (2.4.15)

where Re(Z) and Im(Z) are the real and the imaginary parts, respectively, of impedance Z.

The second term in the denominator is negligible as compared with the first one for usual values of C_{X1}, C_{X2}, R_{X1} and R_{X2} and at frequencies with which we are working. As an example consider:

\[ C_{X1} = C_{X2} = 100 \text{ pF} \]

\[ R_{X1} = R_{X2} = 1 \Omega \]

\[ \omega = 2\pi \times 1,000 \text{ rad/s} \]
then:

\[(c_{x1} + c_{x2})^2 = (2 \times 10^{-10})^2 = 4 \times 10^{-20} \gg\]

\[\omega c_{x1} c_{x2} (r_{x1} + r_{x2})^2 = (2\pi \times 10^3 \times 10^{-20} \times 2)^2 = 1.6 \times 10^{-32}\]

At frequencies of the order of $10^9$ Hz or at values of $r_{x1}$ and $r_{x2}$ of the order of $10^6 \Omega$ the two terms become the same order of magnitude.

Using this approximation the real and imaginary parts of $Z$ become:

\[
\text{Re}(Z) = r_{x1} + r_{x2} \quad (2.4.16)
\]

\[
\text{Im}(Z) = -\frac{\omega c_{x1} c_{x2} (r_{x1} + r_{x2})^2}{c_{x1} + c_{x2}} \quad (2.4.17)
\]

The magnitude of the imaginary part is very small as compared with that of the real part and thus to a very good approximation the circuit shown in Fig. 2.4.5 is equivalent to two resistances, $r_{x1}$ and $r_{x2}$, connected in series. Now, the impedance of the standard arm, $Z_s$, has the following composition:

\[\text{Fig. 2.4.6}\]

Network for the standard arm (switch in position 1)

The situation is completely analogous for switch-position 2.
The equation for the network shown in fig. 2.4.6 is:

\[ Z_s^{(1)} = Z_{s1}^{(1)} + R_{x1} + R_{x2} \quad (2.4.18) \]

where \( Z_s^{(1)} \) is the total impedance for the standard arm. The superscript in brackets indicates the position of the switch.

\[ \frac{1}{Z_{s1}^{(1)}} = \frac{1}{R_s^{(1)}} + j\omega(C_s + C_{d1}^{(1)}) \quad (2.4.19) \]

\[ Z_{s1}^{(1)} = \frac{R_s^{(1)}[1 - j\omega(C_s + C_{d1}^{(1)})R_s^{(1)}]}{1 + \omega^2(C_s + C_{d1}^{(1)})^2 (R_s^{(1)})^2} \quad (2.4.20) \]

For switch position 2, (2.4.18) and (2.4.20) become:

\[ Z_s^{(2)} = Z_{s1}^{(2)} + R_{y1} + R_{y2} \quad (2.4.21) \]

\[ Z_{s1}^{(2)} = \frac{R_s^{(2)}[1 - j\omega(C_s + C_{d1}^{(2)})R_s^{(2)}]}{1 + \omega^2(C_s + C_{d1}^{(2)})^2 (R_s^{(2)})^2} \quad (2.4.22) \]

\( C_s \) is the parallel capacitance of the variable standard resistor. It has a known value, which practically does not change on switching from position 1 to 2. \( C_{d1} \) is the capacitance originating in the differential capacitor.

The expressions for \( Z_s^{(1)} \) and \( Z_s^{(2)} \) can be separated into a real and an imaginary part. The terms containing \( C_s \) or \( C_{d1} \) at power 2 or more, or containing the product \( C_sC_{d1} \) are neglected because they are very small as compared to the others. Thus we obtain:

\[ \text{Re}(Z_s^{(1)}) = R_s^{(1)} + R_{x1} + R_{x2} \quad (2.4.23) \]

\[ \text{Re}(Z_s^{(2)}) = R_s^{(2)} + R_{y1} + R_{y2} \quad (2.4.24) \]
\[ \text{Im}(Z_s^{(1)}) = -\omega(C_s + C_{d1}^{(1)})(R_s^{(1)})^2 \] (2.4.25)

\[ \text{Im}(Z_s^{(2)}) = -\omega(C_s + C_{d1}^{(2)})(R_s^{(2)})^2 \] (2.4.26)

The equations of the unknown arm.

If fig. 2.3.2 is compared with fig. 2.4.3 it can be seen that \( Z_a \) is equivalent to \( C_{x2} \) and \( Z_b \) to \( C_{y1} \) (for switch-position 1). Thus the network for the unknown impedance \( Z_x \) is (again for switch-position 1):

\[ \text{Network for the unknown impedance } Z_x \]

(Switch position 1)

An equivalent circuit given in fig. 2.4.8:

\[ \text{Equivalent network for the unknown impedance } Z_x \text{ for the Switch in position 1} \]
The total impedance of the unknown arm is:

\[ Z_x^{(1)} = \frac{1}{Z_1^{(1)}} + \frac{1}{Z_2^{(1)}} + R_{x2} \quad (2.4.27) \]

where

\[ Z_1^{(1)} = \frac{1}{\frac{1}{R_x} + j\omega C_x} + R_{y1} \quad (2.4.28) \]

\[ Z_2^{(1)} = R_{x1} - \frac{j}{\omega C_{d2}} \quad (2.4.29) \]

then:

\[ Z_x^{(1)} = \frac{\frac{R_x}{1 + j\omega R_x C_x} + R_{y1}}{\frac{R_x}{1 + j\omega R_x C_x} + R_{y1}} \left[ \frac{R_{x1} - \frac{j}{\omega C_{d2}}}{1} \right] + R_{x2} \quad (2.4.30) \]

The numerator:

\[ \frac{R_x R_{x1} \omega C_{d2}^{(1)} + R_{y1} R_{x1} \omega C_{d2}^{(1)} + \omega R_{y1} R_x C_x - j(R_x - R_{y1} R_{x1} R_x C_{d2}^{(1)}) C_x \omega^2 + R_{y1})}{(1 + j\omega R_x C_x) \omega C_{d2}^{(1)}} \quad (2.4.31) \]

The denominator of (2.4.30) is:

\[ \frac{R_x \omega C_{d2}^{(1)} + (R_{y1} + R_{x1}) \omega C_{d2}^{(1)} + R_x C_x - j[1 - \omega^2 R_x C_{d2}^{(1)} C_x (R_{y1} + R_{x1})]}{(1 + j\omega R_x C_x) \omega C_{d2}^{(1)}} \quad (2.4.32) \]
Therefore (2.4.27) becomes:

\[
Z_x^{(1)} = \frac{(R_x R_{x1} + R_y R_{x1}) \omega C_{d2}^{(1)} + \omega R_{y1} R_x C_x - j(R_x + R_y - R_{y1} R_{x1} R_x C_{d2}) (1) C_x \omega^2}{(R_x + R_y + R_{x1}) \omega C_{d2}^{(1)} + \omega R_x C_x - j[1 - \omega^2 R_x C_{d2}^{(1)} C_x (R_{y1} + R_{x1})]} + R_{x2}
\]

\[(2.4.33)\]

\[C_x \text{ and } C_{d2}^{(1)} \text{ are small:}\]

\[C_x = 10 - 20 \times 10^{-12} \text{ F}\]

\[C_{d2}^{(1)} = 50 \times 10^{-12} \text{ F}\]

and therefore the terms containing the product of the two capacitances can be neglected. Equality (2.4.33) becomes:

\[
Z_x^{(1)} = \frac{(R_x R_{x1} + R_y R_{x1}) \omega C_{d2}^{(1)} + \omega R_{y1} R_x C_x - j(R_x + R_y)}{(R_x + R_y + R_{x1}) \omega C_{d2}^{(1)} + \omega R_x C_x - j} + R_{x2}
\]

\[(2.4.34)\]

Relation (2.4.34) can be separated into an imaginary and a real part by multiplying and dividing by:

\[[(R_x + R_y + R_{x1}) \omega C_{d2}^{(1)} + \omega R_x C_x + j]

\[
\text{Re}(Z_x^{(1)}) = \frac{[(R_x + R_y) R_{x1} \omega C_{d2}^{(1)} + \omega R_{y1} R_x C_x][(R_x + R_y + R_{x1}) \omega C_{d2}^{(1)} + \omega R_x C_x] + R_{y1} + R_{x1}}{[(R_x + R_y + R_{x1}) \omega C_{d2}^{(1)} + \omega R_x C_x]^2 + 1}
\]

\[(2.4.35)\]

Neglecting the terms containing \(C_x^2\), \((C_{d2}^{(1)})^2\), \(C_x C_{d2}^{(1)}\) or higher powers of \(C_x\) and \(C_{d2}^{(1)}\) (2.4.35) becomes:

\[
\text{Re}(Z_x^{(1)}) = R_x + R_y + R_{x2}
\]

\[(2.4.36)\]
The imaginary part after the same simplifications used for the real part is:

\[ \text{Im}(Z_x^{(1)}) = \omega R_{y_1} R_x C_x - \omega C_{d_2}^{(1)} (R_x + R_{y_1})^2 \]  \hspace{1cm} (2.4.37)

For switch-position 2 analogous considerations lead to:

\[ \text{Re}(Z_x^{(2)}) = R_x + R_{y_1} + R_{x_2} \]  \hspace{1cm} (2.4.38)

\[ \text{Im}(Z_x^{(2)}) = \omega R_{y_1} R_x C_x - \omega C_{d_2}^{(2)} (R_x + R_{y_1})^2 \]  \hspace{1cm} (2.4.39)

When the bridge is balanced the real part of the impedance of the standard arm should be equal to the real part of the impedance of the unknown arm (2.4.10):

\[ \text{Re}(Z_s^{(1)}) = \text{Re}(Z_x^{(1)}) \]  \hspace{1cm} (2.4.40)

\[ \text{Re}(Z_s^{(2)}) = \text{Re}(Z_x^{(2)}) \]  \hspace{1cm} (2.4.41)

or

\[ R_s^{(1)} + R_{x_1} + R_{x_2} = R_x + R_{y_1} + R_{x_2} \]  \hspace{1cm} (2.4.42)

\[ R_s^{(2)} + R_{y_1} + R_{y_2} = R_x + R_{x_1} + R_{y_2} \]  \hspace{1cm} (2.4.43)

Taking the sum of (2.4.42) and (2.4.43) we obtain:

\[ R_s^{(1)} + R_s^{(2)} = 2R_x \]
Therefore the unknown resistance is given by:

\[ R_x = \frac{R_s(1) + R_s(2)}{2} \]  \hspace{1cm} (2.4.44)

Thus the impedances of the leads have been eliminated. This is in fact the "4 leads method". It must be mentioned that in the case of our bridge the "4 leads method" works only if a series of other conditions are fulfilled: stray capacitances and the resistance of the leads must be small and the frequency used should not be very high.
2.5. **Results**

The bridge was checked by connecting into the unknown arm a series of known resistances. The results are shown in tables 2.5.1, 2.5.2 and 2.5.3.

<table>
<thead>
<tr>
<th>Date</th>
<th>Unknown (R_x)</th>
<th>Readings (of the standard: (R_s))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Omega)</td>
<td>Frequency</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 kHz</td>
</tr>
<tr>
<td>6.03.67</td>
<td>11110.0</td>
<td>11109.1</td>
</tr>
<tr>
<td>22220.0</td>
<td>22216.4</td>
<td>22216.0</td>
</tr>
<tr>
<td>33330.0</td>
<td>33323.0</td>
<td>33322.0</td>
</tr>
<tr>
<td>44440.0</td>
<td>44428.</td>
<td>44427.</td>
</tr>
<tr>
<td>55550.0</td>
<td>55536.</td>
<td>55534.</td>
</tr>
<tr>
<td>66660.0</td>
<td>66645.</td>
<td>66643.</td>
</tr>
<tr>
<td>77770.0</td>
<td>77754.</td>
<td>77748.</td>
</tr>
<tr>
<td>88880.0</td>
<td>88861.</td>
<td>88855.</td>
</tr>
<tr>
<td>99990.0</td>
<td>99966.</td>
<td>99959.</td>
</tr>
<tr>
<td>111100.</td>
<td>111071.</td>
<td>111065.</td>
</tr>
</tbody>
</table>

**Notes:**

1. A decade resistor Model GR-1432-L was used in the unknown arm.

2. 6 decade resistance units Type 510 AA, A, B, C, D and E connected in series and mounted in a shielding metal box were used as standard.

3. The decade resistor of the unknown arm was grounded to the ground post of the Impedance Comparator.

4. No difference was found between readings in "Guarded" and "Unguarded" positions.
5. The readings in all 4 positions of the switch were practically identical.

<table>
<thead>
<tr>
<th>Date</th>
<th>Unknown (R\textsubscript{x}) (\Omega)</th>
<th>Readings (of the standard: R\textsubscript{s}) (\Omega)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Frequency</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 kHz</td>
</tr>
<tr>
<td>29.03.67</td>
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<tr>
<td>11111.1</td>
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<td>99983.</td>
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</table>

Notes:

1. A decade resistor Model ESI- DB 62 of a total resistance of 111,111 \(\Omega\) in steps of 0.1 \(\Omega\) was used in the unknown arm.

2. 6 decade resistance units Type GR-510 AA, A, B, C, D and E connected in series was used as standard.

3. The decade resistor of the unknown arm was grounded to the ground post of the Impedance Comparator.

4. A slight difference at high resistance was found between readings in "Guarded" position and "Unguarded" position. The values in the table 2.5.2 are for "Guarded" position. For \(R_x = 111,111 \Omega\)
the corresponding readings in the "Unguarded" position were:
111093 (1 kHz), 111083 (2 kHz), 111075 (3.5 kHz) and 111067
(5 kHz) Ω.
5. The readings in all 4 positions of the switch were identical.

<table>
<thead>
<tr>
<th>Date</th>
<th>Unknown ( (R_x) ) Ω</th>
<th>Readings (of the standard: ( R_s )) Ω</th>
<th>Frequency</th>
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</table>

Notes:
1. A decade resistor Model GR-1432 L of a total value of 111,110 Ω
   in steps of 10 Ω was used as unknown.
2. A decade resistor Model ESI-DB 62 of a total resistance of
   111,111 Ω in steps of 0.1 Ω was used as standard.
3. The decade resistor in the unknown arm was grounded to the ground
   post of the Impedance Comparator.
4. The readings were taken in "Guarded" position. They were identical for the four positions of the switch.

5. These readings were taken right before the actual resistance of the solution was measured. They were intended to be a check of the bridge. More check-readings will be shown when the measurements for the solutions are presented.

6. The same connectors used to connect the conductance cell to the bridge were used to connect the decade resistor to the bridge.

The readings are within the combined accuracy of the two boxes. Each of GR decade resistor boxes has an accuracy of 0.025% and the ESI box has an accuracy of 0.01%. Therefore, when comparing two GR resistors the difference between them should be no greater than 0.05%; when comparing the ESI decade resistor to a GR decade resistor this difference should not be greater than 0.035%.

The readings show a certain frequency dependence. The dependence seems to be changing for different sets of measurements. We think this is due to small stray capacitance-inductance effects which could be changing from day to day due to changes in external conditions. The simplest equivalent circuit for the decade resistor is shown in fig. 2.5.1.$^{31}$

![Fig. 2.5.1](image-url)
Its total impedance is obtained from:

\[
\frac{1}{Z} = \frac{1}{R + \omega L} + j\omega C
\]

(2.5.1)

L is the equivalent inductance in series with the resistance R, and C is the equivalent capacitance across the terminals of the resistor. Then:

\[
Z = \frac{R + \omega L j}{(1 - \omega^2 LC) + j\omega CR}
\]

(2.5.2)

The real part of (2.5.2) is:

\[
\text{Re}(Z) = \frac{R}{(1 - \omega^2 LC)^2 + \omega^2 C^2 R^2}
\]

(2.5.3)

An increase, a decrease or no change at all in the resistance readings with the increase in frequency can be explained through (2.5.3) having the right values for C and L.

Again we must note that the variation with the frequency is smaller than or equal to the combined accuracy of the decade resistors being compared.
3. **THE CELL**

3.1. **Generalities**

The design of the cell depends primarily on the nature and the range of concentration of the solutions to be measured. Thus there are cells for low, moderate or high concentration, for aqueous solutions or for molten salts, for salts, acids or bases, etc.\(^{37}\)

Another important factor in determining the cell design is the minimization of the stray capacitances. The Parker effect belongs to this group; it is the capacitance effect between the cell leads and the cell solution. It can be avoided by spacing the leads well away from those parts of the cell containing the solution.\(^{38}\)

Among the more recent cell designs for use with moderately dilute solutions, the most noteworthy one is that of Ives and Pryor.\(^{24}\)

Their cell is a double cell: two conductance cells built as similar as possible, except for the distances between the electrodes (a different distance gives a different cell constant), are joined in such a way that they can be filled with the same solution at the same time. Also, the resistance of the solution in the two cells can be measured under exactly the same conditions. It was hoped that the difference between the two resistances would be free, by cancellation, of any errors due to stray capacitances, electrode effects and the like.\(^{39}\)

3.2. **Equivalent circuits and frequency dependence of the conductance cell.**

One of the most critical conditions to fulfill in accurate conductance work is the independence of the measured resistance from
the frequency of the ac used. We are considering here only low frequencies. The effect of high frequencies (of the order of MHz) upon conductance and dielectric constant which has been investigated from a theoretical point of view by Debye and Falkenhagen is a completely different matter.\(^40\)

The problem of frequency dependence is intimately connected with the cell design and the electrode processes.

Different cell designs were not able to eliminate completely the frequency dependence although a proper cell design could bring it to limits which are negligible for many purposes. The best result obtained by a proper cell design is that of Ives and Pryor. Their double cell, mentioned before, shows a residual frequency dependence of 0.01% (measurements at 1150 and 3880 Hz).

A great deal of work has gone into the analysis of the factors which contribute to the change of a metal-solution interface across which a current flows. The usual approach is to find a combination of resistors, capacitors and inductors which can represent this change. The variables which should be considered when looking for such an equivalent circuit are:

a. the type of electrolyte.

b. roughness and inhomogeneity of the electrode surface.

c. presence of trace impurities at the surface of the electrodes.

d. the faradaic and the nonfaradaic impedances.
The last item in this list has received the greatest attention. The nonfaradaic impedance is the impedance of the electrical double layer which behaves like a condenser in series with the ohmic resistance of the solution. The current is carried by charging and discharging of the electrical double layer. The faradaic impedance is connected with the faradaic path of the current. By this path the current crosses the interface of the metal-electrolyte system by virtue of an electrochemical reaction such as reduction or oxidation of water or some ion. The faradaic admittance (the admittance is the inverse of impedance) adds to the admittance of the double layer which is why it is proper to think of the two admittances as two impedances in parallel.

It must be noted that the faradaic admittance should be very small in usual conductance work (as in our case) as the voltage swing across the cell will not normally exceed 100 mV and, moreover, the compounds with which we were working belong to class I by Grahame's classification. According to Grahame, if substances of class I are present alone there is no faradaic current and no faradaic admittance. "Class I" is made up, mainly, of substances which do not participate in electrochemical reactions. However, in normal conductance work some electrolysis will occur perhaps due to some impurities or, more likely, through depolarizing action of dissolved oxygen.
Grahame's equivalent circuit for a system consisting of
from an electrolyte solution and an electrode is: 41

![Grahame's equivalent circuit](image)

Fig. 3.2.1

$C_{dl}$ is the double layer capacity. $R_{soln}$ is the ohmic resistance of
the solution. The series combination $R_F$ and $\mathcal{W}$ represents the
faradaic impedance. $R_F$ is a pure resistance and $\mathcal{W}$ is an impedance
called "Wartburg impedance". Wartburg impedance has some special
properties which makes it different from any combination of capacitors
and resistors. $\mathcal{W}$ is made up from a resistor $R_W$ in series with a
capacitor $C_W$. $R_W$ and $C_W$ are given by:

$$R_W = \frac{\eta}{\omega}^{1/2}$$

$$C_W = \frac{1}{\eta \omega}^{1/2} \quad (3.2.1)$$

where $\eta$ is a constant.

The equivalent circuit of fig. 3.2.1 is valid only for certain
substances (class I and II by Grahame's classification) in a cell with
smooth and homogeneous electrodes and in the presence of an inert
electrolyte or of a considerable faradaic current.
Feates, Ives and Pryor propose a different circuit:

![Fig. 3.2.2 Feates, Ives and Pryor equivalent circuit](image)

$R_F$ is a faradaic impedance considered here to be purely resistive. $C_o$ represents "stray" capacitances which are due to the dielectric properties of the cell solution, capacitance between cell connections and the like. The other symbols have the same meaning as before.

Some of the assumptions on which these two models (fig. 3.2.1 and 3.2.2) are based are very difficult to meet in practice. For example, little is known about the role of surface roughness. Only recently has this element received some attention and the theory is not yet able to predict what the influence of, say, some microscopic scratches on the electrode would have on the frequency dependence of the electrochemical measurement.

The usual approach to the problem of frequency dependence is to try, firstly, to build a cell which will give resistance readings which do not change with the frequency. This is not easy because the problem of constructing conductance cells is more craftsmanship than an exact science at the present time.

Failing this, which is not unusual, the second approach is to correct for the observed frequency dependence. There are several formulas which can be used for this correction. They have a common factor: all are empirical. The formulas were obtained by finding
a polynomial, having frequency as the variable parameter, which best fitted the observed variation with the least number of adjustable constants.

A brief summary of these methods:

1. Jones and Christian method.\textsuperscript{45}

\[ R_{\text{obs}} = R_{\text{soln}} + \frac{A}{\omega^{1/2}} \]  \hspace{1cm} (3.2.2)

where \[ \omega = 2\pi xf \]  \hspace{1cm} (3.2.3)

2. Brody, Nichol and Fuoss method.\textsuperscript{46, 47}

\[ R_{\text{obs}} = R_{\text{soln}} + \frac{A}{\omega^{1/2}} + \frac{B}{\omega} \]  \hspace{1cm} (3.2.4)

Depending on the cell and the nature of the solution one of the terms is often negligible.

3. Feates, Ives and Pryor method.\textsuperscript{24, 39}

\[ \Delta R_{\text{obs}} = \Delta R_{\text{soln}} + \frac{A}{f} \]  \hspace{1cm} (3.2.5)

where \( \Delta R_{\text{obs}} \) represents the difference of the resistance readings taken for the two individual cells of the double cell.

3.3. The total impedance \( Z_x \) of the equivalent circuit of the cell

It was shown in subsection 2.4 that the balance condition for the bridge is:

\[ Z_s = Z_x \]  \hspace{1cm} (2.4.10)
where $Z_s$ is the impedance of the standard arm and $Z_x$ is the unknown impedance. In our case the unknown impedance is the impedance of the conductivity cell with the electrolyte solution in it.

Feates, Ives and Pryor equivalent circuit

The total impedance of the circuit of fig. 3.2.2 is given by:

$$\frac{1}{Z_x} = \frac{1}{Z_1} + j\omega C_0 \quad \text{or} \quad Z_x = \frac{Z_1}{1 + j\omega C_0 Z_1} \quad (3.3.1)$$

where

$$Z_1 = R_{\text{so1n}} + \frac{1}{\frac{1}{R_F} + j\omega C_{\text{d1}}} \quad (3.3.2)$$

Then

$$Z_x = \frac{R_F}{R_{\text{so1n}} + \frac{1}{1 + j\omega C_{\text{d1}}R_F}} \frac{R_F}{1 + j\omega C_0 \left[ R_{\text{so1n}} + \frac{1}{1 + j\omega C_{\text{d1}}R_F} \right]} = \frac{(R_F + R_{\text{so1n}}) + j\omega C_{\text{d1}}R_FR_{\text{so1n}}}{(1 - \omega C_0 C_{\text{d1}}R_FR_{\text{so1n}}) + j\omega (C_{\text{d1}}R_F + C_0 R_F + C_0 R_{\text{so1n}})} \quad (3.3.3)$$

The real part of (3.3.3) is:

$$\text{Re}(Z_x) = \frac{(R_F + R_{\text{so1n}}) + C_{\text{d1}}^2 R_FR_{\text{so1n}}\omega^2}{1 + [R_F^2(C_0 + C_{\text{d1}})^2 + C_0^2 R_{\text{so1n}}^2(R_{\text{so1n}} + 2R_F)] \omega^2 + (C_{\text{d1}}R_FR_{\text{so1n}})^2 \omega^4} \quad (3.3.4)$$

which is of the form:

$$\text{Re}(Z_x) = \frac{A + B\omega^2}{1 + C\omega^2 + D\omega^4} \quad (3.3.5)$$
Though the circuit is not very complicated the expression for its impedance is not simple. It will be difficult to predict what the variation of \( \text{Re}(Z_X) \), which is the actual reading, will be with the change in \( \omega \). One thing is evident: no extrapolation to zero or infinite frequency will give \( R_{\text{soln}} \).

Simpler relations can be obtained using some approximations.

1. Neglecting the capacitance \( C_0 \): \(^{48}\)

\[
\text{Re}(Z_X) = \text{Re}(Z_1) = R_{\text{soln}} + \frac{R_F}{1 + C_{d1} R_F^2 \omega^2} \tag{3.3.6}
\]

Relation (3.3.6) predicts a decrease in the resistance readings with the increase in frequency. \( \text{Re}(Z_X) \) approaches the value of \( R_{\text{soln}} \) when \( \omega \) tends to infinity:

\[
\lim_{\omega \to \infty} \text{Re}(Z_X) = R_{\text{soln}} \tag{3.3.7}
\]

Relation (3.3.6) can be solved exactly for \( R_{\text{soln}}, R_F \) and \( C_{d1} \) provided that readings at least three different frequencies are taken.

2. In (3.3.3) neglect \( R_F \) in the numerator and \( R_F C_0 \) in the denominator. Both these terms should be much smaller than \( R_{\text{soln}} \) and \( (C_0 R_{\text{soln}} + C_{d1} R_F) \) respectively. Then:

\[
\text{Re}(Z_X) = \frac{R_{\text{soln}}}{1 + C_0^2 R_{\text{soln}}^2 \omega^2} \tag{3.3.8}
\]

Expression (3.3.8) predicts, as 3.3.6 predicted, a decrease
in the resistance readings \((\text{Re}(Z_x'))\) as the frequency increases.

However, as opposed to \((3.3.6)\):

\[
\lim_{\omega \to 0} \text{Re}(Z_x') = R_{\text{soln}} \tag{3.3.9}
\]

Taking some arbitrary values for \(R_{\text{soln}}, R_F, C_{d1}, C_0\) and \(\omega\), \(\text{Re}(Z_x')\) can be calculated by all three formulas, i.e. \((3.3.4), (3.3.6)\), and \((3.3.8)\). In this way we can obtain some idea of the difference between \(\text{Re}(Z_x')\), that is, the experimental reading, and \(R_{\text{soln}}\) which is the quantity we want. The results are given in table 3.3.1.

**Graham equivalent circuit**

The total impedance of the circuit shown in fig. 3.2.1 is given by:

\[
Z_x = R_{\text{soln}} + \frac{1}{\frac{1}{R_F + \frac{j \omega C_{d1}}{\omega^{1/2}} + j \omega C_{d1}}} \tag{3.3.10}
\]

where

\[
-\omega = R_w - \frac{j}{\omega C_w} = \frac{n}{\omega^{1/2}} - \frac{j}{\omega^{1/2}} = \frac{n(1 - j)}{\omega^{1/2}} \tag{3.3.11}
\]

Then

\[
Z_x = R_{\text{soln}} + \frac{1}{\frac{1}{R_F + \frac{n(1 - j)}{\omega^{1/2}}} + j \omega C_{d1}} \tag{3.3.12}
\]

\[
= R_{\text{soln}} + \frac{R_F \omega^{1/2} + n - nj}{(\omega^{1/2} + n C_{d1} \omega) + j(\omega^{3/2} C_{d1} R_F + \omega C_{d1} n)}
\]
The real part of (3.3.12) is:

\[
\Re(Z_x) = R_{\text{soln}} + \frac{(R_F^{1/2} + n)(\omega^{1/2} + nC_{d1}\omega) - n(\omega^{3/2}C_{d1}R_F + \omega C_{d1}n)}{\left(\omega^{1/2} + nC_{d1}\omega\right)^2 + \left(\omega^{3/2}C_{d1}R_F + \omega C_{d1}n\right)^2}
\]

\[
= R_{\text{soln}} + \frac{n + R_F^{1/2}}{\omega^{1/2} + 2nC_{d1}\omega + 2n^2C_{d1}\omega^{3/2} + 2nR_FR_F^{1/2} + R_{d1}\omega^{5/2}}
\]

(3.3.13)

The result is more complicated in this case as compared with the previous case.

The first observation is that:

\[
\lim_{\omega \to \infty} \Re(Z_x) = R_{\text{soln}}
\]

(3.3.14)

which is in agreement with (3.3.7).

The second observation is that the reading, \(\Re(Z_x)\), is decreasing as the frequency is increasing. This is the same conclusion as in the case of the first circuit studied.

The introduction of a parallel capacitance, \(C_o\), in the Grahame's circuit to take care of any stray capacitance was proposed by Robinson and Stokes. The circuit has the following aspect:

![Fig. 3.3.1](image-url)
The solution of this circuit leads to even more complicated expressions than in the previous cases. In fact, Robinson and Stokes neglected the capacitance $C_0$ when they discussed the circuit of fig. 3.3.1.

If the faradaic part of the circuit of fig. 3.2.1 is completely neglected as the case should be when only substances of class I (Grahame's classification) are present in solution and if the capacitance $C_0$ mentioned above is introduced, the circuit which now looks like:

\[
\begin{array}{c}
\text{R}_{\text{soln}} \\
\text{C}_{d1} \\
\text{C}_0
\end{array}
\]

has the total impedance given by:

\[
\frac{1}{Z_x} = \frac{1}{R_{\text{soln}}} - \frac{j}{\omega C_d} + j\omega C_0 \quad \therefore Z_x = \frac{R_{\text{soln}} C_{d1}\omega - j}{\omega(c_{d1} + C_0) + j\omega C_{d1} C_0 R_{\text{soln}}}
\]

(3.3.15)

The real part of $Z_x$ is:

\[
\text{Re}(Z_x) = \frac{R_{\text{soln}} C_{d1}\omega^2(c_{d1} + C_0) - \omega^2 C_{d1} C_0 R_{\text{soln}}}{\omega^2(c_{d1} + C_0)^2 + (\omega^2 C_{d1} C_0 R_{\text{soln}})^2}
\]

\[= \frac{R_{\text{soln}} C_{d1}^2}{(C_{d1}^2 + C_0)^2 + \omega^2(C_{d1} C_0 R_{\text{soln}})^2}
\]

(3.3.16)
When $\omega = 0$:

$$\text{Re}(Z_x) = \frac{R_{\text{soln}}}{(C_{d1} + C_0)^2} \left( \frac{C_{d1}}{C_{d1} + C_0} \right)^2$$

(3.3.17)

If $C_{d1} \gg C_0$, as should be the case, then:

$$\text{Re}(Z_x) = R_{\text{soln}}$$

Using the same values for $R_{\text{soln}}$, $C_{d1}$ and $R_F$ as in the case of the Feates, Ives and Pryor circuit and taking some arbitrary $\eta$'s, we calculated $\text{Re}(Z_x)$ from (3.3.13). The results are given in table 3.3.2. They give us an idea of the difference between $\text{Re}(Z_x)$ and $R_{\text{soln}}$ under several different conditions.

Notes to Tables 3.3.1 and 3.3.2

Every parameter, i.e. $\omega$, $R_{\text{soln}}$, $R_F$, $C_0$, $C_{d1}$, and $\eta$ was varied over a wide range of values. The values were chosen to approach the values used when taking the actual measurements (for $\omega$ and $R_{\text{soln}}$) or they were educated guesses for $R_F$, $C_0$, $C_{d1}$. The value of $\eta$ is a plain guess since we could not find any estimate of its value in the literature.

For every possible combination of the parameters mentioned above $\text{Re}(Z_x)$ was calculated by using expressions 3.3.6, 3.3.8, 3.3.4 and 3.3.13. It must be remembered that 3.3.6 and 3.3.8 are approximations of 3.3.4. Of the two 3.3.8 gave results which were very close to the values obtained by using the complete expression.
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<th>$R_F$ (Ω)</th>
<th>$C_0$ (F)</th>
<th>$C_{dl}$ (F)</th>
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Table 3.3.1. (cont’d) The equivalent circuit of Feates, Ives and Pryor. Calculation of \( \text{Re}(Z_d) \) of expressions (3.3.6), (3.3.8) and (3.3.4)

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Note. The numbers in this table are written exactly in the same way as they are on the computer output (see "Detailed calculations - 3.3.1").
Table 3.3.2. The equivalent circuit of Graebe: Calculation of $\text{Re}(Z_2)$ of expression (3.3.13).

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Table 3.3.2. (cont’d) The equivalent circuit of Graeme: Calculation of Re(Z_w) of expression (3.3.13).

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<th>No.</th>
<th>Freq</th>
<th>Re(X)</th>
<th>R_F</th>
<th>C_d</th>
<th>η = 0.1</th>
<th>η = 1</th>
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</table>

Note: The numbers in this table are written exactly in the same way as they are on the computer output (see "Detailed calculations - 3.3.2").
In the case of relations 3.3.4 and 3.3.8 the readings at 1,000 Hz were the closest to the actual value of \( R_{\text{soln}} \) in every case. For these two relations the value of \( C_0 \) is the most critical one (\( C_0 \) represents any stray capacitance in parallel with the cell) with respect to both the actual value of \( \text{Re}(Z_x) \) and the change with frequency. Any value higher than 100 pF produces a considerable change in the value of \( \text{Re}(Z_x) \) over the range of frequencies used (1,000 to 10,000 Hz) and also a large difference between \( \text{Re}(Z_x) \) and \( R_{\text{soln}} \).

Regarding Grahame's equivalent circuit (fig. 3.2.1) and its impedance (expression 3.3.13), the Wartburg impedance hardly affected the value of \( \text{Re}(Z_x) \) even when \( n \) was increased by a factor of \( 10^4 \).

To conclude, \( \text{Re}(Z_x) \) represents a very good approximation of \( R_{\text{soln}} \) at low frequencies (1,000 Hz) provided that the stray capacitances are kept small (< 100 pF).

The computer program used to compute tables 3.3.1 and 3.3.2 is given in appendix 3.3.1.

3.4. Conclusions

A series of methods for adjusting the measured resistance of a solution for its frequency dependence are being used. All of them are empirical. If a more exact treatment is tried, it is observed that different equivalent circuits lead to completely different conclusions with respect to the point at which the measured value approaches the true \( R_{\text{soln}} \).
It is very difficult to recommend one method over another since no conclusive evidence pointing toward any of them exists. The empirical methods of extrapolation are extremely unsatisfactory. Very often the frequency dependence observed for KCl solutions, when determining the cell constant, is different from that observed when measuring the solution of the compound studied.

It seems to us that the best way to proceed in this matter, at least until the exact nature of the frequency dependence is known better, is to try to obtain a cell and a network which gives a very small frequency dependence. The frequencies used need not be greater than 5 kHz. The readings at different frequencies should be treated independently. For comparison with other sets of data a "standard frequency" of, say, 1,000 Hz can be used (see appendix 3.3.1). Thus the data published will have a consistency which is lacking now.

In our case we did exactly the things advocated above: the cell constant was determined for four different frequencies. These values were used to calculate the dissociation constant of some organic acids at the same four different frequencies.

3.5. Our Cell

From the beginning we decided to use a double cell of the Feates, Ives and Pryor type.24

The first cell built for us is shown in fig. 3.5.1. Some typical readings taken with it are shown in columns 3 and 4 of table 3.5.1.
Table 3.5.1. Typical resistance readings taken with cells 1 and 2

<table>
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<tr>
<th>Concentration of the Solution g KCl/kg H₂O</th>
<th>Frequency Hz</th>
<th>Resistance of the Solution (Ω) Cell</th>
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<td></td>
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<td>1000</td>
<td>4951.6 638.06 - -</td>
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<tr>
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We had two main reasons for discarding this cell. The first, and the most important one, was the fact that we could not obtain a cell constant with a precision better than, approximately, ± 0.5%. Also the ratio of the two cell constants, which should be a constant, changed erratically. We were unable to pinpoint exactly the cause of this inaccuracy. The individual measurements leading to the cell constant, weighings, resistance measurements, temperature measurements, were performed with an accuracy much better than 0.5%. We strongly suspected that gas bubbles on the electrodes were the main cause of our troubles. One way to eliminate gas bubbles was to degas the solution. We did not do this because we were afraid that the concentration of the solution might change during the degassing process and also we considered the fact that the cell was not built to hold a vacuum.
The second reason for discarding cell no. 1 was its frequency dependence though, as it could be seen from table 3.5.1, up to 5 kHz the variation is small.

Cell no. 2 was built based on the same principle as cell 1. It had smaller electrodes, smaller volume and the different parts of the cell were farther apart as compared to cell no. 1. It did not represent any remarkable improvement over cell no. 1 though it showed a better frequency dependence. Typical readings are shown in columns 5 and 6 of table 3.5.1.

Cell no. 3 is shown in fig. 3.5.2. It was different in its concept from the previous two cells. It was still a double cell. The difference consisted in the fact that the two cells were made as identical as possible; the difference in the cell constants being obtained by using different internal diameters for the tubes connecting the electrode compartments (tube A, fig. 3.5.2). The ratio of the cell constants was approximately the same as the ratio of the squared internal diameters of tube A. This ratio was closer to 1:2, for cell no. 3, as compared with the ratio of the previous two cells which was closer to 1:8. Other differences between cell no. 3 and cells nos. 1 and 2 were the following:

a. The cell had no stirring. It was observed during our work with cell no. 1 that the stirring did not affect the results in any way; the resistance readings were the same with no stirring or after stirring, provided that all other parameters did not change (temperature for example). It was shown by Stokes\(^\text{49}\) that the Soret effect does not appear when the change in the temperature
is slow. If a cell containing an electrolyte solution is transferred suddenly to a higher temperature and resistance readings are taken after the temperature equilibrium is established the readings will be lower for a non-stirred solution. If the transfer is to a lower temperature the resistance readings will be higher for the non-stirred solution. This is a consequence of the Soret effect. The difference in the readings range from several tenths to a few hundreds of one per cent. The key word here is "suddenly". If the change in the temperature is done slowly then the specific conductance of the mixed solution is the same as that of the non-mixed solution. Thus in our case since the change in the temperature of the bath was done gradually, the Soret effect was absent. This agrees with our experimental observations. It must be, also, remembered that we were doing equilibrium work. The situation might be different in kinetic studies, where the stirring could prove to be essential.

b. Only one lead was provided from each electrode. The "4 leads" method requires two leads from each electrode or 4 leads per cell. Cells nos. 1 and 2 had two leads per electrode. In the case of cell no. 3, the 4 leads were provided by attaching a "Tee adapter" (BNC type, Amphenol part no. 31-208) to the end of each of the leads. This type of construction makes the glass-blowing much easier.

As was shown before (subsection 2.4) the 4 leads method is used in order to eliminate the resistance (or the impedance) of the leads. In our case the resistance of the lead from the electrode
to the "tee adapter" is not eliminated. However since this part of the lead is made from very high conductance metals, its resistance should be very small. The construction of the lead from the electrode to the connector is shown schematically in fig. 3.5.3.

This construction of the cell eliminated the problems we had in the determination of the cell constant. Some residual effects were probably still present because the precision of our cell constant was only 0.05% while some of the more recent work in conductance claimed precisions of 0.01% or better. 50

The improvement could be rationalized if we assumed that a "tunnel" effect took place in the cell. The glass tube A connecting the two electrode compartments had a diameter of approximately 9 mm. while the diameter of the electrode was approximately 20 mm. Thus the outer part of the electrodes had a much smaller role in the transmission of the current (this we call "tunnel effect"). Since the gas bubbles had a tendency to form at the edge of the electrodes, their effects were greatly diminished. The evidence for a so called "tunnel effect" is the fact that different cell constants are obtained by changing the diameter of the tube A.

Cell no. 3 presented a much smaller frequency dependence. It can be seen from the resistance readings for KCl solutions ("Detailed calculations - 5.10.1") or organic acid solutions ("Detailed calculations - 8.3.1") that its frequency variation resembles very well the variation shown by a decade resistor box when connected in the unknown arm.

This small variation was explained in the case of the decade
resistor box by the small capacitance which shunts the box and by an inductance in series with \( R_x \) (see fig. 2.5.1). In the case of the conductance cell it was very likely that the same type of effects caused the frequency variation though their origin was different. Here, as in the case of the decade resistor, the relative variation of the readings, for frequencies between 1,000 and 5,000 Hz, was approximately the same as the relative precision of their absolute values.

A fourth cell (fig. 3.5.4) of the same design as cell no. 3 was built. In cell no. 4 the tubes connecting the two individual cells to the central part of the double cell (tubes B in fig. 3.5.4) were thick wall, capillary tubes. In cell no. 3 they were made of normal glass tube of approximately 3 mm. i.d. This modification of cell no. 4 was done in order to minimize any current flow through tubes B. No significant difference in the behaviour of cells 3 and 4 was found. It was more difficult to fill and empty cell no. 4 because the column of liquid in the capillary tubes very often broke leaving gas bubbles trapped in them. To avoid this the process of filling and emptying the cell had to be done very slowly.

3.6. The connectors

The connectors used to connect the cell to the bridge were specially made. One connector per electrode and therefore, four connectors for the double cell were used.

Each connector provided "4-way" connections. They are shown in fig. 3.6.1. When one part of the double cell was being measured the other part was grounded to the ground post of the bridge
by means of receptacle no. 2 and a special cap which connected the central pin to the outside shield. The metal sheet connecting the outside part of receptacles no. 2, 1 and 4 assured that all the shields of the leads attached to them were grounded to the ground post of the bridge.

The same connectors were used when checking the bridge with the decade resistor box.
Fig. 3.5.1  Cell No. 1
Fig. 3.5.2  Cell No. 3
Fig. 3.5.4 Cell No. 4
All connections spot welded

FIG. 3.5.3.

CELL LEAD
To Leads # 2 or 4 (e.g. $x_2, y_2, x_4, or y_4$)

To ground when measuring the other part of the double cell

To leads # 1 or 3 (e.g. $x_1, y_1, x_3, or y_3$)

Bulkhead receptacle
Amphend part # 31-221
Solder
Plastic block
Metal sheet

FIG. 3.6.1.
THE CONNECTOR USED TO CONNECT THE CELL TO THE BRIDGE
4. **THE TEMPERATURE CONTROL**

The resistance has a temperature coefficient of approximately 2% per centigrade degree. Therefore, if an accuracy of 0.01% is sought the temperature control must be better than ± 0.005°C. The system of baths we used to obtain the constant temperature is shown in fig. 4.1.

The temperature was measured with a calibrated (by Leeds & Northrup Company, Philadelphia, 1961) platinum thermometer from Leeds & Northrup Company. The resistance readings were taken by the "4 leads" method with a dc Müller Bridge (No. 8067 Leeds & Northrup) and a Mercury Commutator (No. 8068 Leeds & Northrup). The Müller Bridge was air-thermostated at 35°C. A dc Galvanometer (Leeds and Northrup No. 2430-2) with a sensitivity of 0.48 microvolts/milimeter was used to detect the balance point.51

Calendar's formula was used to calculate the temperature from the resistance readings. This calculation was incorporated as a subroutine into the computer programs calculating the cell constant and the conductivity of solutions.

The setup is capable of keeping the temperature constant within 0.003°C (in bath no. 3).

The thermometer was regularly checked at the ice point (1 - 2 times a week). No difference was found between readings taken with ice from an ice machine (connected to the distilled water supply of the building) and ice made from conductivity water exposed to air. The contacts of the bridge and the mercury commutator required a daily cleaning.
Figure 4.1.1

Notes. 1. The cooling system of bath no. 1 was taken from an old refrigerator.
2. $T \approx T_1 - 15^\circ C ; \ T_1 \approx T_2 - 5^\circ C ; \ T_2 \approx T_3$. 
5. **DETERMINATION OF CELL CONSTANT IN CONDUCTANCE MEASUREMENTS**

5.1. **Introduction**

For a conductor the resistance, $R$, is defined as:

$$ R = R_{sp} \times \frac{l}{s} \quad (5.1.1) $$

where:

- $R_{sp}$ is the specific resistance, i.e. the resistance of a cube of material 1 cm long and with an area of 1 cm$^2$
- $l$ is the length of the conductor
- $s$ is the cross section

In conductance measurements (5.1.1) takes the form:

$$ \Lambda = \frac{1000 L_{sp}}{c} \quad (5.1.2) $$

where:

- $c$ is the concentration of the solute in gram-equivalents per litre or in moles per litre
- $L_{sp}$ is the specific conductivity of solution
- $\Lambda$ is the equivalent or molar conductance (depending on the units used for concentration) of solution

The specific conductance is calculated from:

$$ L_{sp} = \frac{k}{R_{obs}} \quad (5.1.3) $$

where $k$ is the cell constant and $R_{obs}$ the observed resistance.

The cell constant $k$ is found by applying equation (5.1.3) to a solution of known specific conductivity.

Generally for such determinations KCl solutions are used, although other standards have been proposed.\textsuperscript{52}
5.2. The conductivity of KCl solutions

The best data available for the specific conductivity of KCl solutions are those of Jones and Bradshaw.\textsuperscript{53} However, for the purpose of calibrating a cell, i.e. to determine a cell constant, the equation given by Lind, Zwolenik and Fuoss\textsuperscript{54} is more convenient. The relation was established based on a weighted average of 9 sets of figures by different workers, all of which are based on the Jones and Bradshaw standards. The equation is:

\[ \Lambda = 149.93 - 94.65 + 58.74 \log c + 198.4c \]  \hspace{1cm} (5.2.1)

where \(c\) is the concentration in grams - equivalents per litre.

Equation (5.2.2) is valid at 25\(^\circ\)C and has an accuracy of approximately 0.013%.

For other temperatures the problem of obtaining the cell constant is more difficult because the amount of experimental data available is small.

There are two ways to obtain the cell constant for temperatures other than 25\(^\circ\)C:

a. to calculate the change in the cell constant with the temperature from geometrical considerations.

b. to use the published data on the conductance of KCl solutions and the theoretical conductance equations.

5.3. The change in the cell constant with temperature. Geometrical considerations\textsuperscript{55}

The change in the cell constant with temperature depends on the geometry of the cell and the nature of materials used for its construction.
The usual shape of electrode compartments in a conductance cell is shown in fig. 5.3.1. Two electrodes of area \( A \) at a distance \( l \) apart are connected to the leads by platinum wire sealed into the cell at a distance \( d \) from the electrodes.

A change in temperature, say increase, has the effect of increasing area \( A \), distance \( d \) and distance \( s \).

If the cell constant is considered to be:

\[
k = \Sigma \frac{1}{A}
\]

(5.3.1)

where the sum is taken over regions of uniform current density. The length of the region is \( l \) and \( A \) is cross-sectional area normal to the current.

From (5.3.1) and fig. 5.3.1:

\[
\ln(k) = \ln(1) - \ln(A) = \ln(s - 2d) - \ln(A)
\]

(5.3.2)

Differentiating with respect to \( T \) (temperature):

\[
\frac{1}{k} \frac{dk}{dT} = \frac{1}{l} \frac{dl}{dT} - \frac{1}{A} \frac{dA}{dT}
\]

(5.3.3)

and:

\[
\frac{dl}{dT} = \frac{ds}{dT} - 2 \frac{dd}{dT}
\]

(5.3.4)

\[
\frac{dA}{dT} = (A^{1/2} + A^{1/2} \alpha_{pt})^2 - A = 2\alpha_{pt}
\]

(5.3.5)

\[
\frac{ds}{dT} = \alpha_g s \quad : \quad \frac{dd}{dT} = \alpha_{pt} d
\]

(5.3.6)

where \( \alpha_g \) and \( \alpha_{pt} \) are the linear expansion coefficients of glass and platinum respectively.

Expression (5.3.5) results from considering area \( A \) as a
square. The side, $(A)^{1/2}$, becomes $A^{1/2}(1 + \alpha_{pt})$ after expansion. The term in $\alpha_{pt}^2$ was neglected. The same relation holds if the electrodes are considered circular. Hence:

\[
\frac{1}{k} \frac{dk}{dT} = \frac{1}{s - 2d} \left( \alpha_g s - 2\alpha_{pt}d \right) - 2\alpha_{pt}
\]

\[
= \alpha_g s - 2\alpha_{pt} \frac{s - d}{s - 2d}
\]

(5.3.7)

If $s$ and $d$ are known the change in $k$ can be calculated. $(1/k) \times (dk/dT) \times 100$ will give the % change per $1^\circ\text{C}$.

For our cells nos. 3 and 4 the situation is somewhat different due to their different construction. The electrode compartment is represented schematically in fig. 5.3.2. Expression (5.3.3) is still valid. However, in this case both $l$ and $A$ refer to the glass tube connecting the electrodes.

\[
\frac{1}{k} \frac{dk}{dT} = \frac{1}{l} \frac{dl}{dT} - \frac{1}{A} \frac{dA}{dT} = \alpha_g - 2\alpha_g = -\alpha_g
\]

(5.3.8)

If the glass is Pyrex the % change per $1^\circ\text{C}$ is $3.6 \times 10^{-4}$ $(c^0)^{-1}$.

Note that to obtain the above result we assumed that the area of the electrodes which lies outside the area $A$ does not participate in the electrical conductance. This is probably not exactly so, though, this participation is small. Also we expect this peripheral conductance path to have a temperature coefficient similar to the main conductance path.
FIG. 5.3.1.
SCHEMATIC REPRESENTATION OF THE ELECTRODE COMPARTMENT OF A CONDUCTANCE CELL

FIG. 5.3.2.
SCHEMATIC REPRESENTATION OF THE ELECTRODE COMPARTMENT IN OUR CELLS No. 3 and 4
5.4. The conductance of KCl solutions vs. temperature

The most recent conductance equation is given by Onsager, Fuoss and Skinner.\textsuperscript{56}

\[ \Lambda = \Lambda^0 - S c^{1/2} + E_1 c \ln(6E_1 c) + L_1 c - K_{Acf_\pm}^2 \Lambda^0 \]  \hspace{1cm}(5.4.1)

where:

\[ S = a^1 \Lambda^0 + \beta \]  \hspace{1cm}(5.4.2)

\[ a^1 = 0.8204 \times \frac{10^6}{(DT)^{3/2}} \]  \hspace{1cm}(5.4.3)

Note: In the original paper due to a misprint, probably, a "\pm" sign appears instead of "\times" sign.

\[ \beta = \frac{82.50}{n(DT)^{1/2}} \]  \hspace{1cm}(5.4.4)

\[ E_1 = E_1^{1} \Lambda^0 - E_2 \]  \hspace{1cm}(5.4.5)

\[ E_1^{1} = \frac{2.942 \times 10^{12}}{(DT)^3} \]  \hspace{1cm}(5.4.6)

\[ E_2 = \frac{0.4333 \times 10^{8}}{n \times (DT)^2} \]  \hspace{1cm}(5.4.7)

\[ L_1 = L_2 \]  \hspace{1cm}(5.4.8)

\[ L_1 = 3.202E_1^{1} \Lambda^0 - 3.420E_2 - \alpha^1 \beta \]  \hspace{1cm}(5.4.9)

\[ b = \frac{16.708 \times 10^{-4}}{\alpha DT} \]  \hspace{1cm}(5.4.10)
\[ L_2 = 2E_1^{1/4} h + \frac{44E_1^{1/2}}{3b} - 2E_1 \ln(b) \]  
(5.4.11)

\[ h = \frac{2b^2 + 2b - 1}{b^3} \]  
(5.4.12)

\[ f_{\pm}^2 = \exp \left( -8.405 \times 10^6 \frac{c^{1/2}}{(DT)^{3/2}} \right) \]  
(5.4.13)

\[ K_A = \frac{4\pi Na^3}{3000} \exp(b) \]  
(5.4.14)

\( \gamma \) is the degree of dissociation  
\( c \) is the concentration in moles/litre  
\( a \) is the distance of closest approach  
\( D \) is the dielectric constant of the solvent  
\( \eta \) is the viscosity of the solvent  
\( T \) is the temperature in kelvins.

Relation (5.4.1) applies to 1-1 electrolytes in solvents of higher dielectric constant.

Another conductance equation is that of Falkenhagen, Leist and Kelbg.\(^{51, 58}\)

\[ \Lambda = \Lambda^0 - (B_1 \Lambda^0 + B_2) \frac{c^{1/2}}{1 + Bac^{1/2}} \]  
(5.4.15)

where for 1:1 electrolytes:

\[ B_1 = \frac{0.8204 \times 10^6}{(DT)^{3/2}} \]  
(5.4.16)

\[ B_2 = \frac{82.5}{\eta(DT)^{3/2}} \]  
(5.4.17)
\[ B = \frac{50.29 \times 10^8}{(DT)^{1/2}} \]  
(5.4.18)

D, \eta, a, c and T have the same significance as in the previous equation.

\[ \lambda^0, \text{ the conductance at infinite dilution, for KCl, can be calculated from Harned and Owen expression:}^{59} \]

\[ \lambda^0_T = \lambda^0_{25} + a(T - 25) + b(T - 25)^2 + c(T - 25)^3 \]  
(5.4.19)

where T is in °C.

The constants \( \lambda^0_{25} \), a, b and c for K\(^+\) and Cl\(^-\) are:

<table>
<thead>
<tr>
<th></th>
<th>( \lambda^0_{25} )</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(^+)</td>
<td>73.50</td>
<td>1.43262</td>
<td>0.40563 \times 10^{-2}</td>
<td>-0.3183 \times 10^{-4}</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>76.35</td>
<td>1.54037</td>
<td>0.46500 \times 10^{-2}</td>
<td>-0.1285 \times 10^{-4}</td>
</tr>
<tr>
<td>KCl</td>
<td>149.85</td>
<td>2.97299</td>
<td>0.87063 \times 10^{-2}</td>
<td>-0.4468 \times 10^{-4}</td>
</tr>
</tbody>
</table>

Expression (5.4.19) has an accuracy of 0.02%.

As mentioned before (subsection 5.2), for KCl solutions at 25°C an empirical equation is available which gives the conductance as a function of concentration:

\[ \Lambda = 149.93 - 94.65c^{1/2} + 58.74c \times \log(c) + 198.4c \]  
(5.2.1)

From an experimental point of view the sequence of operations for determining the cell constant is:

1. Prepare a solution of KCl of known concentration, say \( c_1 \)
2. Measure its resistance at the temperatures wanted: \( T_1, T_2, \ldots, T_n \)
3. Calculate the conductance \( \Lambda_{11}, \Lambda_{12}, \ldots, \Lambda_{1n} \) of the solution
corresponding to \( c_1 \) and \( T_1, \ldots, T_n \). \( \Lambda \)'s are calculated by using one of the theoretical or empirical conductance equations available, e.g. (5.4.1) or (5.4.15).

4. Repeat steps 1 to 4 for a series of different concentrations \( c_2, \ldots, c_n \).

5. Calculate the cell constant at \( T_1, \ldots, T_n \) by means of expressions (5.1.2) and (5.1.3).

To compare the results obtained for the different concentrations, \( c_1, \ldots, c_n \), the temperatures at which the measurements are taken should be the same in all cases. It is very difficult and time consuming from an experimental point of view to try to reproduce a temperature within 0.005°C. An easier way is to take a series of readings at \( T'_1, T'_2, \ldots, T'_n \) in the interval of the temperature we want to cover. It is preferable that \( T'_1, T'_2, \ldots, T'_n \) be close to \( T_1, T_2, \ldots, T_n \) however this is not essential. From these readings a relation between \( R \) (resistance) and \( T \) can be obtained:

\[
R = f(T) \quad (5.4.20)
\]

From it, by interpolation, the resistance values at \( T_1, T_2, \) etc. are calculated.

Note that this procedure replaces only step no. 2 from the sequence shown above. The rest of the steps are not changed.

The relation \( R \) vs. \( T \) could be one of the theoretical conductance equations, e.g. (5.4.1) or (5.4.15). However, these types of equations are not the most suitable for a least square fitting of the data. Thus, for the purpose of interpolation only, we looked for a polynomial-like function for (5.4.20).
The relations considered were:

\[ R = A + BT \]  \hspace{1cm} (5.4.21)
\[ R = A + BT + CT^2 \]  \hspace{1cm} (5.4.22)
\[ R = A + BT + CT^2 + DT^3 \]  \hspace{1cm} (5.4.23)
\[ R = A + BT + CT^2 + DT^3 + ET^4 \]  \hspace{1cm} (5.4.24)
\[ R = A + B/T \]  \hspace{1cm} (5.4.25)
\[ R = A + B/T^2 + C/T^2 \]  \hspace{1cm} (5.4.26)
\[ R = A + B/T + C/T^2 + D/T^3 \]  \hspace{1cm} (5.4.27)
\[ R = A + B/T + C/T^2 + D/T^3 + E/T^4 \]  \hspace{1cm} (5.4.28)
\[ \ln R = A + B/T \]  \hspace{1cm} (5.4.29)
\[ \ln R = A + B/T + C\ln T \]  \hspace{1cm} (5.4.30)
\[ R = A + B\ln T \]  \hspace{1cm} (5.4.31)
\[ R = A + B\ln T + C/T \]  \hspace{1cm} (5.4.32)
\[ \ln 2/R = A + B/T \]  \hspace{1cm} (5.4.33)
\[ \ln 1/R = A + B/T + C\ln T \]  \hspace{1cm} (5.4.34)

The expressions (5.4.21) to (5.4.34) were tested on five different sets of experimental data. The detailed results are given in "Detailed calculations - 5.4.1". The computer program is given in appendix 5.4.1. A summary of these results is presented in tables 5.4.1 and 5.4.2.
Table 5.4.1: The temperature and resistance ranges used for testing expressions (5.4.21) to (5.4.34).

<table>
<thead>
<tr>
<th>Set.</th>
<th>No. of points</th>
<th>Temperature range °C</th>
<th>Resistance range Ω</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Minimum</td>
<td>Maximum</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>19.402</td>
<td>40.367</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>19.402</td>
<td>40.367</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>19.697</td>
<td>39.530</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>19.859</td>
<td>40.741</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>19.859</td>
<td>40.741</td>
</tr>
</tbody>
</table>

Eight significant figures were used in the computer programs used for these calculations. In one instance (relations (5.4.21) to (5.4.24)) the number of significant figures was increased to 20. This did not significantly change the previous results.

The best equation for our purposes is (5.4.23). It is the relation which uses the smallest number of adjustable parameters to give a % MSD smaller than the precision of the experimental data.
Table 5.4.2: The results of the fitting obtained with expressions (5.4.21) to (5.4.34)

<table>
<thead>
<tr>
<th>Set</th>
<th>5.4.21</th>
<th>5.4.22</th>
<th>5.4.23</th>
<th>5.4.24</th>
<th>5.4.25</th>
<th>5.4.26</th>
<th>5.4.27</th>
<th>5.4.28</th>
<th>5.4.29</th>
<th>5.4.30</th>
<th>5.4.31</th>
<th>5.4.32</th>
<th>5.4.33</th>
<th>5.4.34</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ω</td>
<td>12.67</td>
<td>0.82</td>
<td>0.15</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>1.33</td>
<td>0.086</td>
<td>0.016</td>
<td>0.009</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ω</td>
<td>98.9</td>
<td>6.8</td>
<td>0.8</td>
<td>0.4</td>
<td>998.1</td>
<td>670.8</td>
<td>211.6</td>
<td>130.3</td>
<td>998.1</td>
<td>388.6</td>
<td>376.</td>
<td>347.</td>
<td>998.1</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>1.33</td>
<td>0.092</td>
<td>0.011</td>
<td>0.005</td>
<td>13.4</td>
<td>9.03</td>
<td>2.85</td>
<td>1.75</td>
<td>13.4</td>
<td>5.23</td>
<td>5.06</td>
<td>4.67</td>
<td>13.4</td>
</tr>
<tr>
<td>3</td>
<td>Ω</td>
<td>5.62</td>
<td>0.34</td>
<td>0.1</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>1.22</td>
<td>0.074</td>
<td>0.021</td>
<td>0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ω</td>
<td>546.</td>
<td>39.2</td>
<td>15</td>
<td></td>
<td>3490.</td>
<td>2073.</td>
<td>2088.</td>
<td>1021.</td>
<td>3486.</td>
<td>605.</td>
<td>2276.</td>
<td>470.</td>
<td>3486.</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>1.51</td>
<td>0.11</td>
<td>0.036</td>
<td></td>
<td>9.62</td>
<td>2.96</td>
<td>3.00</td>
<td>2.82</td>
<td>9.61</td>
<td>1.67</td>
<td>6.28</td>
<td>1.30</td>
<td>9.61</td>
</tr>
<tr>
<td>5</td>
<td>Ω</td>
<td>329.</td>
<td>28.</td>
<td>2.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>1.50</td>
<td>0.13</td>
<td>0.009</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

No. of adj. param. 2 3 4 5 2 3 4 5 2 3 2 3 2 3

Notes: 1. Mean square deviation was calculated from:

$$\text{MSD} = \left( \frac{(R_{\text{obs}} - R_{\text{calc}})^2}{M - 1} \right) \%$$

where $M$ is the number of experimental points, $M$, $R_{\text{min}}$, and $R_{\text{max}}$ are taken from Table 5.4.1.

2. The % mean square deviation was obtained by dividing the mean square deviation in ohms by the $(R_{\text{max}} + R_{\text{min}})/2$ and multiplying the result by 100. $R_{\text{max}}$ and $R_{\text{min}}$ are given in Table 5.4.1.
5.5 Viscosity of water vs. temperature.

In 1952 The National Bureau of Standards (US) adopted a new standard for the viscosity of water. The standard is:

\[ \eta_{20} = 1.002 \times 10^{-2} \text{ poise} \]

The previous standard was:

\[ \eta_{20} = 1.005 \times 10^{-2} \text{ poise} \]

Among the equations giving the change in the viscosity of water with temperature, that of Coe and Godfrey and that of Manning reproduce the experimentally measured viscosities. Both equations have the same form.

The first one is:

\[ \log_{10} \frac{\eta}{\eta_{20}^0} = \frac{1.2348(20-T) - 0.001467(20-T)^2}{T + 96} \]

(5.5.1)

where \( T \) is the temperature in °C.

A series of experimentally determined \( \eta \)'s and their corresponding values calculated from (5.5.1) are shown in table 5.5.1.

The second one is:

\[ \log_{10} \frac{\eta_{20}}{\eta} = \frac{1.37023(T-20) + 0.000836(T-20)^2}{T + 109} \]

(5.5.2)
Table 5.5.1: The viscosity of water at different temperatures

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>( \eta \times 10^{-2} ) (poise)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eq. (5.5.1)</td>
</tr>
<tr>
<td>0</td>
<td>1.787</td>
</tr>
<tr>
<td>5</td>
<td>1.517</td>
</tr>
<tr>
<td>10</td>
<td>1.290</td>
</tr>
<tr>
<td>15</td>
<td>1.132</td>
</tr>
<tr>
<td>20</td>
<td>1.002</td>
</tr>
<tr>
<td>25</td>
<td>0.8903</td>
</tr>
<tr>
<td>30</td>
<td>0.7975</td>
</tr>
<tr>
<td>35</td>
<td>0.7194</td>
</tr>
<tr>
<td>40</td>
<td>0.6531</td>
</tr>
</tbody>
</table>

References

1. R.C. Hardy and R.L. Cottington, J. Res. Nat. Bur. Stand., 42, 573 (1949). The paper gives the ratio \( \eta/\eta_{20} \). \( \eta \) was calculated using the value of \( 1.002 \times 10^{-2} \) for \( \eta_{20} \).


Equation (5.5.1) will be used for further computations.

5.6. The dielectric constant of water vs. temperature

Some of the equations available in the literature giving the dielectric constant of water as a function of temperature are:

\[
D = 78.57 \times (1 - 0.00461(T-25) + 0.0000155(T-25)^2) \quad (5.6.1)
\]
\[ D = 78.54 - 0.004579(T-25) + 1.19 \times 10^{-5}(T-25)^2 + 28 \times 10^{-9}(T-25)^3 \]  
\[ (5.6.2) \]

and finally:

\[ D = 87.74 - 0.4008T + 9.398 \times 10^{-4}T^2 - 1.410 \times 10^{-6}T^3 \]  
\[ (5.6.3) \]

In our computations an average of the values given by the three formulas (5.6.1), (5.6.2) and (5.6.3) was used.

5.7. **The density of KCl solutions**

Conductance equations (subsection 5.4) require that the concentration, \( c \), be expressed in gram-equivalents per litre.

Experimentally it is more convenient to prepare the solutions by weight, i.e. grams solute per kilogram of solution. Hence, an expression connecting the two concentrations is needed.

Such a formula is given by Harned and Cook: 

\[ \frac{c}{c^1} = d_0 + Nc \]  
\[ (5.7.1) \]

where \( c \) is moles solute per litre solution; \( c^1 \) moles solute per 1,000 grams solution; \( d_0 \) the density of water at the temperature considered and \( N \) an isothermal constant.

Using the data from the "International Critical Tables" the authors give \( d_0 \) and \( N \) for a series of temperatures. These values are given in table 5.7.1. The accuracy of expression (5.7.1) is \( \pm 0.04\% \).
Table 5.7.1

<table>
<thead>
<tr>
<th>t°C</th>
<th>(d_0)</th>
<th>N</th>
<th>t°C</th>
<th>(d_0)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.9998679</td>
<td>0.0263</td>
<td>20</td>
<td>0.9982323</td>
<td>0.0270</td>
</tr>
<tr>
<td>5</td>
<td>0.9999919</td>
<td>0.0265</td>
<td>25</td>
<td>0.9970739</td>
<td>0.0272</td>
</tr>
<tr>
<td>10</td>
<td>0.9997277</td>
<td>0.0266</td>
<td>30</td>
<td>0.9956756</td>
<td>0.0273</td>
</tr>
<tr>
<td>15</td>
<td>0.9991265</td>
<td>0.0267</td>
<td>35</td>
<td>0.9940594</td>
<td>0.0274</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>0.9922455</td>
<td>0.0276</td>
</tr>
</tbody>
</table>

The concentration in gram-equivalents/litre is given by:

\[
c = c' d
\]  

(5.7.2)

where \(d\) is the density of the solution. Hence, if the density is known the concentration in mol/kg soln can be converted to g-equiv/l soln (1:1 electrolytes).

To obtain a relation between density and concentration, the data for the densities of KCl solutions from International Critical Tables \(^{67}\) were fitted into an expression of the form:

\[
d = A + Bc^n + Cc^{n^2} + \ldots
\]  

(5.7.3)

where \(c^n\) is the concentration of the solution in g solute/kg solution.

The fitting was done by least square method. Polynomials of 1st degree going up to 6th degree were tested. Seven pairs of data, concentration-density, were considered for each temperature with the exception of 20°C where 14 pairs of data were considered.
The FORTRAN program used is given in appendix 5.7.1 and the detailed results are shown in "Detailed Calculation - 5.7.1". The differences between the values from the "Tables" and the calculated values were of the order:

for 1st degree polynomial : 0.02%
for 2nd degree polynomial : 0.001%
for 3rd degree polynomial : 0.00005%

Note that the 1st degree polynomial of (5.7.3) and (5.7.1) are equivalent.

In computing the density of KCl solutions when calculating the cell constant, the 2nd degree polynomial was used:

\[ d = A + Bc^n + Cc^n^2 \]  

(5.7.4)

The coefficient of this polynomial are given in table 5.7.2.

<table>
<thead>
<tr>
<th>T°C</th>
<th>A</th>
<th>B x 10^4</th>
<th>C x 10^7</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.9999195</td>
<td>6.68457</td>
<td>1.44298</td>
</tr>
<tr>
<td>10</td>
<td>0.9997984</td>
<td>6.46723</td>
<td>1.63842</td>
</tr>
<tr>
<td>20</td>
<td>0.9982438</td>
<td>6.34431</td>
<td>1.65746</td>
</tr>
<tr>
<td>25</td>
<td>0.9971496</td>
<td>6.27002</td>
<td>1.84153</td>
</tr>
<tr>
<td>30</td>
<td>0.9957496</td>
<td>6.23002</td>
<td>1.84153</td>
</tr>
<tr>
<td>35*</td>
<td>0.994134</td>
<td>6.192</td>
<td>1.842</td>
</tr>
<tr>
<td>40</td>
<td>0.9923100</td>
<td>6.15804</td>
<td>1.90814</td>
</tr>
</tbody>
</table>

*obtained by interpolation
It was found that for concentrations smaller than 3g KCl/sol the term in $c^2$ (5.7.4) made no significant contribution to the density.*

Details of the calculation are given in "Detailed calculations - 5.7.1".

5.8. **Jones-Bradshaw standard KCl solutions**

The expressions for the viscosity of water (5.5.1), dielectric constant of water (5.6.1, 5.6.2 and 5.6.3), density of KCl solutions (5.7.4) and the conductance equations (5.4.1, 5.4.5 and 5.2.1) were checked against two of the Jones-Bradshaw standard KCl solutions.

The two solutions were:

Table 5.8.1

<table>
<thead>
<tr>
<th>soln no.</th>
<th>Concentration g KCl/kg soln in vacuum</th>
<th>Spec. conductance $x 10^3$</th>
<th>25°C</th>
<th>25°C</th>
<th>20°C</th>
<th>25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.746558 (0.01N)</td>
<td>1.27572</td>
<td>1.41145</td>
<td>127.523</td>
<td>141.291</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.745263 (0.01D)</td>
<td>-</td>
<td>1.40877</td>
<td>-</td>
<td>141.267</td>
<td></td>
</tr>
</tbody>
</table>

* In International Critical Tables the density is given to 8 significant figures for concentrations smaller than 0.7g/Kg at 20°C and to 6 significant figures in all other cases.
The specific conductance is related to the equivalent conductance by the relation:

\[
\text{Equiv. conductance } (\Lambda_e) = \frac{\text{Specific conductance} \times 1000}{\text{Concentration in equiv/l}} \quad (5.8.1)
\]

The units of concentration were changed from g KCl/kg soln to equiv/l through relation (5.7.4) using the coefficients of table 5.7.2. The results are given in table 5.8.2.

**Table 5.8.2**

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Solution 1</th>
<th>Solution 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Density g/cm³</td>
<td>Concentration equiv/l</td>
</tr>
<tr>
<td>20</td>
<td>0.998718</td>
<td>0.0100007</td>
</tr>
<tr>
<td>25</td>
<td>0.997618</td>
<td>0.00998967</td>
</tr>
<tr>
<td>30</td>
<td>0.996215</td>
<td>0.00997562</td>
</tr>
<tr>
<td>35</td>
<td>0.994596</td>
<td>0.00995941</td>
</tr>
<tr>
<td>40</td>
<td>0.992770</td>
<td>0.00994112</td>
</tr>
</tbody>
</table>

These values of concentration, c, together with the values for the viscosity of water (5.5.1) and the dielectric constant of water (5.6.1 - 5.6.3) were used to calculate the equivalent conductance, \( \Lambda_e \), from (5.4.1), (5.4.15) and (5.2.1). Expressions (5.4.1) and (5.4.15) required a value for "a", the distance of closest approach. Two values were used: \( a = 3.5 \) Å and \( a = 4.0 \) Å. The results are summarized in table 5.8.3. The last column contains, for comparison, Jones-Bradshaw values.
Table 5.8.3

Equivalent conductance (mho)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Rel. (5.4.1)</th>
<th>Rel. (5.4.15)</th>
<th>Rel. (5.2.1)</th>
<th>Jones-Bradshaw values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a = 3.5 A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solution 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>127.080</td>
<td>127.591</td>
<td>-</td>
<td>127.563</td>
</tr>
<tr>
<td>25</td>
<td>140.777</td>
<td>141.340</td>
<td>141.278</td>
<td>141.291</td>
</tr>
<tr>
<td>30</td>
<td>154.877</td>
<td>155.491</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>35</td>
<td>169.348</td>
<td>170.014</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>184.158</td>
<td>184.878</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Solution 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>127.086</td>
<td>127.597</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>140.784</td>
<td>141.346</td>
<td>141.284</td>
<td>141.267</td>
</tr>
<tr>
<td>30</td>
<td>154.885</td>
<td>155.498</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>35</td>
<td>169.356</td>
<td>170.173</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>184.168</td>
<td>184.887</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The empirical expression (5.2.1) gave the closest values to the Jones-Bradshaw standards. It was surprising that the difference between the values obtained using the Onsager-Fuoss-Skinner equation (5.4.1) and the Jones-Bradshaw standards was so large.

We decided to use (5.4.15) \((a = 3.5 \, \text{Å})\) for further computations. Its results were closer to the standard values than those obtained with 5.4.1. Furthermore 5.4.15 allows us to check the constancy of the cell constant over a range of temperatures.
The "Detailed calculations" are given in 5.8.1 and the computer program used for these calculations is given in appendix 5.8.1.

5.9. **Conductivity water and solvent correction**

The solvent correction is one of the critical points of the conductance method when very accurate results are sought. The best conductivity water used to prepare the solutions for the conductance measurements has a specific conductance of $1 \times 10^{-7}$ mho. A dilute solution of a salt or acid (concentration around 0.001N) has a specific conductance of approximately $10^{-4}$ - $10^{-5}$ mho. Depending on the nature of the ions causing the conductance of the solvent and the nature of the solute, the solvent correction can be as large as 1% or be very small and thus negligible. It is obvious that if the nature of the ions present in the "pure" solvent is not known the uncertainty in the measured conductance due to solvent correction is going to be very large. For the example given above it could amount to 1% of the measured conductance. This is, in fact, the critical point of the solvent correction: the nature of the ions causing the solvent conductance is not always known exactly. Through a series of distillations or passages through ion-exchange resins, or both, it is hoped that the conductivity water obtained at the end is completely demineralized. In this case the residual conductance is assumed to be due to $H^+$, $OH^-$, and $HCO_3^-$ ions which result from the self-dissociation of the water and from the reaction of $CO_2$ (very small amounts) with water. Some experimental results fit this assumption. 69
In this case the equilibria present are:

\[ H_2O \xrightleftharpoons{K_w} H^+ + OH^- \]  \hspace{1cm} (5.9.1)

\[ H_2CO_3 \xrightleftharpoons{K_I} H^+ + HCO_3^- \]  \hspace{1cm} (5.9.2)

\[ HCO_3^- \xrightleftharpoons{K_{II}} H^+ + CO_3^{2-} \]  \hspace{1cm} (5.9.3)

The dissociation constants involved are known quantities. Also known are the infinite conductances of the ions present. Hence it is easy to compute the concentration of CO\(_2\) which gives the measured solvent conductance when equilibria (5.9.1), (5.9.2) and (5.9.3) are the only ones present.\(^70\)

The problem is solved by writing down the expressions for the constants involved and also the equation for the electrical balance of the medium:

\[ [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \]  \hspace{1cm} (5.9.4)

\[ K_w = [H^+] \times [OH^-] = [OH^-] = K_w/[H^+] \]  \hspace{1cm} (5.9.5)

\[ K_I = \frac{[H^+] [HCO_3^-]}{[H_2CO_3]} = \frac{[H^+] [HCO_3^-]}{c - [HCO_3^-] - [CO_3^{2-}]} \]  \hspace{1cm} (5.9.6)

\[ K_{II} = \frac{[H^+] [CO_3^{2-}]}{[HCO_3^-]} \]  \hspace{1cm} (5.9.7)

where \(c\) is the concentration of CO\(_2\).
From the last two expressions:

\[
[HCO_3^-] = \frac{K_Ic}{K_I + \frac{K_{II}c}{[H^+]}} + [H^+] \quad (5.9.8)
\]

\[
[CO_3^{2-}] = \frac{K_{II}c}{K_I[H^+] + K_{II}[H^+] + [H^+]^2} \quad (5.9.9)
\]

Substituting (5.9.5), (5.9.8) and (5.9.9) in (5.9.4) the following relation is obtained:

\[
[H^+]^4 + K_I[H^+]^3 + (K_{II} - K_W - K_Ic)[H^+]^2 -
\]

\[
(K_WK_I + 2K_{II}c)[H^+] - K_{II}K_W = 0 \quad (5.9.10)
\]

Equation (5.9.10) can be solved for [H^+]. Once [H^+] is known [HCO_3^-] and [CO_3^{2-}] can be calculated.

If the dissociation of HCO_3^- is considered negligible (equilibrium 5.9.3) (5.9.10) takes the following form:

\[
[H^+]^3 + K_I[H^+]^2 - (cK_I + K_W)[H^+] - K_WK_I = 0 \quad (5.9.11)
\]

and:

\[
[OH^-] = \frac{K_W}{[H^+]} \quad (5.9.12)
\]

\[
[HCO_3^-] = \frac{K_Ic}{K_I + [H^+]} \quad (5.9.13)
\]

The symbols have exactly the same significance as before.
If the concentration of the ions is known the conductance of the solvent can be calculated from:

$$\Lambda_{H_2O} = \Lambda^o_{H^+}[H^+] + \Lambda^o_{OH^-}[OH^-] + \Lambda^o_{HCO_3^-}[HCO_3^-] +$$

$$\Lambda^o_{CO_3^{2-}}[CO_3^{2-}]$$

(5.9.14)

If the dissociation of $HCO_3^-$ is neglected then the last term in (5.9.14) is zero. In (5.9.14) we used the conductance at infinite dilution ($\Lambda^o$'s) for the ions. The approximation is justified at the very small concentrations with which we are dealing.

A series of tables were computed which give the specific conductance of water as a function of $CO_2$ concentration, at 25°C. The computation was done for both cases, i.e. with and without equilibrium 5.9.3 present. When the dissociation of the $HCO_3^-$ ion was considered the resulting concentration of the $CO_3^{2-}$ ion was very small thus justifying the assumption that equilibrium 5.9.3 is negligible. The "Detailed Calculations" are given in 5.9.1 and 5.9.2. The computer programs used for these calculations are given in appendices 5.9.1 and 5.9.2.

Notice that in these calculations we used the so called "apparent" dissociation constant of $H_2CO_3$, that is, the equilibrium constant for the reaction:

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$$
The "true" ionization constant of carbonic acid is defined as being the equilibrium constant for the reaction:

\[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \]

At 25°C the "apparent" dissociation constant, \( K_I \), is \( 4.45 \times 10^{-7} \) while the "true" dissociation constant is \( 1.72 \times 10^{-4.71} \).

The situation is somewhat different if the solvent conductance is caused by some other ions, e.g. ions from the glass.

If we denote these ions by \( G^+ \) and \( G^- \) then the electrical balance equation and the equilibria present in the solvent are:

\[ [\text{H}^+] + [G^+] = [\text{OH}^-] \quad [G^-] \quad (5.9.15) \]

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad (5.9.16) \]

\[ G^- + \text{H}^+ \rightleftharpoons \text{GH} \quad (5.9.17) \]

These relations lead to an equation in \([\text{H}^+]\):

\[ [\text{H}^+]^3 + [\text{H}^+]^2(K_{\text{GH}} + [G^+]) - K_w[H^+] - K_wK_{\text{GH}} = 0 \quad (5.9.18) \]

If the nature of the ions \( G^+ \) and \( G^- \) is known and also, if \( K_{\text{GH}} \) is a known quantity then, exactly analogous to the previous case, (5.9.18) can be solved for a series of assumed \([G^+]\) and \( \Lambda_{\text{H}_2\text{O}} \) calculated from an equation similar to 5.9.14. A table giving the solvent conductance as a function of \([G^+]\) is then obtained. This table, as the previous one which gives the solvent conductance as a function of \( \text{CO}_2 \) concentration, can be used to find the concentration of the species
causing the solvent conductance. This value is used later to calculate the solvent correction.

Solvent correction

It has been mentioned before that the solvent correction depends on the nature of the ions present in the "pure" solvent and on the nature of the solute.

With regard to the nature of the ions in the solvent usually it is assumed that the impurity is CO$_2$. No direct proof of this exists. In many cases the experimental conditions are such that the presence of CO$_2$ in very unlikely. In such cases the presence of trace amounts of ions from the slow dissolving glass could be an equally valid, if not better, assumption.

In a very few cases some compound is added intentionally to the solvent as in the baryta method.$^{69}$

With regard to the nature of the solute, some special cases of interest to us will be treated in more detail.

Salt of a strong acid and a strong base

The typical example for this group of solutes is potassium chloride, which is used to obtain the cell constant.

The solvent correction in this case is what is called a "normal correction" and consists of:$^{24,72}$

$$L_{sp,corr} = L_{sp,obs} - L_{sp,H_2O}$$  \hspace{1cm} (5.9.19)

where $L_{sp}$ is the specific conductivity
or in terms of resistances:

\[
\frac{1}{R_{\text{corr}}} = \frac{1}{R_{\text{obs}}} - \frac{1}{R_{H_2O}} \tag{5.9.20}
\]

To obtain an idea of the magnitude of the corrections, take some arbitrary values:

\[
R_{\text{obs}} = 30,000 \, \Omega \\
R_{H_2O} = 3 \times 10^7 \, \Omega \\
R_{\text{corr}} = 30,033 \, \Omega \\
\%	ext{ correction} = 0.11
\]

The above values correspond (if the cell constant is 3) to a potassium chloride solution of \(1 \times 10^{-3}\) N concentration and conductivity water of \(1 \times 10^{-7}\) mho specific conductance.

If the specific conductance of water is known with a 10% accuracy the uncertainty in the solution conductance is 0.01% 

Salt of a weak acid and a strong base

The typical salts belonging to this group are the sodium or potassium salts of some organic acids (acetic, benzoic). The problem of solvent correction for these salts was studied by Jeffery, Vogel and Lowry and Ives.\(^{69,73}\)

They assume that the conductivity water contains \(CO_2\) only. Then, the equilibria present are:

\[
MA \rightleftharpoons M^+ + A^- \tag{5.9.21}
\]

\[
H_2O \underset{K_w}{\rightleftharpoons} H^+ + OH^- \tag{5.9.22}
\]
\[ H_2CO_3 \rightleftharpoons K_I H^+ + HCO_3^- \]  
\[ A^- + H^+ \rightleftharpoons AH \]  
\[ K_d \]  
(5.9.23)  
(5.9.24)  
(5.9.24)

The relation for the electrical balance is:
\[ [H^+] + [M^+] = [OH^-] + [HCO_3^-] + [A^-] \]  
(5.9.25)

If:
\[ [M^+] = c_M \]  
and
\[ [CO_2] = c \]  
(5.9.26)

then the following equalities can be written assuming negligible
\[ [CO_3^{2-}] \] :
\[ [HCO_3^-] = \frac{K_I c}{[H^+] + K_I} \]  
(5.9.27)
\[ [OH^-] = \frac{K_w}{[H^+]} \]  
(5.9.28)
\[ [A^-] = \frac{K_d c_M}{[H^+] + K_d} \]  
(5.9.29)

Substituting relations (5.9.26) to (5.9.29) into (5.9.25) an equation of fourth degree in \([H^+]\) is obtained:
\[ [H^+]^4 + p[H^+]^3 + q[H^+]^2 - r[H^+] - s = 0 \]  
(5.9.30)

where:
\[ p = K_I + K_d + c_M \]
\[ q = K_I c_M + K_d K_I - K_I c - K_w \]
\[ r = K_I K_d c + K_W K_I + K_W K_d \]  
\[ s = K_I K_W K_d \]

Equation (5.9.30) is solved for \([H^+]\) and then \([A^-], [HCO_3^-]\) and \([OH^-]\) are calculated using the appropriate expressions. The solvent correction is:

\[
\Lambda_{corr} = \Lambda_{obs} + \left\{ \Lambda_{A^-}^O - (c_M - [A^-]) - \Lambda_{H^+}^O[H^+] - \Lambda_{HCO_3^-}^O[HCO_3^-] - \Lambda_{OH^-}^O[OH^-] \right\} \frac{1}{c_M}
\]  
\[ (5.9.32) \]

When the impurity in the conductivity water consists of some other ions the calculation of the solvent correction should follow a similar path.

An example of such a calculation is given in "Det. calc. - 5.9.4". The results are summarized in table 5.9.1.

<table>
<thead>
<tr>
<th>Assumed values:</th>
<th>(c_M = 5.0 \times 10^{-4}) g-equiv/l</th>
<th>(c_M = 5.0 \times 10^{-3}) g-equiv/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L_{sp,H_2O} \times 10^7)</td>
<td>0.986</td>
<td>1.103</td>
</tr>
<tr>
<td>(c \times 10^7)</td>
<td>2.89</td>
<td>3.61</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Results:</th>
<th>([H^+] \times 10^8)</th>
<th>([A^-] \times 10^4)</th>
<th>([HCO_3^-] \times 10^7)</th>
<th>([OH^-] \times 10^7)</th>
<th>(\Lambda_{corr - \Lambda_{obs}})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.112</td>
<td>5.605</td>
<td>6.505</td>
<td>1.308</td>
<td>1.359</td>
</tr>
<tr>
<td></td>
<td>4.996</td>
<td>4.996</td>
<td>4.995</td>
<td>4.999</td>
<td>4.999</td>
</tr>
<tr>
<td></td>
<td>2.592</td>
<td>3.206</td>
<td>4.258</td>
<td>2.807</td>
<td>3.503</td>
</tr>
<tr>
<td></td>
<td>1.972</td>
<td>1.798</td>
<td>1.550</td>
<td>7.705</td>
<td>7.417</td>
</tr>
<tr>
<td></td>
<td>-0.112</td>
<td>-0.111</td>
<td>-0.112</td>
<td>-0.027</td>
<td>-0.027</td>
</tr>
<tr>
<td></td>
<td>(\Lambda_{corr})</td>
<td>104.06</td>
<td>100.56</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\( \Lambda_{\text{corr}} \) was calculated from: 74

\[
\Lambda_{\text{corr}} = 105.88 - 83.87 \, c^\pm + 122.9 \, c(1 - 0.2274 \, c^\mp)
\]

This equation reproduces the conductance of aqueous solutions of sodium benzoate.

Other constants used in the calculation are:

\( K_w = 1.008 \times 10^{-14} \)  
(Ref. 75)

\( K_I = 4.47 \times 10^{-7} \)  
(Ref. 76)

\( \Lambda_{HCO_3}^0 = 44.50 \)  
(Ref. 77)

\( \Lambda_{H}^0 = 350.15 \)  
(Ref. 78)

\( \Lambda_{OH^-}^0 = 199.18 \)  
(Ref. 78)

\( K_d = 6.3 \times 10^{-5} \)  
(Ref. 74)

(the dissociation constant of benzoic acid)

\( \Lambda_{A^-}^0 = 31.85 \)  
(Ref. 74)

(the limiting conductance of the benzoate anion)

The solvent correction is fairly large, 0.1%, for concentrations of the order of \( 5.0 \times 10^{-4} \) g-equiv/l. For more concentrated solutions, say when the concentration is greater than \( 5.0 \times 10^{-3} \) g-equiv/l, the solvent correction is very small and it can be neglected. Note also that an increase of 50\% in the CO\(_2\) concentration did not alter significantly the solvent correction.
Besides this method of correction the published data on this type of salt were corrected in several other ways:

a. No correction at all.\textsuperscript{74,79}

b. Normal solvent correction.\textsuperscript{80}

c. A part (arbitrarily established) is assumed to be due to a salt impurity and as such is subtracted from the measured conductance of the salt solution. The rest of the solvent conductance is assumed to be due to CO\textsubscript{2}. Nothing is done with this part of the solvent conductance because the solutions are considered to have a slight acidic character and because of this the dissociation of the carbonic acid is negligible.\textsuperscript{81}

d. A graphic interpolation method. The interpolation is between the uncorrected values and the values to which the normal solvent correction was applied.\textsuperscript{18,82,83}

**Weak acid**

The organic acids we studied (benzoic acids) belonged to this group.

The same considerations as in the case of a salt of a weak acid and a strong base are valid here. If the solvent impurity is CO\textsubscript{2}, upon the addition of a weak acid, HA, the equilibria present are:

\begin{align*}
    \text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^- \\
    \text{H}_2\text{CO}_3 & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \\
    \text{HA} & \rightleftharpoons \text{H}^+ + \text{A}^-
\end{align*}

\textit{(5.9.33)}
Note that the concentration of ion $A^-$ is smaller than it would have been if no $CO_2$ had been present.

The electrical balance equation is:

$$[H^+] = [OH^-] + [A^-] + [HCO_3^-]$$  \hspace{1cm} (5.9.34)

The concentration of the various species is given by:

$$[OH^-] = \frac{K_w}{[H^+]}$$  \hspace{1cm} (5.9.35)

$$[HCO_3^-] = \frac{K_I c}{K_I + [H^+]}$$  \hspace{1cm} (5.9.36)

$$[A^-] = \frac{K_{dHA} c}{K_d + [H^+]}$$  \hspace{1cm} (5.9.37)

where $c_{HA}$ is the total concentration of the acid HA and $c$ is the total concentration of the $CO_2$.

Substituting (5.9.35), (5.9.36) and (5.9.37) into (5.9.34) a relation completely analogous to (5.9.30) is obtained:

$$[H^+]^4 + p[H^+]^3 + q[H^+]^2 - r[H^+] - s = 0$$  \hspace{1cm} (5.9.30)

where:

$$p = K_d + K_I$$

$$q = K_I K_d - K_I c - K_w - K_{dHA}$$  \hspace{1cm} (5.9.38)

$$r = K_I K_d (c + c_{HA}) + K_w (K_d + K_I)$$

$$s = K_w K_I K_d$$
Relation (5.9.30) can be solved for $[H^+]$ and hence $[A^-]$, $[OH^-]$ and $[HCO_3^-]$ are calculated.

The solvent correction is:

$$
\Lambda_{\text{corr}} = \Lambda_{\text{obs}} + (\Lambda_A^0 - ([H^+] - [A^-]) - \Lambda_{OH^-}^0 - [OH^-]) - \Lambda_{HCO_3^-}^0 - [HCO_3^-]) \frac{1}{c_{HA}}
$$

(5.9.39)

Another possibility is:

$$
\Lambda_{\text{corr}} = \Lambda_{\text{obs}} - (\Lambda_{H^+}^0([HCO_3^-] + [OH^-]) + \Lambda_{OH^-}^0 - [OH^-]) + \Lambda_{HCO_3^-}^0 - [HCO_3^-]) \frac{1}{c_{HA}}
$$

(5.9.40)

An example of such a calculation is given below (see also "Detailed calculations - 5.9.3"). All values are for 25°C.

$$
K_w = 1.008 \times 10^{-14}
$$

(Ref. 75)

$$
K_I = 4.45 \times 10^{-7}
$$

(Ref. 76)

$$
\Lambda_{HCO_3^-} = 44.50
$$

(Ref. 59, 77)

$$
\Lambda_{H^+} = 350.15
$$

(Ref. 78)

$$
\Lambda_{OH^-} = 199.18
$$

(Ref. 78)

Assumed values:

$$
\Lambda_A^0 = 30.15
$$

$$
K_d = 4.9 \times 10^{-5}
$$
(These two values correspond to the values for the infinite conductance of the phenylacetate anion and the dissociation constant of phenylacetic acid, respectively. - J.F.J. Dippy and F.R. Williams, J. Chem. Soc., 161 (1934)).

\[
\begin{align*}
    c_{HA} &= 5.0 \times 10^{-4} \text{ g-equiv/l soln} \\
    c &= 2.9 \times 10^{-7} \text{ g-equiv/l soln}
\end{align*}
\]

The concentration of CO\textsubscript{2} corresponds to a specific conductance of 0.986 \times 10^{-7} mho (see "Detailed calculations - 5.9.2").

The results are:

\[
\begin{align*}
    [H^+] &= 1.383 \times 10^{-4} \text{ grams-equiv/litre soln} \\
    [A^-] &= 1.383 \times 10^{-4} \text{ grams-equiv/litre soln} \\
    [HCO_3^-] &= 9.27 \times 10^{-10} \text{ grams-equiv/litre soln} \\
    [OH^-] &= 7.29 \times 10^{-11} \text{ grams-equiv/litre soln}
\end{align*}
\]

Thus the solvent correction (using (5.9.40) which gives a larger correction) is of the order of $8 \times 10^{-4}$ while \(\Lambda_{obs}\) is approximately 99 mho. Thus if it is assumed that the sole impurity in the conductivity water is CO\textsubscript{2}, it is perfectly justified not to apply any solvent correction to the measured values of acid solutions.

If however the impurity is something else, depending on its nature the solvent correction could have any value from zero to the value of the normal solvent correction.
The most common assumption is that the impurity is CO2 and thus the measured conductivities are not corrected.

Other solvent corrections applied to the acid solutions are:

- normal solvent correction.80,84
- part of the solvent conductance (a fixed value of 1 x 10^{-7} mho, arbitrarily chosen) is assumed to be due to some salt impurity and as such is subtracted from the conductance of the solution. The remaining part (A_{H2O} - 1 x 10^{-7}) is neglected since it is considered to be due to CO2.81

Preparation of conductivity water and its conductance

The apparatus for obtaining conductivity water is shown in fig. 5.9.1 and is a modification of that used by Robertson and Van der Linde.85

The resistance of the water was measured by following exactly the same procedure used with the KCl solution with the obvious exception of adding the salt, although, an empty tube identical to that used in adding KCl was put into the water. (see subsection 5.10)

The resistance was measured in the temperature range of 20 to 40°C. The detailed results of these measurements are shown in "Detailed Calculations - 5.9.5". As in the case of KCl solutions, the experimental data were fitted in different polynomials in order to obtain, by interpolation, the conductance value at any temperature in the specified range. The expressions tried were the same as in the case of KCl. The detailed results of these calculations are
shown in "Detailed calculations - 5.4.1, sets 6 and 7". A summary is given in tables 5.9.1 and 5.9.3.

Table 5.9.2

<table>
<thead>
<tr>
<th>Set</th>
<th>No. of points</th>
<th>Cell constant</th>
<th>Temperature range °C</th>
<th>Resistance range ohms</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>5</td>
<td>0.060</td>
<td>19.365</td>
<td>40.518</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.397x10^5</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>2.8345</td>
<td>19.690</td>
<td>40.378</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.753x10^7</td>
</tr>
</tbody>
</table>

As in the case of potassium chloride expression (5.4.23) was used for further computations.

Because of the high resistance of conductivity water, when its conductance was measured a resistance was connected in parallel with the cell containing the water sample. The value of the parallel resistance was 100,000 Ω when using cell No. 3 and 110,000 Ω when using cell No. 4.

The detailed results of the measurements of solvent resistance are given in "Det. calc. - 5.9.5". In table 5.9.4 the average specific conductance of our water is given at five different temperatures together with literature data. The table also includes a series of values calculated from an equation given by Marsh and Stokes.78 The equation which gives the theoretical specific conductance of water is:

\[ \text{L}_{\text{sp}, \text{H}_2\text{O}} \times 10^7 = 0.5498 + 2.9328 \times 10^{-2}(T-25) + 6.0629 \times 10^{-4}(T-25)^2 \]
\[ + 4.269 \times 10^{-6}(T-25)^3 \]

(5.9.41)

where T is the temperature in °C.
### Table 5.9.3

<table>
<thead>
<tr>
<th>Set</th>
<th>Relation</th>
<th>5.4.21</th>
<th>5.4.22</th>
<th>5.4.23</th>
<th>5.4.24</th>
<th>5.4.25</th>
<th>5.4.26</th>
<th>5.4.27</th>
<th>5.4.28</th>
<th>5.4.29</th>
<th>5.4.30</th>
<th>5.4.31</th>
<th>5.4.32</th>
<th>5.4.33</th>
<th>5.4.34</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Ω</td>
<td>14890</td>
<td>1825</td>
<td>155</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>2.75</td>
<td>0.34</td>
<td>0.029</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>x 10^4</td>
<td>x 10^4</td>
<td>x 10^4</td>
<td>x 10^4</td>
<td>x 10^4</td>
<td>x 10^4</td>
<td>x 10^4</td>
<td>x 10^4</td>
<td>x 10^4</td>
<td>x 10^4</td>
<td>x 10^4</td>
<td>x 10^4</td>
<td>x 10^4</td>
<td>x 10^4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>7.27</td>
<td>2.98</td>
<td>0.062</td>
<td>16.3</td>
<td>4.96</td>
<td>10.6</td>
<td>3.12</td>
<td>6.87</td>
<td>2.27</td>
<td>16.1</td>
<td>3.42</td>
<td>6.87</td>
<td>2.27</td>
<td>16.1</td>
</tr>
</tbody>
</table>

| No. of adj. param. | 2 | 3 | 4 | 5 | 2 | 3 | 4 | 5 | 2 | 3 | 2 | 3 | 2 | 3 |

Notes: 1. Mean square deviation is calculated from:

\[
MSD = \left( \frac{(R_{\text{obs}} - R_{\text{calc}})^2}{\text{No. of points} - 1} \right)^{\frac{1}{2}}
\]

2. % Mean square deviation is calculated from:

\[
MSD(\%) = \frac{MSD \text{ (in } \Omega)}{R_{\text{max}} + R_{\text{min}}} \times 100
\]

\[R_{\text{max}} \text{ and } R_{\text{min}} \text{ are given in Table (5.9.2)}\]
Table 5.9.4: Calculated and observed values for the specific conductivity of water

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Specific conductivity of water x 10^7 mho</th>
<th>Equation (5.9.41)</th>
<th>Our water (av. value)</th>
<th>Ref. 1</th>
<th>Ref. 2</th>
<th>Ref. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.4179</td>
<td>0.745</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.8*</td>
</tr>
<tr>
<td>25</td>
<td>0.5498</td>
<td>0.922</td>
<td>5</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.7121</td>
<td>1.15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>0.7121</td>
<td>1.43</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1.141</td>
<td>1.78</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
<td></td>
<td>9</td>
<td>21</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Temperature not specified.


5.10. Determination of cell constant of cells No. 3 and No. 4

The preparation of potassium chloride for conductivity measurements.

The procedure described by Bates and Pinching was followed. "Fisher reagent grade" potassium chloride was recrystallized twice from conductivity water. This salt was used to prepare a saturated solution at room temperature. Conductivity water was used for the solution. The solution was filtered through a sintered glass funnel. Previous to this operation the funnel was thoroughly cleaned and steamed for a few hours. Chlorine gas (from a small cylinder) was bubbled for 15 minutes through the filtered solution. Then the solution was boiled for 10 minutes to remove any free halogens it might contain. When the solution cooled, to the room temperature, the potassium chloride was precipitated from it by bubbling in gaseous HCl from a small cylinder. The precipitated
salt was collected on a sintered glass funnel, washed a few times with small portions of conductivity water and dried for 12 hours in an oven at 180°C.

The dry salt was placed in a Vycor tube (10 mm o.d.). The tube was evacuated and sealed off. Then it was placed in a tubular, electrical furnace. The salt was melted in a small zone while the tube was moving slowly through the furnace. Two passes top-bottom were performed. The operation had a rough similarity to a zone refining procedure. We tried to use a commercial "Fisher zone refiner" with the Vycor tube containing the potassium chloride salt. It did not work. The heat generated by the two heating coils of the instrument was not sufficient to melt the salt inside the tube.

The middle part of the salt from the Vycor tube was used for the conductance measurements.

The preparation of solutions of potassium chloride

The solutions were made up by weight.

The salt was weighed by difference in a small Pyrex tube of approximately 5 mm diameter and 4 cm in length closed at one end. Previously these tubes were steamed and stored in a desiccator. A Mettler microbalance was used for weighings.

The water was collected directly into a 2 l flask (fig. 5.10.1) from the conductivity water apparatus. The whole system was under a slight positive nitrogen pressure.

The weight of the water was obtained by difference. A Mettler P-1200 was used for these weighings. The balance has a readability of 0.02 g.
The procedure for the preparation of a solution is as follows:

a. the flask is steamed for 30 minutes, rinsed four times with conductivity water and air dried.

b. the flask is filled with purified nitrogen. The filling is done by connecting the flask to a vacuum line and to a purified nitrogen line (see next) through a 2-way stopcock. The flask is evacuated, then filled with nitrogen, evacuated again and so on. The cycle is repeated six times. The last time the flask is filled with nitrogen a slightly positive pressure is created in the flask.

c. the empty flask is weighed. When this operation is completed the flask is connected to the conductivity water apparatus. Parts A and B are flushed with purified nitrogen for 30 minutes. Then stopcock C is closed and D is opened admitting water into the flask. Note that the flask is kept under a positive nitrogen pressure at all times.

d. when enough water is collected, stopcock D is closed and the flask is disconnected from the conductivity water apparatus. The flask with water is weighed. Then the small tube containing the solute, directly from the microbalance, is placed in part A of the flask.

e. the flask is connected to the purified nitrogen line. Stopcock C is opened and nitrogen flushed through A and B for approximately 5 minutes. Then, with the nitrogen still going, C is closed and D is opened letting the tube
containing the salt fall inside the flask. D is closed maintaining in this way a small positive pressure inside the flask.

f. the flask is disconnected from the nitrogen line and shaken vigorously. In this way the small tube containing the solute is broken allowing its contents to come in contact with the solvent.

In the case of potassium chloride solutions the flask is continuously shaken, with an automatic shaker, for one hour to make sure the dissolution is complete. In the case of organic acid solutions the flask is left in the shaker overnight.

Before each run the cell is steamed for 20 minutes, rinsed four times with conductivity water, and air dried overnight. The cell is filled with the solution to be measured just before starting a run. The filling is done in the following way: the cell is attached to the flask containing the solution through the ground glass joint F (see fig. 5J0.2). The flask itself is attached to the purified nitrogen line. The cell is flushed with nitrogen for 40 minutes, approximately. Stopcocks C (flask), H and M are opened during this time. To admit the solution into the cell stopcock M is closed, stopcocks L, D and E are opened and stopcock C is closed, in this order. To empty the cell, stopcock C is opened, stopcocks E and L are closed, and M is opened. Thus the cell is emptied by nitrogen pressure. The filling and emptying operations are repeated twice. Then a small amount of solution is admitted into the cell and evacuated. This is repeated three times. Finally the cell is
FIG. 5.10.1.

FLASK USED TO PREPARE THE SOLUTIONS FOR CONDUCTIVITY MEASUREMENTS
FIG. 5.10.2.

CONDUCTIVITY CELL - (SCHEMATIC)
filled with solution. When the cell is completely filled, stopcock C is opened and stopcocks E and M are closed. After approximately 15 seconds H is closed and C and D are closed. Thus a slight positive pressure of nitrogen is created inside the cell. Now the cell is ready to be placed in the thermostat bath.

The purification of nitrogen

Nitrogen was purified by passing it through two washing towers, connected in series, 3/4 filled with the following mixture: sodium chunks (10 g), benzophenone (50 g) and tetracycline (500 cm³). Before it is ready for use, the mixture must be stirred for approximately 12 hr in a closed flask, at room temperature. The colour, which is yellow at the beginning, turns to a deep blue when the mixture is ready for use. A few more sodium chunks are added to each of the two towers before the mixture is poured into them. A trap with glass beads and a cold (liquid nitrogen) trap connected after and in series with the washing towers prevented any carry-over.

Vacuum correction

All weighings were corrected for the buoyancy of air.

The weight of an object measured in air is corrected by the following formula:

\[ w_v = w_a + w_a \left( \frac{0.0012}{d} - \frac{0.0012}{d_1} \right) \]  \hspace{1cm} (5.10.1)

where \( w_v \) is the corrected weight, \( w_a \) is the weight of the object in air, \( d_1 \) is the density of the material used for the weights and \( d \) is the density of the object.

We used \( d_1 = 7.8 \) (stainless steel) and \( d = 1.984 \) for KCl and \( d = 1.0 \) for water.
Calculation of the cell constant

Schematically the cell constant is calculated in the following way:

1. The experimental results, resistance and temperature (five pairs for every solution), are fitted by least square method into a polynomial of the form (5.4.23). The least square method is carried out assuming errors in both resistance and temperature and using weighed values. The mathematical details are shown in appendix (5.10.1).

2. Values of resistance at five temperatures; 20, 25, 30, 35 and 40°C are obtained by interpolation from the above polynomial.

3. A "normal" solvent correction (equation (5.9.20)) is applied to the values calculated in point 2. The values for the resistance of water are those given in table 5.9.4.

4. The experimental value of concentration, in units of g solute/kg solution, corrected for the buoyancy of air is transformed to g-equiv solute/l solution at each of the five temperatures mentioned above.

5. The equivalent conductance of each solution, at each of the five temperatures is calculated using equation (5.4.15).

6. Finally the cell constant is obtained using relations (5.1.2) and (5.1.3) which combine to give:

\[ k = L \cdot \left( R = \frac{AcR}{1000} \right) \]  

(5.10.2)

where \( k \) is the cell constant, \( R \) is the resistance (in Ω), \( c \) is the concentration of the solution (in g-equiv/l) and \( \Lambda \) is the equivalent conductance of the KCl solution calculated from (5.4.15).
"Det. calculations 5.10.2 - 5.10.4" give the complete calculations and results. A summary of these results follows.

The cell constant was calculated separately for each individual cell of a double cell, i.e. cells nos. 3A, 3B, 4A and 4B, and also for the double cell as a whole. The latter was obtained from:

\[
k = \frac{Ac(R_A - R_B)}{1000}
\]  \hspace{1cm} (5.10.3)

where \(R_A\) and \(R_B\) are the resistance values of the two individual cells of the double cell at 20, 25, ..., 40°C as calculated by interpolation from (5.4.23) and after the solvent correction was applied. We will call this type of cell constant "differential cell constant".

In all cases the change in the cell constant with temperature was within the experimental error and as such we calculated an average cell constant from the values at the five temperatures. There were 18 values in the case of cells nos. 3A and 3B (4 solutions at 5 temperatures with two points left out as they, obviously, were "bad" points) and 25 values in the case of cells nos. 4A and 4B (5 solutions at 5 temperatures). It must be mentioned that the constants for cells nos. 4A and 4B showed a change with temperature slightly beyond the experimental error. This became evident when the mean square deviation for the average cell constant at all temperatures had double the value of the mean square deviation at each of the five individual temperatures. Nevertheless we decided to use a unique cell constant at all temperatures (and all frequencies as we will see later) since its mean square deviation, as large as it was, was predictable on experimental grounds:
<table>
<thead>
<tr>
<th>Estimated relative error</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Weight of the solute (by difference)</td>
</tr>
<tr>
<td>b. Weight of the solvent (by difference)</td>
</tr>
<tr>
<td>c. Solvent correction (due to variation in the solvent conductance)</td>
</tr>
<tr>
<td>d. Interpolation method (R vs. T)</td>
</tr>
<tr>
<td>e. Frequency variation</td>
</tr>
<tr>
<td><strong>Total</strong></td>
</tr>
</tbody>
</table>

There are other sources of error in an experiment of this type as those related to the purity of the solute used and to the transfer of the solute into the flask containing the solvent. However we have no quantitative data for them.

Referring to the Feates, Ives and Pryor double cell,\(^{39}\) it should be noted that the accuracy of the cell constants was of the order of 0.06% for one of the individual cells and of the order of 0.4% for the other. In taking the difference of the two cell constants the results improved dramatically to ± 0.005%. This remarkable fact was attributed to a cancellation of errors due to electrode effects (ion absorption, transfer resistance, etc.). It is very likely that other cancellations occurred at the same time. The experimental details predict a larger error.

The average cell constants at different frequencies are given in table 5.10.1.
Table 5.10.1: Average cell constants and their mean square deviation

<table>
<thead>
<tr>
<th>Freq. Hz</th>
<th>3A</th>
<th>3B</th>
<th>4A</th>
<th>4B</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>4.8466 ± 0.0017</td>
<td>2.8456 ± 0.0013</td>
<td>2.4691 ± 0.0009</td>
<td>1.6967 ± 0.0005</td>
<td>2.0013 ± 0.0012</td>
<td>0.7724 ± 0.0006</td>
</tr>
<tr>
<td>2000</td>
<td>4.8453 ± 0.0017</td>
<td>2.8447 ± 0.0012</td>
<td>2.4691 ± 0.0008</td>
<td>1.6967 ± 0.0005</td>
<td>2.0008 ± 0.0013</td>
<td>0.7724 ± 0.0007</td>
</tr>
<tr>
<td>3500</td>
<td>4.8444 ± 0.0017</td>
<td>2.8442 ± 0.0012</td>
<td>2.4692 ± 0.0008</td>
<td>1.6969 ± 0.0004</td>
<td>2.0004 ± 0.0014</td>
<td>0.7724 ± 0.0006</td>
</tr>
<tr>
<td>5000</td>
<td>4.8441 ± 0.0016</td>
<td>2.8441 ± 0.0012</td>
<td>2.4694 ± 0.0008</td>
<td>1.6970 ± 0.0004</td>
<td>2.0003 ± 0.0015</td>
<td>0.7724 ± 0.0006</td>
</tr>
</tbody>
</table>

It can be seen from the above table that the "differential" cell constants do not show any improvement over the average cell constants. In fact the mean square deviation is larger in the case of the former. This is not unexpected since the "differential" cell constants, as the name implies, are the result of a difference and it is well known that the error of the result of a difference is the sum of the absolute errors of the individual quantities. In some cases when taking the difference a cancellation of the systematic errors may occur and thus the "differential" cell constant can have a smaller mean square deviation. This happens in our case with the one "bad" point of solution 3, for cells 3A and 3B. In taking the difference the error, which is probably the same in both cell constants (very likely a wrong temperature value), cancels out and the point becomes "good" when calculating the "differential" cell constant of cell no. 3.
With respect to the frequency the average cell constants or the "differential" cell constants show a variation which is within the experimental error. Because of this we decided to calculate "overall" averages: a single value for every individual cell, i.e. nos. 3A, 3B, 4A and 4B, which is the average of the values at all five temperatures and four frequencies used by us. These values and their mean square deviation are given in table 5.10.2.

Table 5.10.2: Cell constants and their mean square deviation for temperatures from 20 to 40°C and frequencies between 1000 and 5000 Hz.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Cell constant</th>
<th>Mean sq. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3A</td>
<td>4.8451</td>
<td>0.0019</td>
</tr>
<tr>
<td>3B</td>
<td>2.8446</td>
<td>0.0014</td>
</tr>
<tr>
<td>3</td>
<td>2.0007</td>
<td>0.0014</td>
</tr>
<tr>
<td>4A</td>
<td>2.4692</td>
<td>0.0008</td>
</tr>
<tr>
<td>4B</td>
<td>1.6968</td>
<td>0.0004</td>
</tr>
<tr>
<td>4</td>
<td>0.7724</td>
<td>0.0006</td>
</tr>
</tbody>
</table>

For the sake of comparison, we calculated the cell constant, at 25°C only, by using the conductance equation (5.2.1) to obtain $A$. The results are given in table 5.10.3. They are significantly different from those obtained when using relation (5.4.15) (table 5.10.2).

We will see, however, when discussing the errors involved in the determination of the dissociation constant of an acid by conductance methods, that the accuracy of the cell constant has very
little effect on the accuracy of the limiting conductance and of the
dissociation constant.

Table 5.10.3: Cell constants (calculated via relation 5.2.1) and
their mean square deviation

<table>
<thead>
<tr>
<th>Cell</th>
<th>Cell constant</th>
<th>Mean sq. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3A</td>
<td>4.8351</td>
<td>0.0023</td>
</tr>
<tr>
<td>3B</td>
<td>2.8381</td>
<td>0.0017</td>
</tr>
<tr>
<td>3</td>
<td>1.9970</td>
<td>0.0009</td>
</tr>
<tr>
<td>4A</td>
<td>2.4638</td>
<td>0.0013</td>
</tr>
<tr>
<td>4B</td>
<td>1.6933</td>
<td>0.0010</td>
</tr>
<tr>
<td>4</td>
<td>0.7705</td>
<td>0.0004</td>
</tr>
</tbody>
</table>
6. **CALCULATION OF DISSOCIATION CONSTANT OF A WEAK ACID FROM CONDUCTANCE DATA**

6.1. **Introduction**

Consider the reaction:

\[ HA \rightleftharpoons H^+ + A^- \]  
(6.1.1)

The chemical potential relationship for system (6.1.1) is:

\[ \mu_{HA} = \mu_{H^+} + \mu_{A^-} \]  
(6.1.2)

and also:

\[ \frac{RT \ln \frac{c_{H^+}c_{A^-}f_{H^+}f_{A^-}}{c_{HA}f_{HA}}}{c_{HA}f_{HA}} = \mu_{HA}^0 - \mu_{H^+}^0 - \mu_{A^-}^0 \]  
(6.1.3)

where \( f \) is the molar activity coefficient and \( c \) is the concentration in moles/litre.

Since \( \mu^0 \) is constant at a given temperature, \( K \), the thermodynamic ionization constant at constant pressure, can be defined as:

\[ \mu_{HA}^0 - \mu_{A^-}^0 - \mu_{H^+}^0 = RT \ln K \]  
(6.1.4)

Hence

\[ K = \frac{c_{H^+}c_{A^-}f_{H^+}f_{A^-}}{c_{HA}f_{HA}} \]  
(6.1.5)

If we define \( \alpha \), the degree of dissociation, as being:

\[ \alpha = \frac{\text{concentration of free ions of the solute}}{\text{stoichiometric concentration of the solute}} \]  
(6.1.6)

and if we denote the stoichiometric concentration with \( c \) then:
\[ c_{H^+} = c_{A^-} = c\alpha \]  \hspace{1cm} (6.1.7)

\[ c_{HA} = c(1 - \alpha) \]

Substitution of (6.1.7) in (6.1.5) yields:

\[ K = \frac{c^2 \alpha^2 f_{H^+}f_{A^-}}{(1 - \alpha)c f_{HA}} = \frac{c\alpha^2 f_{H^+}f_{A^-}}{1 - \alpha f_{HA}} \]  \hspace{1cm} (6.1.8)

which is equivalent to Ostwald's dilution law.

According to the classical theory of conductance, \( \alpha \) can be computed from:

\[ \alpha = \frac{\Lambda}{\Lambda^e} \]  \hspace{1cm} (6.1.9)

where \( \Lambda \) is the equivalent conductance at concentration \( c \) and \( \Lambda^e \) is the equivalent conductance at infinite dilution.

Relation (6.1.9) makes no allowance for the change in ionic mobilities with the concentration. A more correct value of \( \alpha \) is given by: \(^88\)

\[ \alpha = \frac{\Lambda}{\Lambda^e} \]  \hspace{1cm} (6.1.10)

where \( \Lambda^e \) is the equivalent conductance of the solute in a completely dissociated state and at a concentration \( c\alpha \).

If we define: \(^89\)

\[ f_{HA} = 1 \]

\[ f_{H^+}f_{A^-} \equiv f_{\pm}^2 \]
substitution of (6.1.10) into (6.1.8) gives:

\[ K = \frac{\Lambda^2 c f^2}{(\Lambda^e - \Lambda)\Lambda^e} \]  

(6.1.11)

Expression (6.1.11) is the basic relation for calculating the ionization constant \( K \) from conductance data. The values of \( \Lambda \) and \( c \) are obtained experimentally and substituted into 6.1.11 yielding \( K \).

6.2. Calculation of "f", the activity coefficient

The activity coefficient is defined as the ratio of activity over the concentration of the ion.\(^9\)

Depending on the units used to express the concentration there are the following types of coefficients:

a. Molal activity coefficient, when concentration is expressed in moles solute/kg solvent.

b. Molar activity coefficient when concentration is in moles solute/litre solution.

c. Rational activity coefficient when concentration is in mole fraction.

The relations between these activity coefficients are as follows:

\[ f_{\pm} = y_{\pm} \left( d + 0.001c(\nu w_A - w_B) \right) \]  

(6.2.1)

\[ f_{\pm} = \gamma_{\pm} \left( d - 0.001cw_B \right) = \gamma_{\pm} \frac{c^1d_0}{c} \]  

(6.2.2)

or:

\[ f_{\pm} = \gamma_{\pm}(1 + 0.001c^1w_B) \frac{d_0}{d} \]  

(6.2.3)
\[ y_\pm = \gamma_\pm (1 + 0.001 \nu w_A c^1) \quad (6.2.4) \]

where:
\[ \nu \] is the number of ions formed by the ionization of one mole of solute.
\[ w_A \] is the molecular weight of the solvent.
\[ w_B \] is the molecular weight of the solute.
\[ d \] is the density of the solution.
\[ d_0 \] is the density of the pure solvent.
\[ c^1 \] is the number of moles of solute per kilogram of solvent.
\[ c \] is the number of moles of solute per litre of solution.
\[ f_\pm \] is the mean molar activity coefficient.
\[ \gamma_\pm \] is the mean molal activity coefficient.
\[ y_\pm \] is the mean rational activity coefficient.

For very dilute solutions:
\[ c^1 d_0 = c \]

and thus:
\[ f_\pm = \gamma_\pm \quad (6.2.5) \]

Also for very dilute solutions (c<5.0 x 10^{-3} moles/litre) of 1:1 electrolytes, in water the following relation holds:

\[ y_\pm = \gamma_\pm (1 + 0.001 \times 2 \times 18 \times 0.005) = \gamma_\pm (1 + 1.8 \times 10^{-4}) = 1.00018 \gamma_\pm = \gamma_\pm \quad (6.2.6) \]

From Debye-Hückel theory.\(^{91}\)
\[ \ln y_{\pm} = \frac{|z^+ z^-| e_0^2}{2DkT} \cdot \frac{\kappa}{1 + \kappa a} \] (6.2.7)

where:

\[ \kappa = \left( \frac{8\pi N_A e_0^2}{1000 DkT} \right) \cdot \left[ \frac{z^+}{2} \left( \frac{z^2}{z_+^2} + \frac{z^2}{z_-^2} \right) \right]^{\frac{1}{2}} \] (6.2.8)

\( z^+ \) and \( z^- \) are the charges on the positive and negative ions, respectively.

\( e_0 \) is the charge of the electron in esu.

\( D \) is the dielectric constant of the solvent.

\( k \) is Boltzmann constant.

\( T \) is the absolute temperature.

\( N_A \) is Avogadro's number.

\( a \) is called distance of closest approach and here is taken to be the sum of the radii of the oppositely charged ions.

The substitution of (6.2.8) into (6.2.7) yields:

\[ \log y_{\pm} = - \frac{A |z^+ z^-| c^2}{1 + B a c^2} \] (6.2.9)

where:

\[ A = \left( \frac{2\pi N_A}{1000} \right)^{\frac{1}{2}} \frac{e_0^3}{2 \cdot 303} \cdot \frac{1}{(DkT)^{\frac{1}{2}}} \] (6.2.10)

\[ B = \left( \frac{8\pi N_A e_0^2}{1000 DkT} \right)^{\frac{1}{2}} \] (6.2.11)

It is interesting to note that:

\[ \kappa = B c^{\frac{1}{2}} \] (6.2.12)
For very dilute solutions 6.2.9 becomes:

$$\log y = - A|z_+z_-|c^{3_2}$$

(6.2.13)

In relation (6.2.9) the numerator accounts for the effect of long-range coulombic forces. The denominator takes into consideration the short-range interaction between ions. The model on which the derivation of (6.2.9) is based is that of two non-deformable spheres of equal radii.

To take into consideration the other forces existent in the solution, e.g. interaction between ions and solvent molecules and interactions between non-rigid ions, a new term may be added to (6.2.9):\(^92\)

$$\log y = - \frac{A|z_+z_-|c^{3_2}}{1 + B a c^{3_2}} + bc$$

(6.2.14)

An equation similar to 6.2.14 but with only one adjustable parameter is given by Guggenheim:\(^93\)

$$\log y = - \frac{A|z_+z_-|c^{3_2}}{1 + c^{3_2}} + bc$$

(6.2.15)

Davies\(^94\) considers $b$ as being:

$$b = 0.1 |z_+z_-|$$

(6.2.16)

Useful reviews in the problem of activity coefficients can be found in references 95 and 96.
Calculation of $\Lambda^0$, $\Lambda^e$, and $K$

6.3. "Direct" method

The method is based on the following two assumptions:

1. Aqueous solutions of NaCl, HCl and the sodium salt of the acid being measured are completely dissociated.

2. At low concentrations, the equivalent conductances of the ionic constituents of strong electrolytes are independent of the nature of the associated ions, i.e. they follow Kohlrausch's law of independent migration.

$\Lambda^e_{HA}$, the equivalent conductance of a completely dissociated acid HA is:

$$\Lambda^e_{HA} = \Lambda_{H^+} + \Lambda_{A^-} = \Lambda_{H^+} + \Lambda_{Cl^-} + \Lambda_{Na^+} + \Lambda_{A^-} - \Lambda_{Na^+} - \Lambda_{Cl^-}$$  \hspace{1cm} (6.3.1)

or:

$$\Lambda^e_{HA} = \Lambda_{HCl} + \Lambda_{NaA} - \Lambda_{NaCl}$$  \hspace{1cm} (6.3.2)

Equations are available in the literature for the conductance of NaCl and HCl. Thus for NaCl at 25°C:

$$\frac{\Lambda + 59.78c^{\frac{1}{2}}}{1 - 0.2273c^{\frac{1}{2}}} = 149.86 + 141.9c + 29.24c\log c - 180.6c^2$$  \hspace{1cm} (6.3.3)

and for HCl at 25°C a similar equation:

$$\frac{\Lambda + 59.78c^{\frac{1}{2}}}{1 - 0.2273c^{\frac{1}{2}}} = 426.16 + 169c$$  \hspace{1cm} (6.3.4)
If a similar equation is available or is obtained experimentally for NaA then a relation of the form:

$$\Lambda_{HA}^e = \Lambda^0 + Bc^{1/2} + Cc + Dc\log(c) + Ec^{3/2} + Fc^2$$  \hspace{1cm} (6.3.5)

is obtained.

$$\Lambda^0, B, C...$$ are the algebraic sums of the respective coefficients in (6.3.3), (6.3.4) and in the relation for NaA.

Equation (6.3.5) can be written as:

$$\Lambda^e = \Lambda^0 - (\alpha^1 \Lambda^0 + \beta)c^{1/2} + B^1c(1 - \alpha^1 c^{1/2})$$  \hspace{1cm} (6.3.6)

which is nothing less than Onsager limiting equation plus an empirical term. The empirical term ($B^1...$) is adjusted in such a way that the equation fits the experimental data of the electrolyte measured. The values of the constants $\alpha^1$ and $\beta$ are predicted theoretically.

Onsager's equation is:

$$\Lambda = \Lambda^0 - \left[ \frac{0.9834 \times 10^6}{(DT)^{3/2}} q_1 \Lambda^0 + \frac{28.94z_i}{(DT)^{1/2} \eta_0} \right] (z_+ + z_-)^{1/2}c^{1/2}$$  \hspace{1cm} (6.3.7)

$$q_1 = \frac{z_+z_-}{1 + q^{1/2}}$$  \hspace{1cm} (6.3.8)

$$q = \frac{z_+z_- (\lambda^0_+ + \lambda^0_-)}{(z_+ + z_-) (z_+ \lambda^0_- + z_- \lambda^0_+)}$$  \hspace{1cm} (6.3.9)

$\eta_0$ is the viscosity of the solvent and the rest of the symbols have the same significance as before.
The first term in the brackets of (6.3.7) accounts for the time of relaxation effect and the second term for the electrophoretic effect. The equation refers only to the ionic part of a dissolved electrolyte.

For a uni-univalent electrolyte (6.3.7) becomes:

$$\Lambda^e = \Lambda^o - \left[ \frac{8.204 \times 10^5}{(DT)^{3/2}} \Lambda^o + \frac{82.50}{(DT)^{1/n_o}} \right] \frac{1}{2} c^2$$  \hspace{1cm} (6.3.10)

which for a given solvent and temperature is of the form:

$$\Lambda^e = \Lambda^o - [\alpha_1 \Lambda^o + \beta] c^{1/2} = \Lambda^o - S c^{1/2}$$  \hspace{1cm} (6.3.11)

where \( S \), which is generally called "Onsager slope", was defined in (5.4.2)

If HA is a weak acid (6.3.5) becomes:

$$\Lambda^e_{HA} = \Lambda^o + B(c_a)^{1/2} + C(c_a) + D(c_a) \log(c_a) + E(c_a)^{3/2} + F(c_a)^2$$  \hspace{1cm} (6.3.12)

To obtain \( \Lambda^e_{HA} \) from (6.3.12), the method of successive approximations is used. In the first approximation \( \alpha \) is given by:

$$\alpha = \frac{\Lambda}{\Lambda^o}$$  \hspace{1cm} (6.3.13)

This value of \( \alpha \) and the respective \( c \) are substituted into (6.3.12) and \( \Lambda^e_{HA} \) calculated. The next approximation for \( \alpha \) is:

$$\alpha = \frac{\Lambda}{\Lambda^e_{HA}}$$  \hspace{1cm} (6.3.14)
The new $\alpha$ is substituted into 6.3.12 again and a new $\Lambda^e_{HA}$ is obtained. The procedure is repeated until $\alpha$ and $\Lambda^e_{HA}$ are constant within the accuracy of the experimental results.

The value of $\alpha$ can now be introduced into the expression:

$$K^1 = \frac{ca^2}{1 - \alpha} \quad (6.3.15)$$

and

$$K = K^1 \frac{f_H^+f_A^-}{f_{HA}} \quad (6.3.16)$$

If $f_{HA} = 1$ (the undissociated acid is a nonelectrolyte) and

$$\log(f_H^+f_A^-) = \log(f_+^2) = - \frac{A (ca)^{3/2}}{1 + Ba(ca)^{3/2}} \quad (6.3.17)$$

we obtain:

$$\log K^1 = \log K + \frac{2A(ca)^{3/2}}{1 + Ba(ca)^{3/2}} \quad (6.3.18)$$

Plotting $\log K^1$ vs. $(ca)^{3/2}/(1 + Ba(ca)^{3/2})$ (or vs. $(ca)^{3/2}$ at low concentrations) a straight line should be obtained. Its intercept is $\log K$.

If $\log(K)$ is calculated for every individual value of $c$ it is observed that $K$ decreases as $c$ increases. $^{101}$

This decrease is probably due to:

a. increase in the viscosity of the solutions with the concentration $^{102}$
b. dimerization $^{103}$
The increase in the viscosity can be taken into consideration by applying a correction factor given by Einstein's equation:

\[ \Lambda^n = \Lambda \left(1 + \frac{5}{2} \frac{4\pi R^3}{3} \cdot \frac{N_A c}{1000}\right) \]  \hspace{1cm} (6.3.19)

where:

- \( \Lambda^n \) is the corrected value of conductivity.
- \( \Lambda \) is the observed conductivity.
- \( R \) is the hydrodynamic radius of the solute.

The second effect provides a way of calculating the dimerization constant \( K_D \). Consider the system:

\[
\begin{align*}
HA & \rightleftharpoons H^+ + A^- \\
(\text{HA})_2 & \rightleftharpoons 2 \text{ HA} \\
K &= \frac{a^2 c^2 f_\pm^2}{[\text{HA}]^2} f_\pm^2
\end{align*}
\]  \hspace{1cm} (6.3.20)

Hence:

\[
[\text{HA}] = \frac{2 a^2 c f_\pm^2}{K}
\]

\[
[(\text{HA})_2] = \frac{1}{2}(c - ac - [\text{HA}])
\]

\[
K_D = \frac{[\text{HA}]^2}{[(\text{HA})_2]} = \frac{2(acf_\pm)^4}{\frac{a^2 c^2 f_\pm^2}{K}}\frac{2}{K^2(c - ac - \frac{acf_\pm^2}{K})}
\]

\[
= \frac{2(acf_\pm)^4}{K[cK - acK - (acf_\pm)^2]} \hspace{1cm} (6.3.21)
\]
Using a value of $K$ determined at low concentrations and $\alpha$ calculated from viscosity corrected conductances, $K_d$ can be obtained at different concentrations.

**Conclusions** To calculate $K$, the dissociation constant of an acid HA in aqueous solution, this method requires the determination of the conductance of a salt, NaA or KA at different concentrations. The data are then fitted into a relation of the form (6.3.4) (or (6.3.5)). Together with the data existent in the literature for HCl and NaCl or KCl, a conductance equation is obtained for HA.

The method which seems simple to apply at 25°C, where enough data on KCl, NaCl and HCl exist, but becomes more difficult to use at other temperatures where data on these compounds are scarce.

Once $\Lambda^0$ is known, $\Lambda^e$, $\alpha$ and $f_\pm$ can be calculated. Then using (6.1.11) the dissociation constant $K$ is obtained.

We wrote a computer program which follows the procedure described by Dippy and Williams. The procedure was applied to a series of published data. The program is given in appendix 6.3.1 and the "Det. Cal." in 6.3.1. A summary of the results and a comparison with other methods of calculation can be found in table 6.10.1.

### 6.4. Ives method

This method makes use of the equations (6.1.11), (6.2.13) and (6.3.11). The result is as follows:

$$K = \frac{\Lambda^2 c f_\pm^2}{[\Lambda^0 - S(ac)^{1/2}][\Lambda^0 - S(ac)^{1/2} - \Lambda]}$$

$$= \Lambda^2 c \times 10^{-2A(ac)^{1/2}} \frac{1}{[\Lambda^0 - S(ac)^{1/2}][\Lambda^0 - S(ac)^{1/2} - \Lambda]} \quad (6.4.1)$$
Rearranging:

$$\Lambda + S(ac)^{1/2} = \Lambda^0 - \frac{\Lambda^2 c \times 10^{-2} A(ac)^{1/2}}{\Lambda^0 - S(ac)^{1/2}} \cdot \frac{1}{K}$$  \hspace{1cm} (6.4.2)

or:

$$y = \Lambda^0 - \frac{1}{K} x$$  \hspace{1cm} (6.4.3)

By plotting $y$ vs. $x$ a straight line should be obtained with the slope of $1/K$ and intercept $\Lambda^0$.

The calculation is done by successive approximations using the method of least squares to obtain $\Lambda^0$ and $1/K$. The calculation proceeds in the following way:

a. A reasonable value is chosen as a first approximation of $\Lambda^0$.

   The final result is not dependent on the value chosen.

b. $A$ is calculated from (6.2.10).

c. $S$ is calculated from (6.3.10) and (6.3.11).

d. $\Lambda^e$ is obtained from (6.3.11) in the following way:

$$\Lambda^e = \Lambda^0 - S(ac)^{1/2}$$  \hspace{1cm} (6.4.4)

and

$$\alpha = \frac{\Lambda}{\Lambda^e}$$  \hspace{1cm} (6.1.10)

Consider:

$$\Lambda^e = \Lambda^0 - \delta(\Lambda^0)$$  \hspace{1cm} (6.4.5)
Then:

\[
\delta(\Lambda^0) = \Lambda^0 - \Lambda^e = \Lambda^0 - \left[ \Lambda^0 - S \frac{\Lambda}{\Lambda^e} c^{x/2} \right] = S \left[ \frac{c\Lambda}{\Lambda^0 - \delta(\Lambda^0)} \right]^{1/2}
\]

(6.4.6)

\[
\frac{S(\Lambda c)^{1/2}}{(\Lambda^0)^{1/2} \left( 1 - \frac{\delta(\Lambda^0)}{\Lambda^0} \right)^{1/2}} = \frac{(\Lambda c)^{1/2}}{(\Lambda^0)^{1/2} \left\{ 1 - \frac{1}{2} \frac{\delta(\Lambda^0)}{\Lambda^0} + \frac{1}{8} \left[ \frac{\delta(\Lambda^0)}{\Lambda^0} \right]^2 + \ldots \right\}}
\]

If the third term in the series expansion is neglected we obtain the following expression:

\[
[\delta(\Lambda^0)]^2 - 2\Lambda^0 \delta(\Lambda^0) + 2S(\Lambda^0 \Lambda c)^{1/2} = 0
\]

(6.4.7)

Relation (6.4.7) is solved for \(\delta(\Lambda^0)\). Substituting the result into (6.4.5) we obtain:

\[
\Lambda^e = [(\Lambda^0)^2 - 2S(\Lambda^0 \Lambda c)^{1/2}]^{1/2}
\]

(6.4.8)

Relation (6.4.8) is solved by successive approximations. The starting value for \(\Lambda^e\) is \(\Lambda^0\).

Another way to obtain \(\Lambda^e\) is directly from (6.4.4) written as:

\[
\Lambda^e = \Lambda^0 - S \frac{\Lambda^e}{\Lambda^e} c^{1/2}
\]

(6.4.9)

by successive approximations. Again the first approximation to \(\Lambda^e\) is \(\Lambda^0\). This is the approach we used in our calculations (appendix 6.4.1 and "Detailed Calculations - 6.4.1").

e. \(\alpha\), the degree of dissociation is calculated from (6.1.10).
f. \(x\) and \(y\) are calculated for each pair, \(\Lambda\) and \(c\), of experimental data:
\[ y = \Lambda + S(ac)^{1/2} \]  
(6.4.10)

\[ x = \frac{\Lambda^2 c \times 10^{-2} A(ac)^{1/2}}{\Lambda^0 - S(ac)^{1/2}} \]  
(6.4.11)

g. The next approximation for \( \Lambda^0 \) is given by the intercept of the \( x - y \) plot.

The whole set of operations is repeated until \( \Lambda^0 \) is constant within the accuracy of the experiment.

As mentioned before the slope and the intercept of the line are obtained by the method of least squares. The equations giving them are:

\[ \Lambda^0 = \frac{\Sigma x \Sigma xy - \Sigma x^2 \Sigma y}{(\Sigma x)^2 - \Sigma x^2} \]  
(6.4.12)

\[ \frac{1}{K} = \frac{\Sigma xy - \Sigma x \Sigma y}{(\Sigma x)^2 - \Sigma x^2} \]  
(6.4.13)

The sums are taken over the whole set of I experimental points (\( \Lambda \) and c).

The computer program which uses Ives method for calculating \( \Lambda^0 \) and \( K \) from conductance data is shown in appendix 6.6.1. Four sets of published experimental data were used to check the program. The results, \( \Lambda^0 \) and \( K \), are given in table 6.4.1.
Table 6.4.1: Ives method for calculating $\Lambda^0$ and $K$. Comparison between literature values and those calculated here.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Compound</th>
<th>Conc. (max.) g-equiv/l x 10^{-3}</th>
<th>No. of pts.</th>
<th>$\Lambda$</th>
<th>$K \times 10^5$ Publish.</th>
<th>$K \times 10^5$ Calc. here</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetic acid</td>
<td>4.07</td>
<td>5</td>
<td>391.6</td>
<td>392.1</td>
<td>1.759</td>
</tr>
<tr>
<td>2</td>
<td>Picric acid</td>
<td>1.2</td>
<td>10</td>
<td>380.2</td>
<td>380.2</td>
<td>212300.</td>
</tr>
<tr>
<td>3</td>
<td>Iodoacetic acid</td>
<td>2.1</td>
<td>4</td>
<td>390.4</td>
<td>390.4</td>
<td>66.80</td>
</tr>
<tr>
<td>4</td>
<td>Di-iso-propylcyanoacetic acid</td>
<td>2.5</td>
<td>6</td>
<td>375.25</td>
<td>375.13</td>
<td>278.16</td>
</tr>
</tbody>
</table>


The agreement between the published values and the values calculated using the computer program no. AD11 - SUBROUTINE IVES ranges from fair to good. The differences between our values and some of the earlier figures, e.g. acetic acid, can be blamed on the different values for the universal constants, the dielectric constant of water, and the viscosity of water. We find no explanation for the difference between our values and the more recently published figures, and especially, for the large difference for the dissociation constant.
of picric acid.\textsuperscript{106}

**Conclusions.** This method uses the extrapolation of a straight line (6.4.3) to determine $\Lambda^0$ and $K$ for an acid, HA, from the measured values of conductance and concentration of the solutions of the acid only.

The limitations and especially the errors involved in an extrapolation method will be discussed in more detail in subsection 6.5. We will mention here only that the plots $x$ vs. $y$ remained linear for $c \leq 4.0 \times 10^{-3}$ g-equiv/l. For higher concentrations the deviations from the linearity were large.

6.5. **Errors in the determination of the dissociation constant and the limiting conductance by extrapolation methods.**

Ives' method (6.4) is part of a larger group of methods. These methods are characterized by the fact that they use data on acid conductance, only, to calculate both the limiting conductance, $\Lambda^0$, and the dissociation constant, $K$, of the acid. The methods use different expressions, functions of conductance "$\Lambda$", and concentration "$c$" which graphically or analytically are able to render $\Lambda^0$ and $K$. Generally on plotting, these relations give straight lines. From the slope and the intercept of the line, $\Lambda^0$ and $K$ are obtained.

Ives was the first to note that a constant relative error in the conductance values produced a large change in $\Lambda^0$ and a very small one in $K$.\textsuperscript{104} This was confirmed later by Belcher and by Shedlovsky, who concluded that any extrapolation method is unreliable as far as $\Lambda^0$ is concerned for acids whose dissociation constant $K \leq 10^{-5}$.\textsuperscript{80,107} Kilpatrick\textsuperscript{108} made a more complete investigation of the errors involved in the extrapolation method. Ives relation
was used for this purpose (6.4.2). Other extrapolation methods should give similar results.

The results are interesting and, we feel, almost completely neglected by the workers in this field when estimating the accuracy of their results. We will present these results in detail here and apply them to some of the published data to estimate their accuracy. A few different possible types of errors will be examined in their relation to \( \Lambda^0 \) and \( \Lambda \).

1. A constant relative error in the conductance values such as a wrong cell constant leads to the following errors:

a. In \( \Lambda \):

\[
\frac{\Delta \Lambda}{\Lambda} = \frac{\Delta L}{L} \sum_{i=1}^{I} \frac{L_i}{\delta L_i} \delta \frac{\Lambda}{\delta L_i} = \frac{\Delta L}{L} \sum_{i=1}^{I} \frac{L_i}{\delta L_i} \delta \frac{\Lambda}{\delta L_i} \quad (6.5.1)
\]

where:

\[
\frac{\delta \Lambda}{\delta L_i} = \frac{1}{L_i} \left[ \Lambda_i \left\{ U_i \frac{\delta \Lambda}{\delta x_i} + r_i \frac{\delta \Lambda}{\delta y_i} + \frac{m_i}{I} \sum_{j=1}^{k} \left( W_j \frac{\delta \Lambda}{\delta x_j} + t_j \frac{\delta \Lambda}{\delta y_j} \right) \right\} \right] \quad (6.5.2)
\]

\[
\frac{\delta \Lambda}{\delta L_i} = \frac{Q_i}{L_i}
\]

\[
U_i = \frac{X_i}{\Lambda_i} \left[ 2 + \frac{\Lambda^0 - \Lambda^e_i}{3 \Lambda^e_i - \Lambda^0} (1 - h \Lambda^e_i) \right] \quad (6.5.3)
\]

\[
r_i = 1 + \frac{1}{\Lambda_i} \left[ \Lambda_i \left( \frac{\Lambda^0 - \Lambda^e_i}{3 \Lambda^e_i - \Lambda^0} \right) \right] \quad (6.5.4)
\]
\[ m_i = U_i \frac{\delta \Lambda^0}{\delta x_i} + r_i \frac{\delta \Lambda^0}{\delta y_i} \] 
\[ 1 = 1 - \left[ \sum_i W_i \frac{\delta \Lambda^0}{\delta x_i} + t_i \frac{\delta \Lambda^0}{\delta y_i} \right] \] 
\[ W_i = x_i \left[ \frac{1}{3 \Lambda_i^e - \Lambda^0} \left( \frac{\alpha^1 \Lambda_i^e + \beta}{\alpha^1 \Lambda^0 + \beta} \right) [h(\Lambda^0 - \Lambda_i^e) - 2] \right] \] 
\[ t_i = \frac{2 \Lambda_i^e(\alpha^1 \Lambda_i^e + \beta)}{(3 \Lambda_i^e - \Lambda^0)(\alpha^1 \Lambda^0 + \beta)} \] 
\[ h = \frac{2.3026 \times 2A}{\alpha^1 \Lambda^0 + \beta} \] 
\[ \frac{\delta K}{\delta x_i} = \frac{1}{\Sigma x \Sigma y - k \Sigma x y} \{ 2[\Sigma x_i - \Sigma x] + K[\Sigma y_i - \Sigma y] \} \] 
\[ \frac{\delta K}{\delta y_i} = \frac{K[\Sigma x_i - \Sigma x_i]}{\Sigma x \Sigma y - I \Sigma x y} \] 
\[ \frac{\delta \Lambda^0}{\delta x_i} = \frac{1}{(\Sigma x)^2 - I \Sigma x^2} \{ [\Sigma x y - y_i \Sigma x - 2x_i \Sigma y] + 2 \Lambda^0[\Sigma x_i - \Sigma x] \} \] 
\[ \frac{\delta \Lambda^0}{\delta y_i} = \frac{x_i \Sigma x - \Sigma x^2}{(\Sigma x)^2 - I \Sigma x^2} \]
The other symbols have the same significance as before (see subsections 6.3 and 6.4). For the sake of clarity they will be repeated here:

\[ \alpha^1 = \frac{8.204 \times 10^5}{(DT)^{3/2}} \]  \hspace{1cm} (6.5.14)

\[ \beta = \frac{82.50}{(DT)^{1/2} n_0} \]  \hspace{1cm} (6.5.15)

\[ A = \frac{1.8123 \times 10^6}{(DT)^{3/2}} \]  \hspace{1cm} (6.5.16)

\[ x = \frac{\Lambda^2 c}{10^{-2A} \left( \frac{cA}{\Lambda e} \right)^{1/2}} \]  \hspace{1cm} (6.5.17)

\[ y = \Lambda + (\alpha^1 \Lambda + \beta) \left( \frac{cA}{\Lambda e} \right)^{1/2} \]  \hspace{1cm} (6.5.18)

\[ \Lambda^e = \Lambda^0 - (\alpha^1 \Lambda^0 + \beta) \left( \frac{cA}{\Lambda e} \right)^{1/2} \]  \hspace{1cm} (6.5.19)

\[ L_i = \frac{\Lambda_i c_i}{1000} \]  \hspace{1cm} (6.5.20)

I is the number of experimental points \( \Lambda, c \).

The sums in (6.5.6) to (6.5.13) are from 1 to I.

b. In \( \Lambda^0 \):

\[ [\Delta \Lambda^0] / \Delta L = \frac{\Delta L}{L} \sum_{i=1}^{I} L_i \frac{\delta \Lambda^0}{\delta L_i} \]  \hspace{1cm} (6.5.21)
\[ \frac{\delta \Lambda}{\delta L_i} = \frac{m_i \Lambda_i}{L_i} \]  

(6.5.22)

2. A constant absolute error in the conductance values, e.g. a wrong solvent correction, leads to the following errors:

a. In \( K \):

\[ [\Delta K]_{\Delta L} = \Delta L \sum_{i=1}^{I} \frac{\delta K}{\delta L_i} \]  

(6.5.23)

b. In \( \Lambda^0 \):

\[ [\Delta \Lambda^0]_{\Delta L} = \Delta L \sum_{i=1}^{I} \frac{\delta \Lambda^0}{\delta L_i} \]  

(6.5.24)

3. A constant relative error in the concentration leads to the following errors:

a. In \( K \):

\[ [\Delta K]_{\Delta C} = \frac{\Delta C}{C} \sum_{i=1}^{I} c_i \frac{\delta K}{\delta c_i} \]  

(6.5.25)

\[ \frac{\delta K}{\delta c_i} = \frac{1}{c_i} \left\{ c_i \left[ v_i \frac{\delta K}{\delta x_i} + s_i \frac{\delta K}{\delta y_i} + \frac{n_i}{I} \sum_{j=1}^{I} \left( w_j \frac{\delta K}{\delta x_j} + t_j \frac{\delta K}{\delta y_j} \right) \right] - Q_i \right\} \]  

(6.5.26)

\[ \frac{1}{c_i} [P_i - Q_i] \]
where:

\[ V_i = \frac{X_i}{C_i} \left[ 1 + \frac{\Lambda^0_i - \Lambda^e_i}{3 \Lambda^e_i - \Lambda^0_i} (1 - h \Lambda^e_i) \right] \]  
\[ (6.5.27) \]

\[ S_i = \frac{1}{C_i} \left[ \Lambda^e_i \left( \frac{\Lambda^0_i - \Lambda^e_i}{3 \Lambda^e_i - \Lambda^0_i} \right) \right] \]  
\[ (6.5.28) \]

\[ n_i = V_i \frac{\delta \Lambda^0_i}{\delta x_i} + S_i \frac{\delta \Lambda^0_i}{\delta y_i} \]  
\[ (6.5.29) \]

b. In \( \Lambda^0 \):

\[ [\Delta \Lambda^0]_{\Delta c} = \frac{\Delta c}{c} \sum_{i=1}^{I} c_i \frac{\delta \Lambda^0_i}{\delta c_i} \]  
\[ (6.5.30) \]

\[ \frac{\delta \Lambda^0_i}{\delta c_i} = \frac{1}{C_i} \left[ \frac{n_i c_i}{I} - \frac{m_i \Lambda_i}{I} \right] \]  
\[ (6.5.31) \]

We wrote a computer program which calculates \([\Delta K]_{\Delta L}^{\Delta L} \), \([\Delta \Lambda^0]_{\Delta L}^{\Delta L} \), \([\Delta K]_{\Delta c}^{\Delta c} \) and \([\Delta \Lambda^0]_{\Delta c}^{\Delta c} \) having as input data "k" pairs of \( \Lambda - c \) values and the values of \( \Lambda^0 \) and \( K \).

The computer program is given in appendix 6.5.1. The "Detailed Calculations - 6.5.1" contains, 6 examples for which the data was taken from the literature. The first example is that given in the original Kilpatrick paper and it was used as a check for the computer program. The results obtained here agree very well with
those published. 108

It was found that Kilpatrick's example 108 is typical for the acids with which we are mostly concerned. For discussion we will consider the second example, which uses Shedlovsky and MacInnes data on acetic acid. 109

The results of the calculations were as follows:

\[
\frac{[\Delta K]_{\Delta L}}{L} = -0.015 \frac{\Delta L}{L}
\]

\[
\frac{[\Delta \lambda^0]_{\Delta L}}{\lambda^0} = 1.01 \frac{\Delta L}{L}
\]

\[
[\Delta K]_{\Delta L} = -15.9 \Delta L
\]

\[
[\Delta \lambda^0]_{\Delta L} = 1.73 \times 10^8 \Delta L
\]

\[
\frac{[\Delta K]_{\Delta C}}{C} = 0.98 \frac{\Delta C}{C}
\]

\[
\frac{[\Delta \lambda^0]_{\Delta C}}{\lambda^0} = -1.0 \frac{\Delta C}{C}
\]

The average specific conductance for the data considered is approximately 4.2 x 10^{-5} mho. If we assume a constant relative error of 0.02% in the specific conductance (due mainly to uncertainty in the cell constant, say) then:
\[
\frac{[\Delta K]_{\Delta L}}{K} = -0.015 \times 0.02 = 0.0003\%
\]

\[
\frac{[\Delta \Lambda^0]_{\Delta L}}{\Lambda^0} = 1.01 \times 0.02 = 0.02\%
\]

Hence a constant relative error in \( L \) (specific conductivity) causes a negligible error in \( K \) and a very small one in \( \Lambda^0 \).

A constant absolute error in the conductance value, \( \Delta L \), is more difficult to estimate and to detect. Its main origin should be the solvent conductance or the conductance caused by any other impurity present in the solution. If the only impurity in the solution is CO\(_2\) then \( \Delta L \) should be zero (see subsection 5.9). However, if this is not the case, the problem becomes complicated because, as we mentioned before, it is necessary to know the nature of the ions present as impurities to calculate \( \Delta L \). Tentatively we take the value estimated by Belcher as being due to salt impurity:\(^{31} \)

\[
\Delta L = 1.0 \times 10^{-7} \text{ mho}.
\]

Then:

\[
\frac{[\Delta K]_{\Delta L}}{K} = \frac{15.9 \times 1.0 \times 10^{-7}}{1.75 \times 10^{-5}} \times 100 = 9.1\%
\]

\[
\frac{[\Delta \Lambda^0]_{\Delta L}}{\Lambda^0} = \frac{1.73 \times 10^8 \times 1.0 \times 10^{-7}}{390.0} \times 100 = 4.4\%
\]

Both these errors are extremely high. Even if \( \Delta L \) is reduced by a factor of 10, i.e. \( \Delta L = 1.0 \times 10^{-8} \) mho, the error in \( K \) of 0.9% is higher than the error currently estimated for this type
of data. It is very likely that the true value of $\Delta l$ lies somewhere between these two extreme values, closer to the latter. It must not be forgotten that some solvent corrections calculated by the Fuoss-Shedlovsky-Kay method (subsection 6.7) were as high as $3.0 \times 10^{-7}$ mho. Unfortunately the solvent correction (or more correctly the "impurity" correction in the specific conductance) has to be very precise to have any positive effect on $\Delta k$ and $\Delta \lambda^0$. A superestimation of this correction causes the same error in $\Delta k$ and $\Delta \lambda^0$ as is caused by neglecting it completely or underestimating it.

The relative error in the concentration can be estimated at approximately $0.004\%$. Then:

$$\frac{[\Delta K]_{AC}}{K} = 0.98 \times 0.004 = 0.004\%$$

$$\frac{[\Delta \lambda^0]_{AC}}{\lambda^0} = 1.0 \times 0.004 = 0.004\%$$

Recapitulating, the error in $\lambda^0$ and $K$ and their origin are:

Table 6.5.1

<table>
<thead>
<tr>
<th>Origin</th>
<th>$Error(%)$ in:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant relative error in conductance of 0.02%</td>
<td>$\lambda^0$ 0.0003 $K$ 0.02</td>
</tr>
<tr>
<td>Constant absolute error in the specific conductance of $2 \times 10^{-8}$ mho.</td>
<td>1.8 0.89</td>
</tr>
<tr>
<td>Constant relative error in concentration of 0.004%</td>
<td>$0.004$ 0.004</td>
</tr>
<tr>
<td>Total</td>
<td>1.8 0.91</td>
</tr>
</tbody>
</table>
It is important to know that the linearity of the $x - y$ plot is not affected by systematic errors larger than those considered above. Thus these types of errors are not taken into account when the mean square deviations of the $y$ and eventually of the $x$ variables are calculated.

Kilpatrick has also shown that the error remains approximately the same for acids with dissociation constants in the range $3 \times 10^{-3} - 5 \times 10^{-5}$.

**Random errors in a linear plot**

The equation of a straight line is:

$$y = a + bx$$  \hspace{1cm} (6.5.32)

If the coefficients 'a' and 'b' are computed by the method of least squares, then their probable error is given by:

$$p_a = r_e \left( \frac{\Sigma x_i^2}{D} \right)^{1/2}$$  \hspace{1cm} (6.5.33)

$$p_a = r_e \left( \frac{1}{D} \right)^{1/2}$$  \hspace{1cm} (6.5.34)

where:

$$r_e = 0.6745 \left[ \frac{\Sigma d_i^2}{(1-2)} \right]^{1/2}$$  \hspace{1cm} (6.5.36)

$$D = \Sigma x_i^2 - (\Sigma x_i)^2$$  \hspace{1cm} (6.5.37)

$$d_i = y_{obs} - y_{calc}$$  \hspace{1cm} (6.5.38)

$I =$ no. of experimental points.
Very often $\Lambda^0$ and $K$ are not exactly the slope or the intercept of the linear plots. They are calculated from the intercept and the slope of the plot in a different way for each of the methods of extrapolation. Hence the actual error in $\Lambda^0$ and $K$ due to random errors is not $P_a$ and $P_b$ exactly; it is $P_a$ and $P_b$ multiplied by certain factors. The expressions which must be used to calculate the errors in $\Lambda^0$, $K$ and $L_W$ (see 6.7.7) from $P_a$ and $P_b$ are given in table 6.5.2.

**Table 6.5.2: Expressions for calculating the probable random errors in $K$, $\Lambda^0$ and $L_W$.**

<table>
<thead>
<tr>
<th>Expression used for calculating</th>
<th>Error in $K$</th>
<th>Error in $\Lambda^0$</th>
<th>Error in $L_W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(6.4.2)$</td>
<td>$P_b \times (K)^2$</td>
<td>$P_a$</td>
<td>$-$</td>
</tr>
<tr>
<td>$(6.6.10)$</td>
<td>$P_b \times K/\text{slope}$</td>
<td>$P \times (\Lambda^0)^2$</td>
<td>$-$</td>
</tr>
<tr>
<td>$(6.7.5)$</td>
<td>$P_b(2 \times \frac{\text{slope}}{\Lambda^0} + P_b)$</td>
<td>$-$</td>
<td>$P_a$</td>
</tr>
</tbody>
</table>

For the same set of experimental data, i.e. the MacInnes and Shedlovsky data on acetic acid, the value of $\Lambda^0$ and $K$ and their errors are:

**Expression used for extrapolation**

<table>
<thead>
<tr>
<th>Expression used for extrapolation</th>
<th>$K \times 10^5$</th>
<th>$\Lambda^0$</th>
<th>$L_W \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(6.4.2)$</td>
<td>1.7473±</td>
<td>391.17±</td>
<td>$-$</td>
</tr>
<tr>
<td></td>
<td>0.0018</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>$(6.6.10)$</td>
<td>1.7473±</td>
<td>391.2±</td>
<td>$-$</td>
</tr>
<tr>
<td></td>
<td>0.0004</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>$(6.7.5)$</td>
<td>1.7473±</td>
<td>$-$</td>
<td>$(6. \pm 0.4)$</td>
</tr>
<tr>
<td></td>
<td>0.0004</td>
<td></td>
<td>$10^{-8}$</td>
</tr>
</tbody>
</table>
Errors in the determination of the dissociation constant of acids when the limiting conductance, \( \Lambda^0 \), is known

As was shown, the errors of the extrapolation method are rather large. It is frequently said\(^1\) that one way to overcome this is to obtain the limiting conductance separately, e.g. from the salt conductance.

We will here try to obtain explicit expressions for the errors in the dissociation constant \( K \), when \( \Lambda^0 \) is given, as a function of the errors in the conductance \( \Lambda \) and in the concentration \( c \). The treatment is similar to that of Kilpatrick for the extrapolation method.

If \( \Lambda^0 \) is known, \( K \) can be calculated from (6.1.11):

\[
K = \frac{\Lambda^2 c f^{2}_\pm}{(\Lambda^e - \Lambda) \Lambda^e} \quad (6.1.11)
\]

where:

\[
\Lambda^e = \Lambda^0 - y \sqrt{\Lambda} \frac{\Lambda e}{\Lambda} c \quad (6.4.9)
\]

\[
f^{2}_\pm = \exp \left[ -A \left( \frac{c}{\Lambda^e} \right)^{1/2} \times 2.303 \right] \quad (6.5.39)
\]

From (6.1.11):

\[
dK = \frac{\delta K}{\delta \Lambda} \, d\Lambda + \frac{\delta K}{\delta c} \, dc + \frac{\delta K}{\delta \Lambda^e} \, d\Lambda^e + \frac{\delta K}{\delta f^{2}_\pm} \, df^{2}_\pm \quad (6.5.40)
\]

\[
\frac{\delta K}{\delta \Lambda} = \frac{cf^{2}_\pm}{\Lambda e} - \frac{(2\Lambda^e - \Lambda)\Lambda}{(\Lambda^e - \Lambda)^2} = n \quad (6.5.41)
\]
\[ \frac{\delta K}{\delta c} = \frac{2f_{\pm}^2}{A^e(A^e - A)} = p \quad (6.5.42) \]

\[ \frac{\delta K}{\delta A^e} = -\frac{\Lambda^2 cf_{\pm}^2(2A^e - A)}{[A^e(A^e - A)]^2} = q \quad (6.5.43) \]

\[ \frac{\delta K}{\delta f_{\pm}} = \frac{2\Lambda^2 cf_{\pm}}{A^e(A^e - A)} = r \quad (6.5.44) \]

From (6.4.9):

\[ dA^e = -\frac{(\Lambda^0 - A^0)A^e}{3A^e - \Lambda^0}(\frac{dc}{c} + \frac{dA}{\Lambda}) = m(\frac{dc}{c} + \frac{dA}{\Lambda}) \quad (6.5.45) \]

From (6.5.39):

\[ df_{\pm} = \frac{\delta f_{\pm}}{\delta A^e} dA^e + \frac{\delta f_{\pm}}{\delta A} dA + \frac{\delta f_{\pm}}{\delta c} dc \quad (6.5.46) \]

\[ \frac{\delta f_{\pm}}{\delta A^e} = \exp \left\{ -\Lambda \left( \frac{c}{A^e} \right)^{1/2} \times 2.303 \right\} x \left[ 2.303A(cA)^{1/2} \frac{1}{2(A^e)^{3/2}} \right] \]

\[ = -\frac{cA}{(A^e)^{3/2}} = t \quad (6.5.47) \]

\[ \frac{\delta f_{\pm}}{\delta A} = S \left( \frac{c}{A^e} \right)^{1/2} = u \quad (6.5.48) \]

\[ \frac{\delta f_{\pm}}{\delta c} = S \left( \frac{A}{cA} \right)^{1/2} = v \quad (6.5.49) \]
Substituting relations (6.5.41) to (6.5.49) into (6.5.40)

we obtain:

$$dK = n \cdot d\Lambda + p \cdot dc + mq \left( \frac{dc}{c} + \frac{d\Lambda}{\Lambda} \right) + r \left( \frac{tm}{c} + v \right) dc + r \left( \frac{tm}{\Lambda} + u \right) d\Lambda$$ \hspace{1cm} (6.5.50)

Whence:

$$\frac{\delta K}{\delta c} = (p + rv) + \frac{m}{c} (q + rt)$$ \hspace{1cm} (6.5.51)

$$\frac{\delta K}{\delta \Lambda} = (n + ru) + \frac{m}{\Lambda} (q + rt)$$ \hspace{1cm} (6.5.52)

and the error in $K$ is:

$$\Delta K = \left[ \left( \frac{\delta K}{\delta c} \Delta c \right)^2 + \left( \frac{\delta K}{\delta \Lambda} \Delta \Lambda \right)^2 \right]^{1/2}$$ \hspace{1cm} (6.5.53)

$\Delta c$ and $\Delta \Lambda$ are the errors in "c" and "\Lambda" respectively.

Note that $\Lambda^0$ was considered free from errors. Generally this is not the case.\textsuperscript{108} If the error in $\Lambda^0$ is considered then (6.4.45) takes the form:

$$\Delta \Lambda^e = 2\Lambda^e \left( \frac{1 - \alpha^1 \left( \frac{c\Lambda^e}{\Lambda^0} \right)^{1/2}}{3\Lambda^e - \Lambda^0} \right) d\Lambda^0 + m \left( \frac{dc}{c} + \frac{d\Lambda}{\Lambda} \right) = m^1 d\Lambda^0 + m \left( \frac{dc}{c} + \frac{d\Lambda}{\Lambda} \right)$$ \hspace{1cm} (6.5.54)

Then (6.5.50) becomes:

$$dK = (n + \frac{qm}{\Lambda} + ru + \frac{rnm}{\Lambda}) d\Lambda + (p + \frac{qm}{c} + rv + \frac{rnm}{c}) dc + (qm^1 + rnm^1) d\Lambda^0$$ \hspace{1cm} (6.5.55)
Note:

\[ q \bar{m}^1 + r \bar{m}^1 = \frac{\delta K}{\delta \Lambda^0} \]  

(6.5.56)

Then:

\[ \Delta K = \left[ \left( \frac{\delta K}{\delta c} \Delta c \right)^2 + \left( \frac{\delta K}{\delta \Lambda} \Delta \Lambda \right)^2 + \left( \frac{\delta K}{\delta \Lambda^0} \Delta \Lambda^0 \right)^2 \right]^{1/2} \]  

(6.5.57)

As an example, the same MacInnes and Shedlovsky data on acetic acid were considered:

\[ K = 1.75 \times 10^{-5} \quad \Lambda = 48.15 \]
\[ c = 1.028 \times 10^{-3} \quad \Lambda^e = 388.3 \]
\[ c_1 = \left( \frac{c^e}{\Lambda^e} \right) = 1.275 \times 10^{-4} \quad f_\pm = 0.987 \]
\[ \Lambda^0 = 390.0 \]

Then:

\[ m = -0.85 \quad m^1 = 1.0 \quad n = 0.784 \times 10^{-6} \]
\[ p = 1.72 \times 10^{-2} \quad q = -0.99 \times 10^{-7} \quad r = 3.56 \times 10^{-5} \]
\[ s = -0.58 \quad t = 1.69 \times 10^{-5} \quad u = -1.36 \times 10^{-4} \]
\[ v = -6.4 \]

\[ \frac{\delta K}{\delta c} = 1.72 \times 10^{-2} \quad \frac{\delta K}{\delta \Lambda} = 0.78 \times 10^{-6} \quad \frac{\delta K}{\delta \Lambda^0} = -0.99 \times 10^{-7} \]
Then:

$$\frac{[\Delta K]}{K} = \frac{1}{K} \frac{\delta K}{\delta c} \frac{\Delta c}{c} = \frac{1.72 \times 10^{-2} 	imes 1.028 \times 10^{-3}}{1.75 \times 10^{-5}} \frac{\Delta c}{c} = 1.01 \frac{\Delta c}{c}$$

$$\frac{[\Delta K]}{K} = \frac{1}{K} \frac{\delta K}{\delta \Lambda} \frac{\Delta \Lambda}{\Lambda} = \frac{0.78 \times 10^{-6} \times 48.15}{1.75 \times 10^{-5}} \frac{\Delta \Lambda}{\Lambda} = 2.2 \frac{\Delta \Lambda}{\Lambda}$$

$$\frac{[\Delta K]}{K} = \frac{1}{K} \frac{\delta K}{\delta \Lambda^0} \frac{\Delta \Lambda^0}{\Lambda^0} = \frac{-0.99 \times 10^{-7} \times 390}{1.75 \times 10^{-5}} \frac{\Delta \Lambda^0}{\Lambda^0} = 2.2 \frac{\Delta \Lambda^0}{\Lambda^0}$$

If we assume:

$$\frac{\Delta c}{c} = 4.0 \times 10^{-5}$$

$$\frac{\Delta \Lambda}{\Lambda} = 2.0 \times 10^{-4}$$

$$\frac{\Delta \Lambda^0}{\Lambda^0} = 5.0 \times 10^{-4}$$

Then from (6.5.57):

$$\frac{\Delta K}{K} = 11.9 \times 10^{-4}$$

Therefore a much higher accuracy in K can be achieved if \(\Lambda^0\) is determined separately.
6.6. Fuoss - Shedlovsky method

For a uni-univalent weak electrolyte, Fuoss and Shedlovsky give the following conductance formula:

\[ \Lambda = \alpha [\Lambda^0 - S(\text{ca})^{3/2}] \]  \hspace{1cm} (6.6.1)

Relation (6.6.1) is solved for \( \alpha \) yielding:

\[ \alpha = \frac{\Lambda}{\Lambda^0} \cdot \frac{1}{F(z)} \quad \text{and} \quad z = \frac{S(\text{ca})^{1/2}}{(\Lambda^0)^{3/2}} \]  \hspace{1cm} (6.6.2)

Substitution of (6.5.2) into (6.1.8) gives:

\[ \frac{F}{\Lambda} = \frac{1}{\Lambda^0} + \frac{ca f_\pm^2}{FK(\Lambda^0)^2} \]  \hspace{1cm} (6.6.3)

where \( F(z) \) is:

\[ F(z) = 1 - z(1 - z(1 - z(\ldots)^{-1})^{-1})^{-1} \]

\[ = \frac{4}{3} \cos^2 \left( \frac{1}{3} \cos^{-1} \left( \frac{3}{2}(3z)^{1/2} \right) \right) \]  \hspace{1cm} (6.6.4)

A plot of (6.6.3) as \( F/\Lambda \) vs. \( ca f_\pm^2/F \) should be linear with slope \( 1/[K_F(\Lambda^0)^2] \) and intercept \( 1/\Lambda^0 \).

Shedlovsky proposed yet another form for (6.6.1):

\[ \Lambda = \alpha \Lambda^0 - \frac{S}{\Lambda^0} (\text{ca})^{1/2} \]  \hspace{1cm} (6.6.5)
which was derived from Onsager's limiting law:

\[ \Lambda^e = \Lambda^0 - (\alpha^1 \Lambda^0 + \beta)(c\alpha)^{1/2} \]  \hspace{1cm} (6.6.6)

and 6.1.10. Together these two relations give:

\[ \Lambda = \alpha \Lambda^0 - \alpha (\alpha^1 \Lambda^0 + \beta)(c\alpha)^{1/2} \]  \hspace{1cm} (6.6.7)

which is solved for \( \alpha \):

\[ \alpha = S(z) \frac{\Lambda}{\Lambda^0} \]  \hspace{1cm} (6.6.8)

where:

\[ S(z) = (z/2 + (1 + (z/2)^2)^{1/2})^2 \]  \hspace{1cm} (6.6.9)

Substitution of (6.6.8) into (6.1.10) gives:

\[ \frac{1}{\Lambda S} = \frac{1}{\Lambda^0} + \frac{1}{K_S(\Lambda^0)^2} c\Lambda S \]  \hspace{1cm} (6.6.10)

By plotting (6.6.10), i.e. \( 1/\Lambda S \) vs. \( c\Lambda S \), a straight line is obtained whose slope is \( 1/K_S \) and intercept is \( 1/K_S(\Lambda^0)^2 \).

Note that the two equations, (6.6.3) and (6.6.10), have the same intercept, \( 1/\Lambda^0 \), but different slopes. Equation (6.6.10) rather than (6.6.3) is recommended by the authors to be used in the range:

\[ 10^{-5} < K < 1 \]

When \( K < 10^{-3} \) both equations give the same result. When \( K = 10^{-6} \) neither one gives an accurate \( K \) or \( \Lambda^0 \).
The relation connecting the two constants, $K_F$ and $K_S$, is:

$$\frac{1}{K_S} = \frac{1}{K_F} + \frac{(s)^2}{(\Lambda^0)^2} \quad (6.6.11)$$

A computer program which calculates $\Lambda^0$ and $K$ from the plot of relation (6.6.10) is given in appendix (6.6.1). The program (SUBROUTINE SHFS) is part of a larger program (AD11). Some published data and the corresponding results obtained with the SUBROUTINE SHFS are given in table 6.6.1.

There is not much published work which uses this method for calculating $\Lambda^0$ and $K$. As was shown in subsection 6.5 the errors involved in any extrapolation method are rather large and, most probably, because of this workers from the Shedlovsky school seem to prefer the "direct" method of calculation (see subsection 6.3). However the agreement is good between the values calculated here by the Shedlovsky-Fuoss method and those obtained by other methods (for the same experimental data).

**Conclusions** These methods, as Ives method, use the extrapolation of straight lines (6.6.3 and 6.6.10) to obtain $\Lambda^0$ and $K$ of an acid from a series of "$\Lambda - c$" experimental data. $\Lambda$ is the conductance of the acid solutions and $c$ the concentration of these solutions.

A comparison between these methods and other methods of extrapolation can be found in subsection 6.9.
Table 6.6.1: A comparison between the values of $\Lambda^0$ and $K$ for a series of acids calculated by the Shedlovsky-Fuoss method and other methods.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref.</th>
<th>Max. conc. g-equiv/l $\times 10^3$</th>
<th>Published data $\Lambda^0$</th>
<th>$K \times 10^5$</th>
<th>Method of calc.</th>
<th>Calculated here by the Shedlovsky-Fuoss method $\Lambda^0$</th>
<th>$K \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>1</td>
<td>3.44</td>
<td>390.71</td>
<td>1.753</td>
<td>1</td>
<td>391.2</td>
<td>1.747</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>2</td>
<td>2.84</td>
<td>391.86</td>
<td>1.734</td>
<td>2</td>
<td>393.6</td>
<td>1.720</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>3</td>
<td>3.44</td>
<td>391.3</td>
<td>1.745</td>
<td>2</td>
<td>391.2</td>
<td>1.747</td>
</tr>
<tr>
<td>Mesoic acid</td>
<td>4</td>
<td>1.35</td>
<td>376.9</td>
<td>36.6</td>
<td>1</td>
<td>376.4</td>
<td>36.79</td>
</tr>
</tbody>
</table>


3. Idem, pg. 126. The data used are those of ref. 1.

6.7. A modified Fuoss-Shedlovsky method (Shedlovsky-Kay method)

The problem of solvent correction in conductance measurements was analysed in subsection 5.9 of this thesis. It was found that if the solvent is water and its conductance is due to the carbonic acid and water dissociation, the addition of the acid whose conductance is being measured greatly reduces these two dissociations and thus the solvent correction becomes negligible. However in most of the cases we are not sure about the nature of the ions causing the solvent conductance and thus we obviously do not know with any certainty whether or not a solvent correction should be applied and if so how it should be applied. Shedlovsky and Kay proposed a method to correct for the solvent conductance which by-passes the need for knowing the solvent conductance and its origin.

The conductance of a solution is considered as being given by:

\[ \Lambda = \frac{1000}{c} \left( \frac{1}{R_{\text{obs}}} - \frac{1}{R_w} \right) = \frac{1000}{c} \left( L_{\text{obs}} - L_w \right) \]  

(6.7.1)

where \( R_{\text{obs}} \) is the measured resistance of the solution and \( R_w \) is the resistance of the solvent. L's are specific conductivities. If the dissociation constant is given by:

\[ K_S = \frac{a^2 c}{1 - a} f_{\pm}^2 \]  

(6.7.2)

and

\[ \alpha = S(z) \frac{A}{\Lambda^0} \]  

(6.6.8)
then:

\[ K_S^{1/2} = \frac{\alpha c^{1/2}}{(1 - \alpha)^{1/2}} f_\pm = \frac{S(z)\Lambda}{\Lambda_0} f_\pm c^{1/2} \]

(6.7.3)

Substituting for \( \Lambda \) from (6.7.1) and rearranging:

\[ K_S^{1/2} (1 - S(z) \frac{1000}{c \Lambda_0} (L_{\text{obs}} - L_w)) = \frac{1000f_\pm c^{1/2} S(z)}{c \Lambda_0} (L_{\text{obs}} - L_w) \]

(6.7.4)

Hence:

\[ L_{\text{obs}} - L_w = \Lambda^0 K_S^{1/2} \frac{c^{1/2}}{1000Sf} (1 - \frac{1000SL_{\text{obs}}}{c \Lambda_0} (1 - \frac{L_{\text{obs}}}{L_w})) \]

(6.7.5)

In the first approximation:

\[ 1 - \frac{L_{\text{obs}}}{L_w} = 1 \]

and thus (6.7.5) becomes:

\[ L_{\text{obs}} = L_w + \Lambda^0 K_S^{1/2} \frac{c^{1/2}}{1000Sf} (1 - \frac{1000SL_{\text{obs}}}{c \Lambda_0}) \]

(6.7.6)

which is of the form:

\[ y = L_w + K_S^{1/2} \Lambda^0 x \]

(6.7.7)

A plot of \( y \) vs. \( x \) has the intercept \( L_w \) and the slope \( K_S^{1/2} \Lambda^0 \).

In the second approximation the complete equation, i.e. (6.7.5), can be used.
Thus the method renders the specific conductance of the solvent and the product $K_S^{1/2} \Lambda^0$. From this product either $K_S$ or $\Lambda^0$ can be obtained. The usual procedure is to obtain $\Lambda^0$ by some other method and to calculate $K_S$ from this product.

We tried to combine the two methods, i.e. the Fuoss-Shedlovsky and the Shedlovsky-Kay methods, into a single one. In this combined method, which we call the Fuoss-Shedlovsky-Kay method, $\Lambda^0$ is determined from a $x - y$ plot of the Fuoss-Shedlovsky method. Then this $\Lambda^0$ and the same values of concentration-conductance are used for a $x - y$ plot of the Shedlovsky-Kay method. From this plot $L_w$ is obtained. New values of conductance are calculated by applying (6.7.1). The new $\Lambda$'s are used for a new Fuoss-Shedlovsky plot from which a new $\Lambda^0$ is obtained. Then this value is used for a new Shedlovsky-Kay $x - y$ plot (expression 6.7.5 or 6.7.6). The procedure is repeated until $\Lambda^0$ does not change by more than a pre-established amount (approximately 0.1%).

The computer program performing this type of calculation is given in appendix 6.6.1 (SUBROUTINE SHFS). Examples are given in "Detailed calculations - 6.6.1". In table 6.8.1 we summarize and compare the results obtained by the three extrapolation methods presented here.

As a general observation for the Fuoss-Shedlovsky-Kay method: in the cases where the iteration method described above worked $L_w$ had reasonable values, in the range of $10^{-8}$ mho. However, the probable error of $L_w$ was so large that it took away any meaning $L_w$ could have had. Also it is worth noting that the dissociation constant and the limiting conductance did not change much when the new values for the conductance were used (i.e. $\Lambda_{\text{new}} = \Lambda_{\text{old}} - L_w$).
6.8. The Fuoss-Onsager-Skinner conductance equation applied to the determination of the dissociation constant and the limiting conductance of weak acids

We mentioned the conductance equation of Fuoss-Onsager and Skinner in subsection 5.4 of this thesis. For convenience the equation is given again below:

\[ \Lambda = \Lambda^0 - (\alpha^1\Lambda^0 + \beta)(ca)^{1/2} + (E_1^{-1}\Lambda^0 - E_2^{-1}) ca\ln(6E_1^{-1}ca) \]

\[ + L^1ca - K_Acaf_{\pm}^2\Lambda \]  \hspace{1cm} (5.4.1)

or:

\[ \Lambda + E_2^{-1}ca\ln(6E_1^{-1}ca) + \beta(ca)^{1/2} = \Lambda^0[1 - \alpha^1(ca)^{1/2} + E_1^{-1}ca\ln(6E_1^{-1}ca)] \]

\[ + L^1ca - K_Acaf_{\pm}^2\Lambda \]  \hspace{1cm} (6.8.1)

where:

\[ E_1^{-1} = 2.942 \times 10^{12}/(DT)^3 \]  \hspace{1cm} (5.4.6)

\[ E_2^{-1} = 0.4333 \times 10^8/[\eta(DT)^2] \]  \hspace{1cm} (5.4.7)

\[ \alpha^1 = 0.8204 \times 10^6/(DT)^{3/2} \]  \hspace{1cm} (5.4.3)

\[ \beta = 82.50/[\eta(DT)^{1/2}] \]  \hspace{1cm} (5.4.4)

Relation (6.8.1) is of the form:

\[ V = Ax + By + Cz \]  \hspace{1cm} (6.8.2)

If \( \Lambda^0 \) is known in a first approximation then \( x, y \) and \( z \) can be calculated from a series of experimental data, \( \Lambda \) and \( c \). Then by method of least squares the coefficients \( A, B \) and \( C \) are determined.
Since:

\[ \Lambda^0 = A \]

the value of A represents the next approximation to \( \Lambda^0 \). New values of x, y and z are calculated and the procedure is repeated until A (or \( \Lambda^0 \)) is constant within certain limits, e.g. 0.01%.

This procedure is similar to that employed by Kay, Hawes and Kay, Evans and Kay, or Swain and Evans for analysis of the conductance data of some salts in different solvents.

In fact we checked the computer program performing this type of calculation by using some of the data from the papers quoted above. The computer program is given in appendix 6.8.1 and the detailed results of these calculations are given in "Detailed calculations - 6.8.1". A summary of the results is given in table 6.8.1. The agreement between the published values and the values obtained here is good. Some disagreements occur in the case of compounds which are completely dissociated in solution. This is expected since we used for the calculations the conductance equation which is applicable to associated solutes. It must also be mentioned that the original papers quote the standard deviation while here the probable error is calculated.
Table 6.8.1: A comparison between published data and the results obtained here when using Fuoss-Onsager-Skinner conductance equation

<table>
<thead>
<tr>
<th>Compound Solvent Temperature</th>
<th>Reference</th>
<th>Published</th>
<th>Calculated here</th>
<th>a*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\Lambda^0$</td>
<td>$K_D$ (A)</td>
<td>$\Lambda^0$</td>
</tr>
<tr>
<td>Me₄NCl in H₂O, 25°C</td>
<td>116</td>
<td>120.39±</td>
<td>-</td>
<td>2.4±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.06</td>
<td>0.1</td>
<td>0.08</td>
</tr>
<tr>
<td>Bu₄NI in H₂O, 25°C</td>
<td>116</td>
<td>96.28±</td>
<td>0.32±</td>
<td>3.0±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.03</td>
<td>0.09</td>
<td>1.0</td>
</tr>
<tr>
<td>KF in H₂O at 25°C</td>
<td>50</td>
<td>128.86±</td>
<td>-</td>
<td>3.3±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.04</td>
<td>0.1</td>
<td>0.07</td>
</tr>
<tr>
<td>CsCl in 100% EtOH at 25°C</td>
<td>115</td>
<td>48.33±</td>
<td>(6.34±</td>
<td>4.2±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>x 10⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium benzoate in H₂O, 25°C</td>
<td>50</td>
<td>105.58±</td>
<td>-</td>
<td>4.2±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.03</td>
<td>0.2</td>
<td>0.01</td>
</tr>
<tr>
<td>KCl in 38.37% EtOH at 25°C</td>
<td>115</td>
<td>57.022±</td>
<td>-</td>
<td>2.71±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.004</td>
<td>0.01</td>
<td>0.16</td>
</tr>
</tbody>
</table>

* This value is not calculated in our program; it must be given. In this case it was taken from the original papers.

The results obtained for weak acid solutions are given in detail in "Detailed calculations - 6.8.1". A summary is shown in table 6.10.1. The agreement between the results obtained by this method and the results obtained by other methods varies. In some cases the results are identical (or almost identical) to those
obtained by extrapolation methods or "direct" methods. In other cases they are quite different. One is inclined to say that the method based on the Fuoss-Onsager-Skinner equation is more reliable than an extrapolation method because of the fact that it does not involve any extrapolation. However the situation is not that simple. The values of the coefficients A, B and C (equation 6.8.1) are very sensitive to errors in A and c. To see exactly how sensitive they are we took a typical set of conductance data and we assumed certain errors in A and c. The conductance and the concentration values were corrected for these errors and then $A^0$ and $K$ were calculated by applying the method based on Fuoss-Onsager-Skinner conductance equation. The conductance data considered were those of MacInnes and Shedlovsky on acetic acid.\(^97\) This set of data gives practically the same final results, i.e. $A^0$ and $K$, independent of the method used to calculate them.

The details of these calculations are given in "Detailed calculations - 6.8.2". A summary of the results obtained is shown in table 6.8.2.

From table 6.8.2 it can be seen that any error in A or c results in large errors in $A^0$ and $K$. Unfortunately this happens without making the fitting worse. The closeness of fit is therefore no criterion for judging whether the results obtained are valid or not.

The errors in $A^0$ and $K$ which result as a consequence of errors in A and c are much larger in this method than in the extrapolation methods.
As in the case of the extrapolation method it is particularly disturbing to see how large errors in $\Lambda^0$ and $K$ result from a small constant absolute error in the conductance values (see "runs" no. 2 to 5 in table 6.8.2).

In conclusion it can be said that any limiting conductance $\Lambda^0$ or dissociation constant $K$ calculated by this method is unreliable unless we are completely sure that the experimental conductance values, especially, are free from errors, particularly any constant absolute error such as those caused by impurities in the solution or by the solvent conductance.
Table 6.8.2: The limiting conductance $\Lambda^0$ and the dissociation constant $K$ obtained from a set of conductance data which was corrected for "hypotetical" experimental errors in $\Lambda$ or $c$ values.

<table>
<thead>
<tr>
<th>&quot;Run&quot;</th>
<th>Conductance</th>
<th>Concentration</th>
<th>Limiting conductance $\Lambda^0$</th>
<th>Dissociation const. $K \times 10^5$</th>
<th>Error of the fitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\Lambda$</td>
<td>$c$</td>
<td>$390.72 \pm 0.51$</td>
<td>$1.752 \pm 0.004$</td>
<td>$0.18$</td>
</tr>
<tr>
<td>2</td>
<td>$\Lambda - 5 \times 10^{-7}/c$</td>
<td>$c$</td>
<td>$308.93 \pm 2.2$</td>
<td>$2.91 \pm 0.04$</td>
<td>$0.95$</td>
</tr>
<tr>
<td>3</td>
<td>$\Lambda - 1 \times 10^{-7}/c$</td>
<td>$c$</td>
<td>$371.78 \pm 0.66$</td>
<td>$1.856 \pm 0.006$</td>
<td>$0.24$</td>
</tr>
<tr>
<td>4</td>
<td>$\Lambda - 1 \times 10^{-8}/c$</td>
<td>$c$</td>
<td>$388.77 \pm 0.50$</td>
<td>$1.762 \pm 0.004$</td>
<td>$0.17$</td>
</tr>
<tr>
<td>5</td>
<td>$\Lambda + 1 \times 10^{-7}/c$</td>
<td>$c$</td>
<td>$411.23 \pm 0.85$</td>
<td>$1.653 \pm 0.005$</td>
<td>$0.28$</td>
</tr>
<tr>
<td>6</td>
<td>$\Lambda \times 1.05$</td>
<td>$c$</td>
<td>$410.32 \pm 0.53$</td>
<td>$1.839 \pm 0.004$</td>
<td>$0.18$</td>
</tr>
<tr>
<td>7</td>
<td>$\Lambda \times 1.01$</td>
<td>$c$</td>
<td>$394.65 \pm 0.51$</td>
<td>$1.770 \pm 0.004$</td>
<td>$0.18$</td>
</tr>
<tr>
<td>8</td>
<td>$\Lambda \times 0.99$</td>
<td>$c$</td>
<td>$386.81 \pm 0.51$</td>
<td>$1.735 \pm 0.004$</td>
<td>$0.17$</td>
</tr>
<tr>
<td>9</td>
<td>$\Lambda \times 0.95$</td>
<td>$c$</td>
<td>$371.14 \pm 0.49$</td>
<td>$1.665 \pm 0.004$</td>
<td>$0.17$</td>
</tr>
<tr>
<td>10</td>
<td>$\Lambda$</td>
<td>$c \times 0.999$</td>
<td>$390.73 \pm 0.51$</td>
<td>$1.750 \pm 0.004$</td>
<td>$0.18$</td>
</tr>
<tr>
<td>11</td>
<td>$\Lambda$</td>
<td>$c \times 1.001$</td>
<td>$390.73 \pm 0.51$</td>
<td>$1.754 \pm 0.004$</td>
<td>$0.18$</td>
</tr>
</tbody>
</table>

2. In "run" no. 1 the concentration and the conductance data were unchanged from those published. In "runs" no. 2 to 5 a constant absolute error in the specific conductance was assumed. The errors assumed range from $-5 \times 10^{-7}$ to $+1 \times 10^{-7}$ mho. In "runs" no. 6 to 9 a constant relative error in the conductance values was assumed. The errors range from $+5\%$ to $-5\%$ of the conductance value. In "runs" no. 10 and 11 a constant relative error of $\pm 0.1\%$ in the concentration value was assumed.
6.9. Other methods of computation

A series of other conductance formulas are available in the literature. We tried to apply a variety of them to the calculation of \( \Lambda^o \) and/or \( K \). Our trials failed. We will give a brief account of what was tried for no other reason than to prevent others from repeating the same thing in the future. This does not mean that we are the first ones to try these calculations. What it means is that they were not reported before (at least in a publication) by anybody. One may deduce from the fact that nobody used them, though they were available, that these formulas did not give proper results. However a built-in human characteristic is "to try, maybe...". Very often the negative results are as important as the positive ones. However the former remain unknown to the large majority of those who might be interested.

The general expression for conductance is:\[117\]

\[
\Lambda = \Lambda^o - \Lambda_I - \Lambda_{II} \tag{6.9.1}
\]

where \( \Lambda^o \) is the limiting value of the molar conductance at infinite dilution; \( \Lambda_I \) refers to the relaxation effect and \( \Lambda_{II} \) refers to the electrophoretic effect.

The methods presented so far make use of the Onsager limiting equation in which:

\[
\Lambda_I = \frac{\sigma^2 - \sigma_{\infty}^2}{1 + \frac{q^2}{k^2}} \cdot \frac{k}{3DkT} \Lambda^o \tag{6.9.2}
\]
\[ \Lambda_{II} = \frac{N_A}{54\pi \times 10^{11}} (v_+e_+^2 + v_-e_-^2) \]  
(6.9.3)

\[ e_i = z_i e_0 \]  
(6.9.4)

The model on which the Onsager limiting law is based is one in which the ions are represented as point charges. Onsager and Fuoss\textsuperscript{118} using a model of charged spheres with the diameter "a" found for the electrophoretic term:

\[ \Lambda_{II} = \frac{N_A}{54\pi \times 10^{11}} \times \frac{v_+e_+^2 + v_-e_-^2}{\eta} \times \frac{\kappa}{1 + \kappa a} \]  
(6.9.5)

Taking into consideration the same distance "a" (the distance of closest approach between the centres of the two oppositely charged ions) Kaneko gives for the relaxation time term the following expression:\textsuperscript{119}

\[ \Lambda_I = \frac{e_+e_-}{3DkT} \cdot \frac{q}{1 - q} \cdot \frac{\kappa}{(1 + \kappa a)\kappa a} \{\exp[(1 - q^2)\kappa a] - 1\} \]  
(6.9.6)

Falkenhagen, Leist and Kelbg\textsuperscript{57} give for a 1:1 electrolyte the following conductance formula:

\[ \Lambda = (\Lambda^0 - \frac{82.5}{n(\Delta T)^{\frac{1}{2}}} \frac{c^\frac{3}{2}}{1 + \kappa a})(1 + \frac{\Delta X}{X}) \]  
(6.9.7)

in which the second term in the first set of brackets refers to the electrophoretic effect and the term \(\Delta X/X\) to the relaxation effect.
\[ \frac{\Delta X}{X} \text{ in one of the forms is:} \]

\[ \frac{\Delta X}{X} = -\frac{e_0^2}{3DKT} \cdot \frac{q}{1 + q^{\frac{1}{2}}} \cdot \frac{\kappa}{(1 + \kappa a)(1 + \kappa a q^{\frac{1}{2}} + \kappa^2 a^2/6)} \quad (6.9.8) \]

Wishaw and Stokes combining (6.9.7) with:

\[ \frac{\Delta X}{X} = -\frac{e_0^2}{3DKT} \cdot \frac{0.2929}{1 + \kappa a} \cdot \frac{e^{0.2929 \kappa a} - 1}{0.2929 \kappa a} \quad (6.9.9) \]

and introducing a viscosity correction factor obtained:

\[ \Lambda = (\Lambda^0 - \frac{BC^{\frac{1}{2}}}{1 + BAC^{\frac{1}{2}}})(1 - \frac{a_1 C^{\frac{1}{2}}}{1 + BAC^{\frac{1}{2}}} \cdot F) \frac{n^0}{n} \quad (6.9.10) \]

where:

\[ \frac{n^0}{n} = \frac{1}{1 + \frac{5}{2} \cdot \frac{4\pi R^3}{3} \cdot \frac{N_A C}{1000}} \quad (6.9.11) \]

\[ \frac{q}{1 + q^{\frac{1}{2}}} = 0.2929 \]

\[ F = \frac{\exp(0.2929 \kappa a) - 1}{0.2929 \kappa a} \quad (6.9.12) \]
For weak electrolytes (6.9.10) takes the form:

\[ \Lambda = \left( \Lambda^0 - \frac{\beta (ca)^{\frac{1}{2}}}{1 + Ba(ca)^{\frac{1}{2}}} \right) \left( 1 - \frac{\alpha^1 (ca)^{\frac{1}{2}}}{1 + Ba(ca)^{\frac{1}{2}}} \times F \right) \frac{n^0}{n} \]  

(6.9.13)

Note that (6.8.13) rearranges to:

\[ \Lambda^0 = \frac{1}{\alpha \left( 1 - \frac{\alpha^1 (ca)^{\frac{1}{2}}}{1 + Ba(ca)^{\frac{1}{2}}} \right) F} \frac{n^0}{n} \Lambda + \frac{\beta (ca)^{\frac{1}{2}}}{1 + Ba(ca)^{\frac{1}{2}}} \]  

(6.9.14)

Robinson and Stokes\textsuperscript{121} give a conductance formula similar to (6.8.7):

\[ \Lambda = \Lambda^0 - \frac{\alpha \Lambda^0 + \beta}{1 + \kappa a} c^{\frac{1}{2}} \]  

(6.9.15)

For weak electrolytes and correcting for the viscosity (6.8.15) rearranges to:

\[ \Lambda^0 = \frac{\frac{\Lambda}{\alpha} + \frac{\beta (ca)^{\frac{1}{2}} n^0}{1 + \kappa a n}}{\frac{n^0}{n} \left( 1 + \frac{\alpha^1 (ca)^{\frac{1}{2}}}{1 + \kappa a} \right)} \]  

(6.9.16)

If \( \alpha \), the degree of dissociation is obtained by some other available formula, e.g. (6.3.14) and (6.4.9), then (6.9.14) or (6.9.16) can be used to obtain \( \Lambda^0 \) for a series of experimental data, \( \Lambda \) and \( c \), using a certain value for "a". The \( \Lambda^0 \) so obtained could be used to calculate new \( \alpha \)'s (second approximations). The new \( \alpha \)'s are used to
calculate the new $\Lambda^0$'s. The procedure could be repeated until $\alpha$ and $\Lambda^0$ fail to change within certain limits.

Appendix 6.9.1 contains a computer program which performs the calculation described above. The data used in the trial run are those of Ives on acetic acid. The results indicate that neither formula leads to the convergence of $\Lambda^0$ and the formulae are therefore of little use to us.

The Kelbg conductance formula contains the following terms:

$$\Lambda_I = \frac{e_0^2}{6DKT} (q - q^2) \frac{\kappa}{(1 + \kappa a)(1 + 2\kappa a/2 + \kappa^2 a^2/6)}$$  \hspace{1cm} (6.9.17)

$$\Lambda_{II} = \frac{e_0^2 N_A}{27\pi 10^{11} n} \cdot \frac{\kappa}{1 + \kappa a}$$  \hspace{1cm} (6.9.18)

Combining (6.9.1), (6.9.17) and (6.9.18):

$$\Lambda^0 = \Lambda + \Lambda_I + \Lambda_{II}$$  \hspace{1cm} (6.9.19)

Appendix 6.9.2 contains a computer program in which $\Lambda^0$ is obtained from (6.9.19) and $\alpha$ from (6.3.14) and (6.4.9). The calculation is repeated until $\Lambda^0$ converges to a certain value. It can be seen from the computer output that this does not occur: the value of $\Lambda^0$ is decreasing continuously from its first approximation of 392 mho. MacInnes and Shedlovsky data on acetic acid are used in the trial run.
Fuoss-Onsager equation

Another failure occurred when we tried to use the new Fuoss-Onsager conductance equation in the form described below.

Using a model of charged spheres of diameter "a" Fuoss and Onsager obtained the following equation:

\[ \Lambda = \Lambda^0 - (\alpha \Lambda^0 + \beta)c^{1/2} + cB(\kappa a) \]  

(6.9.20)

where all the symbols with the exception of \( B(\kappa a) \) were defined previously. \( B(\kappa a) \) has a rather complicated expression:

\[ B(\kappa a) = \frac{(kab)^2}{c} \left[ \frac{(1 + 2b)\phi_1}{b_2} - \phi_2 \right] \Lambda^0 + \frac{8kab}{c^{1/2}} \left( \frac{\phi_3 + \phi_4}{\phi_1} \right) + a^{1/2} \beta \]

(6.9.21)

where \( \phi \)'s are auxiliary functions which depend primarily on \( \kappa a \). They can be found in the original paper.

An approximation to the conductance equation is:

\[ \Lambda = \Lambda^0 - Sc^{1/2} + E^1c\log(c) + Jc \]

(6.9.22)

If we note:

\[ \Lambda^1 = \Lambda + Sc^{1/2} - E^1c\log(c) \]

(6.9.23)

then:

\[ \Lambda^1 = \Lambda^0 + Jc \]

(6.9.24)

\[ E^1 = 2.303 \left[ \frac{(kab)^2}{24c} \Lambda^0 - \frac{kab\beta}{16c^{1/2}} \right] \]

(6.9.25)
Relation (6.9.24) should give a straight line on plotting \( \Lambda^1 \) vs. \( c \). The intercept is \( \Lambda^0 \) and the slope is \( J \). For weak electrolytes \( c \) should be replaced consistently by \( c_\alpha \) and \( \Lambda \) by \( \Lambda^e \).

Appendix 6.9.3 presents a computer program which uses (6.3.14) to calculate \( \alpha \), (6.4.9) to calculate \( \Lambda^e \) and (6.9.24) to calculate the next approximation to \( \Lambda^0 \). The results were not satisfactory because the second approximation to \( \Lambda^0 \) was very much dependent on the first one.

6.10. **Conclusions**

Table 6.10.1 presents a complete summary of the limiting conductance and of the dissociation constant of a series of organic acids obtained from literature conductance data by several different methods of calculation.

The intention of this table is to provide a basis for choosing the most appropriate method of calculation of \( K \) and \( \Lambda^0 \) from conductance data. By "most appropriate" we understand the method which leads to the smallest errors in \( \Lambda^0 \) and \( K \) and which is least sensitive to experimental errors in \( \Lambda \) and \( c \).

As the most important conclusion we have to repeat what most of the workers in this field have observed: the methods which calculate \( \Lambda^0 \) and \( K \) from a unique set of experimental data are very sensitive to systematic and random errors in the conductance values, especially. The methods which determine \( \Lambda^0 \) from the conductance of the salt solutions and \( K \) from the conductance of the acid solutions lead to the smallest errors in \( \Lambda^0 \) and \( K \). Obviously the experimental work in this case is at least twice as large, compared to the methods which require the conductance of the acid solutions only.
Another goal of table 6.10.1 is to provide a check for our computer programs which calculate $\Lambda^0$ and $K$ from conductance data. In general the values obtained here agree with those published. The small differences between the published values and those calculated here which appear in certain cases can be attributed, at least in part, to the different values for the universal constants used in the two computations. Only in one of the cases considered by us, so far is the difference between the published value of the dissociation constant and that calculated by us so large that a reexamination of the published data seems necessary. We are referring to the case of picric acid.\textsuperscript{106} We cannot find any obvious explanation for this difference. It is interesting that the value of the limiting conductance is the same in both cases. Another important difference is the fact that the original paper states explicitly that the Ives and the Fuoss-Shedlovsky methods of calculation lead to the same results; this is not the case here: the two methods agree as far as $\Lambda^0$ is concerned. However they give completely different results for the dissociation constant $K$.

Another point of interest with regard to picric acid or any other acid of similar strength is the large error in $K$ as compared to the error in $\Lambda^0$ or as compared to equivalent errors in the case of weaker acids. The large error in $K$ suggests that in the case of a strong acid, as picric acid, the slope of the linear plot of extrapolation methods is more sensitive to experimental errors than the intercept. This is exactly the reverse of the situation encountered in the case of weak acids ($K$ between $10^{-3}$ and $10^{-5}$, approximately). Recall that in extrapolation methods the intercept gives the limiting conductance and the slope gives the dissociation constant.
We applied a "Kilpatrick" type errors analysis (see subsection 6.5) to the data for picric acid. The detailed results are given in "Detailed calculations - 6.10.1". Table 6.10.2 presents a summary of these results.

Table 6.10.2: Error analysis for picric acid.

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<th>Origin of error</th>
<th>Error (%)</th>
</tr>
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<tr>
<td>Constant relative error in the conductance of 0.02%</td>
<td>-0.21</td>
</tr>
<tr>
<td>Constant absolute error in the specific conductance of 2 x 10^{-8} mho</td>
<td>86.</td>
</tr>
<tr>
<td>Constant relative error in the concentration of 0.004%</td>
<td>0.09</td>
</tr>
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</table>

It can be seen that an absolute error in the specific conductance leads to a very large error in the dissociation constant. In contrast the influence of the experimental errors on \( \Lambda^0 \) is small. These observations could explain why the limiting conductance is obtained very accurately independent of the method of calculation while the value for the dissociation constant shows a large uncertainty.
Table 6.10.1: Calculation of the dissociation constant and the limiting conductance of weak acids from conductance data. A comparison between different methods of calculation.

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<th>Compound</th>
<th>No. of exp. points mg-equiv/l soln.</th>
<th>Max. conc.</th>
<th>$\lambda^0$</th>
<th>$K$</th>
<th>Met. of error calc.</th>
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<th>Prob. of error</th>
<th>ε₀ Value</th>
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<td></td>
<td>3.3</td>
<td>0.12</td>
<td></td>
<td></td>
<td>0.61</td>
<td>0.06</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>In method 4 the iteration did not converge</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>3.3</td>
<td></td>
<td>380.20*</td>
<td>1.281</td>
<td>0.37</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>3.3</td>
<td>0.74</td>
<td>negative</td>
<td></td>
<td></td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>- calculated here</td>
<td>18</td>
<td>3.3</td>
<td></td>
<td>380.35</td>
<td>0.94</td>
<td>0.05</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>(sets 1 + 2)</td>
<td></td>
<td></td>
<td>0.03</td>
<td></td>
<td></td>
<td>0.81</td>
<td>0.04</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>3.3</td>
<td></td>
<td>380.36</td>
<td>2.0</td>
<td>1.1</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>3.3</td>
<td></td>
<td>380.20*</td>
<td>380.20</td>
<td>negative</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

* Assumed value

**Methods:**

1. "Direct" method: 1a. ε₀ from salt conductance and equation (6.3.2).
   1b. K_D from acid conductance and equation (6.3.16).
   1c. K_D from acid conductance and equation (6.3.15) and (6.3.18).

2. Ives method (subsection 6.4).

3. Fuoss-Shedlovsky method (subsection 6.6).


5. "Direct" (Dippy's) method for calculating K_D (subsection 6.3).

6. Method based on the Onsager-Fuoss-Skinner conductance equation (subsection 6.8).
References:
7. THE DETERMINATION OF THE LIMITING CONDUCTANCE (THE CONDUCTANCE AT ZERO CONCENTRATION) OF SODIUM BENZOATE AT TEMPERATURES BETWEEN 20° AND 40°C

7.1. Introduction

In subsection 6.5 we analysed the errors which were involved in the determination of the dissociation constant of acids by the conductance method. It was shown there that the errors could be rather large if the limiting conductance \( \Lambda^0 \) and the dissociation constant \( K \) were determined simultaneously by the so-called extrapolation methods. However if \( \Lambda^0 \) was determined separately, the accuracy of both, the limiting conductance and the dissociation constant improved considerably.

We determined the limiting conductance of sodium benzoate in aqueous solution for temperatures between 20° and 40°C. These values combined with the values of \( \Lambda^0 \) for hydrogen and sodium ions would give us the desired \( \Lambda^0 \) for benzoic acid.

7.2. Materials

Sodium benzoate from "Fisher Scientific" was used. The compound was recrystallized twice from conductivity water, washed with absolute ethanol and dried at 65°C and 0.1 mm of Hg for 48 hours. Particular care was taken with all the glassware used for the recrystallization. All the pieces used were previously steamed for at least half an hour, and rinsed with conductivity water.

The water used to prepare the solutions was obtained in the same way as described in subsection 5.9. Its specific conductance at 20° was approximately \( 7.4 \times 10^{-8} \) mho. The exact values are given in table 5.9.4.
7.3. The conductance measurements

The preparation of the solutions and the conductance measurements followed the same procedure as in the case of KCl (see subsection 5.10).

The resistance of five independently prepared solutions was measured at five different temperatures from 19.7 to 40.3°C, approximately, and four different frequencies: 1000, 2000, 3500 and 5000 Hz. The measurements were made in order of increasing temperature. The temperature control was ±0.002°C. The complete set of measurements for one solution, i.e. 20 readings, 5 temperatures with 4 frequencies at each temperature, took approximately 15 hours. The measurements were carried out without stopping, in one day.

The equipment used was the same as for the KCl solutions. The resistance readings for each solution were smoothed out by fitting them into a polynomial of the form:

\[ R = A + BT + CT^2 + DT^3 \]

where T is the temperature in °C. Once A, B, C, and D were found, we could interpolate for values of R at 20, 25, 30, 35 and 40°C.

The solutions were made up by weight, i.e. grams solute/kilogram solution. All the weights were corrected for the buoyancy of air. The density of sodium benzoate used for this correction was assumed to be 1.0. The transformation to concentration units of gram-equivalents/litre solution was done through the relation:

\[ c(\text{g-equiv/l soln}) = d \times c(\text{g/kg soln})/M \]  

(7.3.0)
where \( d \) is the density of water at the temperature considered (see table 7.3.1) and \( M \) is the molecular weight of sodium benzoate. It was taken to be 144.105.

Table 7.3.1: The density of water at temperature in the range 20 to 40°C

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Density g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.9982323</td>
</tr>
<tr>
<td>25</td>
<td>0.9970739</td>
</tr>
<tr>
<td>30</td>
<td>0.9956756</td>
</tr>
<tr>
<td>35</td>
<td>0.9940594</td>
</tr>
<tr>
<td>40</td>
<td>0.9922455</td>
</tr>
</tbody>
</table>


Cells nos. 3A and 3B were used for measurements. The cell constants employed in the calculations are those given in table 5.10.1. For convenience they are given again below:

<table>
<thead>
<tr>
<th>Frequency Hz</th>
<th>Cell constant Cell 3A</th>
<th>Cell 3B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>4.8466</td>
<td>2.8456</td>
</tr>
<tr>
<td>2000</td>
<td>4.8453</td>
<td>2.8447</td>
</tr>
<tr>
<td>3500</td>
<td>4.8444</td>
<td>2.8442</td>
</tr>
<tr>
<td>5000</td>
<td>4.8441</td>
<td>2.8441</td>
</tr>
</tbody>
</table>
The complete experimental values and calculations are given in "Detailed calculations - 7.3.1 and 7.3.2".

7.4. Calculation of the limiting conductance of sodium benzoate

The procedure of Saxton and Meier\(^79\) was followed. In this procedure the conductance-concentration experimental data are fitted by the method of least squares into an expression of the form:

\[
\frac{\Lambda + Bc^{1/2}}{1 - \alpha_1c^{1/2}} = \Lambda^0 + Ac \tag{7.4.1}
\]

or:

\[
\frac{\Lambda + Bc^{1/2}}{1 - \alpha_1c^{1/2}} = \Lambda^0 + Ac + BClogc \tag{7.4.2}
\]

where all the symbols have the usual significance (see section 6, for example).

The computer program used for calculating the limiting conductance for sodium benzoate is given in appendix 7.4.1. The program was checked by recalculating \(\Lambda^0\) from the Saxton and Meier data\(^79\) on sodium benzoate. A summary of the results is given in table 7.4.1:

Table 7.4.1: A comparison between the published results and the results obtained here for the Saxton-Meier data on sodium benzoate

<table>
<thead>
<tr>
<th></th>
<th>(\Lambda^0)</th>
<th>A</th>
<th>B</th>
<th>MSD*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Published (7.4.1)</td>
<td>82.34</td>
<td>99.9</td>
<td>-</td>
<td>?</td>
</tr>
<tr>
<td>Calculated here - expression (7.4.1)</td>
<td>82.30</td>
<td>105.0</td>
<td>-</td>
<td>0.022</td>
</tr>
<tr>
<td>Calculated here - expression (7.4.2)</td>
<td>82.22</td>
<td>58.82</td>
<td>-28.4</td>
<td>0.005</td>
</tr>
</tbody>
</table>

* Mean Square deviation
Note: Saxton and Meier treated $\alpha^1$ of expressions (7.4.1) and (7.4.2) as an adjustable parameter. It had the value of 78.62 as compared to the value employed here of 60.11, theoretically derived.

The experimental conductance-concentration values obtained by us were treated in two different ways. In the first set of calculations the conductance values were not corrected for the conductance of water. In the second set of calculations they were corrected for the solvent conductance. The solvent correction used is that discussed in subsection 5.9 of this thesis. This correction assumes that the solvent conductance is due to CO$_2$ dissolved in the water. To calculate the correction, the limiting conductances of all ions involved are needed. Also needed are the dissociation constants of benzoic acid, carbonic acid and the ionic product of water. The values used by us are given below.

The limiting conductance of H$^+$ was calculated from:$^{78}$

\[
\Lambda^0_{H^+} = 350.15 + 4.8324(T-25) + 3.06 \times 10^{-3}(T-25)^2 - 4.828 \times 10^{-5}(T-25)^3
\] (7.4.3)

T: Temperature in °C.

the limiting conductance of OH$^-$ from:$^{78}$

\[
\Lambda^0_{OH^-} = 199.18 + 3.3604(T-25) + 3.06 \times 10^{-3}(T-25)^2 + 4.828 \times 10^{-5}(T-25)^3
\] (7.4.4)

and the limiting conductance of Na$^+$ from:$^{59}$

\[
\Lambda^0_{Na^+} = 50.15 + 1.0916(T-25) + 4.715 \times 10^{-3}(T-25)^2 - 1.15 \times 10^{-5}(T-25)^3
\] (7.4.5)
To obtain the limiting conductance for the bicarbonate ion, the procedure was a bit more involved. The data available in the literature were:

(i) \( \Lambda^0_{\text{HCO}_3^-}(18^\circ) = 40.7 \)

This value was calculated from the limiting conductance of \( \text{NaCO}_3\text{H}^{126} \) minus the limiting conductance of \( \text{Na}^+:^{127} \)

\[
\Lambda^0_{\text{HCO}_3^-}(18^\circ) = \Lambda^0_{\text{NaHCO}_3}(18^\circ) - \Lambda^0_{\text{Na}^+}(18^\circ) = 83.5 - 42.8 = 40.7
\]

(ii) \( \Lambda^0_{\text{HCO}_3^-}(25^\circ) = 44.5^{128} \)

The two literature values of \( \Lambda^0_{\text{HCO}_3^-} \), at 18 and 25°C, were used to obtain A and B from the relation:\(^24\)

\[
\log(\Lambda^0) = A + B/T
\] (7.4.6)

where T is the temperature in degrees kelvin.

The results were:

\[
A = 3.01463
\]

\[
B = -480.88
\]

Using these two values and (7.4.6) we calculated the limiting conductance for \( \text{HCO}_3^- \) at the temperatures of interest to us.

The limiting conductance of benzoate ion was obtained by subtracting the limiting conductance of sodium ion from the limiting conductance of sodium benzoate obtained by us from the uncorrected (for solvent conductance) values of conductance.

The limiting conductances of the different ions involved in
the calculation of solvent conductance for aqueous solutions of sodium benzoate are summarized in table 7.4.2.

Table 7.4.2: The limiting conductance of ions at temperatures between 20 and 40°C

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$\Lambda^0_{H^+}$</th>
<th>$\Lambda^0_{OH^-}$</th>
<th>$\Lambda^0_{Na^+}$</th>
<th>$\Lambda^0_{HCO_3^-}$</th>
<th>$\Lambda^0_{BzO^-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>325.74</td>
<td>182.46</td>
<td>44.81</td>
<td>41.8</td>
<td>28.8</td>
</tr>
<tr>
<td>25</td>
<td>350.15</td>
<td>199.18</td>
<td>50.15</td>
<td>44.5</td>
<td>32.5</td>
</tr>
<tr>
<td>30</td>
<td>374.04</td>
<td>216.05</td>
<td>55.72</td>
<td>47.3</td>
<td>36.3</td>
</tr>
<tr>
<td>35</td>
<td>397.37</td>
<td>233.04</td>
<td>61.53</td>
<td>50.2</td>
<td>40.3</td>
</tr>
<tr>
<td>40</td>
<td>420.06</td>
<td>250.11</td>
<td>67.55</td>
<td>53.2</td>
<td>44.5</td>
</tr>
</tbody>
</table>

*BzO^-: benzoate ion.

The equilibrium constants used in the calculation of solvent correction for sodium benzoate aqueous solutions are given in table 7.4.3.

Table 7.4.3: The dissociation constant of some acids

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$K_1(H_2CO_3)$</th>
<th>$K(HOBz)$</th>
<th>$K_w(H_2O)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>$4.147 \times 10^{-7}$</td>
<td>$6.19 \times 10^{-5}$</td>
<td>$0.6809 \times 10^{-14}$</td>
</tr>
<tr>
<td>25</td>
<td>$4.452 \times 10^{-7}$</td>
<td>$6.28 \times 10^{-5}$</td>
<td>$1.008 \times 10^{-14}$</td>
</tr>
<tr>
<td>30</td>
<td>$4.710 \times 10^{-7}$</td>
<td>$6.24 \times 10^{-5}$</td>
<td>$1.469 \times 10^{-14}$</td>
</tr>
<tr>
<td>35</td>
<td>$4.914 \times 10^{-7}$</td>
<td>$6.17 \times 10^{-5}$</td>
<td>$2.089 \times 10^{-14}$</td>
</tr>
<tr>
<td>40</td>
<td>$5.058 \times 10^{-7}$</td>
<td>$6.04 \times 10^{-5}$</td>
<td>$2.919 \times 10^{-14}$</td>
</tr>
</tbody>
</table>
References:

The limiting conductance was calculated by both equations, i.e. (7.4.1) and (7.4.2). The error of the fitting or the error in \( \Lambda^0 \) did not improve on going from an equation with two adjustable parameters (7.4.1) to an equation with three adjustable parameters (7.4.2). In fact the error in the limiting conductance increased on going from (7.4.1) to (7.4.2). We consider the values of the limiting conductance of sodium benzoate obtained from equation (7.4.1) from the solvent-corrected conductance values as the best results. A complete summary of the results obtained by us is given in table 7.4.3.

Table 7.4.3: Values for the limiting conductance of sodium benzoate in aqueous solution obtained in the present work

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Set 1: cond. values not corr. for solv. cond.</th>
<th>Set 2: cond. values are corr. for solvent conductance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(7.4.1)</td>
<td>(7.4.2)</td>
</tr>
<tr>
<td>20</td>
<td>73.51</td>
<td>74.03</td>
</tr>
<tr>
<td>25</td>
<td>82.50</td>
<td>83.25</td>
</tr>
<tr>
<td>30</td>
<td>91.91</td>
<td>92.65</td>
</tr>
<tr>
<td>35</td>
<td>101.66</td>
<td>102.27</td>
</tr>
<tr>
<td>40</td>
<td>111.82</td>
<td>112.43</td>
</tr>
</tbody>
</table>
The computer programs used to calculate the results of table 7.4.3 and the complete results are given in "Detailed calculations 7.4.2 and 7.4.3".

Finally the limiting conductances of table 7.4.3, column 4, were fitted into a relation of the form:

\[ \log(\Lambda^0) = A + \frac{B}{T} \] (7.4.6)

where \( T \) is the absolute temperature.\textsuperscript{24}

The complete results are given in "Detailed calculations - 7.4.4 and 7.4.5". A summary is given in table 7.4.4.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Limiting conductance ((\Lambda^0)_{\text{NaOBr}})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Obs.</td>
</tr>
<tr>
<td>20</td>
<td>73.59</td>
</tr>
<tr>
<td>25</td>
<td>82.62</td>
</tr>
<tr>
<td>30</td>
<td>92.06</td>
</tr>
<tr>
<td>35</td>
<td>101.87</td>
</tr>
<tr>
<td>40</td>
<td>112.10</td>
</tr>
</tbody>
</table>

Another relation used in the literature to express the change in \( \Lambda^0 \) with temperature is a polynomial of the form:\textsuperscript{59}

\[ \Lambda^0 = \Lambda^0(25^\circ) + A(T-25) + B(T-25)^2 + C(T-25)^3 \] (7.4.7)
We used (7.4.7) to fit our data and found that even the second degree polynomial (7.4.9) expresses the change with temperature very well. Expressions quoted in table 7.4.4 and not given so far are:

\[ \Lambda^0 = \Lambda^0(25^\circ) + A(T-25) \]  \hspace{1cm} (7.4.8)

\[ \Lambda^0 = \Lambda^0(25^\circ) + A(T-25) + B(T-25)^2 \]  \hspace{1cm} (7.4.9)

Certainly our data do not cover a wide enough range of temperature to enable us to tell exactly which of the four relations best represents the variation of \( \Lambda^0 \) with temperature.

7.5. Errors in the limiting conductance due to errors in the experimental concentration and conductance values

In part 6.5 of this thesis we analysed the errors in \( \Lambda^0 \) and \( K \) which result as a consequence of the systematic or random errors in the experimental quantities \( \Lambda \) and \( c \) when using the "extrapolation" methods of calculation. It was shown there that the errors in \( \Lambda^0 \) and \( K \) can be reduced if these two quantities are not determined simultaneously from a unique set of data but separately from two independent sets of data. Usually the limiting conductance is determined from the conductance of salt solutions.

It is interesting to see what the magnitude of the error is in \( \Lambda^0 \) determined by such a method, i.e. \( \Lambda^0 \) and \( K \) are determined separately, as a function of the errors in conductance and concentration. The treatment follows the same pattern as that of subsection 6.5.
From (7.4.2), \( \Lambda^0 \) is given by:

\[
\Lambda^0 = \frac{\Lambda + \beta c^2 - Ac - B\log c}{1 - \alpha^1 c^2}
\]  \hspace{1cm} (7.5.1)

Substituting for \( \Lambda \):

\[
\Lambda = \frac{1000\kappa}{c}
\]

\[
\Lambda^0 = \frac{\frac{1000\kappa}{c} + \beta c^2 - Ac - B\log c}{1 - \alpha^1 c^2}
\]  \hspace{1cm} (7.5.2)

The differential of (7.5.2) is:

\[
d\Lambda^0 = \frac{\delta \Lambda^0}{\delta \kappa} d\kappa + \frac{\delta \Lambda^0}{\delta c} dc
\]  \hspace{1cm} (7.5.3)

where:

\[
\frac{\delta \Lambda^0}{\delta \kappa} = \frac{1000}{c(1 - \alpha^1 c^2)}
\]  \hspace{1cm} (7.5.4)

and

\[
\frac{\delta \Lambda^0}{\delta c} = \frac{\left[ -\frac{1000\kappa}{c^2} + \frac{\beta}{2c^2} - A - B(\log c + 0.4343) \right](1 - \alpha^1 c^2)}{(1 - \alpha^1 c^2)^2}
\]

\[
+ \frac{\alpha^1}{2c^2} \left[ \frac{1000\kappa}{c} + \beta c^2 - Ac - B\log c \right]
\]

\[
\frac{\delta \Lambda^0}{\delta c} = \frac{\left[ -\frac{1000\kappa}{c^2} + \frac{\beta}{2c^2} - A - B(\log c + 0.4343) \right](1 - \alpha^1 c^2)}{(1 - \alpha^1 c^2)^2}
\]

\[
+ \frac{\alpha^1}{2c^2} \left[ \frac{1000\kappa}{c} + \beta c^2 - Ac - B\log c \right]
\]

\[
\frac{\delta \Lambda^0}{\delta c} = \frac{\Lambda^0 - 2\Lambda + \beta c^2 + 0.4343 Bc}{c(1 - \alpha^1 c^2)} + \frac{\alpha^1 \Lambda^0}{2c^2(1 - \alpha^1 c^2)}
\]  \hspace{1cm} (7.5.5)
For the usual concentration range of $10^{-3}$ g-equiv/l (7.5.5) can be approximated to:

$$\frac{\delta \Lambda^0}{\delta c} = \Lambda^0 \frac{2\Lambda}{c} + \frac{a^1\Lambda^0}{2c^2}$$  \hspace{0.5cm} (7.5.6)

and (7.5.4) to:

$$\frac{\delta \Lambda^0}{\delta \kappa} = \frac{1000}{c}$$

The error in $\Lambda^0$ resulting from an error in $\Lambda$ (or $\kappa$) is:

$$\frac{\Delta \Lambda^0}{\Lambda^0} = \frac{1}{\Lambda^0} \frac{\Delta \kappa}{\kappa} \Lambda$$  \hspace{0.5cm} (7.5.7)

An error in the concentration $c$ brings about an error in the limiting conductance which is given by:

$$\frac{\Delta \Lambda^0}{\Lambda^0} = 1 \frac{\Delta c}{c} (\Lambda^0 - 2\Lambda + a^1\Lambda^0 c^2)$$  \hspace{0.5cm} (7.5.8)

In conclusion it can be said that experimental errors in the conductance and concentration values have a negligible effect on the accuracy of the limiting conductance.

7.6. **Comparison with published values**

The limiting conductance of sodium benzoate was determined by several workers. Curiously enough, all the determinations were made at 25°C, only.

The results obtained are given in table 7.6.1.
Table 7.6.1: Published values for the limiting conductance of sodium benzoate.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Limiting conductance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>82.34</td>
<td>1</td>
</tr>
<tr>
<td>25</td>
<td>83.3 and 83.6</td>
<td>2</td>
</tr>
<tr>
<td>25</td>
<td>83.08</td>
<td>3</td>
</tr>
<tr>
<td>25</td>
<td>82.62 ± 0.03</td>
<td>4</td>
</tr>
</tbody>
</table>

References:
4. Present work.

Besides these values, the limiting conductance of potassium benzoate was determined at 25°C by Brockman and Kilpatrick and more recently by Swain and Evans. We can compare these values with out results if we refer to the limiting conductance of the benzoate ion.

The limiting conductance of the sodium ion at 25°C is 50.1559 and of the potassium ion is 73.5059. If these two values are subtracted from the values of A° of sodium benzoate and potassium benzoate, respectively we obtain, in both cases, the limiting conductance of the benzoate ion. These values are given in table 7.6.2.
Table 7.6.2: Limiting conductance of benzoate ion.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Limiting conductance of benzoate ion</th>
<th>Original data</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>32.38</td>
<td>KOBz</td>
<td>1</td>
</tr>
<tr>
<td>25</td>
<td>32.08</td>
<td>KOBz</td>
<td>2</td>
</tr>
<tr>
<td>25</td>
<td>32.47</td>
<td>NaOBz</td>
<td>3</td>
</tr>
</tbody>
</table>

References:
3. Present work

We must mention, however, that we believe a valid direct comparison between the different values quoted above cannot be made. This is not because there were differences in the experimental techniques. In fact it is a very good practice to compare results obtained by different techniques. (What happens if they do not agree? Which is the good one?) We are referring in the present case, mainly, to the type of solvent correction applied to the raw experimental data and to the equation employed for calculating \( \Lambda^0 \). Each of the values given in tables 7.6.1 and 7.6.2 were obtained by conductance methods which were different in their details. More important, however, is that in each case a different solvent correction and/or a different equation was used to obtain the limiting conductance. Also, depending on the time when the measurements were taken, different conductance standards might have been used. Thus Saxton and Meier
results are based on Parker and Parker standards$^{133}$ and not on the currently accepted standards of Jones and Bradshaw.$^{53}$

To prove this point we took the Jeffery and Vogel data$^{132}$ on sodium benzoate and used them to calculate $\Lambda^0$ by the same method as that described in subsection 7.4. The value obtained was 84.90 ± 0.25 as compared with the published value of 83.08 (see "Detailed calculations - 7.6.1").

7.7. Conclusions

The limiting conductance of sodium benzoate in aqueous solution was determined, by the conductance method, at temperatures between 20 and 40°C. In this range the limiting conductance can be expressed by one of the following expressions:

\[
\log \Lambda^0_{\text{NaOB}_2} = 4.7251 - 837.5/T \quad (7.7.1)
\]

\[
\Lambda^0_{\text{NaOB}_2} = (82.91 ± 0.24) + (1.920 ± 0.024)(T-25) \quad (7.7.2)
\]

\[
\Lambda^0_{\text{NaOB}_2} = (82.63 ± 0.00) + (1.846 ± 0.000)(T-25) + (0.0079 ± 0.0000)(T-25)^2 \quad (7.7.3)
\]

where $T$ is the temperature in °C.
8. **THE DETERMINATION OF THE DISSOCIATION CONSTANT OF BENZOIC, BENZOIC-2-d AND BENZOIC-d₅ ACIDS IN AQUEOUS SOLUTION BY CONDUCTANCE METHOD AT TEMPERATURES BETWEEN 20 AND 40°C**

8.1. **Introduction**

The dissociation constant of benzoic acid has been measured by many people using different methods during the last 40 years. Most of the measurements were taken at 25°C. Only a few of them covered a wider temperature range. The review "Dissociation constants of organic acids in aqueous solution" by Kortum, Vogel and Andrusow²³ lists 14 determinations with only two of them over a range of temperatures. Of the 12 remaining, 11 are at 25°C and one at 18°C. Since the review came out in 1961, a few more papers on the same subject have appeared. The most important of these is that by Wilson, Gore, Sawbridge and Cardenas-Cruz.¹³⁰ Beside measuring the dissociation constant of benzoic acid over a temperature range of 15 to 40°C, they measured the dissociation constants of a series of substituted benzoic acids over the same temperature range.

The dissociation constant of benzoic-d₅ acid has not been determined as such though the isotope effect

\[
\frac{K_{C_6H_₅COOH}}{K_{C_6D₅COOH}}
\]

has been measured by Erlenmeyer and Epprecht¹ and by Streitwieser and Klein.¹³³ In addition the last group of workers measured the isotope effect benzoic acid/benzoic-2,6-d₂ acid.

The dissociation constant of benzoic-2-d acid has not been measured before.
8.2. Materials

Benzoic acid

Benzoic acid was obtained from "Analar" (analytical reagent). The compound was purified in a "Fisher Zone Refiner".

The benzoic acid was placed in a 4 mm i.d. Pyrex tube, 20 inches long, closed at one end. When the tube was completely filled with the acid, the second end was closed. A small flame on the sides of the tubes helped to pack the tube with compound by melting it and eliminating in this way the largest part of the empty space between the powder particles.

The tube was left in the zone refiner for 72 hours. It took approximately 2 hours per pass (up-down passes). A grey-brown fraction started to accumulate at the bottom of the tube after 3 passes. At the end of the operation two quite well defined zones were present in the tube. The bottom one, approximately 3 inches long obviously contained the impurities. Although it did not show any visible difference from the rest, the compound in the upper part of the Pyrex tube was discarded as well. Thus only the compound in the middle part of the tube was used for the conductance measurements.

The compound was identified by its IR spectrum (see section 18) and its melting point. The melting point was measured with a Mettler FP-1 instrument (capillary melting point apparatus) equipped with a Bausch-Lomb recorder. The rate of temperature increase was 0.2°C/min. The melting point was (122.0 - 122.5)±0.1°C.
Benzoic-\(d_5\) acid

The benzoic-\(d_5\) acid has been prepared by the exchange of sodium benzoate or benzoic acid with \(D_2O\) in the presence of a platinum catalyst (platinum oxide prereduced with deuterium gas)\(^{134}\) or from benzene-\(d_6\) through the bromo-and Grignard compounds.\(^{133}\)

We used the exchange procedure. A typical run is described below.

Platinum oxide, in a \(D_2O\) suspension, was reduced by bubbling deuterium gas through the liquid. The \(D_2O\) amount at this point is approximately 1/2 of the total amount per run. When the reduction was completed (the suspension turns from brown to black) the platinum plus deuterium oxide mixture was placed in a thick wall Pyrex tube (25 mm i.d., 35 cm long) which contained the benzoic acid and/or sodium benzoate. The second half of the \(D_2O\) was added, the tube closed with a ground-glass stopper and the contents frozen slowly in liquid nitrogen. Then the tube was sealed off. When the sealed part cooled we checked it very carefully for strains in the glass. If no strains were present the tube was taken out of the liquid nitrogen and allowed to defrost in the fume hood. When the defrosting was completed the tube was placed in a heated shaker (hydrogenation type) and kept there for the required time. The temperature in the shaker was controlled with a Variac. The quantities used, the conditions of the reaction, and the exchange results are shown in table 8.2.1.

When the reaction was terminated, the Variac, controlling the heat, was turned off, the shaker allowed to cool and the tube containing the reaction mixture was taken out and opened. Sodium
hydroxide solution (10%) was added until all the acid in the tube dissolved. Then the contents were filtered to remove the platinum particles and the filtrate was split into two parts. One part was evaporated in a beaker on a hot plate providing the sodium benzoate for the next exchange. To the second part we added HCl (10% solution). The precipitated benzoic acid was extracted three times with 20 ml portions of ether. The combined ether extracts were washed twice with 10 ml of water, poured into a beaker and then placed in the fume hood to let the ether evaporate. When all the ether was apparently gone the beaker was placed in a vacuum desiccator and kept there for 8 hours, at 30°C. A small portion of the dry acid was sublimed in vacuum and used to obtain the NMR spectrum. The remaining acid was used for the next exchange.

The progress of exchange was followed by NMR. The carboxylic proton provided the internal standard. The NMR spectra were obtained with a Jeol-NMR spectrograph, in CDCl₃ or CCl₄ solution at room temperature.

The melting point of benzoic-d₅ acid was measured with a Mettler-FP1 instrument equipped with a Bausch-Lomb recorder. The rate of temperature increase was 0.2°C/min. The melting point obtained was (122.0 - 122.5)±0.1°C which is identical to the melting point of benzoic acid.
### Table 8.2.1

<table>
<thead>
<tr>
<th>Exchange</th>
<th>Benzoic acid</th>
<th>Sodium benzoate</th>
<th>Platinum oxide</th>
<th>Deuterium oxide</th>
<th>Temp.</th>
<th>Time of reaction</th>
<th>% exchange</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gm</td>
<td>gm</td>
<td>gm</td>
<td>cm³</td>
<td>°C</td>
<td>hrs.</td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>-</td>
<td>9.7</td>
<td>0.0945</td>
<td>40₁</td>
<td>130</td>
<td>48</td>
<td>40²</td>
</tr>
<tr>
<td>1.2</td>
<td>-</td>
<td>3.5</td>
<td>0.1263</td>
<td>21₁</td>
<td>130</td>
<td>163</td>
<td>55</td>
</tr>
<tr>
<td>1.3</td>
<td>-</td>
<td>3.2</td>
<td>0.0933</td>
<td>12</td>
<td>150</td>
<td>161</td>
<td>75</td>
</tr>
<tr>
<td>1.4</td>
<td>-</td>
<td>2.7</td>
<td>0.1458</td>
<td>16</td>
<td>130</td>
<td>164</td>
<td>90</td>
</tr>
<tr>
<td>2.1</td>
<td>5.3</td>
<td>5.3</td>
<td>0.1824</td>
<td>30₁</td>
<td>130</td>
<td>145</td>
<td>84</td>
</tr>
<tr>
<td>2.2</td>
<td>5.2</td>
<td>1.2</td>
<td>0.1120</td>
<td>24</td>
<td>130</td>
<td>144</td>
<td>96</td>
</tr>
<tr>
<td>2.3</td>
<td>1.7</td>
<td>4.2</td>
<td>0.1026</td>
<td>15</td>
<td>165</td>
<td>400</td>
<td>98</td>
</tr>
</tbody>
</table>

### Notes:
1. 97% D₂O; for all other exchanges 99% D₂O was used.
2. Meta and para hydrogens exchanged.
It can be seen from table 8.2.1 that the exchange proceeded with more difficulty when only sodium benzoate was used. In Brown and Garnett's case,\textsuperscript{134} the exchange with sodium benzoate proceeded faster than that with benzoic acid.

**Benzoic-2-d acid**

The preparation of benzoic-2-d acid was reported by Weldon and Wilson\textsuperscript{135} and by Renaud, Kovachic and Leitch.\textsuperscript{136} The synthesis is illustrated by the series of reactions:

\[
\begin{align*}
\text{CH}_3 & \quad \text{Br} \\
\text{ether} & \quad \text{Mg} \\
\text{MgBr} & \quad \text{D}_2\text{O} \\
\text{oxid.} & \quad \text{alk. K}_2\text{MnO}_4
\end{align*}
\]

The critical step is the preparation of the Grignard compound and its subsequent decomposition with D\textsubscript{2}O. The apparatus used for the preparation of the Grignard compound is illustrated in fig. 8.2.1.

The main condition for a successful preparation of a Grignard compound and especially one which is going to be used in the preparation of a deuterated compound is that all the glassware used should be perfectly dry. In order to dry our apparatus three, 25 ml portions of dichloroethane were added to flask D. Each fraction was refluxed for 20 minutes through the whole length of condenser F and flask D and its attachments. Then the dichloroethane was distilled off through condenser F.
FIG. 8.2.1.

APPARATUS USED FOR THE PREPARATION OF TOLUENE-2-d
Next the installation was evacuated, filled with dry nitrogen, evacuated, flamed, evacuated, filled with dry nitrogen and so on for a period of two hours. In the last 1/2 hour of this operation 5.1 g (0.21 g-mol) of magnesium for Grignard compounds (Fisher Scientific) were added to flask D. At the time a slight positive pressure of nitrogen was present in the system to keep the atmospheric air out of it. In fact even during the reaction a positive pressure was present in the system for the same reason. The nitrogen stream and the vacuum were connected to the system through the 2-way stop-cock K.

The o-bromotoluene (Eastman Organic Chemicals. Cat. No. 47) was purified by fractional distillation in a separate set-up just before the preparation of the Grignard compound. This distillation was essential for a successful isotopic preparation because the initial o-bromotoluene contained as much as 10% toluene. The purified o-bromotoluene (31.5 g or 0.2 g-mol) was added to the dropping funnel H.

The ether was refluxed over LiAlH₄ in flask C for 3 hours (stop-cock I closed). Then by opening the stop-cock the ether was admitted into the dropping funnel G. It took, approximately, 20 minutes to collect 200 ml. of ether. The ether was added to the flask D by creating a slight vacuum in part B of the apparatus and by opening stop-cock M. The o-bromotoluene was added dropwise during a period of 1 hour. The reaction was initiated by slight heating of the reaction mixture and by adding a crystal of HgI₂ to the flask D. As is well known, the reaction between magnesium and bromo-compound is fairly violent. It was controlled by removing the heating mantle N and
replacing it, when necessary, by an ice bath. The slight positive pressure in the system was maintained by admitting dry nitrogen through the two-way stop-cock K. When the addition of the bromotoluene was terminated, the reaction mixture was kept refluxing for a further 60 minutes. At the end of this period visual inspection of the reaction flask showed some unreacted magnesium present. The colour of the contents of the flask D changed from clear, colourless, at the beginning of the reaction to a pale yellow, a yellow-green and finally a clear dark-green colour at the end of the reaction.

The decomposition of the Grignard compound with D₂O. When the reaction flask cooled to room temperature (after approximately 30 minutes) the Grignard compound was decomposed by adding D₂O to the reaction flask with a 20 ml. syringe through the septum Q. It took approximately 1 hour to add 18 ml. of D₂O. The addition had to be done very slowly because the reaction between the Grignard compound and D₂O is very energetic. Continuous stirring was essential to assure that all the Grignard compound reacted with the D₂O. The quantity of deuterium oxide used is much more than the required stoichiometric amount. We found that this excess was necessary to make sure that all the Grignard compound was decomposed. At the end of this part of the reaction the mixture in flask D was a white precipitate (Mg(OH)₂) and a pale yellow liquid. The large amount of precipitate which forms presents some problems as far as the magnetic stirring is concerned. To overcome any stoppage of the magnetic bar a fairly strong magnet has to be used.

The reaction mixture was filtered and the liquid fractionally
distilled in a spinning band column. The fraction at 110-112°C was collected.

Oxidation of toluene. The procedure described by Vogel for the oxidation of a side chain by alkaline permanganate was followed.\textsuperscript{137}

To a 500 ml. flask equipped with a reflux condenser we added 300 ml. of water, 2 gm. of sodium carbonate, 16 g of potassium permanganate and 6.5 ml. of toluene-2-d. The mixture was refluxed with stirring for a period of 4 hours. At the end of this period the reaction flask was cooled and 25 ml. of 10\% sulphuric acid were added slowly. The reaction mixture was heated for a further 30 minutes and then cooled. The contents of the reaction flask were transferred to a one litre beaker and placed in the fume hood. The excess manganese dioxide was removed by the addition of sodium bisulphite. The precipitated acid was filtered, washed with water, dissolved in sodium hydroxide solution and precipitated back with 10\% sulphuric acid. The precipitated acid was filtered, washed with water and dried in air for 24 hours. Then it was recrystallized twice from water and finally sublimed under vacuum twice.

The compound was characterized by NMR spectrum. The carboxylic proton served as internal standard. The NMR spectrum indicated 0.98 D atoms/molecule.

The melting point of benzoic-2-d acid was measured with a Mettler-FP1 instrument equipped with a Bausch-Lomb recorder. The rate of temperature increase was 0.2°C/min. The melting point obtained was (122.0 - 122.5)±0.1°C which is identical with that of benzoic acid.
The NMR spectrum of benzoic-2-d acid

\[ \text{COOH} \]

\[
\begin{array}{c}
\text{D} \\
\text{O}
\end{array}
\]

Solvent: CDCl$_3$
Sweeptime: 250s
Sweepwidth: 1000 cps
8.3. Conductivity measurements

The procedure followed was exactly the same as in the case of potassium chloride solutions (see subsection 5.10) or sodium benzoate solutions (see subsection 7.3).

The complete experimental results and calculations are presented in "Detailed calculations - 8.3.1 to 8.3.6".

8.4. Calculation of the limiting conductance of benzoic acid

The most accurate method for obtaining the limiting conductance of benzoic acid is to calculate it from the limiting conductances of sodium benzoate, sodium and hydrogen ions (potassium benzoate can be used for this purpose as well):

\[ \Lambda_{\text{HOBz}}^0 = \Lambda_{\text{NaOBz}}^0 - \Lambda_{\text{Na}^+}^0 + \Lambda_{\text{H}^+}^0 \]  \hspace{1cm} (8.4.1)

All the values on the RHS of (8.4.1) are known. They were given in tables 7.4.2 and 7.4.3. For convenience they are given again in table 8.4.1.

Table 8.4.1: Limiting conductance of sodium benzoate, sodium and hydrogen ions and benzoic acid.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>( \Lambda_{\text{NaOBz}}^0 )</th>
<th>( \Lambda_{\text{Na}^+}^0 )</th>
<th>( \Lambda_{\text{H}^+}^0 )</th>
<th>( \Lambda_{\text{HOBz}}^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>73.59</td>
<td>44.81</td>
<td>325.74</td>
<td>354.57</td>
</tr>
<tr>
<td>25</td>
<td>82.62</td>
<td>50.15</td>
<td>350.15</td>
<td>382.62</td>
</tr>
<tr>
<td>30</td>
<td>92.06</td>
<td>55.72</td>
<td>374.04</td>
<td>410.38</td>
</tr>
<tr>
<td>35</td>
<td>101.87</td>
<td>61.53</td>
<td>397.37</td>
<td>437.71</td>
</tr>
<tr>
<td>40</td>
<td>112.10</td>
<td>67.55</td>
<td>420.06</td>
<td>464.61</td>
</tr>
</tbody>
</table>
In section 6 of this thesis different methods for the calculation of the dissociation constant and the limiting conductance of an acid were discussed. It was shown there that the so-called "extrapolation methods" are sensitive to inherent systematic errors in concentration and especially in conductance values. That is why the K and \( \Lambda^0 \) values determined by extrapolation methods have, generally, a probable error much larger than the one which is usually given and the one which represents the uncertainty due to random errors in the experimental quantities, only.

A large amount of the published data was treated by extrapolation methods only, either because the salts of the respective acids are very difficult to handle, or because the work involved is out to a half, which is not a negligible advantage. In cases where no comparable data exist, such as determinations by some other method, it is very difficult to say what the exact error of these figures are because the original error in the experimental quantity is not generally known. Our data on the isotopic benzoic acids prove this point very well. The acids considered by us are: benzoic acid, benzoic-2-d acid and benzoic-d\(_5\) acid.

![Chemical structures](image)

Benzoic acid

Benzoic-2-d acid

Benzoic-d\(_5\) acid
In the case of these three acids, it can be assumed to an excellent approximation that their limiting conductances are the same.133,138

Treatment of experimental data by extrapolation methods (Ives or Fuoss-Shedlovsky method) yields widely different \( \Lambda^0 \) values for the three acids. The complete results are given in "Detailed calculations - 8.4.1, 8.4.2 and 8.4.3". An example is shown in table 8.4.2.

Table 8.4.2: Limiting conductance of benzoic acids calculated by extrapolation methods.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp.</th>
<th>Ives method</th>
<th>Fuoss-Shedlovsky method</th>
<th>Calculated from salt conductance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
<td>25</td>
<td>373.0±1.0</td>
<td>372.0±0.9</td>
<td>382.62±0.05</td>
</tr>
<tr>
<td>Benzoic-2-d</td>
<td>25</td>
<td>384.1±0.9</td>
<td>383.9±1.0</td>
<td>382.62±0.05</td>
</tr>
<tr>
<td>acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzoic-d5</td>
<td>25</td>
<td>378.0±0.7</td>
<td>377.5±0.7</td>
<td>382.62±0.05</td>
</tr>
<tr>
<td>acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The limiting conductance determined by extrapolation methods or from the salt conductance has the useful property of being a linear function of temperature within the range in which we are working, i.e. 20 to 40°C. This is shown in fig. 8.4.1 where the values of the limiting conductance for the three acids were plotted against temperature. These values were also fitted analytically, by the method of least squares, into the expression:

\[
\Lambda^0 = A + BT
\] (8.4.2)
where $T$ is the temperature in degrees kelvin. The results of the fitting are given in "Detailed calculations - 8.4.5 to 8.4.8" and table 8.4.3.

Only for the purpose of checking relation 8.4.2, the values of $\Lambda^0$ for hydrogen ion (calculated from (7.4.3)) and for sodium ion (calculated from 7.4.5) were fitted by (8.4.2). The results are given in "Detailed calculations - 8.4.4", table 8.4.4 and fig. 8.4.1. The values fit the straight line remarkably well.

The fact that the limiting conductances were linear in temperature led us to try to apply a correction factor to the limiting conductances obtained by the Ives or Fuoss-Shedlovsky method hoping to obtain in this way the correct values for them. The usefulness of such a correction factor becomes apparent when one tries to calculate the dissociation constant for almost any acid at a temperature other than 25°C. For a large majority of acids the limiting conductance determined from the salt conductance is found at one temperature only. Most often this temperature is 25°C. Thus if accurate dissociation constants for other temperatures are desired, one has to measure the salt conductance at every one of these temperatures in order to obtain the respective $\Lambda^0$'s. If the "correction factor method" works the salt conductance has to be measured at one temperature only or the published values at 25°C can be used. This "reference" value together with the values of $\Lambda^0$ obtained by an extrapolation method are used to obtain the correct limiting conductance at any other temperature. The correction factor $F$ is simply:

$$F = \Lambda^0(\text{true}) - \Lambda^0(\text{obs})$$

(8.4.3)
FIG. 8.4.1.

THE LIMITING CONDUCTANCE (OBTAINED BY THE IVES METHOD) VS.
TEMPERATURE FOR A SERIES OF BENZOIC ACIDS
where $\Lambda^0(\text{true})$ is the "reference" limiting conductance obtained from salt conductance for example. $\Lambda^0(\text{obs})$ is the value of $\Lambda^0$ as it is obtained by one of the extrapolation methods. The correct limiting conductance at a temperature $T$ is then:

$$\Lambda^0(\text{calc}) = \Lambda^0(\text{obs}) + F$$  (8.4.4)

We checked these very simple relations with our data on the three benzoic acids. The results are shown in "Detailed calculations - 8.4.2" and table 8.4.5. It can be seen that the largest difference between $\Lambda^0(\text{true})$ and $\Lambda^0(\text{calc})$ is around 0.3% which represents a much better accuracy than the one that can be obtained by an extrapolation method alone and it is only slightly worse than the usual accuracy of the limiting conductance obtained from the salt conductance.

Actually we used the limiting conductances determined from the conductance of sodium benzoate (section 7) to calculate the dissociation constant for the three isotopic benzoic acids. However, in the case of the other acids studied by us, the method just described was used to obtain their limiting conductance at temperatures other than 25°C.
Table 8.4.3: A comparison between observed and calculated values of limiting conductance of some benzoic acids.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Benzoic acid Obs.</th>
<th>Calculated</th>
<th>Benzoic acid Obs.</th>
<th>Calculated</th>
<th>Benzoic-2-d acid Obs.</th>
<th>Calculated</th>
<th>Benzoic-d₅ acid Obs.</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( A = -1258.99 )</td>
<td></td>
<td>( A = -1255.96 )</td>
<td></td>
<td>( A = -1247.04 )</td>
<td></td>
<td>( A = -1225.90 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( B = 5.5054 )</td>
<td></td>
<td>( B = 5.4646 )</td>
<td></td>
<td>( B = 5.4708 )</td>
<td></td>
<td>( B = 5.3784 )</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>354.52</td>
<td>354.91</td>
<td>346.80</td>
<td>345.99</td>
<td>356.62</td>
<td>356.72</td>
<td>350.31</td>
<td>350.77</td>
</tr>
<tr>
<td>25</td>
<td>382.62</td>
<td>382.44</td>
<td>372.99</td>
<td>373.31</td>
<td>384.14</td>
<td>384.08</td>
<td>377.98</td>
<td>377.67</td>
</tr>
<tr>
<td>30</td>
<td>410.38</td>
<td>409.97</td>
<td>399.77</td>
<td>400.63</td>
<td>411.62</td>
<td>411.48</td>
<td>405.61</td>
<td>404.56</td>
</tr>
<tr>
<td>35</td>
<td>437.71</td>
<td>437.50</td>
<td>427.38</td>
<td>427.96</td>
<td>438.64</td>
<td>438.79</td>
<td>430.26</td>
<td>431.45</td>
</tr>
<tr>
<td>40</td>
<td>464.61</td>
<td>465.02</td>
<td>456.22</td>
<td>455.28</td>
<td>464.82</td>
<td>466.14</td>
<td>458.63</td>
<td>458.34</td>
</tr>
</tbody>
</table>

Notes: 1. The \( \Lambda^0 \)'s obtained by the Ives method are given here. In "Detailed calculations - 8.4.5 to 8.4.7" the \( \Lambda^0 \)'s obtained by the Fuoss-Shedlovsky method can be found. The results are completely similar in both cases.

2. Calculated from \( \Lambda^0_{\text{HOBz}} = \Lambda^0_{\text{NaOBz}} - \Lambda^0_{\text{Na}^+} + \Lambda^0_{\text{H}^+} \)

3. All the "Calculated" values are obtained from relation: \( \Lambda^0 = A + BT \) (8.4.2)
Table 8.4.4: A comparison between "observed" and calculated values of limiting conductance of hydrogen and sodium ions.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Hydrogen ion</th>
<th>Sodium ion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Obs.¹</td>
<td>Calculated*</td>
</tr>
<tr>
<td>20</td>
<td>325.74</td>
<td>326.15</td>
</tr>
<tr>
<td>25</td>
<td>350.15</td>
<td>349.77</td>
</tr>
<tr>
<td>30</td>
<td>374.04</td>
<td>373.40</td>
</tr>
<tr>
<td>35</td>
<td>397.37</td>
<td>397.02</td>
</tr>
<tr>
<td>40</td>
<td>420.06</td>
<td>420.64</td>
</tr>
</tbody>
</table>

* Calculated from: \( \Lambda^0 = A + B(T-25) \) (7.4.8)

T: Temperature in °C

Reference:


Table 8.4.5: A comparison between $\Lambda^0(\text{true})$, $\Lambda^0(\text{obs})$ and $\Lambda^0(\text{calc})$ for some benzoic acids.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$\Lambda^0(\text{true})^1$</th>
<th>Benzoic acid</th>
<th>Benzoic-2-d acid</th>
<th>Benzoic-d$_5$ acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Lambda^0(\text{obs})$</td>
<td>$\Lambda^0(\text{calc})$</td>
<td>$\Lambda^0(\text{obs})$</td>
<td>$\Lambda^0(\text{calc})$</td>
</tr>
<tr>
<td>20</td>
<td>354.52</td>
<td>345.99</td>
<td>355.30</td>
<td>356.72</td>
</tr>
<tr>
<td>25</td>
<td>382.62</td>
<td>373.31</td>
<td>382.62</td>
<td>384.08</td>
</tr>
<tr>
<td>30</td>
<td>410.38</td>
<td>400.63</td>
<td>409.94</td>
<td>411.43</td>
</tr>
<tr>
<td>35</td>
<td>437.71</td>
<td>427.96</td>
<td>437.27</td>
<td>438.79</td>
</tr>
<tr>
<td>40</td>
<td>464.61</td>
<td>455.28</td>
<td>464.59</td>
<td>466.14</td>
</tr>
</tbody>
</table>

Notes: 1. $\Lambda^0(\text{true})$ is the limiting conductance obtained from: $\Lambda^0(\text{true}) = \Lambda^0_{\text{NaOBz}} - \Lambda^0_{\text{Na}^+} + \Lambda^0_{\text{H}^+}$

2. The values obtained by the Ives method are quoted as $\Lambda^0(\text{obs})$ (see table 8.4.3, also). The calculation employing $\Lambda^0$'s obtained by the Fuoss-Shedlovsky method is given in "Detailed calculation - 8.4.5 to 8.4.7".
8.5. Calculation of the dissociation constants of benzoic acids

So far we have shown that accurate values for the limiting conductance of an acid are obtained by combining the limiting conductance of one of its salts with the known conductances of hydrogen ion and the ion of the salt according to Kohlrausch's law of independent migration of ions.

The calculation of the dissociation constant from conductance data presents an interesting problem. It was shown in section 6 of this thesis that to obtain accurate \( K \) values the limiting conductance \( \Lambda^0 \) has to be known beforehand. Once \( \Lambda^0 \) is known different methods are available for calculating the dissociation constant of an acid. Though the methods are similar and are based on the same basic formulas, they lead to slightly different results with the same data. This is particularly annoying when accurate \( K \)'s are sought, say 0.1% accuracy, and it is found that the methods of calculation lead to differences which are larger than the expected accuracy.

Initially we used three methods for calculating the dissociation constant:

(i) the Ives method
(ii) the Fuoss-Shedlovsky method
(iii) the direct (Dippy) method.

The methods were described in section 6 of this thesis. The first two methods listed above were used without iteration because the limiting conductance \( \Lambda^0 \) was already known.
The results obtained by applying these methods, with the values of $\Lambda^0$ obtained in the present work, to a series of published conductance data and to the data obtained in the present work are shown in the first part of table 8.5.1. In the second part of table 8.5.1 the dissociation constants of benzoic acid obtained by methods other than conductance are shown, for comparison. It can be seen (see also table 6.10.1) that as a rule the errors shown by the Ives method are larger than the errors shown by the other two methods. This was considered to be due probably to the fact that Ives' formula contains a term in $\Lambda^2$ which leads to a magnification of the experimental error in the conductance values which is reflected in the final $K$ value. 139

Of the remaining two methods we are inclined to consider the results obtained by the Fuoss-Shedlovsky method to be closer to the true values. This choice is based on the fact that the Fuoss-Shedlovsky method contains an implicit extrapolation to $c = 0$. This extrapolation removes any dependence that $K$ might show with respect to concentration. The "Direct" method, as is used here, does not contain such an extrapolation though sometimes its use is recommended. 87

Table 8.5.2 presents a comparison between the only published values for the dissociation constant of benzoic acid at temperatures between 20 and 40°C and the results obtained in the present work (the values obtained by the Fuoss-Shedlovsky method are quoted).
Our results compare favorably with other published results and their precision is of the same order of magnitude as the best ones yet published. At the particular temperature of 25° the difference between our value and the very precise value obtained by Brockman and Kilpatrick could be due to the difference in the conductance standards used in the two works. Their value was obtained based on Parker and Parker conductance standards while our value was based on the theoretical conductance equation of Fuoss, Shedlovsky and Skinner.

At the other four temperatures (see table 8.5.3) we believe that our measurements are more accurate than the ones published before.

The dissociation constants of the two other acids, i.e. benzoic-2-d acid and benzoic-d₅ acid are given in table 8.5.3 and discussed in connection with the isotope effect $K_H/K_D$ (subsection 8.7).
Table 8.5.1: The dissociation constant of benzoic acid at 25°C. A comparison between the published values and the values obtained in the present work.

<table>
<thead>
<tr>
<th>Method</th>
<th>Ref.</th>
<th>Published</th>
<th>K x 10^5 calculated here (Λ^0 = 382.62)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ives method</td>
<td>Fuoss-Shedlovsky method</td>
</tr>
<tr>
<td>Conductance</td>
<td>1</td>
<td>6.312</td>
<td>382.10</td>
<td>6.319±0.004</td>
<td>6.304±0.001</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>6.493</td>
<td>380.15</td>
<td>6.45±0.01</td>
<td>6.420±0.003</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6.295</td>
<td>381.96</td>
<td>6.17±0.03</td>
<td>6.199±0.006</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6.27</td>
<td>383.1</td>
<td>6.14±0.08</td>
<td>6.28±0.02</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>6.27</td>
<td>388.3</td>
<td>6.58±0.4</td>
<td>6.43±0.04</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6.373</td>
<td>381.3</td>
<td>6.53±0.02</td>
<td>6.428±0.005</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>-</td>
<td>-</td>
<td>6.41±0.02</td>
<td>6.247±0.004</td>
</tr>
<tr>
<td>Electrometric</td>
<td>8</td>
<td>6.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrometric</td>
<td>9</td>
<td>6.295</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrometric</td>
<td>10</td>
<td>6.081</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrophotometric</td>
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<td>6.261</td>
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<td></td>
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<tr>
<td>Spectrophotometric</td>
<td>12</td>
<td>6.278</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Potentiometrically</td>
<td>13</td>
<td>6.166</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 8.5.1 (cont.)

References:

7. Present work.
Table 8.5.2: The dissociation constant of benzoic acid at temperatures between 20 and 40°C. A comparison between the published values and the results obtained in the present work.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Method</th>
<th>K x 10^5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>1</td>
<td>Electrometric</td>
<td>6.237</td>
</tr>
<tr>
<td>2</td>
<td>Conductance</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Electrometric</td>
<td>6.13</td>
</tr>
</tbody>
</table>

References:
5. Present work.
8.6. Calculation of the thermodynamic functions for the ionization of benzoic, benzoic-2-d and benzoic-d5 acids

The thermodynamic functions for the ionization of benzoic, benzoic-2-d and benzoic-d5 acids have been calculated by using the Clarke & Glew (13.2.26) and the Harned & Robinson formulae. Both these formulas are discussed in section 13 of this work. The complete results are given in "Detailed calculation - 8.6.1 to 8.6.3". A summary of the results is given in tables 8.6.1 to 8.6.4.

In subsection 8.5 we calculated the dissociation constant of benzoic acids by employing three different methods. The results obtained were different in each of the three cases. Here we calculated, for benzoic acid, three separate sets of thermodynamic functions corresponding to each of the three sets of dissociation constants. The results are presented in table 8.6.5. The absolute values of the results are quite different from one set to another. The trend, however, is the same for every set. Since the dissociation constants determined by the Fuoss-Shedlovsky method were the preferred ones, the corresponding set of thermodynamic values must be considered as the best one.

A comparison between the published values for the thermodynamic functions for the ionization of benzoic acid and the results obtained here is given in table 8.6.5. The comparison is done at two temperatures because most often the agreement at one temperature does not mean agreement at other temperatures. Also, as was shown by Wilson et al. and by Clarke and Glew, the values obtained are dependent to a certain extent on the equations used to fit the experimental data. The values of Δ G° agree fairly well among different workers. The Δ H° values
present large variations in going from one set to another. The situation is identical for $\Delta S^0$ values which seem to follow, together with $\Delta H^0$, the so-called "compensation law". It cannot be said with certainty which of the values are the correct ones. Indeed we are very far from the point of being able to predict such values. It is significant, however, that our values are closer than any other to the values obtained by Smolyakov and Primanchuk. Their values, though not very accurate, cover a range of temperatures much wider than that of any other set of data (25 - 90°C).

Because the data, i.e. $K$ values, were fitted very well by the Clarke & Glew equation with three coefficients, we are very reluctant to attach any significance to the $d(\Delta C_P)/dT$ quantity. Moreover in all cases this quantity is only barely significant at the 95% confidence level.

The thermodynamic quantities for the three isotopic acids were compared in the form of "$\Delta\Delta$" values, e.g.:

$$\Delta\Delta G^0 = \Delta G^0(\text{benzoic acid}) - \Delta G^0(\text{benzoic-2-d acid})$$

A summary of "$\Delta\Delta$" values is given in table 8.6.6.

Because of the high relative errors of the double differences the only significant "$\Delta\Delta$" values seem to be the values of $\Delta\Delta G^0$. If one takes into consideration the differences in the inductive effects and the steric requirements of the carbon-deuterium and carbon-hydrogen bonds, and if the deuterium atom is treated as another substituent, one would expect the benzoic acids containing deuterium in their molecule to have larger $\Delta G^0$ values than ordinary benzoic acid (with
no deuterium in its molecule, see subsection 14.7). This is indeed the case for benzoic-d₅ acid; it is not, however, true for benzoic-2-d acid. Referring to some calculations which are presented in a later section (section 18) of this thesis, the experimental ratios \( K_H/K_D \) in benzoic acid system were reproduced by semitheoretical calculations involving the calculation of vibrational frequencies of the acids and their respective anions. The assumptions we made there were that the force constants corresponding to internal coordinates in the vicinity of the carboxylate group increased in going from the unionized to the ionized state. Such an increase is observed if one compares the force constants of the corresponding internal coordinates in acetic acid and acetate ion.\(^{140-143}\) An increase of only 10% in the force constants of some internal coordinates in the benzoate ions reproduced the experimental result for the \( K(\text{benzoic acid})/K(\text{benzoic-2-d acid}) \) ratio. To reproduce the experimental ratio \( K(\text{benzoic acid})/K(\text{benzoic-d₅ acid}) \) we had to make an additional assumption that the increase in the force constants was slightly less for the deuterated anion. Thus an increase in the force constants of 10% for the benzoate anion and 9.5% for the benzoate-d₅ anion led to a calculated \( K_H/K_D \) ratio which was in very good agreement with the observed one. The same assumptions applied to the previous pair of acids, i.e. benzoic and benzoic-2-d acids, again led to a very good agreement between the calculated and the observed \( K_H/K_D \) ratios.

An increase in the force constants in the ionized state can be caused, both by the changes in the electronic structure, and by the tighter solvation of the ions as compared to the respective
acids, especially in the region of the negatively charged carboxylate group. The slightly smaller force constants in the deuterated anions imply a slightly less strong interaction between the deuterated anion and solvent water which is to be expected in view of the fact that a C-D bond is less polarizable and slightly shorter than a C-H bond.
Table 8.6.1: The thermodynamic functions for the ionization of benzoic acid. Results obtained from the Clarke & Glew formula with 3 coefficients.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>K x 10^{-5}</th>
<th>pK*</th>
<th>ΔG^0 cal/mol</th>
<th>ΔH^0 cal/mol</th>
<th>ΔS cal/(deg. mol)</th>
<th>ΔC_p cal/(deg.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>6.226</td>
<td>4.2058</td>
<td>5641.5±0.1</td>
<td>241 ±8</td>
<td>-18.42±0.03</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>6.249</td>
<td>4.2042</td>
<td>5735.5±0.1</td>
<td>14 ±5</td>
<td>-19.19±0.02</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>6.232</td>
<td>4.2054</td>
<td>5833.4±0.1</td>
<td>-213.8±2.4</td>
<td>-19.95±0.01</td>
<td>-45.5±0.8</td>
</tr>
<tr>
<td>35</td>
<td>6.177</td>
<td>4.2092</td>
<td>5935.0±0.1</td>
<td>-441 ±5</td>
<td>-20.69±0.02</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>6.089</td>
<td>4.2155</td>
<td>6040.3±0.1</td>
<td>-669 ±9</td>
<td>-21.43±0.03</td>
<td></td>
</tr>
</tbody>
</table>

Benzoic acid (Fuoss-Shedlovsky method)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>K x 10^{-5}</th>
<th>pK*</th>
<th>ΔG^0 cal/mol</th>
<th>ΔH^0 cal/mol</th>
<th>ΔS cal/(deg. mol)</th>
<th>ΔC_p cal/(deg.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>6.360</td>
<td>4.1965</td>
<td>5629.0±0.2</td>
<td>435 ±15</td>
<td>-17.72±0.05</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>6.409</td>
<td>4.1932</td>
<td>5720.6±0.1</td>
<td>90 ±9</td>
<td>-18.89±0.03</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>6.394</td>
<td>4.1942</td>
<td>5817.9±0.2</td>
<td>-255 ±5</td>
<td>-20.03±0.01</td>
<td>-68.9±1.5</td>
</tr>
<tr>
<td>35</td>
<td>6.321</td>
<td>4.1992</td>
<td>5920.8±0.1</td>
<td>-599 ±9</td>
<td>-21.16±0.03</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>6.196</td>
<td>4.2079</td>
<td>6029.4±0.2</td>
<td>-944 ±16</td>
<td>-22.27±0.05</td>
<td></td>
</tr>
</tbody>
</table>

Benzoic acid (Ives method)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>K x 10^{-5}</th>
<th>pK*</th>
<th>ΔG^0 cal/mol</th>
<th>ΔH^0 cal/mol</th>
<th>ΔS cal/(deg. mol)</th>
<th>ΔC_p cal/(deg.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>6.185</td>
<td>4.2087</td>
<td>5645.3±0.1</td>
<td>189 ±9</td>
<td>-18.61±0.03</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>6.201</td>
<td>4.2075</td>
<td>5740.1±0.1</td>
<td>-8 ±5</td>
<td>-19.28±0.02</td>
<td></td>
</tr>
<tr>
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<td>-19.93±0.01</td>
<td>-39.3±0.9</td>
</tr>
<tr>
<td>35</td>
<td>6.133</td>
<td>4.2123</td>
<td>5939.4±0.1</td>
<td>-401 ±5</td>
<td>-20.58±0.02</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>6.054</td>
<td>4.2180</td>
<td>6043.8±0.1</td>
<td>-598 ±9</td>
<td>-21.21±0.03</td>
<td></td>
</tr>
</tbody>
</table>

Benzoic acid (Dippy method)

* Results obtained after fitting the observed values in Clarke & Glew formula.
Table 8.6.2: The thermodynamic functions for the ionization of benzoic acid. Results obtained from Clarke & Glew formula with 4 coefficients.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>K x 10^5*</th>
<th>pK*</th>
<th>ΔG° cal/mol</th>
<th>ΔH° cal/mol</th>
<th>ΔS° cal/(deg. mol)</th>
<th>ΔC° p cal/(deg. mol)</th>
<th>d(ΔC° p)/dT cal/(deg. mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>6.227</td>
<td>4.2057</td>
<td>5641.4±0.1</td>
<td>212 ±14</td>
<td>-18.52±0.05</td>
<td>-37.0±3.6</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>6.248</td>
<td>4.2043</td>
<td>5735.6±0.1</td>
<td>15.8±3.5</td>
<td>-19.18±0.01</td>
<td>-41.3±1.9</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>6.232</td>
<td>4.2054</td>
<td>5833.3±0.1</td>
<td>-202 ±5</td>
<td>-19.91±0.02</td>
<td>-45.6±0.6</td>
<td>-0.9±0.4</td>
</tr>
<tr>
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<td>6.179</td>
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<td>5934.8±0.1</td>
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<td>-20.69±0.01</td>
<td>-49.9±2.0</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>6.088</td>
<td>4.2155</td>
<td>6040.3±0.1</td>
<td>-701 ±15</td>
<td>-21.53±0.05</td>
<td>-54.3±3.7</td>
<td></td>
</tr>
</tbody>
</table>

Benzoic acid (Fuoss-Shedlovsky method)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>K x 10^5*</th>
<th>pK*</th>
<th>ΔG° cal/mol</th>
<th>ΔH° cal/mol</th>
<th>ΔS° cal/(deg. mol)</th>
<th>ΔC° p cal/(deg. mol)</th>
<th>d(ΔC° p)/dT cal/(deg. mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>6.362</td>
<td>4.1964</td>
<td>5628.9±0.1</td>
<td>370 ±9</td>
<td>-17.94±0.03</td>
<td>-50.6±2.3</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>6.405</td>
<td>4.1935</td>
<td>5720.9±0.1</td>
<td>94.2±2.2</td>
<td>-18.87±0.01</td>
<td>-59.9±1.2</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>6.394</td>
<td>4.1942</td>
<td>5817.9±0.1</td>
<td>-228.4±3.4</td>
<td>-19.94±0.01</td>
<td>-69.2±0.4</td>
<td>-1.9±0.2</td>
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<tr>
<td>35</td>
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<td>4.1990</td>
<td>5920.5±0.1</td>
<td>-597.3±2.3</td>
<td>-21.15±0.01</td>
<td>-78.4±1.2</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>6.194</td>
<td>4.2080</td>
<td>6029.6±0.1</td>
<td>-1013 ±9</td>
<td>-22.49±0.03</td>
<td>-87.7±2.3</td>
<td></td>
</tr>
</tbody>
</table>

Benzoic acid (Ives method)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>K x 10^5*</th>
<th>pK*</th>
<th>ΔG° cal/mol</th>
<th>ΔH° cal/mol</th>
<th>ΔS° cal/(deg. mol)</th>
<th>ΔC° p cal/(deg. mol)</th>
<th>d(ΔC° p)/dT cal/(deg. mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>6.186</td>
<td>4.2086</td>
<td>5645.2±0.1</td>
<td>154 ±12</td>
<td>-18.73±0.04</td>
<td>-29.5±3.1</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>6.200</td>
<td>4.2076</td>
<td>5740.2±0.1</td>
<td>-5.6±3.0</td>
<td>-19.27±0.01</td>
<td>-34.5±1.6</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>6.183</td>
<td>4.2088</td>
<td>5838.1±0.1</td>
<td>-190 ±5</td>
<td>-19.89±0.02</td>
<td>-39.4±0.5</td>
<td>-1.0±0.3</td>
</tr>
<tr>
<td>35</td>
<td>6.135</td>
<td>4.2122</td>
<td>5939.2±0.1</td>
<td>-400.0±3.1</td>
<td>-20.57±0.01</td>
<td>-44.4±1.7</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>6.053</td>
<td>4.2180</td>
<td>6043.9±0.1</td>
<td>-634 ±13</td>
<td>-21.33±0.04</td>
<td>-49.4±3.2</td>
<td></td>
</tr>
</tbody>
</table>

* Results obtained after fitting the observed values into Clarke & Glew equations.
Table 8.6.3: The thermodynamic functions for the ionization of benzoic, benzoic-2-d and benzoic-d$_5$ acids. Results obtained from the Clarke & Glew formula with 3 coefficients.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>K x 10$^{+5*}$</th>
<th>pK*</th>
<th>$\Delta$G° cal/mol</th>
<th>$\Delta$H° cal/mol</th>
<th>$\Delta$S° cal/(deg. mol)</th>
<th>$\Delta$C° p cal/(deg. mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>6.226</td>
<td>4.2058</td>
<td>5641.5±0.1</td>
<td>241 ±8</td>
<td>-18.42±0.03</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>6.249</td>
<td>4.2042</td>
<td>5735.5±0.1</td>
<td>14 ±5</td>
<td>-19.19±0.02</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>6.232</td>
<td>4.2054</td>
<td>5833.4±0.1</td>
<td>-213.8±2.4</td>
<td>-19.95±0.01</td>
<td>-45.5±0.8</td>
</tr>
<tr>
<td>35</td>
<td>6.177</td>
<td>4.2092</td>
<td>5935.0±0.1</td>
<td>-441 ±5</td>
<td>-20.69±0.02</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>6.089</td>
<td>4.2155</td>
<td>6040.3±0.1</td>
<td>-669 ±9</td>
<td>-21.43±0.03</td>
<td></td>
</tr>
</tbody>
</table>

Benzoic acid (Fuoss-Shedlovsky method)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>K x 10$^{+5*}$</th>
<th>pK*</th>
<th>$\Delta$G° cal/mol</th>
<th>$\Delta$H° cal/mol</th>
<th>$\Delta$S° cal/(deg. mol)</th>
<th>$\Delta$C° p cal/(deg. mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>6.362</td>
<td>4.1964</td>
<td>5628.9±0.1</td>
<td>211 ±5</td>
<td>-18.48±0.02</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>6.383</td>
<td>4.1950</td>
<td>5723.0±0.1</td>
<td>11.8±2.5</td>
<td>-19.16±0.01</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>6.387</td>
<td>4.1961</td>
<td>5820.4±0.1</td>
<td>-187.9±1.3</td>
<td>-19.82±0.01</td>
<td>-39.9±0.4</td>
</tr>
<tr>
<td>35</td>
<td>6.318</td>
<td>4.1994</td>
<td>5921.1±0.1</td>
<td>-387.5±2.7</td>
<td>-20.47±0.01</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>6.239</td>
<td>4.2049</td>
<td>6025.1±0.1</td>
<td>-587 ±5</td>
<td>-21.12±0.02</td>
<td></td>
</tr>
</tbody>
</table>

Benzoic-2-d acid (Fuoss-Shedlovsky method)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>K x 10$^{+5*}$</th>
<th>pK*</th>
<th>$\Delta$G° cal/mol</th>
<th>$\Delta$H° cal/mol</th>
<th>$\Delta$S° cal/(deg. mol)</th>
<th>$\Delta$C° p cal/(deg. mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>6.072</td>
<td>4.2167</td>
<td>5556.1±0.2</td>
<td>222 ±17</td>
<td>-18.54±0.06</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>6.093</td>
<td>4.2151</td>
<td>5750.5±0.2</td>
<td>21 ±9</td>
<td>-19.22±0.03</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>6.080</td>
<td>4.2161</td>
<td>5848.2±0.2</td>
<td>-179 ±5</td>
<td>-19.88±0.02</td>
<td>-40.1±1.7</td>
</tr>
<tr>
<td>35</td>
<td>6.035</td>
<td>4.2194</td>
<td>5949.3±0.2</td>
<td>-379 ±10</td>
<td>-20.54±0.03</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>5.960</td>
<td>4.2248</td>
<td>6053.6±0.2</td>
<td>-580 ±18</td>
<td>-21.18±0.06</td>
<td></td>
</tr>
</tbody>
</table>

* Results obtained after fitting the observed values in Clarke & Glew formula.
Table 8.6.4: The thermodynamic functions for the ionization of benzoic, benzoic-2-d, and benzoic-d₅ acids. Results obtained from the Clarke and Glew formula

| Temp. °C | K x 10^5* | pK*  | ΔG° cal/mol | ΔH° cal/mol | ΔS° (deg. mol) | ΔC° cal/mol | d(ΔC°)/dT cal/mol
|----------|-----------|------|-------------|-------------|---------------|-------------|------------------|

**Benzoic acid (Fuoss-Shedlovsky method)**

| 20       | 6.227     | 4.2057 | 5641.4±0.1  | 212 ±14     | -18.52±0.05   | -37.0±3.6   |
| 25       | 6.248     | 4.2043 | 5735.6±0.1  | 15.8±3.5    | -19.18±0.01   | -41.3±1.9   |
| 30       | 6.232     | 4.2054 | 5833.3±0.1  | -202 ±5     | -19.91±0.02   | -45.6±0.6   |
| 35       | 6.179     | 4.2091 | 5934.8±0.1  | -440.5±3.7  | -20.69±0.01   | -49.9±2.0   |
| 40       | 6.088     | 4.2155 | 6040.3±0.1  | -701 ±15    | -21.53±0.05   | -54.3±3.7   |

**Benzoic-2-d acid (Fuoss-Shedlovsky method)**

| 20       | 6.362     | 4.1964 | 5628.9±0.1  | 225 ±10     | -18.43±0.03   | -43.9±2.6   |
| 25       | 6.384     | 4.1949 | 5722.9±0.1  | 10.9±2.5    | -19.16±0.01   | -41.9±1.3   |
| 30       | 6.367     | 4.1961 | 5820.4±0.1  | -193.6±3.9  | -19.84±0.02   | -39.9±0.4   |
| 35       | 6.318     | 4.1995 | 5921.2±0.1  | -387.9±2.7  | -20.47±0.01   | -37.9±1.4   |
| 40       | 6.239     | 4.2049 | 6025.1±0.1  | -572 ±11    | -21.07±0.04   | -35.9±2.7   |

**Benzoic-d₅ acid (Fuoss-Shedlovsky method)**

| 20       | 6.073     | 4.2166 | 5655.9±0.2  | 163 ±31     | -18.74±0.11   | -23.3±8.0   |
| 25       | 6.091     | 4.2153 | 5750.7±0.2  | 25 ±8       | -19.20±0.03   | -31.8±4.1   |
| 30       | 6.080     | 4.2161 | 5848.2±0.1  | -154 ±12    | -19.80±0.04   | -40.3±1.4   |
| 35       | 6.038     | 4.2191 | 5949.0±0.2  | -377 ±8     | -20.53±0.03   | -48.8±4.3   |
| 40       | 5.958     | 4.2249 | 6053.7±0.2  | -642 ±33    | -21.38±0.11   | -57.2±8.2   |

* Results obtained after fitting the observed values in Clarke & Glew equation.
Table 8.6.5: The thermodynamic functions for the ionization of benzoic acid in water. A comparison between published data and the results obtained in the present work.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Ref.</th>
<th>K x 10^4</th>
<th>pK</th>
<th>ΔG°</th>
<th>ΔH°</th>
<th>ΔS°</th>
<th>ΔC°</th>
<th>d(ΔC°)/dT</th>
<th>Method of calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td></td>
<td></td>
<td></td>
<td>cal/mol</td>
<td>cal/mol</td>
<td>(deg. mol)</td>
<td>cal/mol</td>
<td>(deg. mol)</td>
<td>cal/mol</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>6.281</td>
<td>4.202</td>
<td>5734.6 ±0.88</td>
<td>150 ±24</td>
<td>-18.7 ±0.08</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>6.295</td>
<td>4.201</td>
<td>5732 ±5.7</td>
<td>104 ±150</td>
<td>-18.9 ±0.5</td>
<td>-49.0</td>
<td>-</td>
<td>H&amp;R</td>
</tr>
<tr>
<td>25</td>
<td>4</td>
<td>6.12</td>
<td>4.212</td>
<td>5746.7 ±0.86</td>
<td>-155</td>
<td>-19.8</td>
<td>-</td>
<td>-</td>
<td>C&amp;G/2 coeff.</td>
</tr>
<tr>
<td>25</td>
<td>5</td>
<td>6.24</td>
<td>4.205</td>
<td>5737</td>
<td>0.9</td>
<td>-19.2</td>
<td>-24.7</td>
<td>-</td>
<td>H&amp;R</td>
</tr>
<tr>
<td>25</td>
<td>6</td>
<td>6.249</td>
<td>4.2042</td>
<td>5735.5 ±0.1</td>
<td>14 ±5</td>
<td>-19.19 ±0.02</td>
<td>-45.5 ±0.8</td>
<td>-</td>
<td>C&amp;G/3 coeff.</td>
</tr>
<tr>
<td>25</td>
<td>6</td>
<td>6.248</td>
<td>4.2043</td>
<td>5735.6 ±0.1</td>
<td>15.8 ±3.5</td>
<td>-19.18 ±0.01</td>
<td>-41.3 ±1.9</td>
<td>-0.9 ±0.4</td>
<td>C&amp;G/4 coeff.</td>
</tr>
<tr>
<td>35</td>
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<td>6.166</td>
<td>4.209</td>
<td>5936</td>
<td>-674</td>
<td>-21.4</td>
<td>-</td>
<td>-</td>
<td>C&amp;G/2 coeff.</td>
</tr>
<tr>
<td>35</td>
<td>2</td>
<td>6.237</td>
<td>4.205</td>
<td>5926</td>
<td>-390</td>
<td>-20.5</td>
<td>-49.8</td>
<td>-</td>
<td>H&amp;R</td>
</tr>
<tr>
<td>35</td>
<td>5</td>
<td>6.21</td>
<td>4.207</td>
<td>5933</td>
<td>-250.3</td>
<td>-20.1</td>
<td>-25.5</td>
<td>-</td>
<td>H&amp;R</td>
</tr>
<tr>
<td>35</td>
<td>6</td>
<td>6.177</td>
<td>4.2092</td>
<td>5935.0 ±0.1</td>
<td>-441 ±5</td>
<td>-20.69 ±0.01</td>
<td>-45.5 ±0.8</td>
<td>-</td>
<td>C&amp;G/3 coeff.</td>
</tr>
<tr>
<td>35</td>
<td>6</td>
<td>6.179</td>
<td>4.2091</td>
<td>5934.8 ±0.1</td>
<td>-440.5 ±3.7</td>
<td>-20.69 ±0.02</td>
<td>-49.9 ±2.0</td>
<td>-0.9 ±0.4</td>
<td>C&amp;G/4 coeff.</td>
</tr>
</tbody>
</table>

Note: C&G: Clarke and Glew formulae (13.2.26)

H&R: Harned and Robinson formulae (13.2.10)

B&B: Briegleb and Bieber method.
Table 8.6.5 (cont.)

References:

4. Data of ref. 3 recalculated by Clarke & Glew method by the authors of ref. 2.
6. Present work.
Table 8.6.6: "ΔΔ" values for some pairs of isotopic benzoic acids.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Temp. °C</th>
<th>ΔΔG° cal/mol</th>
<th>ΔΔH° cal/mol</th>
<th>ΔΔS° cal/(deg. mol)</th>
<th>ΔΔC° cal/(deg. mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Benzoic acid) -</td>
<td>20</td>
<td>12.6 ± 0.2</td>
<td>31 ± 13</td>
<td>0.06 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>(Benzoic-2-d acid)</td>
<td>25</td>
<td>12.5 ± 0.2</td>
<td>2 ± 7</td>
<td>-0.03 ± 0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>13.0 ± 0.2</td>
<td>-25.9 ± 3.7</td>
<td>-0.13 ± 0.02</td>
<td>-5.6 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>13.9 ± 0.2</td>
<td>-54 ± 8</td>
<td>-0.22 ± 0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>15.2 ± 0.2</td>
<td>-82 ± 14</td>
<td>-0.31 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>(Benzoic acid) -</td>
<td>20</td>
<td>-14.6 ± 0.3</td>
<td>19 ± 25</td>
<td>0.12 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>(Benzoic-d₅ acid)</td>
<td>25</td>
<td>-15.0 ± 0.3</td>
<td>-7 ± 14</td>
<td>0.03 ± 0.05</td>
<td>-5.4 ± 2.5</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-14.8 ± 0.3</td>
<td>-35 ± 7</td>
<td>-0.07 ± 0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>-14.3 ± 0.3</td>
<td>-62 ± 15</td>
<td>-0.15 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-13.3 ± 0.3</td>
<td>-89 ± 27</td>
<td>-0.25 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>(Benzoic-2-d acid) -</td>
<td>20</td>
<td>-27.2 ± 0.3</td>
<td>-11 ± 22</td>
<td>0.06 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>(Benzoic-d₅ acid)</td>
<td>25</td>
<td>-27.5 ± 0.3</td>
<td>-9 ± 12</td>
<td>0.06 ± 0.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-27.8 ± 0.3</td>
<td>-9 ± 6</td>
<td>0.06 ± 0.03</td>
<td>0.2 ± 2.1</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>-28.2 ± 0.3</td>
<td>-9 ± 13</td>
<td>0.07 ± 0.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-28.5 ± 0.3</td>
<td>-7 ± 23</td>
<td>0.06 ± 0.08</td>
<td></td>
</tr>
</tbody>
</table>

Note: The results obtained from Clarke & Glew equation with 3 coefficients were used to compile this table.
9. **THE DETERMINATION OF THE DISSOCIATION CONSTANTS OF PHENYLACETIC AND PHENYLACETIC - α-d₂ ACIDS BY CONDUCTANCE METHODS AT TEMPERATURES BETWEEN 20 AND 40°C**

9.1. **Introduction**

The dissociation constant of phenylacetic acid was determined by the conductance methods of Jeffery and Vogel, Dippy and Williams, Smolyakov and Primanchuk, and Barnes. Electrometric methods have also been used for the determination of the dissociation constant of phenylacetic acid.

The published values for the dissociation constant are listed in table 9.5.1.

All the determinations but one, have been done at one temperature. In most of the cases this temperature was 25°C. Only Smolyakov and Primanchuk's measurements cover a range of temperatures.

The dissociation constant of phenylacetic-α-d₂ acid was measured at 25°C by Barnes. The isotope effect:

\[
\frac{K_{C_6H_5CH_2COOH}}{K_{C_6H_5CD_2COOH}}
\]

was also measured by Halevi, Nussim and Ron.

9.2. **Materials**

Phenylacetic acid. It was obtained from Anachemia (AC-7204). It was purified by recrystallization from water (twice) followed by distillation under vacuum (three times).

Attempts to purify it in a "Zone Refiner" failed. Tubes with one end or both ends closed were used, up-down and down-up passes
passes were tried. In all cases the compound seemed to decompose rather than purify. The colour of the starting material was a very pale yellow. In the "Zone Refiner" the colour became darker and darker as the exposure time increased.

Phenylacetic-\(\alpha\)-d\(_2\) acid. It was prepared by:

a. Reduction of ethyl benzoate with lithium aluminum deuteride, treatment with thionyl chloride and conversion to the Grignard reagent which was carbonated to the acid.

b. Exchange (with D\(_2\)O) and decarboxylation of phenylmalonic acid.

c. Exchange of the sodium or potassium salt with D\(_2\)O in basic medium.

In the present work the phenylacetic-\(\alpha\)-d\(_2\) acid was prepared by a method which is similar to the third method listed above, of which, of course, we had no knowledge at the time.

To a 500 ml, 3-neck flask, equipped with a reflux condenser, a thermometer and a magnetic stirrer we added in order: 15.4 g of acid, 77 ml of D\(_2\)O (99%), 155 ml of freshly distilled dioxane and 4.0 g of freshly cut sodium. The sodium was the last reagent to be added and its addition was done very slowly (approximately 40 minutes). After the D\(_2\)O was added to the flask a stream of dry nitrogen was passed through it during the reaction. The reaction mixture was refluxed for six hours (the thermometer showed 88°C). At the end of this period the dioxane and the water were distilled off. The remaining solid was dissolved in water and the organic acid precipitated by the addition of HCl (1:1). A NMR spectrum showed 91% deuteration of the protons. The carboxylic hydrogen served as the internal standard.
A second exchange was carried out using: 13.6 g of acid from the first exchange, 50 ml of D₂O and 100 ml of dioxane. The conditions of the reaction were exactly the same as for the first exchange with the exception of the time of reaction. This time the mixture was refluxed for 24 hours. The final product was recovered in the same manner as before.

The acid was recrystallized from water and distilled under vacuum three times. The purified acid amounted to 11 g. NMR spectrum (fig. 9.2.2) showed over 97% deuteration of the α protons and no exchange of the aromatic protons.

The melting points of the two acids were measured with Mettler-FP1 instrument (capillary melting point apparatus) equipped with a Bausch-Lomb recorder. The rate of temperature increase was 0.2°C/min. The melting points of the two compounds were:

a. Phenylacetic acid: (76.9-77.3) ± 0.1°C
   (lit. value: 144 76.5-77°C)

b. Phenylacetic-α-d₂ acid: (74.3-75.0) ± 0.1°C

9.3. The conductance measurements

The procedure followed was exactly the same as the one described earlier in the case of potassium chloride and sodium benzoate.

The complete experimental results and the calculations leading to the concentration and conductance values are given in "Detailed calculations - 9.3.1 to 9.3.4".

No solvent correction was applied to the resistance readings.
The NMR spectrum of phenylacetic-\(\alpha'-d_2\) acid

Solvent: CDCl$_3$

Sweep time: 250 s

Sweep width: 1000 cps
9.4. The limiting conductance of phenylacetic acid

We have shown (subsection 7.5) that the most accurate determination of the limiting conductance of a weak acid is via the limiting conductance of one of its salts with a strong base.

Literature values for the limiting conductance of salts of phenylacetic acid are not very numerous. The existing ones are listed in table 9.4.1.

Table 9.4.1: The literature values for the limiting conductance of salts of phenylacetic acid.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref.</th>
<th>Temp.</th>
<th>Limiting conductance salt</th>
<th>Limiting cond. phenylacetate ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium phenylacetate</td>
<td>1</td>
<td>25</td>
<td>80.7</td>
<td>30.55</td>
</tr>
<tr>
<td>Sodium phenylacetate</td>
<td>2</td>
<td>25</td>
<td>84.49; 84.60</td>
<td>34.34; 34.45</td>
</tr>
<tr>
<td>Potassium phenylacetate</td>
<td>3</td>
<td>25</td>
<td>107.4</td>
<td>33.90</td>
</tr>
</tbody>
</table>

References:

If we refer to the limiting conductance of the phenylacetate ion which is obtained by subtracting the limiting conductance of sodium or potassium ion from the limiting conductance of sodium or potassium phenylacetate, it can be seen that the value obtained by Dippy and Williams is significantly different from the other two.
It is very difficult to assess the reliability of any of the three (or four) figures quoted in table 9.4.1. The only complete set of experimental data published is that of Jeffery and Vogel. Since their method of calculation is different from the one employed in the present work (see sodium benzoate, subsection 7.4), we decided to recalculate the limiting conductance for sodium phenylacetate using the method of calculation described in subsection 7.4 with Jeffery and Vogel's data. The results obtained are:

\[ \Lambda^0_{C_6H_5CH_2COO^-Na^+} = 83.54 \pm 0.12 \text{ by relation (7.4.1)} \]

\[ \Lambda^0_{C_6H_5CH_2COO^-Na^+} = 84.63 \pm 0.15 \text{ by relation (7.4.2)} \]

The details of the calculation are given in "Detailed calculation - 9.4.1". Briefly we must mention here that the original paper gives the conductance values having already a "normal" solvent correction (see subsection 5.9). Since our method of calculation requires the conductance values to be the ones directly measured, we have recalculated these values by using the specific conductance of water given in the original paper. From here on the procedure follows exactly the one employed in the case of sodium benzoate. The "Detailed calculations" are given in 9.4.1.

The value of the limiting conductance of sodium phenylacetate obtained here, i.e. 83.53, is then used to calculate the limiting conductance of phenylacetic acid at 25°C.

If we combine the limiting conductance of sodium phenylacetate with the limiting conductance of sodium and hydrogen ion we obtain the
limiting conductance of the phenylacetic acid:

\[ \Lambda_{C_6H_5CH_2COOH}^0 = \Lambda_{C_6H_5CH_2COO}^-Na^+ \Lambda_Na^+ + \Lambda_H^+ \]

Using the literature values:

\[ \Lambda_Na^+(25^\circ C)^{59} = 50.15 \]

and:

\[ \Lambda^0_H+(25)_{78} = 350.15 \]

we obtain for the limiting conductance of the phenylacetic acid at 25°C:

\[ \Lambda_{C_6H_5CH_2COOH}(25) = 383.54 \]

This value is different from the values used by other workers, even by those whose experimental data we used to calculate \[ \Lambda_{C_6H_5CH_2COONa}^0 \] here (Jeffery and Vogel's data). The reason for this is the fact that different values for \[ \Lambda_H^+ \] and \[ \Lambda_Na^+ \] were used. For a summary of these values see table 9.4.2.
Table 9.4.2: Limiting conductance of some ions used in the
determination of the limiting conductance of
phenylacetic acid.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>( \Lambda_{C_6H_5COONa}^0 )</th>
<th>( \Lambda_{H^+}^0 )</th>
<th>( \Lambda_{Na^+}^0 )</th>
<th>( \Lambda_{C_6H_5CH_2COOH}^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>84.52</td>
<td>348.0</td>
<td>49.82</td>
<td>382.7</td>
</tr>
<tr>
<td>2</td>
<td>80.7</td>
<td>349.72</td>
<td>50.10</td>
<td>380.32</td>
</tr>
<tr>
<td>3</td>
<td>*</td>
<td></td>
<td></td>
<td>381.7</td>
</tr>
</tbody>
</table>

* Potassium phenylacetate, potassium chloride and hydrochloric acid used.

References:

For the other four temperatures (20, 30, 35 and 40°C) the limiting conductance was calculated by the "correction factor" method described in subsection 8.4.

The limiting conductance values for phenylacetic and phenylacetic-\( \alpha\)-d\(_2\) acids obtained by the Ives and Fuoss-Shedlovsky extrapolation methods (see "Detailed calculations - 9.4.2 and 9.4.3") were fitted to the equation:

\[
\Lambda^0 = A + BT
\]  

(8.4.2)

where \( T \) is the temperature in kelvins. The observed and the calculated values, by (8.4.2), are given in table 9.4.3.
The "reference point", necessary to correct the limiting conductances thus obtained, was the limiting conductance at 25°C (383.54) obtained here.

The corrected limiting conductance values for the two acids obtained by this method are listed in Table 9.4.4. Detailed results are given in "Detailed calculations - 9.4.4 and 9.4.5". The average value given in the last column of Table 9.4.4 was used in the calculation of the dissociation constants of the phenylacetic and phenylacetic-α-d₂ acids.

Table 9.4.3: The "observed" and the calculated (by 8.4.2) values of the limiting conductance of phenylacetic and phenylacetic-α-d₂ acids.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Limiting conductance</th>
<th>Phenylacetic acid</th>
<th>Phenylacetic-α-d₂ acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed</td>
<td>Calculated</td>
<td>Observed</td>
</tr>
<tr>
<td>A = -1122.08</td>
<td>331.85</td>
<td>332.35</td>
<td>337.23</td>
</tr>
<tr>
<td>B = 4.9614</td>
<td>357.16</td>
<td>357.16</td>
<td>362.34</td>
</tr>
<tr>
<td>20</td>
<td>382.63</td>
<td>381.97</td>
<td>387.96</td>
</tr>
<tr>
<td>25</td>
<td>407.47</td>
<td>406.78</td>
<td>413.43</td>
</tr>
<tr>
<td>35</td>
<td>430.73</td>
<td>431.58</td>
<td>437.94</td>
</tr>
</tbody>
</table>

Note: The Λ₀'s obtained by Fuoss-Shedlovsky method are listed here. The results obtained with Λ₀'s from Ives' extrapolation are given in "Detailed calculations - 9.4.4 and 9.4.5".
Table 9.4.4: The corrected values of the limiting conductance obtained by extrapolation methods.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Phenylacetic acid</th>
<th>Fuoss-Sheldovsky</th>
<th>Lves method</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>358.91</td>
<td>358.73</td>
<td>358.19</td>
<td>358.53</td>
</tr>
<tr>
<td>25</td>
<td>383.54</td>
<td>383.54</td>
<td>383.54</td>
<td>383.54</td>
</tr>
<tr>
<td>30</td>
<td>408.17</td>
<td>408.89</td>
<td>408.79</td>
<td>408.55</td>
</tr>
<tr>
<td>35</td>
<td>432.79</td>
<td>433.24</td>
<td>434.94</td>
<td>433.56</td>
</tr>
<tr>
<td>40</td>
<td>457.42</td>
<td>457.96</td>
<td>459.29</td>
<td>458.57</td>
</tr>
</tbody>
</table>

Note: The average values listed in the last column were used in the calculation of the dissociation constants of the two acids.
9.5. The calculation of the dissociation constants of phenylacetic and phenylacetic-α-d₂ acids

The same methods of calculation employed for the benzoic acid (see subsection 8.5) were used here. The methods are:

a. Ives method
b. Fuoss-Shedlovsky method
c. Direct (Dippy's) method

These methods were analysed in detail in part 6 of this work. The first two methods, i.e. the Ives and Fuoss-Shedlovsky methods, were used without iteration since Λ⁰ values were obtained separately. The limiting conductances used for the calculation of the dissociation constants at 20, 25, 30, 35 and 40°C are listed in the last column of table 9.4.4.

The methods listed above and the limiting conductance at 25°C given in table 9.4.4 were used to calculate the dissociation constants of phenylacetic acid and phenylacetic-α-d₂ acid from some of the published conductance data (in fact for all available conductance data) and the data were used to compare these results with the ones obtained from data collected in the present work. These results are given in tables 9.5.1 and 9.5.2. "Detailed calculations" are given in 9.4.1 to 9.5.4.

It can be seen that the values obtained for the dissociation constant of phenylacetic acid at 25°C vary over a relatively wide range when we consider the supposed accuracy of the data. We think that Barnes' results and the results obtained here are the most accurate ones obtained up to present time. As far as the difference between the two sets of results is concerned, we would like to think
that it is due to the slightly different conductance standards used in the two works. We recall that we had to use in the present work not the usual Jones and Bradshaw standards but the Fuoss, Onsager and Skinner conductance equation for obtaining the cell constant since we performed our experiments at five different temperatures and since Jones and Bradshaw standards are given at 18 and 25°C, only.

The dissociation constants for the two acids over the entire temperature range are given in table 9.5.3.
### Table 9.5.1: The dissociation constant of phenylacetic acid at 25°C. A comparison between the published values and the values calculated here.

<table>
<thead>
<tr>
<th>Method</th>
<th>Ref.</th>
<th>Published</th>
<th>Calculated here$^a$: $K \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\Lambda^0$</td>
<td>$K \times 10^5$</td>
</tr>
<tr>
<td>Conductance</td>
<td>1</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Conductance</td>
<td>2</td>
<td>380.4</td>
<td>4.96</td>
</tr>
<tr>
<td>Conductance</td>
<td>3</td>
<td>382.7</td>
<td>4.884</td>
</tr>
<tr>
<td>Conductance</td>
<td>4</td>
<td>380.3</td>
<td>4.874</td>
</tr>
<tr>
<td>Conductance</td>
<td>5</td>
<td>381.7</td>
<td>4.886</td>
</tr>
<tr>
<td>Conductance</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrometric</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrometric</td>
<td>8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**

a. $\Lambda^0 = 383.54$

b. Only the experimental points corresponding to $c < 4.0 \times 10^{-3}$ moles/litre were considered. It was shown in section 6 that the Ives and Fuoss-Shedlovsky methods cannot be applied to concentrations higher than this value. For uniformity the same concentration range was used with the Dippy method.
Table 9.5.1 (cont.)

References:

6. Present work.
Table 9.5.2: The dissociation constant of phenylacetic-α-d₂ acid at 25°C. A comparison between the published values and the values calculated here.

<table>
<thead>
<tr>
<th>Method</th>
<th>Ref.</th>
<th>Calculated here$^a$: $K \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ives method</td>
</tr>
<tr>
<td>Conductance</td>
<td>1</td>
<td>5.095±0.018</td>
</tr>
<tr>
<td>Conductance</td>
<td>2</td>
<td>4.756±0.009</td>
</tr>
</tbody>
</table>

Notes: $^a. \Lambda^0 = 383.54$

References:


2. Present work.
Table 9.5.3: The dissociation constants of phenylacetic and phenylacetic-α-d₂ acids and the isotope effect $K_H/K_D$ at temperatures between 20 and 40°C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K \times 10^5$</td>
<td>$K_{H/K_D}$</td>
<td>$K \times 10^5$</td>
<td>$K_{H/K_D}$</td>
<td>$K \times 10^5$</td>
</tr>
<tr>
<td>Phenylacetic acid</td>
<td>4.840±0.004</td>
<td>-</td>
<td>4.850±0.004</td>
<td>-</td>
<td>4.819±0.004</td>
</tr>
<tr>
<td>Phenylacetic-α-d₂ acid</td>
<td>4.794±0.005</td>
<td>1.010</td>
<td>4.806±0.004</td>
<td>1.009</td>
<td>4.775±0.004</td>
</tr>
<tr>
<td></td>
<td>Fuoss-Shedlovsky method</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenylacetic acid</td>
<td>4.745±0.013</td>
<td>-</td>
<td>4.763±0.013</td>
<td>-</td>
<td>4.740±0.012</td>
</tr>
<tr>
<td>Phenylacetic-α-d₂ acid</td>
<td>4.710±0.014</td>
<td>1.007</td>
<td>4.727±0.013</td>
<td>1.008</td>
<td>4.705±0.012</td>
</tr>
</tbody>
</table>

Notes: 1. The probable errors are quoted in this table.
2. Fuoss-Shedlovsky method used without iteration.
3. The limiting conductances are those given in table 9.3.4 (last column).
4. Of the two set of results of table 9.5.3 we give preference to the values obtained by Fuoss-Shedlovsky method for the same reasons as those presented in the case of benzoic acids (see subsection 8.5).
5. Estimated precision of the isotope effect: 0.2% (or ± 0.002) (Fuoss-Shedlovsky method).
9.6. Calculation of the thermodynamic functions for the ionization of phenylacetic and phenylacetic-α-d₂ acids

The thermodynamic functions for the ionization of phenylacetic and phenylacetic-α-d₂ acids were calculated by using the Clarke and Glev formula\textsuperscript{149} (see section 13) with 3 and 4 coefficients.

The results obtained are given in tables 9.6.2 and 9.6.3 and "Detailed calculations 9.6.1 and 9.6.2".

Table 9.6.1 presents a comparison between the only set of thermodynamic quantities for the ionization of phenylacetic acid published until now and some of the results obtained in the present work. The agreement between the two sets of data is fair, only. We think that the results obtained here are better since they originate from a more accurate set of dissociation constants (see subsection 9.5). At the same time we consider the results obtained from the Clarke & Glew equation with 3 coefficients as the better ones although the 4 coefficient equation indicates that there is some probability that the change in $\Delta C^0_p$ with temperature is real though it is small. Because the change is so small it is not possible to obtain the exact temperature coefficient of $\Delta C^0_p$ when the data cover only a small temperature range.

The two isotopic acids have dissociation constants which differ only slightly and because of this the thermodynamic functions are approximately the same within the error at 68% confidence level (the errors quoted in the tables of this work represent the 50% confidence level).

Comparison of the thermodynamic functions for the ionization of phenylacetic acid with those for the ionization of acetic acid
reveal the same type of pattern which is followed by some other organic acids. More specifically we refer to the entropy and heat capacity of ionization which change in opposite directions upon substitution. In this particular case the substitution of a hydrogen with a phenyl group in acetic acid results in a decrease in entropy and an increase in the heat capacity of ionization. The respective values are given in table 9.6.4. The values for diethylacetic acid quoted in the same table are just another example illustrating this fact. Further examples can be found in the literature.\textsuperscript{44,150}

It is interesting to note that the heat capacity of ionization of phenylacetic acid is approximately equal to the heat capacities of ionization of m- and p-toluic acids (see subsection 14.7, for example) which suggests that the "size" of the "intensified" structure around the undissociated acid molecules is approximately the same for the three acids and that the tight hydration shell around the anions is approximately the same also. This is expected in the case when \( \Delta C_p \) is directly dependent on these two phenomena as we have assumed that it is in subsection 14.7 of this work.

The fact that the entropy of ionization of phenylacetic acid differs from that of m- and p-toluic acids suggests that besides the "primary" solute-solvent interactions, other weaker "secondary" interactions bring small contributions to the overall value for the \( \Delta S^0 \) of ionization.

As far as the differences in the thermodynamic functions of ionization of the two isotopic acids, are concerned, i.e. phenylacetic acid and phenylacetic-\( \alpha \)-d\(_2\) acid, only those between the \( \Delta G^0 \) values are
significant. Referring to calculations which are presented in a later part of this thesis (section 20), the experimental $K_H/K_D$ ratio was reproduced by making two assumptions.

1. The valence force constants corresponding to the internal coordinates involving the atoms of the carboxylate group and the atoms in its vicinity are approximately 10% larger than the equivalent force constants in the phenylacetic acid.

2. The same force constants in phenylacetate-$\alpha$-$d_2$ are, approximately 9.8% larger than the equivalent force constants in phenylacetic-$\alpha$-$d$ acid.

The vibrational analysis of acetic acid - acetate ion system has shown that the force constants are larger in the anion for equivalent internal coordinates.140-143

The slight difference (0.2% approximately) in some of the force constants of the two anions was assumed to be due to the slight difference between the anion-solvent interactions in the two cases. The shorter C-D band and its smaller polaizability could account for the weaker interactions phenylacetate-$\alpha$-$d_2$-water assumed here, as compared with phenylacetate - water interactions.

We must mention that the numbers we have used to increment the force constants in going from the acid molecule to the respective anion, i.e. 9.8 and 10%, were purely arbitrarily chosen; there are certainly many other combinations of such numbers which will give the same value for the $K_H/K_D$ ratio.
<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Ref.</th>
<th>$K \times 10^5^*$</th>
<th>pK*</th>
<th>$\Delta G^0$</th>
<th>$\Delta H^0$</th>
<th>$\Delta S^0$</th>
<th>$\Delta C_p^0$</th>
<th>$d(\Delta C_p^0)/dT$</th>
<th>Method of calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1</td>
<td>4.96</td>
<td>5876</td>
<td>-881.8</td>
<td>-22.70</td>
<td>-25.17</td>
<td></td>
<td></td>
<td>H&amp;R-13.2.10</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>4.849</td>
<td>5885.8±0.1</td>
<td>83.2±3.7</td>
<td>-20.02±0.01</td>
<td>-58.6±0.7</td>
<td></td>
<td></td>
<td>C&amp;G-13.2.26/3 coef.</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>4.850</td>
<td>5885.6±0.1</td>
<td>84.9±2.2</td>
<td>-20.03±0.01</td>
<td>-62.2±1.2</td>
<td>0.74±0.22</td>
<td></td>
<td>C&amp;G-13.2.26/4 coef.</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>4.847</td>
<td>5886.2±0.3</td>
<td>83 ±19</td>
<td>-20.02±0.06</td>
<td>-57.6±3.3</td>
<td></td>
<td></td>
<td>H&amp;R-13.2.10</td>
</tr>
<tr>
<td>35</td>
<td>1</td>
<td>4.69</td>
<td>6107</td>
<td>-1137</td>
<td>-23.53</td>
<td>-25.99</td>
<td></td>
<td></td>
<td>H&amp;R-13.2.10</td>
</tr>
<tr>
<td>35</td>
<td>2</td>
<td>4.751</td>
<td>6095.7±0.1</td>
<td>669.0±3.9</td>
<td>-21.95±0.01</td>
<td>-58.6±0.7</td>
<td></td>
<td></td>
<td>C&amp;G-13.2.26/3coef.</td>
</tr>
<tr>
<td>35</td>
<td>2</td>
<td>4.750</td>
<td>6095.8±0.1</td>
<td>669.8±2.3</td>
<td>-21.96±0.01</td>
<td>-54.8±1.2</td>
<td>0.74±0.22</td>
<td></td>
<td>C&amp;G-13.2.26/4 coef.</td>
</tr>
<tr>
<td>35</td>
<td>2</td>
<td>4.750</td>
<td>6096.1±0.3</td>
<td>669 ±20</td>
<td>-21.95±0.06</td>
<td>-59.5±3.4</td>
<td></td>
<td></td>
<td>H&amp;R-13.2.10</td>
</tr>
</tbody>
</table>

Notes: *Results obtained after fitting the observed values to the respective equations.
Methods of calculation: H&R - Harned and Robinson; equation (13.2.10).
C&G - Clarke and Glew; equation (13.2.26) with three or four coeff.

2. Present work (see Detailed calculations - 9.6.1).
Table 9.6.2: The thermodynamic functions for the ionization of phenylacetic and phenylacetic-α-d$_2$ acids. Results obtained from Clarke and Glew formula with 3 coefficients.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>K x 10$^5$</th>
<th>pK*</th>
<th>$\Delta G^0$ cal/mol</th>
<th>$\Delta S^0$ cal/(mol deg)</th>
<th>$\Delta C_p^0$ cal/(mol deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.840</td>
<td>4.3151</td>
<td>5788.1±0.1</td>
<td>210 ±7</td>
<td>-19.03±0.02</td>
</tr>
<tr>
<td>25</td>
<td>4.849</td>
<td>4.3143</td>
<td>5885.8±0.1</td>
<td>-83.2±3.7</td>
<td>-20.02±0.01</td>
</tr>
<tr>
<td>30</td>
<td>4.819</td>
<td>4.3171</td>
<td>5988.3±0.1</td>
<td>-376.1±1.9</td>
<td>-20.99±0.01</td>
</tr>
<tr>
<td>35</td>
<td>4.751</td>
<td>4.3232</td>
<td>6095.7±0.1</td>
<td>-669.0±3.9</td>
<td>-21.95±0.01</td>
</tr>
<tr>
<td>40</td>
<td>4.651</td>
<td>4.3324</td>
<td>6207.8±0.1</td>
<td>-962 ±7</td>
<td>-22.90±0.02</td>
</tr>
</tbody>
</table>

Phenylacetic acid (Fuoss-Shedlovsky method)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>K x 10$^5$</th>
<th>pK*</th>
<th>$\Delta G^0$ cal/mol</th>
<th>$\Delta S^0$ cal/(mol deg)</th>
<th>$\Delta C_p^0$ cal/(mol deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.795</td>
<td>4.3193</td>
<td>5793.7±0.1</td>
<td>226 ±9</td>
<td>-18.99±0.03</td>
</tr>
<tr>
<td>25</td>
<td>4.805</td>
<td>4.3183</td>
<td>5891.2±0.1</td>
<td>-77 ±5</td>
<td>-20.02±0.02</td>
</tr>
<tr>
<td>30</td>
<td>4.775</td>
<td>4.3211</td>
<td>5993.8±0.1</td>
<td>-380.8±2.6</td>
<td>-21.03±0.01</td>
</tr>
<tr>
<td>35</td>
<td>4.707</td>
<td>4.3273</td>
<td>6101.5±0.1</td>
<td>-684 ±5</td>
<td>-22.02±0.02</td>
</tr>
<tr>
<td>40</td>
<td>4.605</td>
<td>4.3368</td>
<td>6214.0±0.1</td>
<td>-988 ±9</td>
<td>-23.00±0.03</td>
</tr>
</tbody>
</table>

Phenylacetic-α-d$_2$ acid (Fuoss-Shedlovsky method)

* Results obtained after fitting the observed values in Clarke and Glew equation.
Table 9.6.3: The thermodynamic functions for the ionization of phenylacetic and phenylacetic-α-d₂ acids. Results obtained from Clarke & Glew formula with 4 coefficients.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>K x 10⁵*</th>
<th>pK*</th>
<th>ΔG⁰ cal/mol</th>
<th>ΔH⁰ cal/mol</th>
<th>ΔS⁰ cal/(deg. mol)</th>
<th>ΔC_p⁰ cal/(deg. mol)</th>
<th>d(ΔC_p⁰)/dT cal/(deg² mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.840</td>
<td>4.3152</td>
<td>5788.2±0.1</td>
<td>235 ±9</td>
<td>-18.94±0.03</td>
<td>-65.9±2.2</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>4.850</td>
<td>4.3142</td>
<td>5885.6±0.1</td>
<td>-84.9±2.2</td>
<td>-20.03±0.01</td>
<td>-62.2±1.2</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>4.819</td>
<td>4.3171</td>
<td>5988.3±0.1</td>
<td>-386.6±3.4</td>
<td>-21.03±0.01</td>
<td>-58.5±0.4</td>
<td>0.74±0.22</td>
</tr>
<tr>
<td>35</td>
<td>4.750</td>
<td>4.3233</td>
<td>6095.8±0.1</td>
<td>-669.8±2.3</td>
<td>-21.96±0.01</td>
<td>-54.8±1.2</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>4.652</td>
<td>4.3324</td>
<td>6207.7±0.1</td>
<td>-934 ±9</td>
<td>-22.81±0.03</td>
<td>-51.1±2.3</td>
<td></td>
</tr>
</tbody>
</table>

Phenylacetic acid (Fuoss-Shedlovsky method)

Phenylacetic-α-d₂ acid (Fuoss-Shedlovsky method)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>K x 10⁵*</th>
<th>pK*</th>
<th>ΔG⁰ cal/mol</th>
<th>ΔH⁰ cal/mol</th>
<th>ΔS⁰ cal/(deg. mol)</th>
<th>ΔC_p⁰ cal/(deg. mol)</th>
<th>d(ΔC_p⁰)/dT cal/(deg² mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.794</td>
<td>4.3193</td>
<td>5793.7±0.1</td>
<td>262 ±9</td>
<td>-18.87±0.03</td>
<td>-70.8±2.3</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>4.806</td>
<td>4.3182</td>
<td>5891.0±0.1</td>
<td>-79.6±2.2</td>
<td>-20.03±0.01</td>
<td>-65.7±1.2</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>4.775</td>
<td>4.3211</td>
<td>5993.8±0.1</td>
<td>-395.3±3.5</td>
<td>-21.08±0.01</td>
<td>-60.6±0.4</td>
<td>1.02±0.23</td>
</tr>
<tr>
<td>35</td>
<td>4.705</td>
<td>4.3274</td>
<td>6101.6±0.1</td>
<td>-685.4±2.3</td>
<td>-22.03±0.01</td>
<td>-55.5±1.2</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>4.606</td>
<td>4.3367</td>
<td>6213.9±0.1</td>
<td>-950 ±9</td>
<td>-22.88±0.03</td>
<td>-50.3±2.4</td>
<td></td>
</tr>
</tbody>
</table>

* Results obtained after fitting the observed values into Clarke & Glew equations.
Table 9.6.4: The thermodynamic functions for the ionization of some organic acids in water at 25°C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref.</th>
<th>$\Delta G^0$ (cal/mol)</th>
<th>$\Delta H^0$ (cal/mol)</th>
<th>$\Delta S^0$ (cal/(deg. mol))</th>
<th>$\Delta C_p^0$ (cal/(deg. mol))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>1</td>
<td>6487.9</td>
<td>-105</td>
<td>-22.1</td>
<td>-37.1</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>3</td>
<td>-</td>
<td>-98</td>
<td>-22.1</td>
<td>-37.0</td>
</tr>
<tr>
<td>Phenylacetic acid</td>
<td>2</td>
<td>5885.8</td>
<td>-83.2</td>
<td>-20.02</td>
<td>-52.6</td>
</tr>
<tr>
<td>Diethylacetic acid</td>
<td>1</td>
<td>6458.7</td>
<td>-2030</td>
<td>-28.47</td>
<td>-28.8</td>
</tr>
</tbody>
</table>

2. Present work.
THE DETERMINATION OF THE DISSOCIATION CONSTANTS OF
\( o\)-TOLUIC ACID AND \( o\)-TOLUIC-\( d_7 \) ACID BY CONDUCTANCE
METHOD AT TEMPERATURES BETWEEN 20 and 40\( ^\circ \)C.

10.1 Introduction.

The dissociation constant of \( o\)-toluic acid has been
determined by Dippy and Lewis using the conductance method at 25\( ^\circ \)C.\(^{17}\) Other methods have also been used to determine the dissociation
costant. The methods and the respective results are listed in
table 10.5.1. The only determination for the dissociation constant
over a temperature range have been done recently and belong to
Wilson, Gore, Sawbridge and Cardenas-Cruz.\(^{130}\) They determined the
dissociation constant of \( o\)-toluic acid between 15 and 40\( ^\circ \)C electro-
metrically. Their results are listed in table 10.5.2.

The dissociation constant of \( o\)-toluic-\( d_7 \) acid has not
been obtained before. In fact as far as we are aware, this acid
has not been prepared as such before.

Materials

\( o\)-Toluic acid. It was bought from Eastman (Eastman Organic
chemicals cat. No. 1646).

The acid was purified in a Fisher "Zone Refiner". The
compound was placed in a Pyrex tube, \( \frac{1}{4} \)" diameter and approximately
20 inches long. After the tube was filled with the acid it was
sealed. During the filling operation the tube was heated with a
microburner. The acid melted and thus we achieved a more compact
packing of the compound in the tube.

The tube was kept in the "Zone Refiner" for 5 days (approxi-
mately 120 hours). A "pass" (up-down) took slightly less than
2 hours and therefore the compound was submitted to at least 60 passes.

The acid was identified by its IR and NMR Spectra and its melting point (see next).

\textbf{o-Toluic-d\textsubscript{7} acid.} It was prepared by exchange of o-toluic acid and its sodium salt with D\textsubscript{2}O on a prereduced platinum catalyst. The procedure was described in subsection 8.2 in connection with the preparation of benzoic-d\textsubscript{5} acid. The quantities used, temperatures, and times of reaction are shown in table 10.2.1. The progress of the exchange reaction was followed by NMR. The carboxylic proton served as an internal standard. Before its NMR spectrum was taken every sample was carefully purified by sublimation under vacuum (3 sublimations for every sample). This was absolutely necessary to obtain sharp, well defined peaks for the acidic proton which played the role of the standard.

In a separate experiment we tried to exchange the aromatic deuterium atoms of o-toluic-d\textsubscript{7} acid for hydrogens. A sample of o-toluic-d\textsubscript{7} acid (0.44 gm) was placed in a 200 ml flask. 60 ml of 81\% H\textsubscript{2}SO\textsubscript{4} and 2 ml of benzene were added. The benzene was added to bring the acid into a liquid phase. The mixture was shaken at room temperature for 14 hours. After this period the acid was extracted with benzene from the reaction mixture. The NMR spectrum showed no difference between it and the starting material.

The melting points were measured with a Mettler FPI capillary melting point apparatus equipped with a Bausch-Lomb recorder. The temperature increment was 0.2°C min. The melting points of the two acids were:
a) o-toluic acid (103.7-104.3) ± 0.2°C  
(literature values: 104-105°C\textsuperscript{151}, 105°C\textsuperscript{152}) 
b) o-toluic-d\textsubscript{7} acid (104.4-104.9) ± 0.2°C

Table 10.21. The exchange conditions for o-toluic acid and its sodium salt.

<table>
<thead>
<tr>
<th>Exchange</th>
<th>Acid Na Salt</th>
<th>Pt0</th>
<th>D\textsubscript{2}O</th>
<th>Temp.</th>
<th>Time</th>
<th>% exchange Methyl protons</th>
<th>Aromatic protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>g</td>
<td>g</td>
<td>mg</td>
<td>cm\textsuperscript{3}</td>
<td>°C</td>
<td>hrs</td>
<td>66</td>
</tr>
<tr>
<td>2</td>
<td>5.7</td>
<td>3.5</td>
<td>188.2</td>
<td>20*</td>
<td>170</td>
<td>210</td>
<td>86</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>3.2</td>
<td>139.7</td>
<td>15</td>
<td>170</td>
<td>237</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>3.8</td>
<td>1.4</td>
<td>108.0</td>
<td>15</td>
<td>170</td>
<td>502</td>
<td>&gt;96</td>
</tr>
</tbody>
</table>

* 97% D\textsubscript{2}O

10.3 The conductance measurements.

The conductance measurements were taken in the same manner as for the measurements with potassium chloride solutions (subsection 5.10) and sodium benzoate solutions (subsection 7.3).

The detailed results are given in "Detailed calculations - 10.3.1 and 10.3.2". The calculations leading to the values of Λ (conductance) and c (concentration) at the five temperatures considered in the present thesis followed the same pattern as those for the other compounds (potassium chloride, sodium benzoate, etc.). Their details and the results are given in "Detailed Calculations - 10.3.3 and 10.3.4".
The NMR spectrum of o-toluic-d₇ acid

Solvent: CDCl₃
Sweeptime: 10min.
Sweepwidth: 9 x 2 ppm
No solvent correction was applied to the present readings.

10.4 The limiting conductance of _o_-toluic acid.

Dippy and Lewis have determined the limiting conductance of sodium _o_-toluate at 25^0C by the conductance method. They obtained the values of 81.2 and 81.9 (average 81.55).

If we combine this average value with the limiting conductance values of the sodium and hydrogen ions we obtain the limiting conductance value of _o_-toluic acid:

\[
\lambda^o_{o\text{-toluic acid}} (25) = \lambda^o_{\text{sodium}} (25) - \frac{\Lambda^o_{\text{Na}^+} (25) + \Lambda^o_{\text{H}^+} (25)}{2}
\]

\[
= 81.55 - 50.15 + 350.15 = 381.55
\]

This value was used as the reference point for calculating the limiting conductances at the other four temperatures: i.e., 20, 30, 35 and 40^0C by the "correction factor" method (see subsection 8.4).

The limiting conductance values obtained by the Ives and Fuoss-Shedlovsky extrapolation methods ("observed" limiting conductance) and the calculated values (by relation 8.4.2) are given in table 10.4.1 and "Detailed calculations - 10.4.1 to 10.4.4". The corrected values are listed in table 10.4.2.

The average values given in the last column of this table were used for the calculation of the dissociation constants of the _o_-toluic and _o_-toluic-d7 acids.

Note that, as before, we assumed that the limiting conductances of the two isotopic acids were equal. The fact that the corrected values of \( \lambda^o \) (table 10.4.2) are the same for the two acids, within the accuracy of the method, is positive evidence in support of this assumption.
Table 10.4.1 The "observed" and the calculated values (by 8.4.2) of the limiting conductance of \( o \)-toluic and \( o \)-toluic-\( d_7 \) acids.

<table>
<thead>
<tr>
<th>Temp. (^\circ)C</th>
<th>( o )-toluic acid</th>
<th>( o )-toluic-( d_7 ) acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed (^2)</td>
<td>Calculated</td>
</tr>
<tr>
<td>A=1190.5</td>
<td></td>
<td>A= -1187.6</td>
</tr>
<tr>
<td>B= 5.2546</td>
<td></td>
<td>B= 5.2218</td>
</tr>
<tr>
<td>20</td>
<td>342.50</td>
<td>349.89</td>
</tr>
<tr>
<td></td>
<td>343.26</td>
<td>343.16</td>
</tr>
<tr>
<td>25</td>
<td>375.68</td>
<td>376.16</td>
</tr>
<tr>
<td></td>
<td>368.99</td>
<td>369.27</td>
</tr>
<tr>
<td>30</td>
<td>403.43</td>
<td>402.43</td>
</tr>
<tr>
<td></td>
<td>395.43</td>
<td>395.38</td>
</tr>
<tr>
<td>35</td>
<td>428.14</td>
<td>428.70</td>
</tr>
<tr>
<td></td>
<td>421.86</td>
<td>421.49</td>
</tr>
<tr>
<td>40</td>
<td>455.02</td>
<td>454.98</td>
</tr>
<tr>
<td></td>
<td>447.37</td>
<td>447.60</td>
</tr>
</tbody>
</table>

1. Not considered in the fitting.
2. \( \Lambda^0 \)'s obtained by the Fuoss-Shedlovsky method are listed here.
   The calculations involving \( \Lambda^0 \)'s obtained by Ives extrapolation method are given in "Detailed calculations 10.4.3 and 10.4.4".
   The results are completely similar to those given in table 10.4.1.

10.5 The calculation of the dissociation constants of \( o \)-toluic acid and \( o \)-toluic-\( d_7 \) acid.

The three methods of calculation used in the present work were applied to the calculation of the dissociation constants of the two \( o \)-toluic acids. The methods are:
Table 10.4.2. The corrected values of the limiting conductances obtained by extrapolation methods

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Corrected values of the limiting conductance</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ɑ-toluic acid</td>
<td>ɑ-toluic-d7 acid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ives method</td>
<td>Fuoss-Shedlovsky method</td>
<td>Ives method</td>
</tr>
<tr>
<td>20</td>
<td>355.23</td>
<td>355.28</td>
<td>355.43</td>
</tr>
<tr>
<td>25</td>
<td>381.55</td>
<td>381.55</td>
<td>381.55</td>
</tr>
<tr>
<td>30</td>
<td>407.87</td>
<td>407.82</td>
<td>407.67</td>
</tr>
<tr>
<td>35</td>
<td>434.18</td>
<td>434.10</td>
<td>433.79</td>
</tr>
<tr>
<td>40</td>
<td>460.50</td>
<td>460.37</td>
<td>459.91</td>
</tr>
</tbody>
</table>
a. Ives method.

b. Fuoss-Shedlovsky method.

c. "Direct" (Dippy) method.

The first two methods were used without iteration because the $\Lambda^0$'s were already known. The detailed calculations are given in "Detailed calculations - 10.5.2 to 10.5.4".

The observations we made for the benzoic acids are valid here too. We are referring mainly to the fact that the Ives method seems to be much more sensitive to experimental errors which is reflected in the larger error of the calculated quantities and to the fact that the results obtained by this method are quite different from those obtained by the other two methods mentioned above. This is as evident in the case of $o$-toluic acid as it is in the case of $o$-toluic-d7 acid.

Among the three methods we prefer the results obtained by the Fuoss-Shedlovsky method for the same reasons as those presented in subsection 8.5.

A summary of the results obtained in the present work is given in table 10.5.2.

The only other determination of the dissociation constant of $o$-toluic acid by conductance method belongs to Dippy and Lewis.\textsuperscript{17} For comparison we recalculated the dissociation constant of $o$-toluic acid from their data using the universal constants, dielectric constant, viscosity and the limiting conductance values accepted in the present thesis. The results are shown in table 10.5.2. It can be seen that the accuracy of our results compares very favorable with that of those published previously.
As we mentioned before, the only other set of determinations covering a range of temperatures is that of Wilson, Gore, Sawbridge and Cardenas-Cruz. The results obtained here differ significantly from their results. We have no immediate explanation for this fact.

10.6. Calculation of the thermodynamic functions for the ionization of o-toluic and o-toluic-d₇ acids in water.

The thermodynamic functions for the ionization of o-toluic and o-toluic-d₇ acids in water were calculated by using the Clarke & Glew and Harned & Robinson formulas (see section 13). From the results obtained with the two sets of formulas, we prefer those obtained by Clarke & Glew formulas for the same reasons as those shown in section 13. The complete results are given in "Detailed calculations-10.6.1 and 10.6.2." A summary of the results obtained with Clarke & Glew formulas is given in tables 10.6.1 and 10.6.2.

We want to call attention to one "abnormality": it can be seen from table 10.6.1 that in the case of o-toluic acid when the 20°C point by the Fuoss-Shedlovsky method) is not considered the calculated ΔC_p changes by approximately 20 cal/(deg.mol). This fact together with the observation we made in subsection 10.4 (table 10.4.) that the Λₒobs (20°C) did not fit relation (8.4.2) suggest that indeed something "abnormal" affects the values of Λ and Λₒ at this particular temperature. We were unable to identify the cause of this so-called "abnormality". Thus in the following discussions we are referring to the thermodynamic functions of o-toluic acid obtained from four Λ values (25, 30, 35, and 40°C) obtained by the Fuoss-Shedlovsky method, only. It is interesting to note, however, that this "abnormality" does not
seem to affect the value of $K$ at $20^\circ$C obtained by the "Direct" method although the same $\Delta^0$ was used in both methods. Furthermore, the thermodynamic functions calculated from five or four $K$ values obtained by the "Direct" method agree very well with the thermodynamic functions calculated from four $K$ values obtained by the Fuoss-Shedlovsky method ($20^\circ$C point excluded).

The values of the thermodynamic functions for the ionization of $\alpha$-toluic acid in water are compared with the values of the thermodynamic functions for the ionization in water of benzoic, $m$- and $p$-toluic, and mesitoic acids in subsection 14.7. Table 10.6.3 presents a comparison between the results obtained in the present work and those found in the literature. The agreement is fair, only.

Table 10.6.4 contains the "$\Delta \Delta$" values for the isotopic pair of acids, e.g.:

$$\Delta \Delta G^0 = \Delta G^0(\alpha\text{-toluic acid}) - \Delta G^0(\alpha\text{-toluic-d}_7 \text{ acid})$$

The differences in the $\Delta G^0$ values, the only ones which are significant, can be explained by referring to calculations which are presented in section 20 of this thesis. There a rough vibrational analysis of the two $\alpha$-toluic acids and their respective anions has shown that the experimental $K_H/K_D$ ratio can be reproduced if one makes the following assumptions.

1. The force constants corresponding to those internal coordinates involving the carboxyl group and the atoms in its vicinity are larger in the anions than in their respective acids. The increase in the force constants in going from the acid to the anion is slightly larger in the case of undeuterated acid.

And/or:

2. The force constants corresponding to those internal coordinates
Table 10.5.1. The dissociation constant of o-toluic acid at $25^\circ$C. A comparison between the published values and the values calculated here.

<table>
<thead>
<tr>
<th>Method</th>
<th>Ref.</th>
<th>Published</th>
<th>Ives method</th>
<th>Fuoss-Shedlovsky method</th>
<th>&quot;Direct(Dippy's)&quot; method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductance</td>
<td>1</td>
<td>381.2</td>
<td>1.235</td>
<td>1.258+0.048</td>
<td>1.260+0.014</td>
</tr>
<tr>
<td>Conductance</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>1.261+0.003</td>
<td>1.246+0.001</td>
</tr>
<tr>
<td>Spectrophotometric</td>
<td>3</td>
<td>-</td>
<td>1.265</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrometric</td>
<td>4</td>
<td>-</td>
<td>1.191</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: $\Delta^0 = 381.55$ (see table 10.4.2)


2. Present work.


<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>$K \times 10^4$</td>
</tr>
<tr>
<td>o-Toluic acid (Electrometric; ref. 1)</td>
<td>1.331</td>
</tr>
<tr>
<td>o-Toluic acid</td>
<td>1.294±0.001</td>
</tr>
<tr>
<td>o-Toluic acid-d$_7$ acid</td>
<td>1.207±0.001</td>
</tr>
<tr>
<td>&quot;Direct&quot;(Dippy's) method</td>
<td>1.274±0.002</td>
</tr>
<tr>
<td>o-Toluic acid-d$_7$ acid</td>
<td>1.189±0.003</td>
</tr>
</tbody>
</table>

Notes. 1. Estimated precision of the isotope effect $K_{H/K_D}$: 0.2% (Fuoss-Shedlovsky method)


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in which C₁₋C₁₂ bond (fig. 19.2.1) is involved are somewhat stronger in o-toluic-d₇ acid than the corresponding force constants in o-toluic acid. Such a difference can be justified if the angle between the plane of the carboxyl group and the plane of the benzene ring is smaller in o-toluic-d₇ acid than in o-toluic acid as a result of the smaller steric requirements of a -CD₃ group as compared with a -CH₃ group. In other words this amounts to a smaller steric interference with the stabilization of the acid molecule by π-electron delocalization.

The differences between the ΔH₀, ΔS₀, and ΔCp values of the isotopic acids as they were obtained here are not really significant. However stretching a little the significance of the numbers given in table 10.6.4 one can see that the ΔΔ values have the expected sign. Thus for example in section 14.7 we explain the more negative entropy of ionization of o-toluic acid as compared with benzoic or other toluic acids to be caused by the restricted rotation of the methyl group in the o-toluate anion due to its proximity to the tightly hydrated carboxylate group. In the case of a -CD₃ group, because of its smaller steric requirements, the restriction is smaller resulting in a more positive entropy of ionization for o-toluic-d₇ acid as compared to o-toluic acid.
Table 10.6.1 The thermodynamic functions for the ionization of α-toluic acid in water

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$Kx10^4$</th>
<th>$pK^*$</th>
<th>$\Delta G^0$ cal/mol</th>
<th>$\Delta H^0$ cal/mol</th>
<th>$\Delta S^0$ cal/(deg.mol)</th>
<th>$\Delta C_P^0$ cal/(deg.mol)</th>
<th>$\Delta C_V^0$ cal/(deg$^2$.mol)</th>
<th>Method of calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.292</td>
<td>3.8886</td>
<td>5216.0±0.8</td>
<td>-1138 ±54</td>
<td>-21.70±0.18</td>
<td>Clarke &amp; Grew equation with three coefficients.</td>
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<th>$\Delta H^0$ cal/mol</th>
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* Results obtained after fitting the observed values by Clarke & Grew equation.
Table 10.6.2 The thermodynamic functions for the ionization of o-toluic-d$_7$ Acid in water.

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<th>$\Delta H^0$ (cal/mol)</th>
<th>$\Delta S^0$ (cal/mol)</th>
<th>$\Delta G_p^0$ (degee/mol)</th>
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(K values obtained by the "Direct" method)

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<th>$\Delta H^0$ (cal/mol)</th>
<th>$\Delta S^0$ (cal/mol)</th>
<th>$\Delta G_p^0$ (degee/mol)</th>
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* Results obtained after fitting the observed values by Clarke & Grew equation.
Table 10.6.4 "ΔΔ" values for the isotopic pair of acids: (α-toluic) - (α-toluic-d7)

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Note. The results obtained from the Clarke & Glew equation with 3 coefficients were used for the compilation of this table.
Table 10.6.3 The thermodynamic functions for the ionization of o-toluic acid in water. A comparison between published data and the results obtained in the present work.

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<th>Ref.</th>
<th>K x 10^4</th>
<th>pK</th>
<th>ΔG⁰</th>
<th>ΔH⁰</th>
<th>ΔS⁰</th>
<th>ΔC⁰</th>
<th>d(ΔC⁰)/dt</th>
<th>Method of calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>2</td>
<td>-</td>
<td>5284</td>
<td>-1400</td>
<td>-22.4</td>
<td>-30.6</td>
<td>-</td>
<td>-</td>
<td>C&amp;G/2 coeff.</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>1.265</td>
<td>3.803</td>
<td>5311.4±4.3</td>
<td>-1022±117</td>
<td>-21.24±0.39</td>
<td>-</td>
<td>-</td>
<td>C&amp;G/3 coeff.</td>
</tr>
<tr>
<td>25</td>
<td>3</td>
<td>1.246</td>
<td>3.9045</td>
<td>5326.8±0.5</td>
<td>-1157±45</td>
<td>-21.75±0.15</td>
<td>-51.3±5.9</td>
<td>-</td>
<td>C&amp;G/3 coeff.</td>
</tr>
<tr>
<td>25</td>
<td>4</td>
<td>1.237</td>
<td>3.9075</td>
<td>5330.7±0.1</td>
<td>-1135±5</td>
<td>-21.69±0.02</td>
<td>-51.1±0.9</td>
<td>-</td>
<td>C&amp;G/3 coeff.</td>
</tr>
<tr>
<td>25</td>
<td>4</td>
<td>1.237</td>
<td>3.9075</td>
<td>5330.9±0.1</td>
<td>-1133±4</td>
<td>-21.68±0.01</td>
<td>-47.0±2.3</td>
<td>-0.8±0.4</td>
<td>C&amp;G/4 coeff.</td>
</tr>
<tr>
<td>35</td>
<td>1</td>
<td>1.225</td>
<td>3.917</td>
<td>5524</td>
<td>-1011</td>
<td>-21.2</td>
<td>-</td>
<td>-</td>
<td>C&amp;G/2 coeff.</td>
</tr>
<tr>
<td>35</td>
<td>3</td>
<td>1.153</td>
<td>3.9381</td>
<td>5552.8±0.4</td>
<td>-1670±20</td>
<td>-23.44±0.07</td>
<td>-51.3±5.9</td>
<td>-</td>
<td>C&amp;G/3 coeff.</td>
</tr>
<tr>
<td>35</td>
<td>4</td>
<td>1.147</td>
<td>3.9405</td>
<td>5556.1±0.1</td>
<td>-1646±5</td>
<td>-23.37±0.02</td>
<td>-51.1±0.9</td>
<td>-</td>
<td>C&amp;G/3 coeff.</td>
</tr>
<tr>
<td>35</td>
<td>4</td>
<td>1.147</td>
<td>3.9404</td>
<td>5555.9±0.1</td>
<td>-1645±5</td>
<td>-23.37±0.01</td>
<td>-55.4±2.4</td>
<td>-0.8±0.4</td>
<td>C&amp;G/4 coeff.</td>
</tr>
</tbody>
</table>

Note. C&G: Clarke and Glew formula (13.2.26)

3. Present work: K values obtained by the Fuoss-Shedlovsky method.
4. Present work: K values obtained by the "Direct" method.
11. THE DETERMINATION OF THE DISSOCIATION CONSTANT OF MESITOIC ACID AND MESITOIC-dg ACID IN AQUEOUS SOLUTION BY THE CONDUCTANCE METHOD AT TEMPERATURES BETWEEN 20 AND 40ºC.

11.1 Introduction.

The dissociation constant of mesitoic acid has been determined by the conductance\(^{18}\), electrometric\(^{153}\) and spectrophotometric\(^{130}\) methods. The published values are given in table 11.5.1.

The dissociation constant of mesitoic-dg acid has not been measured before and in fact this acid has not been prepared before.

11.2 Materials

Mesitoic acid. It was bought from K & K Laboratories, Inc. (Cat. No. 4188).

The acid was purified in a Fisher "Zone Refiner". The acid was placed in a Pyrex tube of \(\frac{1}{4}\)"o.d. and approximately 10 inches long, closed at one end. The compound, in a powder form, was melted by heating the outside part of the Pyrex tube with a microburner. The intention as to obtain a very compact packing of compound in the tube. Then the tube was sealed and placed in the Zone Refiner. It was kept there for 3 days. Up-down passes were used. A pass took approximately 1 hour. The acid was identified by its IR and NMR Spectra and the melting point (see next).

Mesitoic-dg acid. It was prepared from mesitylene-dg by the procedure recommended by Varvoglis and Alexandrou\(^{154}\) which is illustrated by the series of reactions shown below.

\[
\begin{align*}
\text{ClCOCOCI} + 2\text{AlCl}_3 & \rightleftharpoons \text{AlCl}_4^{+} + \text{AlCl}_4^{-} \\
\text{HCl} + \text{R} - \text{C-CO.AICl}_4 & \text{C-O} \quad \text{R} - \text{C} - \text{AICl}_4 \\
& \text{H}_2\text{O}
\end{align*}
\]
Approximately 8 cm$^3$ mesitylene-d$_9$ dissolved in 40 cm$^3$ of carbon disulfide were placed in a 250 ml, 3 neck flask (flask A) equipped with a dropping funnel, reflux condenser, thermometer and a mechanical stirrer; 15.2 gm. of AlCl$_3$ were weighed in a dry box, under a current of nitrogen, and then added very quickly to flask A. A mixture of 4.6 cm$^3$ of oxalyl chloride with 15 cm$^3$ of carbon disulfide was poured in the dropping funnel. Flask A was cooled to -20°C on an ice-salt bath. The oxalyl chloride-carbon disulfide mixture was added very slowly to it, never letting the temperature go over 0°C. It took approximately 21/2 hours to add the whole amount of the mixture. The reaction mixture was stirred for another 24 hours at room temperature. At the end of this period it had a very bright purple colour. Then the stirring was stopped and the contents of flask A were poured into a beaker containing 200 gm of ice and 25 cm$^3$ of concentrated HCl. In this way the organic acid was precipitated and then separated by filtration. The acid was redissolved in NaOH solution, precipitated again with HCl, filtered, washed and, finally purified by vacuum sublimation (3 times). Five grams of pure acid were obtained. The deuterated acid was identified by its NMR spectrum and its melting point.

The melting points of mesitoic and mesitoic-d$_9$ acids were measured with a Mettler-FP1 capillary melting point apparatus equipped with a recorder. The rate of temperature increase was 0.2°C/min. The melting points of the two acids were:

a. Mesitoic acid: (153.5 - 154.1) ± 0.1°C.

Literature values: 156.6-157.1°C$^{18}$, 155.5°C$^{162}$

b. Mesitoic-d$_9$ acid: (151.0 - 152.2) ± 0.1°C

Preparation of mesitylene-d$_9$. Mesitylene-d$_9$ was prepared from mesitylene by exchange with D$_2$O over prerduced (with D$_2$) platinum
catalyst. The procedure was exactly the same as in the case of the exchange of benzoic acid with D₂O. The starting material was identified by its IR and NMR spectra.

In a typical run PtO₂ was reduced by bubbling deuterium gas through a suspension of platinum oxide in D₂O. When the reduction was completed (the colour of the suspension changes from brown to black) the suspension was added to a heavy-wall Pyrex tube containing the mesitylene. More D₂O was added to complete the required amount. The tube was sealed off, taken out of the liquid nitrogen, defrosted slowly in air and placed in a shaker which could be heated. The quantities used, temperatures and times of reaction are shown in table 11.2.1. The exchange was followed by NMR. We used either an internal standard or an external standard to measure the extent of the exchange. The internal standard was a known amount of chloroform which was added to a known amount of mesitylene. In the case of the external standard we used a coaxial tube in which the small central tube contained CHCl₃+TMS. This tube was calibrated against pure mesitylene. The same tube was used to take all the NMR spectra. The results are shown in the last column of table 11.2.1 (no. 3). It can be seen that in the case of series no. 3 the results are not very consistent with the probable exception of those for the last two runs. We think that this is due not to any special chemical reaction but rather to more and uninteresting phenomena of instrument trouble.

In series No. 1 and 2, the exchange of the hydrogen for deuterium atoms proceeded with much more ease. Factors which probably contributed to this were the higher relative amount of PtO₂ and D₂O used and the quality or the PtO₂ used which was from a different source for these two series of exchanges than the PtO₂ in series no. 3.
Table 11.2.1. The exchange of mesitylene with D$_2$O on platinum catalyst.

<table>
<thead>
<tr>
<th>No.</th>
<th>Exchange</th>
<th>Mesitylene</th>
<th>PtO$_2$</th>
<th>D$_2$O</th>
<th>Temp.</th>
<th>Time</th>
<th>% exchange</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>cm$^3$</td>
<td>gm</td>
<td>cm$^3$</td>
<td>°C</td>
<td>hrs.</td>
<td>Aromatic</td>
<td>Aliphatic</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>5.7</td>
<td>0.7756</td>
<td>25</td>
<td>135</td>
<td>49</td>
<td>50</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>0.3147</td>
<td>10</td>
<td>175</td>
<td>234</td>
<td>86</td>
<td>91</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>20</td>
<td>1.3465</td>
<td>120*</td>
<td>135</td>
<td>323</td>
<td>80</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18</td>
<td>1.0765</td>
<td>100</td>
<td>135</td>
<td>588</td>
<td>94</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>50</td>
<td>0.5099</td>
<td>50*</td>
<td>170</td>
<td>142</td>
<td>52</td>
<td>45</td>
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<td></td>
<td></td>
<td>2</td>
<td>0.9595</td>
<td>80*</td>
<td>130</td>
<td>131</td>
<td>40!</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>0.7149</td>
<td>60*</td>
<td>130</td>
<td>134</td>
<td>44</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>0.3677</td>
<td>20</td>
<td>135</td>
<td>184</td>
<td>53</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>0.2905</td>
<td>20</td>
<td>135</td>
<td>313</td>
<td>50!</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>0.1382</td>
<td>20</td>
<td>135</td>
<td>292</td>
<td>75</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7</td>
<td>0.2290</td>
<td>18</td>
<td>130</td>
<td>136</td>
<td>72!</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>0.1710</td>
<td>20</td>
<td>130</td>
<td>309</td>
<td>75</td>
<td>94</td>
</tr>
</tbody>
</table>

Note: * 97% D$_2$O.
It was shown by Rader and Smith\textsuperscript{155} that the rate of reduction of aromatic hydrocarbons with hydrogen on a platinum catalyst is directly proportional to the amount of catalyst used.

Garnett and Solich\textsuperscript{156} have shown how important a role the quality of the catalyst plays in D\textsubscript{2}O/Pt exchanges.

We must mention, however, that at the time our only interest was to obtain deuterated mesitylene on the side chains and that is why we did not follow the problems of hydrogen-deuterium exchange in more detail. A number of papers deal with this subject in detail.\textsuperscript{157, 158}

The mesitylene (10\text{cm}^3), almost completely deuterated on the side chains (94\% deuteration) and only partly deuterated at the ring positions (75\% deuteration), was treated with concentrated HCl\textsuperscript{159}(500 cm\textsuperscript{3}) in a 1-neck round bottom flask provided with a stopper and a magnetic stirrer. The mixture was stirred at room temperature for 88 hours. At the end of this period the contents of the flask were extracted four times with carbon disulfide (20, 10, 10 and 5 cm\textsuperscript{3} portions). The CS\textsubscript{2} extracts were combined, washed with water and dried over CaCl\textsubscript{2} for 24 hours. This solution of mesitylene-d\textsubscript{9} in CS\textsubscript{2} was used for the preparation of mesitoic-d\textsubscript{9} acid described previously. The NMR spectrum of a sample of this solution showed that the ring deuterium atoms were exchanged for hydrogen atoms while the side chains remained unchanged.

The deuterium-hydrogen coupling constant. The NMR spectrum of mesitylene-d\textsubscript{11} (94\% D in the ring and 97\% D in the side chains) shows a very nice quintet (1:3:5:3:1) due to the -CHD\textsubscript{2} group from which the coupling constant $J_{H_\text{a}D_\alpha}$ can be measured. The value obtained is 2.1 cps.
Tiers observed a coupling constant of 2.38 cps in the -CHD₂ group of toluene. MacDonald, Shannon and Sternhell obtained 2.23 cps for the -CHD₂ group of toluene and 2.22 cps from the NMR spectra of the same group in partly deuterated xylenes.

The shift upfield of the proton resonance of group -CHD₂ in partly deuterated mesitylene is 0.05 ppm as compared to the resonance of the protons of the methyl groups of mesitylene. MacDonald, Shannon and Sternhell observed a shift upfield of approximately 0.03 ppm for the proton resonance of the -CHD₂ group in partly deuterated toluene and xylenes as compared to the proton resonance of the -CH₃ group in toluene and xylenes.

11.3 The conductance measurements.

The procedure followed for the preparation of the solutions and for taking the conductance measurements was exactly the same as that described in the case of potassium chloride and sodium benzoate (see subsections 5.10 and 7.3).

The experimental results and the calculations leading to the values of the conductance (Λ) and the concentration (c) at each of the five temperatures considered in the present thesis are given in "Detailed calculations - 11.3.1 to 11.3.4".

11.4 The limiting conductance of mesitoic acid.

The only published value for the limiting conductance of a salt of mesitoic acid belongs to Dippy, Hughes and Laxton:

\[ \Lambda^0_{Na \text{ salt of mesitoic acid}} = 77.3 \]
Using the values of $\Lambda_0^+_{H^+}$ and $\Lambda_0^+_{Na^+}$ accepted in the present work of 350.15 and 50.15 respectively, we obtain:

$$\Lambda_0^{mesitoic\ acid\ (25^\circ C)} = 377.3$$

Due to the fact that the above mentioned authors used slightly different values for the limiting conductance of hydrogen and sodium ions, the value for the limiting conductance of the acid in the original paper is 376.9.

At the other four temperatures considered in the present thesis, the limiting conductance values were obtained by the so-called "correction factor" method described in subsection 8.4. A series of values [observed values] for the limiting conductance of the two acids, mesitoic and mesitoic-dg acids, at temperatures between 20 and 40°C were obtained by the extrapolation methods of Ives and Fuoss-Shedlovsky (see subsections 6.4, 6.6, and 6.7.) These values were smoothed by fitting them by the method of least squares in the equation:

$$\Lambda_0^+ = A + BT \quad (8.4.2)$$

The observed and the calculated values are given in table 11.4.1, and "Detailed calculations 11.4.1 and 11.4.2."

Then taking the value of the limiting conductance of mesitoic acid at 25°C obtained from the salt conductance as reference point, we corrected the calculated values obtained from (8.4.2) according to the equation:

$$\Lambda_0^+ (corrected) = \Lambda_0^+ (calculated) + F$$

where $F$ is given by:

$$F = \Lambda_0^+ (25^\circ C, \text{reference}) - \Lambda_0^+ (25^\circ C, \text{calculated})$$

The corrected values for the limiting conductance of the two acids at each one of the five working temperatures are given in table 11.4.2 and "Detailed calculations - 11.4.1 and 11.4.2."
It can be seen from table 11.4.2 that the agreement between the corrected $\Lambda^o$'s for the two acids is not as good as for other pairs of isotopic acids considered in the present thesis (see for example subsections 8.4, 9.4, etc.). It is very difficult to say what is causing this disagreement. It is possible that some kind of error in the experimental data affects the $\Lambda^o$ values obtained by extrapolation methods in a different way for each one of the two acids considered here. In fact we calculated the limiting conductance values which are going to be used in the calculation of the dissociation constants according to this hypothesis: we took the average of the four limiting conductance values, at each of the five temperatures, to be the correct value. These averages are given in the last column of table 11.4.2. However there always remains the interesting possibility that we are dealing here with a case in which the limiting conductances of the two isotopic acids are different: it is a possibility which would be worth investigating by determining the limiting conductances of the sodium salt, say, of the two isotopic acids.

11.5 The calculation of the dissociation constants of mesitoic acid and of mesitoic-d$_9$ acid.

The same three methods of calculation employed throughout this thesis were used to calculate the dissociation constants of mesitoic and mesitoic-d$_9$ acids. The methods are:

a. Ives method
b. Fuoss-Shedlovsky method
c. "Direct" (Dippy) method

The first two methods were used without iteration. The limiting conductance values listed in the last column of table 11.4.2 were used instead.
Table 11.4.1. The observed and the calculated values (by 8.4.2) of the limiting conductance of mesitoic acid and mesitoic-d$_9$ acid.

<table>
<thead>
<tr>
<th>Temp. $^\circ$C</th>
<th>Limiting conductances</th>
<th></th>
<th>Limiting conductances</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mesitoic acid</td>
<td>Mesitoic-d$_9$ acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Observed*</td>
<td>Calculated</td>
<td>Observed*</td>
<td>Calculated</td>
</tr>
<tr>
<td>A = -1229.55</td>
<td></td>
<td></td>
<td>A = -1198.76</td>
<td></td>
</tr>
<tr>
<td>B = 5.3982</td>
<td></td>
<td></td>
<td>B = 4.8634</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>352.35</td>
<td>352.93</td>
<td>326.70</td>
<td>326.93</td>
</tr>
<tr>
<td>25</td>
<td>380.09</td>
<td>379.92</td>
<td>351.38</td>
<td>351.26</td>
</tr>
<tr>
<td>30</td>
<td>407.58</td>
<td>406.91</td>
<td>375.82</td>
<td>375.57</td>
</tr>
<tr>
<td>35</td>
<td>434.38</td>
<td>433.90</td>
<td>399.97</td>
<td>399.89</td>
</tr>
<tr>
<td>40</td>
<td>460.16</td>
<td>460.89</td>
<td>423.99</td>
<td>424.21</td>
</tr>
</tbody>
</table>

Note. * The $\Lambda^0$'s obtained by the Fuoss-Shedlovsky method are listed here. The calculations involving the $\Lambda^0$'s obtained by the Ives extrapolation method are given in "Detailed calculations - 11.4.1 and 11.4.2". The results are similar to those given in table 11.4.1.
**Table 11.4.2.** The corrected values of the limiting conductance obtained by extrapolation methods.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Corrected values of the limiting conductance.</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mesitoic acid</td>
<td>Mesitoic-d$_g$ acid</td>
</tr>
<tr>
<td></td>
<td>Ives method</td>
<td>Fuoss-Shedlovsky method</td>
</tr>
<tr>
<td>20</td>
<td>350.31</td>
<td>350.31</td>
</tr>
<tr>
<td>25</td>
<td>377.30</td>
<td>377.30</td>
</tr>
<tr>
<td>30</td>
<td>404.29</td>
<td>404.29</td>
</tr>
<tr>
<td>35</td>
<td>431.28</td>
<td>431.28</td>
</tr>
<tr>
<td>40</td>
<td>458.26</td>
<td>458.27</td>
</tr>
</tbody>
</table>

Note. * The average values listed in the last column of this table were used in the calculation of the dissociation constants of the two isotopic acids.
We recalculate the dissociation constant of mesitoic acid from the only set of conductance data published so far, using the three methods mentioned above and the $\Lambda^0$ of table 11.4.2. A complete comparison of the published data and the results obtained in the present work is given in table 11.5.1.

The complete results are given in table 11.5.2 and "Detailed calculations - 11.5.1 and 11.5.4". Again, for comparison only, table 11.5.2 contains the results obtained by Wilson, Gore, Sawbridge and Cardenas-Cruz$^{130}$ for the dissociation constant of mesitoic acid. They constitute the only other set of results covering a range of temperatures.

11.6 Calculation of the thermodynamic functions for the ionization of mesitoic and mesitoic-d$_9$ acids in water.

The thermodynamic functions for the ionization of mesitoic and mesitoic-d$_9$ acids were calculated by using the Clarke & Glew expression and the Harned & Robinson formula (see section 13). The complete results are given in "Detailed calculations - 11.6.1 and 11.6.2". A summary of the results is given in tables 11.6.1 and 11.6.2.

Table 11.6.3 presents a comparison between the published data and the results obtained here. The agreement for the $\Delta S^0$ and $\Delta H^0$ values is poor. No $\Delta C_p^0$ values were found in the literature. Again as in the case of the other acids (see for example subsection 8.6), the the Clarke & Glew equation with three adjustable parameters fitted the experimental data very well. Because of this we do not attach any significance to the quantity $d(\Delta C_p^0)/dT$ obtained from Clarke & Glew expression with four adjustable parameters. Furthermore this quantity was relatively small and had a high degree of uncertainty in it.

Not much can be said about the $\Delta A$ quantities given in table 11.6.4. They are small and probably reflect small changes in solventsolute interactions in going from one species to the other. Although
no calculations of the type carried out for benzoic acid (section 18) or \( \sigma \)-toluic acid (section 19) system were carried out in the mesitoic acid system, undoubtedly the same type of arguments as those used in the two former systems would explain the \( \Delta \Delta G \) values in the later system. The \( \Delta \Delta C_{p}^{\sigma} \) value would have the right sign if the arguments we used to explain the \( \Delta C_{p}^{\sigma} \) difference between the \( \sigma \)-toluic and \( \sigma \)-toluic-d\(_7\) acids (subsection 10.6) or between mesitoic, benzoic and toluic acids (subsection 14.7) were applied here.

The thermodynamic functions of ionization of mesitoic acid are discussed and compared with those of benzoic and toluic acids in subsection 14.7.
Table 11.5.1. The dissociation constant of mesitoic acid at 25°C. A comparison between the published values and the values calculated here.

<table>
<thead>
<tr>
<th>Method</th>
<th>Ref.</th>
<th>Published</th>
<th>Calculated here: $K 	imes 10^4$ ($\Lambda^0 = 377.3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\Lambda^0$</td>
<td>$K \times 10^4$</td>
</tr>
<tr>
<td>Conductance</td>
<td>1</td>
<td>376.9</td>
<td>3.66</td>
</tr>
<tr>
<td>Conductance</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Electrometric</td>
<td>3</td>
<td>-</td>
<td>2.851</td>
</tr>
<tr>
<td>Spectrophotometric</td>
<td>4</td>
<td>-</td>
<td>3.581</td>
</tr>
</tbody>
</table>

References:
2. Present work.
Table 11.5.2. The dissociation constants of mesitoic acid and mesitoic-dg acid and the isotope effect $K_H/K_D$ at temperatures between 20 and 40°C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature (°C)</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K \times 10^4$</td>
<td>$K_H/K_D$</td>
<td>$K \times 10^4$</td>
<td>$K_H/K_D$</td>
<td>$K \times 10^4$</td>
<td>$K_H/K_D$</td>
</tr>
<tr>
<td>Mesitoic acid</td>
<td>4.037</td>
<td>-</td>
<td>3.581</td>
<td>-</td>
<td>3.258</td>
<td>-</td>
</tr>
<tr>
<td>Spectrophotometric</td>
<td>Ref. 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuoss-Shedlovsky method</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesitoic acid</td>
<td>3.802±0.007</td>
<td>-</td>
<td>3.551±0.006</td>
<td>-</td>
<td>3.301±0.006</td>
<td>-</td>
</tr>
<tr>
<td>(Ref. 2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesitoic-dg acid</td>
<td>3.781±0.006</td>
<td>1.006</td>
<td>3.531±0.004</td>
<td>1.006</td>
<td>3.282±0.004</td>
<td>1.006</td>
</tr>
<tr>
<td>(Ref. 2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


2. Present work.
Table 11.6.1. The thermodynamic functions for the ionization of mesitoic acid mesitoic-d₉ acids. Results obtained from Clarke and Glew formula with 3 coefficients.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Kx10⁴ *</th>
<th>pK*</th>
<th>ΔG° cal/mol</th>
<th>ΔH° cal/mol</th>
<th>ΔS° cal/(deg.mol)</th>
<th>ΔC_p° cal/deg.mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3.802</td>
<td>3.4200</td>
<td>4587.4±0.1</td>
<td>-2252.3±2.7</td>
<td>-23.33±0.01</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>3.551</td>
<td>3.4497</td>
<td>4706.2±0.1</td>
<td>-2499.5±1.5</td>
<td>-24.17±0.01</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>3.301</td>
<td>3.4814</td>
<td>4829.1±0.1</td>
<td>-2746.6±0.8</td>
<td>-24.99±0.01</td>
<td>-49.4±0.3</td>
</tr>
<tr>
<td>35</td>
<td>3.055</td>
<td>3.5149</td>
<td>4956.1±0.1</td>
<td>-2993.8±1.6</td>
<td>-25.80±0.01</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>2.817</td>
<td>3.5502</td>
<td>5087.0±0.1</td>
<td>-3241.0±2.8</td>
<td>-26.60±0.01</td>
<td></td>
</tr>
</tbody>
</table>

* Results obtained after fitting the observed values in Clarke & Glew equations.
Table 11.6.2. The thermodynamic functions for the ionization of mesitoic and mesitoic-dg acids. Results obtained from Clarke & Glew formula with 4 coefficients.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Kx10 *</th>
<th>pK*</th>
<th>ΔG° cal/mol</th>
<th>ΔH° cal/mol</th>
<th>ΔS° cal/(deg.mol)</th>
<th>ΔC° P cal/(deg.mol)</th>
<th>d(ΔC° P)/dT cal/(deg².mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3.802</td>
<td>3.4200</td>
<td>4587.4±0.1</td>
<td>-2242 ±4</td>
<td>-23.30±0.01</td>
<td>-52.3±1.0</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>3.551</td>
<td>3.4496</td>
<td>4706.1±0.1</td>
<td>-2500.1±1.0</td>
<td>-24.17±0.01</td>
<td>-50.8±0.5</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>3.301</td>
<td>3.4814</td>
<td>4829.1±0.1</td>
<td>-2750.7±1.6</td>
<td>-25.00±0.01</td>
<td>-49.4±0.2</td>
<td>0.3±0.1</td>
</tr>
<tr>
<td>35</td>
<td>3.055</td>
<td>3.5150</td>
<td>4956.1±0.1</td>
<td>-2994.1±1.1</td>
<td>-25.80±0.01</td>
<td>-48.0±0.6</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>2.817</td>
<td>3.5502</td>
<td>5087.0±0.1</td>
<td>-3230 ±4</td>
<td>-26.56±0.01</td>
<td>-46.5±1.1</td>
<td></td>
</tr>
</tbody>
</table>

Mesitoic acid

Mesitoic-dg acid

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Kx10 *</th>
<th>pK*</th>
<th>ΔG° cal/mol</th>
<th>ΔH° cal/mol</th>
<th>ΔS° cal/(deg.mol)</th>
<th>ΔC° P cal/(deg.mol)</th>
<th>d(ΔC° P)/dT cal/(deg².mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3.781</td>
<td>3.4224</td>
<td>4590.7±0.1</td>
<td>-2253 ±5</td>
<td>-23.35±0.02</td>
<td>-47.9±1.2</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>3.531</td>
<td>3.4521</td>
<td>4709.5±0.1</td>
<td>-2500.5±1.2</td>
<td>-24.18±0.01</td>
<td>-51.1±0.6</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>3.282</td>
<td>3.4839</td>
<td>4832.6±0.1</td>
<td>-2763.9±1.8</td>
<td>-25.06±0.01</td>
<td>-54.3±0.2</td>
<td>-0.6±0.1</td>
</tr>
<tr>
<td>35</td>
<td>3.035</td>
<td>3.5178</td>
<td>4960.1±0.1</td>
<td>-3043.2±1.2</td>
<td>-25.97±0.01</td>
<td>-57.4±0.6</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>2.793</td>
<td>3.5539</td>
<td>5092.3±0.1</td>
<td>-3338 ±5</td>
<td>-26.92±0.02</td>
<td>-60.6±1.2</td>
<td></td>
</tr>
</tbody>
</table>

* Results obtained after fitting the observed values into Clarke & Glew equations.
Table 11.6.3. The thermodynamic functions for the ionization of mesitoic acid in water. A comparison between published data and the results obtained in the present work.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Ref.</th>
<th>Kx10^4</th>
<th>pK</th>
<th>ΔG^0 (cal/mol)</th>
<th>ΔH^0 (cal/mol)</th>
<th>ΔS^0 / (cal/(deg.mol))</th>
<th>ΔC_p^0 / (cal/(deg.mol))</th>
<th>d(ΔC_p^0)/dT / (cal/(deg^2.mol))</th>
<th>Method of calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1</td>
<td>3.581</td>
<td>3.448</td>
<td>4705.4±2.8</td>
<td>-4364±77</td>
<td>-30.41±0.26</td>
<td>-</td>
<td>-</td>
<td>C&amp;G/2 coeff</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>3.551</td>
<td>3.4497</td>
<td>4706.2±0.1</td>
<td>-2499.5±1.5</td>
<td>-24.17±0.01</td>
<td>-49.4±0.3</td>
<td>-</td>
<td>C&amp;G/3 coeff</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>3.551</td>
<td>3.4496</td>
<td>4706.1±0.1</td>
<td>-2500.1±1.0</td>
<td>-24.17±0.01</td>
<td>-50.8±0.5</td>
<td>0.3±0.1</td>
<td>C&amp;G/4 coeff</td>
</tr>
<tr>
<td>35</td>
<td>1</td>
<td>2.891</td>
<td>3.541</td>
<td>4994</td>
<td>-3428</td>
<td>-27.3</td>
<td>-</td>
<td>-</td>
<td>C&amp;G/2 coeff</td>
</tr>
<tr>
<td>35</td>
<td>2</td>
<td>3.055</td>
<td>3.5149</td>
<td>4956.1±0.1</td>
<td>-2993.8±1.6</td>
<td>-25.80±0.01</td>
<td>-49.4±0.3</td>
<td>-</td>
<td>C&amp;G/3 coeff</td>
</tr>
<tr>
<td>35</td>
<td>2</td>
<td>3.055</td>
<td>3.5150</td>
<td>4956.1±0.1</td>
<td>-2994.1±1.1</td>
<td>-25.80±0.01</td>
<td>-48.0±0.6</td>
<td>0.3±0.1</td>
<td>C&amp;G/4 coeff</td>
</tr>
</tbody>
</table>

Note: C&G: Clarke and Glew formula (13.2.26).

2. Present work.
Table 11.6.4. ΔΔ values for the isotopic pair of acids: (mesitoic acid) - (mesitoic-d_9 acid).

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>ΔΔG^0 cal/mol</th>
<th>ΔΔH^0 cal/mol</th>
<th>ΔΔS^0 cal/(deg.mol)</th>
<th>ΔΔC^0 cal/(deg.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>-3.3±0.2</td>
<td>-21 ±8</td>
<td>-0.06±0.02</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>-3.2±0.2</td>
<td>2.5±4.5</td>
<td>0.02±0.02</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>-3.5±0.2</td>
<td>26.3±2.4</td>
<td>0.10±0.02</td>
<td>4.8±0.8</td>
</tr>
<tr>
<td>35</td>
<td>-4.1±0.2</td>
<td>50. ±5</td>
<td>0.17±0.02</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>-5.3±0.2</td>
<td>74 ±9</td>
<td>0.25±0.02</td>
<td></td>
</tr>
</tbody>
</table>

Note. The results obtained from Clarke & Glew formula (13.2.26) with 3 coefficients were used in the compilation of this table.
THE DETERMINATION OF THE DISSOCIATION CONSTANTS OF \textit{m}-TOLUIC AND \textit{p}-TOLUIC ACIDS AT TEMPERATURES BETWEEN 20 AND 40\textdegree C BY CONDUCTANCE METHOD.

12.1 Introduction

The dissociation constants of \textit{p}-toluic acid and \textit{m}-toluic acid have been determined conductometrically,\textsuperscript{163} electrometrically,\textsuperscript{153} and spectrophotometrically.\textsuperscript{130}

The published values are summarized in table 12.5.1

The only determinations covering a range of temperatures are those of Wilson, Gore, Sawbridge and Cardenas-Cruz.\textsuperscript{130} Their results for the interval of 20 to 40\textdegree C are given in table 12.5.2.

12.2. Materials

\textit{m}-Toluic acid. It was obtained from Eastman (Eastman Organic Chemicals Cat. No. 2288).

The acid was purified in a Fisher Zone Refiner. The compound was placed in a tube $\frac{1}{4}$" i.d. and approximately 20 inches long. After filling it with the acid the tube was sealed. The compound was kept in the Zone Refiner for one week. Up-down passes were used. One pass took approximately two hours. The compound from the middle part of the tube was used for the conductivity measurements.

\textit{p}-Toluic acid. It was bought from Eastman (Eastman Organic Chemicals Cat. No. 1459).

It was purified in exactly the same way as the \textit{m}-toluic acid.

Note.

\textit{Pt/D}_2\text{O} exchanges with \textit{m}-toluic and \textit{p}-toluic acid. We tried to prepare deuterated \textit{m}-toluic acid and deuterated \textit{p}-toluic acid by \textit{Pt/D}_2\text{O} exchange. Our attempts were only partly successful. The procedure we followed was described in the case of the exchange of benzoic acid (see subsection 8.2). The quantities and the conditions of the
reactions are summarized in table 12.2.1.

In the case of \textit{m-}toluic acid, the protons of the methyl group and hydrogens 4 and 5 of the ring exchanged fairly rapidly and almost completely. The difficult part was the exchange of the remaining aromatic protons, \textit{i.e.}, hydrogens 2 and 6. Since in the case of the exchange of \textit{o-}toluic acid (subsection 10.2), we had no special problems with the hydrogen next to the carboxyl group it is very likely that in the present case the hydrogen 2 was the difficult one to exchange. This hydrogen sits between the carboxyl and the methyl group and therefore is sterically hindered. It was reported that a very strong steric effect was detected in the platinum-catalyzed exchange of heavy water with several monosubstituted benzenes. 158

Treatment of the deuterated \textit{m-}toluic acid (190 mg) in 2cm$^3$CCl$_4$ with concentrated HCl (10 cm$^3$) with continuous stirring at room temperature for 48 hours, left the organic acid unchanged. Undoubtedly this is due to the deactivating effect of the carboxyl group in an electrophilic substitution. 164

Attempts to exchange the hydrogen atoms of \textit{o-}toluic acid for deuterium atoms were equally unsuccessful. The situation in this case was complicated by the low solubility of \textit{o-}toluic acid in the usual NMR solvents (CCl$_4$, CDCl$_3$, etc.) and by the very broad acid peak. It must be recalled that the acid peak was used as an internal standard for measuring the extent of deuteration. The fact that the acid peak was very broad and in many cases did not appear at all (though the sample was carefully washed, dried and sublimed under vacuum 2 times) made of it a very unreliable standard. Because of the low isotope purity of the deuterated \textit{m} and \textit{o-}toluic acids we did not measure their dissociation constants.
As a note of interest we want to mention that while the acid itself or the sodium salt underwent exchange to a certain extent, when we used the potassium salt of the acid the exchange was zero.

Recently Atkinson, Csakvary, Herbert and Stuart \textsuperscript{148} reported the exchange of the methyl hydrogens with D\textsubscript{2}O in basic media in a series of carboxylic acids including the three toluic acids.

The acids were identified by their IR and NMR spectra and by their melting points. The melting points were measured with a Mettler-FP1 capillary melting point instrument equipped with a recorder. The rate of temperature increased was 0.2\textdegree C/min. The results obtained were as follows:

a. \textit{m}-Toluic acid: (111.5-111.9) \pm 0.1\textdegree C
(Literature values: 110-111\textdegree C, \textsuperscript{151} 111-113\textdegree C, 165 112.5\textdegree C. \textsuperscript{152}, \textsuperscript{163})

b. \textit{m}-Toluic-\textit{d7} acid: (110.5-111.0) \pm 0.1\textdegree C

c. \textit{p}-Toluic acid: (179 - 180.1) \pm 0.1\textdegree C
(Literature values: 179 -180\textdegree C, \textsuperscript{153}, \textsuperscript{165} 179.5\textdegree C, \textsuperscript{152})

d. \textit{p}-Toluic-\textit{d7} acid: (178.5-179.5) \pm 0.1\textdegree C

12.3 \textbf{Conductance measurements}

The procedure followed for preparing the solutions of the two acids and for taking the conductivity measurements was exactly the same as the one used for the potassium chloride and sodium benzoate solutions. The only new factor here was the fact that we used cell no.4 for taking the conductivity measurements for \textit{m}-toluic acid. We had no special reason for doing this except the desire to see how this cell behaves in such measurements. We found no difference between this cell and cell no. 3 which was used more often.

\textit{p}-Toluic acid is noteworthy for its low solubility even in some organic solvents. The solutions of this acid required longer times in the automatic shaker in order to get the solid into solution. The
The infrared spectrum of 2-toluic acid.

CHCl3 solution
Method: ATR
Wavenumber: 4000 - 400 cm⁻¹
Cell: 0.1 mm HgCl2
Reference: CHCl3 in 0.1 mm HgCl2
higher errors in the final results for this acid, i.e., in K's, reflects the difficulty encountered in dissolving it.

12.4 The limiting conductances of m-toluic and p-toluic acids.

The only published determinations of the limiting conductance of a salt of m-toluic and p-toluic acids are those of Dippy and Lewis. They determined the limiting conductance of the sodium salts of these two acids at 25°C by conductance method.

The limiting conductance of the sodium salt of m-toluic acid obtained by them was:

\[ \Lambda^0_{Na \text{ salt of } m-\text{toluic acid}} (25^\circ C) = 79.3; 80.1 \text{ (average: 79.7)} \]

The limiting conductance of the sodium salt of p-toluic acid obtained was:

\[ \Lambda^0_{Na \text{ salt of } p-\text{toluic acid}} (25^\circ C) = 80.0; 80.2 \text{ (average: 80.1)} \]

These values were combined with the limiting conductance values of sodium and hydrogen ions, at 25°C, in order to obtain the limiting conductances for the acids. Using:

\[ \Lambda^0_{H^+} = 350.15 \]
\[ \Lambda^0_{Na} = 50.15 \]

we obtained for the acids:

\[ \Lambda^0_{m-\text{toluic acid}} = 379.7 \]
\[ \Lambda^0_{p-\text{toluic acid}} = 380.1 \]

For the other four temperatures (20, 30, 35 and 40°C) the \( \Lambda^0 \) values were determined by the "correction factor" method described in subsection 8.4.
The limiting conductance values at 25°C given above were used as reference points.

The "observed" values of $\Lambda^0$ for the two acids (obtained from the Ives and Fuoss-Shedlovsky extrapolation methods) and the calculated values (by 8.4.2) are given in table 12.4.1 and "Detailed calculations - 12.4.1 and 12.4.2". The corrected values are given in the same "Detailed calculations" and in table 12.4.2.

The average values of the corrected limiting conductance were used in the calculation of the dissociation constants of $m$-toluic and $p$-toluic acids.

12.5 The calculation of the dissociation constant of $m$-toluic and $p$-toluic acids.

The dissociation constants of $m$-toluic and $p$-toluic acids were calculated by the same three methods employed throughout this work:-

a. Ives method
b. Fuoss-Shedlovsky method
c. Direct (Dippy's) method

The $\Lambda^0$'s from table 12.4.2 were used in the calculation of $K$'s. The 'Detailed calculations" are given in 12.5.1 to 12.5.4. A summary of these results is presented in tables 12.5.1 and 12.5.2.

Among the three sets of results obtained, one for each method of calculation, we prefer those obtained by the Fuoss-Shedlovsky method for the same reasons as those presented in the case of benzoic acid (see subsection 8.4)

In table 12.5.2, the only other set of dissociation constants covering a range of temperatures published so far is given for comparison with our results. The agreement between the two sets of values is poor. It is also interesting to note that while in our case the dissociation constants of $m$-toluic and $p$-toluic acids present a maximum somewhere in
the neighbourhood of 25°C and 35°C, respectively, the values of Wilson et al. do not show any maximum but rather increase continuously in the interval 15-40°C.

12.6 Calculation of the thermodynamic functions for the ionization of \( m- \) and \( p- \) toluic acids in water.

The thermodynamic functions for the ionization of \( m- \) and \( p- \) toluic acids in water were obtained by employing the Clarke & Glew and Harned & Robinson formulas (see section 13). The results obtained with the Clarke & Glew formula are preferred for the same reasons that were given in subsections 8.6 and 13.3. The complete results are given in "Detailed calculation - 12.6.1 and 12.6.2". A summary is presented in tables 12.6.1 and 12.6.2. Tables 12.6.3 and 12.6.4 contain a summary of the thermodynamic functions for the ionization of \( m- \) and \( p- \) toluic acids, respectively, obtained here and those found in the literature. As in the case of the other acids studied in the present work such data are very rare and the agreement between difficult sets of values ranges from fair to poor. The thermodynamic functions of ionization of these two acids are discussed in subsection 14.7 where they are compared to the thermodynamic functions of ionization of benzoic, \( o- \) toluic and mesitoic acids.
Table 12.2.1. Pt/D₂O exchange of m-toluic acid.

<table>
<thead>
<tr>
<th>Exchange #</th>
<th>Acid</th>
<th>Na salt</th>
<th>PtO₂</th>
<th>D₂O</th>
<th>Temp.</th>
<th>Time of reaction</th>
<th>% exchange Methyl</th>
<th>% exchange Aromatic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.5</td>
<td>3.2</td>
<td>140</td>
<td>30*</td>
<td>165</td>
<td>154</td>
<td>81</td>
<td>65</td>
</tr>
<tr>
<td>2</td>
<td>7.4</td>
<td>3.3</td>
<td>117</td>
<td>20*</td>
<td>165</td>
<td>264</td>
<td>90</td>
<td>73</td>
</tr>
<tr>
<td>3</td>
<td>8.4</td>
<td>0.8</td>
<td>87</td>
<td>18</td>
<td>165</td>
<td>160</td>
<td>93</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>6.8</td>
<td>1.6</td>
<td>60</td>
<td>14</td>
<td>165</td>
<td>398</td>
<td>?</td>
<td>77</td>
</tr>
<tr>
<td>5</td>
<td>6.1</td>
<td>1.0</td>
<td>94</td>
<td>15</td>
<td>165</td>
<td>240</td>
<td>?</td>
<td>77</td>
</tr>
<tr>
<td>6</td>
<td>5.7</td>
<td>1.2</td>
<td>108</td>
<td>13</td>
<td>165</td>
<td>288</td>
<td>94</td>
<td>85</td>
</tr>
<tr>
<td>7</td>
<td>3.8</td>
<td>1.9</td>
<td>96</td>
<td>13</td>
<td>165</td>
<td>139</td>
<td>96</td>
<td>90</td>
</tr>
</tbody>
</table>

Note. * 97% D₂O. For the other exchanges 99% was used.
Table 12.4.1. The "observed" (obtained by extrapolation methods) and the calculated values (by 8.4.2) of the limiting conductance of m-toluic and p-toluic acids.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Limiting conductance.</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m-Toluic acid</td>
<td>p-Toluic acid</td>
</tr>
<tr>
<td></td>
<td>Observed</td>
<td>Calculated</td>
</tr>
<tr>
<td></td>
<td>A = -1228.6</td>
<td>B = 5.3942</td>
</tr>
<tr>
<td>20</td>
<td>352.10</td>
<td>352.70</td>
</tr>
<tr>
<td>25</td>
<td>379.78</td>
<td>379.67</td>
</tr>
<tr>
<td>30</td>
<td>407.36</td>
<td>406.64</td>
</tr>
<tr>
<td>35</td>
<td>434.27</td>
<td>433.62</td>
</tr>
<tr>
<td>40</td>
<td>459.71</td>
<td>460.59</td>
</tr>
</tbody>
</table>

Note. The \( \Lambda^0 \)'s obtained by the Fuoss-Shedlovsky extrapolation method are listed in this table. The results obtained with \( \Lambda^0 \)'s from the Ives extrapolation method are given in "Detailed calculations - 12.4.1 and 12.4.2". They are similar to those listed here.
Table 12.4.2. The corrected values of the limiting conductance obtained by extrapolation methods.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Corrected values of the limiting conductance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m-Toluic acid</td>
</tr>
<tr>
<td></td>
<td>Ives method</td>
</tr>
<tr>
<td>20</td>
<td>352.61</td>
</tr>
<tr>
<td>25</td>
<td>379.70</td>
</tr>
<tr>
<td>30</td>
<td>406.80</td>
</tr>
<tr>
<td>35</td>
<td>433.89</td>
</tr>
<tr>
<td>40</td>
<td>460.99</td>
</tr>
</tbody>
</table>

Note. The average values listed in columns 4 & 7 were used in the calculation of the dissociation constant of m-toluic and p-toluic acid respectively.
Table 12.5.1 The dissociation constants of m-toluic and p-toluic acids at 25°C. A comparison between published values and the values calculated here.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>Ref.</th>
<th>Published</th>
<th>Calculated here</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\Lambda^o$</td>
<td>$K \times 10^5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\Lambda^o$</td>
<td>$K \times 10^5$</td>
</tr>
<tr>
<td>m-Toluic acid</td>
<td>Conductometric</td>
<td>1</td>
<td>379.3</td>
<td>5.35</td>
</tr>
<tr>
<td></td>
<td>Conductometric</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Spectrophotometric</td>
<td>3</td>
<td>-</td>
<td>5.321</td>
</tr>
<tr>
<td></td>
<td>Electrometric</td>
<td>4</td>
<td>-</td>
<td>5.14</td>
</tr>
<tr>
<td>p-Toluic acid</td>
<td>Conductometric</td>
<td>1</td>
<td>379.7</td>
<td>4.24</td>
</tr>
<tr>
<td></td>
<td>Conductometric</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Spectrophotometric</td>
<td>2</td>
<td>-</td>
<td>4.290</td>
</tr>
<tr>
<td></td>
<td>Electrometric</td>
<td>4</td>
<td>-</td>
<td>3.86</td>
</tr>
</tbody>
</table>

2. Present work  
<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature (°C)</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-Toluic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Electrometric - ref. 1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-Toluic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>acid-conductometric</td>
<td>(ref. 2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ives method of calc.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuoss-Shedlovsky method</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;Direct&quot; (Bippys) method</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>_ Direct_ (Bippys) method</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>_ Direct_ (Bippys) method</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 12.5.2. The dissociation constants of m-toluic and p-toluic acid at temperatures between 20 and 40°C (x10^5).

2. Present work.
Table 12.6.1. The thermodynamic functions for the ionization of m-toluic and p-toluic acids. Results obtained from Clarke and Glew formula with 3 coefficients.

<table>
<thead>
<tr>
<th>Temp. $^\circ$C</th>
<th>$K \times 10^5$</th>
<th>pK*</th>
<th>$\Delta G^\circ$ cal/mol</th>
<th>$\Delta H^\circ$ cal/mol</th>
<th>$\Delta S^\circ$ cal/(deg.mol)</th>
<th>$\Delta C^\circ$ cal/(deg.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5.518</td>
<td>4.2582</td>
<td>5711.8±0.1</td>
<td>400 ±6</td>
<td>-18.12±0.02</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>5.558</td>
<td>4.2551</td>
<td>5804.9±0.1</td>
<td>99.1±3.4</td>
<td>-19.14±0.01</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>5.551</td>
<td>4.2557</td>
<td>5903.1±0.1</td>
<td>-201.9±1.8</td>
<td>-20.14±0.01</td>
<td>-60.2±0.6</td>
</tr>
<tr>
<td>35</td>
<td>5.498</td>
<td>4.2598</td>
<td>6006.3±0.1</td>
<td>-502.9±3.6</td>
<td>-21.12±0.01</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>5.406</td>
<td>4.2672</td>
<td>6114.3±0.1</td>
<td>-804 ±6</td>
<td>-22.09±0.02</td>
<td></td>
</tr>
</tbody>
</table>

m-Toluic acid

<table>
<thead>
<tr>
<th>Temp. $^\circ$C</th>
<th>$K \times 10^5$</th>
<th>pK*</th>
<th>$\Delta G^\circ$ cal/mol</th>
<th>$\Delta H^\circ$ cal/mol</th>
<th>$\Delta S^\circ$ cal/(deg.mol)</th>
<th>$\Delta C^\circ$ cal/(deg.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.191</td>
<td>4.3777</td>
<td>5872.1±0.1</td>
<td>754.7±0.8</td>
<td>-17.46±0.01</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>4.265</td>
<td>4.3701</td>
<td>5961.8±0.1</td>
<td>462.6±0.4</td>
<td>-18.44±0.01</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>4.303</td>
<td>4.3662</td>
<td>6056.5±0.1</td>
<td>170.5±0.2</td>
<td>-19.42±0.01</td>
<td>-58.4±0.1</td>
</tr>
<tr>
<td>35</td>
<td>4.306</td>
<td>4.3659</td>
<td>6155.9±0.1</td>
<td>-121.6±0.5</td>
<td>-20.37±0.01</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>4.276</td>
<td>4.3690</td>
<td>6260.2±0.1</td>
<td>-413.6±0.8</td>
<td>-21.31±0.01</td>
<td></td>
</tr>
</tbody>
</table>

p-Toluic acid

* Results obtained after fitting the observed values in Clarke & Glew equations.
Table 12.6.2. The thermodynamic functions for the ionization of m-toluic and p-toluic acids. Results obtained from Clarke & Glew formula with 4 coefficients.

<table>
<thead>
<tr>
<th>Temp</th>
<th>Kx10^5 *</th>
<th>pK*</th>
<th>ΔG° cal/mol</th>
<th>ΔH° cal/mol</th>
<th>ΔS° cal/(deg.mol)</th>
<th>ΔC° cal/(deg.mol)</th>
<th>d(ΔC°)/dT cal/(deg^2.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5.519</td>
<td>4.2581</td>
<td>5711.7±0.1</td>
<td>376 ±6</td>
<td>-18.20±0.02</td>
<td>-53.2±1.6</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>5.557</td>
<td>4.2551</td>
<td>5805.0±0.1</td>
<td>100.7±1.6</td>
<td>-19.13±0.01</td>
<td>-56.7±0.8</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>5.551</td>
<td>4.2557</td>
<td>5903.1±0.1</td>
<td>-191.9±2.5</td>
<td>-20.11±0.01</td>
<td>-60.3±0.3</td>
<td>-0.7 ±0.2</td>
</tr>
<tr>
<td>35</td>
<td>5.499</td>
<td>4.2597</td>
<td>6006.1±0.1</td>
<td>-502.1±1.7</td>
<td>-21.12±0.01</td>
<td>-63.8±0.9</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>5.405</td>
<td>4.2672</td>
<td>6114.4±0.1</td>
<td>-830 ±7</td>
<td>-22.18±0.02</td>
<td>-67.3±1.7</td>
<td></td>
</tr>
</tbody>
</table>

m-Toluic acid

<table>
<thead>
<tr>
<th>Temp</th>
<th>Kx10^5</th>
<th>pK*</th>
<th>ΔG° cal/mol</th>
<th>ΔH° cal/mol</th>
<th>ΔS° cal/(deg.mol)</th>
<th>ΔC° cal/(deg.mol)</th>
<th>d(ΔC°)/dT cal/(deg^2.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.191</td>
<td>4.3777</td>
<td>5872.0±0.1</td>
<td>751.4±0.4</td>
<td>-17.47±0.01</td>
<td>-57.5±0.1</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>4.265</td>
<td>4.3701</td>
<td>5961.8±0.1</td>
<td>462.8±0.1</td>
<td>-18.44±0.01</td>
<td>-58.0±0.1</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>4.303</td>
<td>4.3662</td>
<td>6056.5±0.1</td>
<td>171.9±0.2</td>
<td>-19.41±0.01</td>
<td>-58.4±0.1</td>
<td>-0.09±0.01</td>
</tr>
<tr>
<td>35</td>
<td>4.306</td>
<td>4.3659</td>
<td>6155.9±0.1</td>
<td>-121.5±0.1</td>
<td>-20.37±0.01</td>
<td>-58.9±0.1</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>4.276</td>
<td>4.3690</td>
<td>6260.2±0.1</td>
<td>-417.1±0.5</td>
<td>-21.32±0.01</td>
<td>-59.4±0.1</td>
<td></td>
</tr>
</tbody>
</table>

p-Toluic acid

* Results obtained after fitting the observed values into Clarke & Glew equations.
Table 12.6.3. The thermodynamic functions for the ionization of m-toluic acid in water. A comparison between the published data and the results obtained in the present work.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Ref.</th>
<th>Kx10^5</th>
<th>pK</th>
<th>ΔG° cal/mol</th>
<th>ΔH° cal/mol</th>
<th>ΔS° cal/(deg.mol)</th>
<th>ΔC° cal/(deg.mol)</th>
<th>d(ΔC°)/dT cal/(deg^2.mol)</th>
<th>Method of calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>3</td>
<td>?</td>
<td>-</td>
<td>5785</td>
<td>70</td>
<td>-19.2</td>
<td>-32.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>5.321</td>
<td>4.269</td>
<td>5825.4±3.4</td>
<td>1201±93</td>
<td>-15.30±0.81</td>
<td>-</td>
<td></td>
<td>C&amp;G/2 coeff.</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>5.558</td>
<td>4.2551</td>
<td>5804.9±0.1</td>
<td>99.1±3.4</td>
<td>-19.14±0.01</td>
<td>-60.2±0.6</td>
<td></td>
<td>C&amp;G/3 coeff.</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>5.557</td>
<td>4.2551</td>
<td>5805.0±0.1</td>
<td>100.7±1.6</td>
<td>-19.13±0.01</td>
<td>-56.7±0.8</td>
<td>-0.7±0.2</td>
<td>C&amp;G/4 coeff.</td>
</tr>
<tr>
<td>35</td>
<td>1</td>
<td>5.754</td>
<td>4.244</td>
<td>5985</td>
<td>914</td>
<td>-16.4±</td>
<td>-</td>
<td></td>
<td>C&amp;G/2 coeff.</td>
</tr>
<tr>
<td>35</td>
<td>2</td>
<td>5.498</td>
<td>4.2598</td>
<td>6006.3±0.1</td>
<td>-502.9±3.6</td>
<td>-21.12±0.01</td>
<td>-60.2±0.6</td>
<td></td>
<td>C&amp;G/3 coeff.</td>
</tr>
<tr>
<td>35</td>
<td>2</td>
<td>5.499</td>
<td>4.2597</td>
<td>6006.1±0.1</td>
<td>-502.1±1.7</td>
<td>-21.12±0.01</td>
<td>-63.8±0.9</td>
<td>-0.7±0.2</td>
<td>C&amp;G/4 coeff.</td>
</tr>
</tbody>
</table>

Note. C&G: Clarke and Glew formula (13.2.26).

2. Present work.
Table 12.6.4. The thermodynamic functions for the ionization of p-toluic acid in water. A comparison between published data and the results obtained in the present work.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Ref.</th>
<th>$K \times 10^5$</th>
<th>pK</th>
<th>$\Delta G^0$ cal/mol</th>
<th>$\Delta H^0$ cal/mol</th>
<th>$\Delta S^0$ cal/(deg.mol)</th>
<th>$\Delta C_p^0$ cal/(deg.mol)</th>
<th>$d(\Delta C_p^0)/dT$ cal/(deg$^2$.mol)</th>
<th>Method of calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>4.290</td>
<td>4.362</td>
<td>5952.4±3.0</td>
<td>1101±82</td>
<td>-16.27±0.27</td>
<td>-</td>
<td>-</td>
<td>C&amp;G/2 coeff.</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>4.265</td>
<td>4.3701</td>
<td>5961.8±0.1</td>
<td>462.6±0.4</td>
<td>-18.44±0.01</td>
<td>-58.4±0.1</td>
<td>-0.09±0.01</td>
<td>C&amp;G/3 coeff.</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>4.265</td>
<td>4.3701</td>
<td>5961.8±0.1</td>
<td>462.8±0.1</td>
<td>-18.44±0.01</td>
<td>-58.0±0.1</td>
<td>-0.09±0.01</td>
<td>C&amp;G/4 coeff.</td>
</tr>
<tr>
<td>35</td>
<td>1</td>
<td>4.645</td>
<td>4.336</td>
<td>6114</td>
<td>1160</td>
<td>-16.1</td>
<td>-</td>
<td>-</td>
<td>C&amp;G/2 coeff.</td>
</tr>
<tr>
<td>35</td>
<td>2</td>
<td>4.306</td>
<td>4.3659</td>
<td>6155.9±0.1</td>
<td>-121.6±0.5</td>
<td>-20.37±0.01</td>
<td>-58.4±0.1</td>
<td>-0.09±0.01</td>
<td>C&amp;G/3 coeff.</td>
</tr>
<tr>
<td>35</td>
<td>2</td>
<td>4.306</td>
<td>4.3659</td>
<td>6155.9±0.1</td>
<td>-121.5±0.1</td>
<td>-20.37±0.01</td>
<td>-58.9±0.1</td>
<td>-0.09±0.01</td>
<td>C&amp;G/4 coeff.</td>
</tr>
</tbody>
</table>

Note. C&G: Clarke and Glew formula (13.2.26).

2. Present work.
13. **THE CALCULATION OF THE THERMODYNAMIC QUANTITIES $\Delta G^\circ$, $\Delta H^\circ$, $\Delta S^\circ$ AND $\Delta C_p$ FOR THE IONIZATION OF WEAK ORGANIC ACIDS IN AQUEOUS SOLUTION.**

13.1 **Definitions.**

The change in any extensive property which accompanies the ionization of a weak electrolyte is regarded as being the difference between the values of the property for one mole of completely ionized solute and for one mole of nonionized solute in their standard states. In both cases the standard states are hypothetical ideal solutions of unit concentration at the fixed temperature concerned. Ideality is defined in the sense of Henry's law, i.e. it considers the solute-solvent interactions to be absent.

The dissociation constant $K$ at constant pressure is related to the standard free energy change, $\Delta G^\circ$, by the relation:

$$ -RT \ln K_p = \Delta G^\circ \quad (13.1.1) $$

The standard enthalpy change, $\Delta H^\circ$, is given by:

$$ \Delta H^\circ = -T^2 \left[ \frac{\delta}{\delta T} \left( \frac{\Delta G^\circ}{T} \right) \right] \quad (13.1.2) $$

The standard entropy change, $\Delta S^\circ$, is:

$$ \Delta S^\circ = -\left[ \frac{\delta}{\delta T}(\Delta G^\circ) \right] = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (13.1.3) $$
Finally the standard heat capacity change at constant pressure is given by:

\[ \Delta C_p^o = \left[ \frac{\delta H}{\delta T} \right]_p \]  \hspace{1cm} (13.1.4)

The significance of each of these changes in relation to the molecular structure will be analysed in section 14.

13.2 The representation of the variation of the dissociation constant K with temperature.

The first expression proposed to represent the change in K with the temperature belongs to Harned and Embree 166:

\[ \log K = \log K_M - 1(T - T_M)^2 \]  \hspace{1cm} (13.2.1)

where \( T_M \) is the temperature at which the dissociation constant K attains its maximum value \( K_M \). "1" is a constant characteristic of each acid.

If it is assumed that the enthalpy change, \( \Delta H^o \), can be represented as a polynomial in T (temperature in °K), i.e.:

\[ \Delta H^o = A - BT - DT^2 \]  \hspace{1cm} (13.2.2)

then 167:
\[ \Delta G^o = -RT \ln K_p = A + BT \ln T - CT + DT^2 \]  
(13.2.3)

\[ \Delta S^o = (C - B) - B \ln T - 2DT \]  
(13.2.4)

\[ \Delta C_p^o = -B - 2DT \]  
(13.2.5)

Everett and Wynne-Jones \(^{168}\) used an equation identical to (13.2.3) but without the term in \(T^2\):

\[ \Delta G^o = -RT \ln K_p = A + BT \ln T - CT \]  
(13.2.6)

\[ \Delta H^o = A - BT \]  
(13.2.7)

\[ \Delta S^o = (C - B) - B \ln T \]  
(13.2.8)

\[ \Delta C_p^o = -B \]  
(13.2.9)

and they were able to represent their experimental data with deviations of the order of \(\pm 0.0005\) pK units, which was much better than the experimental accuracy of the dissociation values themselves.

Harned and Robinson proposed another equation \(^{167}\):

\[ \Delta G^o = -RT \ln K_p = A + CT + DT^2 \]  
(13.2.10)

\[ \Delta H^o = A - DT^2 \]  
(13.2.11)

\[ \Delta S^o = -C - 2DT \]  
(13.2.2)

\[ \Delta C_p^o = -2D^\circ \]  
(13.2.3)
This equation was based on the fact that their experimental EMF measurements, which lead to $K$, were represented within the experimental error ($0.05 \text{ mv}$) and over the temperature range used ($0 - 60^\circ \text{C}$) by a quadratic equation in $T$.

Much later, Feates and Ives \cite{169} investigated a series of 15 equations as potential candidates for representing the variation of $K$ with temperature. From the 15 equations only 3 were able to represent the data within the experimental error. These three equations were:

$$\frac{\Delta G^o}{RT} = -\ln K_p = A + BT + CT^2 + DT^3 + ET^4 \quad (13.2.14)$$

$$\frac{\Delta G^o}{RT} = -\ln K_p = A + BT + CT^2 + DT^3 + ET^4 + FT^5 \quad (13.2.15)$$

$$\Delta G^o = -RT \ln K_p = A + BT + CT^2 + DT^3 + ET^4 + FT^5 \quad (13.2.16)$$

It is interesting to note that among the equations investigated and rejected were those of the form (13.2.3) and (13.2.6) which later on proved to have the correct mathematical form. It is very likely that the rejection of these equations was caused by an overestimation of the experimental accuracy. Ives and Marsden \cite{44} investigated in more detail the equations (13.2.14) to (13.2.16) and concluded that the addition of the term in $T^4$ and $T^5$ is not
statistically justified. Their new equation has the form:

\[
\frac{\Delta G^{\circ}}{RT} = - \ln K_p - C_1 = AX_1 + BX_2 + CX_3 + C_2
\]  \hspace{1cm} (13.2.17)

where:

\[X_1 = Y\]

\[X_2 = 3Y^2 - 20\]

\[X_3 = (5Y^3 - 59Y)/6\]

\[Y = (T - 25)/5\]

\[T = \text{temperature in } ^{\circ}\text{C.}\]

\[\Delta H^{\circ} = - \frac{RT^2}{5} \left[ A + 6BY + C \left( \frac{15Y - 59}{6} \right) \right]
\]  \hspace{1cm} (13.2.18)

\[\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T}\]

\[\Delta C_p^{\circ} = - \frac{2RT}{5} \left[ A + B \left( 6Y + \frac{3T}{5} \right) + C \left( \frac{15Y^2}{6} - 59 - \frac{YT}{5} \right) \right]
\]  \hspace{1cm} (13.2.19)

Note that all the expressions examined so far were empirical. They were characterised by the fact that they fitted the observed variation of K with T.

Recently Clarke and Glew\textsuperscript{149} developed a series of new equations which, for the first time, were not completely empirical. Their equations were logically and mathematically correct derivations from the integrated van't Hoff equation:
\[ R \ln K_p = A + B/T \]  

(13.2.20)

where \( A = \Delta S^o \) and \( B = -\Delta H^o \) are mean values over short temperature ranges.

The extension of (13.2.20) is based on the assumption that \( K_p, \Delta G^o, \Delta H^o \) and \( \Delta S^o \) are well-behaved functions of \( T \).

The thermodynamic quantities at temperature \( T^oK \) are related by:

\[ R \ln K_p = -\frac{\Delta G_T^o}{T} = \Delta S_T^o - \frac{\Delta H_T^o}{T} \]  

(13.2.21)

where \( \Delta G_T^o, \Delta H_T^o \) and \( \Delta S_T^o \) are functions of \( T \) only.

In the Clarke and Glew treatment a reference temperature \( \theta \) is chosen. The change in the thermodynamic functions are obtained at this particular temperature.

The value of \( \Delta H^o \) at any temperature \( T \), i.e. \( \Delta H_T^o \), is expressed as a perturbation on the value of \( \Delta H^o \) at the reference temperature \( \theta^oK \), i.e. \( \Delta H_{\theta}^o \), by using Taylor's

Footnote: A function is well-behaved when \( ^{170} \):

a. it is single-valued

b. it is continuous

c. the integral of the square of the absolute value of the function is finite, the limits of integration being the entire range of its variables.
series expansion:

\[
\Delta H^\circ_T = \Delta H^\circ_\theta + \Delta C_{p\theta}^\circ (T - \theta) + \frac{1}{2} \left( \frac{d\Delta C_{p\theta}^\circ}{dT} \right)_\theta (T-\theta)^2 + \\
\frac{1}{6} \left( \frac{d^2 C_{p\theta}^\circ}{dT^2} \right)_\theta (T-\theta)^3 + \frac{1}{24} \left( \frac{d^3 \Delta C_{p\theta}^\circ}{dT^3} \right)_\theta (T-\theta)^4 \tag{13.2.22}
\]

Similarly \( \Delta S^\circ_T \) can be expressed as:

\[
\Delta S^\circ_T = \Delta S^\circ_\theta + \int_\theta^T \frac{\Delta C_{pT}^\circ}{T} \, dT \tag{13.2.23}
\]

where:

\[
\Delta C_{pT}^\circ = \Delta C_{p\theta}^\circ + \left( \frac{d\Delta C_{p\theta}^\circ}{dT} \right)_\theta (T-\theta) + \frac{1}{2} \left( \frac{d^2 C_{p\theta}^\circ}{dT^2} \right)_\theta (T-\theta)^2 + \\
+ \frac{1}{6} \left( \frac{d^3 \Delta C_{p\theta}^\circ}{dT^3} \right)_\theta (T-\theta)^3 \tag{13.2.24}
\]

Substituting the expressions for \( \Delta H^\circ_T \) and \( \Delta S^\circ_T \) (integrated) into (13.2.21) the following, rather complex, expression is obtained:

\[
R \ln K_p = -\frac{\Delta G^\circ_\theta}{T} + \Delta H^\circ_\theta \left( \frac{1}{\theta} - \frac{1}{T} \right) + \Delta C_{p\theta}^\circ \left( \frac{\theta}{T} - 1 + \ln \frac{T}{\theta} \right) + \\
\frac{\theta}{2} \left( \frac{d\Delta C_{p\theta}^\circ}{dT} \right)_\theta \left( \frac{T}{\theta} - \frac{\theta}{T} - 2 \ln \frac{T}{\theta} \right) + \\
\frac{\theta^2}{12} \left( \frac{d^2 \Delta C_{p\theta}^\circ}{dT^2} \right)_\theta \left[ \left( \frac{T}{\theta} \right)^2 - 6 \frac{T}{\theta} + 3 + 2 \frac{\theta}{T} + 6 \ln \frac{T}{\theta} \right] + \\
\frac{\theta^3}{72} \left( \frac{d^3 \Delta C_{p\theta}^\circ}{dT^3} \right)_\theta \left[ \left( \frac{T}{\theta} \right)^3 - 6 \left( \frac{T}{\theta} \right)^2 + 18 \frac{T}{\theta} - 10 - 3 \frac{\theta}{T} - 12 \ln \frac{T}{\theta} \right] \tag{13.2.25}
\]

Under the usual experimental conditions:

\[(T-\theta) \ll \theta\]
A new variable "X" is defined as:

\[ X = \frac{T - \theta}{\theta} \]

and thus (13.2.25) can be rewritten as a function of X:

\[
R \ln K_p = - \frac{\Delta G}{\theta} + \frac{\Delta H}{\theta} \left[ \frac{X}{1 +} \right] + \Delta C_p^\circ \left[ \sum_{n=1}^{\infty} \frac{n}{n+1} \frac{n}{n+2} (-X)^{n-1} \right] + \\
\frac{\theta}{2} \left( \frac{d\Delta C}{dt} \right)_\theta \left[ \sum_{n=1}^{\infty} \frac{n}{n+2} (-X)^{n-1} \right] + \\
\frac{\theta^2}{6} \left( \frac{d^2\Delta C}{dt^2} \right)_\theta \left[ \sum_{n=1}^{\infty} \frac{n}{n+3} (-X)^{n-1} \right] + \\
\frac{\theta^3}{24} \left( \frac{d^3\Delta C}{dt^3} \right)_\theta \left[ \sum_{n=1}^{\infty} \frac{n}{n+4} (-X)^{n-1} \right] \tag{13.2.26}
\]

which is of the form:

\[
R \ln K_p = b_0 + b_1 u_1 + b_2 u_2 + b_3 u_3 + b_4 u_4 + b_5 u_5 \tag{13.2.27}
\]

As pointed out by the authors, equation (13.2.25) and its equivalent (13.2.26) are most general since the six constants, \( \Delta G^\circ/\theta \) to \( (d^3 \Delta C_p^\circ/dt^3)_\theta \), can take any finite value. The only assumption involved, and a very reasonable one, is that \( (d^3 \Delta C_p^\circ/dt^3)_\theta \) is a constant and thus any higher derivative of \( \Delta C_p^\theta \) in the Taylor's expansion is zero. If it is desired however, higher derivatives can be included in the series expansion leading to new terms in equation (13.2.26) of the form:

\[
\frac{\theta^r}{(r+1)!} \left( \frac{d^r \Delta C}{dt^r} \right)_\theta \left[ \sum_{n=1}^{\infty} \frac{n}{n+r-1} (-X)^{n-1} \right] \tag{13.2.28}
\]

where "r" is the order of the derivative.
Equation (13.2.26) can be written in a general form:

\[ R \ln K_p = - \frac{\Delta G^0}{\Theta} + \sum_{s=0}^{s-1} \frac{d^s \Delta H^0}{d T^s} \Theta^s + \sum_{n=1}^{n} \frac{n}{n+1} (-\chi)^{n-1} \]  

which is equivalent to \((q = 4):\)

\[ RT \ln K_p = A + B/T + C \ln T + DT + ET^2 + FT^3 \]  

where:

\[ A = f(\Delta G^0, \Delta H^0, \ldots, d^3 \Delta C_p^0/dT^3) \]

\[ B = f(\Delta H^0, \ldots, d^3 \Delta C_p^0/dT^3) \]

\[ \ldots \]

\[ F = f(d^3 \Delta C_p^0/dT^3) \]

The general equation (13.2.29) can be used with as many terms as we desire or better still, with as many terms as the precision of the experimental results, \(T\) and especially \(K_p\), allow us to use.

The present obtainable accuracies, in the best cases, would give us \(\Delta C_p^0 dT\), although even the validity of the
previous constant, i.e. \( \Delta C_{p0} \), has been questioned by some authors\(^{171}\).

Note that one of the earlier equations used for calculating \( \Delta G^o \), \( \Delta H^o \), ..., i.e. (13.2.6), has the same form as (13.2.30) with three coefficients. The meaning of the coefficients, however, is different in the two cases.

Clarke and Glew\(^{149}\) pointed out that while a number of equations fit the variation of \( K \) with temperature well, only the equations represented in a general form by (13.2.29) provide good, unbiased estimates for the change in the thermodynamic functions.

13.3 Calculation of the thermodynamic functions from the dissociation constants of acids.

A computer program to calculate the thermodynamic functions for the ionization of acids was written. The program employs Clarke and Glew's formula\(^{149}\) (13.2.26) with three and four adjustable coefficients.

The second part of the same program calculates the thermodynamic functions of ionization using Harned and Robinson formulas (13.2.10 to 13.2.13)\(^{167}\). The complete program is given in appendix 13.3.1.

The entire program was checked against some of the published data. The results are given in table 13.3.1 and "detailed calculations - 13.3.1".
The agreement between the values obtained by us and those obtained by Clarke and Glew \(^{149}\) and by Wilson, Gore, Sawbridge and Cardenas-Cruz \(^{130}\) when using relation (13.2.26) is good.

The errors in the thermodynamic functions calculated from Harned and Robinson formula (13.2.10) were obtained from the covariance matrix of the least square equations. \(^{172}\)

If \(X\) is:

\[ X = f(x_1, x_2, x_3, \ldots) \]  \hspace{1cm} (13.3.1)

where \(f\) represents any function then the variance of \(X\) is given by \(^{173}\):

\[
V(X) = \left(\frac{\delta X}{\delta x_1}\right)^2 V(x_1) + \left(\frac{\delta X}{\delta x_2}\right)^2 V(x_2) + \ldots + 2 \frac{\delta X}{\delta x_1} \cdot \frac{\delta X}{\delta x_2} \operatorname{cov}(x_1 x_2) + \frac{\delta X}{\delta x_1} \cdot \frac{\delta X}{\delta x_3} \operatorname{cov}(x_1 x_3) + \ldots
\]  \hspace{1cm} (13.3.2)

In our case the explicit expressions for the errors in the thermodynamic functions calculated from relations (13.2.10) to (13.2.13) were:

\[
P.E.(\Delta G^\circ) = 0.6745 \sigma (a_{11} + T^2 a_{22} + T^4 a_{33} + 2T a_{12} + 2T^2 a_{13} + 2T^3 a_{23})^{1/2} \]  \hspace{1cm} (13.3.3)

where P.E. stands for "Probable Error" and which is 0.6745 of \(\sigma\), the standard error.
\[ \sigma = \left[ \frac{N}{N - 3} \left( \sum_{i=1}^{N} (A + CT_i + DT_i^2) - RTlnK_i \right)^2 \right]^{1/2} \] (13.3.4)

\( N \) is the number of experimental points \( T_i - K_i \).

\( a_{11}, a_{22}, \ldots, a_{12}, \ldots \) are elements of the covariance matrix which is nothing less than the inverted matrix of the coefficients of the least square equations.

Analogous:

\[ \text{P.E.}(\Delta H^0) = 0.6745\sigma \left( a_{11} + \frac{T^4a_{33} - 2T^2a_{13}}{T^4a_{33}} \right)^{1/2} (13.3.5) \]

\[ \text{P.E.}(\Delta S^0) = 0.6745\sigma \left( a_{22} + \frac{4T^2a_{33} + 4Ta_{23}}{T^2a_{33}} \right)^{1/2} (13.2.6) \]

\[ \text{P.E.}(\Delta C_p^0) = 0.6745\sigma \left( 4T^2a_{33} \right)^{1/2} (13.3.7) \]

The errors in the thermodynamic functions calculated from the Clarke and Glew equation were obtained from their general errors formula given in their original paper. The explicit expressions used to calculate the errors for the equation with three adjustable coefficients were:

\[ \text{P.E.}(\Delta G_\theta) = -0.6745\sigma\theta(1/N + \bar{u}_1^2a_{22} + 2\bar{u}_1\bar{u}_2a_{23} + \bar{u}_2^2a_{33})^{1/2} (13.3.8) \]

where:

\[ \sigma = \left[ \frac{N}{N - 3} \left( \sum_{i=1}^{N} (RTlnK_{i,\text{obs}} - (b_0 + b_{1u_1} + b_{2u_2}) \right)^2 \right]^{1/2} \] (13.3.9)
\[
\overline{u}_1 = -\frac{\sum_{i=1}^{N} u_1(T_i)}{N}; \quad \overline{u}_2 = -\frac{\sum_{i=1}^{N} u_2(T_i)}{N} \quad (13.3.10)
\]
\[
u_1 = \frac{x}{1+x} = x \sum_{N=1}^{\infty} (-x)^{N-1}; \quad \nu_2 = x^2 \sum_{N=1}^{\infty} \frac{N}{N+1} (-x)^{-1}
\]

And:
\[
P.E.(\Delta H_\theta^\circ) = 0.6745\sigma(a_{22})^{1/2} \quad (13.3.11)
\]
\[
P.E.(\Delta S_\theta^\circ) = 0.6745\sigma[1/N + (1+\overline{u}_1)^2a_{22} + \\
2(1+\overline{u}_1)\overline{u}_2a_{23} + \overline{u}_2^2a_{33}]^{1/2} \quad (13.3.12)
\]
\[
P.E.(\Delta C_{p\theta}^\circ) = 0.6745\sigma(a_{33})^{1/2} \quad (13.3.13)
\]

For the case with four adjustable parameters the expressions for P.E.(\Delta H_\theta^\circ) and P.E.(\Delta C_{p\theta}^\circ) remained the same. P.E.(\Delta G_\theta^\circ)
became:
\[
P.E.(\Delta G_\theta^\circ) = -0.6745\sigma\theta(1/N + \overline{u}_1^2a_{22} + 2\overline{u}_1\overline{u}_2a_{23} + \overline{u}_2^2a_{33} + \\
2\overline{u}_1\overline{u}_3a_{24} + 2\overline{u}_2\overline{u}_3a_{34} + \overline{u}_3^2a_{44})^{1/2} \quad (13.3.14)
\]
\[
\overline{u}_3 = -\frac{\sum_{i=1}^{N} u_3(T_i)}{N} \quad (13.3.15)
\]

where:
\[
u_3 = \frac{x^3}{N+2} \sum_{N=1}^{\infty} \frac{N}{N+1} (-x)^{N-1}
\]
P.E.($\Delta S_\theta^o$) became:

$$\text{P.E.}(\Delta S_\theta^o) = 0.6743\left(\frac{1}{N} + (1+\bar{\nu}_1)^2 a_{22} + 2(1+\bar{\nu}_1)\bar{\nu}_2 + \bar{\nu}_2^2 a_{33} + 2(1+\bar{\nu}_1)\bar{\nu}_3 a_{24} + 2\bar{\nu}_2\bar{\nu}_3 a_{34} + \bar{\nu}_3^2 a_{44}\right) / 2$$  (13.3.16)
Table 13.3.1. The thermodynamic functions for the ionization of some acids.

A comparison of different methods of calculation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref</th>
<th>T (°C)</th>
<th>( \Delta G^0 ) (cal/mol)</th>
<th>( \Delta H^0 ) (cal/mol)</th>
<th>( \Delta S^0 ) (cal/deg.mol)</th>
<th>( \Delta C_p^0 ) (cal/deg.mol)</th>
<th>( d(\Delta C_p^0)/dT ) (cal/deg(^2)mol)</th>
<th>Formula used for calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanoacetic acid (data from ref.1)</td>
<td>2</td>
<td>25</td>
<td>3.3876</td>
<td>3369.34±0.18</td>
<td>-882.7±2.8</td>
<td>-39.16±0.49</td>
<td>-</td>
<td>13.2.26/3 coeff.</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>25</td>
<td></td>
<td>3369.38±0.12</td>
<td>-882.7±1.9</td>
<td>-14.26±0.01</td>
<td>-39.17±0.33</td>
<td>13.2.26/3 coeff.</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>25</td>
<td></td>
<td>3369.36±0.17</td>
<td>-891.6±6.6</td>
<td>?</td>
<td>-39.07±0.45</td>
<td>0.18±0.12 13.2.26/4 coeff.</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>25</td>
<td></td>
<td>3369.40±0.11</td>
<td>-891.6±4.5</td>
<td>-14.29±0.02</td>
<td>-39.07±0.31</td>
<td>0.18±0.08 13.2.26/4 coeff.</td>
</tr>
<tr>
<td>Diisopropylcyanoacetic acid (data from ref.4)</td>
<td>4</td>
<td>5</td>
<td>4.0449</td>
<td>3044.7±0.5</td>
<td>-2783±29</td>
<td>-31.9±3.3</td>
<td>-</td>
<td>13.2.17</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>5</td>
<td></td>
<td>3045.5±0.1</td>
<td>-2804±5</td>
<td>-21.03±0.02</td>
<td>-29.5±0.3</td>
<td>13.2.26/3 coeff.</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>5</td>
<td></td>
<td>3045.7±0.1</td>
<td>-2780±9</td>
<td>-20.94±0.03</td>
<td>-32.8±1.1</td>
<td>0.17±0.06 13.2.26/4 coeff.</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>5</td>
<td></td>
<td>3045.4±0.2</td>
<td>-2819±7</td>
<td>-21.08±0.02</td>
<td>-27.5±0.3</td>
<td>13.2.10</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>25</td>
<td>2.7816</td>
<td>3485.7±0.5</td>
<td>-3402±11</td>
<td>-23.10±0.03</td>
<td>-29.6±0.07</td>
<td>13.2.17</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>25</td>
<td></td>
<td>3486.9±0.1</td>
<td>-3394.4±1.4</td>
<td>-23.08±0.01</td>
<td>-29.5±0.3</td>
<td>13.2.26/3 coeff.</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>25</td>
<td></td>
<td>3486.9±0.1</td>
<td>-3402.7±3.7</td>
<td>-23.11±0.01</td>
<td>-29.4±0.2</td>
<td>0.17±0.06 13.2.26/4 coeff.</td>
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<tr>
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<td>3</td>
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<td></td>
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<td>-23.06±0.01</td>
<td>-29.5±0.3</td>
<td>13.2.10</td>
</tr>
<tr>
<td>Compound</td>
<td>Ref</td>
<td>T 0C</td>
<td>Kx10^5</td>
<td>ΔG cal/mol</td>
<td>ΔH cal/mol</td>
<td>ΔS° cal/deg.mol</td>
<td>ΔC_p° cal/deg.mol</td>
<td>d(ΔC_p°)/dT cal/deg.²mol</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----</td>
<td>------</td>
<td>--------</td>
<td>------------</td>
<td>-------------</td>
<td>----------------</td>
<td>---------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>Benzoic acid (data from ref.5)</td>
<td>5</td>
<td>25</td>
<td>6.281</td>
<td>5734.6±0.9</td>
<td>150±24</td>
<td>-18.7±0.08</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>25</td>
<td></td>
<td>5734.4±0.6</td>
<td>150±16</td>
<td>-18.72±0.06</td>
<td>-82.5±3.9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>25</td>
<td></td>
<td>5735</td>
<td>155</td>
<td>-18.7</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>25</td>
<td></td>
<td>5734±0.6</td>
<td>154±18</td>
<td>-18.72±0.06</td>
<td>-81.5±4.0</td>
<td>-</td>
</tr>
<tr>
<td>Benzoic acid (data from ref.6)</td>
<td>6</td>
<td>25</td>
<td>6.247</td>
<td>5735.5±0.1</td>
<td>13.8±4.6</td>
<td>-19.19±0.02</td>
<td>-45.5±0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>25</td>
<td></td>
<td>5733.5±0.1</td>
<td>13.8±6.8</td>
<td>-19.18±0.02</td>
<td>-45.5±1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>25</td>
<td></td>
<td>5735.6±0.1</td>
<td>15.8±3.5</td>
<td>-19.18±0.01</td>
<td>-41.3±1.9</td>
<td>-0.86±0.36</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>25</td>
<td></td>
<td>5733.6±0.1</td>
<td>15.8±5.2</td>
<td>19.18±0.02</td>
<td>-41.3±2.8</td>
<td>-0.86±0.54</td>
</tr>
</tbody>
</table>
Table 13.3.1 (concluded).

References:
3. Present work (see "Detailed Calculations - 13.3.1").
6. This thesis - subsection 8.6.
7. R. E. Robertson, personal communication.

Note: References 2, 4, 5, 7 quote standard errors. Reference 3 gives probable errors. The relation between the two types of errors is: Probable error = 0.6745 x standard error.
14. THE SIGNIFICANCE OF THE CHANGE IN THE THERMODYNAMIC FUNCTIONS 
UPON IONIZATION IN RELATION TO MOLECULAR STRUCTURE.

14.1 Introduction

What exactly do the quantities $\Delta G^o$, $\Delta H^o$, .... indicate? This is a good question because the difficulties one encounters when an exact interpretation of the results is sought are, at the present time, insurmountable. Too many unknown factors could or do affect these thermodynamic quantities and therefore any progress in this direction depends on finding new ways, experimental or theoretical, for isolating and measuring quantitatively or at least semiquantitatively some of these suspected factors.

A number of reviews have been published in connection with the significance of the thermodynamic quantities, obtained from equilibrium constants, reaction rates and calorimetry, in relation to molecular structure. Among the early reviews the most important are those of Harned and Owen 174 and Everett and Wynne-Jones 168. Among the more recent, those of Ives and Marsden 44, King 175, and Robertson 176 are of particular interest to us.

We will try here to summarise the significance of each of the thermodynamic quantities especially as they relate to the molecular structure.
First, however, a brief recapitulation of meaning of the thermodynamic quantities will be given.

14.2 The thermodynamic quantities.

The first law of thermodynamics can be formulated as (for a system of constant mass):

\[ dE = q - w \]  \hspace{1cm} (14.2.1)

where \( E \) is the energy (internal energy) of the system, \( q \) is the heat absorbed by the system from or evolved to the surroundings or by the surroundings on the system.

The work \( w \) may consist of many components: mechanical, electrical, gravitational, etc. If the work is only mechanical, e.g. expansion by an infinitesimal volume \( dV \) at a constant pressure \( p \), then:

\[ dE = q - pdV \]  \hspace{1cm} (14.2.2)

The second law which applies to reversible processes is formulated as:

\[ dS = q/T \]  \hspace{1cm} (14.2.3)

and states that if a quantity of heat \( q \) is absorbed in a reversible change at temperature \( T \), the entropy \( S \) of the system is increased by the amount \( dS \).
The third law states that the entropy of each pure crystalline substance at the absolute zero of temperature is itself zero:

\[ S_0 = 0 \]

The first and the second law can be combined (by eliminating \( q \) from 14.2.2 and 14.2.3) to give:

\[ dE = TdS - dV \]  
(14.2.4)

The heat content, or the enthalpy, of a system is defined as:

\[ H = E + pV \]  
(14.2.5)

and any infinitesimal change in \( H \) is given by:

\[ dH = dE + pdV + Vdp = q + Vdp \]  
(14.2.6)

and if the change takes place at constant pressure:

\[ (dH)_p = q_p \]

which says that the increase in the heat content at constant pressure equals the heat absorbed.

When the amount of the pure substance is one gram-mole, the heat capacity or the specific heat at constant pressure is defined as being:
\[ C_p = \frac{dq_p}{dT} = (\frac{dH}{dT})_p \] 

(14.2.7)

The Gibbs free energy of the system is defined as:

\[ G = H - TS \] 

(14.2.8)

An analogous quantity is the Helmholtz free energy:

\[ A = E - TS \] 

(14.2.9)

from which it can be seen that if \( E \) is the total energy of
the system and \( A \) is the free energy then "TS" is the "bound"
energy.

If we want to allow for the admission or generation
of molecules the equation for the first law must be replaced
by \(177\):

\[ dE = q - w + \sum \mu_i dN_i \] 

(14.2.10)

where the summation sign covers every kind of molecule in the
system and \( \mu \) is the chemical potential which can be defined in
different ways:

\[ \mu_i = (\frac{\delta E}{\delta N_i})_{S,V,N_j} ... = (\frac{\delta A}{\delta N_i})_{T,V,N_j} ... = (\frac{\delta H}{\delta N_i})_{S,p,N_j} ... = (\frac{\delta G}{\delta N_i})_{T,p,N_j} ... \]
In statistical mechanics it is shown that:

$$S = k \ln W$$  \hspace{1cm} (14.2.11)

where $k$ is Boltzmann's constant and $W$ is given by:

$$W = \frac{N!}{N_1!N_2!N_3!...} \frac{N_1!}{\Pi(N_i!)}$$  \hspace{1cm} (14.2.12)

where $N$ is the total number of molecules in the system; $N_1$ is the number of molecules having energy $\varepsilon_1$; $N_2$ is the number of molecules having energy $\varepsilon_2$ and so on. It is often said that the entropy measures the disorder of a system. It can be seen why this is so: in a more ordered system the range of energy is smaller and thus the denominator of expression (14.2.12) is larger.

Also from statistical mechanics it can be shown that 178:

$$H = -kT \ln \frac{\sum \Omega(N,V,E)e^{-E/kT}}{N}$$  \hspace{1cm} (14.2.13)

$$G = -kT \ln \frac{\sum \Omega(N,V,E)e^{-E/kT}e^{-\beta pV}}{E,V}$$  \hspace{1cm} (14.2.14)

where:

$$\ln \Omega(N,V,E) = \frac{TS}{kT}$$

$\Omega$ being the grand canonical partition function.
When one tries to relate changes in the thermodynamic quantities to molecular structure, the important question is, "What is the correct basis for comparing the predictions of a molecular model with the results of the thermodynamic measurements?"

Bell 179 has pointed out that a molecular model predicts energies or effects on the energies of molecules in vacuum, at absolute zero. In these conditions according to (14.2.8):

\[ H_0 = G_0 \]

At other temperatures and in the presence of other molecules (e.g. solvent molecules) the kinetic energy from the solvent molecules, for example, is superimposed on the model energies. We have shown that \( H \) and \( G \) represent essentially two different ways of averaging the molecular energies (14.2.13 and 14.2.14) and because of this it is not obvious which of the two quantities better approaches the model energies.

It is generally agreed though, for reasons which are not exactly "clean cut", that the free energies are likely to be more appropriate for comparison with molecular models 44, 179-181.
The clearest argument for this, which we could find in the literature, belongs to Bell \textsuperscript{179}. We start with the ideal situation: a reaction taking place in vacuum and at absolute zero temperature. For such a reaction:

\[ \Delta H_0 = \Delta G_0; \quad \Delta S_0 = 0 \]

Then we raise the temperature to \( T^0K \). Now:

\[ \Delta H_T = \Delta H_0 + \int_0^T \Delta c_p \, dT \]  \hspace{1cm} (14.2.15)

\[ \Delta G_T = \Delta H_0 + \int_0^T \Delta c_p \, dT - T \int_0^T \Delta c_p \, d\ln T \]  \hspace{1cm} (14.2.16)

Now suppose that the model is slightly modified by the introduction of a substituent. Call the first model "model 1" and the second model "model 2". Consider the small changes between the two models:

\[ \delta \Delta H_T = \Delta H_T ( \text{model 1} ) - \Delta H_T ( \text{model 2} ) \]

\[ = \delta \Delta H_0 + \int_0^T \delta \Delta c_p \, dT \]

or:

\[ \delta \Delta H_T - \delta \Delta H_0 = \int_0^T \delta \Delta c_p \, dT \]  \hspace{1cm} (14.2.17)
Analogously:

$$\delta\Delta G_T - \delta\Delta H_0 = \int_0^T \delta\Delta C_{pT} dT - T \int_0^T \delta\Delta C_{pT} d(T\ln T) \quad (14.2.18)$$

Since the RHS of (14.2.18) is probably smaller than the RHS of (14.2.17) it follows that $\delta\Delta G_T$ is closer to $\delta\Delta H_0$ than $\delta\Delta H_T$ is and therefore the changes in the free energies approximate better the changes in the energy of the models.

Consider now the same reactions taking place in solution. The thermodynamic quantities for the reaction in solution are related to those of the gas-phase reaction that we saw above by:

$$\delta\Delta H_S - \delta\Delta H_T = \delta(\Sigma H^S) \quad (14.2.19)$$

$$\delta\Delta G_S - \delta\Delta G_T = \delta(\Sigma H^S - T\Sigma S^S) \quad (14.2.20)$$

where $H^S$ and $S^S$ are the heats and the entropies of solution and the summations are over all the species involved in the reactions.

The enthalpies and entropies of solution of a series of similar substances in a given solvent can be related by an expression of the form:

$$T\Sigma S^S = \alpha H^S + \beta \quad (14.2.21)$$

where $\alpha$ and $\beta$ are constants characteristic of the solvent. The constant $\alpha$ is always positive, having a value between
0.4 and 1.0. Therefore if such a relation applies to the compounds under study it follows that:

\[(\delta\Delta G_s - \delta\Delta G_T) < (\delta\Delta H_s - \delta\Delta H_T)\]  \hspace{1cm} (14.2.22)

which means that \(\Delta G_T\) is less affected by the solvent as compared with \(\Delta H_T\). Therefore even in solution the changes in the free energy of the system should approximate the molecular models better than the changes in \(\Delta H_T\). At the same time, because the quantities \(\Delta H_T, \Delta S_T,\) and \(\Delta C_p\) are affected more by the changes in the temperature and the solvent, they should provide better information about the solute-solvent interactions.

14.3 The thermodynamic quantities and the ionization of weak organic acids in solution

Ionization in solution may be viewed as occurring in a series of successive steps:

a. destruction of molecule-solvent interaction.

b. the ionization of the solute.

c. generation of a new set of interactions between ions and the solvent.

The ionization of the solute, i.e., step b, can be also broken down into a series of simpler steps:
HA ⇌ H⁺ + A⁻; energy: \( D_e \) (bond dissociation energy)

H ⇌ H⁺ + e; energy: \( I \) (ionization potential)

A + e ⇌ A⁻; energy: \(-E\) (electron affinity)

Overall: \( HA ⇌ H⁺ + A⁻ \); energy: \( \Delta H_g = D_e + I - E \) \( \text{(14.3.1)} \)

King \(^{182}\) calls \( \Delta H_g \) "proton affinity".

The thermodynamic quantities involved in the other two steps, i.e., steps a and c, are the hydration enthalpies and entropies of the unionized molecule HA and of the ions H⁺ and A⁻.

Schematically the ionization of an acid in solution can be represented as follows:

\[
\begin{align*}
(HA)_{\text{gas}} & \overset{1}{\rightleftharpoons} (H⁺)_{\text{gas}} + (A⁻)_{\text{gas}} \\
2 \uparrow & \quad \downarrow \uparrow 4 \quad \downarrow \uparrow 4 \\
HA, x \text{H}_2\text{O} & \rightleftharpoons H⁺, y \text{H}_2\text{O} + A⁻, z \text{H}_2\text{O} \quad \text{(14.3.3)}
\end{align*}
\]

The changes in an extensive property \( X \) associated with these processes must satisfy the relation \(^{44}\):

\[
\Delta X_1 = \Delta X_2 + \Delta X_3 + \Delta X_4 \quad \text{(14.3.4)}
\]

King \(^{183}\) has calculated the thermodynamic properties of some proton transfer reactions in the gaseous state and has concluded that:
a. Translational, rotational and vibrational motions intrinsic to the molecules and ions have a very minor effect on the behaviour of acids and bases. The change in the free energy is largely due to $\Delta H_g$, the proton affinity. For hydrogen halides, for example, King calculated that the term $T\Delta S_g$ in the expression:

$$\Delta G_g = \Delta H_g - T\Delta S_g$$  (14.3.5)

amounts to only 2% of the value of $\Delta H_g$.

b. The contributions of translational, rotational and vibrational motion to changes in entropy and heat capacities besides being small are, generally, very close for similar acids.

The free energy change for the ionization of hydrogen halides in solution has been calculated according to the scheme shown above and it was concluded that none of the factors played a determining role but rather the final values were a result of an interplay of all of them 184, 185.

Another way to analyse the significance of the thermodynamic quantities is to divide them into an internal part, intrinsic to the molecules and ions, and an external or environmental part, arising from the interaction of these particles with the solvent 186, 190:
\[ \Delta X = \Delta X_{\text{int}} + \Delta X_{\text{ext}} \] (14.3.6)

Ives and Marsden \(^{44}\) divide \(\Delta X\), the change in the thermodynamic property into two parts which they call "reaction part" in which the solvent (water) is not directly concerned and a "hydration part" in which water is solely concerned.

\(\Delta X_{\text{int}}\) corresponds largely to reaction 14.3.2. In particular, \(\Delta H_{\text{int}}\) corresponds primarily to the proton affinity and thus any arguments concerning resonance stabilization of the anions or inductive effects on bond dissociation energies apply to \(\Delta H_{\text{int}}\).

Pitzer and King \(^{188, 189}\) have shown that the difference between the internal entropies of an acid and its anion is small and nearly constant for a series of similar acids. The situation is identical for \(\Delta C_p,_{\text{int}}\). Thus when we compare two similar acids \(\Delta S_{\text{int}}\) and \(\Delta C_p,_{\text{int}}\) nearly cancel out. Any residual contribution from \(\Delta S_{\text{int}}\) is probably due to internal rotations which are frozen out or released by ionization.

To a good approximation the entropy change in the ionization of an acid might be considered to be due entirely to \(\Delta S_{\text{ext}}\). Thus we have:

\[ \Delta S = \Delta S_{\text{ext}} \] (14.3.7)
\[ \Delta H = \Delta H_{\text{int}} + \Delta H_{\text{ext}} \]  \hspace{1cm} (14.3.8)

According to Hepler and Leffler\(^{190, 191}\), there is a proportionality between \(\Delta S_{\text{ext}}\) and \(\Delta H_{\text{ext}}\); especially for "symmetrical" reactions, e.g.:

\[
\text{H-R-COOH} + \text{X-R-COO}^- \Leftrightarrow \text{H-R-Coo}^- + \text{X-R-CooH}
\]

\[ \Delta H_{\text{ext}} = \beta \Delta S_{\text{ext}} \]  \hspace{1cm} (14.3.9)

It follows from (14.3.7), (14.3.8) and (14.3.9) that:

\[ \Delta H = \Delta H_{\text{int}} + \beta \Delta S_{\text{ext}} = \Delta H_{\text{int}} + \beta \Delta S \]  \hspace{1cm} (14.3.10)

Therefore if \(\beta\) is known \(\Delta H_{\text{int}}\) can be estimated after the values for \(\Delta H\) and \(\Delta S\) are found experimentally. Brown and Newsom\(^{192, 193}\) have investigated linear enthalpy-entropy relations and published a series of \(\beta\) values.

Summing up what was said to this point, the change in the thermodynamic quantities in the ionization of acids can be divided into two parts: the first part called "internal" (intrinsic, reaction) and the second part called "external" (environmental, hydration). For symmetrical reactions the entropy term \(\Delta S\) is almost completely \(\Delta S_{\text{ext}}\) and:

\[ \Delta H_{\text{ext}} = \beta \Delta S_{\text{ext}} \]  \hspace{1cm} (14.3.11)
Thus any change in solute-solvent and solvent-solvent interactions in going from the unionized to the ionized state is reflected in $\Delta S$. Any change in the internal energy of the molecule will be reflected in $\Delta H_{\text{int}}$ and/or $\Delta G$.

14.4 Entropy change and the solute-solvent and solvent-solvent interactions.

It was shown in the preceding subsection that the entropy change in the ionization of an acid is almost entirely due to changes in solute-solvent and solvent-solvent interactions. Note that solute-solute interactions are completely neglected as ideal solutions are assumed.

The problem here is to determine how the total change can be divided among these two interactions and consequently to find which one is more important and also to find how a change in the molecular structure affects the ratio of the two. It must be pointed out at the beginning that the exact answers to these problems have not yet been found.

In general the reaction:

$$HA, x H_2O \rightleftharpoons H^+, y H_2O + A^-, z H_2O \quad (14.3.3)$$

occurs with a loss of entropy, i.e., $\Delta S^0$ has negative values:

$$\Delta S^0 = S^0_{\text{products}} - S^0_{\text{reactants}}$$
It is generally agreed that the loss in entropy is a result of more ordered structure in the solute-solvent system due to a preferential solvent orientation about an electrical charge.

The differences between the entropies of ionization of similar acids are more difficult to explain. Various theories have been proposed; none of them, however, is in a quantitative form. For the solvent water the situation is even more complicated by the fact that no agreement has been reached on the structure of liquid water. (Summaries of the actual state of this problem are given in reference number 176 and 194.)

One way by which the variation in $\Delta S$ has been related to changes in the molecular structure has been to compare the values of $\Delta S$ for the ionization of an unsubstituted acid with the $\Delta S$ values for the same acid with different substituents in the molecule. Examples of such series are:

<table>
<thead>
<tr>
<th>Unsubstituted acid</th>
<th>Substituted acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>Propionic, butyric, monochloroacetic, etc.</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>ortho-Toluic, meta-toluic, etc.</td>
</tr>
</tbody>
</table>

The introduction of a substituent in the molecule could affect the solution structure in two ways. Firstly the
substituent could reduce the number of water molecules influenced by the charge in the ionized state. The energy and the entropy of the ion is increased by this solvent exclusion. The classical example is the reaction:

\[ \text{NMe}_3\text{H}^+ + \text{NH}_3 \rightleftharpoons \text{NMe}_3 + \text{NH}_4^+ \]

whose \( \Delta S^0 = -14.5 \text{ cal/(deg.mol)} \) is explained by the shielding action of the methyl groups which hinder the solvent orientation in the ion \( \text{NMe}_3\text{H}^+ \), resulting in a higher entropy for it.

The same argument in a reversed direction has been proposed by Ives and Marsden \(^{44}\) for explaining the variation of \( \Delta S \) for the ionization of some aliphatic acids (acetic, propionic, isobutyric, ....) For these acids the entropy of ionization decreases with increased substitutions.

The explanation, according to Ives and Marsden, consists in the fact that the increased substitution increases the radial extent and the stability of hydration in the ionized state.

A second effect of the substituents is that they may interact directly with water. For hydrophobic substituents such as alkyl groups, the interaction with water leads to partial formation of hydrogen bonds around these groups. This has a two-fold effect. One is the fact that water
molecules bonded around the alkyl groups bring a more orderly structure in the solvent. The second effect is the orientation of water about the alkyl groups which gives rise to a loss in the freedom of motion of water molecules and is thought to be the cause of the large decrease in the entropy and the increase in the heat capacity associated with the introduction of saturated hydrocarbons into water\textsuperscript{195}.

The heat capacity increases because the non-polar solute or the non-polar groups in solute molecules cause the water to have more and/or stronger structure\textsuperscript{196} than normal. As the temperature is raised this extra structure "melts" causing extra heat to be absorbed.

This effect is used to explain the variation in the entropy of ionization with the change in substitution in aliphatic acids (chain lengthening and chain branching) in the following way. A disordered region is created outside the hydration shell and the degree of disorder is inversely proportional to the distance from this shell. An alkyl group because of its structure strengthening ability will counteract this disorder thus lowering the entropy of the ion. Thus the entropy of ionization of a branched chain acid should be more negative than that of an unbranched acid\textsuperscript{197}.

Another explanation of the effect of the chain branching and lengthening upon the entropy of ionization is the restrictions imposed on the internal rotations of solute
molecules due to electrostatic and nonelectrostatic contributions 150, 198, 199.

Finally, another phenomenon which could contribute to the value of the entropy of ionization is the so-called "chelation" effect. This is sterically possible, for example, for higher homologues of aliphatic acids and involves the assumption of a coiled configuration of the acid anion which is stabilized by the hydrogen bond linking of the hydrogen of the terminal methyl group with the carboxylate oxygen atom. This effect will promote dissociation and will lower the entropy of the anion.

Attempts to explain the changes in $\Delta S$ with the change in substitution in a more quantitative way have been very few and not successful. We will discuss them in subsection 14.6 when discussing the significance of $\Delta G$ in relation to the molecular structure.

It is worth pointing out again that it is very unlikely that any theory will succeed until the more fundamental questions of water structure and the modes of interaction between the solute and the solvent molecules (solute-solute, solvent-solvent and solute-solvent interactions) are clarified.

In subsection 14.3 we mentioned that arguments involving inductive effects, bond dissociation energies, etc., apply to $\Delta H_{\text{int}}$, only.
However, acetic acid, for example, has an entropy of ionization which is approximately 5 cal/(deg.mol) more negative than that of monochloroacetic acid. This has been attributed to a more oriented structure of the solvent around the polar groups. \textsuperscript{169, 197}

The more negative entropy of ionization of \textit{m}-nitrophenol as compared to that of \textit{p}-nitrophenol was attributed, again, to a more ordered structure around the anion of the former due to its relatively more concentrated charge. A more concentrated charge, presumably, interacts more strongly with the water molecules. \textsuperscript{190}

For the monohalogenated acids the difference in the entropies of ionization was explained by a solvation in the unionized state which is proportional to the field intensity at the halogen atom field, which is inversely proportional to the atomic size (dipole solvation). In the ionized state, however, the presence of the halogen presumably exerts a general leveling effect (how this happens is not clear) leading to entropies of ionization which will increase in their negative values from fluoro- to iodo-acetic acids \textsuperscript{169}.

A last note in connection with the entropies: King\textsuperscript{200}, using the Harned and Robinson expression (13.2.10) has shown that it is absurd to attach too much significance to variations smaller than 0.1 cal/(deg.mol) in $\Delta S^0$. We agree with this, not
so much because of the experimental precision (the experimental precision of \( \Delta S^0 \) can be as high as \( \pm 0.03 \text{ cal/(deg. mol)} \)), but because we cannot interpret these small differences.

14.5 The change in the heat capacity in the ionization of acids in water.

Leffler \(^{191}\) has pointed out that, although from a microscopic point of view the enthalpy, the entropy, and the free energy are fundamental quantities, from the point of view of statistical mechanics they are derivable quantities. The fundamental quantity from the statistical mechanics point of view is the heat capacity. \(^{191}\)

The theoretical calculation of heat capacity of organic molecules together with its experimental determination for temperatures which range from 0 to \( T^0 \text{K} \) would be a very strong connecting link between the experimental physical-organic chemistry and the principles of theoretical chemistry. As the situation stands at the present time, however, the heat capacities cannot be calculated for complex molecules and experimentally the heat capacities are determined from more accessible quantities such as free energies. The heat capacities can be determined directly by calorimetry. Ahluwalia and Cobble \(^{201}\) reported heat capacities determined calorimetrically with an accuracy of 0.5 cal/(deg.mol).
The limited obtainable precision of $\Delta C_p$ values constitutes a hindrance to their use in the interpretation of molecular structure. It is understandable why someone does not attach much significance to differences which are smaller than the experimental precision. However, this is only an easy excuse, because it seems to us that we are not prepared to interpret small differences (see the entropy case!).

The usual experimental precision is of the order of 5-10 cal/(deg.mol)$^{200}$ with a limited number of experimental data claiming precision of the order of $\pm 1-2$ cal/(deg.mol).$^{44,176}$ In this context it seems to us that the precision of the $\Delta C_p$ values given in Everett and Wynne-Jones classical paper $^{168}$ was over-estimated.

As with the other thermodynamic quantities, $\Delta C_p$ can be considered as the sum of two terms:

$$\Delta C_p = \Delta C_{p,ext} + \Delta C_{p,int} \quad (14.5.1)$$

$\Delta C_{p,int}$ refers to reaction (14.3.2) or, according to Ives and Marsden $^{44}$, to the "solute reaction proper":

$$(HA)_{\text{aqueous phase}} \rightleftharpoons (H^+ + A^-)_{\text{aqueous phase}} \quad (14.5.2)$$

The difference between the two definitions consists of the fact that the $\Delta C_p$ of "reaction proper" includes,
besides the effects of the gas phase reaction, all the modifications imposed by the solvent upon the solute such as any decrement of heat capacity due to loss of rotational freedom in the anion as compared with the unionized molecule.

The second part of the $\Delta C_p$ refers to reaction (14.3.3) or, according to Ives and Marsden, to the "associated solvent reaction" expressed by:

$$x H_2O^{HA} + (y + z - x) H_2O^S \rightleftharpoons y H_2O^{H^+} + z H_2O^A^-$$  \hspace{1cm} (14.5.3)

where $H_2O^{HA}$ indicates the hydration of the molecules HA, $H_2O^S$ represents solvent water, and so on.

The two definitions are related because $\Delta C_p$ of reaction (14.5.3) is the major contributor to any $\Delta C_{p,ext}$. Reaction (14.5.3) expresses the fact that the properties of water are modified by the influence of the solute on the solvent. Ives and Marsden give the $\Delta C_p$ for reaction (14.5.3):

$$\Delta C_p^h = (\delta y \over \delta T)_p (\overline{H}_{H_2O^{H^+}} - \overline{H}_{H_2O^S}) +$$

$$+ (\delta z \over \delta T)_p (\overline{H}_{H_2O^{A^-}} - \overline{H}_{H_2O^S}) -$$

$$+ (\delta x \over \delta T)_p (\overline{H}_{H_2O^{HA}} - \overline{H}_{H_2O^S}) +$$

$$+ y(\overline{C}_{p,H_2O^{H^+}} - \overline{C}_{p,H_2O^S}) + z(\overline{C}_{p,H_2O^{A^-}} - \overline{C}_{p,H_2O^S}) -$$

$$- x(\overline{C}_{p,H_2O^{HA}} - \overline{C}_{p,H_2O^S})$$  \hspace{1cm} (14.5.4)
or in more general terms:

\[
\Delta C_p^\text{h} = \left[ n^h (\Delta C_p) + \frac{\delta n^h}{\delta T} (\Delta H) \right] - \\
\left[ n^h (\Delta C_p) + \frac{\delta n^h}{\delta T} (\Delta H) \right]
\]  \hspace{1cm} (14.5.5)

where \( n^h \) terms are \((y+z)\) or \(x\), as appropriate, and \( \Delta C_p \)
and \( \Delta H \) terms can be identified by reference to (14.5.4)
equation (14.5.4). The first term in the RHS of (14.5.5)
relates to the hydration of ions and the second term to
the hydration of molecules.

To summarize, \( \Delta C_p \) of ionization can be divided into:

a. \( \Delta C_p = \Delta C_p,\text{int} + \Delta C_p,\text{ext} \)  \hspace{1cm} (14.5.1)

b. \( \Delta C_p = \Delta C_p,^r + \Delta C_p,^h \)  \hspace{1cm} (14.5.6)

or

c. \( \Delta C_p = \Delta C_p,\text{int} + \Delta C_p,\text{solute}^- + \Delta C_p,\text{solute}^+ + \Delta C_p,\text{solvent}^- \)  \hspace{1cm} (14.5.7)

where \( \Delta C_p,\text{solvent}^- \) refers to the influence of the solvent
upon the solute and \( \Delta C_p,\text{solute}^- \) refers to the influence of
solute upon the solvent.
In the final analysis these divisions are a bit futile since no experimental or theoretical separation of the $\Delta C_p$'s has been devised. It can be said, however, that the dominant term in the RHS of (14.5.7) is the last one, which takes into account the influence of the solute on the solvent structure. The forces by which the solute acts on the solvent and vice versa are 169:

a. short range forces of hydrogen bonding producing co-operative order in the structure of water.
b. short and long range forces of solute-solvent interaction producing short and long range, respectively, non-co-operative order.

It is not clear, yet, if $\Delta C_p$ is a constant with respect to temperature or not. The assumption that $\Delta C_p$ is constant over the usual temperature range of 5-50$^\circ$C fits the majority of kinetic and equilibria data. The relatively high error in $\Delta C_p$'s derived from equilibrium constants or reaction rates is the main hindrance to the solution of this problem. Ives and Marsden 44 reported the only experimental values in which the change in $\Delta C_p$ with the temperature seems to be significant.

The change in $\Delta C_p$ with $T$ or the constancy of $\Delta C_p$ over an interval of temperature both can be explained
qualitatively, at least, by assuming different relative variations of the forces described above with the temperature.

Qualitatively there are different pictures of what actually happens when a molecule goes into solution from the gaseous state and when this molecule dissociates into ions.

There is evidence that nonpolar molecules interact with water forming so-called "icebergs" whose size is directly proportional to the size of the solute molecule and which causes enthalpy and entropy losses. For acids and bases, however, the most important type of water-solute interaction is hydrogen bonding. The presence of a polar group in the molecule of an acid or base may lead to dipole-dipole interactions with water molecules. Both these facts show that the hydration of the initial state plays a role in the final values of $\Delta C_p$ (and $\Delta S$).

In the ionic state the most accepted picture is that of the three regions surrounding an ion:

1. An innermost structure-forming region of polarized, relatively immobilized and electrostricted water molecules.
2. A middle structure-broken region which has a more random organization than the ordinary water.
3. An outer region in which water has its normal liquid structure.

The breaking of the structure in the middle part is due, presumably, to the competition between the two ordered structures which bound this region.

The large, negative heat capacities of ions in solution are due to the loss of kinetic freedom imposed upon the solvent molecules by the ionic field and by the breaking of the structure, which is somewhat like the effect of the temperature rise upon the water structure. The dependence on temperature of all these factors, i.e. the interaction of a multifunctional polar molecule with water, the ionic hydration, etc., is not known and that is why no predictions about the dependence of $\Delta C_p$ on temperature can be made.

Everett and Wynne-Jones \textsuperscript{168} consider that $\Delta C_{p,\text{solute-solvent}}$ is made up of two parts:

1. A first part, called the electrostatic contribution, comprises the phenomena concerned with the restriction of movement of the molecules of the medium. This contribution can be calculated approximately from Born's formula \textsuperscript{202}.

2. A second part is called orientational contribution and
comprises the contribution to $\Delta C_p$ due to hydration of undissociated molecules and ions which was discussed above. This is the major contribution of the two.

The $\Delta C_{p,solvent-solute}$ refers, as was said before, to the influence of the solvent upon the solute. It is concerned with the restriction of the intramolecular rotations and the constraints on the motion of the molecules and ions caused by the surrounding water molecules.

Finally, the third term of expression (14.5.7) $\Delta C_{p,int}$ is generally small and approximately the same for similar acids. King's calculations 203 show that translational, rotational and vibrational motions intrinsic to the molecules and ions have a very minor effect on $\Delta C_p$.

As far as the relationship between $\Delta C_p$ and molecular structure is concerned, again only qualitative pictures are used.

The first thing which is important to note is that since the electrostatic contributions are small and since the hydrogen ion (in whatever form) is the same for all acids, the differences between $\Delta C_p$ of ionization of two or more similar acids come from differences in the orientating power of the anions. The orientation power is controlled by the electrostatic potential near the surface of the ion. The potential depends on:
a. the distribution of the charge in the ion. The more localized the charge, the stronger the orientating power and, therefore, a more negative $\Delta C_p$.

b. a steric effect. If the charge is screened from the solvent by a steric effect, then $\Delta C_p$ has a less negative value.

c. the presence of inductive groups in the molecule which tend to increase or decrease the charge at the carboxyl group.

**Summary.**

We want to summarize here the kind of information which can be obtained from the entropies and the heat capacities of ionization of weak organic acids in water.

The first thing which must be underlined is that the entropy and heat capacity of ionization are not dependent on the internal energy of the molecule ($\Delta E_0$) (see subsection 14.2).

Secondly, it must be noted that both these quantities have negative values.

It is generally agreed that the major contribution to $\Delta S$ and $\Delta C_p$ of ionization comes from the so-called "orientational" effect, which has to do with the reorganization of water structure due to the ionization of the solute. Thus, the main trends and the sign of $\Delta S$ and $\Delta C_p$ are explained
by the various influences the solute exerts on the solvent. It is obvious that, because our lack of knowledge about the detailed structure of the solvent water (pure or containing a solute), these influences are merely working hypotheses or, if stronger terms are used, speculations with some experimental bases, the so-called educated guesses.

A much smaller contribution comes from the action of the solvent on the solute, as is due to the influence the solvent exerts upon the translational, rotational, and vibrational modes of the solute molecules. In this context, the quantity $\Delta S$ is more sensitive to changes in such motions which, combined with its higher accuracy, makes the entropy of ionization a potentially good source of information about the changes in molecular motions in ionization and how they relate to various substituents or, in more general terms, how they relate to the molecular structure. Here again we do not know the details of such motions and this is an obvious hindrance to any interpretation of this kind.

14.6 The free energy of ionization in relation to molecular structure.

It was shown in subsection 14.2 that if the zero point energy change of ionization, $\Delta H_0$, is inaccessible,
then $\Delta G$ is the thermodynamic function which approaches it better than any other function because $\Delta G$ is much less sensitive to complications introduced by the solvent. Alternatively, Hepler has proposed the use of $\Delta H_{\text{int}}$ as a criterion for discussing resonance stabilization, inductive effects and the like.

The quantity $\Delta G$ is preferred to $\Delta H_{\text{int}}$ because it is obtained directly as an experimental quantity, while $\Delta H_{\text{int}}$ is obtainable by calculation in only a very approximate form.

Particular care should be taken when comparing the free energies of ionization of different acids, or in essence the dissociation constants, because according to (13.2.1):

$$\log K = \log K_\text{M} - 1(T - T_\text{M})^2$$

(13.2.1)

each acid has a specific temperature at which the dissociation constant attains its maximum value though, for a large number of acids, the quantity "1" has nearly the same value: $5.0 \times 10^{-5}$ deg$^{-2}$ 166.

As with the other thermodynamic functions $\Delta G$ can be considered as made up from:

$$\Delta G = \Delta G_{\text{int}} + \Delta G_{\text{ext}}$$

(14.6.1)
In the simplest semi-quantitative approach, $\Delta G_{\text{int}}$ is assumed to be independent of temperature and $\Delta G_{\text{ext}}$ to be of electrostatic origin.

According to Born's formula, the part of electrostatic origin is given by:

$$\Delta G_{\text{el}} = \frac{N e^2}{2D} \left( \sum_{\text{products}} \frac{z^2}{r} - \sum_{\text{reactants}} \frac{z^2}{r} \right) \quad (14.6.2)$$

D: dielectric constant

The other thermodynamic functions are obtained by the differentiation of (14.6.2). The usual assumption in differentiation is that function $\phi$:

$$\phi = \sum_{\text{products}} \frac{z^2}{r} - \sum_{\text{reactants}} \frac{z^2}{r} \quad (14.6.3)$$

is independent of temperature; this is because very little is known about its dependence on $T$. Thus the expression which is obtained for $\Delta S$, for example, is:

$$\Delta S_{\text{el}} = C \phi_{\epsilon} \frac{\delta \ln D}{\delta T} p = C \phi_{\epsilon} \frac{\delta}{\delta T} \left( \frac{1}{D} \right) \quad (14.6.4)$$

where:

$$C = \frac{N e^2}{2}$$

Other electrostatic theories which have been proposed are those of Bjerrum and of Kirkwood and Westheimer.

These theories were, at their best, only partially
successful. Various authors 44, 205 have discussed their applicability and their limitations and we do not intend to repeat the arguments here because they are not relevant to our problem.

A different and a more complete approach is to consider the dissociation constant given by 206:

$$K_p = Q \exp(-\Delta E/RT)$$  \hspace{1cm} \text{ (14.6.5)}

where:

$$Q = \frac{Q_{H^+} Q_{A^-}}{Q_{HA}}$$  \hspace{1cm} \text{ (14.6.6)}

is the ratio of partition functions (the electronic partition functions are omitted) and $\Delta E$ is the energy difference between the ions and acid molecule. It is formed from the following contributions:

$$\Delta E = \Delta E_\sigma + \Delta E_\pi + \Delta E_{st} + \Delta E_s(T)$$  \hspace{1cm} \text{ (14.6.7)}

$\Delta E_\sigma$ is the energy difference associated with localized bonds; $\Delta E_\pi$ is associated with delocalized bonds; $\Delta E_{st}$ corresponds to the interaction between nonbonded atoms and includes what is usually called the steric hindrance energy and finally $\Delta E_s(T)$ is connected with the solvation energy and is the only term which is temperature dependent.

Some theoretical calculations have been carried out for some of the individual terms of (14.6.7), e.g.
However, no spectacular success has been reported. The last quantitative approach to the relationship between structure and acidity we want to discuss is the Hammett and Ingold-Taft equations. These equations exemplify a different approach to the problem from those mentioned so far. The problem of finding some quantitative relationship between the structure and dissociation constants or reaction rates was approached from the experimental side: first empirical correlations were found from the experimental results and only later were they explained and still are being explained from a theoretical point of view.

The Hammett treatment and Taft extension work deal with the following type of reactions:

\[ \text{R}_0\text{Y} + \text{Z} \leftrightarrow \text{P}_0; \text{Equilibrium constant: K}_0 \]  

(14.6.8)

\[ \text{RY} + \text{Z} \leftrightarrow \text{P}; \text{Equilibrium constant: K} \]  

(14.6.9)

where Z is a reagent in the broader sense of the work, i.e. encompassing the reagent itself and the conditions of the reaction as well. \( \text{P}_0 \) and P are products. \( \text{R}_0\text{Y} \) is an arbitrary standard reagent where \( \text{R}_0 \) is a radical or a substituent and Y is a functional group. The alteration of the structure from \( \text{R}_0 \) to R changes the equilibrium constant
of the reaction from $K_o$ to $K$. The Hammett and Ingold-Taft equations predict the value of $K$, knowing $K_o$ and the structural changes involved.

The difference between the standard free energy changes in reactions (14.6.8) and (14.6.9) is:

$$\Delta \Delta G^0 = \Delta G^0(14.6.9) - \Delta G^0(14.6.8) =$$

$$\Delta \Delta E - RT \ln(\Pi Q) \quad (14.6.10)$$

$\Delta \Delta E$ is the potential energy (to a good approximation this is the ground state electronic energy) change accompanying the combination of reactions (14.6.8) and (14.6.9), i.e. the reaction:

$$RY + P_o \rightleftharpoons R_o Y + P; \text{Equilibrium constant:} \frac{K}{K_o} \quad (14.6.11)$$

$Q$ is the ratio of partition functions:

$$\frac{Q_{R_o Y} Q_P}{Q_{R Y} Q_{P_o}} \quad (14.6.12)$$

The $\Delta \Delta E$ term is considered to be the sum of:

$$\Delta \Delta E = \Delta \Delta E_p + \Delta \Delta E_r + \Delta \Delta E_s \quad (14.6.13)$$

$\Delta \Delta E_p$ is due to the polar interactions between the groups $R$ and $Y$. They are associated with coulombic forces which result from charge separation within the groups $R$ and $Y$. 
Polar interactions are transmitted through $\sigma$-bonds or by direct, spatial interaction.

$\Delta\Delta E_r$ reflects the resonance interactions and $\Delta\Delta E_s$ expresses the steric interactions. Equation (14.6.13) is very similar to (14.6.7). $E_p$ can be equated to $E_o$, $E_r$ to $E_n$, and $E_s$ to $E_{st}$. The solvation effects were not considered as a separate entity in this treatment, but rather as a part of each of the three interactions listed above.

The Hammett equation is:

$$\log \frac{K}{K_0} = \rho \sigma = \rho \log \frac{K'}{K'_0} \quad (14.6.14)$$

where $K$ is the ionization constant of an acid with the general formula:

$$X - R - Y \quad Y = -\text{COOH}$$

in which $X$ is a given substituent. $K_0$ is the ionization constant of the same acid with $X = H$. $K'$ is the ionization constant of benzoic acid containing substituent $X$ in the molecule and $K'_0$ is the ionization constant of benzoic acid, both these ionizations being considered in water and at 25°C.

The Hammett equation applies specifically to meta and para substituted benzene derivatives. For these compounds it is assumed that the only non-zero term in equation (14.6.12) is $\Delta\Delta E_p$, i.e.:
\[ \Delta G^0 = \Delta G_p \]

Different justifications were given for this approximation. One of them, that of Hepler, seems to be clearer than the other explanations, though it is not any more rigorous.

The explanation is based on a series of assumptions already presented when discussing the significance of entropy of ionization (subsection 14.4). The enthalpy and the entropy of reaction (14.6.11) are considered to be sums of internal and external contributions:

\[ \Delta H = \Delta H_{\text{int}} + \Delta H_{\text{ext}} \]
\[ \Delta S = \Delta S_{\text{int}} + \Delta S_{\text{ext}} \]

\(\Delta S_{\text{int}}\) for a reaction such as (14.6.11) is very close to zero (see subsection 14.4). Then:

\[ \Delta S = \Delta S_{\text{ext}} \]

As pointed out in (14.3.9), \(\Delta H_{\text{ext}}\) is linearly related to \(\Delta S\) 191-193:

\[ \Delta H_{\text{ext}} = \beta \Delta S \quad (14.3.9) \]

where \(\beta\) has the dimensions of absolute temperature and is characteristic of a certain series of reactions. For reaction (14.6.11):

\[ \Delta G^0 = \Delta H - T\Delta S \]
which can be rearranged to:

\[
\frac{\Delta G^0}{\Delta H_{\text{int}}} = 1 + \frac{(b - T)\Delta S}{\Delta H_{\text{int}}} \tag{14.6.15}
\]

In general the second term on the RHS of (14.6.15) is much smaller than 1 and thus:

\[\Delta G^0 = \Delta H_{\text{int}}\]

Comparing this with the Hammett equation:

\[\log \frac{K}{K_0} = \rho \sigma\]

and with:

\[\Delta \Delta G^0 = -RT \ln \frac{K}{K_0}\]

Hence:

\[\rho \sigma = -\frac{\Delta \Delta G^0}{2.303 RT} = -\frac{\Delta \Delta H_{\text{int}}}{2.303 RT} = \frac{\Delta \Delta H_{\text{int}}}{2.303 RT}\]

\[\left[\frac{C}{2.303 RT}\right] \left[\frac{-\Delta \Delta H_{\text{int}}}{C}\right] \tag{14.6.16}\]

\(\rho\) is identified with \(C/(2.303 \text{ RT})\) and \(\sigma\) with \(-\Delta \Delta H_{\text{int}}/C\)

Jaffé \(^{210}\) has shown that \(\rho\) is linear in \(1/T\) as equation (14.6.16) predicts and Helper has shown that \(\sigma^*\)'s (Taft constants) are proportional to \(\Delta \Delta H_{\text{int}}\) values.

It must be pointed out that this demonstration is valid for a given solvent only, and it was given originally for the water case.
$\Delta \Delta H_{\text{int}}$ is not, by definition, dependent on the solvation energies. $\Delta \Delta E_r$ and $\Delta \Delta E_s$ have been expected to be negligible for the majority of meta and para substituted benzene derivatives (when they are not, the Hammett equation is not applicable in the form 14.6.14). Therefore, the only contribution to $\Delta \Delta H_{\text{int}}$, which we recall approximates $\Delta \Delta \text{G}^0$ is $\Delta \Delta E_p$. Thus the constant $\sigma$ is a measure of the electron withdrawing ($\sigma$ positive) or electron donating ($\sigma$ negative) power of a substituent $X$ as compared with hydrogen ($\sigma=0$). The polar effects can be further divided into 213:

a. inductive polar effects which act along single bonds and by a direct electrostatic effect which acts through the space ($\sigma'$).

b. resonance polar effects within the substituent $R$. This effect must be clearly distinguished from the resonance effects which involve both $R$ and $Y$ (one way to define resonance interaction is to say that it requires at least two valence bond structures or canonical forms for the $R - Y$ bond).

Roberts and Moreland $^{214}$ obtained, independently, the $\sigma'$ values for a series of substituents. They used a close geometrical model of the benzene ring, namely the completely saturated bicyclo $2.2.2$ octane ring in the 4-substituted bicyclo$[2.2.2]$octane-1-carboxylic acids
and esters. Because the compounds were saturated, the only effect present was the inductive polar effect. Once this effect is known, the differences:

\[
\sigma_p - \sigma' \quad \text{and} \quad \sigma_m - \sigma'
\]

should give the polar resonance contribution. As expected, \((\sigma_m - \sigma')\) values are small though, interestingly enough, not zero; in general, they are approximately 1/3 of the value of \((\sigma_p - \sigma')\). Two explanations are available for the non-zero values of the \((\sigma_m - \sigma')\) difference. The first one is that, because of the shorter distance to the reaction center, the inductive effect is somewhat larger in the meta position. The second explanation is that the meta position has some resonance interaction with the ortho position, which in turn influences the reaction center.

The proportionality constant \(\rho\) depends on the conditions and the nature of the reaction. It is a measure of the susceptibility of a given reaction series to polar substituents. The reference reaction and solvent are the ionization of benzoic acids in water at 25\(^{\circ}\)C for which \(\rho = 1\).

By far the most usual assumption about \(\rho\) is that it is the same for the meta and para positions of the benzene ring. As expected, because of the special effects
affecting the ortho position, this position is not considered in the present argument (see "ortho effect" in this subsection).

Hine 218 has shown, however, that this equality does not hold and that, to fit the available equilibrium constants of meta and para substituted benzenes, different \( \rho \) constants should be used, i.e. a \( \rho_p \) and a \( \rho_m \).

When the resonance interaction between substituents in the meta and para position and the reaction center (or functional group) is non-zero, the Hammett equation in the form given by (14.6.14) does not apply. A new term has to be added to take care of this situation:

\[
\log \frac{K}{K_0} = \sigma_p + \psi
\]  

(14.6.17)

where \( \sigma_p \) gives the polar effect, as before, and \( \psi \) is related to the resonance effect.

A last point we want to examine and which is directly connected with the present work is the so-called "ortho effect". Before doing so however, it is necessary to examine another linear free energy relation developed by Taft.

**Ingold-Taft equation** (A generalised Hammett equation) 216,217

As stated before, the original Hammett equation applies to meta and para substituted benzenes in which the substituents are far away from the reaction center. Taft 217
proposed a generalised form of the Hammett equation which is applicable to compounds with substituents adjoining the reaction center in both aliphatic and aromatic compounds:

$$\log \frac{k}{k_0} = \rho^* \sigma^*$$  \hspace{1cm} (14.6.18)

The constant $\rho^*$ gives the susceptibility of a given reaction series to polar substituents. Note that since (14.6.18) measures the proportionality of the polar effects, the other interactions, i.e. steric and resonance, must remain constant within the reaction series.

The constant $\sigma^*$ is defined by the relationship:

$$\sigma^* = \frac{1}{2.48} \left[ \log \left( \frac{k}{k_0} \right)_B - \log \left( \frac{k}{k_0} \right)_A \right]$$  \hspace{1cm} (14.6.19)

This equation applies to rates of hydrolysis of esters of the type RCOOR' and measures the net polar effect of substituent R directly adjoining the reaction centre.

In (14.6.19) $k$ refers to the rate of hydrolysis of a given compound and $k_0$ to the rate of hydrolysis of the standard compound (benzoate esters - aromatic series and acetate esters - aliphatic series). The subscript A refers to acidic conditions and B to basic conditions.

The basic assumptions of equation (14.6.19) are:

a. steric and resonance effects do not change in changing
from acidic to alkaline hydrolysis;
b. the acidic hydrolysis is, to a good approximation, not dependent on polar effects.
As with the $\sigma$ constants, $\sigma^*$'s are negative for electron-releasing substituents and positive for electron-withdrawing substituents.

We recall that $\sigma'$ constants measured the inductive polar effects of meta and para substituents of the benzene ring. Since both these constants, i.e. $\sigma'$ and $\sigma^*$, measure the same polar effect, the ratio of the two must be a constant. This is indeed the case, the ratio being:

$$\frac{\sigma'}{\sigma^*} = +0.450 \quad (14.6.20)$$

**Steric effect constant.**

Since the acidic hydrolysis of esters is not dependent on the polar effects to a great extent ($\rho^*$ is small = -0.2 to +0.5), the ratio:

$$\log\left(\frac{K}{K_0}\right)_A = E_s \quad (14.6.21)$$
could be a measure of the total steric and resonance effects of a given substituent relative to a standard. Taft considers $E_s$ as being a measure of the total steric effect only, not being at all clear where the resonance effect is taken in the consideration.
For aliphatic compounds, $E_s$ values for a series of substituents in $\alpha$- and $\beta$- positions can be directly related to the effective size of the substituent (Van der Waals radii given by Pauling)\(^{219}\).

There is one important difference between the polar constants and the steric and resonance constants $E_s$: $\sigma$'s are additive while $E_s$'s are not.

Another way to calculate the steric effect is to use relation:

$$\log\frac{k}{k_0} = \sigma \rho + \psi \quad (14.6.22)$$

We recall that $\psi$ measured the resonance effect between substituents in para and meta positions of the benzene ring and the reaction center. The constant $\psi$ can be used to measure the steric effects of a substituent when such a substituent does not have any resonance interaction with the reaction center. In this context it was observed that for the ionization of a normal series of 4-substituted-2, 6-dimethylbenzoic acids, (i.e. substituents without resonance interaction with the functional group), $\psi$ remains constant and therefore can be considered as a measure of the steric effects of the two methyl groups adjacent to the carboxyl group \(^{220}\).

A Hammett-type equation which expresses the
proportionality between the rates of reactions or equilibrium constants and the steric requirements of the substituents was given by Taft in the form of:

$$\log \frac{k}{k_0} = \delta E_s$$  \hspace{1cm} (14.6.23)

where $\delta$ is a reaction constant independent of the nature of the substituent. Relation (14.6.23) has a much smaller range of validity as compared with the Hammett equation. A number of reactions which follow (14.6.23) is given by Taft.

The factors which contribute to $\sigma^*$ values are:

a. intrinsic electronegativities of the atoms of the substituent groups especially that of the first atom of the group;
b. resonance within the group;
c. electrostatic field effects especially from unpaired electrons within the group;
d. hybridization; and
e. electron density of the first atom of the group.

Qualitatively, $\sigma^*$ constants can be correlated with the Pauling electronegativity values and with the bond charge separation (obtained by dividing the bond moment by the interatomic distance.).

When both the polar effects and the steric effects vary simultaneously with the nature of the substituent, then a more general equation has to be used:
\[ \log \frac{k}{k_0} = \rho \sigma^* + \delta E_s \]  

(14.6.24)

where the symbols have the same significance as before.

The "ortho-effect".

This effect is of particular interest for the present work. One of the assumptions on which the Hammett equation is based is that steric interactions between the substituent and the functional group, i.e. term \( \Delta E_s \) of (14.6.13), is zero. Indeed it was observed that the equation does not apply to derivatives of benzene with ortho-substituents, for example. Peltier 223 has shown that in such compounds there are in effect two types of steric interactions operating.

1. An external steric effect which represents an actual steric blockage to the reagent approach. This effect, obviously, is a function of the volume of the substituent in the ortho position.

2. An internal steric effect due to steric proximity of the substituent(s) and the functional group. This effect acts by deflecting the functional group out from the plane of the benzene ring. This deflection results in a change in conjugation which, in its turn, affects the polar and resonance effects.

In the specific case of benzoic acids, the reaction:
\[ R - \text{COOH} \rightleftharpoons R - \text{COO}^- + H^+ \]

is probably very little affected by the external steric effect because of the small size of the proton. Therefore, the effect to be considered is the internal steric effect. The dissociation constant of benzoic acid is approximately three times as small as that of formic acid. This is attributed to the conjugation which exists between the ring and the carboxyl group in benzoic acid. This conjugation has a net effect of diminishing the partial positive charge which exists on the carbon atom of the carboxyl group with consequent decrease in the acidity. The effect of an ortho substituent, e.g. a methyl group, is to decrease the conjugation by deflecting the carboxyl group out of the plane of the benzene ring. According to Smith the resonance interaction decreases very rapidly with increase in the angle between the plane of the ring and the plane of the carboxyl group, becoming negligible for an angle of 60°. 224 Therefore, any effect which decreases the conjugation will increase the acidity.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{COO}^-
\end{array}
\]

Therefore, the deflection of the carboxyl group out of the
ring plane will always increase the dissociation constant. Similarly the resonance interaction between the substituent and the functional group will be decreased by the deflection of the substituent out of the plane of the benzene ring. On the other hand, the inductive effect is assumed not to be affected by this deflection.

Certainly when we talk about ortho substituents, we must not forget the solvent effect on the dissociation constant, which plays a very important role. It is very likely that, in the case of ortho-substituted benzoic acids, the solvent acts in the way which was postulated by Ives and Marsden to explain the effects of chain branching and lengthening upon the acidity of aliphatic acids (see 14.5), i.e. the substituent increases the number of water molecules under the influence of the negative charge of the anion and increases the stability of the solvation with consequent decrease in the entropy of ionization. The standard entropy of ionization of o-toluic acid is approximately 5 cal/(deg.mol) more negative than that of m- or p-toluic acids, (see also subsection 14.7).

If all other effects but the steric ones remained the same for para- and ortho- substituted compounds (a very unlikely situation), the steric interaction could be measured from the ratio :
\[
\frac{K_{\text{ortho}}}{K_{\text{para}}}
\]

Finally, it has been shown by various authors \cite{220,223,226} that the additivity rule does not hold for polysubstituted benzene derivatives. This is undoubtedly a result of the steric interactions between the substituents and the functional group on one hand and the various substituents among themselves on the other hand.

Note that in the discussion about free energy of ionization and molecular structure, no mention was made about the ratio of the partition functions of expression (14.6.5) or (14.6.10).

Consider again the two basic equilibria:

\[
\begin{align*}
R_0Y + Z & \rightleftharpoons P_0 \quad \text{Equilibrium constant: } K_0 \quad (14.6.8) \\
RY + Z & \rightleftharpoons P \quad \text{Equilibrium constant: } K \quad (14.6.9)
\end{align*}
\]

\[
RY + P_0 \rightleftharpoons R_0Y + P
\]

where, say, \(R_0Y\) and \(RY\) are two similar acids. The ratio of the two equilibrium constants is given by:

\[
\frac{K}{K_0} = \frac{Q_{R_0Y} \cdot Q_P}{Q_{RY} \cdot Q_{P_0}} \exp\left(\frac{\Delta E - \Delta E_0}{RT}\right) \quad (14.6.25)
\]

and:
\[ \Delta \Delta G^0 = -RT \ln \frac{K}{K_0} = -RT \ln \left( \frac{Q_{RO}Q_P}{Q_{RY}Q_{PO}} \right) + \Delta \Delta E \]  

(14.6.26)

The common procedure is to assume that any difference in \( \Delta \Delta G^0 \) is due to differences in the various contributions making up \( \Delta \Delta E \). This assumption is widespread, probably because "it is not possible as yet to calculate their ratio (viz. of partition functions) for an equilibrium in solution from statistical theory"\textsuperscript{130}.

This statement in our opinion overlooks an important paper which appeared a few years ago. We are referring to the paper by Bell and Crooks \textsuperscript{7} in which the difference between the dissociation constants of formic and formic-d\textsubscript{1} acids was rationalized in terms of zero point energy difference and translational, rotational and vibrational partition function contributions.

The two equilibria involved in this study are:

\[ \text{HCOOH} \rightleftharpoons \text{HCOO}^- + \text{H}^+ \quad \text{Equilibrium constant: } K_H \]

\[ \text{DCOOH} \rightleftharpoons \text{DCOO}^- + \text{H}^+ \quad \text{Equilibrium constant: } K_D \]

These two reactions are completely analogous to reactions (14.6.8) and (14.6.9). Because of this obvious analogy, it is surprising that no similar treatment was tried to explain the change in the dissociating constant with different substituent groups in molecule in the case of two similar acids. The treatment is not simple, and what
is more important, it requires the complete analysis of
the infrared and Raman spectra of all the species involved.
This type of data is particularly scarce in the literature.

We propose, however, as a separate part of this
work, to carry out such a calculation in the series of
benzoic, o-toluic and phenylacetic acids (see sections
18 - 20).

14.7 A discussion of the thermodynamic functions of ionization
of benzoic, toluic and mesitoic acids.

The results obtained in the present work for the
thermodynamic functions of ionization of benzoic acid and
a series of methyl-substituted benzoic acids are collected
in table 14.7.1. It has been pointed out before (see, for
example, subsection 8.6) that we do not want to attach any
significance to the values of $d(\Delta C^0_p)/dT$ obtained here
because of the small values these quantities have through-
out this work and because of their relative high errors.
This is why we limit our discussion to the values given in
table 14.7.1. This discussion is essentially of a
qualitative nature.

In this section we have reviewed, so far, some of
the interpretations given to the thermodynamic functions
in relation to molecular structure. It has been shown that
a thermodynamic quantity of ionization can be considered
as being formed from two parts:

\[ \Delta X = \Delta X_{\text{int}} + \Delta X_{\text{ext}} \]  

(14.3.6)

The first component, \( \Delta X_{\text{int}} \), is an internal part, intrinsic to the molecules and ions; the second component, \( \Delta X_{\text{ext}} \), is an external part arising from the interaction of solute molecules and ions with the solvent molecules.

The standard free energies (\( \Delta G^0 \)) of ionization.

In subsection 14.2 we have argued that the free energies of ionization are the thermodynamic quantities which reflect best the changes in the molecular structures, or, in other words, are better than the enthalpies of ionization for comparison with molecular models. At zero kelvins and in absolute vacuum, the free energies and the enthalpies become equal. Therefore, if we accept this point of view, the effect of changes in molecular structure, e.g. replacing a hydrogen atom of the benzene ring in benzoic acid by a methyl group, should be better reflected in the \( \Delta G^0 \) of ionization. From table 14.7.1 we find that the order of the \( \Delta G^0 \) of ionization is:

mesitoic < o-toluic < benzoic < m-toluic < p-toluic

This is a well-known sequence. The lowering of the dissociation constant of benzoic acid by a methyl group
in the meta position has been explained by the electron-supplying inductive effect of the methyl group (+I) which stabilized the undissociated acid molecule, due to the fact that the two nearest ends of the two "dipoles" have opposite sign 227:

\[ \text{H}_3\text{C}^+ \text{CO}_2\text{H} \]

and destabilizes the respective anion because of the interaction between the negative charge on the carboxylate group and the negative end of the "dipole":

\[ \text{H}_3\text{C}^- \text{CO}_2^- \]

The further decrease in the dissociation constant (or increase in $\Delta G^0$) in going to p-toluic acid is explained by the additional resonance effect (+R) of a methyl group in the para position. It is true that the +I effect should be less effective in this position than it is in the meta position because it is farther away from the reaction center; however, this decrease is more than offset by the +R effect 228.

In o-toluic acid a new effect comes in: the steric effect. UV work has shown that in o-toluic acid the plane
of the carboxyl group is twisted with respect to the plane of the benzene ring. The angle between the two planes is 36°. The effect of this twisting is to decrease the π-electron delocalization between the ring and the carboxyl group. This leads to a destabilization of the acid as compared with benzoic acid and thus leads to a net decrease in the free energy of ionization of o-toluic acid. As expected, two ortho-methyl groups in 2,6-dimethylbenzoic acid or in mesitoic acid, for example, increase even more the angle between the carboxyl group plane and the ring plane (in 2,6-dimethylbenzoic acid the angle is 62° by UV work 229 and 53° by X-ray methods 230). The π-electron delocalization is further diminished, leading to even larger dissociation constants. Note that, as expected, the carbon-carbon bond between the carboxyl group and the ring increases in length from benzoic acid (1.48 Å) to 2,6-dimethylbenzoic acid (1.525 Å). 231

The enthalpies of ionization.

To analyse the change in ΔH° with the position of the methyl substituent on the benzene ring, we refer to expression (14.3.8):

$$\Delta H^o = \Delta H_{\text{int}} + \Delta H_{\text{ext}}$$  \hspace{1cm} (14.3.8)

If we try to arrange the acids of table 14.7.1 on a scale according to their ΔH° values, the job is difficult, since the acids change places on this relative scale as the
temperature changes. The job becomes easy, however, if we refer instead to \( \Delta H_{\text{int}} \) and \( \Delta H_{\text{ext}} \) values. These two quantities can be calculated from the Hepler relation:

\[
\Delta H^0 = \Delta H_{\text{int}} + \beta \Delta S_{\text{ext}}
\]

(14.3.10)

The values of \( \Delta S_{\text{ext}} \) and \( \Delta H_{\text{int}} \) for the five acids are given in table 14.7.2. Two assumptions were made in compiling this table:

1. \( \beta = 280^\circ K \)
   
2. \( \Delta S_{\text{ext}} = \Delta S^0 \)

As expected, the \( \Delta H_{\text{int}} \) values follow the same sequence as \( \Delta G^0 \) values and they are temperature independent (see subsection 14.6).

In table 14.7.3 we have calculated the double differences:

\[
\Delta \Delta H^0 = \Delta H^0 \text{ (methyl-substituted benzoic acid)} -
\]

\[
\Delta H^0 \text{ (benzoic acid)} = \Delta \Delta H_{\text{int}} + \beta \Delta \Delta S_{\text{ext}}
\]

Again, as expected, the \( \Delta \Delta H_{\text{int}} \) values follow the same sequence as the \( \Delta \Delta G^0 \) values and, moreover, the two quantities are approximately equal. This shows that the contribution from the differences in the hydrational stabilization energies to the overall free energy differences is small. The positive \( \Delta \Delta H_{\text{int}} \) values for \( m \)-toluic and \( p \)-toluic acids
reflect the stabilization, as compared with benzoic acid, of these acids by the inductive and electron delocalization (in the case of \( p \)-toluic acid) effects, and reflect the destabilization of their anions as compared with the benzoate anion. Similarly, the negative values for \( \Delta \Delta H_{\text{int}} \) for \( o \)-toluic and mesitoic acids reflect the destabilization of the acids as they are compared with benzoic acid.

The entropies of ionization.

Two other papers in the literature give the entropies of ionization of benzoic acid and some methyl-substituted benzoic acids. Unfortunately, one of them does not discuss the entropy values at all and the other one makes only a brief reference to them.

The interesting feature of the experimental result for the entropy of ionization of methyl-substituted benzoic acids is that the ortho-substituted compounds show a more negative entropy than benzoic acid or other methyl-substituted benzoic acids (\( m \)-toluic and \( p \)-toluic acids, for example, have approximately the same entropy of ionization as benzoic acid). In subsections 14.3 and 14.4 we have shown that the entropy change in the ionization of an acid can be assumed to be due almost entirely to changes in the solute-solvent and solvent-solvent interactions. This assumption is even more valid for the differences in the
entropies of ionization of similar acids.

The effect of an ortho group resembles the effect of chain branching at the α-carbon in the series of straight chain carboxylic acids. King and King have explained that the more negative entropy of ionization of branched acids is due to differences in the entropies of the respective ions. They assumed that in the ionization process, a first hydration shell of highly ordered and tightly bound water molecules forms around the carboxylate group, and a disordered region is created outside this innermost solvation shell. The first region does not extend at all or extends only slightly towards the back of the charged group. An alkyl group will project into the disordered region and because of its strengthening ability will counteract this disorder making, in this way, the positive contribution of the disordered region to the entropy is smaller. The entropy of ionization of a branched chain acid should, therefore, be more negative than that of an unbranched acid. An alternative explanation proposed by King and King is that the compressed, tightly bound water about charged groups, e.g. the carboxylate group, could restrict rotation of alkyl groups next to them. They estimated an entropy decrease due to such an effect to be 1-2 cal/(mol.deg) for a methyl group.
Ives and Marsden 44, disagreeing with the above explanations, proposed a new one: the branching of the chain increases the radial extent and the stability of hydration in the ionized state. Such an effect lowers the entropy of the ionized state and therefore the branched acids would have a more negative entropy of ionization.

In trying to explain the more negative entropy of ionization of o-toluic and mesitoic acids and the almost equal entropy of ionization of m- and p-toluic as compared with benzoic acid, we prefer the explanation of the restricted internal rotation. The same explanation has been used by Hamilton and Robertson to rationalize the entropy of activation in the hydrolysis of methyl esters of a series of alkyl-substituted benzenesulphonates in water. They estimated that the loss in entropy due to restricted rotation of a methyl group is approximately 2 cal/(mol.deg). This value fits our experimental data well. The rotations of the meta and para methyl groups are not affected by the primary solvation shell of the negatively charged carboxylate group and, therefore, the entropies of ionization of these two acids are approximately equal to the entropy of ionization of benzoic acid. In the o-toluic and mesitoic acids the restricted rotations of the methyl groups result in a loss of entropy of approximately 2.5 and 5 ca./(mol.deg), respectively.
It must be said, however, that any of the other two explanations could rationalize our experimental data as well.

**The heat capacities of ionization.**

The values obtained in the present work for the heat capacities of ionization of benzoic, toluic and mesitoic acids were somewhat surprising, especially when compared with each other. The paper by Everett and Wynne-Jones \(^{168}\) is the only published work giving the heat capacities of ionization of the same acids (except mesitoic acid). The agreement between the two sets is fair for benzoic acid and poor for the toluic acids.

It is known at the present time, that non-polar solutes promote structure formation in water or, in other words, more and/or stronger water-water H-bonds exist in solution than in pure water \(^{196, 232}\). Different terms have been used for this type of "hydration". \(^{233}\) We prefer the term of "intensified" structure because it gives an actual physical feeling of what is happening in solution.

When a molecule ionizes, the electric field of the ion decouples the H-bonds between water molecules and thus, upon ionization, extensive solvent reorganization
takes place in the solution, shown by the large changes in the entropies and the heat capacities of ionization. The currently accepted picture of water-ion interaction is that of a primary hydration shell of tightly bound water molecules followed by a secondary shell of "more fluid than normal" water and finally the "normal" water. The large negative heat capacities of ionization are probably due to the loss in the kinetic freedom imposed upon solvent molecules, participating in the first hydration shell of the ions, combined with the breaking down of the "intensified" structure which existed around the undissociated acid molecules. The second of these phenomena could explain qualitatively why the heat capacity of ionization of \textit{m}- and \textit{p}-toluic acids is more negative than that of benzoic acid: more of the "intensified" water structure exists around the molecules of the two toluic acids than around the benzoic acid molecule. Upon ionization, therefore, more structure is broken down in the case of \textit{m}- and \textit{p}-toluic acids leading to more negative heat capacities. The negative contribution to the heat capacity of ionization of the first hydration shell around the anion is probably almost the same for these three acids. One might argue that the methyl groups in \textit{m}-toluic and \textit{p}-toluic acids are far from the carboxyl group (6-8 Å) and therefore the solvent structure around them is not broken down or indeed is not affected by the ionization process. King and King\textsuperscript{197} assumed, arbitrarily, that the range of influence of the carboxylate group is about 5 Å. Ives
and Marsden, however, have strongly objected against this value: they felt that it must be increased although they did not propose any new limit.

The less negative heat capacity of ionization of o-toluic acid as compared with the two other toluic acids can be explained if we consider the following:

a. The "intensified" structure around the methyl group in an ortho position is less than that around a methyl group in the para position. Indeed, because of the proximity of the carboxylate and methyl group, in o-toluic acid the total "intensified" structure around the molecule is certainly less than that around a molecule of p-toluic acid, for example. Therefore there is a smaller amount of water structure to be "melted" during the ionization process of o-toluic acid as compared, say, to p-toluic acid.

b. The proximity of the methyl and the carboxylate group inhibit to some extent the tight solvation characteristic of the ionized state. If the water molecules from this first solvation shell of the o-toluate ion have somewhat more rotational freedom than the water molecules in the first hydration shell of the m- or p-toluate ion, this will tend to make \( \Delta C_p^0 \) of ionization of o-toluic acid more positive as compared with \( \Delta C_p^0 \) of m- or p-toluic acid.

c. Finally, one has to consider the effect of the rotation
of the methyl group on the heat capacities of ionization of toluic acids. We can assume that in the ionized state the methyl group in all three toluic acids has its rotation restricted because of the tight solvation characteristic for this state. Also, we can keep in mind the fact that $\Delta C^0_P$ is the difference between the heat capacity of the anion and the heat capacity of the undissociated acid. In the undissociated $o$-toluic acid the rotation of the methyl group is much more restricted than in the two other undissociated toluic acids. Therefore, the net change in the rotation of the methyl group is smaller in the case of $o$-toluic acid than in $m$- or $p$-toluic acid. Consequently the negative contribution to the heat capacity of ionization is larger in the case of $m$- and $p$-toluic acids than in the case of $o$-toluic acid.

Obviously the net difference between the heat capacities of ionization of benzoic and toluic acids is a combination of these factors and probably others.

In the case of mesitoic acid, the situation is even more complex because of the increased substitution. The factors which affect the heat capacity of ionization of the toluic acids affect also the heat capacity of ionization of mesitoic acid. The relative contributions of each
of these factors are changed, however, leading to a heat capacity that is slightly different from that of o-toluic acid as expected.
Table 14.7.1. The thermodynamic functions for the ionization of some methyl substituted benzoic acids. Results obtained from Clarke & Glew formula with 3 coefficients.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$K 	imes 10^5$ *</th>
<th>$pK*$</th>
<th>$\Delta G^0$ cal/mol</th>
<th>$\Delta H^0$ cal/mol</th>
<th>$\Delta S^0$ cal/(deg.mol)</th>
<th>$\Delta C_p^0$ cal/(deg.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>6.226</td>
<td>4.2058</td>
<td>5641.5 ±0.1</td>
<td>241 ±8</td>
<td>-18.42 ±0.03</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>6.249</td>
<td>4.2042</td>
<td>5735.5 ±0.1</td>
<td>14 ±5</td>
<td>-19.19 ±0.02</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>6.232</td>
<td>4.2054</td>
<td>5833.5 ±0.1</td>
<td>-218.3 ±2.4</td>
<td>-19.95 ±0.01</td>
<td>-45.5 ±0.8</td>
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<tr>
<td>35</td>
<td>6.177</td>
<td>4.2092</td>
<td>5935.0 ±0.1</td>
<td>-441 ±5</td>
<td>-20.69 ±0.02</td>
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</tr>
<tr>
<td>40</td>
<td>6.089</td>
<td>4.2155</td>
<td>6040.2 ±0.1</td>
<td>-669 ±8</td>
<td>-21.43 ±0.03</td>
<td></td>
</tr>
</tbody>
</table>

**p-Toluic acid**

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$K$</th>
<th>$pK*$</th>
<th>$\Delta G^0$ cal/mol</th>
<th>$\Delta H^0$ cal/mol</th>
<th>$\Delta S^0$ cal/(deg.mol)</th>
<th>$\Delta C_p^0$ cal/(deg.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
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<td>12.46</td>
<td>5326.8 ±0.5</td>
<td>-1157 ±45</td>
<td>-21.75 ±0.15</td>
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</tr>
<tr>
<td>25</td>
<td>12.02</td>
<td>3.9201</td>
<td>5437.7 ±0.4</td>
<td>-1413 ±19</td>
<td>-22.60 ±0.06</td>
<td>-51.3 ±5.9</td>
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<tr>
<td>30</td>
<td>11.53</td>
<td>3.9381</td>
<td>5552.8 ±0.4</td>
<td>-1670 ±20</td>
<td>-23.44 ±0.07</td>
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</tr>
<tr>
<td>35</td>
<td>11.00</td>
<td>3.9585</td>
<td>5672.0 ±0.5</td>
<td>-1926 ±47</td>
<td>-24.26 ±0.15</td>
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</table>

**m-Toluic acid**

<table>
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<tr>
<th>Temp. °C</th>
<th>$K$</th>
<th>$pK*$</th>
<th>$\Delta G^0$ cal/mol</th>
<th>$\Delta H^0$ cal/mol</th>
<th>$\Delta S^0$ cal/(deg.mol)</th>
<th>$\Delta C_p^0$ cal/(deg.mol)</th>
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<tr>
<td>20</td>
<td>5.518</td>
<td>4.2582</td>
<td>5711.8 ±0.1</td>
<td>400 ±6</td>
<td>-18.12 ±0.02</td>
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<tr>
<td>25</td>
<td>5.558</td>
<td>4.2551</td>
<td>5804.9 ±0.1</td>
<td>99.1 ±3.4</td>
<td>-19.14 ±0.01</td>
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<td>5.551</td>
<td>4.2557</td>
<td>5903.1 ±0.1</td>
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<td>-20.14 ±0.01</td>
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<td>5.406</td>
<td>4.2672</td>
<td>6114.3 ±0.1</td>
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<td>-22.09 ±0.02</td>
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**p-Toluic acid**

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$K$</th>
<th>$pK*$</th>
<th>$\Delta G^0$ cal/mol</th>
<th>$\Delta H^0$ cal/mol</th>
<th>$\Delta S^0$ cal/(deg.mol)</th>
<th>$\Delta C_p^0$ cal/(deg.mol)</th>
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<td>4.3777</td>
<td>5872.1 ±0.1</td>
<td>754.7 ±0.8</td>
<td>-17.46 ±0.01</td>
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<td>25</td>
<td>4.265</td>
<td>4.3701</td>
<td>5961.8 ±0.1</td>
<td>462.6 ±0.4</td>
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<td>4.3662</td>
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<td>-58.4 ±0.1</td>
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<td>4.3659</td>
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<td>6260.2 ±0.1</td>
<td>-413.6 ±0.8</td>
<td>-21.31 ±0.01</td>
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**Mesitoic acid**

<table>
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<tr>
<th>Temp. °C</th>
<th>$K$</th>
<th>$pK*$</th>
<th>$\Delta G^0$ cal/mol</th>
<th>$\Delta H^0$ cal/mol</th>
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<td>-3241.0 ±2.8</td>
<td>-26.60 ±0.01</td>
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</table>

* Results obtained after fitting the observed values (K obtained by the Fuoss-Shedlovsky method) into Clarke & Glew equations.
Table 14.7.2. The thermodynamic functions $\Delta S$ and $\Delta H_{int}$ for the ionization of benzoic and a series of methyl substituted benzoic acids.

<table>
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<tr>
<th>Compound</th>
<th>Temp.</th>
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<th>$\Delta S^{o}$</th>
<th>$\Delta H_{int}$</th>
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<td>2 cal/mol</td>
<td>3 cal/mol</td>
</tr>
<tr>
<td>Benzoic acid</td>
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<td>5158</td>
<td>5399</td>
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<td></td>
<td>25</td>
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Notes. 1. Taken from table 14.7.1.
2. $\beta$ assumed to be 280°K.
3. Calculated from relation (14.3.10).
Table 14.7.3. "ΔΔ" values for the thermodynamic functions of ionization of toluic and mesitoic acids with respect to benzoic acid.

<table>
<thead>
<tr>
<th>System</th>
<th>Temp. °C</th>
<th>ΔΔG° cal/mol</th>
<th>ΔΔH° cal/mol</th>
<th>ΔΔS° cal/(deg.mol)</th>
<th>ΔΔCp° cal/(deg.mol)</th>
<th>βΔΔS° cal/mol</th>
<th>ΔΔH int cal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(o-Toluic acid) -</td>
<td>20</td>
<td>-408.7±0.6</td>
<td>-1171 ±50</td>
<td>-2.56±0.17</td>
<td>-717</td>
<td>-454</td>
<td></td>
</tr>
<tr>
<td>(Benzoic acid)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-395.8±0.5</td>
<td>-1195 ±21</td>
<td>-2.65±0.07</td>
<td>-5.8±6.7</td>
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<td>-453</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-382.2±0.5</td>
<td>-1229 ±25</td>
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<tr>
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<td>40</td>
<td>-368.2±0.6</td>
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<td>40</td>
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<td>-135 ±14</td>
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<td>-185</td>
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<tr>
<td>(p-Toluic acid) -</td>
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<td>230.6±0.2</td>
<td>514 ± 9</td>
<td>0.96±0.04</td>
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<td>269</td>
<td>245</td>
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<td>(Benzoic acid)</td>
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<td>-4.91±0.04</td>
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<td>-1375</td>
<td>-1118</td>
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Notes. 1. β assumed to be 280°K.
2. Calculated from relation (14.3.10).
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Notes. 1. β assumed to be 280°K.
2. Calculated from relation (14.3.10).
14.8 The Hammett and Taft-Ingold equations and secondary deuterium isotope effects.

The secondary deuterium isotope effects pose the very challenging problem of defining their real cause. Though such effects have been studied for a good number of years and used successfully to clarify many structural and mechanistic problems, they escaped all the attempts which tried to find their origins. A series of different causes were postulated and we deal with them and their experimental evidence elsewhere. Here we limit ourselves to listing some of the proposed explanations for the secondary deuterium isotope effects: steric effects $^{10,234,235}$, inductive effects $^{133}$, hyper-conjugation $^{16}$, and zero-point energy differences $^{12}$.

According to some of the proposed linear free energy relationships, it would be possible to separate the inductive and the steric effects of deuterium provided that the appropriate data were available. Besides this problem, (availability of the data), it seems to us that the possibility of such a separation is highly unlikely. This pessimistic view is based on the fact that the accuracy of such expressions is approximately ±20%, only. To give an example which is of interest for the present work, let us consider the dissociation constants of aliphatic acids. There are two relations available for calculating their values in aqueous solution at 25°C.
1. \[ pK = 4.76 - 1.721 \sigma^* \quad (14.8.1) \]

2. \[ pK = 4.66 - 1.62 \sigma^* \quad (14.8.2) \]

These two expressions correspond to the reaction:

\[ R - COOH \Leftrightarrow R - COO^- + H^+ \quad (14.8.3) \]

and assume that only polar effects are operating in going from one acid to another.

A third relation \(^{212}\) corresponding to the reaction:

\[ R - CH_2 - COOH \Leftrightarrow R - CH_2 - COO^- + H^+ \quad (14.8.4) \]

gives results which are so much different from the ones obtained from (14.8.1) and (14.8.2) that we did not consider it in our calculations. Table 14.8.1 gives the calculated and the observed values for the pK's of the first few terms of the aliphatic acid series.

The average difference between the values rendered by the two formulas is approximately 0.09 pK units which represents ±20% in the values of the dissociation constants.

The usefulness of such relations depends very much on their use. If they are used, for example, to obtain an approximate idea of an equilibrium constant or a reaction rate then they are very useful. They should not be used, in our opinion, to interpret differences which are smaller than their accuracy, in terms of molecular structure, electronic properties and others.
Table 14.8.1. The observed and the calculated pK values for a few aliphatic acids. (R = COOH) in water at 25°C.

<table>
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<tr>
<th>R</th>
<th>σ*&lt;sup&gt;a&lt;/sup&gt;</th>
<th>pK&lt;sub&gt;calc&lt;/sub&gt; (14.7.1)</th>
<th>pK&lt;sub&gt;calc&lt;/sub&gt; (14.7.2)</th>
<th>pK&lt;sub&gt;obs&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
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<tr>
<td>H-</td>
<td>0.49</td>
<td>3.92</td>
<td>3.86</td>
<td>3.75</td>
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<tr>
<td>CH₃⁻</td>
<td>0.0</td>
<td>4.76</td>
<td>4.66</td>
<td>4.76</td>
</tr>
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<td>4.88</td>
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<td>CH₃-CH₂-CH₂⁻</td>
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<td>4.85</td>
<td>4.82</td>
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<td>(CH₃)₂-CH⁻</td>
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<td>4.97</td>
<td>4.85</td>
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<tr>
<td>CH₃-(CH₂)₃⁻</td>
<td>-0.13</td>
<td>4.98</td>
<td>4.87</td>
<td>4.84</td>
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<td>(CH₃)₂-CH-CH₂⁻</td>
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<td>4.86</td>
<td>4.78</td>
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<td>(CH₃)₃-C⁻</td>
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<td>5.28</td>
<td>5.15</td>
<td>5.03</td>
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<tr>
<td>Ph-CH₂⁻</td>
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<td>4.39</td>
<td>4.31</td>
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<tr>
<td>Ph&lt;sub&gt;2&lt;/sub&gt;CH⁻</td>
<td>0.11&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.57</td>
<td>4.48</td>
<td>?</td>
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<tr>
<td>CH₃&lt;sup&gt;3&lt;/sup&gt;C</td>
<td>0.645&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.65</td>
<td>3.62</td>
<td>3.96</td>
</tr>
</tbody>
</table>


<sup>c</sup> Composite values.
In the case of secondary deuterium isotope effects, as a general rule the difference between the reaction rates or equilibrium constants of isotopic compounds is small and because of this \( \sigma \) or \( \sigma^* \) values are not significantly different for substituents containing hydrogen and deuterium as compared with the probable errors of the Hammett and Taft-Ingold equations. The difference between the deuterium and hydrogen compounds has been used, however, for qualitative predictions.

Streitwieser and Klein \(^{133}\) calculated:

\[
\sigma^*(-CD_3) = -0.0081
\]

(14.8.5)

from the difference \( (pK_D - pK_H) \) for acetic acid. From the same difference for pivalic acid \(^{133}\), the \( \sigma^* \) constant for the \( (CD_3)_3C^- \) group can be calculated:

\[
\sigma^*[(CD_3)_3C^-] - \sigma^*[(CH_3)_3C^-] = -0.0105
\]

Since \( \sigma^* \) for the t-Bu group is approximately three times the \( \sigma^* \) value of one methyl group (see table 14.8.1) and taking into account the damping factor (2.8), we obtain:

\[
\sigma^*(-CD_3) = -0.0098
\]

(14.8.6)

which is in fair agreement with the previous value (14.8.5).
Similarly, the difference $\sigma^*(D) - \sigma^*(H)$ can be obtained from the data for the two isotopic formic acids $71, 237$:

$$\sigma^*(-D) - \sigma^*(-H) = -0.019$$

There is no simple way, however, in which this value can be correlated with the previous values for the $-\text{CD}_3$ group. By our previous argument this is not to be taken as definite proof that different types of effects are operating in each of the three cases analysed here. The negative sign of the above examples was interpreted as an indication of the stronger electron repelling power of C-D bond as compared with C-H bond $^1$.

In the same context Barnes$^2 238$ and our measurements on phenylacetic and phenylacetic-$/alpha$-$d_2$ acids yielded:

$$pK_D - pK_H = 0.0039 \pm 0.0004$$

which gives:

$$\sigma^*_D - \sigma^*_H = -(pK_D - pK_H)/\rho^* = -0.0023$$

The difference, experimentally significant, cannot be correlated by the value of the $\sigma^*$ constant with any of the previous values.
Abstract.

In part A of this thesis we discuss the conductance method as it is applied to the determination of the dissociation constants of weak acids and we present the experimental results for the dissociation constant and the thermodynamic functions for the ionization of the following acids: benzoic, benzoic-2-d, benzoic-d5, o-toluic, o-toluic-d7, m-toluic, p-toluic, mesitoic, mesitoic-d9, phenylacetic, and phenylacetic-a-d2. The determinations were done in aqueous solutions at temperatures between 20 and 40°C. The dissociation constants were determined by using a modified Ives-Feates-Pyor double conductance cell, an impedance bridge, and Fuoss-Shedlovsky extrapolation method. We estimate that the dissociation constants are reliable within 0.1 to 0.2%. The thermodynamic functions of ionization were calculated by using Clarke and Glew equations. The temperature coefficient of the heat capacity of ionization found was not considered to be significant. The secondary deuterium isotope effects, \( K_H/K_D \), were found to be constant over the temperature range employed in this work.

In part B calculations of the Wolfsberg-Stern type are carried out in the benzoic, o-toluic, and phenylacetic acid systems in order to obtain an idea of the type of force constant changes that would lead to calculated values for the ratio \( K_H/K_D \) in good agreement with the experimental ones. It was found that the assumption of a slight increase in the
force constants of those internal coordinates of the anions which were located in the vicinity of the carboxylate group led to a good agreement between the calculated and the experimentally obtained results.
15. A REVIEW OF SOME OF THE THEORIES OF THE SECONDARY DEUTERIUM ISOTOPE EFFECTS ON EQUILIBRIUM CONSTANTS.

15.1 History.

In 1913, F. Soddy observed (in connection with "radio-elements"): "Whenever, by expulsion of $\alpha$ or $\beta$-rays, two or more elements come to occupy the same place in the periodic table, then independently of all other considerations such as atomic weight, the disintegration series to which the element belongs, its radioactive character and the nature of radioactive changes in which it is produced or by which it is transformed, these elements occupying the same place are not separable from one another and are, so far as is known, identical in chemical character". Soddy concluded that: "The places at the end of the periodical table, and probably elsewhere in the table, thus represent not single homogeneous elements as has hitherto been supposed, but groups of elements identical in chemical character. To express this newly discovered complexity of matter the terms "isotopic elements" or "isotopes" have been coined....This material identity extends far beyond the chemical properties in the narrow sense and embraces probably nearly all the common physical properties...."

Though isotopes are defined in present-day textbooks essentially in the same way Soddy defined them,
what makes them very valuable to present-day science
are the small differences in the physical and chemical
behaviour of the molecules containing different isotopes
of the same element. Both pure and applied science have
an invaluable tool in the use of isotopes. Certainly
the prime requirement for using isotopes to elucidate
structures, mechanisms, compositions, etc. is to under-
stand their mode of action, i.e. why the small differences
mentioned above arise.

Urey 4, Bigeleisen and Wolfsberg 5 have developed
theories which deal with isotope effects. Urey treats
the thermodynamic properties of isotopic substances and
Bigeleisen and Wolfsberg the isotope effects in chemical
kinetics.

In 1932, Urey, Brickwedge and Murphy 240, 241
reported the discovery of an isotope of hydrogen: H2. A
number of systematic arrangements of known nuclear species
predicted the existence of H2 and H3 for some years 242-245.
In 1931, Birge and Menzel 246, bringing to a common
standard the chemical and mass spectrograph results for
the atomic weight of hydrogen, showed that the discrepancy
(as far as hydrogen is concerned) could be removed by
postulating the existence of an isotope of hydrogen of
mass two.
Because of the particular position of deuterium among the isotopes, any isotope effects are expected to be greatly enhanced in its case; that is (together with its easy availability) probably why deuterium is the most studied isotope.

15.2 The theory of equilibrium constants of exchange reactions.

In the first part of this thesis we have determined the deuterium secondary isotope effects on a series of equilibrium reactions. Thus, a brief review of the theory of isotope effects on equilibrium constants is appropriate.

Consider a closed, one-phase system at pressure $p$, temperature $T$, containing the number of molecules $N_A$, $N_B$, $N_C$, $N_1$, $N_2$, ..., and being at equilibrium. Equilibrium with respect to the chemical reaction can be represented by $247$:

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C$$

(15.2.1)

where $\nu_A$, ..., are small integers. Species 1, 2, ..., are present but do not participate in the reaction.

In statistical mechanics it is shown that a function $K(T)$ can be derived having the following form:

$$K(T) = \frac{\left(\frac{q_c}{V}\right)^{\nu_C}}{\left(\frac{q_A}{V}\right)^{\nu_A} \left(\frac{q_B}{V}\right)^{\nu_B}}$$

(15.2.2)
K is called the equilibrium constant and is a function of temperature only. The q's are the partition functions for the respective molecular species. Expression (15.2.1) assumes that the zeros of energy for each molecular species are self consistent with each other.

The calculation of K for isotope exchange reactions has received particular attention \(^4, 14, 248\).

Isotope exchange reactions are defined as processes by which two isotopes of the same element Z, e.g. \(^1Z\) and \(^mZ\), exchange places:

\[
x^1Z + y^mZ \xrightleftharpoons{K_1}{K_2^2} y^1Z + x^mZ
\]

(15.2.3)

where \(K_1\) and \(K_2\) refer to isotopes \(^1Z\) and \(^mZ\) respectively. The equilibrium constant for such a reaction in the gas phase is:

\[
K = \frac{q_{A2} \cdot q_{B1}}{q_{A1} \cdot q_{B2}}
\]

(15.2.4)

where subscripts A and B refer to species XZ and YZ respectively. Subscripts 1 and 2 refer to isotopes \(^1Z\) and \(^mZ\) respectively. q is the partition function for unit volume. More schematically, the above reaction can be represented by:
\[ A_1 + B_2 \xrightleftharpoons[K_2]{K_1} B_1 + A_2 \]  \hspace{1cm} (15.2.5)

An example of the type of reaction presented, in a general form, in (15.2.5) is the following equilibrium:

a. First consider the ionization of two isotopic acids:

\[ \text{RH}_n\text{COOH} + \text{H}_2\text{O} \xrightleftharpoons[K_H]{K_D} \text{RH}_n\text{COO}^- + \text{H}_3\text{O}^+ \]  \hspace{1cm} (15.2.6)

\[ \text{RD}_n\text{COOH} + \text{H}_2\text{O} \xrightleftharpoons[K_D]{K_H} \text{RD}_n\text{COO}^- + \text{H}_3\text{O}^+ \]

b. The equilibrium constants for the two reactions are given by:

\[ K_H = \frac{[\text{RH}_n\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{RH}_n\text{COOH}]} \]  \hspace{1cm} (15.2.7)

\[ K_D = \frac{[\text{RD}_n\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{RD}_n\text{COOH}]} \]

c. The ratio \( K_H/K_D \) is:

\[ K = \frac{K_H}{K_D} = \frac{[\text{RH}_n\text{COO}^-][\text{RD}_n\text{COOH}]}{[\text{RD}_n\text{COO}^-][\text{RH}_n\text{COOH}]} \]  \hspace{1cm} (15.2.8)

which is nothing else but the equilibrium constant for the exchange reaction:
\[ \text{R}_\text{H}_\text{n} \text{COOH} + \text{R}_\text{D}_\text{n} \text{COO}^- \rightleftharpoons K \text{R}_\text{H}_\text{n} \text{COO}^- + \text{R}_\text{D}_\text{n} \text{COOH} \quad (15.2.9) \]

which is the same type as (15.2.3) or (15.2.5).

On calculating \( K \), the first approximation employed is the Born-Oppenheimer approximation, i.e.: the electronic and nuclear motions can be considered separately. In this case, the partition function \( q \) can be written as:

\[ q = q_e \times q_n \quad (15.2.10) \]

where \( q_e \) is the partition function for electronic motion and \( q_n \) the partition function for nuclear motion.

**The electronic partition function.**

The expression for the electronic partition function is 249:

\[ q_e = \omega_{e_1} \exp(-\epsilon_1/kT) \quad (15.2.11) \]

where only the electronic ground state energy \( \epsilon_1 \) is considered (separation in electronic energy levels is large) and \( \omega_{e_1} \) is the degeneracy of the electronic ground state.

In an exact quantum-mechanical treatment of a system, all the particles and their interactions have to be included in a single Schrödinger equation. Even for the simplest system
the solution of such an equation is a formidable task and in most instances an impossible job (at least for the time being).

In the Born-Oppenheimer approximation, because the electrons are much lighter as compared with the nuclei and, hence, move much faster on the average, the nuclei are considered fixed while studying the electronic motion. The approach to the problem is to study the motion of the electrons for a given fixed configuration of the nuclei. The potential energy for such a motion (i.e. the potential energy in the Schrödinger equation) is made up of electron-electron, electron-nucleus, and nucleus-nucleus coulombic interactions. The last of these interactions is constant for a given, fixed configuration. Denote the dependence of the electronic energy on the internuclear distance by $U_e(r)$. This function can be accurately calculated only for the simplest cases: one and two electrons. In more complicated cases, it must be approximated or deduced semiempirically from experimental information.

A series of phenomena or properties which are considered essentially, as being of electronic nature, that is, they are a reflection of the electronic distribution and/or electronic motion within the molecule, have been shown to be sensitive to isotope substitution. Thus, the properties
or phenomena are: the polarizability, the dipole moment, nuclear quadrupole coupling constant, nuclear magnetic resonance, molecular refraction, optical activity, etc. A discussion of isotope effects on these properties is given by Halevi \(^{250}\) and Weston \(^{251}\).

In the theoretical treatment of isotope effects on reaction rates of Bigeleisen \(^{252}\), Urey \(^{4}\) or Melander \(^{253}\), a necessary assumption is that the potential energy function is invariant under isotopic substitution.

How are the two, apparently opposite points of view, reconciled? There are two ways:

a. An estimate of the electronic isotope effects on reaction rates belongs to Weston. For the simplest case, that of H and D atoms, the difference in the electronic energy levels caused by the small difference in the reduced mass of the electron-proton as compared with the electron-deuteron system amounts to 30 cm\(^{-1}\). For a more complex molecule, no exact calculation is possible. As was said before, recourse is made to the Born-Oppenheimer approximation which makes it possible to solve separately the wave-equations for electronic and nuclear motions. According to this approximation the interaction between the two types of motion, which is in fact the effect being considered, is proportional to the ratio of the
electron mass to some sort of average nuclear mass for the molecule. Hence, in a common molecule the effect of deuterium substitution is an order of magnitude smaller than the 30 cm\(^{-1}\).

The difference in this interaction effect between two molecules, e.g. the reactant and the product, should be vanishingly small as compared with the possible differences in vibrational frequencies.

b. A second explanation, advanced by both Halevi and Weston, is that the isotope effects on the "electronic" properties or phenomena enumerated above is not as much a result of differences in the electronic energy of different isotopic species as a result of vibrational origin: the anharmonicity of the vibrations involving hydrogen atoms will lead to different average bond lengths and bond angles in deuterated and normal molecules.

**Nuclear partition function.**

In calculating the partition function for a polyatomic molecule, the methods and the approximations used for a diatomic molecule are directly extended.\(^{254}\)

As we saw before, by varying the location of the nuclei relative to each other, the electronic energy of the ground state \(U_e\) varies; consequently the work required
to change the internuclear distance \( r \) is determined by \( U_e(r) \). That is, \( U_e(r) \) serves as the potential function for the nuclear motion. Since for \( n \geq 3 \) (\( n \) is the number of nuclei) \( U_e \) is a function of at least three variables, \( U_e(r) \) will be represented by a surface in a space of at least four dimensions. If the molecule is a stable one, the \( U_e \) surface necessarily has a minimum (in some cases several equivalent minima). The nuclear configuration corresponding to the minimum in \( U_e \) is the stable configuration of the molecule.

An exact calculation of the potential surface from quantum-mechanics is a difficult mathematical problem; thus, an approximation to the exact solution or, more often, empirical expressions, which will fit the experimental data are used to calculate it.

A third approximation (the first one being the Born-Oppenheimer approximation) used in the case of diatomic molecules and passed on to the polyatomic molecules is the separability of the vibrational and rotational motions from each other.

The rotational motion (two or three degrees of freedom) is made separable by assuming that, as far as rotation is concerned, the molecule has the rigid structure corresponding to the minimum on the potential surface.

The translational motion (three degrees of freedom) of the center of mass is also separable.
Thus, because the Hamiltonian for one molecule is, approximately, separable:

\[ H = H_t + H_r + H_v + H_e \] (15.2.12)

The energy itself can then be expressed as a sum of separate contributions:

\[ \varepsilon = \varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e \] (15.2.13)

where \( t \): translation, \( r \): rotation, \( v \): vibration, \( e \): electronic.

The partition function can be written as:

\[ q = q_t q_r q_v q_e \] (15.2.14)

The electronic partition function has, already, been mentioned.

The translational partition function.

The expression for the translational partition function is:

\[ q_t = \left( \frac{2\pi kT \sum_i m_i}{\hbar^2} \right)^{3/2} V \] (15.2.15)

where the sum is over all the atoms in the molecule. \( V \) is
the volume in which the molecule is located; \( k \) is the Boltzmann constant; \( T \) is the temperature; \( m \) is the atomic mass; \( h \) is Planck's constant.

Rotational partition function.

The rotational partition function has the following expression 256:

\[
q_r = \frac{\pi^2}{\sigma} \left( \frac{8\pi^2 I_x kT}{h^2} \right)^{1/2} \left( \frac{8\pi^2 I_y kT}{h^2} \right)^{1/2} \left( \frac{8\pi^2 I_z kT}{h^2} \right)^{1/2} \tag{15.2.16}
\]

\( \sigma \) is the symmetry number: the number of different ways in which a molecule can achieve, by rotation, the same (i.e. counting like atoms as indistinguishable) orientation in space. \( I_x, I_y, I_z \) are the three principal moments of inertia.

The above expression can be rewritten as:

\[
q_r = \frac{\pi^2}{\sigma} \left( \frac{T^3}{\Theta \Theta \Theta} \right)^{1/2} \tag{15.2.17}
\]

where \( \Theta \) is the characteristic temperature for rotation and is given by:

\[
\Theta = \frac{h^2}{8\pi^2 I k} \tag{15.2.18}
\]
Vibrational partition function.

The vibrational partition function is given by 257:

\[
q_v = \prod_{i=1}^{n'} \frac{e^{-\Theta_i/2T}}{1-e^{-\Theta_i/T}}
\]  

where \(n' = 3n - 6\) (or \(3n - 5\) for linear molecules). The symbol \(\Theta_i = \hbar\nu_i/k\) and is called the characteristic temperature for vibration. The \(\nu_i\)'s are the normal frequencies of vibration. They are obtained from vibrational spectra.

Expression (15.2.19) holds when the vibration is almost harmonic. For precise calculations it is necessary to include anharmonic terms in the vibrational energy.

The complete partition function.

To obtain the complete partition function, we have to combine the expressions (15.2.11), (15.2.15), (15.2.16), (15.2.19) accordingly with expression (15.2.14). The result is:

\[
q = \left(\frac{2\pi kT}{h^2} \sum_{i=1}^{n} m_i \right)^{3/2} \frac{\pi^{3/2}}{\sigma} \left(\frac{8kT}{h^2} \cdot I_{x} I_{y} I_{z}\right)^{3/2} \prod_{j=1}^{n'} \frac{e^{-\hbar\nu_j/2kT}}{1-e^{-\hbar\nu_j/kT}} \left(\omega_{e_1} e^{-\epsilon_1/kT}\right)
\]  

(15.2.20)
or per unit volume (divide (15.2.20) by $V$):

$$q = \left(\frac{2\pi kT_i \Sigma m_i}{\hbar^2}\right)^{3/2} \frac{3/2}{\pi} \left(8\frac{kT}{\hbar^2} \cdot I_x I_y I_z\right) \frac{1/2}{\pi} \frac{n_i}{1 - e^{-\Theta_i/2T}} \cdot \omega_{e_1} e^{-\varepsilon_1/kT} \quad (15.2.21)$$

15.3 The equilibrium constant and the partition function in the case of exchange reactions.

Returning to expression (15.2.4):

$$K = \frac{q_{A_2}/q_{A_1}}{q_{B_2}/q_{B_1}} \quad (15.2.4)$$

consider one of the fractions $q_2/q_1^4$:

$$\frac{q_2}{q_1} = \frac{q_{t2}}{q_{t1}} \times \frac{q_{r2}}{q_{r1}} \times \frac{q_{v2}}{q_{v1}} \times \frac{q_{e2}}{q_{e1}} \quad (15.3.1)$$

From the translational factor there is left only:

$$\frac{q_{t2}}{q_{t1}} = \left(\frac{1}{\sum \frac{m}{i}} \frac{2}{1} \right)^{3/2} \quad (15.3.2)$$

From the rotational factor:

$$\frac{q_{r2}}{q_{r1}} = \frac{\sigma_{i} I_x I_y I_z}{\sigma_{j} I_x I_y I_z} \quad (15.3.3)$$
From the vibrational factor:

\[
\frac{q_{VR}}{q_{V1}} = \prod_{j=1}^{n'} \frac{e^{-\hbar v_{2j}/2kT}}{1-e^{-\hbar v_{2j}/kT}} \frac{1-e^{-\hbar v_{1j}/2kT}}{e^{-\hbar v_{1j}/kT}}
\]  \hspace{1cm} (15.3.4)

Thus, assuming \( \epsilon_1 = \epsilon_2 \) and \( \omega_1 = \omega_2 \):

\[
\frac{q_2}{q_1} = \left( \sum_{i=1}^{n} \frac{m_{2i}}{m_{1i}} \right)^{3/2} \frac{\sigma_1(I_{x2}I_{y2}I_{z2})^{\frac{1}{2}}}{\sigma_2(I_{x1}I_{y1}I_{z1})^{\frac{1}{2}}} \frac{n'}{e^{-\hbar v_{2j}/2kT}} \frac{1-e^{-\hbar v_{1j}/kT}}{1-e^{-\hbar v_{1j}/2kT}}
\]  \hspace{1cm} (15.3.5)

The complete expression for the equilibrium constant is 4:

\[
K = \frac{q_{A2}}{q_{A1}} \frac{q_{B2}}{q_{B1}} \left( \sum_{i=1}^{n} \frac{m_{A2i}}{m_{A1i}} \right)^{3/2} \frac{\sigma_{A1}(I_{xA2}I_{yA2}I_{zA2})^{\frac{1}{2}}}{\sigma_{A2}(I_{xA1}I_{yA1}I_{zA1})^{\frac{1}{2}}} \frac{\sigma_{B1}(I_{xB2}I_{yB2}I_{zB2})^{\frac{1}{2}}}{\sigma_{B2}(I_{xB1}I_{yB1}I_{zB1})^{\frac{1}{2}}}
\]  \hspace{1cm} (15.3.6)

\[
\frac{n'}{\prod_{i=1}^{n'} e^{-\hbar v_{2i}/2kT}} \frac{1-e^{-\hbar v_{A1i}/kT}}{e^{-\hbar v_{A1i}/2kT}} \frac{1-e^{-\hbar v_{B1i}/kT}}{e^{-\hbar v_{B1i}/2kT}}
\]
15.4 Urey treatment \(^4\).

Perform the following mathematical operations on (15.3.5):

a. Multiply left and right sides of equation (15.3.5) by \(\left(\frac{m_1}{m_2}\right)^{\frac{3n''}{2}}\) where \(m_1\) and \(m_2\) are the atomic weights of the isotopic atoms being considered; \(n''\) is the number of isotopic atoms being exchanged.

b. Multiply and divide the right side by the ratio:

\[
\prod_{i} \frac{u_{1i}}{u_{2i}} \quad \text{where} \quad u = \frac{h\nu}{kT} \quad (\nu \text{ in } s^{-1})
\]

Then (15.3.5) becomes:

\[
\left(\frac{m_1}{m_2}\right)^{\frac{3n''}{2}} \frac{q_2}{q_1} = \left(\frac{M_2}{M_1}\right)^{3/2} \frac{a_1}{a_2} \left(\frac{x_1 x_2 y_1 y_2 z_1 z_2}{x_1' y_1' z_1'}\right) \prod_{i} \frac{e^{-h\nu_{2i}/2kT}}{1-e^{-h\nu_{1i}/kT}}.
\]

\[
1-e^{-h\nu_{1i}/kT} \prod_{i} \frac{u_{1i}}{u_{2i}} \frac{u_{2i}}{u_{1i}} \frac{\left(\frac{m_1}{m_2}\right)^{\frac{3n''}{2}}}{\left(\frac{M_1}{M_2}\right)^{3/2}}
\]

(15.4.1)

where \(M\)'s are the molecular masses of the respective molecules.

According to the Teller-Redlich product rule \(^{258,259}\), the following relation holds:
\[
\left( \frac{I_{x2}I_{y2}I_{z2}}{I_{x1}I_{y1}I_{z1}} \right)^{\frac{1}{2}} \left( \frac{M_2}{M_1} \right)^{3/2} \left( \frac{m_1}{m_2} \right)^{\frac{3n''}{2}} \frac{u_{1i}}{u_{2i}} = 1
\]  (15.4.2)

Thus, relation (15.4.2) reduces to:

\[
\left( \frac{m_1}{m_2} \right)^{\frac{3n''}{2}} \frac{q_2}{q_1} = \frac{\sigma_1}{\sigma_2} \prod_{i=1}^{n'} u_{2i} u_{1i} e^{\frac{-hv_{2i}/2kT}{1-e}} \frac{1-e^{-hv_{1i}/kT}}{1-e^{-hv_{2i}/kT}}
\]  (15.4.3)

The expression on the left side is nothing but the equilibrium constant for the exchange reaction between the compound considered and the separated atoms, i.e.:

\[
A^1Z_n + n^mZ \underset{K_2}{\rightarrow} A^mZ_n + n^1Z
\]  (15.4.4)

This expression will be denoted as \(q_2^'/q_1^'\). \(K\), the equilibrium constant for the general exchange reaction is then:

\[
\frac{K_1}{K_2} = K = \frac{q_{A_2}^q B_1^r}{q_{A_1}^q B_2^r} = \frac{\sigma_{A1}}{\sigma_{A2}} \prod_{i=1}^{n'} \frac{u_{A2i} e^{-u_{A2i}/2}}{u_{A1i} 1-e^{-u_{A2i}}} \frac{\sigma_{B1}}{\sigma_{B2}} \prod_{i=1}^{n'} \frac{u_{B2i} e^{-u_{B2i}/2}}{u_{B1i} 1-e^{-u_{B2i}}}
\]

\[
= \frac{\left[ \begin{array}{c} 1-e^{-u_{A1i}} \\ e^{-u_{A1i}/2} \\ 1-e^{-u_{B1i}} \\ e^{-u_{B1i}/2} \end{array} \right]}{q_{A2}^q B_1^r/q_{A1}^q B_2^r}
\]  (15.4.5)
Since atoms always balance out in any chemical equilibrium, the term \((m_1/m_2)^{3n''/2}\) will cancel out. Thus, it is possible to calculate the ratio of the partition functions from a knowledge of the vibrational frequencies.

Equation (15.4.3) can be put in a more convenient form for the purpose of calculations. Define:

\[
\chi_i = \frac{u_{1i} + u_{2i}}{4}, \quad \delta_i = \frac{u_{1i} - u_{2i}}{2} \tag{15.4.6}
\]

Expanding in terms of \(\delta_i\)'s, we get:

\[
\ln \frac{q_2'}{q_1} = \ln \sigma_1 + \sum_{i=1}^{n'} \ln \frac{u_{2i}}{u_{1i}} + \sum \left[ \coth x_i \delta_i + \frac{1}{12} \coth x_i (\coth^2 x_i - 1) \delta_i^3 + \ldots \right] 
\tag{15.4.7}
\]

In case of small \(u\)'s, i.e. either low frequencies or high temperatures, the right side of (15.4.7) is expanded to give:

\[
\frac{q_2'}{q_1} = \frac{\sigma_1}{\sigma_2} \Pi \left[ 1 - \frac{1}{24} (u_{2i}^2 - u_{1i}^2) \right] \tag{15.4.8}
\]

where:
\[
\frac{q_2'}{q_1'} = \frac{m_1}{m_2} \frac{3n''/2}{q_2} \frac{q_2}{q_1} \quad (15.4.9)
\]

To correct for the anharmonicity of the vibrations, a sufficiently good approximation in the case of polyatomic molecules is to add to equation (15.4.7) a term \(\Delta E'/kT\) in which \(\Delta E'\) is the contribution to the zero point energy difference from the anharmonic terms. If the coefficients of the anharmonic terms are negative (the usual case), \(\Delta E'\) is negative and decreases the calculated value of \(q_2/q_1\).

Further corrections should be made for the case in which the rotational partition function has not reached classical values.

The high temperature limit (classical limit) is:

\[
T \gg \frac{h\nu}{k} = \Theta
\]

and the following approximation holds:

\[
e^{-\Theta/2T} \rightarrow \frac{1-(\Theta/2T + \cdots)}{1-[1-(\Theta/1 + \cdots)]} \rightarrow \frac{T}{\Theta} = \frac{h\nu}{kT}
\]

then:

\[
\frac{q_2'}{q_1'} = \frac{\sigma_1}{\sigma_2} \pi \frac{h\nu_{2i}}{kT} \cdot \frac{kT}{h\nu_{1i}} \cdot \frac{h\nu_{1i}}{kT} \rightarrow \frac{\sigma_1}{\sigma_2}
\]
that is, the ratio of the symmetry numbers.

15.5 Bigeleisen, Wolfsberg, and Stern treatments 5.

Consider (15.4.3) written in a slightly different way:

\[
\frac{\sigma_2}{\sigma_1} \cdot \frac{q_2}{q_1} \prod_{i=1}^{n''} \left( \frac{m_{1i}}{m_{2i}} \right)^{3/2} = \prod_{i=1}^{n'} \left[ \frac{u_{2i}}{u_{1i}} \cdot \frac{u_{1i}-u_{2i}}{2} \cdot \frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}} \right]
\]

(15.5.1)

\[u \equiv h\nu/kT\]

(15.5.2)

Define:

\[u_{1i} = u_{2i} + \Delta u_i\]

(15.5.3)

\[
\frac{\sigma_2}{\sigma_1} f = \frac{\sigma_2}{\sigma_1} \frac{q_2}{q_1} \prod_{i=1}^{n'} \left( \frac{m_{1i}}{m_{2i}} \right)^{3/2} = \prod_{i=1}^{n'} \left[ \frac{u_i}{u_i+\Delta u_i} \cdot e^{\Delta u_i/2} \cdot \frac{1-e^{-u_i}}{1-e^{-u_i+\Delta u_i}} \right]
\]

(15.5.4)

where \(u_i\) refers to the frequency of the molecule containing isotope 2, arbitrarily taken as the heavier of the two.

The product \(\prod \left( \frac{m_{1i}}{m_{2i}} \right)^{3/2}\) will cancel out in any equilibrium (see 15.4.5) and thus, there is left:

\[
\frac{\sigma_2}{\sigma_1} f = \frac{\sigma_2}{\sigma_1} \frac{q_2}{q_1} \prod_{i=1}^{n'} \left[ \frac{u_i}{u_i+\Delta u_i} \cdot e^{\Delta u_i/2} \cdot \frac{1-e^{-u_i}}{1-e^{-u_i+\Delta u_i}} \right]
\]

(15.5.5)
The high temperature approximation (first quantum correction) \(^{260,261}\).

In this approximation both \(u\) and \(\Delta u\) are small:

\[
\Delta u = u^{1}_{11} - u^{21} = \frac{\hbar c}{kT} (\nu^{11} - \nu^{21})
\]  

(15.5.6)

with \(\nu\) in cm\(^{-1}\).

This is the case for the isotopes of all elements, except for hydrogen and for low temperatures.

While the approximation does not provide good quantitative answers, it does provide an insight into the nature and the causes of isotope effects, including those of hydrogen.

Form 1.

Expression (15.5.5) can be written as (see appendix 15.5.1):

\[
\frac{\sigma^{2}}{\sigma^{1}} f = \frac{n^{r}}{n} (1 + G(u)\Delta u) = 1 + \sum_{i=1}^{n^{r}} G(u_{i})\Delta u_{i}
\]  

(15.5.7)

where:

\[
G(u) = \frac{1}{2} - \frac{1}{u} + \frac{1}{eu-1}
\]  

(15.5.8)

Expansion of \(G(u)\) in powers of \(u\) yields \(u/12\) as the leading term. Thus, for small \(u\) and using the approximation:
\[ u_{1i} = \frac{(u_{1i} + u_{2i})}{2}. \]  \hspace{1cm} (15.5.9)

\[ \frac{\sigma_2}{\sigma_1} f = 1 + \sum_{i=1}^{n'} \frac{u_i}{12} \Delta u_i = 1 + \sum_{i=1}^{n'} \frac{u_{1i}^2 - u_{2i}^2}{24}. \] \hspace{1cm} (15.5.10)

Form 2.

Define:

\[ \gamma_i = 12 \frac{G(u_i)}{u_i} \] \hspace{1cm} (15.5.11)

and thus (15.5.7) is now:

\[ \frac{\sigma_2}{\sigma_1} f = 1 + \sum_{i=1}^{n'} \gamma_i \frac{u_i}{12} \Delta u_i \] \hspace{1cm} (15.5.12)

A plot of \( \gamma_i \) vs. \( u_i \) shows that the variation is a slow one and because of this it is convenient to define \( \bar{\gamma} \) such that 262:

\[ \frac{\sigma_2}{\sigma_1} f = 1 + \bar{\gamma} \sum_{i=1}^{n'} \frac{u_{1i}^2 - u_{2i}^2}{24}. \] \hspace{1cm} (15.5.13)

If one has some idea of the magnitude of \( u \)'s which make the major contribution to \( \sum \Delta (u_i^2) \), \( \bar{\gamma} \) can be guessed with a sufficiently good accuracy.
The use of the correction term $\bar{\nu}$ extends the method of the first quantum correction to values of $\nu$, where the first quantum correction itself is inadequate. Form 3.252

The sum of all the frequencies of a molecule has the form:

$$4\pi^2 \sum_{k} \nu_k^2 = \sum_{i=1}^{n'} \frac{A_{jj}}{m_j}$$  \hspace{1cm} (15.5.14)$$

where $\nu_k$ is the normal frequency of vibration and the sum is taken over $3n - 6 (3n - 5)$ modes of vibration; $m_j$ is the atomic mass of atom $j$ and $A_{jj}'s$ are force constants in terms of Cartesian coordinates; if all the atoms in the molecule except the one which is going to be isotopically substituted are fixed in position, then $A_{jj}$ is the sum of the three restoring force constants corresponding to the displacement of the isotopic atom in three mutually perpendicular directions:

$$A_{jj} = A_{jj}^{xx} + A_{jj}^{yy} + A_{jj}^{zz}$$ \hspace{1cm} (15.5.15)$$

For the difference between two isotopic molecules, relation (15.5.14) becomes:

$$4\pi^2 \sum_{k} (\nu_{1k}^2 - \nu_{2k}^2) = \sum_{j=1}^{n'} \frac{A_{jj}(\frac{1}{m_{1j}} - \frac{1}{m_{2j}})}$$  \hspace{1cm} (15.5.16)$$
The use of the correction term $\gamma$ extends the method of the first quantum correction to values of $u$, where the first quantum correction itself is inadequate.

Form 3.252

The sum of all the frequencies of a molecule has the form:

$$4\pi^2 \sum_k \nu_k^2 = \sum_{i=1}^{n'} A_{ij}/m_j$$  \hspace{1cm} (15.5.14)

where $\nu_k$ is the normal frequency of vibration and the sum is taken over $3n - 6$ ($3n - 5$) modes of vibration; $m_j$ is the atomic mass of atom $j$ and $A_{ij}$'s are force constants in terms of Cartesian coordinates; if all the atoms in the molecule except the one which is going to be isotopically substituted are fixed in position, then $A_{jj}$ is the sum of the three restoring force constants corresponding to the displacement of the isotopic atom in three mutually perpendicular directions:

$$A_{jj} = A_{jj}^{xx} + A_{jj}^{yy} + A_{jj}^{zz}$$  \hspace{1cm} (15.5.15)

For the difference between two isotopic molecules, relation (15.5.14) becomes:

$$4\pi^2 \sum_k (\nu_k^2 \nu_{1k} - \nu_{2k}^2) = \sum_{j=1}^{n'} A_{jj}(\frac{1}{m_{1j}} - \frac{1}{m_{2j}})$$  \hspace{1cm} (15.5.16)
where the fact that $A_{jj}$ is independent of the isotopic form is used.

Using the G-matrix of Wilson (15.5.14) can be written as:

$$4\pi^2 \Sigma \nu_k = \sum_{tt', t, t'} F_{tt'} G_{tt'} t, t' = 1... 3n-6(3n-5)$$  (15.5.17)

$F_{tt'}$'s are force constants and $G_{tt'}$'s are elements of the G-matrix (see subsections 16.3 and 16.4).

Furthermore:

$$4\pi^2 \Sigma \nu_k^2 = \sum_{tt', t, t'} F_{tt'} \Sigma_{\alpha} H_{tt'}^\alpha \alpha = 1... n$$

$$t, t' = 1... 3n-6(3n-5)$$  (15.5.18)

$$H_{tt'}^\alpha = \overline{s}_{t\alpha} \cdot \overline{s}_{t'\alpha}$$

where the elements "$\overline{s}_{t\alpha}$" depend on the geometry of the molecule, only. (See 16.3.3)

In the case of isotopic molecules:

$$4\pi^2 \sum_{k=1}^{3n-6} (\nu_{1k}^2 - \nu_{2k}^2) = \sum_{tt', t, t'} \Sigma_{\alpha} H_{tt'}^\alpha (1\alpha) (2\alpha)$$

(15.5.19)
In case of the equilibrium represented in (15.2.5):

\[ A_1 + B_2 \rightleftharpoons B_1 + A_2 \]  

(15.2.5)

the equilibrium constant \( K \) is:

\[
K = \frac{q_{A2}}{q_{A1}} \times \frac{q_{B1}}{q_{B2}} = \frac{1}{24} \left[ \frac{3n-6}{\Sigma (u_{1i}^2 - u_{2i}^2)_A + \Sigma (u_{2j}^2 - u_{1j}^2)_B} \right] 
\]

(15.5.20)

where \( u = \frac{h \nu}{kT} \).

Substituting for \( u^2 \) in (15.5.20) and using (15.5.16), \( K \) becomes:

\[
K = \frac{1}{24} \left( \frac{\hbar}{kT} \right)^2 \frac{1}{4\pi^2} \left[ \Sigma A_{ii}^A \left( \frac{1}{m_{1i}} - \frac{1}{m_{2i}} \right) - \Sigma A_{jj}^B \left( \frac{1}{m_{1j}} - \frac{1}{m_{2j}} \right) \right]
\]

\[
= \frac{1}{24} \left( \frac{\hbar}{kT} \right)^2 \left[ \Sigma \left( A_{ii}^A - A_{ii}^B \right) \left( \frac{1}{m_{1i}} - \frac{1}{m_{2i}} \right) \right] 
\]

(15.5.21)

where the last sum needs to be taken over the isotopically substituted atoms only.
Similarly using (15.5.19), $K$ becomes:

$$K = \frac{1}{24} \left( \frac{\hbar}{kT} \right)^2 \left[ \sum_{t,t'=1}^{n-6} F_{\alpha \alpha} A_{tt'} \left( \mu_{\alpha} H_{tt'} - \mu_{\alpha} H_{tt'} \right) - \sum_{p,p'=1}^{31-6} B_{\beta \beta} A_{pp'} \left( \mu_{\beta} H_{pp'} - \mu_{\beta} H_{pp'} \right) \right]$$  \hspace{1cm} (15.5.22)

According to Wolfsberg and Stern, the sum should be taken only over those elements $H_{tt'}$, which involve an isotopic atom; that is, both coordinates $S_{t\alpha}$ and $S_{t'\alpha}$ (16.3.1) refer to a particular isotopic atom $\alpha$; only then:

$$G_{tt'}^{(1)} - G_{tt'}^{(2)} = 0$$

**Note.**

This is a very good approximation; however, it is not a rigorous conclusion because it implies that no changes in geometry occur at any other position but the isotopic one.

Form 4 264.

For sufficiently small values of $u$ ($= \hbar \nu/kT$), the equation in logarithmic form can be expanded in powers of $1/T$. The first non-vanishing term involves $1/T^2$ and is given below:

$$\ln \frac{K_H}{K_D} = \ln K = \frac{1}{24} \left[ \sum_{i=1}^{3n-6} \left( u_{1i}^2 - u_{2i}^2 \right) - \sum_{j=1}^{31-6} \left( u_{1j}^2 - u_{2j}^2 \right) \right]$$  \hspace{1cm} (15.5.23)
Substitutions for \( u^2 \) analogous to those made in "Form 3" lead to:

\[
\ln K = \frac{1}{24} \left( \frac{\hbar}{kT} \right)^2 \sum_i \left( A_{ii} - A_{ij} \right) \left( \frac{1}{m_{1i}} - \frac{1}{m_{2i}} \right) \quad (15.5.24)
\]

\( i \): all isotopically substituted atoms.

or:

\[
\ln K = \frac{1}{24} \left( \frac{\hbar}{kT} \right)^2 \left[ \sum_{t, t'} \left[ \sum_{tt'} A_{tt'} G^{(1)}_{tt'} - G^{(2)}_{tt'} \right] - \sum_{pp'} \left[ F_{pp'} \right] \right] \quad (15.5.25)
\]

As in the case of "Form 2", for "Forms 3 and 4" a new term, \( \overline{\gamma} \), can be introduced to extend the validity of the equations for \( K \) to larger \( u \) values. \( \overline{\gamma} \) is defined by the Bigeleisen-Mayer \((G(u)\) function (relation 15.5.11):

\[
\overline{\gamma} = \frac{12G(\overline{u})}{\overline{u}} \quad (15.5.11)
\]

where \( \overline{u} \) is some average frequency which is responsible for the isotope effect (or the frequency which makes the most important contribution to the isotope effect).

Wolfsberg and Stern have investigated the application of the "gamma-bar method" in a series of theoretical calculations. They conclude that the high temperature approximation in its simple form, or in its "gamma-bar"
form is very useful for qualitative reasoning about isotope effects.

The direct conclusion, which can be most easily seen from (15.5.21) or (15.5.24), is that, unless

\[ A^A_{11} - A^B_{11} \neq 0 \quad (15.5.26) \]

at the position of isotopic substitution, i.e. the diagonal Cartesian force constants of the isotopically substituted atom are different in the reactant and the product, the isotope effect vanishes.\(^6, 265\)

It was found that this prediction of the high temperature approximation is reasonably correct, even at room temperature.\(^266\)

The deviations from it were found to increase as the force constants in the molecule became larger and with decrease in the number of bonds separating the isotopic position(s) from the reaction site at which major changes in force constants were taking place.

The prediction that the isotope effect primarily depended on the magnitude of the force constant changes rather than on their actual value was found to be reasonably accurate.

No force constant change calculations (nfcc).\(^{255}\)

The same authors carried out a series of calculations in which the force constants and the geometry were
the same in both the reactant and the product (or the transition state) at the positions involving the isotopic substitution. The isotope effect calculated in this way, by means of equation (15.4.5), was small. In the cases of β-, γ-, and δ- deuterium, the isotope effect was <0.1% per deuterium atom at temperatures above 300°K. For α- deuterium, the isotope effects were larger: up to 0.5% at 300°K and 5% at 100°K. A study of the isotope effect vs. force constant (a series of different force constants was used) showed that the change in the calculated isotope effect was small. The effects were also small when the only change between the reactant and the product was an angle involving nonisotopic atoms, and, also, when the change was only in the mass of an atom one or two bonds removed from the isotopic atom.

Low temperature approximation. 260

At low temperatures the factor

\[
\begin{align*}
\prod_{i=1}^{n'} & \frac{1 - e^{-\frac{h\nu_{A1i}}{kT}}}{1 - e^{-\frac{h\nu_{A2i}}{kT}}} \\
\prod_{j=1}^{m'} & \frac{1 - e^{-\frac{h\nu_{B1j}}{kT}}}{1 - e^{-\frac{h\nu_{B2j}}{kT}}}
\end{align*}
\]

(15.5.27)
in (15.4.5) (called the "vibrational excitation factor") becomes unity and thus $K$ becomes:

$$K = \frac{\sigma_{A_1}}{\sigma_{A_2}} \cdot \frac{n' u_{A_{2i}}}{\prod_{i=1}^{n} u_{A_{1i}}} \cdot \frac{-h\nu_{A_{2i}}/2kT}{e^{-h\nu_{A_{1i}}/2kT}} \cdot \frac{-h\nu_{B_{2i}}/2kT}{e^{-h\nu_{B_{1i}}/2kT}}$$

(15.5.28)

where the first two ratios of ratios have their origin in the translational and rotational partition functions; the last ratio of ratios arises from zero point energies and is written as ZPE by Wolfsberg and Stern.

The terms (see 15.4.1)

$$\frac{\sigma_{A_1}}{\sigma_{A_2}} \cdot \frac{\begin{bmatrix} I_{xA_2} & I_{yA_2} & I_{zA_2} \\ I_{xA_1} & I_{yA_1} & I_{zA_1} \\ I_{xB_2} & I_{yB_2} & I_{zB_2} \\ I_{xB_1} & I_{yB_1} & I_{zB_1} \end{bmatrix}^{1/2}}{M_{A_2} \cdot \begin{bmatrix} M_{A_1} \\ M_{B_2} \\ M_{B_1} \end{bmatrix}}$$

can be calculated on the basis of geometrical considerations and masses of the atoms. This term is equivalent to the two ratios of ratios mentioned above (15.5.28).

If the ZPE term can be calculated, $K$ can be obtained. The reverse is also true: if the isotope effect is measured at one (low) temperature and ZPE for one pair of molecules is known, then the ZPE for the second pair of molecules can be obtained.
It was found by Wolfsberg and Stern that this approximation gives results in agreement with those obtained by the complete equation (15.4.5) at 500K.

**Cutoff procedure**

The procedure is based on the relation:

\[
\ln K = \frac{1}{24} \left( \frac{\hbar}{kT} \right)^{3n-6} \sum_{t, t' = 1}^{3n-6} F_{t t'} (G_{t t}^{(1)} - G_{t t}^{(2)}) A_{t t'} - \\
\sum_{p, p' = 1}^{31-6} F_{p p'} (G_{p p}^{(1)} - G_{p p}^{(2)}) B_{p p'}
\]

(15.5.25)

The isotope effect or the contribution to it is zero if no force constant change and/or if no geometry changes occur between the reactants and the products. In other words, the parts of the molecule which do not undergo any change in going from A to B (reaction 15.2.5) can be neglected (cutoff) on calculating K. One of the restrictions imposed upon the cutoff procedure is that the neglected atoms do not participate together with the coordinates of the isotopic positions or of the positions undergoing a change during the reaction (force constant or geometrical change) in the definition of some internal coordinates (see subsection 16.3).

It was found that the best agreement was obtained when the cutoffs were the same in both the reactant and the product (or transition state) and when the mass of the cutoff fragment was added to the mass of the terminal (last
before cutoff) atom.

The procedure has been found to be a valid one. The corollary of this fact is that one needs to know only what is happening in the neighborhood of the isotopic position(s) in order to calculate the isotope effect.

15.6 Streitwieser's approximation. 267

The approximation deals specifically with the deuterium secondary isotope effect and is based on the following assumptions.

1. Deuterium substitution will change significantly only those vibrational frequencies which involve the vibration of the isotopically substituted hydrogen atoms.

2. The C-H stretching and bending frequencies are sufficiently large at room temperature.

3. In substitution of one or more atoms by an isotope the forces binding the individual atoms are not altered. Due to the different masses of the isotopic species the frequencies of vibration are changed.

For a heterodiatomic molecule, this effect is given by:

\[ \nu_1 = \nu \left( \frac{\mu_1}{\mu_2} \right)^{\frac{1}{2}} \]  

(15.6.1)
where \( i \) refers to the isotopic species and \( \mu \) is the reduced mass of the diatomic vibrator.

An isolated C-H stretching vibration can be considered as a vibration of the hydrogen atom against the molecular frame work. Thus:

\[
\nu(X-D) = \nu(X-H) \left( \frac{\mu_D}{\mu_H} \right) = \nu(X-H) \cdot \left( \frac{m_H}{m_D} \right)^{1/2}
\]  

(15.6.2)

Hence:

\[
\frac{\nu(X-H)}{\nu(X-D)} = \left( \frac{m_D}{m_H} \right)^{1/2} = 2^{1/2}
\]  

(15.6.3)

The observed values for some diatomic and polyatomic molecules are smaller than \( 2^{1/2} \):

\[
\frac{\nu_{HBr}}{\nu_{DBr}} = 1.39
\]

\[
\frac{\nu_{CH_3OH}}{\nu_{CD_3OH}} = 1.35
\]

(15.6.4)

\[
\frac{\nu_{CHCl_3}}{\nu_{CDCl_3}} = 1.34
\]

The authors use:

\[
\frac{\nu_H}{\nu_D} = 1.35
\]  

(15.6.5)

Consider expression (15.4.5):
\[
\frac{\sigma_{B_2}}{\sigma_{B_1}} = K \frac{\pi \frac{n'}{u_{A_{2i}}} \frac{e^{-u_{A_{2i}}/2}}{1-e^{-u_{A_{2i}}/2}}}{\pi \frac{n'}{u_{A_{1i}}} \frac{e^{-u_{A_{1i}}/2}}{1-e^{-u_{A_{1i}}/2}}} \]

\[
\frac{\sigma_{A_2}}{\sigma_{A_1}} = \frac{\pi \frac{l'}{u_{B_{2j}}} \frac{e^{-u_{B_{2j}}/2}}{1-e^{-u_{B_{2j}}/2}}}{\pi \frac{l'}{u_{B_{1j}}} \frac{e^{-u_{B_{1j}}/2}}{1-e^{-u_{B_{1j}}/2}}} \]  \tag{15.4.5}

The first two assumptions lead to an approximate cancelation of the first and last ratio of ratios in the RHS of (15.4.5).

Taking the logarithm of (15.4.5) and neglecting the ratio of the symmetry numbers:

\[
\ln K = \frac{1}{2} \left[ \sum \left( u_{A_{1i}} - u_{A_{2i}} \right) - \sum \left( u_{B_{1j}} - u_{B_{2j}} \right) \right]
\]

\[
= \frac{hc}{2kT} \left[ \sum \left( \nu_{A_{1i}} - \nu_{A_{2i}} \right) - \sum \left( \nu_{B_{1j}} - \nu_{B_{2j}} \right) \right] \]  \tag{15.6.6}

For hydrogen and deuterium (15.6.6) becomes:

\[
\ln K = \frac{hc}{2kT} \left[ \sum \left( \nu_i(H) - \nu_i(D) \right)_A - \sum \left( \nu_j(H) - \nu_j(D) \right)_B \right] \]  \tag{15.6.7}

with \( \nu \) in cm\(^{-1}\); the sums are only over the bending and stretching modes of C-H bonds which involve isotopic substitution, i.e. in which H is replaced by D.

Using relation (15.5.30) and substituting for the universal constants:
\[ \ln K = \frac{0.186}{T} \sum_i \left[ \nu_{A(H)} - \nu_{B(H)} \right]_i \]  

Equation (15.6.8) is a very approximate one; it is a very crude high temperature approximation combined with nfcc and cutoff methods of calculation. At the same time, any other vibration which is not C-H bending or stretching is neglected though it may contribute significantly to the isotope effect.

15.7 Halevi's treatment

Halevi considers the potential energy of a C-H bond and that of a C-D bond and the way this potential is affected by an incoming reactant.

The basic idea is that the potential energy of the product (or the transition state) has the same dependence on the displacement of the isotopic atoms as the reactant. The change in potential energy between the reactant and the product is expressed as (see appendix 15.7.1):

\[ \delta V = V_e + \sum_r \left( a_r x_r + \frac{1}{2} b_r x_r^2 \right) + \sum_{r > s} c_{rs} x_r x_s + \ldots \]  

(15.7.1)

where the first sum is taken over isotopically replaceable hydrogen atoms and the second (double) sum over the isotopic positions and all other positions that have important
cross terms with them. If only the sum over \( r \) is retained, we would be treating CH displacements (stretching and deformation modes) as a set of independent diatomic molecules C-H. The double sum allows us to include coupling between the vibrational modes.

For the case of hydrogen and deuterium (15.7.1) becomes:

\[
\Delta \delta V = \sum_r \left[ a_r (\overline{x}_r(D) - \overline{x}_r(H)) \right] + \frac{1}{2} b_r \left[ \overline{x}_r^2(D) - \overline{x}_r^2(H) \right] \\
+ \sum_r \sum_{r<s} c_{rs} \left[ \overline{x}_r(D) \overline{x}_s(D) - \overline{x}_r(H) \overline{x}_s(H) \right] + \ldots \quad (15.7.2)
\]

where \( x \) is the displacement of the H and D atoms, respectively, with respect to the equilibrium position; \( a, b, \) and \( c \) are constants.

As Halevi himself points out, (15.7.2) cannot be used to carry out any isotope effect calculations. It can be used to rationalize observed isotope effects in terms of current physical organic chemistry concepts: hyperconjugation, hybridization, etc. (see subsection 15.10).

15.8 Zero point energy effect

The "zero point energy effect" is an approximate method of calculating the isotope effect and is invoked quite frequently.
Starting with (15.4.5), the approximations made are:

1. For fairly heavy molecules, the substitution of one or more hydrogen atoms for heavier isotopes will not affect the molecular mass or the moment of inertia to any appreciable extent; thus, the ratio of atomic masses and moments of inertia should approach unity and to an even better approximation cancel each other out.

2. The exponential $e^{-u}$ is small compared with unity at room temperature and thus the ratio containing expressions in "$1-e^{-u}$ will cancel out. What is left is:

$$K = \exp \left\{ \left[ \Sigma (u_{A_1} - u_{A_2}) - \Sigma (u_{B_1} - u_{B_2}) \right] \right\} \quad (15.8.1)$$

which is the zero point energy difference.

Thus, an isotope effect is obtained when the difference between the energies of the ground state vibrational level of the reactant and the product (or the transition state) is different for the isotopic molecules. A well-known diagram 269 is used to demonstrate this point:
15.9 The theoretical calculation of an isotope exchange reaction in solution.

The theoretical calculations presented so far are valid for gas-phase reactions. Most experiments, on the other hand, are carried out in the liquid phase where the perturbing influences are strong. It is generally assumed that the external influences have little isotopic specificity.\(^{270}\)

Consider an equilibrium in solution via a hypothetical gas-phase path \(^{248}\):

\[
(x \ XH_y \)_\text{liq}_1 + (y \ YD_x \)_\text{liq}_2 \xrightleftharpoons{K_1} (x \ XH_y + y \ YD_x \)_\text{gas} \xrightleftharpoons{K_2} (x \ XD_y \)_\text{gas} + (y \ YH_x \)_\text{liq}_2
\]

Equation (15.9.1)

\(XH_y\) and \(XD_y\) are in one liquid phase and \(YD_x\) and \(YH_x\) in another liquid phase. Then:
\[ K_S = K_1 K_2 K_3 \]  \hspace{1cm} (15.9.2)

where \( K_S \) is the liquid-phase equilibrium constant; \( K_1 \) is the equilibrium constant for the formation of \( x \) molecules of gaseous \( XH_y \) and \( y \) molecules of gaseous \( YD_x \) from the respective liquid phases; \( K_2 \) is the gas phase equilibrium constant and \( K_3 \) is the equilibrium constant for the formation of \( x \) molecules of liquid \( XD_y \) and \( y \) molecules of liquid \( YH_x \) from gaseous state.

\[ K_1 = \left( \frac{P_1^H}{N_1^H} \right)^x \left( \frac{P_2^D}{N_2^D} \right)^y \quad K_3 = \left( \frac{N_1^D}{P_1} \right)^x \left( \frac{N_2^H}{P_2} \right)^y \]  \hspace{1cm} (15.9.3)

where \( p \)'s are partial vapour pressures and \( N \)'s are the mole fractions in their respective liquid phase.

If the liquid phases consist only of the isotopic species of a single compound, Raoult's law can be assumed to hold, and thus:

\[ \frac{P_1^H}{N_1^H} = p_1^{oH} \quad \text{and} \quad \frac{P_1^D}{N_1^D} = p_1^{oD} \]  \hspace{1cm} (15.9.4)

\[ K_S = K_2 \left( \frac{p_1^{oH}}{P_1^{oH}} \right)^x \left( \frac{P_2^{oD}}{P_2} \right)^y \]  \hspace{1cm} (15.9.5)
where \( p^0 \)'s are the vapour pressures of pure isotopic species.

When the liquid phases are not pure liquids, but solutions, then:

\[
K_1 = \left( \frac{p_1^{\text{H}_2\text{O}} f_1^\text{H}}{p_1^{\text{D}_2\text{O}} f_1^\text{D}} \right)^x \left( \frac{p_2^{\text{H}_2\text{O}} f_2^\text{H}}{p_2^{\text{D}_2\text{O}} f_2^\text{D}} \right)^y
\]

and

\[
K_3 = \left( \frac{1}{p_1^{\text{D}_2\text{O}} f_1^\text{D}} \right)^x \left( \frac{1}{p_2^{\text{H}_2\text{O}} f_2^\text{H}} \right)^y
\]

where \( f \)'s are the activity coefficients (representing the departures from Raoult's law). If it is assumed that:

\[
f_1^\text{H} = f_1^\text{D} \quad \text{and} \quad f_2^\text{H} = f_2^\text{D}
\]

then a relation identical with (15.9.5) is obtained for this case.

The results hold even in the case in which there is only one condensed phase, as in the case of an exchange reaction between a solute and water.

A comparison of the theoretical and experimental equilibrium constants in the liquid phase has been made for the deuterium exchange of water and ethanethiol, and water and \( n \)-pentyl alcohol.\(^{271} \) The agreement was good.

The reaction studied was of the type:

\[
\text{RH + HOD} \rightleftharpoons \text{RD} + \text{HOH}
\]

(15.9.7)
where RH was ethanethiol \((C_2H_5SH)\) or n-pentyl alcohol \((C_5H_{11}OH)\).

The equilibrium constant for the gas phase reaction \(K_g\) was obtained from \(^{272, 273}\):

\[
K_g = K_1 \frac{P_{RD}P_{HOH}}{P_{RH}P_{HOD}} \tag{15.9.8}
\]

where \(K_1\) is the liquid phase equilibrium constant and is obtained experimentally from the relation:

\[
K_1 = \frac{[RD][HOH]}{[RH][HOD]} \tag{15.9.9}
\]

\(P_{HOH}/P_{HOD}\) was taken as 1.074 at \(25^\circ\).

The ratio \(P_{RD}/P_{RH}\) was found to be 0.855 for n-pentyl alcohol and 0.911 for ethanethiol. Thus, the experimental values for \(K_g\) were 0.50 and 0.21 for n-pentyl alcohol-water system and ethanethiol-water system respectively.

The \(K_g\) values calculated by the means of (15.4.5) and using a series of approximations (e.g. change in mass and moments of inertia neglected, only certain frequencies considered in computing the products over vibrational modes) gave the following results: 0.49 for n-pentyl alcohol-water and 0.24 for ethanethiol-water with an estimated uncertainty of 0.04 due to frequency values.
15.10 **Secondary deuterium isotope effects and physical organic chemistry concepts.**

In the preceding pages, methods of calculating isotope effects have been described. Depending on the complexity of the reactions studied, these calculations are of various degrees of difficulty. Though the calculations will reproduce in a semiquantitative way the effects observed experimentally, it is more difficult to sense from them the actual physical phenomenon behind the isotope effects.

To obtain a better understanding of these physical phenomena is one of the reasons (another could be the strong organic background of most physical organic chemists). Why it is a custom to rationalize the isotope effects in terms of common organic chemistry concepts such as, non-bonded interactions, hybridization, hyperconjugation, inductive effects, etc.

These concepts, while they are in general lacking in quantitative rigor, give a picturesque image of what is happening during a reaction. The same thing is valid when these concepts are applied to isotope effects; they give us a physical feeling of the quantities measured (i.e. the isotope effect) while quantitatively, the best they can do is to explain and predict trends.
In the following pages these concepts are described as they relate to deuterium isotope effects.

**A classification of secondary deuterium isotope effects.**

The deuterium isotope effects are classified in the following groups:

1. **Primary:** referring to isotope effects in cases in which a bond to an isotopic atom is broken or formed during a reaction. An example:

$$\begin{align*}
\ce{H} & \quad \ce{C} - \ce{H(D)} + \ce{B^-} \quad \xrightarrow{\text{K_H(K_D)}} \quad \ce{C} - \ce{H(CH_3)} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}$$

$$K_H/K_D \approx 12$$

2. **Secondary:** referring to isotope effects occurring during a reaction in which a bond to an isotopic atom is neither broken nor formed. The secondary effects can be divided in two further groups:

2a. Secondary isotope effects of the first kind (or α-secondary).

2b. Secondary isotope effects of the second kind (or β, γ, etc.-secondary). The two types of effects are illustrated below:

$$\begin{align*}
\ce{D} & \quad \ce{C} - \ce{H} + \ce{B^-} \quad \xrightarrow{\text{K_D}} \quad \ce{C} - \ce{D(CH_3)} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}$$

$$\begin{align*}
\ce{H} & \quad \ce{C} - \ce{H} + \ce{B^-} \quad \xrightarrow{\text{K_D}} \quad \ce{C} - \ce{H(CD_3)} \\
\text{CD}_3 & \quad \text{CD}_3
\end{align*}$$
In neither case is a bond to a deuterium atom ruptured. The participation of the isotopic atom is different in the two cases. In (15.10.2) the C-D bond undergoes a spatial reorientation, from tetrahedral to plane trigonal. In (15.10.3) the -CD$_3$ maintains its configuration throughout the reaction.

The magnitude of the two effects is different: the secondary isotope effects of the first kind tend to be somewhat larger than those of the second kind.

The criterion for classifying secondary isotope effects into the first or second kind is, as shown above, whether or not bonds to isotopic atoms have undergone spatial reorientation. It was proposed by Halevi. Streitwieser has given other criteria, namely, that secondary deuterium isotope effects of the first kind are those in which hybridization changes occur, and that secondary isotope effects of the second kind are those effects "that behave like inductive effects".

Halevi's objection to the Streitwieser criteria is that "a classification scheme based on the presence or absence of significant structural changes in the region of isotopic substitution is likely to survive longer than one based on theoretical concepts, no matter how well established these seem to be at the time". It seems to us
that Halevi's criterion is not any better than Streitwieser's: structural changes are based on theoretical concepts (e.g. postulated mechanisms) rather than on direct observation of such changes during the reaction. A simpler criterion is to consider a secondary deuterium isotope effect of the first kind when a reaction center is located at an atom containing an isotopic bond; those of the second kind occur when the reaction does not take place at the carbon atom containing the isotopic bond.

Nonbonded interactions (steric effects) and secondary isotope effects. 234, 276

Nonbonded interaction theory is based on the contention that nonbonded repulsions between the atoms of a molecule have a strong influence on the structure and thermochemical properties of the respective compound.

It has been considered that, since chlorine atoms are large and repel atoms strongly while hydrogen atoms are small and quite negligible in comparison, bond angles, lengths, and energies in the series \( \text{CH}_n\text{Cl}_{4-n} \) would show marked variations if nonbonded interactions were large. The smallness of such effects in this series was interpreted as an indication that atoms were greatly whittled down on the side of the covalent bonds and hence exhibited small repulsions. 277
Bartell explains the absence of such effects in tetrahedral compounds by the fact that, in these compounds, the interactions between pairs H...H, C...C, Cl...Cl, H...C, H...Cl, etc. are very similar in magnitude and thus balance out (or are obscured). What makes it possible for small hydrogen atoms to compete in repulsive force with larger atoms (carbon, chlorine, ...) is the fact that the larger atom is further away from the central atom and the resulting increase in the nonbonded distances closely compensates for the larger size.

Whereas the balance of repulsions masks their effect in tetrahedral molecules, the change in the number of repulsions upon going to trigonal and linear molecules leads to marked effects. Thus, in a trigonal or linear molecule the number of nonbonded interactions is smaller as compared with tetrahedral molecules. This, presumably, makes the C-X bond in a compound of the type

\[
\begin{array}{c}
X \\
\mid \\
X - C - \ldots \\
\mid \\
X
\end{array}
\]

(A)

greater than in one of the type
or, in other words, the number of nonbonded interactions tending to lengthen the single bond is reduced in compounds B and C. Thus, it was found that the number of nonbonded repulsions decreased in those cases in which the bond lengths were observed to decrease and bond energy to increase.234, 276

The origin of nonbonded interactions leading to secondary deuterium isotope effects is ascribed to the fact that the amplitudes of vibration of hydrogen atoms are larger than the amplitudes of deuterium atoms. Thus, the nonbonded repulsions averaged over the atomic vibrations are greater for hydrogen atoms than for deuterium atoms and, therefore, the relief associated with a transformation from a tetrahedral to a trigonal form is greater in molecules containing hydrogen than in those containing deuterium \((K_H > K_D)\). Conversely, increased steric compression in the product or transition state leads to an inverse isotope effect \((K_D > K_H)\).

Examples of steric kinetic isotope effects are provided by the rates of racemization of 9,10-dihydro-4,
5-dimethylphenanthrenes

\[
\begin{align*}
\text{k}_1 \times 10^4 \text{ (s}^{-1}) & : \\
5.92 & 6.21 & 6.70 & 6.99 \\
\text{k}_D/\text{k}_H & : 1.05 & 1.13 & 1.18 \\
\text{(in benzene at } 42^\circ \text{C)} \\
\text{or of 2,2'-dibromo-4,4'-dicarboxybiphenyl} & \\
\end{align*}
\]

\[
\begin{align*}
\text{k}_1 \times 10^{-5} \text{ (s}^{-1}) & : \\
6.48 & 7.71 \text{ (in EtOH at } -19.8^\circ \text{C)} \\
\text{k}_H/\text{k}_D & : 1.19 \\
\text{or from the rates of reaction of methyl-d}_3\text{-pyridines with alkyl iodides} & \\
\begin{array}{ccc}
\text{Pyridine} & \text{Alkyl iodide} & \text{k}_D/\text{k}_H \text{ at } 25^\circ \text{C} \\
4\text{-Methyl-d}_3 & \text{Methyl} & 1.001 \pm 0.01 \\
3\text{-Methyl-d}_3 & \text{Methyl} & 1.009 \pm 0.01 \\
2\text{-Methyl-d}_3 & \text{Methyl} & 1.030 \pm 0.01 \\
2,6\text{-Dimethyl-d}_6 & \text{Methyl} & 1.095 \pm 0.01 \\
\end{array}
\end{align*}
\]
These results were interpreted to indicate that the electronic effect of the -CD$_3$ group does not differ significantly from that of -CH$_3$. The only significant difference is the steric requirements of the two groups. This difference shows up in the reaction of 2-methylpyridine and 2,6-dimethylpyridine.

Wilson $^{280}$ has criticized the steric hindrance theory "....extremely little is known about forces between nonbonded atoms within a given molecule. In most cases there is at present no solid evidence that the force is repulsive or attractive."

Hyperconjugation and secondary deuterium isotope effects.

In 1934, Wheland $^{281}$ explained the greater stability of ethyl as compared with methyl radicals by a new type of resonance interaction involving structures similar to those shown below:

\[
\begin{align*}
\text{H} & \quad \leftrightarrow \quad \text{H} \\
\text{H} - \text{C} - \text{CH}_2 & \leftrightarrow \quad \text{H}^+ \quad \text{C} = \text{CH}_2 & \leftrightarrow \quad ... \\
\text{H} & \quad \downarrow \quad \text{H}
\end{align*}
\]

This type of resonance was examined later by Mulliken $^{282,283}$ using an MO approach and was labelled "hyperconjugation".

In general, conjugation phenomena are classified into following groups $^{284,285}$.
1. Conjugation: in the case of a pair of adjacent $\pi$-bonds.

2. Hyperconjugation: in the case of a $\pi$-bond interacting with a $\sigma$-bond.

3. Second order hyperconjugation: in the case of a pair of $\sigma$ bonds.

Mulliken's definitions include, besides $\pi$ bonds, a lone $\pi$ electron, a $\pi$ electron pair or quartet, or a $\pi$ electron vacancy.

A more detailed classification is discussed by Mulliken elsewhere. 286

The evidence for hyperconjugation or vice versa, i.e. experimental results which are explained by hyperconjugation, is as follows: bond lengths (the shortening of a carbon-carbon single bond adjacent to a double or triple bond) 287, heats of combustion and/or Baker-Nathan order of reactivity in electron-demanding reactions. 288, 289

One of the predictions of the Bigeleisen-Mayer-Wolfsberg theory in its high temperature approximation (relation 15.5.21), is that, unless the diagonal Cartesian force constants at the position of isotopic substitution change in going from the reactant to the transition state, the isotope effects will vanish.

Hyperconjugation is used in the theory of secondary isotope effects to rationalize these force constant changes. 16
For example, a developing carbonium ion can withdraw electrons from a neighbouring C-H bond making this bond weaker in the transition state.

As it is well known, hyperconjugation is one of the controversial problems of today's chemistry. Until the whole problem is put on more quantitative grounds not much can be said, except to add hyperconjugation to the list of the possible causes for isotope effects with its relative importance still unknown.

Dewar's remarks describe the situation very well: "Much of the present day controversy concerning conjugation and hyperconjugation is based on a failure to recognize the quite arbitrary nature of the resonance and bond delocalization. An accurate quantum mechanical description would contain nothing that could be identified with either".

Hybridization and secondary deuterium isotope effects.

Two things are generally implied when one talks about hybridization: the geometry and the s, p, ....character of the respective bonds. Walsh has shown that a number of properties can be correlated with the hybridization.

For a relationship between hybridization and isotope effects to exist, the reaction studied must occur with a change in the hybridization which could affect the isotopic positions. Primary and secondary (of the first kind) isotope
effects would be involved in these reactions.

The trigonal configuration will favour a deuterated molecule because of the smaller mean-square amplitude of the C-D stretching modes and the shorter mean length. Also, since an sp² carbon is more electronegative, it is easier to shorten the C-H bond than to stretch it (see appendix 15.10.1). Then both these effects operate in the same direction:

\[ K_D > K_H \]

**Inductive effects and secondary deuterium isotope effects.**

The properties of chemical bonds are very frequently rationalized in terms of electronic displacements. The basic assumption is that various atoms and groups have different tendencies to attract or repel electrons. The tendency of a substituent to acquire a negative or positive charge and in this way to induce a positive or a negative charge on the rest of the molecule is known as the inductive effect.

A number of workers refer to "inductive effects" (electrostatic action transmitted through chains of atoms) and to "field effects" (electrostatic action transmitted through the empty space or through the solvent molecules).

Using the generally accepted convention of Ingold, a group is said to have a -I effect if it acquires electronic
charge and a +I effect if it donates charge and becomes positively charged.

Streitwieser and Klein explained the secondary deuterium isotope effects on the dissociation constant of acetic, pivalic, and benzoic acids by assuming an inductive effect.

Studies of electronic properties of hydrogen and deuterium compounds show that in C-D bond, because it is slightly shorter, the electron density is shifted somewhat closer to C than in a C-H bond. As pointed out in 15.2, any difference in the "electronic" properties of the two classes of compounds can be traced back to a vibrational origin. The isotope effects on some of these properties are described next.

The dipole moment of a vibrating polyatomic molecule can be expressed as:

\[ \mu = \nu_e + \sum \left( \frac{\delta \mu}{\delta Q_i} \right)_e Q_i + \sum \sum \left( \frac{\delta^2 \mu}{\delta Q_i \delta Q_j} \right)_e Q_i Q_j + \ldots \]  (15.10.17)

where \( Q_i \) are the normal coordinates; \( \nu_e \) is the dipole moment at the equilibrium configuration and the derivatives are evaluated at the equilibrium configuration of the nuclei.

Halevi gives essentially the same expression for the dipole moment, the only difference being that the normal coordinates are replaced by internal coordinates: bond
stretching, etc. Halevi's expression is:

\[
\mu = \mu_e + \sum_i \left( \frac{\delta \mu}{\delta x_i} \right)_e x_i + \frac{1}{2} \sum_i \left( \frac{\delta^2 \mu}{\delta x_i^2} \right)_e x_i^2 + \sum_{i>j} \left( \frac{\delta^2 \mu}{\delta x_i \delta x_j} \right)_e x_i x_j \]

(15.10.18)

where \(i, j = 1 \ldots 3n-6\) (3n-5) and \(x\)'s are the differences in the interatomic distances and bond angles from their equilibrium values. In particular, for a diatomic molecule \(HX\), (15.10.18) is:

\[
\mu = \mu_e + \left[ \frac{\delta \mu}{\delta x} \right] x + \frac{1}{2} \left[ \frac{\delta^2 \mu}{\delta x^2} \right] x^2 + \ldots \]

(15.10.19)

where \(x = r_r - r_e\), with \(r_e\) the equilibrium internuclear distance and \(r\) the instantaneous nuclear distance.

The average dipole moment is obtained by averaging term by term:

\[
\bar{\mu} = \mu_e + \left[ \frac{\delta \mu}{\delta x} \right] \bar{x} + \frac{1}{2} \left[ \frac{\delta^2 \mu}{\delta x^2} \right] \bar{x}^2 + \ldots \]

(15.10.20)

The difference in the dipole moment \(\Delta \mu\) between two molecules, \(HX\) and \(DX\) is:

\[
\Delta \mu = \bar{\mu}_{DX} - \bar{\mu}_{HX} = \left( \frac{\delta \mu}{\delta x} \right)_e (\bar{x}_{DX} - \bar{x}_{HX}) + \left[ \frac{\delta^2 \mu}{\delta x^2} \right]_e (\bar{x}^2_{DX} - \bar{x}^2_{HX}) + \ldots \]

(15.20.21)
As a rule, $x_{DX} < x_{HX}$. The sign of the derivatives is a difficult problem which has not been resolved up to now and thus, not even the sign of $\Delta \mu$ can be predicted.

The direction and the magnitude of the dipole moment in HD was calculated by Kolos and Wolniewicz. They obtained the following results:

\[
\begin{align*}
\text{H} & \quad \text{D} \\
\mu & = 1.54 \times 10^{-3} \text{D}
\end{align*}
\]

Substitution of hydrogen for deuterium in molecules possessing an electric dipole enhances the magnitude of the dipole when the substitution takes place at the positive end of the dipole.

Examples:

\[
\begin{align*}
\text{F - CH}_3 & \quad \text{F - CD}_3 \\
= 1.8471 \text{ D} & \quad = 1.8583 \text{ D} \\
\text{F}_3\text{C - H} & \quad \text{F}_3\text{C - D} \\
= 1.6461 \text{ D} & \quad = 1.6468 \text{ D}
\end{align*}
\]

The values shown above are in agreement with the larger electron density on the C atom of a C-D bond, as compared to a C-H bond.

Another piece of evidence pointing to the larger electron releasing power of deuterium is the nuclear quadrupole coupling constant (see appendix 15.10.2 for a brief
explanation of the nuclear quadrupole coupling.

In general, the nuclear quadrupole coupling constant is a measure of the departure of the electron distribution from spherical symmetry about the nucleus.

If, in deuteration, the nuclear quadrupole coupling constant decreases, this is a good indication that the respective bond has become more ionic and vice versa.

An increase in the nuclear quadrupole coupling constant upon deuteration was observed in the case of SbH₃ and AsH₃. The increase was assigned to a shorter C-D bond which led to a larger coupling.

A decrease in nuclear quadrupole coupling constant, eqQ, (see appendix 15.10.2) upon deuteration was observed in the methyl halides. The decrease was attributed to a decrease in the C-halogen separation with the probable result that the asymmetry of the charge distribution at the nucleus was reduced. This also agreed with the greater electron density on the carbon atom of a C-D bond as compared with the C-H bond (see appendix 15.10.2).

Nuclear magnetic resonance.

The first example of a deuterium isotope effect in PMR was observed by Wimett: the chemical shift of H in HD increased as compared with H₂.

Later Tiers observed that the protons of -CH₂D
group of α-deuterotoluene are 0.015 ± 0.002 ppm more shielded than are those of CH₃ group of toluene.

Similar shifts have been observed in FMR (fluorine magnetic resonance).

These shifts indicate a greater electron donating power for deuterium than for hydrogen.

Gutowsky has qualitatively analysed the origins of these shifts.

Emsley, Feeney and Sutcliffe gave a semiquantitative treatment of the problem in their book on NMR.

The chemical shift $\sigma$ arises from the diamagnetic shielding of the nucleus by the electrons surrounding it. In the case of isotopic molecules, the change in the shielding constant is probably due to a change in the dynamic state of the molecule, i.e. a change in the bond angles and bond lengths (different amplitudes of vibration).

If the variation of $\sigma$ with the internuclear distance $R$ is given by a polynomial of the type:

$$\sigma(R) = \sigma(R_e) + \sigma'(R_e)(R-R_e) + \frac{1}{2} \sigma''(R_e)(R-R_e)^2 + ... \quad (15.10.22)$$

where $R_e$ is the equilibrium internuclear distance and since:

$$\sigma_{obs} = \int_o^\infty \psi^2 \sigma(R) dR \quad (15.10.23)$$
where $\psi$ is the nuclear wave function for the ground vibrational state, then:

$$\sigma_{\text{obs}} = \sigma(R_e) + <R-R_e>\sigma'(R_e) + <(R-R_e)^2>\sigma''(R_e) + \ldots \quad (15.10.24)$$

where $<>$ denote a quantum mechanical average over the motion:

$$<R-R_e> = \int_0^\infty \psi^2(R-R_e) dR \quad (15.10.25)$$

The function $\psi$ is determined by the nature of the potential field $V(R)$ in which the nuclei move. If $V(R)$ contains both harmonic and anharmonic terms:

$$V(R) = f(R-R_e)^2 - g(R-R_e)^3 \quad (15.10.26)$$

then $\psi$ is:

$$\psi = \psi_0 + gh^{1/2}e^{-k_e} - 5/4 \left( \frac{3}{2\sqrt{2}} \psi_1 + \frac{1}{2\sqrt{3}} \psi_3 \right) \quad (15.10.27)$$

where $\mu$ is the reduced mass and $\psi_0$, $\psi_1$, and $\psi_3$ are the ground, first and third excited states for the corresponding harmonic oscillator ($g\epsilon=0$).

Using (15.10.25), $<R-R_e>$ and $<(R-R_e)^2>$ are:
\[ <R-R_e> = \frac{3}{2} g h \mu^{-1} f^{-3/2} \]
\[ <(R-R_e)^2> = \frac{1}{2} h \mu^{-1/2} f^{-1/2} \] (15.10.28)

and thus:

\[ \sigma_{\text{obs}} = \sigma(R_e) + \frac{3}{2} g h \mu^{-1} f^{-3/2} \sigma'(R_e) + \frac{1}{4} h \mu^{-1/2} f^{-1/2} \sigma''(R_e) \] (15.10.29)

The values of \(g\) and \(f\) may be obtained from the vibrational spectrum of the molecule and the constants \(\sigma(R_e), \sigma'(R_e),\) and \(\sigma''(R_e)\) may be determined if the variation of \(\sigma\) with \(R\) is known. Conversely, if \(\sigma(R_e), \sigma'(R_e),\) and \(\sigma''(R_e)\) are known or can be calculated, \(\sigma_{\text{obs}}\) can be obtained. Calculations of this sort for \(H_2, HD,\) and \(D_2\) agree with the observed values.\(305 - 307\)

Studies of proton spin-spin coupling constants show that \(J_{HH}\) must exhibit an angular dependence and thus, an isotope effect should be observed if interatomic angles in two isotopic molecules are different.\(308, 309\)

In most cases, the effect is too small to be detected.\(310, 311\) One case in which such an effect has been observed is SiH\(_3\)D (\(J_{HD} = 0.427 \pm 0.003\) cps) and SiHD\(_3\) (\(J_{HD} = 0.412 \pm 0.004\) cps).\(312\)
15.11 Secondary deuterium isotope effects and the substituent effects.

From an experimental point of view, the substitution of hydrogen for deuterium has, qualitatively, the same effect as the introduction of any other substituent in the molecule.

From a more theoretical point of view, the situation is different. The isotopes have a unique characteristic: the electronic partition functions (or the electronic potential energy surfaces) are the same for isotopically different molecules. This is not true for other substituents. This leads to the conclusion that the isotope effects are due entirely to the nuclear motion and, moreover, it can be shown to be mainly of vibrational origin (see also subsection 15.5).

That is why Thornton says it is not right to discuss isotope effects in the same terms as the effects of methyl vs. tert-butyl, since, in the latter, shifts in electronic potential energy must be considered besides shifts in vibrational energy.

To demonstrate his point, Thornton considers the following equilibria:

\[ \text{H} - \text{C}_6\text{H}_4 - \text{COOH} \rightleftharpoons \text{H} - \text{C}_6\text{H}_4 - \text{COO}^- + \text{H}^+ \]

\[ \text{D} - \text{C}_6\text{H}_4 - \text{COOH} \rightleftharpoons \text{D} - \text{C}_6\text{H}_4 - \text{COO}^- + \text{H}^+ \quad (15.11.1) \]

\[ \text{Cl} - \text{C}_6\text{H}_4 - \text{COOH} \rightleftharpoons \text{Cl} - \text{C}_6\text{H}_4 - \text{COO}^- + \text{H}^+ \]
The energies of these reactions (free energies, average energies,...) can be broken up into different components (and ignoring effects on solvation energies):

$$\Delta E_H = E_{\text{products}} - E_{\text{reactants}}$$

$$= (E_{\text{COO}^-/R} + E_{R/\text{COO}^-} + E_{H/\text{COO}^-} + E_{\text{COO}^-/H}) - (E_{\text{COOH}/R} + E_{R/\text{COOH}} + E_{H/\text{COOH}} + E_{\text{COOH}/H})$$

Similarly:

$$\Delta E_D = (E_{\text{COO}^-/R} + E_{R/\text{COO}^-} + E_{D/\text{COO}^-} + E_{\text{COO}^-/D}) - (E_{\text{COOH}/R} + E_{R/\text{COOH}} + E_{D/\text{COOH}} + E_{\text{COOH}/D})$$

$$\Delta E_{Cl} = (E_{\text{COO}^-/R} + E_{R/\text{COO}^-} + E_{Cl/\text{COO}^-} + E_{\text{COO}^-/Cl}) - (E_{\text{COOH}/R} + E_{R/\text{COOH}} + E_{Cl/\text{COOH}} + E_{\text{COOH}/Cl})$$

R stands for "ring", i.e. $-C_6H_4-$, and a term $E_{\text{COO}^-/R}$ means the effect of $-\text{COO}^-$ on R and so on.

Some of the terms appearing in (15.11.2) to (15.11.4) are identical for the three expressions: $E_{R/\text{COO}^-}$, $E_{\text{COO}^-/R}$, $E_{\text{COOH}/R}$, $E_{R/\text{COOH}}$. 
Consider $\Delta E_H - \Delta E_D$:

$$\Delta E_{HD} \equiv \Delta E_H - \Delta E_D =$$

$$\left\{ \left[ (E_{\text{COO}^-/H} - E_{\text{COO}^-/D}) + (E_{H/\text{COO}^-} - E_{D/\text{COO}^-}) \right] - \right.$$

$$\left. \left[ (E_{\text{COOH}/H} - E_{\text{COOH}/D}) + (E_{H/\text{COOH}} - E_{D/\text{COOH}}) \right] \right\}$$

(15.11.5)

Because H and D generate the same potential energy surface for the -COO$^-$ or -COOH group, or in other words, the effect of H on -COO$^-$ and -COOH is the same as that of D, the following relations hold:

$$E_{H/\text{COOH}} = E_{D/\text{COOH}} \quad \text{and}$$

$$E_{H/\text{COO}^-} = E_{D/\text{COO}^-}$$

(15.11.6)

On the other hand:

$$E_{\text{COO}^-/H} \neq E_{\text{COO}^-/D} \quad \text{and}$$

$$E_{\text{COOH}/H} \neq E_{\text{COOH}/D}$$

(15.11.7)

because of the vibrational differences of H and D.

Thus
\[ \Delta E_{HD} = \Delta E_H - \Delta E_D = \]

\[ (E_{COOH/D} - E_{COOH/H}) + (E_{COO^-/H} - E_{COO^-/D}) \]

where it can be seen that the isotope effect is an effect on the isotopic atom, rather than an effect of the isotopic atom.

No such simplifications occur in the case of \( \Delta E_{C1} \) (as 15.11.6). In this case, a combined effect takes place: effect of the substituent (in this case Cl) on the reaction site group (COO\(^-\) or -COOH) and the effect of the reaction site group on the substituent.

15.12 Conclusions.

The origins of secondary isotope effects have been examined in the light of the published theories.

Several explanations are currently employed by the workers in this field to rationalize their results:

1. Force constant changes on going from the initial state to the transition state or product.

2. Geometry changes at the position of the isotopic substitution on going from the initial state to the transition state or product.

3. Difference in zero-point energies between H-compounds and D-compounds.

The above explanations are what we might call "theoretical" because they originate, or they are used in
theoretical calculations of secondary isotope effects. This type of calculations tries to reproduce the results of experimentally known isotope effects and to predict isotope effects for any other case. More recent calculations of this type try to reproduce and to predict the temperature dependence of isotope effects. As a general observation: any isotope effect can be explained by choosing the proper parameters.

The "zero-point energy" difference enters as a separate term in any calculation involving isotope effects. Alone it cannot explain the isotope effects, though quite often it is used in this sense.

Another "group" of explanations on hand are:

1. Hyperconjugation
2. Nonbonded interactions
3. Hybridization
4. Inductive effects

We find it difficult to characterize this group by a single name. It is not "theoretical" because all the above terms have resisted all the attempts to pin them down in a rigorous mathematical treatment. At the same time, it is not "experimental" because it is made of concepts rather than experimental facts. Nevertheless, the four explanations
shown above can be reduced to two phenomena easier to visualize: differences in the vibrational amplitudes (or differences in the effective bond length due probably to anharmonicity) and differences in the polarizabilities of the C-H and C-D bonds.
16. THE CALCULATION OF THE VIBRATIONAL FREQUENCIES OF A MOLECULE FROM ITS MOLECULAR STRUCTURE AND THE FORCE CONSTANT MATRIX.

16.1 Introduction

In section 15 we have shown that it is possible to calculate the isotope effects on an equilibrium constant, if all the vibrational frequencies of all the species involved in the equilibrium are known.

The vibrational frequencies can be obtained experimentally or by calculations. The approach from the experimental side presents great difficulties. If we consider the isotope effects on the dissociation of an acid, i.e. the reaction:

\[ R_H - COOH + R_D - COO^- \underset{K}{\overset{K}{\rightleftharpoons}} R_H - COO^- + R_D - COOH \]

to calculate the equilibrium constant \( K \), which is in fact \( K_H/K_D \), we must know the complete set of vibrations of all four species involved. In one case only, was enough experimental data available to allow the calculation of \( K \). This was the classical case of the pair of formic-formic-1. For the acids studied in the present work, no complete vibrational analyses are available in the literature.

It is well known that it is possible to obtain the vibrational frequencies of a molecule if its geometry and the force constants of the vibrations are known. In recent years,
this approach has been used for theoretical studies of isotope effects. Wolfsberg, Stern, Willi,\textsuperscript{322} Kaplan and Thornton\textsuperscript{323}, among others, predicted the isotope effects on a series of reaction rates or equilibrium constants by assuming certain geometries of the reactants and of the products or the transition states and by using force constants from similar compounds or similar bonds.

This approach, which we call "semi-theoretical", allows one to change force constants or the geometries of the species in such a way that the calculated isotope effects match the experimental ones, and thus implicitly allow one to study the effect upon the isotope effects of such changes.

In our case, we will use this approach for studying the secondary deuterium isotope effects on the dissociation constants of a series of aromatic acids. In contrast with the Wolfsberg and Stern treatment, we will try to use the best available data for the geometries of the molecules and for the force constants involved. Whenever available, the experimentally observed frequencies will be used for obtaining force constants, or for comparing with the calculated frequencies of the vibrations.

16.2 \textbf{The calculation of the vibrational frequencies.}

The vibrational frequencies are obtained by solving
the secular equation:

$$|GF - EA| = 0 \quad (16.2.1)$$

$G$ is a matrix whose elements are obtained from the geometry of the molecule (see subsection 16.3). $F$ is the matrix for the force constants (see subsection 16.4). $E$ is the unit matrix and $\Lambda$ the column matrix of the sought values since:

$$\Lambda_i = \left( \frac{\nu_i}{1302.9} \right)^2 \quad (16.2.2)$$

where $\nu_i$ is the vibrational frequency in cm$^{-1}$. The secular equation (16.2.1) can be solved in different ways. Some of the methods for solving it are summarized by Wilson, Decius, and Cross.$^{324}$ In the present work, we use a method given by Miyazawa.$^{325}$ In this method, the sequence of operations is (in matrix notation):

a. Calculate the eigenvector matrix $A$ and the eigenvalues of the matrix $G$ ($\Gamma$ is the diagonal matrix of the eigenvalues):

$$GA = \Lambda \Gamma \quad (16.2.3)$$

b. Calculate a diagonal matrix $B$ whose non-zero elements $B_{ii}$ are given by:

$$B_{ii} = \frac{1}{\nu_i^2} \quad (16.2.4)$$
c. Calculate a matrix $W$:

$$W = AB$$  \hspace{1cm} (16.2.5)

d. Calculate a matrix $H$:

$$H = W'FW$$  \hspace{1cm} (16.2.6)

where $W'$ is the transpose of $W$.

e. Solve the equation:

$$HC = CA$$  \hspace{1cm} (16.2.7)

i.e. find the eigenvalues $\Lambda$ of matrix $H$. These eigenvalues are the quantities sought. From them the vibrational frequencies are calculated, in $\text{cm}^{-1}$, using (16.2.2).

**Potential energy distribution.**

The potential energy of a molecule is given by the expression:

$$V = \frac{1}{2} \sum_{i,j} F_{ij} S_i S_j$$  \hspace{1cm} (16.2.8)

where $S$ is the column matrix of the internal coordinates.

The internal coordinates are related to the normal coordinates by the expression:
\[ S = LQ \quad (16.2.9) \]

where \( Q \) is the matrix of the normal coordinates and \( L \) is a transformation matrix.

If we substitute (16.2.9) in (16.2.8), then the potential energy of the molecule for a given normal vibration \( \nu_k \) is:

\[ V = \frac{1}{2} \sum_{i,j} L_{ik} L_{jk} K_{ij} \quad (16.2.10) \]

\( L \), the transformation matrix, is given by (following the same notation as before) \(^{326}\):

\[ L = WC \quad (16.2.11) \]

The usefulness of relation (16.2.10) is in assigning frequencies to a particular type of vibration. \(^{351}\) Thus, if the largest term in (16.2.10) occurs when:

\[ i = j \]

that is, the maximum term in \( V \) is:

\[ \frac{1}{2} \sum_{i} K_{ii} = \frac{1}{2} \sum_{i} S_{ii} \]

\[ (16.2.12) \]
then the frequency $\nu_k$ is called the $S_i$ characteristic frequency.

If $S_i$ corresponds to a change in a C-C bond distance, for example, then $\nu_k$ is called a C-C stretching frequency.

If there is not one single large term, but two or more of the same magnitude, then the frequency $\nu_k$ results from a combination of the vibrations leading to these terms of the same magnitude in the potential energy distribution.

A computer program which calculates the vibrational frequencies of a molecule and the corresponding potential energy distribution when the $G$ and $F$ matrices are known is given in appendix 16.2.1.

16.3 The $G$ matrix.

The construction of the $G$ matrix follows the procedure given by Wilson, Decius and Cross.

The $G$ matrix is obtained from the geometry of the molecule under consideration. Consider a molecule with $N$ atoms. Any displacement in space of the molecule as a whole, or of the individual atoms, can be expressed by a set of $3N$ Cartesian coordinates. Alternately, the displacement of the atoms relative to each other can be expressed by a set of
$3N - 6$ ($3N - 5$ in case of linear molecules) internal coordinates, i.e. coordinates which are unaffected by translations or rotations of the molecule as a whole. Examples of such coordinates are the changes in the lengths or angles between the chemical bonds. If we denote the Cartesian coordinates by $X$ and the internal coordinates by $S$, the relationship between the two sets is of the form:

$$S_j = \sum_{i=1}^{3N} B_{ji} X_i \quad j = 1, 2, \ldots, 3N-6 (3N-5) \quad (16.3.1)$$

where $B_{ji}$ are constants determined by the geometry of the molecule.

The displacement of an atom $\alpha$ can be described by a vector $\vec{X}_\alpha$ whose components, along the three Cartesian axes are $X^x_\alpha$, $X^y_\alpha$, and $X^z_\alpha$. Likewise, the coefficients $B_{ji}$ can be grouped in sets of three, each set being associated with one atom. Each set can be considered as a vector $\vec{S}_j$ associated with internal coordinate $j$ and atom $\alpha$:

$$S_j = \sum_{\alpha=1}^{N} \vec{S}_{j\alpha} \cdot \vec{X}_\alpha \quad (16.3.2)$$

The $G$ matrix which we seek is defined by:

$$G_{jk} = \sum_{i=1}^{3N} \frac{1}{m_i} B_{ji} B_{ki} \quad j, k = 1, 2, \ldots, 3N-6 (3N-5)$$
\[ = \sum_{\alpha=1}^{N} \mu_{\alpha} \vec{S}_{ja} \cdot \vec{S}_{ka} \]  

(16.3.3)

where \( \mu_{\alpha} = 1/m_{\alpha} \).

Each element \( G_{jk} \) corresponds to one pair of internal coordinates \( S_j \) and \( S_k \). Note that:

\[ G_{jk} = G_{kj} \]

and if the internal coordinates \( S_j \) and \( S_k \) are orthogonal to each other:

\[ G_{jk} = 0 \]

Calculation of "B" elements.

From (16.3.1) the "B" elements are nothing less than the components of the vectors \( \vec{S}_{ja} \) along the Cartesian axes. Thus:

\[ \vec{S}_{ja} = \vec{B}_{ja}^X \vec{T} + \vec{B}_{ja}^Y \vec{J} + \vec{B}_{ja}^Z \vec{K} \]  

(16.3.4)

where the superscripts identify the three Cartesian axes and \( \vec{T}, \vec{J}, \) and \( \vec{K} \) are the unit vectors along these axes.

General expressions for the vectors \( \vec{S}_{ja} \) corresponding to the most common type of internal coordinates have been
given in a series of papers by Wilson, Decius, and Cross and are summarized in their book. They are described next.

**Bond stretching (code no. 1).**

The internal coordinate in this case is the increase in the bond length between two atoms:

\[ S_j = \Delta r_{12} \]

\[ S_{j1} = -e_{12} \quad \text{and} \quad (16.3.5) \]

\[ S_{j2} = e_{12} \quad \text{(16.3.6)} \]

"\( e_{12} \)" is the unit vector directed from atom 1 toward atom 2. It is given by:

\[ e_{12} = \frac{r_{12}}{r_{12}} \quad \text{(16.3.7)} \]

where \( r_{12} \) is the vector directed from atom 1 toward atom 2 and \( r_{12} \) is the distance between atoms 1 and 2. The vector \( r_{12} \) has components along the Cartesian axes which are given, in terms of the Cartesian coordinates, by:

\[ r_{12}^x = x_2^x - x_1^x \]

\[ r_{12}^y = y_2^y - y_1^y \quad \text{(16.3.8)} \]
\[ r_{12}^z = x_2^z - x_1^z \]

The distance \( r_{12} \) between the two atoms is given by:

\[ r_{12} = \left[ (r_{12}^x)^2 + (r_{12}^y)^2 + (r_{12}^z)^2 \right]^{\frac{1}{2}} \] (16.3.9)

The element \( B_{j1}^x \) is the component of \( S_j \) along the \( x \) axis and it is given in terms of the Cartesian coordinates of the atoms by:

\[ B_{j1}^x = -e_{12}^x = -\frac{r_{12}^x}{r_{12}} = \]

\[ \frac{x_2^x - x_1^x}{\left[ (x_2^x - x_1^x)^2 + (x_2^y - x_1^y)^2 + (x_2^z - x_1^z)^2 \right]^{\frac{1}{2}}} \] (16.3.10)

The other \( B \) elements have analogous expressions.

The vectors \( S_j \), corresponding to the atoms which are not directly involved in the stretching of the bond 1-2 (these atoms are comprised of all the atoms of the molecule, except atoms 1 and 2) are zero.

Valence angle bending (code no. 2). 328

\[ S_j = \Delta \phi \text{ or} \frac{\Delta \phi}{R \Delta \phi} \]
The internal coordinate in this case is the change in the angle $\phi$ between the two bonds 1-3 and 2-3. The vectors $\vec{s}_j$ for the three atoms involved in this type of coordinate are given by:

$$\vec{s}_{j1} = \frac{\cos \phi \vec{e}_{31} - \vec{e}_{32}}{r_{31} \sin \phi}$$  \quad (16.3.11)$$

$$\vec{s}_{j2} = \frac{-\cos \phi \vec{e}_{32} - \vec{e}_{31}}{r_{32} \sin \phi}$$  \quad (16.3.12)$$

$$\vec{s}_{j3} = \frac{(r_{31} - r_{32} \cos \phi)\vec{e}_{31} + (r_{32} - r_{31} \cos \phi)\vec{e}_{32}}{r_{31} r_{32} \sin \phi}$$  \quad (16.3.13)$$

$$= -\vec{s}_{j1} - \vec{s}_{j2}$$

The unit vectors $\vec{e}_{31}$ and $\vec{e}_{32}$ and the distances, $r_{31}$ and $r_{32}$ are obtained in the same manner as in the case of the stretching internal coordinate.

The new terms appearing in expressions (16.3.11) to (16.3.13) are $\cos \phi$ and $\sin \phi$. They are obtained from:

$$\cos \phi = \vec{e}_{31} \cdot \vec{e}_{32} = e_{31}^x \cdot e_{32}^x + e_{31}^y \cdot e_{32}^y + e_{31}^z \cdot e_{32}^z$$

$$\sin \phi = (1 - \cos^2 \phi)^{1/2}$$  \quad (16.3.14)
Note that the units of the bending internal coordinate are different from those of stretching. This leads to different units for the stretching force constant (dynes/cm) and for the bending force constant (dynes.cm).

If we want to use the same type of units for both types of coordinates, we have to consider as the bending internal coordinate, not the change in angle $\phi$, i.e. $\Delta \phi$, but $(r_{31}r_{32})^{1/2} \Delta \phi$ (or $r_{31} \Delta \phi$ or $r_{32} \Delta \phi$). In this way, the bending force constant will have the same dimensions as the stretching force constant.

**Modified valence angle bending (code no. 5).**

In the case of an atom of multiplicity $m$ ($m$ is the number of bonds which meet at the atom in question) a maximum of $m(m-1)/2$ valence angle bending coordinates can be defined. Only $m-1$ coordinates, however, are locally independent, the remainder being local redundancies. Such a case occurs in the benzene molecule, for example:

```
  \[ \begin{array}{c}
    H_j \\
    \phi_1 \\
    C_j \\
    \phi_2 \\
    C_{j-1} \quad C_{j+1}
  \end{array} \]
```

Three valence angle bendings ($m(m-1)/2$) can be defined around each of the carbon atoms ($m=3$). From these three coordinates only two are independent ($m-1$). A convenient way to overcome
this problem is to combine two of the three bendings in a modified valence angle bending according to:

\[ \beta = \frac{1}{2}(\phi_1 - \phi_2) \] (16.3.15)

The second independent coordinate is provided by the deformation of the angle \( \alpha \).

**Out-of-plane wagging (code no. 3)**

![Top view diagram](image)

\[ S_j = \Delta \theta \text{ or } \frac{RA \theta}{R} \]

![Side view diagram](image)

The internal coordinate in this case is the change in the angle \( \theta \) formed by the bond 1-4 with the plane defined by atoms 2,3, and 4. A special case of this type of coordinate occurs when all four atoms are coplanar in the equilibrium position.
The expressions for the vectors \( \vec{S}_j \) for the four atoms involved in this type of coordinate are:

\[
\vec{S}_{j1} = \frac{1}{r_{14}} \left( \frac{\vec{e}_{42} x \vec{e}_{43}}{\cos \phi_1 \sin \phi_1} - \tan \theta \vec{e}_{41} \right) \tag{16.3.16}
\]

\[
\vec{S}_{j2} = \frac{1}{r_{42}} \left[ \frac{\vec{e}_{43} x \vec{e}_{41}}{\cos \phi_1 \sin \phi_1} - \tan \theta \left( \vec{e}_{42} - \cos \phi_1 \vec{e}_{43} \right) \right] \tag{16.3.17}
\]

\[
\vec{S}_{j3} = \frac{1}{r_{43}} \left[ \frac{\vec{e}_{41} x \vec{e}_{42}}{\cos \phi_1 \sin \phi_1} - \tan \theta \left( \vec{e}_{43} - \cos \phi_1 \vec{e}_{42} \right) \right] \tag{16.3.18}
\]

\[
\vec{S}_{j4} = -\vec{S}_{j1} - \vec{S}_{j2} - \vec{S}_{j3} \tag{16.3.19}
\]

Terms of the form \( r_{41}, \ldots, \vec{e}_{42}, \ldots \) appeared in the expressions for the other two internal coordinates and they have similar expressions here. The terms which are new are the vector products, e.g. \( \vec{e}_{43} x \vec{e}_{41} \), and \( \cos \theta \).

The vector products are calculated in terms of the Cartesian coordinates from:

\[
\begin{vmatrix}
I & J & K \\
\vec{e}_{42}^x & \vec{e}_{42}^y & \vec{e}_{42}^z \\
\vec{e}_{43}^x & \vec{e}_{43}^y & \vec{e}_{43}^z \\
\end{vmatrix}
\]

\[
\vec{e}_{42} x \vec{e}_{43} =
\begin{vmatrix}
\vec{e}_{42}^x & \vec{e}_{42}^y & \vec{e}_{42}^z \\
\vec{e}_{43}^x & \vec{e}_{43}^y & \vec{e}_{43}^z \\
\end{vmatrix}
\]
Hence:

\[(\overrightarrow{e_{42}} \times \overrightarrow{e_{41}})^{x} = (e_{41}^{y} \overrightarrow{e_{42}} - e_{41}^{z} \overrightarrow{e_{42}})\]

\[(\overrightarrow{e_{42}} \times \overrightarrow{e_{41}})^{y} = (e_{42}^{x} \overrightarrow{e_{41}} - e_{42}^{z} \overrightarrow{e_{41}})\]

\[(\overrightarrow{e_{42}} \times \overrightarrow{e_{41}})^{z} = (e_{42}^{y} \overrightarrow{e_{41}} - e_{42}^{z} \overrightarrow{e_{41}})\]

(16.3.20)

where \(e_{41}^{x}\), for example, is given by:

\[e_{41}^{x} = (x_{1}^{x} - x_{4}^{x})/r_{41}\]

(16.3.21)

The trigonometric functions are given by:

\[\sin \theta = \frac{(\overrightarrow{e_{42}} \times \overrightarrow{e_{43}}) \cdot \overrightarrow{e_{41}}}{\sin \angle_{1}}\]

\[\cos \theta = (1 - \sin^{2} \theta)^{1/2}\]

(16.3.22)

and the double product \((\overrightarrow{e_{42}} \times \overrightarrow{e_{43}}) \cdot \overrightarrow{e_{41}}\) is obtained from:

\[(\overrightarrow{e_{42}} \times \overrightarrow{e_{43}}) \cdot \overrightarrow{e_{41}} = (\overrightarrow{e_{42}} \times \overrightarrow{e_{43}})^{x} \cdot e_{41}^{x} + (\overrightarrow{e_{42}} \times \overrightarrow{e_{43}})^{y} \cdot e_{41}^{y} + (\overrightarrow{e_{42}} \times \overrightarrow{e_{43}})^{z} \cdot e_{41}^{z}\]

(16.3.23)
When the internal coordinate is $\Delta e$, the units of the corresponding force constant are dynes.cm. If the internal coordinate is considered to be $R \Delta \theta$ where, usually:

$$R = r_{41}$$  \hspace{1cm} (16.3.24)

then the units of the corresponding force constant are dynes/cm.

**Torsion (code no. 4).** 330, 331

The internal coordinate in this case is the change in angle $\tau$, the angle formed by the plane containing atoms 1, 2, and 3, and by the plane containing atoms 2, 3, and 4.

The expressions for the vectors $\bar{S}_j$ of the four atoms involved in this type of coordinate are:

$$\bar{S}_{j1} = -\frac{\bar{e}_{12} \bar{e}_{23}}{r_{12} \sin^2 \phi_2}$$  \hspace{1cm} (16.3.25)
\[
\overline{S}_{j2} = \left[ \frac{1}{r_{12}\sin\phi_2} - \left( \frac{\cos\phi_2}{\sin\phi_3} + \frac{\cos\phi_2}{\cos\phi_2} \frac{1}{r_{23}} \right) \frac{\overline{e}_{12} \overline{e}_{23}}{\sin\phi_2} \right] \overline{e}_{23} \sin\phi_3
\]

\[
\frac{\sin\phi_3}{r_{23}\sin\phi_3} \overline{e}_{23} \times \left( \frac{\overline{e}_{12} \overline{e}_{23}}{\sin\phi_2} \right) (16.3.26)
\]

\[
\overline{S}_{j3} = \left[ \frac{1}{r_{43}\sin\phi_3} - \left( \frac{\cos\phi_2}{\sin\phi_2} + \frac{\cos\phi_3}{\sin\phi_3} \frac{1}{r_{32}} \right) \frac{\overline{e}_{43} \overline{e}_{32}}{\sin\phi_3} \right] \overline{e}_{32} \sin\phi_2
\]

\[
\frac{\sin\phi_2}{r_{32}\sin\phi_2} \overline{e}_{32} \times \left( \frac{\overline{e}_{43} \overline{e}_{32}}{\sin\phi_3} \right) (16.3.27)
\]

\[
\overline{S}_{j4} = \frac{\overline{e}_{43} \overline{e}_{32}}{r_{43}\sin^2\phi_3} (16.3.28)
\]

The unit vectors \(\overline{e}_{12}, \ldots\) and the distances \(r_{12}, \ldots\) have expressions analogous to (16.3.7), (16.3.8), and (16.3.9).

The trigonometric functions are given by:

\[
\cos \varphi = \frac{(\overline{e}_{12} \overline{e}_{23}) \cdot (\overline{e}_{23} \overline{e}_{34})}{\sin\phi_2 \cdot \sin\phi_3}
\]
\[ \cos \phi_2 = \bar{e}_{21} \cdot \bar{e}_{23} \quad (16.3.29) \]

\[ \cos \phi_3 = \bar{e}_{32} \cdot \bar{e}_{34} \]

The double vectorial products appearing in (16.3.26) and (16.3.27) are calculated from:

\[ \bar{e}_{23} \times (\bar{e}_{12} \times \bar{e}_{23}) = (\bar{e}_{23} \cdot \bar{e}_{23}) \bar{e}_{12} + (\bar{e}_{23} \cdot \bar{e}_{12}) \bar{e}_{23} = \]

\[ \bar{e}_{12} + \cos \phi_2 \bar{e}_{23} \quad (16.3.30) \]

and:

\[ \bar{e}_{32} \times (\bar{e}_{43} \times \bar{e}_{32}) = \bar{e}_{43} + \cos \phi_3 \bar{e}_{32} \quad (16.3.31) \]

A computer program which calculates the G matrix of a molecule is given in appendix 16.3.1.

16.4 **Calculation of force constants (F matrix).**

The potential energy of a molecule is some function of the displacement, \( X \), of its atoms. For small values of the displacement, the potential energy \( V \) may be expressed as a power series in \( X \):
\[ 2V = 2V_o + 2 \sum_{i=1}^{3N} \left( \frac{\delta V}{\delta x_i} \right) x_i + \sum_{i,j=1}^{3N} \left( \frac{\delta^2 V}{\delta x_i \delta x_j} \right) x_i x_j + \ldots \]

\[ = 2V_o + 2 \sum_{i=1}^{3N} f_{i} x_i + \sum_{i,j=1}^{3N} f_{ij} x_i x_j + \ldots \quad (16.4.1) \]

By choosing the zero of energy so that the energy of the equilibrium configuration is zero, \( V_o \) may be eliminated. Furthermore, at the equilibrium position, all \( x_i \)'s are zero and the potential energy is at a minimum and therefore:

\[ \frac{\delta V}{\delta x_i} = 0 \]

Thus, from expression (16.4.1), there remains only (neglecting any higher terms):

\[ 2V = \sum_{i,j=1}^{3N} f_{ij} x_i x_j \quad (16.4.2) \]

where \( f_{ij} \)'s are constants given by:

\[ f_{ij} = \left( \frac{\delta^2 V}{\delta x_i \delta x_j} \right) \quad (16.4.3) \]

The exact values the constants \( f_{ij} \) take for a given molecule depend very much on the type of coordinates used for describing
the displacement of the atoms.

All 3N Cartesian coordinates, or even better 3N-6 (3N-5) internal coordinates, are necessary to completely describe the displacements of the atoms. When the internal coordinates are used, the expression for the potential energy takes the form:

\[ 2V = \sum_{i,j=1}^{3N-6} F_{ij} S_i S_j \]  
(16.4.4)

where S's represent internal coordinates. In the most general case \((3N-6) \cdot (3N-6+1)/2\), \(F_{ij}\) constants are needed to completely define the potential energy of a molecule, since:

\[ F_{ij} = F_{ji} \]

This number, however, applies to unsymmetrical molecules belonging to the point group \(C_1\). The symmetry of a molecule implies further relations among the \(F\) constants which reduce the number of independent parameters necessary to define the potential energy.

In subsection 16.2, we have shown how the frequency of vibrations can be calculated if all \(G\) and \(F\) elements of a molecule are known. The converse is also true, i.e. if the
G matrix and the vibrational frequencies are known, the $F$ elements can be calculated. Except in the case of very symmetrical molecules, however, the number of constants $F_{ij}$ is larger than the number of fundamental frequencies $\nu$ (or $\lambda$). During the years a series of approximations have been employed to reduce the number of independent force constants $F_{ij}$. 

The central force field (CFF).

In this approximation, the set of internal coordinates is the complete set of interatomic distances. It is assumed that the forces holding the atoms in their equilibrium positions act along the lines joining pairs of atoms, only, and that every pair of atoms is connected by such a force. This type of force field yields diagonal terms, only. Though convenient, CFF has not been very successful in predicting frequencies.

Valence force field (VFF).

This type of force field is associated with a set of internal coordinates composed, most of the time, of stretching, bending, out of plane wagging, and torsion of chemical bonds. The constants $F_{ij}$ will thus represent forces which resist compression or extension of valence bonds, and/or which oppose bending or torsion of bonds. Interaction constants between different types of vibration can be introduced in order to
obtain a more accurate description of the force field. These constants take into account the change in the stiffness of a bond resulting from the distortions of the other bonds. Such a force field in its complete form has a large number of independent force constants, generally, much larger than the number of frequencies available to calculate them. In such a case, certain assumptions, such as, for example, to neglect some of the interaction constants must be made. Note that this type of force field does not contain any interaction constant between non-bonded atoms.

**Urey-Bradley force field (UBFF).**

This type of force field is a hybrid between central force field and the valence force field. Basically, the Urey-Bradley field is a diagonal valence force field with some central forces terms between non-bonded atoms.

In its basic form, this type of force field contains fewer interaction constants than the valence force field, and because of this, it has been more widely used for treatment of large molecules. The VFF has been restricted to accurate treatment of small molecules. In recent years, however, the VFF has been used for the treatment of some large molecules.

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The usual approach for solving the problem of having more force constants than frequencies is to obtain additional data from deuterium substituted molecules or to assume that the
force constants are transferable among a series of related molecules and to use the combined frequency data to determine them.

We think that the transferability of force constants from one molecule to another is an elegant way to rationalize the similarities and the differences between molecules, though this criterion alone might lead to conclusions which are not unique.334

In our particular case, since no complete vibrational analysis of benzoic acid, of its salts, nor of any of the toluic acids and their salts, is available at the present time, and because a detailed vibrational analysis is outside the scope of this work, we are going to adopt the transferability approach, i.e. values of force constants determined for similar molecules will be used for our compounds. A limited number of force constants, however, will be calculated from the vibrational frequencies available in the literature. In all cases, the criterion for a good "transfer" will be the frequency fit though, again, under closer analysis this might not prove to be the best one.334

Calculation of force constants.

We used the method described by Mann, Shimanouchi, Meal, and Fano 335 to calculate the force constants when matrix G and some experimental frequencies are given.
In matrix notation, the calculation proceeds as follows:

1. Construct the following matrices:

   a. G matrix (see 16.3): \( n \times n \) (\( n = 3N - 6, 3N - 5 \)) matrix.
   
   b. \( \nu \) matrix: \( m \times 1 \). This is a column matrix containing \( m \) experimental frequencies (\( m < n \)) in \( \text{cm}^{-1} \).
   
   c. \( F^0 \) matrix: a \( n \times n \) matrix containing \( n \) independent (adjustable) force constants (\( \text{mdyn/Å} \)) in their initial (zero-th) approximation.

2. Calculate an initial set of vibrational frequencies from:

   \[
   |GF^0 - EA| = 0 \quad (16.4.5)
   \]

   \[
   \nu^0_i = 1302.9 \times A^0_i
   \]

3. Calculate a \( n \times n \) diagonal weight matrix \( W \) whose non-zero elements are given by:

   \[
   W_{ii} = \frac{1}{(\nu^0_i)^2} \quad (16.4.6)
   \]

   If \( m < n \), the weight factors corresponding to the missing frequencies are obtained from:
\[ W_{ii} = \frac{0.1}{(v^0_i)^2} \]  \hspace{1cm} (16.4.7)

4. Calculate a Jacobian matrix \( J \) of size \( 1 \times n \) whose elements are given by:

\[ J_{ij} = -\frac{\Delta v_i}{\Delta F_j} \]  \hspace{1cm} (16.4.8)

The Jacobian matrix is obtained in the following way: an increment of 0.01 mdyn/A is given to one of the independent force constants, i.e.:

\[ \Delta F_j = 0.01 \]  \hspace{1cm} (16.4.9)

the other force constants being left unchanged. This new set of force constants is used to calculate \( n \) frequencies of vibration. The difference between these frequencies and those calculated in the zeroth approximation provide the quantity \( \Delta v_i \).

The operation is repeated for all independent force constants.

5. Calculate a matrix \( V \) whose elements are given by:

\[ v_i = \nu^\text{obs}_i - \nu^0_i \]  \hspace{1cm} (16.4.10)
where the superscripts indicate the approximation.

6. The correction to the initial (zero-th) approximation of force constants is given by:

\[ \Delta F = (J'WJ)^{-1} J'WV \]  \hspace{1cm} (16.4.11)

where the primes stand for "transpose". Thus, the new for force constants are:

\[ F^1_j = F^0_j + \Delta F \]  \hspace{1cm} (16.4.12)

7. The new values for the force constants are introduced in the matrix \( F^0 \), obtaining matrix \( F^1 \).

8. The next approximation to the vibrational frequencies is obtained from:

\[ |GF^1 - EA^1| = 0 \]  \hspace{1cm} (16.4.13)

9. Steps 5 to 9 are repeated until the mean square deviation calculated from:

\[ MSD = \left[ \sum_{i=1}^{m} \left( \frac{v_{obs}^i - v_{calc}^i}{v_{obs}^i} \right)^2 / (m-1) \right]^{1/2} \]  \hspace{1cm} (16.4.14)

reaches a certain preestablished value, or until the
values $\Delta F_j$ are smaller than 0.01 mdyn/A, say.

To be completely correct step 4, i.e. the calculation of the $J$ matrix, should be included in each iteration (i.e. steps 4 to 9 are repeated instead of 5 to 9). However the change in the Jacobian matrix from one iteration to the other is small and in practice it might be sufficient to calculate the $J$ matrix only once.

The computer program performing this series of calculations is given in appendix 16.4.1.
The benzene ring was the main part of the compounds with which we were working. It was therefore an important requirement to have available the force constants corresponding to the vibrations of the benzene ring if any frequency calculations for these compounds, e.g. benzoic acid, toluic acids, were to be carried out.

17.1 The in-plane vibrations of the benzene molecule.

A relatively large number of vibrational analyses are available in the literature for the planar vibrations of the benzene molecule. 333, 334, 336-341

These analyses though similar in the general procedure used differ in details: the choice of the internal coordinates, the values of the interatomic distances and atomic weights, the symmetry considerations, the values of the observed frequencies, the type of force field considered, etc.
As a result, similar force constants in different force fields vary over quite a wide range of values. To decide which is the best force field and which one approaches the physical reality best is a difficult problem. In our case, we eventually decided to use Duinker and Mills general valence force field, which, besides fulfilling our main requirements for the present work, i.e. giving good agreement between the observed and the calculated frequencies and being relatively simple, has some theoretical support. The force constants belonging to this field are given in tables 17.1.2 and 17.1.4.

The internal coordinates used to calculate the G matrix for the "in plane" vibrations of benzene were:

(i) C-C-C (ring angle) bending (6\(\alpha\) coordinates).
(ii) C-H bond bending with respect to the external bisector of the ring angle (6\(\beta\) coordinates).

This \(\beta\) coordinate is obtained by taking the difference:

\[
\beta = (\phi_1 - \phi_2)
\]

where \(\phi_1\) and \(\phi_2\) are illustrated below:
Note that $\beta$ is positive when the C-H bond bends toward the $C_{j+1}$ atom. This is the most accepted convention and it is exactly opposite to that used by Duinker and Mills.

(iii) C-H bond stretching (6 "s" coordinates).
(iv) C-C bond stretching (6"t" coordinates).

The nomenclature $\alpha$, $\beta$, $s$ and $t$ used here for the different types of coordinates is taken from Wilson, Decius and Cross.\textsuperscript{342}

The internal coordinates and the corresponding $G$ matrix were calculated by the method shown in subsection 16.3. The values for the bond lengths, bond angles, and atomic weights used in the calculation were\textsuperscript{343}:

- bond lengths:  
  - C-H $1.084\,\text{Å}$
  - C-C $1.397\,\text{Å}$

- bond angles:  
  - CCC $120^\circ$
  - CCH $120^\circ$
- atomic weights: $m_H = 1.0078$ amu
  $m_C = 12.011$ amu

The "Detailed calculations" are given in 17.1.1. The G
matrix elements obtained here agreed exactly in sign and
value with those given by Wilson, Decius, and Cross. The frequencies for the in-plane vibrations of
benzene were calculated by the method shown in subsection
16.2. The results obtained in the present work are compared
with the values from the original paper by Duinker and
Mills and with the observed values in table 17.1.3. Note
that Duinker and Mills general valence force field gives
a value for the $B_{1u}$ frequency in agreement with the Mair and
Horning assignment which is generally accepted today.
The "Detailed calculations" are given in 17.1.2.

(continued p. 497)
Table 17.1.1. The $G$ matrix elements for the in-plane vibrations of benzene.

<table>
<thead>
<tr>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>$a_5$</th>
<th>$a_6$</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
<th>$\beta_3$</th>
<th>$\beta_4$</th>
<th>$\beta_5$</th>
<th>$\beta_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_a^1$</td>
<td>$G_a^2$</td>
<td>$G_a^3$</td>
<td>$G_a^4$</td>
<td>$G_a^3$</td>
<td>$G_a^2$</td>
<td>$0$</td>
<td>$G_{\alpha\beta}^1$</td>
<td>$G_{\alpha\beta}^2$</td>
<td>$0$</td>
<td>$-G_{\alpha\beta}^2$</td>
<td>$-G_{\alpha\beta}^1$</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$s_1$</td>
<td>$s_2$</td>
<td>$s_3$</td>
<td>$s_4$</td>
<td>$s_5$</td>
<td>$s_6$</td>
<td>$t_1$</td>
<td>$t_2$</td>
<td>$t_3$</td>
<td>$t_4$</td>
<td>$t_5$</td>
<td>$t_6$</td>
</tr>
<tr>
<td>$G_{s\alpha}^1$</td>
<td>$G_{s\alpha}^2$</td>
<td>$G_{s\alpha}^3$</td>
<td>$G_{s\alpha}^4$</td>
<td>$G_{s\alpha}^3$</td>
<td>$G_{s\alpha}^2$</td>
<td>$G_{t\alpha}^1$</td>
<td>$G_{t\alpha}^2$</td>
<td>$G_{t\alpha}^3$</td>
<td>$G_{t\alpha}^4$</td>
<td>$G_{t\alpha}^3$</td>
<td>$G_{t\alpha}^2$</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$s_1$</td>
<td>$G_{s}^1$</td>
<td>$G_{s}^2$</td>
<td>$G_{s}^3$</td>
<td>$G_{s}^4$</td>
<td>$G_{s}^3$</td>
<td>$G_{s}^2$</td>
<td>$G_{st}^1$</td>
<td>$G_{st}^2$</td>
<td>$G_{st}^3$</td>
<td>$G_{st}^4$</td>
<td>$G_{st}^3$</td>
</tr>
<tr>
<td>$t_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: The notation used in Table 17.1.1 follows exactly that given by Wilson, Decius, and Cross.

Table 17.1.2. Duinker and Mills general valence force field (mdyn/Å) for the in-plane vibrations of benzene.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\alpha_3$</th>
<th>$\alpha_4$</th>
<th>$\alpha_5$</th>
<th>$\alpha_6$</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
<th>$\beta_3$</th>
<th>$\beta_4$</th>
<th>$\beta_5$</th>
<th>$\beta_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>0.563</td>
<td>-0.050</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.050</td>
<td>0.0</td>
<td>0.042</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.042</td>
<td></td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>0.000</td>
<td>0.024</td>
<td>-0.019</td>
<td>-0.027</td>
<td>-0.019</td>
<td>0.024</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$s_1$</th>
<th>$s_2$</th>
<th>$s_3$</th>
<th>$s_4$</th>
<th>$s_5$</th>
<th>$s_6$</th>
<th>$t_1$</th>
<th>$t_2$</th>
<th>$t_3$</th>
<th>$t_4$</th>
<th>$t_5$</th>
<th>$t_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>-0.010</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.316</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.316</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>0.000</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.336</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.336</td>
</tr>
<tr>
<td>$s_1$</td>
<td>5.125</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$t_1$</td>
<td>7.015</td>
<td>0.531</td>
<td>-0.531</td>
<td>0.531</td>
<td>-0.531</td>
<td>0.531</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note. The values of table 17.1.2 correspond to the notation shown in table 17.1.1 for G matrix elements. In the case of the F matrix, the G's are replaced by F's.

Table 17.1.3. A comparison between the observed and published values and the values obtained in the present work for the in-plane vibrations of benzene using the Duinker and Mills general valence force field.

<table>
<thead>
<tr>
<th>Symmetry species</th>
<th>Frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed</td>
</tr>
<tr>
<td>$A_{1g}$</td>
<td>3073</td>
</tr>
<tr>
<td>$E_{1u}$</td>
<td>3064</td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>3057</td>
</tr>
<tr>
<td>$E_{2g}$</td>
<td>3056</td>
</tr>
<tr>
<td>$E_{2g}$</td>
<td>1599</td>
</tr>
<tr>
<td>$E_{1u}$</td>
<td>1482</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>1350</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>1309</td>
</tr>
<tr>
<td>$E_{2g}$</td>
<td>1178</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>1146</td>
</tr>
<tr>
<td>$E_{1u}$</td>
<td>1037</td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>1010</td>
</tr>
<tr>
<td>$A_{1g}$</td>
<td>993</td>
</tr>
<tr>
<td>$E_{2g}$</td>
<td>606</td>
</tr>
</tbody>
</table>

Table 17.1.4. In-plane vibrations of benzene. Internal coordinates and the corresponding force constants.

<table>
<thead>
<tr>
<th>Internal coordinate</th>
<th>Force constant (mdyn/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C-H stretching - C-H stretching interaction:</strong></td>
<td></td>
</tr>
<tr>
<td>( s_j-s_j )</td>
<td>5.125</td>
</tr>
<tr>
<td>( s_j-s_{j+1} )</td>
<td>0.0</td>
</tr>
<tr>
<td>( s_j-s_{j+2} )</td>
<td></td>
</tr>
<tr>
<td>( s_j-s_{j+3} )</td>
<td></td>
</tr>
<tr>
<td><strong>C-H stretching - C-C stretching interaction:</strong></td>
<td></td>
</tr>
<tr>
<td>( t_j-t_j )</td>
<td>7.015</td>
</tr>
<tr>
<td>( t_j-t_{j+1} )</td>
<td>0.531</td>
</tr>
<tr>
<td>( t_j-t_{j+2} )</td>
<td></td>
</tr>
<tr>
<td>( t_j-t_{j+3} )</td>
<td>-0.531</td>
</tr>
<tr>
<td>Internal coordinate</td>
<td>Force constant $c_0$ (mdyn/Å)</td>
</tr>
<tr>
<td>---------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>CCC bending - CCC bending interaction:</td>
<td></td>
</tr>
<tr>
<td>$\alpha_j - \alpha_j$</td>
<td>0.563</td>
</tr>
<tr>
<td>$\alpha_j - \alpha_{j+1}$</td>
<td>-0.050</td>
</tr>
<tr>
<td>$\alpha_j - \alpha_{j+2}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\alpha_j - \alpha_{j+3}$</td>
<td>0.0</td>
</tr>
<tr>
<td>HCC bending - HCC bending interaction:</td>
<td></td>
</tr>
<tr>
<td>$\beta_j - \beta_j$</td>
<td>0.881</td>
</tr>
<tr>
<td>$\beta_j - \beta_{j+1}$</td>
<td>0.024</td>
</tr>
<tr>
<td>$\beta_j - \beta_{j+2}$</td>
<td>-0.019</td>
</tr>
<tr>
<td>$\beta_j - \beta_{j+3}$</td>
<td>-0.027</td>
</tr>
<tr>
<td>Internal coordinate</td>
<td>Force constant ( \omega ) (mdyn/A)</td>
</tr>
<tr>
<td>---------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td><strong>C-H stretching - C-C stretching interaction:</strong></td>
<td></td>
</tr>
<tr>
<td>( s_j-t_j )</td>
<td>0.</td>
</tr>
<tr>
<td>( s_j-t_{j+1} )</td>
<td></td>
</tr>
<tr>
<td>( s_j-t_{j+2} )</td>
<td></td>
</tr>
<tr>
<td><strong>C-H stretching - CCC bending interaction:</strong></td>
<td></td>
</tr>
<tr>
<td>( s_j-\alpha_j )</td>
<td>-0.010</td>
</tr>
<tr>
<td>( s_j-\alpha_{j+1} )</td>
<td>0.</td>
</tr>
<tr>
<td>( s_j-\alpha_{j+2} )</td>
<td></td>
</tr>
<tr>
<td>( s_j-\alpha_{j+3} )</td>
<td></td>
</tr>
<tr>
<td><strong>C-H stretching - HCC bending interaction:</strong></td>
<td></td>
</tr>
<tr>
<td>( s_j-\beta_j )</td>
<td>0.</td>
</tr>
<tr>
<td>( s_j-\beta_{j+1} )</td>
<td></td>
</tr>
<tr>
<td>( s_j-\beta_{j+2} )</td>
<td></td>
</tr>
<tr>
<td>( s_j-\beta_{j+3} )</td>
<td></td>
</tr>
<tr>
<td>Internal coordinate</td>
<td>Force constant $\alpha_0$ (mdyn/A)</td>
</tr>
<tr>
<td>---------------------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>C-C stretching - CCC bending interaction:</td>
<td></td>
</tr>
<tr>
<td>$t_j-\alpha_j$</td>
<td>0.316</td>
</tr>
<tr>
<td>$t_j-\alpha_{j+1}$</td>
<td></td>
</tr>
<tr>
<td>$t_j-\alpha_{j+2}$</td>
<td>0.</td>
</tr>
<tr>
<td>C-C stretching - HCC bending interaction:</td>
<td></td>
</tr>
<tr>
<td>$t_j-\beta_j$</td>
<td>-0.336</td>
</tr>
<tr>
<td>$t_j-\beta_{j+2}$</td>
<td></td>
</tr>
<tr>
<td>$t_j-\beta_{j+3}$</td>
<td>0.</td>
</tr>
<tr>
<td>CCC bending - HCC bending interaction:</td>
<td></td>
</tr>
<tr>
<td>$\alpha_j-\beta_j$</td>
<td>0.</td>
</tr>
<tr>
<td>$\alpha_j-\beta_{j+1}$</td>
<td></td>
</tr>
<tr>
<td>$\alpha_j-\beta_{j+3}$</td>
<td>0.042</td>
</tr>
</tbody>
</table>

17.2 The out-of-plane vibrations of benzene molecule.

The internal coordinates used to obtain the G matrix for the out-of-plane vibrations of benzene were the out-of-plane wagging of the C-H bond (6 coordinates) and the torsion around the C-C bond (6 coordinates). The B elements corresponding to these internal coordinates were calculated by the expressions given in section 16.3. The values and the signs of the G elements obtained here were identical to those given by Wilson, Decius, and Cross \textsuperscript{345} with the exception of the $G_{\gamma_6}$ elements which had the reverse sign. Our signs for the $G_{\gamma_6}$'s correspond to the usual convention of the "right-hand rule" for the vector product \textsuperscript{347} and, furthermore, they are probably identical with the G elements used by Miller and Crawford \textsuperscript{348} and by Kakiuti and Shimanouchi \textsuperscript{349} because, as it will be seen below, their force fields combined with our G elements gave the correct values for the out-of-plane vibrations of benzene.

The out-of-plane vibrations of benzene have been studied much less than the planar ones. Two of the valence force fields which reproduce the observed values for the out-of-plane vibrations are given in tables 17.2.2, 17.2.3, and 17.2.5. A third valence force field, that of Whiffen \textsuperscript{337}, is not given in here because he used a different torsional coordinate.
The elements of the G and F matrices can be listed in a tabular form as follows:

Table 17.2.1. The G elements for the out-of-plane vibrations of benzene.

<table>
<thead>
<tr>
<th>$\gamma_1$</th>
<th>$\gamma_2$</th>
<th>$\gamma_3$</th>
<th>$\gamma_4$</th>
<th>$\gamma_5$</th>
<th>$\gamma_6$</th>
<th>$\delta_1$</th>
<th>$\delta_2$</th>
<th>$\delta_3$</th>
<th>$\delta_4$</th>
<th>$\delta_5$</th>
<th>$\delta_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_1^\gamma$</td>
<td>$g_2^\gamma$</td>
<td>$g_3^\gamma$</td>
<td>$g_4^\gamma$</td>
<td>$g_5^\gamma$</td>
<td>$g_6^\gamma$</td>
<td>$g_1^\delta$</td>
<td>$g_2^\delta$</td>
<td>$g_3^\delta$</td>
<td>$g_4^\delta$</td>
<td>$g_5^\delta$</td>
<td>$g_6^\delta$</td>
</tr>
</tbody>
</table>

where $\gamma$ stands for the out-of-plane wagging coordinate and $\delta$ for the torsion coordinate. In the case of the F matrix, the G's of table 17.2.1 are replaced by F's, the signs, the subscripts, and the superscripts remaining the same.

From the symmetry force constants given by Miller and Crawford, we calculated a valence force field, assuming that the force constants $F_3^\delta$, $F_4^\delta$ and the symmetry force constant $"F_1^\delta + 2F_2^\delta + F_3^\delta"$ were zero. This VFF is given in table 17.2.2 following the conventions of table 17.2.1.

The observed and the calculated frequencies using this VFF are given in table 17.2.4.

The Kakiuti and Shimanouchi VFF is given in table 17.2.3.
Table 17.2.2. Miller and Crawford $^{348}$ valence force field (mdyn/A) for the out-of-plane vibrations of benzene.

<table>
<thead>
<tr>
<th>$\gamma_1$</th>
<th>$\gamma_2$</th>
<th>$\gamma_3$</th>
<th>$\gamma_4$</th>
<th>$\gamma_5$</th>
<th>$\gamma_6$</th>
<th>$\delta_1$</th>
<th>$\delta_2$</th>
<th>$\delta_3$</th>
<th>$\delta_4$</th>
<th>$\delta_5$</th>
<th>$\delta_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_1$</td>
<td>.378</td>
<td>-.057</td>
<td>.007</td>
<td>-.026</td>
<td>.007</td>
<td>-.057</td>
<td>-.088</td>
<td>.042</td>
<td>.002</td>
<td>-.002</td>
<td>-.042</td>
</tr>
<tr>
<td>$\delta_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.111</td>
<td>-.046</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
</tr>
</tbody>
</table>

Table 17.2.3. Kakiuti and Shimanouchi $^{349}$ valence force field (mdyn/A) for the out-of-plane vibrations of benzene.

<table>
<thead>
<tr>
<th>$\gamma_1$</th>
<th>$\gamma_2$</th>
<th>$\gamma_3$</th>
<th>$\gamma_4$</th>
<th>$\gamma_5$</th>
<th>$\gamma_6$</th>
<th>$\delta_1$</th>
<th>$\delta_2$</th>
<th>$\delta_3$</th>
<th>$\delta_4$</th>
<th>$\delta_5$</th>
<th>$\delta_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_1$</td>
<td>.398</td>
<td>-.072</td>
<td>.000</td>
<td>.000</td>
<td>-.072</td>
<td>-.130</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
<td>.130</td>
</tr>
<tr>
<td>$\delta_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.181</td>
<td>-.012</td>
<td>.000</td>
<td>.000</td>
<td>-.012</td>
</tr>
</tbody>
</table>
The observed and the calculated frequencies corresponding to this force field are given in table 17.2.4.

We used both force fields to calculate the frequencies for the out-of-plane vibrations of benzene. The results are given in "Detailed Calculations - 17.2.1" and are summarized in table 17.2.4.

Table 17.2.4. Observed and calculated frequencies for the out-of-plane vibrations of benzene.

<table>
<thead>
<tr>
<th>Symmetry species</th>
<th>Miller and Crawford valence force field.</th>
<th>Kakiuti and Shimanouchi valence force field.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Frequencies (cm(^{-1}))</td>
<td>Frequencies (cm(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>Observed Calc. Calc. (ref. 1) Calc. (ref. 3)</td>
<td>Observed Calc. Calc. (ref. 2) Calc. (ref.3)</td>
</tr>
<tr>
<td>(B_{2g})</td>
<td>? 993 997</td>
<td>985 1013 1007</td>
</tr>
<tr>
<td>(E_{2u})</td>
<td>985 958 955</td>
<td>970 984 978</td>
</tr>
<tr>
<td>(E_{1g})</td>
<td>850 851 851</td>
<td>849 837 833</td>
</tr>
<tr>
<td>(B_{2g})</td>
<td>685 693 699</td>
<td>703 698 700</td>
</tr>
<tr>
<td>(A_{2u})</td>
<td>671 678 678</td>
<td>671 684 681</td>
</tr>
<tr>
<td>(E_{2u})</td>
<td>404 403 402</td>
<td>405 398 399</td>
</tr>
</tbody>
</table>

3. Present work.
It can be seen from table 17.2.4, that both valence force fields give a satisfactory agreement between the observed and the calculated values. We have chosen Kakiuti and Shimanouchi's force field for further use because of its simpler form, i.e. it does not contain as many interaction constants as the Miller and Crawford force field.
Table 17.2.5 Out-of-plane vibrations of benzene. Internal coordinates and the corresponding force constants.

<table>
<thead>
<tr>
<th>Internal coordinate</th>
<th>Force constants (mdyn/A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ref. 1</td>
</tr>
<tr>
<td>C-H out-of-plane wagging($\gamma_j$) - C-H out of plane wagging interaction:</td>
<td></td>
</tr>
<tr>
<td>![Structure 1]</td>
<td>0.378</td>
</tr>
<tr>
<td>![Structure 2]</td>
<td>-0.057</td>
</tr>
<tr>
<td>![Structure 3]</td>
<td>0.007</td>
</tr>
<tr>
<td>![Structure 4]</td>
<td>-0.026</td>
</tr>
<tr>
<td>Internal coordinate</td>
<td>Force constants (mdyn/A)</td>
</tr>
<tr>
<td>----------------------------------------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>C-C torsion ( (\delta_j) ) -</td>
<td></td>
</tr>
<tr>
<td>C-C torsion interaction :</td>
<td></td>
</tr>
<tr>
<td><img src="image1" alt="Hexagon" /></td>
<td>0.111</td>
</tr>
<tr>
<td><img src="image2" alt="Hexagon" /></td>
<td>-0.046</td>
</tr>
<tr>
<td><img src="image3" alt="Hexagon" /></td>
<td>0.</td>
</tr>
<tr>
<td><img src="image4" alt="Hexagon" /></td>
<td>0.</td>
</tr>
<tr>
<td>C-H out-of-plane wagging -</td>
<td></td>
</tr>
<tr>
<td>C-C torsion interaction :</td>
<td></td>
</tr>
<tr>
<td><img src="image5" alt="Hexagon" /></td>
<td>-0.088</td>
</tr>
<tr>
<td><img src="image6" alt="Hexagon" /></td>
<td>0.042</td>
</tr>
<tr>
<td><img src="image7" alt="Hexagon" /></td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ref. 1</td>
</tr>
<tr>
<td></td>
<td>Ref. 2</td>
</tr>
<tr>
<td></td>
<td>0.181</td>
</tr>
<tr>
<td></td>
<td>-0.012</td>
</tr>
<tr>
<td></td>
<td>0.</td>
</tr>
<tr>
<td></td>
<td>0.</td>
</tr>
<tr>
<td></td>
<td>-0.130</td>
</tr>
<tr>
<td></td>
<td>0.</td>
</tr>
<tr>
<td></td>
<td>0.</td>
</tr>
</tbody>
</table>
Table 17.2.5 (cont.)

References:


18. THE CALCULATION OF THE SECONDARY DEUTERIUM ISOTOPE EFFECTS ON THE DISSOCIATION CONSTANT OF BENZOIC ACID.

18.1 Introduction.

In this and the following parts relation (15.4.5) is used to predict values for the ratio, $K_H/K_D$. $K_H$ is the ionization constant of the undeuterated acid and $K_D$ is the ionization constant of the acid completely deuterated or deuterated at certain positions in the molecule, only.

Relation 15.4.5 is given below in a more convenient form:

$$
\frac{K_1}{K_2} = \frac{\prod_{i=1}^{3n_A-6} \frac{u_{A_i^2}}{u_{A_i^1}} \prod_{i=1}^{3n_A-6} \frac{1 - \exp(-u_{A_i^1})}{1 - \exp(-u_{A_i^2})}}{\prod_{j=1}^{3n_B-6} \frac{u_{B_{1j}^2}}{u_{B_{1j}^1}} \prod_{j=1}^{3n_B-6} \frac{1 - \exp(-u_{B_{1j}^1})}{1 - \exp(-u_{B_{1j}^2})}} \tag{18.1.1}
$$

$$
\exp \left[ \frac{3n_A-6}{\sum_{i=1}^{3n_A-6} \frac{u_{A_i^2} - u_{A_i^1}}{2}} \right]
\exp \left[ \frac{3n_B-6}{\sum_{j=1}^{3n_B-6} \frac{u_{B_{1j}^2} - u_{B_{1j}^1}}{2}} \right]
$$

The subscripts have the following meaning:

$A$ : refers to the undissociated acid molecule.

$B$ : refers to the anion.

$1$ : refers to the lighter isotope.

$2$ : refers to the heavier isotope.

$n_A$ : is the number of atoms in the undissociated acid molecule.

$n_B$ : is the number of atoms in the respective anion. In the case of monocarboxylic acids:

$$
n_B = n_A - 1
$$
\[ u \text{ is given by:} \]

\[ u = \frac{hv}{kT} = \frac{1.4385v}{T} \quad (18.1.2) \]

where \( v \) is a normal vibrational frequency (\( \text{cm}^{-1} \)), \( T \) is the absolute temperature in kelvins, and \( u \) is a dimensionless quantity.

Following the notation of Stern and Wolfsberg,\(^\text{265} (18.1.1) \) can be split into three contributions.

2. A term which arises from translational and rotational partition functions:

\[ \text{VP} = \frac{\sum_{i=1}^{3n_A-6} \frac{u_{A_2i}}{u_{A_1i}}}{\sum_{j=1}^{3n_B-6} \frac{u_{B_2j}}{u_{B_1j}}} \quad (18.1.3) \]

b. A term which arises from the excitation of vibrations:

\[ \text{EXP} = \frac{\sum_{i=1}^{3n_A-6} \frac{1 - \exp(-u_{A_1i})}{1 - \exp(-u_{A_2i})}}{\sum_{j=1}^{3n_B-6} \frac{1 - \exp(-u_{B_1j})}{1 - \exp(-u_{B_2j})}} \quad (18.1.4) \]
c. A term which arises from the vibrational zero point energies:

\[
ZPE = \exp\left[\frac{3n_A-6}{\sum_{i=1}^{i=1} (u_{A_1i} - u_{A_2i})}\right] = \exp\left[\frac{3n_B-6}{\sum_{j=1}^{j=1} (u_{B_1j} - u_{B_2j})}\right]
\]

Thus:

\[
\frac{K_1}{K_2} = \text{VP} \times \text{EXP} \times \text{ZPE}
\]

Therefore to calculate the ratio \( K_1/K_2 \) all that is needed is all the vibrational frequencies of the species involved in the equilibrium. In our case the vibrational frequencies were obtained by the method shown in section 16. The computer program which calculates \( K_1/K_2 \) is given in appendix 18.1.1.

18.2 The vibrational frequencies of benzoic acid.

From the outset it must be mentioned that no complete vibrational analysis for benzoic acid exists in the literature. By complete vibrational analysis we mean an analysis similar to those published for benzene (see section 17), i.e. an analysis in which all the fundamental vibrational frequencies are identified and a force field developed. Such vibrational analyses have been published for simple carboxylic acids such as formic or acetic acids.
Parts of the spectrum of benzoic acid are analysed in papers discussing the spectra of monosubstituted benzene derivatives, \(^{352-355}\) the infrared absorption bands associated with the carboxylic group, \(^{356-360}\) and, briefly, the infrared spectrum of benzoic acid. \(^{361-365}\)

Those observed frequencies belonging to the infrared spectrum of benzoic acid which were tentatively assigned to the fundamental vibrations of benzoic acid molecule are given in columns 4 to 8 of table 18.2.4.

**Calculation of the vibrational frequencies of benzoic acid.**

The vibrational frequencies of benzoic acid were calculated by the method shown in section 16.

**The G matrix.** The molecular structure of benzoic acid was taken from the work by Sim, Robertson and Goodwin. \(^{231}\) This must be considered as an approximation, only, since the above mentioned paper reports the molecular structure of benzoic acid in the solid state while our work deals with benzoic acid in dilute aqueous solutions. The interatomic distances and the bond angles are shown in fig. 18.2.1. The distance O-H was calculated by interpolation from the Lippincott and Schroeder table \(^{366}\) taking the O ... O distance from the benzoic acid crystal.

The \(\text{C}_{12-0}^{14-1}_{15}\) angle was assumed to be 107.8° which is the value for the equivalent angle in formic acid. \(^{368}\)

The computer program which calculates the G matrix of a molecule (appendix 16.3.1) requires the spherical coordinates of the atoms. These coordinates were calculated manually from the interatomic distances and bond angles and are given in table 18.2.1. If the interatomic distances shown in fig. 18.2.1 are compared with
the corresponding values obtained when the B elements were calculated ("Detailed calculations- 18.2.1") small differences can be noted. They are due to our approximate calculation of the spherical coordinates. These differences do not affect the calculated isotope effect since they appear in both isotopic species. The effect they might have on the absolute values of the vibrational frequencies is certainly much smaller than the effect that the approximations involved in choosing of the force constants has (see next). This observation is valid for all the molecules treated in this part of the thesis.

The internal coordinates were defined using the Decius method. According to this method for the benzoic acid molecule a minimum of 45 internal coordinates must be defined in terms of the four basic types, i.e. stretching, valence angle bending, out-of-plane wagging and torsion (see subsection 16.3). These 45 coordinates contain 6 cyclic redundancies. In our case because of the symmetry of the molecule we have chosen to define 47 internal coordinates. Therefore the set of internal coordinates used here contains two additional local redundancies besides the six cyclic ones. The complete description of these 47 coordinates is given in table 18.2.2.

The complete G matrix is given in "Detailed calculations- 18.2.1."

The F matrix. In the absence of any force constant matrix for benzoic acid, in the literature, the F matrix was built up by transferring force constants from similar molecules and groups of atoms. Thus, as expected, the largest part of the F matrix of benzoic acid is composed of force constants of the benzene molecule (continued p. 515)
FIG. 18.2.1.
THE STRUCTURE OF BENZOIC ACID

REFERENCES: 1. G.A. Sim, J.M. Robertson and T. H. Goodwin,
Acta Cryst., 8,157 (1955)

23,1099 (1955)

23,210 (1955)
Table 18.2.1. The Spherical coordinates of the atoms of benzoic acid.

<table>
<thead>
<tr>
<th>No.</th>
<th>Type</th>
<th>R</th>
<th>$A_x$</th>
<th>$A_y$</th>
<th>$A_z$</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C</td>
<td>1.42</td>
<td>90</td>
<td>0</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>1.39</td>
<td>30.7</td>
<td>59.3</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>1.37</td>
<td>31.3</td>
<td>121.3</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>1.41</td>
<td>90</td>
<td>180</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
<td>1.39</td>
<td>149.1</td>
<td>120.9</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>1.39</td>
<td>149.5</td>
<td>59.5</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>7</td>
<td>H</td>
<td>2.47</td>
<td>30.7</td>
<td>59.3</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>8</td>
<td>H</td>
<td>2.45</td>
<td>31.3</td>
<td>121.3</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>9</td>
<td>H</td>
<td>2.49</td>
<td>90</td>
<td>180</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>10</td>
<td>H</td>
<td>2.45</td>
<td>149.1</td>
<td>120.9</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>11</td>
<td>H</td>
<td>2.47</td>
<td>149.5</td>
<td>59.5</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>12</td>
<td>C</td>
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<td>90</td>
<td>0.8</td>
<td>90.8</td>
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</tr>
<tr>
<td>13</td>
<td>O</td>
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<td>90</td>
<td>16.000</td>
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<td>72.1</td>
<td>19.0</td>
<td>91.1</td>
<td>16.000</td>
</tr>
<tr>
<td>15</td>
<td>H</td>
<td>4.65</td>
<td>78.1</td>
<td>11.9</td>
<td>90</td>
<td>1.0078</td>
</tr>
</tbody>
</table>

Notes. 1. The axes are defined in fig. 18.2.1. "$z$" axis is perpendicular to the plane of the ring.

2. "$R$" is the distance measured from point $A$ to a given atom. $A_x$ is the angle which is made by $R$ with the positive direction of the $x$ axis. $A_y$ and $A_z$ have similar definitions. $M$ is the atomic mass in amu.

3. The molecule is planar with the exception of atoms $C_{12}$ and $O_{14}$. 
Table 18.2.2. The valence internal coordinates used for calculating the G matrix of benzoic acid.

<table>
<thead>
<tr>
<th>Int. crd. no.</th>
<th>Atoms involved</th>
<th>Code* no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 7</td>
<td>1</td>
<td>$\nu_{\text{CH}}$</td>
<td>C-H stretching.</td>
</tr>
<tr>
<td>2</td>
<td>3 8</td>
<td>1</td>
<td>$\nu_{\text{CH}}$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4 9</td>
<td>1</td>
<td>$\nu_{\text{CH}}$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5 10</td>
<td>1</td>
<td>$\nu_{\text{CH}}$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6 11</td>
<td>1</td>
<td>$\nu_{\text{CH}}$</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1 2</td>
<td>1</td>
<td>$\nu_{\text{CC}}$</td>
<td>C-C ring stretching.</td>
</tr>
<tr>
<td>7</td>
<td>2 3</td>
<td>1</td>
<td>$\nu_{\text{CC}}$</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>3 4</td>
<td>1</td>
<td>$\nu_{\text{CC}}$</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>4 5</td>
<td>1</td>
<td>$\nu_{\text{CC}}$</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5 6</td>
<td>1</td>
<td>$\nu_{\text{CC}}$</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>6 1</td>
<td>1</td>
<td>$\nu_{\text{CC}}$</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1 12</td>
<td>1</td>
<td>$\nu_{\text{CX}}$</td>
<td>$\text{C}<em>1$-$\text{C}</em>{12}$ stretching.</td>
</tr>
<tr>
<td>13</td>
<td>13 12</td>
<td>1</td>
<td>$\nu_{\text{C}=\text{O}}$</td>
<td>C=O stretching.</td>
</tr>
<tr>
<td>14</td>
<td>12 14</td>
<td>1</td>
<td>$\nu_{\text{C}-\text{O}}$</td>
<td>C-O stretching.</td>
</tr>
<tr>
<td>15</td>
<td>14 15</td>
<td>1</td>
<td>$\nu_{\text{OH}}$</td>
<td>O-H stretching.</td>
</tr>
<tr>
<td>16</td>
<td>6 2 1</td>
<td>2</td>
<td>$\alpha_{\text{CCC}}$</td>
<td>C-C-C ring angle bending.</td>
</tr>
<tr>
<td>17</td>
<td>1 3 2</td>
<td>2</td>
<td>$\alpha_{\text{CCC}}$</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>2 4 3</td>
<td>2</td>
<td>$\alpha_{\text{CCC}}$</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>3 5 4</td>
<td>2</td>
<td>$\alpha_{\text{CCC}}$</td>
<td></td>
</tr>
<tr>
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<td>4 6 5</td>
<td>2</td>
<td>$\alpha_{\text{CCC}}$</td>
<td></td>
</tr>
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<td>5 1 6</td>
<td>2</td>
<td>$\alpha_{\text{CCC}}$</td>
<td></td>
</tr>
<tr>
<td>Int. crd. no.</td>
<td>Atoms involved</td>
<td>Code no.</td>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------</td>
<td>----------</td>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>22</td>
<td>7 1 3 2</td>
<td>5</td>
<td>$\beta_{CH}$</td>
<td>C-H bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>23</td>
<td>8 2 4 3</td>
<td>5</td>
<td>$\beta_{CH}$</td>
<td>$C_1 - C_{12}$ bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>24</td>
<td>9 3 5 4</td>
<td>5</td>
<td>$\beta_{CH}$</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>10 4 6 5</td>
<td>5</td>
<td>$\beta_{CH}$</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>11 5 1 6</td>
<td>5</td>
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<td></td>
</tr>
<tr>
<td>27</td>
<td>12 6 2 1</td>
<td>5</td>
<td>$\beta_{\phi}$</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>13 14 12</td>
<td>2</td>
<td>$\alpha_{OOC}$</td>
<td>O=C-O bending.</td>
</tr>
<tr>
<td>29</td>
<td>1 13 14 12</td>
<td>5</td>
<td>$\beta_{\phi}$</td>
<td>Ring-COOH bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>30</td>
<td>15 12 14</td>
<td>2</td>
<td>$\alpha_{HOC}$</td>
<td>H-O-C bending.</td>
</tr>
<tr>
<td>31</td>
<td>7 1 3 2</td>
<td>3</td>
<td>$\gamma_{CH}$</td>
<td>C-H out-of-plane wagging.</td>
</tr>
<tr>
<td>32</td>
<td>8 2 4 3</td>
<td>3</td>
<td>$\gamma_{CH}$</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>9 3 5 4</td>
<td>3</td>
<td>$\gamma_{CH}$</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>10 4 6 5</td>
<td>3</td>
<td>$\gamma_{CH}$</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>11 5 1 6</td>
<td>3</td>
<td>$\gamma_{CH}$</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>12 6 2 1</td>
<td>3</td>
<td>$\gamma_{\phi}$</td>
<td>$C_1 - C_{12}$ out-of-plane wagging.</td>
</tr>
<tr>
<td>37</td>
<td>14 13 1 12</td>
<td>3</td>
<td>$\gamma_{C-OH}$</td>
<td>C-OH out-of-plane.</td>
</tr>
<tr>
<td>38</td>
<td>1 2 3 4</td>
<td>4</td>
<td>$\delta_{CC}$</td>
<td>Torsion around a C-C ring bond</td>
</tr>
<tr>
<td>39</td>
<td>2 3 4 5</td>
<td>4</td>
<td>$\delta_{CC}$</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>3 4 5 6</td>
<td>4</td>
<td>$\delta_{CC}$</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>4 5 6 1</td>
<td>4</td>
<td>$\delta_{CC}$</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>5 6 1 2</td>
<td>4</td>
<td>$\delta_{CC}$</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>6 1 2 3</td>
<td>4</td>
<td>$\delta_{CC}$</td>
<td></td>
</tr>
<tr>
<td>Int. crd. no.</td>
<td>Atoms involved</td>
<td>Code* no.</td>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------</td>
<td>-----------</td>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>44</td>
<td>14 12 1 6</td>
<td>4</td>
<td>$\delta_{CX}$</td>
<td>Torsion around $C_1 - C_{12}$ bond.</td>
</tr>
<tr>
<td>45</td>
<td>15 14 12 1</td>
<td>4</td>
<td>$\delta_{C-OH}$</td>
<td>Torsion around $C_{12}-OH$ bond.</td>
</tr>
<tr>
<td>46</td>
<td>13 12 1 2</td>
<td>4</td>
<td>$\delta_{CX}$</td>
<td>Torsion around $C_1 - C_{12}$ bond (one of the coordinates no. 44 and 46 is locally redundant).</td>
</tr>
<tr>
<td>47</td>
<td>13 1 14 12</td>
<td>3</td>
<td>$\gamma_{C=O}$</td>
<td>$C=O$ bond out-of-plane wagging (locally redundant)</td>
</tr>
</tbody>
</table>

Notes. * This number corresponds to the code no. shown in subsection 16.3.
(see section 17). These force constants were transferred as such, that is, as scaled force constants with no adjustment for the slightly different scale factors in the two molecules. The force constants for the internal coordinates involving the carboxyl group were taken from the F matrix of acetic acid. Some of them were adjusted by trial and error to fit the observed frequencies of benzoic acid.

All the elements of the F matrix of benzoic acid are described in table 18.2.3.

The calculated vibrational frequencies of benzoic acid. The G and F matrices described above were used to calculate the 39 vibrational frequencies of benzoic acid. As expected, the 8 cyclic and local redundancies in the G matrix appeared as zero roots when solving the secular equation (16.2.1). The "Detailed calculations" are given in 18.2.1. The calculated vibrational frequencies are shown in column 2 of table 18.2.4. In columns 4 to 8 some of the observed frequencies published in the literature and obtained in the present work are given. The agreement between the calculated and observed values is good. The potential energy distribution shows a more complex pattern than the experimental assignments. This is expected for such a large molecule.

The ir spectra of benzoic acid and of all other acids studied in the present work were obtained on a "Perkin-Elmer", Model 457 spectrophotometer (as KBr disks).

The calculated vibrational frequencies of benzoic-2-d acid. The geometry of the molecule of benzoic-2-d acid was assumed to be identical with the geometry of the benzoic acid molecule (table 18.2.1 and fig. 18.2.1) with the exception of atom no. 7. In benzoic-2-d
acid this atom is a deuterium atom; consequently we assumed that its distance from the origin of our system of axes was 0.009 Å shorter \((R = 2.465 \text{ Å})\) than the value for the corresponding H atom.\(^{369}\) The atomic mass of deuterium was taken as being 2.0147 amu. The internal coordinates were the same as those used for benzoic acid (table 18.2.2).

For the coordinates involving the new C-D bond new symbols were used:

<table>
<thead>
<tr>
<th>Int. crd. no.</th>
<th>Atoms involved</th>
<th>Code no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 7</td>
<td>1</td>
<td>(\nu_{\text{CD}})</td>
<td>C-D stretching.</td>
</tr>
<tr>
<td>22</td>
<td>7 1 3 2</td>
<td>5</td>
<td>(\beta_{\text{CD}})</td>
<td>C-D bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>31</td>
<td>7 1 3 2</td>
<td>3</td>
<td>(\gamma_{\text{CD}})</td>
<td>C-D out-of-plane wagging.</td>
</tr>
</tbody>
</table>

The Detailed Calculations of the \(G\) matrix of benzoic-2-d acid are given in 18.2.2.

The elements of the \(F\) matrix were identical (in \(\text{mdyn/Å}\)) to those of the \(F\) matrix of benzoic acid (table 18.2.3) with the exception of the \(\beta_{\text{D}} - \beta_{\text{D}}\) and \(\gamma_{\text{D}} - \gamma_{\text{D}}\) diagonal force constants, which had to be adjusted because of the slightly different scaling factors. The off-diagonal elements involving the deuterium atom were not adjusted since in their case the difference was negligible. The elements of the \(F\) matrix are given in column 3 of table 18.2.3.

The calculated vibrational frequencies together with the potential energy distribution are given in columns 2 and 3 of table 18.2.5. Column 4 of the same table gives the observed frequencies from the spectrum of benzoic-2-d acid (as KBr disk) obtained in the present work. The agreement between the two sets is good.

The calculated vibrational frequencies of benzoic-d\(_5\) acid.

The molecular structure of benzoic-d\(_5\) acid was assumed to be the same as that of benzoic acid (table 18.2.1 and fig. 18.2.1)
with the exception of carbon-deuterium bonds which were assumed to be 0.009 Å shorter than the corresponding carbon-hydrogen bonds. The atomic mass of deuterium was taken to be 2.0147 amu.

The internal coordinates used to compute the G matrix were identical to those of benzoic acid. Different subscripts have been used for the symbols of those coordinates which involve the deuterium atoms. These new symbols are given on the next page.
<table>
<thead>
<tr>
<th>Int. crd. no.</th>
<th>Atoms involved</th>
<th>Code no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 7</td>
<td>1</td>
<td>$\nu_{\text{CD}}$</td>
<td>C-D stretching.</td>
</tr>
<tr>
<td>2</td>
<td>3 8</td>
<td>1</td>
<td>$\nu_{\text{CD}}$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4 9</td>
<td>1</td>
<td>$\nu_{\text{CD}}$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5 10</td>
<td>1</td>
<td>$\nu_{\text{CD}}$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6 11</td>
<td>1</td>
<td>$\nu_{\text{CD}}$</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>7 1 3 2</td>
<td>5</td>
<td>$\beta_{\text{CD}}$</td>
<td>C-D bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>23</td>
<td>8 2 4 3</td>
<td>5</td>
<td>$\beta_{\text{CD}}$</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>9 3 5 4</td>
<td>5</td>
<td>$\beta_{\text{CD}}$</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>10 4 6 5</td>
<td>5</td>
<td>$\beta_{\text{CD}}$</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>11 5 1 6</td>
<td>5</td>
<td>$\beta_{\text{CD}}$</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>7 1 3 2</td>
<td>3</td>
<td>$\gamma_{\text{CD}}$</td>
<td>C-D out-of-plane wagging.</td>
</tr>
<tr>
<td>32</td>
<td>8 2 4 3</td>
<td>3</td>
<td>$\gamma_{\text{CD}}$</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>9 3 5 4</td>
<td>3</td>
<td>$\gamma_{\text{CD}}$</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>10 4 6 5</td>
<td>3</td>
<td>$\gamma_{\text{CD}}$</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>11 5 1 6</td>
<td>3</td>
<td>$\gamma_{\text{CD}}$</td>
<td></td>
</tr>
</tbody>
</table>

The "Detailed calculations" of the G matrix of benzoic-d$_5$ acid are given in 18.2.3.

As in the case of benzoic-2-d acid, the diagonal force constants corresponding to internal coordinates $\beta_{\text{CD}}$ and $\gamma_{\text{CD}}$ were adjusted for the different scaling factors. The remaining elements of the F matrix were exactly the same as those of benzoic acid. The complete set of force (continued p. 539)
Table 18.2.3. The elements of the $F$ matrices of benzoic, benzoic-2-d and benzoic-d$_5$ acids.

Part 1: diagonal elements.

<table>
<thead>
<tr>
<th>The element of the G matrix</th>
<th>Value of the corresponding force constant (mdyn/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>No.</td>
</tr>
<tr>
<td>( \nu_{CH} )</td>
<td></td>
</tr>
<tr>
<td>( H_{15} )</td>
<td></td>
</tr>
<tr>
<td>( H_{11} )</td>
<td></td>
</tr>
<tr>
<td>( \nu_{CC} )</td>
<td>6-11</td>
</tr>
<tr>
<td>( \nu_{CX} )</td>
<td>12</td>
</tr>
<tr>
<td>The element of the G matrix</td>
<td>Value of the corresponding force constant (mdyn/Å)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>Description</td>
<td>No.*</td>
</tr>
<tr>
<td>νC=O</td>
<td>13</td>
</tr>
<tr>
<td>νC-O</td>
<td>14</td>
</tr>
<tr>
<td>νOH</td>
<td>15</td>
</tr>
<tr>
<td>αCCC</td>
<td>16-21</td>
</tr>
<tr>
<td>βCH</td>
<td>22-26</td>
</tr>
</tbody>
</table>

Table 18.2.3 (cont.)

<table>
<thead>
<tr>
<th>Description</th>
<th>No.</th>
<th>Benzoic acid</th>
<th>Benzoic-2-d acid</th>
<th>Benzoic-d$_5$ acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta\phi_X$</td>
<td>27</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$\alpha\text{OCO}$</td>
<td>28</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>$\beta\text{CX}$</td>
<td>29</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$\alpha\text{HOC}$</td>
<td>30</td>
<td>0.72</td>
<td>0.72</td>
<td>0.72</td>
</tr>
<tr>
<td>$\gamma\text{CH}$</td>
<td>31-35</td>
<td>0.398</td>
<td>$\gamma_{CD} = 0.405$</td>
<td>$\gamma_{CD} = 0.405$</td>
</tr>
<tr>
<td>$\gamma\phi_X$</td>
<td>36</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
</tr>
</tbody>
</table>
Table 18.2.3 (cont.)

<table>
<thead>
<tr>
<th>The element of the G matrix</th>
<th>Value of the corresponding force constant (mdyn/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Description</td>
</tr>
<tr>
<td>γ&lt;sub&gt;C-OH&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>δ&lt;sub&gt;CC&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>δ&lt;sub&gt;CX&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>δ&lt;sub&gt;C-OH&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>γ&lt;sub&gt;C=O&lt;/sub&gt;</td>
<td></td>
</tr>
</tbody>
</table>

*This number is the number of the internal coordinate given in table 18.2.2.*
<table>
<thead>
<tr>
<th>The element of the G matrix</th>
<th>Value of the corresponding force constant (mdyn/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Benzoic acid</td>
</tr>
<tr>
<td>$\nu_{C_j}C_{j+1}-\nu_{C_{j+1}}C_{j+2}$</td>
<td>0.531</td>
</tr>
<tr>
<td>$\nu_{C_j}C_{j+1}-\nu_{C_{j+3}}C_{j+4}$</td>
<td>-0.531</td>
</tr>
<tr>
<td>$\nu_{C_j}C_{j+1}-\nu_{C_{j+2}}C_{j+3}$</td>
<td>0.316</td>
</tr>
<tr>
<td>$\nu_{C_j}C_{j+1}-\alpha_{C_{j-1}}C_jC_{j+1}$</td>
<td>0.336</td>
</tr>
<tr>
<td>$\nu_{C_{j+1}}C_{j+1}H(D)$</td>
<td>0.336</td>
</tr>
<tr>
<td>$\nu_{C_1}C_2-\beta_0$</td>
<td>-0.35</td>
</tr>
<tr>
<td>$\nu_{C=0}-\nu_{C-0}$</td>
<td>0.5</td>
</tr>
<tr>
<td>$\nu_{C-0}-\nu_{OH}$</td>
<td>0.3</td>
</tr>
<tr>
<td>The element of the G matrix</td>
<td>Value of the corresponding force constant (mdyn/Å)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>Description</td>
<td>Benzoic acid</td>
</tr>
<tr>
<td>$\alpha_{C_j-1}C_jC_{j+1}\alpha_{C_jC_{j+1}C_{j+2}}$</td>
<td>-0.05</td>
</tr>
<tr>
<td>$\beta_{C_jH(D)}\beta_{C_{j+1}H(D)}$</td>
<td>0.024</td>
</tr>
<tr>
<td>$\beta_{C_jH(D)}\beta_{C_{j+2}H(D)}$</td>
<td>-0.019</td>
</tr>
<tr>
<td>$\beta_{C_jH(D)}\beta_{C_{j+3}H(D)}$</td>
<td>-0.027</td>
</tr>
<tr>
<td>$\beta_{C_2H(D)}\beta_{O_x}$</td>
<td>0.03</td>
</tr>
<tr>
<td>$\beta_{C_6H(D)}\beta_{O_x}$</td>
<td>0.03</td>
</tr>
<tr>
<td>$\beta_{C_3H(D)}\beta_{O_x}$</td>
<td>-0.02</td>
</tr>
<tr>
<td>$\beta_{C_5H(D)}\beta_{O_x}$</td>
<td>-0.03</td>
</tr>
<tr>
<td>$\beta_{C_4H(D)}\beta_{O_x}$</td>
<td>-0.03</td>
</tr>
<tr>
<td>The element of the G matrix</td>
<td>Value of the corresponding force constant (mdyn/Å)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>Description</td>
<td>Benzoic acid</td>
</tr>
<tr>
<td>$\alpha_{C_{j-1}C_{j}C_{j+1}}^{B_{C_{j+1}}H(D)}$</td>
<td>0.042</td>
</tr>
<tr>
<td>$\alpha_{C_1C_2C_3}^{B\phi X}$</td>
<td>-0.05</td>
</tr>
<tr>
<td>$\alpha_{OOC}^{\alpha HOC}$</td>
<td>0.02</td>
</tr>
<tr>
<td>$\gamma_{C_{j}H(D)}^{C_{j+1}H(D)}$</td>
<td>-0.072</td>
</tr>
<tr>
<td>$\gamma_{C_{2}H(D)}^{\gamma \phi X}$</td>
<td>-0.075</td>
</tr>
<tr>
<td>$\delta_{C_{j}C_{j+1}}^{\delta_{C_{j+1}C_{j+2}}}$</td>
<td>-0.012</td>
</tr>
<tr>
<td>$\gamma_{C_{j}H(D)}^{\delta_{C_{j}C_{j+1}}}$</td>
<td>-0.13</td>
</tr>
<tr>
<td>$\delta_{C_{1}C_{2}}^{\gamma \phi X}$</td>
<td>-0.14</td>
</tr>
</tbody>
</table>
Table 18.2.4 The calculated and the observed frequencies of vibrations of benzoic acid.

<table>
<thead>
<tr>
<th>No.</th>
<th>Calculated frequency</th>
<th>Observed frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wave number ( \text{cm}^{-1} )</td>
<td>Wave number ( \text{cm}^{-1} )</td>
</tr>
<tr>
<td>1</td>
<td>3565 ( \nu_{\text{OH}}(100) )</td>
<td>3560 1 IR, R Gas, 200°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3545 4 IR CCl(_4) soln., 0.0082 mol/l</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3537 9 IR CCl(_4) soln., &lt;0.01 mol/l</td>
</tr>
<tr>
<td>2</td>
<td>3074 ( \nu_{\text{CH}}(99) )</td>
<td>3077 2 IR Crystal</td>
</tr>
<tr>
<td>3</td>
<td>3072 ( \nu_{\text{CH}}(99) )</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3072 ( \nu_{\text{CH}}(99) )</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3071 ( \nu_{\text{CH}}(98) )</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3070 ( \nu_{\text{CH}}(99) )</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1752 ( \nu_{\text{C}=\text{O}}(52) )</td>
<td>1764 1 IR, R Gas, 200°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1737 4 IR CCl(_4) soln., 0.0082 mol/l</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1742 9 IR CCl(_4) soln., &lt;0.01 mol/l</td>
</tr>
</tbody>
</table>
Table 18.2.4 (cont.).

<table>
<thead>
<tr>
<th>No.</th>
<th>Calculated frequency</th>
<th>Observed frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wave number cm⁻¹</td>
<td>Ref. Type² of spectrum</td>
</tr>
<tr>
<td>8</td>
<td>ν_{CC}(77)</td>
<td>1602 3 IR Nujol mull</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1600 10 IR KBr disk, 1.8 wt %</td>
</tr>
<tr>
<td>9</td>
<td>ν_{CC}(40), ν_{CX}(15), β_{CH}(25)</td>
<td>1582 3 IR Nujol mull</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1580 10 IR KBr disk, 1.8 wt %</td>
</tr>
<tr>
<td>10</td>
<td>ν_{CC}(70), β_{CH}(35)</td>
<td>1493 3 IR Nujol mull</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1496 10 IR KBr disk, 1.8 wt %</td>
</tr>
<tr>
<td>11</td>
<td>ν_{CC}(63), β_{CH}(27)</td>
<td>1449 3 IR Nujol mull</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1453 10 IR KBr disk, 1.8 wt %</td>
</tr>
<tr>
<td>12</td>
<td>ν_{CC}(74), β_{CH}(38)</td>
<td>1448</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>ν_{CC}(40), β_{CH}(53)</td>
<td>1320</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>β_{CH}(79)</td>
<td>1327 10 IR KBr disk, 1.8 wt %</td>
</tr>
<tr>
<td>15</td>
<td>β_{CH}(81)</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>α_{HOC}(81)</td>
<td>1180 10 IR KBr disk, 1.8 wt %</td>
</tr>
<tr>
<td>17</td>
<td>β_{CH}(95)</td>
<td>1176 3 IR Nujol mull</td>
</tr>
<tr>
<td>No.</td>
<td>Wave number cm(^{-1})</td>
<td>Approximate description (^3)</td>
</tr>
<tr>
<td>-----</td>
<td>----------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>18</td>
<td>1148</td>
<td>(\gamma_{O}(27)), (\gamma_{C-O}(34)), (\gamma_{C=O}(34))</td>
</tr>
<tr>
<td>19</td>
<td>1106</td>
<td>(\nu_{CC}(25)), (\nu_{C-O}(21)), (\alpha_{CCC}(17)), (\beta_{CH}(15))</td>
</tr>
<tr>
<td>20</td>
<td>1081</td>
<td>(\nu_{CC}(51)), (\beta_{CH}(37))</td>
</tr>
<tr>
<td></td>
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</tr>
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<tr>
<td>26</td>
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<td>(\gamma_{CH}(122))</td>
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<tr>
<td>36</td>
<td>323</td>
<td>(\nu_{\text{CX}}(29)), (\alpha_{\text{CCC}}(28)), (\alpha_{\text{OCO}}(31))</td>
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Table 18.2.4 (cont.).

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<td>39</td>
<td>138</td>
<td>(\delta_{\Delta CX}(95))</td>
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</tbody>
</table>

Notes:

1. The "Potential energy distribution" is given in per cent contribution to \(\lambda\) by the diagonal force constants for the respective coordinates. Since the off-diagonal contributions may be negative, the sum of the diagonal contributions may exceed 100 per cent. Only contributions equal to or greater than 15 per cent were included in this table.

2. R stands for Raman spectrum and IR for infrared spectrum.

3. The symbols used to indicate the types of coordinates were defined in Table 18.2.2.
References.

10. Present work.
Table 18.2.5. The calculated and the observed frequencies of vibrations of benzoic-2-d acid.

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<td>Wave number cm$^{-1}$</td>
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<tr>
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<td>3073</td>
<td>$\nu_{CH}(99)$</td>
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<tr>
<td>3</td>
<td>3072</td>
<td>$\nu_{CH}(99)$</td>
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<tr>
<td>4</td>
<td>3072</td>
<td>$\nu_{CH}(99)$</td>
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<tr>
<td>5</td>
<td>3071</td>
<td>$\nu_{CH}(99)$</td>
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<tr>
<td>6</td>
<td>2284</td>
<td>$\nu_{CD}(95)$</td>
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<tr>
<td>7</td>
<td>1751</td>
<td>$\nu_{C=O}(53)$</td>
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<td>8</td>
<td>1644</td>
<td>$\nu_{CC}(78)$</td>
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<tr>
<td>9</td>
<td>1550</td>
<td>$\nu_{CC}(39)$  , $\nu_{CX}(21)$, $\nu_{C=O}(16)$</td>
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<td>1464</td>
<td>$\nu_{CC}(76)$  , $\beta_{CH}(23)$</td>
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<td>12</td>
<td>1448</td>
<td>$\nu_{CC}(68)$  , $\beta_{CH}(42)$</td>
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<td>13</td>
<td>1367</td>
<td>$\nu_{CC}(35)$  , $\beta_{CH}(60)$</td>
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<td>1258</td>
<td>$\nu_{CC}(30)$  , $\beta_{CH}(44)$</td>
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<td>15</td>
<td>1184</td>
<td>$\alpha_{HOC}(80)$</td>
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<td>16</td>
<td>1179</td>
<td>$\beta_{CH}(103)$</td>
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<tr>
<td>17</td>
<td>1146</td>
<td>$\gamma_{C-OH}(33)$, $\gamma_{\delta X}(25)$, $\gamma_{C=O}(33)$</td>
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<td>18</td>
<td>1139</td>
<td>$\nu_{CC}(26)$  , $\beta_{CH}(42)$</td>
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<td>19</td>
<td>1104</td>
<td>$\nu_{CC}(27)$  , $\alpha_{CCC}(18)$, $\beta_{CH}(17)$</td>
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<td>No.</td>
<td>Wave number $\text{cm}^{-1}$</td>
<td>Calculated frequency</td>
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<tr>
<td>-----</td>
<td>-----------------------------</td>
<td>----------------------</td>
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<tr>
<td>21</td>
<td>1000</td>
<td>$\gamma_{\text{CH}}(132)$, $\delta_{\text{CC}}(20)$</td>
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<td>615</td>
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<td>$\alpha_{\text{CCC}}(28)$, $\alpha_{\text{OCO}}(48)$</td>
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<td>560</td>
<td>$\delta_{\text{CC}}(25)$, $\delta_{\text{C-OH}}(76)$</td>
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<td>497</td>
<td>$\beta_{\text{OH}}(17)$, $\beta_{\text{CX}}(45)$</td>
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<td>488</td>
<td>$\gamma_{\text{CH}}(19)$, $\gamma_{\text{OH}}(53)$, $\delta_{\text{CC}}(82)$</td>
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Table 18.2.5 (cont.)

Notes.

1. The "Potential energy distribution" is given in per cent contribution to $\lambda$ by the diagonal force constants of the respective coordinates. Since the off-diagonal contributions may be negative, the sum of the diagonal contributions may exceed 100 per cent. Only contributions equal to or greater than 15 per cent were included in this table.

2. Infrared spectrum of di-azoic-2-d acid as KBr disk, 1.1 wt %, taken on a Perkin-Elmer, Model 457 spectrophotometer.

3. The symbols used to indicate the types of coordinates were defined in table 18.2.2 and subsection 18.2.
Table 18.2.6. The calculated and the observed frequencies of vibrations of benzoic-d$_5$ acid.

<table>
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<th>No.</th>
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<th>Calculated frequency</th>
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<th>Observed$^2$ frequency Wave number (cm$^{-1}$)</th>
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<td>3</td>
<td>2285</td>
<td>$\nu_{CD}$ (94)</td>
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<tr>
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<td>Wave number</td>
<td>Observed frequency</td>
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<td>(%)</td>
<td>cm⁻¹</td>
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<td>γ(CD)(12) , γ(CX)(15) , δ(CC)(22)</td>
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<td>δ(CC)(48)</td>
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<td>318</td>
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<td>202</td>
<td>β(CX)(56) , β(CX)(27)</td>
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</tr>
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<td>185</td>
<td>γ(CD)(11) , δ(CC)(40)</td>
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</tr>
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<td>39</td>
<td>134</td>
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</tbody>
</table>
Notes.

1. The "Potential energy distribution" is given in per cent contribution to $\lambda$ by the diagonal force constants of the respective coordinates. Only contributions equal to or greater than 10 per cent were included in this table.

2. Infrared spectrum of benzoic-d$_3$ acid as KBr disk, 1.7 wt %, taken on a Perkin-Elmer, Model 457 spectrophotometer.

3. The symbols used to indicate the types of coordinates were defined in table 18.2.2 and subsection 18.2.
constants of benzoic-d$_5$ acid is given in column 4 of table 18.2.3.

The calculated vibrational frequencies, the corresponding potential energy distribution and some observed vibrational bands are given in table 18.2.6. The agreement between the calculated and the observed frequencies is good.

18.3 The vibrational frequencies of the benzoate ion.

As in the case of benzoic acid (subsection 18.2), no complete vibrational analysis exists for the benzoate ion. Several papers, 370-372 however, report and assign bands of the infrared and/or Raman spectra of benzoate ion. The wave numbers of these bands, their table 18.3.3 with special reference to the spectra of sodium benzoate.

The calculation of the vibrational frequencies of benzoate ion.

The calculation followed the method shown in section 16. The G matrix. The crystal structure of potassium hydrogen dibenzoate has been studied by Skinner, Stewart and Speakman using x-ray methods. 373 We used their results to calculate the spherical coordinates of all the atoms of the benzoate ion. The carbon-hydrogen distances were assumed to be 1.08 Å. The molecular structure of the benzoate ion is shown in fig. 18.3.1 and the corresponding spherical coordinates are given in table 18.3.1.

We defined 45 internal coordinates for the benzoate ion (table 18.3.2) which included six cyclic and three local redundundancies. These coordinates together with the spherical coordinates and atomic masses were used to obtain the G matrix of the benzoate ion ("Detailed calculations - 18.3.1"). As in the case of benzoic acid, we consider the G matrix obtained here as
a good approximation, only, to the G matrix of the benzoate ion in aqueous solution since the molecular structure of the benzoate ion in this medium is probably not identical to the molecular structure of the benzoate ion in the crystalline form.

The F matrix. The elements of the force constant matrix are described in table 18.4.1. Most of them were transferred directly from the F matrix for the benzene molecule (section 17). Initial values for the force constants corresponding to the internal coordinates of the carboxylate group were those belonging to the carboxylate group in the acetate ion. These initial values were adjusted by trial and error to fit some observed vibrational frequencies tentatively assigned to the vibrations of the carboxylate group in the benzoate ion.

Some of the force constants were then varied in order to see how the ratio $K_H/K_D$ (subsection 18.1) depends on them. This point will be discussed in more detail in subsection 18.4.

The calculated vibrational frequencies of the benzoate ion.

The set of frequencies resulting from set no. 8 of force constants (table 18.4.1) is given in column 2 of table 18.3.3. The corresponding potential energy distribution is given in column 3 of the same table. The agreement with the observed frequencies and with the experimental assignments ranges from fair to good, which is to be expected in view of the approximate treatment used in the present work. The calculated potential energy distribution proved to be more complex than the experimental assignments a fact which is in agreement with similar work in other systems. The wave number of vibration no. 8 (table 18.3.3), which corresponds to out-of-plane (continued p. 546)
FIG. 18.3.1.

THE STRUCTURE OF BENZOATE ION

Table 18.3.1. The spherical coordinates of the atoms of the benzoate ion.

<table>
<thead>
<tr>
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<th>Type</th>
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<th>$A_y$</th>
<th>$A_z$</th>
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<td>12.011</td>
</tr>
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<td>C</td>
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<td>4</td>
<td>C</td>
<td>1.40</td>
<td>90</td>
<td>180</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
<td>1.38</td>
<td>149.6</td>
<td>120.4</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>1.38</td>
<td>149.6</td>
<td>59.6</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>7</td>
<td>H</td>
<td>2.44</td>
<td>30</td>
<td>60</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>8</td>
<td>H</td>
<td>2.44</td>
<td>30</td>
<td>120</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>9</td>
<td>H</td>
<td>2.48</td>
<td>90</td>
<td>180</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>10</td>
<td>H</td>
<td>2.46</td>
<td>149.6</td>
<td>120.4</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>11</td>
<td>H</td>
<td>2.46</td>
<td>149.6</td>
<td>59.6</td>
<td>90</td>
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</tr>
<tr>
<td>12</td>
<td>C</td>
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<td>90</td>
<td>0</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>13</td>
<td>O</td>
<td>3.69</td>
<td>107.1</td>
<td>17.1</td>
<td>90</td>
<td>16.000</td>
</tr>
<tr>
<td>14</td>
<td>O</td>
<td>3.68</td>
<td>73.2</td>
<td>16.8</td>
<td>90</td>
<td>16.000</td>
</tr>
</tbody>
</table>

Notes: 1. $A_x$ is the angle which R makes with the positive direction of the x axis. $A_y$ and $A_z$ have similar definitions. R is the distance from the origin to the respective atom and M is the atomic mass in amu.

2. "z" axis is perpendicular to the plane of the ring.

3. The molecule is planar.
Table 18.3.2. The valence internal coordinates used for calculating the \( G \) matrix of benzoate ion.

<table>
<thead>
<tr>
<th>Int. crd. no.</th>
<th>Atoms involved</th>
<th>Code (^1) no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 7</td>
<td>1</td>
<td>( \nu_{CH} )</td>
<td>C-H stretching.</td>
</tr>
<tr>
<td>2</td>
<td>3 8</td>
<td>1</td>
<td>( \nu_{CH} )</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4 9</td>
<td>1</td>
<td>( \nu_{CH} )</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5 10</td>
<td>1</td>
<td>( \nu_{CH} )</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6 11</td>
<td>1</td>
<td>( \nu_{CH} )</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1 2</td>
<td>1</td>
<td>( \nu_{CC} )</td>
<td>C-C ring stretching.</td>
</tr>
<tr>
<td>7</td>
<td>2 3</td>
<td>1</td>
<td>( \nu_{CC} )</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>3 4</td>
<td>1</td>
<td>( \nu_{CC} )</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>4 5</td>
<td>1</td>
<td>( \nu_{CC} )</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5 6</td>
<td>1</td>
<td>( \nu_{CC} )</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>6 1</td>
<td>1</td>
<td>( \nu_{CC} )</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1 12</td>
<td>1</td>
<td>( \nu_{CX} )</td>
<td>( C_1-C_{12} ) stretching.</td>
</tr>
<tr>
<td>13</td>
<td>13 12</td>
<td>1</td>
<td>( \nu_{C-O} )</td>
<td>C-O stretching.</td>
</tr>
<tr>
<td>14</td>
<td>12 14</td>
<td>1</td>
<td>( \nu_{C-O} )</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>6 2 1</td>
<td>2</td>
<td>( \alpha_{CCC} )</td>
<td>C-C-C ring angle bending.</td>
</tr>
<tr>
<td>16</td>
<td>1 3 2</td>
<td>2</td>
<td>( \alpha_{CCC} )</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2 4 3</td>
<td>2</td>
<td>( \alpha_{CCC} )</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>3 5 4</td>
<td>2</td>
<td>( \alpha_{CCC} )</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>4 6 5</td>
<td>2</td>
<td>( \alpha_{CCC} )</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>5 1 6</td>
<td>2</td>
<td>( \alpha_{CCC} )</td>
<td></td>
</tr>
</tbody>
</table>
Table 18.3.2 (cont.)

<table>
<thead>
<tr>
<th>Int.crd. no.</th>
<th>Atoms involved</th>
<th>Code no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>7 1 3 2</td>
<td>5</td>
<td>$\beta_{CH}$</td>
<td>C-H bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>22</td>
<td>8 2 4 3</td>
<td>5</td>
<td>$\beta_{CH}$</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>9 3 5 4</td>
<td>5</td>
<td>$\beta_{CH}$</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>10 4 6 5</td>
<td>5</td>
<td>$\beta_{CH}$</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>11 5 1 6</td>
<td>5</td>
<td>$\beta_{CH}$</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>12 6 2 1</td>
<td>5</td>
<td>$\beta_{0x}$</td>
<td>C$<em>1$-C$</em>{12}$ bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>27</td>
<td>13 14 12</td>
<td>2</td>
<td>$\alpha_{OCO}$</td>
<td>O-C-O bending.</td>
</tr>
<tr>
<td>28</td>
<td>1 13 14 12</td>
<td>5</td>
<td>$\beta_{CX}$</td>
<td>C$<em>1$-C$</em>{12}$ bending with respect to the external bisector of the O-C-O angle.</td>
</tr>
<tr>
<td>29</td>
<td>7 1 3 2</td>
<td>3</td>
<td>$\gamma_{CH}$</td>
<td>C-H out-of-plane wagging.</td>
</tr>
<tr>
<td>30</td>
<td>8 2 4 3</td>
<td>3</td>
<td>$\gamma_{CH}$</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>9 3 5 4</td>
<td>3</td>
<td>$\gamma_{CH}$</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>10 4 6 5</td>
<td>3</td>
<td>$\gamma_{CH}$</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>11 5 1 6</td>
<td>3</td>
<td>$\gamma_{CH}$</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>12 6 2 1</td>
<td>3</td>
<td>$\gamma_{0x}$</td>
<td>C$<em>1$-C$</em>{12}$ out-of-plane wagging.</td>
</tr>
<tr>
<td>35</td>
<td>13 1 14 12</td>
<td>3</td>
<td>$\gamma_{C-O}$</td>
<td>C-O out-of-plane wagging.</td>
</tr>
<tr>
<td>36</td>
<td>1 2 3 4</td>
<td>4</td>
<td>$\delta_{CC}$</td>
<td>Torsion around a C-C ring bond.</td>
</tr>
<tr>
<td>37</td>
<td>2 3 4 5</td>
<td>4</td>
<td>$\delta_{CC}$</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>3 4 5 6</td>
<td>4</td>
<td>$\delta_{CC}$</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>4 5 6 1</td>
<td>4</td>
<td>$\delta_{CC}$</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>5 6 1 2</td>
<td>4</td>
<td>$\delta_{CC}$</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>6 1 2 3</td>
<td>4</td>
<td>$\delta_{CC}$</td>
<td></td>
</tr>
</tbody>
</table>
Table 18.3.2 (cont.)

<table>
<thead>
<tr>
<th>Int.crd. no.</th>
<th>Atoms involved</th>
<th>Code no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>14 12 1 6</td>
<td>4</td>
<td>$\delta_\phi X$</td>
<td>Torsion around C₁-C₁₂ bond (one of the coordinates no. 42-43 is locally redundant).</td>
</tr>
<tr>
<td>43</td>
<td>13 12 1 2</td>
<td>4</td>
<td>$\delta_\phi X$</td>
<td>-COO$^-$ out-of-plane wagging (locally redundant)</td>
</tr>
<tr>
<td>44</td>
<td>1 13 14 12</td>
<td>3</td>
<td>$\gamma_{CX}$</td>
<td>C-0 out-of-plane wagging. (locally redundant).</td>
</tr>
<tr>
<td>45</td>
<td>14 13 1 12</td>
<td>3</td>
<td>$\gamma_{C-0}$</td>
<td></td>
</tr>
</tbody>
</table>

Notes: 1. This number corresponds to the code no. shown in subsection 16.3.
bendings of the bonds of the carboxylate group is probably high. This fact, however, should not make any difference in the calculated $K_W/K_D$ ratio since the force constants for the two isotopic anions are the same and the internal coordinates contributing to this vibration do not involve the isotopic positions(s). This observation is valid for any other similar case.

**The calculated vibrational frequencies of the benzoate-2-d ion.**

The spherical coordinates and the atomic masses of the atoms of benzoate-2-d ion were assumed to be the same as those of the atoms of benzoate ion (table 18.3.1) with the exception of atom no. 7 which in this case was a deuterium atom. Its distance from the origin was assumed to be 0.009 Å shorter than the distance for the corresponding hydrogen atom of the benzoate ion. The atomic mass of the deuterium atom was taken to be 2.0147 amu. The internal coordinates had the same definitions as those of the benzoate ion (table 18.3.2). For those internal coordinates involving the new carbon-deuterium bond new symbols were used:

<table>
<thead>
<tr>
<th>Int. crd. no.</th>
<th>Atoms involved</th>
<th>Code no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 7</td>
<td>1</td>
<td>$\nu_{CD}$</td>
<td>C-D stretching.</td>
</tr>
<tr>
<td>21</td>
<td>7 1 3 2</td>
<td>5</td>
<td>$\beta_{CD}$</td>
<td>C-D bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>29</td>
<td>7 1 3 2</td>
<td>3</td>
<td>$\gamma_{CD}$</td>
<td>C-D out-of-plane wagging.</td>
</tr>
</tbody>
</table>

The "Detailed calculations" for the G matrix of benzoate-2-d ion are given in 18.3.2.

The F matrix was the same as that used for the benzoate ion with the exception of diagonal force constants corresponding to the in-plane and out-of-plane bending of the carbon-deuterium
bond. The scaling factors for these two coordinates are slightly different from those of the corresponding carbon-hydrogen bond which, consequently, leads to slightly different scaled force constants. Some of the force constants were varied in order to match the calculated and the observed $K_H/K_D$ isotope effects (see subsections 18.1 and 18.4). The frequencies and the potential energy distribution corresponding to set no. 8 of force constants (table 18.4.1) are given in table 18.3.4.

The calculated vibrational frequencies of the benzoate-$d_5$ ion. The molecular structure of benzoate-$d_5$ anion was assumed to be the identical to that of benzoate ion (table 18.3.1 and fig. 18.3.1) with the exception of carbon-deuterium bonds which were assumed to be 0.009 Å shorter than the corresponding carbon-hydrogen bonds. The atomic mass of deuterium atom was taken to be 2.0147 amu. The internal coordinates used for computing the G matrix of benzoate-$d_5$ ion were identical to those used for the G matrix of benzoate ion (table 18.3.2). The subscripts of the symbols corresponding to the internal coordinates in which the deuterium atoms are involved were modified as follows:
<table>
<thead>
<tr>
<th>Int. crd. no.</th>
<th>Atoms involved</th>
<th>Code no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 7</td>
<td>1</td>
<td>$\nu_{CD}$</td>
<td>C-D stretching.</td>
</tr>
<tr>
<td>2</td>
<td>3 8</td>
<td>1</td>
<td>$\nu_{CD}$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4 9</td>
<td>1</td>
<td>$\nu_{CD}$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5 10</td>
<td>1</td>
<td>$\nu_{CD}$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6 11</td>
<td>1</td>
<td>$\nu_{CD}$</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>7 1 3 2</td>
<td>5</td>
<td>$\beta_{CD}$</td>
<td>C-D bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>22</td>
<td>8 2 4 3</td>
<td>5</td>
<td>$\beta_{CD}$</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>9 3 5 4</td>
<td>5</td>
<td>$\beta_{CD}$</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>10 4 6 5</td>
<td>5</td>
<td>$\beta_{CD}$</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>11 5 1 6</td>
<td>5</td>
<td>$\beta_{CD}$</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>7 1 3 2</td>
<td>3</td>
<td>$\gamma_{CD}$</td>
<td>C-D out-of-plane wagging.</td>
</tr>
<tr>
<td>30</td>
<td>8 2 4 3</td>
<td>3</td>
<td>$\gamma_{CD}$</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>9 3 5 4</td>
<td>3</td>
<td>$\gamma_{CD}$</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>10 4 6 5</td>
<td>3</td>
<td>$\gamma_{CD}$</td>
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</tr>
<tr>
<td>33</td>
<td>11 5 1 6</td>
<td>3</td>
<td>$\gamma_{CD}$</td>
<td></td>
</tr>
</tbody>
</table>

The "Detailed calculations" of the G matrix are given in 18.3.3.

The force constants belonging to the F matrix of benzoate-$d_5$ anion were varied in order to match the calculated and the observed $K_H/K_D$ isotope effect. This point is discussed in more detail in the next subsection (subsection 18.4). The vibrational frequencies and the potential energy distributions corresponding to set no. 2 of force constants, i.e. to the set (continued p. 558)
Table 18.3.3. The calculated and the observed frequencies of vibrations of benzoate ion (sodium benzoate).

<table>
<thead>
<tr>
<th>No.</th>
<th>Calculated frequency</th>
<th>Observed frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Potential energy distribution)</td>
<td>Wave number cm⁻¹</td>
</tr>
<tr>
<td></td>
<td>Approximate description (%)</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>1</td>
<td>$v_{CH}(98)$</td>
<td>3110</td>
</tr>
<tr>
<td>2</td>
<td>$v_{CH}(98)$</td>
<td>3108</td>
</tr>
<tr>
<td>3</td>
<td>$v_{CH}(98)$</td>
<td>3073</td>
</tr>
<tr>
<td>4</td>
<td>$v_{CH}(98)$</td>
<td>3072</td>
</tr>
<tr>
<td>5</td>
<td>$v_{CH}(98)$</td>
<td>3070</td>
</tr>
<tr>
<td>6</td>
<td>$v_{CC}(36)$, $v_{CH}(12)$</td>
<td>1702</td>
</tr>
<tr>
<td>7</td>
<td>$v_{CC}(31)$, $v_{C-O}(14)$</td>
<td>1666</td>
</tr>
<tr>
<td>8</td>
<td>$v_{C-O}(39)$, $v_{C-X}(39)$</td>
<td>1581</td>
</tr>
<tr>
<td>9</td>
<td>$v_{CC}(36)$, $v_{CH}(19)$, $v_{C-O}(8)$</td>
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</tr>
<tr>
<td>10</td>
<td>$v_{CC}(35)$, $v_{CH}(20)$</td>
<td>1547</td>
</tr>
</tbody>
</table>

Assignment: CO₂ sym. def.
Table 18.3.3 (cont.).

<table>
<thead>
<tr>
<th>No.</th>
<th>Calculated frequency</th>
<th>Observed frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wave number</td>
<td>Approximate description (^{3})</td>
</tr>
<tr>
<td></td>
<td>cm(^{-1})</td>
<td>(Potential energy distribution (^{1}))</td>
</tr>
<tr>
<td>11</td>
<td>1450</td>
<td>(\nu_{CC}(14), \nu_{CX}(10), \nu_{C-O}(11),) (\beta_{CH}(40))</td>
</tr>
<tr>
<td>12</td>
<td>1414</td>
<td>(\nu_{C-O}(19), \beta_{CH}(44))</td>
</tr>
<tr>
<td>13</td>
<td>1370</td>
<td>(\nu_{C-O}(24), \nu_{CH}(54))</td>
</tr>
<tr>
<td>14</td>
<td>1304</td>
<td>(\nu_{CC}(33))</td>
</tr>
<tr>
<td>15</td>
<td>1218</td>
<td>(\beta_{CH}(78))</td>
</tr>
<tr>
<td>16</td>
<td>1162</td>
<td>(\nu_{CC}(18), \beta_{CH}(57))</td>
</tr>
<tr>
<td>17</td>
<td>1102</td>
<td>(\nu_{CC}(22), \nu_{C-O}(22), \alpha_{CCC}(12))</td>
</tr>
<tr>
<td>18</td>
<td>1052</td>
<td>(\nu_{CC}(33), \beta_{CH}(19))</td>
</tr>
<tr>
<td>19</td>
<td>1035</td>
<td>(\gamma_{CH}(36), \delta_{CC}(10))</td>
</tr>
<tr>
<td>20</td>
<td>1022</td>
<td>(\nu_{CC}(34), \alpha_{CCC}(19))</td>
</tr>
<tr>
<td>21</td>
<td>1019</td>
<td>(\gamma_{CH}(57))</td>
</tr>
<tr>
<td>No.</td>
<td>Calculated frequency</td>
<td>Observed frequency</td>
</tr>
<tr>
<td>------</td>
<td>---------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td></td>
<td>Wave number (cm⁻¹)</td>
<td>Approximate description (Potential energy distribution)</td>
</tr>
<tr>
<td>22</td>
<td>998</td>
<td>$\nu_{\text{CC}}(33)$, $\alpha_{\text{CCC}}(19)$</td>
</tr>
<tr>
<td>23</td>
<td>974</td>
<td>$\gamma_{\text{CH}}(48)$</td>
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<td>24</td>
<td>856</td>
<td>$\gamma_{\text{CH}}(81)$</td>
</tr>
<tr>
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<td></td>
<td></td>
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<td>25</td>
<td>798</td>
<td>$\gamma_{\text{CH}}(20)$, $\gamma_{\theta X}(14)$, $\delta_{\text{CC}}(19)$</td>
</tr>
<tr>
<td>26</td>
<td>741</td>
<td>$\nu_{\text{CC}}(13)$, $\nu_{\text{CX}}(13)$, $\nu_{\text{C-O}}(24)$, $\alpha_{\text{CCC}}(25)$</td>
</tr>
<tr>
<td>27</td>
<td>709</td>
<td>$\gamma_{\text{CH}}(28)$, $\delta_{\text{CC}}(17)$</td>
</tr>
<tr>
<td>28</td>
<td>627</td>
<td>$\alpha_{\text{CCC}}(69)$</td>
</tr>
<tr>
<td>29</td>
<td>62</td>
<td>$\nu_{\text{C-O}}(11)$, $\alpha_{\text{CCC}}(31)$, $\alpha_{\text{OCO}}(42)$</td>
</tr>
<tr>
<td>30</td>
<td>532</td>
<td>$\gamma_{\text{CH}}(10)$, $\gamma_{\theta X}(10)$, $\delta_{\text{CC}}(31)$</td>
</tr>
<tr>
<td>31</td>
<td>514</td>
<td>$\nu_{\text{C-O}}(17)$, $\beta_{\theta X}(14)$, $\beta_{\text{CX}}(41)$</td>
</tr>
</tbody>
</table>
Table 18.3.3 (cont.)

<table>
<thead>
<tr>
<th>No.</th>
<th>Calculated frequency</th>
<th>Observed frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Approximate description (Potential energy distribution)</td>
<td>Wave number (cm⁻¹)</td>
</tr>
<tr>
<td>32</td>
<td>γCH(12), δCC(42)</td>
<td>424</td>
</tr>
<tr>
<td>33</td>
<td>νCX(27), αCCC(27), αOCO(22)</td>
<td>334</td>
</tr>
<tr>
<td>34</td>
<td>βdx(48), βCX(17)</td>
<td>223</td>
</tr>
<tr>
<td>35</td>
<td>γCH(12), δCC(41)</td>
<td>204</td>
</tr>
<tr>
<td>36</td>
<td>δdx(70)</td>
<td>171</td>
</tr>
</tbody>
</table>

Notes.

1. The "Potential energy distribution" is given in per cent contribution to λ by the diagonal force constants of the respective coordinates. Only contributions equal to or greater than 10 per cent were included in this table (with one exception in frequency no. 9).

2. R stands for Raman spectrum and IR for infrared spectrum.

3. The symbols used to indicate the type of coordinates were defined in table 18.3.2.
Table  18.3.3 (cont.)

References .
4. Present work .
Table 18.3.4. The calculated frequencies of vibrations of benzoate-2-d ion.

<table>
<thead>
<tr>
<th>No.</th>
<th>Wave number cm(^{-1})</th>
<th>Calculated frequency</th>
<th>Approximate description(^2) (Potential energy distribution(^1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3109</td>
<td>(\nu_{CH}) (98)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3073</td>
<td>(\nu_{CH}) (99)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3072</td>
<td>(\nu_{CH}) (99)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3070</td>
<td>(\nu_{CH}) (99)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2311</td>
<td>(\nu_{CD}) (93)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1686</td>
<td>(\nu_{CC}) (37), (\nu_{CX}) (14)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1652</td>
<td>(\nu_{CC}) (35), (\nu_{C-O}) (14)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1581</td>
<td>(\gamma_{OH}) (10), (\gamma_{C-O}) (39), (\gamma_{CX}) (39)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1556</td>
<td>(\nu_{CC}) (33), (\nu_{C-O}) (12), (\beta_{CH}) (15)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1524</td>
<td>(\nu_{CC}) (34), (\beta_{CH}) (17)</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1445</td>
<td>(\nu_{CC}) (14), (\nu_{C-O}) (13), (\beta_{CH}) (41)</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1412</td>
<td>(\nu_{CC}) (11), (\nu_{C-O}) (13), (\beta_{CH}) (52)</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1309</td>
<td>(\nu_{CC}) (22), (\nu_{C-O}) (13), (\beta_{CH}) (33)</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1304</td>
<td>(\nu_{CC}) (58)</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1173</td>
<td>(\nu_{CC}) (16), (\beta_{CH}) (59)</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>1146</td>
<td>(\nu_{CC}) (21), (\beta_{CH}) (42)</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>1100</td>
<td>(\nu_{CC}) (23), (\nu_{C-O}) (20), (\alpha_{CCC}) (14)</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>1030</td>
<td>(\nu_{CC}) (39), (\alpha_{CCC}) (11)</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>1027</td>
<td>(\gamma_{CH}) (39)</td>
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<tr>
<td>20</td>
<td>984</td>
<td>(\gamma_{CH}) (52)</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>982</td>
<td>(\nu_{CC}) (32), (\alpha_{CCC}) (28)</td>
<td></td>
</tr>
</tbody>
</table>
Table 18.3.4 (cont.)

<table>
<thead>
<tr>
<th>No.</th>
<th>Wave number $\text{cm}^{-1}$</th>
<th>Calculated frequency</th>
<th>Approximate description(^2) (Potential energy distribution(^1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>933</td>
<td>$\gamma_{CD}(12)$</td>
<td>$\gamma_{CH}(21)$, $\delta_{CC}(11)$</td>
</tr>
<tr>
<td>23</td>
<td>882</td>
<td>$\nu_{CC}(26)$</td>
<td>$\beta_{CD}(45)$</td>
</tr>
<tr>
<td>24</td>
<td>828</td>
<td>$\gamma_{CD}(11)$</td>
<td>$\gamma_{CH}(17)$</td>
</tr>
<tr>
<td>25</td>
<td>779</td>
<td>$\gamma_{CH}(52)$</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>740</td>
<td>$\nu_{CC}(14)$</td>
<td>$\nu_{CX}(13)$, $\nu_{C-O}(24)$, $\alpha_{CCC}(24)$</td>
</tr>
<tr>
<td>27</td>
<td>641</td>
<td>$\gamma_{CD}(13)$</td>
<td>$\gamma_{CH}(16)$, $\delta_{CC}(23)$</td>
</tr>
<tr>
<td>28</td>
<td>623</td>
<td>$\alpha_{CCC}(57)$</td>
<td>$\alpha_{OCC}(12)$</td>
</tr>
<tr>
<td>29</td>
<td>617</td>
<td>$\alpha_{CCC}(40)$</td>
<td>$\alpha_{OCC}(31)$</td>
</tr>
<tr>
<td>30</td>
<td>529</td>
<td>$\gamma_{\Theta X}(12)$</td>
<td>$\delta_{CC}(29)$</td>
</tr>
<tr>
<td>31</td>
<td>506</td>
<td>$\nu_{C-O}(17)$</td>
<td>$\beta_{\Theta X}(13)$, $\beta_{CX}(42)$</td>
</tr>
<tr>
<td>32</td>
<td>408</td>
<td>$\gamma_{CH}(11)$</td>
<td>$\delta_{CC}(43)$</td>
</tr>
<tr>
<td>33</td>
<td>332</td>
<td>$\nu_{CX}(26)$</td>
<td>$\alpha_{CCC}(27)$, $\alpha_{OCC}(22)$</td>
</tr>
<tr>
<td>34</td>
<td>220</td>
<td>$\beta_{\Theta X}(47)$</td>
<td>$\beta_{CX}(16)$</td>
</tr>
<tr>
<td>35</td>
<td>202</td>
<td>$\delta_{CC}(41)$</td>
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</tr>
<tr>
<td>36</td>
<td>170</td>
<td>$\delta_{CC}(10)$</td>
<td>$\delta_{\Theta X}(70)$</td>
</tr>
</tbody>
</table>

Notes.

1. The "Potential energy distribution" is given in per cent contribution to $\lambda$ by the diagonal force constants of the respective coordinates. Only contributions equal to or greater than 10 per cent were included in this table.

2. The symbols used to describe the types of coordinates were defined in tables 18.3.2 and subsection 18.3.
<table>
<thead>
<tr>
<th>No.</th>
<th>Wave number (cm(^{-1}))</th>
<th>Calculated frequency</th>
<th>Approximate description (^2) (Potential energy distribution (^1)) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2306 (\nu_{CD}(94))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2304 (\nu_{CD}(92))</td>
<td></td>
<td></td>
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<tr>
<td>3</td>
<td>2286 (\nu_{CD}(93))</td>
<td></td>
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<tr>
<td>4</td>
<td>2283 (\nu_{CD}(93))</td>
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</tr>
<tr>
<td>5</td>
<td>2280 (\nu_{CD}(90))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1677 (\nu_{CC}(38), \nu_{CX}(15))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1639 (\nu_{CC}(34), \nu_{C-O}(17))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1569 (\gamma_{\phi X}(10), \gamma_{C-O}(40), \gamma_{CX}(39))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1526 (\nu_{CC}(36), \nu_{C-O}(20))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1493 (\nu_{CC}(38), \nu_{CX}(11))</td>
<td>(\nu_{C-O}(13))</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1307 (\nu_{CC}(32), \beta_{CD}(20))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1301 (\nu_{CC}(29), \nu_{C-O}(19), \beta_{CD}(19))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1289 (\nu_{CC}(66))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1091 (\beta_{CD}(73))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1052 (\nu_{CC}(15), \nu_{C-O}(20), \alpha_{CCC}(21))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>950 (\nu_{CC}(24), \alpha_{CCC}(26))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>927 (\gamma_{CD}(19), \delta_{CC}(18))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>880 (\beta_{CD}(76))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>851 (\nu_{CC}(20), \beta_{CD}(37))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>847 (\beta_{CD}(72))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>823 (\nu_{CC}(19), \beta_{CD}(45))</td>
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<td></td>
</tr>
</tbody>
</table>
### Table 18.3.5 (cont.)

<table>
<thead>
<tr>
<th>No.</th>
<th>Wave number cm(^{-1})</th>
<th>Calculated frequency</th>
<th>Approximate description(^2) (Potential energy distribution(^1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>820</td>
<td>(\gamma_{CD}(47))</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>790</td>
<td>(\gamma_{CD}(37))</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>715</td>
<td>(\nu_{CC}(14)), (\nu_{CX}(10)), (\nu_{C-O}(24)), (\alpha_{CCC}(17)), (\alpha_{OCO}(10))</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>673</td>
<td>(\gamma_{CD}(76))</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>656</td>
<td>(\gamma_{CD}(31)), (\gamma_{\phi X}(13))</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>610</td>
<td>(\alpha_{CCC}(34)), (\alpha_{OCO}(37))</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>601</td>
<td>(\alpha_{CCC}(65))</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>555</td>
<td>(\gamma_{CD}(29)), (\delta_{CC}(17))</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>497</td>
<td>(\nu_{C-O}(16)), (\beta_{\phi X}(11)), (\beta_{CX}(43))</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>470</td>
<td>(\gamma_{CD}(15)), (\gamma_{\phi X}(11)), (\delta_{CC}(24))</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>379</td>
<td>(\delta_{CC}(50))</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>328</td>
<td>(\nu_{CX}(26)), (\alpha_{CCC}(27))</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>213</td>
<td>(\beta_{\phi X}(48)), (\beta_{CX}(15))</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>191</td>
<td>(\gamma_{CD}(12)), (\delta_{CC}(44))</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>166</td>
<td>(\delta_{\phi X}(70))</td>
<td></td>
</tr>
</tbody>
</table>

**Notes.**

1. The "Potential energy distribution" is given in per cent contribution to \(\lambda\) by the diagonal force constants of the respective coordinates. Only contributions equal to or greater than 10 per cent were included in this table.

2. The symbols used to describe the types of coordinates were defined in table 18.3.2 and subsection 18.3.
which leads to the best agreement between the calculated and the observed isotope effect, are given in table 18.3.5.

The calculated $K_H/K_D$ isotope effects.

**Benzoic acid - benzoic-2-d acid system.**

Stern and Wolfsberg\(^2\) have shown that in order to obtain a $K_H/K_D$ ratio different from unity some diagonal force constants must change in going from reactants to products. Thus we have varied the force constants for the products of acid dissociation, i.e. the respective anions, and have calculated the corresponding vibrational frequencies and the ratio $K_H/K_D$. In all cases the force constants of the reactant molecules, i.e. the acid molecules, were kept constant (table 18.2.3). The force constants which were varied in the products and their respective $K_H/K_D$ values are given in table 18.4.1. The "Detailed calculations" can be found in 18.4.1.

Sets nos. 1 and 2 (table 18.4.1) in which the force constants of the internal coordinates involving the isotopic atom (atom no. 7) were not changed confirmed the Stern and Wolfsberg\(^2\) statement: "the isotope effect is 1.000 in absence of force constant changes between the reactants and the products at the position(s) of the isotopic substitution."

In sets 3 to 9 we have assumed that the force constants corresponding to the internal coordinates which are in the vicinity of the carboxyl group increase in going from the unionized state to the ionized state (see also subsection 8.6). Thus in set no. 3 the changes were the increases in the force constants corresponding to $C_2$-$H(D)_7$ and $C_6$-$H_{11}$ stretching and in-plane bendings. The resultant isotope effect of 0.966 is almost entirely due to the zero point energy (ZPE) factor of (18.1.1).
It is interesting to note that the entire ZPE factor originates in carbon-hydrogen (deuterium) stretchings (see "Detailed calculations- 18.4.1").

In sets nos. 4 and 9 an additional assumption was introduced: the increase in the force constants was slightly different in the benzoate and benzoate-2-d ions. In sets nos. 5 to 8, the force constants corresponding to the internal coordinates which were located in the neighbourhood of the carboxylate group were varied by various, arbitrarily chosen, amounts. Set no. 8 gave the best agreement with the experimentally observed isotope effect though none of the calculated $K_{H}/K_{D}$ ratios were very far off.

We have seen that the change in the thermodynamic quantities for the ionization of a carboxylic acid in water is a result, primarily, of the more ordered structure of the solvent water molecules around the anion (and in particular around the carboxylate group) as compared to the acid molecules (section 14). Here, we have assumed that this more ordered structure leads to an increase in the force constants. In other words, we have assumed that it is more difficult for a bond to bend, for example, in this more ordered structure. Certainly this is an oversimplified picture and explanation of what happens in the actual system.

From table 18.4.1 it can be seen that the experimental $K_{H}/K_{D}$ ratio was reproduced almost exactly when:

1. the increase in the force constants for both anions, i.e. benzoate and benzoate-2-d, was identical (10% increase, set no. 8); and

2. the increase in the force constants of the benzoate-2-d
anion was slightly less (by 0.5%) than that for benzoate anion (set no. 9).

In subsection 8.6 it was said that a slightly smaller increase in the force constants of the benzoate-2-d anion could mean a slightly weaker interaction between this anion and solvent water than between benzoate anion and water. This weaker interaction could be explained by taking into account the fact that the C-D bond is shorter and less polarizable as compared to a C-H bond. In this particular system, however, this additional assumption is not really necessary since the observed isotope effect is in very good agreement with that calculated from set no. 8 of force constants.

**Benzoic acid - Benzoic-d₅ acid system.**

One set of force constants for the benzoate anion and two sets for the benzoate-d₅ anion were used to calculate the vibrational frequencies and the corresponding $K_H/K_D$ isotope effect. The force constants for the two reactant molecules, i.e. benzoic acid and benzoic-d₅ acid, were kept unchanged and are those given in table 18.2.3. The force constants corresponding to the internal coordinates of the two anions and the results of the calculation of the isotope effect are given in table 18.4.2. The complete calculations are given in "Detailed calculations - 18.4.2."

Set no. 1 of force constants (table 18.4.2) is identical to one of the two sets which gave the best agreement between the calculated and the observed isotope effect in the previous system studied, i.e. set no. 8 (table 18.4.1) of benzoic acid - benzoic-2-d acid system, with the exception of diagonal force constants corresponding to in-plane bending and out-of-plane wagging of the bonds in which the hydrogen has been replaced by
deuterium (different scaling factors). The force constants of set no. 2 are identical to those of set no. 1 for the benzoate ion. For the benzoate-d$_5$ ion the force constants were obtained from those of set no. 1 by multiplying some of them by 0.995 and leaving others unchanged*. The force constants which were multiplied by 0.995 correspond to the internal coordinates which are in the vicinity of the carboxylate group. The agreement between the calculated and the observed $K_H/K_D$ values is very good. A good agreement was also obtained in the previous system, i.e. benzoic acid - benzoic-2-d acid, when the same procedure was applied to obtain the force constants of the benzoate-2-d ion (set no. 9).

The assumption that the force constants in the benzoate-d$_5$ ion are very slightly smaller than those of the benzoate ion is more plausible than in the case of benzoate-2-d anion because of the increased number of deuterium atoms in the first of these anions.

In both systems studied here, i.e. benzoic acid - benzoic-2-d acid and benzoic acid - benzoic-d$_5$ acid, the calculated $K_H/K_D$ ratio was practically temperature independent in the interval from 20 to 40°C (see "Detailed calculations 18.4.1 and 18.4.2"). This result is in very good agreement with the experimental observations (table 8.5.3).

*Footnote. Inadvertently a value of 0.483 instead of 0.493 was used for one of the force constants ($\gamma_{CX}$). This fact, however, does not influence the final results in any way since the corresponding internal coordinate is not a major component of any of the vibrational frequencies of the anions (see table 18.3.3, 18.3.4 and 18.3.5).
Table 18.4.1. The elements of the F matrices of benzoate and benzoate-2-d anions and the corresponding calculated $K_H/K_D$ isotope effect

<table>
<thead>
<tr>
<th>Internal coordinate</th>
<th>(\nu_{CH(D)})</th>
<th>(\nu_C)</th>
<th>(\nu_C)</th>
<th>(\beta_{C,H叙(D)})</th>
<th>(\beta_C)</th>
<th>(\gamma_{CH(D)})</th>
<th>(\gamma_C)</th>
<th>(\delta_{C叙})</th>
<th>(\gamma_C)</th>
<th>(\gamma_{CH叙})</th>
</tr>
</thead>
<tbody>
<tr>
<td>In the acid</td>
<td>5.125 5.125</td>
<td>5.125 5.125</td>
<td>5.125 5.125</td>
<td>5.125 5.125</td>
<td>5.125 5.125</td>
<td>5.125 5.125</td>
<td>5.125 5.125</td>
<td>5.125 5.125</td>
<td>5.125 5.125</td>
<td>5.125 5.125</td>
</tr>
<tr>
<td>In the anion</td>
<td>5.300 5.300</td>
<td>5.300 5.300</td>
<td>5.300 5.300</td>
<td>5.300 5.300</td>
<td>5.300 5.300</td>
<td>5.300 5.300</td>
<td>5.300 5.300</td>
<td>5.300 5.300</td>
<td>5.300 5.300</td>
<td>5.300 5.300</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Value of the corresponding force constant (mdyn/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>\nu_{CH(D)})</td>
</tr>
<tr>
<td>\nu_C)</td>
</tr>
<tr>
<td>\nu_{CH叙(D)})</td>
</tr>
<tr>
<td>\beta_{C,H叙(D)})</td>
</tr>
<tr>
<td>\beta_C)</td>
</tr>
<tr>
<td>\alpha_{OCO})</td>
</tr>
<tr>
<td>\gamma_{CH(D)})</td>
</tr>
<tr>
<td>\gamma_C)</td>
</tr>
<tr>
<td>\gamma_{CH叙})</td>
</tr>
<tr>
<td>\gamma_{CH叙(D)})</td>
</tr>
</tbody>
</table>

Total isotope effect:

<table>
<thead>
<tr>
<th>Value of the total isotope effect (mdyn/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.979</td>
</tr>
</tbody>
</table>

Notes:

a. Isotope effect obtained experimentally in the present work.

b. This internal coordinate was used in the G matrices of the two anions only.

c. The off-diagonal force constants corresponding to the internal coordinates not shown in the table and all off-diagonal force constants were identical to those of benzoic acid and benzoic-2-d acid (Table 18.2.3).

d. Bz(H): Benzoate anion; Bz(2-d): Benzoate-2-d anion.

e. Calculated from relations (18.1.3), (18.1.4), and (18.1.5).
Table 18.4.2. The elements of the F matrices of benzoate and benzoate-d₈ anions and the corresponding calculated $K_{H}/K_{D}$ isotope effect

<table>
<thead>
<tr>
<th>Internal coordinate</th>
<th>Value of the corresponding force constant (mdyn/A)</th>
<th>In the acids</th>
<th>In the anions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Bz(H)⁴</td>
<td>Bz(d₈)⁴</td>
</tr>
<tr>
<td>$\nu_{C_6H(D)_7}$</td>
<td>5.125</td>
<td>5.125</td>
<td>5.250</td>
</tr>
<tr>
<td>$\nu_{C_6H(D)_{11}}$</td>
<td>5.125</td>
<td>5.125</td>
<td>5.250</td>
</tr>
<tr>
<td>$\nu_{\beta}$</td>
<td>5.0</td>
<td>5.0</td>
<td>5.1</td>
</tr>
<tr>
<td>$\nu_{C_6H(OH)}$</td>
<td>9.20</td>
<td>9.20</td>
<td>6.80</td>
</tr>
<tr>
<td>$\nu_{C_6H-O_{13}}$</td>
<td>5.50</td>
<td>5.50</td>
<td>5.50</td>
</tr>
<tr>
<td>$\beta_{C_6H(D)_7}$</td>
<td>0.881</td>
<td>0.896</td>
<td>0.969</td>
</tr>
<tr>
<td>$\beta_{C_6H(D)_{11}}$</td>
<td>0.881</td>
<td>0.896</td>
<td>0.969</td>
</tr>
<tr>
<td>$\sigma_{OCO}$</td>
<td>1.000</td>
<td>1.000</td>
<td>1.100</td>
</tr>
<tr>
<td>$\delta_{\beta}$</td>
<td>0.900</td>
<td>0.900</td>
<td>0.990</td>
</tr>
<tr>
<td>$\sigma_{\beta_{CX}}$</td>
<td>1.000</td>
<td>1.000</td>
<td>1.100</td>
</tr>
<tr>
<td>$\gamma_{C_{6H(D)_{7}}}$</td>
<td>0.398</td>
<td>0.405</td>
<td>0.438</td>
</tr>
<tr>
<td>$\gamma_{C_{6H(D)_{11}}}$</td>
<td>0.398</td>
<td>0.405</td>
<td>0.438</td>
</tr>
<tr>
<td>$\gamma_{\beta_{DX}}$</td>
<td>0.450</td>
<td>0.450</td>
<td>0.495</td>
</tr>
<tr>
<td>$\gamma_{\beta_{OCO}}$</td>
<td>0.400</td>
<td>0.400</td>
<td>0.444</td>
</tr>
<tr>
<td>$\delta_{\beta_{DX}}$</td>
<td>0.100</td>
<td>0.100</td>
<td>0.158</td>
</tr>
<tr>
<td>$\gamma_{\beta_{CX}}$</td>
<td>0.450⁵</td>
<td>0.450⁵</td>
<td>0.495</td>
</tr>
<tr>
<td>$\gamma_{\beta_{OCO}}$</td>
<td>0.350</td>
<td>0.350</td>
<td>0.385</td>
</tr>
<tr>
<td>VP (298.15⁰K)</td>
<td>0.993</td>
<td></td>
<td>1.032</td>
</tr>
<tr>
<td>EXP (298.15⁰K)</td>
<td>1.009</td>
<td></td>
<td>1.007</td>
</tr>
<tr>
<td>ZPE (298.15⁰K)</td>
<td>0.991</td>
<td></td>
<td>0.984</td>
</tr>
</tbody>
</table>

Total isotope effect:

$K_{H}/K_{D} = VP, EXP, ZPE$

1.025⁴

0.992

1.022

Notes:

a. Isotope effect obtained experimentally in the present work (subsection 8.6).

b. This internal coordinate was used in the G matrices of the two anions, only.

c. The diagonal force constants corresponding to the internal coordinates not shown in this table and all off-diagonal force constant were identical to those of benzoic and benzoate-d₈ acids, respectively (Table 18.2.3).

d. Bz(H): Benzoate anion; Bz(d₈): Benzoate-d₈ anion.
19. THE CALCULATION OF THE SECONDARY DEUTERIUM ISOTOPE EFFECTS IN \( o\)-TOLUIC ACID - \( o\)-TOLUIC-D\(_7\) ACID SYSTEM

19.1 Introduction

In this section we apply the method of calculation described in the previous section to the \( o\)-toluic acid - \( o\)-toluic-d\(_7\) acid system in order to calculate the \( K_H/K_D \) ratio; essentially we carry out an approximate vibrational analysis of the molecular species involved in the system mentioned above, i.e. the two acids and their anions.

No complete vibrational analysis exists in the literature for any of the four molecules belonging to this system. The published values of some of the vibrational frequencies of \( o\)-toluic acid are given in columns 4 to 7 of table 19.2.4.

19.2 The calculated vibrational frequencies of \( o\)-toluic and \( o\)-toluic-d\(_7\) acids.

The \( G \) matrix. The molecular structure of \( o\)-toluic acid assumed in the present work is shown in fig. 19.2.1 and the coordinates of all the atoms are given in table 19.2.1. The structure is essentially identical to the molecular structure of benzoic acid (subsection 18.2) with the following rather obvious exceptions:

a. The presence of a methyl group in the \( o\)-position. The methyl group was assumed to be tetrahedral. The carbon - hydrogen and the carbon (methyl) - carbon (ring) bond lengths were assumed to be equal to the equivalent bond lengths in toluene. 375
b. The carboxyl group is not in the plane of the benzene ring. It was assumed that the plane of the carboxyl group makes an angle of 36° with the plane of the benzene ring.

To calculate the G matrix we have defined 59 internal coordinates. Of these 59 coordinates, 54 were defined according to Decius' rules. Because of the symmetry of the molecule, we have defined five more coordinates which, therefore, represent local redundancies. The definition of the internal coordinates and their symbols are given in table 19.2.1.

The complete calculations of B and G elements (see subsection 16.3) are given in "Detailed calculations - 19.2.1".

The F matrix. For corresponding internal coordinates the force constants of o-toluic acid were assumed to be equal to those of benzoic acid (subsection 18.2). The force constants corresponding to the internal coordinates involving the atoms of the methyl group were taken from the work by Schachtschneider and Snyder on n-paraffins although the situations are far from being identical. The complete set of force constants is given in table 19.2.3.

The calculated vibrational frequencies of o-toluic acid

The vibrational frequencies of o-toluic acid were obtained from the G and F matrices by solving the secular equation (16.2.1). The "Detailed calculations" are given in 19.2.2 and a summary of the results is given in columns 2 and 3 of table 19.2.4. The calculated vibrational frequencies are in fair agreement with the limited number of reported observed frequencies.

(continued p. 583)
\[ \begin{align*}
&< C_1 C_2 C_3 : 118^\circ \\
&< C_2 C_3 C_4 : 123^\circ \\
&< C_3 C_4 C_5 : 118^\circ \\
&< C_4 C_5 C_6 : 122^\circ \\
&< C_5 C_6 C_1 : 120^\circ \\
&< C_6 C_1 C_2 : 119^\circ \\
&< O_{13} C_{12} C_1 : 122^\circ \\
&< O_{14} C_{12} C_1 : 118^\circ \\
&< C_{12} O_{14} H_{15} : 107.8^\circ 
\end{align*} \]

**FIG. 19.2.1.**

THE ASSUMED STRUCTURE OF \( \alpha \)-TOLUIC ACID
Table 19.2.1: The spherical coordinates of the atoms of γ-toluic acid.

<table>
<thead>
<tr>
<th>No.</th>
<th>Atom type</th>
<th>R</th>
<th>A_x</th>
<th>A_y</th>
<th>A_z</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C</td>
<td>1.416</td>
<td>90</td>
<td>0</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>1.390</td>
<td>30.7</td>
<td>59.3</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>1.365</td>
<td>31.3</td>
<td>121.3</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>1.410</td>
<td>90</td>
<td>180</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
<td>1.370</td>
<td>149.1</td>
<td>120.9</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>1.390</td>
<td>149.5</td>
<td>59.5</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>7</td>
<td>H</td>
<td>2.474</td>
<td>30.7</td>
<td>59.3</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>8</td>
<td>H</td>
<td>2.450</td>
<td>31.3</td>
<td>121.3</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>9</td>
<td>H</td>
<td>2.494</td>
<td>90</td>
<td>180</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>10</td>
<td>H</td>
<td>2.454</td>
<td>149.1</td>
<td>120.9</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>11</td>
<td>C</td>
<td>2.900</td>
<td>149.5</td>
<td>59.5</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>12</td>
<td>C</td>
<td>2.890</td>
<td>90</td>
<td>0.8</td>
<td>90.8</td>
<td>12.011</td>
</tr>
<tr>
<td>13</td>
<td>O</td>
<td>3.720</td>
<td>103.3</td>
<td>16.51</td>
<td>99.60</td>
<td>16</td>
</tr>
<tr>
<td>14</td>
<td>O</td>
<td>3.656</td>
<td>75.61</td>
<td>18.17</td>
<td>79.50</td>
<td>16</td>
</tr>
<tr>
<td>15</td>
<td>H</td>
<td>4.096</td>
<td>86.13</td>
<td>4.17</td>
<td>87.53</td>
<td>1.0078</td>
</tr>
<tr>
<td>16</td>
<td>H</td>
<td>3.420</td>
<td>167</td>
<td>77</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>17</td>
<td>H</td>
<td>3.422</td>
<td>138.2</td>
<td>52.14</td>
<td>74.96</td>
<td>1.0078</td>
</tr>
<tr>
<td>18</td>
<td>H</td>
<td>3.422</td>
<td>138.2</td>
<td>52.14</td>
<td>105</td>
<td>1.0078</td>
</tr>
</tbody>
</table>

Notes: 1. $A_x$, $A_y$ and $A_z$ are the angles made by vector R with the three coordinate axes. R is the distance from origin to the respective atom. M is the atomic mass in amu.

2. The origin of the coordinate system is in the centre of the benzene ring. The benzene ring is located in the xy plane; the z axis is perpendicular to this plane.

3. The angle between the plane of the carboxyl group and the plane at the benzene ring makes an angle at 36°.
Table 19.2.2: The valence internal coordinates used to calculate the G matrix of \textit{p}-toluic acid.

<table>
<thead>
<tr>
<th>Int.crd. no.</th>
<th>Atoms involved</th>
<th>Code* no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 7</td>
<td>1</td>
<td>$\nu_{CH}$</td>
<td>$C_{\text{ring}}$-$H_{\text{ring}}$ stretching</td>
</tr>
<tr>
<td>2</td>
<td>3 8</td>
<td>1</td>
<td>$\nu_{CH}$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4 9</td>
<td>1</td>
<td>$\nu_{CH}$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5 10</td>
<td>1</td>
<td>$\nu_{CH}$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6 11</td>
<td>1</td>
<td>$\nu_{C,4C_{\text{methyl}}}$</td>
<td>$C_{\text{ring}}$-$C_{\text{methyl}}$ stretching</td>
</tr>
<tr>
<td>6</td>
<td>1 2</td>
<td>1</td>
<td>$\nu_{CC}$</td>
<td>$C_{\text{ring}}$-$C_{\text{ring}}$ stretching</td>
</tr>
<tr>
<td>7</td>
<td>2 3</td>
<td>1</td>
<td>$\nu_{CC}$</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>3 4</td>
<td>1</td>
<td>$\nu_{CC}$</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>4 5</td>
<td>1</td>
<td>$\nu_{CC}$</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5 6</td>
<td>1</td>
<td>$\nu_{CC}$</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>6 1</td>
<td>1</td>
<td>$\nu_{CC}$</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1 12</td>
<td>1</td>
<td>$\nu_{CX}$</td>
<td>$C_{1}$-$C_{12}$ stretching</td>
</tr>
<tr>
<td>13</td>
<td>13 12</td>
<td>1</td>
<td>$\nu_{C=0}$</td>
<td>C=O stretching</td>
</tr>
<tr>
<td>14</td>
<td>12 14</td>
<td>1</td>
<td>$\nu_{C-O}$</td>
<td>C-O stretching</td>
</tr>
<tr>
<td>15</td>
<td>14 15</td>
<td>1</td>
<td>$\nu_{OH}$</td>
<td>O-H stretching</td>
</tr>
<tr>
<td>16</td>
<td>6 2 1</td>
<td>2</td>
<td>$\alpha_{CCC}$</td>
<td>C-C-C ring angle bending</td>
</tr>
<tr>
<td>17</td>
<td>1 3 2</td>
<td>2</td>
<td>$\alpha_{CCC}$</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>2 4 3</td>
<td>2</td>
<td>$\alpha_{CCC}$</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>3 5 4</td>
<td>2</td>
<td>$\alpha_{CCC}$</td>
<td></td>
</tr>
<tr>
<td>Int. crd. no.</td>
<td>Atoms involved</td>
<td>Code* no.</td>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------</td>
<td>-----------</td>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>20</td>
<td>4 6 5</td>
<td>2</td>
<td>$\alpha_{CCC}$</td>
<td></td>
</tr>
<tr>
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<td>5 1 6</td>
<td>2</td>
<td>$\alpha_{CCC}$</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>7 1 3 2</td>
<td>5</td>
<td>$\beta_{CH}$</td>
<td>$C_{ring-H_{ring}}$ in-plane bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>23</td>
<td>8 2 4 3</td>
<td>5</td>
<td>$\beta_{CH}$</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>9 3 5 4</td>
<td>5</td>
<td>$\beta_{CH}$</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>10 4 6 5</td>
<td>5</td>
<td>$\beta_{CH}$</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>11 5 1 6</td>
<td>5</td>
<td>$\beta_{C_{r_{m}}C_{r}}$</td>
<td>$C_{ring-C_{methyl}}$ in-plane bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>27</td>
<td>12 6 2 1</td>
<td>5</td>
<td>$\beta_{RX**}$</td>
<td>$C_{-C_{12}}$ in-plane bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>28</td>
<td>13 14 12</td>
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<td>$\alpha_{OOC}$</td>
<td>$O=C-O$ bending</td>
</tr>
<tr>
<td>29</td>
<td>1 13 14 12</td>
<td>5</td>
<td>$\beta_{CX}$</td>
<td>$C_{ring-COOH}$ in-plane bending with respect to the external bisector of the right angle.</td>
</tr>
<tr>
<td>30</td>
<td>15 14 12</td>
<td>2</td>
<td>$\alpha_{HOC}$</td>
<td>$H-O-C$ bending</td>
</tr>
<tr>
<td>31</td>
<td>7 1 3 2</td>
<td>3</td>
<td>$\gamma_{CH}$</td>
<td>$C_{ring-H_{ring}}$ out-of-plane wagging</td>
</tr>
<tr>
<td>32</td>
<td>8 2 4 3</td>
<td>3</td>
<td>$\gamma_{CH}$</td>
<td></td>
</tr>
<tr>
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<td>9 3 5 4</td>
<td>3</td>
<td>$\gamma_{CH}$</td>
<td></td>
</tr>
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<td>$\gamma_{CH}$</td>
<td></td>
</tr>
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<td>35</td>
<td>11 5 1 6</td>
<td>3</td>
<td>$\gamma_{C_{r_{m}}C_{r}}$</td>
<td>$C_{ring-C_{methyl}}$ out-of-plane wagging</td>
</tr>
<tr>
<td>Int. crd. no.</td>
<td>Atoms involved</td>
<td>Code no.</td>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
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<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>36</td>
<td>12 6 2 1</td>
<td>3</td>
<td>$\gamma_{\text{RX}}^{**}$</td>
<td>$C_1$-$C_{12}$ out-of-plane wagging</td>
</tr>
<tr>
<td>37</td>
<td>14 13 1 12</td>
<td>3</td>
<td>$\gamma_{\text{C-OH}}$</td>
<td>C-Oh out-of-plane wagging</td>
</tr>
<tr>
<td>38</td>
<td>1 2 3 4</td>
<td>4</td>
<td>$\delta_{\text{CC}}$</td>
<td>Torsion around a C-C ring bond.</td>
</tr>
<tr>
<td>39</td>
<td>2 3 4 5</td>
<td>4</td>
<td>$\delta_{\text{CC}}$</td>
<td></td>
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</tr>
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<td>41</td>
<td>4 5 6 1</td>
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<td>$\delta_{\text{CC}}$</td>
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</tr>
<tr>
<td>42</td>
<td>5 6 1 2</td>
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<td>$\delta_{\text{CC}}$</td>
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</tr>
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<td>$\delta_{\text{CC}}$</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>14 12 1 6</td>
<td>4</td>
<td>$\delta_{\text{CX}}$</td>
<td>Torsion around $C_1$-$C_{12}$ bond</td>
</tr>
<tr>
<td>45</td>
<td>15 14 12 1</td>
<td>4</td>
<td>$\delta_{\text{C-OH}}$</td>
<td>Torsion around C-OH bond</td>
</tr>
<tr>
<td>46</td>
<td>13 12 1 2</td>
<td>4</td>
<td>$\delta_{\text{CX}}$</td>
<td>Torsion around $C_1$-$C_{12}$ bond (locally redundant)</td>
</tr>
<tr>
<td>47</td>
<td>13 1 14 12</td>
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<td>$\gamma_{\text{C=O}}$</td>
<td>CO out-of-plane wagging</td>
</tr>
<tr>
<td>48</td>
<td>16 11</td>
<td>1</td>
<td>$\nu_{\text{C}_m\text{H}_m}$</td>
<td>\text{CH}_m$-$H\text{CH}_m$ methyl stretching</td>
</tr>
<tr>
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<td>17 11</td>
<td>1</td>
<td>$\nu_{\text{C}_m\text{H}_m}$</td>
<td></td>
</tr>
<tr>
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<td>$\nu_{\text{C}_m\text{H}_m}$</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>6 16 11</td>
<td>2</td>
<td>$\alpha_{\text{C}_{\text{ring-C}_m\text{H}_m}}$</td>
<td>$\text{C}_{\text{ring-C}}$-$\text{methyl-H}$ methyl angle bending</td>
</tr>
</tbody>
</table>
Table 19.2.2 (cont.)

<table>
<thead>
<tr>
<th>Int. crd. no.</th>
<th>Atoms involved</th>
<th>Code* no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>6 17 11</td>
<td>2</td>
<td>$\alpha_{C_r C_m H_m}$</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>6 18 11</td>
<td>2</td>
<td>$\alpha_{C_r C_m H_m}$</td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>16 17 11</td>
<td>2</td>
<td>$\alpha_{H_m C_m H_m}$</td>
<td>$H_{methyl}^{-C_{methyl}^{-H_{methyl}}}$ angle bending</td>
</tr>
<tr>
<td>55</td>
<td>17 18 11</td>
<td>2</td>
<td>$\alpha_{H_m C_m H_m}$</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>18 16 11</td>
<td>2</td>
<td>$\alpha_{H_m C_m H_m}$</td>
<td>(one of the coordinates nos. 51-56 is locally redundant)</td>
</tr>
<tr>
<td>57</td>
<td>16 11 6 1</td>
<td>4</td>
<td>$\delta_{C_r C_m}$</td>
<td>Torsion around $C_6-C_{11}$ bond (two of the coordinates 57-59 are locally redundant)</td>
</tr>
<tr>
<td>58</td>
<td>17 11 6 5</td>
<td>4</td>
<td>$\delta_{C_r C_m}$</td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>18 11 6 5</td>
<td>4</td>
<td>$\delta_{C_r C_m}$</td>
<td></td>
</tr>
</tbody>
</table>

Note: *This number corresponds to the code no. shown in subsection 16.3.

** $R = \text{\underline{o-CH}}_3 - \text{C}_6\text{H}_4 -$ **
Table 19.2.3. The elements of the $F$ matrix of $o$-toluic acid. Part 1: diagonal elements.

<table>
<thead>
<tr>
<th>The element of the $G$ matrix</th>
<th>Description</th>
<th>No.*</th>
<th>Value of the corresponding force constant $^0$ (mdyn/A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{C_1C_m}$</td>
<td><img src="image" alt="Diagram" /></td>
<td>5</td>
<td>5.125</td>
</tr>
<tr>
<td>$\nu_{OH}$</td>
<td><img src="image" alt="Diagram" /></td>
<td>15</td>
<td>7.0</td>
</tr>
<tr>
<td>$\beta_{C_1C_m}$</td>
<td><img src="image" alt="Diagram" /></td>
<td>26</td>
<td>0.462</td>
</tr>
<tr>
<td>The element of the $G$ matrix</td>
<td>Description</td>
<td>No.*</td>
<td>Value of the corresponding force constant $\gamma_0$ (mdyn/Å)</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-------------</td>
<td>------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>$\gamma_{C_r C_m}$</td>
<td><img src="image1" alt="Diagram" /></td>
<td>35</td>
<td>0.209</td>
</tr>
<tr>
<td>$\nu_{C_m H_m}$</td>
<td><img src="image2" alt="Diagram" /></td>
<td>48-50</td>
<td>4.703</td>
</tr>
<tr>
<td>$\alpha_{C_r C_{H_{m m}}}$</td>
<td><img src="image3" alt="Diagram" /></td>
<td>51-53</td>
<td>0.266</td>
</tr>
<tr>
<td>$\alpha_{H_m H_m C_m}$</td>
<td><img src="image4" alt="Diagram" /></td>
<td>54-57</td>
<td>0.455</td>
</tr>
<tr>
<td>$\delta_{C_r C_m}$</td>
<td><img src="image5" alt="Diagram" /></td>
<td>57-59</td>
<td>0.011</td>
</tr>
</tbody>
</table>

* This number corresponds to the internal coordinate number given in table 19.2.2.
<table>
<thead>
<tr>
<th>The element of the G matrix</th>
<th>Value of the corresponding force constant $\kappa_0$ (mdyn/A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{C_{j-1}C_j^{-}}C_{j}C_m$</td>
<td>0.336</td>
</tr>
<tr>
<td>$\beta_{C_{j-1}H^{-}}C_{j}C_m$</td>
<td>0.024</td>
</tr>
<tr>
<td>$\beta_{C_{j-2}H^{-}}C_{j}C_m$</td>
<td>-0.019</td>
</tr>
<tr>
<td>$\beta_{C_{j-3}H^{-}}C_{j}C_m$</td>
<td>-0.027</td>
</tr>
<tr>
<td>$\beta_{C_{j}C_m^{-}}\beta_{RX}$</td>
<td>0.030</td>
</tr>
<tr>
<td>$\beta_{C_{j}C_m^{-}}\alpha_{C_{j}}C_{j+1}C_{j+2}$</td>
<td>-0.042</td>
</tr>
<tr>
<td>$\gamma_{C_{j}C_m^{-}}\gamma_{C_{j-1}H}$</td>
<td>-0.072</td>
</tr>
<tr>
<td>Description</td>
<td>Value of the corresponding force constant (mdyn/A)</td>
</tr>
<tr>
<td>-------------</td>
<td>---------------------------------------------------</td>
</tr>
<tr>
<td>$\gamma_{C_j C_m} - \gamma_{RX}$</td>
<td>-0.075</td>
</tr>
<tr>
<td>$\gamma_{C_j C_m} - \delta C_j C_{j+1}$</td>
<td>0.140</td>
</tr>
<tr>
<td>$\nu_{C_m H_m} - \nu_{C_m H_m'}$</td>
<td>0.38</td>
</tr>
<tr>
<td>$\alpha_{C_j C_m H_m} - \nu_{C_j C_m}$</td>
<td>0.080</td>
</tr>
<tr>
<td>$\alpha_{C_j C_m C_m} - \nu_{C_j C_{j+1}}$</td>
<td>0.110</td>
</tr>
<tr>
<td>$\alpha_{C_j C_m C_m} - \alpha_{C_j C_m H_m'}$</td>
<td>-0.022</td>
</tr>
</tbody>
</table>

Note. Only the non-zero force constants which are different or new from those of benzoic acid (table 18.2.3) are given in this table.
<table>
<thead>
<tr>
<th>No.</th>
<th>Wave number cm(^{-1})</th>
<th>Calculated frequency</th>
<th>Wave number cm(^{-1})</th>
<th>Ref.</th>
<th>Type</th>
<th>The state of the compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3548</td>
<td>(\nu_{\text{OH}}(100))</td>
<td>3555</td>
<td>1</td>
<td>IR</td>
<td>Gas, 200°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3515</td>
<td>2</td>
<td>IR</td>
<td>CHCl(_3) soln., 2.69% wt/vol</td>
</tr>
<tr>
<td>2</td>
<td>3074</td>
<td>(\nu_{\text{CH}}(98))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3072</td>
<td>(\nu_{\text{CH}}(98))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3071</td>
<td>(\nu_{\text{CH}}(97))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3070</td>
<td>(\nu_{\text{CH}}(99))</td>
<td>3069</td>
<td>1</td>
<td>IR</td>
<td>Gas, 200°C</td>
</tr>
<tr>
<td>6</td>
<td>2964</td>
<td>(\nu_{\text{C}_m\text{H}_m}(98))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2962</td>
<td>(\nu_{\text{C}_m\text{H}_m}(98))</td>
<td>2945</td>
<td>1</td>
<td>IR</td>
<td>Gas, 200°C</td>
</tr>
<tr>
<td>8</td>
<td>2883</td>
<td>(\nu_{\text{C}_m\text{H}_m}(98))</td>
<td></td>
<td>2888</td>
<td>IR</td>
<td>Liquid, 190°C</td>
</tr>
<tr>
<td>9</td>
<td>1755</td>
<td>(\nu_{\text{CC}}(11), \nu_{\text{CX}}(10))</td>
<td>1760</td>
<td>1</td>
<td>R</td>
<td>Gas, 300°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1770</td>
<td>1</td>
<td>IR</td>
<td>Gas, 200°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1743</td>
<td>1</td>
<td>IR</td>
<td>Liquid, 190°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1693</td>
<td>2</td>
<td>IR</td>
<td>CHCl(_3) soln., 2.69% wt/vol</td>
</tr>
<tr>
<td>No.</td>
<td>Calculated frequency</td>
<td>Wave number cm(^{-1}) (Potential energy distribution(^1))</td>
<td>Approximate description</td>
<td>Observed frequency</td>
<td>The state of the compound</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>---------------------</td>
<td>---------------------------------------------------------------</td>
<td>-------------------------</td>
<td>-------------------</td>
<td>---------------------------</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>(\nu_{CC}(50))</td>
<td>1662</td>
<td></td>
<td></td>
<td>Gas, 200°C</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>(\nu_{CC}(33), \beta_{CH}(21))</td>
<td>1560, 1575</td>
<td>160, 1575</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CHCl(_3) soln., 2.69% wt/vol</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>(\nu_{CC}(41))</td>
<td>1539</td>
<td></td>
<td></td>
<td>Gas, 200°C</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>(\nu_{CC}(42), \beta_{CH}(15))</td>
<td>1480, 1490</td>
<td>1490, 1490</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CHCl(_3) soln., 2.69% wt/vol</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>(\alpha_{H_m_C_m_H_m}(91))</td>
<td>1472</td>
<td>1482</td>
<td>IR</td>
<td>Gas, 200°C</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>(\alpha_{H_m_C_m_H_m}(81))</td>
<td>1470</td>
<td>1457</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>(\nu_{CC}(41), \beta_{CH}(23))</td>
<td>1437</td>
<td>1450, 1448</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CHCl(_3) soln., 2.69% wt/vol</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>(\nu_{CC}(25), \beta_{CH}(13))</td>
<td>1380</td>
<td>1383, 1385</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\alpha_{C_m_C_m_H_m}(19), \alpha_{H_m_C_m_H_m}(17))</td>
<td>1380</td>
<td>1383, 1385</td>
<td>IR</td>
<td>CHCl(_3) soln., 2.69% wt/vol</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>(\nu_{CC}(24), \beta_{CH}(29))</td>
<td>1342</td>
<td>1340</td>
<td>IR</td>
<td>Gas, 200°C</td>
<td></td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>No.</th>
<th>Calculated frequency</th>
<th>Wave number cm⁻¹</th>
<th>Approximate description (potential energy distribution)</th>
<th>Wave number cm⁻¹</th>
<th>Ref.</th>
<th>Type of spectrum</th>
<th>The state of the compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>ν_C(20), β_C(30)</td>
<td>1265</td>
<td></td>
<td>1272</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1270</td>
<td></td>
<td></td>
<td></td>
<td>CHCl₃ soln., 2.69% wt/vol</td>
</tr>
<tr>
<td>20</td>
<td>ν_C(26), β_C(15),</td>
<td>1243</td>
<td></td>
<td>1270</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
</tr>
<tr>
<td></td>
<td>γ_C-H(12), α_C-H(11)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CHCl₃ soln., 2.69% wt/vol</td>
</tr>
<tr>
<td>21</td>
<td>β_C(64)</td>
<td>1174</td>
<td></td>
<td>1182</td>
<td>1</td>
<td>IR</td>
<td>Gas, 200°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1171</td>
<td></td>
<td></td>
<td></td>
<td>KBr disk, 1.03 wt %</td>
</tr>
<tr>
<td>22</td>
<td>β_C(19), ν_C-O(17)</td>
<td>1164</td>
<td></td>
<td>1165</td>
<td>2</td>
<td>IR</td>
<td>CHCl₃ soln., 2.69% wt/vol</td>
</tr>
<tr>
<td></td>
<td>γ_C=O(15)</td>
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<td></td>
<td></td>
<td>KBr disk, 1.03 wt %</td>
</tr>
<tr>
<td>23</td>
<td>ν_C(11), ν_C=O(11),</td>
<td>1147</td>
<td></td>
<td>1144</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
</tr>
<tr>
<td></td>
<td>β_C(11), α_HOC(39)</td>
<td></td>
<td></td>
<td>1142</td>
<td>2</td>
<td>IR</td>
<td>CHCl₃ soln., 2.69% wt/vol</td>
</tr>
<tr>
<td>24</td>
<td>ν_C(17), β_C(12)</td>
<td>1131</td>
<td></td>
<td>1090</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
</tr>
<tr>
<td></td>
<td>α_HOC(36)</td>
<td></td>
<td></td>
<td>1090</td>
<td>2</td>
<td>IR</td>
<td>CHCl₃ soln., 2.69% wt/vol</td>
</tr>
<tr>
<td>25</td>
<td>ν_C(17), α_CCC(15)</td>
<td>1063</td>
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<td>1058</td>
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<td>R</td>
<td>Gas, 300°C</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td>1052</td>
<td>1</td>
<td>IR</td>
<td>Gas, 200°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1057</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
</tr>
</tbody>
</table>
Table 19.2.4 (cont.)

<table>
<thead>
<tr>
<th>No.</th>
<th>Wave number cm(^{-1})</th>
<th>Approximate description (potential energy distribution)</th>
<th>Wave Number cm(^{-1})</th>
<th>Ref.</th>
<th>Type of spectrum</th>
<th>The state of the compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>1027 (\alpha_{C_r C_m H_m}^{(62)})</td>
<td>1040</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>1006 (\nu_{CC}^{(44)})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>998 (\gamma_{CH}^{(46)})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>994 (\alpha_{C_r C_m H_m}^{(62)})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>959 (\gamma_{CH}^{(55)})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>873 (\gamma_{CH}^{(51)})</td>
<td>835</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>809 (\nu_{C_r C_m}^{(14)}, \nu_{CC}^{(12)}, \alpha_{CCC}^{(32)})</td>
<td>805</td>
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<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>768 (\gamma_{CH}^{(29)})</td>
<td>769</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>726 (\gamma_{CH}^{(17)}, \delta_{CC}^{(15)})</td>
<td>725</td>
<td>1</td>
<td>R</td>
<td>Gas, 300°C</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>696 (\delta_{CC}^{(19)})</td>
<td>740</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>588 (\alpha_{CCC}^{(28)}, \alpha_{OCO}^{(28)})</td>
<td>690</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Calculated frequency</td>
<td>Observed frequency</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
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<tr>
<td></td>
<td>Wave number cm⁻¹</td>
<td>Approximate description</td>
<td>Wave number cm⁻¹</td>
<td>Ref.</td>
<td>Type of spectrum</td>
<td>The state of the compound</td>
</tr>
<tr>
<td>37</td>
<td>574</td>
<td>$\gamma_{CH}(10)$, $\delta_{CC}(32)$</td>
<td>577</td>
<td>1</td>
<td>IR</td>
<td>Gas, 200°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>570</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
</tr>
<tr>
<td>38</td>
<td>560</td>
<td>$\delta_{C-OH}(66)$</td>
<td>535</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
</tr>
<tr>
<td>39</td>
<td>521</td>
<td>$\nu_{C\rightarrow C}(10)$, $\alpha_{CCC}(29)$</td>
<td>535</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
</tr>
<tr>
<td>40</td>
<td>439</td>
<td>$\gamma_{RX}(10)$, $\delta_{CC}(16)$</td>
<td>535</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
</tr>
<tr>
<td>41</td>
<td>359</td>
<td>$\gamma_{C\rightarrow C}(11)$, $\delta_{CC}(30)$</td>
<td>535</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
</tr>
<tr>
<td>42</td>
<td>346</td>
<td>$\gamma_{C\rightarrow C}(10)$, $\delta_{CC}(12)$</td>
<td>535</td>
<td>2</td>
<td>IR</td>
<td>KBr disk, 1.03 wt %</td>
</tr>
<tr>
<td>43</td>
<td>282</td>
<td>$\beta_{C\rightarrow C}(12)$</td>
<td>299</td>
<td>1</td>
<td>R</td>
<td>Gas, 300°C</td>
</tr>
<tr>
<td>44</td>
<td>233</td>
<td>$\gamma_{C\rightarrow C}(44)$</td>
<td>299</td>
<td>1</td>
<td>R</td>
<td>Gas, 300°C</td>
</tr>
<tr>
<td>45</td>
<td>171</td>
<td>$\beta_{C\rightarrow C}(10)$, $\beta_{RX}(11)$, $\delta_{CC}(26)$</td>
<td>299</td>
<td>1</td>
<td>R</td>
<td>Gas, 300°C</td>
</tr>
</tbody>
</table>
Table 19.2.4 (cont.)

<table>
<thead>
<tr>
<th>No.</th>
<th>Calculated frequency</th>
<th>Observed frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wave number cm$^{-1}$</td>
<td>Approximate description (potential energy distribution)</td>
</tr>
<tr>
<td>46</td>
<td>158</td>
<td>$\beta_{RX}(10)$, $\delta_{CC}(21)$, $\delta_{C_rC_m}(11)$</td>
</tr>
<tr>
<td>47</td>
<td>134</td>
<td>$\gamma_{C_rC_m}(12)$, $\delta_{CC}(27)$, $\delta_{C_rC_m}(16)$</td>
</tr>
<tr>
<td>48</td>
<td>122</td>
<td>$\gamma_{C_rC_m}(15)$, $\delta_{CX}(56)$</td>
</tr>
</tbody>
</table>
Table 19.2.4 (cont.)

Notes: 1. The "Potential energy distribution" is given in per cent contribution to $\lambda$ by the diagonal force constants of the respective coordinates. Only contribution equal to or greater than 10 per cent were included in this table.

2. R stands for Raman spectrum and IR for infrared spectrum.

3. The symbols used to indicate the type of the internal coordinate were defined in table 19.2.2.

References:


2. Present work. The spectra were taken with a Perkin-Elmer Model 457 spectrophotometer as KBr disk or chloroform solution.
The calculated vibrational frequencies of o-toluic-d₇ acid

The molecular structure of o-toluic-d₇ acid were assumed to be identical to that of the undeuterated acid with the exception of carbon-deuterium bonds which were assumed to be 0.009 Å shorter than the corresponding carbon-hydrogen bonds.

The internal coordinates for the G matrix of o-toluic-d₇ acid had the same definitions as those of o-toluic acid. New symbols were used for the coordinates which involved the deuterium atoms. These coordinates are listed below. (For the numbering system, see the first entry in Table 19.2.3.)

<table>
<thead>
<tr>
<th>Int. crd. no.</th>
<th>Atoms involved</th>
<th>Code no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 7</td>
<td>1</td>
<td>ν&lt;sub&gt;CD&lt;/sub&gt;</td>
<td>C&lt;sub&gt;r&lt;/sub&gt;ing-D&lt;sub&gt;r&lt;/sub&gt;ing stretching</td>
</tr>
<tr>
<td>2</td>
<td>3 8</td>
<td>1</td>
<td>ν&lt;sub&gt;CD&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4 9</td>
<td>1</td>
<td>ν&lt;sub&gt;CD&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5 10</td>
<td>1</td>
<td>ν&lt;sub&gt;CD&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>7 1 3 2</td>
<td>5</td>
<td>β&lt;sub&gt;CD&lt;/sub&gt;</td>
<td>C&lt;sub&gt;r&lt;/sub&gt;ing-D&lt;sub&gt;r&lt;/sub&gt;ing in-plane</td>
</tr>
<tr>
<td>23</td>
<td>8 2 4 3</td>
<td>5</td>
<td>β&lt;sub&gt;CD&lt;/sub&gt;</td>
<td>bending with respect to the external bisector of the ring angle</td>
</tr>
<tr>
<td>24</td>
<td>9 3 5 4</td>
<td>5</td>
<td>β&lt;sub&gt;CD&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>10 4 6 5</td>
<td>5</td>
<td>β&lt;sub&gt;CD&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>7 1 3 2</td>
<td>3</td>
<td>γ&lt;sub&gt;CD&lt;/sub&gt;</td>
<td>C&lt;sub&gt;r&lt;/sub&gt;ing-D&lt;sub&gt;r&lt;/sub&gt;ing out-of-plane</td>
</tr>
<tr>
<td>32</td>
<td>8 2 4 3</td>
<td>3</td>
<td>γ&lt;sub&gt;CD&lt;/sub&gt;</td>
<td>wagging</td>
</tr>
<tr>
<td>33</td>
<td>9 3 5 4</td>
<td>3</td>
<td>γ&lt;sub&gt;CD&lt;/sub&gt;</td>
<td></td>
</tr>
</tbody>
</table>
The symbol R in the case of o-toluic-d$_7$ acid stands for o-CD$_3$-C$_6$D$_4$-group.

The complete set of B and G elements of o-toluic-d$_7$ acid are given in "Detailed calculations-19.2.3."

In a second set of calculations of the G matrix of o-toluic-d$_7$ acid, we have assumed that the plane of the carboxyl group makes an angle of 33°, instead of 36°, with the plane of the benzene ring.

The complete sets of B and G elements are given in "Detailed calculations 19.2.4." To differentiate between the two situations we denote the former case by "o-toluic-d$_7$ acid (φ=36°)" and the latter case by "o-toluic-d$_7$ acid (φ=33°)".

The force constants corresponding to the internal coordinates of o-toluic-d$_7$ acid generally were identical to those of o-toluic acid.
Some of the diagonal force constants corresponding to the internal coordinates involving the carbon-deuterium bonds had to be adjusted for the different scaling factors. In the case of o-toluic-d₇ acid (θ=33°) we varied the force constants corresponding to the internal coordinates which involved the C₁-C₁₂ bond when we tried to take into account the increased π-electron communication between the ring and the carboxyl group. The force constants which were changed in going from o-toluic acid to o-toluic-d₇ acid are given in table 19.4.1.

The calculated vibrational frequencies corresponding to set no. 6 of force constants (table 19/4.1) are given in table 19.2.5 and they are compared with some observed frequencies obtained in the present work.

19.3 The calculated vibrational frequencies of o-toluate and o-toluate-d₇ anions

The G matrix. The molecular structure of the o-toluate anion was assumed to be identical to that of the benzoate ion (subsection 18.3) with the same exceptions as in the case of o-toluic acid, i.e.:

a. The presence of a methyl group in the o-position. As in the case of o-toluic acid, the bond angles and the bond lengths of the methyl group were assumed to equal those of the methyl group in the toluene molecule.

b. The plane of the carboxylate group makes an angle of ϕ=36° with the plane of the benzene ring.

(continued p. 590)
Table 19.2.5. *The calculated and the observed frequencies of vibrations of \( \alpha \)-toluic-d\(_7\) acid.*

<table>
<thead>
<tr>
<th>No.</th>
<th>Wave number cm(^{-1})</th>
<th>Calculated frequency</th>
<th>Approximate description (^1) (Potential energy distribution (^3)) (%)</th>
<th>Observed (^2) frequency</th>
<th>Wave number cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3548</td>
<td>( \nu_{\text{OH}} ) (100)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2288</td>
<td>( \nu_{\text{CD}} ) (93)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2283</td>
<td>( \nu_{\text{CD}} ) (92)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2281</td>
<td>( \nu_{\text{CD}} ) (94)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2280</td>
<td>( \nu_{\text{CD}} ) (92)</td>
<td></td>
<td></td>
<td>2280</td>
</tr>
<tr>
<td>6</td>
<td>2212</td>
<td>( \nu_{\text{C}_{m\text{D}} m} ) (97)</td>
<td></td>
<td></td>
<td>2240</td>
</tr>
<tr>
<td>7</td>
<td>2210</td>
<td>( \nu_{\text{C}_{m\text{D}} m} ) (97)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2084</td>
<td>( \nu_{\text{C}_{m\text{D}} m} ) (94)</td>
<td></td>
<td></td>
<td>2125</td>
</tr>
<tr>
<td>9</td>
<td>1760</td>
<td>( \nu_{\text{CX}} ) (11)  , ( \nu_{\text{C} = 0} ) (45)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1649</td>
<td>( \nu_{\text{CC}} ) (47)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1538</td>
<td>( \nu_{\text{CC}} ) (24)  , ( \nu_{\text{CX}} ) (17)  , ( \nu_{\text{C-0}} ) (14)</td>
<td></td>
<td></td>
<td>1547</td>
</tr>
<tr>
<td>12</td>
<td>1502</td>
<td>( \nu_{\text{C}_{\text{r}} \text{C}} ) (52)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1449</td>
<td>( \nu_{\text{CC}} ) (59)</td>
<td></td>
<td></td>
<td>1425</td>
</tr>
<tr>
<td>14</td>
<td>1367</td>
<td>( \nu_{\text{CC}} ) (45)</td>
<td></td>
<td></td>
<td>1351</td>
</tr>
<tr>
<td>15</td>
<td>1255</td>
<td>( \nu_{\text{CC}} ) (37)</td>
<td></td>
<td></td>
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</tbody>
</table>
Table 19.2.5 (cont.)

<table>
<thead>
<tr>
<th>No.</th>
<th>Calculated frequency</th>
<th>Approximate description</th>
<th>Observed frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wave number cm⁻¹</td>
<td>(Potential energy distribution) %</td>
<td>Wave number cm⁻¹</td>
</tr>
<tr>
<td>16</td>
<td>1240</td>
<td>ν_CrC_m (13), ν_CC (15), β_CD (10)</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>1154</td>
<td>γ_Rx (10), γ_C-OH (19), γ_C=O (16)</td>
<td>1170</td>
</tr>
<tr>
<td>18</td>
<td>1140</td>
<td>α_HOC (81)</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>1067</td>
<td>α_D_mC_mD_m (94)</td>
<td>1083</td>
</tr>
<tr>
<td>20</td>
<td>1066</td>
<td>α_D_mC_mD_m (94)</td>
<td>1048</td>
</tr>
<tr>
<td>21</td>
<td>1059</td>
<td>α_CCC (16), β_CD (20)</td>
<td>1038</td>
</tr>
<tr>
<td>22</td>
<td>1011</td>
<td>α_CrC_mD_m (23), α_D_mC_mD_m (20)</td>
<td>1027</td>
</tr>
<tr>
<td>23</td>
<td>994</td>
<td>ν_CC (13), β_CD (32)</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>866</td>
<td>α_CCC (10), β_CD (50)</td>
<td>885</td>
</tr>
<tr>
<td>25</td>
<td>854</td>
<td>ν_CC (17), β_CD (40)</td>
<td>860</td>
</tr>
<tr>
<td>26</td>
<td>842</td>
<td>ν_CD (17), δ_CC (17)</td>
<td>846</td>
</tr>
<tr>
<td>27</td>
<td>840</td>
<td>β_CD (46)</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>805</td>
<td>γ_CD (24), α_CrC_mD_m (25)</td>
<td>817</td>
</tr>
<tr>
<td>29</td>
<td>781</td>
<td>γ_CD (38)</td>
<td>775</td>
</tr>
<tr>
<td>30</td>
<td>770</td>
<td>α_CrC_mD_m (60)</td>
<td>758</td>
</tr>
<tr>
<td>No.</td>
<td>Wave number cm(^{-1})</td>
<td>Calculated frequency</td>
<td>Approximate description (Potential energy distribution(^1))</td>
</tr>
<tr>
<td>-----</td>
<td>------------------------</td>
<td>----------------------</td>
<td>----------------------------------------------------------</td>
</tr>
<tr>
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<td>743</td>
<td>(\alpha_{\text{CC}}(26)), (\beta_{\text{CD}}(13))</td>
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</tr>
<tr>
<td>32</td>
<td>720</td>
<td>(\gamma_{\text{CD}}(33))</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>676</td>
<td>(\nu_{\text{CC}}(16)), (\gamma_{\text{CD}}(23))</td>
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</tr>
<tr>
<td>34</td>
<td>646</td>
<td>(\gamma_{\text{CD}}(28))</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>579</td>
<td>(\alpha_{\text{CC}}(33)), (\alpha_{\text{OCO}}(35))</td>
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</tr>
<tr>
<td>36</td>
<td>573</td>
<td>(\gamma_{\text{CD}}(36))</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>561</td>
<td>(\delta_{\text{C-OH}}(80))</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>524</td>
<td>(\delta_{\text{CC}}(31))</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>487</td>
<td>(\alpha_{\text{CC}}(19)), (\delta_{\text{CC}}(15))</td>
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</tr>
<tr>
<td>40</td>
<td>424</td>
<td>(\beta_{\text{CX}}(11)), (\gamma_{\text{RX}}(11)), (\delta_{\text{CC}}(16))</td>
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</tr>
<tr>
<td>41</td>
<td>336</td>
<td>(\nu_{\text{CX}}(15)), (\alpha_{\text{CCC}}(15)), (\beta_{\text{CrC}<em>m}(12)), (\alpha</em>{\text{OCO}}(17))</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>328</td>
<td>(\gamma_{\text{CrC}<em>m}(12)), (\delta</em>{\text{CC}}(32))</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>267</td>
<td>(\beta_{\text{CrC}<em>m}(15)), (\beta</em>{\text{RX}}(10)), (\delta_{\text{CX}}(10))</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>213</td>
<td>(\gamma_{\text{CrC}_m}(41))</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>157</td>
<td>(\beta_{\text{CrC}<em>m}(16)), (\beta</em>{\text{RX}}(14)), (\delta_{\text{CC}}(14))</td>
<td></td>
</tr>
</tbody>
</table>
Table 19.2.5 (cont.)

<table>
<thead>
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<th>No.</th>
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</tr>
</thead>
<tbody>
<tr>
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<td>Wave number cm⁻¹</td>
<td>Approximate description (Potential energy distribution) (%)</td>
</tr>
<tr>
<td>46</td>
<td>145</td>
<td>$\gamma_{\text{C},m}$ (12), $\delta_{\text{CC}}$ (26)</td>
</tr>
<tr>
<td>47</td>
<td>120</td>
<td>$\gamma_{\text{C},m}$ (16), $\delta_{\text{CX}}$ (52)</td>
</tr>
<tr>
<td>48</td>
<td>99</td>
<td>$\delta_{\text{CC}}$ (15), $\delta_{\text{C},m}$ (46)</td>
</tr>
</tbody>
</table>

Notes:
1. The "Potential energy distribution" is given in per cent contribution to $\lambda$ by the diagonal force constants of the respective coordinates. Only contributions equal to or greater than 10 per cent were included in this table.
2. Infrared spectrum of o-toluic-d$_7$ acid as KBr disk, 0.81 wt%, taken on a Perkin-Elmer Model 457 spectrophotometer.
3. The symbols used to indicate the coordinates were defined in table 19.2.2 and subsection 19.2.
4. The frequencies given in this table correspond to set no. 6 of force constants (table 19.4.1).
The spherical coordinates of the atoms in \( o \)-toluate ion are given in table 19.3.1.

We have defined 57 internal coordinates of which 51 have been defined according to Decius' rules. The remaining 6 coordinates represent local redundancies and are defined because of the symmetry of the molecule. The complete definitions of the internal coordinates are shown in table 19.3.2. The complete sets of B and G elements are given in "Detailed calculations - 19.3.1."

**The \( F \) matrix.** The majority of force constants corresponding to the internal coordinates of \( o \)-toluate ion were equal to the force constants of equivalent coordinates in the \( o \)-toluic acid molecule. Some of the diagonal force constants, those corresponding to internal coordinates involving the atoms of the carboxylate and methyl groups, were varied in order to match the calculated \( K_H/K_D \) ratio with the experimental value. This point is discussed in more detail in the next subsection. The force constants which were changed in going from the acid molecule to the anion molecule and the force constants of the anion which were varied in our calculations are listed in table 19.4.1.

A summary of the vibrational frequencies corresponding to set no. 4 of force constants of table 19.4.1 is given in table 19.3.3. The "Detailed calculations" are given in 19.4.1.

(continued p. 601)
<table>
<thead>
<tr>
<th>No.</th>
<th>Atom type</th>
<th>R</th>
<th>A_x</th>
<th>A_y</th>
<th>A_z</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>1.390</td>
<td>90.</td>
<td>0.</td>
<td>90.</td>
<td>12.011</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>1.390</td>
<td>30.3</td>
<td>59.7</td>
<td>90.</td>
<td>12.011</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>1.380</td>
<td>30.3</td>
<td>120.3</td>
<td>90.</td>
<td>12.011</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>1.380</td>
<td>90.</td>
<td>180.</td>
<td>90.</td>
<td>12.011</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
<td>1.390</td>
<td>150.</td>
<td>120.</td>
<td>90.</td>
<td>12.011</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>1.390</td>
<td>150.</td>
<td>60.</td>
<td>90.</td>
<td>12.011</td>
</tr>
<tr>
<td>7</td>
<td>H</td>
<td>2.474</td>
<td>30.3</td>
<td>59.7</td>
<td>90.</td>
<td>1.0078</td>
</tr>
<tr>
<td>8</td>
<td>H</td>
<td>2.464</td>
<td>30.3</td>
<td>120.3</td>
<td>90.</td>
<td>1.0078</td>
</tr>
<tr>
<td>9</td>
<td>H</td>
<td>2.464</td>
<td>90.</td>
<td>180.</td>
<td>90.</td>
<td>1.0078</td>
</tr>
<tr>
<td>10</td>
<td>H</td>
<td>2.474</td>
<td>150.</td>
<td>120.</td>
<td>90.</td>
<td>1.0078</td>
</tr>
<tr>
<td>11</td>
<td>C</td>
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</tr>
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<td>0.</td>
<td>90.</td>
<td>12.011</td>
</tr>
<tr>
<td>13</td>
<td>O</td>
<td>3.666</td>
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<td>17.2</td>
<td>100.02</td>
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</tr>
<tr>
<td>14</td>
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<td>80.1</td>
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<td>H</td>
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<td>16</td>
<td>H</td>
<td>3.422</td>
<td>138.19</td>
<td>52.14</td>
<td>74.96</td>
<td>1.0078</td>
</tr>
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<td>17</td>
<td>H</td>
<td>3.422</td>
<td>138.19</td>
<td>52.14</td>
<td>105.04</td>
<td>1.0078</td>
</tr>
</tbody>
</table>
Table 19.3.1 (cont.)

Notes: 1. R is the distance between origin and the respective atom. $A_x$, $A_y$, and $A_z$ are the angles made by vector R and the coordinate axes. M is the atomic mass of the atom in amu.

2. The origin of the coordinate system is at the center of the benzene ring. The benzene ring is located in the xy plane; the z axis is perpendicular to this plane.

3. The angle between the plane of the carboxylate group and the plane of the benzene ring is 36°.
Table 19.3.2: The valence internal coordinates used to calculate the G matrix of the p-toluate ion.

<table>
<thead>
<tr>
<th>Int.crd. no.</th>
<th>Atoms involved</th>
<th>Code* no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 7</td>
<td>1</td>
<td>$\nu_{CH}$</td>
<td>$C_{\text{ring}}$-$H_{\text{ring}}$ stretching</td>
</tr>
<tr>
<td>2</td>
<td>3 8</td>
<td>1</td>
<td>$\nu_{CH}$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4 9</td>
<td>1</td>
<td>$\nu_{CH}$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5 10</td>
<td>1</td>
<td>$\nu_{CH}$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6 11</td>
<td>1</td>
<td>$\nu_{C_C_m}$</td>
<td>$C_{\text{ring}}$-$C_{\text{methyl}}$ stretching</td>
</tr>
<tr>
<td>6</td>
<td>1 2</td>
<td>1</td>
<td>$\nu_{CC}$</td>
<td>$C_{\text{ring}}$-$C_{\text{ring}}$ stretching</td>
</tr>
<tr>
<td>7</td>
<td>2 3</td>
<td>1</td>
<td>$\nu_{CC}$</td>
<td></td>
</tr>
<tr>
<td>8</td>
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<td></td>
</tr>
<tr>
<td>9</td>
<td>4 5</td>
<td>1</td>
<td>$\nu_{CC}$</td>
<td></td>
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<tr>
<td>10</td>
<td>5 6</td>
<td>1</td>
<td>$\nu_{CC}$</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>6 1</td>
<td>1</td>
<td>$\nu_{CC}$</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1 12</td>
<td>1</td>
<td>$\nu_{CX}$</td>
<td>$C_1$-$C_{12}$ stretching</td>
</tr>
<tr>
<td>13</td>
<td>13 12</td>
<td>1</td>
<td>$\nu_{C-O}$</td>
<td>C-O stretching</td>
</tr>
<tr>
<td>14</td>
<td>12 14</td>
<td>1</td>
<td>$\nu_{C-O}$</td>
<td></td>
</tr>
<tr>
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<td>$\alpha_{CCC}$</td>
<td>C-C-C ring angle bending</td>
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<tr>
<td>16</td>
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<td>2</td>
<td>$\alpha_{CCC}$</td>
<td></td>
</tr>
<tr>
<td>17</td>
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<td>2</td>
<td>$\alpha_{CCC}$</td>
<td></td>
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<td>Int. crd. no.</td>
<td>Atoms involved</td>
<td>Code* no.</td>
<td>Symbol</td>
<td>Description</td>
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<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>19</td>
<td>4 6 5</td>
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<td>( \alpha_{\text{CCC}} )</td>
<td>C(_{\text{ring-H}}) ring in-plane bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>20</td>
<td>5 1 6</td>
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</tr>
<tr>
<td>21</td>
<td>7 1 3 2</td>
<td>5</td>
<td>( \beta_{\text{CH}} )</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>8 2 4 3</td>
<td>5</td>
<td>( \beta_{\text{CH}} )</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>9 3 5 4</td>
<td>5</td>
<td>( \beta_{\text{CH}} )</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>10 4 6 5</td>
<td>5</td>
<td>( \beta_{\text{CH}} )</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>11 5 1 6</td>
<td>5</td>
<td>( \beta_{\text{C}_r \text{C}_m} )</td>
<td>C(_{\text{ring-C}}) methyl in-plane bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>26</td>
<td>12 6 2 1</td>
<td>5</td>
<td>( \beta_{\text{RX}**} )</td>
<td>C(<em>1)-C(</em>{12}) bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>27</td>
<td>13 14 12</td>
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<td>( \alpha_{\text{OCO}} )</td>
<td>O-C-O bending</td>
</tr>
<tr>
<td>28</td>
<td>1 13 14 12</td>
<td>5</td>
<td>( \beta_{\text{CX}} )</td>
<td>C(<em>1)-C(</em>{12}) bending with respect to the external bisector of the O-C-O angle.</td>
</tr>
<tr>
<td>29</td>
<td>7 1 3 2</td>
<td>3</td>
<td>( \gamma_{\text{CH}} )</td>
<td>C(_{\text{ring-H}}) ring out-of-plane wagging</td>
</tr>
<tr>
<td>30</td>
<td>8 2 4 3</td>
<td>3</td>
<td>( \gamma_{\text{CH}} )</td>
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</tr>
<tr>
<td>31</td>
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<td>( \gamma_{\text{CH}} )</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>10 4 6 5</td>
<td>3</td>
<td>( \gamma_{\text{CH}} )</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>11 5 1 6</td>
<td>3</td>
<td>( \gamma_{\text{C}_r \text{C}_m} )</td>
<td>C(_{\text{ring-C}}) methyl out-of-plane wagging</td>
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<tr>
<td>Int.crd. no.</td>
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<td>Code no.</td>
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<td>Description</td>
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<tr>
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<tr>
<td>34</td>
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<td>3</td>
<td>$\gamma_{RX}^{**}$</td>
<td>$C_1\text{-}C_{12}$ out-of-plane wagging</td>
</tr>
<tr>
<td>35</td>
<td>13 14 12</td>
<td>3</td>
<td>$\gamma_{C-O}$</td>
<td>C-O out-of-plane wagging</td>
</tr>
<tr>
<td>36</td>
<td>1 2 3 4</td>
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<td>$\delta_{CC}$</td>
<td>Torsion around a C-C ring bond</td>
</tr>
<tr>
<td>37</td>
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<td>4</td>
<td>$\delta_{CC}$</td>
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</tr>
<tr>
<td>38</td>
<td>3 4 5 6</td>
<td>4</td>
<td>$\delta_{CC}$</td>
<td></td>
</tr>
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<td>4 5 6 1</td>
<td>4</td>
<td>$\delta_{CC}$</td>
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<td>5 6 1 2</td>
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<td>$\delta_{CC}$</td>
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</tr>
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<td>41</td>
<td>6 1 2 3</td>
<td>4</td>
<td>$\delta_{CC}$</td>
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</tr>
<tr>
<td>42</td>
<td>14 12 1 6</td>
<td>4</td>
<td>$\delta_{RX}^{**}$</td>
<td>Torsion around $C_1\text{-}C_{12}$ bond (one of the coordinates no. 42 and 43 is locally redundant)</td>
</tr>
<tr>
<td>43</td>
<td>13 12 1 2</td>
<td>4</td>
<td>$\delta_{RX}$</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>1 13 14 12</td>
<td>3</td>
<td>$\gamma_{CX}$</td>
<td>Out-of-plane wagging of $C_1\text{-}COO$ bond (locally redundant)</td>
</tr>
<tr>
<td>45</td>
<td>14 13 12</td>
<td>3</td>
<td>$\gamma_{C-O}$</td>
<td>C-O out-of-plane wagging (locally redundant)</td>
</tr>
<tr>
<td>46</td>
<td>15 11</td>
<td>1</td>
<td>$\nu_{C_m H_m}$</td>
<td>$C_{\text{methyl}}\text{-}H_{\text{methyl}}$ stretching</td>
</tr>
<tr>
<td>47</td>
<td>16 11</td>
<td>1</td>
<td>$\nu_{C_m H_m}$</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>17 11</td>
<td>1</td>
<td>$\nu_{C_m H_m}$</td>
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Table 19.3.2 (cont.)

<table>
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<th>Atoms involved</th>
<th>Code* no.</th>
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<th>Description</th>
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<tbody>
<tr>
<td>49</td>
<td>6 15 11</td>
<td>2</td>
<td>$\alpha_{C_{r}C_{m}H_{m}}$</td>
<td>C\text{ring}-C\text{methyl}-H\text{methyl} angle bending</td>
</tr>
<tr>
<td>50</td>
<td>6 16 11</td>
<td>2</td>
<td>$\alpha_{C_{r}C_{m}H_{m}}$</td>
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</tr>
<tr>
<td>51</td>
<td>6 17 11</td>
<td>2</td>
<td>$\alpha_{C_{r}C_{m}H_{m}}$</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>15 16 11</td>
<td>2</td>
<td>$\alpha_{C_{m}C_{m}H_{m}}$</td>
<td>H\text{methyl}-C\text{methyl}-H\text{methyl} angle bending</td>
</tr>
<tr>
<td>53</td>
<td>16 17 11</td>
<td>2</td>
<td>$\alpha_{C_{m}C_{m}H_{m}}$</td>
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</tr>
<tr>
<td>54</td>
<td>17 15 11</td>
<td>2</td>
<td>$\alpha_{H_{m}C_{m}H_{m}}$</td>
<td>(one of the coordinates no. 49-54 is locally redundant)</td>
</tr>
<tr>
<td>55</td>
<td>15 11 6 1</td>
<td>4</td>
<td>$\delta_{C_{r}C_{m}}$</td>
<td>Torsion around C\text{6}-C\text{11} bond (two of the coordinates 55-57 are locally redundant)</td>
</tr>
<tr>
<td>56</td>
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<td>4</td>
<td>$\delta_{C_{r}C_{m}}$</td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>17 11 6 5</td>
<td>4</td>
<td>$\delta_{C_{r}C_{m}}$</td>
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</tbody>
</table>

Notes: * This number corresponds to the code no. shown in subsection 16.3.

** R $\equiv \text{O-CH}_3 - \text{C}_6\text{H}_4 -$
Table 19.3.3: The calculated vibrational frequencies of \( o \)-toluate ion.

<table>
<thead>
<tr>
<th>No.</th>
<th>Wave number cm(^{-1})</th>
<th>Frequency ( \nu ) ( \text{(cm}^{-1}) )</th>
<th>Approximate description(^2) (Potential energy distribution(^1)) ( \text{(%)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3109</td>
<td>( \nu_{\text{CH}} ) ( (98) )</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3073</td>
<td>( \nu_{\text{CH}} ) ( (99) )</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3072</td>
<td>( \nu_{\text{CH}} ) ( (99) )</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3071</td>
<td>( \nu_{\text{CH}} ) ( (98) )</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2965</td>
<td>( \nu_{\text{C-H}} ) ( (98) ) ( \text{m} , \text{m} )</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2962</td>
<td>( \nu_{\text{C-H}} ) ( (99) ) ( \text{m} , \text{m} )</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2879</td>
<td>( \nu_{\text{C-H}} ) ( (98) ) ( \text{m} , \text{m} )</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1743</td>
<td>( \nu_{\text{CC}} ) ( (29) )</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1672</td>
<td>( \nu_{\text{CC}} ) ( (37) ) , ( \nu_{\text{CX}} ) ( (11) )</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1565</td>
<td>( \nu_{\text{CC}} ) ( (24) ) , ( \nu_{\text{CX}} ) ( (11) ) , ( \beta_{\text{CH}} ) ( (11) )</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1559</td>
<td>( \nu_{\text{CC}} ) ( (34) ) , ( \nu_{\text{C-O}} ) ( (10) ) , ( \beta_{\text{CH}} ) ( (15) )</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1534</td>
<td>( \nu_{\text{C-O}} ) ( (18) ) , ( \gamma_{\text{CX}} ) ( (23) ) , ( \gamma_{\text{C-O}} ) ( (11) )</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1482</td>
<td>( \nu_{\text{C-C}} ) ( (11) ) , ( \nu_{\text{CC}} ) ( (17) ) , ( \beta_{\text{CH}} ) ( (13) ) , ( \alpha_{\text{C-C}} ) ( \text{m} , \text{m} ) ( (10) )</td>
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</tr>
<tr>
<td>14</td>
<td>1473</td>
<td>( \alpha_{\text{C-C}} ) ( \text{m} , \text{m} ) ( (77) )</td>
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</tr>
<tr>
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<td>1470</td>
<td>( \alpha_{\text{C-C}} ) ( \text{m} , \text{m} ) ( (91) )</td>
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</tr>
<tr>
<td>16</td>
<td>1412</td>
<td>( \nu_{\text{CC}} ) ( (12) ) , ( \beta_{\text{CH}} ) ( (47) )</td>
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<tr>
<td>17</td>
<td>1395</td>
<td>( \nu_{\text{C-O}} ) ( (19) ) , ( \beta_{\text{CH}} ) ( (26) )</td>
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<tr>
<td>No.</td>
<td>Wave number ( \text{cm}^{-1} )</td>
<td>Frequency</td>
<td>Approximate description² (Potential energy distribution¹) (%)</td>
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<td>----------------------------------------------------------</td>
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<td>18</td>
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<td>( \nu_{CC}(41) ), ( \beta_{CH}(20) )</td>
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<td>( \nu_{CX}(13) ), ( \nu_{CC}(13) ), ( \beta_{CH}(10) ), ( \alpha_{C_rC_mH_m}(18) ), ( \alpha_{H_mC_mH_m}(16) )</td>
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<tr>
<td>21</td>
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<td>( \nu_{CC}(17) ), ( \beta_{CH}(53) )</td>
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<td>1119</td>
<td>( \nu_{CC}(26) ), ( \nu_{C-O}(10) ), ( \beta_{CH}(22) )</td>
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</tr>
<tr>
<td>23</td>
<td>1071</td>
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<tr>
<td>24</td>
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<td>( \alpha_{C_rC_mH_m}(38) )</td>
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<td>1024</td>
<td>( \gamma_{CH}(40) )</td>
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<td>( \gamma_{CH}(53) )</td>
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<td>( \gamma_{CH}(44) )</td>
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<td>31</td>
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Table 19.3.3 (cont.)

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<td>$\gamma_{\text{CH}} (11)$, $\delta_{\text{CC}} (36)$</td>
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<td>$\nu_{\text{C}_r\text{C}<em>m} (10)$, $\alpha</em>{\text{CCC}} (31)$</td>
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</tr>
<tr>
<td>37</td>
<td>$\beta_{\text{CX}} (13)$, $\delta_{\text{CC}} (13)$</td>
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</tr>
<tr>
<td>38</td>
<td>$\gamma_{\text{C}_r\text{C}<em>m} (14)$, $\delta</em>{\text{CC}} (29)$</td>
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</tr>
<tr>
<td>39</td>
<td>$\nu_{\text{CX}} (11)$, $\beta_{\text{C}<em>r\text{C}<em>m} (19)$, $\alpha</em>{\text{OCO}} (10)$, $\beta</em>{\text{CX}} (12)$</td>
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</tr>
<tr>
<td>40</td>
<td>$\alpha_{\text{CCC}} (15)$, $\beta_{\text{C}_r\text{C}_m} (12)$</td>
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</tr>
<tr>
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<td>$\gamma_{\text{CH}} (10)$, $\gamma_{\text{C}_r\text{C}<em>m} (26)$, $\delta</em>{\text{CC}} (12)$</td>
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<td>$\delta_{\text{CC}} (25)$</td>
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<td>43</td>
<td>$\beta_{\text{RX}} (13)$, $\delta_{\text{CC}} (16)$</td>
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<tr>
<td>44</td>
<td>$\gamma_{\text{C}<em>r\text{C}<em>m} (15)$, $\delta</em>{\text{RX}} (34)$, $\delta</em>{\text{C}_r\text{C}_m} (19)$</td>
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<td>45</td>
<td>$\delta_{\text{CC}} (33)$, $\delta_{\text{C}_r\text{C}_m} (24)$</td>
<td></td>
</tr>
</tbody>
</table>
Notes:

1. The "Potential energy distribution" is given in per cent contribution to $\lambda$ by the diagonal force constants of the respective coordinates. Only contributions equal to or greater than 10 per cent were included in this table.

2. The symbols used to describe the types of coordinates were defined in table 19.3.2.

3. The frequencies given in this table correspond to set no. 4 of force constants of table 19.4.1.
The calculated vibrational frequencies of o-toluate-d₇ anion.

The molecular structure of o-toluate-d₇ anion was assumed to be identical to that of the o-toluate ion with the exception of the carbon-deuterium bond lengths which were assumed to be 0.009 Å shorter than the corresponding carbon-hydrogen bonds.

As in the case of o-toluic-d₇ acid, we have calculated two G matrices for o-toluate-d₇ anion. For the first one we assumed that the angle between the plane of the carboxylate group and the plane of the benzene ring was 36°. For the second G matrix we assumed that this angle was 33°.

The internal coordinates of o-toluate-d₇ anion had exactly the same definitions as the internal coordinates of o-toluate ion (table 19.3.2). For those internal coordinates which involved the deuterium atoms new symbols were used.

These symbols and the respective coordinates are listed below.

<table>
<thead>
<tr>
<th>Int.cr. no.</th>
<th>Atoms involved</th>
<th>Code no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 7</td>
<td>1</td>
<td>v_CD</td>
<td>C_{ring-D-ring} stretching</td>
</tr>
<tr>
<td>2</td>
<td>3 8</td>
<td>1</td>
<td>v_CD</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4 9</td>
<td>1</td>
<td>v_CD</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5 10</td>
<td>1</td>
<td>v_CD</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>7 1 3 2</td>
<td>5</td>
<td>\beta_{CD}</td>
<td>C_{ring-D-ring} in-plane</td>
</tr>
<tr>
<td>22</td>
<td>8 2 4 3</td>
<td>5</td>
<td>\beta_{CD}</td>
<td>bending with respect to the external bisector of the ring angle.</td>
</tr>
<tr>
<td>23</td>
<td>9 3 5 4</td>
<td>5</td>
<td>\beta_{CD}</td>
<td></td>
</tr>
<tr>
<td>Int. crd. no.</td>
<td>Atoms involved</td>
<td>Code no.</td>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------</td>
<td>----------</td>
<td>--------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>24</td>
<td>10 4 6 5</td>
<td>5</td>
<td>$\beta_{CD}$</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>7 1 3 2</td>
<td>3</td>
<td>$\gamma_{CD}$</td>
<td>$C_{ring-D-ring}$ out-of-plane wagging</td>
</tr>
<tr>
<td>30</td>
<td>8 2 4 3</td>
<td>3</td>
<td>$\gamma_{CD}$</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>9 3 5 4</td>
<td>3</td>
<td>$\gamma_{CD}$</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>10 4 6 5</td>
<td>3</td>
<td>$\gamma_{CD}$</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>15 11</td>
<td>1</td>
<td>$\nu_{C_m\text{D}_m}$</td>
<td>$C_{methyl-D_methyl}$ stretching</td>
</tr>
<tr>
<td>47</td>
<td>16 11</td>
<td>1</td>
<td>$\nu_{C_m\text{D}_m}$</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>17 11</td>
<td>1</td>
<td>$\nu_{C_m\text{D}_m}$</td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>6 15 11</td>
<td>2</td>
<td>$\alpha_{C_r\text{C}_m\text{D}_m}$</td>
<td>$C_{ring-C_{methyl-D_methyl}}$ angle bending</td>
</tr>
<tr>
<td>50</td>
<td>6 16 11</td>
<td>2</td>
<td>$\alpha_{C_r\text{C}_m\text{D}_m}$</td>
<td></td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>52</td>
<td>15 16 11</td>
<td>2</td>
<td>$\alpha_{D_m\text{C}_m\text{D}_m}$</td>
<td>$D_{methyl-C_{methyl-D_methyl}}$ angle bending</td>
</tr>
<tr>
<td>53</td>
<td>16 17 11</td>
<td>2</td>
<td>$\alpha_{D_m\text{C}_m\text{D}_m}$</td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>17 15 11</td>
<td>2</td>
<td>$\alpha_{D_m\text{C}_m\text{D}_m}$</td>
<td></td>
</tr>
</tbody>
</table>
The symbol R in the case of the \( \alpha \)-toluate-d\(_7\) anion stands for the \( \alpha \)-CD\(_3\)-C\(_6\)D\(_4\) group. The elements of the two \( G \) matrices are given in "Detailed calculations - 19.3.2".

The force constants corresponding to the internal coordinates of the \( \alpha \)-toluate-d\(_7\) anion were in general equal to those of the \( \alpha \)-toluate anion. The force constants are given in table 19.4.1. Some of the force constants listed there appear to have different values in the \( \alpha \)-toluate and \( \alpha \)-toluate-d\(_7\) anions because of the different scaling factors used. Some other force constants were made different in the two anions on purpose. This point is discussed in detail in the next subsection.

The vibrational frequencies corresponding to set no. 8 (table 19.4.1) of force constants are given in table 19.3.4.

19.4 The calculated \( K_H/K_D \) isotope effects

As in the previous section a series of sets of vibrational frequencies for the species involved in the equilibrium:

\[ \alpha \)-toluic acid + \( \alpha \)-toluate-d\(_7\) anion \rightleftharpoons \alpha \)-toluic-d\(_7\) acid + \( \alpha \)-toluate anion \]

were calculated by varying some of the diagonal force constants in order to obtain a calculated \( K_H/K_D \) value which approaches the experimentally obtained value, and in doing so to try to find, eventually, some of the factors which are affecting this ratio.

(continued p. 608)
<table>
<thead>
<tr>
<th>No.</th>
<th>Wave number cm(^{-1})</th>
<th>Calculated frequency</th>
<th>Approximate description(^3) (Potential energy distribution(^1)) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2306</td>
<td>(\nu_{CD}(92))</td>
<td></td>
</tr>
<tr>
<td>2</td>
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<td>(\nu_{CD}(93))</td>
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<tr>
<td>3</td>
<td>2282</td>
<td>(\nu_{CD}(92))</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2281</td>
<td>(\nu_{CD}(92))</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2214</td>
<td>(\nu_{C_mD_m}(95))</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2210</td>
<td>(\nu_{C_mD_m}(97))</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2078</td>
<td>(\nu_{C_mD_m}(94))</td>
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</tr>
<tr>
<td>8</td>
<td>1709</td>
<td>(\nu_{CC}(33))</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1658</td>
<td>(\nu_{CC}(37), \nu_{CX}(14))</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1542</td>
<td>(\nu_{CC}(29), \nu_{CX}(12), \nu_{C-O}(27))</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1529</td>
<td>(\nu_{C-O}(10), \nu_{C-O}(26), \nu_{CX}(27))</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1501</td>
<td>(\nu_{CC}(39), \nu_{C-O}(11))</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1423</td>
<td>(\nu_{C_mC_m}(19), \nu_{CC}(22), \nu_{C-O}(13))</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1284</td>
<td>(\nu_{CC}(65))</td>
<td></td>
</tr>
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<td>15</td>
<td>1275</td>
<td>(\nu_{CC}(33), \beta_{CD}(17))</td>
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<tr>
<td>16</td>
<td>1239</td>
<td>(\nu_{CC}(22), \beta_{CD}(15))</td>
<td></td>
</tr>
<tr>
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<td>1068</td>
<td>(\beta_{CD}(36), \alpha_{D_mC_mD_m}(20))</td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Wave number cm(^{-1})</td>
<td>Calculated frequency</td>
<td>Approximate description (^3) (Potential energy distribution (^1) (%)</td>
</tr>
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<td>--------------------------</td>
<td>----------------------</td>
<td>---------------------------------</td>
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<tr>
<td>18</td>
<td>1066</td>
<td>(\alpha_{D_mC_mD_m}) (74)</td>
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</tr>
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<td>19</td>
<td>1066</td>
<td>(\alpha_{D_mC_mD_m}) (80)</td>
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<td></td>
</tr>
<tr>
<td>22</td>
<td>904</td>
<td>(\gamma_{CD}(13)), (\gamma_{RX}(10)), (\delta_{CC}(17))</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>863</td>
<td>(\alpha_{CCC}(11)), (\beta_{CD}(46))</td>
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<td>25</td>
<td>839</td>
<td>(\nu_{CC}(13)), (\beta_{CD}(58))</td>
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<td>26</td>
<td>818</td>
<td>(\gamma_{CD}(19)), (\alpha_{C_mC_mD_m}(32))</td>
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<tr>
<td>27</td>
<td>795</td>
<td>(\gamma_{CD}(36)), (\delta_{CC}(11))</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>771</td>
<td>(\alpha_{C_mC_mD_m}(52))</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>735</td>
<td>(\alpha_{CCC}(11)), (\gamma_{CD}(19)), (\alpha_{C_mC_mD_m}(11))</td>
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</tr>
<tr>
<td>30</td>
<td>729</td>
<td>(\gamma_{CD}(26))</td>
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</tr>
<tr>
<td>31</td>
<td>689</td>
<td>(\nu_{CC}(14)), (\nu_{C-O}(11)), (\gamma_{CD}(17))</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>666</td>
<td>(\gamma_{CD}(41))</td>
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</tr>
<tr>
<td>33</td>
<td>611</td>
<td>(\alpha_{CCC}(39)), (\alpha_{OCO}(30))</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>578</td>
<td>(\gamma_{CD}(40))</td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Wave number cm⁻¹</td>
<td>Calculated frequency $\delta_{\text{CC}}$</td>
<td>Approximate description $^3$ (Potential energy distribution $^1$) ($%$)</td>
</tr>
<tr>
<td>-----</td>
<td>------------------</td>
<td>------------------------------------------</td>
<td>---------------------------------------------------------------------</td>
</tr>
<tr>
<td>35</td>
<td>524</td>
<td>$\delta_{\text{CC}}$ (40)</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>488</td>
<td>$\nu_{\text{C}<em>r\text{C}<em>m}$ (10), $\alpha</em>{\text{CCC}}$ (22), $\delta</em>{\text{CC}}$ (14)</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>442</td>
<td>$\beta_{\text{CC}}$ (14), $\delta_{\text{CC}}$ (14)</td>
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</tr>
<tr>
<td>38</td>
<td>347</td>
<td>$\gamma_{\text{C}_r\text{C}<em>m}$ (15), $\delta</em>{\text{CC}}$ (31)</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>340</td>
<td>$\nu_{\text{CX}}$ (16), $\alpha_{\text{CCC}}$ (15), $\beta_{\text{C}_r\text{C}<em>m}$ (14), $\alpha</em>{\text{OCO}}$ (14)</td>
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<tr>
<td>40</td>
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<td>$\alpha_{\text{CCC}}$ (12), $\beta_{\text{C}_r\text{C}<em>m}$ (16), $\beta</em>{\text{RX}}$ (13)</td>
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<tr>
<td>41</td>
<td>227</td>
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</tr>
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<td>42</td>
<td>164</td>
<td>$\gamma_{\text{C}_r\text{C}<em>m}$ (10), $\delta</em>{\text{CC}}$ (26)</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>143</td>
<td>$\beta_{\text{C}<em>r\text{C}<em>m}$ (11), $\beta</em>{\text{RX}}$ (14), $\gamma</em>{\text{C}_r\text{C}<em>m}$ (11), $\delta</em>{\text{CC}}$ (12)</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>135</td>
<td>$\delta_{\text{CC}}$ (34), $\delta_{\text{RX}}$ (24)</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>100</td>
<td>$\delta_{\text{CC}}$ (13), $\delta_{\text{C}_r\text{C}_m}$ (59)</td>
<td></td>
</tr>
</tbody>
</table>
Table 19.3.4 (cont.)

Notes:
1. The "Potential energy distribution" is given in per cent contribution to $\lambda$ by the diagonal force constants of the respective coordinates. Only contributions equal to or greater than 10 per cent were included in this table.
2. The symbols used to describe the types of coordinates were defined in table 19.3.2 and subsection 19.3.
3. The frequencies given in this table correspond to set no. 8 of force constants of table 19.4.1.
The starting point of these calculations was to find a set of force constants for \( o \)-toluic acid which led to a set of calculated frequencies which was in good agreement with the observed values. We have discussed this point in more detail in subsection 19.2. Once this set was found, it was kept constant for all the subsequent calculations. For the force constants of \( o \)-toluate anion we retained the values of the force constants of \( o \)-toluic acid for those internal coordinates which were similar in the two molecules. For those internal coordinates which were not present in the acid molecule or underwent drastic changes in going from the acid to the anion state we used the values of the force constants of the corresponding internal coordinates in benzoate anion. The force constants chosen in this way formed our basic set. This set is given in column 5 of table 19.4.1.

In sets nos. 1 and 2 of table 19.4.1 the force constants of the deuterated species were assumed to be equal to those of their undeuterated counterparts with the exception of some scaling factors. The difference between sets 1 and 2 was the value of the angle \( \phi \) in the deuterated compounds. In the first case this angle had a value of 36° which was equal to the value in the undeuterated molecules and the second case it had a value of 33°. This change in the value of the angle \( \phi \) resulted in a very small change in the total isotope effects or even in the individual components of these effects. Note that the calculated isotope effects are small, to be
expected in a "no force constants change" calculation (nfcc), which is what sets nos. 1 and 2 represent in effect.

In sets nos. 3 and 4 (table 19.4.1) we made the same assumption that we made in the previous section, that is we increased by 10% the force constants corresponding to those internal coordinates of the two anions which involved the atoms of the carboxylate group and those of its immediate vicinity. In set no. 3 we included the internal coordinates of the methyl group in the group of internal coordinates whose force constants were increased. In set no. 4 the force constants corresponding to the internal coordinates of the methyl group were not increased. The total isotope effects corresponding to sets no. 3 and 4 of force constants were small and the two values were almost equal although the differences between the individual factors were larger.

In sets nos. 5 and 6 (table 19.4.1) a second assumption was made. It is known that the presence of a group in the ortho position leads to a deflection of the carboxyl group out of the plane of the benzene ring. We have assumed that because of the smaller steric requirements of a \(-\text{CD}_3\) group as compared with a \(-\text{CH}_3\) group the angle between the plane of the carboxyl group and the plane of the benzene ring is smaller in the case of \(\text{o-toluic-d}_7\) acid. Ossorio by UV studies has shown that this angle has a value of 36° in \(\text{o-toluic acid}\). We have arbitrarily chosen a value of 33° for the angle in \(\text{o-toluic-d}_7\) acid. The deflection of the
carboxyl group out of plane of the benzene ring leads to a decrease in the $\pi$-electron communication between this group and the ring. Looking at this effect from a slightly different angle, the bond $C_1-C_{12}$ (fig. 19.2.1) is weaker in $o$-toluic acid as compared with benzoic acid, for example, where the carboxyl group and the benzene ring are in the same plane. If we apply the same argument to the $o$-toluic - $o$-toluic-$d_7$ pair of acids we see that the $C_1-C_{12}$ bond in $o$-toluic-$d_7$ acid should be slightly stronger than the same bond in $o$-toluic acid. Thus in sets no. 5 and 6 we increased by 10, and 3% respectively the force constants of those internal coordinates of $o$-toluic-$d_7$ acid which involve the $C_1-C_{12}$ bond. We must point out that the 10 and 3% values were arbitrarily chosen. It can be seen that set no. 6 (3% increase) gave a better agreement with the experimental value for the $K_H/K_D$ ratio.

In sets nos. 7 and 8 of table 19.4.1 we used the same approximation which we used successfully in the benzoic acid system (section 18). In this approximation, it is assumed that certain force constants in the deuterated anion, e.g. $o$-toluate-$d_7$, are slightly smaller than the similar force constants in the undeuterated anion. As we mentioned in a earlier subsection (subsection 10.6) we think that one effect which could lead to such differences is small differences in the solute-solvent interaction between the two anions. As we pointed out in subsection 10.6 we assume that the smaller force constants of certain internal coordinates of the deuterated
anion reflect slightly weaker solute-solvent interactions. This could be due, for example, to the smaller length and smaller polarizability of the carbon-deuterium bonds as compared with carbon-hydrogen bonds. In set no. 7 we have used a value of 36° for the angle \( \phi \) and in set no. 8 a value of 33°. No significant difference was observed between the final results of the two sets.

Finally in sets no. 9 and 10 (table 19.4.1) the three assumptions which we made, and used separately in sets 3 to 8 were combined into one calculation. The difference between the calculations carried out in sets no. 9 and 10 is again the value used for angle \( \phi \). The final results of these two sets are in fair agreement with the observed values. The agreement can be improved by further adjustments of the force constants. The conclusions, however, would be the same.

The calculated isotope effects show an almost negligible variation between 20 and 40°C (see "Detailed Calculations - 19.2.1"). This is in good agreement with the experimental values (table 10.6) except for the experimental value at 20°C which is approximately 1% larger than the others. This disagreement is difficult to explain in view of our limited knowledge of the details of these systems, however, one is tempted to think that a larger than estimated error in the experimental value at 20°C is causing the 1% difference in the \( K_H/K_D \) ratio.
To conclude, we must note that the approximations we made in the previous system studied, i.e. benzoic acid system, led to a good agreement between the calculated and the observed values in this system, also. A new effect, however, seems to appear in this particular system, namely a small difference between the steric requirements of a -CD₃ and a -CH₃ group. This difference seems to be relatively more important in the undissociated state. It leads to small differences in the value of angle φ and consequently to small differences in the diagonal force constants of the internal coordinates involving a ring-carboxyl group bond.
<table>
<thead>
<tr>
<th>Internal coordinates</th>
<th>a1</th>
<th>a2</th>
<th>a3</th>
<th>a4</th>
<th>a5</th>
<th>a6</th>
<th>a7</th>
<th>a8</th>
<th>a9</th>
<th>a10</th>
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</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>a1</td>
<td>a2</td>
<td>a3</td>
<td>a4</td>
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<td>a6</td>
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<td>a8</td>
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<td>a10</td>
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<tr>
<td>g-Toluate</td>
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<td>125</td>
<td>125</td>
<td>125</td>
<td>125</td>
<td>125</td>
<td>125</td>
<td>125</td>
<td>125</td>
<td>125</td>
</tr>
<tr>
<td>g-Toluate-d4</td>
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<td>125</td>
<td>125</td>
<td>125</td>
<td>125</td>
<td>125</td>
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<tr>
<td>Force constants (kcal/mol)</td>
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<td>a5</td>
<td>a6</td>
<td>a7</td>
<td>a8</td>
<td>a9</td>
<td>a10</td>
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<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Vp,exp</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Total force constant</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
</tbody>
</table>

a. Isotope effect observed experimentally in the present work (face subsection 10.13).

b. This number refers to the coordinates number in the structure (see Table 15.6.2).

A. The symbols used at the head of the present section have the following significances: OT-d4: g-Toluate-d4; OT-d5: g-Toluate-d5; OT-d6: g-Toluate-d6.

b. The diagonal force constants are shown in the table and all off-diagonal force constants were kept constant and were equal for the four species involved in the above calculations. These force constants are given in Table 15.2.3.

c. v in the angle made by the plane of the carboxyl group with the plane of the benzene ring.

d. Calculated from equations (11.1.3.5), (11.1.4.4), and (11.1.2.5).
20. THE CALCULATION OF THE SECONDARY DEUTERIUM ISOTOPE EFFECTS
IN THE PHENYLACETIC ACID - PHENYLACETIC-α-d₂ ACID SYSTEM.

20.1 Introduction.

The method of calculation described in subsection 18.1
which was used to calculate the secondary detuerium isotope
effects in the benzoic acid system (section 18) was used in the
system presented in this section to calculate the $K_H/K_D$ ratio
for phenylacetic acid - phenylacetic-α-d₂ acids at a
series of temperatures.

No complete vibrational analysis exists for these two
acids, i.e. phenylacetic and phenylacetic-α-d₂ acids, nor for
any of their anions. The available data in the literature for
vibrational bands of the infrared spectra of phenylacetic acid
has been summarized in columns 4 to 8 of table 20.2.4.

20.2 The calculated vibrational frequencies of phenylacetic acid
and phenylacetic-α-d₂ acid.

The G matrix.

The molecular structure of phenylacetic acid was taken
from the work by Manojlovic and Speakman.377 Because their
work gives the crystal structure of potassium hydrogen
bisphenylacetate, the use of their results in our problem, i.e.
phenylacetic acid in aqueous solution, represents an approxima-
tion. At the same time, we do not think that small changes in
the bond angles and bond lengths will make any significant
contribution to the ratio $K_H/K_D$, especially when the structure of the undeuterated and deuterated species is assumed to be the same (see section 19). The molecule is represented schematically in fig. 20.2.1 and the spherical coordinates of the atoms are given in table 20.2.1. These coordinates were obtained after the original Cartesian system of coordinates was rotated and translated to bring the origin at $C_{12}$ from its original location at $H_{18}$ (see footnote).

We have defined 57 internal coordinates, which included six cyclic and three local redundancies. The

Footnote.

The initial system of coordinates was first rotated by using the following expressions:

$$X_1 = 0.28142X - 0.32916Y - 0.90136Z$$
$$Y_1 = 0.77345X - 0.47483Y + 0.41916Z$$
$$Z_1 = -0.56616X - 0.81539Y + 0.12100Z$$

where $(X, Y, Z)$ are the old coordinates and $(X_1, Y_1, Z_1)$ are the new coordinates. The constants in the above expressions are the direction cosines of the new axes with respect to the old coordinate system.

After the above rotation, the system was translated to the new origin at $C_{12}$. 
definitions of the internal coordinates and their symbols are given in table 20.2.2. The complete G matrix of phenylacetic acid is given in "Detailed calculations - 20.2.1".

The F matrix.

The force constants corresponding to the internal coordinates of phenylacetic acid came mainly from the F matrix of the benzene molecule (subsections 17.1 and 17.2). Other force constants, those corresponding to the internal coordinates of the -CH₂COOH group, were obtained from the work by Nakamoto and Kishida on acetic acid 351 and by Schachtschneider and Snyder on n-paraffins. 326 Some of the force constants were adjusted, by trial and error, to fit some of the observed vibrational frequencies of phenylacetic acid. The final set of values is given in column 2 of table 20.2.3.

The calculated vibrational frequencies of phenylacetic acid.

The 48 vibrational frequencies of phenylacetic acid (3n-6) were calculated by solving the secular equation 16.2.1. The "Detailed calculations" are given in 20.2.2, and a summary of the results is given in columns 2 and 3 of table 20.2.4.

The calculated vibrational frequencies of phenylacetic-α-d₂ acid.

The molecular structure of phenylacetic-α-d₂ acid was assumed to be identical to that of phenylacetic acid, with the exception of the two new carbon-deuterium bonds which
were assumed to be 0.009 Å shorter than the corresponding carbon-hydrogen bonds.\(^{369}\)

The internal coordinates for the \(G\) matrix of phenylacetic-\(α\)-\(d_2\) acid had the same definitions as those of phenylacetic acid (table 20.2.2). New symbols were used for those internal coordinates involving the new carbon-deuterium bonds. (For numbering system, see fig. 20.2.1.).

<table>
<thead>
<tr>
<th>Int. crd. no.</th>
<th>Atoms involved</th>
<th>Code Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>12 13</td>
<td>(ν_{CD_α})</td>
<td>(C_12-D_α) stretching</td>
</tr>
<tr>
<td>7</td>
<td>12 14</td>
<td>(ν_{CD_α})</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>13 15 12</td>
<td>(α_{D_aCC})</td>
<td>(D_α-C_12-C_15) or (D_α-C_12-C_1) bending</td>
</tr>
<tr>
<td>32</td>
<td>15 14 12</td>
<td>(α_{D_aCC})</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>14 1 12</td>
<td>(α_{D_aCC})</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>1 13 14</td>
<td>(α_{D_aCC})</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>13 14 12</td>
<td>(α_{D_aCD_α})</td>
<td>(D_α-C_12-D_α) bending (locally redundant)</td>
</tr>
</tbody>
</table>

\(R\), in the case of phenylacetic-\(α\)-\(d_2\) acid, becomes \(C_6H_5CD_2\)-group.
The complete G matrix of phenylacetic-α-d₂ acid is given in "Detailed calculations - 20.2.3".

The force constants belonging to the F matrix of phenylacetic-α-d₂ acid were identical to those of the F matrix of phenylacetic acid, with the exception of the diagonal force constants corresponding to some of the internal coordinates involving the C-D bonds, which had to be adjusted because of the different scaling factors. The complete set of force constants is given in column 3 of table 20.2.3.

The calculated frequencies of phenylacetic-α-d₂ acid are given in column 2 of table 20.2.5. Some observed frequencies from the infrared spectrum of this acid, obtained in the present work, are given in column 4 of the same table. The "Detailed calculations" are given in 20.2.4.

(continued p. 641)
NOTE: The Z axis is perpendicular to the plane of the ring
the origin of the coordinates system being at C_{12}.

FIG. 20.2.1.

THE STRUCTURE OF PHENYLACETIC ACID

B24, 323 (1968).

Table 20.2.1. The spherical coordinates of the atoms of phenylacetic acid.

<table>
<thead>
<tr>
<th>Atom No.</th>
<th>Type</th>
<th>R</th>
<th>$A_x$</th>
<th>$A_y$</th>
<th>$A_z$</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C</td>
<td>1.516</td>
<td>90</td>
<td>180</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>2.505</td>
<td>61.82</td>
<td>151.82</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>3.783</td>
<td>71.78</td>
<td>161.78</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>4.286</td>
<td>90.12</td>
<td>179.87</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
<td>3.799</td>
<td>108.40</td>
<td>161.60</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>2.525</td>
<td>118.55</td>
<td>151.45</td>
<td>90</td>
<td>12.011</td>
</tr>
<tr>
<td>7</td>
<td>H</td>
<td>2.689</td>
<td>37.72</td>
<td>127.72</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>8</td>
<td>H</td>
<td>4.650</td>
<td>62.93</td>
<td>152.93</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>9</td>
<td>H</td>
<td>5.388</td>
<td>90.20</td>
<td>179.80</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>10</td>
<td>H</td>
<td>4.681</td>
<td>117.21</td>
<td>152.71</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>11</td>
<td>H</td>
<td>2.716</td>
<td>141.97</td>
<td>128.03</td>
<td>90</td>
<td>1.0078</td>
</tr>
<tr>
<td>12</td>
<td>C</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>12.011</td>
</tr>
<tr>
<td>13</td>
<td>H</td>
<td>1.077</td>
<td>157.32</td>
<td>70.87</td>
<td>101.73</td>
<td>1.0078</td>
</tr>
<tr>
<td>14</td>
<td>H</td>
<td>1.104</td>
<td>50.64</td>
<td>70.64</td>
<td>134.31</td>
<td>1.0078</td>
</tr>
<tr>
<td>15</td>
<td>C</td>
<td>1.522</td>
<td>72.41</td>
<td>69.02</td>
<td>27.93</td>
<td>12.011</td>
</tr>
<tr>
<td>16</td>
<td>O</td>
<td>2.359</td>
<td>98.75</td>
<td>81.91</td>
<td>11.96</td>
<td>16.000</td>
</tr>
<tr>
<td>17</td>
<td>O</td>
<td>2.403</td>
<td>50.18</td>
<td>62.17</td>
<td>52.41</td>
<td>16.000</td>
</tr>
<tr>
<td>18</td>
<td>H</td>
<td>3.400</td>
<td>89.65</td>
<td>77.91</td>
<td>12.10</td>
<td>1.0078</td>
</tr>
</tbody>
</table>
Table 20.2.1 (cont.)

Notes. 1. $A_x$, $A_y$, and $A_z$ are the angles made by the vector $\mathbf{R}$ with the three coordinate axes. $R$ is the distance between origin and the respective atom and $M$ is the atomic mass in amu.

2. The origin of the spherical coordinate system is located at atom $C_{12}$. The benzene ring is in the "xy" plane and the "z" axis is perpendicular to this plane.
Table 20.2.2. The valence internal coordinates used for calculating the G matrix of phenylacetic acid.

<table>
<thead>
<tr>
<th>Int. crd. no.</th>
<th>Atoms involved</th>
<th>Code(^1) no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 7</td>
<td>1</td>
<td>(\nu)\text{CH}</td>
<td>(\text{C}<em>{\text{ring}})-(\text{H}</em>{\text{ring}}) stretching</td>
</tr>
<tr>
<td>2</td>
<td>3 8</td>
<td>1</td>
<td>(\nu)\text{CH}</td>
<td>(\text{C}<em>{\text{ring}})-(\text{H}</em>{\text{ring}}) stretching</td>
</tr>
<tr>
<td>3</td>
<td>4 9</td>
<td>1</td>
<td>(\nu)\text{CH}</td>
<td>(\text{C}<em>{\text{ring}})-(\text{H}</em>{\text{ring}}) stretching</td>
</tr>
<tr>
<td>4</td>
<td>5 10</td>
<td>1</td>
<td>(\nu)\text{CH}</td>
<td>(\text{C}<em>{\text{ring}})-(\text{H}</em>{\text{ring}}) stretching</td>
</tr>
<tr>
<td>5</td>
<td>6 11</td>
<td>1</td>
<td>(\nu)\text{CH}</td>
<td>(\text{C}<em>{\text{ring}})-(\text{H}</em>{\text{ring}}) stretching</td>
</tr>
<tr>
<td>6</td>
<td>12 13</td>
<td>1</td>
<td>(\nu)\text{CH}_\alpha</td>
<td>(\text{C}<em>{12}-\text{H}</em>\alpha) stretching</td>
</tr>
<tr>
<td>7</td>
<td>12 14</td>
<td>1</td>
<td>(\nu)\text{CH}_\alpha</td>
<td>(\text{C}<em>{12}-\text{H}</em>\alpha) stretching</td>
</tr>
<tr>
<td>8</td>
<td>1 2</td>
<td>1</td>
<td>(\nu)\text{CC}</td>
<td>(\text{C}<em>{\text{ring}})-(\text{H}</em>{\text{ring}}) stretching</td>
</tr>
<tr>
<td>9</td>
<td>2 3</td>
<td>1</td>
<td>(\nu)\text{CC}</td>
<td>(\text{C}<em>{\text{ring}})-(\text{H}</em>{\text{ring}}) stretching</td>
</tr>
<tr>
<td>10</td>
<td>3 4</td>
<td>1</td>
<td>(\nu)\text{CC}</td>
<td>(\text{C}<em>{\text{ring}})-(\text{H}</em>{\text{ring}}) stretching</td>
</tr>
<tr>
<td>11</td>
<td>4 5</td>
<td>1</td>
<td>(\nu)\text{CC}</td>
<td>(\text{C}<em>{\text{ring}})-(\text{H}</em>{\text{ring}}) stretching</td>
</tr>
<tr>
<td>12</td>
<td>5 6</td>
<td>1</td>
<td>(\nu)\text{CC}</td>
<td>(\text{C}<em>{\text{ring}})-(\text{H}</em>{\text{ring}}) stretching</td>
</tr>
<tr>
<td>13</td>
<td>6 1</td>
<td>1</td>
<td>(\nu)\text{CC}</td>
<td>(\text{C}<em>{\text{ring}})-(\text{H}</em>{\text{ring}}) stretching</td>
</tr>
<tr>
<td>14</td>
<td>1 12</td>
<td>1</td>
<td>(\nu)\text{\theta}X</td>
<td>(\text{C}<em>{1}-\text{C}</em>{12}) stretching</td>
</tr>
<tr>
<td>15</td>
<td>12 15</td>
<td>1</td>
<td>(\nu)\text{R-COOH}</td>
<td>(\text{C}<em>{12}-\text{C}</em>{15}) stretching(^2)</td>
</tr>
<tr>
<td>16</td>
<td>15 16</td>
<td>1</td>
<td>(\nu)\text{C-O}</td>
<td>(\text{C}<em>{15}-\text{O}</em>{16}) stretching</td>
</tr>
<tr>
<td>17</td>
<td>15 17</td>
<td>1</td>
<td>(\nu)\text{C=O}</td>
<td>(\text{C}<em>{15}-\text{O}</em>{17}) stretching</td>
</tr>
<tr>
<td>18</td>
<td>16 18</td>
<td>1</td>
<td>(\nu)\text{OH}</td>
<td>O-H stretching</td>
</tr>
<tr>
<td>19</td>
<td>6 2 1</td>
<td>2</td>
<td>(\alpha)\text{CCC}</td>
<td>C-C-C ring angle bending</td>
</tr>
<tr>
<td>20</td>
<td>1 3 2</td>
<td>2</td>
<td>(\alpha)\text{CCC}</td>
<td>C-C-C ring angle bending</td>
</tr>
</tbody>
</table>
Table 20.2.2 (continued).

<table>
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<tr>
<th>Int. crd. no.</th>
<th>Atoms involved</th>
<th>Code(^1) no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>2 4 3</td>
<td>2</td>
<td>(a_{\text{CCC}})</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>3 5 4</td>
<td>2</td>
<td>(a_{\text{CCC}})</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>4 6 5</td>
<td>2</td>
<td>(a_{\text{CCC}})</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>5 1 6</td>
<td>2</td>
<td>(a_{\text{CCC}})</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>12 6 2 1</td>
<td>5</td>
<td>(\beta_{\varnothing X})</td>
<td>(C_1-C_{12}) bending with respect to the external bisector of the ring angle</td>
</tr>
<tr>
<td>26</td>
<td>7 1 3 2</td>
<td>5</td>
<td>(\beta_{\text{CH}})</td>
<td>(C_{\text{ring}}-H_{\text{ring}}) bending with respect to the external bisector of the ring angle</td>
</tr>
<tr>
<td>27</td>
<td>8 2 4 3</td>
<td>5</td>
<td>(\beta_{\text{CH}})</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>9 3 5 4</td>
<td>5</td>
<td>(\beta_{\text{CH}})</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>10 4 6 5</td>
<td>5</td>
<td>(\beta_{\text{CH}})</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>11 5 1 6</td>
<td>5</td>
<td>(\beta_{\text{CH}})</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>13 15 12</td>
<td>2</td>
<td>(\alpha_{H_{\alpha} \text{CC}})</td>
<td>(H_{\alpha}-C_{12}-C_{15}) or (H_{\alpha}-C_{12}-C_{1}) bending</td>
</tr>
<tr>
<td>32</td>
<td>15 14 12</td>
<td>2</td>
<td>(\alpha_{H_{\alpha} \text{CC}})</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>14 1 12</td>
<td>2</td>
<td>(\alpha_{H_{\alpha} \text{CC}})</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>1 13 12</td>
<td>2</td>
<td>(\alpha_{H_{\alpha} \text{CC}})</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>15 1 12</td>
<td>2</td>
<td>(\alpha_{C_1-C_{12}C_{15}})</td>
<td>(C_1-C_{12}-C_{15}) bending</td>
</tr>
<tr>
<td>36</td>
<td>13 14 12</td>
<td>2</td>
<td>(\alpha_{H_{\alpha} \text{CH}})</td>
<td>(H_{\alpha}-C_{12}-H_{\alpha}) bending (locally redundant)</td>
</tr>
<tr>
<td>37</td>
<td>12 16 17 15</td>
<td>5</td>
<td>(\beta_{\text{R-COOH}})</td>
<td>(\text{R-COOH}) bending</td>
</tr>
<tr>
<td>38</td>
<td>16 17 15</td>
<td>2</td>
<td>(\alpha_{\text{OCO}})</td>
<td>(O-C=O) bending</td>
</tr>
<tr>
<td>Int. crd. no.</td>
<td>Atoms involved</td>
<td>Code^1 no.</td>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------</td>
<td>------------</td>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>39</td>
<td>18 15 16</td>
<td>2</td>
<td>a_{HOC}</td>
<td>H-O-C bending</td>
</tr>
<tr>
<td>40</td>
<td>12 6 2 1</td>
<td>3</td>
<td>γ_{\text{X}}</td>
<td>C_{1}-C_{12} out-of-plane wagging</td>
</tr>
<tr>
<td>41</td>
<td>7 1 3 2</td>
<td>3</td>
<td>γ_{\text{CH}}</td>
<td>C_{-\text{ring}}-H_{\text{ring}} out-of-plane wagging</td>
</tr>
<tr>
<td>42</td>
<td>8 2 4 3</td>
<td>3</td>
<td>γ_{\text{CH}}</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>9 3 5 4</td>
<td>3</td>
<td>γ_{\text{CH}}</td>
<td></td>
</tr>
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<td>44</td>
<td>10 4 6 5</td>
<td>3</td>
<td>γ_{\text{CH}}</td>
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<tr>
<td>45</td>
<td>11 5 1 6</td>
<td>3</td>
<td>γ_{\text{CH}}</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>12 16 17 15</td>
<td>3</td>
<td>γ_{R-\text{COOH}}</td>
<td>R-COOH\textsuperscript{2} out-of-plane wagging</td>
</tr>
<tr>
<td>47</td>
<td>6 1 2 3</td>
<td>4</td>
<td>δ_{\text{CC}}</td>
<td>Torsion around C_{\text{ring}}-C_{\text{ring}} bond</td>
</tr>
<tr>
<td>48</td>
<td>1 2 3 4</td>
<td>4</td>
<td>δ_{\text{CC}}</td>
<td></td>
</tr>
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<td>49</td>
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<td>δ_{\text{CC}}</td>
<td></td>
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<td>50</td>
<td>3 4 5 6</td>
<td>4</td>
<td>δ_{\text{CC}}</td>
<td></td>
</tr>
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<td>51</td>
<td>4 5 6 1</td>
<td>4</td>
<td>δ_{\text{CC}}</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>5 6 1 2</td>
<td>4</td>
<td>δ_{\text{CC}}</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>13 12 1 2</td>
<td>4</td>
<td>δ_{\text{X}}</td>
<td>Torsion around C_{12}-C_{1} bond (locally redundant)</td>
</tr>
<tr>
<td>54</td>
<td>14 12 1 6</td>
<td>4</td>
<td>δ_{\text{X}}</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>17 15 12 13</td>
<td>4</td>
<td>δ_{R-\text{COOH}} \textsuperscript{2}</td>
<td>Torsion around C_{15}-C_{12} bond</td>
</tr>
<tr>
<td>56</td>
<td>16 15 12 14</td>
<td>4</td>
<td>δ_{R-\text{COOH}} \textsuperscript{2}</td>
<td>(locally redundant)</td>
</tr>
<tr>
<td>57</td>
<td>18 16 15 12</td>
<td>4</td>
<td>δ_{\text{C-O}}</td>
<td>Torsion around C-O bond</td>
</tr>
</tbody>
</table>
Notes. 1. This number corresponds to the code no. shown in subsection 16.3.

2. \( R : \text{C}_6\text{H}_5\text{CH}_2^- \)
Table 20.2.3. The elements of the $F$ matrices of phenylacetic acid and phenylacetic-$\alpha$-$d_2$ acid$^1$.

Part 1: diagonal elements.

<table>
<thead>
<tr>
<th>The element of the $G$ matrix</th>
<th>Value of the corresponding force constant (mdyn/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phenylacetic acid</td>
</tr>
<tr>
<td>$v_{\text{CH}_\alpha}$</td>
<td>5.</td>
</tr>
<tr>
<td>$v_\varnothing X$</td>
<td>4.5</td>
</tr>
<tr>
<td>$v_{\text{R-COOH}}$</td>
<td>4.8</td>
</tr>
<tr>
<td>$v_{\text{C-O}}$</td>
<td>4.5</td>
</tr>
<tr>
<td>The element of the G matrix</td>
<td>Value of the corresponding force constant (mdyn/Å)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td></td>
<td>Phenylactic acid</td>
</tr>
<tr>
<td>νC=0</td>
<td>10.9</td>
</tr>
<tr>
<td>α²H(D)²CC</td>
<td>0.58 (0.29)²</td>
</tr>
<tr>
<td>α²H(D)²CC</td>
<td>0.55 (0.29)²</td>
</tr>
<tr>
<td>α²C¹C¹2C₁₅</td>
<td>0.39</td>
</tr>
<tr>
<td>α²H(D)²CH(D)α</td>
<td>0.47</td>
</tr>
<tr>
<td>βR- COOH</td>
<td>0.8</td>
</tr>
<tr>
<td>The element of the G matrix</td>
<td>Value of the corresponding force constant (mdyn/Å)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td></td>
<td>Phenylacetic acid</td>
</tr>
<tr>
<td>α₀CO</td>
<td>0.75</td>
</tr>
<tr>
<td>γ₀X</td>
<td>0.4</td>
</tr>
<tr>
<td>γₐ-COOH</td>
<td>0.42</td>
</tr>
<tr>
<td>δ₀X</td>
<td>0.05</td>
</tr>
<tr>
<td>δₐ-COOH</td>
<td>0.1</td>
</tr>
<tr>
<td>δC-0</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Table 20.2.3. Part 2: off-diagonal elements.

<table>
<thead>
<tr>
<th>The element of the G matrix</th>
<th>Value of the corresponding force constant (mdyn/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phenylacetic acid</td>
</tr>
<tr>
<td>νCH(D)ₐ⁻νCH(D)ₐ (C common)</td>
<td>0.04</td>
</tr>
<tr>
<td>νR-COOH⁻νØX</td>
<td>0.06</td>
</tr>
<tr>
<td>νR-COOH⁻αH(D)ₐ CC</td>
<td>0.24 (0.17)²</td>
</tr>
<tr>
<td>νØX⁻αH(D)ₐ CC</td>
<td>0.24 (0.17)²</td>
</tr>
<tr>
<td>νØX⁻αC₁C₁₂C₁₅</td>
<td>0.23</td>
</tr>
<tr>
<td>νR-COOH⁻αC₁C₁₂C₁₅</td>
<td>0.23</td>
</tr>
<tr>
<td>αH(D)ₐ CC⁻αH(D)ₐ CC (C-C common)</td>
<td>-0.01</td>
</tr>
<tr>
<td>αH(D)ₐ CC⁻αH(D)ₐ CC (C-H common)</td>
<td>0.014</td>
</tr>
</tbody>
</table>
Table 20.2.3 (cont.)

Notes.

1. Only the non-zero force constants which are different or new from those of benzoic acid (table 18.2.3) are given in this table.

2. The first number represents the value of the force constant scaled by the C-H distance. The value in the brackets is scaled by the C-C distance.
Table 20.2.4. The calculated and the observed frequencies of vibrations of phenylacetic acid.

<table>
<thead>
<tr>
<th>No.</th>
<th>Calculated frequency</th>
<th>Wave number(^{-1}) cm(^{-1})</th>
<th>Approximate description(^{2})</th>
<th>(Potential energy distribution(^{1})) (%)</th>
<th>Observed frequency</th>
<th>Wave number(^{-1}) cm(^{-1})</th>
<th>Ref.</th>
<th>Type(^{2})</th>
<th>The state of the compound</th>
<th>Assignment(^{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\nu_{\text{OH}}(100))</td>
<td>3567</td>
<td>(\nu_{\text{CH}}(98))</td>
<td>AA(^{4}) 3577</td>
<td>3-5</td>
<td>IR</td>
<td>Gaseous phase,</td>
<td>200(^{\circ})C</td>
<td>(\nu_{\text{OH}})</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(\nu_{\text{CH}}(98))</td>
<td>3075</td>
<td>(\nu_{\text{CH}}(98))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(\nu_{\text{CH}}(98))</td>
<td>3073</td>
<td>(\nu_{\text{CH}}(99))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(\nu_{\text{CH}}(98))</td>
<td>3071</td>
<td>(\nu_{\text{CH}}(98))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(\nu_{\text{CH}}(98))</td>
<td>3071</td>
<td>(\nu_{\text{CH}}(98))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>(\nu_{\text{CH}}(98))</td>
<td>3070</td>
<td>(\nu_{\text{CH}}(98))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>(\nu_{\text{CH}_{\alpha}}(97))</td>
<td>3058</td>
<td>(\nu_{\text{CH}_{\alpha}}(98))</td>
<td>AA 3048 3048</td>
<td>4</td>
<td>IR</td>
<td>Gaseous phase,</td>
<td>150(^{\circ})C</td>
<td>(\nu_{\text{CH}_{\alpha}})</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>(\nu_{\text{CH}_{\alpha}}(98))</td>
<td>3002</td>
<td>(\nu_{\text{CH}_{\alpha}}(98))</td>
<td>AA 2997 2997</td>
<td>4</td>
<td>IR</td>
<td>Gaseous phase,</td>
<td>150(^{\circ})C</td>
<td>(\nu_{\text{CH}_{\alpha}})</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>(\nu_{\text{C}=\text{O}}(70))</td>
<td>1798</td>
<td>(\nu_{\text{C}=\text{O}}(70))</td>
<td>1730 1799</td>
<td>1</td>
<td>IR</td>
<td>Dioxane soln</td>
<td>Gaseous phase,</td>
<td>(\nu_{\text{C}=\text{O}})</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>(\nu_{\text{CC}}(45))</td>
<td>1639</td>
<td>(\nu_{\text{CC}}(45))</td>
<td>AA 1799 1799</td>
<td>3-5</td>
<td>IR</td>
<td>Gaseous phase,</td>
<td>150(^{\circ})C</td>
<td>(\nu_{\text{C}=\text{O}})</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>(\nu_{\text{CC}}(53))</td>
<td>1619</td>
<td>(\nu_{\text{CC}}(53))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 20.2.4 (continued)

<table>
<thead>
<tr>
<th>No.</th>
<th>Wave number (cm(^{-1}))</th>
<th>Approximate description (^1)</th>
<th>Calculated frequency (Potential energy distribution (^2), %)</th>
<th>Wave number (cm(^{-1}))</th>
<th>Ref.</th>
<th>Type (^3)</th>
<th>The state of the compound</th>
<th>Assignment (^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>1565 (\alpha_{\text{HCC}}(18), \alpha_{\text{HCH}}(64),) (\delta_{\text{R-COOH}}(10))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IR</td>
<td>KBr disk, 4.46 wt %</td>
<td>(\alpha_{\text{HCC}})</td>
</tr>
<tr>
<td>13</td>
<td>1509 (\nu_{\text{CC}}(25), \beta_{\text{CH}}(38))</td>
<td></td>
<td>1492 (6) IR</td>
<td></td>
<td></td>
<td></td>
<td>(\alpha_{\text{HCC}})</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1466 (\nu_{\text{CC}}(21), \beta_{\text{CH}}(37))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IR</td>
<td>Gaseous phase, 150°C</td>
<td>(\alpha_{\text{HCC}})</td>
</tr>
<tr>
<td>15</td>
<td>1379 (\nu_{\text{R-COOH}}(18), \alpha_{\text{HCC}}(32))</td>
<td></td>
<td>AA 1401 (4) IR</td>
<td></td>
<td></td>
<td>IR</td>
<td>Gaseous phase, 150°C</td>
<td>(\nu_{\text{H}}) (\alpha_{\text{CC}})</td>
</tr>
<tr>
<td>16</td>
<td>1350 (\nu_{\text{CC}}(16), \beta_{\text{CH}}(42))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IR</td>
<td>Gaseous phase, 150°C</td>
<td>(\nu_{\text{H}}) (\alpha_{\text{HOC}})</td>
</tr>
<tr>
<td>17</td>
<td>1303 (\nu_{\text{CC}}(15), \nu_{\text{C-O}}(11),) (\alpha_{\text{HCC}}(30))</td>
<td></td>
<td>AA 1279 (3-5) IR</td>
<td></td>
<td></td>
<td>IR</td>
<td>Gaseous phase, 150°C</td>
<td>(\nu_{\text{C-O}}) (\nu_{\text{R-COOH}})</td>
</tr>
<tr>
<td>18</td>
<td>1300 (\nu_{\text{CC}}(47), \beta_{\text{CH}}(12))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IR</td>
<td>Gaseous phase, 150°C</td>
<td>(\alpha_{\text{HOC}})</td>
</tr>
<tr>
<td>19</td>
<td>1252 (\nu_{\text{CC}}(14), \nu_{\text{BX}}(20),) (\beta_{\text{CH}}(11), \alpha_{\text{HCC}}(13))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IR</td>
<td>Gaseous phase, 150°C</td>
<td>(\alpha_{\text{HOC}})</td>
</tr>
<tr>
<td>20</td>
<td>1220 (\alpha_{\text{HCC}}(56))</td>
<td></td>
<td>1230 (1) IR</td>
<td></td>
<td></td>
<td>IR</td>
<td>Solid or liquid</td>
<td>(\alpha_{\text{HCC}})</td>
</tr>
<tr>
<td>21</td>
<td>1194 (\beta_{\text{CH}}(78))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IR</td>
<td>Solid or liquid</td>
<td>(\alpha_{\text{HOC}})</td>
</tr>
</tbody>
</table>

\(^1\) Potential energy distribution

\(^2\) Calculated frequency

\(^3\) Assignment
Table 20.2.4 (continued).

<table>
<thead>
<tr>
<th>No.</th>
<th>Wave number cm(^{-1})</th>
<th>Calculated frequency (^2) Approximate description (^1) (Potential energy distribution %)</th>
<th>Wave number cm(^{-1})</th>
<th>Ref.</th>
<th>Type (^3)</th>
<th>The state of the compound</th>
<th>Assignment (^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>1192</td>
<td>$\alpha_{\text{HOC}}(83)$</td>
<td>AA 1192</td>
<td>3-5</td>
<td>IR</td>
<td>Gaseous phase, 150(^{\circ})C</td>
<td>$\alpha_{\text{HOC}}$</td>
</tr>
<tr>
<td>24</td>
<td>1103</td>
<td>$\nu_{\text{CC}}(12), \beta_{\text{CH}}(16)$</td>
<td>AA 1068</td>
<td>4</td>
<td>IR</td>
<td>Gaseous phase, 150(^{\circ})C</td>
<td>$\nu_{\text{CC}}(26), \beta_{\text{CH}}(12)$, $\gamma_{\text{R-COOH}}(21)$</td>
</tr>
<tr>
<td>25</td>
<td>1053</td>
<td>$\nu_{\text{CC}}(26), \beta_{\text{CH}}(12)$</td>
<td>1071</td>
<td>6</td>
<td>IR</td>
<td>KBr disk, 4.46 wt %</td>
<td>$\gamma_{\text{R-COOH}}$</td>
</tr>
<tr>
<td>26</td>
<td>1021</td>
<td>$\nu_{\text{CC}}(35), \alpha_{\text{CCC}}(20)$</td>
<td>AA 846</td>
<td>4</td>
<td>IR</td>
<td>Gaseous phase, 150(^{\circ})C</td>
<td>$\nu_{\text{R-COOH}}(13), \nu_{\text{C-O}}(18)$</td>
</tr>
<tr>
<td>27</td>
<td>1008</td>
<td>$\gamma_{\text{CH}}(41)$</td>
<td></td>
<td></td>
<td></td>
<td>Solid or liquid</td>
<td>$\gamma_{\text{CH}}(43)$</td>
</tr>
<tr>
<td>28</td>
<td>998</td>
<td>$\nu_{\text{CC}}(41), \alpha_{\text{CCC}}(19)$</td>
<td></td>
<td></td>
<td></td>
<td>Solid or liquid</td>
<td>$\gamma_{\text{CH}}(56)$</td>
</tr>
<tr>
<td>29</td>
<td>985</td>
<td>$\gamma_{\text{CH}}(56)$</td>
<td></td>
<td></td>
<td></td>
<td>Solid or liquid</td>
<td>$\alpha_{\text{HCC}}(25), \gamma_{\text{CH}}(12)$</td>
</tr>
<tr>
<td>30</td>
<td>974</td>
<td>$\alpha_{\text{HCC}}(25), \gamma_{\text{CH}}(12)$</td>
<td></td>
<td></td>
<td></td>
<td>Solid or liquid</td>
<td>$\gamma_{\text{CH}}(82)$</td>
</tr>
<tr>
<td>31</td>
<td>934</td>
<td>$\gamma_{\text{CH}}(43)$</td>
<td>928</td>
<td>1</td>
<td>IR</td>
<td>Solid or liquid</td>
<td>$\nu_{\text{R-COOH}}(13), \nu_{\text{C-O}}(18)$</td>
</tr>
<tr>
<td>32</td>
<td>835</td>
<td>$\gamma_{\text{CH}}(82)$</td>
<td></td>
<td></td>
<td></td>
<td>Solid or liquid</td>
<td>$\gamma_{\text{CH}}(83)$</td>
</tr>
<tr>
<td>33</td>
<td>817</td>
<td>$\nu_{\text{R-COOH}}(13), \nu_{\text{C-O}}(18)$</td>
<td>AA 846</td>
<td>4</td>
<td>IR</td>
<td>Gaseous phase, 150(^{\circ})C</td>
<td>$\nu_{\text{R-COOH}}(13), \nu_{\text{C-O}}(18)$</td>
</tr>
<tr>
<td>No.</td>
<td>Wave number cm$^{-1}$</td>
<td>Approximate description$^1$</td>
<td>Wave number cm$^{-1}$</td>
<td>Ref.</td>
<td>Observed frequency type$^2$</td>
<td>The state of the compound</td>
<td>Assignment$^3$</td>
</tr>
<tr>
<td>-----</td>
<td>----------------------</td>
<td>-----------------------------</td>
<td>----------------------</td>
<td>------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>34</td>
<td>782</td>
<td>$\gamma_{\beta x}(11), \gamma_{\beta x}(17)$, $\delta_{\text{CC}}(10)$</td>
<td></td>
<td></td>
<td>IR</td>
<td>KBr disk, 4.46 wt %</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>737</td>
<td>$\gamma_{\text{CH}}(17)$</td>
<td>750</td>
<td>6</td>
<td>IR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>688</td>
<td>$\gamma_{\text{CH}}(17), \delta_{\text{CC}}(26)$</td>
<td></td>
<td></td>
<td>IR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>622</td>
<td>$\alpha_{\text{CCC}}(63)$</td>
<td>602</td>
<td>2</td>
<td>IR</td>
<td>Nujol mull</td>
<td>$\alpha_{\text{CCC}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>601</td>
<td>6</td>
<td>IR</td>
<td>KBr disk, 4.46 wt %</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>585</td>
<td>$\delta_{\text{CC}}(13), \delta_{\text{C-O}}(42)$</td>
<td></td>
<td></td>
<td>IR</td>
<td>Gaseous phase, 150$^0$C</td>
<td>$\gamma_{R-COOH}$</td>
</tr>
<tr>
<td>39</td>
<td>558</td>
<td>$\nu_{\beta x}(10), \gamma_{\text{CH}}(10)$, $\delta_{\text{CC}}(22), \delta_{\text{C-O}}(13)$</td>
<td>546</td>
<td>2</td>
<td>IR</td>
<td>Nujol mull</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>AA 582</td>
<td>4</td>
<td>IR</td>
<td>Gaseous phase, 150$^0$C</td>
<td>$\gamma_{R-COOH}$</td>
</tr>
<tr>
<td>40</td>
<td>518</td>
<td>$\nu_{\text{C-O}}(10), \alpha_{\text{CCC}}(15), \beta_{\beta x}(10), \beta_{R-COOH}(19), \alpha_{\text{OCO}}(20)$</td>
<td>535</td>
<td>2</td>
<td>IR</td>
<td>Nujol mull</td>
<td>$\alpha_{\text{OCO}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>AA 536</td>
<td>3-5</td>
<td>IR</td>
<td>Gaseous phase, 150$^0$C</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>482</td>
<td>$\alpha_{\text{CCC}}(23), \alpha_{\text{OCO}}(10)$</td>
<td></td>
<td>476</td>
<td>2</td>
<td>IR</td>
<td>Nujol mull</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>479</td>
<td>6</td>
<td>IR</td>
<td>KBr disk, 4.46 wt %</td>
</tr>
</tbody>
</table>

$^1$ Potential energy distribution

$^2$ Ref. = Reference

$^3$ Assignment

---

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Table 20.2.4 (continued).

<table>
<thead>
<tr>
<th>No.</th>
<th>Wave number cm(^{-1})</th>
<th>Approximate description(^1)</th>
<th>Wave number cm(^{-1})</th>
<th>Observed frequency</th>
<th>Ref.</th>
<th>Type</th>
<th>The state of the compound</th>
<th>Assignment(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>452</td>
<td>(\alpha_{OCO}(13)), (\gamma_\phi(13)) (\delta_{CC}(23))</td>
<td>395</td>
<td>IR</td>
<td>2</td>
<td>Nujol mull</td>
<td>(\alpha_{OCO})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>390</td>
<td>IR</td>
<td>6</td>
<td>KBr disk, 4.46 wt %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>398</td>
<td>(\gamma_{CH}(13)), (\delta_{CC}(40))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>338</td>
<td>(\beta_\phi(31)), (\beta_{R-COOH}(31))</td>
<td>356, 351, 325</td>
<td>IR</td>
<td>2</td>
<td>Nujol mull</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>240</td>
<td>(\delta_{CC}(36))</td>
<td>266, 252, 225</td>
<td>IR</td>
<td>2</td>
<td>Nujol mull</td>
<td></td>
<td>266 : ((\beta_\phi) + (\gamma_\phi))</td>
</tr>
<tr>
<td>46</td>
<td>125</td>
<td>(\alpha_{HCC}(10)), (\alpha_{C_1C_1C_2C_15}(20)), (\delta_{R-COOH}(19))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>108</td>
<td>(\alpha_{HCC}(14)), (\alpha_{C_1C_1C_2C_15}(12)), (\delta_{R-COOH}(28))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>65</td>
<td>(\delta_{\phi}(74)), (\delta_{R-COOH}(10))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 20.2.4 (continued).

Notes. 1. The "Potential energy distribution" is given in per cent contribution to $\lambda$ by the diagonal force constants for the respective coordinates. Only contributions equal to, or greater than, 10 per cent were included in this table.

2. IR stands for infrared spectrum.

3. The symbols used to indicate the types of coordinates were defined in table 20.2.2.

4. AA refers to the spectrum of acetic acid.


6. Present work. The spectrum was taken on a Perkin-Elmer, Model 457 Spectrophotometer.
Table 20.2.5. The calculated and the observed frequencies of vibrations of phenylacetic-α-d₂ acid.

<table>
<thead>
<tr>
<th>No.</th>
<th>Calculated frequency</th>
<th>Approximate description (^1,\text{(Potential energy distribution}^3\text{)})</th>
<th>Observed (^2\text{ frequency} \text{ Wave number} \text{ cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3567</td>
<td>(v_{\text{OH}}(100))</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3074</td>
<td>(v_{\text{CH}}(99))</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3073</td>
<td>(v_{\text{CH}}(98))</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3071</td>
<td>(v_{\text{CH}}(98))</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3071</td>
<td>(v_{\text{CH}}(98))</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3070</td>
<td>(v_{\text{CH}}(98))</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2288</td>
<td>(v_{\text{CD}}(96))</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2197</td>
<td>(v_{\text{CD}}(95))</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1794</td>
<td>(v_{\text{C} = \text{O}}(71))</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1638</td>
<td>(v_{\text{CC}}(45))</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1615</td>
<td>(v_{\text{CC}}(54))</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1509</td>
<td>(v_{\text{CC}}(25), \beta_{\text{CH}}(38))</td>
<td>1500</td>
</tr>
<tr>
<td>13</td>
<td>1461</td>
<td>(v_{\text{CC}}(22), \beta_{\text{CH}}(40))</td>
<td>1452</td>
</tr>
<tr>
<td>14</td>
<td>1349</td>
<td>(v_{\text{R-COOH}}(22), v_{\text{C-O}}(12), \beta_{\text{CH}}(16))</td>
<td>1349</td>
</tr>
<tr>
<td>15</td>
<td>1343</td>
<td>(v_{\text{CC}}(15), \beta_{\text{CH}}(40))</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>1299</td>
<td>(v_{\text{CC}}(55), \beta_{\text{CH}}(11))</td>
<td></td>
</tr>
</tbody>
</table>
Table 20.2.5 (Continued).

<table>
<thead>
<tr>
<th>No.</th>
<th>Calculated frequency</th>
<th>Wave number cm(^{-1})</th>
<th>Approximate description(^1) (Potential energy distribution(^3))</th>
<th>Observed(^2)</th>
<th>Frequency cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>(\nu_{\phi X}(24))</td>
<td>1268</td>
<td></td>
<td></td>
<td>1255</td>
</tr>
<tr>
<td>18</td>
<td>(\alpha_{HOC}(81))</td>
<td>1194</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>(\beta_{CH}(76))</td>
<td>1192</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>(\nu_{CC}(18), \beta_{CH}(54))</td>
<td>1158</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>(\alpha_{D_{\alpha}CD_{\alpha}}(50))</td>
<td>1150</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>(\alpha_{D_{\alpha}CC_{(25)}, \gamma_{R-COOH}(42)})</td>
<td>1098</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>(\nu_{CC}(29), \beta_{CH}(23))</td>
<td>1082</td>
<td></td>
<td></td>
<td>1080</td>
</tr>
<tr>
<td>24</td>
<td>(\alpha_{D_{\alpha}CC_{(21), \gamma_{R-COOH}(11)})</td>
<td>1030</td>
<td></td>
<td></td>
<td>1040</td>
</tr>
<tr>
<td>25</td>
<td>(\nu_{CC}(32), \alpha_{CCC}(22))</td>
<td>1021</td>
<td></td>
<td></td>
<td>1025</td>
</tr>
<tr>
<td>26</td>
<td>(\gamma_{CH}(43))</td>
<td>1006</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>(\nu_{CC}(33), \alpha_{CCC}(16))</td>
<td>998</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>(\gamma_{CH}(58))</td>
<td>984</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>(\gamma_{CH}(42))</td>
<td>935</td>
<td></td>
<td></td>
<td>945</td>
</tr>
<tr>
<td>30</td>
<td>(\alpha_{D_{\alpha}CC_{(69)})</td>
<td>880</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>(\gamma_{CH}(82))</td>
<td>835</td>
<td></td>
<td></td>
<td>848</td>
</tr>
<tr>
<td>32</td>
<td>(\alpha_{D_{\alpha}CC_{(29)})</td>
<td>822</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>(\gamma_{\phi X}(10), \gamma_{CH}(22))</td>
<td>771</td>
<td></td>
<td></td>
<td>780</td>
</tr>
<tr>
<td>34</td>
<td>(\nu_{CC}(10), \nu_{\phi X}(13), \alpha_{CCC}(26), \alpha_{D_{\alpha}CC}(12))</td>
<td>755</td>
<td></td>
<td></td>
<td>740</td>
</tr>
<tr>
<td>No.</td>
<td>Calculated frequency</td>
<td>Observed frequency</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>----------------------</td>
<td>--------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wave number cm⁻¹</td>
<td>Approximate description (Potential energy distribution) (%)</td>
<td>Wave number cm⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>717 (\nu_{\text{R-COOH}}(14), \nu_{\text{C-O}}(21),\gamma_{\text{CH}}(15))</td>
<td>698</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>687 (\gamma_{\text{CH}}(16), \delta_{\text{CC}}(28))</td>
<td>666</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>618 (\sigma_{\text{CCC}}(67))</td>
<td>612</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>582 (\delta_{\text{CC}}(11), \delta_{\text{C-O}}(51))</td>
<td>585</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>551 (\gamma_{\phi X}(11), \gamma_{\text{CH}}(10),\delta_{\text{CC}}(23))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>489 (\alpha_{\text{CCC}}(22), \alpha_{\text{O-C}}(32))</td>
<td>473</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>444 (\alpha_{\text{O-C}}(10), \gamma_{\phi X}(12),\delta_{\text{CC}}(21))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>435 (\beta_{\phi X}(14), \beta_{\text{R-COOH}}(27),\delta_{\text{R-COOH}}(14))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>397 (\gamma_{\text{CH}}(13), \delta_{\text{CC}}(40))</td>
<td>389</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>335 (\beta_{\phi X}(34), \beta_{\text{R-COOH}}(27))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>240 (\delta_{\text{CC}}(46))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>125 (\alpha_{\text{D}<em>{\alpha\text{CC}}}(10), \alpha</em>{\text{C}_1\text{C}_2\text{C}_1\text{C}<em>5}(20),\delta</em>{\text{R-COOH}}(19))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>108 (\alpha_{\text{D}<em>{\alpha\text{CC}}}(14), \alpha</em>{\text{C}_1\text{C}_2\text{C}_1\text{C}<em>5}(12),\delta</em>{\text{R-COOH}}(29))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>64 (\delta_{\phi X}(75))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 20.2.5 (continued).

Notes.  1. The "Potential energy distribution" is given in per cent contribution to $\lambda$ by the diagonal force constants of the respective coordinates. Only contributions equal to, or greater than, 10 per cent were included in this table.

2. Infrared spectrum of phenylacetic-$\alpha$-$d_2$ acid as KBr disk, 2.6 wt %, taken on a Perkin-Elmer Model 457 Spectrophotometer.

3. The symbols used to indicate the coordinates were defined in table 20.2.2 and subsection 20.2.
20.3 The calculated vibrational frequencies of phenylacetate and phenylacetate-α-d₂ anions.

The G matrix.

The molecular structures of the phenylacetate ion and the phenylacetate-α-d₂ ion were assumed to be identical to those of the respective acids with the obvious exception of atom H₁₈, absent in the anions, and with the exception of the carbon-oxygen bonds, which were assumed to be nearly equal in length (see subsection 18.3). The spherical coordinates of the two oxygen atoms in the anions are given in table 20.1.1.

Fifty-four internal coordinates were defined for each of the anions. The internal coordinates of the phenylacetate ion are given in table 20.3.2. Those of the phenylacetate-α-d₂ anion were identical, with the exception of the symbols used to represent the coordinates involving the carbon-deuterium bonds. These coordinates are given below:
<table>
<thead>
<tr>
<th>Int. crd. no.</th>
<th>Atoms involved</th>
<th>Code no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>12 13</td>
<td>1</td>
<td>(v_{\text{CD}_\alpha})</td>
<td>(\text{C}<em>{12}-\text{D}</em>\alpha) stretching</td>
</tr>
<tr>
<td>7</td>
<td>12 14</td>
<td>1</td>
<td>(v_{\text{CD}_\alpha})</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>13 15 12</td>
<td>2</td>
<td>(\alpha_{\text{DCC}})</td>
<td>(\text{D}<em>\alpha-\text{C}</em>{12}-\text{C}<em>{15}) or (\text{D}</em>\alpha-\text{C}<em>{12}-\text{C}</em>{1})</td>
</tr>
<tr>
<td>31</td>
<td>15 14 12</td>
<td>2</td>
<td>(\alpha_{\text{DCC}})</td>
<td>bending</td>
</tr>
<tr>
<td>32</td>
<td>14 1 12</td>
<td>2</td>
<td>(\alpha_{\text{DCC}})</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>1 13 12</td>
<td>2</td>
<td>(\alpha_{\text{DCC}})</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>13 14 12</td>
<td>2</td>
<td>(\alpha_{\text{DCC}})</td>
<td>(\text{D}<em>\alpha-\text{C}</em>{12}-\text{D}_\alpha) bending (locally redundant)</td>
</tr>
</tbody>
</table>

The fifty-four coordinates included six cyclic and three local redundancies. The complete G matrices of the two anions are given in "Detailed calculations - 20.3.1 and 20.3.2".

**The F matrix.**

The force constants for the phenylacetate and phenylacetate-\(\alpha\)-d\(_2\) ions were, generally, equal to those used to compute the vibrational frequencies of the respective acids (subsection 20.2). The force constants which were changed in going from the acids to anions are listed in table 20.4.1.

The calculated vibrational frequencies of the two isotopic phenylacetate ions and their potential energy distribution (corresponding to set no. 1 of force constants of table 20.4.1) are given in tables 20.3.3 and 20.3.4. For comparison
we included some vibrational frequencies of acetate and propionate ions in table 20.3.3, where the vibrational frequencies of the phenylacetate ion are given.

Table 20.3.1. The spherical coordinates of the atoms of the phenylacetate ion.

<table>
<thead>
<tr>
<th>Atom No.</th>
<th>Type</th>
<th>R</th>
<th>$A_x$</th>
<th>$A_y$</th>
<th>$A_z$</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>0</td>
<td>2.216</td>
<td>98.21</td>
<td>81.61</td>
<td>11.78</td>
<td>16.000</td>
</tr>
<tr>
<td>17</td>
<td>0</td>
<td>2.400</td>
<td>50.29</td>
<td>62.19</td>
<td>51.29</td>
<td>16.000</td>
</tr>
</tbody>
</table>

Note. The coordinates of atoms 1 to 15 are identical to those in the phenylacetic acid molecule (Table 20.2.1).
Table 20.3.2. The valence internal coordinates used for calculating the G matrix of phenylacetate ion.

<table>
<thead>
<tr>
<th>Int. crd. No.</th>
<th>Atoms involved</th>
<th>Code no.</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 7</td>
<td>1</td>
<td>( \nu_{\text{CH}} )</td>
<td>( \text{C}<em>{\text{ring}}-\text{H}</em>{\text{ring}} ) stretching</td>
</tr>
<tr>
<td>2</td>
<td>3 8</td>
<td>1</td>
<td>( \nu_{\text{CH}} )</td>
<td>( \text{C}<em>{\text{ring}}-\text{H}</em>{\text{ring}} ) stretching</td>
</tr>
<tr>
<td>3</td>
<td>4 9</td>
<td>1</td>
<td>( \nu_{\text{CH}} )</td>
<td>( \text{C}<em>{\text{ring}}-\text{H}</em>{\text{ring}} ) stretching</td>
</tr>
<tr>
<td>4</td>
<td>5 10</td>
<td>1</td>
<td>( \nu_{\text{CH}} )</td>
<td>( \text{C}<em>{\text{ring}}-\text{C}</em>{\text{ring}} ) stretching</td>
</tr>
<tr>
<td>5</td>
<td>6 11</td>
<td>1</td>
<td>( \nu_{\text{CH}} )</td>
<td>( \text{C}<em>{\text{ring}}-\text{C}</em>{\text{ring}} ) stretching</td>
</tr>
<tr>
<td>6</td>
<td>12 13</td>
<td>1</td>
<td>( \nu_{\text{CH}_{\alpha}} )</td>
<td>( \text{C}<em>{\text{12}}-\text{H}</em>{\alpha} ) stretching</td>
</tr>
<tr>
<td>7</td>
<td>12 14</td>
<td>1</td>
<td>( \nu_{\text{CH}_{\alpha}} )</td>
<td>( \text{C}<em>{\text{12}}-\text{H}</em>{\alpha} ) stretching</td>
</tr>
<tr>
<td>8</td>
<td>1 2</td>
<td>1</td>
<td>( \nu_{\text{CC}} )</td>
<td>( \text{C}<em>{\text{ring}}-\text{C}</em>{\text{ring}} ) stretching</td>
</tr>
<tr>
<td>9</td>
<td>2 3</td>
<td>1</td>
<td>( \nu_{\text{CC}} )</td>
<td>( \text{C}<em>{\text{ring}}-\text{C}</em>{\text{ring}} ) stretching</td>
</tr>
<tr>
<td>10</td>
<td>3 4</td>
<td>1</td>
<td>( \nu_{\text{CC}} )</td>
<td>( \text{C}<em>{\text{ring}}-\text{C}</em>{\text{ring}} ) stretching</td>
</tr>
<tr>
<td>11</td>
<td>4 5</td>
<td>1</td>
<td>( \nu_{\text{CC}} )</td>
<td>( \text{C}<em>{\text{ring}}-\text{C}</em>{\text{ring}} ) stretching</td>
</tr>
<tr>
<td>12</td>
<td>5 6</td>
<td>1</td>
<td>( \nu_{\text{CC}} )</td>
<td>( \text{C}<em>{\text{ring}}-\text{C}</em>{\text{ring}} ) stretching</td>
</tr>
<tr>
<td>13</td>
<td>6 1</td>
<td>1</td>
<td>( \nu_{\text{CC}} )</td>
<td>( \text{C}<em>{\text{ring}}-\text{C}</em>{\text{ring}} ) stretching</td>
</tr>
<tr>
<td>14</td>
<td>1 12</td>
<td>1</td>
<td>( \nu_{\beta X} )</td>
<td>( \text{C}<em>{1}-\text{C}</em>{12} ) stretching</td>
</tr>
<tr>
<td>15</td>
<td>12 15</td>
<td>1</td>
<td>( \nu_{\text{R-COO}^2} )</td>
<td>( \text{C}<em>{12}-\text{C}</em>{15} ) stretching</td>
</tr>
<tr>
<td>16</td>
<td>15 16</td>
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<td>( \nu_{\text{C}-\text{O}} )</td>
<td>( \text{C}_{\text{O}} ) stretching</td>
</tr>
<tr>
<td>17</td>
<td>15 17</td>
<td>1</td>
<td>( \nu_{\text{C}-\text{O}} )</td>
<td>( \text{C}_{\text{O}} ) stretching</td>
</tr>
<tr>
<td>18</td>
<td>6 2 1</td>
<td>2</td>
<td>( \alpha_{\text{CCC}} )</td>
<td>( \text{C}_{\text{C}}-\text{C} ) ring angle bending</td>
</tr>
<tr>
<td>19</td>
<td>1 3 2</td>
<td>2</td>
<td>( \alpha_{\text{CCC}} )</td>
<td>( \text{C}_{\text{C}}-\text{C} ) ring angle bending</td>
</tr>
<tr>
<td>20</td>
<td>2 4 3</td>
<td>2</td>
<td>( \alpha_{\text{CCC}} )</td>
<td>( \text{C}_{\text{C}}-\text{C} ) ring angle bending</td>
</tr>
<tr>
<td>Int. crd. no.</td>
<td>Atoms involved</td>
<td>Code no.</td>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------</td>
<td>----------</td>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>21</td>
<td>3 5 4</td>
<td>2</td>
<td>(a_{CCC})</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>4 6 5</td>
<td>2</td>
<td>(a_{CCC})</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>5 1 6</td>
<td>2</td>
<td>(a_{CCC})</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>12 6 2 1</td>
<td>5</td>
<td>(\beta_{\phi X})</td>
<td>(C_1-C_{12}) bending with respect to the external bisector of the ring angle</td>
</tr>
<tr>
<td>25</td>
<td>7 1 3 2</td>
<td>5</td>
<td>(\beta_{CH})</td>
<td>(C_{ring-H_{ring}}) bending</td>
</tr>
<tr>
<td>26</td>
<td>8 2 4 3</td>
<td>5</td>
<td>(\beta_{CH})</td>
<td>with respect to the external bisector of the ring angle</td>
</tr>
<tr>
<td>27</td>
<td>9 3 5 4</td>
<td>5</td>
<td>(\beta_{CH})</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>10 4 6 5</td>
<td>5</td>
<td>(\beta_{CH})</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>11 5 1 6</td>
<td>5</td>
<td>(\beta_{CH})</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>13 15 12</td>
<td>2</td>
<td>(a_{H_\alpha CC})</td>
<td>(H_\alpha-C_{12}-C_{15}) or</td>
</tr>
<tr>
<td>31</td>
<td>15 14 12</td>
<td>2</td>
<td>(a_{H_\alpha CC})</td>
<td>(H_\alpha-C_{12}-C_1) bending</td>
</tr>
<tr>
<td>32</td>
<td>14 1 12</td>
<td>2</td>
<td>(a_{H_\alpha CC})</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>1 13 12</td>
<td>2</td>
<td>(a_{H_\alpha CC})</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>15 1 12</td>
<td>2</td>
<td>(a_{C_1 C_{12} C_{15}})</td>
<td>(C_1-C_{12}-C_{15}) bending</td>
</tr>
<tr>
<td>35</td>
<td>13 14 12</td>
<td>2</td>
<td>(a_{H_\alpha CH_\alpha})</td>
<td>(H_\alpha-C_{12}-H_\alpha) bending (locally redundant)</td>
</tr>
<tr>
<td>36</td>
<td>12 16 17 15</td>
<td>5</td>
<td>(\beta_{R-COO2})</td>
<td>(R-COO^-) bending</td>
</tr>
<tr>
<td>37</td>
<td>16 17 15</td>
<td>2</td>
<td>(\alpha_{OCO})</td>
<td>(O-C-O) bending</td>
</tr>
<tr>
<td>38</td>
<td>12 6 2 1</td>
<td>3</td>
<td>(\gamma_{\phi X})</td>
<td>(C_1-C_{12}) out-of-plane wagging</td>
</tr>
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</table>
Table 20.3.2 (continued).

<table>
<thead>
<tr>
<th>Int. crd. no.</th>
<th>Atoms involved</th>
<th>Code(^1) no.</th>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
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<td>C(<em>{\text{ring}})-H(</em>{\text{ring}}) out-of-plane wagging</td>
</tr>
<tr>
<td>40</td>
<td>8 2 4 3</td>
<td>3</td>
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<td></td>
</tr>
<tr>
<td>41</td>
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<td>3</td>
<td>(\gamma_{CH})</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>10 4 6 5</td>
<td>3</td>
<td>(\gamma_{CH})</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>11 5 1 6</td>
<td>3</td>
<td>(\gamma_{CH})</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>12 16 17 15</td>
<td>3</td>
<td>(\gamma_{R-COO}^2)</td>
<td>R-COO(^-) out-of-plane wagging</td>
</tr>
<tr>
<td>45</td>
<td>6 1 2 3</td>
<td>4</td>
<td>(\delta_{CC})</td>
<td>Torsion around C(<em>{\text{ring}})-C(</em>{\text{ring}}) bond</td>
</tr>
<tr>
<td>46</td>
<td>1 2 3 4</td>
<td>4</td>
<td>(\delta_{CC})</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>2 3 4 5</td>
<td>4</td>
<td>(\delta_{CC})</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>3 4 5 6</td>
<td>4</td>
<td>(\delta_{CC})</td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>4 5 6 1</td>
<td>4</td>
<td>(\delta_{CC})</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>5 6 1 2</td>
<td>4</td>
<td>(\delta_{CC})</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>13 12 1 2</td>
<td>4</td>
<td>(\delta_{\phi X})</td>
<td>Torsion around C(<em>1)-C(</em>{12}) bond</td>
</tr>
<tr>
<td>52</td>
<td>14 12 1 6</td>
<td>4</td>
<td>(\delta_{\phi X})</td>
<td>(locally redundant)</td>
</tr>
<tr>
<td>53</td>
<td>17 15 12 13</td>
<td>4</td>
<td>(\delta_{R-COO}^2)</td>
<td>Torsion around C(<em>{15})-C(</em>{12}) bond</td>
</tr>
<tr>
<td>54</td>
<td>16 15 12 14</td>
<td>4</td>
<td>(\delta_{R-COO}^2)</td>
<td>(locally redundant)</td>
</tr>
</tbody>
</table>

Notes. 1. This number corresponds to the code no. shown in subsection 16.3.

2. R : \(\text{C}_6\text{H}_5\text{CH}_2\)
Table 20.3.3. The calculated frequencies of vibrations of phenylacetate ion.

<table>
<thead>
<tr>
<th>No.</th>
<th>Calculated frequency</th>
<th>Observed frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wave number cm(^{-1})</td>
<td>Approximate description(^2)</td>
</tr>
<tr>
<td></td>
<td>3076 (\nu_{CH}(98))</td>
<td>(Potential energy, distribution) (%):</td>
</tr>
<tr>
<td>1</td>
<td>3073 (\nu_{CH}(95))</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3071 (\nu_{CH}(98))</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3002 (\nu_{CH\alpha}(98))</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Calculated frequency</td>
<td>Wave number cm(^{-1})</td>
</tr>
<tr>
<td>-----</td>
<td>----------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>13</td>
<td>1498 ν(<em>{CC})(22), β(</em>{CH})(32)</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1481 ν(<em>{CC})(10), ν(</em>{O_X})(23), ν(_{C_O})(17), (β_CH)(18)</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1372 ν(_{CC})(38), (β_CH)(20)</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>1338 ν(_{CC})(12), (β_CH)(14), (α_H_CC)(42)</td>
<td>Ac 1341 1</td>
</tr>
<tr>
<td>17</td>
<td>1326 ν(_{CC})(13), (β_CH)(26), (α_H_CC)(16)</td>
<td>Ac 1333 3</td>
</tr>
<tr>
<td>18</td>
<td>1231 (α_H_CC)(62)</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>1212 ν(<em>{CC})(17), ν(</em>{O_X})(16), (β_CH)(22)</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1191 (β_CH)(77)</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>1158 ν(_{CC})(16), (β_CH)(49)</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>1124 ν(<em>{CC})(21), (β_CH)(26), γ(</em>{R_COO})(11)</td>
<td>Ac 1046 1</td>
</tr>
<tr>
<td>23</td>
<td>1083 ν(<em>{CC})(19), (β_CH)(12), γ(</em>{R_COO})(34)</td>
<td>Ac 1045 2</td>
</tr>
<tr>
<td>24</td>
<td>1032 ν(_{CC})(47)</td>
<td></td>
</tr>
</tbody>
</table>

\(^2\) Approximate description includes potential energy and distribution of the modes.

\(^3\) Type of spectrum includes IR (infrared) or other types as noted.
<table>
<thead>
<tr>
<th>No.</th>
<th>Calculated frequency</th>
<th>Observed frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wave number cm⁻¹</td>
<td>Approximate description (%)</td>
</tr>
<tr>
<td>25</td>
<td>1010</td>
<td>( \gamma_{\text{CH}} (37) )</td>
</tr>
<tr>
<td>26</td>
<td>999</td>
<td>( \nu_{\text{CC}} (25), a_{\text{CCC}} (24) )</td>
</tr>
<tr>
<td>27</td>
<td>984</td>
<td>( \gamma_{\text{CH}} (58) )</td>
</tr>
<tr>
<td>28</td>
<td>974</td>
<td>( \gamma_{\text{CH}} (19) )</td>
</tr>
<tr>
<td>29</td>
<td>930</td>
<td>( a_{\text{H}, \text{CC}} (11), \gamma_{\text{CH}} (32) )</td>
</tr>
<tr>
<td>30</td>
<td>856</td>
<td>( \nu_{\text{R-COO}} (23), \nu_{\text{C-O}} (30) )</td>
</tr>
<tr>
<td>31</td>
<td>835</td>
<td>( \gamma_{\text{CH}} (80) )</td>
</tr>
<tr>
<td>32</td>
<td>796</td>
<td>( \gamma_{\text{CH}} (13), \gamma_{\text{CH}} (16), \delta_{\text{CC}} (10) )</td>
</tr>
<tr>
<td>33</td>
<td>762</td>
<td>( a_{\text{CCC}} (14), \gamma_{\text{CH}} (11) )</td>
</tr>
<tr>
<td>34</td>
<td>695</td>
<td>( \gamma_{\text{CH}} (24), \delta_{\text{CC}} (19) )</td>
</tr>
<tr>
<td>35</td>
<td>610</td>
<td>( \nu_{\text{CC}} (10), a_{\text{CCC}} (52) )</td>
</tr>
<tr>
<td>36</td>
<td>599</td>
<td>( a_{\text{OCO}} (16), \gamma_{\text{CH}} (11), \delta_{\text{CC}} (22) )</td>
</tr>
</tbody>
</table>
Table 20.3.3 (continued)

<table>
<thead>
<tr>
<th>No.</th>
<th>Calculated frequency</th>
<th>Wave number</th>
<th>Approximate description² (Potential energy, distribution)</th>
<th>Wave number</th>
<th>Observed frequency</th>
<th>Ref.</th>
<th>Type³</th>
<th>The state of the compound</th>
<th>Assignment of spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td>549</td>
<td>α_{CC}(14), β_{R-COO}(13), δ_{CC}(11)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>508</td>
<td>β_{R-COO}(13), δ_{CC}(14)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>473</td>
<td>α_{CC}(15), γ_{θX}(10), δ_{CC}(17)</td>
<td>Ac 465</td>
<td>499</td>
<td>2</td>
<td>IR</td>
<td></td>
<td>Solid sodium acetate</td>
<td>γ_{R-COO}</td>
</tr>
<tr>
<td>40</td>
<td>398</td>
<td>γ_{CH}(13), δ_{CC}(40)</td>
<td>Pr 499</td>
<td>3</td>
<td>R</td>
<td></td>
<td></td>
<td>Conc. aq. soln. of sodium propionate</td>
<td>γ_{R-COO}</td>
</tr>
<tr>
<td>41</td>
<td>345</td>
<td>β_{θX}(31), β_{R-COO}(25)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>245</td>
<td>δ_{CC}(36)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>128</td>
<td>α_{H_{CC}}(11), α_{C_{1}C_{12}C_{15}}(19), δ_{R-COO}(20)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>115</td>
<td>α_{H_{CC}}(13), α_{C_{1}C_{12}C_{15}}(12), δ_{R-COO}(25)</td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>45</td>
<td>67</td>
<td>δ_{θX}(74)</td>
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</tbody>
</table>
Table 20.3.3. (continued)

Notes. 1. The "Potential energy distribution" is given in per cent contribution to $\lambda$ by the diagonal force constants of the respective coordinates. Only contributions equal to, or greater than 10 per cent were included in this table.

2. The symbols used to describe the types of coordinates were defined in table 20.3.2.

3. IR: infrared spectrum; R - Raman spectrum

4. Ac: acetate ion; Pr: propionate ion


Table 20.3.4. The calculated vibrational frequencies of phenylacetate-α-d₂ ion.

<table>
<thead>
<tr>
<th>No.</th>
<th>Wave number cm⁻¹</th>
<th>Frequency Approximate description² (Potential energy distribution¹) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3076</td>
<td>νₐ₈ (98)</td>
</tr>
<tr>
<td>2</td>
<td>3074</td>
<td>νₐ₈ (99)</td>
</tr>
<tr>
<td>3</td>
<td>3073</td>
<td>νₐ₈ (98)</td>
</tr>
<tr>
<td>4</td>
<td>3072</td>
<td>νₐ₈ (98)</td>
</tr>
<tr>
<td>5</td>
<td>3071</td>
<td>νₐ₈ (98)</td>
</tr>
<tr>
<td>6</td>
<td>2290</td>
<td>νₐ₈ (96)</td>
</tr>
<tr>
<td>7</td>
<td>2197</td>
<td>νₐ₈ (95)</td>
</tr>
<tr>
<td>8</td>
<td>1694</td>
<td>νₐ₈ (48)</td>
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<tr>
<td>9</td>
<td>1681</td>
<td>νₐ₈ (48)</td>
</tr>
<tr>
<td>10</td>
<td>1598</td>
<td>νₐ₈ (70)</td>
</tr>
<tr>
<td>11</td>
<td>1525</td>
<td>νₐ₈ (21), β₈ (32)</td>
</tr>
<tr>
<td>12</td>
<td>1496</td>
<td>νₐ₈ (23), β₈ (33)</td>
</tr>
<tr>
<td>13</td>
<td>1476</td>
<td>νₐ₈ (11), νₐ₈ (22), νₐ₈ (18), ν₈ (20)</td>
</tr>
<tr>
<td>14</td>
<td>1370</td>
<td>νₐ₈ (40), β₈ (18)</td>
</tr>
<tr>
<td>15</td>
<td>1328</td>
<td>νₐ₈ (21), β₈ (41)</td>
</tr>
<tr>
<td>16</td>
<td>1239</td>
<td>νₐ₈ (20), ν₈ (26)</td>
</tr>
<tr>
<td>17</td>
<td>1192</td>
<td>β₈ (78)</td>
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<tr>
<td>18</td>
<td>1166</td>
<td>β₈ (58)</td>
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</table>
Table 20.3.4. (continued)

<table>
<thead>
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</thead>
<tbody>
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<td>Wave number $\text{cm}^{-1}$</td>
</tr>
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<td>24</td>
<td>1007</td>
</tr>
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<td>25</td>
<td>993</td>
</tr>
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<td>26</td>
<td>984</td>
</tr>
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<td>28</td>
<td>887</td>
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<td>604</td>
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<tr>
<td>37</td>
<td>523</td>
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<td>38</td>
<td>468</td>
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</tbody>
</table>
Table 20.3.4 (continued)

<table>
<thead>
<tr>
<th>No.</th>
<th>Wave number cm(^{-1})</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Approximate description(^2) (Potential energy distribution(^1)) (%)</td>
</tr>
<tr>
<td>39</td>
<td>450</td>
<td>(\alpha_{\text{CCC}}(18), \beta_{\text{O}}(13), \delta_{\text{R-COO}}(10))</td>
</tr>
<tr>
<td>40</td>
<td>398</td>
<td>(\gamma_{\text{CH}}(13), \delta_{\text{CC}}(40))</td>
</tr>
<tr>
<td>41</td>
<td>341</td>
<td>(\beta_{\text{O}}(33), \beta_{\text{R-COO}}(21))</td>
</tr>
<tr>
<td>42</td>
<td>244</td>
<td>(\delta_{\text{CC}}(36))</td>
</tr>
<tr>
<td>43</td>
<td>127</td>
<td>(\gamma_{\text{CH}}(12), \alpha_{\text{C}_1\text{C}_2\text{C}<em>3}(19), \delta</em>{\text{R-COO}}(20))</td>
</tr>
<tr>
<td>44</td>
<td>114</td>
<td>(\gamma_{\text{CH}}(14), \delta_{\text{R-COO}}(26))</td>
</tr>
<tr>
<td>45</td>
<td>66</td>
<td>(\delta_{\text{O}}(75))</td>
</tr>
</tbody>
</table>

Notes. 1. The "Potential energy distribution" is given in per cent contribution to \(\lambda\) by the diagonal force constants of the respective coordinates. Only contributions equal to, or greater than 10 per cent were included in this table.

2. The symbols used to indicate the internal coordinates were defined in table 20.3.2 and subsection 20.3.
20.4 The secondary deuterium isotope effects in phenylacetic acid - phenylacetic-α-d₂ system.

In subsection 9.5, we obtained the dissociation constants and the thermodynamic functions for the ionization of phenylacetic and phenylacetic-α-d₂ acids in aqueous solutions in the temperature range of 20 to 40°C. The experimental ratio $K_H/K_D$ was found to be $1.009 \pm 0.002$ at 50% confidence level.

In this subsection, we tried to reproduce the experimental value by using relation 18.1.1. To accomplish this, the vibrational frequencies of phenylacetate and phenylacetate-α-d₂ ions were calculated, using several different sets of force constants. In the first instance, we found, by trial and error, a set of force constants which gave a reasonably good agreement between the calculated frequencies for the phenylacetate anion and some observed frequencies of the acetate ion. The frequencies of the acetate ion to which we referred were those assigned to internal coordinates which are changed very little by the substitution of a hydrogen atom, in the methyl group, by a phenyl group. We compared the calculated frequencies of the phenylacetic ion with those of the acetate ion because no vibrational analysis was available in the literature for the former ion. The same
force constants adjusted by the proper scaling factors
(where this was required) were then used to calculate the
vibrational frequencies of the phenylacetic-α-d_2 ion.
These force constants are given in set no. 1 of table 20.4.1
and the actual vibrational frequencies calculated from them
are given in tables 20.3.3 and 20.3.4.

We have shown in the benzoic acid system (section
18) that an increase in the force constants in going from the
acid to the anion lead to a calculated $K_H/K_D$ ratio which was
in a good agreement with the experimental value. The
increase in the force constants was attributed to the
tighter solvation or stronger solute-solvent interactions in
the anion state, although other causes might contribute to
this increase. We used the same approach here. The force
constants corresponding to the internal coordinates of the
carboxylate group and of those bonds which are in its immediate
vicinity, i.e. those involving the α-carbon, α-hydrogen, and
α-deuterium atoms were increased by various amounts in sets
1 to 5 (see table 20.4.1).

In sets no. 3 and 4, a second approximation was used.
The approximation was similar to that used in the two previous
systems analysed, i.e. the force constants in the deuterated
anion were increased by a slightly smaller amount than those
of the undeuterated anion. In the case of the benzoic acid
and o-toluic acid systems, we rationalized this assumed difference as being a result of the smaller polarizability and the shorter carbon-deuterium bonds as compared with the carbon-hydrogen bonds. The differences between the force constants of the deuterated and undeuterated anions in these systems were of the order of 0.5%. In the case of the phenylacetate ion any difference which might exist between the interactions of the two anions and the solvent water molecules would be minimized because the isotopic bonds, i.e. Cα-Hα and Cα-Dα, are in that region of the carboxylate group (back) which is probably least affected by solvation. Thus, in this system, the differences between the force constants of the two anions were smaller; they were of the order of 0.1-0.2%. Set no. 4 gave the best agreement with the experimental K_H/K_D values. The calculated isotope effects were constants in the temperature range of 20 to 40°C, thus, being in good agreement with the experimental results. The "Detailed calculations" are given in 20.4.1.

In conclusion, it can be said that the calculations carried out in this system indicate that the experimental results obtained in subsection 9.5 can be reproduced if we assume that a very small difference (of the order of 0.1-0.2%) exists between the valence force constants of the two isotopic
anions in aqueous solution. Such a difference can be due, for example, to the different solute-solvent interactions which are caused by the differences in length and polarizability between carbon-hydrogen and carbon-deuterium bonds.
Table 20.4.1. The elements of the F matrices of phenylacetate and phenylacetate-α - d₄ anions and the corresponding calculated K₆/K₅ isotope effects.

<table>
<thead>
<tr>
<th>Internal coordinate</th>
<th>In the acids</th>
<th>In the anions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PhAc A⁵⁺</td>
<td>PhAc A⁵⁻</td>
</tr>
<tr>
<td>νCH(D)x</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>βR-CO</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>αK(D)CH(C)h</td>
<td>0.58</td>
<td>0.59</td>
</tr>
<tr>
<td>αK(D)CH(C)k</td>
<td>0.29</td>
<td>0.29</td>
</tr>
<tr>
<td>αK(D)CH(C)l</td>
<td>0.55</td>
<td>0.56</td>
</tr>
<tr>
<td>αK(D)CH(C)r</td>
<td>0.29</td>
<td>0.29</td>
</tr>
<tr>
<td>αK(D)CH(C)s</td>
<td>0.39</td>
<td>0.39</td>
</tr>
<tr>
<td>αK(D)CH(C)t</td>
<td>0.470</td>
<td>0.477</td>
</tr>
<tr>
<td>βR-COO</td>
<td>0.800</td>
<td>0.800</td>
</tr>
<tr>
<td>αOCO</td>
<td>0.750</td>
<td>0.750</td>
</tr>
<tr>
<td>αQX</td>
<td>0.400</td>
<td>0.400</td>
</tr>
<tr>
<td>αQ-COO</td>
<td>0.420</td>
<td>0.420</td>
</tr>
<tr>
<td>αR-CO</td>
<td>0.050</td>
<td>0.050</td>
</tr>
<tr>
<td>αR-COO</td>
<td>0.100</td>
<td>0.100</td>
</tr>
</tbody>
</table>

VP (298,15°C)°      | 1.007      | 1.017      | 1.067      | 1.044      | 1.027      |
EXP (298,15°C)°      | 0.994      | 0.994      | 0.984      | 0.985      | 0.986      |
ZPE (298,15°C)°      | 1.000      | 0.985      | 0.970      | 0.979      | 0.985      |

Total isotope effects (298.15°C)°: 1.009a

1.001  0.995  1.018  1.006  0.997

Notes:

a. Isotope effects obtained experimentally in the present work.

b. The diagonal force constants corresponding to the internal coordinates not shown in this table and all off-diagonal force constants were identical to those of phenylactic and phenylactic-α - d₄ acids (Table 20.2.3).

c. PhAc A(H): phenylactic acid; PhAc A(D): phenylactic-α - d₄ acid; PhAc (H): phenylacetic ion; PhAc (D): phenylacetic-α - d₄ ion.

d. The first number represents the coordinate number in the acids (Table 20.2.2) and the second number (in parentheses) the coordinate number in the anions (Table 20.3.2). Although in a physical sense all these coordinates are identical their values appear to be different because different scaling factors were used.

e. Calculated from relations (18.1.3), (18.1.4), and (18.1.5).
Future work.

A series of assumptions made in this thesis can and should be checked by experimental work.

The first assumption which should be checked is that the limiting conductances of the undeuterated and deuterated anions are equal.

More detailed vibrational analyses should be carried out in some of the systems analysed here, or indeed any similar system, to see how "real" the changes are in the force constants assumed in the present work. When time permits the analyses of the mesitoic acids should also be undertaken, to see whether the assumptions employed in the \( o \)-toluic acid system can be extended to the doubly \( o \)-substituted case.

To complete the data for this system one should measure the dissociation constant of deuterated \( m \)- and \( p \)-toluic acids. Finally the measurement of the dissociation constant of toluic acids deuterated at the methyl groups only should provide more light and an interesting check of the assumptions made in this work.
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318. W. Kauzmann, ref. 170, p. 484ff.
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C THIS PROGRAM CALCULATES THE REAL PART OF A CELL IMPEDANCE FROM
C ARBITRARILY CHOSEN VALUES FOR RSOLN, RF, CO AND CDL.
C FEATES, IVES AND PRYOR'S EQUIVALENT CELL CIRCUIT.
DIMENSION F(5),WCT(5),REZXW(5)

REWIND 2
READ 1, N
WRITE (2) N

1 FORMAT (13,6((1X,E7.4)))
PI = 3.14159
F(1) = 1000, *2, *PI
F(2) = 2000, *2, *PI
F(3) = 3500, *2, *PI
F(4) = 5000, *2, *PI
F(5) = 10000, *2, *PI
PRINT 5

DO 2 M = 1, N
READ 1, M, RSOLN, RF, CO, CDL
WRITE (2) RSOLN, RF, CDL
PRINT 6

DO 3 MM = 1, 5
REZX = RSOLN * RF / (1.0 *(F(MM) * CDL * RF) ** 2)
REZX2 = RSOLN / (1.0 *(F(MM) * CO * RSOLN) ** 2)
AUX1 = (CDL * RF * CO * RF) ** 2 * RSOLN / (CDL * CO * (2.0 * RF * RSOLN)) ** 2

2 AUX2 = (CO * CDL * RF * RSOLN) ** 2 */ (F(MM) ** 4)
REZX = AUX / (1.0, * AUX1 + AUX2)
PRINT 4, M, F(MM), RSOLN, RF, CDL, REZX1, REZX2, REZX
CONTINUE

3 FORMAT (1H,13,4X,F6,0,5X,4(E8,1,3X),2X,3(E14,7,3X))
4 FORMAT (1HO)

C GRAHAM'S EQUIVALENT CIRCUIT

REWIND 2
READ (2) N
PRINT 6
PRINT 9
PRINT 12
DO 7 M = 1, N
READ (2) RSOLN, RF, CDL
PRINT 6

DO 8 MM = 1, 5
WCT(M1) = 0.1 *(10.0 * (M1-1))
AUX1 = (F(MM) * CDL * RF / WCT(M1) / SORT(F(MM))) ** 2
AUX1 = (F(MM) * CDL * RF / WCT(M1) / SORT(F(MM))) ** 2
10 REZXW(M1) = RSOLN * (RF + WCT(M1) / SORT(F(MM))) / (AUX + AUX1)
8 PRINT 11, M, F(MM), RSOLN, RF, CDL, (REZXW(M1), M1=1, 5)
7 CONTINUE

9 FORMAT (9X,"FREQ","8X,"RSOLN","7X,"RF","9X,"CDL","36X,"REZXW")
11 FORMAT (1H,13,4X,F6,0,5X,3(E8,1,3X),2X,5(E12,5,2X))
12 FORMAT (1HO,55X,"WCT = 0","1","6X,"WCT = 1","10","6X,"WCT = 100")
Appendix 3.3.1. Notes

The symbols used in the computer program relate to the symbols used in the text in the following way:

<table>
<thead>
<tr>
<th>Computer symbol</th>
<th>Text symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>FREQ</td>
<td>$\omega$ - the frequency in sec$^{-1}$ ($\omega = 2\pi f$)</td>
</tr>
<tr>
<td>RSOLN</td>
<td>$R_{soln}$</td>
</tr>
<tr>
<td>RF</td>
<td>$R_F$</td>
</tr>
<tr>
<td>CO</td>
<td>$C_0$</td>
</tr>
<tr>
<td>CDL</td>
<td>$C_{dl}$</td>
</tr>
<tr>
<td>REZX1</td>
<td>Re($Z_x$) calculated from 3.3.6</td>
</tr>
<tr>
<td>REZX2</td>
<td>Re($Z_x$) calculated from 3.3.8</td>
</tr>
<tr>
<td>REZX</td>
<td>Re($Z_x$) calculated from 3.3.4</td>
</tr>
<tr>
<td>REZW</td>
<td>Re($Z_x$) calculated from 3.3.13</td>
</tr>
<tr>
<td>WCT</td>
<td>$\eta$ - the constant of Hartburg impedance</td>
</tr>
</tbody>
</table>
DO 5 K7 = 1,10
DIMENSION TEMP(10),Y1(10),X1(10),XX(10,10),YY(10),COEFF(10),Y2(10)
DIMENSION DIF(10)
M1 = 5
READ 1, M
1 FORMAT(12)
   DO 2 L = 1, M
      READ 3, TEMP(L), Y1(L)
   2 X1(L) = TEMP(L) - 20.
3 FORMAT (6(3X, 13.6))
   DO 5 M2 = 2, M1
   DO 6 L = 1, M2
   DO 6 J = 1, M2
       SUM = 0.
       SUM1 = 0.
   DO 6 K = 1, M
       J1 = J + L - 2
       SUM = SUM + X1(K)**J1
       XX(L,J) = SUM
   IF (J-1)6,7,6
   7 L1 = L - 1
       SUM1 = SUM1 + (X1(K)**L1)*Y1(K)
       YY(L) = SUM1
6 CONTINUE
   CALL EQUAT(XX, YY, COEFF, M2)
   SUM3 = 0.
   DO 9 L = 1, M
       SUM2 = 0.
   DO 10 J = 1, M2
   10 SUM2 = SUM2 + COEFF(J)*(X1(L)**(J-1))
      Y2(L) = SUM2
      DIF(L) = Y1(L) - Y2(L)
   PRINT 3, TEMP(L), Y1(L), Y2(L), DIF(L)
   SUM3 = SUM3 + DIF(L)**2
9 CONTINUE
   AM = M
   DEV = (SUM3/(AM - 1.))**0.5
   PRINT 4, DEV
4 FORMAT (1H ,12HDEVIATION = E15.8)
5 CONTINUE
   CALL EXIT
END
DO 5 M7 = 1,10
DIMENSION TEMP(10), Y1(10), X1(10), XX(10,10), YY(10), COEFF(10), Y2(10)
DIMENSION DIF(10)
M1 = 5
READ 1, M
1 FORMAT (I2)
DO 2 L = 1, M
READ 3, TEMP(L), Y1(L)
2 X1(L) = 1./(TEMP(L) - 20.)
3 FORMAT (6(3XE15.6))
   R = A + B/(T-20)
   R = A + B/(T-20) + ... + E/(T-20)²
DO 5 M2 = 2, M1
DO 6 L = 1, M2
DO 6 J = 1, M2
SUM = 0.
SUM1 = 0.
SUM = SUM + X1(K)**J1
XX(L,J) = SUM
IF (J < 1) 6, 7, 6
7 L1 = L - 1
SUM1 = SUM1 + (X1(K)**L1)*Y1(K)
YY(L) = SUM1
6 CONTINUE
CALL EQUAT(XX, YY, COEFF, M2)
SUM3 = 0.
DO 9 L = 1, M
SUM2 = 0.
DO 10 J = 1, M2
SUM2 = SUM2 + COEFF(J)*(X1(L)**(J-1))
Y2(L) = SUM2
10 DIF(L) = Y1(L) - Y2(L)
PRINT 3, TEMP(L), Y1(L), Y2(L), DIF(L)
SUM3 = SUM3 + DIF(L)*DIF(L)
9 CONTINUE
AM = M
DEV = (SUM3/(AM - 1.))**0.5
PRINT 4, DEV
4 FORMAT (1H, 12HDEVIAITION = E15.8)
5 CONTINUE
CALL EXIT
END
DIMENSION TEMP(10),RES(10),XX(10),ZZ(10),YY(10),A(10,10),B(10)
DIMENSION X(10),RES2(10),DIF(10)
DO 13 M = 1,10
READ 1,M
1 FORMAT(12)
DO 2 L = 1,M
READ 3,TMP(L),RES(L)
XX(L) = 1./((TMP(L) - 20.)
ZZ(L) = LOGF(TMP(L) - 20.)
YY(L) = LOGF(RES(L))
2 CONTINUE
3 FORMAT(6(3XE13.6))
SY = 0.
SX = 0.
SYX = 0.
SXX = 0.
DO 4 N = 1,M
SY = SY + YY(N)
SX = SX + XX(N)
SYX = SYX + YY(N)*XX(N)
4 SXX = SXX + XX(N)**2
M1 = 2
10 A(1,1) = M
A(1,2) = SX
A(2,1) = SX
A(2,2) = SXX
B(1) = SY
B(2) = SYX
CALL EQUAT(A,B,X,M1)
SUM = 0.
DO 5 N = 1,M
IF(M1 - 2)6,9,8
9 Y2 = X(1) + X(2)*XX(N)
GO TO 12
8 Y2 = X(1) + X(2)*XX(N) + X(3)*ZZ(N)
12 RES2(N) = EXPF(Y2)
DIF(N) = RES(N) - RES2(N)
PRINT 3,TMP(N),RES(N),RES2(N),DIF(N)
5 SUM = SUM + DIF(N)**2
AM = M
DEV = (SUM/(AM - 1.))**0.5
PRINT 6,DEV
6 FORMAT(1H,17HMEAN DEVIATION = E15.8)
IF(M1 - 2)13,14,13
14 SYZ = 0.
SXZ = 0.
SZZ = 0.
SZ = 0.
DO 7 N = 1,M
SYZ = SYZ + YY(N)*ZZ(N)
SXZ = SXZ + XX(N)*ZZ(N)
SZZ = SZZ + ZZ(N)**2
7 SZ = SZ + ZZ(N)
A(1,3) = SZ
A(2,3) = SXZ
A(3,1) = SZ
EQUATIONS:
ln(R) = A + B/(T-20)
ln(R) = A + B/(T-20) + Cln(T-20)
\[ A(3,2) = SXZ \]
\[ A(3,3) = SZZ \]
\[ B(3) = SYZ \]
\[ M1 = 3 \]
\[ \text{GO TO 10} \]
13 CALL EXIT
END

```
00003 0001
00007 0010
00017 10000000-1
00027 20000000-2
00037 00000000000
00041 0002
00051 50000000-0
00055 0003
00065 TEMP 00155 00165 RES 00255 00265 XX 00355 00365 ZZ 004
01565 B 01655 01665 X 01755 01765 RES2 01855 01865 DIF 019
01967 L 01977 SY 01987 SX 01997 SYX
02015 M1 02025 SUM 02035 Y2 02045 AM
02075 SXZ 02085 SZZ 02095 SZ 02100 EQUAT

0013 05614 0001 02156 0002 02746 0003 02788 0004 03226 0010 03370 0005
0009 03662 0012 03940 0006 04708 0014 04850 0007 05330

05678 CORES USED
39999 NEXT COMMON
END OF COMPILATION
```

MAIN 14300 05678 LOADED
EQUAT 19976 02738 LOADED
03 22716 00510 LOADED
02 23226 01158 LOADED
01 24384 00850 LOADED
DIMENSION TEMP(10), RES(10), XX(10), ZZ(10), YY(10), A(10, 10), B(10)
DIMENSION X(10), RES2(10), DIF(10)
DO 15 M = 1, 10
READ 1, H
1 FORMAT (I2)
DO 2 L = 1, M
READ 3, TEMP(L), RES(L)
XX(L) = LOGF(TEMP(L) - 20.)
ZZ(L) = 1./(TEMP(L) - 20.)
YY(L) = RES(L)
2 CONTINUE
3 FORMAT (6(3XE13.6))
SY = 0.
SX = 0.
SYX = 0.
SXX = 0.
DO 4 N = 1, M
SY = SY + YY(N)
SX = SX + XX(N)
SYX = SYX + YY(N)*XX(N)
SXX = SXX + XX(N)**2
4 M1 = 2
10 A(1, 1) = M
A(1, 2) = SX
A(2, 1) = SX
A(2, 2) = SXX
B(1) = SY
B(2) = SYX
CALL EQUAT(A, B, X, M1)
SUX = 0.
DO 5 N = 1, M
IF(M1 - 2)8, 9, 8
9 Y2 = X(1) + X(2)*XX(N)
GO TO 12
8 Y2 = X(1) + X(2)*XX(N) + X(3)*ZZ(N)
12 RES2(N) = Y2
DIF(N) = RES(N) - RES2(N)
PRINT 3, TEMP(N), RES(N), RES2(N), DIF(N)
5 SUM = SUM + DIF(N)**2
AM = M
DEV = (SUX/(AM - 1.))**0.5
PRINT 6, DEV
6 FORMAT (1H1, 17HMEAN DEVIATION = E15.8)
IF(M1 - 2)15, 14, 15
14 SYZ = 0.
SXZ = 0.
SZZ = 0.
DO 7 N = 1, M
SYZ = SYZ + YY(N)*ZZ(N)
SXZ = SXZ + XX(N)*ZZ(N)
SZZ = SZZ + ZZ(N)**2
7 SZ = SZ + ZZ(N)
A(1, 3) = SZ
A(2, 3) = SXZ
A(3, 1) = SZ
Equations:
R = A + B ln(T - 20)
R = A + B ln(T - 20) + C/(T - 20)
A(3,2) = SXZ
A(3,3) = SZZ
B(3) = SYZ
M1 = 3
GO TUR 10
15 CONTINUE
CALL EXIT
END

00003 0001
00007 0010
00017 20000000-2
00027 10000000-1
00037 00000000RR
00041 0002
00051 50000000-0
00055 0003
00065 TEMP 00155 00165 RES 00255 00265 XX 00355 00365 ZZ 00455
01565 B 01655 01665 X 01755 01765 RES2 01855 01865 DIF 01955
01967 L 01977 SY 01987 SX 01997 SYX
02015 M1 02025 SUM 02035 YZ 02045 AM
02075 SXZ 02085 SZZ 02095 SZ 02100 EQUAT
DIMENSION TEMP(10),RES(10),XX(10),ZZ(10),YY(10),A(10,10),B(10)
DIMENSION X(10),RES2(10),DIF(10)
DO 15 M = 1,10
READ 1,M
1 FORMAT(12)
DO 2 L = 1,M
READ 3,TEMP(L),RES(L)
XX(L) = 1./(TEMP(L) - 20.)
ZZ(L) = LOGF(TEMP(L) - 20.)
YY(L) = LOGF(1./RES(L))
2 CONTINUE
3 FORMAT (6(3XE13.6))
SY = 0.
SX = 0.
SYX = 0.
SXX = 0.
DO 4 N = 1,M
SY = SY + YY(N)
SX = SX + XX(N)
SYX = SYX + YY(N)*XX(N)
4 SXX = SXX + XX(N)**2
M1 = 2
10 A(1,1) = M
A(1,2) = SX
A(2,1) = SX
A(2,2) = SXX
B(1) = SY
B(2) = SYX
CALL EQUAT(A,B,X,M1)
SUM = 0.
DO 5 N = 1,M
IF(M1 - 2)8,9,8
5 SUM = SUM + DIF(N)**2
AM = M
DEV = (SUM/(AM - 1.))**0.5
PRINT 6,DEV
6 FORMAT (1H1,17HMEAN DEVIATION = E15.8)
IF(M1 - 2)15,14,15
9 Y2 = X(1) + X(2)*XX(N)
GO TO 12
8 Y2 = X(1) + X(2)*XX(N) + X(3)*ZZ(N)
12 RES2(N) = EXPF(-Y2)
DIF(N) = RES(N) - RES2(N)
PRINT 3,TEMP(N),RES(N),RES2(N),DIF(N)
5 SUM = SUM + DIF(N)**2
AM = M
DEV = (SUM/(AM - 1.))**0.5
PRINT 6,DEV
6 FORMAT (1H1,17HMEAN DEVIATION = E15.8)
IF(M1 - 2)15,14,15
14 SYZ = 0.
SXZ = 0.
SZZ = 0.
SZ = 0.
DO 7 N = 1,M
SYZ = SYZ + YY(N)*ZZ(N)
SXZ = SXZ + XX(N)*ZZ(N)
SZZ = SZZ + ZZ(N)**2
7 SZ = SZ + ZZ(N)
A(1,3) = SZ
A(2,3) = SXZ
A(3,1) = SZ
Equations:
\[ \ln(1/R) = A + B/(T-20) \]
\[ \ln(1/R) = A + B/(T-20) + C\ln(T-20) \]
A(3,2) = SXZ
A(3,3) = SZZ
B(3) = SYZ
M1 = 3
GO TO 10
15 CONTINUE
CALL EXIT
END

00003 0001
00007 0010
00017 10000000-1
00027 20000000-2
00037 00000000RR
00041 0002
00051 50000000-0
00055 0003
00065 TEMP 00155 00165 RES 00255 00265 XX 00355 00365 ZZ 00455
01565 B 01655 01665 X 01755 01765 RESZ 01855 01865 DIF 01955
01967 L 01977 SY 01987 SX 01997 SYX
02015 M1 02025 SUM 02035 Y2 02045 .AM
02075 SXZ 02085 SZZ 02095 SZ 02100 EQUAT
SUBROUTINE EQUAT(A,B,X,M)
DIMENSION A(10,10),b(10),X(10)
MM = M-1
UU 20 I1 = 1,MM
UU 20 K = I1,MM
N = K + 1
DD = A(N,I1)/A(I1,I1)
UU 50 J = I1,M
D = A(I1,J)*DD
30 A(N,J) = A(N,J) - D
b(N) = b(N) - b(I1)*DD
20 CONTINUE
X(M) = b(M)/A(M,M)
UU 50 L = 2,M
N = N+1-L
KK = N+1
X(N) = b(N)/A(N,N)
UU 50 K = KK,M
50 X(N) = X(N) - A(N,K)*X(K)/A(N,N)
UU 60 NK = 1,M
60 PRINT 101,NK,X(NK)
101 FORMAT (1H, 11HCOEFFICIENT, 2XI3, 5H = E15.8)
102 FORMAT (4(E15.8))
103 FORMAT (5(2XE15.8))
RETURN
END
CURVE DENSITY VS. GRAMS KCL/KGS. SOLUTION

TEMPERATURE = 20, 0, 10, 25, 30, 40
DIMENSION XX(20), YY(20), SX(40), SYX(20), DIFF(20), Y2(30), RT(20)
DIMENSION A(20, 20), B(I, 20), X(20)
DIMENSION X10(20), DEN(20)

PRINT 202.

202 FORMAT (1H0, 5X5HXX(N), 12X5HYY(N))
M2 = 14
DO 351 M7 = 1, 6
DO 10 N = 1, M2
READ 201, X10(N), YY(N)
XX(N) = X10(N) * X10
10 PRINT 201, XX(N), YY(N)

201 FORMAT (1F15.9, 2XF15.9, 2XF15.9)
M1 = M2 - 1
MIM = 2*M1
DO 210 NN = 1, MIM
SXI = 0.
DO 200 N = 1, M2
200 SXI = SXI + (XX(N) * NN)
210 SX(NN) = SXI
DO 230 NN = 1, M2
SYX = 0.
N1 = NN - 1
DO 220 N = 1, M2
220 SYX = SYX + YY(N) * (XX(N) * NN)
230 SYX(NN) = SYX
DO 351 M = 2, M2
DO 300 I = 1, M
300 J = I + J - 2
IF (JJ = 0) 310, 309, 310
309 A(I, 1) = M2
GU TU 308
310 A(I, J) = SX(JJ)
308 CONTINUE
B(I) = SYX(I)
300 CONTINUE
C CALCULATION OF THE COEFFICIENTS OF THE CURVE
DO 11 I = 1, M
11 PRINT102, (A(I, J), J = 1, M), B(I)
MM = M-1
DO 20 II = 1, MM
DO 20 K = 1, MM
N = K + 1
DO 20 I = N, N
20 D = A(N, II) / A(I, II)
DO 430 J = I, M
430 D = A(I, J) * D + D
IF (II = 129, 25, 29
29 IF (J - II) 28, 26, 28
26 IF (A(N, J) = D) 27, 25, 27
27 CORRC = A(N, J) - D
GU TU 28
25 CORRC = 0.
28 D = A(I, J) * DD + CORRC
430 A(N, J) = A(N, J) - D
B(N) = B(N) - B(1)*DD

20 CONTINUE
X(M) = B(M)/A(N,N)
DO 50 L = 2, M
N = M+1-L
KK = N+1
X(N) = B(N)/A(N,N)
DO 50 K = KK, M
50 X(N) = X(N) - A(N,K)*X(K)/A(N,N)
DO 60 NK = 1, M
60 PRINT 101, NK, X(NK)
101 FORMAT(1H0, 1OHCOEFFICIENT, 2X13, 5H = E15.8)
102 FORMAT(6(2XE15.8)/6(2XE15.8)/6(2XE15.8)/6(2XE15.8))/
K1 = M2 + 1
DO 320 N = 1, M2
Y22 = 0.
DO 330 NJ = 1, M
NJJ = NJ - 1
330 Y22 = Y22 + X(NJ)*((X(N)**NJ))
320 Y2(N) = Y22
DO 350 N = 1, M2
DIF(N) = YY(N) - Y2(N)
350 PRINT 130, XX(N), YY(N), Y2(N), DIF(N)
351 CONTINUE
M2 = 7
130 FORMAT(1H0, 17HCONC.TAB(G/KG) = F12.7, 3X18HDENS.TAB.(G/CC) = F11.8,
13X19HDENS.CALC.(G/CC) = F11.8/7HDIF. = E15.8)
CALL EXIT
END
APPENDIX 5.8.1

Calculation of the concentration of the KCl solutions in g-equiv/l from g KCl/kg soln.

```
DIMENSION A(5), B(5), C(5), GCUNC(5), DENS(5), CONC(10), T(5)

GMKCL  = 74.555
A(1)  = 0.999244
b(1)  = 0.3443e-4
C(1)  = 1.65746e-7
A(2)  = 0.9971496
b(2)  = 0.2700e-4
C(2)  = 1.84153e-7
A(3)  = 0.9957496
b(3)  = 0.2300e-4
C(3)  = 1.84153e-7
A(4)  = 0.994134
b(4)  = 0.192e-4
C(4)  = 1.842e-7
A(5)  = 0.992310
b(5)  = 0.1504e-4
C(5)  = 1.90814e-7
DU 11 M = 1,10
READ 1
PRINT 1
1 FORMAT (1X,10X45H
READ 10,CUNC(M)
PRINT 10,CUNC(M)
10 FORMAT (F10.6)
DU 12 N = 1,5
AN = N
T(N) = 15. + 5.*AN
DENS(N) = A(N) + b(N)*CUNC(M) + C(N)*(CONC(M)**2)
GCUNC(N) = CONC(M)*DENS(N)/GMKCL
PRINT 13, T(N), DENS(N), GCUNC(N)
12 CONTINUE
13 FORMAT (3XF8.5,5XF13.9,5XF17.11)
PUNCH 14, (GCUNC(N), N = 1,5)
14 FORMAT (5(F11.8))
11 CONTINUE
CALL EXIT
END
```
C FALKENHAGEN ET ALL. CONDUCTANCE EQUATION
1
1AL(5)
2DO 5 LL = 1, 20
3READ 1, (CONC(N), N=1, 5)
4FORMAT (5(F11.8))
5A = 3.5E-8
6DO 5 LL = 1, 2
7PRINT 6, LL, L, A
8FORMAT (1H/2(3X13), 3XE12.5)
9DO 2 N = 1, 5
10AN = N
11T(N) = 15., + 5.*AN
12AUX2 = T(N) = 25.
13D1 = 78., 57*(1., + 0.0046*AUX2+0.0000155*(AUX2**2))
14D2 = 78., 54*(-0.00459*AUX2+0.000019*(AUX2**2))
15D3 = 87., 74-0.0, 4008*T(N)+7.398E-4*(T(N)**2)+1.41E-6*(T(N)**3)
16D(N) = (D1 + D2 + D3)/3.
17AUX1 = 20., = T(N)
18VISC(N) = EXP((2., 30258*(1.2348*AUX1-0.001467*(AUX1**2))/((T(N)+96.))
19=4.60316)
20AL0(N) = 149.85+9.7299*AUX2+8.7063E-3*(AUX2**2)+4.468E-5*(AUX2**3)
21AUX = D(N)+T(N) + 273.15
22B1(N) = 0.8204E6/(AUX**1.5)
23B2(N) = 82.50/(VISC(N)*(AUX**0.5))
24S(N) = B1(N)+AL0(N) + B2(N)
25B(N) = 50.29*(AUX**(-0.5)) + 1.0E+08
26AL(N) = AL0(N) - S(N)+SQRNT(1.+B(N)*A=SQRNT(CONC(N))
27PRINT 3, T(N), B1(N), B2(N), S(N), B(N)
28FORMAT (6(2XE13.6))
29DO 4 N = 1, 5
30PRINT 3, T(N), D(N), VISC(N), AL0(N), CONC(N), AL(N)
31A = 4.0E-8
32CALL EXIT
33END

50E-07
29781E+00 0.538696E+02 0.849379E+02 0.329037E+08
29276E+00 0.605633E+02 0.949403E+02 0.328796E+08
29799E+00 0.675968E+02 0.105326E+03 0.328567E+08
26344E+00 0.748763E+02 0.116070E+03 0.328349E+08
27904E+00 0.824250E+02 0.127152E+03 0.328139E+08
26656E+02 0.100201E+01 0.135208E+03 0.100006E+01
34651E+02 0.890312E+02 0.149850E+03 0.998566E+02
32782E+02 0.797460E+02 0.164927E+03 0.997561E+02
41255E+02 0.791590E+02 0.180406E+03 0.995941E+02
50660E+02 0.653086E+02 0.196253E+03 0.994112E+02

10E-07
29781E+00 0.538696E+02 0.849379E+02 0.329037E+08
29276E+00 0.605633E+02 0.949403E+02 0.328796E+08
29799E+00 0.675968E+02 0.105326E+03 0.328567E+08
26344E+00 0.748763E+02 0.116070E+03 0.328349E+08
27904E+00 0.824250E+02 0.127152E+03 0.328139E+08
26656E+02 0.100201E+01 0.135208E+03 0.100006E+01
34651E+02 0.890312E+02 0.149850E+03 0.998566E+02
32782E+02 0.797460E+02 0.164927E+03 0.997561E+02
41255E+02 0.790308E+02 0.180406E+03 0.995941E+02
50660E+02 0.653086E+02 0.196253E+03 0.994112E+02

10E-07
CONSAGER, FUSS AND SKINNER CONDUCTANCE EQUATION

DIMENSION CONC(5),A1(3)
PI = 3.14159
AV = 6.02486E23
READ 5,M9
DO 4 L = 1,M9
READ 2,(CONC(N),N=1,5)
A1(1) = 3.0E-08
A1(2) = 3.5E-08
A1(3) = 4.0E-08
DO 4 LL = 1,3
A = A1(LL)
PRINT 5,L,LL,A
REWIND 2
DO 1 N = 1,5
AN = N
T = 15, + AN*5,
AUX2 = T = 25,
D1 = 78.575*(1,-0.00406*AUX2+0.0000155*(AUX2**2))
D2 = 78.540-0.004579*AUX2+0.00001194*(AUX2**2)
D3 = 87.740-0.4008*T+9.3984*(T**2)+1.6416*T*(T**3)
D1= (D1 + D2 + D3)/3;
AL0 = 149.85*2.97299*AUX2+8.7063E3*(AUX2**2)+4.468E5*(AUX2**3)
AUX2 = 20, - T
VISC = EXP((2.30258*(1,2348*AUX2+0.001467*(AUX2**2))/(T + 96)))
1-4,60316)
AUX2 = D1*(T + 273.15)
ALPH = 0.82046/AUX2**1.5
BET0 = 82.50/(VISC*(AUX2**0.5))
S = ALPH*AL0 + BET0
E1PR = 2.942E12/(AUX2**3)
E2PR = 0.4333E8/(VISC*(AUX2**2))
EPR = E1PR*AL0 - E2PR
AL1 = 3.202E1PR*AL0 = 3.42E2PR + ALPH*BET0
B = 16,708E4/(AUX2*A)
HB = (2.0*(B**2)+2.1*B = 1.0)/(B**3)
AL2B = 2.0*E1PR*AL0 = HB*44.1*E2PR/(3.0*B = 2.0*E1PH*ALOG(B)
AL = AL1 + AL2B
WRIE (2) E1PR,E2PR,EPR,R,HB,AL1,AL2B,AL,ALPH,BET0,S
F2 = EXP(-8.4056*(CONC(N)**0.5)/(AUX2**1.5))
ASSOC = 4.0*PI*AV6*(A+3)*EXP(B)/3000;
ALL = AL0 - S*(CONC(N)**0.5)*EPR*CONC(N)*ALOG(6.0*E1PR*CONC(N))
1+AL*CONC(N) = ASSOC*CONC(N)*F2*AL0

IF(N=2)B,7,B
7 ALL1 = 149.93 = 94.65*(CONC(2)**0.5) + 58.74*CONC(2)*ALOG(10.00)
1/2,30258 + 198.4*CONC(2)
PRINT 11,T,D1,VISC,AL0,CONC(N),F2,ASSOC,ALL,ALL1
GO TO 1
8 PRINT 11,T,D1,VISC,AL0,CONC(N),F2,ASSOC,ALL
1 CONTINUE
PRINT 10
REWIND 2
DO 4 N = 1,5
READ (2) E1PR,E2PR,EPR,R,HB,AL1,AL2B,AL,ALPH,BET0,S
<table>
<thead>
<tr>
<th>OFFSETS</th>
<th>PRINT 3, E1PR, E2PR, EPR, B, HB, AL1, AL2B, AL, ALPH, BETO, S</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>4 CONTINUE</td>
</tr>
<tr>
<td>52</td>
<td>2 FORMAT (5(F11.8))</td>
</tr>
<tr>
<td>53</td>
<td>3 FORMAT (1H1, 11I2X, E10.4)</td>
</tr>
<tr>
<td>54</td>
<td>5 FORMAT (1HO, 2X, I5, 2X, I5, 3X, E10.4)</td>
</tr>
<tr>
<td>55</td>
<td>10 FORMAT (1HO)</td>
</tr>
<tr>
<td>56</td>
<td>11 FORMAT (9(1X, E13.6))</td>
</tr>
<tr>
<td>57</td>
<td>CALL EXIT</td>
</tr>
<tr>
<td>58</td>
<td>END</td>
</tr>
</tbody>
</table>

|            | 0.3000E+07  |
| 796666E+02 | 0.100201E+01 |
| 794651E+02 | 0.149850E+03 |
| 772782E+02 | 0.164927E+03 |
| 761253E+02 | 0.180406E+03 |
| 750060E+02 | 0.196253E+03 |

|            | 0.2328E+02  |
| 924E+01    | 0.238E+01   |
| 900E+01    | 0.237E+01   |
| 904E+02    | 0.301E+02   |
| 902E+02    | 0.325E+02   |
| 904E+02    | 0.301E+02   |
| 902E+02    | 0.325E+02   |
| 904E+02    | 0.301E+02   |
| 902E+02    | 0.325E+02   |

|            | 0.2044E+01  |
| 392E+01    | 0.2041E+01  |
| 390E+01    | 0.2038E+01  |
| 394E+02    | 0.2035E+01  |
| 202E+02    | 0.2032E+01  |

|            | 0.1349E+01  |
| 892E+01    | 0.1343E+01  |
| 900E+01    | 0.1346E+01  |
| 904E+02    | 0.1347E+01  |
| 202E+02    | 0.1349E+01  |

|            | 0.1402E+03  |
| 892E+01    | 0.1402E+03  |
| 900E+01    | 0.1402E+03  |
| 904E+02    | 0.1402E+03  |
| 202E+02    | 0.1402E+03  |

|            | 0.1627E+03  |
| 892E+01    | 0.1627E+03  |
| 900E+01    | 0.1627E+03  |
| 904E+02    | 0.1627E+03  |
| 202E+02    | 0.1627E+03  |

|            | 0.2479E+03  |
| 892E+01    | 0.2479E+03  |
| 900E+01    | 0.2479E+03  |
| 904E+02    | 0.2479E+03  |
| 202E+02    | 0.2479E+03  |

|            | 0.3309E+03  |
| 892E+01    | 0.3309E+03  |
| 900E+01    | 0.3309E+03  |
| 904E+02    | 0.3309E+03  |
| 202E+02    | 0.3309E+03  |

|            | 0.3600E+03  |
| 892E+01    | 0.3600E+03  |
| 900E+01    | 0.3600E+03  |
| 904E+02    | 0.3600E+03  |
| 202E+02    | 0.3600E+03  |

|            | 0.3025E+03  |
| 892E+01    | 0.3025E+03  |
| 900E+01    | 0.3025E+03  |
| 904E+02    | 0.3025E+03  |
| 202E+02    | 0.3025E+03  |

|            | 0.2000E+03  |
| 892E+01    | 0.2000E+03  |
| 900E+01    | 0.2000E+03  |
| 904E+02    | 0.2000E+03  |
| 202E+02    | 0.2000E+03  |

|            | 0.1203E+03  |
| 892E+01    | 0.1203E+03  |
| 900E+01    | 0.1203E+03  |
| 904E+02    | 0.1203E+03  |
| 202E+02    | 0.1203E+03  |

|            | 0.2397E+03  |
| 892E+01    | 0.2397E+03  |
| 900E+01    | 0.2397E+03  |
| 904E+02    | 0.2397E+03  |
| 202E+02    | 0.2397E+03  |

|            | 0.3025E+03  |
| 892E+01    | 0.3025E+03  |
| 900E+01    | 0.3025E+03  |
| 904E+02    | 0.3025E+03  |
| 202E+02    | 0.3025E+03  |

|            | 0.2937E+03  |
| 892E+01    | 0.2937E+03  |
| 900E+01    | 0.2937E+03  |
| 904E+02    | 0.2937E+03  |
| 202E+02    | 0.2937E+03  |

|            | 0.2397E+03  |
| 892E+01    | 0.2397E+03  |
| 900E+01    | 0.2397E+03  |
| 904E+02    | 0.2397E+03  |
| 202E+02    | 0.2397E+03  |

|            | 0.2937E+03  |
| 892E+01    | 0.2937E+03  |
| 900E+01    | 0.2937E+03  |
| 904E+02    | 0.2937E+03  |
| 202E+02    | 0.2937E+03  |
REAL KH2CO3, KHLHCO3, LHLHLOH, LHLH, KHCO3, LCO3
DIMENSION CONC(2), CH(2), COH(2), CHC03(2), LW(2), COF(5), RRO(5), XIROT(15), CCO(3)(2)

KH2CO3 = 4.45E-07
KHLHCO3 = 4.69E-11
KH = 1.008E-14
LHLHCO3 = 4.45, 50
LHLH = 69.13
LHLH = 350.15
LHLH = 199.18

APPENDIX 5.9.1

The specific conductance of water. The concentration of bicarbonate and carbonate species are considered.

PRINT 11, KH2CO3
PRINT 16, KHCO3
PRINT 17, LCO3
PRINT 14, LHLH
PRINT 18

PRINT 12, KH
PRINT 13, LHLHCO3
PRINT 17, LCO3
PRINT 14, LHLH
PRINT 18

FORMAT (1HO, "FIRST DISSOCIATION CONSTANT OF CARBONIC ACID =", E10, 4)
FORMAT (1HO, "SECOND DISSOCIATION CONSTANT OF CARBONIC ACID =", E10, 4)

DO 1 N1 = 1, 500
DO 2 N = 1, 2
FN = N + (N1 - 1) * 2
CONC(N) = 4.1E-9 * FN
COF(1) = 1,
COF(2) = KH2CO3
COF(3) = KH2CO3 * KHCO3 - KW * KH2CO3 * CONC(N)
COF(4) = -KW * KH2CO3 * 2, 0 * KH2CO3 * KHCO3 * CONC(N)
COF(5) = -KH2CO3 * KHCO3 * KW
CALL PLRTS(COF, RRO, XIROT, 1, NRO)
DO 6 N2 = 1, 4
IF (XIROT(N2) .GE. 7, 6, 7)
7 RRO(N2) = 0.1
6 CONTINUE
CH(N) = MAX1(RRO(1), RRO(2), RRO(3), RRO(4))
COH(N) = KW / CH(N)
CHC03(N) = KH2CO3 * CONC(N) / (KH2CO3 + KH2CO3 + KHCO3 / CH(N) + CH(N))
CCO3(N) = KHCO3 * CHC03(N) / CH(N)

2 LW(N) = LH * CH(N) + LHLH * LHCO3 + LHLH * LCO3 * CCO3(N)
FN = FN - 1,
1 PRINT 3, FN, (LW(N), CONC(N), CH(N), COH(N), CHC03(N), CCO3(N), N=1, 2)
3 FORMAT (14, 2X, E9.3, 1X, 5X, E9.3, 1X)
CALL EXIT
END
SUBROUTINE PLRTS(C,RR,RI,NN,IND)
DIMENSION C(1),RR(1),RI(1)
N=NN
I=1

IF(N) 23, 23, 30
30 P=10,0/C(1)
DO 4 J=1,N
4 C(J)=P*C(J+1)
ISW=N/2
ISW=ISW+ISW-N

1 P=C(N-1)+1,E=12
2 Q=C(N)
3 IF(I=N+1) 5, 14, 2
4 RR(I)=Q
5 RI(I)=0,0
6 IND=N

7 GO TO 24
5 IC=I
6 BI=C(N-2)
7 IF(BI) 7, 28, 7
8 BI=1,0/BI
9 P=P*BI

10 DO 10 J=1,N
11 RR(J)=C(J)-P*BI=Q*BI
12 IF(J=N) 9, 10, 10
13 RI(J)=RR(J)-P*BI=Q*BI
14 CONTINUE
15 R(N-1)=RI(N-1)-RR(N-1)
16 B2=1,0
17 B3=RI(N-1)
18 B4=RI(N-2)
19 IF(I=N+2) 3, 6, 3
20 3 B2=RI(N-3)
21 B1=B4+B4-B3*B2
22
23 IF(ABS(B2)) 47, 48, 48
24 47 IF(ABS(B3)) 49, 50, 50
25 49 P=P*B2
26 Q=Q-B3
27 IC=IC+1
28 IF(ABS(B2)) 47, 48, 48
29 48 IF(ABS(B3)) 49, 50, 50
30 50
31 IF(ISW) 32, 23, 24
32 ISW=1
IND = I-1
J = N
\( \text{N} = \text{N} + 1 \)
\( C(\text{N}) = 0 \)

33 \( C(J+1) = C(J) + C(J) \)
34 \( J = J - 1 \)
35 \( \text{IF}(J) = 34, 34, 33 \)
36 \( C(1) = C(1) + 1, 0 \)
37 \( \text{GO TO 1} \)
38 \( \text{IF}(P) = 27, 16, 27 \)
39 \( B4 = 4.0 \times 0/(P \times P) \)
40 \( \text{IF}(\text{ABS}(B4) - 1.0, E=12) = 15, 15, 16 \)
41 \( \text{RR}(1) = P \)
42 \( \text{RR}(1+1) = Q \times P \)
43 \( \text{GO TO 19} \)
44 \( \text{RR}(1) = -5 \times P \)
45 \( \text{RR}(1+1) = \text{RR}(1) \)
46 \( B1 = P \times P - 4.0 \times Q \)
47 \( \text{IF}(B1) = 17, 19, 18 \)
48 \( \text{RI}(1) = 5 \times \text{SQRT}(-B1) \)
49 \( \text{RI}(1+1) = -\text{RI}(1) \)
50 \( \text{GO TO 20} \)
51 \( \text{B1} = 5 \times \text{SQRT}(B1) \)
52 \( \text{RR}(1) = \text{RR}(1) + B1 \)
53 \( \text{RR}(1+1) = \text{RR}(1+1) + B1 \)
54 \( \text{RI}(1) = 0, 0 \)
55 \( \text{RI}(1+1) = 0, 0 \)
56 \( I = I + 2 \)
57 \( \text{IF}(I-N) = 1, 1, 35 \)
58 \( \text{IF}(I\%2) = 23, 23, 36 \)
59 \( K = \text{IND} + 1 \)
60 \( \text{DO 38 } J = K, N \)
61 \( \text{IF}(\text{ABS}(K1(J)) - 1.0, E=12) = 37, 37, 38 \)
62 \( \text{DO 37 } I = \text{RI}(J+1), 0 \)
63 \( \text{CONTINUE} \)
64 \( \text{GO TO 24} \)
65 \( \text{DO 40 } K = J, N \)
66 \( \text{RR}(K) = \text{RR}(K+1) \)
67 \( \text{RI}(K) = \text{RI}(K+1) \)
68 \( \text{IND} = N - 1 \)
69 \( \text{GO TO 24} \)
70 \( \text{DO 22 } J = 1, N \)
71 \( \text{GO TO 14} \)
72 \( \text{IND} = 1 - 1 \)
73 \( \text{RETURN} \)
74 \( \text{GO TO 8} \)
75 \( \text{END} \)
REAL KH2CO3, KW, LHC03, LH, LOH, LW
DIMENSION CONC(2), CH(2), COH(2), CHCO3(2), LH(40), COF(5), RROT(5), XI(5)

11 FORMAT (1HO, "FIRST DISSOCIATION CONSTANT OF CARBONIC ACID \(\alpha_1\), E10.4)
12 PRINT 11, LW
13 FORMAT (1HO, "IONIC PRODUCT OF WATER \(\alpha_0\), E10.4)
14 PRINT 12, KW
15 FORMAT (1HO, "CONDUCTIVITY BICARBONATE ION \(\alpha_2\), E10.4)
16 PRINT 13, LHC03
17 FORMAT (1HO, "CONDUCTIVITY HYDROGEN ION \(\alpha_3\), E10.4)
18 PRINT 14, LH
19 FORMAT (1HO, "CONDUCTIVITY HYDROXYL ION \(\alpha_4\), E10.4)
20 PRINT 15, LOH
21 FORMAT (1HO, "NO.", COND, H2O, CONC, CO2, CONC, H+, CONC, OH-)
22 DO 1 N = 1, 500
23 DO 2 N = 1, 2
24 FN = N * (N1 - 1) * 2
25 CONC(N) = FN * 1.0, E-9
26 Q = -CONC(N) * KH2CO3 - KW
27 COF(1) = 1.
28 COF(2) = P
29 COF(3) = Q
30 COF(4) = R
31 CALL PFRMTS(COF, RROT, XI07, 3, RROT)
32 CH(N) = AMAX1(RROT(1), RROT(2), RROT(3))
33 COH(N) = KW/CH(N)
34 CHCO3(N) = CONC(N) * KH2CO3/(KH2CO3 + CH(N))
35 2 LW(N) = LH + CH(N) + LOH + COH(N) + LHC03 + CHCO3(N)
36 FN = FN - 1.
37 PRINT 1, FN, (LW(N), CONC(N), CH(N), COH(N), CHCO3(N), N=1, 2)
38 FORMAT (14, 2X, 2(E11.5, 1X, E11.5, 1X, E11.5, 1X, E11.5, 1X, E11.5, 5X))
39 CALL EXIT
40 END

(Appendix 5.9.2 continued on p. 710)
1 AL(5), F0(5), ALL(5), VY(5), XY(5), XCAL(5), YCAL(5), RAD(4), FB(5), FC(5),
2 FD(5), CONC(5), WY(5), CELLC(5)

READ 500, M8

500 FORMAT (12, 3XF10.5)
DO 351 M7 = 1, M8
PRINT 1
1 FORMAT(80H)
READ 500, M2, R0
PRINT 109, R0, M2

109 FORMAT(1X, 'TEMP = F8.4, 5X14')
CALL TEMP(R0, M2, XX)
READ 202, (YM(N), N = 1, 5)
READ 10, CONC1
PRINT 11, CONC1

10 FORMAT (F10, 6)
11 FORMAT (1X, 'CONCENTRATION IN-GM-SOLUTE/KG-SOLUTION = ', F10.6)
DO 351 M10 = 1, 4
READ 1
PRINT 1
READ 202, (YY(N), N = 1, M2)

202 FORMAT (1X, 5(E10.4))
M = 4
DO 210 L = 1, 4
DO 210 J = 1, 4
SX = 0,
SYX = 0,
DO 210 K = 1, M2
J1 = J * L - 2
SX = SX + XX(K) ** J1
A(L, J) = SX
IF(J-1)210, 210, 210

210 CONTINUE
CALL EQAT(A, B, X, M)
DO 304 N = 1, 4
304 FORMAT (1X, 5(E10.4))
R = D304 N = 1, 4
SFAA = 0,
SFAB = 0,
SFAC = 0,
SFAD = 0,
SFBD = 0,
SFCD = 0,
SPDD = 0,
SFAO = 0,
SPBO = 0,
SFCO = 0,
SPDO = 0,
DO 505 N = 1, M2
FA = -1,
WX(N) = 1, 1/4, E-6
WY(N) = 1, E8/(YY(N)*YY(N))
FX(N) = -X(2) - 2*X(3)*XX(N) - 3*X(4)*XX(N)*XX(N)
FY = 1,
AL(N) = FX(N)*FX(N)/WX(N) + FY/WY(N)
FB(N) = -XX(N)
FC(N) = -XX(N)*XX(N)
FD(N) = -XX(N)*XX(N)*XX(N)
F0(N) = YY(N) - X(1) - X(2)*XX(N) - X(3)*XX(N)*XX(N) - X(4)*XX(N)*XX(N)*XX(N)

DO 507 N = 1, M2
SFAA = SFAA + FA*FA/AL(N)
SFAB = SFAB + FA*FB(N)/AL(N)
SFAC = SFAC + FA*FC(N)/AL(N)
SFAD = SFAD + FA*FD(N)/AL(N)
SFBD = SFBD + FB(N)*FD(N)/AL(N)
SFCD = SFCD + FC(N)*FD(N)/AL(N)
SFDD = SFDD + FD(N)*FD(N)/AL(N)
SFAO = SFAO + FO(N)*FA/AL(N)
SFBO = SFBO + FO(N)*FB(N)/AL(N)
SFCO = SFCO + FO(N)*FC(N)/AL(N)
SFDO = SFDO + FO(N)*FD(N)/AL(N)

A(1, 1) = SFAA
A(1, 2) = SFAB
A(1, 3) = SFAD
A(1, 4) = SFBD
B(1) = SFAO
A(2, 1) = SFAB
A(2, 2) = SFAC
A(2, 3) = SFAD
A(2, 4) = SFBD
B(2) = SFBO
A(3, 1) = SFAC
A(3, 2) = SFAD
A(3, 3) = SFDO
A(3, 4) = SFDD
B(3) = SFDO
A(4, 1) = SFAD
A(4, 2) = SFBD
A(4, 3) = SFCD
A(4, 4) = SFDD
B(4) = SFDO
CALL EQUAT(A, B, X, M)
DO 501 N = 1, M2
ALL(N) = (F0(N) - X(1) - X(2)*XX(N) - X(3)*XX(N)*XX(N) - X(4)*XX(N)*XX(N)*XX(N))/AL(N)

DO 506 N = 1, M
X(N) = RAD(N) - X(N)
PRINT 101, N, X(N)

101 FORMAT(1H1, 11HCOEFFICIENT, 2X13, 5H 3 E15, 8)

SUM = 0
SUM1 = 0
DO 504 N = 1, M2
VX(N) = ALL(N)*FX(N)/WX(N)
VY(N) = ALL(N)*FY/WY(N)
SUM = SUM + VX(N) * VX(N)
SUM1 = SUM1 + VX(N) * VX(N)
XCAL(N) = XX(N) - VX(N)
YCAL(N) = YY(N) - VY(N)
PRINT 502, XX(N), XCAL(N), VX(N), YY(N), YCAL(N), VY(N)

504 CONTINUE

502 FORMAT (6(1X, E13.6))
DO 503 K = 1, 5

AK = K
XY(K) = 15. + 5. * AK
YY(K) = X(1) + X(2) + XY(K) + X(3) + (XY(K) * 2) + X(4) + (XY(K) * 3)
PRINT 502, YY(K), YW(K)
503 YY(K) = YY(K) * YW(K) / (YW(K) + YY(K))
PUNCH 203, (YY(K), K = 1, 5)

203 FORMAT (1X, 5F10.2)
CALL CONCTR(CONC, CONC1)
CALL FALKEN(CONC, AL, XY)

DO 406 N = 1, 5

CELLC(N) = AL(N) * CONC(N) * YY(N) / 1000
406 PRINT 405, XY(N), CELLC(N), YY(N), AL(N)

405 FORMAT (1H , "TEMPERATURE = ", F7.3, 5X, "CELL CONSTANT = ", E14.6, 4X,
1 "RESISTANCE = ", F11.3, 4X, "CONDUCTANCE = ", F9.4)

408 FORMAT (5(5X, F10.5))

351 CONTINUE
CALL, EXIT
END
SUBROUTINE TEMP(R0,M2,XX)
DIMENSION RT(5),XX(5)
READ 201,(RT(N),N = 1,M2)
APPENDIX 5.10.1 (cont.)
201 FORMAT (10(F8.4))
C CALCULATION OF TEMPERATURE BY CALENDAR EQUATION
C = 39.2596E-4
DELT = 1.492
R100 = R0 * 100. *C*R0
DO 30 N = 1,M2
PT = 100.*(RT(N) - R0)/(R100 - R0)
T = PT
10 CHECK = T
CORR = DELT*(T/100. - 1.)*(T/100.)
T = PT + CORR
IF (CHECK = T)30,30,10
30 XX(N) = T
DO 15 N = 1,M2
15 PRINT 203,RT(N),XX(N)
203 FORMAT (F9.4,3XF8.3,3XF13.4)
RETURN
END
SUBROUTINE EQUAT(A, B, X, M)

DIMENSION A(4, 4), B(4), X(4)

M = M + 1

DO 20 I = 1, M
  DO 20 K = I, M
    N = K + 1
    DD = A(N, K) / A(K, K)
    DO 30 J = I, M
      D = A(K, J) * DD
      30 A(N, J) = A(N, J) - D
    B(N) = B(N) - B(K) * DD
  CONTINUE

DO 50 L = 2, M
  N = M - L + 1
  KK = N + 1
  X(N) = B(N) / A(N, N)
  DO 50 K = KK, M
    50 X(N) = X(N) - A(N, K) * X(K) / A(N, N)
  DO 60 N = 1, M
    60 PRINT 101, NK, X(NK)
101 FORMAT (1H1, 11HCOEFFICIENT, 2X, 13, 5H = D15.8)

RETURN
END
SUBROUTINE FALKEN(CONC, AL, T)

C FALKENHAGEN ET ALL, CONDUCTANCE EQUATION

1AL(5)

A = 3.5E-8

DO 2 N = 1, 5

AUX2 = T(N) - 25

D1 = 78.57 * (1.0046 * AUX2 + 0.0000155 * (AUX2 ** 2))

D2 = 78.54 + 0.004579 + AUX2 + 0.0000119 + (AUX2 ** 2)

D3 = 87.74 - 0.4008 * T(N) + 9.396E-4 * (T(N) ** 2) - 1.841E-6 * (T(N) ** 3)

D(N) = (D1 + D2 + D3) / 3

AUX1 = 20.0 - T(N)

VISC(N) = EXP((2.30258 * (1.2348 * AUX1 - 0.001467 * (AUX1 ** 2)) / (T(N) ** 96)) - 1/4, 60316

AL0(N) = 149.85 + 2.97299 + AUX2 + 8.7063E-3 * (AUX2 ** 2) - 4.468E-5 * (AUX2 ** 3)

AUX = D(N) + (T(N) * 273.15)

B1(N) = 0.8204E6 / (AUX ** 1.5)

B2(N) = 8.250 / (VISC(N) * (AUX ** 0.5))

S(N) = B1(N) * AL0(N) - B2(N)

B(N) = 50.29 % (AUX ** (-0.5)) * 1.0E-08

AL(N) = AL0(N) - S(N) * SQRT(CONC(N)) / (1 + B(N) * A * SQRT(CONC(N))")

CONTINUE

RETURN

END
SUBROUTINE CONCTR(GCONC, CONC)
DIMENSION GCONC(5), DENS(5)
GMKCL = 74,555
DO 12 N = 1, 5
AN = N
T = 15. + 5.*AN
DENS(1) = 0.998244+6.3443E-4*CONC
DENS(2) = 0.9971496+6.2700E-4*CONC
DENS(3) = 0.9957496+6.2300E-4*CONC
DENS(4) = 0.994134+6.192E-4*CONC
DENS(5) = 0.992310+6.15804E-4*CONC
GCONC(N) = CONC*DENS(N)/GMKCL
12 PRINT 13, T, DENS(N), GCONC(N)
13 FORMAT (3XF8.3, 5XF13.9, 5XF17.11)
RETURN
END
DIMENSION CELLC(5,5)

READ 9,N2
DO 12 M3 = 1,N2
READ 1
PRINT 1
READ 9,M1
SUM = 0,
SUM1 = 0,
SUM2 = 0,
SUM3 = 0,
SUM4 = 0,
SUM5 = 0,
DO 3 M = 1,M1
READ 4, (CELLC(M,N),N=1,5)
DO 5 N1 = 1,5
5 SUM = SUM * CELLC(M,N1)
SUM1 = SUM1 * CELLC(M,1)
SUM2 = SUM2 * CELLC(M,2)
SUM3 = SUM3 * CELLC(M,3)
SUM4 = SUM4 * CELLC(M,4)
SUM5 = SUM5 * CELLC(M,5)
CONTINUE
FORMAT(80H)
FORMAT(5(5X,F10,5))
FM1 = M1
AV = SUM/(FM1=5)
AV1 = SUM1/FM1
AV2 = SUM2/FM1
AV3 = SUM3/FM1
AV4 = SUM4/FM1
AV5 = SUM5/FM1

C CALCULATE MSD
SUM = 0,
SUM1 = 0,
SUM2 = 0,
SUM3 = 0,
SUM4 = 0,
SUM5 = 0,
DO 6 M = 1,M1
DO 7 N = 1,5
DIF = CELLC(M,N) - AV
7 SUM = SUM * DIF**2
SUM1 = SUM1 + (CELLC(M,1) - AV1)**2
SUM2 = SUM2 + (CELLC(M,2) - AV2)**2
SUM3 = SUM3 + (CELLC(M,3) - AV3)**2
SUM4 = SUM4 + (CELLC(M,4) - AV4)**2
SUM5 = SUM5 + (CELLC(M,5) - AV5)**2
CONTINUE
SD = SORT(SUM/(FM1=5) = 1))
SD1 = SORT(SUM1/(FM1 = 1))
SD2 = SORT(SUM2/(FM1 = 1))
SD3 = SORT(SUM3/(FM1 = 1))
SD4 = SORT(SUM4/(FM1 = 1))
53    SD5 = SQRT(SUM5/(FM1 - 1))
54    DO 8 M = 1,M1
55    8 PRINT 9,H,(CELLC(M,N),N=1,5)
56    9 FORMAT(I5,5(3X,F10,5))
57    PRINT 11,AV1,AV2,AV3,AV4,AV5
58    PRINT 11,SD1,SD2,SD3,SD4,SD5
59    PRINT 10,AV,SD
60    12 CONTINUE
61    10 FORMAT(1H0,"CELL CONSTANT (OVERALL AVERAGE) =",F10.5,5X,"MEAN SQUARE DEVIATION =",F10.5)
62    11 FORMAT(1H0,4X,5(3X,F10,5))
63    END
DIMENSION XY(5),YY(5),CONC(5),CELLC(5),AL(5),C(5)

XY(1) = 20,
XY(2) = 25,
XY(3) = 30,
XY(4) = 35,
XY(5) = 40,
READ 500, M8

500 FORMAT (12,3XF10,5)
     "differential" cell
     constant .

1 FORMAT (60H)

READ 10, CONC1
PRINT 11, CONC1

10 FORMAT (F10,6)

11 FORMAT (1X, "CONCENTRATION IN CM SOLUTE/KG SOLUTION = ", F10,6)

DO 351 M10 = 1,4
READ 1
PRINT 1
READ 202, (YY(N), N=1,5)
READ 202, (C(N), N=1,5)
DO 2 N = 1,5

2 YY(N) = YY(N) - C(N)

202 FORMAT (1X, 5(E10,4))

CALL CONCTR(CONC, CONC1)
CALL FALKEN(CONC, AL, XY)
DO 406 N = 1,5

CELLC(N) = AL(N)*CONC(N)*YY(N)/1000,

406 PRINT 405, XY(N), CELLC(N), YY(N), AL(N)

PUNCH 1
PUNCH 408, (CELLC(N), N=1,5)

AL1 = 149.93 - 94.85*SORT(CONC(2)) + 58.74*CONC(2)*ALOG(CONC(2))/2,

CELLC(2) = AL1*CONC(2)*YY(2)/1000,

PRINT 405, XY(2), CELLC(2), YY(2), AL1

405 FORMAT (1H, "TEMPERATURE = ", F7,3,5X, "CELL CONSTANT = ", E14, 6, 4X,
     "RESISTANCE = ", F11,3,4X, "CONDUCTANCE = ", F9,4)

408 FORMAT (5(5X, F10,5))

351 CONTINUE

CALL EXIT

END
SUBROUTINE CONCTR(GCONC, CONC)
DIMENSION GCONC(5), DENS(5)
GHKCL = 74,555
DO 12 N = 1,5
AN = N
T = 15, * 5, * AN
DENS(1) = 0.998244*6.3443E-4*CONC
DENS(2) = 0.997149*6.2700E-4*CONC
DENS(3) = 0.995749*6.2300E-4*CONC
DENS(4) = 0.994134*6.1920E-4*CONC
DENS(5) = 0.992310*6.1580E-4*CONC
GCONC(N) = CONC*DENS(N)/GHKCL
PRINT 13, T, DENS(N), GCONC(N)
FORMAT (3XF8.3, 3XF13.9, 3XF17.11)
RETURN
END
SUBROUTINE FALKEN(CONC,AL,T)
C FALKENHAGEN ET AL., CONDUCTANCE EQUATION
1AL(5)
A = 3.5E-8
D0 2 N = 1.5
AUX2 = T(N) = 25,
D1 = 78,57+(1,-0,0046*AUX2+0,0000155*(AUX2**2))
D2 = 78,54+0,004579*AUX2+0,0000119*(AUX2**2)
D3 = 87,74-0,4008*T(N)+9,398E-4*(T(N)**2)-1,41E-6*(T(N)**3)
D(N) = (D1 + D2 + D3)/3,
D(N) = D(N) = EXP((2,30258*(1,2348*AUX1-0,001467*(AUX1**2))/(T(N)+96)),)
1-4,60316.
AL0(N)=149,85+2,97299*AUX2+8,7063E=3*(AUX2**2)+4,468E=5*(AUX2**3)
AUX = D(N)*T(N) + 273,15
B1(N) = 0,8204E+6/(AUX**1,5)
B2(N) = 82,50/(VISC(N)=(AUX**0,5))
S(N) = B1(N)*AL0(N) + B2(N)
B(N) = 50,29*(AUX**(-0,5))*1,0E+08
AL(N) = AL0(N) - S(N)*SQR(T(CONC(N)))/(1+B(N)**SQR(T(CONC(N))))
2 CONTINUE
20 RETURN
21 END
REAL KH2CO3,KW,LHCO3,LH,LOH,LW
DIMENSION CONC(2),CH(2),COH(2),CHCO3(2),LW(40),COF(5),RROT(5),XIRO

1T(5)
kh2co3 = 4.45e-07
kw = 1.006e-14
lhco3 = 14.50
lh = 350.15
loh = 199.15
p = kh2co3
r = -kw/kh2co3

print 11,kh2co3
11 format(1h0,"FIRST DISSOCIATION CONSTANT OF CARBONIC ACID =",e10.4)
print 12,kw
12 format(1h0,"IONIC PRODUCT OF WATER =",e10.4)
print 13,lhco3
13 format(1h0,"CONDUCTIVITY BICARBONATE ION =",e10.4)
print 14,lh
14 format(1h0,"CONDUCTIVITY HYDROGEN ION =",e10.4)
print 15,loh
15 format(1h0,"CONDUCTIVITY HYDROXYL ION =",e10.4)
print 17
17 format(1h0,"NO, COND,H2O CONC,CO2 CONC,H+ CONC,OH- CONC,HCO3-
2 CONC,LHCO3")
di 1 n1 = 1,500
do 2 n = 1,2
fn = n*(n1-1)/2
do 2 conc(n) = 10.0e-07 + fn*1.0e-08
q = -conc(n)-kh2co3-kh
cof(1) = 1
cof(2) = p
cof(3) = q
cal p1r(1) = r
ch(n) = max(1, rrot(1), rrot(2), rrot(3))
cof(n) = kw/ch(n)
chco3(n) = conc(n)*kh2co3/(kh2co3 + ch(n))
lw(n) = lh*ch(n) + loh*coh(n) + lhco3*chco3(n)
f = fn
1 print 3,fn,(lw(n),conc(n),ch(n),coh(n),chco3(n),n=1,2)
3 format(14,2x,2(1e11.5,1x,1e11.5,1x,1e11.5,1x,1e11.5,1x,1e11.5,1x))
call exit
end
REAL KH2CO3, KW, LHC03, LH, LOH, KHA, LA
DIMENSION COF(5), RROT(5), XIROT(5)
READ 20, KHA, LA, CHA, CO2

20 FORMAT(5(2X,E13.6))
KH2CO3 = 4.45E-07
KW = 1.008E+14
LHC03 = 44.50
LH = 350.15
LOH = 199.18
PRINT 11, KH2CO3

11 FORMAT(1HO,"FIRST DISSOCIATION CONSTANT OF CARBONIC ACID =","E10.4)
PRINT 12, KW
12 FORMAT(1HO,"IONIC PRODUCT OF WATER =","E10.4)
PRINT 13, LHC03
13 FORMAT(1HO,"CONDUCTIVITY BICARBONATE ION =","E10.4)
PRINT 14, LH
14 FORMAT(1HO,"CONDUCTIVITY HYDROGEN ION =","E14.7)
PRINT 15, LOH
15 FORMAT(1HO,"CONDUCTIVITY HYDROXYL ION =","E10.4)
PRINT 21, KHA
21 FORMAT(1HO,"DISSOCIATION CONSTANT ACID =","E14.7)
PRINT 22, LA
22 FORMAT(1HO,"INFINITE CONDUCTANCE ANION =","E14.7)
PRINT 23, CHA
23 FORMAT(1HO,"CONCENTRATION ACID =","E14.7)
PRINT 24, CO2
24 FORMAT(1HO,"CONCENTRATION CO2 =","E14.7)

COF(1) = 1,
COF(2) = KHA + KH2CO3
COF(3) = KH2CO3*KHA - KH2CO3*CO2 - KW - KHA*CHA
COF(4) = -KH2CO3*CO2*KHA - KW*KH2CO3 - KW*KHA - KHA*CHA*KH2CO3
COF(5) = -KW*KH2CO3*KHA
CALL PLRTS(COF, RROT, XIROT, 4, NROT)
DO 6 N2 = 1, 4
6 CONTINUE

IF (XIROT(N2))7, 6, 7
7 RROT(N2) = 0.
6 CONTINUE
CH = AMAX1(RROT(1), RROT(2), RROT(3), RROT(4))
COH = KW/CH
PRINT 4

1,"CONC, HCO3", 7X,"CONC, OH-", 6X,"CORRECT, 1", 6X,"CORRECT, 2")
CHCO3 = CO2*KH2CO3/(CH+KH2CO3)
CA = CHA*KHA/(CH*KHA)
CORR1 = LOH*COH + LHC03*CHCO3
CORR2 = LOH*COH + LHC03*CHCO3 + LH*CHC03
PRINT 3, CHA, CC02, CH, CA, CHC03, COH, CORR1, CORR2
CNDSL = 1000.*2.8391/(CHA*54073.8) - CORR1/CHA
PRINT 3, CNDSL
CNDSL = 1000.*2.8391/(CHA*54073.8) - CORR2/CHA
PRINT 3, CNDSL
3 FORMAT(3X,8(E13.6,3X))
CALL EXIT
END
REAL KH2CO3, KHA, LHC03, LH, LOH, KHA, LA
DIMENSION COF(5), RROT(5), XIROT(5)
READ 17, M9

17 FORMAT (15)
DO 16 M10 = 1, M9
READ 20, KHA, LA, CH, CC02
20 FORMAT (5(2X, E13.6))
KH2CO3 = 4.45E-07
KW = 1.008E-14
LHC03 = 44.50
LH = 350.15
LOH = 199.18
PRINT 11, KH2CO3

11 FORMAT (1H1, "FIRST DISSOCIATION CONSTANT OF CARBONIC ACID =", E10.4)
PRINT 12, KW
12 FORMAT (1H0, "IONIC PRODUCT OF WATER =", E10.4)
PRINT 13, LHC03
13 FORMAT (1H0, "CONDUCTIVITY BICARBONATE ION =", E10.4)
PRINT 14, LH
14 FORMAT (1H0, "CONDUCTIVITY HYDROGEN ION =", E10.4)
PRINT 15, LOH
15 FORMAT (1H0, "CONDUCTIVITY HYDROXYL ION =", E10.4)
PRINT 21, KHA
21 FORMAT (1H0, "DISSOCIATION CONSTANT ACID =", E10.4)
PRINT 22, LA
22 FORMAT (1H0, "INFINITE CONDUCTANCE ANION =", E10.4)
PRINT 23, CM
23 FORMAT (1H0, "CONCENTRATION SALT =", E10.4)
PRINT 24, CC02
24 FORMAT (1H0, "CONCENTRATION CO2 =", E10.4)

COF(1) = 1,
COF(2) = KHA + KH2CO3 + CM
COF(3) = KH2CO3*KHA - KH2CO3*CC02 = KW*KH2CO3
COF(4) = -KH2CO3*CC02*KHA - KW*KH2CO3 - KHA
COF(5) = -KH*KH2CO3*KHA
CALL PLRTS(COF, RROT, XIROT, N ROT)
DO 6 N2 = 1, 4
IF (XIROT(N2)) \ 7, 5, 7
7 RROT(N2) = 0 1
6 CONTINUE
CH = AMAX1(RROT(1), RROT(2), RROT(3), RROT(4))
COH = KH/CH
PRINT 4

4 FORMAT (1H0, 5X, "CONC.HA", 8X, "CONC.CO2", 8X, "CONC.H+", 9X, "CONC.A-", 9X
1, "CONC.HCO3", 7X, "CONC.CH+", 6X, "CORRECT.1", 6X, "CORRECT.2")
CHCO3 = CC02*KH2CO3/(CH*KH2CO3)
CA = CM*KHA/(CH*KHA)
CORH1 = (LA*(CH-CA)) - LH = CH = LHC03 + CHCO3 + LOH = COH) / CM
PRINT 3, CM, CC02, CH, CA, CHC03, COH, CORR1
16 CONTINUE
3 FORMAT (3X, B(13, 6, 3X))
CALL EXIT
END
DIMENSION YY(5),XX(5), A(4,4), B(4), X(4), W(5), Y(5), FX(5),
1, AL(5), F0(5), AL1(5), VY(5), YY(5), XCAL(5), YCAL(5), RAD(4), FB(5), FC(5),
2, FD(5), CUNC(5), YW(5)

DIMENSION RPAR(4, 2), XY(5)

APPENDIX 5.9.5

Calculation of water resistance.

DO 351 M11 = 1, 2
READ 500, M8
DO 351 M7 = 1, M8
READ 1
PRINT 1
1 FORMAT(80H)

READ 500, M2, RO.
500 FORMAT (12, 3*(I10, 5))
PRINT 109, RO, M2
109 FORMAT (1H, 3X, T10, 5 = F9.4, 5X(4))
CALL TEMP(R0, M2, XX)
DO 351 M10 = 1, 4
READ 1
PRINT 1
READ 202, (YY(N), N = 1, M2)
202 FORMAT (1X, 5*(E10, 4))
PRINT 600

DO 407 N = 1, 5
YY1 = YY(N) + RPAR(M10, M11)/(RPAR(M10, M11) - YY(N))
PRINT 502, XX(N), RPAR(M10, M11), YY(N), YY1
407 YY(N) = YY1

M = 4
DO 210 L = 1, 4
DO 210 J = 1, 4
SX = 0
SYX = 0
DO 210 K = 1, M2
J1 = J + L - 2
SX = SX + XX(K)*J1
A(L, J) = SX
210 CONTINUE

IF(J-1)210, 200, 210
200 L1 = L - 1
SYX = SYX + (XX(K)*J1)*YY(K)
B(L) = SYX
210 CONTINUE

CALL EQUAT(A, B, X, M)
DO 304 N = 1, 4
304 RAD(N) = X(N)
SFAA = 0
SFAY = 0
C THIS PROGRAM CALCULATES THE DISSOCIATION CONST. OF AN ACID BY DIPPY

C METHOD

DIMENSION C(40),AL(40),UK(40)

READ 4,L1

4 FORMAT(13)

DO 26*L2 = 1,L1

READ 1

PRINT 1

1 FORMAT(90H

1)

READ 2,T

PRINT 2,T

2 FORMAT(1H0,19H

F8.3)

C CALCULATION OF D DIELECTRIC CONSTANT

C DRAKE, ... (PHYS.REV., II, 35, 613, 1930)

D1 = 78.57*(1.0052610*(T-25.)+0.0000155*((T-25.)*2))

C WYMAN AND INGALLS (J. AM. CHEM. SOC., 60, 1182, 1938)

D2 = 8.548*0.00579*(T-25.)*0.0000119*((T-25.)*2)+28*E-9*(T-25.)*2

C MALMBERG AND MARYOTT (J. RES. NAT. BUR. STAND., 56, 1, 1956)

D3 = 87.74-0.4008*T+9.398E-4*T*1.5+1.410E-5*T*T

C AVERAGE VALUE

D = (D1 + D2 + D3)/3.

PRINT 201

201 FORMAT(1H0,5X1HT,16X2HU1,16X2HD2,16X2HD3,16X1HD)

PRINT 202,T,U1,D2,D3,D

202 FORMAT(F9.4,4(7XF11.4))

AUX = 20. - T

VISCT = EXP(2.30258*(1.00348*AUX-0.001467*(AUX**2)))/(T+96.) = 4.60316

TK = 1 + 273.16

ALPHA1 = 8.20785/((D*TK)**1.5)

BET = 8.72/((D*TK)**0.5)*VISCT

PRINT 3,ALPHA1,BET

3 FORMAT(1H0,31HCOEFF, IN ONSAGER EQ, ALPH1 = E14,8,4X7HBETA = E14,18)

READ 2,ALO

PRINT 2,ALO

READ 4, M

PRINT 8

8 FORMAT(1H0,2H =.3X,16HCONC(MOLE/LITER),10H COND(MH))

DO 36 = L2,1,M

READ 6,C(N),AL(N)

PRINT 7,N,C(N),AL(N)

6 FORMAT(E12.3,F9.4)

7 FORMAT(I3,5X,E14,6,3X,F9.4)

READ 18,R

18 FORMAT(F8.1)

A = 1.8123E+15/((D*TK)**1.5)

B = 50.29+18/SQRT(D*TK)

PRINT 19,A,B

16 FORMAT(1H0,3X4HA = E14,8,8X4HB = E14,8)

PRINT 20

20 FORMAT(1H0,2H =.4X,10HCONC,(M/L),3X,10HCOND,(MHO),14H EQ,COND,(MH 10),9H DQ,DISS,,3X,9HACT,COEF,,4X,11HDISS,FUNCTION,20H THERMODYN,DIS
25.C

SUMDK = 0.
ONGSLP = ALPH * ALO + BEI
DO 19 N = 1, M
ALE = SORT(ALO**2 - 2 * ONGSLP * SORT(ALO * AL(N) * C(N)))
ALPH = AL(N)/ALE
CI = ALPH * C(N)
  ALN = A * SORT(CI )/(1.0 * BOR * SORT(CI ))
F = 10.0 * (ALN - 1)
DK1 = ALPH**2 * C(N)/(1.0 - ALPH)
DK(N) = DK1 * (F**2)
SUMDK = SUMDK + DK(N)

19 PRINT 21, N, C(N), AL(N), ALE, ALPH, F, DK1, DK(N)
21 FORMAT(13, 3X, E14.6, 3X, F8.6, 3X, F8.5, 3X, F8.5, 2(5X, E14.6))
22 PRINT 23, DKA
23 FORMAT(1HU, 3X, 46HTHERMODYNAMIC DISASSOCIATION CONSTANT=ART, MEAN = , E
111.4)
SUMDIF = 0.
DO 23 N = 1, M
DIF = DK(N) - DKA
23 SUMDIF = SUMDIF + DIF**2
DEV = SORT(SUMDIF/(AM - 1))
PRINT 24, DEV
26 CONTINUE
24 FORMAT(1HU, 23HMEAN SQUARE DEVIATION = E11.4)
CALL EXIT
END
DEMAYO, CALCULATION 0

1 DIMENSION C(40), SAL(40), AL(40), ALE(40), CI(40), X(40), Y(40), U(40),
   R(40), V(40), S(40), W(40), T(40), DALOX(40), DALOY(40), FM1(40), FN(40),
   DLOS(40), DLOC(40), DKSL(40), DKE(40), DXX(40), DXY(40)
   ALPH = 0.2274
   BETA = 59.79
   A = 0.5065
   READ 1, M1
   DO 61 N = 1, M1
   READ 51
   PRINT 51
   51 FORMAT (80H)

1 READ 4, ALO, DISS
   PRINT 4, ALO, DISS
   4 FORMAT (21H)
   1, E14.7
   READ 1, M

1 FORMAT (13, 8(2X, E14.7))
   B = ALPH * ALO + BETA
   FJ = 2.303 * 2. * A / B
   PRINT 1, M, B, FJ
   PRINT 10
   SX = 0.
   SY = 0.
   SXX = 0.
   SXY = 0.
   PRINT 55
   55 FORMAT (1H0, "N", 7X, "C(N)", 12X, "SAL(N)", 9X, "AL(N)", 12X, "CI(N)", 11X,
   1"ALE(N)", 11X, "X(N)", 12X, "Y(N)"
   DO 3 N = 1, M
   READ 2, C(N), AL(N)
   SAL(N) = AL(N) * C(N) / 1000.
   CHK = ALO
   ALE(N) = ALO - B * SQRT(C(N) * AL(N) / CHK)
   IF (ABS(CHK - ALE(N)) < 0.0115, 5, 6
   6 CHK = ALE(N)
   GO TO 7
   5 CI(N) = AL(N) * C(N) / ALE(N)
   X(N) = AL(N) * CI(N) / (10. * 2. + A * SQRT(CI(N)))
   Y(N) = ALO - X(N) / DISS
   PRINT 1, N, C(N), SAL(N), AL(N), CI(N), ALE(N), X(N), Y(N)
   AUX = (ALO - ALE(N)) / (3. * ALE(N) - ALO)
   U(N) = X(N) * (2. + AUX * (1. - FJ * ALE(N))) / AL(N)
   R(N) = 1. + ALE(N) * AUX / AL(N)
   V(N) = X(N) * (1. + AUX * (1. - FJ * ALE(N))) / C(N)
   S(N) = ALE(N) * AUX / C(N)
   AUX = (ALPH * ALE(N) + BETA) / (3. * ALE(N) - ALO) * B
   W(N) = X(N) * AUX * (FJ * (ALO - ALE(N)) + 2.)
   T(N) = 1. - 2. * ALE(N) * AUX
   SX = SX + X(N)
   SY = SY + Y(N)
   SXX = SXX + X(N) * 2
   SXY = SXY + X(N) * Y(N)
   3 FORMAT (E12.3, F9.3)
FM = M
AUX = 1/(SX*SY - FM*XY)
PRINT 10
10 FORMAT (1HO)
PRINT 52
12 FORMAT (1HO, "N", 7x, "R(N)", 13x, "S(N)", 9x, "T(N)", 12x, "U(N)", 14x, "V(N)
1")
DO 8 N = 1,M
52 DNX(N) = AUX*(2*(FM*X(N) - SX) - DISS*(FM*Y(N) - SY))
57 DNY(N) = AUX*DISS*(FM*X(N) - SX)
59 PRINT 1,N,R(N),S(N),T(N),U(N),V(N),W(N)
60 AUX = 1/(SX**2 - FM*SX)
61 PRINT 10
62 PRINT 53
63 53 FORMAT (1HO, "N", 6x, "DKX(N)", 11x, "DKY(N)", 6x, "DALOX(N)", 10x, "DALOY(N)
1")
DO 9 N = 1,M
64 DALOX(N) = AUX*((SX + Y(N)*SX - 2*X(N)*SY) - 2*ALO*(FM*X(N) -
1))
65 DALOY(N) = AUX*(X(N)*SX - SX)
66 PRINT 1,N,DNX(N),DKY(N),DALOX(N),DALOY(N)
68 SWT DK = 0.
69 DO 11 N = 1,M
70 SWT DK = SWT DK + W(N)*DKX(N) + T(N)*DKY(N)
71 SL = 0.
72 DO 12 N = 1,M
73 FM(N) = DALOX(N)*U(N) + DALOY(N)*R(N)
74 FN(N) = DALOX(N)*V(N) + DALOY(N)*S(N)
75 SL = SL + W(N)*DALOX(N) + T(N)*DALOY(N)
76 FL = 1. - SL
77 S2 = 0.
78 DO 13 N = 1,M
79 S2 = S2 + W(N)*DKX(N) + T(N)*DKY(N)
80 PRINT 10
81 PRINT 54
82 54 FORMAT (1HO, "N", 5x, "DLOSL(N)", 8x, "DLOC(N)", 7x, "DKSL(N)", 11x, "DKC(N
1)"
DO 14 N = 1,M
83 DLOSL(N) = FM(N)*AL(N)/(FL*SAL(N))
84 DLOC(N) = (FN(N)*C(N)/FL - FM(N)*AL(N)/FL)/C(N)
85 Q = AL(N)*(U(N)*DKX(N) + R(N)*DKY(N) + FM(N)*S2/FL)
86 P = C(N)*(V(N)*DKX(N) + S(N)*DKY(N) + FN(N)*S2/FL)
87 DKSL(N) = Q/SAL(N)
88 DKC(N) = (P - Q)/C(N)
90 14 PRINT 1,N,DLOSL(N),DLOC(N),DKSL(N),DKC(N)
C CONSTANT RELATIVE ERROR IN SPECIFIC CONDUCTANCE
91 PRINT 21
92 21 FORMAT (1HO,5x"CONSTANT RELATIVE ERROR IN SPECIFIC CONDUCTANCE")
93 S1 = 0.
94 S2 = 0.
95 DO 22 N = 1,M
96 S1 = S1 + SAL(N)*DLOSL(N)
97 S2 = S2 + SAL(N)*DKSL(N)
98 FACT = S2/SAL
23 FORMAT(1H0,"THE RELATIVE ERROR IN K IS ",E14.7," OF THE RELATIVE ERROR IN SPECIFIC CONDUCTANCE")
FACT = S1/ALO
PRINT 24, FACT
24 FORMAT(1H0,"THE RELATIVE ERROR IN THE LIMITING CONDUCTANCE IS ",E14.7," OF THE RELATIVE ERROR IN SPECIFIC CONDUCTANCE")
C CONSTANT ABSOLUTE ERROR IN SPECIFIC CONDUCTANCE
PRINT 34
34 FORMAT(1H0,5X,"CONSTANT ABSOLUTE ERROR IN SPECIFIC CONDUCTANCE")
S1 = 0.
S2 = 0.
DO 31 N = 1,M
   S2 = S2 + DKSL(N)
31 S1 = S1 + DLOSL(N)
PRINT 32,S2
32 FORMAT(1H0,"THE ERROR IN K IS ",E14.7," OF THE CONSTANT ABSOLUTE ERROR IN SPECIFIC CONDUCTANCE")
PRINT 33,S1
33 FORMAT(1H0,"THE ERROR IN THE LIMITING CONDUCTANCE IS ",E14.7," OF THE CONSTANT ABSOLUTE ERROR IN THE SPECIFIC CONDUCTANCE")
C CONSTANT RELATIVE ERROR IN CONCENTRATION
PRINT 44
44 FORMAT(1H0,5X,"CONSTANT RELATIVE ERROR IN CONCENTRATION")
S1 = 0.
S2 = 0.
DO 41 N = 1,M
   S2 = S2 + DKC(N)*C(N)
41 S1 = S1 + DLOC(N)*C(N)
FACT = S2/DISS
FACT1 = S1/ALO
PRINT 42,FACT
42 FORMAT(1H0,"THE RELATIVE ERROR IN K IS ",E14.7," OF THE RELATIVE ERROR IN CONCENTRATION")
PRINT 43,FACT1
43 FORMAT(1H0,"THE RELATIVE ERROR IN THE LIMITING CONDUCTANCE IS ",E14.7," OF THE RELATIVE ERROR IN CONCENTRATION")
61 CONTINUE
129 CALL EXIT
130 END
DIMENSION C(20),AL(20)
READ 102, M8
DO 3 M7 = 1, M8
READ 1
PRINT 1
1 FORMAT (80H1)
RE X 2, T
PRINT 2, T
2 FORMAT (1H0, 1H0, F8, 3)
C CALCULATION OF DIELECTRIC CONSTANT
C. DRAKE, JR., (PHYS. REV., 11, 39, 613, 1930)
D = 78.57 × (1.0 - 0.0000155(T - 25))
C WYMAN AND INGALLS (J. AM. CHEM. SOC., 50, 1182, 1938)
D = 78.54 × (1.0 - 0.000115(T - 25))
C. MALMHEUG AND MARYOTT (J. RES. NAT. BUR. STAND., 56, 1, 1956)
D = 78.74 × (1.0 - 0.000115(T - 25))
C AVERAGE VALUE
D = (D1 + D2 + D3) / 3
PRINT 201
201 FORMAT (1H0, 5X1HT, 16X2HD1, 16X2HD2, 16X2HD3, 16X1HD)
PRINT 202, T, D1, D2, D3, D
202 FORMAT (F9, 4, 4(7XF11, 4))
AUX = 20.4 × T
VISCA = EXP(2.30258 × (1.2348 × AUX - 0.01467 × AUX**2) / (T - 96), 1) × 4, 60316
TK = T + 273.16
ALPHA = 8.204E5 × ((D × TK)**1.5)
BET = 82.50 / (((D × TK)**0.5) × VISCA)
PRINT 115, ALPH, BET
115 FORMAT (1H0, "CQSCF", IN ONSAGER EQ., ALPH =", E14, 8, 4X, "BETA =", E14, 18)
READ 2, ALO
PRINT 2, ALO
ALO = ALO
READ 102, M, COMP
PRINT 110
110 FORMAT (1H0, 6X5HCONC, 12X5HCOND, 1)
DO 30 N = 1, M
READ 101, C(N), AL(N)
30 PRINT 102, N, C(N), AL(N)
101 FORMAT (E12, 3, F9, 4)
102 FORMAT (13, 1XE14, 8, 5(1XE14, 8))
AN = M
CALLIVES1(M, AN, VISCA, D, TK, ALO, ALPH1, BET, C, AL, COMP)
PRINT 1
ALO = ALO
5 CALL SHFS(M, AN, VISCA, D, TK, ALO, ALPH1, BET, C, AL, COMP)
PRINT 1
CALLIVES1(M, AN, VISCA, D, TK, ALO, ALPH1, BET, C, AL, COMP)
3 CONTINUE
CALL EXIT
END
SUBROUTINE IVES1(M, AN, VISC, D, TK, ALO, ALPH1, BET, C, AL, COMP)

C CALCULATION OF DISSOCIATION CONSTANT
C IVES METHOD

DIMENSION C(20), AL(20), ALPH(20), CI(20), ALE(20), X(20), Y(20)

ALO1 = ALO
A = 1.8123E6/((D*TK)**1.5)
PRINT 110, A

110 FORMAT(1X,0,3X4HA = E14.8)

GAM = ALPH1*ALO*BET
SY = 0.
SX = 0.
SXY = 0.
SXX = 0.
DO 10 N = 1, M

10 CHK = ALO

ALE1 = ALO - GAM*SORT(AL(N)*C(N)/CHK)
CHK1 = ABS(CHK-ALE1)
IF(CHK1-COMP)12, 12, 11

11 CHK = ALE1
GO TO 13

12 ALPH(N) = AL(N)/ALE1

ALE(N) = ALE1
CI(N) = SORT(ALPH(N)*CI(N))
Y(N) = AL(N)*GAM*CI(N)
X(N) = AL(N)*AL(N)*C(N)*(10.**(-2.*A*CI(N)))/(ALO-GAM*CI(N))
SY = SY + Y(N)
SX = SX + X(N)
SXY = SXY + X(N)*Y(N)
SXX = SXX + X(N)*X(N)

10 CONTINUE
CHECK = (SX*SXY-SXX*SY)/(SX*SX-AN*SXX)
DK = (SX*SX-AN*SXX)/(AN*SXY-SX*SY)
PRINT106, CHECK, DK

CHK2 = ABS(CHECK-ALO)
IF(CHK2-COMP)15, 15, 14

14 ALO = CHECK
GO TO 16

15 SUM = 0.
SUMX = 0.
SUMXX = 0.
DO 17 N = 1, M

17 YY = CHECK - X(N)/DK
DIF = Y(N) - YY
SUM = SUM + DIF*DIF
SUMX = SUMX + X(N)
SUMXX = SUMXX + X(N)*X(N)
PRINT 102, N, X(N), Y(N), YY, DIF

102 FORMAT(I3,1XE14.8,5(1XE14.8))

17 CONTINUE

502 FORMAT(2(3XE13.6))
RE = 0.6745*SQR(SUM/(AN-2.))
D1 = AN*SUMXX - SUMX*SUMX
PA = RE*SQR(SUMXX/D1)
PB = RE*SQR((AN/D1)**(DK*2))
SUBROUTINE

53    SUM = SORT(SUM/(AN - 1))
54    PRINT 104
55    PRINT 105
56    DO 20 N = 1, M
57    20 PRINT 102, N, C(N), AL(N), ALPH(N), ALE(N), X(N), Y(N)
58    PRINT 103, CHECK, DK
59
60    103 FORMAT (1HO, 4X23HLIMITING CONDUCTANCE = E14.6, 6X24HDISSOCIATION CO
61    INSTANT = E14.8)
62    PRINT 111, SUM, PA, PB
63    111 FORMAT (1HO, "MEAN SQ.DEV. = ", E14.6, 3X, "PROBABLE ERROR IN LIM. COND.
64    1 = ", E14.6, 3X, "PROBABLE ERROR IN DISS. CONST. = ", E14.6)
65    104 FORMAT (1HO, 4X13HCONEC'TRATION, 2X11HCONDUCTANCE, 4X12HDEGREE DISS.,
66    14X11HIONIC COND., 7X4HX(N), 11X4HY(N))
67    105 FORMAT (1HO, 6X10HMOL/LITER, 7X3HMHO, 28X3HMHO)
68    106 FORMAT (E15.8, 10XE15.8, 10XE15.8, 10XE15.8)
69    ALO = ALO1
70    RETURN
71    END
SUBROUTINE SHFS(M, AN, VISC, D, TK, ALO, ALPH1, BET, C, AL, COMP)
C CALCULATION OF DISSOCIATION CONSTANT
C FUOSS - SHELDOVSKY METHOD
DIMENSION C(20), AL(20), ALPH(20), F(20), X(20), Y(20), CI(20), CAPS(20),
1 X5(20)
READ 108, R
PRINT 108, R
108 FORMAT (E8.1)
104 FORMAT (1H0, 4X13HCONCENTRATION, 1X11HCONDUCTANCE, 3X12HDEGREE DISS., 4
1X1HACT, 6X4HX(N), 10X4HY(N), 10X2HYY, 13X3HDF)
A = 1.8123E+06/((D*TK)**1.5)
B = 50.29E+08/SQRT(D*TK)
PRINT110, A, B
110 FORMAT (1H0, 3X4HA = E14.9, 8X4HB = E14.8)
M4 = 0
M5 = 0
24 M6 = 0
23 GAM = ALPH1*ALO+BET
SY = 0.
SX = 0.
SXY = 0.
SX = 0.
DO 10 N = 1, M
Z = GAM* SQRT(C(N)*AL(N))/(ALO**1.5)
S = (Z/Z2, + SQRT(1,+(Z/Z2)**2))*2
ALPH(N) = S*AL(N)/ALO
22 C DEBYE - HUKEL FORMULA
C CALCULATION OF ACTIVITY COEFFICIENT
CI(N) = ALPH(N)*C(N)
24 ALNF = A* SQRT(CI(N))/((1, +B*R* SQRT(CI(N)))
25 F(N) = 10, 0**(-ALNF)
26 X(N) = C(N)*AL(N)*S*F(N)*F(N)
27 Y(N) = I,/(AL(N)*S)
28 SX = SX + X(N)
29 SY = SY + Y(N)
30 SXY = SXY + X(N)*Y(N)
31 SX = SX + X(N)*X(N)
32 10 CONTINUE
109 FORMAT (5(E14.8)/4(E14.8))
YO = (SX*SXY-SXX*SY)/(SX*SX-AN*SXX)
SL = (AN*SXY-SX*SY)/(AN*SXX-SX*5X)
PRINT 117, YO, SL
117 FORMAT (1H0,"INTERCEPT = ",E14.7," SLOPE = ",E14.7)
CHK = 1./YO
38 IF (ABS(CHK - ALO) - 0.3)69, 69
39 69 ALO = CHK
40 25 GO TO 28
41 ALO = CHK
42 DK = 1./(SL*(ALO**2))
43 PRINT 111, CHK, DK
44 111 FORMAT (1H0, 30H LAMDA ZERO FROM THE INTERCEPT = F8.3, 8X, 23HDISSOCIATION CONSTANT = E14.7)
46 22 PRINT 104
47 PRINT 105
105 FORMATT(1HO,6X10HMOLE/LITER,7X3HMO)
    SUM = 0;
    SUMX = 0;
    SUMXX = 0;
    DO 20 N = 1,M
      YY = 1./ALO + SL*X(N)
      DIF = YIN(N) - YY
      SUM = SUM + DIF*DIF
      SUMX = SUMX + X(N)
      SUMXX = SUMXX + X(N)*X(N)
    20 PRINT 102,N,C(N),AL(N),ALPH(N),F(N),X(N),Y(N),YY,DIF
102 FORMAT (13,1XE13,7,7(1XE13,7))
    RE = 0.6745*SQRT(SUM/(AN-2.))
    D1 = AN*SUMXX - SUMX*SUMX
    PA = RE*SQRT(SUMXX/D1)*(ALO**2)
    PB = RE*SQRT(AN/D1)*DK/SL
    DEV = (SUM/(AN - 1.))**0.5
    PRINT 103, ALO, DK
    PRINT 116, DEV, PA, PB
116 FORMAT(1HO,"MEAN SQ.DEV. = ",E14,6,3X,"PROBABLE ERROR IN LIM.COND.
      1 = ",E14,6,3X,"PROBABLE ERROR IN DISS.CONST. = ",E14,6)
103 FORMAT (1HO,4X23H, LIMITING CONDUCTANCE = E14,8,6X24H DISSOCIATION CO
      INSTANT = E14,8)
104 CAPW1 = 1,E20
105 N7 = 2
106 N9 = 1
32 CONTINUE
72 SX5 = 0;
74 SCAPS = 0;
75 SCAX5 = 0;
76 SX5X5 = 0;
77 DO 40 N = 1,M
    CAPS(N) = AL(N)*C(N)
    Z = GAM*SQRT(C(N)*AL(N))/(ALO**1.5)
    S = (2/2., * SQRT(1.+ (Z/2.)**2)**2
    IF(N7-1)44,45,44
    44 X5(N) = (C(N)**0.5)/(S*F(N))**((1.+ S*AL(N))/ALO)**0.5
    45 GO TO 46
    46 X5(N) = (C(N)**0.5)/(S*F(N))**((1.+ S*AL(N))/ALO)**0.
    15)
    SX5 = SX5 + X5(N)
    SCAPS = SCAPS + CAPS(N)
    SCAX5 = SCAX5 + CAPS(N)*X5(N)
    SX5X5 = SX5X5 + X5(N)*X5(N)
40 CONTINUE
48 CAPW = (SX5X5*SCAPS - SX5*SCAX5)/(AN*SX5X5 - SX5*SX5)
49 SL5 = (AN*SCAX5 - SX5*SCAPS)/(AN*SX5X5 - SX5*SX5)
48 CONTINUE
55 FORMAT (1HO,33HCALCULATION WITH WATER CORRECTION)
59 PRINT 114, CAPW, SL5
114 FORMAT (1HO,3X7HCAPW = E14,7,5X6HSL5 = E14,7)
70 IF (N7 - 1)50,51,50
50 CHK3 = CAPW
99 N7 = 1
100 GO TO 32
101 51 COMP2 = 0.05
102 CHK4 = ABS(CAPW/CHK3 - 1)
103 IF (COMP2 - CHK4)53,52,52
104 53 N9 = N9 + 1
105 IF (N9 = 5)54,54,56
106 54 CHK3 = CAPW
107 GO TO 32
108 56 PRINT 57
109 57 FORMAT(1HO,"INTERESTEDISSISION IS DIVERGENT")
110 GO TO 72
111 52 CONTINUE
112 IF (ABS(CAPW1) = ABS(CAPW))59,42,58
113 58 SUM = 0
114 SUMX = 0
115 SUMXX = 0
116 DO 43 N = 1,M
117 Y6 = CAPW + SL5*X5(N)
118 DIF = CAPS(N) - Y6
119 SUMX = SUMX + X5(N)
120 SUMXX = SUMXX + X5(N)**2
121 SUM = SUM + DIF*DIF
122 PRINT 102,N,CAPS(N),Y6,DIF
123 CONTINUE
124 DK1 = SL5/SL5/(AL0**2)
125 PRINT 112,AL0,DK1
126 112 FORMAT(1HO,3X12HLIM, COND1 = E14,8,3X15HDISS, CONST1 = E14,8)
127 DEV = (SUM/(AN - 1.,))**0.5
128 RE = 0.6745*SQRT(SUM/(AN-2.,))
129 D1 = AN*SUMXX - SUMXX**2
130 PA = RE*SQRT(SUMXX/D1)
131 PB = NE*SQRT(AN/D1)
132 PB = PB**2,0*SQRT(DK1)/AL0 * (PB/AL0)**2
133 PRINT 118,DEV,PA,PB
134 118 FORMAT(1HO,"MEAN SO,DEV,",E14,6,3X,"PROBABLE ERROR IN SPEC,COND,
135 1H20 =",E14,6,3X,"PROBABLE ERROR DISS,CONST,",",E14,6)
136 SUM = 0
137 DO 61 N = 1,M
138 AL1 = (CAPS(N) - CAPW)/C(N)
139 DIF = AL(N) - AL1
140 PRINT 102,N,C(N),AL(N),AL1,DIF
141 61 AL(N) = AL1
142 DEV = (SUM/(AN - 1.,))**0.5
143 PRINT 119,DEV
144 119 FORMAT(1HO,"MEAN SQUARE DEVIATION = ",E14,6)
145 CAPW1 = CAPW
146 GO 10 42
147 42 PRINT 60
148 59 FORMAT(1HO,"SECOND TIME AROUND WATER RESISTANCE HAS INCREASED, CA
149 1LCULATION WAS STOPPED,")
150 42 CONTINUE
151 M6 = M6 + 1
63 IF (ABS(DK-DK1)/DK - 0.001) > 62.62.66
66 IF (M6 - 4) > 23.64.64
64 PRINT 65
65 FORMAT (1HO,"INTERACTION DOES NOT CONVERGE, STOP CALCULATION")
GO TO 72
62 IF(M5) > 70.71.70
71 ALO1 = ALO
M5 = 1
GO TO 23
70 IF (ABS(ALO-ALO1) - 0.3) > 72.72.73
73 M4 = M4 + 1
72 IF (M4-3) > 71.71.64
72 CONTINUE
RETURN
END
C NEW ONSAGER-FUOSS-SKINNER EQUATION

DIMENSION C(40), AL(40), GAM(40), F(40), X(40), Y(40), Z(40), V(40), A(8, 18), B(4), COEF(4), PE(4)

READ 4, L1
DO 26 L2 = 1, L1
L3 = 0
READ 1
PRINT 1
1 FORMAT (80H)

READ 2, T
PRINT 2, T
READ 2, ALO

2 FORMAT (1HO, 19H)

READ 4, M, COMP
AM = M

4 FORMAT (I3, 1X, E14.7)
AM = M
PRINT 8
8 FORMAT (1HO, 2H =, 3X, 16HCONC(MOLE/LITER), 10H COND(MHO))
DO 5 N = 1, M
READ 6, C(N), AL(N)
PRINT 7, N, C(N), AL(N)
6 FORMAT (E12.3, F9.4)
7 FORMAT (I3, 5X, E12.6, 3X, F9.4)
READ 18, R

18 FORMAT (F8.1)
T = T + 273.16
D = 78.47
VISC = 0.008903
ALPH1 = 8.024E5/((D*DS)**1.5)
BET = 82.50/((D*DS)**0.5*VISC)
PRINT 3, ALPH1, BET
3 FORMAT (1HO, 7(2X, E12.5))
E11 = 2.942E12/((D*DS)**3)
E12 = 0.433E08/((VISC*DS)**2))
PRINT 3, E11, E12
L4 = 0

24 PRINT 2, ALO
GAM1 = ALPH1*ALO + BET
DO 9 N = 1, M
9 GAM(N) = AL(N)/(ALO-GAM1*(((C(N)*AL(N))/ALO)**0.5))
11 CONTINUE

SXX = 0
SXY = 0
SXZ = 0
SXV = 0
SYY = 0
SYZ = 0
SYV = 0
SZZ = 0
SZV = 0
SVV = 0
DO 11 N = 1, M

APPENDIX 6.8.1
Calculation of K and \( \Lambda^0 \) by a method based on the Fuoss-Onsager-Skinner conductance equation.
52  \( C_i = C(N) \times \text{GAM}(N) \)
53  \( F(N) = \exp(-4.203E06 \times \text{SORT}(C)) / ((D+T) \times 1.5) \)
54  \( X(N) = 1, - \text{ALPH}_1 \times \text{SORT}(C) + E11 \times C_i \times \text{ALOG}(6 \times E11 \times C_i) \)
55  \( Y(N) = C_i \)
56  \( Z(N) = -C_i \times F(N) \times F(N) \times \text{AL}(N) \)
57  \( V(N) = A(N) + \text{BET} \times \text{SORT}(C) + E12 \times C_i \times \text{ALOG}(6 \times E11 \times C_i) \)
58  \( \text{SX} \times X(N) \times X(N) \)
59  \( \text{SY} \times Y(N) \times Y(N) \)
60  \( \text{SZ} \times Z(N) \times Z(N) \)
61  \( \text{SV} \times V(N) \times V(N) \)
62  \( \text{SY} \times Y(N) \times Y(N) \)
63  \( \text{SZ} \times Z(N) \times Z(N) \)
64  \( \text{SV} \times V(N) \times V(N) \)
65  \( \text{SY} \times Y(N) \times Y(N) \)
66  \( \text{SZ} \times Z(N) \times Z(N) \)
67  \( \text{SV} \times V(N) \times V(N) \)
68  \text{CONTINUE} \)

69  \( A(1,1) = \text{SX} \times X(N) \times X(N) \)
70  \( A(1,2) = \text{SY} \times Y(N) \times Y(N) \)
71  \( A(1,3) = \text{SZ} \times Z(N) \times Z(N) \)
72  \( B(1) = \text{SV} \times V(N) \times V(N) \)
73  \( A(2,1) = \text{SX} \times X(N) \times X(N) \)
74  \( A(2,2) = \text{SY} \times Y(N) \times Y(N) \)
75  \( A(2,3) = \text{SZ} \times Z(N) \times Z(N) \)
76  \( B(2) = \text{SV} \times V(N) \times V(N) \)
77  \( A(3,1) = \text{SX} \times X(N) \times X(N) \)
78  \( A(3,2) = \text{SY} \times Y(N) \times Y(N) \)
79  \( A(3,3) = \text{SZ} \times Z(N) \times Z(N) \)
80  \( B(3) = \text{SV} \times V(N) \times V(N) \)
81  \( M1 = 3 \)
82  \text{CALL ADMI}(M1, A) \)
83  \text{DO 51 N = 1, M1} \)
84  \text{SUM = 0,} \)
85  \text{DO 52 N1 = 1, M1} \)
86  \text{SUM = SUM + A(N, N1) * B(N1)} \)
87  \text{COEF(N) = SUM} \)
88  \text{PRINT 33, N, COEF(N)} \)
89  \text{FORMAT(1H, "COEFFICIENT", 13, 4X, E14, 7)} \)
90  \text{IF (ABS(ALO = COEF(1)) < COMP)14, 14, 15} \)
91  \text{ALO = COEF(1)} \)
92  \text{GAM1 = ALPH1 * AL0 * BET} \)
93  \text{DO 1 N = 1, M} \)
94  \text{C} = C(N) * GAM(N) \)
95  \text{CHK = GAM(N)} \)
96  \text{GAM(C) = AL(N) / (ALO + GAM1 * SORT(C)) + (E11 * ALO - E12) * C1 * ALOG(6 * E11 * C1)} \)
97  \text{CHK = COEF(2) * C1)} \)
98  \text{IF (GAM(N) = 21, 27, 27) \)
99  \text{IF (ABS(GAM(N) - CHK) = 0.0001) 12, 12, 28} \)
100 \text{CONTINUE} \)
101 \text{L3 = L3 + 1} \)
102 \text{IF (L3 - 10)11, 11, 14} \)
103 \text{IF (L3 - 5)22, 22, 23} \)
104 \text{ALO = ALO + 1,} \)
105 \text{CONTINUE}
GO TO 24
14 CONTINUE
ALO = COEF(1)
PRINT 10
10 FORMAT('1H0','N',6X,'CONC',9X,'OBS;COND',,CALC;COND','7X,'DIF',8X
1'DEG,DISS','5X,'ACT,COEF','7X,'V(N)',9X,'V CALC','9X,'DIF')
SUM = 0,
SUM1 = 0,
DO 37 N = 1,M
CI = C(N)*GAM(N)
V1 = COEF(1)*X(N) + COEF(2)*Y(N) + COEF(3)*Z(N)
DIF = V(N) - V1
SUM = SUM + DIF**2
AL2 = V1 - BET*SORT(CI) - E12*CI*ALOG(6,E11*CI)
DIF1 = AL2 = AL(N)
SUM1 = SUM1 + DIF1**2
120 PRINT 17,N,C(N),AL(N),AL2,DIF1,GAM(N),F(N),V(N),V1,DIF
17 FORMAT('1H0',2X,'E12.5')
SD = (SUM/(AM-3))**0.5
PRINT 19,SD
124 FORMAT('1H0',5X,'E14.7')
SD = (SUM1/(AM-3))**0.5
PRINT 19,SD
DISS = 1./COEF(3)
PRINT 20,COEF(1),DISS
20 FORMAT('1H0',3X,'E14.7')
CALL CALER(A,AM,ML,UNIT,PE)
PEDIS = PE(3)/COEF(3)**2
PRINT 100,PE(1),PEDIS
100 FORMAT('1H0',5X,'E14.6')
GO TO 26
23 PRINT 25,N
25 FORMAT('1H0',5X,'E14.6')
26 CONTINUE
CALL 'EXIT
END
SUBROUTINE CALER(A1, AM, M1, SUM, PE)

DIMENSION A1(6,8), PE(4), COV(4,4)
AM1=M1
DFREE=AM-AM1
IF (DFREE)3,2,3

2 DFREE=1,

3 S = SQRT(SUM/DFREE)

PS=S*0.6745

4 PRINT 4,S,PS

5 PRINT 7

6 PRINT 8

7 FORMAT (1H0, "ESTIMATE OF RESIDUAL VARIANCE=", E14:7,3X, "PROBABLE ERROR OF THE FITTING=", E14:7)

8 PRINT 9

9 FORMAT (1H0, "ERRORS IN THE COEFFICIENTS")

10 FORMAT (1H0, "COEFFICIENT", 5X, "PROBABLE ERROR")

11 DO 5 N=1,M1

12 PE(N) = PS*SQRT(A1(N,N))

13 PRINT 6,N,PE(N)

14 PRINT 9

15 FORMAT (7X, I3, 9X, E14:7)

16 DO 10 M1=1,M1

17 DO 11 N=1,M1

18 COV(N1,N) = S*S*A1(N1,N)

19 PRINT 12,N1,(N,COV(N1,N), N=1,M1)

20 FORMAT (1H0, "COVARIANCES")

21 RETURN

22 END

APPENDIX 6.8.1 (cont.)
SUBROUTINE ADIV(N, A)
DIMENSION A(0:N), AUX(N, N)
N1 = N + 1
N2 = 2*N
DO 10 I = 1, N
  DO 10 J = N1, N2
    IF (J - I - N) 11, 12, 11
  11 A(I, J) = 0.
  GO TO 10
  12 A(I, J) = 1.
  CONTINUE
C MATRIX INVERSION
  DO 4 I = 1, N
    AUX2 = A(I, I)
    M = 2*N + 1 - I
    DO 3 J = 1, M
      3 A(I, J) = A(I, J) / AUX2
    DO 1 L = 1, N
      IF (L - I) 6, 1, 6
    CONTINUE
  6 CONTINUE
  DO 2 L1 = 1, M
    2 AUX(I, L1) = A(I, L1) * A(L, L1)
  DO 5 L1 = 1, M
    5 A(L, L1) = A(L, L1) - AUX(I, L1)
  CONTINUE
  M1 = M - 1
  DO 4 K1 = 1, N
    DO 4 K = 1, M1
      4 A(K1, K) = A(K1, K+1).
RETURN
END
SUBROUTINE ADIV(N,A)
DIMENSION A(8,8), AUX(8,8)
N1 = N + 1
N2 = 2*N
DO 10 I = 1,N
DO 10 J = N1,N2
IF (J-I-N) 11,12,11

11 A(I,J) = 0.
GO TO 10

12 A(I,J) = 1.
CONTINUE

C. MATRIX INVERSION
DO 4 I = 1,N
AUX2 = A(I,1)
M = 2*N + 1 - I
DO 3 J = 1,M
3 A(I,J) = A(I,J)/AUX2
DO 1 L = 1,N
IF (I-L) 6,1,6
CONTINUE

6 CONTINUE
DO 2 L1 = 1,M
2 AUX(I,L1) = A(I,L1)*A(L,1)
DO 5 L1 = 1,M
5 A(L,L1) = A(L,L1) - AUX(I,L1)
CONTINUE
M1 = M - 1
DO 4 K1 = 1,N
DO 4 K = 1,M1
4 A(K1,K) = A(K1,K+1).
RETURN
END
NEW ONSAGER-FUOSS-SKINNER EQUATION

```fortran
DIMENSION CC(100), AL(100), GAM(100), F(100), X(100), Y(100), Z(100), 
1V(100), A(8,8), B(4), COEF(4), PE(4)

DIMENSION CC(100), AL(100), F(9), FC(5)

READ 4, L1
DO 26 L2 = 1, L4
L3 = 0
READ 1
PRINT 1

1 FORMAT (80H )

READ 2, T
PRINT 2, T
READ 2, AL0

2 FORMAT (1H0, 19H )

READ 4, M, COMP.

AM = M

4 FORMAT (13, 1X, E14, 7)

AM = M
PRINT 8

8 FORMAT (1H0, 2H =, 3X, 16HCONC(MOLE/LITER), 10H COND(MHQ))

DO 5 N = 1, M
READ 6, CC(N), AL(N)

5 PRINT 7, N, CC(N), AL(N)

6 FORMAT (E12, 3, F9, 4)

7 FORMAT (13, 5X, E12, 6, 3X, F9, 4)

READ 18, R

18 FORMAT (F8, 1)

T = T * 273, 16
D = 78, 47
VISC = 0, 008903
ALPH1 = 8, 204E5/(D*T)**1, 5
BET = 82, 50/(D*T)**0, 5*VISC

PRINT 3, ALPH1, BET

3 FORMAT (1H0, 7(2X, E12, 5))

E11 = 2, 942E12/(D*T)**3
E12 = 0, 4333E08/(VISC*(D*T)**2)

PRINT 3, E11, E12

AL01 = AL0

FL(1) = 0
FL(2) = 5, 0E-07
FL(3) = 1, 0E-07
FL(4) = 1, 0E-08
FL(5) = -1, 0E-07
FL(6) = 1, 05
FL(7) = 1, 01
FL(8) = 0, 99
FL(9) = 0, 95
FC(1) = 1
FC(2) = 0, 999
FC(3) = 1, 001

AL01 = AL0
DO 26 KKK = 1, 3
DO 26 KK = 1, 9
```

APPENDIX 6.8.2

Analysis of errors involved in the determination of \( K \) and \( \sigma \) by a method based on Fuoss-Onsager-Skinner conductance equation.
IF(KKK-1)201,200,201
201 IF(KK-1)201,208,26
208 DO 202 N = 1,M
202 C(N) = CC(N)*FC(KK)
206 AL(N) = ALL(N) - 1000,4FL(KK)/C(N)
209 FORMAT(1H0,2(13,3X),"CONC FACTOR = ",F7,3,4X,"COND FACTOR = ",E14.7)
210 L4 = 0
24 PRINT 2,ALO
25 GAM1 = ALPH1*ALO + BET
9 GAM(N) = AL(N)/((ALO-GAM1*(C(N)*AL(N)/ALO)**0,5))
11 CONTINUE
74 SXZ = 0
75 SYY = 0
76 SXZ = 0
77 SXV = 0
78 SYY = 0
79 SYZ = 0
80 SVV = 0
81 SZZ = 0
82 SZZ = 0
83 SVV = 0
84 DO 13 N = 1,M
13 CONTINUE
85 CI = C(N)*GAM(N)
86 F(N) = EXP(-4,203E06*SORT(CI))/(D*T)**1,5)
87 X(N) = 1. - ALPH1*SORT(CI) + E11*CI*ALOG(6,E11*CI)
88 Y(N) = CI
89 Z(N) = -CI*F(N)*F(N)*AL(N)
90 V(N) = AL(N) + BET*SORT(CI) + E12*CI*ALOG(6,E11*CI)
91 SXZ = SXZ + X(N)*X(N)
92 SXX = SXZ + X(N)*Y(N)
93 SXZ = SXZ + X(N)*Z(N)
94 SXZ = SXZ + X(N)*Z(N)
95 SYY = SYY + Y(N)*Y(N)
96 SYZ = SYZ + Y(N)*Z(N)
97 SYZ = SYZ + Y(N)*Z(N)
98 SZZ = SZZ + Z(N)*Z(N)
99 SZZ = SZZ + Z(N)*Z(N)
100 SVV = SVV + V(N)*V(N)
101 SVV = SVV + V(N)*V(N)
102 A(1,1) = SXX
103 A(1,2) = SXY
104 A(1,3) = SXZ
```
105  B(1) = SXV
106  A(2,1) = SXY
107  A(2,2) = SYY
108  A(2,3) = SYZ
109  B(2) = SYV
110  A(3,1) = SXZ
111  A(3,2) = SYZ
112  A(3,3) = SZZ
113  B(3) = SZV
114  M1 = 3
115  CALL ADMIV(M1,A)
116  DO 51 N = 1, M1
117       SUM = 0,
118       DO 52 N1 = 1, M1
119       52 SUM = SUM + A(N,N1) * B(N1)
120       COEF(N) = SUM
121  51 PRINT 33, N, COEF(N)
122  33 FORMAT(1X, "COEFFICIENT", I3, 4X, E14, 7)
123  IF (ABS(ALO - COEF(1)) < COMP) 14, 14, 15
124  15 ALO = COEF(1)
125     GAM1 = ALPH1 * ALO * BET
126     DO 12 N = 1, M
127  28 CI = C(N) * GAM(N)
128     CHK = GAM(N)
129     GAM(N) = AL(N) / (ALO - GAM1 * SORT(CI) * (E11 * ALO - E12) * CI * ALOG(6, E11 * CI))
130     1*COEF(2)*CI
131     IF (GAM(N) .LT. 21,27,27
132  27 IF (ABS(GAM(N) - CHK) .LT. 0.0001) 12, 12, 28
133     L3 = L3 + 1
134  21 IF (L3 .LT. 10) 11, 11, 14
135     L4 = L4 + 1
136  22 IF (L4 .LT. 5) 22, 22, 23
137     ALO = ALO + 1,
138     GO TO 24
139  14 CONTINUE
140     ALO = COEF(1)
141  PRINT 10
143     1*DEG, DISS", 5X, "ACT, COEF", 7X, "V(N)", 9X, "V, CALC", 9X, "DIF")
144     SUM = 0,
145     SUM1 = 0,
146     DO 32 N = 1, M
147     V1 = COEF(1) * X(N) + COEF(2) * Y(N) + COEF(3) * Z(N)
148     DIF = V(N) - V1
149     SUM = SUM + DIF**2
150     AL2 = V1 - BET * SORT(CI) - E12 * CI * ALOG(6, E11 * CI)
151     DIF1 = AL2 - AL(N)
152     SUM1 = SUM1 + DIF1**2
153  32 PRINT 17, N, C(N), AL(N), AL2, DIF1, GAM(N), F(N), V(N), V1, DIF
154  17 FORMAT(13, 9(2X, E12, 5))
155     SD = (SUM/(AM - 3, 1)**0.5
156  PRINT 19, SD
```
157  19 FORMAT (1H0,5X,5HMSD = ,E14,7)
158         SD = (SUM1/(AM-3,))**0.5
159         PRINT 19, SD
160  160 DISS = 1./COEF(3)
161         PRINT 20, COEF(1), DISS
162  20 FORMAT (1H0,3X,11H LIM,COND, = ,E14,7,5X,10HDISS,CT, = ,E14,7)
163         CALL CALER(A,AM,M1,SUM,PE)
164         PEDIS = PE(3)/(COEF(3)**2)
165         PRINT 100, PE(1), PEDIS
166  100 FORMAT(1H0,"PROBABLE ERROR LIM,COND, = ",E14,6,5X,"PROBABLE ERROR DISS CONST, = ",E14,6)
167         GO TO 26
168  23 PRINT 25, N
169  25 FORMAT (1H0,"DEGREE OF DISSOCIATION NEGATIVE FOR DATA NO; ",I3,3X,
170         1"STOP CALCULATION,")
171  26 CONTINUE
172         CALL EXIT
173         END
C HISHAW AND STOKES FORMULA

n = 2
AH = -N
DU 3N N = 1,M
READ 101,C(N),AL(N)
30 PRINT 101,C(N),AL(N)

T = 293.000
TK = T + 273.16

C CALCULATION OF D: DIELECTRIC CONSTANT

C DRAKE,...(PHYS.REV., 11, 35,613,1930)

UI = 7.85.57*(1/-0.00661*(T=25.)*0.0015*21)

C WYKAN AND INGALLS (J.AM. CHEN.SOC. 60,1182,1938)

U2 = 7.85.54*0.004579*(T=25.)*0.001519*21+28.4*9*(T=25.)*

C HALSEBERG AND HARRYTT (J.RES.NAT.BUR.STAND. 56,1,1956)

U3 = 87.74-0.4008*T + 9.398E-4*T*T - 1.410E-6*T*T*T

C AVERAGE VALUE

D = (U1 + U2 + U3)/3.

PRINT 201

PRINT 202, T, U1, U2, U3, D

201 FORMAT (I9, 2F16.5, 1X, I9, 2F16.5, 1X)

202 FORMAT (F9.4, 7XF11.4, 7XF11.4, 7XF11.4)

C CALCULATION OF DISSOCIATION CONSTANT

CUMP = 0.01

VISCA = 0.003949

ALPH1 = 8.147E5/(1D*T)*(1.5*1.5)

GAT = 8.146/(1D*T)*(0.5*VISCA)

PRINT 115, ALPH1, BET

AV = 0.02257523

BOLT1 = 1.380543-16

ED = 4.602928E-10

PI = 3.141593

AUX = SQRTF(D*BOLT1*T*1000.)

A = ED*ED*ED*SQRTF(2.*PI*AV)/(AVD*BOLT1*T)

B = SQRTF(2.*PI*ED*ED*AV)/AUX

PRINT110, A, B

B1 = 8.29E5/(1D*T)*(1.5*1.5)

B2 = 8.29/(VISCA*SQRTF(D*T))

K = 10

R1 = 2.6E-8

DC 70 J = 1, K

AJ = J

R(J) = R1 + 0.2E-8*AJ

SAWO = 0.

DO 60 N = 1, N

VICK = 1./(1+PI*AV*C(N)*(R(J)*3)/300.)

ALD = 291/5

GAM = ALPH1*ALU+BET

65 CHK = ALD

63 ALE1 = ALD - GAM*SQRTF(AL(N)*C(N)/CHK)

CHK1 = ABSF(CHK- ALE1)

IF (CHK1 = CUMP) 62, 62, 61

61 CHK = ALE1

GO TO 63

62 ALE(N) = ALE1
ALPH(n) = AL(m) / ALE(n)
CAP(n) = SQRTF(PI*A*T*EO*EO*C(n)*ALPH(n)/(125.*D*BULK*TK))
F1 = 1./(1.+CAP(n)*R(J)/2.+(CAP(n)*R(J))**2)/6.)
B3 = CAP(n)**R(J)
CA = SQRTF(C(n)*ALPH(n))
ALU1 = AL(n)/(ALPH(n)*(1.-B1*CA*F1/(1.+B3))*VICR)-B2*CA/(1.+B3)
PRINT(14,ALU1,ALU2(n),CAP(n),ALPH(n))
66 ALU2(n) = ALU1
66 SALU = SALU+ALU2(n)
PRINT 142, SALU
ALO3(J) = SALU/AN
DEV = 0.
DO 80 N = 1,M
80 DEV = DEV + ABSF(ALU2(N)-ALO3(J))
PRINT 143, DEV
DEV1(J) = DEV/AN
C CALCULATION OF ACTIVITY COEFFICIENT
C DEBYE - HUKEL FORMULA
DO 90 N = 1,M
CI(N) = ALPH(N)*C(N)
ALAF = A*SQRTF(CI(N))/(1.+B1*R(J)*SQRTF(CI(N)))
F(N) = EXPF(-ALNF)
PRINT 136, F(N)
G(N) = 1.0000000 - ALPH(N)
G1(N) = ALPH(N)*F(N)
DK(N) = CI(N)/(G1(N)**2)/G(N)
190 PRINT 145, G(N), ALPH(N), G1(N)
DKM = 0.
DO 95 N = 1,M
95 DKM = DKM + DK(N)
PRINT 144, DKM
PRINT 131
DO 100 N = 1,M
100 PRINT130, N, CI(N), AL(N), ALE(N), ALPH(N), F(N), ALU2(N), DK(N)
DKI(J) = DKM/AN
PRINT 133
70 PRINT 136, R(J), ALO3(J), DEVI(J), DKI(J)
101 FORMAT (E12.3, F9.4)
110 FORMAT(1X,H0,3X4HA = E14.8, 8X4HB = E14.8)
115 FORMAT(1X,H0, 3HCUEFF. IN ONSAGER EO. ALPH1 = E14.8, 4X7HBETA = E14.18)
130 FORMAT(13,3(2XE15.8)/5XE15.8,3(2XE15.8))
131 FORMAT(1H0, 6X13HCONCENTRATION, 5X11HCONDUCTANCE, 6X11HIUNIC COND, /6X 112HDGEEK DISS, 6X10HACT. COEF., 8X10HLIM. COND., 6X12HDISS. CONST.)
133 FORMAT(1H0, 4X11HIUNIC DIST., 7X10HLIM. COND., 7X9HMEAN DEVI., 7X12HOIS 1S. CONST.)
136 FORMAT(4(2XE15.8))
140 FORMAT(1H0, 4HIUNIC COND. = E15.8)
141 FORMAT(1H0, 5HL0 = E11.4, 3X5HLE = E11.4, 3X8HKAPPA = E12.5, 3X10HD. DJ 1SS. = E12.5)
142 FORMAT(1H0, 7HSALO = E15.8)
143 FORMAT (1H0, 6HDEV = E15.8)
144 FORMAT (1H0, 6HOHI = E15.8)
145 FORMAT (1H0, 7HG(N) = E15.8, 5X10HALPH(N) = E15.8, 5X8HG1(N) = E15.8)
CALL EXIT
END
C RISTOFFLER AND STOKES FORMULA

\[ m = 5 \]
\[ DU = 31 \cdot h = 1.2 \]
\[ AN = m \]
\[ DU = 30 \cdot n = 1.2 \]
\[ READ 101, \text{C}(N), \text{AL}(N) \]
\[ T = 29,000 \]
\[ TK = T + 273.16 \]

C CALCULATION OF DIELECTRIC CONSTANT

\[ \text{DRAKE} \ldots \text{(PHYS. REV., 11, 35, 613, 1930)} \]
\[ D_1 = 78.57 \cdot \left(1 - 0.00461 \cdot (T - 25) + 0.0000155 \cdot (T - 25)^2 \right) \]

H. YAMAN AND INC. GALL (J. AM. CHEM. SOC., 60, 1162, 1930)
\[ D_2 = 78.54 - 0.004579 \cdot (T - 25) + 0.0000119 \cdot (T - 25)^2 + 28 \cdot 10^{-9} \cdot (T - 25)^2 \]

C NAHBERG AND HAKROTTI (J. RES. NAT. BUR. STAND., 56, 1, 1956)
\[ D_3 = 67.74 + 0.4008 \cdot T + 9.395 \cdot 10^{-4} \cdot T^2 - 1.410 \cdot 10^{-6} \cdot T^3 \cdot T^4 \]

C AVERAGE VALUE
\[ D = \frac{D_1 + D_2 + D_3}{3} \]

PRINT 201

F201 FORMAT(1H0, 5X1H7, 15X2HD1, 15X2HD2, 15X2HD3, 15X1HD)

C CALCULATION OF DISSOCIATION CONSTANT

\[ C_{OM} = 0.01 \]
\[ VISC = 0.008903 \]
\[ ALPH1 = 5.1475 \cdot \left( \frac{(D \cdot TK)^2}{2} \right) \]
\[ BET = 81.86 \cdot \left( \frac{(D \cdot TK)^2}{2} \right) \cdot VISC \]

PRINT 115, ALPH1, BET

AV = 6.02257E23

SOLT = 1.38055E16

EO = 4.80296E-10

PI = 3.141593

AUX = SQRTF(D*BULT*TK*1000)
\[ A = \frac{E_{0} \cdot C_{OM} \cdot AUX \cdot (2 \cdot \pi \cdot AV)}{(AUX \cdot D \cdot BOLT \cdot TK)} \]
\[ b = \frac{2 \cdot \pi \cdot AV \cdot E_{0} \cdot (E_{0} \cdot AV) / AUX}{273.16} \]

PRINT 110, ATD

\[ b_1 = 8.20E5 \cdot \left( \frac{(D \cdot TK)^2}{2} \right) \]
\[ D_2 = 62.0 \cdot \left( VISC \cdot \left( \frac{SQRTF(D \cdot TK)}{TK} \right) \right) \]

K = .10

R1 = 2.47E-6

DO 70 J = 1, K

R(J) = R1 + 0.2E-8 * AJ

SALU = 0.

DO 60 N = 1, n

VICK = 1 / (1 + PI*AV*G(N)*(R(J)**3)/300.)

ALU = 391.5

GAM = ALPH1*ALU*BET

CHK = ALU

ALE = ALU - GAM * SQRTF(ALU(N)*C(N)/CHK)

CHK1 = ABSF(CHK - ALE)

IF(CHK1 = COMPD) 62, 02, 61

CHK = ALE

GO TO 62
62 \text{ALC}(n) = \text{ALC1}
\text{ALP}(n) = \text{AL}(n)/\text{ALE}(n)
\text{CAP}(n) = \sqrt{TF_{(1^{*}AV^{*}LO*EO*C(n)^{*}ALP(n)}/(125*O*\text{ULT*TK})}}
F1 = 1.7/(1.+\text{CAP}(n)^{*}K(J)/2.1\text{+(CAP}(n)^{*}R(J))^{{**}2}/6.1)
DS = \text{CAP}(n)^{*}K(J)
CA = \sqrt{TF_{(C(n)^{*}\text{ALP}(n))}}
\text{CAPR} = \text{CAP}(n)^{*}R(J)
\text{ALU1} = (\text{AL}(n)/\text{ALP}(n)+B2*CA*VIRC/(1.+\text{CAPR}))/(VIRC*(1-B1*CA)/(1.+CA
1.1))
66 \text{ALU2}(n) = \text{ALU1}
\text{PRINT141,ALU1,ALP(n),CAP(n),ALP(n)}
60 \text{SALU} = \text{SALU}+\text{ALU2}(n)
\text{PRINT 142,SALU}
\text{ALO3(J)} = \text{SALU}+\text{AN}
\text{DEV} = 0.
\text{DO 80 N = 1,11}
80 \text{DEV} = \text{DEV} + \text{ABSFL} (\text{ALU2}(n),\text{ALO3(J)})
\text{PRINT 143,DEV}
\text{DEVI(J)} = \text{DEV}+\text{AN}
C \text{CALCULATION OF ACTIVITY COEFFICIENT}
C \text{DEVEY - HUREL FORMULA}
\text{DO 190 N = 1,11}
C1(n) = \text{ALP}(n)^{*}C(n)
\text{ALNF} = A*\sqrt{TF(C1(n))}/(1.+B*K(J)^{*}\text{SQRTF(C1(n))})
F(N) = \text{EXPF}(A-\text{ALNF})
\text{PRINT 136,F(N)}
G(N) = 1.000000 = \text{ALPH}(N)
G1(n) = \text{ALPH}(n)^{*}F(n)
\text{DK(N) = C(N)^{*}(G1(N)**2)/G(N)}
190 \text{PRINT 145,G(N),ALPH(N),G1(N)}
\text{DKM} = 0.
\text{DO 95 N = 1,11}
95 \text{DKM = DKM + D}(K(N))
\text{PRINT 144,DKM}
\text{PRINT 131}
\text{DO 100 N = 1,11}
100 \text{PRINT 130,NT,C(n),AL(n),ALE(n),ALP(n),F(n),ALO2(n),DK(N)}
\text{UK1(J) = DKM/AN}
\text{PRINT 129}
70 \text{PRINT 136,R(J),ALO3(J),DEVI(J),DKI(J)}
N = 10
31 \text{CONTINUE}
101 \text{FORMAT(E12.3,F9.4)}
110 \text{FORMAT(1H0,3X4HA = E14.8,6X4HB = E14.8)}
115 \text{FORMAT(1H0,31HCOEFF: IN UNSAFIEK EQ: ALPH1 = E14.0,4X7MULTA = E14.18)}
130 \text{FORMAT(1S,31X2E15.8)/5XE15.8,3(2XE15.8))}
131 \text{FORMAT(1H0,6X13HCENTRATKATU,5X11HCONDUCTANCE,6X11HIUNIC COND.\text{/6X}}
112\text{DEGREE DISS,5X10MACT, COEF.,8X10MLIM,COND.,6X12HDISS. CONST.)}
133 \text{FORMAT(1H0,4X11HIUNIC DIST.,7X10HMLIM, COND.,7X9HMEAN DEVS,7X12HDIS}
15. CONST.)}
136 \text{FORMAT(4.12X15.8))}
140 \text{FORMAT(1H0,14HIUNIC COND. = E15.8)}
141 \text{FORMAT(1H0,5SHLU = E11.4,3X5MLE = E11.4,3X8HAKPPA = E12.5,3X10HD.DI}
135. = E12.5}
142 \text{FORMAT(1H0,7HSLU = E15.8)}
145 \text{FORMAT(1H0,7MDE = E15.8)}
144 FORMAT (1H0,6HUKH = E15.8)
145 FORMAT (1H0,7HG(N) = E15.8,5X10HALPH(N) = E15.8,5X8HG1(N) = E15.8)
CALL EXIT
END
DIMENSION CI(30),AL(30),F(30),ALU(30),ALP(30),ALM(30),CAP(30)

APPENDIX 6.9.2

Calculation of K and A^0

by a method based on
Kelbg et al. conductance equation.

D = 32, N = 1, M
A = N
READ IO1, E(N), AL(N)
30 PRINT 101, C(N), AL(N)
T = 20, 000
TK = T + 273.16

C CALCULATION OF DIELECTRIC CONSTANT

C DRAKE, .... (PHYS. REV., II, 35, 613, 1930)
D1 = 78.577(1.00461*(T-25*)+0.000155*(T-25*)**2)

C WYMAN AND INGALLS (J. A R. C H E M. S O C . 60, 1182, 1938)
D2 = 75.74 0.00437*(T-25)+0.0001019*(T-25*)**2+20.9*(T-25.1**13)

C HALNBERG AND HARRY T (J. R. S. B U R. S T A N D. 56, 1, 1956)
D3 = 87.7*4.0*4008*T+9.398E-4*T*T-1.4*10E-6*T*T*T

C AVERAGE VALUE

D = (D1 + D2 + D3)/3
PRINT 201
PRINT 202, T, 01, 02, 03, 0

201 FORMAT(9,19,7X,F11.4,7XF11.4,7XF11.4,7XF11.4)

202 FORMAT(9,19,7X,F11.4,7XF11.4,7XF11.4,7XF11.4)

C CALCULATION OF DISSOCIATION CONSTANT

COMP = 0.5
VISC = 0.0006903
ALPH = 8.147E5/((D*TK)**1.5)

BET = 0.67/(((D*TK)**0.5)*VISC)
PRINT 115, ALPH, BET
AV = 0.02257E23
BOLT = 1.38053E-16
CU = 4.8029EO-10
PI = 3.141593

AUX = SQRT(D*BOLT*TK*1000.)
A' = EU*EU*O*SQRTF(Z*PI*AV)/(AUX*D*BOLT*TK)
B = SQRTF(CU*PI*EO*EU*AV)/AUX
PRINT 110, A, B
R = 3.106

PRINT 138
60 300, N = 1, M
ALU = 392
512 CHK = ALU

512 CHK = ALU

GA = ALPH*ALU + BET

301 AL1 = ALU - GA - SQRTF(ALU(2) - C(N)/CHK)

CHK1 = ABSF(AL1 - CHK)

IF(CHK1 = COMP)302, 302, 301

301 CHK = AL1

GO TO 302

302 ALPH2 = AL(U)/AL1

CAP1 = SQRTF(P1*AV*EU*EO*C(N)*ALPH2/(125.*D*BOLT*TK))
CAPR = CAP1*R

AL1 = EU*EU*(Z - SQRTF(Z()))*ALU*CAP1/(6.*D*BOLT*TK*(1.+CAPR)*(1.+CA

1PR*SQRTF(Z)/2.*((CAPR**2)**6.))

AL2 = EU*EO*AV*CAP1/(2.*PI*(10.***11)*VISC*(1.+CAPR))

ALU1 = AL(U)/ALPH2 + AL1 + AL2
PRINT 141, ALU1, AL1, AL2, CAP1
C  CALCULATION OF ACTIVITY COEFFICIENT - DEBYE-HUKEL FORMULA

CI(N) = ALPH(N) * C(N)
ALNF = A * SQRTF(CI(N)) / (1. + B * K * SQRTF(CI(N)))
P(N) = EXP(-ALNF)
DK(N) = AL(N) * AL(N) * C(N) * F(N) * F(N) / ((ALE(N) - AL(N)) * ALE(N))

500  PRINT 137,N,C(N),AL(N),ALE(N),ALPH(N),CAP(N),CAPQ(N),P(N),ALOZ(N),
10K(N)
N = 10
32 CONTINUE
101 FORMAT (E12.3,F9.4)
110 FORMAT (IH0,3X4HA = E14.8,8X4HB = E14.8)
111 FORMAT (IH0,51HCOEFF. IN UNSAUR Eq. ALPH1 = E14.8,4X7HACTA = E14.
18)
130 FORMAT (IH0,6X12HCONCENTRATION,5X11HCONDUCTANCE,6X11H1UNIC.,6X
11DUGREE DISS.,10X5HKAPPA,11X7HKAPPA*R,9X10HACT. COEF.,6X10HLLm,
2COND.,6X12HDISS. CONST.)
137 FORMAT (I3,4(2XE15.8)/5XE15.8,4(2XE15.8))
141 FORMAT (IH0,5H0 = E11.4,3X5HLE = E11.4,6X5HL2 = E12.5,5X6HKAPPA =
1 E12.5)
CALL EXIT
END
METHOD BASED ON AN EXTENDED FORM OF ONSAGER EQUATION

DIMENSION C(20), AL(20), ALPH(20), ALE(20), C(20), Y(20), F(20), Y5(20)

D = .78, 47
VISC = .0008903
COMP = 0, 1
READ 102, M8

102 FORMAT(13,6(3X,E14.7))
DO 16, M8 = 1, M8
READ 1
PRINT 1

1 FORMAT(80H)

1 READ 2, T
PRINT 2, T

2 FORMAT(1HO, 19H)
READ 2, ALO
PRINT 2, ALO
READ 102, M
AM = M

DO 30 N = 1, M
READ 101, (C(N), A(N))
30 PRINT 101, (C(N), A(N))
READ 103, R

101 FORMAT(E12, 3, F9, 4)
103 FORMAT(E8, 1)

TK = T + 273, 15
ALPH1 = 8, 204 * E05 / (D * TK)**1, 5
BET = 82, 50 / ((D * TK)**0, 5 * VISC)
PRINT 115, ALPH1, BET

115 FORMAT(IHO, "COEFF. IN ONSAGER EQ. ALPH1 = ", E14, 7, 4X, "BETA = ", E14

1, 7)

B = 50, 29E+08/SORT(D * TK)
A = 1, 8123E+06 / ((D * TK)**1, 5)
AB = 16, 708E-04 / (D * TK)
J = 0

J = J + 1
IF(J = 1015, 16, 15)

15 GAH = ALPH1 * ALO * BET
BE = (B * AB)**2 / 24, ALO = B * AB * BET / 16, )**2, 3026

SX = 0,
SY = 0,
SXX = 0,
SYX = 0,

PRINT 173, GAM, AB, B, BE

173 FORMAT(1HO, 4(3X, E15, 8))
DO 40 N = 1, M

CHK = ALO
ALE1 = ALO - GAM * SQRT(AL(N) * C(N) / CHK)
CHK1 = ABS(CHK - ALE1)
IF(CHK1 = COMP) 12, 12, 14

11 CHK = ALE1
GO TO 43

12 ALPH(N) = AL(N) / ALE1
ALE(N) = ALE1
CI(N) = C(N) + ALPH(N)
Y(N) = ALE(N) * GAH*(CI(N)*10^0.5) + BE*CI(N) + ALOG10(CI(N))
SY = SY + Y(N)
SX = SX + CI(N)
SYX = SYX + Y(N)*CI(N)
SXX = SXX + CI(N)*CI(N)
PRINT 102, N, ALE(N), ALPH(N), CI(N), Y(N)

40 CONTINUE

CHK = ALO
ALO = (SY*SXX - SYX*SX)/(AM*SXX - SX*SX)
AJ = (SY*SX - AM*SYX)/(SX*SX - AM*SXX)
PRINT 172, ALO, AJ

172 FORMAT(1H0,3X,"LIMITING COND. =",E14.7,3X,"J = "E14.7)

CHK2 = ABS(ALO - CHK)
IF(CHK2 = COMP)41,41,14

41 CONTINUE

SX5 = 0
SY5 = 0
SYX5 = 0
SXX5 = 0
DO 50 N = 1, M
ALNF = A*(CI(N)*10^0.5)/(1, + B*RE*(CI(N)*10^0.5))
F(N) = 10,*(ALNF)
Y5(N) = C(N)*((ALPH(N)*F(N))*2)
SX5 = SX5 + ALPH(N)
SY5 = SY5 + Y5(N)
SYX5 = SYX5 + ALPH(N)*Y5(N)
SXX5 = SXX5 + ALPH(N)*ALPH(N)

50 CONTINUE

DK = (SY5*SXX5 - SYX5*SX5)/(AM*SXX5 - SX5*SX5)
DK1 = (SY5*SX5 - AM*SYX5)/(AM*SXX5 - SX5*SX5)
PRINT 176, DK, DK1

176 FORMAT(1H0,3X,"DISSOCIATION CONSTANT =",E15.8,3X,E15.8)

SX5 = 0
SXX5 = 0
SY5 = 0
SYX5 = 0
DO 89 N = 1, M
Y5(N) = CI(N)*ALPH(N)*F(N)*F(N)/(1, + ALPH(N))
PRINT 177, C(N), Y5(N)
SYX5 = SYX5 + Y5(N)*CI(N)
SXX5 = SXX5 + CI(N)*CI(N)
SY5 = SY5 + Y5(N)
SX5 = SX5 + CI(N)

89 CONTINUE

DK2 = SY5/AM
PRINT 176, DK2
DK = (SY5*SXX5 - SYX5*SX5)/(AM*SXX5 - SX5*SX5)
DK1 = (SY5*SX5 - AM*SYX5)/(AM*SXX5 - SX5*SX5)
PRINT 176, DK, DK1

177 FORMAT(1H0,3X,"CONCENTRATION =",E14.7,5X,"DISSOCIATION CONSTANT =",E14.7)

16 CONTINUE

END
C THIS PROGRAM CALCULATES THE CONDUCTIVITY OF ACID OR SALT SOLUTIONS

2FD(5), CONC(5)

XY(1) = 20,
XY(2) = 25,
XY(3) = 30,
XY(4) = 35,
XY(5) = 40,
READ 500, M8
DO 351 M7 = 1, M8
READ 1
PRINT 1
PUNCH 1

1 FORMAT (80H)

READ 500, M2, R0
500 FORMAT (I2, 3X/F10.5)
PRINT 109, R0, M2
109 FORMAT (1H, 3X/F8.5, 5X/I4)
CALL TEMP(R0, M2, XX)
READ 2, GM, GCONC
PRINT 2, GM, GCONC
2 FORMAT (7(3X/F15.9))
CONC(1) = 0.9982323*GCONC/GM
CONC(2) = 0.9970739*GCONC/GM
CONC(3) = 0.9956756*GCONC/GM
CONC(4) = 0.9940594*GCONC/GM
CONC(5) = 0.9922455*GCONC/GM
DO 351 M9 = 1, 4
READ 1
PRINT 1
READ 3, CELLC
3 FORMAT (F8.5)
READ 202, (YY(N), N = 1, M2)
202 FORMAT (5(F8.1))
M = 4
DO 210 L = 1, 4
DO 210 J = 1, 4
SX = 0,
SYX = 0,
DO 210 K = 1, M2
J1 = J + L - 2
SX = SX + XX(K)*J1
A(L, J) = SX
IF(J-1)210, 200, 210
200 L1 = L-1
SYX = SYX + (XX(K)*L1)*YY(K)
B(L) = SYX
210 CONTINUE
CALL EQUAT(A, B, X, M)
DO 304 N = 1, 4
304 RAD(N) = X(N)
SFAA = 0,

APPENDIX 7.3.2

Calculation of \( A_c \) values of an acid or salt solution from resistance-concentration-temperature experimental results.
51 SFAB = 0,
52 SFAC = 0,
53 SFAD = 0,
54 SFBD = 0,
55 SFCU = 0,
56 SFDO = 0,
57 SFAO = 0,
58 SFBO = 0,
59 SFCU = 0,
60 SFDO = 0,
61 DO 505 N = 1,M2
62 FA = -1,
63 WX(N) = 1, /4,E-6
64 WY(N) = 1, EB/(YY(N)*YY(N))
65 FX(N) = -1, X(2) - 2, X(3)*XX(N) - 3, X(4)*XX(N)*XX(N)
66 FY = 1,
67 AL(N) = FX(N)*FX(N)/WX(N) + FY/WY(N)
68 FB(N) = -XX(N)
69 FC(N) = -XX(N)*XX(N)
70 FD(N) = -XX(N)*XX(N)*XX(N)
71 505 FO(N) = YY(N) - X(1) - X(2)*XX(N) - X(3)*XX(N)*XX(N) - X(4)*XX(N)*XX(N)
72 DO 507 N = 1,M2
73 SFAA = SFAA + FA*FA/AL(N)
74 SFBG = SFBG + FA*FB(N)/AL(N)
75 SFCM = SFCM + FA*FC(N)/AL(N)
76 SFDR = SFDR + FA*FD(N)/AL(N)
77 SFCU = SFCU + FF(1)*FA/AL(N)
78 SFBG = SFBG + FF(N)*FB(N)/AL(N)
79 SFCM = SFCM + FF(N)*FC(N)/AL(N)
80 SFDR = SFDR + FF(N)*FD(N)/AL(N)
81 SFAA = SFAA + FF(N)*FA/AL(N)
82 SFBG = SFBG + FF(N)*FB(N)/AL(N)
83 SFCM = SFCM + FF(N)*FC(N)/AL(N)
84 507 SFDR = SFDR + FO(N)*FD(N)/AL(N)
85 A(1,1) = SFAA
86 A(1,2) = SFAB
87 A(1,3) = SFAC
88 A(1,4) = SFAD
89 B(1) = SFAO
90 A(2,1) = SFAB
91 A(2,2) = SFAC
92 A(2,3) = SFAD
93 B(2) = SFBO
94 A(3,1) = SFAC
95 A(3,2) = SFAD
96 A(3,3) = SFBO
97 A(3,4) = SFCM
98 B(3) = SFCO
99 A(4,1) = SFAD
100 A(4,2) = SFBD
101 A(4,3) = SFCM
102 A(4,4) = SFDR
103 B(4) = SFDO
104 CALL EQUAT(A,B,X,K)
DO 501 N = 1, M
501 ALL(N) = (FO(N) - X(1) - X(2) * XX(N) - X(3) * XX(N) ** 2 - X(4) * XX(N) ** 3) / AL(N)
DO 506 N = 1, M
X(N) = RAD(N) - X(N)
506 PRINT 101, N, X(N)
101 FORMAT(1H11HCOEFFICIENT, 2X13, 5H = E15, 8)
SUM = 0,
SUM1 = 0,
113 DO 504 N = 1, M2
VX(N) = ALL(N) * FX(N) / WX(N)
115 VY(N) = ALL(N) * FY / WY(N)
SUM = SUM + VX(N) * VX(N)
117 SUM1 = SUM1 + VY(N) * VY(N)
118 XCAL(N) = XX(N) - VX(N)
119 YCAL(N) = YY(N) - VY(N)
PRINT 502, XX(N), XCAL(N), VX(N), YY(N), YCAL(N), VY(N)
120 504 CONTINUE
AM = M2
DEV = (SUM / (AM - 1,)) ** 0, 5
DEV1 = (SUM1 / (AM - 1,)) ** 0, 5
PRINT 502, DEV, DEV1
126 502 FORMAT(6(3XE13, 6))
DO 503 K = 1, 5
YY(K) = X(1) + X(2) * XY(K) + X(3) * (XY(K) ** 2) + X(4) * (XY(K) ** 3)
129 503 PRINT 502, XY(K), YY(K)
130 DO 406 N = 1, 5
AL(N) = 10000 * CELLC / (CONC(N) * YY(N))
132 PRINT 2, XX(N), CONC(N), CELLC, YY(N), AL(N)
133 406 PUNCH 405, CONC(N), AL(N)
134 351 CONTINUE
135 405 FORMAT(3PE12, 6, 0PF9, 4)
136 CALL EXIT
137 END
DIMENSION CONC(40), AL(40), Y(40), X(40), CI(40), A(8,8), B(4), COEF(4)

1 FORMAT (I3,3(4X,E14.7))
2 DO 9 L2 = 1, L1
3 READ 8
4 PRINT 8
5 READ 8
6 PRINT 8
7 READ 8
8 PRINT 8
9 8 FORMAT (80H)
10 READ 7, T
11 PRINT 7, T
12 7 FORMAT (1H ,19H, F8.3)
13 READ 1, L
14 DO 2 N = 1, L
15 READ 3, CONC(N), AL(N)
16 PRINT 3, CONC(N), AL(N)
17 2 FORMAT (3PE12.6, 0PF9.4)
18 SCNC = 0.
19 C CALCULATION OF D DIELECTRIC CONSTANT
20 C DRAKE,... (PHYS. REV., II, 35, 613, 1930)
21 D1 = 78.57* (1. - 0.00461*(T-25.) + 0.0000155*(T-25.)**2)
22 C WYMAN AND INGALLS (J. AM. CHEM. SOC., 60, 1182, 1938)
23 D2 = 78.54 - 0.004579*(T-25.) + 0.0000119*(T-25.)**2 + 28.0*10**(-9)*(T-25.)**2
24 C MÄLMBERG AND MARYOTT (J. RES. NAT. BUR. STAND., 56, 1, 1956)
25 D3 = 87.74 - 0.4008*T + 9.398E-4*T*T - 1.410E-6*T*T*T
26 C AVERAGE VALUE
27 D = (D1 + D2 + D3)/3.
28 PRINT 201
29 201 FORMAT (1H, 5X1HT, 16X2HD1, 16X2HD2, 16X2HD3, 16X1HD)
30 PRINT 202, T, D1, D2, D3, D
31 202 FORMAT (F9.4, 4(7XF11.4))
32 AUX = 20. - T
33 VISC = EXP(2.30258*(1.2348*AUX - 0.001467*(AUX**2))/(T+96.) - 4.60316)
34 TK = T + 273.16
35 ALPH1 = 8.147E5/((D*TK)**1.5)
36 BET = 81.86/((D*TK)**0.5)*VISC
37 PRINT 115, ALPH1, BET
38 115 FORMAT(1H0, 31HC) COEFF, IN ONSAGER EQ. ALPH1 = E14.8, 4X7HBETA = E14.18)
39 SX = 0.
40 SY = 0.
41 SYCNC = 0.
42 SCNC = 0.
43 SXCN2 = 0.
44 SYX = 0.
45 SX2 = 0.
46 C THE EQUATION IS Y(N) = A + 8*CONC(N) + D*X(N)
47 DO 4 N = 1, L
48 CI(N) = SORT(30C(N))
49 Y(N) = (AL(N) + BET*CI(N))/(1 - ALPH1*CI(N))
50 X(N) = CONC(N)*ALOG10(CONC(N))
51 SY = SY + Y(N)
SX = SX + X(N)
SCNC = SCNC + CONC(N)
SYCNC = SYCNC + Y(N)*CONC(N)
SXCN2 = SXCN + X(N)*CONC(N)
SCNC2 = SCNC2 + CONC(N)*2
SYX = SYX + Y(N)*X(N)
SX2 = SX2 + X(N)*2
DO 9 M = 2,3
   A(1,1) = L
   A(1,2) = SCNC
   A(1,3) = SX
   A(2,1) = SCNC
   A(2,2) = SCNC2
   A(2,3) = SXCN
   A(3,1) = SX
   A(3,2) = SXCN
   A(3,3) = SX2
   B(1) = SY
   B(2) = SYCNC
   B(3) = SYX
   CALL MATIN(A,B,COEF,M)
   SUM = 0.
   DO 5 N = 1,L
      IF (M-2)11,10,11
   10  AL1 = (1. - ALPH1*CI(N))*COEF(1) + COEF(2)*CONC(N) - BET*CI(N)
      GO TO 12
   11  AL1 = (1. - ALPH1*CI(N))*COEF(1) + COEF(2)*CONC(N) + COEF(3)*CONC
      1(N)*ALOG10(CONC(N))) - BET*CI(N)
   12  DIF = AL(N) - AL1
      SUM = SUM + DIF**2
      PRINT 1,N,AL(N),AL1,DIF
      A1 = L
      DEV = SQRT(SUM/(A1-1.))
      PRINT 6,DEV
   6 FORMAT (1H0,8X5HMSD =E14.7)
   9 CONTINUE
   CALL EXIT
   END
SUBROUTINE MATIN(A,B,P,N)
DIMENSION A(8,8),B(4),P(4),AUX(8,8)
N1 = N + 1
N2 = 2*N
DO 10 I = 1,N
PRINT 9,(A(I,J), J = 1,N),B(I)
10   DO 10 J = N1,N2
     IF (J-I-N)11,12,11
11   A(I,J) = 0.
     GO TO 10
12   A(I,J) = 1.
     CONTINUE
C MATRIX INVERSION
DO 4 I = 1,N
AUX2 = A(I,1)
PRINT 9, AUX2
M = 2*N + 1 - I
DO 3 J = 1,M
3   A(I,J) = A(I,J)/AUX2
   PRINT 9,(A(I,J),J=1,M)
DO 6 L = 1,N
   IF (I - L)6,1,6
2   CONTINUE
DO 2 L1 = 1,M
2   AUX(I,L1) = A(I,L1)*A(L,1)
   PRINT 9, (AUX(I,L1),L1=1,M)
DO 5 L1 = 1,M
5   A(L,L1) = A(L,L1) - AUX(I,L1)
   PRINT 9, A(L,L1)
1   CONTINUE
M1 = M - 1
DO 4 K1 = 1,N
DO 4 K = 1,M1
4   A(K1,K) = A(K1,K+1)
DO 16 I = 1,N
16  PRINT 9,(A(I,J),J = 1,N)
9  FORMAT(6((4XE14.7),/6(4XE14.7))
C SOLVING FOR X
DO 17 I = 1,N
   SUM = 0.
   DO 15 K = 1,N
15   SUM = SUM + A(I,K)*B(K)
   P(I) = SUM
   PRINT 14,I,P(I)
14  FORMAT(1H ,5XI1HCOEFFICIENT,12,2XE14.7)
RETURN
END
C THIS PROGRAM CALCULATES THE INFINITE CONDUCTANCE OF SODIUM BENZOATE
DIMENSION CONC(80),AL(80),Y(80),X(80),C1(80),A(8),B(4),COEF(4)
READ 1,L1
1 FORMAT(13,3X,"CONC =",E14.6,3X,"OBS,COND = ",E14.6,3X,"CALC,COND = ",E14.6,3X,"DF = ",E14.6)
DO 9 L2 = 1,L1
READ 8
PRINT 8
READ 8
PRINT 8
9 FORMAT(80H)

C CALCULATION OF DI DIelectric Constant
D1 = 78.57*(1.0,0.00461*(T-25)+0.0000155*(T-25)**2)
D2 = 78.54-0.004579*(T-25)+0.0000119*(T-25)**2+28.8*9{10.00(T-25)**3}
C AVERAGE VALUE
D = (D1 + D2 + D3)/3,
PRINT 201
201 FORMAT(1H ,5X1HT,16X2HD1,16X2HD2,16X2HD3,16X1HD)
PRINT 202,T,D1,D2,D3,D
202 FORMAT(F9.4,4(7XF11.4))
AUX = 20.-T
VISC = EXP((2.30258*(1.2326*AUX-0.001467*(AUX**2))/(T+96.))-.460316)
TK = T + 273.16
ALPH1 = 8.204E5/((D*TK)**1.5)
BET = 82.50/((D*TK)**0.5)*VISC
PRINT 115,ALPH1,BET
115 FORMAT(1H0,31H0)
C THE EQUATION IS Y(N) = A + B*CONC(N) + D*X(N)
DO 4 N = 1,L
CI(N) = SQRT(CONC(N))
43 Y(N) = (AL(N) + BET*CI(N))/(1.-ALPH1*CI(N))
X(N) = CONC(N) * ALOG10(CONC(N))
SY = SY + Y(N)
SX = SX + X(N)
SCNC = SCNC + CONC(N)
SYCNC = SYCNC + Y(N) * CONC(N)
SXCN = SXCN + X(N) * CONC(N)
SCNC2 = SCNC2 + CONC(N)**2
SYX = SYX + Y(N) * X(N)
SX2 = SX2 + X(N)**2
DO 9 N = 2,3
A(1,1) = L
A(1,2) = SCNC
A(1,3) = SX
A(2,1) = SCNC
A(2,2) = SCNC2
A(2,3) = SXCN
A(3,1) = SX
A(3,2) = SXCN
A(3,3) = SX2
B(1) = SY
B(2) = SYCNC
B(3) = SYX
CALL MAIN(A,B,COEF,M)
SUM = 0.
DO 10 N = 1,L
IF (M-2)11,10,11
10 AL1 = (1, - ALPH1*CI(N))*COEF(1) + COEF(2)*CONC(N) - BET*CI(N)
GO TO 12
11 AL1 = (1, - ALPH1*CI(N))*COEF(1) + COEF(2)*CONC(N) + COEF(3)*CONC
1(N)*ALOG10(CONC(N))) - BET*CI(N)
12 DIF = AL(N) - AL1
SUM = SUM + DIF**2
PRINT 1,N,CONC(N),AL(N),AL1,DIF
A1 = L
DEV = SQRT(SUM/(A1-1,))
PRINT 6,DEV
6 FORMAT (1H0,8X5HMSD =E14,7)
CONTINUE
9 CALL EXIT
11 CALL EXIT
END
SUBROUTINE MATIN(A,B,P,N)
DIMENSION A(8,8),B(4),P(4),AUX(8,8)
N1 = N + 1
N2 = 2*N
DO 10 I = 1,N
DO 10 J = N1,N2
IF (J-I-N)11,12,11
11 A(I,J) = 0.
GO TO 10
12 A(I,J) = 1.
10 CONTINUE
C MATRIX INVERSION
DO 4 I = 1,N
AUX2 = A(I,1)
M = 2*N + 1 - I
DO 3 J = 1,M
3 A(I,J) = A(I,J)/AUX2
DO 1 L = 1,N
IF (I - L)6,1,6
6 CONTINUE
DO 2 L1 = 1,M
2 AUX(I,L1) = A(I,L1)*A(L,1)
DO 5 L1 = 1,M
5 A(L,L1) = A(L,L1) - AUX(I,L1)
1 CONTINUE
M1 = M - 1
DO 4 K1 = 1,N
4 A(K1,K) = A(K1,K+1)
C SOLVING FOR X
DO 17 I = 1,N
SUM = 0.
DO 15 K = 1,N
15 SUM = SUM + A(I,K)*B(K)
P(I) = SUM
17 PRINT 14,1,P(I)
14 FORMAT(1H ,5X,NCOEFFICIENT,I2,2XE14,7)
RETURN
END
C THIS PROGRAM CALCULATES THE INFINITE CONDUCTANCE OF SODIUM BENZOATE
DIMENSION CONC(80), AL(80), Y(80), X(80), CI(80), A(8,8), B(4, COEF(4)
1 DIMENSION AL2(80)
2 3 READ 500, L1
4 500 FORMAT (13)
6 DO 9 L2 = 1, L1
7 READ 8
8 PRINT 8
9 READ 8
10 PRINT 8
11 8 FORMAT (80H
1 12 READ 7, T
13 PRINT 7, T
14 7 FORMAT (1H, 19H
15 16 DO 2 N = 1, L1
17 READ 3, CONC(N), AL2(N)
18 CALL SOLCR(CONC, T, AL2, N, AL)
19 2 CONTINUE
20 3 FORMAT (3PE12.6, 0PF9.4
21 SCNC = 0,
C CALCULATION OF DIELECTRIC CONSTANT
C DRAKE (PHYS. REV., 11, 35, 613, 1930)
22 D1 = 78.5 70 2 1 2 0 0 4 6 1 2 5 0 0 0 0 0 0 2 5 0 0 0 0 0 2 2
23 WYMAN AND INGALLS (J. AM. CHEM. SOC., 60, 1182, 1938)
24 D2 = 78.5 48 2 1 0 0 0 0 0 2 5 0 0 0 0 0 2 2 0 0 0 0 0 2 2
25 MALKBERG AND MARYOTT (J. RES. NAT. BUR. STAND., 56, 1, 1956)
26 D3 = 87.7 46 2 1 0 0 0 0 0 2 5 0 0 0 0 0 2 2 0 0 0 0 0 2 2
27 AVERAGE VALUE
28 D = (D1 + D2 + D3) / 3.
29 PRINT 201
30 201 FORMAT (1H, 5X1HT, 16X2HD, 16X2HD, 16X2HD, 16X2HD)
31 PRINT 202, T, D1, D2, D3, D
32 202 FORMAT (F9.4, 4(7XF11.4)
33 AUX = 28, T
34 VISC = EXP(2.3058*10(-1)*2.248*10(-2)*AUX/10(-20))*10(-30)
35 TK = T + 273.16
36 ALPH1 = 8.2045/(D*TK)**1.5
37 BET = 82.50/(1+(D*TK)**0.5)*VISC
38 PRINT 115, ALPH1, BET
39 115 FORMAT (1HD, 31HCDEFF, IN ONSAGER EQ. ALPH1 = E14.8, 1X7HBETA = E14.8)
40 SX = 0,
41 SY = 0,
42 SYCNC = 0,
43 SX = 0,
44 SX = 0,
45 SX = 0,
46 SX = 0,
47 SYCNC = 0,
48 SYCNC = 0,
49 SX = 0,
50 SX = 0,
51 SX = 0,
52 SX = 0,
53 SX = 0,
54 SX = 0,
55 SX = 0,
56 SX = 0,
57 SX = 0,
58 SX = 0,
59 SX = 0,
60 SX = 0,
61 SX = 0,
62 SX = 0,
63 SX = 0,
64 SX = 0,
65 SX = 0,
66 SX = 0,
67 SX = 0,
68 SX = 0,
69 SX = 0,
70 SX = 0,
71 SX = 0,
72 SX = 0,
73 SX = 0,
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76 SX = 0,
77 SX = 0,
78 SX = 0,
79 SX = 0,
80 SX = 0,
81 SX = 0,
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88 SX = 0,
89 SX = 0,
90 SX = 0,
91 SX = 0,
92 SX = 0,
93 SX = 0,
94 SX = 0,
95 SX = 0,
96 SX = 0,
97 SX = 0,
98 SX = 0,
99 SX = 0,
100 SX = 0,
101 SX = 0,
102 SX = 0,
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104 SX = 0,
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162 SX = 0,
163 SX = 0,
164 SX = 0,
165 SX = 0,
166 SX = 0,
167 SX = 0,
168 SX = 0,
169 SX = 0,
170 SX = 0,
171 SX = 0,
172 SX = 0,
173 SX = 0,
174 SX = 0,
175 SX = 0,
176 SX = 0,
177 SX = 0,
178 SX = 0,
179 SX = 0,
180 SX = 0,
181 SX = 0,
DO N = 1, L
C1(N) = SQRT(CONC(N))
Y(N) = (AL(N) + BET*Cl(N))/(1 - ALPH1*Cl(N))
X(N) = -CONC(N)*ALOG10(CONC(N))
SY = SY + Y(N)
SX = SX + X(N)
SCNC = SCNC + CONC(N)
SYNC = SYNC + Y(N)*CONC(N)
SXNC = SXNC + X(N)*CONC(N)
SCNC2 = SCNC2 + CONC(N)**2
SYX = SYX + Y(N)*X(N)
SX2 = SX2 + X(N)**2
DO M = 2, 3
A(1, 1) = L
A(1, 2) = SCNC
A(1, 3) = SX
A(2, 1) = SCNC
A(2, 2) = SCNC2
A(2, 3) = SXNC
A(3, 1) = SX
A(3, 2) = SXNC
A(3, 3) = SX2
B(1) = SY
B(2) = SYNC
B(3) = SX
CALL MAIN(A, B, COEF, M)
SUM = 0
DO N = 1, L
IF (M = 2) GO TO 12
10 AL1 = (1, -ALPH1*Cl(N))*(COEF(1) - COEF(2)*CONC(N)) - BET*Cl(N)
GO TO 12
11 AL1 = (1, -ALPH1*Cl(N))*(COEF(1) + COEF(2)*CONC(N) + COEF(3)*CONC(N)**2 - ALLOG10(CONC(N)) - BET*Cl(N)
12 DIF = AL(N) - AL1
DIF1 = AL2(N) - AL(N)
SUM = SUM + DIF**2
PRINT 17, N, CONC(N), AL2(N), AL(N), DIF1, AL1, DIF
PRINT 200, A1
AVDIF = SUM1/A1
PRINT 200, AVDIF
200 FORMAT(1HO, **AVERAGE DIFFERENCE BETWEEN OBS. VALUES AND WATER CORR. 1 VALUES IS E14.6)
CALL CALLER(A, A1, H, SUM, PE)
9 CONTINUE
CALL EXIT
END
SUBROUTINE SOLCR(CH, T, AL2, N, AL)
C THIS SUBROUTINE CALCULATES THE WATER CORRECTION FOR THE CONDUCTANCE
C OF SODIUM BENZOATE AQUEOUS SOLUTION.

REAL KH2CO3, KH, LHC03, LH, LOH, KHA, LA
DIMENSION COF(5), RROT(5), XROT(5)
DIMENSION CM(80), KHA(5), LA(5), KH2CO3(5), KW(5), LHC03(5), LH(5), LOH(5)

1)

CC02 = 2.15E-07
KHA(1) = 6.194E-05
KHA(2) = 6.281E-05
KHA(3) = 6.237E-05
KHA(4) = 6.166E-05
KHA(5) = 6.039E-05
KH2CO3(1) = 4.147E-07
KH2CO3(2) = 4.452E-07
KH2CO3(3) = 4.710E-07
KH2CO3(4) = 4.914E-07
KH2CO3(5) = 5.058E-07
KW(1) = 0.6809E+14
KW(2) = 1.008E+14
KW(3) = 1.469E+14
KW(4) = 2.089E+14
KW(5) = 2.919E+14
LAI(1) = 28.70
LAI(2) = 32.35
LAI(3) = 36.18
LAI(4) = 40.13
LAI(5) = 44.28
LHC03(1) = 41.8
LHC03(2) = 44.5
LHC03(3) = 47.3
LHC03(4) = 50.2
LHC03(5) = 53.2
LH(1) = 325.74
LH(2) = 350.15
LH(3) = 374.04
LH(4) = 397.37
LH(5) = 420.06
LOH(1) = 182.16
LOH(2) = 199.18
LOH(3) = 216.53
LOH(4) = 233.04
LOH(5) = 250.11
M = (T-19.015) / 1.

COF(1) = 1.
COF(2) = KH2CO3(M) + KH2CO3(M) + CM(M)
COF(3) = KH2CO3(M) + KHA(M) = KH2CO3(M) + CM(M)
COF(4) = KH2CO3(M) + CM(M) = KW(M) + KH2CO3(M) = KW(M) + KHA(M)
COF(5) = KW(M) + KH2CO3(M) + KHA(M)

CALL PLRTS(COF, RROT, XROT, N, NROT)
DO 6 N2 = 1, 4
6 CONTINUE
52  \[ CH = \text{AMAX1}(RROT(1), RROT(2), RROT(3), RROT(4)) \]
53  \[ \text{COH} = K(W(M)) / CH \]
54  \[ \text{CHCO3} = CC02 \times KH2CO3(M) / (CH + KH2CO3(M)) \]
55  \[ CA = CH(N) \times KHA(M) / (CH + KHA(M)) \]
56  \[ \text{CORR} = \{L(A(M)) \times (CM(N) - CA) = L(H(M) \times CH = LHC03(M) \times \text{CHCO3} = LOH(M) \times \text{COH} \}ight) \]
57  \[ 1 / CH(N) \]
58  \[ AL(N) = AL2(N) = \text{CORR} \]
59  \[ \text{RETURN} \]
60  \[ \text{END} \]
SUBROUTINE MATIN(A,B,P,N)
DIMENSION A(8,8),B(4),P(4),AUX(8,8)

N1 = N + 1
N2 = 2*N
DO 10 I = 1,N
DO 10 J = N1,N2
  IF (J-I-N)11,12,11
     11 A(I,J) = 0,
     GO TO 10
12 A(I,J) = 1,
10 CONTINUE

C MATRIX INVERSION
DO 18 I = 1,N
  AUX2 = A(I,1)
  M = 2*N + 1 - I
  DO 16 J = 1,M
    16 A(I,J) = A(I,J)/AUX2
  DO 18 L = 1,N
  IF (I = L)6,1,6
  CONTINUE
  DO 20 L1 = 1,M
    20 AUX(I,L1) = A(I,L1) + A(L1,1)
  DO 22 L1 = 1,M
    22 A(L1,L1) = A(L1,L1) - AUX(I,L1)
  CONTINUE
  M1 = M - 1
  DO 26 K1 = 1,N
    26 DO 28 K = 1,M1
      28 A(K1,K) = A(K1,K+1)

C SOLVING FOR X
DO 34 I = 1,N
  SUM = 0
  DO 32 K = 1,N
    32 SUM = SUM + A(I,K) + B(K)
  P(I) = SUM
34 PRINT 14,I,P(I)
14 FORMAT(1H1,5X11HC0EFFICIENT,12,2XE14.7)
RETURN
END
SUBROUTINE CALER(A1, AM, M1, SUM, PE)
DIMENSION A1(8, 8), PE(4), COV(4, 4)
AM1=M1
DFREE=AM-AM1
IF (DFREE)<3, 2, 3
2
DFREE=1
3 S = SQRT(SUM/DFREE)
PS=S*0.6745
PRINT 4, S, PS
11 PRINT 7
12 PRINT 8
13 FORMAT (1HO, "ERRORS IN THE COEFFICIENTS")
14 FORMAT (1HO, 3X, "COEFFICIENT", 5X, "PROBABLE ERROR")
15 DO 5 N=1, M1
16 PE(N)=PS*SORT(A1(N,N))
17 5 PRINT 6, N, PE(N)
18 6 FORMAT (7X, I3, 9X, E14.7)
19 PRINT 9
20 9 FORMAT (1HO, "COVARIANCES")
21 DO 10 N1=1, M1
22 DO 11 N=1, M1
23 11 COV(N1, N)=S*S*A1(N1, N)
24 10 PRINT 12, N1, (N, COV(N1, N), N=1, M1)
25 12 FORMAT (1H, I3, 5X, (I3, 2X, E14.7))
26 RETURN
27 END
SUBROUTINE PLRTS(C, RR, RI, NN, IND)
!
DIMENSION C(1), RR(1), RI(1)
!
N=NN
!
I=1
!
IF(N) 23, 23, 30
!
30 P=1, 0/C(1)
!
DO 4 J=1, N
!
4 C(J)=P*C(J+1)
!
ISW=N/2
!
ISW=ISW+ISW-N
!
1 P=C(N-1) + 1, E=12
!
Q=C(N)
!
IF(I-N+1,5, 14,2
!
2 RR(I)=Q
!
15 RI(I)=0, 0
!
IND=N
!
GO TO 24
!
5 IC=1
!
6 B1=C(N+2)
!
7 IF(B1)7, 28, 7
!
8 P=P*B1
!
9 Q=Q*B1
!
24 8 B1=1, 0
!
25 B3=1, 0
!
26 B2=0, 0
!
27 B4=0, 0
!
28 DO 10 J=1, N
!
29 RR(J)=C(J)-P*B1+Q*B2
!
30 IF(J-N+9, 10, 10
!
31 9 RI(J)=RR(J)-P*B3+Q*B4
!
32 B2=B1
!
33 B4=B3
!
34 B1=RR(J)
!
35 B3=RI(J)
!
36 10 CONTINUE
!
37 RI(N-1)=RI(N-1)-RR(N-1)
!
38 B2=1, 0
!
39 B3=RI(N-1)
!
40 B4=RI(N-2)
!
41 IF(I=N+2)3, 6, 3
!
42 3 82=B1
!
43 6 B1=B4+B4+B3*B2
!
44 11 B1=1, 0/B1
!
45 B2=(RR(N-1)*B4+RR(N)*B2)*B1
!
46 B3=(RR(N-1)*B3+RR(N)*B4)*B1
!
47 IF(ABS(B2)/ABS(F)+1, 0)=5, E=12)12, 12, 13
!
48 12 IF(ABS(B3)/ABS(Q)+1, 0)=5, E=12)21, 21, 13
!
49 13 P=P+B2
!
50 Q=Q+B3
!
51 IC=IC+1
!
52 IF(IC=100)8, 8, 31
!
53 31 IF(ISW)32, 23, 24
!
54 32 ISW=1
55  IND=1+1
56  J=N
57  N=N+1
58  C(N)=0,
59  33 C(J+1)=C(J+1)+C(J)
60  J=J-1
61  IF(J)=34,34,33
62  34 C(1)=C(1)+1,0
63  GO TO 1
64  14 IF(P)=27,16,27
65  27 B4 = 4,000/09(P0P)
66  IF (ABS(B4) = 1,E=12)15,15,16
67  15 RR(I)=P
68  RR(I+1)=0/P
69  GO TO 19
70  16 RR(I)=5*P
71  RR(I+1)=RR(I)
72  B1=P+P=4,000
73  IF(B1)=17,19,18
74  17 RI(I)=5*SQT(R*B1)
75  RI(I+1)=RI(I)
76  GO TO 20
77  18 B1=5*SQT(B1)
78  RR(I)=RR(I)+B1
79  RR(I+1)=RR(I+1)=B1
80  19 RI(I)=0,0
81  RI(I+1)=0,0
82  20 I=I+2
83  IF(I)=35,35
84  35 IF(J)=23,23,36
85  36 K=IND+1
86  DO 38 J=K,N
87  IF(ABS(RJ(J)) = 1,E=12)37,37,38
88  37 IF(ABS(RR(J)+1,0) = 1,E=12)39,39,38
89  38 CONTINUE
90  GO TO 24
91  39 DO 40 K=J,N
92  RR(K)=RR(K+1)
93  40 RI(K)=RI(K+1)
94  IND=N+1
95  GO TO 24
96  21 DO 22 J=1,N
97  22 C(J)=RR(J+2)
98  GO TO 14
99  23 IND=1+1
100  24 RETURN
101  28 P=0
102  GO TO 8
103  END
DIMENSION ALOO(5), X(5), Y(5), A(8,8), B(4), PE(4), COEF(4)
READ 6, NPRBS
DO 3 NRB = 1, NPRBS
READ 8
PRINT 8
8 FORMAT (80H)
1
READ 1, ALOO, (ALOO(N), N=1,5)
1 FORMAT (62X, F7.2)
X(1) = -5,
X(2) = 0,
X(3) = 5,
X(4) = 10,
X(5) = 15,
DO 2 N = 1,5
2 Y(N) = ALOG(N)
PRINT 1, Y(N), N=1,5
DO 3 M = 2,4
DO 210 L = -1, M
3 SX = 0,
DO 210 K = 1, 5
J1 = J + L = 2
SX = SX + X(K)**J1
A(L, J) = SX
IF (J-1) 210, 200, 210
200 L1 = L = 1
SYX = SYX + (X(K)**L1)*Y(K)
28 B(L) = SYX
210 CONTINUE
30 CALL MATIN(A, B, COEF, M)
32 SUM1 = 0,
33 DO 4 N = 1, 5
34 SY = COEF(1)
35 DO 5 N1 = 2, M
36 SY = SY + COEF(N1)*(X(N)**(N1+1))
37 YCALC = SY
38 DIF = Y(N) - YCALC
39 SUM1 = SUM1 + DIF*DIF
40 PRINT 6, N, Y(N), YCALC, DIF, SUM1, X(N)
41 6 FORMAT (13, 4(2X, E14.7), 5X, 3(F7.3, 2X))
42 CALL CALER(A, 5, M, SUM1, PE)
43 3 CONTINUE
44 END

APPENDIX 7.4.5
The fitting of $\Lambda^0$ values in a polynomial of the type:

$\Lambda^0 = A + B(T-25) + C(T-25)^2 + \ldots$
THE GE-400 SERIES - FORTRAN ASA (MTPS)

C THIS PROGRAM CALCULATES THE CONDUCTIVITY OF ACID OR SALT SOLUTIONS
2 FD(5), CONC(5)
3 DIMENSION YXK(20)
4 XY(1) = 20
5 XY(2) = 35
6 XY(3) = 35
7 XY(4) = 40
8 XY(5) = 40
9 READ 500, MB
10 DO 351 M2 = 1, MB
11 PRINT 1
12 PUNCH 1
13 FORMAT(80H)
14 READ 500, M2, R0
15 PRINT 109, R0, M2
16 CALL TEMPR(M2, XX)
17 READ 2, GM, GCONC
18 PRINT 2, GM, GCONC
19 FORMAT('0.3X15.9E')
20 PRINT(5, F8,1)
21 CALL CONC(1, 0.99922455*GCONC/GM, 1.000)
22 CALL CONC(2, 0.99922455*GCONC/GM, 1.000)
23 CALL CONC(3, 0.99922455*GCONC/GM, 1.000)
24 CALL CONC(4, 0.99922455*GCONC/GM, 1.000)
25 CALL CONC(5, 0.99922455*GCONC/GM, 1.000)
26 READ 3, CELLC
27 FORMAT(F8.5)
28 DO 406 M9 = 1, 4
29 READ 1
30 PRINT 1
31 READ 202, (YY(N), N = 1, M2)
32 FORMAT(5(F8,1))
33 M = 4
34 DO 210 L = 1, 4
35 DO 210 J = 1, 4
36 SX = 0
37 SYX = 0
38 DO 210 K = 1, M2
39 J1 = J + L - 2
40 SX = SX + XX(K)*XX(J1)
41 CALL A(L,J) = SX
42 IF(J-1)210, 210, 210
43 L1 = L - 1
44 SYX = SYX + (XX(K)*XX(L1))*YY(K)
45 CALL CONTINUE
46 R(L) = SYX
47 210 CONTINUE
48 CALL EQUAT(A, 8, X, H)
49 DO 304 N = 1, 4
50

APPENDIX 7.4.6

Calculation of \( \Lambda - \alpha \) values
and \( \Lambda^0 \) values using Jones-
Jones standards and the
"differential" cell contents.
304 RAD(N) = X(N)
53 SFAA = 0.
54 SFAB = 0.
55 SFAC = 0.
56 SFAD = 0.
57 SFBD = 0.
58 SFDD = 0.
59 SFAO = 0.
60 SFCO = 0.
61 SFDO = 0.
62 DD 505 N = 1, M2
63 FA = -1.
64 WX(N) = 1./4., E-6
65 WY(N) = 1./5. / (YY(N) * YY(N))
66 FX(N) = - X(2) - 2. * X(3) * X(N) - 3. * X(4) * X(N) * X(N)
67 FY = 1.
68 AL(N) = FX(N) * FX(N) / WX(N) + FY / WY(N)
69 FB(N) = - XX(N)
70 FG(N) = - XX(N) * XX(N)
71 FD(N) = - XX(N) * XX(N) * XX(N)
72 FD(N) = Y Y(N) * Y(N) * X(N) * X(N) - X(1) - X(2) * XX(N) - X(3) * XX(N) * XX(N) - X(4) * XX(N) * XX(N)
73 FO(N) = Y Y(N) - X(1) - X(2) * XX(N) - X(3) * XX(N) * XX(N) - X(4) * XX(N) * XX(N)
74 DD 507 N = 1, M2
75 SFAA = SFAA + FA * FA / AL(N)
76 SFAB = SFAB + FA * NB(N) / AL(N)
77 SFAC = SFAC + FA * FC(N) / AL(N)
78 SFAD = SFAD + FA * FD(N) / AL(N)
79 SFBD = SFBD + FB(N) * FD(N) / AL(N)
80 SFCO = SFCO + FC(N) * FD(N) / AL(N)
81 SFDD = SFDD + FO(N) * FD(N) / AL(N)
82 SFAO = SFAO + FO(N) * FA / AL(N)
83 SFBO = SFBO + FO(N) * FB(N) / AL(N)
84 SFCO = SFCO + FO(N) * FC(N) / AL(N)
85 SFDO = SFDO + FO(N) * FD(N) / AL(N)
86 A(1, 1) = SFAA
87 A(1, 2) = SFAB
88 A(1, 3) = SFAC
89 A(1, 4) = SFAD
90 A(2, 1) = SFAB
91 A(2, 2) = SFAC
92 A(2, 3) = SFAD
93 A(2, 4) = SFBD
94 B(1, 1) = SFBD
95 A(3, 1) = SFAD
96 A(3, 2) = SFBD
97 A(3, 3) = SFCO
98 A(3, 4) = SFCO
99 B(3, 1) = SFCO
100 A(4, 1) = SFAD
101 A(4, 2) = SFBD
102 A(4, 3) = SFCO
103 A(4, 4) = SFBD
104
B(4) = 5F0
CALL EQUAT(A,B,X,M)
DO 501 N = 1,M2
501 ALL(N) = (F0(N) - X(1) - X(2) * XX(N) - X(3) * (XX(N) ** 2) - X(4) * (XX(N) ** 3)) / XL(N)
DO 506 N = 1,M
X(N) = AD(N) - X(N)
506 PRINT 101,N,X(N)
101 FORMAT(14,11HCoefficient,2e3,5H = E15,8)
SUM = 0.
SUM1 = 0.
DO 504 N = 1,M2
VX(N) = ALL(N) * FX(N) / WX(N)
VY(N) = ALL(N) * FY / WY(N)
SUM = SUM + VX(N) * VX(N)
SUM1 = SUM1 + VY(N) * VY(N)
XCAL(N) = XX(N) = VX(N)
YCAL(N) = YY(N) = VY(N)
PRINT 502, XX(N), XCAL(N), VX(N), YY(N), YCAL(N), VY(N)
504 CONTINUE
AM = M2
DEV = (SUM / (AM**1.)) ** 0.5
DEV1 = (SUM1 / (AM**1.)) ** 0.5
DO 502 M = 1,M
PRINT 502, DEV, DEV1
502 FORMAT (6{3xe13.5})
503 CONTINUE
DO 406 K = 1,5
YY(K) = X(1) + X(2) * XY(K) + X(3) * (XY(K) ** 2) + X(4) * (XY(K) ** 3)
I = (M9**1. - 1.05 + K)
406 CONTINUE
DO 650 I = 1,M
YYK(I) = YY(K)
650 CONTINUE
DO 503 I = 1,5
PRINT 502, XY(K), YY(K), YYK(I)
503 CONTINUE
DO 405 N = 1,5
AL(N) = 006 * CELLC / (CONC(N) * YY(N))
405 CONTINUE
PRINT 2, XY(N), CONC(N), CELLC, YY(N), AL(N)
READ 1, L31 = 1,2
READ 1, PUNCH 1
READ 3, CELLC
DO 652 I = 1,4
DO 652 N = 1,5
I1 = (I-1)**1 + N
AL(N) = 006 * CELLC / (CONC(N) * YYK(II))
652 CONTINUE
PRINT 2, XY(N), CONC(N), CELLC, YYK(II), AL(N)
650 CONTINUE
FORMAT (3PE12.6,0PF9.4)
CALL EXIT
END
APPENDIX 8.4.1

Calculation of $\Lambda^0$ by
the Ives and Fuoss-Shedlovsky
methods (with iteration).

1 DIMENSION C(100),AL(100)
2 READ 102, M
3 DO 3 M7 = 1,M
4 READ 1
5 PRINT 1
6 1 FORMAT (80H)
    1 READ 2,T
    8 PRINT 2,T
9 2 FORMAT (1H0,19H,F8.3)

C CALCULATION OF DIELECTRIC CONSTANT

C DRAKE, "PHYS. REV., 11, 35, 613, 1930"
10 $D_1 = 78.57*(1.0-0.00461*(T-25.0)+0.000155*(T-25.0)**2)$
11 $D_2 = 78.54*(1.0-0.00479(T-25.0)*1.19E05*(T-25.0)**2)+$
12 1.28*0.09*(T-25.0)**4$

C MALMBERG AND MARYOTT "J. RES. NAT. BUR. STAND., 56, 1, 1956"
13 $D_3 = 87.74-0.4008*T-9.398E-4*T*T = 1.410E6*T*T*T$

C AVERAGE VALUE
14 D = ($D_1 + 2*D_2 + D_3$)/3,
15 PRINT 201
16 201 FORMAT (1H0,5X+HT,16X2HD1,16X2HD2,16X2HD3,16X1HD)
17 PRINT 202,T,D1,D2,D3,D
18 202 FORMAT (F9.4,4(7XF11.4))
19 AUX = 20,-T
20 VISC= EXP(2,30258*(1.2348*AUX+0.01467*(AUX**2)))/(T*96.) = 4.60315
21 TK = T + 273.16
22 ALPH1 = $-8.204E5/((D*TK)**2)$
23 BET = $82.50/((D*TK)**2)*VISC$
24 PRINT 115, ALPH1,BET
25 115 FORMAT (1H0,"COEFF. IN ONSAGER EQ., ALPH1 = ",E14.8,4X,"BET = ",E14.8)
26 READ 2,ALO
27 PRINT 2,ALO
28 ALO1 = ALO
29 READ 102, M,COMP
30 PRINT 110
31 110 FORMAT (1H0,6X5HCONC.,12X5HCOND.)
32 DO 30 N = 1,M
33 30 PRINT 102,N,C(N),AL(N)
34 101 FORMAT (E12,3,F9.4)
35 102 FORMAT (I3,1XE14.8,5(1XE14.8))
36 AN = M
37 CALLIVES1(M,AN,VISC,D,TK,ALO,ALPH1,BET,C,AL,COMP)
38 PRINT 1
39 ALO = ALO1
40 5 CALL SHE'S(M,AN,VISC,D,TK,ALO,ALPH1,BET,C,AL,COMP)
41 3 CONTINUE
42 CALL EXIT
43 END
SUBROUTINE IIVES1(M, AN, VISC, D, TK, ALO, ALPH1, BET, C, AL, COMP)
C CALCULATION OF DISSOCIATION CONSTANT
C IIVES METHOD
DIMENSION C(100), AL(100), ALPH(100), CI(100), ALE(100), X(100), Y(100)
ALO1 = ALO
A = 1.0123E6 / (D * TK)**1.5
PRINT 110, A
110 FORMAT(1H0, 3X4HA = E14.9)
16 GAM = ALPH1 + ALO + BET

SY = 0
SX = 0
SXY = 0
SXX = 0
DO 10 N = 1, M
13 ALE1 = ALO - GAM - SQRT(AL(N) + C(N) / CHK)
15 CHK1 = ABS(CHK = ALE1)
16 IF(CHK1 - COMP) 12, 12, 11
17 11 CHK = ALE1
18 GO TO 13
12 ALPH(N) = AL(N) / ALE1
19 ALE(N) = ALE1
20 CI(N) = SQRT(ALPH(N) + C(N))
22 Y(N) = AL(N) + GAM + CI(N)
23 X(N) = AL(N) + AL(N) + C(N) * (10.0 ** (-2.0 * AIC(N))) / (AL + GAM + CI(N))
24 SY = SY + Y(N)
25 SX = SX + X(N)
26 SXY = SXY + X(N) * Y(N)
27 SXX = SXX + X(N) * X(N)
10 CONTINUE
29 CHECK = (SX * SXY - SXX * SY) / (SX * SX - AN * SXX)
30 DK = (SX * SX - AN * SXX) / (AN * SXY - SX * SY)
31 PRINT 106, CHECK, DK
32 CHK2 = ABS(CHECK - ALO)
33 IF(CHK2 - COMP) 15, 15, 14
34 14 ALO = CHECK
35 GO TO 16
15 SUM = 0
36 SUMX = 0
38 SUMXX = 0
39 DO 17 N = 1, M
40 YY = CHECK = X(N) / DK
41 DIF = Y(N) - YY
42 SUM = SUM + DIF * DIF
43 SUMX = SUMX + X(N)
44 SUMXX = SUMXX + X(N) * X(N)
45 PRINT 102, N, X(N), Y(N), YY, DIF
102 FORMAT (15, 1X, E14.8, 5(1X, E14.8))
17 CONTINUE
502 FORMAT (2(3X = E14.6))
52 RE = 0.6745 * SQRT(SUM/(AN - 2.0))
54 D1 = AN + SUMXX / SUMX * SUMX
51 PA = RE * SQRT(SUMXX / D1)
52 PB = RE * SQRT(AN / D1) * (DK ** 2)
SUM = SQRT(SUM/(AN - 1.0))
PRINT 104
PRINT 105
DO 20 N = 1, M
20 PRINT 102, N, C(N), AL(N), ALPH(N), ALE(N), X(N), Y(N)
PRINT 103, CHECK, DK
103 FORMAT (1H0, 4X23HLIMITING CONDUCTANCE = E14, 8, 6X24HDISSOCIATION CO-
INSTANT = E14, 8)
PRINT 111, SUM, PA, PB
111 FORMAT (1H0, "MEAN-SQ-DEV = ", E14, 6, 3X, "PROBABLE ERROR IN LIM_COND",
1 = ", E14, 6, 3X, "PROBABLE ERROR IN DISS, CONST, = ", E14, 6)
104 FORMAT (1H0, 4X13HCONCENTRATION, 2X11HCONDUCTANCE, 4X12HDEGREE DISS,
14X11HIONIC COND, 7X4HX(N), 11X4HY(N))
105 FORMAT (1H0, 6X10HMOLE/LITER, 7X3HMHO, 28X3HMHO)
106 FORMAT (E15, 8, 10XE15, 8, 10XE15, 8, 10XE15, 8)
ALO = AL01
RETURN
END
SUBROUTINE SHFS(M,AN,VISC,D,Tk,A0,ALPH1,BET,C,AL,COMP)
C CALCULATION OF DISSOCIATION CONSTANT
C FUOSS - SHEDLOVKY METHOD

DIMENSION C(100),AL(100),ALPH(100),F(100),X(100),Y(100),C(100),
1 CAPS(100),X5(100)
READ 108,R
PRINT 108,R
FORMAT (EB,1)
FORMAT (1H0,4X13HCONCENTRATION,1X11HCONDUCTANCE,3X12HDEGREE DISS,4
1X10HACT,6X6HC(N),10X4HY(N),10X2HY,13X3HDF)
A = 1,8123E+06/((D*Tk)**1,5)
B = 50,29E+08/SORT(D*Tk)
PRINT110,A,B
110 FORMAT(1H0,3X4HA = E14,8,8X4HB = E14,8)
M4 = 0
M5 = 0
M6 = 0
23 GAM = ALPH1*A0*BET
APPENDIX 8.4.1 (cont.)
SY = 0
SX = 0
SXY = 0
SXX = 0
DO 10 N = 1,M
20 Z =GAM* SORT(C(N)*AL(N))/(AL0**1,5)
S = (Z/2,1 + SORT(1,1*(Z/2,1)**2)**2
21 ALPH(N) = S*AL(N)/AL0
C DEBYE - HUKEL FORMULA
C CALCULATION OF ACTIVITY COEFFICIENT
CI(N) = ALPH(N)*C(N)
ALNF = A* SORT(CI(N))/(1,B*RESORT(CI(N)))
F(N) = 10,0**(ALNF)
X(N) = C(N)*AL(N)*S*F(N)*F(N)
26 Y(N) = 1,/(AL(N)*S)
27 SXX = SX = X(N)
SXY = SY = Y(N)
SX = SX = X(N)
SXX = SX = X(N)*X(N)
10 CONTINUE
109 FORMAT(5(E14,8)/4(E14,8))
34 Y0 = (SX*SXY=SXX*SY)/(SX*SX=AN*SXX)
35 SL = (AN*SXY*SX=SY)/(AN*SXX*SX=SXX)
36 PRINT 117, Y0,SL
37 117 FORMAT (1H0,"INTERCEPT=-",E14,7," SLOPE=-",E14,7)
38 CHK = 1,1/Y0
39 IF (ABS(CHK = A0) = 0,3)69,69,25
40 ALO = CHK
41 GO TO 23
42 ALO = CHK
43 DK = 1,/(SL*(AL0**2))
44 PRINT 111,CHK,DK
45 111 FORMAT(1H0,30HLANA ZERO FROM THE INTERCEPT=E8,3,8X,23HDISSOCIATI
1ON CONSTANT = E14,7)
46 22 PRINT 104
47 PRINT 105
105  FORMAT(1HO,6X10HMOLE/LITER,7X3HMHO)
   SUM = 0
   SUMX = 0
   SUMXX = 0
   DO 20 N = 1,M
   YY = 1./ALO + SL*X(N)
   DIF = Y(N) - YY
   SUM = SUM + DIF*DIF
   SUMX = SUMX + X(N)
   SUMXX = SUMXX + X(N)*X(N)
   20  PRINT 102,N,C(N),AL(N),ALPH(N),F(N),X(N),Y(N),YY,DIF
102  FORMAT(13,1XE13,7,7(1XE13,7))
   RE = 0,6745*SQRT(SUM/(AN=2,))
   D1 = AN*SUMXX - SUMX*SUMX
   PA = RE*SQRT(SUMXX/D1)*(ALO**2)
   PB = RE*SQRT((AN/D1)**DK/SL)
   64  DEV = (SUM/(AN = 1,))**0.5
   PRINT 103,ALO,DK
66  PRINT 116,DEV,PA,PB
116  FORMAT(1HO,"MEAN SQ,DEV = ",E14,6,3X,"PROBABLE ERROR IN LIM_COND = ",E14,6)
68  103  FORMAT(1HO,4X23H,LIMITING CONDUCTANCE = E14,6,3X,DISSOCIATION COINSTANT = E14,6)
   RETURN
   END
DIMENSION ALO0(5), T(5), ALO(5)
T(1) = 295.15
T(2) = 296.15
T(3) = 306.15
T(4) = 308.15
T(5) = 313.15
N1 = 5
READ 4, NPRBS
DO 8 NPRBS = 1, NPRBS
READ 5
PRINT 5
5 FORMAT(80X)
1 READ 7, N2, N3
7 FORMAT(213)
READ 1, ALO1, (ALO0(N), N=1, N1)
PRINT1, ALO1, (ALO0(N), N=1, N1)
1 PRINT(6(2X, F7, 2))
SX = 0
SY = 0
SXX = 0
DO 2 N = N2, N3
SX = SX + T(N)
SY = SY + ALO0(N)
SXX = SXX + T(N)*T(N)
2 SYX = SYX + T(N)*ALO0(N)
FN1 = N3 - N2 + 1
D = FN1*SXX - SX*SX
A = (SY*SXX - SYX*SX)/D
B = (FN1*SYX - SY*SXX)/D
SUM = 0
DO 11 N = 1, N1
11 ALO(N) = A + B*T(N)
DO 3 N = N2, N3
DIF = ALO0(N) - ALO(N)
PRINT 4, N, ALO0(N), ALO(N), DIF
3 SUM = DIF*DIF + SUM
4 FORMAT(13, 2(3X, F7, 3), 3X, E14, 6)
PRINT 6, A, B
6 FORMAT(1HU, "THE INTERCEPT IS " , E14, 6, 1X, "AND THE SLOPE IS " , E14, 6)
FAC = ALO1 = ALO(2)
DO 9 N = 1, N1
AL02 = FAC + ALO(N)
PRINT 10, N, ALO1, ALO(N), AL02
9 CONTINUE
10 FORMAT(13, 4(3X, F7, 3))
8 CONTINUE
END
DIMENSION ALO0(5), T(5), ALO(5)

T(1) = 293.15
T(2) = 298.15
T(3) = 303.15
T(4) = 308.15
T(5) = 313.15

N1 = 5
READ 4, NPRS
DO 8 NPRB = 1, NPRS
  8  READ 5
  9  PRINT 5
  10  FORMAT(80H
  11              1
  12              7 FORMAT(213)
  15  READ 1, ALO1, (ALO0(N), N=1, N1)
  16  PRINT1, ALO1, (ALO0(N), N=1, N1)
  17  1 FORMAT(6(2X,F7.2))

  SX = 0,
  SY = 0,
  SYX = 0,
  SXX = 0,
  DO 2 N = N2, N3
  2  SX = SX + T(N)
  3  SY = SY + ALO0(N)
  4  SXX = SXX + T(N)*T(N)
  5  SYX = SYX + T(N)*ALO0(N)
  6  FN1 = N3 - N2 + 1
  7  D = FN1*SXX = SX*SX
  8  A = (SY*SXX = SYX=SX)/D
  9  B = (FN1*SYX = SY*SX)/D
 10  SUM = 0,
 11  DO 11 N = 1, N1
 12  11  ALO(N) = A + B*T(N)
 13  DO 3 N = N2, N3
 14  DIF = ALO0(N) - ALO(N)
 15  PRINT 4, N, ALO0(N), ALO(N), DIF
 16  3  SUM = DIF*DIF + SUM
 17  4  FORMAT(13,2(3X,F7.3),3X,E14.6)
 18  PRINT 6, A, B
 19  6  FORMAT(1HU,"THE INTERCEPT IS \n,E14.6,1X,"AND THE SLOPE IS \n,E14.6)""
 20  FAC = ALO1 - ALO(2)
 21  DO 9 N = 1, N1
 22  9  ALO2 = FAC + ALO(N)
 23  PRINT 10, N, ALO1, ALO(N), ALO2
 24  10 CONTINUE
 25  8 CONTINUE
 26  END
APPENDIX 8.5.1

Calculation of $K$ by the Ives and Fuoss-Sheldovsky methods (no iteration).

```fortran
DIMENSION C(100), AL(100)
READ 102, M8
DO 3 M7 = 1, M8

1 FORMAT (80H, 1)
    READ 2, T
    PRINT 2, T

2. FORMAT (1H0, 19H, F8, 3)
C CALCULATION OF DIELECTRIC CONSTANT
C DRAKE, (PHYS. REV., 11, 35, 1930)
D1 = 78.57*1.0, 0.00461*(T-25) + 0.0000155*(T-25)**2)
C WYMAN AND INGALLS (J. AM. CHEM. SOC., 60, 1182, 1938)
D2 = 78.54*1.0, 0.004279*(T-25) + 1.19*E-05*(T-25)**2) +
    1.28*E-09*(T-25)**3)
C MALMBERG AND MARYOTT (J. RES. NAT. BUR. STAND., 56, 1, 1956)
D3 = 87.74*0.400E+T + 9.398E-4*T*T + 1.410E-6*T*T*T

C AVERAGE VALUE
D = (D1 + D2 + D3)/3,
PRINT 201

201 FORMAT (1H0, 5X1HT, 16X2HD1, 16X2HD2, 16X2HD3, 16X1HD)
PRINT 202, T, D1, D2, D3, D

202 FORMAT (F9.4, 4(7XF11.4))

AUX = 20.0/T
VISC = EXP(2.30258*(1.2348*AUX-0.001467*(AUX**2))/(T+961)-4.60316)
Tf = T + 273.16
ALPH1 = 8.204E5/((D*Tf)**1.5)
BET = 82.50/((1.0/Tf)**0.5)*VISC
PRINT 115, ALPH1, BET

115 FORMAT(1H0, "COEFF. IN ONSAGER EQ. ALPH1 = ",E14.8,"X", "BET = ",E14.18)

READ 2, ALO
PRINT 2, ALO
READ 102, M, COMP
PRINT 110

110 FORMAT (1H0, 6X5HCONC., 12X5HCOND.,)
DO 30 N = 1, M
30 READ 101, C(N), AL(N)

CONTINUE

30 CONTINUE

101 FORMAT (E12.3, F9.4)
102 FORMAT (3J, 1XE14.8, 5(1XE14.8))

AN = M
CALL IVES1(M, AN, VISC, D, Tk, ALO, ALPH1, BET, C, AL, COMP)
PRINT 1

CALL SHFS(M, AN, VISC, D, Tk, ALO, ALPH1, BET, C, AL, COMP)
CONTINUE

CALL EXIT
END
```
SUBROUTINE IVES1(M, AN, VISC, D, TK, ALO, ALPH1, BET, C, AL, COMP)
C CALCULATION OF DISSOCIATION CONSTANT
C IVES METHOD

DIMENSION C(100), AL(100), ALPH(100), CI(100), ALE(100), X(100), Y(100)
A = 1.8123E6 / ((D*TK)**1.5)
PRINT 110, A

110 FORMAT (1H40, 3X 4HA = E14.8)
16 GAM = ALPH*ALO + BET

SY = 0,
SX = 0,
SXY = 0,

DO 10 N = 1, M

CHK = ALO

13 ALE1 = ALO - GAM*SORT(AL(N)*C(N)/CHK)

14 CHK1 = ABS(CHK-AL1)
15 IF (CHK1=COMP) 12, 12, 11
16 11 CHK = ALE1
17 GO TO 13
12 ALPH(N) = AL(N)/ALE1

19 ALE(N) = ALE1

20 CI(N) = SORT(ALPH(N)*C(N))
21 Y(N) = AL(N) + GAM*CI(N)
22 X(N) = AL(N)*AL(N)*C(N)*((10, *(-2.0*A*CI(N)))/(ALO-GAM*CI(N))

23 SY = SY + Y(N)
24 SX = SX + X(N)
25 SXY = SXY + X(N)*Y(N)

26 SXX = SXX + X(N)**2

10 CONTINUE

28 CHECK = (SX*SXY-SXX*SY)/(SX*SX-AN*SXX)
29 DK = (SX*SX-AN*SXX)/(AN*SXY-SX*SY)
30 PRINT 106, CHECK, DK
31 15 SUM = 0,
32 SUMX = 0,
33 SUMXX = 0,

DO 17 N = 1, M
34 YY = CHECK - X(N)/DK
35 DIF = Y(N) - YY.
36 SUM = SUM + DIF*DIF
37 SUMX = SUMX + X(N)
38 SUMXX = SUMXX + X(N)**2

40 PRINT 102, N, X(N), Y(N), YY, DIF
41 102 FORMAT (15, 1XE14.6, 6(1XE14.6))
42 17 CONTINUE
43 502 FORMAT (2(3XE13.6))

44 RE = 0.6745*SORT(SUM/(AN**2))
45 D1 = AN*SUMXX - SUMX*SUMX
46 PA = RE*SORT(SUMXX/D1)
47 PB = RE*SORT(AN/D1)*(DK**2)
48 SUM = SORT(SUM/(AN = 1.0))
49 PRINT 104
50 PRINT 105
51 DO 20 N = 1, M
52 20 PRINT 102, N, C(N), AL(N), ALPH(N), ALE(N), X(N), Y(N)
```
53 PRINT 103,ALO,OK
54 103 FORMAT (1H0,4X23HLIMITING CONDUCTANCE = E14,8,6X24HDISSOCIATION CO
      1INSTANT = E14,8)
55 PRINT 111, SUM, PA, PB
56 111 FORMAT (1H0,"MEAN SQ.DEV. = ",E14,6,3X,"PROBABLE ERROR IN LIM,COND.
      1 =",E14,6,3X,"PROBABLE ERROR IN DISS,CONST. =",E14,6)
57 104 FORMAT (1H0,4X13HCONCENTRATION,2X11HCONDUCTANCE,4X12HDEGREE DISS,
      14X11HIONIC COND.,7X4HX(N),11X4HY(N))
58 105 FORMAT (1H0,5X10HMOLE/LITER,7X3HMHO,28X3HMHO)
59 106 FORMAT (F15,3,10XE15,8,10XE15,8,10XE15,8)
60 RETURN
61 END
```
SUBROUTINE SHFS(M, AN, VISC, D, DT, ALO, ALPH1, BET, C, AL, COMP)

C CALCULATION OF DISSOCIATION CONSTANT

C FUSS = SHELDON'S METHOD

DIMENSION C(100), AL(100), ALPH(100), F(100), X(100), Y(100), C1(100),
CAPS(100), X5(100)

READ 100, R

100 FORMAT (100, I)

PRINT 100, R

103 FORMAT (E6, 1)

104 FORMAT (I14, 4X, 14HCONCENTRATION, 1X, 11HCODUCANCE, 3X, 12HDEGREE DISS., 4X,
1X, 10HACT, COEF., 6X, 4HXM(N), 10X, 4HY(N), 10X, 2HYY, 13X, 3HDIF)

A = 1.8123E+06/((D*TK)**1.5)

B = 50.298E+08/SORT(D*TK)

PRINT 110, A, B

110 FORMAT (I14, 3X, 4HA = E14, 8, 8X, 4HB = E14, 8)

M4 = 0

M5 = 0

M6 = 0

APPENDIX 8.5.1 (cont.)

23 GAM = ALPH1*ALO*BET

SY = 0,
SX = 0,

SXY = 0,

DO 10 N = 1, M

Z = GAM*SORT(C(N)*AL(N))/(ALO**1.5)

S = (Z/2, + SORT(1, +(Z/2, **2))**2)

ALPH(N) = S*AL(N)/ALO

C DEBYE = HUEKEL FORMULA

C CALCULATION OF ACTIVITY COEFFICIENT

C(N) = ALPH(N)*C(N)

ALNF = A*SORT(C(N))/C(N)

F(N) = 10.0**(-ALNF)

X(N) = C(N)*AL(N)*S*F(N)*F(N)

Y(N) = 1.0/(AL(N)**S)

SX = SX + X(N)

SY = SY + Y(N)

SXY = SXY + X(N)*Y(N)

SXX = SXX + X(N)**2

10 CONTINUE

109 FORMAT (5(E14, 8)/4(E14, 8))

YO = (SX*SXY-SXX*SY)/(SX*SX-AN*SXX)

SL = (AN*SXY-SX*SY)/(AN*SXX-SX*SX)

PRINT 117, YO, SL

117 FORMAT (1HG, "INTERCEPT = ", E14, 7, " SLOPE = ", E14, 7)

CHK = 1.0/YO

DK = 1.0/(SL*(ALO**2))

PRINT 111, CHK, DK

111 FORMAT (I14, 3OHAMDA ZERU FROM THE INTERCEPT=, F6, 11ON constant =, E14, 7)

12 PRINT 104

22 PRINT 105

105 FORMAT (I14, 6X, 10HMOLE/LITER, 7X, 3HMHO)

SUM = 0.

SUMX = 0.

SUMXX = 0.
DO 20 N = 1, M
YY = Y0 + SL*X(N)
DIF = Y(N) - YY
SUM = SUM + DIF*DIF
SUMX = SUMX + X(N)
SUMXX = SUMXX + X(N)*X(N)
20 PRINT 102, H, C(N), AL(N), ALPH(N), F(N), X(N), Y(N), YY, DIF
102 FORMAT (I3, 1XE13, 7, 7(1XE13, 7))
RE = 0.6745*SQRT(SUM/(AN-2,))
D1 = AN*SUMXX - SUMX*SUMX
PA = RE*SQRT(SUMXX/D1)*(ALO**2)
PB = RE*SQRT(AN/D1)*DK/SL
DEV = (SUM/(AN - 1,))***0.5
PRINT 103, ALO, DK
116 FORMAT (1HO, "MEAN SQ, DEV = ", E14, 6, 3X, "PROBABLE ERROR IN LIM, COND, 1 = ", E14, 6, 3X, "PROBABLE ERROR IN DISS, CONST = ", E14, 6)
103 FORMAT (1HO, 4X23H, LIMITING CONDUCTANCE = E14, 6, 6X24H, DISSOCIATION CO INSTANT = E14, 6)
RETURN
END
THE GE-400 SERIES - FORTRAN ASA (MPS)

C THIS PROGRAM CALCULATES THE DISSOCIATION CONSTANT, \( K \), OF AN ACID BY DIPPY METHOD

DIMENSION C(99), AL(99), DK(99)

READ 4, L1

4 FORMAT(13) DO 26 = L2 = 1, L1

READ 1

1 FORMAT(80H)

PRINT 2, T

T FORMAT(1HG, 19H)

C CALCULATION OF D, DIELECTRIC CONSTANT

C DRAKE, (PHYS REV., 83, 613, 1930)

D1 = 78.57 + (1.0, 0.0461 * (T=25), 0.0000155 * (T=25), 0.02)

C WYMAN AND INGALLS, (J. AM. CHEM. SOC., 60, 1182, 1938)

D2 = 78.54 + (1.0, 0.00479 * (T=25), 0.01196 * 0.5 * (T=25), 0.02) * 28

10E = 0.90 * (T=25), 0.023)

C MALMBERG AND MARYOTT, (J. RES. NAT. BUR. STAND., 56, 1, 1956)

D3 = 87.74 * 0.4000 * T 9.3988 * 4 * 10E = 0.90 * 0.02

C AVERAGE VALUE

D = (D1 + D2 + D3) / 3.

PRINT 201

201 FORMAT(1HG, 5X1HT, 16X2HU1, 16X2HD2, 16X2HD3, 16X1HD)

PRINT 202, 1, D, D1, D2, D3, D

FORMAT (F9.4, 4(1X, F14.4))

AUX = -20. - T

VISC = EXP(2.130258 * (1.2348 + AUX + 0.004167 * AUX * 2) / (T+96)) = 4160316

TK = T * 273.16

ALPH1 = 8.204E5 / ((D * TK) * 0.5)

BET = 82.56 / ((D * TK) * 0.5) / VISC

PRINT 3, ALPH1, BET

FORMAT (2HG, 31HC0EFF 11 - ONSAGER-EQ, ALPH1 = E14, 8, 4X7H8BETA = -E14, 18

READ 24, ALO

PRINT 2, ALO

READ 4, M

PRINT 5, N, M

READ 6, C(N), AL (N)

CONTINUE

6 FORMAT (E12.3, F9.4)

READ 18, R

18 FORMAT (F8.1)

A = 1.8123E+06 / ((D * TK) * 0.5)

B = 30.129E+08 / SQRT(D * TK)

C = 1.9, A, B

16 FORMAT (3X, 4X4HA = E14, 8, 8X4HB = E14, 8)

PRINT 20

20 FORMAT (1HG, 2HNO, 7X, 10HC0NC, (M/L), 3X, 10HC0ND, (MHO), 14H EQ, COND, (MH

10), 9HZ, DG, DISS, 3X, 9HACT, COEF, 4X, 11HD1SS, FUNCTION, 20H THERMODYN, DIS

S, C)

SOMDR = 0

ONGSP = ALPH1 * ALO + BET
DO 19 N = 1, M
   ALEF = SORT(ALO*2=2, 2NGSLP*SORT(ALO*AL(N)*C(N)))
   ALPH = AL(N)/ALET
   CNF = ALPH+C(N)
   ALNF = A*SORC(CN)/F/(1.+B*SORC(CN))
   F = 10. D(N) = ALNF
19   D(K) = ALPH*2*G(N)/(1.+ALNF)
   SUMD = SUMD + DK(N)
   21   FORMAT(13, 3X, E14, 6, 3X, F9, 4, 4X, F8, 3, 3X, F8, 5, 3X, F8, 5, 2(5X, E14, 6))
   AM = M
   D(K) = SUMD/AM
   PRINT-22, D(K)
22   FORMAT(1H0, 39X, 46H THERMODYNAMIC DISSOCIATION CONSTANT ART. MEAN =, E
111.4)
   SUMDF = 0.
   DO 23 N = 1, M
   DIF = D(K) - D(KAV)
   SUMDF = SUMDF + DIF**2
23   DEV = SQR(SUMDF/(AM - 1, 1))
   PRINT-24, DEV
24   CONTINUE
   FORMAT(1H0, 23H MEAN SQUARE DEVIATION = E11, 4)
   CALL EXIT
REAL K, K1

DIMENSION T(20), K(20), A(8, 8), B(4), COEF(4), U1(20), U2(20), U3(20), Y(2)

R = 1.98719

33 READ 100
CALL EDFTST(50, MM)
GO TO (31, 32), MM

31 PRINT 100

100 FORMAT(80H)

1

READ 39, NT, TSTRF
FNT = NT

39 FORMAT(13X, 2X, F5, 2)

DO 40 N = 1, NT
FN = N - 1

40 T(N) = TSTRF + 273.15 + FN*5, 0
READ 1, (K(N), N = 1, NT)
PRINT 1, (K(N), N = 1, NT)

1 FORMAT(5E15, 5)

DO 2 N1 = 1, NT
THETA = T(N1)
PRINT 10, THETA

10 FORMAT(1HU, 20X, "TEMPERATURE =", F7, 2, 2X, "DEGREES KELVIN")

DO 6 NN = 1, NT
X = (T(NN) - THETA)/THETA
U1(NN) = X/(1, 0 + X)
SUM2 = 0
SUM3 = 0

27 IF(X)29, 6, 29

29 SUM2 = 0, 5
SUM3 = 1, 7, 3

30 DO 4 N = 2, 1000
FN = N

31 CHK2 = SUM2
CHK3 = SUM3
L1 = N - 1
PRODX = 1

35 DO 30 L = 1, L1

37 PRODX = PRODX*(-X)
SUM2 = SUM2 + FN/(FN+1, 0)*PRODX
SUM3 = SUM3 + FN/(FN + 2, 0)*PRODX

40 IF(ABS(1, 0 - ABS(CHK2/SUM2)) < 0, 00001) 5, 5, 4
41 IF(ABS(1, 0 - ABS(CHK3/SUM3)) < 0, 00001) 6, 6, 4

42 CONTINUE

6 PRINT 1, NN, N, X, SUM2, SUM3
U2(NN) = SUM2*X*X

3 U3(NN) = SUM3*X*X*X
SY = 0
SYU1 = 0
SYU2 = 0
SYU3 = 0
SU1 = 0
SU2 = 0
SU3 = 0

APPENDIX 13.3.1
Calculation of the thermodynamic functions of ionization by the Clarke & Glew and Harned & Robinson formulas.
SU11 = 0,
SU12 = 0,
SU13 = 0,
SU22 = 0,
SU23 = 0,
SU33 = 0,
DO 7 N = 1, NT
Y(N) = ALOG(K(N)) * R
SY = SY + Y(N)
SYU1 = SYU1 + Y(N) * U1(N)
SYU2 = SYU2 + Y(N) * U2(N)
SYU3 = SYU3 + Y(N) * U3(N)
SU1 = SU1 + U1(N)
SU2 = SU2 + U2(N)
SU3 = SU3 + U3(N)
SU11 = SU11 + U1(N) * U1(N)
SU12 = SU12 + U1(N) * U2(N)
SU13 = SU13 + U1(N) * U3(N)
SU22 = SU22 + U2(N) * U2(N)
SU23 = SU23 + U2(N) * U3(N)
7 SU33 = SU33 + U3(N) * U3(N)
DO 2 M = 3, 4
A(1,1) = FNT
A(1,2) = SU1
A(1,3) = SU2
A(2,1) = SU1
A(2,2) = SU11
A(2,3) = SU12
A(3,1) = SU2
A(3,2) = SU12
A(3,3) = SU22
B(1) = SY
B(2) = SYU1
B(3) = SYU2
IF(M-3)60, 70, 60
60 A(1,4) = SU3
A(2,4) = SU13
A(3,4) = SU23
A(4,1) = SU3
A(4,2) = SU13
A(4,3) = SU23
A(4,4) = SU33
B(4) = SYU3
70 PRINT 28
28 FORMAT(1HO)
CALL MATIN(A, B, COEF, M)
99 PRINT 12
100 AU1 = SU1/FNT
101 AU2 = SU2/FNT
102 AU3 = SU3/FNT
103 SUM = 0.
DO 9 N = 1, NT
IF(M-3)25, 26, 25
25 YCALC = COEF(1) + COEF(2) * U1(N) + COEF(3) * U2(N) + COEF(4) * U3(N)
GO TO 27

26 YCALC = COEF(1) * COEF(2) * U1(N) + COEF(3) * U2(N)

27 DIFF = Y(N) - YCALC

SUM = SUM + DIFF

K(N) = EXP(YCALC/R)

9 PRINT 11, N, U1(N), U2(N), Y(N), YCALC, DIFF, SUM

FM = M

PS = 0.6745 * SQR(T(SUM/(FNT-FM))

11 FORMAT(1H1, '12.1X, R2X, E13.6)

12 FORMAT(1H4, 'N0, "5X, U1(N)", 10X, "U2(N)", 10X, "U3(N)", 11X, "Y(N)", 10X

1, "YCALC", 7X, "DIFFERENCE", 9X, "SUM")

36 PRINT 28

CALL PK(K, K1, T, NT)

PRINT 28

AU11 = 1.0 - AU1

AU12 = U1(N1) + U2(N1) - AU2

AU1 = U1(N1) - AU1

AU2 = U2(N1) - AU2

AU3 = U3(N1) - AU3

37 GTHET = "-COEF(1)*THETA

HTHET = COEF(2)*THETA

DS = Y(N1) + COEF(3)

ERH = T(N1) * PS * SQR(T(A(2,2)))

ERC = PS * SQR(T(A, 3, 3))

129 IF (N-3) = 200, 201, 200

201 ERG = "PS * T(N1) * SQR(T(1.0/FNT + A(2,2) * (AU1**2) + 2.0 * A(2,3) * AU1 * AU2 + A(3,3) * (AU2**2)

132 ERDS = PS * SQR(T(1.0/FNT + A(2,2) * (AU1**2) + 2.0 * A(2,3) * AU11 * AU12 + 2.0 * A(3,3) * (AU12**2))

133 00 TO 202

200 ERG = "PS * T(N1) * SQR(T(1.0/FNT + A(2,2) * (AU1**2) + 2.0 * A(2,3) * AU1 * AU2 + A(3,3) * (AU2**2) + 2.0 * A(2,4) * AU1 * AU3 + 2.0 * A(3,4) * AU2 * AU3 + 2A(4,4) * (AU3**2))

135 ERDS = PS * SQR(T(1.0/FNT + A(2,2) * (AU1**2) + 2.0 * A(2,3) * AU11 * AU12 + 2.0 * A(3,3) * (AU12**2) + 2.0 * A(2,4) * AU1 * AU3 + 2.0 * A(3,4) * AU2 * AU3 + 2A(4,4) * (AU3**2))

136 202 CONTINUE

137 PRINT 13, THETA, GTHET, ERG

138 13 FORMAT(1H1, "TEMPERATURE =", F7.2, 3X, "FREE ENERGY CHANGE (DELTA G) = 1", E13.6, 3X, "PROBABLE ERROR =", E13.6)

139 PRINT 14, THETA, HTHET, ERH

140 14 FORMAT(1H1, "TEMPERATURE =", F7.2, 3X, "ENTALPHY CHANGE (DELTA H) = 1", E13.6, 3X, "PROBABLE ERROR =", E13.6)

141 PRINT 17, THETA, DS, ERDS

142 17 FORMAT(1H1, "TEMPERATURE =", F7.2, 3X, "ENTROPY CHANGE (DELTA S) = 1", E13.6, 3X, "PROBABLE ERROR =", E13.6)

143 PRINT 15, THETA, COEF(3) * ERC

144 15 FORMAT(1H1, "TEMPERATURE =", F7.2, 3X, "DELTA CP = 1", E13.6, 3X, "PROBABLE ERROR =", E13.6)

145 IF (N-3) = 18, 21, 18

146 18 DCPDT = COEF(4) * T * THEITA

147 ERCPT = PS * E2.0 / T(N1) * SQR(T(A(4,4)))

148 PRINT 16, THETA, DCPDT, ERCPT

149 16 FORMAT(1H1, "TEMPERATURE =", F7.2, 3X, "D(DELTA CP)/DT "

150
1 "E13.6,3X,”PROBABLE ERROR = „E13.6)
2 CONTINUE

C HARNED AND ROBINSON CALCULATION

PRINT 100
PRINT 20
20 FORMAT(1HO,”HARNED AND ROBINSON CALCULATION OF THERMODYNAMIC QUANT
ITIES”)

SU1 = 0,
SU2 = 0,
SU3 = 0,
SU4 = 0,
SY = 0,
SYU1 = 0,
SYU2 = 0,
DO 21 N = 1, NT
SU1 = SU1 + T(N)
SU2 = SU2 + T(N)*T(N)
SU3 = SU3 + T(N)**3
SU4 = SU4 + T(N)**4
SY = SY - Y(N)*T(N)
SYU1 = SYU1 - Y(N)*T(N)*T(N)
SYU2 = SYU2 - Y(N)*T(N)**3
A(1,1) = FNT
A(1,2) = SU1
A(1,3) = SU2
A(2,1) = SU1
A(2,2) = SU2
A(2,3) = SU3
A(3,1) = SU2
A(3,2) = SU3
A(3,3) = SU4
B(1) = SY
B(2) = SYU1
B(3) = SYU2
CALL MATIN(A,B,COEF,3)
SUM = 0,
DO 22 N = 1, NT
YCALC = -COEF(1) - COEF(2)*T(N) - COEF(3)*T(N)*T(N)
K1(N) = EXP(YCALC/(R*T(N)))
DIF = Y(N)*T(N) - YCALC
SUM = SUM + DIF
22 PRINT 23,N,Y(N),YCALC,DIF,SUM
23 FORMAT(1H1,”N = “E13.6,2X,”Y(N) = “E13.6,2X,”YCALC = “E13.6,2X,”DIF
1= “E13.6,2X,”SUM = “E13.6)
CALL CALEK(A,FNT,3,SUM,PE,PS)
CALL PK(K,K1,T,NT)
DO 34 N = 1, NT
DG = COEF(1) + COEF(2)*T(N) + COEF(3)*T(N)*T(N)
ERG = PS*SORT(A(1,1) + T(N)*T(N)*A(2,2) + (T(N)**4)*A(3,3) + 2.0)
1T(N)*A(1,2) + 2.0*T(N)*T(N)*A(1,3) + 2.0*(T(N)**3)*A(2,3)
PRINT 14,T(N),DG,ERG
DH = COEF(1) - COEF(3)*T(N)*T(N)
ERH = PS*SORT(A(1,1) + (T(N)**4)*A(3,3) - 2.0*T(N)*T(N)*A(1,3))
PRINT 14,T(N),DH,ERH
199  DS = -COEF(2) - 2.0*COEF(3)*T(N)
200  ERS = PS*SORT(A(2,2) + 4.0*T(N)*A(3,3) + 4.0*T(N)*A(2,3))
201  PRINT 17,T(N),DS,ERS
202  DCP = -2.0*COEF(3)*T(N)
203  ERDCP = PS*SORT(4.0*T(N)*T(N)*A(3,3))
204  PRINT 15,T(N),DCP,ERDCP
205  24 PRINT 28
206  GO TO 33
207  32 CONTINUE
208  END
SUBROUTINE MATIN(A, B, P, N)
DIMENSION A(8,8), B(4), P(4), AUX(8,8), C(8,8), IT(8)
CALL MATI(A, C, IT, N, N, 8, KFLQ)

C CHECK INVERSION
CALL MATH(C, A, AUX, N, N, 8, B)
DO 101 M = 1,N
101 PRINT 102, M, (AUX(M, MH), MH=1,N)
102 FORMAT(1HU, I4, 6(2X, E14, 7), /, 5X, 6(2X, E14, 7)))
DO 110 K1 = 1,N
110 A(K1, K) = C(K1, K)

C SOLVING FOR X
DO 17 -I = 1,N
17 SUM = 0
DO 15 K = 1,N
15 SUM = SUM + A(I, K)*B(K)
P(I) = SUM
16 PRINT 14, I, P(I), (A(I, L), L=1,N), B(I)
14 FORMAT(1H, 5X11HC0EFFICIENT, I2, 2X14, 7, 5X, 5(2X, E14, 7))
RETURN
END
SUBROUTINE CALER(A1,AM,M1,SUM,PE,PS)
DIMENSION A1(8,8),PE(4),COV(4,4)
AM1=M1
DFREE=AM-AM1
IF (DFREE)2,2,3
2 DFREE=1.
3 S=SQR(SUM/DFREE)
PS=S*0.6745
PRINT 4,S,PS
4 FORMAT (1H0,ESTIMATE OF RESIDUAL VARIANCE=",E14.7,3X,"PROBABLE
ERROR OF THE FITTING=",E14.7)
PRINT 7
PRINT 8
7 FORMAT (1H0,ERRORS IN THE COEFFICIENTS")
8 FORMAT (1H0,3X,COEFFICIENT",5X,"PROBABLE ERROR")
DO 5 N=1,M1
5 PE(N)=PS*SQR(A1(N,N))
PRINT 6,N,PE(N)
6 FORMAT (7X,13,9X,E14.7)
PRINT 9
9 FORMAT(1H0,COVARIANCES")
10 DO 11 N=1,M1
11 COV(N1,N)=PS*PS*A1(N1,N)
12 PRINT 12,N1,(N,COV(N1,N),N=1,M1)
12 FORMAT(1H0,13,5X,6(J3,2X,E14.7))
RETURN
END
SUBROUTINE PK(K, K1, T, NT)

REAL K, K1

DIMENSION K(20), K1(20), T(20)

APPENDIX 13.3.1 (cont.)

DO 34 N = 1, NT

DIF = K(N) - K1(N)

PK = -ALOG10(K(N))

PK1 = -ALOG10(K1(N))

DIF1 = PK - PK1

PRINT 35, T(N), K(N), K1(N), DIF, PK, PK1, DIF1

FORMAT('T =', F7, 2X, 'K =', E12, 5, 2X, 'K1 =', E12, 5, 2X, 'DIF =', 1, E11, 4, 5X, 'PK =', F8, 5, 2X, 'PK1 =', F8, 5, 2X)

RETURN

END
Appendix 15.5.1.

Consider:

\[
\frac{\sigma_2}{\sigma_1} f = \prod_{i} \frac{u_i}{u_i + \Delta u_i} \frac{\Delta u_i}{e^{\frac{\Delta u_i}{2}} \frac{1-e^{-u_i}}{1-e^{-u_i}}}
\]  

(15.5.5)

The first factor on the right can be written as:

\[
\frac{u_i}{u_i + \Delta u_i} = \frac{1}{1 + \frac{\Delta u_i}{u_i}} = \frac{1}{1 + \delta}
\]

where \( \delta \ll 1 \). The function \( 1/(1 + x) \) represents the sum of an infinite geometrical progression with the first term \( a = 1 \) and the increment \( r = -x \):

\[
\frac{1}{1 + x} = 1 - x + x^2 - x^3 + ...
\]

Since \( x = \delta \ll 1 \), the terms from \( x^2 \) on can be neglected. We can write now:

\[
\frac{1}{1 + \frac{\Delta u_i}{u_i}} = 1 - \frac{\Delta u_i}{u_i}
\]

\( e^x \) can be expressed as a series:
\[ e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \ldots \]

Taking \( x = \Delta u_i/2 << 1 \), we can limit ourselves to the first two terms only.

Finally, the last fraction on the right side can be multiplied and divided by \( e^{u_i} \):

\[
\frac{1 - e^{(u_i + \Delta u_i)}}{1 - e^{-u_i}} \cdot \frac{e^{u_i}}{e^{u_i} - e^{-u_i}} = \frac{u_i}{e^{u_i}} e^{u_i - u_i - \Delta u_i}
\]

\[ e^{-\Delta u_i} = e^{-x} = 1 - \frac{x}{1!} + \frac{x^2}{2!} - \ldots \]

By taking the first two terms, expression (15.5.10) becomes:

\[
\frac{e^{u_i - 1 + \Delta u_i}}{e^{u_i - 1}} = 1 + \frac{\Delta u_i}{e^{u_i - 1}}
\]

The whole expression (15.5.5) is:

\[
\frac{\sigma_2}{\sigma_1} f = \prod_{i=1}^{n'} \left( 1 - \frac{\Delta u_i}{u_i} \right) \left( 1 + \frac{\Delta u_i}{2} \right) \left( 1 + \frac{\Delta u_i}{e^{u_i - 1}} \right)
\]

Multiplying out and neglecting the terms on \((\Delta u_i)^2\) or higher.
we obtain:

\[ \frac{\sigma^2}{\sigma_1} f = \prod_{i=1}^{n'} (1 + \Delta u_i \left( \frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i-1}} \right)) \]

Once again a multiplication, i-fold, neglecting terms of second and higher powers transforms the product into a sum:

\[ \frac{2}{1} f = 1 + \sum \Delta u_i \left( \frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i-1}} \right) \quad (15.5.7) \]
Appendix 15.7.1.

Consider a vibrating dipole H-X and an incoming reagent with a positive charge:

\[ \bullet \quad \vdots \quad X \quad H \]

\[ r_e \quad R \]

Assuming that HX is not polarized by the reagent, the potential energy of interaction \( \delta V \) will be proportional to the instantaneous dipole moment which changes as the molecule vibrates, according to:

\[
\delta V = C(\mu_e + \left( \frac{d\mu}{dx} \right)_e + \frac{1}{2} \left( \frac{d^2\mu}{dx^2} \right)_e x^2 + \ldots)
\]

The potential energy of the product will be that of the reactant plus the increment \( \delta V \) which can be expressed as a power series in the displacement:

\[
\delta V = V_e + ax + \frac{1}{2}bx^2
\]

If we now consider separately the H-X and D-X bonds and if we average over the displacements, then the isotope effect on the average potential energy is:

\[
\Delta\delta V = \delta V_{DX} - \delta V_{HX} = a(\bar{x}_D - \bar{x}_H) + \frac{1}{2} b(\bar{x}_D^2 - \bar{x}_H^2) + \ldots
\]
Appendix 15.10.1

The calculation shown in this appendix follows that given by Halevi.\textsuperscript{316}

Consider a reacting system consisting of a vibrating HX molecule (reactant) and an incoming positive charge (reagent). The notion of an HX molecule can be extended to include a C-H bond or an H-molecule bond (identical situation with that presented in appendix 15.7.1).

The potential energy of interaction $\delta V$ is (assuming that HX is not polarized):

$$\delta V = C\nu_e + \left[ \frac{d\nu}{dx} \right]_e x + \left[ \frac{d^2\nu}{dx^2} \right]_e x^2 + \ldots$$  \hspace{1cm} (15.10.4)

proportional to the instantaneous dipole moment which changes as the molecule vibrates. The same thing can be expressed as a power series in the displacement:

$$\delta V = V_e + ax + \frac{1}{2} bx^2 + \ldots$$  \hspace{1cm} (15.10.5)

The potential energy of the product is the sum of the potential energy of the reactant plus the energy of interaction:
\[ V_{\text{product}} = V_{\text{reactant}} + \delta V \]  \hspace{1cm} (15.10.6)

where \( V_{\text{reactant}} \) is well represented at the bottom of the potential well by:

\[ V = \frac{1}{2} k x^2 + gx^3 \]  \hspace{1cm} (15.10.7)

where \( g \) is negative since the bond contraction, i.e. \( x \) having a minus sign, increases the potential energy more than an equal extension, i.e. \( x \) positive. If the potential is harmonic, then \( g = 0 \). The potential energy function of the product is:

\[ V_{\text{product}} = V_e + ax + \frac{1}{2} (b+k)x^2 + gx^3 + \ldots \]  \hspace{1cm} (15.10.8)

or if the original potential is harmonic:

\[ V_{\text{product}} = V_e + ax + \frac{1}{2} (b+k)^2 \]  \hspace{1cm} (15.10.9)

Only the square term of the perturbing potential leads to an isotope effect, because only the coefficient of the square term, \( b \), enters the new force constant \( (b+k) \).

If \( V_{\text{reactant}} \) is harmonic and the perturbation linear, i.e.:
\[ V_{\text{reactant}} = \frac{1}{2} kx^2 \]

\[ V = V_e + ax \quad (15.10.10) \]

\[ V_{\text{product}} = V_e + ax + \frac{1}{2} kx^2 \]

no isotope effect takes place: the new force constant, defined by \( \delta^2 V_{\text{product}}/\delta x^2 \), is:

\[ \frac{\delta^2 V_{\text{product}}}{\delta x^2} = k \]

the same as that of \( V_{\text{reactant}} \).

If \( V_{\text{reactant}} \) is anharmonic, i.e. given by (15.10.7) and \( V_{\text{product}} \) given by (15.10.11), an isotope effect will take place even if the perturbing potential is linear in \( x \):

\[ V_{\text{product}} = V_e + ax + \frac{1}{2} kx^2 + gx^3 \quad (15.10.11) \]

The value of \( x \) at the bottom of the potential well is obtained from:

\[ \frac{\delta V_{\text{product}}}{\delta x} = a + kx + 3gx^2 = 0 \quad (15.10.12) \]

and \( x_{\text{min}} \) is:
\[ x_{\text{min}} = \frac{-k \pm \sqrt{k^2 - 12ag}}{6g} \quad (15.10.13) \]

The new force constant is given by:

\[ \left( \frac{\delta^2 V_{\text{product}}}{\delta x^2} \right) = k + 6gx \quad (15.10.14) \]

which, evaluated at the bottom of the potential well, gives:

\[ \left( \frac{\delta^2 V_{\text{product}}}{\delta x^2} \right)_{\text{min}} = (k^2 - 12ag)^{1/2} \quad (15.10.15) \]

Since "k" is positive and "g" negative, the force constant will increase when "a" is positive and decrease when "a" is negative.

Returning to the diatomic reactant C-H: if the displacement of the charge in the bond is as shown below:

\[ \delta^+ \quad \text{C} \rightarrow \text{H} \quad \text{extension} \quad (15.10.16) \]

\[ \delta^- \quad \text{C} \leftarrow \text{H} \quad \text{contraction} \]

then an incoming positive charge (approaching from the "C" side of the bond) should facilitate the contraction of the bond and make the extension of it more difficult. This
leads to the conclusion that "a" must be positive: from
(15.10.9) $V_{\text{product}}$ will increase when $x$ is positive
(extension is more difficult) and $V_{\text{product}}$ will decrease
when $x$ is negative (the contraction is facilitated).
Because "a" is positive, the force constant must increase
in the transition state (or product) and thus, the predicted
isotope effect will be in the direction:

$$K_D > K_H$$

(see 15.7.2).
Appendix 15.10.2.

Nuclear quadrupole moment and the chemical bond.

Generally, a nucleus is described by its mass \( m \), position \( r \), charge \( Ze \), spin number \( I \), magnetic moment \( \mu \), and electric quadrupole moment \( eQ \).

A simple quadrupole is defined for the distribution of charges shown below as being \( \sum_{i} e_i z_i^2 \).

\[
\begin{array}{c}
+e \\
-2e \\
+e
\end{array}
\]

In the case of nuclei, quadrupoles are obtained when the charge distribution is not perfectly spherical. The charge distribution can be considered to have an ellipsoidal shape:

\[
\begin{array}{c}
\text{spin axis}
\end{array}
\]

The signs indicate regions of low (minus sign) or high density of the positive charge while the nucleus, as a whole, possesses a net positive charge. Nuclei with spin quantum number \( I > 0 \) have nuclear quadrupoles. \(^{317}\)

The nuclear quadrupole moment is designated as \( eQ \),
where \( e \) is the charge of the electron and \( Q \) has the dimensions of \( \text{cm}^2 \).

If the charge density is cylindrically symmetrical and constant at all points within the ellipsoid and zero elsewhere then:

\[
eQ = \frac{2}{5} x Ze(c^2 - a^2) = \frac{8}{5} x ZeR^2 \epsilon \quad (15.10.30)
\]

where \( 2c \) is the length of the ellipsoid along the axis of revolution; \( 2a \) is the width of the ellipsoid in the dimension perpendicular to the axis; \( \epsilon \) is the ellipticity:

\[
\epsilon = \frac{c - a}{c + a} \quad (15.10.31)
\]

and \( R \) is the mean radius of the ellipse:

\[
R = \frac{c + a}{2} \quad (15.10.32)
\]

Values of \( Q \) are determined experimentally. When \( c > a \) (\( \epsilon > 0 \)), \( Q \) is positive and when \( c < a \) (\( \epsilon < 0 \)), \( Q \) is negative.

At every nucleus in a molecule there is an electric field due to all other charged particles in the molecule. If a nucleus in the molecule has a quadrupole moment, the
degeneracy of the energy levels of the nucleus (2I+1 fold) is lifted without the application of any external field.

The contribution to the potential energy of the system arising from the interaction of the nuclear quadrupole moment and an axially symmetric field is:

\[ E_Q = eQ \left( \frac{\delta^2 V}{\delta z^2} \right) \frac{3M_I^2 - I(I+1)}{4I(2I-1)} \] (15.10.33)

where \( V \) is the electrostatic potential and is related to the components of the electric field by the relations:

\[ E_x = -\frac{\delta V}{\delta x}, \quad E_y = -\frac{\delta V}{\delta y}, \quad E_z = -\frac{\delta V}{\delta z} \] (15.10.34)

In axially symmetric fields:

\[ \frac{\delta^2 V}{\delta x^2} = \frac{\delta^2 V}{\delta y^2} \] (15.10.35)

Examples of nuclei with axial (cylindrical) symmetry are: Cl nucleus in the \( \text{Cl}_2 \) molecule, in \( \text{HCl} \), or in \( \text{CH}_3\text{Cl} \), all of which are symmetrical-top molecules.

\( \theta \) is the angle made by the axis of the quadrupole with the direction of the electric field.
For the prolate shape ($\varepsilon > 0$) the charges are arranged as above, i.e.

$$+ - - +$$

In the oblate case ($\varepsilon < 0$) the charges are:

$$- + + -$$

The energy levels of the nucleus are split into $(2I+1)/2$ subenergy levels (there are $(2I+1)M_1$ values; however, since $M_1$ is squared in expression (15.10.36) only $(2I+1)/2$ energy levels are obtained). Transitions between these energy levels occur in the radio frequency range: 10 to 1000 Megacycles (Mc) which correspond with wave lengths of the order of 30m to 30cm.

$$Q\left(\frac{\delta^2V}{\delta z^2}\right)$$

is obtained from nuclear quadrupole spectra. Since $Q$, the nuclear quadrupole, is the same for a given nucleus independent of environment, comparisons between $(\delta^2V/\delta z^2)$ can be made for the same nucleus in different molecules. This quantity is given the symbol "q" and is related to the curvature of the electrostatic potential at the nucleus along the axis of cylindrical symmetry. More complicated treatments exist when such symmetry is not present.
A nucleus with \( I = 3/2 \) in an axially symmetric electric field has the degeneracy of its energy levels partly removed according to:

\[
M_I = I, I-1, I-2, \ldots, -(I-1), -I = 3/2, 1/2, -1/2, -3/2.
\]

For \( M_I = \pm 3/2 \):

\[
E'_Q = eQq \cdot \frac{1}{4}
\]

For \( M_I = \pm 1/2 \):

\[
E''_Q = -eQq \cdot \frac{1}{4}
\]

The splitting looks like:

\[
\begin{array}{c}
\text{\( E'_Q \)} \\
\text{\( E''_Q \)} \\
\hline
\text{\( M_I \)}
\end{array}
\]

\( \pm 3/2 \hspace{2cm} \pm 1/2 \)

The frequency of the transition is obtained by applying Einstein's frequency condition:

\[
h\nu = E'_Q - E''_Q = 1/2 \cdot eQq
\]

\[\text{(15.10.36)}\]

The value of \( eQ \) is approximately known from the
hyperfine structure of atomic spectra. The quantity eQq is called the nuclear quadrupole coupling constant; it is usually expressed in frequency units, i.e. as eQq/h Mc. sec^{-1}.

It can be shown that, if we have N electrons placed in \( \psi_1, \psi_2, \ldots, \psi_N \) orbitals, q at a particular nucleus is 320:

\[
q = e \sum_{i=1}^{N} \int |\psi_i|^2 \left[ (3\cos^2 \theta_i - 1)|r_i|^3 \right] d\tau
\]  
(15.10.37)

where \( \theta_i, \psi_i, \) and \( r_i \) are the polar coordinates of the \( i \)th electron relative to an axis whose origin is at the nucleus and in which the direction \( \theta = 0 \) lies along the axis of symmetry.

If \( \Sigma |\psi_i|^2 \) is spherically symmetrical (15.10.37) can be written as 320:

\[
q = - \int_0^\pi (3 \cos^2 \phi - 1) \sin \phi \int_0^{2\pi} d\phi \int_0^\infty r \left( \Sigma |\psi_i|^2 / r_i^3 \right) r_i^2 dr_i
\]  
(15.10.38)

The first integral in (15.10.38) is zero and thus, the whole expression vanishes. Therefore, it can be said that a spherically symmetrical charge distribution makes no contribution to q. This is the case of s-electrons, since s-orbitals are spherically symmetrical. Complete
shells of electrons are in the same category since they have a spherical charge distribution; this also means that q is determined by the valence electrons and therefore, q is a good source of information about the nature of the bonding in molecules. Polarization effects can destroy the spherical distribution of the filled shells of electrons. However, it is believed that the contribution of such an effect to q is small. In an axially symmetric molecule with z as an axis of symmetry:

\[ q_{np_x} = q_{np_y} \quad \text{and} \quad q_{np_z} = -2q_{np_x} \quad (15.10.39) \]

where \( q_{np_x} \), for example, is read as "the contribution to q of an electron in the np_x orbital" where n is the principal quantum number. Relation (15.10.39) is obtained directly from:

\[ q_{np_x} + q_{np_y} + q_{np_z} = 0 \quad (15.10.40) \]

since the three electrons, each one in one of the p orbitals, have spherical symmetry.

Because of the dependence of q on \( 1/r^3 \) (15.10.37), the contribution of the d-electrons is only a fraction of the contribution of the p-electrons (estimated at 10-15%) and
thus, the value of \( q \) at the nucleus will depend mainly on the number of p-orbitals of the atom to which the nucleus belongs.

If we have \( N_x \) of the np\(_x\) type of electrons, \( N_y \) of the np\(_y\) electrons, and \( N_z \) of the np\(_z\) electrons, then \( q \) for the atom is:

\[
q = \left[ N_z - \frac{1}{2}(N_x + N_y) \right] q_{\text{np}_z}
\]  

(15.10.41)

where the first term, i.e. \( N_z - \frac{1}{2}(N_x + N_y) \), is called the number of unbalanced p-electrons in a shell. This number is affected by the hybridization and the (ionic) character of the bonds between the atom under consideration and its neighbour.

The value of the nuclear quadrupole coupling constant for the chlorine atom in different molecular environments is the classical example used to demonstrate the relationship between \( eQq \) and the nature of the chemical bond.

The reasoning goes in the following way: the nuclear quadrupole coupling constant for the Cl atom has a certain value, say \( b \) (actually \( b \) is well known; it is \(-109.7 \text{ Mc.s}^{-1}\) where \( b \) corresponds to an imbalance of one p-electron (the electronic configuration of the Cl atom is \( 1s^22s^22p^63s^23p^5 \)). Any value of \( eQq \) smaller than "\( b \)" shows that the chlorine atom
tends to diminish this imbalance by acquiring a partial ionic character Cl\(^-\). When the imbalance is fully compensated, that is, the electronic configuration becomes \(1s^22s^22p^63s^23p^6\) corresponding to the ion Cl\(^-\), eQq should be zero since all the electronic shells are full. This is observed in KCl in which the chlorine has a nuclear quadrupole coupling constant (eQq) of less than 0.04 Mc.s\(^{-1}\).

Any value of eQq higher than "b" shows a tendency of the chlorine atom to increase the p-electron imbalance by acquiring a partial Cl\(^+\) character, that is, approaching an electronic configuration \(1s^22s^22p^53s^23p^4\). This, presumably, happens in FCl, in which the nuclear quadrupole coupling constant for Cl is -146.0 Mc.s\(^{-1}\).

Similarly, the value eQq = -75.3 Mc.s\(^{-1}\) for the chlorine in methyl chloride (gas) is explained by taking into consideration the inductive effect of the chlorine atom which makes the ionic structure CH\(_3\)Cl\(^+\)Cl\(^-\) a major contributor to the resonance hybrid of the methyl chloride.
DIMENSION X(18,3), WT(18), B(60,18,3)
COMMON B
WRITE (74,997)
C READ IDENTIFICATION STATEMENTS

997 FORMAT (4OHLOAD TAPE 108 WITH THE RING IN ON UNIT 2)
PAUSE
READ 2, NPRBS
REWIND 2
WRITE (2) NPRBS
DO 5 NPRBS = 1,NPRBS

5 PRINT 1,NPRBS
READ 1
PRINT 1
READ 1
PRINT 1
1 FORMAT (80H)

1 PRINT 2, NOAT, NINT, IWT, IPUNCH, ICK, ICK1, ICK2
2 FORMAT (1013)
3 FORMAT (140,H0,10X,"NO. OF ATOMS =",14,5X,"NO. OF INTERNAL COORDINATES 1=".14)

16 IF (IWT) 12, 13, 12
17 12 PRINT 14
18 14 FORMAT (140,H0,10X,"INTERNAL COORDINATES ARE NOT WEIGHTED")
19 GO TO 16
20 13 PRINT 15
21 15 FORMAT (140,H0,10X,"INTERNAL COORDINATES ARE WEIGHTED BY THE BOND LENGTH")
22 16 WRITE (2) NOAT, NINT, IPUNCH
C READ THE POLAR COORD, R IS THE DISTANCE FROM THE GEOMETRICAL CENTER OF C THE MOLECULE TO THE ATOM, AX, AY, AZ ARE THE ANGLES MADE BY R WITH THE C 3 CARTESIAN AXES,
23 CALL CART (NOAT, X, WT)
C READ THE DEFINITION OF THE INTERNAL COORD, AND CALCULATE B, S, C CODE FOR INTERNAL COORDINATES 1-STRETCH, 2-BEND C 3-OUT OF PLANE WAGGING, 4-TORSION C 5-BENDING SPECIAL CASE BENZENE HYDROG,

28 DO 4 N = 1, NINT
29 READ 2, NOINT, NCODE, N1, N2, N3, N4
30 PRINT 6, N, NOINT, NCODE, N1, N2, N3, N4
31 GO TO (7, 8, 9, 10, 61), NCODE
32 7 CALL STRECH (NOINT, X, N1, N2, NOAT, B)
33 GO TO 19
34 8 CALL BEND (NOINT, X, N1, N2, N3, NOAT, B, IWT, ICK)
35 GO TO 19
36 9 CALL OPWAG (NOINT, X, N1, N2, N3, N4, NOAT, B, IWT)
37 GO TO 19
38 10 CALL TORS (NOINT, X, N1, N2, N3, N4, NOAT, B, IWT)
39 GO TO 19
40 61 CALL BEND1 (NOINT, X, N1, N2, N3, N4, NOAT, B, IWT, ICK1, ICK2)
41 19 WRITE (2) NCODE, NOINT
42 DO 20 H7 = 1, NOAT
43 20 WRITE (2) (B(NOINT, M7, H8), H8 = 1, 3), WT(H7)
4 CONTINUE
5 CONTINUE
11 FORMAT(1H1,10X,"PROBLEM NO.",13)
WRITE (74,999)
WRITE (74,998)
998 FORMAT(34HKEEP IT HANDY FOR THE NEXT PROGRAM)
999 FORMAT(53HREMOVE TAPE 108 FROM UNIT 2)
PAUSE
CALL EXIT
END
SUBROUTINE CART (NOAT, X, WT)
C THIS SUBROUTINE READS IN POLAR COORDS. (R, AX, AY, AZ - THE ANGLES MADE BY R WITH THE 3 AXES) AND CALCULATES CARTESIAN COORDINATES, THE ATOMIC WEIGHS OF THE ATOMS. ALSO:
C 1 - X AXIS, 2 - Y AXIS, 3 - Z AXIS
DIMENSION X(18,3), WT(18)

FORMAT(1HO, "NO," , 5X, "ATOM NO," , 7X, "R", 14X, "AX", 11X, "AY", 12X, "AZ", 110X, "WT(NAT)" , 8X, "X(NAT,1)" , 6X, "X(NAT,2)" , 6X, "X(NAT,3)"")

DO 1 N = 1, NOAT
  READ 2, NAT, R, AX, AY, AZ, WT
  X(NAT,1) = R*COS(AX*0.017453278)
  X(NAT,2) = R*COS(AY*0.017453278)
  X(NAT,3) = R*COS(AZ*0.017453278)

1 PRINT 3, N, NAT, R, AX, AY, AZ, WT(NAT), X(NAT,1), X(NAT,2), X(NAT,3)

FORMAT(13,2X,5(E12.5,3X))

RETURN

END

APPENDIX 16.3.1 (cont.)
SUBROUTINE STRECH (NOINT, X, N1, N2, NOAT, B)
C THIS SUBROUTINE CALCULATES THE B ELEMENTS FOR STRECHING AS INTERNAL
C COORDINATE, GIVEN ARE
C COORDINATE, GIVE I THE CART. COORD. OF EACH ATOM (X) AND THE ATOMS
C DEFINING THE INTERNAL COORD.: 
DIMENSION X(18,3), B(60,18,3)
RN2N1 = 0.
 DO 1 N = 1,3
 1 RN2N1 = RN2N1 * (X(N2,N) - X(N1,N))**2
 RN2N1 = SURT(RN2N1)
 PRINT 100,NOINT,RN2N1
 PRINT 101
 DO 10 M = 1,NOAT
 10 IF (N1-M)5,4,5
 5 IF(N2-M)9,7,9
 4 DO 3 N = 1,3
 3 B(NOINT,M,N) = (X(N1,N) - X(N2,N)) / RN2N1
 GO TO 2
 2 GO TO 1
 7 DO 8 N = 1,3
 8 B(NOINT,M,N) = (X(N2,N) - X(N1,N)) / RN2N1
 GO TO 2
 9 DO 6 N = 1,3
 6 B(NOINT,M,N) = 0.
 GO TO 10
 2 PRINT 102,NOINT,M,(B(NOINT,M,N),N=1,3)
 10 CONTINUE
 100 FORMAT (1H0,"INTERNAL COORD. NO. = ",14,5X,"STRECHING",15X,"RN2N1 = "
 1,E14.7)
 101 FORMAT (1H0,"INT. COORD. NO.",2X,"ATOM NO.",5X,"B(NOINT,M,1)",5X,"B(
 1NOINT,M,2)",5X,"B(NOINT,M,3)"
 102 FORMAT (1H0,"X",5X,14,7X,14,5X,3E13X,E14.7)
 RETURN
 END
SUBROUTINE BEND (NOINT, X, N1, N2, N3, NOAT, B, IHT, ICK)
C THIS SUBROUTINE CALCULATES THE B ELEMENTS FOR VALENCE ANGLE BENDING
C COORDINATE, GIVEN 1 THE CART,COORD, (X,S) AND THE ATOMS DEFINING THE
C VALENCE ANGLE (N1,N2,N3). N3 IS THE CENTRAL ATOM.
C CALCULATE THE DISTANCES BETWEEN ATOMS

DIMENSION X(18,3), B(60,10,3), EN3N1(3), EN3N2(3)

RN3N1 = 0,
RN3N2 = 0,
DO 1 N = 1, 3
RN3N1 = RN3N1 * (X(N3, N) - X(N1, N))**2
1 CONTINUE

1 RN3N2 = RN3N2 * (X(N3, N) - X(N2, N))**2
RN3N1 = SQRT(RN3N1)
RN3N2 = SQRT(RN3N2)

PRINT 100, NOINT, RN3N1, RN3N2
100 FORMAT (1H0, "INTERNAL COORD, NO., =", 14, 3X, "VALENCE ANGLE BENDING", 4X, "RN3N1 = "E14.7, 2X, "RN3N2 = "E14.7)

PRINT 101
101 FORMAT (1H0, "INT,COORD, NO., "X, "ATOM NO., "X, "B(NOINT, M, 1), "X, "B("NOINT, H, 2), "X, "B(NOINT, M, 3)"

COSPH = 0,
DO 3 N = 1, 3
EN3N1(N) = (X(N1, N) - X(N3, N))/RN3N1
3 CONTINUE

EN3N2(N) = (X(N2, N) - X(N3, N))/RN3N2

COSPH = COSPH - EN3N1(N)*EN3N2(N)

SINPH = SQRT(1. - COSPH*2)

DO 5 M = 1, NOAT
IF(N1-M)6, 5, 6
21 IF(IHT)15, 14, 15
5 CONTINUE

14 RWT = SQRT(RN3N1*RN3N2)
15 IF(ICK)18, 4, 17

17 RWT = RN3N1
18 RWT = RN3N2
20 GO TO 4
21 GO TO 4
25 GO TO 4
26 GO TO 4
27 GO TO 4
28 GO TO 4
29 GO TO 4
30 GO TO 4
31 B(NOINT, N1, N) = (COSPH*EN3N1(N) - EN3N2(N))/(SINPH*RN3N1)*RWT
32 B(NOINT, N2, N) = (COSPH*EN3N2(N) - EN3N1(N))/(SINPH*RN3N2)*RWT
33 B(NOINT, N3, N) = -B(NOINT, N1, N) - B(NOINT, N2, N)
34 GO TO 2
35 IF(N2-M)7, 2, 7
36 IF(N3-M)8, 2, 8
37 GO TO 9
38 B(NOINT, H, N) = 0,
39 CONTINUE
40 DO 10 M = 1, 3
41 GO TO (11, 12, 13): M1
11 M = N1
42 GO TO 10
12 M = N2
43 GO TO 10
13 M = N3
44 GO TO 10
45 GO TO 10
46 GO TO 10
47 GO TO 10
48 GO TO 10

10 PRINT 102, NOINT, M, (B(NOINT, M, N), N=1, 3)
102 FORMAT (1H, 5X, 14, 7X, 14, 3X, 3X, E14, 7)
49
RETURN
50
END
SUBROUTINE OPWAG(NPOINT, X, N1, N2, N3, N4, NOAT, B, IWT)
C THIS SUBROUTINE CALCULATES THE B ELEMENTS FOR OUT OF PLANE INTERNAL
C COORDINATE, GIVEN THE CART COORD. (X) OF THE ATOMS; THE ATOMS
C DEFINING THE COORDINATE (N1 IS THE END ATOM, N4 IS THE Apex OR CENTRAL
C ATOM AND N2 AND N3 ARE THE ANCHOR ATOMS);
D IMENSION X(18,3), B(60,18,3), EN4N1(3), EN4N2(3), EN4N3(3), E4243(3),
E 1E4142(3), E4341(3)
C CALCULATE THE DISTANCES BETWEEN THE ATOMS
RN4N1 = 0,
RN4N2 = 0,
RN4N3 = 0,
DO 1 N = 1, 3
RN4N1 = RN4N1 + (X(N4,N) - X(N1,N))**2
RN4N2 = RN4N2 + (X(N4,N) - X(N2,N))**2
1 RN4N3 = RN4N3 + (X(N4,N) - X(N3,N))**2
RN4N2 = SQRT(RN4N2)
RN4N3 = SQRT(RN4N3)
PRINT 100, NPOINT, RN4N1, RN4N2, RN4N3
100 FORMAT (1X0,"INTERNAL COORD.NO. =",I4,3X,"OUT OF PLANE WAGGING",5X
C CALCULATE THE UNIT VECTORS
DO 2 N = 1, 3
EN4N1(N) = (X(N1,N) - X(N4,N))/RN4N1
EN4N2(N) = (X(N2,N) - X(N4,N))/RN4N2
2 EN4N3(N) = (X(N3,N) - X(N4,N))/RN4N3
C CALCULATE THE ANGLES AND THE VECTORIAL PRODUCTS
E4243(1) = EN4N2(2)*EN4N3(3) - EN4N2(3)*EN4N3(2)
E4243(2) = EN4N2(3)*EN4N3(1) - EN4N2(1)*EN4N3(3)
E4243(3) = EN4N2(1)*EN4N3(2) - EN4N2(2)*EN4N3(1)
E4142(1) = EN4N1(2)*EN4N2(3) - EN4N1(3)*EN4N2(2)
E4142(2) = EN4N1(3)*EN4N2(1) - EN4N1(1)*EN4N2(3)
E4142(3) = EN4N1(1)*EN4N2(2) - EN4N1(2)*EN4N2(1)
E4341(1) = EN4N3(2)*EN4N1(3) - EN4N3(3)*EN4N1(2)
E4341(2) = EN4N3(3)*EN4N1(1) - EN4N3(1)*EN4N1(3)
E4341(3) = EN4N3(1)*EN4N1(2) - EN4N3(2)*EN4N1(1)
COSPH1 = EN4N2(1)*EN4N3(1)*EN4N2(2)*EN4N3(2)*EN4N2(3)*EN4N3(3)
SINPH1 = SQRT(1. - COSPH1**2)
SINH = (EN4N1(1)*E4243(1)*EN4N1(2)*E4243(2)*EN4N1(3)*E4243(3))/SIN
1PH1
COSPH = SQRT(1. - SINH**2)
TANH = SINH/COSPH
C CALCULATE THE B ELEMENTS
DO 3 M = 1, NOAT
IF (M-N1) 4, 4, 4
3 IF (IWT) 16, 17, 16
4 16 RWT = 1!
GO TO 6
5 RWT = RN4N1
6 DO 18 N = 1, 3
N1(N) = (E4243(N)/(COSPH*SINPH1) - TANH*EN4N1(N))/RN4N1*RWT
18 GO TO 6
1N2(N)/(SINPH1**2))/RN4N3*RWT
43 1B(NOINT,N4,N) = B(NOINT,N1,N) - B(NOINT,N2,N) - B(NOINT,N3,N)
44  GO TO 3
45  4 IF(M-N2)7,3,7
46  7 IF(M-N3)8,3,8
47  8 IF(M-N4)9,3,9
48  9  DO 10 N = 1,3
49 10 B(NOINT,M,N) = 0,
50   3 CONTINUE
51   PRINT 101
52   DO 11 M1 = 1,4
53   GO TO (12,13,14,15),M1
54  12 M = N1
55  GO TO 11
56  13 M = N2
57  GO TO 11
58  14 M = N3
59  GO TO 11
60  15 M = N4
61 11 PRINT 102,NOINT,M,(B(NOINT,M,N),N=1,3)
62 101 FORMAT (1H0,"INT,COORD.NO.",2X,"ATOM NO.",5X,"B(NOINT,M,1)",5X,"B(1NOINT,M,2)",5X,"B(NOINT,M,3)"
63 102 FORMAT (1H1,5X,14,7X,15,3X,3(3X,E14.7))
64  RETURN
65  END
SUBROUTINE TORS (NOINT, X1, N1, N2, N3, N4, NOAT, B, IWT)

DIMENSION X(18,3), B(0,18,3)
DIMENSION EN1N2(3), EN2N3(3), EN3N4(3), E1223(3), E3423(3)

C THIS SUBROUTINE CALCULATES THE B ELEMENTS FOR INTERNAL COORDINATE
C TORSION, GIVEN I THE CART. COORDINATES, THE ATOMS DEFINING THE INT.
C COORD, I N1 AND N4 ARE THE END ATOMS, N2 AND N3 ARE THE CENTRAL ATOMS,
C N1 AND N2 ARE NEARER THE OBSERVER.
C CALCULATE THE DISTANCES BETWEEN ATOMS

RN1N2 = 0,
RN2N3 = 0,
RN3N4 = 0,

DO 1 N = 1, 3
RN1N2 = RN1N2 + (X(N1,N)-X(N2,N))**2
RN2N3 = RN2N3 + (X(N2,N)-X(N3,N))**2
RN3N4 = RN3N4 + (X(N3,N)-X(N4,N))**2

1 RN1N2 = SQRT(RN1N2)
RN2N3 = SQRT(RN2N3)
RN3N4 = SQRT(RN3N4)

PRINT 100, NOINT, RN1N2, RN2N3, RN3N4


C CALCULATE THE UNIT VECTORS

DO 2 N = 1, 3
EN1N2(N) = (X(N2,N)-X(N1,N))/RN1N2
EN2N3(N) = (X(N3,N)-X(N2,N))/RN2N3
EN3N4(N) = (X(N4,N)-X(N3,N))/RN3N4

C CALCULATE THE ANGLES AND THE VECTORIAL PRODUCTS

E1223(1) = EN1N2(2)*EN2N3(3)-EN1N2(3)*EN2N3(2)
E1223(2) = EN1N2(3)*EN2N3(1)-EN1N2(1)*EN2N3(3)
E1223(3) = EN1N2(1)*EN2N3(2)-EN1N2(2)*EN2N3(1)
E3423(1) = EN3N4(2)*EN2N3(3)-EN3N4(3)*EN2N3(2)
E3423(2) = EN3N4(3)*EN2N3(1)-EN3N4(1)*EN2N3(3)
E3423(3) = EN3N4(1)*EN2N3(2)-EN3N4(2)*EN2N3(1)
COSPH3 = -EN1N2(1)*EN2N3(1) = EN1N2(2)*EN2N3(2) = EN1N2(3)*EN2N3(3)
SINPH2 = SQRT(ABS(1.0-COSPH2**2))
SINPH3 = SQRT(ABS(1.0-COSPH3**2))

C CALCULATE THE DIHEDRAL ANGLE TAU !
COSTAU = (-E1223(1)*E3423(1) - E1223(2)*E3423(2) - E1223(3)*E3423(3))/SINPH2*SINPH3)

31 SINTAU = SQRT(1.0 - COSTAU**2)

C SOME CHECK STATEMENTS

PRINT 102, N, C, COSPH2
PRINT 102, N, C, COSPH3
PRINT 102, N, C, COSTAU
PRINT 102, N, C, SINTAU

C CALCULATE THE B ELEMENTS

DO 3 M = 1, NOAT
IF (M-1)4, 5, 4
3 IF (IWT) 16, 17, 16
17 RWT = RN1N2
GO TO 6
40 16 RWT = 1
6 DO 18 N = 1, 3
TORSF

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43 B(NOINT,N1,N) = -E123(N)/(SINPH2*2)*RN1N2*RWT
44 B(NOINT,N2,N) = RWT*((1./(RN1N2*SINPH2) - (COSTAU*COS
1PH2/SINPH2 * COSPH2/SINPH2)*RN2N3)*E123(N)/SINPH2 - COSPH2*SINTAU
2*(EN1N2(N) + COSPH2*EN2N3(N))/(SINPH2*RNN3N3*SINPH2))
45 B(NOINT,N3,N) = RWT*((1. / (RN3N4*SINPH3) - (COSTAU*COS
1SPH2/SINPH2 * COSPH3/SINPH3)*RNN2N3)*E3423(N)/SINPH3 - COSPH2*SINTA
2*(-EN2N3(N) + COSPH3 - EN3N4(N))/(SINPH2*RNN2N3*SINPH3))
46 B(NOINT,N4,N) = -E3423(N)/(SINPH3*2)*RN3N4*RWT
47 GO TO 3
48 IF(M-N2)7,3,7
49 IF(M-N3)8,3,8
50 IF(M-N4)9,3,9
51 DO 10 N = 1,3
52 10 B(NOINT,M,N) = 0,
53 CONTINUE
54 PRINT 101
55 DO 11 M1 = 1,4
56 GO TO (12,13,14,15),M1
57 12 M = N1
58 GO TO 11
59 13 M = N2
60 GO TO 11
61 14 M = N3
62 GO TO 11
63 15 M = N4
64 PRINT 102,NOINT,M,B(NOINT,M,N),N=1,3
66 102 FORMAT (IH : 5X, 14, /X, 14, 3X, 3X, E14, 7))
67 RETURN
68 END
SUBROUTINE BEND1(NOINT, X, N1, N2, N3, N4, NOAT, B, IHW, ICK1, ICK2)
C THIS SUBROUTINE CALCULATES THE B ELEMENTS FOR VALENCE ANGLE BENDING
C OF A SPECIAL CASE THAT IS CORRESPONDING TO BETA INTERNAL COORDINATE
C OF BENZENE (HYDROGEN BENDING),

C N1 AND N4 ARE THE CONON ATOMS, N4 IS THE CENTRAL ATOM.
DIMENSION B(60, 18, 3), X(18, 3), C(60, 3)
CALL BEND(NOINT, X, N1, N2, N4, NOAT, B, IHW, ICK1)

DO 1 MM = 1, 4
   GO TO (10, 11, 12, 13), MM
10 M = N1
   GO TO 14
11 M = N2
   GO TO 14
12 M = N3
   GO TO 14
13 M = N4
   CONTINUE
14 DO 1 N = 1, 3
   C(M,N) = B(NOINT, M, N)
15 CONTINUE
CALL BEND(NOINT, X, N1, N3, N4, NOAT, B, IHW, ICK2)
PRINT 101
101 FORMAT (1H0, "INT, COORD, NO.", 2X, "ATOM NO.", 5X, "B(NOINT, M, 1)", 5X, "B(
NOINT, M, 2)", 5X, "B(NOINT, M, 3)"

DO 4 MM = 1, 4
   GO TO (6, 7, 8, 9), MM
4 M = N1
   GO TO 5
5 M = N2
   GO TO 5
6 M = N3
   GO TO 5
7 M = N4
   DO 3 N = 1, 3
3 B(NOINT, M, N) = (C(M, N) - B(NOINT, M, N))/2.0
PRINT 102, NOINT, M, (B(NOINT, M, N), N=1, 3)
102 FORMAT (1H0, 5X, 14, 7X, 14, 3X, 3X, 3X, E14.7)
4 CONTINUE
RETURN
END
DIMENSION B(60,18,3),WT(18)
COMMON B
WRITE (74,999)
999 FORMAT (23HLOAD_TAPE 108 ON UNIT 2)
PAUSE
REWIND 2
READ (2) NPRBS
DO 1 NPRB = 1,NPRBS
READ (2) NOAT,NINT,IPUNCH
PRINT 100,NPRB
DO 3 NINT1 = 1,NINT
READ (2) NCODE,NINT
DO 4 M7 = 1,NOAT
READ (2) (B(NPOINT,M7,M8),M8=1,3),WT(M7)
CONTINUE
CALL GMATRIX(NINT,NOAT,WT,B,IPUNCH)
CONTINUE
WRITE (74,998)
PAUSE
998 FORMAT(43HREMOVE TAPE 108 FROM UNIT 2, STORE IT AWAY;)
100 FORMAT(1H,10X,"PROBLEM NO.",13)
101 FORMAT(1H,2X,2(I3,2X),3(2X,E14.7),4X,I3,2X,3(2X,E14.7))
102 FORMAT(1H0,2X,"AT ",3X,"IC",7X,"B(IC,AT,1)",6X,"B(IC,AT,2)",7X,"B(IC,AT,3)"
END
SUBROUTINE GMATRIX(NINT,NOAT,WT,B,Punch)
DIMENSION B(60,18,3),WT(18),G(60)
PRINT 11
DO 1 N1 = 1,NINT
DO 2 N2 = 1,NINT
AUX2 = 0,
DO 3 N3 = 1,NOAT
AUX1 = 0,
DO 4 N4 = 1,3
AUX = B(N1,N3,N4)*B(N2,N3,N4)/WT(N3)
4 AUX1 = AUX1 + AUX
3 AUX2 = AUX2 + AUX1
2 G(N2) = AUX2
PRINT 6,N1
IF(IPUNCH)10,1,10
10 DO 8 M = 1,NINT,6
L = M + 5
IF (L-NINT)8,8,9
9 L = NINT
8 PUNCH7,N1,M,(G(N2),N2=M,L)
1 PRINT 5,(G(N2),N2=1,NINT)
7 FORMAT (13,13,6F12,8)
5 FORMAT (1H0,10,(2X,0PE11,4)/(1X,10(2X,0PE11,4))
6 FORMAT (1H0,14)
11 FORMAT (1H0,10X,"G MATRIX")
RETURN
END
THE GE-400 SERIES - FORTRAN ASA (MIPS)

DIMENSION A(1275),G(50),E(50),V(50,50),B(50,50),F(50,50),V1(50,1)
1N(50,50),FW(50),FW1(50,50),HFW(50)
EQUIVALENCE (E,V1,FW,HFW) \{ V1,B,F,W,FW1 \}

READ 20,NCT
DO 300 NCON = 1,NCT
REWIN 2
READ 110
PRINT 110
110 FORMAT(80H)

PRINT 101
101 FORMAT(1H0,10X,"G MATRIX")
C M1 IS THE MATRIX ORDER \{ G MATRIX AND F MATRIX \}
C N8 IS THE NUMBER OF NON-ZERO FORCE CONSTANTS IN THE UPPER TRIANGLE,
READ 28,M1,N8
28 FORMAT(2I3,4X,F10.5)
K = 0
M2 = 0
DO 2 M = 1,M1
M2 = M2 + 1
170 READ 10,N1,N2,G(N),N=N1,M1
202 PRINT 100,M=N1,N2,G(N),N=N1,M1
190 DO 2 N = M2,M1
K = K + 1
210 A(K) = G(N)
10 FORMAT(2I3,6F12.8/(6X,6F12.8))
100 FORMAT(I5,5X,2(I3,2X),6(E14.7,2X)/(29X,6(E14.7,2X)))

M5 = 0
6 CALL EIGENJ(A,M1,50,V,E,1)
26 PRINT 103
103 FORMAT(1H0,5X,"RESULTS : EIGENVALUES")
DO 29 N = 1,M1
7 PRINT 1,N,E(N)
30 FORMAT(15,5X,5(E15.7,3X)/(10X,5(E15.7,3X)))
19 IF (M5) 17,19,17
17 DO 18 N = 1,M1
18 WRITE (2) G(N,M),M=1,M1
8 CONTINUE
DO 35 N = 1,M1
9 B(N,N) = -SQRT\.ABS\{E(N)\}
36 DO 11 N = 1,M1
37 DO 11 M = 1,M1
38 IF (M-N) 12,11,12
39 12 B(N,M) = 0.
41 CONTINUE
CALL MXT(A,0,M1,7,10)
CALL MXH(2,3,4,1)
PRINT 102
REWIN 2
DO 47 M = 1,M1
47 DO 48 N = 1,M1
48 IF (N-M) 49,47,46
49 3 F(M,N) = 0.
50 DO 204 N7 = 1,N8

APPENDIX 16.2.1
Calculation of the vibrational frequencies of a molecule from the G and F matrices.
(Version 1 : for GE 420, 16K computer.)
READ 28, M, N, F(M, N)
DO 205 M = 1, M1
PRINT 100, M1, M, N, (F(M, N), N=1, M1)
WRITE (2) (F(M, N), N=1, M1)
REWIND 4
DO 13 N = 1, M1
READ (4) (V1(M), M=1, M1)
DO 13 M = 1, M1
13 W(N, M) = V1(M)
CALL MTXT(W, M1, 4, 0)
CALL MTXM(2, 4, 3, M1)
REWIND 3
DO 23 N = 1, M1
READ (3) (FW(M), M=1, M1)
DO 23 M = 1, M1
23 FW1(N, M) = FW(M)
CALL MTXT(FW1, M1, 3, 0)
CALL MTXM(4, 3, 2, M1)
REWIND 2
M2 = 0
K = 0
DO 15 N = 1, M1
M2 = M2 + 1
READ (2) (WF(M), M=1, M1)
DO 15 M3 = M2, M1
15 A(K) = WF(M3)
M5 = 1
GO TO 6
17 PRINT 26
26 FORMAT (1H0, 4(5X, "BAND", 3X, "WAVE NUMBER (CM-1)"))
DO 24 N = 1, M1
24 E(N) = SORT(ABS(E(N)))+1302.9
PRINT 25 (N, E(N), N=1, M1)
300 CONTINUE
25 FORMAT (1H1, 4(5X, I4, 5X, E15.7), I1, 4(5X, I4, 5X, E15.7))
END
SUBROUTINE MTEXT(A, M, N, IP)
C THIS PROGRAM TRANSPOSES A MATRIX
DIMENSION A(50, 50), T(50)

N = 1
DO 1 N1 = N, M
DO 2 N2 = N, M
T(N2) = A(N1, N2)
A(N1, N2) = A(N2, N1)
2 A(N2, N1) = T(N2)
1 N = N - 1
10 REWIND NTP
DO 5 N1 = 1, M
12 5 WRITE (NTP)(A(N1, N2), N2 = 1, M)
13 IF (IP) 6, 7, 6
14 6 DO 8 N1 = 1, M
15 8 PRINT 4, N1, (A(N1, N2), N2 = 1, M)
16 4 FORMAT (5, 7, 3X, E14.7, / (9X, E14.7, 6(3X, E14.7)))
17 7 RETURN
18 END
SUBROUTINE HTXM(NTP1,NTP2,NTP3,M)  
C THIS SUBROUTINE MULTIPLIES TWO SQUARE MATRICES  
DIMENSION A(50),B(50),C(50)  

APPENDIX 16.2.1 (cont.)

DO I N = 1,M  
REWIND NTP1  
REWIND NTP3  
DO J L = 1,M  
REWIND NTP2  
READ (NTP1)(A(L),L=1,M)  
READ (NTP2)(B(L),L=1,M)  
SUM = 0  
DO J L = 1,M  
SUM = SUM * D  
WRITE (NTP3)(C(L),L=1,M)  
1 CONTINUE  
RETURN  
END
MAIN
1108 FORTRAN V LEVEL  2206 0009 F600A
COMPIATION WAS DONE ON 29 AUG 68 AT 10:24:01

PROGRAM

AGE USED (BLOCK, NAME, LENGTH)
0001  *CODE  000302
0000  *DATA  124733
0002  *BLANK  000000

APPENDIX 16.2.2
Calculation of the vibrational frequencies
of a molecule from the G and F matrices
(Version 2: for a Univac 1108, 50K computer).

INTERNAL REFERENCES (BLOCK, NAME)
0003  FREQ
0004  POTEN
0005  NRDUS
0006  NI01
0007  NI02
0010  NPRINT
0011  NRDUS
0012  NSTOPS

AGE ASSIGNMENT FOR VARIABLES (BLOCK, TYPE, RELATIVE LOCATION, NAME)

1 034235  1F  0001  000012  112G  0001  000023  120G  0000  03431
2 000104  152G  0001  000122  163G  0001  000134  174G  0001  00013
3 000143  205G  0001  000204  224G  0001  000217  233G  0000  03426
6 034274  5F  0000  034244  53F  0000  034234  57F  0000  03430
7 034304  9F  0000  R  034330  AA  0000  R  106660  AL  0000  R  05237
D 000000  1F  0000  D  106660  FW  0000  R  034232  F1  0000  D  03433
D 070620  G1  0000  D  016134  H  0001  I  034221  IA  0000  I  03417
I 106660  JJ  0000  I  034223  L1  0000  I  034225  M  0001  I  03422
I 034231  M2  0000  I  034233  M5  0000  I  034230  N  0000  R  01604
I 034227  N2  0000  D  070620  V  0000  D  052370  V1  0000  D  03433

* C THIS PROGRAM CALCULATES THE VIBRATIONAL FORCE CONSTANTS OF A MOLECULE
* C REFERENCES
3* C
J.H. SCHACHTSCHNEIDER, SPECTROCHIM. ACTA, 19, 117, 1963
4* C
DIMENSION G(60,60), F(60,60), NUCAL(60), V(60,60), GAM12(60,60), W(60,6)
5* C
10), FW(60,60), H(60,60), 61(1830), V1(3660), IALF(20)
6* C
DOUBLE PRECISION G, F, V, GAM12, W, FW, H, G1, V1
7* C
DIMENSION WT(60,60), ALLF(60,60), AL(60,60), AA(3660), II(3660), JJ(A
8* C
13660)
9* C
EQUIVALENCE (G, W, AA), (WT, V1, ALLF), (V, G1, II), (GAM12, FW, AL, JJ)
10* C
REAL NUCAL
11* C
MR = 60
12* C
READ (1, 57, ERR = 47, END = 47) (IALF(IA), IA=1, 20)
13* C
PRINT 57, (IALF(IA), IA=1, 20)
14* C
57 FORMAT (20A4)
15*       READ 1,M1,L1,CHKPT
16*       1 FORMAT(I3,13,4X,F7.4,2X,I3,13,5X,F5.3,2X,I3,13)
17*       PRINT 53,M1,L1
18*       53 FORMAT(1H0,20HNO. OF INT. COORD.: = ,I4,4X,45HNO. OF NON-ZERO F.CT. IN THE UPPER TRIANG. = ,I5)
20*       C READ MATRIX G
21*       PRINT 2
22*       2 FORMAT(1H0, 'G MATRIX ')
23*       DO 3 M = 1,M1
24*       READ 4,N1,N2,(G(M,N),N=1,M1)
25*       PRINT 5,M1,N1,N2,(G(M,N),N=1,M1)
26*       3 CONTINUE
27*       4 FORMAT(2I3,6(D12.5)/(6X,6(D12.5)))
28*       5 FORMAT(15,5X,2(I3,2X), 6(D14.7,2X)/(20X,6(D14.7,2X)))
29*       C READ THE NON-ZERO ELEMENTS OF F
30*       DO 7 M = 1,M1
31*       DO 7 N = 1,M1
32*       7 F(M,N) = 0.0D+00
33*       DO 8 M2 = 1,L1
34*       READ 1,M2,N,F1
35*       F(M,N) = F1
36*       F(N,M) = F(M,N)
37*       8 CONTINUE
38*       PRINT 9
39*       9 FORMAT(1H0, 'F MATRIX ')
40*       DO 10 M = 1,M1
41*       PRINT 6,M1,L1,M,(F(M,N),N=1,M1)
42*       6 FORMAT(I5,5X,2(I3,2X), 6(E14.7,2X)/(20X,6(E14.7,2X)))
43*       M5 = 0
44*       PRINT 14,M5
45*       14 FORMAT(1H0, 'THE CALCULATED FREQ. AFTER ITERATION NO. = ,I2)
46*       CALL_FREQ(G,F,M1,NUCAL,MR, 1,V,GAM12,W,FW,H,G1,V1,WT)
47*       IF(CHKPT)62,64,62
48*       62 CALL_POTEN(F,W,V,M1,MR,ALLF,AL,NUCAL,AA,II,JJ)
49*       GO TO 64
50*       47 CONTINUE
51*       STOP
52*       END

END OF UNIVAC 1108 FORTRAN V COMPILATION. 0 *DIAGNOSTIC* MESSAGE(S)
TIME = 0 SEC.
TIME = 0 SEC.
TIME = 0 SEC.
TIME = 0 SEC.
TIME = 1 SEC.
TIME = 1 SEC.

*NMPILATION TIME = 2 SEC
SUBROUTINE FREQ(G,F,M1,NICAL,MR,M3,V,GAM12,W,FW,H,G1,V1,WT)
C THIS SUBROUTINE CALCULATES FREQUENCIES OF VIBRATION WHEN G AND F
C MATRICES ARE GIVEN.
C REFERENCE J.H. SCHACHTSCHNEIDER, SPECTROCHIM. ACTA, 19, 117, 1963
REAL NUMCAL
DIMENSION G(60,60), F(60,60), NICAL(60), V(60,60), GAM12(60,60), W(60,60),
1 H(60,60), G1(1830), V1(3660)
DOUBLE PRECISION G,F,V,GAM12,W,FW,H,G1,V1,DSORT
DOUBLE PRECISION WT(60,60)
CALL LINE(G,G1,M1)
CALL EIGEN(G1,V1,M1,0)
CALL RLINE(G,G1,V,V1,M1,MR)
PRINT 102,M1,(G(N,N),N=1,M1)
102 FORMAT(1H,14,G6(2X,D13.6)/*,(5X,6(2X,N13.6)))
DO 2 M = 1,M1
2 DO 2 N = 1,M1
IF(M - N)3,4,3
3 G0 TO 2
4 GAM12(M,N) =DSORT(DABS(G(M,N)))
3 GAM12(M,N) = 0.0
2 CONTINUE
C CALCULATE MATRIX W = V*GAM12
CALL MATM(V,GAM12,W,M1,M1,M1,MR,MR)
C CALCULATE F*W
CALL MATM(F,W,FW,M1,M1,M1,MR,MR)
C TRANSPOSE W = WT
CALL MATT(W,WT,M1,M1,MR)
C CALCULATE H = WT*FW
CALL MATM(WT,FW,H,M1,M1,M1,MR,MR)
C CALCULATE THE EIGENVALUES OF H  HC = C*LAMDA  C = EIGENVECTOR MAT.
LAMDA = EIGENVALUES
CALL LINE(H,G1,M1)
CALL EIGEN(G1,V1,M1,0)
CALL RLINE(H,G1,V,V1,M1,MR)
PRINT 102,M1,(H(N,N)-N=1,M1)
DO 5 M = 1,M1
NUCAL(M) = 1302.9*DSORT(DABS(H(M,M)))
IF(M3)7,5,7
7 PRINT 6,M,NUCAL(M)
5 CONTINUE
6 FORMAT(1H,5X,7.0,13,5X,'CALC. FREQ. (RM-1) = ',F10.3)
RETURN
END
END OF UNIVAC 1108 FORTRAN V COMPILATION. 0 *DIAGNOSTIC* MESSAGE(S)
TIME = 1 SEC.
TIME = 0 SEC.
TIME = 0 SEC.
TIME = 0 SEC.
TIME = 0 SEC.
TIME = 0 SEC.
COMPILATION TIME = 1 SEC
1* subroutine line(G,G1,M1)
2* C THIS SUBROUTINE PUTS THE DOUBLE DIMENSION UPPER TRIANGLE OF A
3* C SYMMETRIC MATRIX IN A LINEAR FORM COLUMNWISE.
4* dimension G(60,60),G1(1830)
5* double precision G,G1
6* K = 0
7* do 1 M = 1,M1
8* do 1 MM = 1,M
9* K = K + 1
10* 1 G1(K) = G(MM,M)
11* return
12* end

end of univac 1108 fortran v compilation. 0 *diagnostic* message(s)
time = 1 sec.
time = 0 sec.
time = 0 sec.
time = 0 sec.
time = 0 sec.
time = 0 sec.
compilation time = 1 sec
1108 FORTRAN V LEVEL 2206.0009 F600A
COMPILATION WAS DONE ON 29 AUG 68 AT 10:24:06

OUTLINE RELINE ENTRY POINT 000114

AGE USED (BLOCK, NAME, LENGTH)

0001  *CODE  000145
0000  *DATA  000022
0002  *BLANK  000000

APPENDIX 16.2.2 (cont.)

RNAI REFERENCES (BLOCK, NAME)

0003  NERR$3

AGE ASSIGNMENT FOR VARIABLES (BLOCK, TYPE, RELATIVE LOCATION, NAME)

1  000032 1L  0001  000012 106G  0001  000015 111G  0001  00005
  0000 000004 0J  0000 000002 0K  0000 000006 0L  0000 00000
  0000 000003 0M  0000 000005 0N

1*  SUBROUTINE RELINE(G6,G1,D, S,M1,MR)
2*  C THIS SUBROUTINE DOES THE FOLLOWINGS -
3*  C  1. SELECTS THE EIGENVALUES FORM A LINEAR FORM AND PUTS THEM INTO
4*  C  A DOUBLE DIMENSION FORM .
5*  C  2. TAKES THE EIGENVECTORS IN A LINEAR FORM AND TRANSFORMS THEM
6*  C  INTO A DOUBLE DIMENSION MATRIX .
7*  DIMENSION G6(60,60),G1(1830),D(1),S(1)
8*  DOUBLE PRECISION G6,G1,D,S
9*  DO 1 M = 1,M1
10*  DO 1 MM = 1,M1
11*  IF(M-MM)1,2,1
12*  2 K = M + (MM*MM-MM-MM)/2
13*  G(M,MM) = G1(K)
14*  1 CONTINUE
15*  NI = MR - M1
16*  IJ = M1*M1 + 1
17*  NM = MR*M1+1
18*  DO 110 K = 1,M1
19*  NM = NM - NI
20*  DO 110 L = 1,M1
21*  IJ = IJ - 1
22*  NM = NM - 1
23*  110 D(NM) = S(IJ)
24*  RETURN
25*  END

END OF UNIVAC 1108 FORTRAN V COMPIILATION.     0 *DIAGNOSTIC* MESSAGE(S)
TIME = 0 SEC.
**K POTEN**

1108 FORTRAN V LEVEL 2206 0009 F600A

Compilaton was done on 29 Aug 68 at 10:24:03

**ROUTINE POTEN ENTRY POINT 000247**

**RANGE USED (BLOCK*, NAME*, LENGTH)**

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<td>0000</td>
<td>DATA</td>
<td>000121</td>
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**APPENDIX 16.2.2 (cont.)**

**EXTERNAL REFERENCES (BLOCK*, NAME*)**

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<td>0004</td>
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<tr>
<td>0005</td>
<td>NIO25</td>
</tr>
<tr>
<td>0006</td>
<td>NIO15</td>
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<tr>
<td>0007</td>
<td>NERR35</td>
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**RANGE ASSIGNMENT FOR VARIABLES (BLOCK*, TYPE*, RELATIVE LOCATION*, NAME*)**

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<th>Relative Location</th>
<th>Name</th>
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<td>114G</td>
<td>0001 000051 121G</td>
<td>0001 000074 136G</td>
</tr>
<tr>
<td>0000</td>
<td>170G</td>
<td>0001 000147 173G</td>
<td>0000 000012 2F</td>
</tr>
<tr>
<td>0000</td>
<td>212G</td>
<td>0000 000052 24F</td>
<td>0000 000060 25F</td>
</tr>
<tr>
<td>0001</td>
<td>6F</td>
<td>0000 000030 7F</td>
<td>0000 000004 J</td>
</tr>
<tr>
<td>0001</td>
<td>M</td>
<td>0000 000001 N</td>
<td>0000 000003 SUM</td>
</tr>
</tbody>
</table>

1* SUBROUTINE POTEN(F*W*V*M1*MR*ALLF*AL*NUCAL*AA*II*JJ)
2* REAL NUCAL
3* DIMENSION F(60,60), W(60,60), V(60,60), AL(60,60), ALLF(60,60)
4* DIMENSION AA(3660), II(3660), JJ(3660), NUCAL(60)
5* DOUBLE PRECISION F*W*V*AL
7* PRINT 3
8* 3 FORMAT(1HO,10X,8HL MATRIX)
9* DO 1 M = 1*M1
10* 1 PRINT 2*M1(AL(M)*N=M1)
11* 2 FORMAT(1HO,13*6(2X,D12.5),(2X,D12.5))
12* PRINT 6
13* 6 FORMAT(1HO,29HPOTENTIAL ENERGY DISTRIBUTION)
14* PRINT 7
15* 7 FORMAT(1HO,22HRELATIVE CONTRIBUTIONS)
16* DO 16 K = 1*M1
17* PRINT 4
18* 4 FORMAT(1HO)
19* PRINT 21*K*NUCAL(K)
20* 21 FORMAT(1HO,16HFREQUENCY NO. = *I4,5X,14HWAVE NUMBER = *F6.1,1X,6H(1CH-1))
21* 22 PRINT 24
23* 24 FORMAT(2H0,6(18H M N CONTRIBUT. ))
24* SUM = 0.
25* DO 18 M = 1,M1
26* DO 18 N = 1,M1
27* ALLF(M,N) = AL(M,K)*AL(N,K)*F(M,N)
28* 18 SUM = SUM + ALLF(M,N)
29* J = 0
30* DO 20 M = 1,M1
31* DO 20 N = 1,M1
32* ALLF(M,N) = ALLF(M,N)/SUM
33* IF(ABS(ALLF(M,N)) = 0.01)20,22,22
34* 22 J = J + 1
35* AA(J) = ALLF(M,N)
36* II(J) = N
37* JJ(J) = M
38* 20 CONTINUE
39* PRINT 25, (JJ(L),II(L),AA(L),L=1,J)
40* 16 CONTINUE
41* 25 FORMAT(1H ,6(2I3,2X,F6.3,4X),/,(1X,6(2I3,2X,F6.3,4X)))
42* RETURN
43* END

END OF UNIVAC 1108 FORTRAN V COMPILATION. 0 *DIAGNOSTIC* MESSAGE(S)
1 TIME = 0 SEC.
2 TIME = 0 SEC.
3 TIME = 1 SEC.
4 TIME = 0 SEC.
5 TIME = 0 SEC.
6 TIME = 0 SEC.

COMPILATION TIME = 1 SEC
MATM
1108 FORTRAN V LEVEL 2206 0009 F600A
Compilation was done on 15 Aug 68 at 09:09:06

OUTLINE MATM ENTRY-POINT 000117

AGE USED (BLOCK, NAME, LENGTH)

| 0001 | *CODE | 000160 |
| 0000 | *DATA | 000037 |
| 0002 | *BLANK | 000000 |

APPENDIX 16.2.2 (cont.)

INAL REFERENCES (BLOCK, NAME)

| 0003 | NERR3S |

AGE ASSIGNMENT FOR VARIABLES (BLOCK, TYPE, RELATIVE LOCATION, NAME)

| 0000017 | 111G | 0001 | 000022 | 114G | 0001 | 000031 | 120G | 000000 |
| 0000006 | K | 0000 | 0000002 | L | 0000 | 0000003 | M | 0000 | 0000 |

1*

2*
SUBROUTINE TO MULTIPLY MATRIX A BY B

3*
USING A COLUMN ORIENTED POST-MULTIPLY METHOD

4*
PLACE THE RESULT IN C

5*
NO MATRIX MAY REPLACE OR OVERLAP ANY OTHER

6*
C

7*
C

8*
DIMENSION A(100,), B(100,), C(100)

9*
DOUBLE PRECISION A*B*C,T

10*
L = 1

11*
M = 1

12*
N = 1

13*
DO 21 I = 1, II

14*
DO 20 K = 1, KK

15*
T = 0.0D+00

16*
DO 10 J = 1, JJ

17*
T = T + A(M) * B(N)

18*
M = M + MM

19*
N = N + 1

20*
C(L) = T

21*
L = L + MM

22*
M = I

23*
N = (K * NN) + 1

24*
M = M + 1

25*
L = M

26*
N = 1

27*
RETURN

28*
END

1* C PURPOSE
2* C COMPUTE EIGENVALUES AND EIGENVECTORS OF A REAL SYMMETRIC MATRIX.
3* C A - ORIGINAL MATRIX DESTROYED IN COMPUTATION
4* C R - RESULTANT MATRIX OF EIGENVECTORS STORED COLUMNWISE.
5* C N - ORDER OF MATRICES A AND R
6* C MV - INPUT CODE - 0 COMPUTE EIGENVALUES AND EIGENVECTORS
7* C 1 COMPUTE EIGENVALUES ONLY
8* C METOD = DIAGNOLIZATION METHOD ORIGINATED BY JACOBI AND ADAPTED BY
9* C VON NEUMANN FOR LARGE COMPUTERS.
10* C REF. : MATHEMATICAL METHODS FOR DIGITAL COMPUTERS EDITED BY
11* C A. RALSTON AND H.S. WILF, JOHN WILEY AND SONS, NEW YORK.
12* C 1962, CHAPTER 7 (IBM SUBROUTINE).
13* C FOR A DOUBLE PRECISION VERSION OF THIS SUBROUTINE REMOVE THE
14* C C FROM THE FIRST COLUMN OF THE NEXT TWO LINES
15* C DOUBLE PRECISION A,R, ANORM, ANRX, THR, X, Y, SINX, SINX2, COSX,
16* C 1.0, COSX2, SINC, RANGE

APPENDIX 16.2.2 (cont.)
DOUBLE PRECISION A, R, ANORM, ANRMX, THR, X, Y, SINX, SINX2, COSX, 
1COSX2, SINC5, RANGE, DSQRT

ALL THE FORTRAN FUNCTIONS MUST BE CHANGED TO DOUBLE PRECISION

FORTRAN FUNCTIONS

SQRT IN STATEMENTS 40, 68, 75 AND 78 MUST BE CHANGED TO DSQRT
STATEMENT 62 MUST BE CHANGED TO DABS

CONSTANT RANGE IN STATEMENT 5 SHOULD BE CHANGED TO 1.0D-12

A(1), R(1)

GENERATE THE IDENTITY MATRIX

5 RANGE = 1.0D-12
IF(MV-1)10,25,10
10 IQ = N
DO 20 J = 1,N
20 IQ = IQ + N
DO 20 I = 1,N
IJ = IQ + I
R(IJ) = 0.0
IF(I = J)20,15,20
15 R(IJ) = 1.0
20 CONTINUE

COMPUTE INITIAL AND FINAL NORMS (ANORM AND ANRMX)
FN = N
25 ANORM = 0.0
DO 35 I = 1,N
30 IA = I + (J+J-J)/2
ANORM = ANORM + A(A)*A(A)
35 CONTINUE
IF(ANORM)165,165,40
ANORM = 1.414*DSQRT(ANORM)
ANRMX = ANORM*RANGE/FN

INITIALIZE INDICATORS AND COMPUTE THRESHOLD THR

IND = 0
THR = ANORM
THR = THR/FN
L = 1
M = L + 1

COMPUTE SIN AND COS

M = (M*M-M)/2
L0 = (L*L-L)/2
LM = L + MQ
62 IF(DABS(A(LM)) - THR)130,65,65
65 IND = 1
66 LL = L + L0
MM = M + MQ
67 X = 0.5*(A(LL) - A(MM))
68 Y = -A(LM)/DSQRT(A(LM)*A(LM) + X*X)
69 IF(X)70,75,75
70 Y = -Y
75 SINX = Y/DSQRT(2.0*(1.0 + (DSQRT(1.0 - Y*Y))))
76 SINX2 = SINX*SINX


76* 78 \text{COSX} = \text{DSORT}(1.0 - \text{SINX2})
77* \text{COSX2} = \text{COSX} \times \text{COSX}
78* \text{SINCS} = \text{SINX} \times \text{COSX}
79* C \text{ROTATE L AND M COLUMNS}
80* C
81* C
82* \text{ILQ} = N \times (L - 1)
83* \text{IMQ} = N \times (M - 1)
84* DO 125 \text{I} = 1 \text{~N}
85* \text{IQ} = (\text{I} \times \text{I} \times 0 - 2)
86* \text{IF} (\text{I} - \text{L}) \times 80 = 0, 115, 80
87* \text{IF} (\text{I} - \text{M}) \times 85, 115, 90
88* 85 \text{IM} = \text{I} + \text{MQ}
89* \text{GO} \text{TO} 0.95
90* 90 \text{IM} = \text{M} + \text{IQ}
91* 95 \text{IF} (\text{I} - \text{L}) \times 100, 105, 105
92* 100 \text{IL} = \text{I} + \text{LQ}
93* \text{GO} \text{TO} 110
94* 105 \text{IL} = \text{L} + \text{IQ}
95* 110 \text{X} = \text{A(IL)} \times \text{COSX} - \text{A(IM)} \times \text{SINX}
96* \text{A(IM)} = \text{A(IL)} \times \text{SINX} + \text{A(IM)} \times \text{COSX}
97* \text{AIL} = \text{X}
98* 115 \text{IF} (\text{MV} - 1) \times 120, 125, 120
99* 120 \text{ILR} = \text{ILQ} + \text{I}
100* \text{IMR} = \text{IMQ} + \text{I}
101* \text{X} = \text{R(ILR)} \times \text{COSX} - \text{R(IMR)} \times \text{SINX}
102* \text{R(IMR)} = \text{R(ILR)} \times \text{SINX} + \text{R(IMR)} \times \text{COSX}
103* \text{R(ILR)} = \text{X}
104* 125 \text{CONTINUE}
105* \text{X} = 2.0 \times \text{A(LM)} \times \text{SINCS}
106* \text{Y} = \text{A(LL)} \times \text{COSX} + \text{A(MM)} \times \text{SINX} + \text{X}
107* \text{X} = \text{A(LL)} \times \text{SINX} + \text{A(MM)} \times \text{COSX} + \text{X}
108* \text{A(LM)} = (\text{A(LL)} - \text{A(MM)}) \times \text{SINCS} + \text{A(LM)} \times (\text{COSX} - \text{SINX})
109* \text{A(LL)} = \text{Y}
110* \text{A(MM)} = \text{X}
111* C
112* C \text{TEST FOR COMPLETION}
113* C \text{TEST FOR M = LAST_COLUMN}
114* C
115* 130 \text{IF} (\text{M} = - \text{N}) \times 135, 140, 135
116* 135 \text{M} = \text{M} + 1
117* \text{GO} \text{TO} 60
118* C
119* C \text{TEST FOR L = SECOND_FROM_LAST_COLUMN}
120* C
121* 140 \text{IF} (\text{L} = -(\text{N}-1)) \times 145, 150, 145
122* 145 \text{L} = \text{L} + 1
123* \text{GO} \text{TO} 55
124* 150 \text{IF} (\text{IND} = 1) \times 150, 155, 160
125* 155 \text{IND} = 0
126* \text{GO} \text{TO} 50
127* C
128* C \text{COMPARE THRESHOLD WITH FINAL NORM}
129* C
130* 160 \text{IF} (\text{THR} - \text{ANRMX}) \times 165, 165, 45
131* C
132* C \text{SORT EIGENVALUES AND EIGENVECTORS
134*  165  IQ = -N
135*  166  DO 185 I = 1,N
136*  167       IQ = IQ + N
137*  168       LL = I + (I*I - I)/2
138*  169       JQ = N*(I - 2)
139*  170       DO 185 J = I,N
140*  171       JQ = JQ + N
141*  172       MM = J + (J*J - J)/2
142*  173       IF(A(LL) - A(MM))170,185,185
143*  174       170  X = A(LL)
144*  175       A(LL) = A(MM)
145*  176       A(MM) = X
146*  177       IF(MV - 1)175,185,175
147*  178       175  DO 180 K = 1,N
148*  179       ILR = IQ + K
149*  180       IMR = JQ + K
150*  181       X = R(ILR)
151*  182       R(ILR) = R(IMR)
152*  183       180  R(IMR) = X
153*  184       185_CONTINUE
154*  185       RETURN
155*  186       END

END_OF_UNIVAC_1108_FORTRAN_V_COMPILATION.  0 *DIAGNOSTIC* MESSAGE(S)
TIME = 1 SEC.
TIME = 0 SEC.
TIME = 0 SEC.
TIME = 1 SEC.
TIME = 1 SEC.

COMPILATION TIME = 3 SEC
OUTINE MATT ENTRY POINT 000062

AGE USED (BLOCK, NAME, LENGTH)

0001 *CODE 000110
0000 *DATA 000021
0002 *BLANK 000000

APPENDIX 16.2.2 (cont.)

RNAL REFERENCES (BLOCK, NAME)

0003 NEBR35

AGE ASSIGNMENT FOR VARIABLES (BLOCK, TYPE, RELATIVE LOCATION, NAME)

1 000013 110G 0001 000015 113G 0000 I 000002 I 0000 I 00000
0 I 000001 L

END OF UNIVAC 1108 FORTRAN V_COMPI LATION. 0 *DI AGNOSTIC* MESSAGE(S)
TIME = 0 SEC.
TIME = 0 SEC.
TIME = 0 SEC.
TIME = 0 SEC.
TIME = 0 SEC.
TIME = 0 SEC.

SUBROUTINE MATT (A, B, II, JJ, M)

Ref. : GE manual.

C SUBROUTINE TO TRANPOSE THE MATRIX A

DOUBLE PRECISION A, B

C PUT THE TRANPOSE MATRIX IN B

C B MUST NOT REPLACE OR OVERLAP A

C

DIMENSION A(100 ), B(100 )

K = 1

L = 1

DO 11 I = 1, JJ

DO 10 J = 1, II

B( L ) = A( K )

L = L + M

K = K + 1

L = I + 1

K = ( I * M ) + 1

RETURN

END

TIME = 0 SEC.
DIMENSION IALF(20), FROA1(54), FROAZ(54), FROB1(54), FROB2(54), 
 1UA1(54), U2(54), U61(53), UB2(54)

READ 1, ICNT

C MA1 IS THE NO. OF FREQUENCIES OF MOLECULE A1
C SIMILARLY FOR MA2, MB1, MB2

DO 2 ICNT1 = 1, ICNT
  READ 3, (IALF(N), N = 1, 20)
  PRINT 3, (IALF(N), N = 1, 20)
  FORMAT(20A4)

READ 1, MA1, MA2, MB1, MB2

C READ THE VIBRATIONAL FREQUENCIES OF THE 4 MOLECULES

PRINT 4

DO 6 N = 1, MA1
  6 READ 7, FROA1(N)

DO 8 N = 1, MA2
  8 READ 7, FROA2(N)

DO 9 N = 1, MB1
  9 READ 7, FROB1(N)

DO 10 N = 1, MB2
  10 READ 7, FROB2(N)

IF(N = MB1) 12, 12, 13

13 PRINT 14, N, FROA1(N), FROA2(N)

GOTO 11

12 PRINT 15, N, FROA1(N), FROB1(N), FROAZ(N), FROB2(N)

11 CONTINUE

14 FORMAT(1H,13,6X,2(F6,0,22X))

15 FORMAT(1H,13,6X,4(F6,0,8X))

C CALCULATE U - S
C REF: M. WOLFSBERG AND M. J. STERN, PURE APPL. CHEM., 8, 229, 1964

T = 288.15

DO 2 N = 1, 5
  2 T = T * 5.0

PRINT 34, I

34 FORMAT(1H0,13,6X,20X,14HTEMPERATURE = (F7,2)

FACT = 1.4385/T

DO 16 N = 1, MA1
  IF(N = MB1) 17, 17, 18
  17 UB1(N) = FACT*FROB1(N)
  UB2(N) = FACT*FROB2(N)

18 UA1(N) = FACT*FROA1(N)

16 UA2(N) = FACT*FROA2(N)

C CALCULATE VP_TERM

TERM = 4*HVP

PRINT 32

32 FORMAT(1H0,13,6X,1H0)

PRINT 24, TERM

24 FORMAT(1H0,13,6X,1HCALCULATION OF A4,7H TERM)
47  PROD = 1,
48  DO 19 N = 1,MA1
49  AUX = UA2(N)/UA1(N)
50  19 PROD = PROD*AUX
51  PRINT 20,MA1,PROD
52  20 FORMAT(1HO, 27HNO, OF VIBRATIONAL MODES = ,14,5X,10HPRODUCT = ,1X,
                   1E14,7)
53  PROD1 = 1,
54  DO 21 N = 1,MB1
55  AUX = UB2(N)/UB1(N)
56  21 PROD1 = PROD1*AUX
57  PRINT 20, MB1, PROD1
58  VP = PROD/PROD1
59  PRINT 22, VP
60  22 FORMAT(1HO, 10HPTERM = ,1X,E14,7)
       C CALCULATE EXP (HERE IS CALLED EXP) TERM
61  TERM = 4HEXP
62  PRINT 32
63  PRINT 24, TERM
64  PROD = 1,
65  DO 23 N = 1,MA1
66  AUX = (1,0 - EXP(-UA1(N)))/(1,0 - EXP(-UA2(N))
67  23 PROD = PROD*AUX
68  PRINT 20, MA1, PROD
69  PROD1 = 1,0
70  DO 25 N = 1,MB1
71  AUX = (1,0 - EXP(-UB1(N)))/(1,0 - EXP(-UB2(N))
72  25 PROD1 = PROD1*AUX
73  PRINT 20, MB1, PROD1
74  EXP = PROD/PROD1
75  PRINT 26, EXP
76  26 FORMAT(1HO, 11HEXPTERM = ,1X,E14,7)
       C CALCULATE ZPE TERM
77  TERM = 4HZPE
78  PRINT 32
79  PRINT 24, TERM
80  SUM = 0.
81  DO 27 N = 1,MA1
82  27 SUM = SUM + (UA1(N) - UA2(N))/2,0
83  PRINT 25, MA1, SUM
84  28 FORMAT(1HO, 27HNO, OF VIBRATIONAL MODES = ,14,5X,7HSUM = ,E14,7)
85  SUM1 = 0.
86  DO 29 N = 1,MB1
87  29 SUM1 = SUM1 + (UB1(N) - UB2(N))/2,0
88  PRINT 28, MB1, SUM1
89  ZPE = SUM/SUM1
90  PRINT 30, ZPE
91  30 FORMAT(1HO, 11HZPE TERM = ,1X, E14,7)
       C CALCULATE K1/K2 (OR KH/KD)
92  R = VP*ZPE
93  PRINT 32
94  PRINT 31, R, VP, EXP, ZPE
95  31 FORMAT(1HO, 23HTOTAL ISOTOPIC EFFECT = ,E14,7,2H, ,5X,20HITS COMPO
1ENTS ARE ,/,45X, 6HVP = ,E14,7,/,45X, 6HEXP = ,E14,7,/,45X, 6HZP
2E = [E14.7]
2 CONTINUE
STOP
END