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Conductimetric determination of reaction rates: the solvolysis of benzhydryl chloride

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A THESIS

CONDUCTIMETRIC DETERMINATION OF REACTION RATES -

THE SOLVOLYSIS OF BENZHYDRYL CHLORIDE

Sumbitted for the Degree of Doctor of Philosophy

of the University of Durham

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This thesis is dedicated to the memory of my father for his initial encouragement.

ACKNOWLEDGEMENT

MEMORANDUM

This thesis is original work, except where acknowledgement by reference, it has formed no part of any other published work, and has not been submitted for any other degree.

The computer programmes used in the calculation of most of the results were all written by Dr. G. Kohnstam.

ABSTRACT

The aim of the thesis was to produce accurate rate measurements, from which an accurate value of $\Delta Cp*$ at constant atmospheric pressure could be calculated and so obtain more information concerning the activation process for the S_n1 solvolysis of benzhydryl chloride. It was hoped that the data would be accurate enough to determine any possible temperature coefficient of $\Delta Cp*$.

The solvolysis of benzhydryl chloride can be followed accurately via the development of acidity, either by titrimetric analysis or conductance measurement of the reaction mixture. It was calculated assuming that conductance and concentration are linearly related, that conductance measurements were capable of producing rate coefficients with a fractional error better than 1×10^{-4}.

Whilst such an assumption has been used in the past, it was found not to be applicable in this case. It was therefore decided to computer fit the rate data using equation I, a relationship between conductance (L) and concentration (c):

$$c \;=\; AL + BL^{3/2} + C \qquad\qquad \text{I}$$

together with the rate equation, equation II:

$$\ln (P_\infty - P) = A - kT \qquad\qquad \text{II}$$

which when combined together yield equation III which was computer fitted:

$$y = \ln(1 - X) = A_1 T + A_2 - \ln \left(1 - A_3 \cdot \frac{X}{1 + X^{\frac{1}{2}}}\right) \qquad \text{III}$$

where $X = L/L_\infty$

$A_1 = -k$

A_2 involves all the Xo terms

$A_3 = A_3^1 /1 + A_3^1$

$A_3^1 = B/A. \ L_\infty^{\frac{1}{2}}$

The rate coefficients calculated from equation III had a fractional error in the range 0.001 to 0.0008, whilst being an order of magnitude better than any obtained in the past, were not as good as the 1×10^{-4} that had been expected. This in turn meant that the activation parameters, particularly ΔCp^*, had disappointing accuracies. One of the causes is without doubt the limited temperature range (now 25°, normally 50°), over which the rate coefficients were determined due to experimental difficulties. Also the introduction of the parameter B/A, is also partly responsible for the poor accuracy of the activation parameters. In the event, no conclusions as to the magnitude of d/dT (ΔCp^*) were possible.

It was also the aim of this thesis to study the same reaction under conditions of constant volume, since suggestions had been made that activation parameters at constant volume might be easier to interpret. However, even greater experimental difficulties were encountered, it was therefore decided to limit the study to obtain accurate rate data at constant atmospheric pressure.

CONTENTS

CHAPTER I

INTRODUCTION AND GENERAL DESCRIPTION OF SN1 AND SN2

REACTIONS

1.1   Nucleophilic Substitution Reactions

This thesis describes an accurate study of a solvolytic reaction of an organic halide, benzhydryl chloride, in 70% aqueous acetone.   Since the leaving group, the halogen, is attached to a saturated carbon atom, such reactions are termed nucleophilic substitution reactions, and designated S_n.[1]   A nucleophilic substitution reaction is a heterolytic reaction involving the following general scheme:- a group X called the leaving group, is displaced from the reaction centre by a nucleophilic reagent Y; there is a transfer of a pair of electrons from the reagent Y to the reaction centre, and from that to the leaving group X:-

$$Y: \; + \; R - X \; \longrightarrow \; Y - R \; + \; :X$$
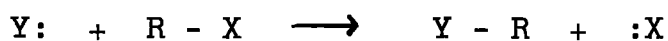
Given that this transfer of charges can be accommodated, the charged states of the reacting species need not be restricted, the above scheme is written generally.   Indeed, solvolytic reactions are not the only reactions occurring by an Sn mechanism.   Other reactions that occur by this same general reaction are the Finkelstein reaction, the Williamson ether synthesis, the Menschutkin reaction, the Hofmann degradation, the various 'Onium ion exchange reactions.

Although many reactions do occur by this mechanism, in many instances the solvent acts as the nucleophile and such reactions can be referred to as solvolysis reactions.   This type of reaction is, kinetically, the most deeply studied;

indeed, accurate activation parameters have in the main only been calculated for such reactions.

1.2   Mechanism of Nucleophilic Substitution

It has generally been accepted that nucleophilic substitution can occur via one of two general mechanisms.[2] This widely held view has recently been questioned[3] and further evidence shows that the original scheme could be an oversimplification.[56, 63]   It is however, convenient to consider the classical scheme first and to defer consideration of the modifications and alternative proposals until later (section 1.5).

1.2.1   The Bimolecular Mechanism (S_n2)

In the bimolecular mechanism both the substrate RX and the substituting group Y undergo simultaneous, although not necessarily identical covalency changes in both molecules. An example of this type of bimolecular substitution is furnished by the reaction of ethyl bromide with hydroxyl ions in ethanol[4]:

$$H\bar{O} + EtBr \rightleftharpoons \left[\overset{\delta-}{OH} \cdots C \cdots \overset{\delta-}{Br} \right] \rightleftharpoons EtOH + Br^-$$

Transition State
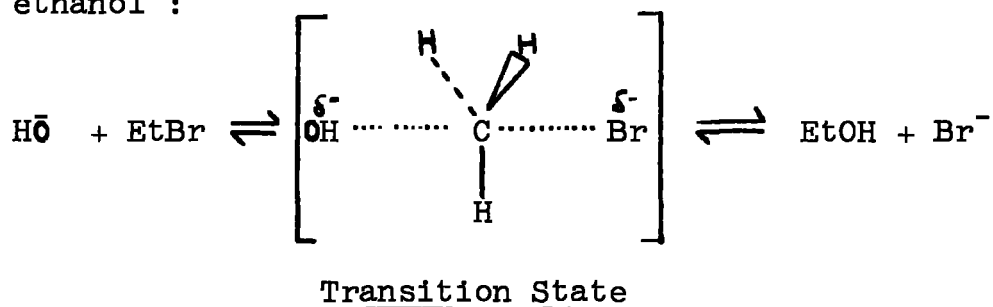
1.2.2   The Unimolecular Mechanism (S_n1)

In the second type of mechanism the products are formed by a two step process.   The scheme is shown below.

The rate determining step, process one, is the ionisation of the substrate RX, to give the carbonium ion R^+. The second step, is merely a reversal of the first. The carbonium ion, then in a third and fast step co-ordinates with the nucleophilic substituting agent Y, which could be a solvent molecule.

$$R - X \quad \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \quad R^+ + X^-$$

$$R^+ + X^- \quad \overset{Y}{\underset{k_3}{\longrightarrow}} \quad \text{Products}$$
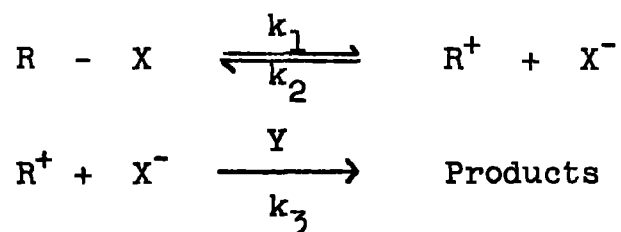
Under these circumstances only the substrate undergoes a covalency change in the rate determining step, and for this reason the reaction is termed unimolecular and is designated $S_n 1$.

The heterolytic cleavage of the carbon halogen bond in the $S_n 1$ mechanism is rate determining, since this process is normally endothermic. The large energy requirements of the rate determining step was one of the earliest arguments against such a mechanism and that the carbonium ion would be too unstable. It was argued, however, that the energy of the heterolysis could be compensated for by the energy of solvation of the ions produced, thus the interactions between the ionic species and the solvent were of primary importance. Tertiary butyl chloride has been shown to hydrolyse via this mechanism in aqueous acetone.[2b]

$$(CH_3)_3C\text{-}CL \rightleftharpoons \left[(CH_3)_3 \ \overset{\delta+}{C} \cdots \cdots Cl^{\delta-} \right] \rightleftharpoons (CH_3)_3 C^+ + Cl^- \quad \underline{\text{slow}}$$

<div align="center">Transition State</div>

$$(CH_3)_3 \ C^+ + H_2O \longrightarrow (CH_3)_3 \ C - OH + H^+ \qquad \underline{\text{fast}}$$
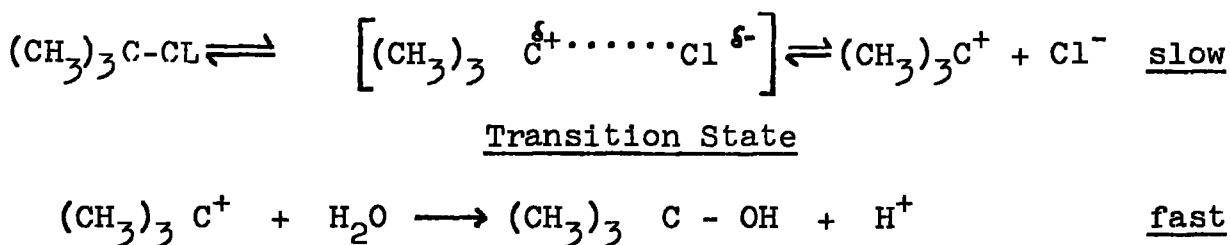
1.3   The Characterisation of Mechanism

1.3.1   Kinetic Form of the Mechanism

When both species, that is the substrate, RX, and the substituting agent, Y, are in small controllable concentrations, then the kinetic form of the reaction can be used to determine the reaction mechanism.

Thus an S_n2 reaction, under normal circumstances, unambiguously requires second order kinetics since there are two molecules involved in the rate determining step.

$$\text{Rate} \;=\; k_2 \left[RX \right] \left[Y \right]$$

However, when solvolytic reactions are considered, the substituting agent, Y, is in large and almost constant excess, under these circumstances the reaction reduces to first order.

The S_n1 reaction scheme is shown below:-

$$RX \; \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \; R^+ + X^- \qquad \underline{slow}$$

$$R^+ \; \underset{H_2O}{\overset{k_3}{\longrightarrow}} \; ROH + H^+ \qquad \underline{fast}$$
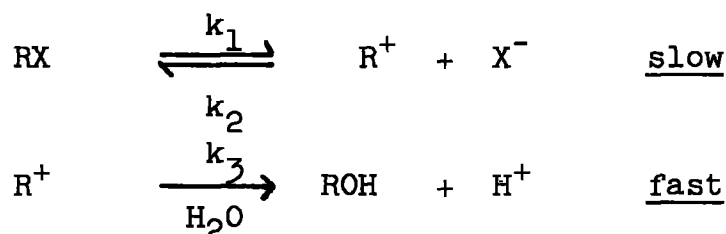
For this reeaction scheme, the rate of disappearance of the alkyl halide may be obtained by a steady state treatment of the very reactive carbonium ion[8]:-

$$-\frac{\partial}{\partial T} \cdot \left(RX \right) = k_1 \left(RX \right) \Big/ \left(\frac{k_2}{k_3} \left(X^- \right) + 1 \right)$$

If $k_2 \left(X \right) / k_3 \lll 1$ throughout the reaction then the equation predicts first order kinetics:-

$$-\frac{\partial}{\partial T} \cdot \left(RX \right) = k_1 \cdot \left(RX \right)$$

However, if the term k_2/k_3 is significant, then the magnitude of $k_2/k_3 \cdot \left(X^-\right)$ will increase as the reaction progresses. The effect will be that the instantaneous rate constant decreases as the reaction proceeds and deviations from first order kinetics will be observed in the presence of small amounts of added X^- ion. Such an effect is called the mass law effect[8], and k_2/k_3 is called the mass law constant and is normally denoted as α.

In addition ionic species are believed to stabilise the polar transition state more than the non-polar initial state so that added electrolytes accelerate the rate of reaction. This is the ionic strength effect[8] and does not necessarily occur with a common ion. Such an accelerating ionic strength effect could cancel a retarding mass law effect so that the net result will depend on the relative sizes of each. Thus, the S_n1 solvolysis could occur by a first order rate equation from which there will be deviations. The effect of the addition of electrolytes is discussed in more detail in section 1.3.2(v).

Irrespective of mechanism, then, the rate equation reduces to first order. The kinetic form of the mechanism, under these circumstances, cannot be used as an indication of the mechanism, and other methods must be used.

1.3.2 Other Criteria

Hughes[7] has reviewed the several methods which may be useful in the determination of the mechanism of a solvolytic reaction. It is important to note, however, that each has limited usefulness and it is essential that they be used together and not in isolation.

1.3.2(i)   Effect of the structural changes in R

In a nucleophilic reaction, the leaving group departs with a pair of electrons which were formerly bonded to the reaction centre R.   The resulting electron deficiency in R is then made up by co-ordination with Y, either con-currently - the S_n2 mechanism - or at a later stage giving the S_n1 mechanism.

If the nature of R is now varied such that there is an increase in electron release to the reaction centre there will be an increasing tendency to react via the S_n1 mechanism. However, the effect is ambiguous in the bimolecular mechanism since it simultaneously facilitates bond fission and inhibits bond formation.   Therefore, such changes in R will have less pronounced effects in S_n2 and, depending upon whether bond fission or bond formation predominates, the rate may be decreased or increased.   A negative charge on Y will accentuate the importance of the inhibition to bond formation.

Since methyl groups release electrons by the inductive effect and such electron release to the reaction centre facilitates the S_n1 mechanism, it follows that the following series should show increasing tendency to react by this mechanism:-

$$H - CH_2 - X \; , \; CH_3 - CH_2 - X \; , \; \begin{array}{c} CH_3 \\ | \\ CH - X \\ | \\ CH_3 \end{array} \; , \; \begin{array}{c} CH_3 \\ | \\ CH_3 - C - X \\ | \\ CH_3 \end{array}$$
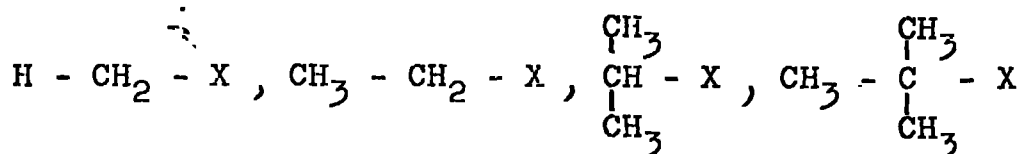
For this series (X = Br), the rates of reaction in aqueous ethanol are in the order Me > Et > i-Pr < t — Bu.   The rate sequence in the first three compounds may be due to polar

effects as already discussed, alternatively steric hindrance to the S_n2 attack may be responsible since electronic effects when the attacking reagent is neutral are likely to be small. However, since the overall effect is small both effects may be operative. Furthermore, added hydroxide ions accelerate the reaction of the first three compounds in the order

$$CH_3X \quad > \quad CH_3CH_2X \quad > \quad (CH_3)_2 CHX$$
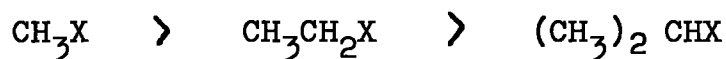
and have no effect on the solvolysis of t-butyl chloride.[9]

It would appear from these data that t-butyl chloride solvolyses by the S_n1 mechanism, even in the presence of added hydroxide ion, and that the other compounds react by S_n2 mechanism, their reactivity decreasing methyl, ethyl, and i-propyl. The bimolecular attack of hydroxide ions on i-propyl bromide does not rule out bimolecular solvolysis by water, a weaker nucleophile. On this basis the solvolysis of this compound could be in the mechanistic borderline, this is discussed further in section 1.4.

A similar transition of mechanism is found for the solvolysis of the α-phenyl substituted series, electron release is by a conjugative process:

$$
H - CH_2 - X \quad , \quad Ph - CH_2 - X \quad , \quad \underset{\underset{Ph}{|}}{\overset{\overset{Ph}{|}}{CH}} - X \quad , \quad Ph - \underset{\underset{Ph}{|}}{\overset{\overset{Ph}{|}}{C}} - X
$$

$$(I) \qquad\qquad (II) \qquad\qquad (III) \qquad\qquad (IV)$$
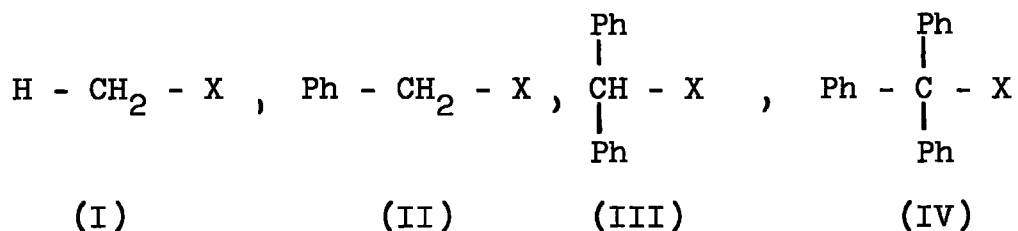
Since there is increasing electron release along this series, there is also increasing facility for reaction

by the S_n1 mechanism.   In this series it is believed
that compounds III and IV react by the unimolecular mechanism,
whilst compound I reacts bimolecularly.   Whilst the solvolysis
of benzyl   halide is not clearly defined and furnishes a
good example when the mechanistic criteria must be applied
with care, since ambiguous conclusions could be reached.[5,6,10,11]

However, from the available evidence and measurements of
the $\Delta Cp^*/\Delta S^*$ ratio (see section 1.3.2.(vi)) solvolysis in
both 50% aqueous ethanol and 50% aqueous acetone takes place
mainly if not entirely by the S_n2 mechanism.[12]

The variation of electron release to the reaction centre
can be studied without the added steric complications which
may result from substitution at or near the reaction centre,
by the introduction of polar substituents into the benzene
ring at a site relatively distant from the reaction centre.
These meta or para substituents alter the rate of reaction
by mesomeric and inductive effects.

The following series of para substituents -

NO_2 H   Me $p - Me C_6 H_4$ PhO $Me O$
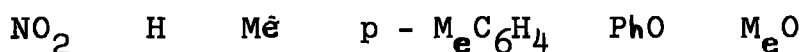
shows increasing tendency to electron release to the reaction
centre, and hence an increasing tendency for reaction by the
unimolecular mechanism.   It has been shown that the p-phenoxy[13]
and the p-methoxy substituents induce the S_n1 mechanism along
the p-substituted benzyl halides in aqueous acetone.   The
p-anisyl and the p-methyl derivatives are regarded as border-
line whilst the parent compound and p-nitro derivative appear
to undergo the bimolecular reaction.[14]

A consideration of the effect of such substitution on the

bimolecular process is ambiguous, since electron release
to the reaction centre inhibits bond formation whilst at
the same time promotes bond fission.   The ease of bond
formation becomes especially important when the attacking
reagent carries a negative charge.   When the attacking
reagent, Y, carries no formal charge, the effect of such
a substitution would depend mainly on the ease of fission
of the C - X bond.   As a result one would expect an increase
in the reaction rate, as in the $S_n 1$ process, but to a smaller
extent since the influence of bond formation is in the
opposite direction and not entirely negligible, see Table 1.1.

TABLE 1.

Substituent effect of k_x/k_H for p — X-benzyl chloride and
p — X — benzhydryl chloride for solvolysis in aqueous
acetone

	X = NO_2	H	Me	Mechanism
p - X - $C_6H_4CH_2Cl$[a]	9.16×10^{-2}	1	8.13	$S_n 2$
p - X - $C_6H_4CH_2Ph$[b]	1.25×10^{-4}	1	21.2	$S_n 1$

a) at 50° in 50% aqueous acetone [14]

b) at 25° in 70% aqueous acetone [15]

When Y carries a negative charge, the effect of polar
substituents on the bond forming process is now important.
This is shown in the bimolecular reaction of radio bromide ions
with p-substituted benzyl bromides in ethylene diacetate[15] and
in the Finkelstein reaction of benzyl chloride[16], see Table 1.2.

TABLE 1.2

Substituent effect, k_x k_H for p - X - benzyl halides
for solvolysis in ethylene diacetate[15] and acetone[16]

Solvent	X = NO_2	CN	Cl	H	Me	t-Bu	OMe
Ethylene diacetate	11.2	10.0	-	1	-	-	6.2
Acetone	6.19	-	2.12	1	1.17	1.35	-

It is noteworthy that the rate coefficients have a minimum value for the parent compound. Electron attracting substituents increase the rate coefficient since they facilitate the approach of the negatively charged substituting agent, Y; whilst the electron releasing groups facilitate the fission of the R - X bond.

Unless used with care, this criterion of mechanism is capable of giving ambiguous results. For example, the rate of solvolysis of methyl, ethyl and i-propyl bromides decrease[17] along the series $Me > Et > i-Pr$ even though there is increasing electron release. An alternative explanation could be steric retardation caused by increasing hindrance to the bimolecular attack.[18] In the case of the neo - pentyl halides[19] congestion in the bimolecular transition state is so great that it inhibits reaction by the S_n2 process, and the observed rate of reaction arises from decomposition by the S_n1 mechanism.

1.3.2(ii)   Effect of Substituting Reagent Y

In an S_n1 reaction the rate determining step - the ionisation of the R - X bond - is independent of the nucleophilic power of Y. If the nucleophile is an ionic species there may be a small medium effect.

On the other hand the bimolecular process requires that the nucleophile is incorporated in the rate determining step. On this basis if an added nucleophile is stronger than the solvent, then the rate should be substantially increased. A further consequence is that for a series of

reactions in which the only variable is the nucleophile, the rate of the S_n2 process will decrease as the nucleophilic strength of the attacking group decreases. It may even be reduced to such an extent that it will be slower than the rate for the ionisation step. The mechanism will now be unimolecular and independent of the nucleophilic strength. For example, the decomposition of trimethyl sulphonium salts in ethanol[2] by the following series of nucleophilic reagents

$$OH^- \; \rangle \; OPh^- \; \rangle \; CO_3^{2-} \rightleftharpoons Br^- \rightleftharpoons Cl^-$$
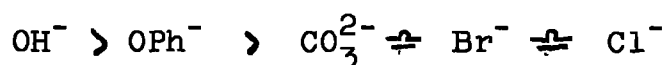
the relatively rapid second order reactions with hydroxide and phenoxide ions were interpreted as involving the S_n2 mechanism. The last three carbonate, bromide and chloride lead to first order kinetics having the same rate coefficient. This could be explained as a unimolecular reaction or a bimolecular reaction with the solvent ethanol.[20]

From these findings, the effect of an added nucleophile may provide a useful test of mechanism. If on the addition of a strong nucleophile the rate is not changed, then the original reaction occurred by the unimolecular mechanism.[21] For example benzhydryl chloride is sterically hindered to bimolecular attack because of the bulky phenyl groups; it has a rate of hydrolysis in aqueous ethanol practically unaffected by added hydroxide ion.[22,23,24] It is not possible to apply the converse of this, since the addition of a powerful nucleophile to a reaction occurring unimolecularly with the solvent, may change the rate coefficient by providing an energetically more favourable reaction path, facilitating reaction by mechanism S_n2. For example chloro

dimethyl ether solvolyses by the unimolecular process in ethanolic solvents, but reacts predominantly by an S_n2 process in the presence of ethoxide ion.[25]

1.3.2(iii)   The Effect of Solvent Changes

Only a simple qualitative treatment of the effect of solvent changes is attempted at this stage.   A more detailed discussion is found in sections 2.3.1 and 2.3.2.

The charges developed on passing to the transition state of an S_n reaction are stabilised by solvent solvation, and a change of solvent will tend to increase or decrease the rate of reaction, depending on whether the transitiion state is more or less polar than the initial state and whether the solvent is more or less polar.   There will be an opposing effect due to changes in the entropy of activation, but this may generally be assumed to be dominated by the change in the enthalpy of activation.[1,15]

Three assumptions must be made regarding the amount of solvation expected in the presence of charged species

i)   solvation will increase with the magnitude of the charge

ii)   if there is an increasing dispersal of a givencharge, the solvation will be less

iii)   the decrease of solvation due to dispersal of a charge will be less than that due to charge destruction

Consideration of the four possible charge types and the charge distribution in the initial state and the transition state, lead to the following predictions for changing to a solvent of increased polarity.   These are shown in Table 1.3.

TABLE 1.3

The predicted effect of solvent changes on rate

coefficients of S_n reactions

a) S_n2 reactions

Charge Type	Charge Disposition		Charge effect in going I.S. $\longrightarrow$ T.S.	Predicted effect of increased solvent polarity
1	$Y^- + RX$	$Y^{\delta-} \cdots R \cdots X^{\delta-}$	dispersed	small decrease
2	$Y + RX$	$Y^{\delta+} \cdots R \cdots X^{\delta-}$	increased	large increase
3	$Y^- + RX^+$	$Y^{\delta-} \cdots R \cdots X^{\delta+}$	dispersed	large decrease
4	$Y + RX^+$	$Y^{\delta+} \cdots R \cdots X^{\delta-}$	dispersed	small decrease

b) S_n1 reactions

1	2	RX	$R^{\delta+} X^{\delta-}$	increased	large increase
3	4	RX^+	$R^{\delta+} X^{\delta-}$	dispersed	small decrease

There is much evidence to show that these predictions are, to a first aproximation, correct.[26,27]   It is possible that a change of solvent may also change the mechanism of the reaction in question, and for example the reaction mechanism may change from S_n2 to S_n1 in changing to a more strongly ionising solvent.

1.3.2(iv)   The Stereochemical course of the substitution[28]

For a bimolecular reaction it can be shown that the arrangement of the transition state which has the minimum energy occurs when the attacking group Y, approaches along the C - X axis, thus:
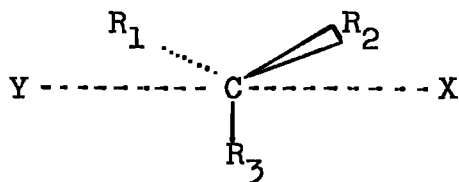
where R_1, R_2 and R_3 occupy a plane perpendicular to the Y - C - X plane. Substitution via this symmetrical transition state will lead to optical inversion at the central carbon atom. On the other hand if substitution occurs via the unimolecular mechanism, racemic products should be produced, unless there are additional asymmetric carbon atoms not at the reaction site. Under these conditions, a planar carbonium ion is formed when there is, theoretically, an equal probability of frontside and backside attack by the attacking reagent, leading to racemic products. It has been observed that partial inversion does occur in some cases. As a result of this Hughes and Ingold postulated shielding by the leaving group, since they found that the longer the life of the carbonium ion, and the greater its separation from its shielding group, the greater the degree of racemisation.

However, net retention of configuration, accompanied by a variable amount of racemisation may be observed and this has been attributed to the protection of the reaction centre by a mainly weak electrostatic bond arising from another group within the molecule. This is a type of neighbouring group participation. Such examples have been reported in the literature.[29]

The stereochemistry of nucleophilic substitution has been discussed in greater depth by Bunton.[30]

1.3.2(v)   The Effect of salt additions

In the case of neutral reactants the transition state for both S_n1 and S_n2 reactions are more polar than the

initial states

$$S_n1 \qquad RX \rightleftharpoons R^{\delta+}\cdots\cdots\cdots X^{\delta-} \qquad T.S.$$

$$S_n2 \qquad Y: \;+\; RX \rightleftharpoons Y^{\delta+}\cdots R\cdots X^{\delta-} \qquad T.S.$$
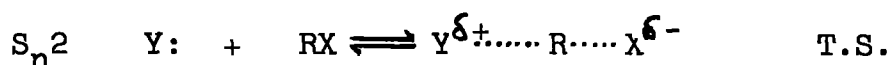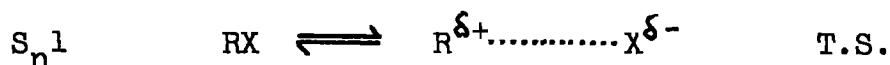
The addition of an inert electrolyte should therefore
increase the stability of the transitiion state by analogy
with ion atmosphere stabilisation of fully developed ions.
This stabilising effect causing an increase in the rate of
the reaction is called the "ionic strength effect".[18]
Since there is greater charge development in the transition
state of an S_n1 reaction compared with the S_n2 reaction,
the addition of an inert salt should give rise to greater
increase in the rate in S_n1 reactions than S_n2 reactions.

In addition to this effect, if the added electrolyte
contains the common ion, X^-, a reversal of the ionisation of
the organic chloride RX can occur, when S_n1 hydrolysis is
retarded. This is the "mass law effect" and obviously
cannot operate in S_n2 reactions.[8]

During unimolecular hydrolysis of an organic halide,
both the common ion and the mass law effect will operate
even without added electrolyte and common ion salts, since
halide ions are formed during the reaction. The two effects
act in opposite directions and the overall result will
depend on the relative sizes of each. For example the
solvolysis of benzhydryl chloride in aqueous acetone gives
good first order kinetics,[31] whereas the corresponding
reaction of t-butyl chloride is accelerated as the reaction

proceeds,[32] whilst that of dichlorodiphenyl methane is progressively retarded.[33]

Recent work[35,36] has shown that the actual behaviour of some electrolytes in mixed organic solvents is more complex than outlined above.   In addition to causing common ion and mass law effects some electrolytes are capable of causing a salt induced medium effect which can be regarded as a change in the effective composition of the solvent caused by specific solvation of the salt by the more polar component of the solvent.   Thus the salt may tend to "dry" the solvent by attracting water molecules into a tightly held solvation shell.   It has also been shown[35,36] that electrolytes have appreciable and different effects on both the initial and transition states (in both the electrostatic and the salt induced medium effects) and it is the combination of these effects which is observed. It is therefore evident that a consideration in terms of transition state effects only could therefore be misleading.

1.3.2(vi)   The Ratio $\Delta Cp^*/\Delta S^*$

This ratio for a given solvent and temperature is independent of the nature of the substrate if the S_n1 mechanism is operating.   This has been demonstrated[36,37] for a variety of substrates showing widely differing entropies of activation.   Under the same conditions a much smaller value for the S_n2 mechanism has been observed.[36] This subject is discussed in more detail in Chapter 2.

1.4 The Mechanistic Change from S_n1 to S_n2 - The Borderline Region

Since this thesis is concerned solely with S_n1 reactions only a brief outline of the problem is given below.

1.4.1 The Borderline Region - General Considerations

A great deal of attention has been paid in the previous sections to compounds which react uniquely either by the S_n1 or the S_n2 mechanism. There is however no sharp break between the two mechanistic processes. If, for example, a compound RX undergoes bimolecular solvolysis and the group R is altered so that there is increased electron release to the reaction and increased steric hindrance to bimolecular nucleophilic attack then RX will eventually react via the S_n1 mechanism. The borderline region is that region in which the mechanism is neither S_n1 or S_n2 and has been subject to much controversy and speculation. The details of the activation process in the borderline region have often been discussed and two different views have emerged.[1,30,45]

Firstly some workers consider that all the individual acts of substitution occur via identical transition states and these require a substantial contribution from the valence bond structure I, and a small but definite contribution from structure II:

$$HS \quad R^+ \quad X^- \qquad\qquad HS \overset{+}{-\!\!\!-} R \quad X^-$$

$$I \qquad\qquad\qquad\qquad II$$
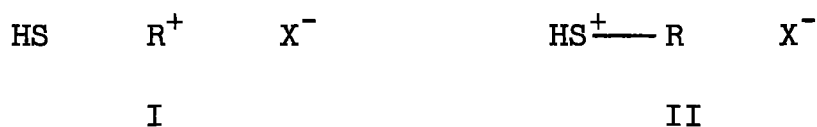
Since the structure I has the greatest contribution this

type of reaction should show many of the features
associated with an S_n1 reaction.   Although showing
unimolecular characteristics, the reaction must still
be regarded as bimolecular as long as II contributes to
the transition state, since solvent participation is an
essential feature of the S_n2 rate determining step.

Secondly, a variety of paths may be available to the
reaction system, some requiring a contribution from II
whilst others do not.   There is in effect a concurrent
operation of S_n1 and S_n2 mechansisms.

It is this question of determining whether a single or
concurrent single mechanisms best describe such reactions
in the borderline region that has aroused considerable
interest.

Winstein, Grunwald and Jones[38] studied solvent effects
on a number of solvolytic reactions thought to proceed by
the S_n1 mechanism.   They proposed[38] a free energy relation-
ship of the form

$$\log k = \log k_0 + mY$$

k_0 is the rate of solvolysis of the particular compound in
the standard solvent, 80% ethanol; k is the rate of solvolysis
of the same compound in a given solvent.   Y is a measure
of the ionising power of the solvent, m is the slope of the
plot of log k versus Y, and may be interpreted as the
susceptibility of the given compound to the ionising power
of the solvent used, relative to t-butyl chloride.   The
m values for the solvolysis of alkyl halides were found to
be lower than those found for unimolecular reactions.

This type of correlation has severe limitations[39-41] and any conclusions based on such a correlation must be made with care.[40]

An alternative explanation of the borderline region[41-44] takes the view that one mechanistic pathway is sufficient for all solvolytic reactions. The gradual variations that occur in behaviour can be accounted for by the variations in nucleophilic and electrophilic participation in the transition state. This view in effect denies the existence of the borderline region and similar conclusions have been reached from gradual variations in the values of the Hammett reaction constant, ρ, for a wide range of solvolytic reactions.[43] Gold[45] pointed out that the variation in the ρ values would be expected if on approaching the borderline region S_n2 reactions gradually become more S_n1 like from a substituent point of view, since bond breaking becomes progressively more important in the transition state.

Kohnstam, Queen and Shilaker[47] showed that in the presence of azide ions, the rate of hydrolysis of p-methoxybenzyl chloride was reduced whilst there was an increase in the rate of the ionisation of the latter compound. This increase in the rate of ionisation was always less than the total rate of disappearance of the substrate. From this data it appears that p-methoxybenzyl azide is formed via both S_n1 and S_n2 pathways. It has been further shown that although p-methoxy and p-phenoxybenzyl chlorides were bimolecularly attacked by nucleophiles in 70% acetone, some ionisation of the C-Cl bond takes place

before nucleophilic attack.[51c]   For the weakest

nucleophiles, nitrate and benzensulphonate ions the

transition state for ionisation has almost been reached

before covalent interaction begins.

The work of Fava and co-workers[48,49] provides further

evidence for the concurrent mechanism, since they reached

similar conclusions by studying the exchange rates of

substituted benzhydryl thiocyanates (with thiocyanate ions)

and substituted triphenyl methyl chlorides (with chloride ions)

in polar solvents.

In conclusion, the available evidence[47,50,51] seems to

support the operation of the concurrent mechanism in the

borderline region for reactions involving non-solvolytic

nucleophiles.   But for solvolytic reactions persuasive

evidence in favour of either view has not yet been published.

In view of the increasing accuracy with which kinetic studies

of solvolytic reactions are being made the question of the

mechanisms in the borderline region may well be resolved.

1.4.2   Recognition of the Mechanism in the Borderline Region - The use of ΔC_p^* in this Region

The use of the criteria discussed in section 1.3 is

limited in the borderline region, since it is here that

reactions will show the general characteristics of both

mechanisms.   It is under these conditions that the value of

the ratio $\Delta C_p^* / \Delta S^*$ may be extremely useful.   It has been

shown[51] that this ratio has separate values for S_n1 and S_n2

reactions.   Details of the behaviour of this ratio in the

mechanistic borderline region are given in Chapter 2 where

it is shown that if even in the borderline region they all go through the same type of transition state it would be expected that there would be a smooth variation of the ratio from its S_n1 value to the S_n2 value, provided of course the structure of the transition state does not alter as the temperature is changed. Any such change in the transition state structure would be expected to be in the direction of a transition state involving less covalent participation by the nucleophile (showing S_n1 characteristics) as the temperature is raised and in turn would require a positive contribution to ΔC_p^* (and hence a reduction in the value of $\Delta C_p^*/\Delta S^*$) since the enthalpy of the transition state tends to increase abnormally with increasing temperature (the greater the S_n1 character of the reaction the greater the enthalpy). As a result $\Delta C_p^*/\Delta S^*$ relatively close to zero would be observed.

However such an observation is also to be expected for the concurrent mechanism since the processes would have different activation energies and would lead to a positive contribution to ΔC_p^*.

1.5   Ion-Pair Intermediates ·

1.5.1   Ion-pair Intermediates in Solvolysis

Whilst the presence of ion pairs in systems involving equilibria between a neutral substrate and its free ions has been known for sometime, the intervention and ionisation of intermediate ion pairs has been postulated increasingly in the last few years.[3]   The situation is complicated further

since the definition of an ion pair is rather obscure and
can be defined in various ways. For example, Bjerrum,[52]
suggested that two ions could be regarded as an ion pair
if they are close enough together to ensure that electro-
static energy is greater than their mean thermal energies.
The distances involved in such an ion pair would be about
3.5Å in water, but over 100Å in a non polar solvent such
as benzene.[53] Another definition of an ion pair by Fuoss[54]
requires that the ionic constituents be in intimate contact.
Evidence for this type of intermediate in the ionisation of
organic substrates, the subject of the present thesis, whether
they are of the former or latter type comes from the consider-
ations shown below.

The ionisation step of a unimolecular reaction leads to
a planar carbonium ion, which is energetically the most
stable configuration. It should therefore follow that
optically active substrates give rise to racemic products
when they undergo unimolecular solvolysis. It has been
found necessary, however, to postulate[55] some sort of
shielding of the carbonium ion by the departing group, to
account for the partial inversion that has been observed
in, for example, the S_n1 solvolysis of α-phenylethyl chloride.
Contrary to this, Winstein[56] suggested that if ionisation
were complete enough for the reaction to be called unimolecular,
the planar carbonium ion would be free from shielding effects,
so that a completely racemic product would be formed. It
was further suggested by Hammett[57] that an explanation of
this sort of behaviour may lie in the formation of an ion
pair prior to complete ionisation. The reaction of this

type of intermediate with the solvent, would lead to inversion of the original configuration. Hence the relative rates at which this ion pair and the carbonium ion react would determine the extent of inversion. In addition it has been considered possible that an intermediate ion pair may return to the initial state either with retention or inversion of the original configuration.

In discussing this possibility, the following scheme is of use to define each coefficient:-

$$RX \quad \xrightarrow{\frac{kt}{HS}} \quad RS \quad + \quad HX$$

$$(+) \quad -RX \quad \xrightarrow{\frac{k\alpha}{HS}} \quad \partial l - RX \quad + \quad \partial l - RS$$

$$(+) \quad -RX \quad \xrightarrow{krac} \quad dl - RX$$
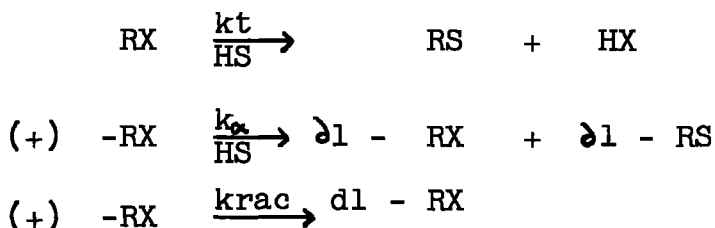
The rate of solvolysis is given by the rate constant k_t, whether measured by titration, conductance or any other method. The observed loss of optical activity is described by the polarimetric rate constant k_α. The difference between the rate constants k_t and k_α gives the rate constant for racemisation of the substrate during the solvolysis. For some optically active compounds it has been found that the rate of racemisation in acetic acid occurs more rapidly than solvolysis, suggesting that inversion may occur by ion pair return as well as by solvolysis.

It was found that for reactants producing long lived carbonium ions, a two fold increase in the rate of acetolysis was induced by the addition of lithium perchlorate:

1) an initial steep rise in the first order titrimetric rate coefficient for small concentrations of salt, called "the special salt effect".

ii) a subsequent increase which was almost linear
with concentration, the normal salt effect.

Bearing these factors in mind, Winstein[56] proposed that
for S_n1 solvolyses of certain substrates in media of low
dielectric constant, the normal ionisation of a neutral
molecule RX is complicated by the intervention of ion pairs
and occurs essentially in three stages.

$$RX \rightleftharpoons \left[R^+ \ X^-\right] \rightleftharpoons R^+ /\!/ X^- \rightleftharpoons R^+ + X^-$$

I   II   III
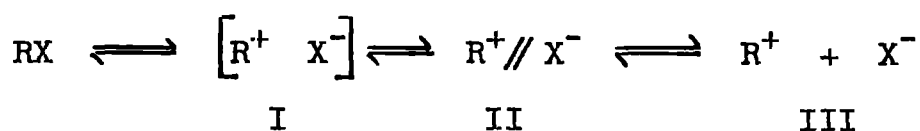
Structure I is called an intimate or internal ion pair and
both ions are surrounded by a common solvation shell.   It
can return to the initial stage by internal return.
Structure II is an external solvent separated ion pair which
can return to structure I or form the fully developed ·
carbonium ion, structure III.   Both ion pairs are capable
of reacting with nucleophilic species but the internal form
(I) is much less reactive.[58]

The special salt effect was attributed[59] to the suppression
of the return from an intermediate ion pair, that is capture
of the ion pair by the added salt.   This compound immediately
reacts with acetic acid to form the products.   Hence external
return is inhibited and a higher rate of acetolysis is
observed.· The presence of the internal ion pair was
deduced from the fact that the special salt effect only
partially closed the gap between the polarimetric rate
constant and the titrimetric rate coefficient.   It has
also been shown[60] that the racemisation of p-chlorobenzhydryl
chloride proceeds more rapidly than exchange with labelled

chlorine and more rapidly than hydrolysis in 80% acetone. Similar results have been reported[61] for the reactions of unsymmetrically deuterated benzhydryl chlorides in 70% acetone. The results are consistent with internal return since benzhydryl chloride reacts by the S_n1 mechanism.[62]

Two ion pairs were therefore necessary to explain the observations.[63] Both the internal and external ion pairs were capable of returning to the covalent substrate with racemisation. Only the external ion pair was capable of reacting with lithium perchlorate causing the special salt effect. This however has been questioned by Hughes and Ingold,[64] who suggested that in the region of the special salt effect, the acceleration was approximately proportional to the salt concentration to the power of one half, thereby representing that the free ions present at low concentrations are in equilibrium with ion pairs of the salt. At higher concentrations, the acceleration could be attributed to the ion pairs of the salt. This is consistent with a poor ionising medium such as acetic acid.

The reaction of ion pairs with nucleophiles in aqueous and organic solvent systems has not yet been unambiguously demonstrated. Indeed it has been concluded from studies of the effects of mixed chlorides and bromides on the rate of hydrolysis of dichloro diphenylmethane in aqueous acetone,[65] that the results of these experiments only require that the free carbonium ion reacts with water and anions in such a solvent. Further data, on the other hand has come from Winstein and Appel[66] from their study of the rates of hydrolysis, azide formation and O^{18} equilibration for triphenylmethyl benzoate in acetone containing small

amounts of water. They[66] concluded that the proportion of reaction occurring via the free carbonium ion increases with increasing water content of the solvent.

Goering and his co-workers[67] also studied the rate of oxygen equilibration, k_{eq} (see below), using discretely labelled esters of 4- nitrobenzoic acid. The rate of equilibration was that which occurred under solvolytic conditions of the unsolvolysed ester:

$$ R - O^{18} \diagdown \!\!\! \underset{O}{\overset{}{C}} - Ar \qquad \xrightarrow{\ k_{eq}\ } \qquad R - O^{18} \diagdown \!\!\! \underset{^{18}O}{\overset{}{C}} - Ar $$
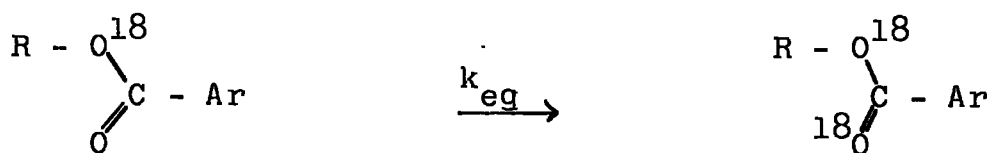
<div align="right">Label Randomised</div>

The rate of equilibration, k_{eq}, provided an independent measure of ion pair return, since k_{rac} could be simultaneously determined if the substrate was optically active. For the solvolysis of trans-5-methyl-2-cyclo-hexenyl-4'-nitrobenzoate, the ratio $k_{eq}/k_{rac} \simeq 2$ was observed in 80% acetone.[67b] These results have been explained by invoking return from two intermediate ion pairs. Only the external ion pair returns with racemisation and equilibration. The excess equilibration $(k_{eq} > k_{rac})$ is also explained as return from an internal ion pair whilst retaining its configuration. The external ion pair also has equivalent oxygen atoms and also returns with oxygen equilibration.

Data relating to 4 substituted benzhydryl-4'- nitrobenzoates (substituents Cl, H, Me, MeO) in 90% acetone are worthy of mention.[68]

Whilst the solvolysis rates vary over the range in excess

of 2,500,. the ratios k_{eq}/k_t and k_{eq}/k_{rac} have the same
order of magnitude. Goering[68] argued that similar
variations in rates of solvolysis, racemisation and
equilibration with substrate and solvent changes implied
that these processes share a common rate controlling step
for unimolecular solvolysis. Thus the ionisation step
for S_n1 solvolysis has been interpreted in terms of two
ion pairs, prior to the formation of the carbonium ion R^+
for many systems.[69]

However Ingold argues differently.[1] Thus these results
can equally well be explained by the fact that at all
degrees of separation after the free energy maximum has
been passed, there is a probability that the counter ions
will recombine. Thus as the distance increases the
probability of R^+ reacting with the solvent increases,
whilst the still finite probability of return decreases.
Similar explanations are possible for racemisation and
equilibration.

This type of interpretation is contrary to the require-
ments of the Transition State Theory[70] which considers that
a chemical reaction occurs when a particular vibrational mode
of the activated complex becomes translational motion. The
activated complex, at the saddle point of the potential energy
curve, is then required to react once this translational
freedom is achieved. However, it may be that intramolecular
processes such as these are beyond the scope of the Transition
State Theory, with its inherent assumptions of the activated
complex, and the stereochemical course of a unimolecular

substitution must still be regarded as being unsettled.[71]

Ion pair intermediates in S_n1 solvolyses may explain the observed racemisation and oxygen equilibration during solvolysis, but it would appear that for solvolysis in aqueous organic solvents ther e is nothing to suggest that they are capable of being captured by external reagents. However, in poor ionising : solvents such as acetic acid, where ion pairs may be more stable relative to a fully developed carbonium ion R^+; such capture of ion pairs might explain the special salt effect.

It has been suggested[3, 67c] that ion pairs are generally capable of capture by external reagents in aqueous organic solvents. Goering and co-workers[67c, 68] cited experiments, mentioned earlier, using O^{18} labelled substrates, which were evidence of ion pair· return from the two types of ion pair. The effect of adding the strong nucleophile, azide ion, was also investigated, and provided the striking result that the seven-fold acceleration of the decomposition of the 4-chloro compound on the addit·on of azide ion was accompanied by the complete suppression of the racemisation of the substrate, observed in the absence of azide ion. There was little or· no change in the rate of equilibration. These results were interpreted[67c] in terms of two ion pairs in the ionisation process. The first ion pair formed is capable of return with equilibration. The second ion pair is capable of return with racemisation. It was suggested that the latter had been captured by the azide ion, thus suppressing racemisation. However it is possible that attack on the benzhydryl compound by the azide ion may well take place by the S_n2 mechanism and,

investigations made at this laboratory[73] are consistent

with the hypothesis of S_n2 attack by azide ions on the

deactivated 4-nitrobenzhydryl chloride.   Although the

studies of Goering were not on such deactivated substrates,

the use of a relatively "poor" leaving group and the poorly

ionising solvent (90% acetone) would tend to favour S_n2

attack.

1.5.2   The Ion Pair Mechanism

From the above discussion it would appear that ion pairs,

under certain conditions, can intervene in S_n1 processes and

authors proposing this view have mainly accepted that bimol-

ecular reactions occur via the one step mechanism originally

proposed by Hughes and Ingold.[1,2b]   However Sneen and Larsen[3]

have recently suggested that all nucleophilic substitutions

proceed via intermediate ion pairs, also called the unified

mechanism.

Results from selected nucleophilic substitutions of

2-octyl sulphonates in 25% and 30% dioxan have been explained[3]

by suggesting that an intermediate ion pair is involved in

the reaction and nothing else.   Furthermore these workers[3]

have postulated that this single mechanism is operative over

the entire range of nucleophilic substitution reactions,

and the mechanism becomes indistinguishable from S_n1 and

S_n2 mechanisms.   The central feature of this reaction, see

below, requires an ion pair as an intermediate

$$RX \underset{-1}{\overset{1}{\rightleftharpoons}} R^+ /\!/ X^- \underset{Y\ \overset{3}{\searrow} RY}{\overset{H_2O\ \overset{2}{\nearrow}\ ROH}{}}$$
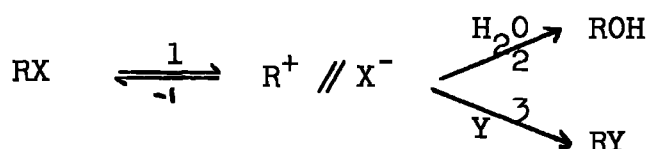
whose formation is rate determining at the S_n1 end; that is when x = k_{-1}/k_2 ≪ 1. Whilst the destruction of this ion pair by nucleophilic attack is rate determining at the S_n2 extreme, that is x ≫ 1; borderline behaviour presumably occurs when the rates of formation and destruction by nucleophilic attack on the intermediate ion pair are similar.

The rate profiles, plots of free energy, G, against the reaction ordinate, highlight these defining conditions which are shown overleaf. A characteristic of such schemes would be a transition in mechanistic type from S_n2 like to S_n1 like as the strength or concentration of the nucleophile is increased. This would place a maximum limit on the observable acceleration. No such behaviour has yet been reported.

Sneen and Larsen[3] have extended their conclusions to results previously reported for the hydrolysis in 70% acetone of 4-methoxybenzyl chloride.[74] This is in direct contrast to a previous interpretation which suggested[74] concurrent S_n1 and S_n2 processes for this reaction system. However, the reaction of 2-octyl sulphonates like those of 4-methoxybenzyl chloride occur in the neighbourhood of the mechanistic borderline region and a re-examination[75] has recently shown that both sets of results are equally consistent with both concurrent S_n1 and S_n2 processes and the unique ion pair mechanism.

Sneen and Larsen[3] have considered their scheme to be of general validity, but a detailed investigation[75,76] has shown that it leads to serious inconsistencies since they assumed that direct S_n2 nucleophilic attack on the substrate does

FREE ENERGY

G

RX

R/X

RY   RS

REACTION ORDINATE

S_N2 LIKE

X » I

G

RX

R/X

RY   RS

REACTION ORDINATE

BORDERLINE

X ~ I

G

RX

R/X

RS
RY

REACTION ORDINATE
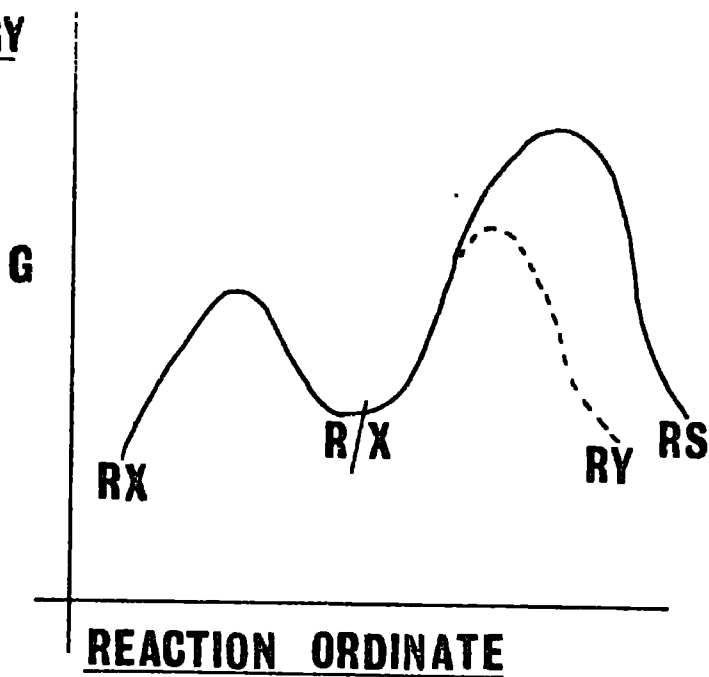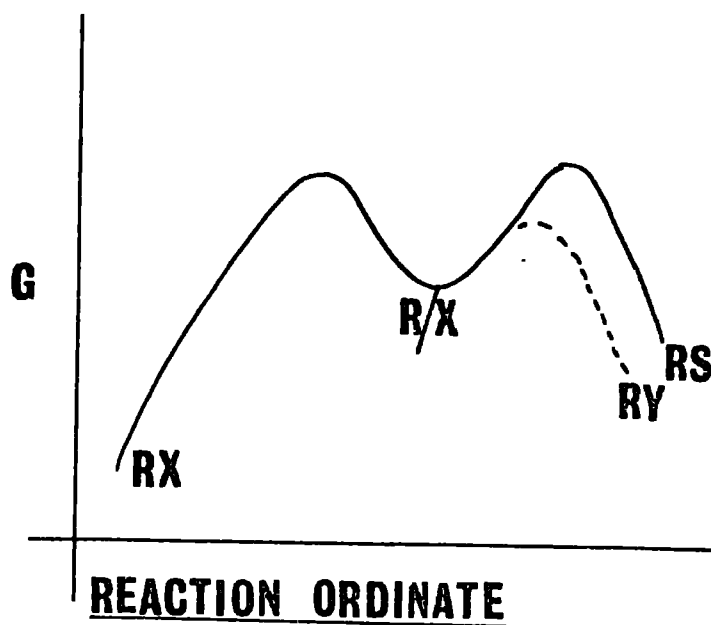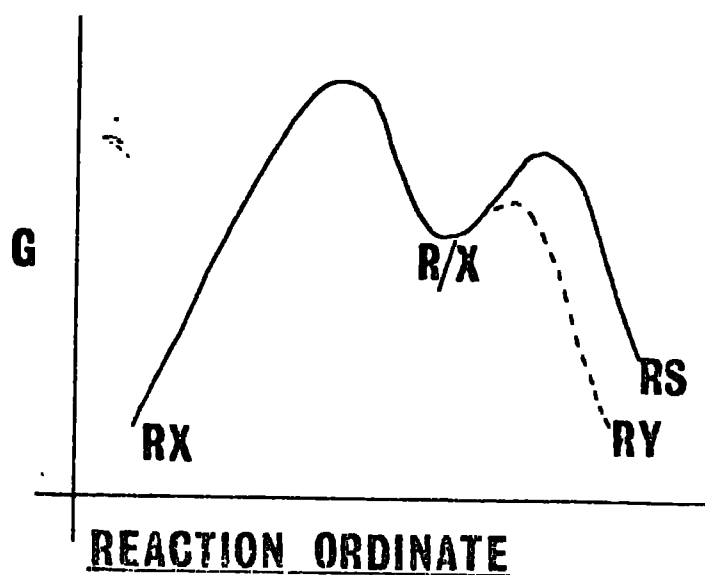
$S_N I$ LIKE

X « I

not occur and they did not envisage the existence of free carbonium ions.   Some examples of the inconsistencies are given below.

If this scheme is generally valid, then the principle of microscopic reversibility requires that any reaction with a common ion, X^-, can only occur with the same ion pair, R^+/X^- to produce the ion pair.   This will therefore have no effect on the hydrolysis rate, there will be no mass law effect.   Retardation by common ion has, however, been observed on a large number of occasions and though it could be that a small effect arises from a negative salt effect by added X^- anions, such an explanation could not account for the substantial retardation which frequently require mass law constants in excess of 100.[77]   Similarly the observed retardations of the hydrolysis of benzhydryl chloride and bromide by lithium chloride and bromide respectively[78] and the acceleration of the hydrolysis of the organic chloride by lithium bromide[78] are perfectly consistent with reaction by the S_n1 mechanism.   The ion pair scheme requires an explanation of why lithium bromide retards the ionisation of the organic bromide but accelerates the ionisation of the structurally similar chloride.   In addition the activation parameters for the hydrolysis of 4-methoxy and 4-phenoxy chloride in aqueous acetone[79] strongly suggest an entirely S_n1 process.   Reaction by ion pair mechanism would require $k_{-1}/k_2 \ll 1$,[3] but the results in the presence of azide ions then require that $k_{-1}/k_2 \doteq 2$ for the methoxy compound,[3] and greater than ten for the phenoxy compound.[76]   These apparent inconsistencies disappear if the strongly nucleophilic azide

ion also undergoes bimolecular reaction with the substrate. Since reaction centres are sterically favourable to S_n2 attack,[79] this explanation seems reasonable.

The ion pair (unified) mechanism has, however, gained wide acceptance and has been used[80] to correlate the rates of substitution of a series of nucleophiles with methyl halides in water, using an empirical linear free energy relationship. A requirement of this unified mechanism when applied to such simple substrates is that the free energy of activation for the overall reation ΔG^* should be greater than that for the formation of the ion pair. It has been calculated[81] that this is not likely to be fulfilled for simple methyl and ethyl halides and therefore they are unlikely to undergo solvolysis via an ion pair in water.

The considerations outlined here cast considerable doubts on the existence of any significant reaction between the intermediate ion pair and external reagents in aqueous organic solvents. No such disadvantages arise on the basis of mechanisms S_n1 and S_n2 in their original form, and it is proposed to discuss the present reaction in these terms.

1.6 Present Study

The present work was aimed at obtaining more information for the S_n1[1,23,31,82,84] solvolysis of benzhydryl chloride from accurate rate coefficients leading to the calculation of accurate activation parameters.

Recently there has been some discussion that the conventional activation parameters for solvolytic reactions in solution,

when determined from kinetic data obtained under constant
atmospheric pressure conditions are difficult to interpret
and that parameters referring to reactions at constant
volume might provide more information.[83,85] It was
initially intended to determine both parameters at constant
volume and at constant pressure for the solvolysis of one
substrate (benzhydryl chloride), although in the event
experimental difficulties prevented the determination of
the constant volume parameters (this is discussed in chapter
3).

The details of the considerations essential for the
determination and interpretation of activation parameters
at constant pressure and the reason for the choice of the
present substrate are given in chapter 2.

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CHAPTER TWO

THE TRANSITION STATE THEORY AND ACTIVATION PARAMETERS

OF SOLVOLYTIC REACTIONS

2.1   Introduction

As long ago as 1887 van't Hoff[1] indicated that the

rate of reaction varied with temperature.   This idea was

later extended by Arrhenius[2] who showed that the variation

of the reaction rate could be expressed by an equation of

the form

$$k \ \ = \ \ A.e^{-E/RT} \hspace{4cm} 2.1$$

where k is the rate constant for reaction, T is the absolute

temperature, and R the gas constant.   A and E were found to

be constant for each particular reaction.   The development

of the collision theory many years later related A to the

"collision number" or "frequency factor".   The quantity E

has now become known as the energy of activation and represents

the energy that a molecule in the initial state must aquire

before it can take part in the reaction.

The relationship required by equation 2.1 has been shown

to be valid within the limits of experimental error on

numerous occasions.   However, Hinselwood[3] pointed out that

E would be temperature dependent if the additional energy of

the activated molecules was distributed among more than two

square terms.   It was pointed out a few years later[4] that

any difference between the heat capacity of normal and

activated molecules would result in temperature dependent

values of E.   The transition state theory has led to

similar conclusions, and has been very successful in relating rate data for reactions in solution to activation parameters. Because of the temperature dependence of E, the Arhenius equation is now better defined in its differential forms:

$$E = RT^2 . \frac{\partial \ln k}{\partial T} \qquad 2.2$$

$$E = -R . \frac{\partial (\ln k)}{\partial (1/T}) \qquad 2.3$$

2.2   The Transition State Theory[5]

The theory is based on the principle that the reactants are considered to pass through a continuous series of configurations en route to the formation of the products. At some stage a state of maximum free energy is reached, the configuration is called the transition state or the activated complex which is assumed to be in equilibrium with reactant molecules.   The activated complex is regarded as a perfectly normal molecule, possessing the usual thermodynamic properties except that motion in one direction - along the reaction ordinate - leads to decomposition at a definite rate.[5]

From the statistical treatment of reaction rates in the transition state theory, the rate coefficient of a single step reaction is given by:-

$$k = K . \frac{kT}{h} . \exp(-\Delta G^*/RT) \frac{\pi_R f_R}{f^*}$$

where ΔG^* is the standard free energy change associated with the activation process, K is the transmission coefficient, the probability that the activated complex will form the products,

its value is normally assumed to be unity. $\bar{k}$ is
Boltzmann's constant, h is Plank's constant, f_R and f^* are
the activity coefficients of the reactants, and activated
complex, respectively. In practice, they are assumed to
be unity for non-electrolytes in dilute solutions.

By replacing ΔG^* by its equivalent $\Delta H^* - T\Delta S^*$ equation
2.4 can be written in the form:-

$$\ln k = \ln \frac{\bar{k}T}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \qquad 2.5$$

where ΔH^* and ΔS^* are the enthalpy and entropy of activation
respectively. Differentiation of this equation with respect
to temperature and comparison with equation 2.2 shows that:

$$E = \Delta H^* + RT \qquad 2.6$$

Equation 2.5 can be written in the form:

$$\ln k = \ln \frac{\bar{k}T}{h} + 1 + \frac{\Delta S^*}{R} - \frac{E}{RT} \qquad 2.7$$

This last equation is the form of the absolute rate equation
usually used in the determination of entropies of activation
for reactions in solution. Using Kirchoff's equations and
equation 2.6, the relationship between the heat capacity of
activation and the energy of activation can be written:

$$\Delta Cp^* = \frac{\partial E}{\partial T} - R \qquad 2.9$$

where ΔCp^* is the heat capacity of activation which represents
the heat capacity change associated with the activation process:

Reactants $\longrightarrow$ Activated Complex

with all the substances in their standard states.

The derivation given above assumes that the quasi-
thermodynamic parameters ΔH^* and ΔS^* show all the properties

of normal thermodynamic functions so that:-

$$\frac{\partial}{\partial T} (\Delta H^*) = T. \frac{\partial}{\partial T} (\Delta S^*) = \Delta Cp^* \qquad 2.10$$

Thus the transition state theory predicts a temperature dependent ΔH^* and hence a temperature dependent E if ΔCp^* differs from zero. This conclusion parallels that reached by De la Mer[4] before the development of the transition state theory provided the normal and activated molecules possessed different heat capacities.

Experimental evidence indicating a significant temperature dependence of E, and hence a significant value of ΔCp^* has only become available in the last twenty years, although some earlier workers[4,9] claimed to have observed such behaviour.

A further equation expressing ΔCp^* can be obtained by differentiating equation 2.2 with respect to temperature:

$$\Delta Cp^* = -R. \frac{\partial}{\partial T} \left(T.^2 \frac{\partial (\ln k)}{\partial (1/T)} \right) -R \qquad 2.11$$

Equation 2.11 demonstrates quite well the difficulty of obtaining accurate values for ΔCp^* from rate data since it is the second differential of the rate coefficient with respect to temperature.

The methods for evaluating the energy, entropy and heat capacity of activation are discussed in Appendix 5.

2.3 ΔCp^* in Solvolytic Reactions[6]

By far the most studied class of reactions, from the kinetic point of view, are the solvolytic reactions involving the mechanisms S_n1 and S_n2. The main reason for this is the

ease and accuracy with which rate measurements are made for such reactions and the magnitude of ΔCp^* is such that it facilitates measurement in such systems. Associated with the activation process for these type of reactions, is considerable development of electrical charge, and therefore considerable solvent reorganization. This accounts almost exclusively for the observation that ΔCp^* has a range of values from -20 to -100 cal. deg.$^{-1}$ [7,8]. Smaller values are to be expected when the reactions involve less drastic changes of polarity in the activation process, as for example the reaction taking place between a neutral substrate and an ion.

It must be stressed that the attempt made below to interpret the observations is based on the implicit assumption that the first step in the reaction sequence determines the rate of reaction so that the observed activation parameters (ΔH^*, ΔS^* and ΔCp^*) are identical with the corresponding parameters for this step. When this requirement is not met, or when the observed rate coefficient refers to two concurrent processes the observed activation parameters are composite quantities which must be resolved into their component contributions before any interpretation can be attempted. This is discussed further in section 2.4.

Table 2.1 shows that without exception, for solvolysis in aqueous organic solvents that the values of ΔCp^* and ΔS^* are negative. Whereas for solvolysis in water only ΔCp^* has negative values whilst ΔS^* can take positive or negative values. There are a further class of reactions where these parameters are numerically smaller, this is the borderline

TABLE 2.1

Kinetic Data for S_n1 and S_n2 Solvolysis in Aqueous Organic Solvent and Water at $50°$ [10]

Solvent	Substrate	ΔCp^*	ΔS^*	$\Delta Cp^*/\Delta S^*$	Mechanism
50% EtOH	$PhCHCl_2$	-59.0	-9.01	+6.55	S_n1
	t-BuCl	-34.0	-5.6	+6.1	S_n1
70% Me_2CO	$4\text{-}NO_2C_6H_4CHPhCl$	-39.8	-9.96	+4.00	S_n1
	$4\text{-}PhO.C_6H_4CH_2Cl$	-43.1	-11.98	+3.60	S_n1
	t-BuCl	-38.0	-10.89	+3.48	S_n1
	t-BuBr	-38.3	-10.20	+3.75	S_n1
50% EtOH	Ph_2CHCl	-31.07	-19.3	+1.61	S_n2
50% Me_2CO	$4\text{-}NO_2C_6H_4CH_2Cl$	-19.7	-23.49	+0.84	S_n2
	n-BuBr	-27.6	-20.82	+1.31	S_n2
	n-PrOTs	-32.1	-15.92	+2.07	S_n2
	$4\text{-}NO_2C_6H_4CH_2OTs$	-18.3	-18.95	+0.97	S_n2
H_2O	t-BuCl	-83	+3.42	-24.3	S_n1
H_2O	t-AmCl	-92	-1.96	+46.9	S_n1
H_2O	CH_2Cl	-86	+0.99	-86.9	S_n1
H_2O	i-PrOBs	-37	-2.78	+13.3	S_n1
H_2O	i-PrOTs	-42	-11.88	+3.54	S_n1
H_2O	MeCl	-49	-8.64	+5.67	S_n2
H_2O	i-PrCl	-38	-5.26	+7.22	S_n2
H_2O	i-PrI	-57	+1.90	-30.0	S_n2
H_2O	MeOBs	-36	-12.04	+3.0	S_n2

region and has been discussed in section 1.4.2 in Chapter 1.
A further feature shown by Table 2.1 is the constancy of the
ratio $\Delta Cp^*/\Delta S^*$ for reactions taking place in aqueous organic
media for S_n1 reaction (the ratio is smaller for reactions
taking place by the S_n2 mechanism). This does not apply to
S_n1 reactions in water where (as pointed out above) ΔS^* is
often positive, although ΔCp^* is always negative. As an
explanation of this behaviour, it was originally thought that
the values of these parameters could be explained by an
electrostatic model.[15] This model described the reaction
processes simply in terms of different electrostatic contribu-
tions to the change in free energy, from the two different
electrical states of the initial and transition states, the
solvent being considered as a continuous dielectric. It
has however been shown that such an approach predicts a
constant $\Delta Cp^*/\Delta S^*$ for S_n1 reactions in all solvents including
water, where clearly this is not observed. Furthermore, the
resulting values are widely different from those observed.

2.3.1   The Solvation Model for Solvolytic Reactions in Aqueous Organic Solvents.

It has long been recognised that an essential feature of
S_n1 solvolysis is the stabilisation of the highly polar
transition state by solvation interaction of solvent dipoles.
Thus comparing the corresponding gas phase reaction with the
reaction in solution, the activation energy is much reduced
by solvation interaction.

For the purpose of this discussion it is assumed that
in aqueous acetone the solvation required by the more polar
transition state is satisfied by the more polar solvent

molecule[6], water.   The movement of these water molecules

in the transition state will now be restricted and so the

entropy and heat capacity of activation will be reduced;

therefore negative values for ΔCp^* and ΔS^*.   Now, if the

contribution due to bond stretching and electrostatic

considerations are small, as they are often shown to be[6],

then solvation alone will control the magnitude of these

parameters.   On this basis then, ΔCp^* and ΔS^* will be

negative and the ratio $\Delta Cp^*/\Delta S^*$ could well be independent

of the substrate.

The changes in the heat capacity of activation associated

with S_n2 processes are generally less negative[6], also S_n2

reactions are also associated[6] with a more negative entropy

of activation.   From this it can be seen that the ratio

$\Delta Cp^*/\Delta S^*$ is smaller for the bimolecular process, relative to

the unimolecular process under the same conditions.   The

different values for the activation parameters of an S_n2 process

compared with those for an S_n1 process can be explained as

follows.   The transition state associated with an S_n2 process

requires that there is a greater distribution of the charge

developed, and the charge development is somewhat less.   As

a result, the increase in solvation upon passage to the

transition state will be less in S_n2, than in S_n1, this gives

rise to a smaller value of ΔCp^* as observed.   This of course

will only be true[6] if the heat capacity loss on covalent

attachment of a water molecule to the activated complex is of

the same order as the loss when a water molecule solvates the

transition state.   Now covalent attachment of a water molecule

would give rise to a substantial loss of entropy upon activation,

hence explaining the more negative values for ΔS^* in the S_n2 process relative to the S_n1 process. Thus the solvation model when presented in the above form can be used, albeit qualitatively, to predict the approximate and relative magnitude of the values of ΔCp^* and ΔS^* for both unimolecular mechanism and the bimolecular process.

A quantitative discussion of these reactions is also possible from the solvation point of view.[6] Kohnstam[6] proposed the following scheme for solvent and solute inter-actions, all solvent-solute and solvent-solvent interactions are identical in both the initial state and the transition state with the exception of the solvent-solute interactions arising from the increased polarity of the transition state. Furthermore, it is reasonable to assume that in aqueous acetone solvent systems, only water is involved in the solvation of the highly polar transition state. Therefore, the contributions to ΔCp^* and ΔS^* due to the solvation of the transition state can be written:

$$\Delta S^* = n_1 (S_s - S_1) \qquad 2.12$$

$$\Delta Cp^* = n_1 (C_s - C_1) \qquad 2.13$$

where n_1 is the effective increase in the solvation number associated with the activation process. S_s and C_s are the molar contributions of a solvated water molecule to the entropy and heat capacity of activation process respectively, S_1 and C_1 are the partial molar entropy and heat capacity of water in the solvent employed. Equations 2.12 and 2.13 then predict that the ratio $\Delta Cp^*/\Delta S^*$ is independent of the nature of n, and hence independent of the nature of the substrate.

A more rigorous check of the validity of equations 2.12

and 2.13 shows[6] that the predicted values of $\Delta Cp^*/\Delta S^*$ agree tolerably well with the observed values in four acetone water mixtures for which data are available, see Table 2.2.

TABLE 2.2

Observed and Calculated Values for the ratio $\Delta Cp^*/\Delta S^*$ for S_n1 Solvolysis at 25°. Based on the Solvation Model[6].

% Acetone	$\Delta Cp^*/\Delta S^*$(obs.)	$\Delta Cp^*/\Delta S^*$ (calc.)
50	3.77	3.03
70	5.24	5.37
80	3.53	4.09
85	3.58	3.62

This is true provided that the heat capacity and entropy loss by water in solvating the transition state is approximately one third the loss that suffered on freezing pure water.[7] This assumption is not at all unreasonable.[11] It appears that this solvation model is applicable qualitatively to solvolysis in aqueous acetone and less particularly to aqueous organic solvents. However, the conclusions drawn could easily be fortuitous since they are based on a rather simplified model of solvation. However, it has been severely criticised[14] on the grounds that this ratio is temperature dependent since:

$$- \quad \Delta S_T^* \quad = \quad A \quad + \quad \Delta Cp^*.\ln T \qquad 2.14$$

As a result it was suggested[14] that at some temperature ΔS^* would become positive (whilst ΔCp^* remained negative) so that the ratio would be a discontinuous function with temperature. However, the criticism was based on the implicit assumption

that ΔCp^* was a constant at all temperatures, whereas it is clearly only justified to make such an assumption over the temperature range studied experimentally. In all cases the temperature at which ΔS^* becomes positive is not only well outside this range but usually arises at a point when the solvent has already solidified. This criticism is thus readily dismissed.

2.3.2 The Solvation Model for Solvolytic Reactions in Water[6,8].

Table 2.1 shows that the constant value for the ratio $\Delta Cp^*/\Delta S^*$ does not hold true for solvolytic reactions in water. It seems that different factors control the magnitude of the ratio and that the results obtained in water cannot be explained in terms of the solvolysis model discussed in section 2.3.1. It is of interest to note that ΔS^* and ΔCp^* do not always have opposite signs. Explanations have already been advanced to explain the behaviour of electrolytes and non-electrolytes in aqueous solution[12] and have formed the basis of the interpretation of ΔCp^* and ΔS^* values for solvolytic reactions in water.[13] From this point of view a neutral organic solute invokes no solvent-solute interactions but increases the solvent-solvent interactions; such a solute enhances the structure of the solvent in its immediate vicinity. On passage to the transition state there is increased polarity which increases the solvent-solute interactions at the expense of the solvent-solvent inter-actions operating in the initial state. Since solvent-solvent interactions increase the heat capacity of the

system under consideration, a breakdown of these same
forces on passage to the transition state has been
considered responsible for the negative values of ΔCp^*.
On the other hand compounds that are easily polarisable
or capable of forming hydrogen bonds with the water, cause
a reduction of the initial state solvation shell, by
enhancing its solvent-solute interactions.   Since the
initial shell is relatively weakly formed with such compounds
there is less disruption of the shell on passing to the
transition state which in its turn causes ΔCp^* to be less
negative.   This conclusion is upheld by experiment as, for
example, in the solvolysis of sulphonates whose value for
ΔCp^* is less negative than the corresponding value for the
hydrolysis of chlorides.

Taking into consideration the entropy changes in such
a system, solvent-solvent interactions make a positive
contribution to the entropy of the system.   Thus on passage
to the transition state, the breakdown of the initial solvation
shell would result in a greater positive contribution to the
entropy than the negative contributions from the increased
solvent-solute interactions formed in the transition state.
From this point of view, changes in the structure alter the
extent of the breakdown of the initial state solvation shell
and will effect the values of ΔCp^* and ΔS^* in different
directions.   A constant value for the ratio $\Delta Cp^*/\Delta S^*$ is
therefore not expected for S_n1 hydrolysis in water.   Further-
more, since the predicted positive value of ΔS^* is observed in
some cases but not in others, then some other factors are of
importance in determining the magnitude of ΔS^*.

Kohnstam[7] suggested that the difference between hydrolysis in an aqueous organic solvent and water is that in the former, the initial state solvation by the organic component of the solvent reduces the solvent-solvent interactions induced by the presence of the substrate. Thus the addition of relatively small am ounts of dioxan or acetone to water in the hydrolysis of t-butyl chloride results in a fall in the value of ΔS^*. This may be because the solvent-solvent interactions are so reduced by the added organic component that they are not further reduced by the activation process. In this case the solvation model would be applicable to the hydrolysis. Further, it has been found[16] that ΔCp^* for the reaction between t-butyl chloride and water and various aqueous ethanol solvents shows a maximum in the region of the solvent composition where the structure of the solvent is changing rapidly with its composition.

The solvent used in this work has been 70% aqueous acetone, and the solvation model discussed in this Chapter describes the best working hypothesis at this present time for the explanation of the results of solvolytic studies in this medium. It will therefore be used to explain the results that may be produced in the present work.

2.4   The Unified Ion Pair Mechanism in Solvolysis

The discussion presented in previous sections is obviously only applicable if the first step is rate determining otherwise the observed value of ΔCp^* is a composite quantity dependent upon the system under consideration. Thus if a reaction has as the rate determining step, the breakdown of

an intermediate, itself formed by a pre-equilibrium

from the reactants, if the concentration of the intermediate

is small

$$A \quad + \quad B \rightleftharpoons AB \qquad AB \xrightarrow{\quad 1 \quad} \quad PRODUCTS$$

then the observed heat capacity is a composite quantity:

$$(\Delta C_p^*) \, obs \qquad = \qquad \Delta C_p^{\;O} \quad + \quad (\Delta C_p^*)_1 \qquad 2.15$$

Where ΔC_p^* is the standard heat capacity change for the

formation of the intermediate AB, and $(\Delta Cp^*)_1$ is the heat

capacity of activation for the rate determining step, step

1 in the above reaction scheme.

For concurrent reactions, $(\Delta Cp^*)_{obs}$ is given by

equation 2.16

$$(\Delta Cp^*)_{obs} \quad = \quad \frac{k_1 \, k_2}{k^2 \, RT} \cdot \quad (E_1 - E_2)^2 + \frac{k_1}{k} \, (\Delta Cp^*)_1 + \frac{k_2}{k} \, (\Delta Cp^*)_2$$

$$\dots\dots\dots\dots 2.16$$

where $k = k_1 + k_2$, and the subscripts refer to the appropriate

processes. This equation shows several features of interest:-

i) if the two processes occur with the same activation
    energy, E, then $(\Delta Cp^*)obs$ is that which would be
    expected from a combination of the individual
    components.

ii) if $E_1 \neq E_2$ there will be an unambiguous positive
    contribution to $(\Delta Cp^*) \, obs$ which will therefore be
    closer to zero than is normally observed, as is
    observed if one considers that the unimolecular
    and bimolecular reactions operate concurrently in the
    borderline region.

The presence of ion pairs in solvolytic systems has been

known for some time, their intervention has been postulated

increasingly in the last few years. In this thesis, the interest

is attached principally to the solvolysis of benzhydryl chloride

which has been considered in the past as a substrate undergoing S_n1 solvolysis in the present solvent system. For example,[17] the retardation of the solvolysis by added chloride ion has been taken to indicate a mass law effect thus requiring the classical S_n1 mechanism. The retardation is such that it could conceivably arise from a negative salt effect (see section 1.3.2(v)). However, such a conclusion has been thought extremely unlikely.[17,19]

It is therefore considered that any scheme for the solvolysis of this substrate must allow for the fully developed carbonium ion so that any any scheme invoking reaction by intermediate ion pair would have to take the form:

$$RX \; \underset{-1}{\overset{1}{\rightleftharpoons}} \; R^+/X^- \; \overset{2}{\longrightarrow} \; R^+ \; + \; X^-$$

with branches labeled 3 and 4 leading to PRODUCTS

where the retarding common ion effect has been omitted, a procedure which is valid for solvolysis carried out in dilute solution and with no added common ion.

Application of the steady state theory to the intermediate R^+/X^- then shows that the observed first order rate coefficient is given by:-

$$k_{obs} = \frac{1 + k_3/k_2}{1 + k_{-1}/k_2 + k_3/k_2} \cdot RX \qquad 2.17$$

noting that

$$\Delta H^*_{obs} = RT^2 \cdot \frac{\partial}{\partial T} \ln k_{obs}$$

then

$$\Delta H^*_{obs} = \Delta H^*_1 + \frac{k_3}{k_2}\left(\Delta H^*_3 - \Delta H^*_2\right)\left(\frac{1}{1 + k_3/k_2} - \frac{1}{1 + k_{-1}/k_2 + k_3/k_2}\right)$$

$$- \frac{k_{-1}/k_2}{1 + k_{-1}/k_2 + k_3/k_2} \ (\Delta H_1^* - \Delta H_2^*) \qquad 2.18$$

Now $\quad \dfrac{\Delta S^*_{obs}}{R} = \ln k_{obs} - \ln \dfrac{kT}{h} + \dfrac{\Delta H^*_{obs}}{R}$

therefore $\dfrac{\Delta S^*_{obs}}{R} = \Delta S_1^* - \ln (1 + k_3/k_2 + k^{-1}/k_2) +$

$$\frac{k_{-1}/k_2 \ \ln k_{-1}/k_2}{1 + k_3/k_2 + k_{-1}/k_2}$$

$$- \frac{k_{-1}/k_2}{1 + K_3/k_2 + k_{-1}/k_2} \cdot \frac{\Delta S_{-1}^* - \Delta S_2^*}{R}$$

$$+ \frac{k_3}{k_2} \left(\frac{\Delta S_3^* - \Delta S_2^*}{R} - \ln \frac{k_3}{k_2} \right) \left(\frac{1}{1 + k_3/k_2} - \frac{1}{1 + k_3/k_2 + k_{-1}/k_2} \right)$$

$$\dotfill 2.19$$

Since $\quad \dfrac{\Delta H_a^* - \Delta H_b^*}{RT} = \dfrac{\Delta S_a^* - \Delta S_b^*}{R} - \ln \dfrac{k_a}{k_b}$

A more complicated expression can be found which relates the observed heat capacity of activation (ΔCp^*) obs to parameters associated with the individual steps as ΔH^*_{obs} and ΔS^*_{obs} have been related.

It is noteworthy that the solvolysis of benzhydryl chloride the 4-nitro and the $4,4^1$ - dinitro derivatives show the same entropy of activation within a very small error (± 0.1 cal.deg^{-1})[18] although the rate coefficients vary over seven orders of magnitude. The simplest way of accounting for this observation is to assume that $k_3/k_2 \ll 1$ (that is neglible hydrolysis of the ion pair) and $k_{-1}/k_2 \gg 1$ (step 2 of the scheme is the

rate determining step) then equations 2.18 and 2.19 reduce to equations 2.20 and 2.21:

$$\Delta H^{*}_{obs} = \Delta H^{*}_{1} - \Delta H^{*}_{-1} + \Delta H^{*}_{2} = H^{*}_{2} - H^{o}_{RX} \qquad 2.20$$

$$\Delta S^{*}_{obs} = \Delta S^{*}_{1} - \Delta S^{*}_{-1} + \Delta S^{*}_{2} = S^{*}_{2} - S^{o}_{RX} \qquad 2.21$$

when it can be seen that each observed activation parameter (including $(\Delta Cp)_{obs}$ which is not shown) simply represents the increase in the appropriate quantity in passing from the substrate to the transition state of step 2. This observation can easily be explained if the difference between the ΔCp^{*} and ΔS^{*} values between these two states is the same for benzhydryl, nitro-and dinitro-benzhydryl chlorides. This is not an unreasonable assumption since the activation parameters depend on structural properties and are independent of the energy required to ionise the C-Cl bond. It must be stressed that under these conditions the scheme is kinetically indistinguishable from one that does not involve an intermediate ion pair. From this point of view ionisation via an intermediate ion pair is not excluded provided the ion pair does not react with the solvent. Alternatively significant hydrolysis via the ion pair ($k_{3}/k_{2} \gg 0.01$) requires a remarkable cancellation of various terms in equation 2.19 in order to lead to the observed constancy of ΔS^{*} observed in the hydrolysis of the benzhydryl nitro derivatives. It was thought that further information could be obtained from an accurate determination of ΔCp^{*}. Although earlier results had shown that $\Delta Cp^{*}/\Delta S^{*}$ was the same as that for other $S_{n}1$ reactions within the limits of experimental error (approximately 10%), it was felt that

values for this parameter and its temperature coefficient
would provide useful information, since it was regarded as
unlikely that the cancellation of terms involving k_3/k_2 and
k_{-1}/k_2 would apply to all three parameters, ΔS^*, ΔCp^* and
$\partial/\partial T$ (ΔCp^*). A value of $\partial/\partial T$ (ΔCp^*) has recently been
reported in the literature,[20] but in fact proved to be
insignificant.[21] Earlier calculations[6] indicated that
rate coefficients with fractional standard errors of approx-
imately 0.002 to 0.004 would be required to achieve this,
an accuracy which is five to ten times better than that
previously reported.

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CHAPTER THREE

ACTIVATION PARAMETERS AT CONSTANT VOLUME

3.1 Introduction

When solvolytic reactions are carried out under conventional conditions of constant pressure, they give rise to significant values of ΔCp^* which have been interpreted in terms of solvent-solute interactions (see section 2.4.3). It has been suggested that the use of mole fraction statistics, implied by constant pressure parameters, is inappropriate to these systems, and it would be better if discussions were based on volume fraction statistics, when the appropriate parameters would be those referring to constant volume conditions.[1,2] However at present constant volume parameters refer mainly to ΔV^* obtained from rate measurements at different pressures. Several extensive reviews[9,10,11,12,13,14] of the kinetic effects of pressure have appeared in the last few years and it is discussed in greater detail in section 3.5.

3.2 Activation Parameter at Constant Volume

The fundamental equation for the effect of pressure on the rate coefficient, k, of a one step chemical reaction, according to the Transition State Theory of Reaction Rates is given by[3]:-

$$\left(\frac{\partial}{\partial p} \cdot \ln k \right)_T = \frac{-\Delta V^*_p}{RT} \qquad 3.1$$

where the volume of activation, $\Delta V^*_p = V^* - V^o$ int, with V^* and V^oint the standard molar volumes of the activated complex and the initial state respectively.

A closely related equation was proposed by van't Hoff in 1901[4].

Many authors, for example Whalley[1], have suggested that activation parameters for chemical reactions might be more easily interpreted if they were determined at constant volume, and that values of ΔCp^*, the heat capacity of activation at constant pressure, may be essentially a consequence of working at constant pressure, and that the heat capacity of activation at constant volume could well be zero.[2]

As an aid to the elucidation of reaction mechanisms, volumes of activation should be at least as valuable as activation parameters at constant pressure since they are easier to interpret qualitatively, although at a rather elementary level. For instance, entropy requires a knowledge of the vibrations, and the enthalpy and free energy a knowledge of both the vibrations and the forces in the reacting molecules. Volumes of activation from this point of view should therefore be useful in elucidating mechanisms on account of their relative simplicity. However, it is only relatively recently that mechanistic information has been obtained from volumes of activation. The principal argument against constant pressure conditions arises from the expansion or contraction of the solvent as the temperature increases or decreases. This in turn results in an additional factor governing the interaction of reactants and the transition state with the solvent. In their original exposition of the Transition State Theory, Evans and Polyani[3] pointed out that these interactions would vary less if the

volume were kept constant, but it is doubtful whether studies of reactions at constant volume would avoid all the difficulties arising from results obtained at constant pressure. When the transition state is formed at constant pressure with a change in volume, only the solvent in its immediate vicinity is disturbed, the rest of the solvent is unaffected. Therefore the same reaction carried out at constant volume requires the compression or expansion of the solvent as a whole to compensate for the relatively large changes in volume over the small region near the transition state. This would complicate the interpretation of such results, and is a contradiction of an earlier suggestion.[1]

Purely thermodynamical arguments cannot establish whether the conventional constant pressure measurements or constant volume conditions would allow the simpler interpretation of activation parameters. The conditions to be preferred will to a certain extent depend on the theoretical model and on the results produced. Results for the same reaction under constant volume and constant pressure conditions would greatly aid the interpretation of the mechanism of that reaction, and it is hoped that reliable values of the heat capacity of activation at constant volume will soon be available. However, because of the relative ease of determining accurate rates at constant pressure, more forceful arguments will have to be presented to persuade workers to change from these conditions to those of constant volume.

3.3   Transition State Theory of Reactions at Constant Volume

This section follows the reasoning given by Whalley in his

review[1].

The rate constant of a one step chemical reaction, according to the Transition State Theory is given by:-

$$k = K. \frac{\overline{k}T}{h} . \exp -\left(\frac{\Delta G_p^*}{RT}\right) . \frac{\pi_R f_r}{f^*} \qquad 3.2$$

Where all the letters and subscripts have the usual significance.

It has been assumed in deriving equation 3.2 that the transition state has been formed at constant pressure. If it has been formed at constant volume, then the rate is given by:-

$$k = K. \frac{\overline{k}T}{h} . \exp \left(-\frac{\Delta F_v^*}{RT}\right) \frac{\pi_R f_r}{f^*} \qquad 3.3$$

Where ΔF_v^* is Hemholtz free energy of activation at constant volume.

However, the concentration of the transition state is always very small and consequently conditions of constant pressure and constant volume are indistinguishable at any stage of the reaction[1]. Differentiating equation 3.3 with respect to temperature gives:-

$$\left(\frac{\partial \ln \left(\frac{k}{T}\right)}{\partial \left(\frac{1}{T}\right)}\right)_v = \frac{-\Delta U_v^*}{R} \qquad 3.4$$

Where ΔU_v^* is the internal energy of activation at constant volume.

Also:-

$$\left(\frac{\partial T. \ln (k/T)}{\partial T}\right)_v = \frac{-\Delta S_v^*}{R} \qquad 3.5$$

Where ΔS_v^* is the entropy of activation at constant volume.

Now:-

$$\left(\frac{\partial G}{\partial p}\right)_T = V \quad \text{and} \quad \left(\frac{\partial A}{\partial V}\right)_T = -p$$

therefore

$$\left(\frac{\partial}{\partial p} \cdot \ln k\right)_T = -\frac{\Delta V_p^*}{RT} \qquad 3.1$$

$$\left(\frac{\partial}{\partial V} \cdot \ln k\right)_T = \frac{\Delta p^*}{RT} \qquad 3.6$$

Where ΔV_p^* is defined as before, Δp^* is the pressure of activation.

The pressure of activation is defined as the change in pressure when a fixed amount of transition state is formed at constant volume. Both equations contain essentially the same information, but equation 3.1 is more useful since pressure is easier to measure than volume.

The determination of other activation parameters for the process at constant volume requires a knowledge of the rates of reaction at various temperatures with the volume of the reaction mixture kept constant. This information is usually obtained by interpolation of the rate constants at a number of different pressures, rather than keeping the reacting volume constant and assuming that the coefficients of expansivity, (α), and compressinility, (β), of the reacting system are the same as in the pure solvent. Any error resulting from this is probably negligibly small when dilute solutions are studied.

The heat capacity of activation at constant volume, ΔC_V^* is given by:-

$$\Delta C_v^* = \left(\frac{\partial \Delta U_v^*}{\partial T} \right)_v \qquad 3.7$$

Where ΔU_v^* is defined as in equation 3.4.

The internal energy of activation is related to the corresponding parameters at constant pressure by:-

$$\Delta U_v^* = \Delta H_p^* - \frac{\alpha}{\beta} \cdot T \cdot \Delta V_p^* \qquad 3.8$$

where the isopiestic thermal expansivity $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$

and the isothermal compressibility $\beta = \frac{-1}{V} \left(\frac{\partial V}{\partial p} \right)_T$

Also ΔC_v^* is related to corresponding parameters at constant pressure by the relation:-

$$\Delta \dot{C}_v^{*} = \Delta Cp^* - \frac{\alpha T}{\beta} \cdot \Delta V_p^* \left(\left(\frac{\ln\left(\alpha \cdot \frac{\Delta V_p^*}{\beta^2} \right)}{T} \right)_p + \frac{\alpha}{\beta} \left(\ln \left(\frac{\Delta V_p^*}{\beta} \right) \right) \right) \qquad 3.9$$

Details of the derivation of the above equation are given by Whalley[1].

No reaction appears to have been studied deeply enough for this equation to be applied.   It must be stressed that the constant pressure parameters (subscript p) in equations 3.8 and 3.9 are not identical with those discussed in the previous Chapters.   They refer to a pressure, p, required to keep the volume of reaction system constant at some arbitrarily chosen value, and it is inevitable that p will increase as the temperature is increased.   Strictly speaking therefore, the comparison should be carried out between the parameters at constant volume and those at constant pressure, say one atmosphere.

3.4   Experimental Technique

The technique of measuring rate constants at various pressures (for reactions in solution) suffers from the inherent defect, that the rate coefficients are relatively insensitive to changes in pressure.   This is in direct contrast to reactions studied at various temperatures whose rate on average will double for each ten degree rise in temperature.   For example, a volume of activation of $-30cm^3$, according to equation 3.10 corresponds to a pressure coefficient of the rate coefficient at 20° of about:-

$$\frac{1}{k} \cdot \frac{\partial k}{\partial p} = -1200 \times 10^{-6} \text{ bar}^{-1} \qquad 3.10$$

Alternatively this means that the rate constant approximately doubles for each kilobar change in pressure.   Thus in order to obtain activation parameters of similar precision to those at constant pressure, the pressure at which the reaction takes place and the rate coefficient must be measured with extreme accuracy.   On the other hand if only volumes of activation are required, then rate coefficients measured to an accuracy of 1% over a pressure range of 1 to 3 kilobars would be sufficient[1] for an accuracy in V_p^* of about ± 1 cm^3.   This clearly is not good enough for the present study.

Until recently the conventional method of rate measurement has been to confine the reaction mixture in a tube with a well fitting movable piston placed in the pressure vessel. After a known time the pressure is released and a sample removed for analysis.   Other samples are treated similarly, being left in the pressure vessel for varying lengths of time.

Various methods have been used to transmit the pressure

from the hydraulic fluid to the reaction vessel for example, a modified hypodermic syringe, mercury, teflon plugs, stainless steel bellows. Whilst the batch method, mentioned earlier, is useful when only a small number of points are required to calculate the rate coefficient, it is obviously better if a physical property of the reaction mixture can be measured in situ. Several such methods have been used, polarimetry, spectrophotometry, electrical conductivity, even dilatometry has been used. This can be done using a manganin resistance gauge, when changes of the order of 0.04 bar can be detected[6].

A further experimental point to be considered is the heat developed when the mixture is compressed. When liquids are compressed adiabatically, their temperature increases according to the relationship:-

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{T}{C_p} \cdot \frac{V}{T} \qquad\qquad 3.11$$

where S is the entropy, V is the volume and Cp is the heat capacity at constant pressure.

For water at atmospheric pressure at 25°, $(\partial T/\partial p)_S$ is of the order of 1.8° k bar^{-1}. However for organic liquids the value of $(\partial T/\partial p)_S$ can be ten times higher than this. Thus the compression of the reaction mixture should be slow since the heat produced has to be dissipated, the temperature equilibrium restored before rate measurements can begin. This factor places a serious limitation on the highest temperature (largest rate coefficient) which can be employed in the determination of activation parameters.

For a full study of a reaction system as indicated in section 3.3 enabling the heat capacity of activation at constant volume to be calculated, the following sets of experimental data have to be obtained:

> the isopiestic thermal expansivity, α, of the solvent, the isothermal compressibility, β, of the solvent, and the effect of pressure on the rate of reaction at given intervals of temperature.

Further experimental details are found in Chapter 6.

3.5 Information derived from Activation Parameters at Constant Volume

The only constant volume parameter which seems to have been studied in any detail in the volume of activation ΔV^*. Although the variation of ΔV^* with pressure has been useful[14], mechanistic information and the sensitivity of reaction rates to pressure changes have generally been based on $\Delta V o^*$ the volume of activation at zero pressure. However, the estimation of $\Delta V o^*$ is not easy[14]. At present, it is generally calculated by graphical methods[1] or from the best fit[14] of the experimental points to the equation:-

$$\ln k = a + bP + cP^2 \qquad 3.12$$

This equation assumes that $\partial V^*/\partial p$ is independent of pressure, but the validity of this assumption, and equation 3.2 may depend on the system under investigation.

According to Whalley[1], the volume of activation may be resolved into two components, ΔV_r^* and ΔV_s^*, Kohnstam[14] also considered a similar resolution of ΔV^*. The principal terms that contribute to ΔV_r^* arise from volume changes from the partial formation of new chemical bonds, stretching or fission of existing bonds, as the reaction system passes to

the transition state.

Contributions to ΔV^*_s arise from volume changes due to the interactions of initial state and the transition state with the solvent. It must be emphasised that these concepts are not precise but are worth discussing qualitatively because they allow a certain insight into the activation processes involved in chemical reactions.[1,14]

3.5.1 The Magnitude of ΔV^*_r

Contributions to ΔV^*_r arise mainly from:

    i)   bond fission

    ii)   bond formation

   iii)   non bonded interactions

   iv)   destruction or formation of cyclic systems

Bond fision mainly contributes to ΔV^*_r because of partial stretching or breaking of a covalent bond during the activation process.[14] Such contributions are normally calculated[1,14] from the Van der Waal's radii of atoms or groups in the vicinity of the reaction centre. ΔV^*_r can readily be calculated provided the extension of the bond being broken is known. Such calculations lead to values of ΔV^*_r in the region of $0.5 - 4$ cm^3.

Similarly the contributions to ΔV^*_r due to bond formation can be obtained from the decrease in the distance between two reacting sites in the transition state. It is important to note that the reduction in volume in forming a new partial bond is greater than the volume increase associated with partial bond destruction for similar reacting systems.

Consequently for a bimolecular reaction involving synchronous fission and formation of new bonds, there is expcected to be a negative value of ΔV^*_r contributing to ΔV^*.

Non bonded interactions having contributions to ΔV^*_r will be expected when the transition state is formed either by compression of sterically hindered groups or the release of such compression in groups whose bonding is not otherwise affected by the formation of the transition state. Therefore depending on whether compression or its release occurs in the activation process, there will be a negative or positive contribution to ΔV^*_r. When the activation process involves the formation of a cyclic transition state from a non cyclic molecule, the creation of such an empty space - too small to be occupied by a solvent molecule - will result in a positive contribution to ΔV^*_r.[7,8] Conversely a negative contribution will occur when a cyclic precursor forms a linear transition state provided there is exclusion of the solvent from the interior of the cyclic structures. The effects of non bonded interactions and the formation or destruction of cyclic intermediates will have very little contribution to make to ΔV^*_r and hence to ΔV^* in S_n1 and S_n2 solvolytic type reactions.

3.5.2   The Magnitude of ΔV^*_s

The interaction between a molecule and its solvent is very complicated and cannot be described at all quantitatively[1] by any detailed theory.

The contribution of solvent effects, ΔV^*_s, to ΔV^*, can be discussed either in terms of a solvation model or an electro-

static model.   In the solvation model[14] a contraction

occurs when the solvent molecules become attached to a

charged centre.   The electrostatic model[1] considers the

electrostatic contribution to the volume when a polar

species is placed in a solvent which is regarded as a

structureless and continuous dielectric.   Both approaches

lead qualitatively to the same conclusions, a negative ΔV^*_s

when charges are created in the activation process, and a

positive value when charges are destroyed or dispersed over

a larger part of the reacting entity.

The effect of solvent changes is usually considered to

be negligible in non polar reactions not involving the

formation or fission of hydrogen bonds.   This is assumed

although it is well known that a neutral substrate initiates

solvent-solute interactions and changes solvent-solvent

interactions.[15]   It is possible that such interactions will

not be greatly altered by the passage to the transition state.

Most discussions involving factors contributing to ΔV^*_s,

however, neglect contributions from neutral species[14],

since the present state of knowledge allows no other meaning-

ful consideration.   This may not be entirely valid particularly

in highly aqueous solvents.

The various processes which can occur during the formation

of a transition state, each making a contribution to the volume

of activation are shown in Table 3.1.

TABLE 3.1

The Effect of Various Processes on Volumes of Activation[14]

Process	Initial State	Transition State	$\ddagger\, \Delta V^*_c$
Bond fission	A - B	A.....B	5
Bond formation	A + B	A.....B	-10 to -15
Charge Creation	A + B	$A^{\delta+}.....B^{\delta-}$	-10 to -30^x
Charge Destruction	$A^+ + B^-$	$A^{\delta+}.....B^{\delta-}$	10 to 30^x
Charge Dispersal	A-B-C	A...B...C	5 to 10^x

$\ddagger\, \Delta V^*_c$ the contribution to ΔV^* from the process under consideration (cm^3)

x These processes do not include contributions from bonding changes.

3.6 ΔV^* for the Solvolysis of Organic Halides

Solvolysis of organic halides is accelerated by an increase in pressure (see section 3.4). The volumes of activation for such reaction lie in the range -15 to -25 cm^3 [14] although values closer to zero have been observed for solvolysis in water[13,16]. It is difficult to predict whether there will be any difference in volumes of activation for S_n1 and S_n2 solvolyses.

In the bimolecular solvolysis, there is a partial stretching of an existing bond, and the partial formation of a new bond; these factors should provide a negative ΔV^*_r [14]. There is also increasing solvation caused by the formation of electric charges in the transition state, resulting in a

negative ΔV^*_s. In direct contrast, in an S_n1 transition
state not only is there a greater concentration of these
charges but their possible greater magnitude should result
in a more negative ΔV^*_s.[14] In opposition to this there is
a positive contribution to ΔV^*_r caused by the fission of an
existing bond.

Bearing all this in mind it is not surprising to find
that the volume of activation for solvolysis of alkyl halides
has often very similar values for the S_n1 and S_n2 mechanisms,
and that ΔV^* does not provide a useful criterion of mechanism.
From this brief discussion, it is likely that the use of ΔV^*
offers very little insight into the nature of the intermolecular
and molecular solvent forces in reactions taking place by
these two mechanisms. This is a result of a lack of values
of ΔV^* for S_n1 and S_n2 reactions, and a lack of a suitable
theory explaining solvent-solvent and solvent-solute inter-
actions. However, experimental results for the same reactions
at both constant pressure and constant volume would further
aid the interpretation of activation parameters.[15a]

3.7   Conclusion

Whilst activation parameters at constant volume would
have undoubtedly provided additional detailed information about
the processes involved in S_n1 reactions, it was felt that
there was not sufficient time to overcome the experimental
problems that were encountered. The present reactions were
therefore only studied under conditions of constant pressure.

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CHAPTER FOUR

ACCURATE RATE COEFFICIENTS

4.1 Introduction

The aim of this work was to obtain rate coefficients
of maximum accuracy for the hydrolysis of benzhydryl chloride
in aqueous acetone.   It was hoped that this aim could be
achieved by following the development of acidity during
solvolysis, either by titrimetric analysis of samples of the
reaction mixture or by measurement of the conductance of the
reaction mixture itself.   The reliability of the rate
coefficients likely to be obtained by these two methods is
considered in this chapter.

4.2 Errors involved in the Determination of the Concentration
     of the Product.

Two types of error contribute to the total error in the
titre (P) of a sample of the reaction mixture.   Firstly, a
titration error arises from errors involved in reading the
burette and from any error in locating the end point.   Both
these errors are independent of the magnitude of the titre,
so that the titration error can be expected to be constant
as the reaction proceeds.   Hence:

$$\delta P_{tit} \;=\; (\delta P_{tit}) \;=\; P_{\infty}.\sigma_T$$

where $\qquad \sigma_T \;=\; \delta P_{tit}/P_{\infty}$

σ_T expresses the titration error as a fraction of the infinity
reading.   Secondly, the titres will also be subject to a
sampling error resulting from errors in the volume of sample

taken for analysis. If the sample volume, V_s, is subject to an error, δV_s the resulting error in the titre will be given by:-

$$\delta P_s = P. \delta V_s / V_s$$

The total error in the titre resulting from the combination of these two independent errors is given by:-

$$\delta P^2 = \delta P_{tit}^2 + \delta P_s^2$$

$$= P_\infty^2 . \sigma_T \left(1 + x^2 \left(\frac{(\delta V_s / V_s)^2}{\sigma_T^2}\right)\right)$$

where $P/P_\infty = X$

$$\therefore \quad \delta P = P_\infty . \sigma_T (1 + x^2)^{\frac{1}{2}} \qquad 4.1$$

Equation 4.1 follows provided that the fractional sampling error, $\delta V_s / V_s$, is of a similar magnitude to the fractional titration error, σ_T, as does occur in practice.

For kinetic runs followed by a conductimetric method, the situation is different. For such a run, the resistances in the conductance bridge are generally accurate to some fraction of their total value. Therefore, the error in a conductance reading, P, is given by:-

$$\delta P = P_\infty . X. \sigma_p \qquad 4.2$$

where $P/P_\infty = X$

$\delta P/P_\infty = \sigma_p$

σ_p expresses the error in a conductance reading as a fraction of the infinity reading.

In the past, kinetic data from conductance measurements have often been treated by assuming a direct proportionality between the observed conductance and concentration similar to

the direct proportionality that exists between the titre and the concentration, provided this assumption causes only a small error.   (See however, the discussion in section 5.2. et seq.)

A comparison of equations 4.1 and 4.2 shows that the actual determination of the "product concentration" will invariably be subject to a smaller error when conductance is employed (since X < 1), unless of course, σ_p is considerably larger than σ_T.   In fact, the converse is likely to apply, since an accurate titrimetric determination of an acid concentration would involve an error of the order of 0.01 mls. in 10 mls, $\sigma_T \doteq 10^{-3}$;   whilst conductance measurements can easily be obtained with a value of σ_p 1 - 2 x 10^{-4}.

On this view the case for employing conductance measurements as opposed to titration appears to be unassailable, but it is necessary to consider how the rate coefficients are obtained in practice before this conclusion can be finally accepted.   This is because the statistical weight factors employed in these calculations will depend on the method of following the reaction.

4.3   The Rate Equations

The integrated first order rate equation for a reaction followed by the development of the product (P) can be expressed in a number of ways, each of which invariably influences the reliability of the final rate coefficient.

Integration of the instantaneous rate equation between limits of zero time (T = 0) and time, T, gives the normal form of the first order equation

$$k = \frac{1}{T} \ln \frac{P_\infty - P_0}{P_\infty - P} \qquad\qquad 4.3$$

or its equaivalent

$$kT = \ln \frac{P_\infty - P_0}{P_\infty - P} \qquad\qquad 4.4$$

from which the rate coefficient is obtained as the mean of the individual rate coefficients (equation 4.3) or as the slope of the appropriate line through the origin (equation 4.4). The estimated standard error of the "best" rate coefficient arises from the random errors (δP) in the P terms, in addition this parameter is subject to systematic "zero" and "infinity" errors which are associated with each k in the equation 4.3 and each kT in equation 4.4. The use of equations 4.3 and 4.4 has been criticised for these reasons,[1] but there is no difficulty in taking several infinity measurements for a reaction which goes to completion. Thus the systematic error in P_∞ , and therefore the infinity error of k can easily be reduced to an insignificantly small amount. Similarly there is no difficulty in carrying out several zero measurements for titration runs when the sealed ampoule technique is used. This unfortunately is not possible for runs followed by change in conductivity. However, equation 4.2 does indicate that the error in a zero measurement resulting from a single determination of P_0 is likely to be small provided the reading is taken at a very early stage of the reaction $(X \ll 1)$. It was therefore considered that the use of equation 4.3 in the present work was worthy of further consideration. Obviously reliable experimental data should give the same final value for the rate constant, irrespective of the method of calculation, this does not necessarily apply

to the estimated standard error of this quantity. However, the method of weighted least squares (see section 4.4) leads to identical expressions for the rate coefficient and its estimated standard error from equation 4.3 and 4.4

Alternatively the systematic error in the zero reading can be avoided by treating the term $\ln (P_\infty - P_0)$, in equation 4.3 as a disposable constant when the integrated rate equation takes the form

$$\ln (P_\infty - P) = A - kT \qquad 4.5$$

The final rate coefficient, k, is then obtained as the slope of the appropriate "best" straight line, but such a rate coefficient is still subject to the systematic error in the infinity reading, although this can be minimised by replicate determinations. In addition the estimated standard error of the resulting rate coefficient is likely to be larger than that from equation 4.3 since it is now calculated from an expression involving two disposable parameters.

Systematic errors can be entirely avoided by writing equation 4.3 in its exponential form and replacing terms involving P_∞ and P_0 by disposable parameters. This equation is shown below (equation 4.6)

$$P = A - Be^{-kT} \qquad 4.6$$

The rate coefficient is obtained from this expression by the the method of non linear least squares (see Appendix 3), but it can be expected to be subject to a relatively large standard error in view of the three disposable parameters involved in equation 4.6.

. Alternatively the infinity error can also be avoided by

applying equation 4.5 to two separate determinations of P separated by a constant time interval ΔT. The resulting expression, the well known Guggenheim equation, can be written in the form:

$$\ln (P_{T + \Delta T} - P_T) = A - kT \qquad 4.7$$

Calculations[2] performed on equation 4.7 have shown that the resulting reliability of the rate coefficients is less than that obtained from equation 4.5 when several infinity measurements have been carried out. As a result of this discussion, rate coefficients were not calculated from equations 4.6 and 4.7 for the present work.

4.4   Weighting Schemes Applied to Rate Data

In effect the rate equation can be written quite generally in the form:-

$$y = f (T,k,a)$$

where y is a function of the P's, or of the P's and the T's, f is a function of the T's (assumed much more accurate than the P terms), the rate coefficient, k, any other disposable parameters, a.

The disposable parameters, including the rate coefficient, are then evaluated from the principle of least squares which requires that:-

$$\sum_{i} \omega_i \cdot \Delta_i^2 \qquad \text{is to be a minimum} \qquad 4.8$$

where Δ_i are the residuals calculated from the differences between the observed, y, and the values calculated from the "best" values of the disposable para-

meters, and w_i, is the statistical weight to be assigned to each experimental point y_i.

This weight factor has often been assumed to be unity in kinetic work, but it is necessary to establish that this assumption is justified before it can be accepted in the present calculations.

For aGaussian distribution of errors, the statistical weight properly assigned to any point y_i is proportional to the reciprocal of its variance, δy_i^2, about its correct value:

that is $\qquad w_i \quad \propto \quad 1/ \delta y_i^2 \qquad\qquad$ 4.9

δy_i can be obtained to a good degree of approximation from the relation between y and the observed quantity P.

Since

$$y \quad = \quad g \ (P)$$

then $\qquad \delta y_i \ = \ \frac{\partial g}{\partial P} \cdot \ \delta P_i \qquad\qquad$ 4.10

Equation 4.10 gives an expression for an error δy_i caused by an error δP_i. Expressions for δP_i are given by equations 4.1 and 4.2, this allows δy_i to be formulated in terms of experimental quantities (P_i, P_∞ .....) and an unknown constants (σ_T or σ_p) and this permits the evaluation of the weight factors w_i from equation 4.9. The calculation of the weight factors, w_i, is outlined below

Writing the rate expression in the form

$$y \quad = \quad f \ (T,k,a)$$

the method of weighted least squares (equation 4.8) gives the "best" value of the rate coefficient:-

$$k \quad = \quad h \ (y,t,w)$$

where the function h depends only on the experimental quantities y and t and does not involve any parameters. The precise nature of h depends on the rate equation employed. An error δy_i in a point y_i causes an error δk_i in k given by:-

$$\delta k_i = \frac{\partial h}{\partial y_i} \cdot \delta y_i$$

and the variance of k is given by:-

$$v(k) = \frac{n}{n-p} \cdot \sum \delta k_i^2$$

where n is the number of experimental points, p the number of disposable parameters.

For expressions under consideration it was always found that

$$v(k) = \frac{n}{n-p} \sum_i w_i h_i' \cdot w_i \delta y_i^2 \qquad 4.11$$

where h' is a function of w and t only.

For a proper weighting procedure (that is, if there is a Gaussian distribution of errors) $w_i \delta y_i^2$ is constant (in practice almost constant) and equal to $\sum w_i \delta y_i^2/n$. Now δy_i can be identified with the observed residuals Δ_i (see equation 4.8), therefore equation 4.11 can be written:-

$$v(k) = \frac{\sum w_i \cdot \Delta_i^2}{n-p} \cdot \sum w_i \cdot h_i'$$

Table 4.1 shows the values of the various functions appropriate to equations 4.3 and 4.5.

TABLE 4.1

Functions Involved in the Solution of Equations 4.3 and 4.5

Function	Equation 4.3	Equation 4.5
f_i	$\dfrac{1}{T_i} \ln \dfrac{P - P_o}{P - P_i}$	$\ln (P_\infty - P_i)$
y_i	k	$A - kT_i$
$\partial y_i / \partial P_i$	$\dfrac{1}{T_i} \dfrac{1}{1 - X_i} \cdot \dfrac{1}{P_\infty}$	$-\dfrac{1}{1 - X_i} - \dfrac{1}{P_\infty}$
y_i (titration)	$\dfrac{1}{T_i} \dfrac{1}{1 - X_i} \cdot \sigma_T$	$\dfrac{1}{1 - X_i} \sigma_T$
(conductance)	$\dfrac{1}{T_i} \dfrac{X_i}{1 - X_i} \cdot \sigma_p$	$\dfrac{X_i}{1 - X_i} \cdot \sigma_p$
w_i (titration)	$T_i^2 (1 - X_i)^2$	$(1 - X_i)^2$
(conductance)	$T_i^2 \cdot \left(\dfrac{1}{X_i} - 1\right)^2$	$\left(\dfrac{1}{X_i} - 1\right)^2$
k	$\dfrac{\sum w_i \cdot y_i}{\sum w_i}$	$\dfrac{\sum w_i \cdot \sum w_i y_i T_i - \sum w_i T_i \sum w_i y_i}{\sum w_i \sum w_i T_i^2 - (\sum w_i T_i)^2}$
$v(k)$	$\dfrac{\sum w_i \Delta_i^2}{n - 1} \cdot \dfrac{1}{\sum w_i} \cdot \dfrac{\sum w_i \Delta_i^2}{n - 2}$	$\dfrac{\sum w_i}{\sum w_i \sum w_i T_i^2 - (\sum w_i T_i)^2}$

4.5   The Fraction of the Reaction over which the
Rate Coefficients have Greatest Reliability

Assuming that the systematic errors have been minimised or avoided, the estimated standard error of the final rate coefficient, obtained from the appropriate rate equation, can be taken to reflect the reliability of this parameter. It seems reasonable to assume that this reliability will be affected by the extent of reaction over which readings have been taken.   Equation 4.3. then allows the calculation of a rate coefficient, k_i, appropriate to each experimental point.   The value of this rate coefficient will be subject to a random error arising from the random error, δP_i, in the appropriate observation P_i.   Thus from equation 4.3, the error in the rate coefficient, δk_i, from a corresponding error δP_i in P_i is given by:-

$$\delta k_i = \frac{1}{T} \cdot \frac{1}{1 - X_i} \cdot \frac{\delta P_i}{P_\infty}$$

Substituting from equations 4.1 and 4.2, the corresponding equations for titration and conductance become:-

$$\frac{\delta k_i}{\sigma_T} \approx \frac{1}{T} \cdot \frac{1}{1 - X_i} \cdot (1 + X_i^2)^{\frac{1}{2}} \qquad 4.11$$

$$\text{and} \quad \frac{\delta k_i}{\sigma_p} = \frac{1}{T} \cdot \frac{1}{1 - X_i} \cdot X_i \qquad 4.12$$

A comparison of these equations shows that for comparable values of σ_T and σ_p, the smaller error occurs in equation 4.12 since $X < 1$.   It must be borne in mind that the optimum range for each δk_i is not necessarily the same for each method.   It can be shown that if the reaction follows good first order kinetics, and since $X < 1$ then

$$T = -\frac{1}{k} \cdot \ln(1-X) \qquad (\text{Assuming } X_0 = 0)$$

Therefore substituting for T in equations 4.11 and 4.12

$$\frac{\delta k_1/k}{\sigma_T} = -\frac{(1+X_1^2)^{\frac{1}{2}}}{(1-X_1)\ln(1-X_1)} \qquad 4.13$$

$$\frac{\delta k_1/k}{\sigma_p} = -\frac{X_1}{(1-X_1)\ln(1-X_1)} \qquad 4.14$$

Equations 4.13 and 4.14 give the fractional error of an individual rate coefficient relative to fractional error of the infinity determination, by the two methods, titration and conductance. The values of $\frac{\delta k_1/k}{\sigma}$ at various points of the reaction are shown graphically in figure 4.1 for titration runs and figure 4.2 for conductance runs. From these figures it is evident that for the titration method, the greatest accuracy is obtained within the range X = 0.2 to 0.9, with $\frac{\delta k_1/k}{\sigma_T}$ having a value of between three and six whilst for the conductance method the most accurate range lies between X = 0.02 to 0.7, with the corresponding value of $\frac{\delta k_1/k}{\sigma_p}$ between one and two. Bearing in mind, that the fractional error of the infinity determination (σ) can be expected to be five times larger for a titration method than for a conductance method, it is clear that equation 4.3 will give the more accurate rate coefficients when the products have been determined by conductimetric methods. These general conclusions only hold provided that the conductance measurements are proportional to the concentration.

It can easily be shown that the approximate two fold

FIGURE 4.1

Plot of $\delta k_{1/2k}/\sigma_T$ vs. X
For a Titration Run

X   PER CENT REACTION

$\dfrac{\delta k_{1/2k}}{\sigma_T}$
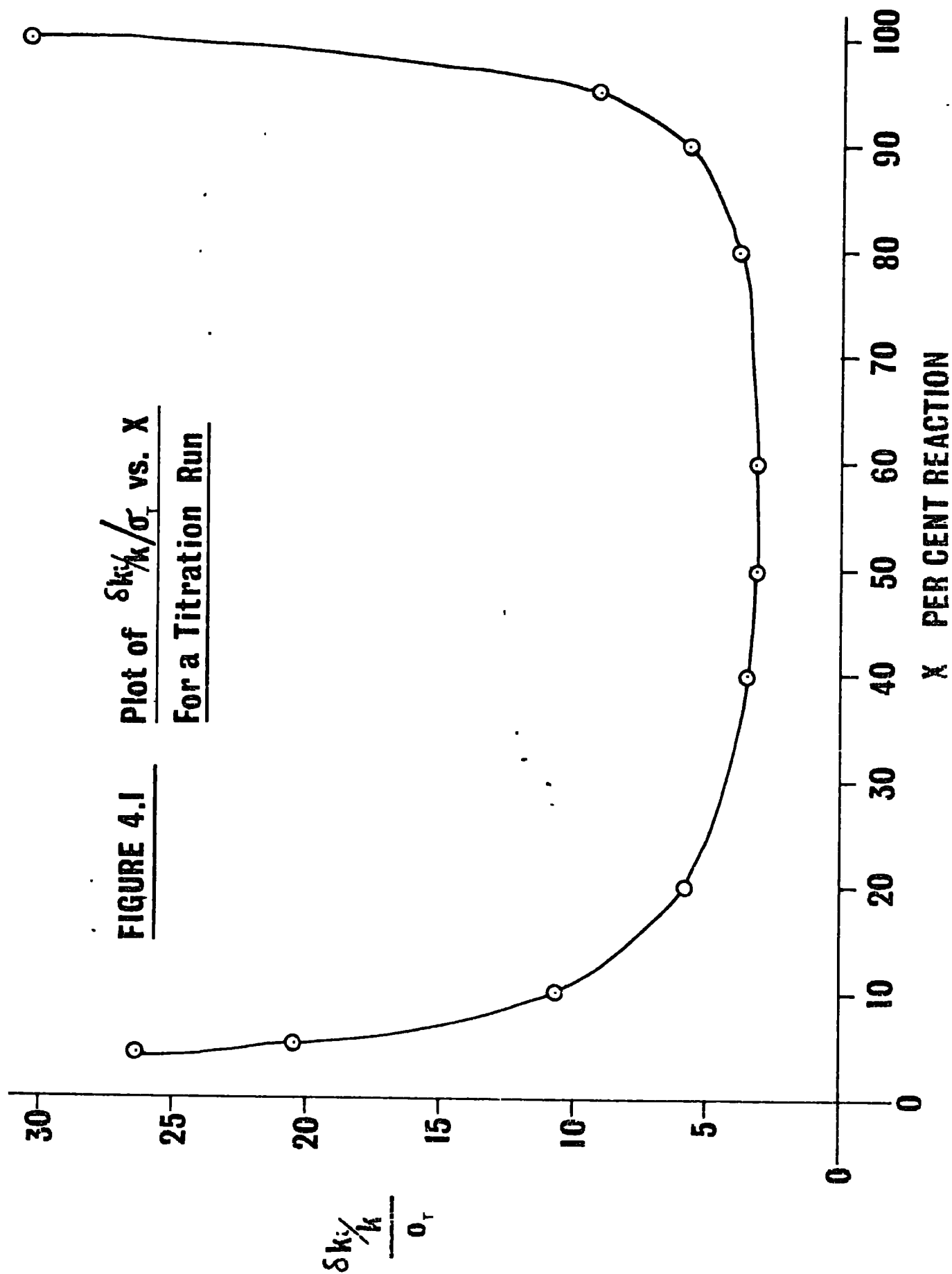
FIGURE 4.2   Plot of $\frac{\delta k_i/k}{0_p}$ vs X
For a Conductance Run
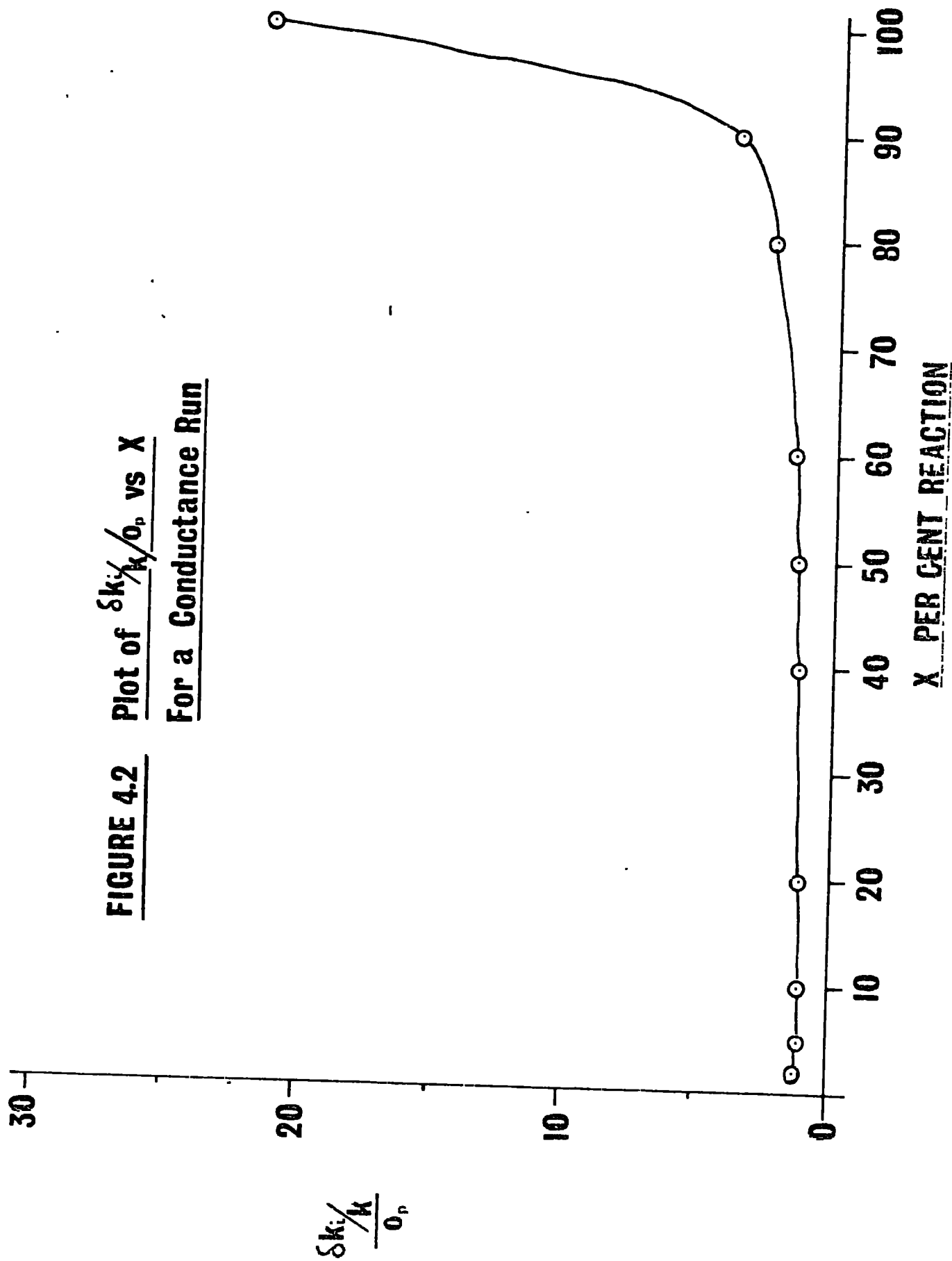
variation of $\dfrac{\delta k_i/k}{\sigma}$ over these ranges corresponds to a

four fold variation in the weight factors, w, a variation

which can be neglected, so that no error arises from the

assumption of unit weight factors for all points under these

conditions.

No similar simplification applies to the calculation of

a rate coefficient from equation 4.5. Moreover, it is

impossible to use a similar technique to find the optimum

range of rate coefficients, since the value of the rate

coefficient can now only be obtained from a consideration

of all the readings taken. However, it is possible to

calculate the standard deviation of the rate coefficient

relative to σ for hypothetical runs. In such runs it may

be assumed that each reading differs by one standard deviation

from its correct value, thus giving an indication of the

reliability of the rate coefficient calculated by the various

methods. The results of such calculations are summarised

in Table 4.2. It can be seen that the accuracy of the rate

coefficient obtained from equation 4.5 does not differ greatly

from that obtained by equation 4.4, particularly for the

conduct imetric runs. This conclusion is reached in spite

of the larger number of disposable parameters involved in

equation 4.5 In complete contrast the use of equations 4.6

and 4.7 leads to a substantial increase in the estimated

standard error of the rate coefficient. Clearly, these

expressions are valuable when no infinity determinations

can be carried out but in this thesis, the additional in-

accuracies caused by the use of equations 4.6 and 4.7 are

clearly greater than any systematic error resulting from

TABLE 4.2

Minimum Erros in the Rate Coefficient

The values quoted refer to fifteen hypothetical and equally spaced observations from the range X_1 to X_{15}

Equation	X_1	X_{15}	$\dfrac{\sigma_k/K}{\sigma_T}$	$\dfrac{\sigma_k/K}{\sigma_p}$
4.4	0.2	0.875	0.858	-
	0.01	0.50	-	0.311
4.5	0.01	0.875	1.389	-
	0.01	0.50	-	0.366
4.6	0.01	0.97	2.972	1.228
4.7	0.01	0.875*	2.592	1.599

*   For each reading in this range, another reading two half lives later has been assumed.

accurately determined values of the infinity reading.

Table 4.2 also shows quite clearly that there is a two to four times increase in accuracy when the reaction is followed by conductance rather than by titration; even if the fractional error of the infinity determinations are the same for both methods.   The greater accuracy of such determinations argues further in favour of the adoption of this method which should give a tenfold improvement in the estimated standard error of the rate coefficient (σ_T approximately five times σ_p). Further improvement in the estimated accuracy can be obtained by increasing the number of determinations in a given run, such improvement is proportional to the square root of the number of determinations.   Thus a further five fold increase in accuracy (decrease in σ_k) should result from kinetic runs involving 300 separate determinations instead of the usual twelve for a typical titration run.

From these considerations, on the assumption that conductance is directly proportional to concentration (see, however, section 5.1) there should be no difficulty in obtaining a value of σ_k/k less than 1×10^{-4}, an accuracy very much better than previously reported.

CHAPTER FOUR - REFERENCES

1.   COLLINS   J.Chem.Phys. 1957, <u>26</u>, 398

2.   KOHNSTAM   private communications.

CHAPTER FIVE

RESULTS AND DISCUSSION OF THE CALCULATED RATE COEFFICIENTS

5.1   Introduction

The present hydrolysis of benzhydryl chloride in 70% acetone was followed by noting the conductance of initially 0.0015m to 0.0030m solutions, between 200 and 500 readings were taken for each run.   Full details of experimental procedures are given in Chapter 6.

It was pointed out in Chapter 4 that conductance measurements offered the best hope of obtaining accurate rate coefficients calculated from equations 4.3, 4.4 and 4.5 although it was stressed in the discussion that the arguments were based on the assumption of direct proportionality between conductance and concentration.   Whilst such an assumption is strictly not correct it has frequently been employed in kinetic work in the past and it was hoped that it might cause no significant error in the present work. A test of the validity of this assumption was provided by the individual rate coefficients which should be independent of the stage of the reaction at which they were determined.

Typical results, shown in Table 5.1, very clearly demonstrate that this assumption is not justified under the present conditions.   The decrease of the individual rate coefficients with increasing extent of reaction, is more marked in the experiment involving the larger initial concentration and always well outside the limits of accuracy with which it was hoped to determine the rate coefficient. These observations are fully consistent with a significant

effect arising from errors as a result of assuming direct proportionality between conductance and concentration.

TABLE 5.1

Individual Rate Coefficients from Equation 4.3*

X	Run 19[+] 10^4k	Run 20[‡] 10^4k
0.05	5.006	5.175
0.10	5.006	5.142
0.15	5.003	5.113
0.20	5.002	5.093
0.30	4.988	5.050
0.50	4.949	5.004
0.70	4.912	4.943

*   Temperature   = 25.007°

+   Initial concentration $1.7 \times 10^{-3}m$

‡   Initial concentration $2.4 \times 10^{-3}m$

X   is the fraction reaction

The obvious way of overcoming this difficulty would have been the experimental determination of the relation between conductance and concentration. In carrying out such a procedure it would have been essential to ensure a very high accuracy in the concentration measurements, bearing in mind that conductance can be measured with an accuracy of 2×10^{-4}. Initial experiments carried out showed that a similar precision for the measurement on hydrochloric acid in the relatively volatile 70% aqueous acetone could only

be achieved with great difficulty, and that the construction
of experimental conductance-concentration curves at each
temperature to be studied would have taken an inordinate
length of time.   The alternative to determining this
relationship was to assume a relationship between these
two quantities in terms containing unknown parameters,
which could then be included in the rate equation as disposable
constants.   The latter procedure was adopted and the various
possibilities are outlined in the following sections.

5.2   Conductance-Concentration Relationships

Two general types of relations between conductance
and concentration were employed, most attention was given
to the empirical relationship, equation 5.1.

$$c_{HC\ell} = A. L + B. L^{3/2} + C + DL^2 \qquad 5.1$$

where $L = \lambda - \lambda_s$, the conduc·tance of the solution
after correction for the solvent conductance.

Equation 5.1 has no theoretical significance, although it
has a form similar to that of the Onsager Equation and may
include an allowance for the self ionisation of the solvent.
This accounts for the inclusion of the constant term, C,
which is included for the sake of completeness, although it
never appears in the rate equation which invariably involves
differences between two concentrations.   A simplified form
of equation 5.1 omitting the final term (D=0) was also
frequently employed.

A theoretically more correct expression is given by
the Onsager Equation:

$$\Lambda = \Lambda_0 - (\alpha \Lambda_0 - \beta)\sqrt{c}$$

where Λ is the equivalent conductance and the subscript $_0$ indicates the equivalent conductance at infinite dilution α and β are constants.

The form of the above equation is inconvenient for the present purposes, but it can be transformed into equation 5.2, which includes another parameter, γ :

$$L = \alpha . c \left(1 + \beta c^{\frac{1}{2}} + \gamma . c \right) \qquad 5.2$$

If the final term of the equation is neglected, ($\gamma = 0$), then only a negligibly smally error arises from writing equation 5.2 in the form:

$$c = \frac{AL}{1 + \dfrac{BL^{\frac{1}{2}}}{1 + CL^{\frac{1}{2}}}} \qquad 5.3$$

Details are shown in Appendix 1.

5.3 Conductance Concentration Relationships Used in the Rate Equation

5.3.1 Equation 5.1 in the Rate Equation 4.4

If the conductance and concentration are related by equation 5.1 substitution in the rate equation, equation 4.4, leads to equation 5.4, details are given in Appendix 2.1

$$y = k = \frac{1}{T} \ln \left(\frac{1 - X_0}{1 - X} \right) + \frac{1}{T} \ln \left(1 + A_3 \frac{X_0}{1 \, x \, X^{\frac{1}{2}}} + A_4 . X_0 \right)$$

$$- \frac{1}{T} \ln \, 1 + A_3 \frac{X}{1 \, x \, X^{\frac{1}{2}}} + A_4 \, X \qquad 5.4$$

where

$$A_3 = \frac{A_3^1}{1 + A_3^1 + A_4^1} \qquad , \qquad A_4 = \frac{A_4^1}{A + A_3^1 + A_4^1}$$

$$A_3^1 = \frac{B}{A} . L_\infty^{\frac{1}{2}} \qquad , \qquad A_4^1 = \frac{D}{A} \, L_\infty$$

If it is assumed that $D = 0$ in equation 5.1, then A_4 and A_4^1 in equation 5.4 becomes zero. Clearly, the first of the three terms on the right hand side of equation 5.4 has much greater significance than the other two, so that the statistical weight factor to be assigned to each experimental point, y_1, can be obtained from this first term alone by the standard methods (see section 4.4), when

$$w \quad \propto \quad \left(\frac{1}{X} - 1\right)^2$$

Initially it was assumed that $D = 0$ and a rate coefficient was obtained from equation 5.4 for a series of arbitrarily chosen values of A_3 to give a minimum error in y, the rate coefficient. The resulting "best" value of A_3, and hence the "best" value of B/A gave identical rate coefficients which showed no regular variation with the stage of reaction, see Table 5.2.

TABLE 5.2

Individual Rate Coefficients at Various Stages of Reaction

The data refer to Solvent III at 25.007°, for Run 19, with B/A = 1.40

X	$10^4 k$
0.15	4.800
0.25	4.802
0.40	4.791
0.55	4.799
0.70	4.803

This suggests that equation 5.1, with $D = 0$, represents a satisfactory relationship between conductance and concentration.

Similar observations applied to all kinetic runs carried out.

Alternatively and probably more correctly, the rate coefficients can be obtained from equation 5.4 by the method of non linear least squares, which again adjusts the parameters to give a minimum weighted error in y. Clearly this procedure should give the same result as the reiteration method in the previous paragraph. These methods were outlined in Appendices 6.1 and 6.3 respectively. It can be seen that in Table 5.3 this prediction applies.

TABLE 5.3

Rate Coefficients for equation 5.4 by Reiteration and Non Linear Least Squares Methods

The data refer to Solvent III at 25.007°

	Reiteration		Non Linear Leat Squares	
Run	$10^4 k$	B/A	$10^4 k$	B/A
19	4.803$\pm$0.00094	1.41	4.803$\pm$0.00113	1.41
20	4.797$\pm$0.00112	1.65	4.797$\pm$0.00160	1.65

The non-linear least squares method leads to a larger estimate of the standard error of the rate coefficient than the reiteration method. Such an observation is only to be expected since these methods involve one and two disposable parameters, respectively; A_3 = B/A is not a disposable parameter in the reiteration method, it is a chosen parameter.

It is important to note that each individual rate coefficient is subject to a systematic error arising from any error in the conductance reading taken at zero time. This type of systematic error has been discussed in section

4.1.   The significance of the zero errors can be obtained
by calculating a series of "final best" rate coefficients
for a given run, corresponding to a choice of different zero
readings in the early stages of reaction.

Typical results of such calculations are shown in Table 5.4
It can be seen that the choice of zero reading has no effect
on Run 20, outside the limits of experimental error, however,
for run 48 there is a substantial variation.   Similar obser-
vations applied to other kinetic runs.   Thus the fact that
a substantial dependence of the value of the final "best"
rate coefficient on the choice of the zero reading was
frequently found, suggested that equation 5.4 was unsuitable

TABLE 5.4

The Effect of the Choice of "Zero" Readings on the
Parameters Calculated from Equation 5.4

	RUN 20a			RUN 48b	
$100.X_o$	$10^4 k$	B/A	$100X_o$	$10^4 k$	B/A
2.7	4.797±0.00019	1.65	0.98	1.433±0.000088	1.92
2.7	4.796±0.00019	1.67	1.3	1.432±0.000085	1.94
3.5	4.798±0.00021	1.65	1.8	1.436±0.000077	1.84
4.0	4.798±0.00022	1.64	2.2	1.439±0.000063	1.77
4.3	4.797±0.00021	1.65	2.7	1.435±0.000085	1.86
4.8	4.797±0.00022	1.65	3.3	1.434±0.000110	1.89
6.3	4.798±0.00023	1.65	3.7	1.440±0.000061	1.74
6.4	4.798±0.00025	1.64	4.5	1.440±0.000065	1.74
			5.4	1.441±0.000065	1.70
			6.2	1.442±0.000065	1.66

a - Solvent III, Temperature = 20.006°   N = 236

b - Solvent III, Temperature = 14.996°   N = 293

for the calculation of accurate rate coefficients.   It has
been already pointed out (see section 4.1) that zero errors
should be small, when the progress of the reaction is followed

by a conduct imetric method, but it now appears they are
not negligibly small.   It is possible that the observations
outlined above arise, at least partly, from an incomplete
supression of the self ionisation of the solvent by the
products in the early stages of the reaction.

5.3.2   Equation 5.1 and the Rate Equation 4.5

The systematic zero errors in the rate coefficient can
be avoided by the use of equation 4.5   The appropriate form
of this expression, together with equation 5.1, the expression
relating conductance and concentration, is readily derived
from equation 5.4 by combining all terms involving measurements
at zero time into a single disposable parameter (A2).
Equation 5.4 can then be written in the form:-

$$y = \ln(1-X) = A\,T + A2 - \ln\left(1 + A_3 \cdot \frac{X_1}{1+X^{\frac{1}{2}}} + A_4 \cdot X\right)$$

$$\ldots\ldots\ldots 5.5$$

where A_1 = $-k$

A_2 involves all the terms continaing X_o.

Details are given in Appendix 2.2.   Anticipating the later
discussion, it can be stated that this expression with $A_4 = 0$
(i.e. D = 0) was finally adopted as giving the most reliable
rate coefficients; no results are therefore given in this
section.   The expression with a non zero value of A_4 should
ideally give the same rate coefficient but with a larger error
in view of the larger number of disposable parameters now
involved.

The effect of choosing A_4(D) as zero and as a disposable

parameter in the best estimate of the rate coefficient calculated from equation 5.5 is illustrated in Table 5.7 where it can be seen that the introduction of A_4 alters the rate coefficient by an amount exceeding the estimated standard error, although it predicts y with better precision (not shown in Table 5.7). This observation is by no means unexpected and illustrates one of the weaknesses of employing a least squares procedure for the determination of one of several disposable parameters in a "theoretical" expression.

5.3.3   Equation 5.2 and Rate Equations 4.3 and 4.4

In principle a rate equation which avoids systematic zero errors can also be obtained by substituting the alternative conductance-concentration relationship (equation 5.2) into the line with intercept equation. For the special case when $\gamma = 0$, it can be shown (see Appendix 2.3) that the resulting rate equation can be written in the form:-

$$y = \ln(L_\infty - L) = A_1 + A_2 T + \ln(1 + Y) - \ln(1 + W) \ldots\ldots 5.6$$

where
$$A_1 = \ln(C_\infty - C_0) - \ln A$$
$$A_2 = -k$$
$$A_3 = B$$
$$A_4 = C$$
$$Y = (A_3 + A_4) \cdot L_\infty^{\frac{1}{2}}$$

and
$$W = A_4 \cdot L_\infty^{\frac{1}{2}} - \frac{A_3}{1 + (A_3 + A_4) \cdot L_\infty^{\frac{1}{2}}} \cdot \frac{L}{L_\infty^{\frac{1}{2}} + L^{\frac{1}{2}}}$$

The mean rate coefficient was obtained from the experimental data by the method of non linear least squares for a number of arbitrarily chosen values of the parameter A_4. The value corresponding to the minimum error in $A_1(k)$ was
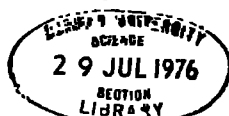
accepted. Table 5.5 shows the results of such calculations for a typical run.

TABLE 5.5

Results Calculated from Equation 5.6

The data refer to Solvent III, Run 19, Temp = 25.007°

A_4	A_1	A_3	$10^4 k$
-5	5.66	0.83	4.783 ± 0.00115
-3	5.66	0.99	4.793 ± 0.00072
-1	5.65	1.15	4.797 ± 0.00048
0	5.65	1.23	4.803 ± 0.00047
1	5.65	1.33	4.805 ± 0.00046
3	5.65	1.53	4.811 ± 0.00048
5	5.64	1.75	4.816 ± 0.00053

It can be seen that whilst the estimated standard error in the rate coefficient is small, the "best" value is relatively insensitive to the chosen value of A_4, in the range A_4 = 0 - 3. Other rate coefficients obtained by this method are shown in Table 5.7.

A rate equation based on the extended form of the Onsager Equation (equation 5.2) was derived in a somewhat different manner using the rate equation 4.3, with an additional disposable parameter replacing terms involved in the zero reading. This equation takes the form:-

$$y = X = (1 - A_4 e^{-A_1 T}) \left(1 + A_2 \left((1 - A_4 e^{-A_1 T})^{\frac{1}{2}} - 1 \right) + A_3 (-A_4 e^{-A_1 T}) \right) \qquad 5.7$$

where $X = L/L_{\infty}$

$A_1 = k$

$$A_2 = \frac{\beta c_{\infty}^{\frac{1}{2}}}{1 + \beta c_{\infty}^{\frac{1}{2}} + \gamma c_{\infty}}$$

$$A_3 = \frac{\gamma c_\infty}{1 + \beta c_\infty^{\frac{1}{2}} + \gamma c_\infty}$$

$$A_4 = 1 - \frac{c_0}{c_\infty} + \frac{\delta^1}{c_\infty}$$

and δ^1 is the unknown error in c_0.

Full details of the derivation are shown in Appendix 2.4.
Equation 5.7 has the advantage that the rate coefficient
is obtained by the minimisation of errors in the experimental
quantity X, instead of a function derived from X (say $\ln(1 - X)$).
However, the values of the parameters A_1, A_2, and A_3 depend
not only on the temperature but also on the initial concen-
tration of the run in question, since it can be seen that
A_2 and A_3 are functions of β and γ and c_∞ .   Clearly any
rate expression can only be considered to give reliable rate
coefficients if it leads to the same value of β^1 and γ for
different runs in the same solvent and at the same temperature.
The evaluation of β and γ from experimentally determined
values of A_2 and A_3 requires further approximation similar
to those in the derivation of equation 5.3 from 5.2.   The
approximation methods employed and the results of the
calculations are not discussed here since it was found that
replicate experiments at the same temperature lead to slightly
different rate coefficients (see Table 5.7).   Moreover, in
spite of the inclusion of a disposable parameter to avoid
errors in the measurement of c_0, it was found that the rate
coefficients (see Table 5.6) did depend to some extent on the
choice of this reading.   Contrary to procedures in the
calculations via equation 5.4 by the method of non linear
least squares, the present procedure involves an initial

TABLE 5.6

Rate Coefficients obtained from Equation 5.7 for Various Zeros

$100.X_0$	$10^8 VY^*$	10^4 k Run 19
3.6	5.97	4.815 ± 0.00175
3.7	5.91	4.815 ± 0.00174
3.8	4.09	4.813 ± 0.00149
3.8	4.10	4.813 ± 0.00150
4.6	3.04	4.809 ± 0.00138
4.6	3.71	4.810 ± 0.00150
5.2	2.80	4.807 ± 0.00139
5.3	2.85	4.808 ± 0.00142
7.5	2.88	4.806 ± 0.00160

$$* \ VY \ = \ \Sigma w \delta y^2/n - 4$$

trial value for A_4, which is based on the chosen zero and arises from the definition of A_4, viz:-

$$A_4 \ = \ 1 - \frac{c_0}{c_\infty} + \frac{\delta^1}{c_\infty}$$

Thus whilst the zero is not included as such, it is required implicitly in the calculation, the existence of a zero error is therefore not surprising. Table 5.6 also shows that the smallest error in the VY, occurs with the minimum value for the estimated standard error of the rate coefficient, as would be expected. Similarly, the error in the rate coefficient obtained from this expression containing four disposable parameters is comparable to that obtained for the four parameter form of equation 5.5 and larger than that obtained from the various three parameter equations.

Before the significant zero error, arising in this type

of calculation was appreciated, rate constants were also calculated on a similar basis using a two parameter Onsager equation (equation 5.3). The resulting rate equation is:-

$$y = \ln\left(\frac{1 + X}{1 + X_0}\right) = -kT - \ln\left(\frac{a + b}{a + b_0}\right) \qquad 5.8$$

where $X = L/L_\infty$

$X_0 = L_0/L_\infty$

$a = 1 + CL_\infty^{\frac{1}{2}}$

$$- b = \frac{\dfrac{BL}{L_\infty^{\frac{1}{2}} + L^{\frac{1}{2}}}}{1 + (B + C) L_\infty^{\frac{1}{2}}}$$

$$- b_0 = \frac{\dfrac{BL_0}{L_\infty^{\frac{1}{2}} + L_0^{\frac{1}{2}}}}{1 + (B + c)L_0^{\frac{1}{2}}}$$

Details are given in Appendix 2.5. Rate coefficients were calculated from equation 5.8 in a similar manner to those calculated for equation 5.6 using arbitrarily chosen values for C. The rate coefficients were calculated for a large number of experiments for this expression. Unfortunately, the results were not examined for any zero errors.

5.4 A Comparison of Equations Used in the Calculation of Rate Coefficients

Table 5.7 shows the variation of the rate coefficients and their associated standard errors obtained for the different rate equations. It can be seen that for equation 5.5 (A_4 = 0 ie D = 0) in equation 5.1 leads to by far the best agreement between the final rate coefficients of replicate kinetic runs. This was surprising because equation 5.5 is based on the simplest relationship that could exist between conductance and concentration, equation 5.1. It may well

be that the introduction of further parameters into this relationship and hence the rate equation[*] helps to decrease the reliability (and hence the value) of the most important parameter, the rate coefficient (see section 5.3.2), since all parameters are obtained via the minimisation of the experimental quantity y.   This may also account for the slightly different values of the rate equation obtained by different equations for the same kinetic run.   As equation 5.5 (A_4 = 0) gave by far the best agreement between the rate coefficients calculated for replicate runs it was decided to base the discussion on the rate coefficients obtained from this expression.

TABLE 5.7

Rate Coefficients of Individual Runs from Different Rate Equations

SOLVENT III Temp. = 25.007	RUN 19	RUN 20
10^4 k Equation 5.5 (D=0)	4.802±0.0009	4.798±0.0008
Equation 5.5 (D≠0)	4.814±0.0030	4.780±0.0034
Equation 5.6	4.803±0.0005	4.786±0.0006
Equation 5.8	4.827±0.0008	4.840±0.0027
Equation 5.7	4.811±0.0016	4.767±0.0017

SOLVENT III Temp. = 10.006

Equ.	RUN 49	RUN 50	RUN 51	RUN 52
(D=0)5.5	0.7538±0.003	0.7530±0.0003	0.7560±0.0002	0.7841±0.0004
5.8	0.7609±0.0001	0.7710±0.0003	0.7740±0.0004	0.7713±0.0004
5.7	0.7479±0.0010	0.7593±0.0070	0.7562±0.0007	0.7552±0.0004

SOLVENT IV Temp. = 20.029

Equ.	RUN 57	RUN 58	RUN 59
(D=0)5.5	2.601±0.0005	2.593±0.0006	2.609±0.0010
5.8	2.651±0.0019	2.644±0.0020	2.658±0.0020
5.7	2.586±0.0014	2.577±0.0021	2.599±0.0014

* The simplified Onsager equation also involves three parameters, even though it is basically a two parameter relationship, equation 5.2 with X= 0.

5.5 Final Form of the Rate Equation

5.5.1 Final Form of Equation 5.5

Having decided to assume zero value for the parameter D in equation 5.1, A_4 can be omitted from equation 5.5 which can therefore be written in the form:-

$$y = \ln(1 - X) = A_1 T' + A_2 - \ln\left(1 + A_3 \cdot \frac{X}{1 + X^{\frac{1}{2}}}\right) \qquad 5.9$$

where $X = L/L_\infty$

$A_1 = -k$

A_2 involves all the X_0 terms

$$A_3 = \frac{A_3^{\frac{1}{3}}}{1 + A_3^{\frac{1}{3}}}$$

$$A_3^{\frac{1}{3}} = \frac{B}{A} \cdot L_\infty^{\frac{1}{2}}$$

All the parameters were obtained by the method of weighted non linear least squares (described in Appendix 3), and hence the rate coefficient from A_1 and B/A from A_3. Ideally, the replicate runs should give precisely the same values for the rate coefficient and B/A within the limits of experimental error, but small variations outside this range were found. This is illustrated in Table 5.8 for a typical temperature.

TABLE 5.8

Results from Equation 5.9 in its Final Form
Data refer to 14.996°, Solvent III, Runs 45 -48

Run	N	10^6VY	10^4k	B/A
45	570	3.289	1.4460±0.00091	1.516±0.025
46	296	1.087	1.4299±0.00051	1.968±0.021
47	299	1.370	1.4262±0.00069	2.061±0.014
48	293	0.873	1.4332±0.00061	1.903±0.014

A summary of results produced from equation 5.9 for all runs carried out will be found in Table 5.13. Table 5.8 shows that the largest value of the rate coefficient at a given temperature is associated with the smallest value of B/A and vice versa, so that the various replicates could be expected to give better agreement between their rate coefficients if B/A was the same for all runs. It seems very likely that the relatively poor agreement between the "best" rate coefficient and the "best" B/A for the individual runs arises from the very nature of the least squares calculation which merely minimises the error in the y's.

In principle, the parameters B/A and the rate coefficient for a particular temperature could be obtained as the means of the values given by equation 5.9 for the individual runs, but such a procedure would make it difficult to decide which experimental points should be rejected as discordant. It seems better to calculate the rate coefficient and B/A from a combined consideration of all the runs carried out at the temperature in question. However, the statistical weight, g, to be assigned to each run* requires some discussion. Although it is attractive to give the same weight to each run, such a weighting scheme is unlikely to be justified especially when different runs involve different numbers of readings (N = 200 to 500) different values for the VY's (see Table 5.8) and as the occasional run was clearly relatively

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* this quantity is quite distinct from the weight factors, w, assigned to each individual reading of a run.

inaccurate (see Table 5.13). Calculations were arranged so that the rate coefficient and the B/A value for each individual run could be calculated, but the exclusion of discordant points was based on the residuals calculated from the values of the rate coefficient and B/A for the temperature in question, i.e. the values of these parameters obtained from a combination of all the runs at that temperature. Details of the calculations are given in Appendix 4.

5.5.2 The Weight Factors Applied to Each Run.

Initially, it was assumed that the weight factors to be assigned to each run could be identified with the reciprocal of the variance of the experimental points:-

$$g \propto \frac{-1}{Vy} \quad ; \quad vy = \frac{\Sigma w_i \, \Delta_i^2}{n - 3}.$$

It was thought that vy represented a measure of the average reliability of the individual points within the run in question but calculations employing this weighting procedure (Programme A82F) led to unexpected results. An alternative scheme (Programme A82M) assigned to each run a weight factor corresponding to the reciprocal of the variance of the best estimate of the rate coefficient for that run; i.e.

$$g \propto \frac{1}{v(k)}$$

Table 5.9 shows the "best" rate coefficient and B/A for each temperature obtained by these two weighting procedures. It shows clearly that these two methods do not give the same results even within the limits of the estimated standard

TABLE 5.9

A summary of the Final Rate Coefficients and B/A values for Each Temperature Obtained from the Two Weighting Procedures

RUN	TEMP.	RUNS	N	A82M		A82F	
				$10^4\,k$	B/A	$10^4\,k$	B/A
III	25.008	19 – 22	811	4.79713 ± 0.00141	1.592 ± 0.012	4.7181 ± 0.00635	1.927 ± 0.0055
III	20.010	41 – 44	986	2.65275 ± 0.00072	1.779 ± 0.0009	2.6680 ± 0.00172	1.591 ± 0.022
III	14.999	45 – 48	1458	1.43120 ± 0.00026	1.942 ± 0.0006	1.4333 ± 0.00066	1.930 ± 0.016
III	10.026	49 – 52	1202	0.75439 ± 0.00017	1.959 ± 0.010	0.75349 ± 0.00040	2.023 ± 0.022
IV	20.029	56 – 59	761	2.59320 ± 0.00096	1.669 ± 0.012	2.5768 ± 0.00179	1.889 ± 0.026
IV	15.014	60 – 64	1088	1.39892 ± 0.00020	1.765 ± 0.005	1.40173 ± 0.00035	1.682 ± 0.010
IV	10.181	65 – 67					
IV	5.021	77,78	1597	0.753008 ± 0.00010	1.838 ± 0.005	0.75145 ± 0.00022	1.937 ± 0.012
IV		87,88					
IV		100, 101	1544	0.379537 ± 0.00012	2.078 ± 0.017	0.37980 ± 0.00032	2.354 ± 0.024
IV	0.821	102					
IV		105-106	1538	0.211698 ± 0.00005	1.872 ± 0.005	0.211568 ± 0.00010	1.918 ± 0.024

error.   The outstanding discrepancy is found for runs
19 - 22 at 25° where the "best" rate coefficients differ
by as much as 2%.

Examination of the calculations for individual runs
showed that the procedure of rejecting discordant points
leads to different discards in the two programmes producing
considerably different results.   For a group of runs at
one temperature which appeared to be accurate as judged by
the magnitude of VY, this term tended to become more accurate
by discarding discordant points (as expected) in calculations
using A82M, but became less accurate when A82F was used.
The converse of this was found for the less accurate runs.
This of course is contrary to the implicit requirement that
the exclusion of divergent points and the adjustment of
disposable parameters should give better results.   Table
5.10 shows that the two programmes (A82M and A82F) yield
very similar rate coefficients of comparable accuracy before
the exclusion of discordant points.   The final values
obtained from calculations via A82M do not differ greatly
from the initial values, and are invariably more accurate.
This is in complete contrast to the results from A82F where
larger differences are apparent between initial and final
calculations and the estimated standard error of the final
rate coefficient is often greater than its initial value.
The most striking discrepancy of this type is found for
runs 19 - 22, and illustrates the different consequences of
the two weighting schemes.

Table 5.11 shows that the initially highly inaccurate

TABLE 5.10

Initial and Final Values of the Mean Rate Constant

			10^4 k A82M	
SOLV,	TEMP*	RUNS	INITIAL	FINAL
III	25	19 - 21	4.7978±0.00166	4.7971±0.00141
	20	41 - 44	2.6628±0.00108	2.6528±0.00072
	15	45 - 48	1.4311±0.00032	1.4312±0.00026
	10	49-52	0.75394±0.00032	0.7544±0.00017
IV	20	56 - 59	2.5915± 0.00112	2.5932±0.00096
	15	60 - 64	1.3987±0.00022	1.3989±0.00020
	10	65-67 77,78	0.7527±0.00024	0.7530±0.00010
	5	87,88, 100,101	0.3775±0.00049	0.3795±0.00012
	0	102 104-106	0.2106±0.00045	0.2117±0.00005
			10^4 k A82F	
III	25	19 - 21	4.7997±0.00195	4.7181±0.00635
	20	41 - 44	2.6666±0.00147	2.6680±0.00172
	15	45 - 48	1.4319±0.00093	1.4333±0.00066
	10	49 - 52	0.7538±0.00033	0.7536±0.00040
IV	20	56 - 59	2.5897±0.00090	2.5768±0.00179
	15	60 - 64	1.3987±0.00039	1.4017±0.00035
	10	65-67 77 .78	0.7525±0.00046	0.7515±0.00022
	5	87,88, 100,101	0.3761±0.00078	0.3798±0.00032
	0	102, 104-106	0.2157±0.00087	0.2116±0.00010

* Approximate temperature, the accurate temperatures
are shown in Table 5.9

TABLE 5.11

Comparison of Initial and Final Values of $10^6(\sum w \delta y^2/n-3)_j$

The data refer to solvent III

| TEMP. | RUN | INITIAL | FINAL VALUES | |
			A82M	A82F
25	19	0.272	0.147	10.661
	20	3.298	0.145	3.161
	21	193.85	221.024	11.479
	22	0.932	0.169	10.002
20	41	7.573	22.80	3.579
	42	1.777	0.880	1.258
	43	1.713	0.308	2.176
	44	0.992	0.713	2.930
15	45	3.461	3.306	1.620
	46	1.773	1.079	1.436
	47	2.016	1.381	2.301
	48	1.634	0.872	2.103
10	49	0.657	0.524	1.491
	50	1.274	0.612	1.174
	51	3.639	0.671	1.905
	52	2.706	2.438	5.573

run 21 apparently becomes more accurate after the rejection
of discordant points in A82F, whilst the other initially
more accurate runs appear to become less reliable, with all
the runs finally indicating reliabilities of the same order.
Calculations using A82M, however, tend to improve the indicated
accuracy of the more reliable runs after the rejection of
discordant points and do not point to a virtually similar
reliability for all the runs in the final calculation.

As the results obtained using A82M are those expected
from a valid weighting procedure, it was decided to base
subsequent discussion on these results.   The anomalous
results provided by the alternative weighting procedure,
applied in A82F were surprising but may be connected with
the fact that the weight factors now have no statistical
significance.   Alternatively some error in the relevant
computer programme may be responsible, although none could
be found, even after a thorough detailed examination of the
programme was undertaken.   This programme was discarded
once it was recognised that acceptable results could be
obtained using the alternative weighting procedure employed
in A82M.

5.6. Rate Coefficients from Programme A82M

The results obtained from the final method of calculation
(programme A82M) using equation 5.9, and statistical weight
factors applied to each run (g $\propto$ $1/V(k)$) are summarised in
Tables 5.13(i) and 5.13(ii).   Table 5.13(i) shows the "best"
value of the rate coefficient for individual runs ($10^4 k_{best}$),
together with the statistical weight factor ($10^{14} g$) assigned

to them.   Table 5.13(ii) show the "best" rate coefficient
and B/A for all replicate runs at a given temperature.

The reliability of these final parameters requires
some consideration.   It has already been pointed out that
the "best" values of the rate coefficient and B/A for the
individual runs may differ from each other by amounts
greater than the estimated standard error (see section 5.5.1).
A better indication of the reproduc ibility of the kinetic
data is probably obtained by calculating the rate coefficient
denoted k*, for individual runs when B/A is assigned the
best value for the combined data at a given temperature.
Values of k* are shown in Table 5.13(i) when it can be
seen that the replicates give much better agreement between
k* than the individual rate coefficients.   Nevertheless,
the k* replicates still show a larger spread of values than
is suggested by the estimated standard error of the final
rate coefficient for the combined data, $\bar{k}$, although the
weighted mean of the k* values $(k*_m)$, (the value $k*_m$ is
equivalent in Table 5.13(ii) to the mean weighted individual)
appears to be in good agreement with the value of $\bar{k}$.   The
range of values of k* can be as wide as 0.4%, approximately
ten times the value of the estimated standard error of the
rate coefficient.   It therefore seems likely that the
method of calculation adopted under estimates the standard
error of the final rate coefficient.   The conclusion is
confirmed by comparison of the rate coefficients obtained
in different solvents and at different temperatures.   In
practice the experimental temperatures and the solvents
were not precisely the same but an accurate correction factor

TABLE 5.13

Parameters Calculated from A82M

i) Parameters for individual runs

SOLV.	TEMP.	RUN	N	$10^4 k_{best}$	B/A	$10^{14} g$	$10^4 k^*$	N_{disc}
III	25.007	19	185	4.8019 ± 0.00087	1.410	1.318	4.7835	-
		20	236	4.7983 ± 0.00080	1.643	1.568	4.8044	7
		21	181	4.3467 ± 0.03392	4.904	0.001	4.7606	-
		22	209	4.8206 ± 0.00099	1.393	1.022	4.8001	1
III	20.006	41	181	2.6748 ± 0.01301	1.955	0.006	2.6835	35
		42	257	2.6675 ± 0.00127	1.611	0.622	2.6554	10
		43	279	2.6460 ± 0.00058	1.844	2.962	2.6513	15
		44	269	2.6671 ± 0.00120	1.720	0.696	2.6635	8
III	14.996	45	570	1.4456 ± 0.00091	1.516	1.217	1.4309	10
		46	296	1.4299 ± 0.00055	1.968	3.286	1.4315	8
		47	299	1.4262 ± 0.00069	2.061	2.127	1.4321	5
		48	293	1.4332 ± 0.00061	1.903	2.655	1.4319	6
III	10.006	49	243	0.75377 ± 0.00026	2.032	14.755	0.75468	3
		50	317	0.75302 ± 0.00026	2.071	14.699	0.75474	27
		51	344	0.75596 ± 0.00023	1.858	19.151	0.75392	15
		52	298	0.74180 ± 0.00041	2.198	5.795	0.75267	2

TABLE 5.13 (continued)

SOLV.	TEMP.	RUN	N	$10^4 k_{best}$	B/A	$10^{14}g$	$10^4 k^*$	N_{disc}
IV	20.029	56	201	2.5326±0.00507	2.632	0.039	2.5873	14
		57	178	2.6005±0.00054	1.600	3.375	2.5957	4
		58	204	2.5925±0.00055	1.596	3.281	2.5880	3
		59	178	2.6091±0.00096	1.664	0.897	2.6092	3
	15.015	60	214	1.3982±0.00026	1.746	15.399	1.3972	3
		61	209	1.3982±0.00053	1.791	3.608	1.3987	8
		62	211	1.4008±0.00028	1.745	12.356	1.3996	6
		63	232	1.3972±0.00032	1.640	9.711	1.3997	2
		64	222	1.4013±0.00033	1.688	8.957	1.3982	2
	10.172	65	215	0.74498±0.00032	2.185	9.641	0.75180	5
		66	316	0.75220±0.00014	1.833	47.967	0.75292	31
		67	324	0.75422±0.00021	1.750	23.181	0.75262	49
		77	336	0.75659±0.00031	1.651	10.352	0.75433	18
		78	406	0.75380±0.00026	1.739	14.841	0.75239	94
	5.016	87	384	0.37363±0.00030	2.793	10.176	0.37815	30
		88	395	0.37334±0.00079	3.906	1.613	0.38577	-
		100	405	0.38152±0.00014	1.698	44.759	0.37917	36
		101	360	0.38004±0.00014	2.035	53.427	0.37971	56
	0.816	102	367	0.21546±0.00033	1.127	9.037	0.21254	68
		104	414	0.21188±0.00007	1.853	120.62	0.21185	71
		105	375	0.21412±0.00067	1.435	2.164	0.21254	43
		106	383	0.21141±0.00007	1.899	188.44	0.21157	66

NOTES TO TABLE 5.13(i)

N =   number of points in each run.

$10^{14}g$ =   statistical weight assigned
to that run in the calculation
of the total mean.

k^* =   the rate coefficient when B/A
is assigned the "best" value
for the combined experiments
at a given temperature.

N_{disc} =   number of discordant points
rejected.

TABLE 5.13

ii) Total means for replicate runs

SOLV.	TEMP.	$10^4 \bar{k}$	$\overline{B/A}$	$k_m^\bullet$	B/A_m
III	25.007	4.79713 ±0.00141	1.592 ±0.012	4.79622	1.593
	20.006	2.65275 ±0.00072	1.779 ±0.009	2.65390	1.774
	14.996	1.43120 ±0.00026	1.942 ±0.006	1.43167	1.933
	10.006	0.75390± 0.00017	1.959 ±0.010	0.75421	1.974
IV	20.029	2.59320 ±0.00096	1.669 ±0.012	2.59392	1.663
	15.015	1.39892 ±0.00020	1.765 ±0.005	1.39857	1.774
	10.172	0.753008±0.00010	1.838 ±0.012	0.752816	1.848
	5.016	0.379537±0.00012	2.078±0.017	0.379428	2.085
	0.816	0.211698±0.00005	1.872 ±0.012	0.211709	1.861

NOTE FOR TABLE 5.13(ii)

$\bar{k}$ = final rate coefficient calculated from the combined experimental data, $\overline{B/A}$ being also calculated from the combined data.

$k_m^\bullet$ = the weighted mean of the $k^\bullet$ values (see Table 5.13(i)).

B/A_m = the corresponding value of B/A for the corresponding $k_m^\bullet$.

could easily be applied from a knowledge of the appropriate activation energies from Table 5.14. These considerations lead to Table 5.12.

TABLE 5.12

Solvent Correction Factors

Temperature	k_{III}/k_{IV} *
20.006	1.02581
14.996	1.02552
10.006	1.02384

* The ratio of the rate coefficients at that particular temperature in each solvent.

Although the value of k_{III}/k_{IV} at 20° and 15° agree within 0.03%, a figure commensurate with the estimated standard error of the rate coefficient, the ratio k_{III}/k_{IV} at 10° differs by 0.2% from the other two values suggesting a rather larger error, of the order of 0.1% for the mean rate coefficient of any run.

5.7 Activation Parameters Derived from Data Calculated from Programme A82M

In general activation parameters are most conveniently obtained from the expression[1]:-

$$\ln k = A + \frac{B}{T} + C.\ln T + D.T^2 \qquad 5.10$$

However, the application of this method to the present work would have involved some loss of accuracy in view of the fact that an allowance in the change of the solvent did not reproduce the rate coefficients to within the accuracy (see

TABLE 5.14

Activation Energies Calculated from all Possible

Temperature Combinations

SOLV.	θ_2	θ_1	θ^{*}	$10^{10}\, w^{\ddagger}$	E_{obs}	$\Delta^{\ddagger}_a$	$\Delta^{\ddagger}_b$
III	25.007	20.006	22.507	8.29	20.575	−	-0.024
		14.996	20.002	34.3	20.626	0.002	-0.013
		10.006	17.507	79.4	20.688	0.016	0.014
	20.006	14.996	17.501	8.91	20.675	0.003	0.001
		10.006	15.006	36.8	20.742	0.022	0.027
	14.996	10.006	12.501	9.47	20.806	0.037	0.045
IV	20.029	15.015	17.522	8.92	20.665	-0.007	-0.009
		10.172	15.101	35.7	20.707	-0.012	-0.006
		5.016	12.523	85.8	20.744	-0.025	-0.017
		0.816	10.423	145	20.814	0.005	0.010
	15.015	10.172	12.594	8.91	20.749	0.018	-0.012
		5.016	10.016	39.4	20.781	-0.036	-0.032
		0.816	7.916	81.9	20.863	0.006	0.002
	10.172	5.016	7.594	10.8	20.810	-0.054	-0.059
		0.816	5.494	36.8	20.919	0.015	0.002
	5.016	0.816	2.916	7.69	21.049	0.086	0.057

* mid point of temperature scale $\quad \ddagger\ w = \left[(T_2 - T_1)/RT_1T_2\right]^2$

+ $\Delta = E_{obs} - E_{calc}$; E_{calc} from a) $E = 21.011 - 0.01936.\theta$

b) $E = 21.078 - 0.03095.\theta$

$+0.00045.\theta^2$

For a) $10^4\ \sum w\Delta^2 = 0.267$ For b) $10^4\ \sum w\Delta^2 = 0.188$

the previous section) expected by the estimated standard error. Activation parameters were therefore calculated from all possible combinations of measurements at two temperatures in a given solvent from the integrated form of the Arrhenius equation[1]. It is shown in Appendix 5.1 that in the present experiments the resulting activation energies refer to the mean of the temperature range, with a negligibly small error. If the same weight factors are assigned to all the rate coefficients, the activation energy calculated from the rate coefficients at temperatures T_1 and T_2 can be assigned a weight.

$$w = \left(\frac{T_2 - T_1}{RT_1 T_2} \right)^2$$

and it can be shown that the activation parameters and their temperature coefficients obtained by this procedure (all possible combinations of pairs of temperatures) are identical with those obtained from equation 5.10. The results are shown in Table 5.14

It is shown in Appendix 5.2 that if the temperature coefficient of the activation energy (E) can be regarded as constant, then

$$E_T = E_{273} + \frac{\partial E}{\partial T} . \theta \qquad 5.11$$

where θ is the temperature in degree Celsius.

A linear variation with temperature of this parameter leads to:-

$$E_T = E_{273} + \Delta c^*_{p273} . \theta + \frac{d}{2} . \theta^2 \qquad 5.12$$

where $\quad \Delta C^*_{p273} \quad = \quad \dfrac{\partial E}{\partial T} \quad - \quad R$

and $\qquad d \qquad = \qquad \dfrac{\partial^2 E}{\partial T^2}$

The "best" values of these parameters in these two equations are shown in Table 5.15 and the resulting residuals (Δa for constant $\partial E/\partial T$, Δ_b for linear variations of $\partial E/\partial T$) are shown in Table 5.14.

TABLE 5.15

The Variation of the Activation Energy with Temperature

EQATION	E_{273} (k cal.)	$\left(C^*_p\right)_{273}$ (cal.deg^{-1})	10^4 d/2 (cal.deg^{-2})	$10^4 \ \Sigma \, w\Delta^2$
5.11	20.011	$-21.36 \pm 8.8^*$	-	0.276
5.12	20.078	-30.54 ± 44.6	4.5 ± 17.1	0.188

*a constant independent of temperature

From these data it is seen that equation 5.12 predicts that the observed activation energies are more reliable than those from equation 5.11 ($10^4 \ \Sigma \, w \Delta^2 = 0.267$ for equation 5.11 and 0.188 for equation 5.12). The parameters involved in equation 5.12, however, are associated with errors in excess of the estimated values of the parameters. No significance can be attached therefore to parameters derived from this particular expression and it can be only concluded that the present results provide no information concerning the temperature dependence of $\partial E/\partial T$. The value of $\partial E/\partial T$ required by the assumption that this parameter is independent of temperature is given by:-

$$\dfrac{\partial E}{\partial T} \quad = \quad -19.86 \ \pm \ 8.8 \ \text{cal.deg.}^{-1}$$

This value could be considered to agree within the limits of experimental error with a previous value[2] of -35.6 ± 2.7 cal.deg.$^{-1}$ for the same system, but the discrepancy between the two values is large and any agreement arises entirely from the substantial error involved in the present result. These results therefore require some comment.

5.8   Accuracy of the Rate Coefficients Calculated from Activation Parameters

The present work aimed at obtaining accurate coefficients, and it has now been established that the resulting activation parameters were not sufficiently accurate to estimate a temperature coefficient of $\partial E/\partial T$ (ΔC_p^*). Furthermore, the assumption of a constant value for this parameter gave a value subject to a larger error than previously reported[2]. One of the causes of this observation arises from the relatively small experimental temperature range (25°) now employed.   Previous determinations[2] of ΔC_p^* including that for benzhydryl chloride[2] have involved rate measurements over a range of $40 - 50^o$.

In the present work, the inevitable time lag, between the mixing of the reactant and the observation of the first reading, for the reaction system at the reaction temperature, meant that the initial reading for kinetic runs carried out above 25° could only be taken when a significant fraction of the reaction had undergone hydrolysis, thus precluding any rate measurements at temperatures higher than 25°.   The electrode system found to give good and reliable conductance readings was unfortunately unsuitable at temperatures below 0°,

when it was subject to considerable condensation by water
in the form of ice on various parts of the reaction vessel
making accurate readings difficult to take.   Since not
enough time was available to redesign the electrode system, it
was hoped that the available results would at least indicate
the accuracy capable of being achieved by this present method.

The reliability of the activation parameters and their
termperature coefficients obviously depends on the accuracy of
the rate coefficients from which they are caluclated.   It is
convenient to express this accuracy as the estimated standard
error of the rate coefficient relative to its value (σ/k),
and it has already been pointed out (section 5.6) that values
of σ/k obtained from the calculation of the reaction rates
may well represent an under estimate.   However, an alternative
value for σ/k can be obtained from the agreement between
the observed energies of activation and the value calculated
from equation 5.11.   If each of the rate coefficients is
subject to the same fractional error:-

$$\Delta = E_{obs} - E_{calc} = \left(\frac{R.T_1 T_2}{T_2 - T_1}\right) . \left(2 \left(\frac{\sigma}{k}\right)^2\right)^{\frac{1}{2}}$$

Thus

$$w \Delta^2 = 2 \left(\frac{\sigma}{k}\right)^2$$

since the weight for each activation energy E, is given by:-

$$w = \left(\frac{T_2 - T_1}{R T_1 T_2}\right)^2$$

Sixteen values of E_{obs} are available (see Table 5.13), then:-

$$\Sigma w \Delta^2 = 32. \left(\frac{\sigma}{k}\right)^2$$

so that

$$\frac{\sigma}{k} = 9.13 \times 10^{-4}$$

since

$$\Sigma w \Delta^2 = 0.267 \times 10^{-4}$$

This value is approximately four times as large as the average value obtained from the estimated standard errors calculated from A82M, and only about two to three times less than values obtained previously from runs where a smaller number of experimental observations were obtained by the less accurate titration[2,3].

It seems very likely that the introduction of the additional disposible parameter, B/A, to express the relationship between conductance and concentration is responsible for the disappointing accuracy of the present rate coefficients. An examination of the results shows that the rate coefficients are not as insensitive to the variation in B/A as had been hoped. The comparison of the "best" rate coefficients for individual runs and the corresponding k^* values (see Table 5.13) indicates that:-

$$\frac{1}{k} \cdot \frac{\partial k}{\partial (B/A)} \simeq 0.025$$

and that the "best" B/A values for reliable individual runs at a given temperature very often differ by more than 0.1. Strictly the parameter B/A should express solely the relationship between the conductance and the concentration, but it will without doubt partly serve to minimise observational errors. On this view a spread of the values of B/A among replicate runs at the same temperature would not be surprising.

On the other hand if these extraneous contributions to
B/A cancel out (see Table 5.13) when all the replicate
runs at a given temperature are combined, the final "best"
value of B/A should reflect solely the nature of the conductance
concentration relationship, and this value should therefore,
alter in a systematic way as the temperature is altered.
Inspection of Table 5.13 shows that for both solvents B/A
tends to increase with decreasing temperature but the change
with temperature does not follow any recognisable pattern
and the value at 0° is certainly anomalous.

Now the assumption of a linear relationship between
the value of B/A and the temperature leads to a set of
values which differ from those quoted in Table 5.13, although
a larger difference is found at 0°. These corrected values
of B/A can be used to give the relevant values of k^* from
$\frac{1}{k} \cdot \frac{\partial k}{\partial(B/A)}$ and hence an alternative rate coefficient (k^*_m)
at a given temperature as a weighted mean of the values of
k^*. Activation energies calculated from these corrected
rate coefficients lead to a value of $\partial E/\partial T$ which is much
closer to the earlier value[2] than those obtained from
results in Table 5.13, but the error of $\partial E/\partial T$ remains
virtually unaltered.

It would appear that the variation of B/A with temperature
is not a linear one, and the values of B/A shown in Table 5.13
could easily be subject to an uncertainty of 0.05. This
would correspond to a σ/k for a rate coefficient of approx-
imately 12×10^{-4} (using a value of $1/k \cdot \partial k/\partial(B/A)$ approx-
imately equal to 0.025), a value very close to σ/k calculated

from the temperature dependence of the activation energy shown above. It therefore seems likely that this uncertainty in B/A is responsible for the relatively poor accuracy of the activation parameters and for the observation that σ/k calculated from these parameters is of the order of four times its direct estimate. This difficulty can only be avoided by the independent determination of the relationship between conductance and concentration to a degree of precision commensurate with the accuracy that is obtained from conductance determinations. Arguments were advanced earlier in this thesis (see section 5.1) showing that this would be a matter of great difficulty in the mixed solvents employed.

It must be concluded therefore that the determination of rate coefficients for solvolysis in the mixed solvent by this method is unlikely to yield the precision (σ/k of the order of 2×10^{-4}) required for the detection of small coefficients of ΔC_p^* or $\partial E/\partial T$. These difficulties are greatly reduced in a pure solvent such as water and indeed Robertson[4] has employed independently observed Onsager parameters in his rate equation for reactions in pure water, although the results obtained only give σ/k approximately 1×10^{-3}.

REFERENCES - CHAPTER FIVE

1.   KOHNSTAM   Adv. in Phys. Org. 1967, 5, 121.

2.   KOHNSTAM   J.Chem.Soc. 1960, 2066.

3.   See for example
      PENTY   Ph. D. Thesis, Durham, 1971.

4.   KOSHY, ROBERTSON, STRACHAN   Canad. J.Chem. 1973, 51, 2958.

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CHAPTER SIX

EXPERIMENTAL DETAILS

6.1   Preparation and Purification of Materials

6.1.1   Benzhydryl Chloride

Dry hydrogen chloride was passed through a solution of benzhydrol (G. P.grade 22g)in 150 mls of dry diethyl ether for fourteen hours at room temperature in the presence of granular calcium chloride.   The ethereal solution was filtered free from calcium chloride, washed with water, 5% sodium bicarbonate, water and finally dried over magnesium carbonate.   The ether and any remaining hydrogen chloride were removed using a rotary evaporator.   The residual yellow viscous oil was then distilled under reduced pressure (b. pt. 84 - 86° at 0.2 mm.Hg.).   The hydrolysable chloride content was never less than 99% of the theoretical amount.   Carbon, hydrogen and chlorine analysis yielded:-

FOUND   Carbon 77%   Hydrogen 5.8%   Chlorine 18.6%

CALCULATED   76.7%   5.4%   17.9%

The resulting compound, a colourless viscous oil at room temperature, was stored at -15° in a blackened bottle until required.

6.1.2   Solvent Preparation

Analar grade acetone was refluxed over sodium hydroxide and potassium permanganate for four hours, then distilled at such a rate that one tenth of the refluxing volume was collected.   The distillate was then fractionated from

excess hydroquinone, generous head and tail fractions
were discarded in all cases, only one tenth of the
fractionating volume was collected.   All solvents were
made up be volume as follows: in order to prepare an X%
solvent, X mls. of acetone prepared as above were added
to 100 - X mls. of demineralised water.   Five litres of
solvent were prepared at any one time.   The solvent was
stored in a glass vessel with a lightly greased well
fitting stopper.   No solvent evaporation was ever observed.
Each batch of solvent was monitored by measuring the rate
of hydrolysis of benzhydryl chloride in that batch at 20°.

6.2   Conductometric   Cells and their Treatment

6.2.1   Cell design

In designing the cells two factors had to be taken into
consideration:-

      i) ease of handling for the faster runs
     ii) prevention of solvent evaporation

Two types of cells were tried.   One in which the electrodes
were built into a side arm (see Figure 6.1); the second type,
eventually used, had dipping electrodes.   The side arm cell
had several disadvantages.   The time taken to dismantle
the cell, inject the substrate, reassemble, dissolve the
substrate and make sure that there were no entrained air
bubbles was in excess of two minutes.   This meant that at
20° the "zero" conductance reading could never be taken
earlier than about 10% of the reaction.   This was too far
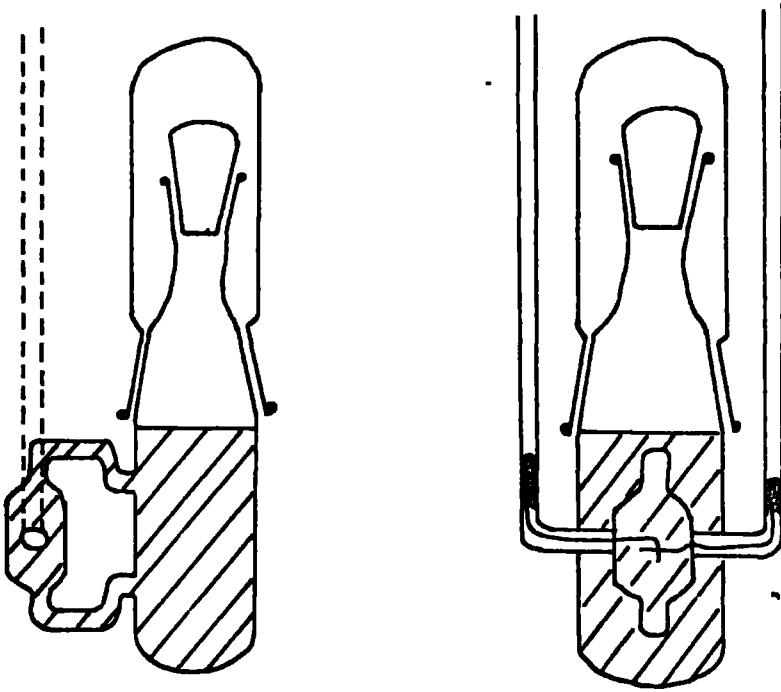into the reaction for the "zero" reading to be accurate.

FIGURE 6.1

Furthermore, solvent evaporation still appeared to take place even though the vessel was double sealed. The greatest defect of this cell was that its cell constant was exceedingly small. Consequently the concentration of the substrate had to be relatively high so that reasonably high readings could be obtained on the conductance bridge. This in turn meant that any concentration-conductance non linearity would be accentuated at these higher concentrations.

As a result of these disadvantages a further cell was designed and made, this is shown in figure 6.2. As well as overcoming all the disadvantages mentioned above, this cell was relatively easy to construct. Solvent evaporation after a run was started, was prevented by filling the cups around the tops of the joints with mercury. The electrode assembly, which was a ring type assembly in order to minimise errors due to electrode movement, was made of thick platinum foil (0.05mm.) and secured to the glass guard by means of glass support beads. Platinum wire was used only to make the connexions to the foil and to come through the glass seals, heavy guage silver wire, hard soldered to the platinum wire, was used for the rest of the length of the electrode arm. Glass tubing was pushed over the silver wires which was then surrounded by cable screening and earthed. The electrode arm was packed with silica sand dried at 120°, the top was sealed off using paraffin wax. Terminals were attached to the leads emerging from the top of the electrode arm. Connexions from here to the conductance bridge were made with crocodile clips and earthed screened cable.

LEADS TO
CONDUCTANCE BRIDGE

PLATINUM WIRE

PLATINUM GLASS
SEALS

MERCURY

BREATHE HOLE

BREATHE HOLE

ELECTRODE
ARM

PLATINUM
FOIL
ELECTRODES

GLASS SUPPORT BEADS

SILVER WIRE

GLASS ARM

GLASS
TUBING

GLASS
TUBING

DRIED
SILICA SAND

PLATINUM ELECTRODES
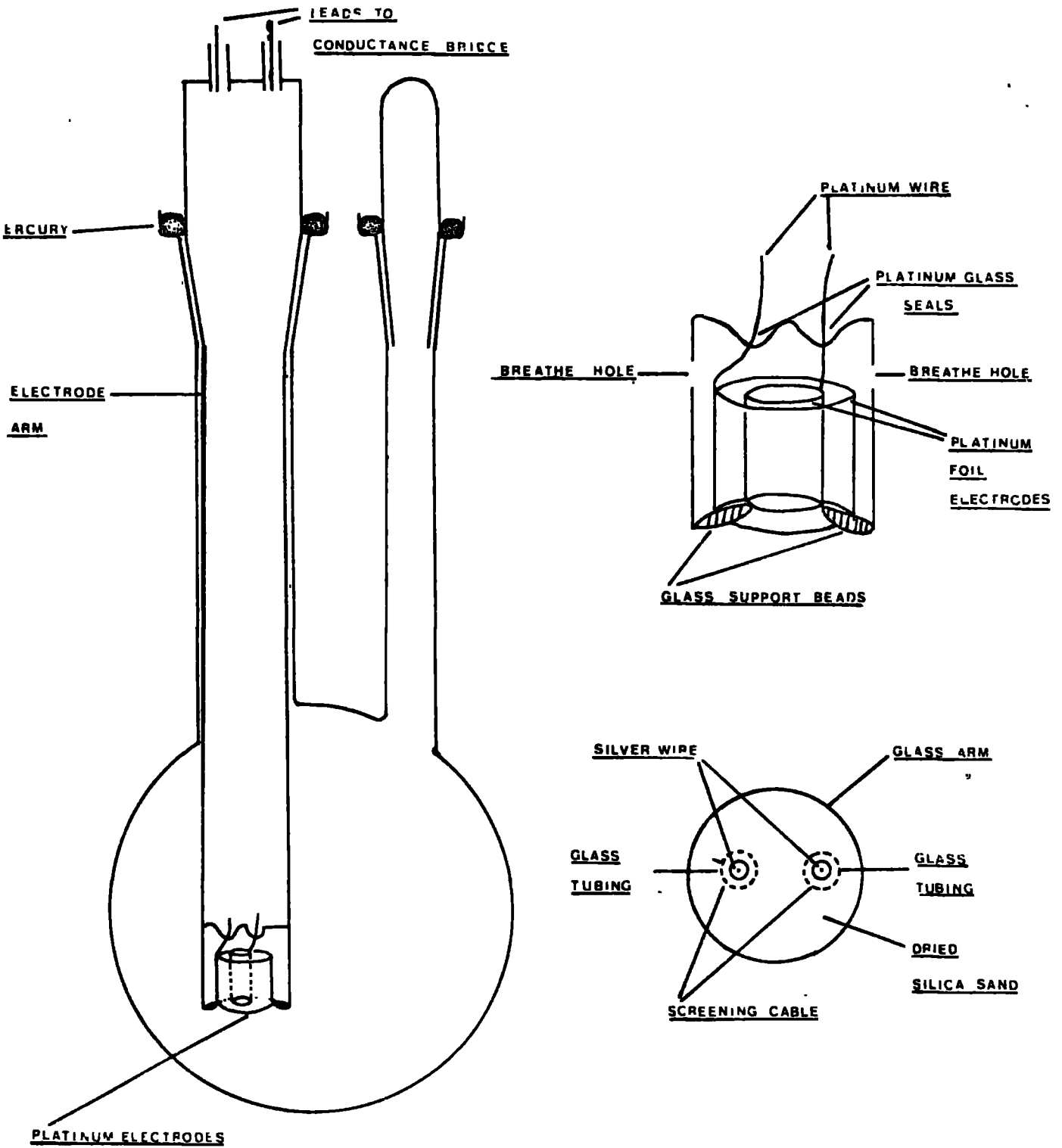
SCREENING CABLE

FIGURE 6.2

6.2.2   Cell Cleaning and Treatment

It was essential before proceeding with the experimental work that the cells and electrodes were thoroughly cleaned. They were stood in 'Analar' grade concentrated nitric acid for several days, and then heated on a water bath at 100° for twenty four hours.   When cold they were rinsed with demineralised water, allowed to stand in water for several days, heated on a water bath for several hours and thoroughly washed again.   They were dried in an oven at 150° for several hours.

Each cell had now to be aged, to avoid surface effects, with the solvent and the electrolyte.   This was achieved by first using them for several kinetic runs.   The rate constants calculated from these initial runs were found to vary by as much as ten per cent.   The cells were fit to be used when reproducible rate constants were produced and the conductance reading at infinite time remained constant within experimental error.

In order to avoid the evaporation of acetone during the preparation of a run, the solvent was pushed by means of nitrogen saturated with 70% solvent vapour, into the cell.

The cells were never allowed to stand in the thermostat bath filled with solvent alone for longer than twelve hours. Furthermore, a spent reaction mixture always remained in the cell until the cell was required for the next run.

6.3   Rate Measurements

6.3.1   Apparatus

All the runs were carried out in thermostat baths of conventional design, filled with water, and temperature control was better than $\pm 0.01^{\circ}$. In fact in a series of experiments with a platinum resistance thermometer and a high precision Wheatsone Bridge, the following variations in temperature were recorded:-

$\pm 0.0056^{\circ}$ $\qquad \pm 0.0041^{\circ}$ $\qquad \pm 0.0056^{\circ}$

Thus the temperature fluctuations in this bath, set at approximately 25° were always less than one hundredth of a degree.

The baths maintained at 0° were filled with a mixture of ethylene glycol and water. Refrigeration units were used in baths at and below 10°. The thermostat baths and the thermostating apparatus were all carefully earthed.

Mercury in glassthermometers were used for the temperature determination of the thermostat bath. They were standardized to $\pm 0.02^{\circ}$ by the National Physical Laboratory.

6.3.2   Measurement of Conductance

All reactions were followed by the development of conductivity over at least two half lives, during which time the conductance changed from 1×10^{-4} mhos to 40×10^{-4} mhos. If necessary, initial readings for the zero concentration in the rate equation were taken as early as possible. This was facilitated by the use of a 16mm. cine camera (see section 6.5) and an accu rate mechanical counter driven by a synchronous

motor. Several solvent conductance readings were taken before the run began.

As pointed out in section 4.2, the reduction in the systematic errors in the conductance reading at infinite time is very important. The infinity readings were never taken before thirteen half lives had elapsed. They were measured over a period of about eight to sixteen hours, and readings were taken at quarter and half hourly intervals throughout. The infinity reading used in the rate measurements, was a mean calculated from the data collected as above.

The conductance measurements were made on a Wayne Kerr Autobalance Universal Bridge B641. The bridge was capable of measuring 1×10^{-2} mhos to 1×10^{-8} mhos in seven ranges with an accuracy of $\pm 0.1\%$ over all ranges. The frequency at which the measurements were made at was 1592 Hz.

6.4   Titrimetric Technique

6.4.1   Determination of Hydrochloric Acid Concentrations

Where this was necessary this was done by titrating in excess of neutral acetone (neutral to lacmoid), which was of commercial grade, distilled from potassium permanganate and sodium hydroxide against a standard sodium hydroxide solution using lacmoid as indicator. The sodium hydroxide was standardised using 0.1N hydrochloric acid, diluted as required.

6.4.2   Determination of Cell Constant

The following technique was used for determining a very approximate conductance concentration ratio, and to

determine a cell constant for each electrode.   About 200mls.
of the solvent were transferred into a round bottomed flask.
An appropriate volume of benzhydryl chloride was added to the
flask from a micro syringe.   The substrate was allowed to
react completely by placing the flask in the 20° thermostat
bath for not less than eighteen hours.   Approximately 90mls.
of this solution was transferred to each of the conductance
cells.   The cells were allowed to equilibrate at the desired
temperature when the conductance readings were taken.   When
this was completed 5 mls. and 10 mls. aliquots were withdrawn
and titrated as outlined in section 6.4.1

6.5   Photographic Technique

During the early part of all runs, and for most of the
20° runs, the conductance changed too rapidly to be followed
accurately using normal techniques.   Therefore, to make
the conductance readings as accurate as possible, the fastest
parts of the runs were recorded on film using a 16 mm. film
camera.

The speed of the sixteen frames per second was fast
enough to prevent any blurring of the needle even in the
fastest runs.   Whilst filming the meter, which is centre
zero, the camera also filmed the mechanical counter, which
had been calibrated against an electric clock.   The film
was developed in Ilford PQX Universal Developer and fixed
in the usual way.   A Kodak Archival Reader gave adequate
magnification for the meter to be read to plus or minus a
quarter of a scale reading (± 0.0005), and the mechanical
counter to ± 0.1 sec.   The film used was Kodak Plus X

Negative Film (ASA 64). The aperture at 16 f.p.s. was f11 at 0.66m. from the object, illuminated by a 75 watt anglepoise lamp.

6.6   Experimental Technique at High Pressure

It was decided at the outset to measure the rate of reaction conductometrically, since this was the technique that was used at atmospheric pressure and was known to be capable of producing accurate rate coefficients.

6.6.1   Apparatus

The inside of the reaction vessel lined with teflon which was machined slightly larger than necessary and cold shrunk fitted into the stainless steel vessel.   Teflon was chosen as the lining material because of its inert qualities, even though it had been suggested that it might have been difficult to remove all surface impurities from it.

The electrodes which were of the spade type were sealed into the steel cap and teflon sealing ring using a commercial grade of Araldite.   Connexions were made from the electrodes to the conductance bridge using earthed co-axial cable.

This system did seem to withstand quite well the small increases in pressure to which it was initially subjected. It was possible that the cell constant of the reaction vessel could well have altered from one run to another due to the increase and decrease in pressure that would have been applied to the reaction vessel.

6.6.2   Difficulties encountered with High Pressure Technique

Because of the high pressures involved, the walls of the reaction vessel were about 40mm. thick with a further 7mm. of extremely well insulating teflon.   As already explained, when a liquid is compressed adiabatically its temperature rises.   This temperature increase can be of the order of 18° per k bar.   Thus, compression to 3 k bar could result in a rise in temperature by as much as 50°.   This large rise in temperature would be "sealed inside" the reaction vessel and would only dissipate slowly through the walls. For some of the faster runs the reaction could well be over 50% completed before temperature equilibrium could be restored.   The pressure would clearly have to be applied to the reaction vessel reasonably quickly, so that the conditions under which the rate is measured are soon applied to the reaction mixture.   An obvious solution to this problem would be to cool the reaction down by an amount carefully estimated in a previous experiment before applying the pressure.   Such a technique would at best only yield a final temperature difference before equilibrium of around $2 - 5^{\circ}$.   When using a conductance technique to follow a kinetic run, it is extremely important that the zero conductance reading or readings be taken as early as possible once the run has commenced.   Assuming that a zero reading could never be taken later than 5% reaction and that temperature equilibrium would at the minimum take ten minutes, it is clear that 5% reaction corresponds to ten minutes at say 20°.   Therefore the fastest run that could be followed would be of the order of 1×10^{-4} sec^{-1}.   For reasons

explained later in this section, one of the results of such a constraint is a reduction in the range over which the reaction can be studied at various temperatures and pressures.

Consider now the temperature range over which the reaction could be studied. Table 6.1 shows the temperature range assuming various maximum half lives, and the mean temperature of the reaction at about room temperature, for two different values of the activation energy. From this table the actual temperature range that can be studied is limited. Furthermore, for a ten day half life, it is necessary that the reaction be followed for about thirty days, during which time temperature and pressure must be kept constant. The apparatus would therefore be fully occupied on one run for thirty days, allowing only one run per month at this particular temperature. Bearing this in mind, the slowest run possible is one with the one day half life. The experimental range of temperatures is thus reduced to about 25° which really is rather small to enable accurate values of ΔC_V^* to be calculated.

TABLE 6.1

Limitations of the Temperature Range for the Present Reaction Study

Minimum Half Life (day)	Maximum Half Life (day)	Temp. Range E = 20kcal.	Temp.Range E = 18 kcal.
100	1	23	25
100	5	37	41
100	10	39	43

It was mentioned earlier that for a volume of activation of about -20 cm^3 a pressure change of one kilobar would cause the rate only to double. It is therefore necessary to study much larger pressure differences to produce comparable changes in reaction rates, compared with temperature changes. In fact, the pressure must be controlled and measured to limits finer than even commercial apparatus could produce. Under these conditions, temperature must be controlled with corresponding accuracy, since its fluctuations would cause pressure differences. The pressure control would extend over a period of many days introducing another severe limitation into the experimental apparatus.

Thus it was decided in view of the time factor, and the experimental facts mentioned above to limit the experimental work to following the reaction at constant pressure only. A complete study at constant pressure would require something of the order of forty runs, that is, a series of runs every five degrees over say, a range of fifty degrees. Whereas a study at constant volume would require something of the order of two hundred runs.

6.7 Calibration of the Solvent and the Cells

The actual method of calibration is described earlier in section 6.4.2. The results are shown in this section.

Two cells were standardised, with two solutions, one approximately 2 x 10^{-3}M and the other was 0.5 x 10^{13}M. The conductance was determined at each of the three temperatures

after which the concentration of the hydrochloric acid was determined by titration. Table 6.2 summarises the results for Cell(I) and Cell(II)   In addition to this calibration, a number of reaction mixtures, after the conductance at infinite time had been determined, were titrated as above.   The results of all measurements are shown in Table 6.3.

TABLE 6.2

Cell (I) Calibration

Temperature $^{\circ}C$	Conductance $x\ 10^{-3}$mhos	Concentration $x\ 10^{-3}$ M
20	3.6725	2.202±0.004
15	3.3250	2.202±0.004
10	2.9936	
20	0.94705	
15	0.85562	0.5320±0.0013
10	0.76815	

Cell (II) Calibration

20	3.7810	
15	3.4159	2.202±0.004
10	3.0876	
20	0.97259	
15	0.87893	0.5302±0.0013
10	0.79009	

The data from Table 6.3 is also shown graphically in figure 6.3.   This clearly demonstrates the non linearity of the conductance-concentration relationship; it also shows that the non linearity is not large.

TABLE 6.3

Summary of Conductance Concentration Measurements

Temperature °C	Conductance x 10^{-3} mhos	Concentration x 10^{-3} M	Cell
20	3.6725	2.202	I
20	0.94705	0.5302	I
20	1.2820	0.7379	I
20	3.7810	2.202	II
20	0.97259	0.5302	II
20	1.3620	0.7659	II
20	1.8839	1.0699	II

This was indicated in the original calculations when it accounted for only a 5% fall in the rate coefficients from 10 - 70% reaction.

FIGURE 6.3

Plot of Conductance-Concentration

Data shown in Table 6.3

⊙ CELL (II)

⊕ CELL (I)
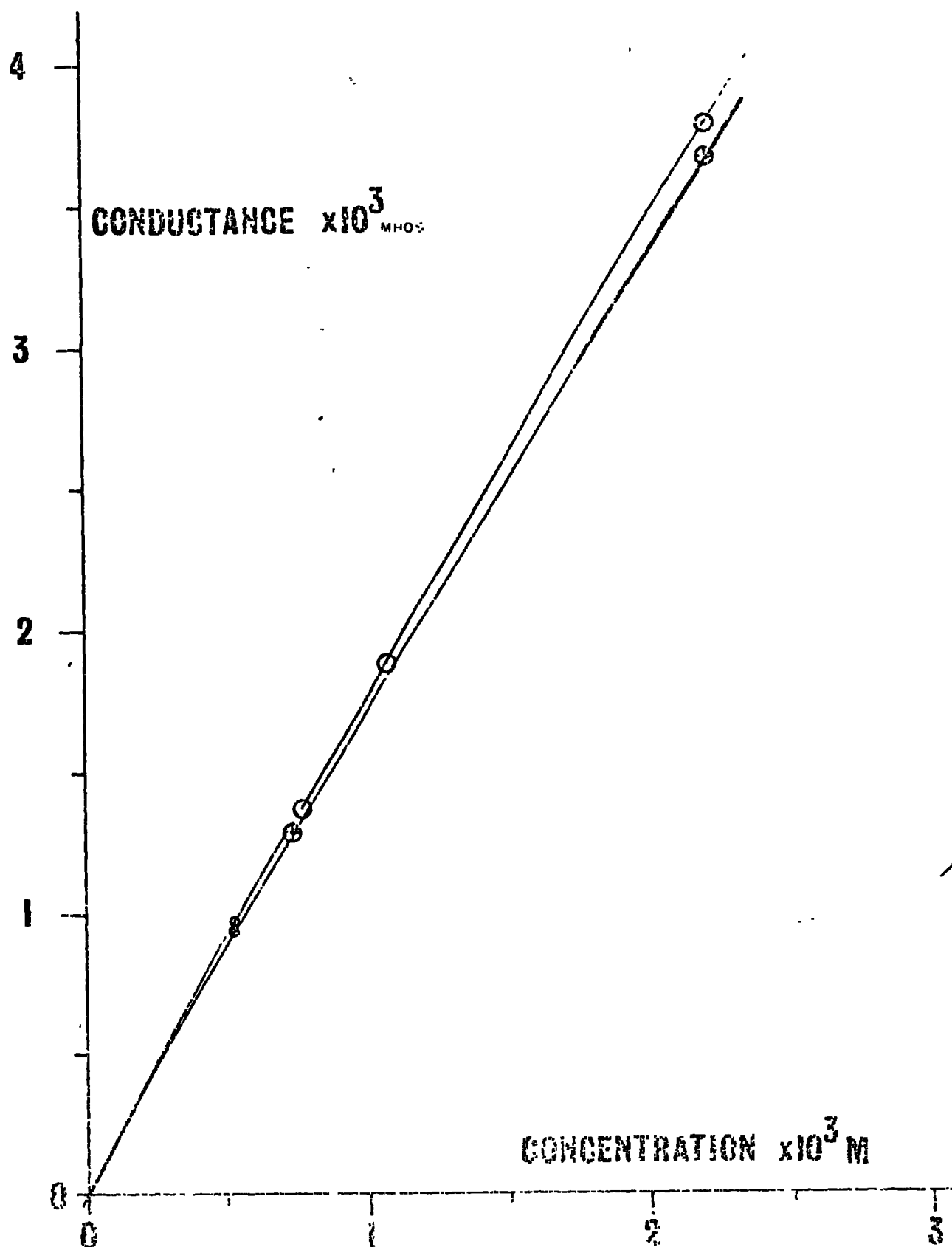
APPENDIX I

THE ONSAGER EQUATION

The Onsager equation can be written in the form:-

$$\Lambda \;=\; \Lambda_o \;-\; (\alpha.\Lambda_o - \beta).\sqrt{c}$$

This form of the equation is inconvenient for the present purpose but it can be transformed into equation A1.1 which includes another parameter , γ :

$$L \;=\; \alpha.c \left(1 \;+\; \beta.c^{\frac{1}{2}} \;+\; \gamma.c\right) \qquad\qquad \text{A1.1}$$

where $L = \lambda - \lambda_s$, the conductance of the solution corrected for that of the solvent, see section 5.2.

If $\gamma = 0$, then

$$c \;=\; \frac{L}{\alpha\left(1 + \beta c^{\frac{1}{2}}\right)}$$

$$\;=\; \frac{L}{\alpha\left(1 \;+\; \dfrac{\beta L^{\frac{1}{2}}}{\alpha^{\frac{1}{2}}.(1 + \frac{1}{2}\beta.c^{\frac{1}{2}})}\right)} \qquad\qquad \text{A1.2}$$

Now $\beta c^{\frac{1}{2}} \ll 1$ so that $1 + \beta.c^{\frac{1}{2}}$ is a small correction term. Very little error will therefore arise,
by writing

$$1 \;+\; \beta.c^{\frac{1}{2}} \;\simeq\; 1 \;+\; \beta.L^{\frac{1}{2}}$$

so that A1.2 can be written in the form

$$c \;=\; \frac{AL}{1 + \dfrac{BL^{\frac{1}{2}}}{1 + CL^{\frac{1}{2}}}} \qquad\qquad \text{A1.3}$$

Equation A1.3 is now in a more convenient form for substituting into various rate equations.

APPENDIX 2

DERIVATION OF RATE EQUATIONS

2.1   Rate Equation 5.4

Using rate equation 4.4

$$kT = \ln\left(\frac{c_\infty - c_o}{c_\infty - c}\right)$$

and the conductance concentration relationship from equation 5.1, then:-

$$kT = \ln\left(\frac{L_\infty - L_o}{L_\infty - L}\right) + \ln\left(1 + \frac{B}{A}\cdot\frac{L_\infty^{3/2} - L_o^{3/2}}{L_\infty - L_o} + \frac{D}{A}\frac{L_\infty^2 - L_o^2}{L_\infty - L_o}\right)$$

$$- \ln\left(1 + \frac{B}{A}\frac{L_\infty^{3/2} - L^{3/2}}{L_\infty - L} + \frac{D}{A}\frac{L_\infty^2 - L^2}{L_\infty - L}\right)$$

Defining $X = L/L_\infty$

$$kT = \ln\left(\frac{1 - X_o}{1 - X}\right) + \ln\left(1 + A_3'\cdot\frac{1 - X_o^{3/2}}{1 - X_o} + A_4'\cdot(1 + X_o)\right)$$

$$- \ln\left(1 + A_3'\cdot\frac{1 - X^{3/2}}{1 - X} + A_4'\cdot(1 + X)\right)$$

$$\dots\dots\dots\dots\dots\dots A2.1$$

where $A_3' = \frac{B}{A}\cdot L_\infty^{\frac{1}{2}}$

$A_4' = \frac{D}{A}\cdot L_\infty$

The terms involving A_3' and A_4' do not vary much as the reaction proceeds.   It is therefore convenient to separate these terms into their constant and variable components. Thus:

$$1 + A_3'\cdot\frac{1 - X^{3/2}}{1 - X} + A_4'\cdot(1 + X)$$

$$= 1 + A_3^1 + A_4^1 + A_3^1\cdot\left(\frac{1 - X^{3/2}}{1 - X} - 1\right) + A_4^1\cdot X$$

$$= (1 + A_3^1 + A_4^1)\left(1 + \frac{A_3^1}{1 + A_3^1 + A_4^1}\cdot\frac{X}{1 + X^2} + \frac{A_4^1}{1 + A_3^1 + A_4^1}\cdot X\right)$$

Substitution of the above equation A2.1 leads to:

$$kT = \ln\left(\frac{1 - X_o}{1 - X}\right) + \ln\left(1 + A_3 \cdot \frac{X_o}{1 + X_o^{\frac{1}{2}}} + A_4 \cdot X_o\right)$$

$$- \ln\left(1 + A_3 \frac{X}{1 + X^{\frac{1}{2}}} + A_4 \cdot X\right) \qquad A2.2$$

where $\quad A_3 = A_3' / (1 + A_3' + A_4')$

$$A_4 = A_4' / (1 + A_3' + A_4')$$

2.2   Rate Equation 5.5

Equation 5.5 is derived from equation 5.4 by combining all terms involving measurements at zero time into a single disposable parameter, A_2.

$$kT = \ln\left(\frac{1 - X_o}{1 - X}\right) + \ln\left(1 + A_3 \cdot \frac{X_o}{1 + X_o^{\frac{1}{2}}} + A_4 \cdot X_o\right)$$

$$- \ln\left(1 + A_3 \cdot \frac{X}{1 + X^{\frac{1}{2}}} + A_4 \cdot X\right)$$

$$y = \ln(1 - X) = A_1 \cdot T + A_2 - \ln\left(1 + A_3 \cdot \frac{X}{1 + X^{\frac{1}{2}}} + A_4 \cdot X\right)$$

where $A_1 = -k$

$$A_2 = \ln(1 - X_o) + \ln\left(1 + A_3 \cdot \frac{X_o}{1 + X_o^{\frac{1}{2}}} + A_4 \cdot X_o\right)$$

2.3   Rate Equation 5.6

This equation avoids the systematic errors that may exist in the zero readings.   It uses the Onsager Equation with the special case, $\delta = 0$, and the line with intercept first order rate equation.   The rate equation can be put in the form:

$$\ln\left(c_\infty - c\right) = \ln\left(c_\infty - c_o\right) - k T$$

Using equation 5.3

$$c_\infty - c = \cfrac{AL_\infty}{1 + \cfrac{BL_\infty^{\frac{1}{2}}}{1 + CL_\infty^{\frac{1}{2}}}} - \cfrac{AL}{1 + \cfrac{BL^{\frac{1}{2}}}{1 + CL^{\frac{1}{2}}}}$$

where $L = \lambda - \lambda_s$.

The above equation can be reduced to:-

$$c_\infty - c = \frac{A(L_\infty - L)}{1 + (B + C)L_\infty^{\frac{1}{2}}} \left(1 + CL_\infty^{\frac{1}{2}} - \cfrac{\cfrac{BL}{L_\infty^{\frac{1}{2}} - L^{\frac{1}{2}}}}{1 + (B + C)L_\infty^{\frac{1}{2}}} \right)$$

$$\dots\dots\dots\dots\dots\dots A2.3$$

Now $\ln\left(c_\infty - c\right) = \text{constant} - kT$ A2.4

where constant $= \ln\left(c_\infty - c_o\right)$

Combining equations A2.3 and A2.4

$$\ln\left(c_\infty - c\right) - kT = \ln\left(\frac{A(L_\infty - L)}{1 + (B + C)L_\infty^{\frac{1}{2}}}\right)$$

$$+ \ln \left(1 + CL_\infty^{\frac{1}{2}} - \cfrac{\cfrac{BL}{L_\infty^{\frac{1}{2}} - L^{\frac{1}{2}}}}{1 + (B + C)L_\infty^{\frac{1}{2}}} \right)$$

writing $A_3 = B$ and $A_4 = C$

$$\ln\left(c_\infty - c_o\right) - kT = \ln A + \ln\left(L_\infty - L\right) - \ln\left(1 + (A_3 + A_4)L_\infty^{\frac{1}{2}}\right)$$

$$+ \ln \left(1 + A_4 L_\infty^{\frac{1}{2}} - \frac{A_3}{1 + (A_3 + A_4)L_\infty^{\frac{1}{2}}} \cdot \frac{L}{L_\infty^{\frac{1}{2}} - L^{\frac{1}{2}}} \right)$$

This can be written in the form:-

$$\ln\left(L_\infty - L\right) = A_1 + A_2 T + \ln(1 + Y) + \ln(1 + W)$$

where $A_1 = \ln\left(c_\infty - c_o\right) - \ln A$

$A_2 = -k$

$A_3 = B$

$A_4 = C$

$Y = (A_3 + A_4) \cdot L_\infty^{\frac{1}{2}}$

$$W = A_4 \cdot L_\infty^{\frac{1}{2}} - \frac{A_3}{1 + (A_3 + A_4)L_\infty^{\frac{1}{2}}} \cdot \frac{L}{L_\infty^{\frac{1}{2}} + L^{\frac{1}{2}}}$$

2.4   Rate Equation 5.7

This rate equation is derived from the mean from zero rate equation

$$kT = \ln\left(\frac{c_\infty - c_0}{c_\infty - c}\right)$$

and the full form of the Onsager Equation.

It is assumed that c_0 is in error by an amount δ'.

$$kT = \ln\left(\frac{c_\infty - c}{c_\infty - c_0 + \delta'}\right)$$

The above equation can be written in its exponential form:

$$c = c_\infty\left(1 - e^{-kT}\left(1 - \frac{c_0}{c_\infty} + \frac{\delta'}{c_\infty}\right)\right)$$

Defining

$$z = c/c_\infty \quad \text{and} \quad A_1 = k$$

and

$$A_4 = 1 - \frac{c_0}{c_\infty} + \frac{\delta'}{c_\infty}$$

and using the extended form of the Onsager Equation (equation 5.2)

$$L = \alpha.c\,(1 + \beta.c^{\frac{1}{2}} + \gamma.c)$$

these equations may be combined to give

$$z = 1 - A_4.e^{-A_1 T} \qquad\qquad A2.5$$

Combining equation A2.5 and the Onsager Equation

$$X = \frac{L}{L_\infty} = z.\frac{1 + \beta.c^{\frac{1}{2}}_\infty . z^{\frac{1}{2}} + \gamma.c_\infty.z}{1 + \beta.c_\infty^{\frac{1}{2}} + \gamma.c_\infty}$$

Defining $Q = 1 + \beta.c^{\frac{1}{2}}_\infty + \gamma.c_\infty$,

$$X = z\left(1 + \frac{\beta.c^{\frac{1}{2}}_\infty}{Q}(z^{\frac{1}{2}} - 1) + \frac{\gamma.c_\infty}{Q}(z - 1)\right)$$

and using $\qquad A_2 = \dfrac{\beta . c_\infty^{\frac{1}{2}}}{Q} \quad$ and $\quad A_3 = \dfrac{\gamma . c_\infty}{Q}$

$$X = z\left(1 + A_2\left(z^{\frac{1}{2}} - 1\right) + A_3(z - 1)\right)$$

Substituting for z from A2.5

$$y = X = \left(1 - A_4 e^{-A_1 T}\right)\left(1 + A_2\left(\left(1 - A_4 e^{-A_1 T}\right)^{\frac{1}{2}} - 1\right) + A_3\left(-A_4 e^{-A_1 T}\right)\right)$$

$$\dots\dots\dots\dots\text{A2.6}$$

where $\qquad X = L/L_\infty$

$$A_1 = k$$

$$A_2 = \frac{\beta . c_\infty^{\frac{1}{2}}}{1 + \beta c_\infty^{\frac{1}{2}} + \gamma . c_\infty}$$

$$A_3 = \frac{\gamma c_\infty^{\frac{1}{2}}}{1 + \beta . c_\infty^{\frac{1}{2}} + \gamma . c_\infty}$$

$$A_4 = 1 - \frac{c_o}{c_\infty} + \frac{\delta'}{c_\infty}$$

2.5 Rate Equation 5.8

It was shown in Appendix 2.3. that

$$c_\infty - c = \frac{A(L_\infty - L)}{1 + (B + C)L_\infty^{\frac{1}{2}}}\left(1 + CL_\infty^{\frac{1}{2}} - \frac{\dfrac{BL}{L_\infty^{\frac{1}{2}} - L^{\frac{1}{2}}}}{1 + (B + C)L_\infty^{\frac{1}{2}}}\right)$$

Using $A_\infty = \dfrac{A}{1 + (B + C)L_\infty^{\frac{1}{2}}} \qquad$ and $a = \quad 1 + CL_\infty^{\frac{1}{2}}$

and $\qquad -b = \dfrac{\dfrac{BL}{L_\infty^{\frac{1}{2}} - L^{\frac{1}{2}}}}{1 + (B + C)L_\infty^{\frac{1}{2}}}$

Then $\quad c_\infty - c = A_\infty(L_\infty - L)(a + b)$

Therefore $\ln\left(L_\infty - L\right) = \ln\left(c_\infty - c\right) - \ln A_\infty - \ln\left(a + b\right)$ A2.7

And at zero time

$$\ln\left(L_\infty - L_0\right) = \ln\left(c_\infty - c_0\right) - \ln A_\infty - \ln\left(a + b_0\right) \qquad \text{A2.8}$$

The rate equation can be put in the form

$$\ln\left(c_\infty - c\right) = \ln\left(c_\infty - c_0\right) + \delta - kT \qquad \text{A2.9}$$

where δ represents any error that is present in the zero reading.

Equation A2.7, A2.8 and A2.9 can now be combined

$$y = \ln\left(\frac{L_\infty - L}{L_\infty - L_0}\right) = \delta - kT - \ln\left(\frac{a + b}{a + b_0}\right) \qquad \text{A2.10}$$

APPENDIX 3

THE METHOD OF NON LINEAR LEAST SQUARES

Many equations can be solved more accurately using non linear least squares methods, rather than reiteration or recycling techniques or a combination of these two methods.

In general, an equation to be solved can be written in the form:-

$$Y = f(y, X) = g(X, a_1, a_2, \ldots\ldots)$$

where a_1, a_2,....a_n are the disposable parameters. It is important to note that the error in y is very much greater than the error in X.

If

$$g = a_1 h_1 + a_2 h_2 + \cdots$$

where h_1, h_2,.... are functions of X only, then ordinary linear least squares may be employed in the method of solution, that is for linear least squares to be applicable g must be a linear function of the disposable parameters and X.   If g is a non linear function of these parameters, then non linear least squares must be used.   Under these conditions the equation has to be reduced to a linear form.

Trial values A_1, A_2, ... can be used for the values of the parameters, from this

$$YY = g(X, A_1, A_2, \ldots\ldots)$$

Taking the Taylor expansion to the first term only, when

$$Y - YY = \alpha_1 . \frac{\partial YY}{\partial A_1} + \alpha_2 . \frac{\partial YY}{\partial A_2} + \ldots \qquad A3.1$$

α_1, ... are constants whose values are not yet known.

The differentials $\partial YY/\partial A_1$, $\partial YY/\partial A_2$, ... can be

evaluated.   Equation A3.1 is now linear in the unknown constants $\alpha_1, \cdots\cdots$.   It is therefore possible using linear least squares to evaluate α_1, $\alpha_2, \cdots\cdots$.

Having found α_1, $\alpha_2, \cdots\cdots$ then $A_1 + \alpha_1$, $A_2 + \alpha_2$, $\cdots\cdots$ is a better approximation to a_1, a_2, $\cdots\cdots$ than A_1, $A_2, \cdots\cdots$.   Thus A_1 takes the value $A_1 + \alpha_1$ etc., when the whole procedure is repeated until the desired degree of precision is achieved, for example that

$$\alpha_1 \; < \; \tfrac{1}{4}.\sigma(a_1) \; = \; \tfrac{1}{4}.\sigma(\alpha_1)$$

or that α_1 is some other fraction of a_1.

The final programme, A82M, is only non linear in the A_3 parameter, and recycling ceases when:-

$$\alpha_3 \; < \; A_3/100$$

APPENDIX 4

CALCULATIONS INVOLVED IN PROGRAMME A82M.

The final form of the rate equation to be solved is given by equation A4.1.

$$y = \ln(1 - X) = A_1 T + A_2 - \ln\left(1 + A_3 \cdot \frac{X}{1 + X^{\frac{1}{2}}}\right)$$

$$\ldots\ldots\ldots\ldots\ldots A4.1$$

where

$$A_1 = -k$$

$$A_2 = \ln(1 - X_0) + \ln\left(1 + A_3 \cdot \frac{X_0}{1 + X_0^{\frac{1}{2}}}\right)$$

$$A_3 = \frac{A^{\frac{1}{3}}}{1 + A^{\frac{1}{3}}}$$

$$A^{\frac{1}{3}} = \frac{B}{A} \cdot L_\infty^{\frac{1}{2}}$$

However, equation A4.1 has the drawback that $A^{\frac{1}{3}}$ (and hence A_3) depends on the run under consideration and is not directly applicable to replicate mean rate coefficient calculations. It therefore, must be written in the form:-

$$y = \ln(1 - X) = A_{2j} - kT - \ln\left(1 + \frac{B}{1 + BL_\infty^{\frac{1}{2}}} \cdot L_\infty^{\frac{1}{2}} \cdot \frac{X}{1 + X^{\frac{1}{2}}}\right)$$

$$\ldots\ldots\ldots\ldots A4.2$$

where $B = B/A$, and the subscript j indicates that the parameter depends on the run in question.

Equation A4.2 can now be solved by non linear least squares methods (see Appendix 3), and equation A4.2 forms the basis of A82M. If equation A4.2 is to be solved by this method, the "best" coefficients have to be found for the relationship:-

$$y = \ln(1 - X) + \ln\left(1 + \frac{\bar{B}}{1 + \bar{B}L_\infty^{\frac{1}{2}}} \cdot L_\infty^{\frac{1}{2}} \cdot \frac{X}{1 + X^{\frac{1}{2}}}\right) \quad \text{A4.3}$$

$$= a_j + a_1 T + a_2 \cdot \frac{\partial y}{\partial \bar{B}}$$

where $\quad a_j = A_{2j}$

$$a_1 = -k$$

$\bar{B}$ is a trial value for B

a_2 is such that $\bar{B} + a_2$ is a better approximation to B than $\bar{B}$

$$\frac{\partial y}{\partial \bar{B}} = \frac{X/(1 + X^{\frac{1}{2}})}{1 + \dfrac{\bar{B}}{1 + \bar{B}L_\infty^{\frac{1}{2}}} \cdot L_\infty^{\frac{1}{2}} \cdot \dfrac{X}{1 + X^{\frac{1}{2}}}} \left(\frac{L_\infty^{\frac{1}{2}}}{1 + \bar{B}L_\infty^{\frac{1}{2}}} - \frac{\bar{B}L_\infty^{\frac{1}{2}} \cdot L_\infty^{\frac{1}{2}}}{(1 + \bar{B}L_\infty^{\frac{1}{2}})^2}\right)$$

$$= \frac{X/(1 + X^{\frac{1}{2}})}{1 + \dfrac{\bar{B}}{1 + \bar{B}L_\infty^{\frac{1}{2}}} \cdot L_\infty^{\frac{1}{2}} \cdot \dfrac{X}{1 + X^{\frac{1}{2}}}} \cdot \frac{L_\infty^{\frac{1}{2}}}{(1 + \bar{B}L_\infty^{\frac{1}{2}})^2}$$

Since the variable terms in equation A4.3 are calculated separately for each run, the A_3 nomenclature used in equation A4.1 can still be used throughout. Therefore equation A4.3 can be rewritten:-

$$y = \ln(1 - X) + \ln(1 + \bar{A}_{3j}^1 \cdot f_x)$$

$$= a_j X_1 + a_1 X_2 + a_2 X_3 \quad\quad \text{A4.4}$$

where each of the terms has the following significance:-

$$f_x = \frac{X}{1 + X^{\frac{1}{2}}}$$

$$\bar{A}_{3j}^1 = \frac{\bar{A}_{3j}}{1 + \bar{A}_{3j}}$$

$$\bar{A}_{3j} = \frac{\bar{B}L_\infty^{\frac{1}{2}}}{1 + \bar{B}L_\infty^{\frac{1}{2}}} \quad \text{with } \bar{B} = \bar{B} + a_2 \text{ for each cycle}$$

$$X_1 \quad = \quad 1$$

$$X_2 \quad = \quad T$$

$$X_3 \quad = \quad \frac{f_x}{1 + \overline{A}_{3j} \cdot f_x} \quad \frac{L_{\infty}^{\frac{1}{2}}}{(1 + \overline{A}_{3j})^2}$$

The programme initially calculates the "best" values for the disposable parameters for a given run, each point is assigned the weight factor:-

$$w \quad = \quad (1/x - 1)^2$$

Using the linear form of the least squares procedure, then:-

$$v_j^1 \quad = \quad \sum_i w_{ji} \, (y_{ji} - a_{1j}X_{j1i} - a_{2j}X_{j3i})^2$$

must be a minimum. Where the subscript j indicates a particular run, and i indicates each point within that run. The values of a_{1j} and a_{2j} are the "best" values of a_1 and a_2 for that run.

The application of the minimum condition:-

$$\frac{\partial v_j}{\partial a_j} \quad = \quad \frac{\partial v_j}{\partial a_{1j}} \quad = \quad \frac{\partial v_j}{\partial a_{2j}} \quad = 0$$

leads to the normal equations:-

$$a_j \, \delta X_{j11} + a_{1j} \delta X_{j12} + a_{2j} \delta X_{j13} = \delta Y_{j1} \qquad \text{A4.5(i)}$$

$$a_j \, \delta X_{j21} + a_{1j} \delta X_{j22} + a_{2j} \delta X_{j23} = \delta Y_{j2} \qquad \text{A4.5(ii)}$$

$$a_j \, \delta X_{j31} + a_{1j} \delta X_{j32} + a_{2j} \delta X_{j33} = \delta Y_{j3} \qquad \text{A4.5(iii)}$$

$$\text{where} \quad \delta X_{jkl} = \delta X_{jlk} = \sum_i w_{ji} \, X_{jkl} \, X_{jli}$$

$$\delta Y_{jk} = \sum_i w_{ji} \, y_{ji} \, X_{jki}$$

Equation A4.5(i) gives

$$a_j = \frac{\delta Y_{j1} - a_{1j}\delta X_{j12} - a_{2j}\delta X_{j13}}{\delta X_{j11}} \qquad A4.6$$

Substitution into A4.5(ii) and A4.5(iii) gives

$$a_{1j}\, qX_{j11} + a_{2j}\, qX_{j12} = qY_{j1}$$

$$a_{1j}\, qX_{j21} + a_{2j}\, qX_{j22} = qY_{j2}$$

where $qX_{jkl} = qX_{j1k}$

$$= \delta X_{j,k+1,l+1} - \frac{\delta X_{j,1,k+1} - \delta X_{j,1,l+1}}{X_{j11}}$$

$$qY_{jk} = \delta Y_{j,k+1} - \frac{\delta Y_{j1} \cdot \delta X_{j,1,k+1}}{X_{j11}}$$

From these equations

$$a_{1j} = \frac{qY_{j1}\, qX_{j22} - qY_{j2}\, qX_{j12}}{D}$$

$$a_{2j} = \frac{qY_{j2}\, qX_{j11} - qY_{j1}\, qX_{j12}}{D}$$

where $D = qX_{j11}\, qX_{j22} - qX_{j12}^2$

The errors of the a_{1j} and a_{2j} are obtained from the errors of the corresponding qY's, an error δy in the ith point is given by:-

$$\delta(qY_{j1})_i = w_{ji}\, \delta Y_{ji} \left(X_{j2i} - X_{j1i} \cdot \frac{\delta X_{j12}}{\delta X_{j11}} \right)$$

$$\delta(qY_{j2})_i = w_{ji}\, \delta Y_{ji} \left(X_{j3i} - X_{j1i} \cdot \frac{\delta X_{j13}}{\delta X_{j11}} \right)$$

Making the approximation that:-

$$w_{ji}\, \delta Y_{ji}^2 \simeq \frac{\sum_1 w_{ji}\, \delta Y_{ji}^2}{n_j} \simeq \frac{v_j^1}{n_j}$$

where n_j is the number of readings taken.

Then

$$\sum_i \delta (qY_{j1})^2_i = \delta X_{j22} - \frac{\delta X_{j12}^2}{\delta X_{j11}} = qX_{j11} \cdot \frac{v_j^1}{n_j}$$

$$\sum_i \delta(qY_{j2})^2_i = qX_{j22} \cdot \frac{v_j^1}{n_j} \qquad\qquad A4.7$$

$$\sum_i \delta(qY_{j1})_i \, \delta(qY_{j2})_i = qX_{j12} \cdot \frac{v_j^1}{n_j}$$

The error in a_{1j} due to an error in the ith point is given by:-

$$\delta(a_{1j})_i = \frac{qX_{j22} \, \delta(qY_{j1})_i - qX_{j12} \, \delta(qY_{j2})_i}{D}$$

Therefore substitution from A4.7, the variance of a_{1j} is given by:-

$$v(a_{1j}) = \frac{n_j}{n_j - 3} \cdot \sum_i \delta(a_{1j})^2_i$$

$$= \frac{qX_{j22}^2 \, qX_{j11} - 2qX_{j22} \, qX_{j12}^2 + qX_{j22} \, qX_{j12}^2 \cdot}{D^2} \frac{v_j^1}{n_j - 3}$$

$$= \frac{qX_{j22}}{D} \cdot \frac{v_j^1}{n_j - 3} \qquad\qquad A4.8$$

In the calculation of a total mean for replicate runs, it is assumed in the calculations that the statistical weight (g_1) assigned to each run is the reciprocal of $v(a_{1j})$ from equation A4.8. This means that each run is weighted according to the accuracy with which it predicts its own "best" rate coefficient.

The programme first of all calculates the "best" rate

coefficient and B/A, together with the variance and the statistical weight factors. No attempt is made yet to discard divergent points. The programme also calculates the "best" rate coefficient for each run when B/A has the same value for each run. This is found by neglecting the last term in equation A4.4, that is $a_2 = 0$, normal least squares treatment then yields:-

$$a_{1j} = \frac{\delta Y_{j2} \, \delta X_{j11} - \delta Y_{j1} \, \delta X_{j12}}{\delta X_{j11} \, \delta X_{j22} - \delta X_{j12}{}^2}$$

$$a_{1j} = \frac{\delta Y_{j2} - \dfrac{\delta Y_{j1} \, \delta X_{j12}}{\delta X_{j11}}}{q X_{j11}}$$

The total mean values for the various parameters can now be calculated. The minimisation conditions now apply to the sum:-

$$v = \sum_j g_1 \left(\sum_1 w_{j1} \, (y_{j1} - a_j X_{j11} - a_1 X_{j2j} - a_2 X_{j31})^2 \right)$$

$$\dots\dots\dots\dots A4.9$$

In this equation a_j depends on the run under consideration, whereas a_1 and a_2 do not. The normal equations take the form:-

$$a_j \delta X_{j11} + a_1 \delta X_{j12} + a_2 \delta X_{j13} = \delta Y_{j1} \qquad A4.10(i)$$

$$\sum_j g_j a_j \, \delta X_{j21} + a_1 \sum_j g_j \delta X_{j22} + a_2 \sum_j g_j \delta X_{j23} = \sum_j g_j \delta Y_{j2} \qquad A4.10(ii)$$

$$\sum_j g_j a_j \delta X_{j31} + a_1 \sum_j g_j \delta X_{j32} + a_2 \sum_j g_j \delta X_{j33} = \sum_j g_j \delta Y_{j3} \qquad A4.10(iii)$$

In equation A4.10(i), j takes the values $1, 2, \dots n$. Using similar arguments to those used in the derivation of equation A4.6, then:-

$$a_j \ = \ \frac{\delta Y_{j1} \ - \ a_1 \delta X_{j12} \ - \ a_2 \delta X_{j13}}{\delta X_{j11}}$$

Substitution for a_j in the other normal equations (A4.10(ii) and A4.10(iii)) leads to

$$a_1 \ QX_{11} \ + \ a_2 \ QX_{12} \ = \ QY_1 \qquad\qquad \text{A4.11(i)}$$

$$a_1 \ QX_{12} \ + \ a_2 \ QX_{22} \ = \ QY_2 \qquad\qquad \text{A4.11(ii)}$$

$$\text{where} \quad QX_{kl} \ = \ \sum_j g_j \ qX_{jkl}$$

$$QY_k \ = \ \sum_j g_j \ qY_{jk}$$

Therefore

$$a_1 \ = \ \frac{QY_1 \ QX_{22} \ - \ QY_2 \ QX_{12}}{D_1} \qquad\qquad \text{4.12(i)}$$

$$a_2 \ = \ \frac{QY_2 \ QX_{11} \ - \ QY_1 \ QX_{12}}{D_1} \qquad\qquad \text{4.12(ii)}$$

$$\text{where } D_1 \ = \ QX_{11} \ QX_{22} \ - \ QX_{12}^2$$

The use of equation A4.9, then produces the variance, v, in the same way as the individual runs. The errors of a_1 and a_2 are worked out by similar methods to those in the individual rate coefficient calculations.

For any experimental point

$$\delta(QY_1)_i \ = \ g_j \ w_{ji} \ \delta Y_{ji} \left(X_{j2i} \ - \ X_{j1i} \cdot \frac{\delta X_{j12}}{\delta X_{j11}} \right)$$

$$\delta(QY_2)_i \ = \ g_j \ w_{ji} \delta Y_{ji} \left(X_{j3i} \ - \ X_{j1i} \cdot \frac{\delta X_{j12}}{\delta X_{j11}} \right)$$

Defining now

$$v_j \ = \ \sum_i w_{ji} \ (y_{ji} \ - \ a_j X_{j1i} \ - \ a_1 \ X_{j2i} \ - \ a_2 \ X_{j3i})^2 \qquad \text{A4.13}$$

v_j is related to v in equation A4.9 by

$$v = \sum_j g_j \, v_j$$

For a given run, the following may be written:-

$$w_{ji} \, \delta Y_{ji}^2 = \frac{\sum w_{ji} \, \delta Y_{ji}^2}{n_j} = \frac{v_j}{n_j}$$

Then using analogous arguments to those used for the individual rate coefficients, then

$$\sum_j \sum_i \delta(QY_1)_i^2 = \sum_j g_j^2 \, q \, X_{j11} \cdot v_j/n_j \qquad \text{A4.14(i)}$$

$$\sum_j \sum_i \delta(QY_2)_i^2 = \sum_j g_j^2 \, qX_{j22} \cdot v_j/n_j \qquad \text{A4.14(ii)}$$

$$\sum_j \sum_i \delta(QY_1)_i \, \delta(QY_2)_i = \sum_j g_j^2 \, qX_{j12} \cdot v_j/n_j$$

Writing
$$G_j = \frac{v_j}{n_j - 3} \cdot g_j^2 \qquad \text{A4.15}$$

$$v(a_1) = \sum_j \sum_i (a_1)^2$$
$$= \frac{1}{D_1^2} \cdot (DY_{11} \cdot QX_{22}^2 - 2DY_{12}QX_{22}QX_{11} + DY_{22}QX_{12}^2)$$

$$v(a_2) = \frac{1}{D_1^2} (DY_{22}QX_{11}^2 - 2DY_{12}QX_{11}QX_{12} + DY_{11}QX_{12}^2)$$

where
$$DY_{kl} = \sum_j G_j \, qX_{jkl}$$

The programme, having done these calculations, is now able to give an improved value for B/A, B, where $B = \bar{B} - a_2$. If at this stage

$$|a_2/B| < 0.01$$

then the programme returns to the beginning of the programme with the redefined value of $\bar{B}$, when all other parameters depending on $\bar{B}$ are recalculated.

Once the stage that

$$a_2 < 0.01 \ \bar{B}$$

then v_j is calculated for each run from A4.13 when the discordant points are discarded such that

$$w_{j1} \ \sum Y_{ji}^2 \ > \ 6.25 \ . \ \frac{v_j}{n_j - 3}$$

The calculation is then repeated until there are no discordant points and $a_2 < 0.01 \ \bar{B}$ when the calculation ends. A flow chart for programme A82M is shown in Table A4.1.

TABLE   A4.1

Flow Chart for Programme A82M

(A) Calculate functions independent of B/A

(B) For a given B/A calculate dependent functions

(C) Calculate "best" parameters for individual runs

Calculate "best" parameters for combined runs

If $a_2 >$ B/A $/100$ then B/A$_{new}$ = B/A$_{old}$ - a_2

Once (D) has been run at least once

If $a_{1new} - a_{1old} < \sigma(a_1)/4$

(D) Discordant points are rejected

If there are rejects

(E) End.
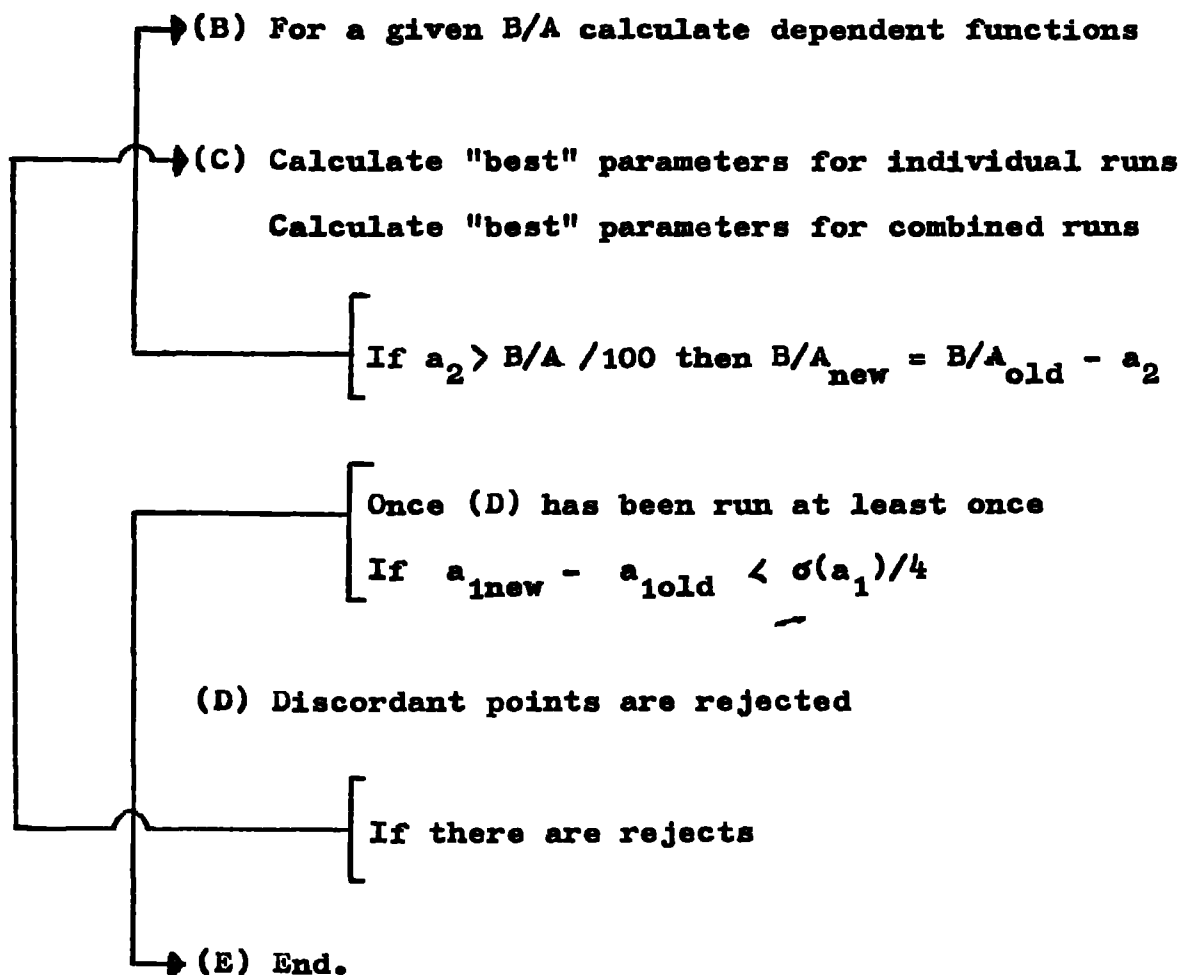
APPENDIX 5

CALCULATION OF ACTIVATION PARAMETERS

5.1 Activation Energies from the Integrated Arrhenius Equation

It is initially assumed that:-

$$\frac{\partial E}{\partial T} = c + dT$$

which on integration gives

$$E = E_o + cT + \frac{d}{2} \cdot T^2 \qquad \text{A5.1}$$

The observed activation energy E_{obs} can be found from the rate coefficient at two temperature, T_1 and T_2, via the Arrhenius Equation:-

$$E_{obs} = \frac{RT_1T_2}{T_2-T_1} \cdot \ln\left(\frac{k_2}{k_1}\right) \qquad \text{A5.2}$$

with a negligibly small error, E_{obs}, is the activation energy at the temperature T_{12}, given by:-

$$T_{12} = \frac{T_1T_2}{T_2-T_1} \cdot \ln\left(\frac{T_2}{T_1}\right) \qquad \text{A5.3}$$

Combining equations A5.1 and A5.2

$$E_{obs} = E_o + c.\frac{T_1T_2}{T_2-T_1} \cdot \ln\left(\frac{T_2}{T_1}\right) + \frac{d}{2} T_1T_2$$

$$\dots\dots\dots\text{A5.4}$$

Using equation A5.4, then for the two ranges of temperature, a and b:-

$$E_{obs}^a - E_{obs}^b = c\left(\frac{T_1^a T_2^a}{T_2^a-T_1^a} \cdot \ln\left(\frac{T_2^a}{T_1^a}\right) - \frac{T_1^b T_2^b}{T_2^b-T_1^b} \cdot \ln\left(\frac{T_2^b}{T_1^b}\right)\right)$$

$$+ \frac{d}{2} \cdot (T_1^a \, T_2^a - T_1^b \, T_2^b) \qquad\qquad A5.5$$

Whilst the assumption that E_{obs} refers to the mean temperature of the interval gives:

$$E_{obs}^a - E_{obs}^b = c\left(\frac{T_1^a + T_2^a}{2} - \frac{T_1^b + T_2^b}{2}\right)$$

$$+ \frac{d}{2} \cdot \left(\left(\frac{T_1^a + T_2^a}{2}\right)^2 - \left(\frac{T_1^b + T_2^b}{2}\right)^2\right) \qquad A5.6$$

The mean approximation (equation A5.6) is most likely to be correct for small temperature intervals, and least likely to be valid for large temperature intervals. The validity of this assumption can easily be tested using the following ranges:-

Range a) $T_2 = 298.167$ $T_1 = 273.976$

Range b) $T_2 = 278.176$ $T_1 = 273.976$

The values of the various parameters (c and d) calculated for the above range are shown in Table A5.1.

It can be seen that the two parameter equation (equation A5.1, with c = -0.01936 kcal., d = 0), calculation via equation A5.6 gives a maximum error in the activation energy, E, of 0.006 kcal.   Whilst for the three parameter equation

TABLE A5.1
Comparison of Results Calculated from Equations A5.5 and A5.6

	Value Calculated from equation A5.5	Value Calculated from equation A5.6	Difference
Coefficient of C	9.665	9.996	-0.331
Coefficient of D	5.477×10^3	5.619×10^3	-142

(equation A5.1, c = -0.1538 kcal. and d = 0.00045 k cal.) the maximum error is 0.013 kcal. It appears from this data that the approximation used in equation A5.6 is acceptable.

5.2   Calculation involved in Equation A5.1

The Relationship

$$E \quad = \quad E_o \quad + \quad c.T \quad + \quad \frac{d}{2} \cdot T^2 \qquad \text{A5.1}$$

is applicable only when T is in degrees absolute. However, it is more convenient to have the temperature expressed in degrees celsius. Therefore A5.1 can be rewritten:-

$$E \quad = \quad E_o \quad + \quad c(273 + \theta) \quad + \quad \frac{d}{2} \cdot (273 + \theta)^2 \quad \text{A5.7}$$
$$\text{where } \theta \text{ is in degrees celsius}$$

Equation A5.7 can be simplified

$$E \quad = \quad E_o \quad + 273.c \quad + \quad 273^2 \cdot \frac{d}{2} \quad + \quad \theta.(c + 273.d) + \frac{d}{2} \cdot \theta^2 \quad \text{A5.8}$$

The first three terms in equation A5.8 correspond to the activation energy at 0°, i.e. E_{273}. Therefore equation A5.8 can be further simplified, assuming d = 0, to:-

$$E \quad = \quad E_{273} \quad + \quad c.\theta \qquad\qquad \text{A5.9}$$

For the two parameter equation (equation A5.9, d = 0) the application of normal weighted least squares gives:-

$$E_{273} \quad = \quad \frac{\Sigma_w \theta^2 \Sigma_{wE} - \Sigma_w \theta \; \Sigma_w \theta E}{\Sigma_w \Sigma_w \theta^2 - (\Sigma_w \theta)^2}$$

$$c \quad = \quad \frac{\Sigma_w \Sigma_w \theta E - \Sigma_w \theta \; \Sigma_{wE}}{\Sigma_w \Sigma_w \theta^2 - (\Sigma_w \theta)^2}$$

$$\text{and} \quad v(c) \quad = \quad \frac{\Sigma_w}{\Sigma_w \Sigma_w \theta^2 - (\Sigma_w \theta)^2} \cdot \Sigma_w \Delta^2 \cdot \frac{16}{5}$$

where $\Delta = E_{obs} - E_{calc}$, and the factor 16/5 from the five independent points among the sixteen points taken.

For the three parameter equation (equation A5.8) a similar least squares consideration yield:-

$$\frac{d}{2} = \frac{Q_{22} Y_1 - Q_{12} Y_2}{D}$$

$$c + 273d = \frac{Q_{11} Y_2 - Q_{12} Y_1}{D}$$

$$E_{273} = \frac{\Sigma wE - (c + 273d)\Sigma w\theta - d/2 \Sigma w\theta^2}{\Sigma w}$$

The various errors are given by:-

$$v(d/2) = \frac{Q_{11}}{D}. \Sigma w\Delta^2. \frac{16}{4}$$

$$v(c+273d) = \frac{Q_{22}}{D}. \Sigma w\Delta^2. \frac{16}{4}$$

$$cv(d/2, c+273d) = \frac{-Q_{12}}{D}. \Sigma w\Delta^2. \frac{16}{4}$$

and

$$v(c) = v(c+273d) - 4. \, cv(d/2, \, c+273d) + 4x273^2. \, v(d/2)$$

where cv represents the co-variance of the two particular parameters

$$Q_{kl} = \Sigma w\theta^{k+1} - \frac{\Sigma w\theta^k \, \Sigma w\theta^l}{\Sigma w}$$

$$Y_k = \Sigma wE\theta^k - \frac{\Sigma w\theta^k \, \Sigma wE}{\Sigma w}$$

$$D = Q_{11}. Q_{22} - Q_{12}^2$$

the factor 16/4 arises this time, since there are now only four independent points.

The weight factors for the solutions of both equations A5.8 and A5.9 are given by:-

$$w \; = \; \left(\frac{T_2 - T_1}{RT_1 \; T_2} \right)^2$$

APPENDIX 6

OTHER SOLUTIONS OF THE FIRST ORDER INTEGRATED RATE EQUATION

6.1   Reiteration Procedure for the Calculation of B/A

Initially equation A2.1 was used to calculate the rate coefficient and B/A, D was assumed to be zero. The procedure used in the programme was to change the value of B/A (starting with B/A = 0) until the rate coefficient had a minimum error. The programme calculated a mean weighted rate constant using B/A = 0, 1, 2, ·····. At some point, the error will increase with increasing B/A. The programme then reverts to its previous value of B/A and smaller increments in B/A are used until a similar condition exists. This cycling was repeated until the error in the mean rate coefficient was a minimum. The programme rejected the discordant points. The whole cycling procedure was repeated until there were no further discards.

Table A6.1 shows mean rate coefficients for replicate runs at a given temperature. It must be emphasised that these "mean" rate constants are merely an average of the data from the programme.

6.2   Solution of Equation 5.6

Equation 5.6 has the form

$$y = \ln\left(L_\infty - L\right) = A_1 + A_2 T + \ln(1 + Y) - \ln(1 + W)$$

TABLE A6.1

RESULTS FOR THE REITERATIVE SOLUTION OF EQUATION A2.1

Solvent	Runs	Temp.	$10^4 k$	B/A
III	19 - 22	25.008	4.795 ± 0.00027	1.55
	41 - 44	20.006	2.660 ± 0.00016	1.69
	45 - 48	14.996	1.437 ± 0.00006	1.79
	49 - 52	10.006	0.7560 ± 0.00004	1.86
IV	56 - 59	20.027	2.600 ± 0.00012	1.63
	60 - 64	15.015	1.399 ± 0.00005	1.75
	65-67,77,78	10.172	0.7525 ± 0.00003	1.84

The details of the derivation are given in Appendix A2.3.
This equation is now in a suitable form to be solved by a
reiterative procedure.   The mechanism of solution was to
assume a range values for the A_4 (=c) parameter and then
to improve the value of the other parameters by a reiteration
procedure, a procedure not unlike that described in Appendix
A6.1.   The parameter A_4 (= c) took the values -5, -3, -1,
0, 1, 3, 5.   The results of such a solution are shown in
Table A6.2.

6.3   Solution of Equation 5.7

Equation 5.7 can be written (see Appendix A2.4) in the
form:-

$$y = X = (1 - A_4 e^{-A_1 T}) \left(1 + A_2 \left(\left(1 - A_4 e^{-A_1 T} \right)^{\frac{1}{2}} - 1 \right) + A_3 (-A_4 e^{-A_1 T}) \right)$$

where the symbols were explained in Appendix A2.4.
Now A_2 and A_3 in the above equation contain an expression:-

$$D = 1 + \beta c_\infty^{\frac{1}{2}} + \gamma c_\infty$$

TABLE   A6.2

Solution of Equation 5.6 by reiteration

The data refer to Solvent III and Temperature = 25.008

RUN	C	10^4 k	$-A_1$	$-B$
19	-5	4.786±0.00115	5.66	0.832
	-3	4.793±0.00073	5.66	0.991
	-1	4.797±0.00048	5.65	1.15
	0	4.803±0.00047	5.65	1.25
	1	4.805±0.00046	5.65	1.33
	3	4.811±0.00048	5.65	1.53
	5	4.815±0.00053	5.64	1.75
20	-5	4.748±0.00116	5.36	0.95
	-3	4.765±0.00060	5.38	1.15
	-1	4.777±0.00055	5.39	1.37
	0	4.786±0.00062	5.33	1.48
	1	4.792±0.00073	5.41	1.58
	3	4.804±0.00090	5.43	1.83
	5	4.813±0.00110	5.45	2.08

for which an approximation has to be found since it involves c_∞ . This was done in the following manner. The Onsager equation may be written:-

$$c = \frac{L}{1 + \beta c_\infty^{\frac{1}{2}} + \gamma c_\infty} \qquad\qquad A6.1$$

where $L = L_\infty / \alpha$

The first approximation is to assume that $D_I = 1$. This in turn means that all terms are negligible compared with unity. This is called Solution I.

For the second approximation, it is assumed that

$$L_\infty = c_\infty$$

Thus $$D_2 = 1 + \beta L_\infty^{\frac{1}{2}} + \gamma L_\infty$$

This is called Solution II.

The third approximation uses equation A6.1, and the second approximation, when:-

$$c_\infty = \frac{L_\infty}{D_2} \qquad \text{and} \qquad c_\infty^{\frac{1}{2}} = \frac{L_\infty^{\frac{1}{2}}}{D_2^{\frac{1}{2}}}$$

Therefore $$D_3 = 1 + \beta \cdot \frac{L_\infty^{\frac{1}{2}}}{D_2^{\frac{1}{2}}} + \cdot \frac{L_\infty^{\frac{1}{2}}}{D_2^{\frac{1}{2}}}$$

This is solution III.

Equation A5.7 is a four parameter equation whose parameters decrease in order of importance:-

$$A_1 \;\gt\; A_2 \;\gt\; A_3 \;\gt\; A_4$$

provided that A_4 is fixed within the limit of δ . The best route to a solution of equation A5.7 is a successive approximation procedure as indicated in Table A6.3. In this way the value of the most important parameter is fixed before

TABLE A6.3

THE METHOD OF SOLUTION OF EQUATION A5.7

Vary	Approximate	Leave
A_1	A_2	A_3 A_4
A_1 A_2	A_3	A_4
A_1 A_2 A_3	A_4	-
A_1 A_2 A_3 A_4	-	-

the least important. The solution is by a non linear least squares procedure. Table A6.4 shows for one run from a series of replicates, the mean value of the parameters for each of the methods of solution.

6.4   Solution of Equation A5.8

Equation A5.8 can be written in the form:-

$$y = \ln\left(\frac{L_\infty - L}{L_\infty - L_0}\right) = \delta - kT - \ln\left(\frac{a + b}{a + b_0}\right) \qquad A5.8$$

The details are given in Appendix 2.5. As undertaken in other solutions (see Appendix 6.2) it is convenient to assume a range of values for the third Onsager parameter (c) and to solve for δ, k and β . For this method of solution δ must be small. This condition will be fulfilled since δ represents an error in a zero reading. The parameters δ, k and β were obtained by a non linear least squares procedure, with the parameter c taking the values

$$-5 \quad -3 \quad -1 \quad 0 \quad 1 \quad 3 \quad 5$$

TABLE A6.4

Solution of Equation 5.7

RUN	SOLN	10^8 VY*	10^4 k	β	γ	10^6
19	I	3.93	4.811±0.00153	1.54±0.036	-2.04±0.49	-13.6±7.9
	II	3.97	4.811±0.00163	-1.50±0.030	3.45±0.43	-14.5±7.9
	III	4.04	4.812±0.00169	-1.46±0.013	3.70±0.32	-15.3±7.9
41	I	20.3	2.645±0.00259	1.05±0.065	VARY TOO MUCH	
	II	24.5	2.643±0.00292	-1.12±0.056	"	"
	III	20.6	2.641±0.00254	-1.14±0.033	"	"
45	I	30.8	1.452±0.00152	2.38±0.068	-8.86±0.95	"
	II	30.7	1.454±0.00164	-2.03±0.052	10.2±0.78	"
	III	30.6	1.455±0.00164	-2.06±0.015	9.18±0.47	"
49	I	32.2	0.748±0.00088	1.60±0.096	10.7±2.01	"
	II	32.0	0.748±0.00099	-1.65±0.082	6.11±1.82	"
	III	32.0	0.748±0.00108	-1.70±0.028	3.96±1.71	"
56	I	13.4	2.583±0.00236	1.12±0.076	"	"
	II	13.5	2.585±0.00264	-1.06±0.068	"	"
	III	13.6	2.580±0;00293	-1.09±0.041	"	"
60	I	5.41	1.399±0.00579	1.83±0.030	1.43±0.46	5.41±5.7
	II	5.36	1.399±0.00632	-1.81±0.021	3.63±0.38	5.39±5.6
	III	5.30	1.400±0.00663	-1.76±0.008	4.31±0.31	5.05±5.6
65	I	14.8	0.753±0.00725	2.33±0.071	"	"
	II	13.3	0.752±0.00787	-2.14±0.060	"	"
	III	13.6	0.753±0.00819	-2.06±0.019	"	"

* VY $= \Sigma w \delta y_i / n-3$

Table A6.5 shows the results for this solution for a few selected runs.

TABLE   A6.5

Solution of Equation 5.8

SOLV.	TEMP.	RUN	C	10^7VY*	10^4 k	β	10^6δ
III	25.008	19	-5	0.57	4.810±0.00070	0.64±0.0044	6.62±0.30
			-3	0.86	4.820±0.00075	0.82±0.0063	7.46±0.34
			-1	1.03	4.826±0.00075	1.00±0.0076	8.60±0.34
			0	1.16	4.829±0.00079	1.09±0.0088	9.02±0.33
			1	1.03	4.831±0.0083	1.19±0.0103	9.57±0.41
			3	1.56	4.835±0.00088	1.39±0.0130	10.3±0.42
			5	1.87	4.839±0.00095	1.62±0.0169	11.2±0.50
III	14.996	45	-5	39.0	1.445±0.00062	0.76±0.0094	10.5±0.18
			-3	41.8	1.448±0.00061	0.90±0.0116	11.2±0.20
			-1	46.4	1.451±0.00062	1.03±0.0144	11.7±0.22
			0	48.1	1.451±0.00063	1.13±0.0163	12.8±0.25
			1	49.8	1.452±0.00064	1.21±0.0180	13.1±0. 27
			3	53.3	1.454±0.00064	1.36±0.0213	13.5±0.29
			5	56.8	1.456±0.00065	1.54±0.0253	13.5±0.32
IV	20,029	56	-5	17.1	2.636±0.00166	0.50±0.0102	0.32±0.90
			-3	19.1	2.641±0.00164	0.58±0.0123	0.14±0.90
			-1	20.7	2.645±0.00162	0.66±0.0146	0.15±0.89
			0	21.5	2.646±0.00161	0.70±0.0158	0.21±0.89
			1	22,3	2.648±0.00161	0.74±0.0170	0.24±0.89
			3	24.0	2.651±0.00161	0.84±0.0197	0.28±0.89
			5	25.6	2.653±0.00161	0.93±0.0226	0.286±0.89

*VY $= \Sigma w \delta y_i / $ n-3