KINETICS IN AQUEOUS SYSTEMS

A Thesis presented for the degree of
Doctor of Philosophy
in the Faculty of Science
of the University of Leicester

by

Jill Rosemary Membrey

September 1975
The experimental work described in this thesis has been carried out by the authoress in the laboratories of the Department of Chemistry of the University of Leicester between October 1971 and August 1974.

No part of this work has been presented or is concurrently being presented for any other degree.

Signed: Jill R. Membrey.

Jill R. Membrey.

September 1975.
To my Parents and Teachers
Thou wilt shew me the path of life: in thy presence is fulness of joy.

Psalm 16, v. 11.
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CHAPTER ONE

Introduction
Recently, the role of water in biochemical systems has received a great deal of attention, and it has become evident that an understanding of the solution behaviour of aqueous non-electrolytes is an essential prerequisite to complete knowledge of the complex processes occurring in biological systems. The aim of the work reported in this thesis was to probe kinetics of chemical reactions in aqueous systems, and thence to examine the relation between kinetic data and the properties of such systems, bearing in mind current ideas concerning aqueous mixtures. The results obtained have been compared with earlier studies of the substrates in related systems (available in the literature), in order to assess the extent to which they conform with previously observed patterns of behaviour. Ultimately, it was hoped to examine kinetics of reactions in systems where the water was associated with the gel state, because of the implications this would hold for processes occurring 'in vivo'.

The opening chapters provide a brief review of the properties of aqueous systems, with particular emphasis on identifying various classes of solute behaviour, a background to the substrates used for kinetics, and an introduction to the thermodynamics of binary solvent mixtures. The latter topic is utilized in the detailed Solubility Analysis which follows, and which forms the basis of conclusions drawn from the experimental work. The kinetics of first-order reactions and methods developed for calculating reaction rate constants are explained in detail. A full description is also given of the apparatus and experimental procedures involved in monitoring the reactions by conductimetric and spectrophoto-
metric methods. The theoretical section also outlines the method for calculating thermodynamic activation parameters from the experimentally observed values of rate constants.

The subsequent four chapters contain the background, results and discussion sections for each of the systems investigated, these being: hydrogen peroxide/water; polyvinylpyrrolidone/water; aqueous sols and gels; urea/water, glycerol/water and propane-1,2- and -1,3- diols/water. Appendices include tables of experimental rate constants, computer programs and other relevant information.

Reference:
CHAPTER TWO

Water and Aqueous Systems
2.1 Introduction

Both the physical appearance of this planet and the life-forms it contains have been moulded and conditioned by the abnormal properties of water, since the substance is known to have existed on earth for at least 600 million years.\(^1\) The storage of large quantities of heat by the oceans, maintenance of sea level, surface freezing of ponds and lakes, and formation of soil are but a few examples of the geological significance of water. Equally, the essential role played by water in life itself is clearly demonstrated by the fact that DNA requires some 30\% of water in order to maintain its native conformation; partial dehydration leads to denaturation.\(^2\)

The importance of water has been recognised since ancient times: the command "Meditate on Water!" appears in a manuscript dating from c. 1000 BC.\(^3\) whilst Greek philosophers included water among their four 'vital elements' (fire, earth, air and water). In the last century, however, water was taken for granted by most chemists, in spite of its universal solvent use. Many of the liquid's physical properties became international standards (boiling point, density, viscosity, etc.), although their basis was little understood. Not until fairly recently have the actual structure of water and the nature of its interactions with other substances been seriously investigated. The classic paper of Bernal and Fowler, describing models for liquid water and aqueous salt solutions, appeared in 1933.\(^4\) This prompted much interest and experiment, from which resulted the "iceberg" description of Frank and Evans, and Samoilov's work on ions in water.\(^5-10\)
In the late 1950's, the term "water structure" became familiar. Frank's "flickering clusters" were introduced, as was the phenomenon of "hydrophobic bonding" due to Kauzmann. Némethy and Scheraga were the first to apply statistical mechanics to the molecular description of water, in a quantitative analysis. Thus, water had become the most frequently studied of all liquids, within a comparatively short space of time.

The results gained so far have been interpreted in terms of either of two models for liquid water. The first of these, the Uniformist model, was based on the proposals of Bernal and Fowler, and envisaged a completely hydrogen-bonded arrangement of molecules throughout the liquid. The importance of bending, rather than breaking, of hydrogen-bonds on elevation of the temperature was suggested by Pople. The alternative has been the Mixture model, which assumes the coexistence of at least two arrangements of water molecules in equilibrium, sensitive to external conditions (e.g. temperature and pressure). Samoilov's interstitial model and the crystalline clathrate hydrate description of Pauling belong to this category. Other models have been suggested, but at present, the choice remains between the two rival theories and has not been definitely resolved. The Mixture model seems to be preferred, however. Support for the latter has been gathered from recent spectroscopic studies, although earlier work had been interpreted in terms of the Continuum model. The presence in water of non-hydrogen-bonded OH groups has been demonstrated by Walrafen. Dielectric and acoustic properties are both consistent with the concept
of water being a mixture of two or more distinguishable species, whilst neutron scattering results have demonstrated the existence of structured regions in the liquid. Experiments performed by Safford indicate that water molecules remain in an ordered region for \(10^{-12}\) seconds, and then jump away. X-ray scattering, however, has shown that the "structure" in liquid water extends only over relatively short distances.

The availability of sophisticated computing techniques has been responsible for growing interest in the application of theoretical calculations to the water molecule and its aggregates in the liquid. Of the results so far published, some seem to conflict with the two state water model, and certainly appear inconsistent with the view of liquid water as a disrupted ice or crystal lattice, in spite of calculations in one case being based on a body-centred cubic ice-VIII lattice. Application of statistical thermodynamics has discounted the idea of large clusters (>60 molecules) at any temperature. Calculations on the water dimer and trimer have suggested the hydrogen-bond strength to be approx. 20.92 kJ mol\(^{-1}\), and also that polarization accounts for a significant proportion of the binding energy, as well as determining the structure of the complex. The earlier proposal of a non-linear hydrogen-bond has not been confirmed, but Frank's concept of hydrogen-bond co-operativity has been clearly demonstrated. Simple electrostatic models for hydrogen-bonding have been shown inappropriate. Sequential trimers (see diagrams below) are found to be more stable at the ice distance \((2.76 \times 10^{-10} \text{m})\) than double acceptors or double donors;
studies of larger aggregates are now in progress.

Figure 2.1

Linear hydrogen-bonded water dimer, trans configuration (ref. 30)

Figure 2.2

The three distinct classes of hydrogen-bond triplets.

From the evidence available, it seems that water does contain broken hydrogen-bonds, with accompanying fluctuations in density; the most attractive approach to the liquid at present is the semi-empirical model of Frank. Water is visualized as a dynamic two-state system, comprising bonded ("bulky") water, with predominantly tetrahedral co-ordination, and non-bonded ("dense") water, the latter having shorter than normal oxygen/oxygen distances. The relationship between these is represented by the equilibrium:
where $\Delta h^* > 0$ and $\Delta V^* < 0$. Thermodynamics can provide no information on the exact nature of the two states, however. $(H_2O)_b$ has been identified with ice or clathrate lattices, whilst $(H_2O)_d$ can refer to water molecules in interstitial sites or cavities, or just a dense fluid between regions of hydrogen-bonded water molecules. The lifetime of the bulky state (between $10^{-10}$ and $10^{-11}$ seconds) is just sufficient for the species to be chemically meaningful, and very much shorter than the half-lives of reactions studied in this project. This model seems most favoured at the present time, especially because the effects of solutes on physical properties of water cannot be readily accounted for by a continuum model. Recently, the analogy of water with an infinitely and randomly branched "gel" of interchanging hydrogen-bonds has been made. However, in this thesis, the mixture model for water will be used in the discussion of the properties of aqueous solutions.

### 2.2 Aqueous Solutions

Considerable interest is currently being shown in the role of water in biological systems. Because the macromolecules present in living cells (proteins, carbohydrates, nucleic acids, etc.) are constructed from small polar and apolar building blocks, an understanding of the simple solution behaviour exhibited by these basic units would seem invaluable to the knowledge of life processes. In spite of the obvious need for this information, very few aqueous systems have so far been investigated in detail. The most well-documented to date include alkali halides, tetra-alkylammonium halides and
the lower monohydric alcohols. The simplest systems amenable to study are aqueous solutions of the rare gases, followed by hydrocarbons and other monofunctional solutes. Such apolar molecules have provided evidence of complex solution behaviour in water, principally through their marked heat capacity effects, entropy and volumetric behaviour. Thus the low solubility of inert gases is a consequence of a marked negative entropy of solution, even though the process is exothermic.

Polar non-electrolytes, in contrast, are more soluble, due to direct interaction between solute and water; solutions here are enthalpy dominated and heat capacities small. Electrolyte solutions are treated quite differently, because the solution process is dominated by intense ion/solvent interactions. Apolar electrolytes (e.g. the alkyl-substituted quarternary ammonium salts) do not conform to expected electrolyte behaviour, however, resembling to a high degree hydrocarbons in solution. These solutes show for the most part "hydrophobic hydration". Other molecules, such as urea seem to behave in a quite unique manner (see Chapter 10).

No adequate theory for solutions exists at present. Interest in apolar solutes originated from the results of Butler, pointing to the importance of entropies of solution, and the discovery of "compensation" between entropy and enthalpy. Eley attributed the observed large negative entropies of solution to the combination of loss of translational motion by the solute, on going from gas phase to solution, and the formation of the corresponding solvent
Frank and Evans' proposal that water became increasingly ordered around a solute ("iceberg formation") received support from a comparison of hydrocarbon clathrate hydrates with hydrocarbon solutions. Pauling's water hydrate model was similarly extended to methane solutions, whilst Némethy and Scheraga attempted to explain the interactions of water and solute in an extension of their statistical mechanical model for water. However, by making use of the semi-empirical approach to water suggested by Frank (see above), a reasonably acceptable picture of solutions can be obtained. It would seem that apolar solutes shift the equilibrium (1) from right to left, such that the proportion or size of clusters is increased (i.e. $(H_2O)_n^+$ increased) - see reference 47. This model is also supported by Ben Naim. In this work, aqueous non-electrolyte systems were studied, and it is useful to consider these in terms of the previously defined classification due to Rowlinson and Franks. This is based on the distinction between solutes exhibiting typically aqueous (TA) solution behaviour, e.g. the hydrocarbons, and those classed as typically non-aqueous (TNA), the hydrophilic substances such as sugars. The former class includes both apolar and mixed solutes, but in each case the apolar groups are dominant, a peculiarity of aqueous solutions. TNA solutes, however, contain a preponderance of polar groups which determine the solution properties, the latter then resembling normal non-aqueous solutions.

The two groups may be distinguished thermodynamically by the relative magnitudes of their molar excess functions of mixing, $X^E$ (see Chapter 3). TA solutes are entropy-
controlled, such that $T|S^E| < |H^E|$, whilst the reverse is true of TNA solutes, where $|H^E| > T|S^E|$. Examples of each type are given below:

I. Typically Aqueous solutes. These include the alcohols + water, acetone + water; $G^E$ is positive, because $T \Delta S^E$ is negative, reflecting the importance of hydrophobic alkyl groups which exert a "structure-forming" action on the water.

II. Typically Non-aqueous solutes. Two groups are possible here: (a) $G^E$ is positive, for example acetonitrile + water. In fact, both $G^E$ and $H^E$ are positive in this case. The cosolvent exerts a depolymerizing effect on the water, and hence may be regarded as a structure-breaker. Such systems

Excess functions for Ethanol/Water at 298K.

At low mole fractions, overlapping of solvent co-spheres around the solute molecules further enhances water/water interactions. Should $G^E$ become large ($> \frac{1}{2}RT$), then the solvent mixtures will phase separate with a Lower Critical Solution Temperature, e.g. triethylamine + water. This point is particularly sensitive to changes in pressure or addition of other solutes, e.g. salts.
show a tendency to phase separate at an Upper Critical Solution Temperature.

(b) $G^E$ is negative, as for dimethylsulphoxide + water, hydrogen peroxide + water (see Chapter 7). Such mixtures are enthalpy-controlled, with exothermic mixing. The strong intercomponent association predominant in these systems leads to an obvious breakdown in water/water interactions, and there
is no tendency to phase separate. The position of the liquid mixtures used here, with regard to the above classification will be dealt with in the later chapters.

Various experimental techniques have been used in the investigation of solutions recently, for example in hydrogen-bonding studies,\textsuperscript{50} examining the extent of solvent structuring,\textsuperscript{51-53} tendency to phase separation,\textsuperscript{54} and the strength of intermolecular interactions.\textsuperscript{55} In the case of monofunctional compounds, interstitial types of solution seem preferred. TNA solutions provide no evidence for clustering or enhancement of water/water interactions, and only short-range interactions are observed. Studies of ternary aqueous systems having an apolar solute as one component (e.g. water/urea/apolar solute,\textsuperscript{56} water/\(R_4N^+\)/hydrocarbon\textsuperscript{57} or water/argon/organic compound\textsuperscript{58}) have also assisted in clarifying the nature of solute/solvent interactions.

2.3 The Gel State

A brief introduction will now be given to this particular type of aqueous system which has been of interest to us. It is known that water often comprises up to 80\% or more of the mass of a living cell. This cell water may contain polymers and colloidal dispersions of particles, or may be in a gel state. Aqueous gels have been previously used as model systems for the living cell, in order to probe the structure and function of water contained therein.\textsuperscript{59} From such studies of macromolecular solutions, the phenomenon of "bound water" has arisen: some workers have concluded that the water surrounding proteins,
for example, has a structure intermediate between that of a liquid and a solid, thus lending structure to the macromolecule and enabling ions to be excluded. In particular, it is observed that cell water does not freeze at 273K. It was hoped, therefore, that some additional information on this matter could be obtained from our work.

After an investigation of the solution properties of the macromolecule polyvinylpyrrolidone, two gel systems were selected (see Chapter 9). The first of these was gelatin, a protein gelling agent whose parent molecule Collagen is the principal protein in mammals, accounting for 60% of the total protein content. Agar, impure agarose, was the alternative used because this polysaccharide gel has become the model for all gelling systems. Polysaccharide gels have biological functions in plant cell walls, animal fluids and connective tissues, as well as many commercial uses.

Although detailed structures of both these gels are not definitely known, a clearer picture is now slowly developing. In 1962, Plodin demonstrated that agarose gels consisted of cross-linked matrices with water trapped in the interstices, the degree of cross-linking being variable. Veis (1964) indicated that gelatin gels could interact by intermolecular hydrogen-bonding between the protein chains, but later evidence has tended to contradict this viewpoint. For example Pilling has demonstrated the gelation of gelatin by hydration and charge interaction alone, without intermolecular hydrogen-bonding. Thus, a mechanism involving hydration is now greatly favoured.

The most recent proposition for the mechanism of gelation
by agarose suggests a resemblance to that of the Carrageenans. The structures of both polysaccharides are given below, for comparison:

\[
\text{Agarose:} \quad [\text{HO}-\text{CH}_2\text{OH}-\text{HO}]_n
\]

\[
\text{Carrageenan:} \quad [\text{O}_3\text{SO}\text{CH}_2\text{OH}-\text{HO}]_n
\]

Computer models have already indicated the possibility of double helix formation by agarose. The schematic representation of the sol→gel transition for i-carrageenan is as follows:

The gel is seen to result from the association of polysaccharide chains to form a three-dimensional network, the junction zones containing double helical regions. Recent evidence suggests the existence of even larger aggregates, also. Inspite of the low concentration of dispersed polysaccharide required for gelling, each network is a very highly associated structure. The related polysaccharides, alginates and pectins gel through the ordering of their polycarboxylic chains, the
process in this case being assisted by packing Ca\(^{2+}\) cations in the polymer chain interstices (the "egg-box junction" model):—

Schematic representation of the sol-gel transition for alginate, involving egg-box junction zones.

The gelation of gelatin appears to involve a different mechanism. On cooling a gelatin solution below 313K, the initially random molecular coil conformation becomes more ordered until a pattern of triple helices is obtained (reversion to the 'collagen fold'). The process is intramolecular, with a low activation energy — see diagram below. At this stage, the flowing species in solution are reasonably spherical and gelling occurs, provided the concentration is

Diagrammatic representation of the nucleation and folding sequences in a portion of the \(\alpha\)-gelatin chain.
sufficiently high, at the point of first contact between spheres. The spheres themselves have been visualized with a diameter of 45 nm and surrounded by a shell of water molecules two or three layers in depth, approximately 1-2 nm thick. Thus, initial contact between the spheres is via the hydration layers, which provide a means of transmitting attractive forces between the particles. Electron micrographs of such gels show a mesh structure, the pore size of which indicates construction from strands formed from aggregation of the individual particles (the "string of beads" model).

Varied techniques have been used for studies of gels: of particular importance were trace diffusion of ions and NMR of agar solutions. Statistical calculations on chain branching and the thermodynamics of the double helix → coil transfer have also been examined; results in the latter case gave the enthalpy change \( \Delta H_r = 5.02 \text{ kJ (mol of residue)}^{-1} \) and entropy \( \Delta S_r = 14.85 \text{ J (mol of residue)}^{-1}\text{K}^{-1} \). Cell water was taken to be more structured than bulk water from early NMR measurements, but later results for agar have been interpreted in terms of a two-state model (see Chapter 9). Water adjacent to the macromolecule is assumed to be modified by the presence of that surface, although rapid exchange occurs between the bulk and "bound" water molecules. The trace diffusion results, for example, may be explained by regarding the gel as a random arrangement of heavily hydrated needles. Some workers have proposed that the free water in polysaccharide gels is a mixture of at least two different states, but this idea has not been confirmed so far. The results of an investigation into the kinetics of reactions in gels are summarized in Chapter 9.
2.4 Substrates used in Kinetics

Studies of solvent effects in aqueous solution on the mechanisms of many varied chemical reactions have been and are being pursued in depth by Robertson, Arnett, Hyne, Kohnstam, Caldin and others. Consequently, the reactions studied in this work have been well-characterized previously and are known for their sensitivity to environment. In each case, the kinetics were first-order, thus facilitating the analysis of data, and the reactions were used as probes, to monitor changes in the aqueous solvent as the composition of the latter was altered.

The first substrate was the organic compound tertiary-butyl chloride, which solvolyses in water according to the equation,

\[
(CH_3)_3Cl + H_2O \rightarrow (CH_3)_3COH + H^+ + Cl^-
\]

The mechanism for reaction is well known as \(S_N^1\) dominated, from the detailed studies to be found in the literature, the original proposal having been made by Ingold and Hughes in 1933. Various techniques have been adopted for kinetic measurements since then (conductometric, as here, and electro-metric), and the rate constant for solvolysis has been found to decrease in aqueous mixtures containing alcohols, acids, ethers, an amide and acetonitrile. Robertson was the first to suggest, and Arnett subsequently agreed, that ground state solvation of the t-butyl chloride could be important towards explaining this observation. More details are given in Chapter 6.

The second substrate was an inorganic complex of iron(II), the tris(5-nitro-1,10-phenanthroline) iron(II) cation, which
Figure 2.3

The tris(5-nitro-1,10-phenanthroline)iron(II) cation.
was chosen because of its size (see Figure 2.3) and also because it was envisaged that its kinetics might be modified considerably by constriction in a gel matrix. The reaction, monitored spectrophotometrically, was dissociation of the coloured ion in the presence of metal ions Ni^{2+} and Zn^{2+}. The latter were required for promotion of the aquation, instead of the more customary acid. Previous studies have shown that rates of aquation of this iron(II)-phenanthroline complex are extremely sensitive to changes in the nature and composition of the medium (see Chapter 9). For comparison with these results, a bimolecular reaction was also investigated in the gel phase: cyanide attack on the analogous 5-methyl complex of iron(II) was selected as fulfilling all the experimental requirements. The bimolecular mechanism of this reaction has been reasonably well characterized, and studies have also been made in mixed solvent systems.

Results for t-butyl chloride solvolysis in mixed aqueous solvents are given in Chapters 7, 8 and 10, while the iron complex dissociation appears in Chapter 9. Firstly, however, it is necessary to examine the relation between the kinetics of reaction of the substrates and the properties of the aqueous media involved. This is accomplished in the following chapter. Close links have already been identified between the thermodynamic properties of aqueous mixtures and both their spectroscopic\textsuperscript{53} and ultrasonic absorption properties.\textsuperscript{54} Moreover, these links have often assisted in the interpretation of the data for a given system. Attempts to establish similar links between thermodynamic properties and the kinetics of reactions in these mixtures have so far been impeded by lack of information.
References

2. 'Water - A Comprehensive Treatise', F. Franks (ed.),
3. Chândogya Upanishad, ca. 1000 BC (?), 7: 10,1. Isabel
   Willcox Translation.
7. O.Ya. Samoilov, 'Structure of Aqueous Electrolyte Solutions
   and Hydration of Ions', Consultants Bureau, N.Y., 1965.
9. J.H. Wang, J. Amer. Chem. Soc., 1951, 73, 510; 1951, 73,
   4181; 1954, 76, 4755.
15. L. Pauling, in 'Hydrogen Bonding', D. Hadzi and
20. References given by Walraffen in (18) above.
36. See for example, refs. (6) and (43); A. Ben-Naim, J. Phys. Chem., 1965, 69, 1922.
37. See refs. (35) and (49), and references therein.


44. See reference (6).


61. References given in (60).
CHAPTER THREE

Thermodynamics of Aqueous Mixtures
3.1 Introduction

In this chapter, an attempt is made to analyse the thermodynamic properties of mixtures in which kinetic measurements have been recorded. Rate constants, and hence the derived thermodynamic activation parameters for reactions in binary aqueous systems are known to depend on the medium composition. This dependence is complex because the activation parameters themselves reflect differences between the thermodynamic quantities describing initial and transition states (see Chapter 6). Investigation has indicated, however, that for the water-rich systems, the most important changes occur in the initial rather than transition state parameters. These conclusions will be examined in an analysis which emphasizes the properties of the solvent to a greater extent than has been done before. The following convention will be used throughout (unless otherwise stated) for the components involved:

Species 1: Water.
Species 2: Substrate undergoing reaction (e.g. t-butyl chloride).
Species 3: Organic cosolvent (e.g. ethanol in ethanol/water mixtures).

3.2 Analysis of Initial State Parameters

In Arnett's thermodynamic studies, the variation of \( H^\circ_2 \) - the standard partial molar enthalpy of a solute - with change in mole fraction of organic cosolvent was observed. The tendency for \( H^\circ_2 \) to increase at low alcohol mole fraction was attributed to the enhancement of water/water interactions by
the cosolvent. The effect of cosolvent on the chemical potential of the solute may be quite different, however. In the previous chapter, the importance of entropy changes in aqueous solutions was stressed. It would seem preferable, therefore, as Arnett suggested, to use entropy data for any detailed analysis of cosolvent effects. Unfortunately, the compilation of such presents a formidable task, since entropy calculations require solute vapour pressures and heats of solution for a whole range of aqueous mixtures (e.g. 2 in a mixture of 1+3). The following analysis was devised in an attempt to solve this problem: enthalpies, Gibbs free energies, and entropies of solution are derived for binary aqueous mixtures, making use of the following information:

(a) Thermodynamics of mixing for the binary mixture of 1+3.
(b) Solubility data for 2 in pure 1 and pure 3.

The basis employed for predictions of gas solubility in mixtures of liquids has been a relatively straightforward analysis by J.P. O'Connell and J.M. Prausnitz.

The final section of the chapter gives some indication of the applications of the analysis, and predictions which can be made from the equations obtained. However, it is necessary to examine individually the two contributory subjects mentioned above, namely the thermodynamics of binary mixtures and the quantitative analysis of solubility data.

3.3 Thermodynamics of Binary Mixtures

In this section, the definition of an ideal mixture is extended to cover non-ideal cases, and typical examples of the latter are given, along with a common theoretical model used
to express excess properties.

The chemical potential of a component \( i \) in an ideal mixture, where Raoult's law is obeyed over the whole range of composition, can be written as

\[
\mu_i = \mu_i^\circ(T,p) + RT \ln x_i \tag{1}
\]

For all values of \( i \),

\[
\mu_i^\circ(T,p) = \mu_i^\circ(T,p) \tag{2}
\]

where \( \mu_i^\circ(T,p) \) represents the chemical potential of pure component \( i \) at the same temperature and pressure. The change in Gibbs free energy on forming a mixture from \( n_1 \) moles of component 1 with \( n_2 \) moles of component 2, at constant temperature and pressure is given by:

\[
\Delta G_{\text{mixing}} = G_{\text{mixture}} - G_{\text{unmixed}} = n_1 \mu_1 + n_2 \mu_2 - n_1 \mu_1^\circ - n_2 \mu_2^\circ = n_1 (\mu_1 - \mu_1^\circ) + n_2 (\mu_2 - \mu_2^\circ)
\]

Therefore, from equation (1),

\[
\Delta G_{\text{mixing}} = RT \left\{ x_1 \ln x_1 + x_2 \ln x_2 \right\}
\]

and,

\[
\frac{\Delta G}{\text{mole}} = \frac{\Delta G}{n_1 + n_2} = RT \left\{ x_1 \ln x_1 + x_2 \ln x_2 \right\} \tag{3}
\]

Clearly, the enthalpy of mixing \( H^m \) must be zero for such a mixture, since

\[
-\frac{H^m}{T^2} = \frac{\partial (G^m/T)}{\partial T} = 0 \tag{4}
\]

and \( x_1 \) and \( x_2 \) are independent of \( T \) and \( p \). The entropy of mixing is given in equation (5), where \( G^m = H^m - TS^m \).

\[
S^m = -\frac{\partial G^m}{\partial T} = -x_1 R \ln x_1 - x_2 R \ln x_2 \tag{5}
\]

The volume of mixing, \( V^m \), like \( H^m \) is zero, since \( V^m = \partial G^m/\partial p = 0 \). Thus, ideality in these mixtures is characterized by complete
uniformity of cohesive forces: the forces between molecules of component 1 must be essentially the same as those between molecules of 2, and equally resemble forces between the unlike molecules 1 and 2. In practice, however, it is found that solutions seldom follow Raoult's law closely over an extended range of concentrations, simply because complete similarity of interaction between the components can rarely be achieved. This, then, leads to the concept of non-ideality; the chemical potentials of components in real mixtures, where Raoult's law is not obeyed, may be represented by writing

\[
\begin{align*}
\mu_1 &= \mu_1^0 + RT \ln x_1 f_1 \\
\mu_2 &= \mu_2^0 + RT \ln x_2 f_2
\end{align*}
\]

Here, \( f_1 \) and \( f_2 \), the rational activity coefficients are defined such that \( f_1 \to 1 \) as \( x_1 \to 1 \); \( f_2 \to 1 \) as \( x_2 \to 1 \).

The change in Gibbs free energy on forming a mixture from components 1 and 2, as above, is now given by

\[
\Delta G^m = n_1 \mu_1 + n_2 \mu_2 - n_1 \mu_1^0 - n_2 \mu_2^0 = RT \left\{ n_1 \ln x_1 f_1 + n_2 \ln x_2 f_2 \right\}
\]

and

\[
\Delta G/\text{mole} = RT \left\{ x_1 \ln x_1 f_1 + x_2 \ln x_2 f_2 \right\} = RT \left\{ x_1 \ln f_1 + x_2 \ln f_2 \right\} + RT \left\{ x_1 \ln x_1 + x_2 \ln x_2 \right\}
\]

\[\Delta G^\text{ideal} + G^E\]

\( G^E \) defines the Excess Gibbs free energy of mixing, the representation of the system's deviations from ideality, and this quantity may be positive or negative, depending on the activity coefficients \( f \). Clearly, if \( f_1 \) and \( f_2 \) > 1, then \( G^E \) is positive; conversely, if both are less than one, \( G^E \) is negative. Values of \( G^E \) may be obtained experimentally direct from vapour pressure measurements, since
\[ P_i / P_i^* = x_i f_i \]  

\( P_i \) is the vapour pressure of \( i \), \( P_i^* \) the vapour pressure of pure solvent 1 at the same temperature. The other related excess quantities can be derived from the free energy function in the normal way, e.g. the excess enthalpy,

\[
H^E = -T^2 \left( \frac{\partial (G^E/T)}{\partial T} \right)_p = -RT \left[ x_1 \frac{\partial \ln f_1}{\partial T} + x_2 \frac{\partial \ln f_2}{\partial T} \right]_p
\]

and entropy,

\[
S^E = - \left( \frac{\partial G^E}{\partial T} \right)_p = -RT \left[ x_1 \frac{\partial \ln f_1}{\partial T} + x_2 \frac{\partial \ln f_2}{\partial T} \right]_p - R(x_1 \ln f_1 + x_2 \ln f_2)
\]

The excess volume is given by:

\[
V^E = \left( \frac{\partial G^E}{\partial V} \right)_T = RT \left[ x_1 \frac{\partial \ln f_1}{\partial T} + x_2 \frac{\partial \ln f_2}{\partial T} \right]_T
\]

The excess heat capacity, \( C_p^E \), may be obtained from

\[
C_p^E = \frac{\partial H^E}{\partial T}
\]

\( H^E \) and \( V^E \) quantities are easily measured, being the heat of mixing and volume change on mixing respectively, since both the enthalpy and volume change on mixing ideally are zero (see above).

In the previous chapter, it has been seen that binary liquid mixtures can be conveniently classified on the basis of their molar excess functions; the definition and some examples of typically aqueous and non-aqueous mixtures have been examined. The diagram below illustrates three typical excess function plots, all of which (as required) become zero in the limit of pure component. In simple mixtures, excess functions are often parabolic in form, and many simple theoretical models give rise to quadratic excess properties:
for example, $X^E$ could be represented by the quadratic expression shown below, since this becomes zero when $x = 0$ and $x = 1$, and has its turning point when $x = 0.5$, $y = A/4$: 

$$X^E \approx x (1 - x) A$$

This function forms the basis for simple curve-fitting functions which can be used to represent the more complex curve shapes which are found in real mixtures. For the systems analysed in this project, the Guggenheim-Scatchard equation (below) was used in fitting $X^E$ data for binary aqueous mixtures:

$$x^E = x_1 (1 - x_1) \sum_{i=0}^{n} A_i (1,2) (1 - 2x)_i$$  \hspace{1cm} (13)$$

where $A_i$ values are regression coefficients. This method works by adding together curves which can ultimately produce any shape. The equation itself has not been tested: it has just been employed as a means of obtaining interpolated values of $G^E$ from the literature data, at specified mole fractions, (e.g. at 0.01 mf intervals over the range $0 < x < 1$. The equation was built into an Algol program, XEFIT, given in Appendix 2, and based upon a standard least squares matrix
procedure for obtaining the $A_i$ coefficients, where $i$ was specified. The best-fitted curve was taken when the standard deviation reached a minimum value, and the corresponding $A_i$ coefficients inserted into a second short program from which the calculated excess functions could be obtained at specified mole fractions. Curves for the resulting values of $X^E$ were then plotted, as necessary. The incorporation of excess Gibbs free energy functions into the final analysis will be demonstrated later in the chapter.

3.4 Solubility and Henry's Law

The second topic relevant to the analysis is Solubility, and thermodynamics deals with this subject in terms of Henry's law, a law which is particularly important for volatile solutes in dilute solutions. Considering a solution consisting of a solute $B$ in solvent $A$, then when the solution is sufficiently dilute, a situation can eventually arise at which each molecule of $B$ is effectively completely surrounded by component $A$. $B$ is then in a uniform environment, even though $A$ and $B$ may form far from ideal solutions at higher concentrations. The escaping tendency of $B$ from its environment is proportional to its mole fraction, but the proportionality constant is no longer given by the vapour pressure of pure $B$ at the same temperature (i.e. $P^*_B$). Henry's law is written as

$$P_B = k' x_B$$

(16)

$k'$ is the Henry's law constant and is clearly dependent on the nature of both solute and solvent. In an ideal solution, if the dissolved species obeys Henry's law, then the solvent must obey Raoult's law. The significance of the two laws in a
non-ideal solution is shown by the diagram.

From this theoretical background stems the interest for our analysis in Henry's law constants; an initial glance at the literature indicates the diverse ways of expressing the solubility of gases in liquids. It has been customary to present data in ways which reflect the method of solubility determination: hence, in order to obtain the necessary values of $k^*$ for systems, a number of conversions from the literature values were made. These were incorporated in the form of various subroutines and procedures into an Algol program HENRI, which was subsequently tested with the remainder of the solubility analysis by Mrs. E. Godfrey, of this department. The solubility measurements most frequently encountered and converted into Henry's law constants (units $N \cdot m^{-2}$) were expressed in either Bunsen or Ostwald coefficients, or simply the number of moles of solute for a given volume of solution. The Bunsen coefficient, $\alpha$, represents the volume of gas at 273.15K and standard pressure absorbed by unit volume of
solvent, whilst Ostwald coefficients \( L \) indicate the volume of gas absorbed by a given volume of solvent (both volumes being measured at the same temperature and pressure).

The density of the solvent figured prominently in the conversion equations required for the quantities named above. Since water was one of the common solvents used for the literature measurements, an expression for its density at specified temperatures was necessary for the analysis of gas solubilities. A program DENSITY, incorporating Kell's equation for the density of water as a function of temperature was used for the calculations:

\[
\rho(t) = \frac{a_0 + a_1 t + a_2 t^2 + \ldots + a_n t^n}{1 + b_1 t}
\]

where \( a_n \) are the coefficients given by Kell, \( t \) is the temperature in Centigrade and \( \rho(t) \) is expressed in g cm\(^{-1}\). The conversion factor required for \( \rho(\text{g cm}^{-3}) \) is

\[
\rho(\text{g cm}^{-3}) = \rho(t)(\text{g cc}^{-1}) \times 0.999972
\]

Finally, on collection and tabulation of the Henry's law constants, the temperature dependence of \( K' \) for a given solute in a given solvent was analysed using the Clarke-Glew expression (see Chapter 6),

\[
R \ln(K/P) = b_0 + b_1 u_t + b_2 u_2 + \ldots
\]

(17)

where \( b_0, b_1, b_2 \ldots \) are regression coefficients and \( u_t, u_2, u_3 \) etc. series functions of the temperature. In the Algol program written for this purpose, the series for each \( u_t \)-function was terminated when the ratio of the \( j \)-th term in this series divided by \( u_t \) was less than 10\(^{-12}\). The program had been tested using solubility data for gases in water, and
the derived parameters agreed with those reported in the literature.

Before the theory of the analysis is embarked upon, it is worthwhile defining the standard states which will be used; the literature has been found to provide not only a clash of units, but a wide discrepancy and mis-use of standard states. This naturally makes the task of collecting data between separate papers extremely difficult. Here, the standard state for a

Gas is the ideal gas at 298K and 101325 N m$^{-2}$.
Water, Cosolvent the pure liquids at 298K and 101325 N m$^{-2}$.
Solute the ideal solute, of hypothetical unit mole fraction

where $f_2^*$ is unity at 298K and 101325 N m$^{-2}$.

($f_2^*$ is the Henry's law activity coefficient)

3.5 Theory of the Analysis

Having collected Henry's law coefficients and excess functions from the available literature, the task of relating the two can now be undertaken, to further the aim of understanding initial state parameters. The analysis of Prausnitz and O'Connell is required for this process, as will be seen later. Firstly, a binary mixture consisting of components 1 and 3 must be considered, at fixed temperature and pressure, and where the chemical potentials are $\mu_1$ and $\mu_3$ respectively. Then,

$$\mu_1 = \frac{\partial G}{\partial n_1}, T, p, n_3 \quad \mu_3 = \frac{\partial G}{\partial n_3}, T, p, n_1$$

(18)

For the binary mixture 1+3, we can write

$$\mu_1 = \mu_1^*(T, p) + RT \ln x_1, (1, 3) f_1, (1, 3)$$

(19)
where \( \mu_1 = \mu_1^o \)
\[ x_i \to 1 \]
\[ f_i \to 1 \]
(\( \mu_1^o \) is the chemical potential of pure 1)

and similarly

\[ \mu_3 = \mu_3^o(T,p) + RT \ln x_3(1,3)f_3(1,3) \]  \( (20) \)

where \( \mu_3^o \)
\[ x_3 \to 1 \]
\[ f_3 \to 1 \]
(\( \mu_3^o \) is the chemical potential of pure 3)

The activity coefficients \( f \) have been defined here according to the symmetric convention. The molar excess Gibbs function for such a mixture is

\[ G^E = x_1RT \ln f_1(1,3) + x_3RT \ln f_3(1,3) \]  \( (21) \)

This may be rearranged as follows:

\[ G^E = \left( \frac{n_1}{n_1 + n_3} \right)RT \ln f_1 + \left( \frac{n_3}{n_1 + n_3} \right)RT \ln f_3 \]  \( (22) \)

or,

\[ (n_1 + n_3)G^E = n_1RT \ln f_1 + n_3RT \ln f_3 \]  \( (23) \)

When differentiated with respect to \( n_1 \) at fixed \( n_3 \), \( (23) \) becomes

\[ RT \ln f_1 + n_1RT \frac{d \ln f_1}{d n_1} + n_3RT \frac{d \ln f_3}{d n_1} = \frac{d}{d n_1} \left( \frac{G^E(n_1 + n_3)}{n_3} \right) \]  \( (24) \)

But the Gibbs-Duhem equation requires that

\[ RT n_1 \left( \frac{d \ln f_1}{d n_1} \right) + RT n_3 \left( \frac{d \ln f_3}{d n_1} \right) = 0 \]  \( (25) \)

Therefore,

\[ RT \ln f_1 = \frac{d}{d n_1} \left( \frac{G^E(n_1 + n_3)}{n_3} \right) \]  \( (26) \)

Now, if it may be assumed that the vapours are ideal, we can apply Raoult's law for a number of binary mixtures; for example, the mixture of 1+2, at fixed temperature,
Also, the mixture of 1+3,
\[
P_1(1,3) = P_1^0 x_1(1,3) f_1(1,3)
\]
\[
P_3(1,3) = P_3^0 x_3(1,3) f_3(1,3)
\]
and the mixture of 2+3,
\[
P_2(2,3) = P_2^0 x_2(2,3) f_2(2,3)
\]
\[
P_3(2,3) = P_3^0 x_3(2,3) f_3(2,3)
\]
Rearrangement of (27) gives
\[
f_1(1,2) = P_1(1,2)/x_1(1,2) P_1^0
\]
\[
f_2(1,2) = P_2(1,2)/x_2(1,2) P_2^0
\]
and of (28) gives
\[
f_1(1,3) = P_1(1,3)/x_1(1,3) P_1^0
\]
\[
f_3(1,3) = P_3(1,3)/x_3(1,3) P_3^0
\]
At this point, it is necessary to consider the solute, species 2, in solvent 1, in terms of Henry's law and the asymmetric convention. The vapour is again assumed to be ideal; then, the gaseous solute 2 in solvent 1 may be represented by the following,
\[
P_2(1,2) = k_2(1,2) x_2(1,2) f_2^*(1,2)
\]
where $k_2(1,2)$ is the Henry's law constant for solute 2 in 1, and $f_2^*(1,2) \to 1$ as $x_2(1,2) \to 0$ (the Asymmetric Convention).
But Raoult's law equally applies here, so that, as in equation (27)
\[
P_2(1,2) = P_2^0 x_2(1,2) f_2(1,2)
\]
and, therefore,
\[
k_2(1,2) f_2^*(1,2) = P_2^0 f_2(1,2)
\]
or,
\[
f_2^*(1,2) = \frac{k_2(1,2)}{P_2^0} f_2(1,2)
\]
Equation (34) provides a relation between the two activity coefficients. Then,

\[
\text{Lt } \frac{f_2(1,2)}{x_1 \to 0} = \frac{k_2(1,2)}{p_2^*} \quad \text{and} \quad \text{Lt } \frac{f_2(1,2)}{x_1 \to 1} = \frac{f_2^*(1,2)}{f_2^*(1,2)}
\]

Equations (35) and (36) may be combined on equating \( P_2^* \):

\[
\frac{f_2(1,2)}{x_1 \to 0} = \frac{f_2(2,3)}{x_1 \to 1} \cdot \frac{k_2'(1,2)}{k_2(2,3)}
\]

Thus, equation (38) relates the behaviour of solute 2 in the mixtures 1+2 and 2+3.

For the tertiary mixture (1,2,3), the following equations hold, making use of the symmetric convention,

\[
\begin{align*}
P_1(1,2,3) &= P_1^* x_1(1,2,3) f_1(1,2,3) \\
P_2(1,2,3) &= P_2^* x_2(1,2,3) f_2(1,2,3) \\
P_3(1,2,3) &= P_3^* x_3(1,2,3) f_3(1,2,3)
\end{align*}
\]

where \( f_i \to 1 \) as \( x_i \to 1 \).

If, however, we choose to treat component 2 as a solute, then Henry's law gives

\[
P_2(1,2,3) = k_2'(1,2,3) x_2(1,2,3) f_2^*(1,2,3)
\]

\[
\text{Lt } \frac{f_2^*(1,2,3)}{x_1 \to 0} = 1
\]

The reference here is the standard state of 2 in pure solvent 1.
As from equation (34), we can write

\[ \frac{f_2(1,2,3)}{f_2^*(1,2,3)} = \frac{k_2'(1,2,3)}{P_x} \]  

(42)

and \( \lim_{x_3 \to 0} f_2(1,2,3) = \frac{k_2'(1,2,3)}{P_x} = \frac{f_2(1,2,3)}{f_2^*(1,2,3)} \)  

(43)

We already have \( \lim_{x_2 \to 0} f_2(1,2) = \frac{f_2(1,2)}{f_2^*(1,2)} = \frac{k_2'(1,2)}{P_x} \) from (35) above.

So far, the analysis is based totally on the thermodynamic description of properties of solutions; at this stage, however, some extra-thermodynamic assumptions are required for the ternary mixture of components 1, 2 and 3. The excess thermodynamic function \( X^E(1,2,3) \) must be necessarily related in some way to the above properties. An expression for \( X^E(1,2,3) \) having the general form shown below is required:

\[ X^E(1,2,3) = f \left[ X^E(1,2), X^E(1,3), X^E(2,3) \right] \]  

(44)

\( X^E(i,j) \) is the corresponding excess function for each binary mixture \( i+j \). O'Connell and Prausnitz assumed that

\[ G^E(1,2,3) = G^E(1,2) + G^E(1,3) + G^E(2,3) \]  

(45)

A general expression for the excess function \( X^E \) for each binary mixture is also needed, having the form

\[ X^E(1,2) = f(x_1) \), e.g. \( G^E(1,2) = f(x_1) \).

The simple parabolic dependence equation has already been mentioned – see section 3.3. Essentially this was the first term in the Guggenheim-Scatchard equation:

\[ G^E(1,2) = x_1(1-x_1)A(1,2) \]  

(46)

for which \( G^E = 0 \) at \( x_1 = 0 \) and \( x_2 = 0 \). Also, the Guggenheim-
Scatchard equation itself, (13), has been previously described. Both of these are relevant to the present discussion and will subsequently figure in the theory.

Finally, a series of equations of the type shown is required, to relate activity coefficients, Henry's law constants and excess functions, e.g.

\[ \ln f_2^* (1,2,3) = f \left[ G^E (1,3) \right] \]

\[ k'_{2} (1,3) = f \left[ G^E (1,3) \right] \]

where \( k'_{2} (1,3) \) is the Henry's law constant for 2 in the 1+3 mixture. From combining these factors, the related thermodynamic quantities may eventually be obtained, all as functions of the excess enthalpy, entropy and heat capacity for the mixture 1+3. The partial molar enthalpy, entropy etc. will be

\[ H_{2} (1,3) = f \left[ H^E (1,3) \right] \]

\[ S_{2} (1,3) = f \left[ S^E (1,3) \right] \]

\[ C_{p,2} (1,3) = f \left[ C_{p}^E (1,3) \right] \]

Firstly, the parabolic dependence of excess functions must be incorporated into the analysis, in particular for the 1+2 mixture. We can write

\[ G^E (1,2) = x_{1} (1 - x_{1}) A(1,2) \]

Then, for species 2 using equation (26),

\[ RT \ln f_{2} = \frac{d}{dn_{2}} \left( \frac{n_{2} A(1,2)}{(n_{1} + n_{2})} \right)_{n_{1}} \]

i.e.

\[ RT \ln f_{2} = \frac{d}{dn_{2}} \left( \frac{n_{1} n_{2} A(1,2)}{(n_{1} + n_{2})} \right)_{n_{1}} \]

\[ = A(1,2)n_{1} \left[ -n_{2}(n_{1} + n_{2})^{-2} + (n_{1} + n_{2})^{-1} \right] \]
i.e. \[ \frac{RT \ln f_2}{RT} = A(1,2)n \left( \frac{-n_2 + n_1 + n_3}{(n_1 + n_2)^2} \right) = x_i^2 A(1,2) \]

This may be rewritten as \[ f_2 = \exp \left( \frac{A(1,2)x_i^2}{RT} \right) \] (47)

because \[ \frac{f_2(1,2)}{f_2^*(1,2)} = \lim_{x_i \to 0} f_2(1,2) \] from equation (35).

Then, clearly, \[ f_2(1,2) = f_2^*(1,2) \exp \left[ \frac{A(1,2)}{RT} \right] \]
or equally \[ f_2^*(1,2) = f_2(1,2) \exp \left[ -\frac{A(1,2)}{RT} \right] \] (48)

Hence \[ \ln f_2^*(1,2) = \ln f_2(1,2) - \frac{A(1,2)}{RT} \] (49)

For the case of the binary mixture 2+3, the parabolic expression requires that

\[ \frac{G^E(2,3)}{RT} = x_3(1 - x_3)A(2,3) \] (50)

and from (47) \[ \frac{RT \ln f_2(2,3)}{RT} = A(2,3)x_3^2 \] (51)

But equation (38) provides

\[ \lim_{x_i \to 0} f_2(1,2) = \lim_{x_i \to 0} f_2(2,3) \cdot \frac{k'(1,2)}{k'(2,3)} \]

Then, \[ \exp \left( \frac{A(1,2)}{RT} \right) = \exp \left( \frac{A(2,3)}{RT} \right) \cdot \frac{k'(1,2)}{k'(2,3)} \] (52)

or \[ A(1,2) = A(2,3) + RT \ln \left( \frac{k'(1,2)}{k'(2,3)} \right) \] (53)

This last equation is useful because it relates the two Henry's law constants, and it is an extrathermodynamic equation as a result of the derivation from the parabolic expression for \( G^E \).

The basic assumption of O'Connell and Prausnitz can now be applied to the ternary system, giving

\[ G^E(1,2,3) = A(1,2)x_1x_2 + A(2,3)x_2x_3 + A(1,3)x_1x_3 \] (54)
or 
\[ G^E(1,2,3) = \frac{A(1,2)n_1n_2 + A(2,3)n_2n_3 + A(1,3)n_1n_3}{(n_1+n_2+n_3)^2} \]  

Comparing equation (26),

\[
RT \ln f_x(1,2,3) = \frac{d}{dn_x} \left( \frac{A(1,2)n_1 + A(2,3)n_2 + A(1,3)n_3}{(n_1+n_2+n_3)^2} \right)
\]

\[
= \frac{A(1,2)n_1 - A(1,2)n_2 + A(2,3)n_3}{(n_1+n_2+n_3)^2} - \frac{A(2,3)n_2 - A(1,3)n_3}{(n_1+n_2+n_3)^2}
\]

\[
= A(1,2)x_1 - A(1,2)x_1x_2 + A(2,3)x_3 - A(2,3)x_2x_3 - A(1,3)x_1x_3
\]

Finally,

\[
RT \ln f_x(1,2,3) = A(1,2)x_1(1-x_2) + A(2,3)x_3(1-x_2) - A(1,3)x_1x_3
\]

Thus, the rational activity coefficient \( f_x \) for component 2 in the ternary liquid is given by

\[
f_x = \exp \left[ A(1,2)x_1(1-x_2) + A(2,3)x_3(1-x_2) - A(1,3)x_1x_3 / RT \right]
\]

The behaviour of component 2 in the mixture can, therefore, be described if the dependence of \( G^E \) on mole fraction for the three binary liquid mixtures is known. The intention is, in fact, to obtain the rational activity coefficient (i.e. \( f^*_x \)) for component 2 when only \( G^E(1,3) \) is available. This requires a definition of \( f_x \), taking as reference the standard state for \( f_x \) in pure 1 (i.e. \( f_x^* \) of course). Comparing with equation (47), we can write

\[
\text{Lt } x_i \rightarrow 1 \quad x_2, x_3 \rightarrow 0
\]

\[
\frac{df_x(1,2,3)}{dx_i} = \exp \left( \frac{A(1,2)}{RT} \right)
\]

\[ (59) \]
Equation (48) gives
\[
\frac{f_2(1,2,3)}{f_2^*(1,2,3)} = \exp \left( \frac{A(1,2)}{RT} \right)
\]  \hspace{1cm} (60)

(57) and (60) may now be combined to obtain an expression for \(f_2^*(1,2,3)\):
\[
\ln f_2^*(1,2,3) = \frac{A(1,2)}{RT} \left[ x_1(1-x_2)-1 \right] + \frac{A(2,3)}{RT} x_3(1-x_2) - \frac{A(1,3)}{RT} x_1 x_3
\]  \hspace{1cm} (61)

Then, for a solution where \(x_2 \to 0\),
\[
\lim_{x_2 \to 0} \ln f_2^*(1,2,3) = \frac{A(2,3)-A(1,2)}{RT} x_3 - \frac{A(1,3)}{RT} x_1 x_3
\]  \hspace{1cm} (62)

Equation (53) can now be used to eliminate \(A(2,3)\) and \(A(1,2)\), giving
\[
\lim_{x_2 \to 0} \ln f_2^*(1,2,3) = x_3 \ln \left( \frac{k'(2,3)}{k'(1,2)} \right) - \frac{x_1 x_3 A(1,3)}{RT}
\]  \hspace{1cm} (63)

This expression, then, has the necessary form, relating the unsymmetric activity coefficient for component 2 with the solubilities of 2 in 3 and 1. In order to obtain an equation containing \(f_2^*\) and the solubility of 2 in a mixture of 1+3, another extra-thermodynamic assumption must be employed.

Following the example of Prausnitz and O'Connell, the previous definition of \(f_2^*\) will be used, as in equation (32),
\[
f_2^*(1,2,3) = \frac{P_2}{x_2 k'_2(1,2)}
\]  \hspace{1cm} (64)

But, from (63) above,
\[
f_2^*(1,2,3) = \left( \frac{k'(2,3)}{k'(1,2)} \right)^{x_3} \cdot \exp \left( \frac{-x_1 x_3 A(1,3)}{RT} \right)
\]  \hspace{1cm} (65)

Combining (64) and (65)
\[
\frac{P_2}{x_2} = k'_2(1,2) \left( \frac{k'(2,3)}{k'(1,2)} \right)^{x_3} \cdot \exp \left( \frac{-G^B(1,3)}{RT} \right)
\]  \hspace{1cm} (66)

The parabolic expression for \(G^B\) has been incorporated into (66).
However, in dilute solutions, \( P_2 = x_2 k'_2(1,2,3) \) \( (67) \)

Replacement of \((67)\) in \((66)\) gives

\[
k'_2(1,2,3) = \left[ k'_1(1,2) \right] x_1 \left[ k'_2(2,3) \right] x_2 \exp \left[ -G^E(1,3)/RT \right]
\]

which may be re-written finally as:

\[
\ln k'_2(1,2,3) = x_1 \ln k'_2(1,2) + x_2 \ln k'_2(2,3) - G^E(1,3)/RT
\]

Thus, the aim of the theory has been successfully reached:

\[(69)\] provides the link between Henry’s law constants for 2 in the binary 1+3 mixture, with similar constants for solute 2 in both individual solvents, 1 and 3, and the excess function for the mixture 1+3. This clearly illustrates the need for analysis of the properties of the 1,3 mixture for \( G^E \), and a search for related solubility data. A more detailed examination is possible, also, since on obtaining \( k'_2(1,2,3) \), a range of thermodynamic functions may be calculated for the transfer of 2 into the 1,3 mixture. These are defined below, taking firstly the free energy term:

(i) For a solute 2 in solution mixture 1,2,3, the chemical potential of 2 is given by

\[
\mu_2(T,p,x_1,x_2,x_3) = \mu_2^* + RT \ln x_2 f_2^*
\]

\[= \mu_2^* + RT \ln \frac{P_2}{k'_2(1,2,3)} \] \( (71)\)

\((71)\) can be rewritten thus,

\[
\mu_2(T,p,x_1,x_2,x_3) = \mu_2(\text{liquid mixture}) + RT \ln \frac{P_2}{P_2^*} - RT \ln \frac{k'_2(1,2,3)}{P_2^*} \]

But for the solute 2 in the gas phase at the same temperature and pressure,
\[
\mu_2(\text{gas, } T, p) = \mu_2^\circ(g) + RT \ln \frac{P_2}{P_2^\circ} \quad (73)
\]

Therefore, at equilibrium, (72) and (73) must be equal,
\[
\mu_2^\circ(g) + RT \ln \frac{P_2}{P_2^\circ} = \mu_2^\circ(l) + RT \ln \frac{P_2}{P_2^\circ} - RT \ln k_2'(1,2,3)/P_2^\circ \quad (74)
\]

Then,
\[
\Delta G_2^\circ(\text{g} \rightarrow \text{mixt.}) = \mu_2^\circ(l) - \mu_2^\circ(g)
= RT \ln \left( \frac{k_2'(1,2,3)}{P_2^\circ} \right) \quad (75)
\]

The importance of this equation is obvious, since the free energy of transfer of 2 from gas to liquid mixture is required, and an expression for the Henry's law constant of 2 in mixture 1,2,3 has already been obtained, (69). This latter may now be inserted into (75):
\[
\Delta G_2^\circ(\text{g} \rightarrow \text{m}) = -RT \ln P_2^\circ + RT \ln k_2'(1,2,3)
\]
i.e.
\[
\Delta G_2^\circ(\text{g} \rightarrow \text{m}) = -RT \ln P_2^\circ + RTx_1 \ln k_2'(1,2) + RTx_3 \ln k_2'(2,3)
- G^E(1,3) \quad (76)
\]

(ii) The enthalpy term is derived below. The Gibbs-Helmholtz equation requires that
\[
\Delta H_2^\circ(\text{g} \rightarrow \text{m}) = -T^2 \frac{d}{dT} \left( \frac{\Delta G_2^\circ(\text{g} \rightarrow \text{m})}{T} \right)_P /dT \quad (77)
\]

Then
\[
\frac{\Delta H_2^\circ(\text{g} \rightarrow \text{m})}{T^2} = \frac{d}{dT} \left[ -RT \ln P_2^\circ + RTx_1 \ln k_2'(1,2) + RTx_3 \ln k_2'(2,3)
- \frac{G^E(1,3)}{T} \right] \quad (78)
\]

and
\[
\Delta H_2^\circ(\text{g} \rightarrow \text{m}) = -RTx_1 \frac{d}{dT} \ln k_2'(1,2) - RTx_3 \frac{d}{dT} \ln k_2'(2,3)
+ T^2 \frac{d}{dT} \left( \frac{G^E(1,3)}{T} \right) \quad (79)
\]

However, for the 1+3 mixture,
\[ H^m = -T^2 \frac{d}{dT} \left( \frac{\delta R(1,3)}{T} \right) \]  
(see equation (4))

where \( H^m \) is the enthalpy of mixing.

Also, for the gas 2 in a given solvent 1,
\[ \Delta G^\circ_2(1) = -RT \ln P^\circ_2 + RT \ln k_2'(1) \]  
(80)

Then \[ -\Delta H^\circ_2(1) = \frac{d}{dT} \left( R \ln k_2'(1) \right) , i.e. \Delta H^\circ_2(1) = -RT^2 \frac{d}{dT} \left( \ln k_2'(1) \right) \]  
(81)

Therefore, by making use of (81) and the equation for \( H^m \), we can write
\[ \Delta H^\circ_2(g \rightarrow m) = x_1 \Delta H^\circ_2(1) + x_3 \Delta H^\circ_2(3) - H^m \]  
(82)

(iii) The related entropy and heat capacity functions are obtainable thus:-
\[ \Delta S^\circ_2(g \rightarrow m) = \frac{-\Delta G^\circ_2(g \rightarrow m) + \Delta H^\circ_2(g \rightarrow m)}{T} \]  
(83)
\[ \Delta C^\circ P_2(g \rightarrow m) = x_1 \Delta C^\circ P_2(1) + x_3 \Delta C^\circ P_2(3) - C^\circ P_E \]  
(84)

(iv) Finally, the specific case for which 1 represents water, and 1 + 3 a binary aqueous mixture must be considered. The relevant transfer functions (1 \( \rightarrow \) mixture 1, 3) can be evaluated thus:-

As with (74), we can write (m denotes mixture)
\[ \mu^\circ_2(m) + RT \ln \frac{P_2}{P^\circ_2} = \mu^\circ_2(1) + RT \ln \frac{k_2'(1,3)}{P^\circ_2} \]  
(85)

Since
\[ \Delta G^\circ_2(1 \rightarrow m) = \mu^\circ_2(1,3) - \mu^\circ_2(1) \]  
(86)
\[ = RT \ln k_2'(1,3) - RT \ln k_2'(1) \]

Using the expression for \( k_2'(1,3) \), (69),
\[ \Delta G_{x}^{\ast}(1 \rightarrow m) = RTx_{i} \ln k_{x}^{\ast}(1) + RTx_{j} \ln k_{x}^{\ast}(3) - G_{x}^{E} - RT \ln k_{x}^{\ast}(1) \]

\[ = RT(x_{i} - 1) \ln k_{x}^{\ast}(1) + RTx_{j} \ln k_{x}^{\ast}(3) - G_{x}^{E} \]

\[ = -x_{3}RT \ln k_{x}^{\ast}(1) + RTx_{3} \ln k_{x}^{\ast}(3) - G_{x}^{E} \] (87)

The other functions are obtained from equations of similar form,

\[ \Delta H_{x}^{\ast}(1 \rightarrow m) = -x_{3} \Delta H_{x}^{\ast}(g \rightarrow 1) + x_{3} \Delta H_{x}^{\ast}(g \rightarrow 3) - H_{x}^{m} \] (88)

\[ \Delta C_{P_{x}}^{\ast}(1 \rightarrow m) = -x_{3} \Delta C_{P_{x}}^{\ast}(g \rightarrow 1) + x_{3} \Delta C_{P_{x}}^{\ast}(g \rightarrow 3) - C_{P}^{E} \] (89)

\[ \Delta S_{x}^{\ast}(1 \rightarrow m) = \frac{\Delta H_{x}^{\ast}(1 \rightarrow m) - \Delta G_{x}^{\ast}(1 \rightarrow m)}{T} \] (90)

3.6 Conclusions

The most important equations from the analysis were brought together as part of two simple computer programs, in order to present the data in a reasonable form. The required input included:

(a) the number of parameters in the Guggenheim-Scatchard equation for \(G_{x}^{E}, H_{x}^{E}\) and \(C_{P_{x}}^{E}\), (derived from XEFIT);

(b) Henry's law constants for solution in water 1, and cosolvent 3, as well as \(\Delta G^{\ast}, \Delta H^{\ast}\) and \(\Delta C_{P}^{\ast}\) quantities for both solutions at 298K;

(c) the actual Guggenheim-Scatchard coefficients, \(A_{x}\), for \(X_{x}^{E}\) at 298K.

Ultimately, from the Prausnitz equation (69), and making use of the Henry's law constants, values of \(\Delta G^{\ast}, \Delta H^{\ast}, \Delta S^{\ast}, T\Delta S^{\ast}\) and \(\Delta C_{P}^{\ast}\) for the transfer of solute from gas phase to mixture were calculated for mole fraction intervals of 0.01 (equations 76, 82, 83, 84). In contrast, the same quantities were printed for the case when \(G_{x}^{E}, H_{x}^{E}, S_{x}^{E}\) and \(C_{P_{x}}^{E}\) were zero, i.e. the ideal mixture.
From equation (76), the theory predicts that a solute will be less soluble (i.e. $\Delta G^\circ$ more positive) in the mixture than in the corresponding ideal solution, when $G^E$ is negative; however, when $G^E$ is positive, the solubility will be greater. This prediction is borne out in several cases, even for aqueous solutions: for example, the solubilities of adenine and thymine reported by Herskovits and Harrington, in different aqueous mixtures. As the theory suggests, these solutes are less soluble in water + ethylene glycol ($G^E$ is negative) than in the ideal mixture, but more soluble in water + methanol, ethanol or n-propanol, where $G^E$ is positive. To illustrate the application of the theory, two systems relevant to the work reported in this thesis will be described: ethanol/water and ethylene glycol/water mixtures. Solubility data for both argon and hydrocarbons are available in the literature for the former system, but argon alone is quoted for glycol. This proves sufficient for a brief discussion of the results, however.

3.6.1 Solubilities in Ethanol/Water mixtures

Data for argon solubility in water were taken from Bunsen coefficients reported by E. Douglas, for the temperature range 278.15 - 303.15K at 1K intervals. The density of water at corresponding temperatures was calculated from the program DENSITY, as mentioned previously. HENRI was used to analyse the solubility data, and the resulting quantities are given below, with those for ethanol. Bunsen coefficients at six temperatures, obtained by A. Lannung, provided the data for argon in ethanol, and density of the latter was calculated by
means of the equation given by Kirk-Othmer. The solution quantities were again obtained from HENRI analysis:

<table>
<thead>
<tr>
<th>Water</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k' = 4.0286 \times 10^9$ N m$^{-2}$</td>
<td>$k' = 1.6317 \times 10^8$ N m$^{-2}$</td>
</tr>
<tr>
<td>$\Delta G^*_2 = 26.2532 \times 10^3$ J mol$^{-1}$</td>
<td>$\Delta G^*_2 = 18.3049 \times 10^3$ J mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta H^*_2 = -11.7101 \times 10^3$ J mol$^{-1}$</td>
<td>$\Delta H^*_2 = -9.7412 \times 10^2$ J mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta C_P^*_2 = 228.4517$ J mol$^{-1}$ K$^{-1}$</td>
<td>$\Delta C_P^*_2 = 0$</td>
</tr>
<tr>
<td>$T\Delta S^*_2 = -37.9633 \times 10^3$ J mol$^{-1}$</td>
<td>$T\Delta S^*_2 = -19.279 \times 10^3$ J mol$^{-1}$</td>
</tr>
</tbody>
</table>

It is clear that the gas is not very soluble in either solvent, but is just slightly more soluble in ethanol: the Henry's law constant is larger for argon in water, and $\Delta G^*$ larger and positive for this solution. The transfer is exothermic for both solvents, although less so for ethanol, but this factor is opposed dramatically by the entropy change (particularly in the case of water). Once again, this characteristic of all aqueous systems is noticeable here.

Excess functions for the ethanol/water mixture are shown in the diagram. Excess Gibbs functions were calculated from vapour pressure data by Dobson and combined with those of Vaslow and Linderstrom for input to XEPIT. Heats of mixing were those determined by Boyne and Williamson, and excess heat capacity data obtained from Arnaud, Avedikian and Morel (see Fig. 3.1). Trends predicted by the Prausnitz analysis, from the combination of solubilities and excess functions, are shown in Figure 3.2.

Actual solubilities of argon in the mixture have been measured by Ben-Naim and Baer, and this enabled a comparison with the Prausnitz calculations to be made. Ben-Naim's data
Figure 3.1 Molar thermodynamic functions of mixing for water and ethanol at 298.15K; $x_2$ is the mole fraction of ethanol.
Figure 3.2 Thermodynamic functions for transfer of argon from gas phase to water + ethanol mixtures at 298.15K. Broken lines indicate calculated values if mixture were ideal; $x_3$ is the mole fraction of ethanol.
do not, however, cover the complete mole fraction range. It was found that the most important experimental features were reflected by the theoretical results, but subtle trends observed at low ethanol mole fractions were not predicted. Thus, the maximum in solubility near $x_2 = 0.1$ and the minimum near $x_2 = 0.15$ ($x_2$ is mole fraction of ethanol) found experimentally were not calculated by the theory. However, argon is more soluble in the binary aqueous mixture than in the ideal mixture, indicating the stabilization arising from the rapid decrease in chemical potential. The dominant factor is clearly the entropy change, and the important rise in $\Delta H^\circ$ observed by Arnett for nearly all solutes is surprisingly absent, at low cosolvent mole fractions.

The choice of argon as a model solute is not a good one, however, since most of the kinetic studies in this project have involved t-butyl chloride as substrate. Ideally, then, a polyatomic gas should be sought: fortunately, some data are available for the hydrocarbons propane and butane in both water and ethanol, and the Prausnitz analysis has been subsequently applied. The diagram for butane only will be shown.

The solubility of both hydrocarbons in water was measured by Wauchope, while data for ethanol were obtained from the work of Kretschmer. The thermodynamic quantities are shown below. Relative to the values given previously for argon, the hydrocarbon solubilities in water are strikingly similar, and the insolubility still accounted for largely by the negative $\Delta S^\circ$. However, both hydrocarbons are much more soluble in ethanol than was argon. The predicted transfer
1. Propane in Ethanol Water

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta G^\circ)</td>
<td>4585 J mol(^{-1})</td>
<td>26100 J mol(^{-1})</td>
</tr>
<tr>
<td>(\Delta H^\circ)</td>
<td>1020 J mol(^{-1})</td>
<td>-21376 J mol(^{-1})</td>
</tr>
<tr>
<td>(\Delta S^\circ)</td>
<td>-3565 J mol(^{-1})</td>
<td>-47476 J mol(^{-1})</td>
</tr>
<tr>
<td>(\Delta C_{P}^\circ)</td>
<td>359 J mol(^{-1}) K(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>

2. Butane in Ethanol Water

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta G^\circ)</td>
<td>4966 J mol(^{-1})</td>
<td>26510 J mol(^{-1})</td>
</tr>
<tr>
<td>(\Delta H^\circ)</td>
<td>1653 J mol(^{-1})</td>
<td>-25577 J mol(^{-1})</td>
</tr>
<tr>
<td>(\Delta S^\circ)</td>
<td>-3313 J mol(^{-1})</td>
<td>-52087 J mol(^{-1})</td>
</tr>
<tr>
<td>(\Delta C_{P}^\circ)</td>
<td>288 J mol(^{-1}) K(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>

functions for solute from gas to liquid mixture are shown in Figure 3.3. Once again, the positive value of \(\Delta H^\circ\) for solutes at low mole fractions of organic cosolvent, expected from Arnett's suggestion, is not apparent. Stabilization of the gas in the liquid mixture relative to that in the ideal mixture is predicted, however, as in the case of argon. The most dramatic feature is the increase in the entropy quantity.

### 3.6.2 Solubilities in Ethylene Glycol/Water mixtures

Finally, it is interesting to compare the results above with those from the analysis in operation for a mixture having negative \(G^E\). Ethylene glycol/water is a convenient example, since not only was this one of the systems studied experimentally when the conductivity equipment was first set up, but also data for argon solubility in glycol were eventually traced (hydrocarbon data were not available). The
Figure 3.3 Thermodynamic functions for transfer of butane from gas phase to water + ethanol mixtures at 298.15K. (See caption to Figure 3.2).
thermodynamic functions listed below for argon in ethylene glycol were obtained from Gjaldbaek and Niemann,¹⁵ and for water as before.

<table>
<thead>
<tr>
<th>Water</th>
<th>Ethylene Glycol</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k' = 4.02859 \times 10^9 ) N m⁻²</td>
<td>( k' = 1.28134 \times 10^9 ) N m⁻²</td>
</tr>
<tr>
<td>( \Delta G^\circ = 26.2532 \times 10^3 ) J mol⁻¹</td>
<td>( \Delta G^\circ = 23.413 \times 10^3 ) J mol⁻¹</td>
</tr>
<tr>
<td>( \Delta H^\circ = -11.710 \times 10^3 ) J mol⁻¹</td>
<td>( \Delta H^\circ = 1.202 \times 10^3 ) J mol⁻¹</td>
</tr>
<tr>
<td>( T\Delta S^\circ = -37.96 \times 10^3 ) J mol⁻¹</td>
<td>( T\Delta S^\circ = -22.211 \times 10^3 ) J mol⁻¹</td>
</tr>
</tbody>
</table>

Argon is clearly more soluble in ethylene glycol, in spite of the endothermic contribution of \( \Delta H^\circ \). The excess function plot for the liquid mixture, Figure 3.4, has been based on heats of mixing by Könnecke, Steinert and Leibnitz,¹⁶ and vapour pressures of Trimble and Potts.¹⁷

From the transfer functions diagram, it appears that the chemical potential of argon in the ethylene glycol/water mixture falls less rapidly than in the ideal mixture, despite the greater solubility of the gas in cosolvent alone. The enthalpy \( \Delta H^\circ \) remains negative at low cosolvent mole fractions, exhibiting similar behaviour to that already observed in ethanol/water mixtures (see Fig. 3.5).

Since it would appear that initial state parameters are important, the above theory may be extended to predictions for other systems. For example, in the case of solvolysis of a substrate in a liquid mixture, the rate constant may increase on addition of the cosolvent, provided the initial state of the substrate is destabilized. Two means of achieving this effect are possible according to the theory, and on some
Figure 3.4
Molar thermodynamic functions of mixing for water and ethylene glycol at 298.15K; $x_2$ is the mole fraction of ethylene glycol.
Thermodynamic functions for transfer of argon from gas phase to water + ethylene glycol mixtures at 298.15K.

(See caption to Figure 3.2).
occasions, these may operate together. Firstly, the solubility of the substrate should be lower in the cosolvent than in water, and secondly $G^E$ for the mixture must be negative. The latter factor may, in some cases, outweigh an increase in solubility. It was these predictions which prompted the measurements reported in Chapter 7, of kinetics of t-butyl chloride solvolysis in water/hydrogen peroxide mixtures, because for this mixture $G^E$ is negative. Then, in the limit, if the transition state is independent of $x_2$, the initial state may be destabilized by added $H_2O_2$, $\Delta G^+$ decreases and the rate constant for the solvolysis increases. This prediction can only be qualitative, however. It is not anticipated that quantitative agreement will be observed because the theory outlined above cannot be expected to hold for such complicated systems as aqueous mixtures. For example, the assumptions made in equations (45) and (46) are probably invalid for these systems. The relevance of predictions made for each of the aqueous systems studied is discussed in Chapters 7 and 10, along with the experimental results.
References

CHAPTER FOUR

Analysis for Rate Constants
4.1 Introduction

In the previous chapter, the thermodynamics of binary aqueous mixtures have been examined in some detail, and the Prausnitz-O'Connell theory employed to assist in predictions of solubility behaviour for solutes in such systems. This chapter commences with a brief discussion of the kinetics exhibited by the substrates used in this work, and the theory behind the physical techniques involved in their measurement. This is followed by a description of the analysis of the information obtained, for first- and pseudo first-order rate constants. Chapter 5 subsequently provides details of the apparatus used for acquiring the experimental data.

4.2 Kinetics and First-order Reactions

The rate of a reaction may be expressed in terms of the concentration of any reactant or of any product, i.e. the rate of decrease in concentration of reactant, or the rate of increase of product. The manner in which the rate varies with these concentrations of reacting substances is indicated by reference to the order of reaction. If it is found experimentally that the rate of reaction is proportional to the $\alpha$th power of the concentration of one reactant $A$, to the $\beta$th power of the concentration of $B$ etc., then

$$\text{Rate} = k [A]^\alpha [B]^\beta \ldots$$  \hspace{1cm} (1)

The overall order of the reaction is given by

$$n = \alpha + \beta + \ldots \ldots$$ \hspace{1cm} (2)

$k$, the rate constant, possesses the numerical value of the reaction rate when the reactants are present at unit concentration. Units of $k$ are dependent on those stated for the
reactants. Definitions of the rate laws for first- and second-order reactions may be made as follows:

\[\text{Rate} = k[A] \quad \text{First-order} \quad (3)\]
\[\text{Rate} = k[A]^2 \text{ or } k[A][B] \quad \text{Second-order} \quad (4)\]

The first-order rate constant has units of reciprocal time \((s^{-1})\), being independent of concentration. Because the systems studied were concerned mainly with first-order kinetics, it will be useful to examine the equations involved in some detail.

Consider a reaction of order \(n\), whose reaction scheme may be represented by the equation

\[n \ A \longrightarrow P\]

and where the initial concentration of reactant \(A\) is \(a_0\). If \((a_0 - x)\) is the amount of \(A\) remaining after time \(t\), the rate of disappearance of \(A\) is given by

\[-\frac{d(a_0 - x)}{dt} = \frac{dx}{dt} = k(a_0 - x)^n \quad (5)\]

This is then integrated subject to the boundary condition that \(x = 0\) when \(t = 0\). If \(n\) is unity, then

\[k = \frac{1}{t} \ln \frac{a_0}{a_0 - x} \quad (6)\]

or

\[\frac{kt}{2.303} = \log_{10} \frac{a_0}{a_0 - x} \quad (7)\]

Clearly, a plot of \(\log[a_0/(a_0 - x)]\) against \(t\) will give a straight line through the origin, with a slope of the value of \(k\).

As well as the rate constant, considerable use is made of the half-life of reaction, for first-order reactions. This is defined as the time required for the concentration of the
reactant to decrease to half its initial value, and may be
found from equation (7) by putting \( (a_o - x) = \frac{1}{2}a_o \),

\[
\log_{10} \frac{a_o}{a} = \frac{k}{2.303} t_{\frac{1}{2}} \quad \rightarrow \quad t_{\frac{1}{2}} = \frac{0.69}{k}
\]

and thus \( t_{\frac{1}{2}} \) is independent of the initial concentration of
reactant. As will be seen later in the chapter, this partic­
ular quantity is of great importance in the analysis of data.

Since it is desirable to obtain data for rate constant
calculations at fixed temperature and as a function of the
concentration of reactant or product, it is convenient to make
use of some physical property of the system under study, which
changes as reaction proceeds. Rather than having to withdraw
and analyse samples of the reaction mixture, these physical
measurements can be made directly on the latter, and the
concentrations of reactant or product deduced accordingly.
This explains the choice of conductivity for following the
solvolysis of t-butyl chloride, where the build-up of chloride
and hydrogen ions can be monitored. Similarly, absorbance
changes can be employed in the case of a given complex of iron,
the latter having a characteristic absorption spectrum in the
visible region. Recording changes in physical properties is
most satisfactory because they are less susceptible to inter­
ference from possible side reactions. The individual
relationships between both conductance and absorbance with
concentration, necessary for the application of rate laws,
will now be discussed.

4.3 Conductance Theory

The resistance of a conductor depends on its dimensions,
such that

\[ R = \rho \frac{1}{A} \]  

(9)

where \( l \) is the length, \( A \) the cross-sectional area, and \( \rho \) the specific resistance (units of ohm m). The conductance is then defined as \( 1/R \), and \( 1/\rho \), the specific electrical conductivity is usually denoted by \( \kappa \) (units ohm\(^{-1}\)m\(^{-1}\)). Reliable conductivity data have been used to demonstrate the fact that solutions of electrolytes follow Ohm's Law. Kohlrausch suggested a more useful quantity for solutions, by means of which the conductivity and concentration of electrolyte may be linked. The molar conductance, \( \Lambda \), is given by

\[ \Lambda = \frac{10^{3} \kappa}{c} \]  

(10)

for a concentration of \( c \) mol dm\(^{-3}\). This enables the current-carrying ability of various electrolytes to be compared, at different concentrations. At low concentrations, the dependence of \( \Lambda \) on \( c \) may be represented by the Onsager equation

\[ \Lambda = \Lambda^{\infty} - S \sqrt{c} \]  

(11)

where \( S \) depends on temperature, solvent viscosity and solvent permittivity. \( \Lambda^{\infty} \) is the molar conductance in the limit \( c \to 0 \).

Conductances are usually measured in practice by the use of any convenient conductance cell, which forms part of a Wheatstone Bridge circuit, wired to a high frequency alternating current source. The cell constant, \( 1/A \) from equation (9) must be determined initially from the measurement of resistance of a solution where \( \Lambda \) is known; the value of \( \Lambda \) for an unknown solution can then be calculated.

Rate constants for t-butyl chloride solvolysis were first
obtained from conductance measurements by Tommila, Tiilikainen and Voipio, and the reaction (see Chapter 2) clearly lends itself to such a method through the production of $H^+$ and $Cl^-$ ions. It is obvious, however, from the previous equations that the conductance reading registered by the bridge during an experiment is not precisely proportional to the concentration of ions present in solution. The proportionality is assumed to hold, for all the experiments described, since the error incurred is, in fact, negligible. Thus, at the low concentrations used in the investigation,

$$\Lambda \approx \Lambda^0$$

and so

$$c \text{ (ions)} = \Lambda^0 k$$

from (10).

Then

Concentration of ions = $\Lambda^0 \frac{1}{A}$ measured conductance

or

Concentration of ions $\propto$ measured conductance

Because the changes in conductance, not absolute values, were recorded, the cell constants were taken as part of a single proportionality constant. In conclusion, Robertson has convincingly illustrated the validity of these assumptions by measuring rate constants for t-butyl chloride solvolysis in water/ethanol at five different initial concentrations of substrate, from $3 \times 10^{-5}$ to $5 \times 10^{-4}$ mol dm$^{-3}$: the resulting values of $k$ were almost identical.

4.4 Absorbance Theory

A direct relationship exists between the absorbance of a solution and concentration of solute, and this forms the basis of the spectrophotometric analysis of kinetic data for rate constants. Thus, the absorbance $A$ of a solution is given by
where \( x \) is the path length of the spectrophotometer cell, \( \varepsilon \) the extinction coefficient at the wavelength \( \lambda \). For a given solution, \( A \) is usually a maximum for a given \( \lambda \), so leading to the definition of \( \varepsilon_{\text{max}} \) and \( \lambda_{\text{max}} \). Kinetic data are usually recorded by following the change in \( A \) at \( \lambda_{\text{max}} \) because here the change in \( A \) is most marked. It has been assumed that no other solute absorbs at the same wavelength. If this should be the case, however, then \( A \) becomes a function of \( \varepsilon \) and \( c \) summed over all solutes which absorb at the wavelength.

Equation (12) applies strictly only for monochromatic light. The SP 800A and SP 1800A spectrophotometers have been used to monitor the decrease in absorption at the \( \lambda_{\text{max}} \), as the starting material disappeared. Conveniently, in the case of the aquation, the products of reaction did not absorb in this particular region of the spectrum. The same was not true of the cyanide substitution, but the absorbance decreased with time.

Having related the data obtained in the experiments with concentrations required by the rate laws, it is now possible to pursue the calculation of rate constants in each case. As will become clear in Chapter 5, all the results were recorded at set time intervals, and first-order kinetics assumed (except for the cyanide reaction). The two methods of obtaining values of \( k \) were those due to Guggenheim and Moore, both of which will be described, along with the relevant parts of the computer programs written to incorporate each method.
4.5 The method of Guggenheim

Guggenheim described a method for calculating the rate constant of a first-order reaction where \( x \), the concentration reacted may be determined directly, but where the initial concentration (or equally the value of \( x \) at infinite time) is not known. Such a method is clearly applicable to a reaction monitored by a physical technique, where the equilibrium or final reading cannot be made. If readings are taken at times \( t_1, t_2, t_3 \) etc. and \( t_1 + \Delta, t_2 + \Delta, t_3 + \Delta \) etc., where \( \Delta \) is a constant increment, then the following equations hold:

\[
\begin{align*}
(\lambda_1 - \lambda_1') &= (\lambda_\infty - \lambda_\infty') e^{-kt_1} \\
(\lambda_1' - \lambda_\infty') &= (\lambda_\infty - \lambda_\infty) e^{-k(t_1 + \Delta)}
\end{align*}
\]

\( \lambda \) and \( \lambda' \) are readings of the particular physical property at \( t_1 \) and \( t_1 + \Delta \) respectively, and the usual first-order equation (6) has been written in exponential form. Similar equations would also hold for \( t_2 \) and \( t_2 + \Delta \). Subtracting (13) from (14) gives

\[
(\lambda_1 - \lambda_1') = (\lambda_\infty - \lambda_\infty') e^{-kt_1}(1 - e^{-k\Delta})
\]

or

\[
kt_1 + \ln(\lambda_1 - \lambda_1') = \ln \left[ (\lambda_\infty - \lambda_\infty')(1 - e^{-k\Delta}) \right]
\]

This equation can be generalized by dropping the subscript 1.

Before the method may be applied to a reaction, care must be taken to ensure that the latter is simple first-order, since certain other more complex reactions (reversible and concurrent first-order types) will give apparent rate constants from the calculations. The interval \( \Delta \) should be two or three times as great as the half-life period of the reaction, for maximum accuracy in the final rate constant. \( k \) is easily obtained from a plot of \( \ln(\lambda - \lambda') \) against \( t \), the slope of the
resulting straight line.

4.5.1 Application to Conductivity Data

The initial analysis of conductivity data involved direct use of the Guggenheim method, as suggested above, by plotting \( \log(\lambda - \lambda') \) against \( t \). Corresponding conductances from the first and third half-lives of the reaction, separated by the constant time-step \( \Delta \), were noted for each cell, logs of the differences taken, and these \( \log(\lambda - \lambda') \) quantities plotted against time (see sample graph). The resulting straight line slopes provided accurate values of \( k \) for the solvolysis. Apart from the tedium of the arithmetical analysis and plotting of points, where many possible errors could arise, the main advantage of this method was found in the clarity of the graphs: runs which were slightly curved, and therefore gave an unsatisfactory value of \( k \) were clearly discernible.

In an attempt to facilitate the calculation of rate constants, a simple computer program based on the method described above was tried (see Appendix 2). This made a comparison of the conductances of the two half-lives, in exactly the same way, and then employed a standard least squares procedure to obtain the best line which would fit the resulting values of \( \log(\lambda - \lambda') \) and time. The gradient of this line was again taken as the rate constant, and the root mean square deviation on this value of \( k \) also calculated. To improve the accuracy of the resulting rate constants, it was subsequently found useful to re-cycle the data through the computer. In this case, use was made of an exact half-life, calculated from the first value of \( k \) obtained, and then the amount of data altered accordingly. However, this naturally
With transference of the data onto punched tape, it was felt desirable to make additions to the basic Guggenheim program, so that not only could the data-tape be checked before calculations (see Chapter 5), but some refinement of the rate constant be achieved by the computer, as an alternative to the manual modification of half-lives described in the previous paragraph. The result was KINFUN (see Appendix 2). The actual analysis for k began by guessing the half-life for the reaction, this being taken as one-third of the time spanning the total number of points on the tape. The data for the first cell were then organised into two half-lives, separated by at least one half-life, enabling a provisional value of k to be calculated from a least squares analysis on this first set of results. The half-life subsequently derived from this provisional rate constant was then used to calculate a second value for k, and so on, a maximum of ten cycles being allocated for this purpose. Thus, the position of the half-lives was being constantly changed, along the conductance curve (see below), as the best value of k was sought.

Simultaneously, each new rate constant was used to determine a set of calculated Y values, (i.e. values of \( \log(\lambda - \lambda') \)) for each given X (time). The total number of data points
available for calculation of the next value of \( k \) was reduced through a loop in the program, which excluded points whose calculated and experimental Y values differed by more than 1%. For the second and following cycles, the rate constant calculation was terminated if the deviation between two successive \( k \) values was less than 1%. When this stage had been reached, the final rate constant was printed out, along with the mean square deviation. Should minimization of the deviation not occur upon completion of the ten cycles, then the last value of \( k \) was printed out, accompanied by a statement indicating its inaccuracy. The whole process was then repeated for the other cells included on the data-tape.

The successor to KINFUN for data analysis, program RABBIT (see Appendix 2) incorporated completely identical procedures for obtaining the most accurate value of the rate constant, but its selection of half-lives was based on a slightly different approach. The first (guessed) half-life was chosen to be one quarter of the total time covered by the tape, and the computer was then instructed to space out three half-lives around the mid-point of the data, hopefully avoiding the less accurate readings which often occurred at the start and end of a tape. The ends of both first and final half-lives were specified initially, and the data printed out for the calculation in decreasing order of time. The central half-life was taken to be 10% longer than the other two, and up to ten cycles of least squares refinement were performed, as before.

Prolonged use of the Guggenheim analysis, for several systems and temperatures, demonstrated that the main
disadvantage was the necessity for readings at constant time intervals: if any readings were missed, then the number of data points available for calculation of $k$ could be substantially reduced. Also, reactions had to be monitored for at least three half-lives, although the data for one of these, the middle one, which usually included the most reliable results, were never used. The Forwin procedure from the analysis developed by Moore showed a considerable improvement on this method, as will be seen later.

4.6 Moore's method of Analysis

This is based on a non-linear least squares method for analysing the kinetic data of a first-order reaction, which, as in the Guggenheim method, has unknown initial and final readings. In this case, however, readings do not have to be recorded at constant intervals, and any length of monitoring time is feasible, although obviously improved accuracy will be achieved the longer a reaction is followed. The data are fitted to a first-order rate law with a normal Gaussian error distribution, the complex calculations involved being facilitated by availability of a digital computer.

As shown previously, for a first-order reaction having rate constant $k$, and being followed by the measurement of some physical property $P$ of the system (e.g. absorbance, conductivity) where $P$ is linearly related to concentrations of reactants or products,

$$\ln \left[ \frac{(P_\infty - P)}{(P_\infty - P_0)} \right] = -kt$$  \hspace{1cm} (17)

$P$ is the value of the physical property at time $t$, $P_0$ at time $t = 0$ (when timing of the reaction commences), and $P_\infty$ at the
end of reaction, i.e. the infinity reading. Rearrangement of (17) gives

\[ P = P_\infty (1 - e^{-kt}) + P_0 e^{-kt} \]  

(18)
a non-linear expression for the dependent variable \( P \) in terms of the independent variable \( t \). Solution of this expression by the method of least squares requires an iterative procedure (hence the use of the computer) starting from approximate values of the unknown parameters. If \( P_0 \) was known accurately, then only \( P_\infty \) and \( k \) would need to be determined; experimentally, however, this is not true, so it is more satisfactory to treat this as a three parameter problem.

The analysis starts by guessing values (see below) for \( k, P_0 \) and \( P_\infty \). Then, at a fixed time \( t \), \( P \) is a function of \( P_0, P_\infty \) and \( k \),

\[ P = P(P_0, P_\infty, k) \]

By differentiation,

\[ \delta P = \left( \frac{\partial P}{\partial P_0} \right) \delta P_0 + \left( \frac{\partial P}{\partial P_\infty} \right) \delta P_\infty + \left( \frac{\partial P}{\partial k} \right) \delta k \]

(19)

This is an expression for \( \delta P \), which may be solved using conventional least squares analysis for the unknowns \( \delta P_0 \), \( \delta P_\infty \) and \( \delta k \). The sum of the squares of the deviations between \( \delta P \) and \( \delta P_{\text{calc}} \) is given by

\[ Q = \sum \left( \delta P - \left[ \left( \frac{\partial P}{\partial P_0} \right) \delta P_0 + \left( \frac{\partial P}{\partial P_\infty} \right) \delta P_\infty + \left( \frac{\partial P}{\partial k} \right) \delta k \right] \right)^2 \]

(20)

Then, for example, dropping subscripts

\[ \frac{dQ}{d\delta P_0} = 2 \sum \left( \frac{\partial P}{\partial P_0} \right) \left( \delta P - \left[ \left( \frac{\partial P}{\partial P_0} \right) \delta P_0 + \left( \frac{\partial P}{\partial P_\infty} \right) \delta P_\infty + \left( \frac{\partial P}{\partial k} \right) \delta k \right] \right) \]

or at the minimum,
This is one of the three normal equations. The other two are:

\[
\sum_{i} \left( \frac{\partial P}{\partial P_i} \right) \delta P = \sum_{i} \left( \frac{\partial P}{\partial P_i} \right)^2 \delta P_i + \sum_{i} \left( \frac{\partial P}{\partial k} \right) \delta P_i + \sum_{i} \left( \frac{\partial P}{\partial k} \right)^2 \delta k \quad (21)
\]

\[
\sum_{i} \left( \frac{\partial P}{\partial P_{\infty}} \right) \delta P = \sum_{i} \left( \frac{\partial P}{\partial P_{\infty}} \right)^2 \delta P_i + \sum_{i} \left( \frac{\partial P}{\partial k} \right) \delta P_i + \sum_{i} \left( \frac{\partial P}{\partial k} \right)^2 \delta k \quad (22)
\]

\[
\sum_{i} \left( \frac{\partial P}{\partial k} \right) \delta P = \sum_{i} \left( \frac{\partial P}{\partial P_{\infty}} \right) \delta P_i + \sum_{i} \left( \frac{\partial P}{\partial k} \right)^2 \delta P_i + \sum_{i} \left( \frac{\partial P}{\partial k} \right)^2 \delta k \quad (23)
\]

Solution of equations (21)-(23) gives values for \(\delta k\), \(\delta P\), and \(\delta P_{\infty}\), the estimated shifts to \(k\), \(P_{\infty}\) and \(P_{\infty}\) respectively, where

\[
k (improved) = k (previous) + \delta k \quad (24)
\]

In order to achieve this, the partial derivatives below, derived from equation (18), are required:

\[
\left( \frac{\partial P}{\partial P_{\infty}} \right)_{k, P_{\infty}} = e^{-kt} \quad \left( \frac{\partial P}{\partial P_{\infty}} \right)_{P_{\infty}, k} = 1 - e^{-kt} \quad \left( \frac{\partial P}{\partial k} \right)_{P_{\infty} - P_{\infty}} = t(P_{\infty} - P_{\infty})e^{-kt} \quad (25)
\]

Hence, initial values for \(k\), \(P_{\infty}\), and \(P_{\infty}\) are needed to commence the analysis; if the experimental data are good, then estimates of the three parameters do not have to be very accurate. \(P_{\infty}\) can be taken as the first observation, for which \(t\) is assumed to be zero. Subsequent readings are then related in time to this. Since the reactions were usually followed for at least three half-lives, sufficiently accurate initial estimates for \(k\) and \(P_{\infty}\) were obtained from the following:

\[
k \approx \frac{2}{(\text{time of last observation})} \quad (26)
\]

\[
P_{\infty} \approx 1.25 \times (\text{last observation}) - 0.25P_{\infty}
\]
These values were used in the computer programs for calculating $\delta P$ over the N experimental data points. For accuracy, N should be as large as possible: in the conductivity experiments, N was on average about 100, but reached a far higher figure in spectrophotometry runs. When the data were reasonably good, only a few cycles of least square refinement proved necessary to converge the sum of the squares of the deviations (equation (20)) to its minimum value. Variation of this factor by less than $10^{-6}$ between successive cycles was used as a convenient test for convergence. The possibility of including a weighting factor in equations (21)-(23), suggested by Moore, was ignored since the standard deviations of each of the observations $P$ were approximately equal for these experiments.

Solution of the three normal equations was achieved by matrix inversion (see below), because on convergence, the diagonal elements of the inverse matrix were directly related to the required standard deviations. As with all matrices found in least squares procedures, this matrix was symmetric. Values for the initial and infinity $P$ readings were obtained from the analysis, as well as the rate constant, and standard deviations on all three parameters; standard deviations on the observations were also calculated.

The complete analysis was incorporated into the HOPE and ROSEMA programs for conductivity, as well as STEVE and ROGUE for spectrophotometry, in the form of three main procedures. The first of these (see Listing in Appendix 2), INVMX (A), which provided a standard means of matrix inversion, was supplied by Dr. T.A. Claxton of this Department. The second,
PCALC was an exact statement of equation (17), and finally, cycling and refinement of the rate constant were carried out by the procedure FORWIN. In all the various programs, FORWIN controlled the calculations.

For the first cycle, $P_o$, $P_\infty$ and $k$ were defined as shown in the equations (26) and then printed under the respective cycle headings, along with the cycle number and square of the residuals, on the output. The three normal equations (21)-(23) were set up, and the related elements arranged in matrix form, for solution. Use was made of PCALC, to define 'delta', the difference between the experimental value of $P$ and its newly-calculated value. After matrix inversion, the increments $\delta k$, $\delta P_o$ and $\delta P_\infty$ were obtained, and if the difference between two successive sum of squares factors ($SDEL$ in the program) for cycles became less than $10^{-6}$, the calculation was terminated, in order that the data and rate constant might be printed. In the case of the second cycle, where this does not apply, then the second calculation commenced with use of new values for $k$, $P_o$ and $P_\infty$, these having been obtained by addition of the previously mentioned increments, as in equation (24). A maximum of 50 cycles was allocated for the continual modification of $k$, and, should minimization still not occur, calculation ceased, the last rate constant was printed and a statement added, indicating its inaccuracy. The data output for all the FORWIN programs included experimental and calculated values for $P$, the differences between them, and standard deviations on $k$, $P_o$ and $P_\infty$, as mentioned earlier.

The two conductivity programs were extremely successful in analysing data for t-butyl chloride solvolyses in all the
systems tried, and this was equally true of STEVE and ROGUE when aquation of the iron complexes was under investigation. However, the ROGUE analysis was found to be unsatisfactory when considering the reaction of cyanide with iron(II). The rate constants and standard deviations obtained in this case were often inconsistent and bore little resemblance to literature values. This prompted selection of an alternative approach (see Chapter 9). For the revised analysis, absorbance data from runs were taken directly from ROGUE outputs, and fed into a PDP 11 computer program based on a simple least squares procedure (see Appendix 2). A guessed range for the infinity reading - not zero for this reaction - was also input, and repeatedly modified until the standard deviation on the rate constant reached a minimum value. The value for $k_n$ at this point was then taken to be correct for that run; results obtained from this method were much improved on those from the 4130 computer.

### 4.7 Conclusions

As familiarity with the 4130 computer analyses grew, it became increasingly observed that good sets of data required, at most, five cycles of refinement only, before the rate constant was reached. The errors on a typical value of $k$ were usually small: for example, a rate constant of $8 \times 10^{-3} \text{s}^{-1}$ would have estimated standard deviation $1 \times 10^{-5}$ or better. This was equally true of the PDP 11 calculations. Reasons for less successful runs were usually sought, in case modifications to the data could lead to improvements in the final rate constant. A few errors, in particular, repeatedly
occurred on the tapes, and became easily recognizable. Completion of the full 50 cycles, without minimization, was indicative either of an error in tape heading, or an alteration in the order of cells (the latter leading to an abrupt change in conductance or absorbance). The calculation always failed after encountering two adjacent readings which were identical numerically, inspite of the fact that one referred to time and the other conductance or absorbance. Strange values for $k$ often resulted when the tape contained a series of wild or missed data points. Whenever possible, these obvious errors were edited out after the initial computer analysis, for the tapes to be subsequently rerun. Poor tapes were ignored and runs repeated, but this process was often hindered by the computer itself: 4130 breakdowns inevitably resulted in a backlog of data-tapes. Thus many runs had to be done without any idea of the results, in order that maximum use should be made of the equipment when available.

When the final conductivity rate constants were examined, it was noticeable that three out of four values obtained for one solution in the glass vessel were often very close, whilst the fourth tended to be slightly different. The same was sometimes true of the four spectrophotometry cells in SP 800A runs. The reason for this discrepancy was not clear. Badly curved runs were always excluded from the analysis. Upon establishing a definite set of rate constants, these were carefully tabulated, along with the corresponding temperature (see next chapter). In almost all cases, four or more independent measurements were made on each solution; lists of actual rate constants obtained are given in Appendix 3.
References

3. E.A. Guggenheim, Phil. Mag., 1926, 2, 538.
CHAPTER FIVE

Kinetic Apparatus
5.1 Introduction

In the previous chapter, it was shown that the rate constants for a given reaction could be calculated by measuring the variation of the conductivity or absorbance with time. In this chapter, two methods of obtaining the required information are described, followed by a summary of the procedures for organising the experimental data before computer analysis.

A major part of this project has been the commission and subsequent testing of apparatus, most of which was constructed by the electronics staff and technicians of the departmental workshop. The aim was to develop systems for monitoring chemical reactions automatically, such that the changes in physical property being measured could be recorded in a form suitable for direct computer analysis. The output from the computer should provide the required reaction rate constants, therefore, completing the cycle (it was hoped) in the shortest possible time.

On perfecting the working of the apparatus, however, completion of the cycle of operations depended markedly on the availability of the University's ICL 4130 computer for data analysis. Unfortunately, this latter machine proved all too easily influenced by external and internal factors (e.g. collapse of the building in which it was housed, as well as temperamental software of the computer itself - particularly card and tape-readers), which led to frequent obstructions in the work turn-round queues. Despite these inconveniences, the efficiency of the method was not in any way impaired; the only effect was a lengthening of the whole procedure.
Since two techniques were employed to follow chemical reactions for the kinetic studies, the two sets of apparatus will be described separately. In essence, they are very similar: the general theme of automation is clearly reflected in both systems.

5.2 Conductivity Apparatus

(a) Introduction The main features of the apparatus are summarised in the block diagram, Figure 5.1. A timer, which effectively controls the complete system, was wired in turn to a divider, ring counter and cell selector. From one to 24 conductivity cells could be connected to this selector, via an array of switches and relays, thus enabling a certain conductivity cell to be selected at some predetermined time interval. The selector was connected to a Conductance bridge, this being the instrument which monitored the changing conductivities of the solutions in the cells C₁, C₂, etc. The bridge was triggered by a signal from the timer, which had been delayed until the cell was selected. When the apparatus was first assembled, the data were recorded by a printer; consequently, a delay on the "Print" command signal had to be included in the circuit, to allow the bridge to balance before the information was recorded. The bridge output was then fed into the printer via a B.C.D. converter. Time information was added at this point, to complete the description of the reaction under study.

This design proved unsatisfactory, however. In practice the printer recorded many meaningless conductance readings, when the bridge remained unbalanced until after the "Print"
Figure 5.1
Conductivity circuit.
command. A suitable modification was incorporated later, when the printer was replaced by a data-logger. It was arranged that if the bridge did not balance within the time allowed, an "Inhibit" command was relayed to the Data Transfer Unit, to prevent that particular reading from being recorded. In general, the D.T.U. collected the time and conductance information and channelled this into a Facit Punch, where the results were punched directly onto 8-track computer paper-tape.

(b) Electronic Components The timer, an Advance Instruments 32 MHz Timer Counter (TC 9), was programmed at the start of each run to trigger the bridge and cell selector at a certain time interval. Time bases of 1 and 10 seconds only were used. The time divider provided a means of extending the range of time intervals further, to include command signals having intervals of 2, 4, 8, 16, 32, 64 and 128 seconds. For a given run, the value actually used was dictated by the rate of reaction, as well as the number of cells to be read. In general, a preliminary 'test' run was tried for each new solution, to obtain some idea of the necessary gap between readings, bearing in mind that each run would be monitored for at least three half-lives. This was more crucial for the Guggenheim analysis of data.

The cell selector had been originally constructed in order that a number of reactions at different temperatures could be monitored simultaneously, but this eventually proved impossible in practice. In fact, the maximum number of cells ever needed at any time was eight; more usually, four were used, since each glass vessel possessed four cell compartments for studying one solution (see later). Facilities for manual
cell selection were also provided. In the last two months of this work, a sudden increase in data errors was traced to dirty contacts in the relays, so the selector mechanism was simplified to read just four cells.

A General Radio 1680A Automatic Capacitance bridge assembly, operating at a frequency of 1 kHz on a fast range, was used to measure the conductances, to five figures in some cases. The bridge display simultaneously showed the corresponding capacitance measurements, but these were ignored. A most useful feature of the display was the "unbalanced" signal, which indicated that the bridge had not settled on a steady reading (usually the result of a very rapid change in conductance). Conductances were recorded in mhos; both on the printer and paper-tape outputs, a code number – the "range" – was added after the conductance digits, to indicate the position of the decimal point. The ranges were as follows:

<table>
<thead>
<tr>
<th>Range</th>
<th>Conductance</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0100.0 mU</td>
</tr>
<tr>
<td>6</td>
<td>010.00 mU</td>
</tr>
<tr>
<td>5</td>
<td>01.000 mU</td>
</tr>
<tr>
<td>most commonly used</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0100.0 μU</td>
</tr>
<tr>
<td>3</td>
<td>010.00 μU</td>
</tr>
<tr>
<td>2</td>
<td>01.000 μU</td>
</tr>
<tr>
<td>1</td>
<td>0100.0 nU</td>
</tr>
</tbody>
</table>

The absolute conductance reading was not actually required, since the rate constant was calculated from the change in conductance (see previous chapter).

The Kienzle D44 printer, which had no facilities for
manual operation, possessed a maximum printing speed of one line per second, and hence this set an upper limit to the number of readings which could be made during a run. The layout of data recorded on this machine is demonstrated by the sample below:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>secs</td>
<td>μV</td>
</tr>
<tr>
<td>1</td>
<td>129</td>
<td>2224</td>
</tr>
<tr>
<td>2</td>
<td>130</td>
<td>4961</td>
</tr>
<tr>
<td>3</td>
<td>131</td>
<td>6634</td>
</tr>
<tr>
<td>4</td>
<td>132</td>
<td>8639</td>
</tr>
<tr>
<td>*</td>
<td>133</td>
<td>2496</td>
</tr>
<tr>
<td>2</td>
<td>134</td>
<td>5111</td>
</tr>
<tr>
<td>3</td>
<td>135</td>
<td>6833</td>
</tr>
<tr>
<td>4</td>
<td>136</td>
<td>8898</td>
</tr>
</tbody>
</table>

As indicated, the first column on the output represented the time of each reading (in seconds), the second column gave the conductance digits and the third column the range. Only four figures were printed for the conductance; the time often required five figures, however, and so the numbers were carefully scrutinised for omitted zeros and ones, before data analysis. To facilitate this process, individual cells were usually marked for easy recognition (as above). This was not a satisfactory situation, however.

With the advent of a data-logging system, the electronic circuit was modified to include a switch for either printing only, or alternatively printing + punching. When the logger had successfully completed its trial period, the printer was phased out of use. The Data Transfer Unit, which then assimilated all the data for subsequent runs, was a Solartron
Section A
Tape
Heading

Section B
Data

Section C
Tape
Ending

No. of Cells
Time interval
Temperature

Figure 5.2
Conductivity data tape, for t-butyl chloride solvolysis.

Data
Conductance
Range

Time

Data for one cell at time 142 s.

Negative number
Halt code
Schlumberger model 3230 attached to a Facit 3245 Paper Tape Punch. A manual data entry unit was also available, enabling headings and endings to be added on all tapes. Two error lights on the punch indicated when the feeding mechanism was faulty, or that the tape had almost run out. For long runs, a secondary winding mechanism was used, by which the punched tape could be safely rewound on a separate spool. Figure 5.2 shows a typical sample of conductivity data tape which has been divided into three parts. Section A is the tape-heading (manually punched), containing the number of cells, time interval between readings, time base and approximate temperature of reaction for each cell in turn. Section B, of which only a fragment is shown, represents the data, recorded automatically in the order mentioned previously for the printer: time, conductance digits and range. These numbers for one individual cell are separated from the next three by carriage return/line feed, and are recognisable thus by the computer as a complete unit. Five figures were allocated for both time and conductance readings. Section C is the tape-ending, which consisted of a negative number and the halt code (see data analysis and computer programs, section 5.4). Similar tapes for spectrophotometry runs are illustrated in section 5.3.

(c) The Conductivity Cell Assembly Reactions were carried out in a pyrex vessel, having electrodes of conventional design but also incorporating some additional features for the specific requirements of this particular method. The standard model (see diagrams 5.3 and 5.4) consisted of a flat bottomed 250 ml. flask, bearing long neck and side-arm. The
Figure 5.3
Conductivity cell assembly
- side view.

Contacts to Selector board

Pipette filler

B 24
Air bleed

B 14
Stopper

Flask

Test Solution

Stirrer bead

U-tube

Capillary

Cell Compartment

Mercury
Figure 6.4
Conductivity cell assembly - front view.

- Contact to Selector board
- Flask
- Mercury
- Four Cell Compartments
- Platinum Electrode
flask base was fused onto a thin U-shaped tube, by means of which the four cell compartments were connected to the flask itself. The neck of the flask held an air-bleed (B 24), surmounted by a rubber pipette filler: this provided the means for blowing solutions over into, and sucking them back from the cell compartments. The stoppered side-arm facilitated addition of the reacting substrate to the solution in the flask; a 2 ml. Rocket syringe with an 8 inch needle was used for this purpose. The mixture was then stirred by a polypropylene-covered magnetic bead.

The four cell compartments had different capacities, with the pairs of electrodes increasingly far apart. Thus, each cell yielded a slightly different conductance reading, enabling a faulty cell to be more quickly recognized. Each electrode consisted of platinum foil mounted on a fine wire, the latter passing through the glass cell wall into a mercury-filled side-arm. Contact was made from the mercury, via a length of tinned copper wire and 'crocodile' clips, to leads which could be plugged directly into the cell selector board.

Later, a simplified version of the vessel was constructed for use at higher temperatures, when one cell compartment alone could be monitored. Less solution was required in this case, so the flask size was reduced to 30 ml. Periodically, each glass assembly was emptied, cleaned and re-annealed.

(d) Temperature Control and Measurement The whole glass assembly was thermostatted at the varying temperatures thus:

The vessel was clamped securely, on the top of a watertight magnetic stirrer, as near to the centre as possible of a zinc-plated thermostat bath (approx. 80 litres capacity).
The water was stirred by a Stuart Turner BS170 pump, fixed on the wooden frame of the bath. Initially, two D.A. Gunn stirrers had been fixed in opposite corners, but these proved unreliable because they often overheated and jammed. Circulation of anti-freeze liquid through copper pipes mounted around the sides of the tank provided cooling for the bath. The anti-freeze was pumped from an adjoining refrigeration unit. Temperature control was maintained by the use of a Red Rod "permanent" heater, together with a contact thermometer (Jumo), which controlled via a relay the second Red Rod "temporary" heater. Temperature control to better than 0.01K was usual, although in some cases control to better than 0.005K could be achieved. Permanent heating was unnecessary for temperatures below 308K, since it was found that the control (temporary) heater could be balanced with the flow of coolant to produce a steady temperature. A layer of polystyrene chips floating on the surface of the tank seemed to enhance thermostatting at low temperatures, and also prevent appreciable evaporation. Methanol was added to the tank for experiments around 273K.

Considerable experimental difficulties were encountered with the refrigeration system, which repeatedly fused until placed on an entirely separate electrical circuit, or broke down due to a lack of oil in the motor. The delicate workings of the contact thermometers were extremely vulnerable, resulting in many minor hold-ups; fortunately, three were available for different temperature ranges. The magnetic stirrers often proved unpredictable, also.

Measurement of the thermostat temperature provided some
inconveniences. Originally, a quartz thermometer (Hewlett Packard, model 2801A) had been used, but this was ultimately superseded by platinum resistance thermometers. The quartz probe then remained as a rough guide to temperature fluctuations in the tank, especially during runs. Initially, the platinum resistance thermometer and bridge were not always available when required, being on infrequent loan from the Thermodynamics Research group. The situation was remedied somewhat when the whole conductivity equipment was rehoused in a neighbouring room. An extension lead to the bridge was then fixed through the wall into the Thermodynamics laboratory.

One of the major reasons for this somewhat drastic operation, namely the moving of the whole equipment, was associated with the mains supply. The whole apparatus clearly depended on a series of pulse signals which commanded the operation of the various components. In addition, the information passed to the data punch was in the form of electrical pulses. Unfortunately, the mains supply in the laboratories was found to carry pulses which strayed into the equipment and set off a series of undesired events. Eventually the problem was solved by running a special mains supply from the central distributor board in the research laboratories. No other apparatus was supplied from this circuit.

The platinum resistance thermometers (Rosemount Engineering Co. WS 104 sensors, serial numbers 245 and 246) were operated in conjunction with a Rosemount Precision Comparison bridge, model VLF 51A, and standard 25 Ohm resistance. Temperatures were obtainable to three decimal places
from tables computed using the standardized data of each individual thermometer (N.P.L. calibrated). At a later stage in the work, when comparing the calculated temperatures for the tank from the 245 and 246, with those obtained from a newly-acquired H. Tinsley & Co. 1-5187 SA thermometer (serial no. 221459), it was discovered that the 245 sensor had become unreliable over part of the temperature range. This was most probably the result of a serious knock which the thermometer had suffered shortly before the test was performed. Consequently, the 245 was then discarded, and all further measurements were made with the 246; the Tinsley thermometer was kept as a standard, to check the accuracy from time to time.

(e) Experimental Procedure When the thermostat bath had reached a steady temperature, the air-bleed/pipette filler was removed from the neck of a conductivity flask, and approximately 80 cm$^3$ of the solution under test were poured into the vessel. The air-bleed was then replaced, and, with a B 14 stopper in the side-arm, the pipette filler was compressed, thus forcing the solution from the flask itself over into the cell compartments. On removing the stopper for a few seconds, the pressure was released and the liquid found its own level, both in the capillaries and the flask. The solution was then allowed at least ten minutes to equilibrate in the thermostat bath, during which time the contents of the flask were gently stirred. The actual length of time depended on the temperature of the reaction and the nature of the solution under test. The electrodes were kept wet throughout. During the equilibration period, leads from the required
number of cells were plugged into the selector board, the time base and multiplier on the clock were set as needed, and the clock started. The bridge, printer, converter and datalogger had all been switched on as early as possible, and the platinum resistance thermometer was clamped firmly in the tank, adjacent to the cell compartments. A tape-heading was manually punched onto the paper tape, to record the number of cells, temperature and time interval between readings, and the tape was then given its own reference code number. For data recorded on the printer, a code number only was written on the top of the paper. Finally, the 2 ml. syringe was cleaned thoroughly with Analar acetone and carefully dried.

When thermostatting was complete, the solution was sucked back into the flask from the cell compartments and given a more vigorous stir, before a small quantity of t-butyl chloride was syringed in via the side-arm. The clock was restarted at this moment, and the solution thoroughly stirred for approximately one half of the reaction half-life. The mixture was then carefully blown back into the cells, in an effort to avoid air bubble formation. Bubbles occluding to the electrodes could lead to serious fluctuations in conductivity. The cell selector was switched on, and times + conductances subsequently recorded at the specified time interval for, normally, about four half-lives. As mentioned earlier, the bridge was allowed a delay of just less than one second in which to balance, before the "Print" command. If a balance point was not reached, then no reading was recorded on the paper tape. Instability of the bridge reading usually arose from either dirty contacts in the cell or plugs, bubbles
adhering to the electrodes, or a rapidly changing conductance
(e.g. a fast reaction, at high temperature).

During each run, small temperature fluctuations were
noted from the quartz thermometer; the Rosemount bridge was
balanced and the resistance ratio of thermometer to standard
recorded normally twice (independently) per run. The average
of the ratios was then used to calculate the exact temperature.

At the end of a run, as the conductance changes grew
small, the cell selector and clock were switched off. An
end-code was manually punched onto the tape, and the latter
removed for analysis. The spent solution was then sucked
back from the cells into the flask and removed by means of a
pump attached to a reservoir (a very efficient method).
Should the next run require a different solution, then the
glass assembly was thoroughly rinsed before use. For runs
extending beyond the normal hours of working, an automatic
clock was incorporated into the circuit. This switched off
the selector and timer at a predetermined interval after the
start of the experiment. Procedures for organization of the
conductivity data by the computer are set out in section 5.4.

5.3 Spectroscopic Techniques

Two spectrophotometers were used to monitor the change in
absorbance with time, because one machine was easily thermost-
atted at lower temperatures and the other had been specifically
modified for work above room temperature. The complete
apparatus in each case was basically the same, one set being a
simpler version of the other.
Figure 5.5
Unicam SP 800A circuit.
(a) **Unicam SP 800**  This system (see Figure 5.5) centred around a Unicam SP 800A spectrophotometer, and was governed, like the Conductivity equipment, by a timer connected in turn to a control unit and cell changer. The control unit directed the movement of the spectrophotometer cell block, through the cell changer, and commanded an adjoining digital voltmeter to sample the absorbance of a particular cell. Finally, the absorbance data, along with the time of the sampling (taken directly from the timer), were channelled into the paper-tape punch and recorded on 8-track computer tape.

The timer, which in fact formed part of the Solartron data-logging unit, was calibrated in multiples of ten seconds, such that the time intervals available for recording readings were strictly limited to 10, 20, 60, 600 and 3600 seconds. The two intervals used in this work were the one minute and ten minutes, only. The lower limit was determined solely by the length of time required for the spectrophotometer cell block to complete its cycle of four cell changes (approximately 30 seconds in all). The rates of reaction were never sufficiently slow to warrant a one hour interval.

The control unit, built by the electronics staff, issued the following sequence of command signals when triggered by the timer:

1. Print Time.
2. Select Cell I.
3. Sample Cell I.
4. Print Absorbance.
5. Select Cell II.
6. Sample Cell II.
7. Print Absorbance.
8. Select Cell III.
9. Sample Cell III.
10. Print Absorbance.
11. Select Cell IV.
12. Sample Cell IV.
13. Print Absorbance.

The "Select" signals passed to the cell changer, whilst the "Sample" command was undertaken by the digital voltmeter. The sequence was complicated by the fact that a suitable time delay had to be inserted between the selection of a cell and printing the absorbance reading, in order to make allowance for movement of the cell block and sampling by the DVM. Ideally, the complete cycle should have been as short as possible, and hence a number of difficulties were encountered before the situation was resolved. The problem was still apparent, however, when absorbance readings were high, for example at the start of a reaction.

The cell changer was mounted on the SP 800 and, as mentioned previously, could be programmed before a run to permit the monitoring of up to four cells. In almost every case, the spectrophotometer's internal timer was not required, so the changer was set to 'remote control'. Absorbances of solutions in the cells were logged by a Solartron Digital Voltmeter LM 1420, and the accompanying drive unit LU 1718 was linked to an Addo punch. The latter possessed no facilities for manual operation, but it did have an unaccountable aptitude for mispunching and adding readings (all zeros) to the tapes during runs, most probably through interference with
Figure 5.6
SP 800 data tape, for the iron(II) complex aquation (analysed by STEVE).
neighbouring machines. Care had to be taken, therefore, in the analysis of results that these meaningless numbers were not included in the computer calculations. The order of data on a typical tape is shown in Figure 5.6; time was always punched first. Four figures were allocated for each absorbance reading, and the individual values separated by carriage return/line feed characters. The example illustrates readings for four cells at the beginning and end of a run, followed by the halt code, which included a negative number.

Because the iron complex studied in these experiments absorbed light in the visible region of the spectrum, the ultraviolet source in the spectrophotometer was not required. A tungsten lamp, which needed frequent replacement, provided the source of illumination. The SP 800 was operated at fixed wavelength throughout; the spectra were monitored at 510 nm, $\lambda_{\text{max}}$ for the complex. The slit width was always 0.07 mm, and reactions were carried out in 10 mm stoppered silica-glass cells. Reaction temperatures were measured in the reference solution cells, using a copper-constantan thermocouple, connected to a Pye 7569 Potentiometer and Cambridge Instrument Co. Spot Galvanometer. The second thermocouple junction was immersed in an ice-water bath at 273K.

The spectrophotometer cell block was cooled by water circulating from a thermostat tank (Townson and Mercer Ltd.), fitted with refrigeration unit, the bath being at a temperature a few degrees below that required. Initially, the circulating pump was a small Stuart Turner no. 10 model, but owing to rapid destruction of the carbon brushes therein, this was eventually replaced by a larger BS 170 pump. The temperature
control within the cell block improved markedly as a result of this change, the flow rate of the water from tank to spectrophotometer having obviously increased. Rates of aquation of the iron complex were measured in this equipment at 289 and 300K; the temperature of each reaction was controlled to better than 0.1K.

(b) **Experimental Procedure** When a steady temperature had been reached in the thermostat bath, the cell block was cooled to the required reaction temperature. Usually this involved connecting pipes to the bath and re-priming the pump, since the spectrophotometer was shared with a colleague, whose work demanded higher operating temperatures. This continual temperature alternation of the cell block naturally hampered attempts to maintain the reproducibility of runs, thus contributing towards the variation in rate constants (see results in Chapter 9).

While the block attained thermal equilibrium (usually some 15 to 20 minutes), the SP 800 pen recorder was set to zero and the digital Voltmeter calibrated internally. The spectrophotometer scale was then calibrated as follows: 100% absorption was simulated, the pen automatically moved to the top of the chart-paper scale, and the DVM was adjusted to read 2000. Similarly, at zero absorption, the pen returned to the base line and the DVM was set to zero. This sequence was repeated until further adjustments proved unnecessary. The wavelength had previously been fixed, and the SP 800 table clamped firmly in position. With the pen carriage switched to 'scan', the cell changer was programmed to read the required number of cells and allowed to complete one cycle of operation,
thus ensuring that Cell I would be selected immediately when monitoring commenced. Spare tape was run out from the punch, in readiness for the run, and a reference code number marked at the start.

Actual preparation of reaction solutions depended on the contents; preparation of sols and gels will be described in Chapter 9. The simplest system, aquation of the iron complex in salt solution required the following procedure: 2 ml. stock salt solution were carefully pipetted into the silica cells, and either 1 ml. of water added (for reference solutions) or 1 ml. complex solution. The final concentration of complex was then approximately $2 \times 10^{-4}$ mol dm$^{-3}$, the intensity of colour being sufficient to produce an off-scale absorbance on the spectrophotometer. Each cell was shaken before being placed into a cell compartment, and at least ten minutes were allowed for equilibration in the cell block, by which time the absorbance of the complex had decreased and was now on scale. The clock was then reset, the time interval selected and monitoring commenced. The reaction was followed until the absorbance approached zero (usually four half-lives).

At the end of each run, the scanner and clock were turned off, the thermocouple temperature was read from one of the reference cells, and spare tape was again run out at the end of the data to provide space for a tape-ending to be inserted manually later. The tape was scrutinised to ensure its first number constituted a time reading (see data analysis). The number of cells and time interval for readings were punched onto data cards, to be input along with program and data tape to the 4130 computer. The cells were removed from the cell
block, washed thoroughly, rinsed in Analar acetone and carefully dried before re-use.

(c) Unicam SP 1800 As Figure 5.7 indicates, this greatly simplified system was controlled by an Advance TC 9 Timer, connected directly to the Data Transfer Unit. Again, a sequence similar to that used for the SP 800 was followed: at the selected time interval, the digital voltmeter sampled the absorbance of cells in the spectrophotometer, and transferred this information into a tape punch, to be recorded on 8-track paper tape. The major difference here, however, was that times were omitted from the recorded data.

Compared with the two previous sets of apparatus, the timer in this case provided a rather restricted choice of time intervals for readings: either 1 second or 10 seconds. As before, the exact interval chosen depended on the half-life of the reaction being studied. Each manually-punched tape heading had to include this time step value, for correct analysis of the absorbance data.

The Data Transfer Unit consisted of a Solartron A 220 digital voltmeter with accompanying A 295 Recorder Drive unit, the former enabling optical densities to be read to five figures, and the latter providing manual as well as automatic punching facilities. The DVM response was adjusted to correspond with the time interval for each run, and because one cell alone could be monitored at a time (due to the lack of cell-change mechanism), the number of readings per line punched on the data tape was set at one, throughout. The Punch was a Facit model 3245, identical to that previously described in
**Figure 5.7**

Unicam SP 1800A circuit.
the Conductivity section. The main features of a sample tape for the cyanide substitution reaction (see Chapter 9) are shown in Figure 5.8. The four labelled sections illustrate the tape heading, absorbances at the start and end of a run, and finally the tape ending.

There appeared to be very few errors through external interference with this equipment, perhaps because a little-used electrical circuit was provided for the mains supply. The data-logger did not mispunch or add extra points, and the agreement between DVM readings and the spectrophotometer scale was excellent. Any meaningless points obtained when switching on the logger at the start of a run were ignored by the program during analysis.

The SP 1800A spectrophotometer (Unicam) was a more modern version of the SP 800A, though identical in function. A fixed wavelength in the visible region was again used (510 nm for both iron complexes), and the decrease in absorbance as reaction proceeded was clearly demonstrated by a meter on the front of the machine. The slit width was kept at 0.3 mm, and reactions carried out in 10 mm stoppered silica cells, the temperature being measured by the same thermocouple arrangement as for the SP 800. As stated above, only one cell could be observed per run because the SP 1800 lacked a remote-controlled cell changer.

Thermostatting of the spectrophotometer cells was achieved by placing them in a block which had been constructed from winding a heating element and a resistance thermometer around a Unicam SP 874 cell housing. The resistance thermometer formed one arm of a Wheatstone bridge circuit; the off-balance
Figure 5.8
SP 1800 data tape, for the cyanide substitution (analysed by PDP 11).
signal was amplified and fed to a phase-sensitive detector which controlled the current to the electrical heater. In this way, proportional temperature control could be achieved, yielding a temperature stability of better than ± 0.01K. In practice, however, this accuracy was rarely reached, since these experiments were undertaken during the Power Crisis (when voltage reductions and fluctuations were common), and the controller had to be switched off overnight, contrary to its usual 24 hour operation. Consequently, when the equipment was actually in use, the temperature stability appeared to vary, with the resulting rate constants varying accordingly. Temperature control during a run, however, was probably better than 0.1K since most reactions were short: none lasted more than 10 minutes. Rates of aquation and cyanide attack on the iron complexes were measured in this apparatus at 308 and 314K.

(d) **Experimental Procedure** Basically, this was much the same as that involved for the SP 800. The temperature controller had first to be switched on, and a minimum of forty minutes allowed for the cell block to reach thermal equilibrium (longer if the mains voltage was reduced). It was found helpful to take test thermocouple measurements from a spare cell containing water only, in one of the empty cell compartments, during this warming period. Meanwhile, the spectrophotometer wavelength was fixed as required, the Data Transfer Unit and punch switched on to stabilize, and the time interval on the clock selected. The digital Voltmeter was then calibrated to read zero absorbance, in accordance with the absorbance meter, by adjusting the SP 1800 zero control.
Because the DVM exhibited a slight tendency to drift from zero, further adjustments were sometimes necessary, especially when the machine had been left for a long period before the run began.

A length of spare tape was run out from the punch, to be followed by the tape heading (added manually). This recorded the number of cells and the time step between readings. A reference code number was usually added. The complex and reference solutions were prepared as previously described, all being thoroughly mixed before being placed in the cell block; between 5 and 10 minutes were normal for equilibration. When the absorbance had reached a suitable level on the meter, logging was commenced and the reaction monitored for almost four half-lives (the aquation) or two (the cyanide substitution). Five figures were allocated by the punch for each absorbance reading. As the peak intensity approached zero, or the infinity value, depending on the reaction concerned, the DVM and clock were turned off and the tape ending - 99999 + halt code - punched at the end of the data. The reaction temperature was noted from potentiometer and thermocouple, and the cells removed, to be carefully washed and dried. The data tape was then wound, in readiness for analysis by computer.

5.4 Organisation of Data
(a) Introduction As was mentioned in Chapter 4, the conductivity data were analysed by a variety of methods, which gradually increased in efficiency and complexity over the period of study. Initially, a simple graphical method was
employed, but the eventual calculations were performed with
the aid of a lengthy program (ROSEMA) stored on Disc in the
ICL 4130 computer. Programs for the analysis of spectro-
photometry data, from both the SP 800 and 1800, were already
available at the time these investigations began, and
incorporated the same basic procedures as the final Conductiv-
ity analysis. For the latter part of the spectrophotometry
work, however, it was seen that a simpler approach to the
calculations had to be adopted, when the type and conditions
of the reaction had altered. The aim of this section is to
illustrate how the data were organized for the rate constant
analysis, the latter having been described in Chapter 4.

(b) Conductance Data As explained in section 5.3(b),
conductance data were originally printed, and the rate
constants were calculated directly using Guggenheim's method.
Hence, after distinguishing the individual cells for the length
of each run, three rough half-lives were marked off on the
paper. Corresponding conductances from the first and third
half-lives, separated by the set time-step $\Delta t$ were then noted
for each cell; the data were analysed by hand.

The natural progression from this simple method led to
consideration of computer analysis. The small program based
on the Guggenheim calculation required accompanying data to be
transferred from the original printer paper onto punched cards.
For reactions having long half-lives and with at least four
cells per run, however, the typing proved extremely time-
consuming. Typing errors also added to the confusion, these
being almost unavoidable. It soon became obvious that more
time was being spent in preparing the results for the computer
than in actually running the experiments.

At this stage, the possibility of a data-logging system was discussed, and when this equipment materialized, the original Guggenheim program was rewritten to read the data directly from paper tape. However, any previous notions of obtaining perfect sets of results soon faded when it became clear that the logger was still on trial, and the electronic circuits had to be repeatedly modified to accommodate it. Obviously, any effective computer program would require some means of distinguishing good from meaningless data points; KINFUN was an attempt to fulfill these requirements. The first part of the program (see Appendix 2) is now described.

The basic requirement of the program was to set up an array of data points for each cell, these points being selected from a tape containing information for more than one cell and, probably, several incorrect readings. Subsequently, the data would be organized into two separate half-lives, connected by at least one half-life, for the final calculation. The computer was commanded to set aside a number of locations in its store for arrays containing the number of cells, temperatures, time multipliers, times of readings and corresponding conductances. The figures were then fed into their correct places, before being printed out to provide a visual record of the tape, along with results from calculations. The end of the data (see Fig. 5.2) was indicated by a negative time, thus enabling the computer to easily ascertain the total number of time points on the tape. A series of checks were then automatically carried out on the whole tape, before the data were divided between arrays for individual cells. These checks
were carried out by procedures written into the program. If any two adjacent time points were not separated by the previously defined time interval, both corresponding conductances were put equal to zero and the position of the error was printed on the output. If a conductance did not follow a time point, as in the specified order of punching, then the missing number was given a zero value and the error recorded. Again, if the range figure was either absent or greater than 7, the conductance was set to zero. When the range had a value between 1 and 7, appropriate factors were used to convert the readings into conductances.

The whole series of readings for each individual cell were then examined, bearing in mind the anticipated exponential increase in conductivity as reaction proceeds. If a new value of $G[I]$ was less than 90% of the previous one, then the former was put equal to zero and "Conductance out of Sequence" printed, along with the position of the error, on the output. The time multiplier then corrected the times before a rough half-life was computed and the least squares procedure begun. It should be noted that a further sequence of loops (including the "Select" procedure) was originally incorporated in both this and subsequent programs, to make allowance for runs monitoring more than one reaction at different temperatures. In such cases, part of the data would then be necessarily omitted from the final calculation. However, for the work undertaken here, this addition to the programs was never required.

The data for analysis of each cell was assembled in another array, omitting the zero-valued points, in readiness
for the Guggenheim calculation (see previous chapter). The major difficulty of this approach was that the analysis used the first few points from each run in every cycle executed by the program. Unfortunately these points were the most likely to be wrong. It became apparent that the bridge balanced more smoothly as reaction progressed, partially a result of the conductance reaching a higher and less sensitive range, and also because the circuits had settled into a regular switching sequence. This naturally suggested a further possible modification to the program. The program RABBIT (Chapter 4) was designed to follow the basic format of the original Kinfun. An additional loop was inserted into the program to make allowance for any two adjacent sets of data points having zero value. Previously, the program had just ground to a halt when confronted with such a situation, but now a command to examine the next and following pairs of points was added. The completed RABBIT, in this form, had a considerable measure of success.

The programs described above were designed to set up the information in a form suitable for the application of Guggenheim's method. As a further development, a new program HOPE was prepared which set up the data in a way suitable for analysis using the procedure FORWIN (see previous chapter). This made use of all the data presented on tape, and incorporated the whole series of tests for the order of the numbers, which had been employed in earlier programs, as well as a few additional ones for the new calculation.

Because a time base of one second was almost invariably used for these experiments, the time procedure soon became
redundant, and, in order to prevent further difficulties arising from modifications to the tape-heading, 'Time' was removed completely. The program was then renamed ROSEMA, and has superseded all the earlier prototypes for the analysis of conductivity tapes through its unfailing accuracy. A few minor features were added to ROSEMA before use: firstly, when the computer found a 'Conductance out of Sequence', it was told to set both this point and its predecessor to zero. The whole store of times and conductances was cleared before a new tape was read, thus enabling two or more tapes to be input consecutively to the 4130, and the total number of tape errors was printed out with the rate constants in each case. This latter sum had never been satisfactorily obtained from previous programs. The only fault encountered with ROSEMA arose when a wild point followed either one or two having a zero value, or a point absent altogether from the series. The computer was then forced to calculate a meaningless rate constant from the whole set of data, including this strange number. The problem was solved at first by editing out the offending points, but with improved data tapes, the necessity for such treatment became increasingly rare.

Each tape-heading and halt code were visually checked before submission of the results for computer analysis, and a special effort was made to examine the very first time point, since this was often mispunched as monitoring began.

(c) Spectrophotometry Data Results from the SP 800 experiments were analysed using the program STEVE, also from disc store in the 4130 computer (see Chapter 4 and Appendix 2). Once again, the data sequence of each tape had to be carefully
scrutinized. The computer store was cleared and a series of arrays allotted for time and absorbance numbers, before each tape was read in. The computer was then instructed that each time point must be separated from the next by the previously defined time interval (obtained from cards input with the tape). If the time was negative, then this indicated the end of the data, and the total number of points was printed out. The time sequence provided a backbone for the calculation, since the computer assumed these points to be correct throughout. If one time was found to be absent, "Timeout" was printed, along with the position of the error, and any related absorbance numbers put equal to zero. The computer was then instructed to seek another time as reference, from which the calculation was continued. Because the timer unit, and hence the data tape recorded times in hours, minutes and seconds, a conversion to seconds was also included in the 'Time' procedure. A loop which took account of the re-setting of the clock after 24 hours, during a long run, was never used.

For the case of two adjacent time points not separated by a complete set of absorbances equivalent to the specified number of cells, "Absorbance out of Sequence" was printed, and all the absorbances involved were given a value of zero. As before, the checking process was resumed upon discovery of another time on the tape. When the order of numbers had been satisfactorily tested, a summary of the tape was printed out. Absorbances for the individual cells were then compared, bearing in mind the decrease in absorbance with time as reaction proceeds. If the difference between any two adjacent points exceeded 50, then "Absorbance out of Sequence" was again
printed; the first absorbance of the pair was given a zero value. With the completion of this final check, the data for each cell (omitting all the zero values) was presented for use in the rate constant evaluation. To assist the program in its difficult task, each tape was carefully examined before submission to the 4130, and any obvious errors, such as additional zero points, were removed.

The program ROQUE used to analyse data from the SP 1800 was much simpler in comparison with STEVE, principally due to the fact each tape only consisted of a list of absorbances for one cell (Fig. 5.8). The program did make provision for any number of cells, however. There was no necessity for time checks or sequence of data tests on the present results, therefore. The time for each reading was obtained directly from multiples of the given time interval. As before, the computer store was cleared and arrays set aside for times and absorbances (see Appendix 2). As the tape was read in, a time was allocated to each absorbance, and the total number of points printed when 99999 (the halt code) was reached. A loop was included in order to eliminate the first three points, usually of doubtful accuracy, and then collect the absorbances for each cell, in preparation for the calculation (Chapter 4). Editing of the SP 1800 tapes was only rarely required, since this equipment proved extremely reliable and produced no wild absorbance points.

Inspite of its creditable performance in analysing the aquation data, ROQUE was found unsatisfactory for the cyanide substitution results (see Chapters 4 and 9). A contributory factor towards this failure was the much narrower absorbance
range covered during reaction, and so a far simpler analytical method was used. Times and absorbances were taken directly from the tapes and fed into the PDP 11 computer.

Thus, the methods of collection and analysis of the experimental data from both conductivity and spectrophotometry techniques have been explained in some detail. The next chapter deals with the calculation and interpretation of activation parameters, obtained from the experimental rate constants.
CHAPTER SIX

Activation Parameters
6.1 Introduction

Various attempts have been made to account for the dependence of kinetic parameters on solvent composition: over thirty years ago, Ingold and Hughes first examined the effects of solvents on relative rates of reactions. The variations in rate constants have, for the most part been examined with reference to electrostatic considerations, where free energy differences have been correlated with some function of the bulk solvent relative permittivity. Examples include log k with $\varepsilon_r$, log k with log $\varepsilon_r$, and some more detailed relationships based on the Kirkwood equation (k is the rate constant, $\varepsilon_r$ the relative permittivity). Such correlations stem from the assumed change in electrical properties of the reactant, on going from the initial to the transition state. These treatments found some success where ion-solvent interactions were large, but had limited analytical value.

Interest in the kinetics of chemical reactions in aqueous mixtures grew, however, from the complex patterns obtained when activation parameters for a given reaction were plotted against solvent composition. Values of $\Delta H^*$ and $\Delta S^*$, the enthalpy and entropy of activation respectively, had been previously determined for many solvolysis reactions, but their superiority over the free energy $\Delta G^*$ in probing solvent effects had still to be demonstrated. The extra experimental work required for determination of $\Delta H^*$ and $\Delta S^*$ had also to be deemed worthwhile. Winstein and Fainberg found that the change in values of these parameters with solvent composition was indeed dramatic, and the need for a more detailed investigation of solvent effects was then clearly indicated.
Finally, Moelwyn-Hughes suggested that the temperature coefficient of $\Delta H^\ddagger$ (i.e. $\Delta C_p^\ddagger$) provided an experimentally accessible quantity which was largely determined by solvent reorganisation. This parameter had already been documented in connection with the temperature dependence of ionization of weak acids: a high degree of accuracy in rates and a wide experimental range are required for its determination, however.

This chapter deals with the derivation of activation parameters from experimental rate constants, through the application of Transition State theory. An introduction to the Algol computer program involved in this analysis, based on the method explained by Clarke and Glew, is given, with a comparison of the calculated results and literature data for the activation parameters of some aqueous systems. Possible interpretations of the quantities in terms of mechanism and reactivity are briefly commented on. Firstly, an outline of Transition State theory (originally proposed by Eyring in 1935) is provided.

6.2 Theoretical Background

The Transition State theory makes allowance for the use of important thermodynamic concepts, but no completely theoretical prediction of rate constants is possible. The species in a reaction process which corresponds to the maximum in the energy curve (see diagram) is the focus of attention here. Referred to as the Activated Complex, or
Transition State, this is formally treated as a molecule, inspite of its ill-defined and transitory existence. In a given reaction, \( A + B \rightarrow \text{products} \) it may be assumed that \( A \) and \( B \) establish an equilibrium concentration of this transition state species, before the reaction proceeds to product formation. Thus:

\[
A + B \rightleftharpoons (AB)^+ \rightarrow \text{products}
\]

The activated complex is, therefore, not a state of stable equilibrium since it lies at a maximum of potential energy.

The rate of overall reaction is dependent upon both the concentration of transition state species, and the rate of their subsequent decomposition to products. The concentration of the activated complex may be written in terms of the equilibrium expression,

\[
k^* = \frac{[A][B]}{[(AB)^*]} \quad \text{or} \quad [(AB)^*] = k^*[A][B]
\]  

(1)

The rate of decomposition of \((AB)^+\) is determined by the frequency at which this complex flies apart; since this frequency factor, \( \nu \), is given by \( (kT/h) \), (where \( k \) is the Boltzmann constant, \( T \) the temperature and \( h \) Planck's constant) then the reaction rate is

\[
\frac{-d[A]}{dt} = k^*[A][B] \frac{kT}{h} = k_r[A][B]
\]  

(2)

The rate constant is given by \( k_r = \frac{kT}{h} k^* \)

(3)

This general expression provided by the Transition State theory for the rate constant of any elementary reaction only becomes of value when the equilibrium constant is interpreted thermodynamically. This is achieved by introduction of the
standard free energy change (as would be done for any ordinary equilibrium constant):

$$\Delta G^\ddagger = -RT \ln K^\ddagger$$  \hspace{1cm} (4)

$K^\ddagger$ is expressed in units of concentration here; $\Delta G^\ddagger$ is the free energy of activation, and represents the difference between the free energy of the activated complex and that of the reactants, when all are in their standard states. Since

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$$  \hspace{1cm} (5)

then,

$$k_r = \frac{kT}{h} e^{-\Delta G^\ddagger / RT} = \frac{kT}{h} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}$$  \hspace{1cm} (6)

Therefore,

$$\Delta H^\ddagger = RT \left( \frac{d \ln K^\ddagger}{dT} \right)_p$$ and $\Delta S^\ddagger = (\Delta H^\ddagger - \Delta G^\ddagger) / T$  \hspace{1cm} (7)

The heat capacity of activation is given by

$$\Delta C_p^\ddagger = \left( \frac{d \Delta H^\ddagger}{dT} \right)_p$$  \hspace{1cm} (8)

The above theory may now be applied to a simple, spontaneous solvolysis reaction, occurring at fixed temperature and pressure. For example, in the reaction:

$$RX + H_2O \rightarrow ROH + H^+ + X^-$$

and where

$$RX + H_2O \rightarrow [\text{ }]^\ddagger$$

The reaction rate constant is assumed to be first-order. Then, taking $RX$ as species 2, $\mu^\ddagger$ the chemical potential of the transition state in its solution standard state, and $\mu_1^\ddagger$ as the chemical potential for the initial state in its solution standard state (at the same temperature and pressure), it follows that

$$\Delta G^\ddagger = \mu^\ddagger - \mu_1^\ddagger$$

$$\Delta H^\ddagger = H^+ - H_2^-$$

$$\Delta S^\ddagger = S^+ - S_2^+$$  \hspace{1cm} (9)
\( H^*, S^* \) are the standard partial molar enthalpy and entropy respectively for the transition state, \( H_2^*, S_2^* \) their equivalents for the initial state. A similar expression holds for the standard partial molar heat capacities, \( \Delta C_p^* = C_p^* - C_p^* \).

The activation parameters are much less sensitive to temperature changes than are rate or equilibrium constants, and are often considered as being practically invariant in a narrow temperature interval. Before progressing to the means of calculating these functions, their variation with cosolvent in a binary aqueous mixture must be mentioned. For a simple first-order reaction, taking the cosolvent as species 3 and water as reference solvent \( (x_3 = 0) \), the change in any thermodynamic function \( \Delta X^* \), on going from a solution in water to one in a binary mixture, is given by

\[
\delta_n \Delta X^* = \Delta X^*(x_3) - \Delta X^*(x_3 = 0)
\]  

\( \delta_n \) is the solvent operator. The dependence of a given \( \Delta X^* \) on \( x_3 \) indicates that the properties of initial and transition states must differ in respect to their dependence on \( x_3 \), i.e. \( \delta_n X^* \neq \delta_n X^* \), although either \( \delta_n X^* \) or \( \delta_n X^* \) may be zero.

These two quantities are transfer functions, representing the effect of cosolvent on a particular partial molar property of the solute or transition state. By definition, \( \delta_n X^* \) cannot be measured; hence, as will be seen, most efforts have been directed towards obtaining \( \delta_n X^* \) for the reactants.

6.3 Temperature Dependence of Rate Constant

The problem of evaluating standard thermodynamic function changes, whether from equilibrium or rate constants depends totally on the accurate fitting of the experimental data to a
representative equation. Many workers have made suggestions for the form of dependence of $k$ upon temperature: these include the original Arrhenius equation, various polynomials in $T$, e.g. $\ln k = A + B/T + C \ln T$, or polynomials in $(T-\theta)$ or $(T-T_0)$, where $\theta$ and $T$ are reference temperatures, e.g.

\[
\ln k = A + B\left(\frac{1}{T} - \frac{1}{T_0}\right) + C \ln\left(\frac{T}{T_0}\right) + \beta_k
\]

Overall, however, there has been little agreement on any particular equation suitable for data covering a wide temperature range, and certainly few authors have attempted a treatment for errors on the thermodynamic functions calculated. The most fundamental analysis has been that of E.C.W. Clarke and D.N. Glew, and this was selected as the basis for the computer program TEMPAN used for our calculations. Their completely general set of equilibrium equations, representing the temperature dependence of equilibrium constants in terms of the standard thermodynamic function changes at a chosen reference temperature have been adapted for use with reaction rate constants.

The Clarke-Glew analysis was based on an extension of the simple Van't Hoff equation:

\[
R \ln K_p = A + B/T
\]  

$K_p$, the equilibrium constant was assumed to be a well-behaved continuous function of $T$, and the related standard thermodynamic function changes ($\Delta G^\circ_T$, $\Delta H^\circ_T$, $\Delta C_P^\circ_T$ etc.) to exhibit similar behaviour. At $T K$, the following equation holds:

\[
R \ln K_p = -\frac{\Delta G^\circ_T}{T} = \Delta S^\circ_T - \left(\frac{\Delta H^\circ_T}{T}\right)
\]

$\Delta G^\circ_T$, $\Delta S^\circ_T$ and $\Delta H^\circ_T$ are functions of $T$ only. A reference
temperature $\theta K$ was then chosen, at which the standard functions and their errors were required, these being $\Delta G_\theta^\pi$, $\Delta S_\theta^\pi$, $\Delta H_\theta^\pi$, $\Delta C_P^\pi$, $(d\Delta C_P/dT)_\theta$, $(d^2\Delta C_P/dT^2)_\theta$ and $(d^3\Delta C_P/dT^3)_\theta$.

$\Delta H_\theta^\pi$ was considered to be a perturbation on the value of $\Delta H_\theta^\pi$ at $\theta$, such that the Taylor's series expansion could be used in its definition, thus:

$$\Delta H_\theta^\pi = \Delta H_\theta^\pi + \Delta C_P^\pi (T-\theta) + 1/2(d\Delta C_P/dT)_\theta (T-\theta)^2 + 1/6(d^2\Delta C_P/dT^2)_\theta (T-\theta)^3 + 1/24(d^3\Delta C_P/dT^3)_\theta (T-\theta)^4$$ (13)

The $\theta$ subscript denotes the value of each function at $\theta$, and the series has been arbitrarily terminated at the third derivative of $\Delta C_P$. The expression for $\Delta S_\theta^\pi$ is

$$\Delta S_\theta^\pi = \Delta S_\theta^\pi + \int_\theta^T (\Delta C_P^\pi/T) \cdot dT$$ (14)

in which $\Delta C_P^\pi$ is defined by the Taylor's series expansion

$$\Delta C_P^\pi = \Delta C_P^\pi + (d\Delta C_P/dT)_\theta (T-\theta) + 1/2(d^2\Delta C_P/dT^2)_\theta (T-\theta)^2 + 1/6(d^3\Delta C_P/dT^3)_\theta (T-\theta)^3$$ (15)

Then, by substituting equation (13) for $\Delta H_\theta^\pi$, and the integrated (14) for $\Delta S_\theta^\pi$, into equation (12), a relationship between $R \ln K_p$ and $T$ is obtained. This is an exact equation in five variables of $T$, and six constants, the latter defining the values for the standard thermodynamic function changes. Replacing $T$ by the variable $x = (T-\theta)/\theta$ facilitates more accurate evaluation of the temperature derivatives.

Consequently, the final equation after simplification becomes:

$$R \ln K_p = -\frac{\Delta G_\theta^\pi}{\theta} + \frac{\Delta H_\theta^\pi}{\theta} \left[ \frac{x}{1+x} \right] + \Delta C_P^\pi \left[ x^2 \sum_{n=1}^{\infty} \frac{n}{n+1} (-x)^{n-1} \right] + \frac{\theta(d\Delta C_P/dT)_\theta x^3}{2} \left[ \sum_{n=1}^{\infty} \frac{n}{n+2} (-x)^{n-1} \right]$$
Here, \( R \ln K_p \) is expressed at any \( T \) as a function of the five independent temperature variables in \( x \), with the constants directly proportional to the standard thermodynamic functions at \( \theta \). Any higher derivatives of \( \Delta C_P \) are assumed to be zero, and \( (d^3 \Delta C_P / dT^3)_\theta \) is a constant; the fourth, fifth and subsequent orders of \( \Delta C_P^* \) at \( \theta \) may be obtained if required, however. In practice, the experimental data proved insufficiently precise for any terms above \( \Delta C_P^* \) itself, so this extension was not needed.

For the evaluation of thermodynamic functions from equilibrium constants, Clarke and Glew assumed that each set of data comprised \( \ln K_p \) values having equal weight and the same standard error. Weight factors could be introduced if required; the temperatures were taken to be accurately known. Application of the method of least squares for fitting equation (16) to a set of \( N \) experimental \( K_p \) measurements required rewriting the expression as a regression:

\[
R \ln K_p = b_0 + b_1 u_1 + b_2 u_2 + b_3 u_3 + b_4 u_4 + b_5 u_5 \tag{17}
\]

Each symbol is defined below:

\[
\begin{align*}
    b_0 &= -\Delta G^*_\theta / \theta \\
    b_1 &= \Delta H^*_\theta / \theta \\
    b_2 &= \Delta C_P^*_\theta \\
    b_3 &= \theta / 2 (d\Delta C_P / dT)_\theta \\
    b_4 &= \theta / 6 (d^2 \Delta C_P / dT^2)_\theta \\
    b_5 &= \theta / 24 (d^3 \Delta C_P / dT^3)_\theta
\end{align*}
\]

The constants \( b_1 \rightarrow b_5 \) are the partial regression coefficients of \( R \ln K_p \) on the corresponding variables below.
\[ u_1 = \left[ \frac{x}{1+x} \right] = \left[ x \sum_{n=1}^{\infty} (-x)^{n-1} \right] \]

\[ u_2 = \left[ x^2 \sum_{n=1}^{\infty} \frac{n}{n+1} (-x)^{n-1} \right] \]

\[ u_3 = \left[ x^3 \sum_{n=1}^{\infty} \frac{n}{n+2} (-x)^{n-1} \right] \]

\[ u_4 = \left[ x^4 \sum_{n=1}^{\infty} \frac{n}{n+3} (-x)^{n-1} \right] \]

bo is eliminated from the equation by substituting the values of the \( u \) variables for the data mean point \((\overline{R \ln Kp}, \overline{u_1}, \overline{u_2}, \overline{u_3}, \overline{u_4}, \overline{u_5})\) into equation (17), giving

\[
(R \ln Kp - \overline{R \ln Kp}) = b_1 (u_1 - \overline{u_1}) + b_2 (u_2 - \overline{u_2}) + b_3 (u_3 - \overline{u_3}) + b_4 (u_4 - \overline{u_4}) + b_5 (u_5 - \overline{u_5})
\] (18)

Equation (18) contains only the five unknown regression coefficients, therefore, and fitting of the expression to the \( N \) data points by the least squares method provides the best estimates of values for \( b_1 - b_5 \). Evaluation of the fifteen elements \( b_{11}, b_{12}, \ldots, b_{55} \) of the inverse matrix permits calculation of the errors on linear functions of the regression coefficients. By substituting the \( b \) coefficients and data into equation (17), a value for \( b_0 \) may be obtained. The residual sum of squares, \( Q(R \ln Kp) \), for the \( N \) observed \((R \ln Kp)\) values about regression equation (17) is given by

\[
Q(R \ln Kp) = \sum_{i=1}^{N} \left[ (R \ln Kp)_{\text{obs}} - (b_0 + b_1 u_1 + b_2 u_2 + b_3 u_3 + b_4 u_4 + b_5 u_5)^2 \right]
\] (19)

The residual mean square error is provided by the square of the standard error \( \sigma(R \ln Kp) \) on a single \((R \ln Kp)_{\text{obs}}\) determination assessed from the six constant equation (17) at \((N-6)\) degrees of freedom.

From the least squares solution of equation (18) and its
inverse matrix, the derived coefficients $b_1$ to $b_5$ together with the data mean values may be employed to predict the standard thermodynamic function changes and errors, both at $\Theta$ and at the general temperature $T K$. Generally, the value for any function $\Delta x^*$ is obtained from:

$$\Delta x^* = W(w_0 R \ln K_p + w_1 b_1 + w_2 b_2 + w_3 b_3 + w_4 b_4 + w_5 b_5)$$  \hspace{1cm} (20)$$

Its standard error can be calculated from the $b$-coefficients. The weight factors $w_0 \rightarrow w_5$ for each thermodynamic function are those set out in Table I of the Clarke-Glew paper.

Values for the functions and errors at reference $\Theta$ are also obtainable from equation (20), when $\Theta$ replaces $T$ and both $x$ and the $u$ variables have zero value.

The completely general equations given above, then, were suggested by Clarke and Glew to be equally applicable both to the constant volume functions $\Delta A^*$, $\Delta B^*$, $\Delta C_V^*$ derived from values of equilibrium constant $K_v$, and to the activation functions $\Delta G^*$, $\Delta H^*$, $\Delta C_P^*$ obtainable from reaction rate constants. The ready solution of equation (16) by the least squares method, possible extension to include any number of independent variables for data of any accuracy over any temperature range, and direct relation to the thermodynamic functions and their errors, made it ideal for fitting and representing the temperature variation of accurate rate constants. A brief discussion of the computer program constructed for this analysis, based on the above theory, is given below.

6.4 Introduction to TEMPAN

Firstly, because equation (16) defines $R \ln K_p$ in terms of the five temperature variables and six constants, the rate
equation must be rewritten in a similar form, for the activation parameters to be obtainable. From equation (6),

\[ k_r = \frac{kT}{h} \exp \left( \frac{-\Delta G^*}{RT} \right) \]

\[ \frac{-\Delta G^*}{RT} = \left[ \ln k_r - \ln \left( \frac{kT}{h} \right) \right] \]

and

\[ \frac{-\Delta G^*}{T} = R \left[ \ln \left( \frac{k_r h}{kT} \right) \right] \]  \hspace{1cm} (21)

i.e.

\[ \frac{-\Delta G^*}{T} = 8.31434 \left[ \ln \left( \frac{k_r \cdot 6.626196}{1.380622 \cdot 10^{11}} \right) \right] \]  \hspace{1cm} (22)

The rate constant \( k_r \) may now be expressed in the same form as \( K_p \) in equation (16).

After reading in the number of data points \( N \) and the reference temperature \( \Theta \), and allocating store space for various arrays, the program TEMPAN is controlled by the values assigned to parameters \( Z, ZZ, ZZZ \) and \( ZZZZ \). These determine the number of constants used in the analysis, such that if all the parameters have a value of unity, then an initial calculation involving the complete set of 6 constants is undertaken, followed by repetition of the process using successively fewer constants (terminating after the 2 constant equation has been reached). Also, if \( ZZZZ \) has zero value, the five constant equation only is used; \( ZZ \) being zero indicates use of four constants (and \( ZZZZ \) becomes zero automatically). Equally, \( ZZ \) must be zero for the three constant equation, and \( Z \) zero for two constants: here, the remaining \( Z \) parameters become zero upon commencement of each calculation.

Prior to application of the least squares procedure, the data consisting of rate constants and corresponding tempera-
tures are read in; the temperature step, dθ, for predicted thermodynamic functions is specified at this stage. Y values are then calculated for each data point, where Y represents the righthand side of equation (22); X values are obtained from the relation X = (T-θ)/θ. The u terms of regression equation (17) are constructed, again for each of the N points, but the required summations to infinity have been replaced by the following: each summation ceases when the value of the final term, divided by the total sum of the series becomes less than 10^{-12}. Mean values of the completed coefficients UA, UB, UC, UD and UE, over the N data points are denoted by UAM, UBm, UCM, UDM, UEM; the mean Y value is YM.

The (5×5) matrix A is then set up, the elements comprising u coefficients and multiples of the differences between these and their mean values. Factors SA, SB, SC, SD and SE refer to results obtained from multiplying the differences (u - U) by (Y - Ȳ), for all N. Procedures for copying the A matrix, and inverting the resulting matrix B (identical to those used in the programs of Chapter 4) are included here. The b constants in equation (17) may, therefore, be calculated from combinations of the elements of the inverse matrix with the factors SA→SE.

Substitution of all b constants and u variables back into (17) provides the calculated values for Y, and subsequently the rate constants, k. QD represents the sum of squares of (Y - Ycalc) differences, i.e. the Q(R ln K) factor of equation (19), and the residual mean square error is given by the quotient QD/DF. DF defines the number of degrees of freedom, and its value obviously varies according to the number of
constants used in the analysis. Finally, each standard thermodynamic function and its standard error may be obtained from the constants \( b_i \rightarrow b_7 \), for reference temperature \( \Theta \).

Predicted functions \( \Delta G_\alpha, \Delta H_\alpha, \Delta S_\alpha, \Delta C_p_\alpha \) etc. are then determined at selected temperature intervals \( \Delta \Theta \) between 273.15 and 353K, making use of the new \( u \) variables (\( UAT, UBT, UCT, UDT, UET \)), calculated as before. The control variable \( W \), dependent on the allotted \( Z, ZZ, ZZZ, ZZZZ \) values determines the number of \( b \) constants in the analysis, and hence deletes the unwanted elements of the \( B \) matrix. All thermodynamic functions are calculated from equation (20), in accordance with the appropriate weighting functions. Expected rate constants for each preselected temperature are also printed. The entire analysis may then be repeated for another value of \( \Theta \), if required. (For program see Appendix 2)

Some results obtained from the TEMPAN analysis, for the solvolysis of t-butyl chloride in water, acetone/water and for benzyl chloride in ethanol/water mixtures are shown in Table I. Rate constants measured by Robertson and Sugamori,\(^4\) Albery and Robinson,\(^5\) Tommila, Tiilikainen and Voipio,\(^6\) and Hyne, Wills and Wonkka,\(^7\) respectively, were used. The table illustrates, for comparison, values of activation parameters calculated by the various authors. The agreement is seen to be extremely good.

6.5 Activation Parameters and Solvent Composition

Having examined in detail the means of calculating these activation parameters, it is now of interest to briefly look at trends in their variation with cosolvent, in aqueous binary
### TABLE 6. I

Comparison of literature and TEMPAN - calculated Activation Parameters.

A. System: t-butyl chloride/water.

1. Robertson's Data (20 points) at 298.15K.

<table>
<thead>
<tr>
<th></th>
<th>$k_r$</th>
<th>$\Delta G^*/kJ \text{ mol}^{-1}$</th>
<th>$\Delta H^*/kJ \text{ mol}^{-1}$</th>
<th>$\Delta S^*/J \text{ K}^{-1} \text{ mol}^{-1}$</th>
<th>$\Delta C_p^*/J \text{ K}^{-1} \text{ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Robertson</td>
<td>$2.9745 \times 10^{-2}$</td>
<td>81.75</td>
<td>96.23</td>
<td>48.57</td>
<td>-347</td>
</tr>
<tr>
<td>TEMPAN 3 const.</td>
<td>$2.9699 \times 10^{-2}$</td>
<td>81.74</td>
<td>94.31</td>
<td>42.14</td>
<td>-348.8</td>
</tr>
<tr>
<td>TEMPAN 2 const.</td>
<td>$3.1032 \times 10^{-2}$</td>
<td>81.63</td>
<td>99.43</td>
<td>59.68</td>
<td></td>
</tr>
</tbody>
</table>

2. Albery's Data (40 points) at 298.15K.

<table>
<thead>
<tr>
<th></th>
<th>$k_r$</th>
<th>$\Delta G^*/kJ \text{ mol}^{-1}$</th>
<th>$\Delta H^*/kJ \text{ mol}^{-1}$</th>
<th>$\Delta S^*/J \text{ K}^{-1} \text{ mol}^{-1}$</th>
<th>$\Delta C_p^*/J \text{ K}^{-1} \text{ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albery</td>
<td>$2.9760 \times 10^{-2}$</td>
<td></td>
<td>93.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEMPAN 3 const.</td>
<td>$2.7513 \times 10^{-2}$</td>
<td>81.93</td>
<td>98.43</td>
<td>55.35</td>
<td>-228.8</td>
</tr>
<tr>
<td>TEMPAN 2 const.</td>
<td>$2.7362 \times 10^{-2}$</td>
<td>81.94</td>
<td>100.28</td>
<td>61.50</td>
<td></td>
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</tbody>
</table>

3. Robertson's + Albery's Data (60 points) at 298.15K.

<table>
<thead>
<tr>
<th></th>
<th>$k_r$</th>
<th>$\Delta G^*/kJ \text{ mol}^{-1}$</th>
<th>$\Delta H^*/kJ \text{ mol}^{-1}$</th>
<th>$\Delta S^*/J \text{ K}^{-1} \text{ mol}^{-1}$</th>
<th>$\Delta C_p^*/J \text{ K}^{-1} \text{ mol}^{-1}$</th>
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</thead>
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<tr>
<td>TEMPAN 3 const.</td>
<td>$2.8084 \times 10^{-2}$</td>
<td>81.88</td>
<td>96.16</td>
<td>47.89</td>
<td>-302.5</td>
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<tr>
<td>TEMPAN 2 const.</td>
<td>$2.8044 \times 10^{-2}$</td>
<td>81.88</td>
<td>98.88</td>
<td>56.99</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 6. I

**B. System: Benzyl chloride/Ethanol - water.**

Hyne's data at 298.15K; 3 constant TEMPAI analysis, (T).

<table>
<thead>
<tr>
<th>mf. Ethanol</th>
<th>k_r(x10^5)</th>
<th>k_r(T)(x10^5)</th>
<th>ΔH^°/kJ mol(^{-1})</th>
<th>ΔH^°(T)/kJ mol(^{-1})</th>
<th>ΔS^°(T)/kJ mol(^{-1})</th>
<th>ΔCp^°(T)/J K(^{-1}) mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.320</td>
<td>1.318</td>
<td>89.57</td>
<td>87.73</td>
<td>100</td>
<td>-176.3</td>
</tr>
<tr>
<td>0.04</td>
<td>0.0992</td>
<td>0.0991</td>
<td>84.8</td>
<td>84.02</td>
<td>101.6</td>
<td>-140.3</td>
</tr>
<tr>
<td>0.08</td>
<td>0.0695</td>
<td>0.0695</td>
<td>80.40</td>
<td>79.18</td>
<td>102.4</td>
<td>-97.3</td>
</tr>
<tr>
<td>0.125</td>
<td>0.0368</td>
<td>0.0368</td>
<td>80.29</td>
<td>78.96</td>
<td>104.04</td>
<td>-97.4</td>
</tr>
<tr>
<td>0.203</td>
<td>0.0123</td>
<td>0.0123</td>
<td>85.38</td>
<td>83.45</td>
<td>106.7</td>
<td>-143.99</td>
</tr>
</tbody>
</table>
TABLE 6.  I

C. System: t-Butyl Chloride/Acetone - water.

Tommila's data at 298.15K; 3 constant TEMPAN analysis (T).
2 constant " " (T2).

<table>
<thead>
<tr>
<th>mf. Acetone</th>
<th>k_r(x10^2)</th>
<th>ΔG/kJ mol^-1</th>
<th>ΔH/kJ mol^-1</th>
<th>ΔS/J mol^-1</th>
<th>ΔCp^* /J K^-1 mol^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.03</td>
<td>82.09</td>
<td>94.59</td>
<td>41.84</td>
<td></td>
</tr>
<tr>
<td>(T) 0.006</td>
<td>0.912</td>
<td>84.6</td>
<td>85.59</td>
<td>3.347</td>
<td>-310.4</td>
</tr>
<tr>
<td>0.052</td>
<td>0.929</td>
<td>84.6</td>
<td>85.62</td>
<td>3.358</td>
<td>-70.62</td>
</tr>
<tr>
<td>(T) 0.151</td>
<td>0.0666</td>
<td>91.128</td>
<td>84.76</td>
<td>-21.34</td>
<td></td>
</tr>
<tr>
<td>(T) 0.0669</td>
<td>0.0054</td>
<td>97.40</td>
<td>82.04</td>
<td>-51.46</td>
<td></td>
</tr>
<tr>
<td>0.283</td>
<td>0.0055</td>
<td>97.33</td>
<td>83.27</td>
<td>-47.17</td>
<td>-215.7</td>
</tr>
<tr>
<td>(T2) 0.505</td>
<td>0.00029</td>
<td>104.56</td>
<td>89.57</td>
<td>-50.21</td>
<td></td>
</tr>
</tbody>
</table>
mixtures. Winstein, Robertson, Tommila and Hyne have all made careful measurements of the effect of binary solvent change on activation parameters for a number of reactions. Free energies, enthalpies and entropies of activation for t-butyl chloride solvolysis in water/ethanol mixtures of all compositions at different temperatures (Winstein and Fainberg) are plotted in the diagram below. Clearly, the free energy $\Delta G^*$ varies smoothly and almost linearly with respect to solvent composition, in spite of the extrema exhibited by enthalpy and entropy functions. These wild fluctuations of $\Delta H^*$ and $\Delta S^*$, especially in the high water end of the solvent spectrum appear peculiar to aqueous solutions, and not aqueous alcohols alone.

![Plot of $\Delta G^*$, $\Delta H^*$ and $-T\Delta S^*$ against mole fraction of water for t-butyl chloride solvolysis in EtOH/H$_2$O at 298.15K.](image)

Arnett subsequently measured heats of solution for a number of non-electrolytes and salts, and discovered that these show endothermic maxima in the same region of water-rich binary solvents where the other properties show extrema. He then concluded that at least 95% of the variation in $\Delta H^*$
for the region of the minimum could be accounted for by changes in the ground-state solvation, leaving the transition state changes negligible, in this particular case.

Robertson found that the solvolysis of t-butyl chloride in water is characterized by large negative values of the heat capacity of activation (see diagram below). If it is assumed that the breakdown of the initial state solvation shell partly determines the enthalpy required in the activation process, then this term will decrease as the temperature increases. Robertson believes this to be the physical basis for a large part of the observed negative temperature coefficients of $\Delta H^*$ in such reactions. The remarkable difference in values of $\Delta C_p^*$ across the same concentration range, for tetrahydrofuran/water and acetonitrile/water mixtures has been correlated with the effect of these two cosolvents on the structural properties of the solvent media. For the high-water region of alcohol/water mixtures, the dramatic changes occurring in $\Delta C_p^*$ and $\Delta S^*$ strongly suggest a reorganization of
solvent structure, and that the involvement in the activation process is in opposition to that in the initial state solvation process.

It is obvious, then, that in order to obtain a complete analysis of transition state thermodynamic quantities, the ground state contributions must be known. Arnett has indicated that these may possibly be extracted from solubility data. As a result of this suggestion, the solubility analysis of Chapter 3 has been applied to the systems studied in this work, as far as is possible. Activation parameters and any conclusions are dealt with in the following chapters.
References

CHAPTER SEVEN

Solvolysis of t-Butyl Chloride in Hydrogen Peroxide/Water mixtures
7.1 Introduction

Kinetic data have been reported for t-butyl chloride hydrolysis in a wide variety of solvent systems. The dependence on mole fraction of thermodynamic activation parameters was illustrated in Figure 2, Chapter 6. The common feature of all these systems was the decrease in rate constant with increase in cosolvent mole fraction, \( x_2 \). It is noteworthy that, in every case, the excess Gibbs free energy \( G^E \) for the liquid mixture was positive, although some mixtures were typically aqueous (monohydric alcohols + water) and others typically non-aqueous (acetonitrile + water). There was a distinct lack of information for reactions in aqueous mixtures where \( G^E \) was negative.

Also, the Prausnitz analysis of Chapter 3 has indicated the solubility behaviour expected for solutes in mixtures having positive \( G^E \) functions: a decrease in rate constant for solvolysis of t-butyl chloride was predicted, arising from stabilization of the initial state. In this context, therefore, it was considered likely that the solubility of the substrate in a mixture where \( G^E \) is negative might decrease, thus destabilizing the initial state and resulting in a significant increase in \( k \). Consequently, it was decided to study the kinetics of solvolysis of t-butyl chloride in water/hydrogen peroxide mixtures.

Hydrogen peroxide is worthy of study, not only because of its importance to industry (particularly for oxidizing purposes), but also as a result of its inorganic character and great resemblance to water. The latter is apparent from similar surface tension and viscosity values. Also, both
liquids are very weak electrolytes and have similar electrical conductivities. H$_2$O$_2$ is also an excellent ionizing solvent, thus allowing the dissociation of electrolytes at all ranges of composition; the reactivity of the compound, however, introduces a restriction on the selection of metal electrodes used for conductivity measurements (see later). The structure of the hydrogen peroxide molecule (see below) clearly demonstrates that this is the outstanding example of a hydrophilic solute. As with water, the dominant interaction between peroxide molecules, or peroxide and water molecules in an aqueous mixture must be that of hydrogen bonding. Each peroxide has two bonding protons and four acceptor sites, compared with the two acceptor sites and protons of the water molecule. Hence, it would be expected that peroxide molecules alone, and with water should form three-dimensional polymers: intercomponent association will be important in aqueous mixtures, obviously.

Physicochemical studies of hydrogen peroxide/water mixtures have been made previously, and these include density measurements, heats of mixing and heats of vaporisation, and other thermodynamic work. The excess function data collected by Giguère et al. have been processed by the program XEFIT and the results used to plot the curves illustrated in Figures 1 and 2. These show that the peroxide/water mixture
Molar thermodynamic functions of mixing for water and hydrogen peroxide at 298.15 K; $x_2$ is the mole fraction of $H_2O_2$. 
is a typically non-aqueous system, for which at the lower temperatures at least (273 and 298K), \( G^E \) is determined largely by \( H^E \). \( TS^E \) values are considerably smaller, and correspond to an increase of order in the solution. The variation in excess heat capacity is noticeably less regular, but nevertheless very small. It has been found\(^5\) that the partial molal volume of \( H_2O_2 \), especially at low temperatures and at low concentrations of peroxide is far from being a linear function of the composition. This has been attributed to the relatively open structure of the water at low temperatures being drawn together by the peroxide molecules entering it. Giguere\(^6\) has suggested that a type of hydrate — not a clathrate hydrate — is formed in mixtures by the intermolecular hydrogen-bonding. The excess thermodynamic mixing functions have been used in the Solubility data analysis (see Section 7.4).

7.2 Experimental Details

The procedure for the experiments followed exactly that described in Chapter 5: it was not found necessary to modify the cell assembly or metal of the electrodes because of the nature of the solvent mixture under investigation. Although decomposition of the peroxide did occur at the platinum electrodes, the majority of runs proved reproducible. It was found that, in order to obtain a reasonable range reading on the conductivity bridge, the reaction mixture had to be thoroughly stirred, before recording commenced.

The hydrogen peroxide (Analar) was used as supplied for mole fraction mixtures 0.03 & 0.17, and diluted with freshly...
**TABLE 7. I**

Sample Titration Figures for Peroxide Solutions.

<table>
<thead>
<tr>
<th>Mole Fraction Peroxide</th>
<th>Equivalent Mls. Thiosulphate Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Pure Solution)</td>
</tr>
</tbody>
</table>
| 1 ml. 6% soln.  
  (0.03 mf)           | 34.4                                    | 34.1                                 |
| 0.3 ml. 18% soln.  
  (0.1 mf)            | 31.25                                   | 31.3                                 |
| 0.15 ml. 30% soln.  
  (0.17 mf)           | 27.25                                   | 27.0                                 |
distilled water for the 0.1 mole fraction; t-butyl chloride was fractionally distilled. The composition of the peroxide mixtures was checked before and after kinetic runs: aliquots were removed, diluted with sulphuric acid and Analar potassium iodide added. The resulting liberated iodine was then titrated against standard Analar sodium thiosulphate solution, the latter having been previously standardised with Analar potassium iodate. Care was taken to ensure that titrations were shielded from direct sunlight, since difficulties had been encountered as a result of the reappearance of the blue colouration due to starch indicator, on allowing the solution to stand for a few seconds.

As the sample titration figures show (Table I), the change in mole fraction arising from peroxide decomposition during a run was found to be negligibly small, although the decomposition itself remained a problem. At high temperatures and in peroxide-rich solutions, oxygen bubbles occluding to the cell electrodes tended to produce wild fluctuations in electrical conductivity. Despite repeated attempts, the rate constant could not be measured in these cases; hence, the highest temperature for reactions was 293K. At lower temperatures and mole fractions, this difficulty persisted but was not as acute. Many runs were ruined, therefore, and the accuracy of the measured rate constants (+ 5%) proved significantly less than the technique is capable of attaining. In order to minimize the problem, fifteen or more runs were made at each temperature and mole fraction: thus, rate data at 273, 278, 283, 288 and 293K for peroxide solutions of mole fraction 0.03, 0.1 and 0.17 were obtained (see Table II).
### TABLE 7. II

Rate Constants for t-Butyl Chloride solvolysis in
Hydrogen Peroxide Mixtures

<table>
<thead>
<tr>
<th>H$_2$O$_2$ Concentration</th>
<th>Rate Constants</th>
<th>Temperature</th>
<th>No. of pts</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03128 mf. H$_2$O$_2$</td>
<td>$k = 1.02468 \times 10^{-3}$</td>
<td>273.59K</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.00171$</td>
<td>273.59K</td>
<td>12</td>
</tr>
<tr>
<td>0.09588 mf. H$_2$O$_2$</td>
<td>$k = 1.81294 \times 10^{-3}$</td>
<td>273.58K</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.015$</td>
<td>273.58K</td>
<td>12</td>
</tr>
<tr>
<td>0.17383 mf. H$_2$O$_2$</td>
<td>$k = 3.197713 \times 10^{-3}$</td>
<td>273.40K</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.091$</td>
<td>273.40K</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>$k = 1.2442 \times 10^{-3}$</td>
<td>278.26K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.014$</td>
<td>278.26K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$k = 3.5636 \times 10^{-3}$</td>
<td>278.26K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.032$</td>
<td>278.26K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$k = 4.8683 \times 10^{-3}$</td>
<td>278.26K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.087$</td>
<td>278.26K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$k = 4.57496 \times 10^{-3}$</td>
<td>283.22K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.011$</td>
<td>283.22K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$k = 7.50798 \times 10^{-3}$</td>
<td>283.22K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.050$</td>
<td>283.22K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$k = 9.51837 \times 10^{-3}$</td>
<td>283.22K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.161$</td>
<td>283.22K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$k = 9.4385 \times 10^{-3}$</td>
<td>288.22K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.026$</td>
<td>288.22K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$k = 1.46510 \times 10^{-2}$</td>
<td>288.115K</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.0358$</td>
<td>288.115K</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>$k = 1.85225 \times 10^{-2}$</td>
<td>288.12K</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.0795$</td>
<td>288.12K</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>$k = 1.88993 \times 10^{-2}$</td>
<td>293.11K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.008$</td>
<td>293.11K</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$k = 2.67146 \times 10^{-2}$</td>
<td>293.110K</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.223$</td>
<td>293.110K</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>$k = 3.28499 \times 10^{-2}$</td>
<td>293.105K</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.225$</td>
<td>293.105K</td>
<td>17</td>
</tr>
</tbody>
</table>


**TABLE 7. III**

Kinetic data for the hydrolysis of t-butyl chloride in water and hydrogen peroxide mixtures.

<table>
<thead>
<tr>
<th>Mole fraction of H$_2$O$_2$</th>
<th>$10^3 k$ (283.2 K) /s$^{-1}$</th>
<th>$10^2 k$ (298 K) /s$^{-1}$</th>
<th>$\Delta H^\ddagger$ /kJ mol$^{-1}$</th>
<th>$\Delta S^\ddagger$ /kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>4.57 ± 0.01</td>
<td>3.77</td>
<td>97.1 ± 0.2</td>
<td>16 ± 0.2</td>
</tr>
<tr>
<td>0.1</td>
<td>7.51 ± 0.05</td>
<td>5.24</td>
<td>90.3 ± 1.3</td>
<td>9.9 ± 1.3</td>
</tr>
<tr>
<td>0.17</td>
<td>9.52 ± 0.16</td>
<td>5.6</td>
<td>78.6 ± 3.9</td>
<td>-1.5 ± 3.9</td>
</tr>
</tbody>
</table>

* extrapolated values at 298 K.*
7.3 Results

As the Table shows, at each temperature, the rate constant for the hydrolysis of t-butyl chloride increased when hydrogen peroxide was added to water.\(^9\)\(^{ab}\) Thermodynamic activation parameters \(\Delta G^*\), \(\Delta H^*\) and \(T\Delta S^*\) were calculated using two regression coefficients in the Clarke-Glew analysis (see Chapter 6). Their dependence on mole fraction of peroxide, \(x_2\), is summarized in Table III and compared in Figure 3 with the corresponding quantities for hydrolysis in mixtures containing t-butyl alcohol\(^10\) and acetonitrile\(^11\). Clearly, the solvolysis results for this system are somewhat unusual, and Figure 3 particularly serves to highlight the contrast in behaviour of the thermodynamic parameters for the mixtures having \(G^E\) positive and negative. The rate data for the peroxide mixtures were insufficiently precise to be analysed using three regression coefficients, and hence to provide meaningful values of \(\Delta C_p^*\), although the analysis did indicate that when \(x_2 = 0.03\), \(-\Delta C_p^*\) was less than in water.

7.4 Analysis of Results

Since the hydrolysis of t-butyl chloride almost certainly involves unimolecular fission of the carbon-chlorine bond, the increase in rate constant cannot be attributed to the presence of a possibly more powerful nucleophile, \(H_2O_2\). The observed trends in activation parameters have, therefore, been examined from two different standpoints, reflecting two common interpretations of kinetic data to be found in the literature. These are, in the first case, based on dielectric considerations, and in the second on the solubility analysis described
Figure 7.3 Thermodynamic activation parameters for t-BuCl solvolysis in aqueous mixtures.
earlier (Chapter 3). The aim in both, however, was to identify the source of the observed changes in the parameters 

\[ \Delta X^* \left\{ \Delta X^* \left( x_1 \right) - \Delta X^* \left( x_1 = 0 \right) \right\} \]

where \( X = G, H \) or \( S \).

From Chapter 6, it is apparent that these changes may stem from modifications to the initial and transition state quantities. For consistency in the analysis, all data have been calculated for the common temperature 298K. Thus, the kinetic data for hydrolysis in water\(^7\) and in the mixtures were extrapolated to 298K using two regression coefficients in the Clarke-Glew analysis.

7.4.1 Dielectric Effects

The properties of hydrogen peroxide/water mixtures are of interest particularly because these solutions are almost isodielectric.\(^1^2\) To a first approximation, therefore, the rate constant for a reaction involving charge separation on going from initial to transition state should be independent of peroxide mole fraction. However, it was considered important to determine whether the small variation in relative permittivity, \( \varepsilon_r \), was sufficient to produce the observed change in rate constant.

It is interesting to note, from the work of Gross and Taylor,\(^1^2\) that despite the higher dipole moment of the hydrogen peroxide molecule, the relative permittivity of pure \( \text{H}_2\text{O}_2 \) is less than that of water at all temperatures for which they can be compared. The fact that a high \( \varepsilon_r \) value is found is characteristic of liquids in which molecular orientation and short-range structure exist as a result of hydrogen-bonding. The lower value of relative permittivity for
**TABLE 7. IV**

Dielectric Data for the Hydrogen Peroxide/Water system.

Mole Fraction of peroxide, $x_2$ | $\varepsilon_r$ | $-d\varepsilon_r/dT$
---|---|---
0  | 78.3  | -0.36  
0.041  | 78.49  | -0.44  
0.064  | 79.2  | -0.41  
0.158  | 79.2  | -0.54  
0.16  | 79.4  | -0.56  
0.22  | 80.4  | -0.54  
0.32  | 80.3  | -0.49  
0.36  | 80.3  | -0.56  
0.38  | 81.1  | -0.55  
0.50  | 82.5  | -0.41  
0.62  | 79.0  | -0.48  
0.75  | 74.9  | -0.59  
0.94  | 72.3  | -0.48  
0.98  | 70.7  | -0.49  
0.98  | 71.1  | -0.49  

Estimated values for the 3 mixtures from the plot were as below:

- 0  | 78.28  | -0.356  
- 0.03  | 78.4  | -0.38  
- 0.10  | 79.0  | -0.46  
- 0.17  | 79.6  | -0.55
Figure 7.4
Dielectric properties of $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ at 298K.
peroxide does suggest that the extent of short-range order in this case is less than in water. Gross and Taylor observed a series of maxima in \( \varepsilon_r \) values for aqueous peroxide solutions, and attributed this phenomenon to the enhancement of the short-range structure and co-ordination in water by the addition of \( \text{H}_2\text{O}_2 \).

For the present analysis, the temperature dependence of the \( \varepsilon_r \) values determined by Gross and Taylor for \( \text{H}_2\text{O}_2/\text{H}_2\text{O} \) mixtures was fitted to a simple series function, as suggested by the authors:

\[
\varepsilon_r = A + Bt + Ct^2
\]

(1)
t was the temperature in degrees Centigrade. Values of \( \varepsilon_r(x_i) \) and \( d\varepsilon_r(x_i)/dT \) at the three specified mole fractions (0.03, 0.1 and 0.17) and 298K were then calculated by extrapolation and interpolation (program BONGO). This was only an approximate calculation, however; due to the insufficiently accurate original data (see Table IV and Figure 4). As the plot shows, a maximum in \( \varepsilon_r \) values occurs around mole fraction 0.5 (\( \varepsilon_r \geq 82 \)), but the temperature derivative exhibits an irregular oscillation in value, about \(-0.5\).

The above results were then used in conjunction with the Kirkwood equation\(^{13}\) for the solvation energy of a solute, having dipole moment \( \mu \), and radius \( a \):

\[
\Delta G^{\circ}(g \rightarrow x_\text{solute}) = -\frac{N \mu^2}{4\pi \varepsilon_0 a^3} \left[ \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \right]
\]

(2)

\( N \) is Avogadro's Number and \( \varepsilon_0 \) the permittivity of free space. The aim was to obtain an expression relating the medium effect on the thermodynamic parameters with change in radius and
dipole moment of the solute, and relative permittivity of the solvent. The Gibbs function for solvation of a solute, at fixed temperature and pressure, in a solvent of composition \( x_2 \), is important in this context:

\[
\Delta G_3^*(g \rightarrow x_2) = \mu_3^*(x_2) - \mu_3^*(g) \tag{3}
\]

By using equation (4), for the first-order rate constant of a solute undergoing chemical reaction at fixed temperature and pressure, the rate constants for reactions taking place in pure water, \( k_1(x_a=0) \) and a mixture, \( k_1(x_2) \) may be related:

\[
k_1 = \frac{kT}{h} \exp \left( - \frac{\Delta G_3^*}{RT} \right) \tag{4}
\]

Therefore,

\[
\frac{k_1(x_2)}{k_1(x_2=0)} = \frac{\exp \left( - \frac{\Delta G_3^*(x_2)}{RT} \right)}{\exp \left( - \frac{\Delta G_3^*(x_2=0)}{RT} \right)} = \exp \left[ - \frac{\Delta G_3^*(x_2) + \Delta G_3^*(x_2=0)}{RT} \right]
\]

i.e. \( \frac{\Delta G_3^*(x_2)}{k_1(x_2)} = \Delta G_3^*(x_2) - \Delta G_3^*(x_2=0) \) \tag{5}

But \( \Delta G_3^*(x_2) - \Delta G_3^*(x_2=0) \) is the change in \( \Delta G^* \) on moving from the pure solvent water to a mixture of mole fraction \( x_2 \), i.e. \( \delta_m \Delta G_3^* \). Hence,

\[
\delta_m \Delta G_3^* = - RT \ln \left( \frac{k_1(x_2)}{k_1(x_2=0)} \right) \tag{6}
\]

Equally, \( \delta_m \Delta G_3^* = \delta_m \mu_3^* - \delta_m \mu_3^* \) \tag{7}

For the transition state,

\[
\delta_m \mu_3^* = (\mu_3^*(x_2) - \mu_3^*(g)) - (\mu_3^*(x_2=0) - \mu_3^*(g)) = \Delta G_3^*(g \rightarrow x_2) - \Delta G_3^*(g \rightarrow x_2=0) \tag{8}
\]
Then, from the Kirkwood equation,

\[ \frac{\partial \mu_3^+}{\partial x_3} = \frac{-N (\mu_3^+(x_2))^2}{4\pi \varepsilon_0 (\varepsilon_3^+(x_2))^3} \left[ \frac{\varepsilon_3(x_2) - 1}{\varepsilon_3(x_2) + 2} \right] + \frac{N (\mu_3^+(x_2 = 0))^2}{4\pi \varepsilon_0 (\varepsilon_3^+(x_2 = 0))^3} \left[ \frac{\varepsilon_3(x_2 = 0) - 1}{\varepsilon_3(x_2 = 0) + 2} \right] \]  

(9)

and a similar equation may be obtained for \( \delta_m \mu_3^+ \). Substitution of these initial and transition state quantities into equation (7) provides the value of \( \delta_m \Delta G_3^+ \). Applying the basic Gibbs-Helmholtz expression leads to derivation of the corresponding enthalpy terms,

\[ -\left[ \frac{H_3}{T^2} \right] = \left[ \frac{d(\mu_\nu/T)}{dT} \right] \]  

(10)

Then

\[ \delta_m \Delta H^+ = \delta_m H_3^+ - \delta_m H_3^+ \]  

(11)

Values of \( d \varepsilon_i(x_2)/dT \) and \( d \varepsilon_i(x_2 = 0)/dT \) are required for use in equation (11). The above analysis, linking the rate constant ratios of equation (6) with the thermodynamic activation parameters was subsequently incorporated into the Algol program \( \text{H202} \). Thus, values of \( k(x_2)/k(x_2 = 0) \) were obtained for a range of values of the radius \( a_3^+ \), and for a range of values of the dipole moment \( \mu_3^+ \) of the transition state.

The analysis assumes that the Continuum theory is both precise and applicable in this case. The parameters involved, however, are not directly known, particularly the radii and dipole moments of initial and transition states with their solvent dependences. In order to permit the calculations, therefore, estimates for these parameters had to be made.

The initial state radius was calculated from the density of t-butyl chloride (0.84 g cm\(^{-3}\))\(^{14} \) and its molecular weight (92.57), giving \( r = 3.519 \times 10^{-10} \) m. The dipole moment, \( \mu_3^+ \), was
taken as 2.13 D, the gas phase value. With regard to the transition state, an indication of the radius of the tertiary-butyl cation \( (\text{C}_3\text{H}_7^+) \) was gained from the work of Franklin on van der Waals radii, and of the chloride anion from Gourary and Adrian; thus, \( r(\text{C}_3\text{H}_7^+) = 2.80 \times 10^{-10} \text{ m} \) and \( r(\text{Cl}^-) \) \( 1.64 \times 10^{-10} \). Consequently, \( r^* = 4.44 \times 10^{-10} \text{ m} \). Baliga and Whalley have, however, measured \( \Delta V \) experimentally for the solvolysis of t-butyl chloride at 273.15K; their result of -2.0 cm\(^3\) mol\(^{-1}\) corresponded to a value of 3.4975x10\(^{-10}\) m for \( r^* \). Clearly the data of Franklin gives \( r^* > r^0 \), whilst that of Whalley indicates the reverse to be the case. Care must be taken here, since the two values are not strictly comparable. The 'ionic' radius completely ignores the presence of solvent, whilst the alternative value obviously takes this into account.

In order to resolve this problem, an initial value for \( r^* \) of 1.319 \times 10^{-10} \text{ m} was built into the program, and stepped by set intervals, to cover the possible radius range. Corresponding dipole moment values were calculated for each new \( r^* \). In all cases, the size of t-butyl chloride and its dipole moment were assumed to be independent of solvent.

For each peroxide mixture, the input to H2O2 consisted of the relative permittivities of both water and the relevant \( \text{H}_2\text{O}_2/\text{H}_2\text{O} \) mixture, with the temperature derivatives of each. The output produced values for the medium effect on partial molar free energy and enthalpy of initial and transition states (i.e., \( \Delta_m \mu, \Delta_m \mu^*, \Delta_m \mu^0, \Delta_m H^* \)), the rate constant ratio (\( k_1/k_0 \)) and the overall change in enthalpy (\( \Delta_m \Delta H \)). In order to reduce the amount of computer output, the range of rate ratios was also specified, around the experimental result —
see Listing in Appendix 2. Some of the results of this calculation are summarized in Figure 5. The dashed curves represent the variation in rate constant ratio with change in dipole moment of the transition state ($\mu^*$), for each given transition state radius. The full curve corresponds to the variation in rate ratio which would be observed if the radius of the transition state was $3.519 \times 10^{-10}$ m, the same as the initial state. The diagram shows that the value of $\Delta V^*$, calculated for the radius $r^* = 3.319 \times 10^{-10}$ m was found to be $-17.7$ cm$^3$ mol$^{-1}$ (cf. Whalley's result above). $\mu_i$ represents the dipole moment of the initial state, $\mu^*(F)$ the value calculated for the transition state, based on the ionic radius quoted earlier ($\mu^* = 21.328$ D). The horizontal line at $k/k_0 = 1.689$ is the observed rate constant ratio for the 0.1 mole fraction peroxide/water mixture, at 298K. These results are discussed in section 7.5.

### 7.4.2 Solubilities

Analysis of solvent effects on the measured rate constants would be relatively straightforward if the solubility data for t-butyl chloride in water/hydrogen peroxide mixtures were available. Unfortunately, that is not the case; indeed, the situation is even less encouraging, because the literature reveals no information concerning solubilities of gases in hydrogen peroxide. Consequently, an attempt has been made to overcome these problems. Although the calculation involves a number of approximations, it makes some useful predictions, and may possibly have wider applications.
Results of H2O2 calculation: dipole moment of Transition state v. rate ratio for t-BuCl solvolysis in H₂O/H₂O₂.
Before the activation parameters for t-butyl chloride solvolysis in hydrogen peroxide/water mixtures can be interpreted, the dependence of the initial state parameters on composition of the solutions is required. For the latter, a plot of the type demonstrated in Chapter 3 must be obtained, in order to characterize the system (see e.g. Fig. 3.2). Since the information needed was not directly available, a model hydrophilic solute was chosen to represent t-BuCl: the hydrocarbon butane. The solubility of this gas is known in water\textsuperscript{21} and ethanol,\textsuperscript{22} Table V, and its solubility in hydrogen peroxide was estimated empirically as follows:

The review of gas solubilities in liquids by Battino and Clever\textsuperscript{18} mentions an empirical observation that a plot of \( \log \alpha \) (\( \alpha \) being the Ostwald coefficient) against the surface tension of a liquid is linear. This is borne out by the diagram, Figure 6, and suggests that the factors controlling surface tension of a liquid also control solubility (an idea which has been the cause of some dispute).\textsuperscript{23,24} Data for the three hydrocarbons methane, propane and butane\textsuperscript{25,26} were collected in the form of Bunsen coefficients, and converted by means of the analysis described in Chapter 3 to Henry's Law coefficients at \( 298.15 \)\,K. The figures are collected in Table VI. Corresponding surface tension values for the liquids were taken from Timmermans\textsuperscript{27} and a plot of log \( k'_3 \) against \( \gamma \) constructed for the three solutes, Figure 7. Since \( \gamma (H_2O_2) \) is approximately 80, then the graph provides a value of 10.15 for \( \log k'_3 \), and the Henry's law coefficient for solubility of butane in \( H_2O_2 \) is \( 1.4 \times 10^{10} \) N m\textsuperscript{-2}. Then, \( \Delta G^\circ_3 = 29.34 \) kJ mol\textsuperscript{-1} for transfer from gas phase to solution. The ideal Gibbs
Figure 7.6 Logarithm of Argon Ostwald coefficients as a function of solvent surface tensions, (ref. 18).

Solvents

- n-Hexane
- Isooctane
- 2,3-Dimethylhexane
- n-Heptane
- 2,4-Dimethylhexane
- 3-Methylheptane
- n-Octane
- n-Nonane
- Methylcyclohexane
- n-Decane
- Cyclohexane
- n-Dodecane
- Carbon tetrachloride
- n-Tetradecane
- Fluorobenzene
- Toluene
- Water
- p-Xylene
- Benzene
- Chlorobenzene
- Carbon disulphide
- Bromobenzene
- Nitromethane
- Iodobenzene
- Nitrobenzene
Figure 7.7
Plot of log (Henry's Law coefficient) for gases against solvent Surface Tension at 298.15 K.

LOG H₂

SURFACE TENSION / DYNES CM⁻¹

Methane

Butane

Propane
### TABLE 7.V
Solubility of Butane in Liquids.

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>Water</th>
<th>Hydrogen Peroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henry's Law Coefficient ($k'$)</td>
<td>$7.52377 \times 10^5$</td>
<td>$4.46824 \times 10^9$</td>
<td>$1.4 \times 10^{10}$</td>
</tr>
<tr>
<td>$\log k'$</td>
<td>5.876435</td>
<td>9.65013</td>
<td>10.15</td>
</tr>
<tr>
<td>$\Delta G^\circ (g\rightarrow l)$</td>
<td>4.97</td>
<td>26.51</td>
<td>29.34</td>
</tr>
</tbody>
</table>

Calculated by the analysis

### TABLE 7.VI
Hydrocarbon Solubilities in Various Solvents.

<table>
<thead>
<tr>
<th>Methane in:</th>
<th>Bunsen Coefficient ($\alpha$)</th>
<th>Henry's Coefficient ($k'$)</th>
<th>$\log k'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>0.564</td>
<td>$3.9204 \times 10^7$</td>
<td>7.59333</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.523</td>
<td>$4.8690 \times 10^7$</td>
<td>7.68744</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.675</td>
<td>$2.9309 \times 10^7$</td>
<td>7.467</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>0.266</td>
<td>$8.0691 \times 10^7$</td>
<td>7.9068</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.489</td>
<td>$7.9239 \times 10^7$</td>
<td>7.8989</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.869</td>
<td>$1.9964 \times 10^7$</td>
<td>7.3003</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.479</td>
<td>$1.1656 \times 10^8$</td>
<td>8.0665</td>
</tr>
<tr>
<td>Water</td>
<td>0.0313</td>
<td>$4.188 \times 10^9$</td>
<td>9.6221</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Propane in:</th>
<th>Bunsen Coefficient ($\alpha$)</th>
<th>Henry's Coefficient ($k'$)</th>
<th>$\log k'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>14.7</td>
<td>$1.8300 \times 10^6$</td>
<td>6.2625</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>7.48</td>
<td>$3.6425 \times 10^6$</td>
<td>6.5614</td>
</tr>
<tr>
<td>Ethanol</td>
<td></td>
<td>$6.4545 \times 10^5$</td>
<td>5.8099</td>
</tr>
<tr>
<td>Hexane</td>
<td>21.6</td>
<td>$9.0045 \times 10^5$</td>
<td>5.9544</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>$3.7871 \times 10^9$</td>
<td>9.5783</td>
</tr>
</tbody>
</table>
function behaviour for butane in $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ could then be drawn on the solubility diagram, leaving the enthalpy and entropy quantities to be computed.

In order to complete the diagram, an estimate of the entropy change was obtained from an empirical equation of R.E. Powell. This required the assumption that hydrogen peroxide does not behave in a manner analogous to water, but rather resembles any simple organic solvent. Powell observed that for solutes in benzene, and approximately in other organic solvents, the following empirical equation was satisfactory:

$$\Delta S^\circ (g\rightarrow l) = -8.368 + \frac{3}{2} R \ln M \quad \text{J mol}^{-1}\text{K}^{-1}$$

where $R$ is the Gas Constant and $M$ the molecular weight of the solute. For butane, therefore,

$$\Delta S_3^\circ = -8.368 + \frac{3}{2} R \ln(58.084) = 42.28 \quad \text{J mol}^{-1}\text{K}^{-1}$$

and $$T\Delta S_3^\circ (g\rightarrow l) = -12.61 \quad \text{kJ mol}^{-1}$$

Hence, $\Delta H_3^\circ$ is $+16.7$ kJ mol$^{-1}$, and the whole diagram is now complete (see Figure 8). From values of the $X^E$ functions for peroxide mixtures, the expected solubility behaviour for the real mixtures was added onto this framework diagram, having been calculated from the Prausnitz-O'Connell analysis (Chapter 3); for example, at $x_4 = 0.5$, $H^E = -1.02$ kJ mol$^{-1}$, $G^E = -0.76$ kJ mol$^{-1}$ and $T S^E = -0.26$ kJ mol$^{-1}$. The completed solubility parameter diagram, for butane in hydrogen peroxide/water mixtures is shown in Figure 8.

Conclusions drawn from the analysis were, firstly, that butane is less soluble in peroxide than water, a fact supported by the vigorous stirring required for the t-BuCl reaction.
Figure 7.8 Values of $\Delta X^+_3 (g \rightarrow l)$ for butane in the system $H_2O_2/H_2O$ at 298K.
mixtures. Secondly, butane is less soluble in the H$_2$O$_2$/H$_2$O mixture than in the ideal mixture. Therefore, if butane is assumed to be a reasonably good model for t-butyl chloride, and the transition state in solvolysis is unaffected by solvent, then these conclusions suggest that the reaction rate constant should increase gradually in the peroxide mixtures. This would be a direct result of the destabilization of the initial state, through the increase in H$_3^-$, and the accompanying rapid increase in TS$^\ddagger$.

Obviously, it is unlikely that the solubility of t-butyl chloride in the H$_2$O$_2$/H$_2$O systems is identical to that of butane, simply because of the polar nature of the molecule. Nevertheless, making the extra-thermodynamic assumption that the variations of solubility parameters with $x_a$ for these solutes are equal enables the transition state properties, $\delta_m X_3^+$ to be calculated from $\delta_m \Delta X_3^+$ and $\delta_m X_3^\ddagger$:

Assume 
$$\delta_m X_3^+(\text{butane}) = \delta_m X_3^+(t\text{-butyl chloride})$$

Then
$$\delta_m X_3^+ = \delta_m \Delta X_3^+ + \delta_m X_3^\ddagger$$

Figure 9 summarizes the calculated thermodynamic and kinetic parameters for the three mole fractions, listed in Table VII. A typical calculation, using results for the 0.03 mole fraction peroxide solution is set out below to illustrate the analysis:

At $x_a = 0.03$, from the outputs of XEPIT, $G^E = -0.0969$ kJ mol$^{-1}$

Since $X_3^\ddagger = X_3^\ddagger (\text{id}) - X^E$

then $X_3^\ddagger = [X(x_a = 1) - X(x_a = 0)] x_a + X(x_a = 0) - X^E$

$$G^E_3 = \left[29.3 - 26.5\right] 0.03 + 26.5 - G^E$$

$$= \left[2.8\right] 0.03 + 26.5 - (-0.0969) = 26.68 \text{ kJ mol}^{-1}$$
Thermodynamic and Kinetic parameters (Table VII).
### TABLE 7. VIIa

Transfer functions for butane from the Gas Phase to Hydrogen Peroxide/Water Mixtures.

<table>
<thead>
<tr>
<th>Peroxide Mole Fraction</th>
<th>$\Delta G^*$ (kJ mol$^{-1}$)</th>
<th>$\delta m \Delta G^*$</th>
<th>$\Delta H^*$ (kJ mol$^{-1}$)</th>
<th>$\delta m \Delta H^*$</th>
<th>$T \Delta S^*$ (kJ mol$^{-1}$K$^{-1}$)</th>
<th>$T \delta m \Delta S^*$ (kJ mol$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>26.68</td>
<td>0.18</td>
<td>-24.3</td>
<td>1.30</td>
<td>-50.98</td>
<td>1.12</td>
</tr>
<tr>
<td>0.10</td>
<td>27.08</td>
<td>0.58</td>
<td>-21.04</td>
<td>4.56</td>
<td>-48.12</td>
<td>3.98</td>
</tr>
<tr>
<td>0.17</td>
<td>27.44</td>
<td>0.94</td>
<td>-18.76</td>
<td>6.84</td>
<td>-46.20</td>
<td>5.90</td>
</tr>
</tbody>
</table>

### TABLE 7. VIIb

Kinetic parameters for t-butyl chloride solvolysis in Hydrogen Peroxide/Water mixtures. (298K)

<table>
<thead>
<tr>
<th>Peroxide Mole Fraction</th>
<th>0</th>
<th>0.03</th>
<th>0.10</th>
<th>0.17</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k/s^{-1}$</td>
<td>3.103.10$^{-2}$</td>
<td>3.77.10$^{-2}$</td>
<td>5.242.10$^{-2}$</td>
<td>5.604.10$^{-2}$</td>
</tr>
<tr>
<td>$k/k_o$</td>
<td>1</td>
<td>1.215</td>
<td>1.689</td>
<td>1.806</td>
</tr>
<tr>
<td>$\Delta G^*$</td>
<td>81.6315</td>
<td>81.144</td>
<td>80.332</td>
<td>80.166</td>
</tr>
<tr>
<td>$\delta m \Delta G^*$</td>
<td>0</td>
<td>-0.488</td>
<td>-1.300</td>
<td>-1.466</td>
</tr>
<tr>
<td>$\Delta H^*$</td>
<td>99.426</td>
<td>97.138</td>
<td>90.273</td>
<td>78.646</td>
</tr>
<tr>
<td>$\delta m \Delta H^*$</td>
<td>0</td>
<td>-2.288</td>
<td>-9.153</td>
<td>-20.78</td>
</tr>
<tr>
<td>$T \Delta S^*$</td>
<td>17.794</td>
<td>15.993</td>
<td>9.941</td>
<td>-1.520</td>
</tr>
<tr>
<td>$T \delta m \Delta S^*$</td>
<td>0</td>
<td>-1.802</td>
<td>-7.853</td>
<td>-19.314</td>
</tr>
</tbody>
</table>

(Thermodynamic quantities expressed in kJ mol$^{-1}$)
<table>
<thead>
<tr>
<th>Peroxide Mole Fraction</th>
<th>0.03</th>
<th>0.1</th>
<th>0.17</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta_n \Delta G^+ )</td>
<td>-0.488</td>
<td>-1.30</td>
<td>-1.466</td>
</tr>
<tr>
<td>( \delta_m \mu^+ )</td>
<td>0.18</td>
<td>0.58</td>
<td>0.94</td>
</tr>
<tr>
<td>( \delta_m \mu^+ )</td>
<td>-0.31</td>
<td>-0.72</td>
<td>-0.53</td>
</tr>
<tr>
<td>( \delta_m \Delta H^+ )</td>
<td>-2.288</td>
<td>-9.153</td>
<td>-20.78</td>
</tr>
<tr>
<td>( \delta_m H^+ )</td>
<td>1.30</td>
<td>4.56</td>
<td>6.84</td>
</tr>
<tr>
<td>( \delta_m H^+ )</td>
<td>-0.99</td>
<td>-4.59</td>
<td>-13.94</td>
</tr>
<tr>
<td>( T \delta_n \Delta S )</td>
<td>-1.802</td>
<td>-7.853</td>
<td>-19.314</td>
</tr>
<tr>
<td>( T \delta_m S^* )</td>
<td>1.12</td>
<td>3.98</td>
<td>5.90</td>
</tr>
<tr>
<td>( T \delta_m S^* )</td>
<td>-0.68</td>
<td>-3.87</td>
<td>-13.41</td>
</tr>
</tbody>
</table>

(Thermodynamic quantities expressed in kJ mol\(^{-1}\))
\[ \delta_m \mu^+ = 26.68 - 26.5 = 0.18 \]

Similarly,
\[ H_3^+ (g\rightarrow m) = [16.7 + 25.6] 0.03 - 25.6 - H^E \]
\[ = [42.3] 0.03 - 25.6 - (-0.102) \]
\[ = -24.3 \text{ kJ mol}^{-1} \]
\[ \delta_m H^+ = -24.3 + 25.6 = 1.3 \]

By subtraction, \[ TS^+_3 (g\rightarrow m) = -50.98 \text{ kJ mol}^{-1} \]
\[ T \delta_m S^+ = -50.98 + 52.1 = 1.12 \]

From the kinetic data, including that of Robertson for rates when \( x_a = 0 \),
\[ \Delta G^+(x_a = 0) = 81.632; \Delta G^+(x_a = 0.03) = 81.144; \delta_m \Delta G^+ = -0.488 \]
\[ \Delta H^+(x_a = 0) = 99.426; \Delta H^+(x_a = 0.03) = 97.138; \delta_m \Delta H^+ = -2.288 \]
\[ T \Delta S^+(x_a = 0) = 17.794; T \Delta S^+(x_a = 0.03) = 15.993; T \delta_m \Delta S^+ = -1.802 \]

Combining initial and transition states, gives:
\[ \delta_m \Delta x^+ = \delta_m x^+ - \delta_m x^o \]
\[ \delta_m \mu^+ = -0.488 + 0.18 = -0.308 \]
\[ \delta_m H^+ = -2.288 + 1.3 = -0.988 \]
\[ T \delta_m S^+ = -1.802 + 1.12 = -0.682 \]

Finally, Figure 10 illustrates the comparison between solution behaviour expected for the non-polar molecule butane in ethanol/water and hydrogen peroxide/water mixtures. The full lines indicate changes in chemical potential, partial molar enthalpy and partial molar entropy, in the event that the water-cosolvent mixture is ideal; the dotted lines represent the real system, according to the Prausnitz-O'Connell theory, in each case. It is noticeable that such a solute would be more soluble in the organic liquid: in this example,
Figure 7.10
Comparison of the effects of added solvent, mole fraction $x_2$, on the initial state for t-BuCl in water.
(a) Added monohydric alcohol; (b) added $\text{H}_2\text{O}$, at 298K.
\[ \Delta G_s = 4.97 \text{ kJ mol}^{-1} \] for butane in ethanol, but 26.5 kJ mol\(^{-1}\) in water, and 29.3 kJ mol\(^{-1}\) in hydrogen peroxide.

7.5 **Discussion**

Although the thermodynamic, and some spectroscopic\(^{29}\) properties of the hydrogen peroxide/water system itself have been investigated, very few studies involving solution in \( \text{H}_2\text{O}_2/\text{H}_2\text{O} \) mixtures have been undertaken. Thermal phase measurements have been made on the system potassium fluoride-\( \text{H}_2\text{O}_2/\text{H}_2\text{O} \),\(^{30}\) yielding information on the existence of compounds \( \text{KF} \cdot \text{H}_2\text{O}_2 \) and \( \text{KF} \cdot 2\text{H}_2\text{O}_2 \). The enthalpy of transfer of sodium chloride from water to aqueous peroxide has been measured calorimetrically for mixtures of up to 0.225 mole fraction \( \text{H}_2\text{O}_2 \).\(^{31}\) The results were in agreement with the idea of the non-planar \( \text{H}_2\text{O}_2 \) molecule having a specific water-structure breaking effect. Gibbs free energies of transfer of sodium fluoride from water to the mixtures have been obtained,\(^{32}\) using ion-selective electrodes, the results being compared with those from NMR measurements. Studies of some alkali metal and halide resonance chemical shifts have been made in mixtures of up to 85% w/w peroxide,\(^{33}\) and here the conclusions drawn were preferential solvation of \( \text{Rb}^+ \), \( \text{Cs}^+ \) and \( \text{F}^- \) by peroxide, with solvation of \( \text{Li}^+ \) by water. It appears, therefore, that little indeed is known of the physicochemical effects of this important inorganic compound on water and its structure.

From the results described in section 3, the most striking observation is that addition of the hydrogen peroxide to \( t\)-butyl chloride in water increases the rate constant for
hydrolysis, whereas addition of organic cosolvents decreases the rate and increases ΔG°. Recent work in these laboratories has also shown that hydrogen peroxide has a novel effect on the rate of aquation of an inorganic iron complex. In the hydrolysis of t-butyl chloride, it is noteworthy that, regardless of cosolvent, ΔH° increases as x increases: hence, if this was the sole parameter determining k, the rate constant would always increase. However, in ethanol/water and similar mixtures, TAS° falls more rapidly with increasing amount of added cosolvent, producing the observed increase in ΔG° and fall in k. The hydrogen peroxide/water mixtures exhibit a marked contrast in behaviour here, since the decrease in TAS° is not as dramatic as the corresponding fall-off in ΔH°. The obvious result is a decrease in value for ΔG°, and increase in rate constant.

As mentioned in Chapter 2, an important factor in the hydrolysis of t-butyl chloride is the need to break down neighbouring water/water interactions around the substrate. This phenomenon is thought to be responsible for the large -ΔC_p° in water. From Chapter 2, the negative g° and H° functions associated with peroxide/water mixtures have been taken as indicative of intercomponent association, leading to the classification of H_2O_2 as a structure-breaker (see also ref. 31). However, this description of hydrogen peroxide is in itself insufficient to account for the increase in rate constant, although it is consistent with the observed tendency for -ΔC_p° to decrease. Acetonitrile (see Chapter 2) is also described as a structure breaker, but here the rate constant decreases.
The marked differences in relative permittivities of acetonitrile, t-butyl alcohol and hydrogen peroxide may account for the different effects on the rate constant. The results shown in Figure 5, based on dielectric calculations demonstrate the obvious dependence of the predicted rate constant ratio on both $\alpha^*$ and $\mu^*$. It is noticeable that the necessary charge development in the transition state (as given by $\mu^*$) can for a specified value of $k(x_a)/k(x_a = 0)$ be minimized if the radius of the transition state is smaller than that of the initial state, i.e. $a^* < a_3$. This would seem to be in accordance with the negative value for $\Delta V^*$ obtained by Whalley et al. for the hydrolysis of t-butyl chloride in water. However, compression to provide a dipole moment value approaching that calculated by assuming complete charge separation in the transition state, i.e. $\mu^*(F)$, would require a much smaller radius: in Fig. 5, for the specified rate constant ratio, $r^*$ would have to be approximately $2 \times 10^{-10}$ m. The corresponding $\Delta V^*$ would then become considerably more negative than the value given by Whalley. From the diagram, the value of $\Delta V^*$ calculated for a transition state radius of $3.319 \times 10^{-10}$ m was $-17.7$ cm$^3$ mol$^{-1}$. The calculation of activation parameters and their modification in the three hydrogen peroxide solutions predicted that $\delta_m \Delta H^*_3$ was negative, and dominated by the value of $\delta_m H^*_3$. The quantitative agreement between theory and experiment was, however, poor. It is unlikely that more could be expected from an analysis based solely on electrostatic considerations.

The discussion involving predicted trends in solubilities is more encouraging. Here, the increase in rate constant stems from both a stabilization of the transition state, and a
The marked differences in relative permittivities of acetonitrile, t-butyl alcohol and hydrogen peroxide may account for the different effects on the rate constant. The results shown in Figure 5, based on dielectric calculations demonstrate the obvious dependence of the predicted rate constant ratio on both \( \alpha^+ \) and \( \mu^+ \). It is noticeable that the necessary charge development in the transition state (as given by \( \mu^+ \)) can for a specified value of \( k(x_2)/k(x_2 = 0) \) be minimized if the radius of the transition state is smaller than that of the initial state, i.e. \( \alpha^+ < \alpha_3 \). This would seem to be in accordance with the negative value for \( \Delta V^+ \) obtained by Whalley et al. for the hydrolysis of t-butyl chloride in water. However, compression to provide a dipole moment value approaching that calculated by assuming complete charge separation in the transition state, i.e. \( \mu^+(F) \), would require a much smaller radius: in Fig. 5, for the specified rate constant ratio, \( r^+ \) would have to be approximately \( 2 \times 10^{-10} \) m. The corresponding \( \Delta V^+ \) would then become considerably more negative than the value given by Whalley. From the diagram, the value of \( \Delta V^+ \) calculated for a transition state radius of \( 3.319 \times 10^{-10} \) m was \(-17.7 \) cm\(^3\) mol\(^{-1}\). The calculation of activation parameters and their modification in the three hydrogen peroxide solutions predicted that \( \delta_H^+ \) was negative, and dominated by the value of \( \delta_H^+ \). The quantitative agreement between theory and experiment was, however, poor. It is unlikely that more could be expected from an analysis based solely on electrostatic considerations.

The discussion involving predicted trends in solubilities is more encouraging. Here, the increase in rate constant stems from both a stabilization of the transition state, and a
destabilization of the initial state, the latter factor being important because $G^E$ for the $H_2O_2/H_2O$ mixture is negative, and also because the solubility in pure $H_2O_2$ of the substrate is predicted to be less than in water. The relevance of initial state considerations to discussions of t-butyl chloride solvolysis has already been demonstrated in Chapter 6. In the same way, the $\delta_m$ quantities for initial and transition state enthalpies and entropies contribute towards the decrease in $\Delta H^+$ and $T\Delta S^+$. 

In conclusion, it was encouraging to find that predictions based on the idea of examining rate data in conjunction with excess functions of mixing were borne out, since these ideas had prompted the measurement of rate constants in hydrogen peroxide/water mixtures in the first place.
References

14. C.R.C. Handbook of Chemistry and Physics, ed. R. Weast,


34. M. Baird, M.J. Blandamer and J. Burgess, unpublished observations.

35. M.J. Blandamer and M.F. Fox, in 'Water - A Comprehensive Treatise' (see ref. 23), vol. 2, ch. 8.

36. M.J. Blandamer, in 'Water - A Comprehensive Treatise', (see ref. 23), vol. 2, ch. 9.
CHAPTER EIGHT

Solvolyis of t-Butyl Chloride, and Aquation of tris(5-NO₂-1,10-phenanthroline)Iron(II) in Polyvinylpyrrolidone/Water mixtures
8.1 Introduction

Realisation of the importance and lack of general understanding of biochemical systems and processes has led to increasing interest in the hydration of macromolecular species, and, in particular, the state of water in hydrophilic polymers. Data for the interactions of a synthetic polymer with water have been obtained, which correlate remarkably with corresponding results available from natural biopolymers such as collagen, ribonuclease and DNA. Equally noteworthy is the fact that, in spite of their grossly different macromolecular structures, the conformations of these three biopolymers in aqueous solutions are strikingly similar. The solvent clearly plays a very significant role, therefore. Stabilizing and destabilizing effects of simple molecules added to such systems are assumed to result from modification of the solvent structure. As a contribution to this work, synthetic water-soluble polymers have been employed to simulate the solution behaviour of proteins in vivo: one such polymer is polyvinylpyrrolidone, (PVP).

As with any discussion of macromolecules, the phenomenon of "bound" water and its relevance to the PVP polymer must be examined. Some authors have concluded that the water surrounding proteins has a structure intermediate between solid and liquid, and that this structure may exclude ions, whilst lending structure to the macromolecule. In the case of cellulose, cellulose acetate and nylon, for example, the sorption of water has been interpreted in terms of theories originally developed to describe the binding of monatomic gases and small molecules to free surfaces. Thus, it has
been suggested that water becomes attached to certain sites on the macromolecule, with additional water molecules adhering to these primary positions, forming layer-like structures. In the case of PVP, which has the structural repeating unit shown, and is miscible with water in all proportions, the extent and exact nature of hydration is in dispute. Dole and Faller\(^5\) have demonstrated that the polymer absorbs a considerable amount of water, and this is confirmed in freezing studies. PVP has, however, neither a terminal polar group, as in the case of polyglycine esters, nor a hydrogen-donating group on the nitrogen atom. The only hydrogen-bonding groups are the carbonyl groups, similar to those on protein backbones, although it has been suggested that such groups do not interact with water.\(^2\)

In connection with its apparent ability to retain water, PVP is used in cosmetics, and particularly as a "cryoprotective agent" in biology.\(^6\) Here, the polymer shields human red blood cells and cells in tissue culture from freezing injury, and yeast cells from death during freeze-drying. Although the freezing behaviour of aqueous PVP solutions has been investigated by several workers,\(^7\) and some insight gained into the amounts of water bound to the macromolecule, the mechanism of the cryoprotective action remains little understood.

In the light of the information already available, therefore, it was considered likely that both the solvolysis of t-butyl chloride and aquation of the iron complex might be substantially modified in the presence of this hydrophilic
polymer. The degree of modification might then provide some idea of the extent of PVP hydration in aqueous solutions.

8.2 Experimental Details

Solutions of polyvinylpyrrolidone were prepared by the gradual addition of weighed amounts of the extremely fine white powdered polymer (BDH, average molecular weight 700,000) to freshly distilled water, accompanied by very vigorous stirring. Dissolution of the polymer was exothermic, indicative of some interaction between the solute and water; solutions were allowed to equilibrate at Room Temperature before use. The rapid increase in viscosity which results from addition of PVP to water produced experimental difficulties for the conductance measurements, and hence placed restrictions on the range of PVP concentrations which could be used. The necessary liquid flow in the cell assembly was reduced, the system became difficult to stir, and hence the preparation of a homogeneous solution within the time limit set by the chemical reaction was not facilitated. Nevertheless, reasonable kinetic data were obtained for solutions containing up to 7.5% by weight of PVP \( w_2 \), inspite of the fact that this was an extremely viscous, sticky liquid. The t-butyl chloride solvolysis followed first-order kinetics over at least three half-lives. Rate data were obtained at 5K intervals over the range 278 to 308K, for solutions where \( w_2 = 0.5, 1, 3, 5 \) and 7.5 (see Table I). At the higher temperatures and low concentrations of PVP, when the solvolysis rate was close to that in pure water, the conductivity cell having one compartment only was used. This reduced the
## TABLE 8. I
Rate Constants for solvolysis of t-butyl-chloride in Polyvinylpyrrolidone/Water mixtures.

<table>
<thead>
<tr>
<th>$W_2 = 0.5$</th>
<th>1.0</th>
<th>3.0</th>
<th>5.0</th>
<th>7.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.58015</td>
<td>±0.024 (8)</td>
<td>±0.009 (6)</td>
<td>±0.007 (8)</td>
<td>±0.033 (7)</td>
</tr>
<tr>
<td>278.182K</td>
<td>278.176K</td>
<td>278.172K</td>
<td>278.165K</td>
<td>278.164K</td>
</tr>
<tr>
<td>2.95444</td>
<td>±0.078 (6)</td>
<td>±0.227 (12)</td>
<td>±0.085 (8)</td>
<td>±0.036 (6)</td>
</tr>
<tr>
<td>283.011</td>
<td>283.095</td>
<td>283.132</td>
<td>283.090</td>
<td>283.118</td>
</tr>
<tr>
<td>6.04747</td>
<td>±0.080 (13)</td>
<td>±0.109 (6)</td>
<td>±0.381 (4)</td>
<td>±0.167 (5)</td>
</tr>
<tr>
<td>288.10</td>
<td>288.098</td>
<td>288.105</td>
<td>288.097</td>
<td>288.108</td>
</tr>
<tr>
<td>11.12783</td>
<td>±0.50 (6)</td>
<td>±0.418 (6)</td>
<td>±0.236 (9)</td>
<td>±0.377 (5)</td>
</tr>
<tr>
<td>293.163</td>
<td>293.159</td>
<td>293.158</td>
<td>293.16</td>
<td>293.142</td>
</tr>
<tr>
<td>22.14365</td>
<td>±1.51 (5)</td>
<td>±1.070 (5)</td>
<td>±1.47 (6)</td>
<td>±0.81 (4)</td>
</tr>
<tr>
<td>298.16</td>
<td>298.086</td>
<td>298.075</td>
<td>298.120</td>
<td>298.196</td>
</tr>
<tr>
<td>39.21962</td>
<td>±0.516 (2)</td>
<td>±14.049 (2)</td>
<td>±16.39 (2)</td>
<td>±0.39 (2)</td>
</tr>
<tr>
<td>303.110</td>
<td>303.085</td>
<td>303.101</td>
<td>303.106</td>
<td>303.106</td>
</tr>
</tbody>
</table>
amount of solution required per run.

For the spectrophotometric measurements, the existing PVP solutions were diluted slightly, and their resulting concentrations subsequently recalculated. Sufficient solid nickel sulphate (Analar) was added to each stock PVP solution to produce a concentration of 0.3 mol dm$^{-3}$; 2 ml of this green liquid were then pipetted into 10 mm spectrophotometer cells. The choice of metal ion and the reason for its presence in the reaction is discussed in the following chapter. To the sample cells were added 1 ml portions of iron complex solution, prepared from addition of iron(II) ammonium sulphate and a slight excess of the 5-NO$_2$-1,10-phenanthroline ligand. Thorough mixing of the components in each sample cell was ensured before being transferred to the thermostatted cell block of the SP 1800A spectrometer. Final concentration of the complex were $2 \times 10^{-4}$ mol dm$^{-3}$, and PVP 0.2 mol dm$^{-3}$. Reference solutions contained 2 ml of the nickel sulphate/PVP solution and 1 ml distilled water. After equilibration, the change in absorbance with time at 510 nm was monitored over at least three half-lives, for each concentration of PVP. The reaction temperature was 308K, and the rate constants are given in Table II.

8.3 Results

As the tables show, the rate constant for t-butyl chloride solvolysis decreases at any given temperature with increase in concentration of PVP, whilst the aquation rate of the iron complex remains unchanged at the concentrations and temperature of experiment. At low temperatures and in
### TABLE 8. II

Rate Constants for the Aquation of Fe(5-NO$_2$-phen)$_2^{2+}$ in PVP/Water mixtures, at 308K.$^a$

<table>
<thead>
<tr>
<th>PVP % ($W_2$)</th>
<th>$10^3k/s^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$2.4\pm0.2$ (4)$^b$</td>
</tr>
<tr>
<td>0.31</td>
<td>$2.24\pm0.02$ (4)</td>
</tr>
<tr>
<td>0.62</td>
<td>$2.38\pm0.2$ (4)</td>
</tr>
<tr>
<td>1.84</td>
<td>$2.18\pm0.06$ (4)</td>
</tr>
<tr>
<td>3.08</td>
<td>$2.20\pm0.04$ (4)</td>
</tr>
</tbody>
</table>

$^b$ number of independent measurements.

Concentration of Ni$^{2+}$ was 0.2 mol dm$^{-3}$, and of complex $2 \times 10^{-4}$ mol dm$^{-3}$.

### TABLE 8. III

Kinetic data for hydrolysis of t-butyl chloride in water containing PVP.

<table>
<thead>
<tr>
<th>PVP</th>
<th>$10^3k(278K)$</th>
<th>$\Delta G^+(298K)$</th>
<th>$\Delta H^+(298K)$</th>
<th>$T\Delta S^+(298K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_2$(%)</td>
<td>/s$^{-1}$</td>
<td>/kJ mol$^{-1}$</td>
<td>/kJ mol$^{-1}$</td>
<td>/kJ mol$^{-1}$</td>
</tr>
<tr>
<td>0$^a$</td>
<td>1.68</td>
<td>81.65</td>
<td>94.37</td>
<td>12.72</td>
</tr>
<tr>
<td>0.5</td>
<td>1.58</td>
<td>82.54</td>
<td>88.5 ± 0.9</td>
<td>5.9 ± 0.9</td>
</tr>
<tr>
<td>1</td>
<td>1.49</td>
<td>83.21</td>
<td>86.1 ± 1.5</td>
<td>3.1 ± 1.5</td>
</tr>
<tr>
<td>3</td>
<td>1.42</td>
<td>83.12</td>
<td>86 ± 3</td>
<td>3.2 ± 3</td>
</tr>
<tr>
<td>5</td>
<td>1.33</td>
<td>83.64</td>
<td>84 ± 5</td>
<td>0.2 ± 5</td>
</tr>
<tr>
<td>7.5</td>
<td>1.09</td>
<td>84.69</td>
<td>82 ± 12</td>
<td>-2.7 ± 12</td>
</tr>
</tbody>
</table>

$^a$ Kinetic data calculated from reference 7, Chapter 7.
solutions containing small amounts of PVP, the t-BuCl rate constants were reproducible to \( \leq 1\% \). However, as either temperature or \( w_x \) increased, the accuracy fell rapidly, this being reflected in the standard deviation on the activation enthalpy, \( \Delta H^+ \) (Table III). As in the case of hydrogen peroxide, the thermodynamic activation parameters were calculated using two regression coefficients in the Glew-Clarke analysis.

At a fixed temperature, the Gibbs free energy of activation \( \Delta G^+ \) increases when PVP is added, causing the decrease in rate constant. This arises from the fact that, as \( w_x \) increases, so \( \Delta H^+ \) and \( T \Delta S^+ \) decrease, but the latter decreases more rapidly, to produce the increase in \( \Delta G^+ \). The activation parameters are compared in Figure 1 with the corresponding values for t-BuCl solvolysis in water, through the medium operators \( \delta \Delta G^+ \), \( \delta \Delta H^+ \) and \( T \delta \Delta S^+ \). The contrast in behaviour pattern with the similar diagram for \( \text{H}_2\text{O}_2 \) (Figure 7.9) is interesting. As a result of the lack of data available concerning systems involving PVP and other solutes, an analysis of the type instigated for hydrogen peroxide was not possible here. Some conclusions have been drawn from the results obtained, however.

8.4 Discussion

As mentioned earlier, the cryoprotective properties of PVP have attracted considerable attention, and much work on freezing of aqueous PVP has been undertaken. It appears that the amount of "bound" water deduced from these experiments is dependent on the path of freezing, indicating that true
Figure 8.1

Medium effects on thermodynamic activation parameters for solvolysis of t-BuCl in polyvinylpyrrolidone/water mixtures, (data below).

<table>
<thead>
<tr>
<th>$w_2$</th>
<th>$\delta_m \Delta G^+$</th>
<th>$\delta_m \Delta H^+$</th>
<th>$T \delta_m \Delta S^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.91</td>
<td>-10.92±1</td>
<td>-11.83</td>
</tr>
<tr>
<td>1</td>
<td>1.32</td>
<td>-13.37±2</td>
<td>-14.69</td>
</tr>
<tr>
<td>3</td>
<td>1.43</td>
<td>-11.66±5</td>
<td>-13.08</td>
</tr>
<tr>
<td>5</td>
<td>2.01</td>
<td>-15.59±6</td>
<td>-17.602</td>
</tr>
<tr>
<td>7.5</td>
<td>3.96</td>
<td>-36.18±9</td>
<td>-40.139</td>
</tr>
</tbody>
</table>
equilibrium is not established. From studies of ice formation patterns, it has been observed that solutions containing greater than 60% PVP show no ice formation at any temperature.\textsuperscript{9} The general consensus of opinion, therefore, seems to be that the polymer immobilizes water, and Jellinek et al. have claimed that this bound water has an ice-like structure.\textsuperscript{9} In agreement with this suggestion is the change noted in the near infrared spectrum of HOD in D\textsubscript{2}O when PVP is added.\textsuperscript{10} These changes are indicative of a marked water-structure forming action. Mackenzie and Rasmussen,\textsuperscript{7a} however, contest the idea that water sorbed to PVP can assume repeating structures exhibiting a truly hexagonal symmetry. Although the polymer is completely miscible with water, it is insoluble in ice.

As indicated earlier, if the water was involved in this tightly organised structure, marked changes in rate constant and activation parameters would be expected when PVP was added to t-butyl chloride or the iron complex in water. Indeed a close correlation might be anticipated between the rate constant and viscosity of the solution. In fact, no such dramatic changes are observed. The kinetic data show a pattern of behaviour which resembles the modest changes exhibited when an organic cosolvent is added to water, in the case of t-BuCl. The near compensation between TΔS\textsuperscript{*} and ΔH\textsuperscript{*} quantities, as well as the slight endothermic maximum in ΔH\textsuperscript{*}, are features similar to those previously reported for other systems.

The kinetic data tend to support the conclusions reached by Glasel,\textsuperscript{2} concerning the state of water in the PVP system. Glasel based his conclusions on deuteron magnetic resonance
data for solutions of the macromolecule in D₂O. This technique allows the interactions of water with various conformations of biopolymers to be measured quantitatively. The relaxation rate for D₂O in PVP, however, was found to be essentially the same as in bulk water, the results being clearly independent of bulk viscosities. This result from NMR suggests, therefore, that the polymer interacts weakly, if at all, with water, presumably as a result of the absence of labile proton donors available for hydrogen-bonding. The proposed interactions of water with the carbonyl group were not experimentally borne out.

From conductance measurements for electrolytes in PVP solutions, it was concluded that ions must be transferred through the polymer coil. Only the volume occupied by the hydrated polymer disturbs the transport of the ions and decreases their mobility; the observed decrease in conductance for ions in PVP solutions is not large. It appears that, from the kinetic viewpoint, the majority of the water in the PVP system is held in a mesh of PVP polymer, and that its structure is not grossly modified. The fact that aquation of tris(5-NO₂-1,10-phenanthroline)iron(II) proceeds normally in PVP solutions obviously tends to confirm this idea, in view of the solvent-sensitivity of the complex (see Chapter 9).

Finally, it is of interest to note the solubility characteristics of salts in PVP solutions. The rates of solution of sodium and potassium chlorides have been measured in water and aqueous PVP at 298K, and the dissolution rate constants found to decrease with increasing bulk solution viscosity. Also, a series of alkyl bromides (Et, nPr, nBu and n-amyl)
have been studied in aqueous solutions of neutral polymers and polyelectrolytes, which included PVP. Here, the solubility of the salts increases with concentration of the neutral polymer; the order of increasing solubility for PVP is as follows: EtBr < PrBr < BuBr. Clearly, the larger the cosolute, the stronger are the stabilizing effects, although all three salts are readily absorbed by PVP solutions. It has been suggested that the cosolute may be incorporated into the cavities produced by the iceberg-enhancing polymer. In the light of this solubility data, therefore, it is possible that t-butyl chloride might be more soluble in aqueous PVP than pure water. This could result in stabilization of the ground state, and hence contribute towards the decrease in rate constant for solvolysis (cf. hydrogen peroxide).

Similar action of PVP is demonstrated in the ability of the polymer to act as a nucleating agent for detergent micelles, stabilizing detergent clusters.
References

CHAPTER NINE

Kinetics of reaction of low-spin Iron(II) complexes in aqueous Gelatin and Agar
9.1 Introduction

The physical state of intracellular water has become a much discussed and controversial topic. The properties of water near interfaces, including biological interfaces, often appear notably different from the properties of bulk water, and these same anomalies have also been detected at liquid-gel interfaces. \(^1\) Evidence for bound water in colloidal materials in insects was found by Robinson in 1928; \(^2\) later, Lloyd and Phillips\(^3\) proposed that "the colloidal properties of a protein are dependent on the ease and degree with which it becomes hydrated." Freundlich\(^4\) indicated that enzyme reactions 'in vivo' should be discussed in the light of the chemistry of gels. However, before considering the very complex question of enzyme kinetics in gels, it seemed important to examine the kinetics of simpler reactions in these systems, and to probe the effects of changing the reaction medium from water to sol to gel.

A brief background to the gel state has already been provided in Chapter 2. Recent NMR data have tended to contradict the conclusions of early workers, who had assumed either (a) that cellular water was more structured than bulk water, or (b) that water-structure adjacent to the surface was modified by the presence of that surface. Tait et al.\(^5\) have shown that the expected gross reduction in rotational freedom of the water molecules in an agarose gel does not occur. The only bound water detectable by NMR in these comparatively dilute systems corresponds to one water molecule per residue. The sol→gel transformation appears difficult to detect by physicochemical methods; for example, no abrupt change in solvent water structure is indicated by dielectric
relaxation or ultrasonic absorption for the system gelatin/water. In agreement with this experimental observation are the calculations of Peniche-Covas et al. which demonstrate the existence of highly-branched sol molecules of size up to 10^8, close to the gel point.

For the present programme of investigation into dynamic processes in sols and gels, gelatin and agar were employed for the reaction media. As described previously, gelatin is a fibrous protein belonging to the same class of hydrophilic colloids as haemoglobin and albumen. The source of agar is a group of red seaweeds, and the gel state is the most typical for this polysaccharide, either in biological or artificial systems. The choice of the reaction to be monitored was limited by a number of factors. Firstly, the substrate(s) had to form a homogeneous system, both in sol and gel states. Secondly, the reaction needed to be sufficiently fast so that the kinetic data could be obtained before appreciable syneresis (dehydration and volume contraction of the gel, on standing) occurred. Finally, the reaction had to be sufficiently slow in order that kinetic data could be obtained after the gel had formed - see experimental procedure below. Two closely related reactions were eventually found to satisfy these conditions: (1) the aquation of tris(5-nitro-1,10-phenanthroline) Iron(II), and (2) the reaction between cyanide ion and tris(5-methyl-1,10-phenanthroline) Iron(II). Earlier attempts to monitor the solvolysis of t-butyl chloride in the agar/water system had failed, as a result of three principle factors: inhomogeneity of the gelling mixture in the cell-assembly vessel, inability to control the temperature of the
system and monitor conductance changes after gelation had occurred.

9.2 Experimental Details

(a) Solutions containing known concentrations of nickel sulphate, zinc sulphate and potassium cyanide (all Analar grade) were prepared using freshly distilled water. Analar potassium sulphate was added to the 0.1 and 0.05 mol dm$^{-3}$ sulphate solutions, in order to maintain the ionic strength at constant level. This then facilitated comparison of the aquation rates of the complex in the presence of varying concentrations of either Ni$^{2+}$ or Zn$^{2+}$ cations. Stock solutions of both the 5-nitro and 5-methyl complexes were prepared from iron(II) ammonium sulphate and a slight excess of the appropriate ligand. Sols were obtained by adding a known weight of either gelatin or agar (BDH purified grade) to the required volume of salt solution (Ni$^{2+}$, Zn$^{2+}$ or CN$^-$). This mixture was warmed gently until the gelling agent had dissolved, and subsequently cooled before addition of the specified volume of complex solution. The sol was then poured into spectrophotometer cells and equilibrated in readiness for monitoring to commence. Gels were similarly prepared, by dissolving the gelling agent in the heated salt solution, cooling this mixture in ice/water and finally adding the required volume of solution containing the complex. Thorough mixing of the components was ensured, before portions of this solution were transferred to 10 mm cells standing in an ice/water bath. After gelation had occurred, the cells were transferred to the thermostatted cell block of either the SP 800A or 1800A
spectrophotometer, depending upon the temperature at which the reaction was to be monitored. The time allowed for each cell to reach thermal equilibrium depended on the system and temperature; this was estimated initially from the variation of solution absorbance with time. For each experimental run, the contents of reference cells comprised a system prepared in the same way as described above, but which did not contain an iron complex.

(b) Kinetics. Rate constants were calculated from the change in optical density at 510 nm, this being at or near the wavelengths of maximum absorption of the tris-ligand complexes. Readings were recorded at preselected time intervals on punched tape, as mentioned in Chapter 5, with the calculations based on Algol programs STEVE and ROGUE (see Chapter 4). In the case of the aquation of the 5-nitro complex, the absorbance decreased to zero as the reaction neared completion; kinetic data here were recorded for over three half-lives. For the cyanide substitution, however, data could be obtained only for approximately two half-lives: the absorbance had decreased by about one-third when the reaction reached completion. Restrictions imposed by the mechanical facilities available in the SP 1800A meant that it was only possible to monitor one cell at a time. The one-second time interval here was realistic for faster reaction rates at the higher temperatures. Difficulties associated with thermal equilibration of sol and gel systems were encountered in the SP 800A spectrophotometer. Hence, in both machines, it proved difficult to reproduce precisely the same temperature for each system studied. In the summary of the data given in the
Tables, the stated temperature is an average over many experimental runs, the deviation being $\pm 0.4K$. Within a given run, the temperature was controlled to better than 0.1K. Rate constants for the cyanide substitution were calculated by means of the simple PDP 11 program (see Chapter 4).

9.3 Results

Aquation of the tris(5-nitro-1,10-phenanthroline) iron(II) cation, as of other iron(II) complexes of (substituted) 1,10-phenanthrolines, occurs through the stepwise equilibria:

\[
\begin{align*}
Fe(LL)_3^{2+} & \rightleftharpoons Fe(LL)_2^{2+} + LL \\
Fe(LL)_2^{2+} & \rightleftharpoons Fe(LL)^{2+} + LL \\
Fe(LL)^{2+} & \rightleftharpoons Fe^{2+aq} + LL
\end{align*}
\]

(where LL = 5-nitro-1,10-phenanthroline)

The three reversible reactions (1) to (3) are forced to proceed from left to right by the addition of a reagent which reacts either with the released ligand molecules or with the aquoiron(II) cation. The rate-determining step is the loss of the first ligand molecule [equation (1)], since this reaction requires a change in spin state from the original inert $d^6$ low-spin configuration of the iron. The usual reagent for promoting this type of aquation is acid, as protonation of the liberated phenanthroline molecules prevents their recombination with the iron. It is well established that the rate-determining ligand loss is essentially independent of acid concentration. Unfortunately it is impossible to use acids in the present work, as they inhibit gel formation. A suggestion was followed, therefore, that the presence of cations such as zinc(II) or nickel(II) in sufficient concentr-
ation led to complete aquation. Aquation in the presence of a large excess of one of these cations follows first-order kinetics. Table I shows that the rate constant of aquation of the complex in the presence of either of these cations is independent both of the nature and of the concentration of the added cation (measured at 289K). The rate constants are close to that reported for aquation of the complex in acid solution. These cations can thus be used as scavengers for the released ligand molecules in the same way as acids; they do not inhibit gel formation in the concentrations used here.

The kinetic results for aquation of the Fe(5-NO₂-phen)²⁺ cation in aqueous solution and gel systems are recorded in Table II. Rate constants were obtained for agar sols and gels at the temperatures 289, 300, 307.5 and 314.6K, and for gelatin at 289K only; the concentrations of Ni²⁺ and Zn²⁺ cations used were 0.2 mol dm⁻³ throughout. When either agar or gelatin is added to form a sol or gel system, the rate constant for aquation remains unchanged and, for the agar system at least, this behaviour has been observed over the range 289-314K.

Reaction of the 5-nitro complex with cyanide ion is too rapid for its kinetics to be monitored under the conditions and restrictions of the present systems (see Experimental section). For solutions containing 0.1 mol dm⁻³ potassium cyanide, for example, a value of 5.3×10⁻² s⁻¹ was observed for the first-order rate constant at 308K. The corresponding figure for cyanide attack on the 5-methyl complex is 1.7×10⁻³ s⁻¹ (7.9×10⁻³ s⁻¹ for 0.5 mol dm⁻³ KCN), at the same temperature. It was decided, therefore, to investigate the kinetics of this
TABLE 9. I
First Order Rate Constants, k, for the Aquation of
Tris(5-Nitro-1,10-Phenanthroline)Iron(II) at 289.0 ± 0.3K
in the Presence of Either Ni\(^{2+}\) or Zn\(^{2+}\)
cation
salt concentration/ mol dm\(^{-3}\) Ni\(^{2+}\) Zn\(^{2+}\)

<table>
<thead>
<tr>
<th>salt concentration/ mol dm(^{-3})</th>
<th>10(^4)k/s(^{-1})</th>
<th>10(^4)k/s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1.90±0.04(3)(^a)</td>
<td>1.87(2)</td>
</tr>
<tr>
<td>0.1(^b)</td>
<td>1.97(2)</td>
<td>1.92±0.03(3)</td>
</tr>
<tr>
<td>0.05(^c)</td>
<td>1.93(1)</td>
<td>1.91(2)</td>
</tr>
</tbody>
</table>

\(^a\)number of independent measurements;
\(^b\)+0.133 mol dm\(^{-3}\)K\(_2\)SO\(_4\);
\(^c\)+0.2 mol dm\(^{-3}\)K\(_2\)SO\(_4\).

TABLE 9. III
Pseudo First Order Rate Constants for the Reaction
between CN\(^-\) and Tris(5-Methyl-1,10-Phenanthroline)Iron (II)
in aqueous Agar Sol and Agar Gel systems,
containing 0.5 mol dm\(^{-3}\)KCN.

temperature/K system     308       313
rate constant 10\(^2\)k/s\(^{-1}\)

<table>
<thead>
<tr>
<th>system</th>
<th>rate constant 10(^2)k/s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>aqueous solution</td>
<td>0.62±0.04(8) 1.2±0.2(11)</td>
</tr>
<tr>
<td>0.1% agar sol</td>
<td>0.54±0.06(6) 1.1±0.05(7)</td>
</tr>
<tr>
<td>0.2% agar gel</td>
<td>0.59±0.05(5) 1.0±0.1(8)</td>
</tr>
</tbody>
</table>

(Results from reference 26)
TABLE 9. II
First Order Rate Constants for the Aquation of Tris(5-Nitro-1,10-
Phenanthroline)Iron(II) Complex in aqueous Sol and Gel systems
containing 0.2 mol dm⁻³ NiSO₄ or ZnSO₄.

<table>
<thead>
<tr>
<th>temperature/K system</th>
<th>289.1±0.2</th>
<th>300±0.4</th>
<th>307.5±0.1</th>
<th>314.6±0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate constant, 10³k/s⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aqueous solution</td>
<td>0.188±0.005(8)</td>
<td>1.12±0.2(8)</td>
<td>2.4±0.2(4)</td>
<td>4.8±0.1(6)</td>
</tr>
<tr>
<td>0.1% agar sol</td>
<td>0.147±0.001(4)</td>
<td>0.95±0.04(8)</td>
<td>2.2±0.1(4)</td>
<td>4.9±0.4(3)</td>
</tr>
<tr>
<td>0.2% agar gel</td>
<td>0.167±0.009(8)</td>
<td>1.0±0.2(7)</td>
<td>1.9±0.2(4)</td>
<td>4.5±0.2(4)</td>
</tr>
<tr>
<td>1% gelatin sol</td>
<td>0.166±0.004(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% gelatin gel</td>
<td>0.17±0.01(8)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
much slower reaction, Fe(5-Me-phen)$_2^{2+}$ with cyanide ion, in aqueous sols and gels. The observed first-order rate constants (cyanide ion was in large excess) are reported for the agar/water system at 308 and 313K, in Table III. As in the case of the aquation reaction, the results appear little affected by the addition of the gelling agent.

9.4 Discussion

The mechanism of aquation of iron(II)-phenanthroline complexes has not been unequivocally established, though all the results to date can be satisfactorily accounted for on the basis of the dissociative mechanism intuitively expected for low-spin d$^6$ complexes of the first-row transition series. Indeed, a recent determination of the activation volume ($\Delta V^\neq +18$ cm$^3$ mol$^{-1}$) for the aquation of Fe(5-NO$_2$-phen)$_3^{2+}$ strongly supports a dissociative mode of activation for this reaction. Additional evidence for this proposal is provided by the correlation observed between kinetic behaviour of t-butyl chloride and that of the Fe(5-NO$_2$-phen)$_3^{2+}$ cation, in various mixed aqueous solvents. The variation of activation parameters with Gibbs functions of mixing for the solvent systems show striking similarities for both substrates. Such results have been demonstrated for cosolvents which include ethanol, glycerol, DMSO, H$_2$O$_2$ and MeCN; the two exceptions are formic and acetic acids.

On the other hand the rate law and activation parameters for the reactions of many low-spin iron(II) complexes, including the Fe(5-Me-phen)$_3^{2+}$ cation, with cyanide ion indicate that these reactions [equation (4)] proceed predominantly by
an associative, bimolecular pathway \(^{10,13}\)

\[
\text{Fe(LL)}_3^{2+} + 2\text{CN}^- \rightarrow \text{Fe(LL)}_2(\text{CN})_2 + \text{LL}
\]  

The two-term rate law given above indicates two parallel reaction pathways, the \(k_1\) term (which is independent of \(\text{CN}^-\)) suggesting a mechanism involving rate-determining loss of a phen ligand. In some cases, it has been possible to compare the \(k_1\) values of the cyanide reaction with known rates of aquation of certain complexes. For example, cyanide attack on the 3,5,6,8-tetramethyl complex gives a value of 0.0007 s\(^{-1}\) for \(k_1\), whereas \(k_1\) for acid aquation is 0.0006 s\(^{-1}\) at 308K. For the specific case of the 5-methyl complex and the cyanide concentration used here, the alternative dissociative reaction path makes a negligible contribution to the overall rate of disappearance: the rate constant for aquation of \(\text{Fe(5-Me-phen)}_3^{2+}\) at 308K is \(1.9 \times 10^{-4}\) s\(^{-1}\). The comparatively high concentration \((0.5 \text{ mol dm}^{-3}\)\) of potassium cyanide used in the experiments served not only to reduce the importance of the \(k_1\) term, but also to avoid side reactions resulting from the presence of HCN or OH\(^-\) in the reaction mixture.

Previous studies have shown that rates of aquation of iron(II)-phenanthroline complexes usually vary significantly with solvent composition in mixed aqueous solvents.\(^{14}\) The rate constant variation for the \(\text{Fe(5-NO}_2\text{-phen)}_3^{2+}\) cation in a series of aqueous systems at 308K is illustrated in Figure 9.1. It is clear that the rates of aquation in ethanol or t-butyl alcohol are approximately three times the value in pure water, at cosolvent mole fractions approaching 0.2, whilst a slightly
Figure 9.1 Rate constant variation for Fe(5-NO₂-phen)²⁺ aquation in mixed aqueous solvents at 308K. \( x_2 \) is the mole fraction of organic component.

(Reference 14)
higher mole fraction of dioxan increases the rate constant to about six times the initial value. At the equivalent mole fraction of formic acid, however, the rate decreases by more than half. Values of \( k \) vary by a factor of greater than 10 overall, therefore. The aquation reactions are also dependent on the nature and concentration of the acid used for protonation of the ligand, as well as being sensitive to the effects of added salts on the structure of solvent water.\(^{15}\) Figure 9.2 shows the dependence of \( k/k_* \) for the aquation of the 5-nitro complex on concentration of added salt, at 308K. At a concentration of 1.5 mol dm\(^{-3}\) \((nBu)_4N^+Br^-\), the rate increases by a factor of 2, whilst decreases in the order: \((Et)_4N^+Br^- < (Me)_4N^+Br^- < KBr \approx CsBr\) are observed for 1.0 mol dm\(^{-3}\) solutions. Overall, the variation covers a range equivalent to about 4 times the initial value. In all cases, the 5-nitro complex is the most sensitive of this class of complexes to solvent variation.

Rate constants for the reaction of this type of low-spin iron(II) complex with cyanide ion are also noticeably dependent on solvent composition.\(^{10}\) In 50\% (v/v) aqueous ethanol, for example, the rates of cyanide attack are very much faster than in water. The trend in \( k_x \) values for the various substituents remains the same as in water, though the range of rates is larger in the mixed solvent. Thus, \( k_x(5-NO_2)/k_x(5,6-Me_2) \) is 130 in water, but 580 in 50\% ethanol. In the case of comparable cyanide reaction with the Schiff base complex of iron(II),\(^{16}\) \( k_x \) increases by a factor of about 10\(^2\) when either the ethanol content of solution is raised from 30 to 80\%, or equally the methanol content rises from 50 to 95\%, for all concentrations of cyanide added.
Figure 9.2 Rate constant variation for Fe(5-NO₂-phen)²⁺ aquation in salt solutions at 308K: X (nBu)₄N Br; † (Et)₄N Br; □ (Me)₄N Br; ▲ KBr; ○ CsBr.

(reference 15)
In view of this known sensitivity of kinetic behaviour to added cosolvents and solutes, the relative insensitivity of the rate constants to the transition sol→gel is at first sight surprising. The results show that there are sufficiently large volumes of water to contain the unwieldy iron(II) complex cation and the $M^{2+}{\text{aq}}$ (metal) cation or $\text{CN}^-{\text{aq}}$ anion in a "free solution" state, and that in these regions the structure of the water closely resembles that in the aqueous solution. To this extent, therefore, the kinetic data support the conclusion concerning the structure of these gels drawn from other experiments. In the polysaccharide gel, the water is trapped in the interstices or "caves" of a loosely interwoven but extensively hydrogen-bonded network, the strands of which contain bundles of double helices. This matrix arrangement gives rise to the characteristic texture and properties of a gel, and has been confirmed by electron microscopy. To some extent, the helices are free and solvated, but some sections are associated to form the cross-linkages. Derbyshire and Duff show that while part of the water is bound to the macromolecule, the remainder can be considered as bulk water, although the self-diffusion of water in the gel is affected by the gel network. Earlier workers recorded a reduction of 15% in the self-diffusion coefficient of water. Derbyshire's estimate for hydration is 0.59 g water for each gramme of agarose present in the gel.

The gelation of a protein gel (see Chapter 2) appears to involve a quite different arrangement. Gelation is a limited aggregation process, in which the spherical gelatin species come together to form strands; the latter then
interact to produce the gel mesh. It is noticeable that higher concentrations of protein are required for gel formation than carbohydrates. Only a small proportion of the water in a protein gel is specifically associated with the gelatin framework. Information concerning gel networks has been obtained from freezing studies,\textsuperscript{24} since the growth of ice crystals is inhibited by the size of the mesh. Crystals may only grow beyond such a mesh and envelop it by being cooled to a temperature appreciably lower than normal.

The results reported here can be contrasted with those of Caldin and Grant\textsuperscript{25} for the reaction of the aquonickel(II) cation with pyridine-2-azo-\textsubscript{p}-dimethylaniline, in which the rate is controlled by the macroscopic viscosity of the solvent, glycerol. In this case, the macroscopic viscosity is indicative of extensive intermolecular association, which in turn affects the dynamics of processes in the system. The dramatic increase in viscosity accompanying the transition sol$\rightarrow$gel reflects only a change in the organisation of the gelling agent, the microscopic viscosity of much of the water apparently being little modified.

If the sol or gel is considered to contain certain amounts of water bound to the macromolecular helices or spheres, then this implies a reduction in the amount of water available for solvation of the reacting species, in the interstices. The concentrations of cyanide ion and complex are relatively greater than in pure water, therefore, indicating a retardation in the rate of cyanide attack (see rate law) in the gel matrix. Since the aquation reaction is first-order, the rate in this case will be unaffected by the available free water.
The hydration figure for agar given earlier (0.59 g per g agarose) suggests that the fraction of bound water present in the systems used would not be very great, owing to the low initial concentrations of agar. This alternative interpretation appears worthy of consideration in future investigations on the gel state.

References


2. W. Robinson, Colloid Symposium Monograph, 1929, no. 5, 199.


6. Unilever Research Report, April 1969. (See also ref. 23)


11. J. Burgess, J.M. Lucie and D.R. Stranks, unpublished
observations.

17. J. Porath, T. Låås, J-C. Janson, J. Chromatography, 1975, 103, 49.
21. Reference given in (5) above.
CHAPTER TEN

Solvolysis of t-Butyl Chloride in Aqueous Urea, Glycerol and Propane-1,2- & -1,3-Diols
10.1 Introduction

The work of Robertson, Tommila, Winstein and Fainberg and others, mentioned in Chapters 3 and 7, has covered solvolysis reactions of organic substrates in many varied aqueous media. A common pattern of behaviour was observed, where all the rate constants appeared to decrease from the value in pure water, inspite of the favourable decrease in activation enthalpy, $\Delta H^*$. $T \Delta S^*$ for these reactions also decreased, however, and being the dominant term, accounted for the subsequent increase in $\Delta G^*$ with increase in cosolvent mole fraction, $x_2$. The behaviour of hydrogen peroxide, illustrated clearly in Chapter 7, appears contrary to these expectations, although polyvinylpyrrolidone apparently conforms to the pattern. It was decided, therefore, to extend the conductivity technique to other previously uninvestigated systems, in an attempt to explore the generality of these ideas.

In the solubility analysis of Chapter 3, the following features were observed for solvolyses in most organic aqueous mixtures:-

(i) The initial state of the substrate was stabilized, leading to an increase in $\Delta G^*$ and resultant decrease in rate constant;

(ii) $\Delta H^*$ decreased because of the increase in partial molar enthalpy of the initial state;

(iii) $T \Delta S^*$ decreased, due to the increase in partial molar entropy of the initial state.

The Prausnitz-O'Connell theory introduced an additional factor, in the thermodynamic functions of mixing, $X^E$, but the overriding trend for any organic aqueous mixture is determined by the
difference between substrate solubilities in the two pure solvents. Ben Naim and Yaacobi have demonstrated that differences in solubility parameters of methane and ethane in a range of organic solvents were small, compared with the large difference between these values and those obtained in pure water. In a generalised plot of thermodynamic parameters for solutions of solutes in aqueous mixtures, as below, it is reasonable to assume that all organic solvents will have similar G, H and S values, grouped in approximately the same area on the pure solvent axis. Therefore, the predicted

pattern of activation parameters for other cosolvent mixtures will closely resemble the behaviour already observed. It is possible, however, that complications may arise at low cosolvent mole fractions (e.g. the Arnett region, Chapter 6).

In the following investigation, aqueous mixtures of a series of polyhydroxylic compounds have been examined and a study made of urea/water mixtures. Urea is of particular interest because of the controversy surrounding its "water-structure breaking" effect.
10.2.1 Urea/water mixtures

Although aqueous solutions of electrolytes have in general received more attention than non-electrolytes, a considerable effort has been made in recent years to gain information on the molecular interactions responsible for the properties of urea/water mixtures. Urea is characterized by its surprisingly high solubility ($\geq 20$ mol dm$^{-3}$ at 298K) and by the almost ideal solutions it forms with water. Among the remarkable properties observed when urea is a component in various systems are the following: urea enhances the solubility of hydrocarbons, inhibits the micellar aggregation of surfactants, and affects the conformational properties of a wide range of water-soluble polymers. Particularly important is the denaturing effect of urea on proteins. Most of its physicochemical properties and much thermodynamic data have been determined. In spite of various studies employing different techniques, the exact effect of urea on the structure of water is far from certain. At present, there are two theories which fit the thermodynamic data, and it was hoped that the present work might contribute something towards this continuing discussion.

10.2.2 Experimental Details

Urea solutions were prepared by adding weighed amounts of the BDH reagent to freshly distilled water, the mixtures being vigorously stirred and allowed to equilibrate at room temperature before transferring to graduated volumetric flasks. This proved necessary as a result of the endothermic dissolution process, particularly noticeable in the case of the most
**TABLE 10. I**

Rate Constants for solvolysis of t-butyl chloride in Urea/Water Mixtures.

$10^3 \text{k/s}^{-1}$

<table>
<thead>
<tr>
<th>Water only</th>
<th>1 mol dm$^{-3}$</th>
<th>2 mol dm$^{-3}$</th>
<th>3 mol dm$^{-3}$</th>
<th>4 mol dm$^{-3}$</th>
<th>6 mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6689</td>
<td>1.622</td>
<td>1.5369</td>
<td>1.4916</td>
<td>1.4399</td>
<td>1.294</td>
</tr>
<tr>
<td>±0.11</td>
<td>±0.042 (8)</td>
<td>±0.03 (8)</td>
<td>±0.014 (8)</td>
<td>±0.0156 (7)</td>
<td>±0.033 (6)</td>
</tr>
<tr>
<td>278.17K</td>
<td>278.141K</td>
<td>278.133K</td>
<td>278.15K</td>
<td>278.136K</td>
<td>278.138K</td>
</tr>
<tr>
<td>3.338</td>
<td>3.21558</td>
<td>3.270</td>
<td>3.1304</td>
<td>2.9798</td>
<td>2.3096</td>
</tr>
<tr>
<td>±0.035</td>
<td>±0.076 (8)</td>
<td>±0.018 (8)</td>
<td>±0.25 (7)</td>
<td>±0.01 (8)</td>
<td>±0.37 (8)</td>
</tr>
<tr>
<td>283.10</td>
<td>283.103</td>
<td>283.077</td>
<td>283.014</td>
<td>283.083</td>
<td>283.071</td>
</tr>
<tr>
<td>7.3454</td>
<td>7.159</td>
<td>6.226</td>
<td>6.065</td>
<td>5.7239</td>
<td>4.843</td>
</tr>
<tr>
<td>±0.046</td>
<td>±0.036 (8)</td>
<td>±0.2 (8)</td>
<td>±0.182 (7)</td>
<td>±0.03 (4)</td>
<td>±0.15 (8)</td>
</tr>
<tr>
<td>288.15</td>
<td>288.116</td>
<td>288.116</td>
<td>288.121</td>
<td>288.128</td>
<td>288.122</td>
</tr>
<tr>
<td>±0.36</td>
<td>±0.21 (4)</td>
<td>±0.16 (2)</td>
<td>±0.12 (4)</td>
<td>±0.23 (2)</td>
<td>±0.11 (4)</td>
</tr>
<tr>
<td>293.18</td>
<td>293.175</td>
<td>293.175</td>
<td>293.187</td>
<td>293.175</td>
<td>293.175</td>
</tr>
<tr>
<td>±0.05</td>
<td>±0.258 (4)</td>
<td>±0.47 (4)</td>
<td>±1.129 (4)</td>
<td>±1.29 (4)</td>
<td>±0.48 (4)</td>
</tr>
<tr>
<td>297.94</td>
<td>297.925</td>
<td>297.925</td>
<td>297.925</td>
<td>297.925</td>
<td>297.925</td>
</tr>
<tr>
<td>44.23</td>
<td>45.13</td>
<td>36.26</td>
<td>36.09</td>
<td>29.53</td>
<td>27.14</td>
</tr>
<tr>
<td>±5</td>
<td>±6 (3)</td>
<td>±0.8 (2)</td>
<td>±1 (3)</td>
<td>±1.76 (3)</td>
<td>±3.75 (4)</td>
</tr>
<tr>
<td>302.58</td>
<td>302.507</td>
<td>302.532</td>
<td>302.510</td>
<td>302.522</td>
<td>302.105</td>
</tr>
</tbody>
</table>
concentrated mixtures. Some form of change in water was clearly demonstrated here. The solutions were not stable for any great length of time, so it was found convenient to prepare small quantities at frequent intervals. Maintaining the exact solution concentrations within the cell assembly vessel proved difficult, especially for the higher concentrations of urea, since accidental dilution was unavoidable. In order to minimise the problem, the cell compartments were repeatedly washed with the test solution before runs. Many runs were ruined as a result of concentration fluctuations, however; temperature changes during modifications to the thermostat tanks, and arising from alterations in the means of temperature measurement were an added inconvenience.

10.2.3 Results

Rate constants for five urea concentrations (1, 2, 3, 4 and 6 mol dm\(^{-3}\)), as well as pure water, were obtained at 5K intervals over the temperature range 278-303K - see Table I. At the highest temperatures, 298 and 303K, the single compartment vessel had to be used, owing to the greatly increased reaction rate. The amount of time allowed for stirring the reaction mixture was reduced accordingly; in a few cases, the reaction was almost over before monitoring began. The error on measured rate constants varies considerably between solutions, but most obviously increases with temperature. This is no doubt a consequence of the shorter reaction monitoring time and fewer conductance measurements on which the rate constant calculations were based.
TABLE 10.11
Activation parameters for the solvolysis of t-buty l chloride in Urea/Water mixtures, at 298.15K.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>1 mol dm$^{-3}$</th>
<th>2 mol dm$^{-3}$</th>
<th>3 mol dm$^{-3}$</th>
<th>4 mol dm$^{-3}$</th>
<th>6 mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>k /s$^{-1}$</td>
<td>2.66 x 10$^{-2}$</td>
<td>2.2779 x 10$^{-2}$</td>
<td>2.150 x 10$^{-2}$</td>
<td>1.8129 x 10$^{-2}$</td>
<td>1.6550 x 10$^{-2}$</td>
</tr>
<tr>
<td>$\Delta G^+$</td>
<td>82.01</td>
<td>82.398</td>
<td>82.541</td>
<td>82.964</td>
<td>83.189</td>
</tr>
<tr>
<td>$\Delta H^+$</td>
<td>94.40 $\pm$ 2.1</td>
<td>89.45 $\pm$ 2.3</td>
<td>88.67 $\pm$ 1.3</td>
<td>82.968 $\pm$ 1.8</td>
<td>86.61 $\pm$ 1.4</td>
</tr>
<tr>
<td>$\Delta S^+$ /J mol$^{-1}$</td>
<td>41.56</td>
<td>23.6</td>
<td>20.57</td>
<td>0.016</td>
<td>11.46</td>
</tr>
<tr>
<td>$T\Delta S^+$</td>
<td>12.39</td>
<td>7.048</td>
<td>6.132</td>
<td>0.004</td>
<td>3.417</td>
</tr>
</tbody>
</table>

All Thermodynamic quantities expressed in kJ mol$^{-1}$, unless otherwise stated.
Thermodynamic activation parameters were again obtained by using two regression coefficients in the Glew-Clarke analysis: see Table II. A gradual increase in $\Delta G^*$ is observed with increasing concentration of urea, while both $\Delta H^*$ and $T \Delta S^*$ decrease (this trend being more marked in the latter case, however). The medium effects on all three quantities are illustrated in Figure 1, in which both $\xi \Delta H^*$ and $T \xi \Delta S^*$ exhibit minima around 4 mol dm$^{-3}$ urea. The compensatory behaviour produces a smooth gradation in $\xi \Delta G^*$. Trends in $\Delta C_p^*$, calculated for the solvolysis using three regression coefficients in the analysis suggest that values for 1-4 mol dm$^{-3}$ urea could be negative and the 6 mol dm$^{-3}$ value positive; the errors are large, however, due to insufficient accuracy in the rate constant data.

10.2.4 Discussion

The system urea + water is indeed a complicated one. Of the thermodynamic data obtained so far, the best are discussed by Stokes, who attempted to explain the observed concentration dependence of the properties by an association model. A set of step-wise equilibria were proposed for urea molecules, dimers etc. as below:

$$U_1 + U_1 \rightleftharpoons U_2$$
$$U_2 + U_1 \rightleftharpoons U_3 \text{ etc.}$$

These data indicate that urea is not a structure-making solute, but do not show that the molecule is necessarily a structure-breaker. The overall implication is that this may be the case, however.
**Figure 10.1**

Medium effects on activation parameters for t-BuCl solvolysis in Urea/water mixtures.

**Figure 10.2** Glycerol/water mixtures.
Medium effects on Thermodynamic Activation parameters,
(data for Figures 10.1 - 10.4).

(a) Urea/water mixtures

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\Delta G^\ddagger$</th>
<th>$\Delta H^\ddagger$</th>
<th>$T \Delta S^\ddagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mol dm$^{-3}$</td>
<td>0.38</td>
<td>-5.02±2</td>
<td>-5.4</td>
</tr>
<tr>
<td>2</td>
<td>0.76</td>
<td>-9.97±2</td>
<td>-10.742</td>
</tr>
<tr>
<td>3</td>
<td>0.91</td>
<td>-10.75±1</td>
<td>-11.658</td>
</tr>
<tr>
<td>4</td>
<td>1.33</td>
<td>-16.45±2</td>
<td>-17.786</td>
</tr>
<tr>
<td>6</td>
<td>1.56</td>
<td>-12.81±1</td>
<td>-14.373</td>
</tr>
</tbody>
</table>

(b) Glycerol/water mixtures

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\Delta G^\ddagger$</th>
<th>$\Delta H^\ddagger$</th>
<th>$T \Delta S^\ddagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 mf</td>
<td>0.57</td>
<td>-6.15±2</td>
<td>-6.718</td>
</tr>
<tr>
<td>0.025</td>
<td>1.12</td>
<td>-10.58±4</td>
<td>-11.693</td>
</tr>
<tr>
<td>0.05</td>
<td>1.86</td>
<td>-12.19±3</td>
<td>-14.049</td>
</tr>
<tr>
<td>0.075</td>
<td>2.28</td>
<td>-11.86±3</td>
<td>-14.134</td>
</tr>
<tr>
<td>0.1</td>
<td>2.8</td>
<td>-13.17±2</td>
<td>-11.701</td>
</tr>
</tbody>
</table>

(c) Propane-1,2-diol/water mixtures

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\Delta G^\ddagger$</th>
<th>$\Delta H^\ddagger$</th>
<th>$T \Delta S^\ddagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025 mf</td>
<td>2.05</td>
<td>-16.82±6</td>
<td>-18.869</td>
</tr>
<tr>
<td>0.05</td>
<td>3.15</td>
<td>-24.76±2</td>
<td>-27.91</td>
</tr>
<tr>
<td>0.1</td>
<td>4.33</td>
<td>-25.56±3</td>
<td>-29.89</td>
</tr>
</tbody>
</table>

(d) Propane-1,3-diol/water mixtures

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\Delta G^\ddagger$</th>
<th>$\Delta H^\ddagger$</th>
<th>$T \Delta S^\ddagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025 mf</td>
<td>2.13</td>
<td>-13.29±1</td>
<td>-15.425</td>
</tr>
<tr>
<td>0.05</td>
<td>2.81</td>
<td>-16.68±5</td>
<td>-19.506</td>
</tr>
</tbody>
</table>

(All values in kJ mol$^{-1}$)
The model proposed by Frank and Franks\textsuperscript{9} is radically different, but provides a good fit to the experimental activity coefficient data. Work done by Wetlauffer et al.\textsuperscript{3} on the thermodynamics of systems containing water/urea/apolar solute was used as the basis for the theory. The authors postulated that the "dense" (non H-bonded) species of water mixes ideally with urea, but that the molecule is barred from the tetrahedrally-ordered water clusters (the "bulky" species). A decision between the theories is difficult: it had been suggested that spectroscopy might be able to differentiate between the two.

NMR, Raman and other recent results lead to the conclusion that the effect of urea on aqueous solutions of simple molecules, surfactants and polymers is due to its power of destroying the long-range order of the aqueous medium.\textsuperscript{10} Thus, hydrogen-bonding is reduced, in favour of extensive short-range, short-lived interactions between water and urea, involving H-bonds to the urea amino groups and possibly the carbonyl. The NMR work does not provide any evidence for long-lived dimers or other aggregates, and recent viscosity studies are in agreement here. The Stokes model, therefore, appears to receive little support; the ideas of Frank and Franks may be closer to reality. Data from conductance measurements,\textsuperscript{11}a transfer studies,\textsuperscript{11}b ultrasonics,\textsuperscript{11}c vapour pressures,\textsuperscript{11}d volume changes\textsuperscript{12} and activity coefficient determinations\textsuperscript{13} have all been interpreted in terms of the structure-breaking theory.

\textit{t}-Butyl chloride in urea/water mixtures showed the same gradual decrease in rate as found in many other organic
cosolvent/water mixtures. In contrast to hydrogen peroxide, also classed as a structure-breaker, there were no dramatic changes in activation parameters. This is somewhat unexpected, in view of the supposed increase in free water resulting from structure-breaking, and also because urea/water has an increased relative permittivity (\( \varepsilon_r \) increases from ~80 in water to almost 100 in a solution of 50% by weight of urea).\(^{14}\)

The latter factor could contribute towards stabilization of the transition state.

Probably more relevant to the present discussion are some of the observations made on tetra-alkylammonium salts and hydrocarbons in the urea/water system. Data for transfer of \( \mathbf{R_4NBr} \) and \( \mathbf{R_4NI} \) salts from water to aqueous urea\(^{11b}\) indicate spontaneous solution which is entropy directed. This has been explained in terms either of complexing, or the structure-breaking effect of urea. The solution of eight hydrocarbons in 7 mol dm\(^{-3}\) urea\(^3\) is found to be similarly favourable, \( \Delta G^* \) becoming more negative with increasing temperature and increasing molecular weight of hydrocarbon. From work on the system glycylglycine/urea/water,\(^{15}\) it has been concluded that urea stabilizes both the nonpolar and peptide groups in amino acids; sodium chloride, in contrast, has an unfavourable \( \Delta G \) for transfer from water to aqueous urea.

It is not unreasonable to suppose, then, that the t-butyl chloride molecule may be readily soluble in urea solutions: the mechanism involved could be similar to that for some of the compounds mentioned above. Thus, the ground state for solvolysis will be stabilized, and the rate constant obviously decrease. Since the magnitude of the observed decrease in \( k \)
is not great, as the concentration of urea increases, it must be concluded that the t-BuCl stabilization cannot be a very large effect. The change in sign for $\Delta C_p^*$ in 6 mol dm$^{-3}$ solutions appears to coincide with recent Ag/AgCl electrode potential measurements, made by Kundu and Mazumdar. These workers proposed an enhancement of structure in urea/water mixtures at higher concentrations, possibly as a result of urea–water complex formation.

As in the case of PVP, the results obtained here tend to support the ideas of Glasel, from his deuteron magnetic resonance work. Urea appears to have little effect on water, and this is reflected in the changes of rates of solvolyses.

10.3.1 Glycerol/water mixtures

The glycerol molecule, like urea, contains three polar hydroxyl groups, all of which are capable of forming hydrogen-bonds. It is, therefore, an example of the Franks 'Typically nonaqueous' class of solutes in water: a polyfunctional hydrophilic compound, associated with specific interactions. No comprehensive picture exists for the typically nonaqueous solutes as yet, but commonly found properties include marked short-range solute/water interactions and a lack of evidence for clustering. Minor stereochemical differences in solute molecules appear to be important (see section 10.4), also. The exothermic nature of the heat of glycerol dissolution indicates extensive hydrogen-bond formation with water.
(comparable to that of the sugars, DMSO and $\text{H}_2\text{O}_2$), and as a result of this, glycerol is assumed to be a water-structure breaker. There appears to be some controversy concerning the exact effect of the molecule on the structure of water, however, and whether some form of solute/solute pairwise attraction exists in solution.\textsuperscript{19}

Among its many varied uses, glycerol is known to stabilise proteins against thermal denaturation,\textsuperscript{20} and has cryoprotective properties useful in the preservation of red blood cells (cf. PVP).\textsuperscript{21} Binary water + glycerol mixtures have often been used as solvents in studies of ionisation constants and acid-base properties of compounds slightly soluble in water.\textsuperscript{22} Since the kinetics of other types of reaction have been modified in the presence of glycerol, principally due to the increased viscosity of the medium,\textsuperscript{23} the effect on t-BuCl solvolysis appeared worthy of investigation.

10.3.2 Experimental Details

Glycerol solutions were prepared by adding approximate volumes of the BDH reagent and freshly distilled water to graduated flasks. The required mole fractions were then obtained by correcting the weights of each component. Each flask was shaken well, to ensure thorough mixing of the two liquids, and this procedure repeated before each run. Maintenance of the correct solution concentrations did not prove to be a problem in this case. Rate constants for five solutions, of glycerol mole fraction 0.01, 0.025, 0.05, 0.075 and 0.1 were obtained at 5K intervals over the temperature range 278-303K.
### TABLE 10. III

*Rate Constants for solvolysis of t-butyl chloride in Glycerol/Water mixtures.*

<table>
<thead>
<tr>
<th></th>
<th>0.01 mf.</th>
<th>0.025 mf.</th>
<th>0.05 mf.</th>
<th>0.075 mf.</th>
<th>0.1 mf.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1.49470$</td>
<td>$1.32776$</td>
<td>$1.14572$</td>
<td>$0.88366$</td>
<td>$0.77371$</td>
</tr>
<tr>
<td>$\pm$</td>
<td>$0.0085$</td>
<td>(9)</td>
<td>$0.015$</td>
<td>(8)</td>
<td>$0.021$</td>
</tr>
<tr>
<td></td>
<td>$278.21K$</td>
<td>$278.208K$</td>
<td>$278.22K$</td>
<td>$278.195K$</td>
<td>$278.205K$</td>
</tr>
<tr>
<td>$\pm$</td>
<td>$0.054$</td>
<td>(7)</td>
<td>$0.021$</td>
<td>(8)</td>
<td>$0.033$</td>
</tr>
<tr>
<td></td>
<td>$283.19$</td>
<td></td>
<td>$283.168$</td>
<td></td>
<td>$283.17$</td>
</tr>
<tr>
<td>$\pm$</td>
<td>$0.077$</td>
<td>(11)</td>
<td>$0.250$</td>
<td>(10)</td>
<td>$0.129$</td>
</tr>
<tr>
<td></td>
<td>$288.19$</td>
<td></td>
<td>$288.185$</td>
<td></td>
<td>$288.173$</td>
</tr>
<tr>
<td>$\pm$</td>
<td>$0.179$</td>
<td>(8)</td>
<td>$0.291$</td>
<td>(10)</td>
<td>$0.144$</td>
</tr>
<tr>
<td></td>
<td>$293.17$</td>
<td></td>
<td>$293.00$</td>
<td></td>
<td>$293.155$</td>
</tr>
<tr>
<td>$\pm$</td>
<td>$0.082$</td>
<td>(4)</td>
<td>$0.421$</td>
<td>(4)</td>
<td>$0.266$</td>
</tr>
<tr>
<td></td>
<td>$298.13$</td>
<td></td>
<td>$298.13$</td>
<td></td>
<td>$298.137$</td>
</tr>
<tr>
<td>$\pm$</td>
<td>$0.223$</td>
<td>(4)</td>
<td>$2.206$</td>
<td>(4)</td>
<td>$0.484$</td>
</tr>
<tr>
<td></td>
<td>$303.105$</td>
<td></td>
<td>$303.070$</td>
<td></td>
<td>$303.080$</td>
</tr>
</tbody>
</table>

Numbers in brackets refer to the number of rate constants on which the averages are based.
### TABLE 10. IV

Activation parameters for the solvolysis of t-butyl chloride in Glycerol/Water mixtures, at 298.15K.

<table>
<thead>
<tr>
<th>$X_2$</th>
<th>0.01</th>
<th>0.025</th>
<th>0.05</th>
<th>0.075</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k/s^{-1}$</td>
<td>$2.464 \times 10^{-2}$</td>
<td>$1.9786 \times 10^{-2}$</td>
<td>$1.464 \times 10^{-2}$</td>
<td>$1.237 \times 10^{-2}$</td>
<td>$1.0014 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\Delta G^+$</td>
<td>82.203</td>
<td>82.747</td>
<td>83.494</td>
<td>83.912</td>
<td>84.43</td>
</tr>
<tr>
<td>$\Delta H^+$</td>
<td>93.27 ± 2.3</td>
<td>88.84 ± 4.1</td>
<td>87.23 ± 2.9</td>
<td>87.56 ± 2.9</td>
<td>86.25 ± 1.5</td>
</tr>
<tr>
<td>$\Delta S^+/J\ mol^{-1}$</td>
<td>37.13</td>
<td>20.44</td>
<td>12.54</td>
<td>12.26</td>
<td>1.816</td>
</tr>
<tr>
<td>$T\Delta S^+$</td>
<td>11.072</td>
<td>6.097</td>
<td>3.741</td>
<td>3.656</td>
<td>6.089</td>
</tr>
</tbody>
</table>

All Thermodynamic quantities expressed in kJ mol$^{-1}$, unless otherwise stated.
10.3.3 Results

The rate constants are shown in Table III, and activation parameters calculated using two regression coefficients in the Glew-Clarke analysis appear in Table IV. Errors on $k$ tend to increase with temperature, though not necessarily with increase in glycerol mole fraction. The reproducibility for a larger number of rate constant determinations was a distinct improvement over that obtainable in the case of urea. Once again, $\Delta g^*$ increases smoothly over the concentration range, while both $\Delta H^*$ and $\Delta S^*$ are seen to decrease. The medium effects on activation parameters are given in Figure 2. Although the errors are large, calculated $\Delta C_p^*$ values appear to be negative, as observed previously for urea.

10.3.4 Discussion

In most cases, the data available for glycerol support the Franks proposal that the molecule is a structure-breaker. Examples include EMF measurements of hydrochloric acid in glycerol/water mixtures,\textsuperscript{24} partial molal volume determinations,\textsuperscript{25} and studies of noble gas solubilities in aqueous glycerol.\textsuperscript{26} In contrast, Khoo has adopted the ideas of Moriamez,\textsuperscript{27} who concluded that pure glycerol is a highly associated liquid, consisting of collinear H-bonded chains. These chains are in turn hydrogen-bonded laterally. Addition of glycerol to water causes depolymerisation of the alcohol, the molecules of which become embedded in the water structure. Khoo has suggested that the glycerol molecule acts to stabilize the ice-like clusters in water, this stabilization reaching a maximum around 10-30% (w/w) glycerol. Further addition of the alcohol
results in structural breakdown, when the bulky molecule can no longer be accommodated successfully. The lack of excess enthalpy of mixing data for glycerol/water is unfortunate, since such results are usually good guides to the structural properties of binary solvent mixtures.

The solvolysis of benzyl chloride has been studied in glycerol/water at temperatures of 323-343K. The results obtained seemed to imply that the constant volume activation parameters were more appropriate for a fundamental discussion of this reaction than the constant pressure parameters. No reason for this observation was suggested by the workers, however.

The t-butyl chloride solvolysis results reported here show trends similar to those observed for urea: gradual decreases in rate constants and smooth changes in activation parameters over the mole fraction range. It is evident that the increased viscosity of the system when glycerol is added plays no dramatic role in determining $\Delta X^+$, (the same as was observed for PVP). This is in contrast to the viscosity effects recorded on such reactions as ligand substitution on Ni$^{2+}$, Co$^{2+}$, Cu$^{2+}$ and Zn$^{2+}$ ions in pure glycerol. In these cases, the kinetics were apparently controlled by the properties of the liquid.

Consideration of solubilities is more difficult for glycerol, due to the lack of information available in the literature. It has been reported that sodium and potassium chloride solubilities in aqueous glycerol decrease uniformly as the water content decreases. Sodium chloride has, however, a marked solubility in both liquids, (more so in
glycerol, on the basis of moles of solute per mole of solvent). The chemical interaction (solvation) terms for transfer of HCl from water to glycerol/water are favourable, but electrostatic factors dominate, resulting in a positive free energy for the process. The dissolution of argon is characterized by a large positive enthalpy change, making the free energy very unfavourable. Unfortunately, the behaviour of hydrocarbons in glycerol solutions is unknown: hence, no conclusions can be drawn with regard to the solubility of t-BuCl. If glycerol is assumed to resemble urea, in structure-breaking ability, it is possible that the substrate would be more soluble in the glycerol/water mixtures, thus stabilizing the ground state, as before.

10.4.1 Propane-1,2-diol/water and Propane-1,3-diol/water mixtures

These isomeric glycols, of formulae \(\text{CH}_3\text{-CH(OH)-CH}_2\text{(OH)}\) and \(\text{(HO)CH}_2\text{-CH}_2\text{-CH}_2\text{(OH)}\) respectively, also belong to the polyfunctional 'typically non-aqueous' class of solutes in water, and were selected originally for comparison with glycerol. This was prompted by some thermodynamic work by Reid and Tibbe on the alcohol series: \(n\text{-propanol, propane-1,2- and -1,3-diols, and glycerol}\). The authors were investigating the effect of increasing hydroxylic substitution on a propane backbone, through measurements of heats of solution in water. The gradation in calculated heat capacity values appeared to reflect the change from structure-making to structure-breaking properties of the solutes, across the series.
Although the 1,2-diol had a slightly more positive $\Delta C_p^\circ$ value, both diols were found roughly half-way between the mono- and tri-hydroxy compounds. A linear relation was noted between $\Delta C_p^\circ$ values and the number of OH groups.

The heat of dilution of propane-1,2-diol has been compared with that of glycerol, and the observation made that the quantity varies inversely with molecular weight. This has been attributed to the number of OH groups present in the molecules, and the extent of molecular association in the pure alcohols. In general, however, the diols have received little attention so far; their effect on the solvolysis of t-butyl chloride was considered worthy of investigation, especially with regard to the increased viscosity of the medium.

10.4.2 Experimental Details

As previously described for glycerol, solutions of both diols were made up by weight, and thorough mixing of the components ensured before use. Three mole fraction mixtures of propane-1,2-diol were prepared ($x_2 = 0.025, 0.05$ and $0.1$), but only two were obtainable for the 1,3-diol ($x_2 = 0.025, 0.05$). When repeated attempts were made to prepare the 0.1 mole fraction mixture, a milky opalescence was observed on each occasion. The same result was obtained in different flasks and with independent samples of 1,3-diol; hence, it was assumed that partial miscibility occurred at this particular cosolvent/water ratio. t-BuCl solvolyses were monitored in the five solutions at temperatures: 278, 283, 288 and 293K. The temperature control for these measurements was particularly good throughout.
10.4.3 Results

Rate constants and activation parameters, calculated as before, are given in Tables V and VI respectively. Errors on k tend to increase with temperature, as expected; a comparison of rate constants between the diols shows that the values for corresponding mole fractions are very similar, but slightly less than the values obtained for glycerol. This difference is reflected in the $\Delta G^*$ values, which are more positive for the diols; trends in activation parameters are the same for the three cosolvents, however. The medium effects in Figures 3 and 4 demonstrate this clearly. The value of $\Delta C_p^*$ for 0.025 mlf 1,2-diol was positive, in contrast to the heat capacities calculated for urea and glycerol. Large errors caused the figures for the other solutions to prove unreliable.

10.4.4 Discussion

As mentioned earlier, studies of propane-diols have been somewhat limited, to volume\textsuperscript{33} and solubility\textsuperscript{34} measurements, with a little thermodynamic work\textsuperscript{35} (usually for comparison with other polyhydric alcohols). The diols have been briefly mentioned in connection with ultrasonics experiments, where their behaviour is typical of that observed for systems where $G^E$ is negative.\textsuperscript{36} A few measurements on enthalpies and volumes of mixing with water show $\Delta H$ and $\Delta V$ to be negative, for the 1,2-diol.\textsuperscript{35} In fact, comparison shows $\Delta H$ to be more negative than the values obtained for methanol and ethanol. Volume changes are of interest, also: although $\Delta V$ values are large and negative for both diols,\textsuperscript{33} the volume contraction
### TABLE 10. V

Rate Constants for solvolysis of t-butyl chloride in Propane-1,2-Diol/Water, Propane-1,3-Diol/Water mixtures.

<table>
<thead>
<tr>
<th></th>
<th>10^3 k/s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Propane-1,2-Diol</td>
</tr>
<tr>
<td>0.025 mf</td>
<td>0.05 mf</td>
</tr>
<tr>
<td>1.234 ±0.008</td>
<td>0.9349 ±0.03</td>
</tr>
<tr>
<td>278.131K</td>
<td>278.104K</td>
</tr>
<tr>
<td>2.0317 ±0.13</td>
<td>1.625 ±0.056</td>
</tr>
<tr>
<td>283.133</td>
<td>283.134</td>
</tr>
<tr>
<td>3.902 ±0.2</td>
<td>3.0327 ±0.14</td>
</tr>
<tr>
<td>288.127</td>
<td>288.122</td>
</tr>
<tr>
<td>7.992 ±0.5</td>
<td>5.0414 ±0.14</td>
</tr>
<tr>
<td>293.072</td>
<td>293.087</td>
</tr>
</tbody>
</table>
TABLE 10. VI

Activation parameters for the solvolysis of t-butyl chloride in Propane-1,2-Diol/Water and Propane-1,3-Diol/Water mixtures, at 298.15K.

<table>
<thead>
<tr>
<th>X₂</th>
<th>(1,2-Diol)</th>
<th>(1,3-Diol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k /s⁻¹</td>
<td></td>
</tr>
<tr>
<td>0.025</td>
<td>1.35 x 10⁻²</td>
<td>0.870 x 10⁻²</td>
</tr>
<tr>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| ΔG⁺  |            |            |            |            |            |            |
| 83.68 |            |            |            |            |            |
| 84.78 |            |            |            |            |            |
| 85.96 |            |            |            |            |            |
| 83.76 |            |            |            |            |            |
| 84.449 |            |            |            |            |            |

| ΔH⁺  |            |            |            |            |            |            |
| 82.60 ± 5.8 |            |            |            |            |            |
| 74.66 ± 1.8 |            |            |            |            |            |
| 73.86 ± 2.6 |            |            |            |            |            |
| 86.13 ± 1  |            |            |            |            |            |
| 82.74 ± 5.5 |            |            |            |            |            |

| ΔS⁺/J mol⁻¹ |            |            |            |            |            |            |
| -3.6        |            |            |            |            |            |
| -33.9       |            |            |            |            |            |
| -40.6       |            |            |            |            |            |
| 7.93        |            |            |            |            |            |
| -5.75       |            |            |            |            |            |

| TΔS⁺  |            |            |            |            |            |            |
| -1.079    |            |            |            |            |            |
| -10.12    |            |            |            |            |            |
| -12.1     |            |            |            |            |            |
| 2.365     |            |            |            |            |            |
| -1.716    |            |            |            |            |            |

All Thermodynamic quantities expressed in kJ mol⁻¹, unless otherwise stated.
Figures 10.3 & 10.4 Medium effects on activation parameters for t-BuCl solvolysis in Propane-1,2-diol/water and Propane-1,3-diol/water mixtures.
for the 1,2- compound is nearly twice that of the 1,3-diol, at the minimum point. Occupation of the free volume, or cavities, in the open water-structure is used to explain the volume loss. The Frank and Ives proposal of an 'interstitial' contribution, available when the solute has a terminal methyl group (secondary OH) for extra cavity occupation has been suggested, in connection with the larger 1,2-diol effect.

Finally, the solubility of some nucleic acid bases and related nucleosides (adenine, thymine, guanosine and uracil) have been measured in aqueous propane-1,2-diol. A correlation between solubility parameters and the effectiveness of the glycol as a denaturant for DNA and RNA was observed. Free energies of transfer for the bases from water to the solution were negative, and three of the compounds were more soluble in the aqueous diol than any other mixture tried. In general, alcohols and glycols have been found to increase the solubilities of DNA, RNA and their model compounds. It is possible, therefore, that the ground state of t-BuCl may be stabilized in the diol/water media, as a result of increased substrate solubility. The rate constant decrease may be accounted for thus, in spite of the negative free energies of mixing for both diols with water. The solubility factors dominate, apparently. Increases in viscosity of the media for solvolysis bear no relation to the modification in kinetics (cf. glycerol), which is not spectacular.
10.5 Conclusions

The observed trends in activation parameters for each of the four systems studied are remarkably similar, and resemble closely the pattern obtained for nearly all aqueous organic mixtures. This observation bears out the original conclusions which were based primarily on supposed modifications to the initial state. Thus, $\Delta G^*$ increases in each system, as a result of the initial state stabilization. In comparison, it is difficult to argue convincingly that the trends in $\Delta H^*$ and $T\Delta S^*$ are as expected, because data for these parameters would be required over the whole mole fraction range. However, the pattern is close to that anticipated. The endothermic maximum in initial state enthalpy, as demonstrated by Arnett (see Chapter 6) is not observed here, although it may occur at mole fractions beyond the range studied in these measurements. No correlation has been discovered between rate constant behaviour and changes in either relative permittivity or viscosity of the reaction medium. This clearly demonstrates the unsatisfactory nature of these approaches when applied to such systems.
References


17. J.S. Rowlinson and F. Franks, ref. given in 'Water - A Comprehensive Treatise' (see ref. 7), vol. 2, ch. 5.

18. F. Franks and D.S. Reid, in 'Water - A Comprehensive Treatise' (see ref. 7), vol. 2, ch. 5.


30. See reference 22.


34. T.T. Herskovits and J.P. Harrington, Biochemistry, 1972, **11**, 4800.


Appendix I

As an extension to the kinetic study of aqueous gel systems reported in Chapter 9, a preliminary investigation was undertaken to observe the effects of alternative types of gelling agent on the rate of aquation of the tris(5-nitro-1,10-phenanthroline)iron(II) cation. In contrast to the naturally-occurring gelatin and agar used earlier, four synthetic polymers were selected, following references to this class of compound in papers by Allan and Norman. The necessary conditions of reaction for the complex, as determined by the equipment (Chapter 5) were maintained, but proved unsuitable for two of the mixtures. Observations made, however, were sufficient to indicate similar behaviour to that exhibited by both agar and gelatin.

The four compounds used were: Cab-O-Sil, Klucel, Natrosol and Cellulose Gum.

(a) Cab-O-Sil (Cabot Corporation, grade M5) was a very finely powdered form of Silica, one of the purest commercially available (99% SiO₂, and practically free from contaminating metallic oxides). Its physical appearance was that of fluffy snow-white 'flakes', having extremely low bulk density and enormous external surface area. It has been used in many industries, and even to improve the texture and properties of food. In the formation of aquasols, the rate of addition of Cab-O-Sil is important to the final viscosity: rapid mixing has been advocated.

When the compound is dispersed in a liquid system, hydrogen-bonding occurs between silica particles (see Fig. 1), and the resulting chain-like formations join together to form...
Figure 1. Hydrogen-bonding action between Cab-O-Sil particles.

Figure 2. Idealized structure of Natrosol.
a network type of structure. This reduces the ability of the liquid to flow and results in increased viscosity. Upon agitation, the network structure breaks down, but reforms after agitation stops (thixotropic behaviour). It is this property which is most frequently employed in the various uses made of the product. Viscosity stability of various systems over wide temperature ranges may be maintained by the addition of Cab-O-Sil.

(b) Natrosol (Hercules Inc., type 250HR) was a non-ionic water-soluble polymer, derived from cellulose by reaction of the latter with sodium hydroxide and ethylene oxide. The result of this reaction is a hydroxyethyl ether, of idealized structure shown in Fig. 2, having greater solubility in water than the parent cellulose. Natrosol was a white, odourless, tasteless, free-flowing powder, which readily dissolved in hot or cold water to give clear, smooth, viscous solutions. Slow addition to water has been recommended, to prevent agglomeration or "lumping". Natrosol solutions do not gel, even up to the boiling point of water, and are known to be compatible with many inorganic salts.

(c) Cellulose Gum (Hercules Inc., type 7HF) was purified sodium carboxymethylcellulose, an anionic water-soluble polymer derived from cellulose. Like Natrosol, it is a cellulose ether, prepared from the reaction of alkali cellulose with sodium monochloroacetate, and rapidly dissolves in both hot or cold water. The structure of the polymer is shown in Fig. 3. The water solubility of cellulose is greatly enhanced by substitution of some of the OH groups. Cellulose gum is used as a thickener, binder and stabilizer,
Figure 3. Idealized structure of Cellulose Gum.

Figure 4. Idealized structure of Hydroxypropyl Cellulose.
and solutions are prepared by agitated dispersion. The latter can provide ranges of viscosity, but their compatibility with salts depends on the ability of the added salt to form a soluble salt of carboxymethylcellulose. If Al$^{3+}$ ions are added, cross-linking to form a gel will occur. 

(d) Klucel (Hercules Inc., grade H) was a hydroxypropyl cellulose, a non-ionic water-soluble cellulose ether, with much the same uses as the above. Prepared by reacting alkali cellulose with propylene oxide, the idealized structure is given in Fig. 4. The polymer is soluble in water below 313K and insoluble above 318K, with a wide range of viscosities. It is an off-white, odourless and tasteless powder, giving clear, smooth solutions with water. Klucel must be stored tightly closed and in a dry atmosphere, owing to its great affinity for moisture (a property shared by all three compounds above). The polymer does not form gels, and inorganic salts are soluble provided the concentrations are not great. Slow dissolution is again recommended, to prevent lumping; Klucel in solution is susceptible to acid hydrolysis, however.

**Experimental Details**

Solutions of all four compounds contained the required concentration of NiSO$_4$ for promotion of the aquation (2 mol dm$^{-3}$), and stock complex solution was used in each case (see Chapter 9). Samples containing 2% by weight of natrosol, cellulose gum and klucel, and 1.5% by weight of cab-O-sil were tested. The first three produced clear green mixtures of varying viscosity, but the cab-O-sil remained cloudy. The order of increasing viscosity was
Cellulose gum > Klucel > Natrosol. Reactions were monitored as previously in the SP 1800A spectrophotometer, at approximately 318K.

Results The Cab-O-Sil solution remained cloudy throughout the run, probably due to its incompatibility with the nickel salt, and hence the results were ignored. Klucel began to precipitate out of solution towards the end of the reaction, but readings obtained over the first two half-lives provided a rough estimate for k. Rate constants were calculated using the PDP 11 program:

\[
\begin{align*}
10^{-3}k &= 5.4947 \pm 0.2 \\
10^{-3}k &= 6.9677 \pm 0.2 \\
10^{-3}k &= 6.1894 \pm 0.2
\end{align*}
\]

Although the accuracy leaves much to be desired, the rate constants appear to be little affected by the polymer present. These results, therefore, follow the trend already observed for aquation of the iron complex in PVP, agar and gelatin solutions. A more detailed study of the synthetic polymers would obviously be required before any conclusions could be drawn, however.

References
Appendix 2  Computer Programs

Listing of METHOD OF GUGGENHEIM

ALGOL;
LIBRARY
ALGOL

LIST;

1 METHOD OF GUGGENHEIM;
2 "BEGIN" "INTEGER" I,NREAD;
3 "REAL" TMULT;
4 "INTEGER" "ARRAY" T[1:5000];
5 "REAL" "PROCEDURE" LSR(X, Y, NREAD);
6 "INTEGER" NREAD;
7 "REAL" "ARRAY" X,Y;
8 "BEGIN" "INTEGER" I;
9 "REAL" DEVSQ, A,B,C,D, INTERCEPT,GRADIENT;
10 "REAL" "ARRAY" DIFF, YCALC[1:NREAD];
11 A:=0;
12 B:=0;
13 C:=0;
14 D:=0;
15 "FOR" I:=1 "STEP" 1 "UNTIL" NREAD "DO" "BEGIN"
16 A:=A+X[I];
17 B:=B+Y[I];
18 C:=C+(X[I]*Y[I]);
19 D:=D+(X[I]*2);
20 "END";
21 "PRINT" SAMELINE,
22 "STEP", "UNTIL", "DO", "BEGIN"
23 YCALC[I]:= GRADIENT *X[I] + INTERCEPT;
24 DIFF[I]:= Y[I] - YCALC[I];
25 "PRINT" "", SAMELINE, FREEPOINT(9), PREFIX("S8");
26 DEVSQ:=DEVSQ+DIFF[I]*2;
27 "END";
28 "PRINT" "";
29 DEVSQ:=DEVSQ/NREAD;
30 "PRINT" "", SCALED(4), "GRADIENT;"
31 "PRINT" "", "REACTION RATE CONSTANT=", SAMELINE;
32 SCALED(6), GRADIENT;
33 "PRINT" "", "ROOT MEAN SQUARE DEVIATION =",
34 SAMELINE,FREEPOINT(8),DEVSQ;
35 "PRINT" "", "S5";
36 "END" OF LINEAR REGRESSION ANALYSIS;
37 D:=1;
38 INSTRING(TITLE,D);
39 "READ" NREAD,TMULT;
"BEGIN" "REAL" "ARRAY" T1, T2, L1, L2, X, Y[1:NREAD];
"PRINT" "EVALUATION OF REACTION RATE CONSTANTS USING THE",
"METHOD OF GUGGENHEIM**",
"D. WADDINGTON,",
"UNIVERSITY OF LEICESTER * 1971",
"DESCRIPTION OF SYSTEM STUDIED",
D := 1;
"OUTSTRING" (TITLE, D);
"PRINT" "S10' DATE /
L2'S10' RUN NUMBER /
L2'S10' TEMPERATURE K
"FOR" I := 1 "STEP" 1 "UNTIL" NREAD "DO"
"READ" T1[I], L1[I];
"FOR" I := 1 "STEP" 1 "UNTIL" NREAD "DO"
"READ" T2[I], L2[I];
"FOR" I := 1 "STEP" 1 "UNTIL" NREAD "DO" "BEGIN"
Y[I] := LN(L2[I] - L1[I]);
X[I] := T1[I] * TMULT;
"END";
"END";
"END" OF PROGRAM;
"INPUT DATA***",
"DATA FOR GRAPH***",
"L3";
"PRINT" "SAMELINE, 'S4'T1, 'S9'L1, 'S10'T2, 'S9'L2, 'S21'X, 'S9'Y",
"L";
"FOR" I := 1 "STEP" 1 "UNTIL" NREAD "DO" "BEGIN"
Y[I] := Y[I] / 2.30259;
"PRINT" 'L', SAMELINE,FREEPOINT(7),
T1[I], 'S2', L1[I], 'S5', T2[I], 'S2', L2[I], 'S12', X[I], 'S2', Y[I]
"END";
"END";
"END" OF PROGRAM;
Listing of KINFUN.

ALGOL;
LIBRARY ALGOL;

&LIST;

1 KINFUN;
2 "BEGIN"
3 "INTEGER" I,N,J,Q,U,V,W,Z,
4 TE,P,J,HOP,MM,
5 JJ,WH,JA,
6 ZZ,ZY,ZM;
7 "REAL" KP,TH,DEUS0,RA,A,R,C,D,INT,GRAD,KRR,
8 RO,AC,TS,TC,TA,YC,
9 THH,GA,GB,DKR;
10 "ARRAY" TC[1:1000], YCALC[1:1000],
11 Y[1:1000], YCALC[1:1000],
12 SC[1:30], SK[1:30],
13 KM[1:90],
14 DIF[1:1000], TR[1:30], TEMP[1:30], TT[1:1000];
15 "PROCEDURE" FINISH;
16 "BEGIN"
17 J:=1-1;
18 "PRINT" '"L'J"=I',SAMELINE,SCALED(9),J;
19 V:=1-1;
20 "FOR" I:= J+1 "STEP" 1 "UNTIL" 8000 "DO" "BEGIN"
21 TC[I]:=0;
22 "END";
23 "PRINT" '"L'TAPE ERRORS TRANSFERS=I',
24 SAMELINE,SCALED(9),TE;
25 "GOTO" MIKE;
26 "END"FINISH;
27 "PROCEDURE" CHECK;
28 "BEGIN"
29 "IF" GCV3 = 0 "THEN" "GOTO" ROBIN;
30 "IF" GCV3 = 0 "THEN" "GOTO" ROBIN;
31 "IF" GCV3 = 0 "THEN" "GOTO" ROBIN;
32 "IF" GCV3 = 0 "THEN" "GOTO" ROBIN;
33 "IF" GCV3 = 0 "THEN" "GOTO" ROBIN;
34 "IF" GCV3 = 0 "THEN" "GOTO" ROBIN;
35 "IF" GCV3 = 0 "THEN" "GOTO" ROBIN;
36 "END";
37 "PRINT" '"L'CONDUCTANCE OUT OF SEQUENCE AT I=',
38 SAMELINE,SCALED(5),"S",T[I];
39 "END";
40 "PROCEDURE" SELECT;
41 "BEGIN"
42 MM:=NM+1;
43 SS[MM]:=SS[MM]+1;
44 "IF" SS[MM]<9K[NM] "THEN" G[C]:0;
"IF" SK[MM]=SS[MM] "THEN" SS[MM]:=0;
"IF" MM=N "THEN" MM:=0;
"END" SELECT;
"PROCEDURE" LSOR;
"BEGIN"
  JA:=0;
  POOLE:
  JA:=JA+1;
  A:=0;
  R:=0;
  C:=0;
  D:=0;
  W:=0;
  "PRINT" '''LSQRSTART';
  "PRINT" '''V=',SAMELINE,SCALED(9),V;
  JJ:=1;
  FOR W:=1 "STEP" 1 "UNTIL" V "DO"
  "BEGIN"
  "IF" Y[w]=0 "THEN" "GOTO" KANGA;
  Q:=Q+1;
  A:=A+TT[w];
  B:=B+Y[w];
  C:=C+(TT[w]*Y[w]);
  D:= D+(TT[w]*2);
  R:=R+Y[w];
  KANGA:
  "END";
  "IF" Q<11 "THEN" "BEGIN"
  V := V;
  "PRINT" '''L'Q<11-LSQR CUT OUT';
  "GOTO" EVGTON;
  "END";
  W:=W-1;
  "PRINT" '''L'SQR';
  "PRINT" SAMELINE,SCALED(9),W, '''S3''',A, '''S3''',B, '''S3''',C,
  "PRINT" SAMELINE,SCALED(9),W, '''S3''',A, '''S3''',B, '''S3''',C;
  GRAD:=(A*B-Q*C)/(A*A-W*D);
  INT:=(D*B-A*C)/(Q*D-A*A);
  KR:=-GRAD;
  TH:=-0.69/KR;
  "PRINT" '''L' PROVK=',SAMELINE,SCALED(9),KR, '''S3''',
  "PRINT" '''L'NO. POINTS IN LSQ CALC=',
  SAMELINE,SCALED(9),Q;
  "IF" ZZ<2 "THEN" "GOTO" EVGTON;
  "FOR" W:=1 "STEP" 1 "UNTIL" V "DO"
  "BEGIN"
  "IF" Y[w]=0 "THEN" "GOTO" DORCH;
  YC:=GRAD*TT[w] + INT;
  AC:=(100*(ABS(YC-Y[w])))/Y[w];
  "IF" AC>1 "THEN" "BEGIN"
  Y[w]:=0;
  "END";
  DORCH:
  "END";
  "IF" JA=2 "THEN" "GOTO" EVGTON;
  "GOTO" POOLE;
  "END LSOR';
  "IF" KR<0 "THEN" "BEGIN"
  "PRINT" '''L'NEGATIVE K SO EXIT';
ZZ:=10;
"GOTO" OTTAMA;
"END";
"END" LSQR;
TE:=0;
"FOR" M:=1 "STEP" 1 "UNTIL" 30 "DO"
"BEGIN" SS[M]:=0;
"END";
MN:=0;
N:=0;
Z:=1;
READ (1);
"PRINT" "F' ANALYSIS OF DATA USING GUGGENHEIM'S METHOD';
"PRINT" "L'M.J.BLANDINER.***DATA INPUT VIA TAPE';
"READ" N;
"FOR" M:=1 "STEP" 1 "UNTIL" N "DO"
"BEGIN"
"READ" TEMP[M], THMCTH[M];
"READ" SKCM3;
"PRINT" "L'NUMBER OF CELLS=',SAMELINE,SCALED(9),N;
"END";
"FOR" , M := 1 "STEP" 1 "UNTIL" 6000 , "D0"
"READ" TC;
"IF" I>1 "THEN" FINISH;
"FOR" Z:=2 "STEP" 1 "UNTIL" W , "DO"
"BEGIN"
"READ" G1;"IF" G1.KO "THEN" FINISH;
"READ" RA;
GL1 := 0;
SELECT;
I := I + 1;
TC := TC;
TC := TC + TS;
"GOTO" HOO;
"END";
"IF" RA < 0 "THEN" FINISH;
"IF" RA = 1 "THEN" GL1 := GL1 * 10 + (-7);
"IF" RA = 2 "THEN" "BEGIN"
GL1 := 0;
"GOTO" ROBIN;
"END";
"IF" RA = 3 "THEN" GL1 := GL1 * 10 + (-5);
"IF" RA = 4 "THEN" GL1 := GL1 * 10 + (-4);
"IF" RA = 5 "THEN" GL1 := GL1 * 10 + (-3);
"IF" RA = 6 "THEN" GL1 := GL1 * 10 + (-2);
"IF" RA = 7 "THEN" GL1 := GL1 * 10 + (-1);
"IF" RA > 7 "THEN" "BEGIN"
GL1 := 0;
"PRINT" "'L'RA>7-TAPE ERROR AT I='",
SAMELINE, SCALED(9), I, "'S'", TC;
TE := TE + 1;
"END";
"IF" I > N "THEN" "BEGIN"
V := I - N;
CHECK;
"END";
"IF" I > (2 * N) "THEN" "BEGIN"
V := I - 2 * N;
CHECK;
"END";
ROBIN:
SELECT;
"END";
MIKE:
FOR" M := 1 "STEP" 1 "UNTIL" N "DO"
"BEGIN"
ZZ := 0;
WW := 1;
"PRINT" "'L'SYSTEM=';
"PRINT" "'L'TEMPERATURE='", SAMELINE, SCALED(9), TEMPCN;
V := 0;
"FOR" Z := 0 "STEP" N "UNTIL" J "DO"
"BEGIN"
V := V + 1;
I := M + Z;
"IF" (I > J) "THEN" "GOTO" MART;
TTE[V] := TMULTCN * TC;
"END";
MART:
Q := ENTER(J/3);
"PRINT" "'L'Q='", SAMELINE, SCALED(9), Q;
V := 0;
HOP := SK[M] * N;
"FOR" Z := 0 "STEP" HOP "UNTIL" J "DO"
"BEGIN"
V := V + 1;
I := N * (SK[M] - 1) + M + Z * HOP * ENTER((2 * Q + N) / HOP);
"PRINT" "'L'", SAMELINE, SCALED(9), I;
"IF" I > J "THEN" "BEGIN"
PRINT "L\'DATA ORUN";
V:=V-1;
Z:=J;
"GOTO" DOC;
"END";
G A:=G[1];
"PRINT" SAMELINE,SCALED(9),G[1];
"IF" G[1]=0 "THEN" "BEGIN"
Y[V]:=0;
GB:=0;
"GOTO" PIGLET;
"END";
I:= N*(SK[M]-1)+M+Z;
"PRINT" SAMELINE,SCALED(9),"S3",I;
"IF" I>J "THEN" "BEGIN"
"PRINT" "L\'DATA ORUN";
V:=V-1;
Z:=J;
"GOTO" DOC;
"END";
"IF" GB>GA "THEN" "BEGIN"
Y[V]:=0;
"GOTO" PARK;
"END";
Y[V]:=LN(GA-GB);
PARK;
"PRINT" SAMELINE,SCALED(9),"S3",,T[V];
GA:=0;
GB:=0;
"GOTO" PIGLET;
"IF" V=0 "THEN" "GOTO" DOC;
"END";
"FOR" ZZ:=1 "STEP" 1 "UNTIL" 10 "DO" "BEGIN"
V:=2;
GA:=T[V];
V:=1;
GB:=T[V];
Q:=ENTIER(TH/(GA-GB));
RQ:=0;
RQ:=RQ*N;
O:=O*N;
Q:=ENTIER(Q+(O/10));
"PRINT" "L\'SAMELINE,SCALED(9),RQ,"S3",Q;
V:=0;
HOP:= SK[M]+N;
"FOR" Z:=0 "STEP" HOP "UNTIL" RQ "DO"
"BEGIN"
V:=V+1;
I:= N*(SK[M]-1) +M+Z+HOP*ENTIER((Z*N)/HOP);
"PRINT" "L", SAMELINE, SCALED(9), I;

"IF" I > J "THEN" "BEGIN"

"PRINT" "L', DATA OVERUN';

Z := J;

"GOTO" CAT;

"END";

"IF" G[1]=0 "THEN" "BEGIN"

Y[L] := 0;

"GOTO" ROO;

"END";

GA := G[1];

"PRINT" SAMELINE, SCALED(9), 'S3', G[1];

I := N*(SKCN-1)+H+Z;

"PRINT" SAMELINE, SCALED(9), 'S3', I,

"PRINT"SAMELINE, SCALED(9), 'S3', G[1];

Mu := TMULT(M)*T[I];

"IF" G[I] = 0 "THEN" "BEGIN"

Y[V] := 0;

"GOTO" ROO;

"END";

GR := G[1];

"IF" GA > GB "THEN" "BEGIN"

Y[V] := 0;

"GOTO" ROO;

"END";

Y[V] := LN(GA-GB);

ROO:

"PRINT" SAMELINE, SCALED(9), Y[V], 'S3', T[V];

"IF" V=RO "THEN" "GOTO" CAT;

"END";

CAT:

I := 1;

GA := T[V];

GB := T[V];

GB := GB-GA;

"PRINT" 'L', TIME LAPSE=', SAMELINE, SCALED(9), GB;

LSOR;

KM[ZZ] := -GRAD;

"IF" ZZ>1 "THEN" "BEGIN"

ZY := ZZ-1;

DKR := 100*ARSKMZY-KM[ZZ]/KM[ZZ];

"IF" DKR<1 "THEN" "BEGIN"

"GOTO" RAT;

"END";

"IF" ZZ=10 "THEN" "BEGIN"

"PRINT" 'L', CATCH-22-DEV>1%, SAMELINE, 

SCALED(9), DKR;

"GOTO" RAT;

"END";

"END";

TH := 0.69/KM[ZZ];

"END";

RAT:

"PRINT" 'L', *****CALCULATED RATE CONSTANT=',
SAMELINE, SCALED(9), KM(73), "S6", ZZ;

"PRINT" "L' NUMBER OF POINTS=";
SAMELINE, SCALED(9), V;

"PRINT" "L'CELL=",
SAMELINE, SCALED(9), W;

THH := TH;

"PRINT" "L'HALF-LIFE(SECONDS)=" SAMELINE, SCALED(9), THH;

THH := THH/60;

"PRINT" "L'HALF-LIFE(MINUTES)=" SAMELINE, SCALED(9), THH;

THH := THH/60;

"PRINT" "L'HALF-LIFE(HOURS)=" SAMELINE, SCALED(9), THH;

"PRINT" "L'COMPARISON OF Y-INPUT AND Y-RESTFIT VALUES=";

"PRINT" "S13'TIME', 'S15'Y', 'S15'YCALC', 'S14'DIFF', 'L';

DEUSO := 0;

Q := 0;

A := 0;

"FOR" W := 1 "STEP" 1 "UNTIL" V "DO"

"BEGIN"

U := 0 + i;

"IF" Y[CWJ] = 0 "THEN" "BEGIN"

Q := Q - 1;

A := A + 1;

"GOTO" TOAD;

"END"

"END"

YCALC[W] := (GRAD*TTLW) + INT;

DIFF [W] := YCWJ - YCALC[W];

"PRINT" "L'SAMELINE, SCALED(9), TTLW;

"S3", YCW], "S3", YCALC[W], "S3", DIFF [W];

DEUSO = DEUSO + DIFF [W]*2;

TOAD:

"END"

"END"

DEUSO := SORT (DEUSO/Q);

"PRINT" "L'ROOT MEAN SQUARE DEVIATION=" SAMELINE, SCALED(9), DEUSO

"PRINT" "L'NO OF POINTS=",
SAMELINE, SCALED(9), V, "S'MINUS POINT JUMPS=",
SAMELINE, SCALED(9), A;

OTTAWA:

"END"

OWL:

"END"

MC

2524 CODE

3088 TOTAL
Listing of RABBIT.

8.0B:CH001050MJP;
SACP
BATCH

SALGOL;
LIBRARY
ALGOL

&LIST:

1   RABBIT;
2   "BEGIN"
3   "INTEGR" L,N,M,J,O,U,V,W,Z,TE,PJ,HOP,MH,
4   JJ,WW,JA,Z7,ZY,ZW;
5   "REAL" KR,TH,DLUSQ,RA,A,B,C,D,INT,GRAD,KHR,
6   TOPTH,ENVF;
7   RD,AC,TS,TA,YC,THH,RA,GB,DKR;
8   "ARRAY" T[1:R,33], G[1:R,33];
9   Y[1:1000], YCALC[1:1000],
10  SSC[1:30], SK[1:30],
11  KM[1:30],
12  DIFF[1:1000], THULT[1:30], TEMPC[1:30], TT[1:1000];
13  "PROCEDURE" FINISH;

   Lines 16-27 of KINFUN.

26  "PROCEDURE" CHECK;
27  "BEGIN"
28  "IF" G[V]=0 "THEN" "GOTO" ROBIN;
29  "IF" G[I]=0 "THEN" "GOTO" ROBIN;
30  GA:=GLV-(0.1*GEVJ);
31  "IF" G[I]<0 "THEN" "BEGIN"
32  "PRINT" ":L:CONDUCTANCE OUT OF SEQUENCE AT I=";
33  SAMELINE,SCALLED(5),I,"S4",T[I];
34  G[I]:=0;
35  G[V]:=0;
36  TE:=TE+1;
37  "END";
38  "END" CHECK;
39  "PROCEDURE" SELECT;
40  "BEGIN"
41  MM:=MM+1;
42  SS[MM]:=SS[MM]+1;
43  "IF" SS[MM]<SK[MM] "THEN" G[I]:=0;
44  "IF" SK[MM]<SS[MM] "THEN" SS[MM]:=0;
45  "IF" MM=N "THEN" MM:=0;
46  "END" SELECT;
47  "PROCEDURE" LSQR;
48  "BEGIN"
49  JA:=0;
50  POOLE;
51  JA:=JA+1;
52  A:=0;
53  B:=0;
C := 0;
Q := 0;
PRINT "' 'LSORSTART';
PRINT "' 'L'V='SAMELINE;SCALED(9),V;
JJ := 1;
FOR W := 1 "STEP" 1 "UNTIL" V "DO"
BEGIN
IF Y[W] = 0 "THEN" "GOTO" Kanga;
END;
PRINT "' 'LSORT";
PR I NT '/7' V ; SAMELINE;SCALED(9)
FOR W := 1 "STEP" 1 "UNTIL" 10 "DO"
BEGIN
IF W < 6 "THEN" "BEGIN"
PRINT "' 'LSOR CUT OUT RESTART';
FOR I := 1 "STEP" 1 "UNTIL" V "DO"
IF Y[I] = W "THEN" "GOTO" OTTAWA;
END;
PRINT "' 'LSQ';
PRINT SAMELINE;SCALED(9),W,"'S3''A,'''S3''B,'''S3''C,
' 'S3'',D;
PRINT "' 'GRAD;'(A*B-Q*D)/(Q*D-A*A);
PRINT "' 'INT;'(D*B-A*C)/(Q*D-A*A);
END;
PRINT "' 'LIMS';
PRINT "' 'DATA INPUT VIA TAPE';
PRINT "' 'NUMBER OF CELLS=',SAMELINE;SCALED(9),N;
FOR W := 1 "STEP" 1 "UNTIL" V "DO"
IF Y[W] = 0 "THEN" "GOTO" DORCH;
Y[W] := GRAD*WC + INT;
AC := 100*(ACS(YC-YCW3))/YCW3;
FOR W := 1 "STEP" 1 "UNTIL" V "DO"
IF JJA = 4 "THEN" "GOTO" EVGTON;
GOTO POOLE:

Lines 102-115 of KINFUN.
FOR M:=1 "STEP" 1 "UNTIL" N "DO"
BEGIN
READ TEMP[M], TMULT[M];
READ SK[M];
PRINT "'L',SAMELINE,SCALED(9),TEMP[M],'S5',TMULT[M]
PRINT SAMELINE,SCALED(9),,'S5',SK[M];
END;
FOR I:= 1 "STEP" 1 "UNTIL" 8000 "DO" "BEGIN"
READ T[I];
IF Ti<0 "THEN" FINISH;
IF I>1 "THEN" "BEGIN"
V:=I-1;
W:=(T[I]-T[V])/TS;
IF W>1 "THEN" "BEGIN"
FOR Z:=2 "STEP" 1 "UNTIL" W "DO" "BEGIN"
TCI:=TCI+TS*(Z-1) - .....
TE:=TE+1;
END;
FOR Z:=1 "STEP" 11 "UNTIL" 10 "DO" "BEGIN"
IF ZZ=I "THEN" GOTO FISH;
V:=2;
IF GA=0 "THEN" "GOTO" BILL;
IF GB=0 "THEN" "GOTO" BILL;
GOTO HEN;
BILL:
V:=4;
GA:=TT(V);
V:=1;
GB:=TT(V);
IF GA=0 "THEN" "GOTO" BILL;
IF GB=0 "THEN" "GOTO" BILL;
GOTO HEN;
Q:=ENTIER(TH/(GB-GA));
FISH:
RQ:=Q;

Lines 143-199 of KINFUN.
Q:=ENTER(Q+(Q/10));
PRINT ""L"",SAMELINE,SCALED(9),RQ,"'S3'",Q;
V:=0;
HOP:=SK[M]*N;
FOR Z:=O "STEP" HOP "UNTIL" J "DO"
BEGIN
V:=V+1;
I:=HOP*ENTER(J/(2*HOP))*M-Z+
HOP*ENTER((3*Q)/(2*HOP))-N*(SK[N]-1);
PRINT ""L",SAMELINE,SCALED(9),I,"'S2'",T[I];
IF I>J "THEN" BEGIN
PRINT ""L",DATA ORUN;""PRINT SAMELINE,SCALED(9),RQ,"'S2'",YCV,J;
IF V>RQ "THEN" GOTO CAT;
END;
GOTO ROO;
END;
GA:=G[I];
PRINT SAMELINE,SCALED(9),"'S2'",G[I];
I:=HOP*ENTER(J/(2*HOP))*M-Z-N*(SK[N]-1);
IF G[I]=0 "THEN" BEGIN
YCV:=0;
GOTO ROO;
END;
IF I<1 "THEN" BEGIN
PRINT ""L",DATA ORUN;""PRINT SAMELINE,SCALED(9),"'S2'",T[I],"'S2'",G[I];
IF V>G[A] "THEN" BEGIN
YCV:=0;
GOTO ROO;
END;
YCV:=LN(GA-GB);
ROO:
T[V]:=TMULT[M]*T[I];
PRINT SAMELINE,SCALED(9),"'S2'",T[V],"'S2'",YCV;
IF V=RQ "THEN" GOTO CAT;
END;
GOTO ROO:
END;
"GOTO" CAT;
NOTE: I=0.69/kM[ZZ];
END;
RAT:

"PRINT" "L'******CALCULATED RATE CONSTANT=";

SANLINE,SCALED(9),KM([Z]),"S6",Z;

"PRINT" "L' NUMBER OF POINTS=";

SANLINE,SCALED(9),V;

"PRINT" "L'CELL=";

SANLINE,SCALED(9),M;

THH:=THH;

"PRINT" "L'HALFLIFE(SECONDS)=";SANLINE,SCALED(9),THH;

THH:=THH/60;

"PRINT" "L'HALFLIFE(MINUTES)=";SANLINE,SCALED(9),THH;

THH:=THH/60;

"PRINT" "L'HALFLIFE(HOURS)=";SANLINE,SCALED(9),THH;

"PRINT" "L'COMPARISON OF Y-INPUT AND Y-BESTFIT VALUES","L";

"PRINT" "S13'TIME','S15'Y','S15'YCALC','S14'DIFF','L";

DEVSQ:=0;

Q:=0;

A:=0;

"FOR" W:=1 "STEP" 1 "UNTIL" V "DO"

"BEGIN"

Q:=Q+1;

"IF" V(W)=0 "THEN" "BEGIN"

Q:=Q-1;

A:=A+1;

"GOTO" TOAD;

"END";

YCALC(W):=(GRAD*TT(W))INT;

DIFF [W]:= Y(W)-YCALC(W);

"PRINT" "$15',Y',YCALC(W)',S3',DIFF [W]';

TOAD;

"END";

DEVSQ:=DEVSQ+DIFF [W]?;

GOT0 TOAD;

"PRINT" "$15'ROOT MEAN SQUARE DEVIATION=';SANLINE,SCALED(9),DEVSQ;

"PRINT" "$15'NO OF POINTS=';

SAMLINE,SCALED(9),V,'S'MINUS POINT JUMPS=';

SAMLINE,SCALED(9),A;

KR:=0;

OTTAWA;

"END";

OHL;

"END";

M;

CODE;

TOTAL

FUN;

RABBIT

DRC
LISTING OF HOPE.

ASSIGN:5:DC:9;HOPE,EG;
SWCP
BATCH

SALGOL;
LIBRARY
ALGOL

LIST;

1  HOPE;
2  "BEGIN"
3  "INTEGER"I,N,M,J,V,W,Z,
4  TE,HOP,MM,JJ,WW,JA,FJ,ZH;
5  "REAL."
6  SS,
7  GA,RA,
8  TA,TC,
9  TS;
10  "ARRAY" T,G[1:8000],
11  SS,SK[1:30],
12  TMULT,TEMP[1:30],
13  TT,P[1:3000];
14
15  "PROCEDURE" FINISH(MIKE);
16  "LABEL" MIKE;
17  "BEGIN"
18  J:=I-1;
19  "PRINT" '"L TOTAL NUMBER OF POINTS,J=','SAMLINE,
20  SCALED(9),J;
21  V:=I-1;
22  "FOR" I:=J+1 "STEP" 1 "UNTIL" 8000 "DO"
23  "BEGIN"
25  "END";
26  "PRINT" '"L TAPE ERRORS=','SAMLINE,
27  SCALED(9),TE;
28  "GOTO" MIKE;
29  "END" FINISH;
30
31  "PROCEDURE" CHECK(NUT);
32  "LABEL" NUT;
33  "BEGIN"
34  "IF" G[V]=0 "THEN" "GOTO" NUT;
35  "IF" G[I]=0 "THEN" "GOTO" NUT;
36  GA:=G[V]-(0.1*G[V]);
37  "IF" G[I]<GA "THEN" "BEGIN"
38  "PRINT" '"L CONDUCTANCE OUT OF SEQUENCE AT I=','
39  SAMLINE,SCALED(9),I,','S4',',T[1];
G[I]:=G[V]:=0;
TE:=TE+1;
"END";
"END"CHECK;
"PROCEDURE" SELECT;
"BEGIN"
MM:=MM+1;
SSCM3:=SSCM3+1;
"IF" SSCM3<SKCMM "THEN" G[I]:=0;
"IF" SKCMM=SSCM3 "THEN" SSCM3:=0;
"IF" MM=N "THEN" MM:=0;
"END"SELECT;

"PROCEDURE" INVMX(B);
"ARRAY" B;
"BEGIN"
"REAL" MAX, EPS;
"INTEGER" SS, L, V; Z; R;
R:=3;
EPS:=2.0*10^-37;
"BEGIN"
"INTEGER" "ARRAY" RR, BR[C1:R];
"FOR" SS:=1 "STEP" 1 "UNTIL" R "DO"
"BEGIN"
MAX:=0;
"FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
"BEGIN"
"FOR" V:=1 "STEP" 1 "UNTIL" SS-1 "DO"
"IF" ABS(MAX)-ABS(BCL[V]) "LE" 0 "THEN"
"PRINT" "'L' INVMX ERROR'; STOP;
STOP;
"END"
"END"
V:=BR[C3];
"FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
BCL[L]:="IF" L=V "THEN" 1 "ELSE" 0;
"FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
"BEGIN"
MAX:=BCL[L];
"IF" L<>V "THEN" "FOR" Z:=1 "STEP" 1 "UNTIL" R "DO"
BCL[Z]:=BCL[Z+1]/MAX;
"END"
"END";
"FOR" Z:=1 "STEP" 1 "UNTIL" R "DO"
RA[Z]:=Z;
"END"
"BEGIN"
"IF" i=1 "THEN" "BEGIN"
PO:=P[i];
"IF" T[i]>=20 "THEN" INC:=T[i];
"END";
"IF" T[i]<INC "THEN" "BEGIN" PO:=P[i];
INC:=T[i];
"END";
"IF" T[i] > LARGET "THEN" "BEGIN"
SI := I;
LARGET:=T[i];
"END";
K:=2/LARTAG;
PINF:=1.25*P[S]+0.25*PO;
"IF" INC>20 "THEN" "BEGIN"
"FOR" I:=1 "STEP" 1 "UNTIL" N "DO" T[i]:=T[i]-INC;
"END";
"PRINT" "L2'CYCLE RATE CONSTANT INFINITY', SAMELINE, 'S6'ZERO', 'S7'NEW SUM', 'S5'OLD SUM', 'L';
"PRINT" 'S7'SECONDS(-1) READING', 'S6' READING (SQUARES OF RESIDUALS), 'L';
L1:
E[13]:=E[23]:=E[33]:=SDEL:=0;
"FOR" I:=1 "STEP" 1 "UNTIL" 3 "DO"
"FOR" J:=1 "STEP" 1 "UNTIL" 3 "DO" A[i,j]:=0:
"BEGIN"
S:=EXP(-K*T[i]);
DPDK:=T[i]*S*(PINF-PO);
DPDINF:=1-S;
ALP,1]):A[1,1]]+DPDK*DPDINF;
AC,2,3]:=[AC,3,3]+DPDINF*DPDINF;
AC,3,1]:=[AC,1,3]+DPDINF*DPDINF;
AC,2,3]:=[AC,3,1]+DPDINF*DPDINF;
DELTA:=P[i]-PCALC(PINF,K,T[i],PO);
SDEL:=SDEL+DELTA*DELTA;
E[23]:=E[23]+DELTA*DPDK;
E[33]:=E[33]+DELTA*DPDK;
END";
"ELSE" "PRINT" SAMELINE, SCALED(9), CYCLE, 'S5', K, 'S3', PINF, 'S2', PO, 'S3',
SDEL, 'S3', 'L';
"ELSE" "PRINT" SAMELINE, SCALED(9), CYCLE, 'S3', K, 'S3', PINF, 'S2', PO, 'S2', SDDEL, 'S3', 'L';
INVX(A);
"FOR" I:=1 "STEP" 1 "UNTIL" 3 "DO"
"FOR" J:=1 "STEP" 1 "UNTIL" 3 "DO"
BEGIN"
"IF" J<i "THEN" A[I, J]:=A[J, I];
"END";
CYCLE := CYCLE+1;
"IF" ABS(SDEL-SSDEL) "LE" -.6 "THEN" "GOTO" EXIT;
"IF" SDEL < SSDEL "THEN" "BEGIN"
STK := K;
STINF := PINF;
STP0 := PO;
SSDEL := SDEL;
"END";
K := K+DELK;
PINF := DELINF+PINF;
PO := PO+DELPO;
"IF" CYCLE=51 "THEN"
"PRINT" ""L2" PROGRAM TERMINATED AFTER 50 CYCLES'',''L2'';
"IF" CYCLE=51 "THEN" "GOTO" EXIT;
"GOTO" L1;
EXIT:
"PRINT" ''L4'POINT'',''S5'TIME'',''S8'CALCULATED'',
SAMELINE,''S6'ERROR'',''L'';
"PRINT'' ''S8'(SECONDS)'',''S5'READING','SAMELINE,
''S8'READING'',''S6'IN READING'',''L2'';
"FOR'' I:=1 "STEP'' 1 "UNTIL'' N ''DO''
"BEGIN";
ST := SCALC(STINF,STK,TL13,STP0);
"PRINT'' ''L4'ESD(OBSERVATION)'=''SAMELINE,
SCALED(9),SQRT(SSDEL/(N-3));
"PRINT'' ''L''=''S9'RATE CONSTANT=''SAMELINE,
SCALED(9),STK,
'',''S5'','
''S'SECOND(-1)'';
"PRINT'' ''L'ESD(RATE CONSTANT)=''SAMELINE,
SCALED(9),SQRT(A[2, 1]*SSDEL/(N-3))),''S'SECOND(-1)'';
"PRINT'' ''L'CALCULATED INFINITY READING=''SAMELINE,
SCALED(9),STINF;
"PRINT'' ''L'ESD(INFINITY)=''SAMELINE,
SCALED(9),SQRT(A[2, 2]*SSDEL/(N-3))),''L2'';
FINISH:
"END"FORWIN;

"PROCEDURE" TIME;
"BEGIN"
"FOR'' I:=1 "STEP'' 1 "UNTIL'' 8000 ''DO''
TL13 := TS*TL13;
"END''TIME;

"PROCEDURE" SETUP;
"BEGIN"
FJ := 0;
HOP := N*SK[M];
"FOR'' I:=M "STEP'' HOP "UNTIL'' J ''DO''
"BEGIN"
FJ := FJ+1;
"IF'' TL13=0 ''THEN'' "BEGIN"
FJ := FJ-1;
"GOTO'' PARIS;
"END";
T[I]:=T[I];
"IF" G[I]<0 "THEN" "BEGIN"
FJ:=FJ-1;
"GOTO" PARIS;
"END";
PFJ1:=G[I];
PARIS:
"END";
"PRINT" '"L.NUMBER OF POINTS='$,SAMELINE,
SCALED(9),FJ;
"END"SETUP;
"PRINT" '"F.ANALYSIS OF DATA BY FORWINS';
"BEGIN"
"PRINT" '"L.M.J.BLANUAMER.***DATA INPUT VIA TAPE';
READER(1);
"READ" N;
"PRINT" '"L.NUMBER OF CELLS='$,SAMELINE,SCALED(9),N;
"READ" TS;
"FOR" M:=1 "STEP" 1 "UNTIL" N "DO"
"BEGIN"
"READ" TEMP[M], TMULT[M];
"READ" SKM[M];
"PRINT" '"L',SAMELINE,SCALED(9),TEMP[M],"S5",TMULT[M]
"PRINT" SAMELINE,SCALED(9),"S5",SKM[M];
"END";
"FOR" I:=1 "STEP" 1 "UNTIL" 8000 "DO" "BEGIN"
"READ" T[I];
"IF" T[I]<0 "THEN" FINISH(MIKE);
"IF" I>1 "THEN" "BEGIN"
V:=I-1;
W:=(T[I]-T[I])/TS;
"IF" W>1 "THEN" "BEGIN"
"FOR" Z:=2 "STEP" 1 "UNTIL" W "DO" "BEGIN"
I:=V+Z-1;
T[I]:=T[I]+TS*(Z-1);
G[I]:=0;
TE:=TE+1;
SELECT;
"END";
TA:=T[I];
I:=I+1;
T[I]:=TA+TS;
"END";
"END";
MOO:
"READ" G[I];
"IF" G[I]<0 "THEN" FINISH(MIKE);
TC:=T[I]+TS;
"IF" G[I]=TC "THEN" "BEGIN"
G[I]:=0;
SELECT;
I:=I+1;
TC:=TC;
"READ" G[I];
"GOTO" FARM;
"END";
"READ" RA;
"IF" RA=TC "THEN" "BEGIN"
G[I]:= 0;
SELECT;
I:=I+1;
T[I]:=TC;
TC:=T[I]+TS;
"GOTO" M00;
"END";
"IF" RA<0 "THEN" FINISH(MIKE);
"IF" RA=1 "THEN" G[I]:= G[I]*10(-7);
"IF" RA=2 "THEN" "BEGIN"
G[I]:=0;
"GOTO" ROBIN;
"END";
"IF" RA=3 "THEN" G[I]:=G[I]*10(-(5));
"IF" RA=4 "THEN" G[I]:=G[I]*10(-(4));
"IF" RA=5 "THEN" G[I]:=G[I]*10(-(3));
"IF" RA=6 "THEN" G[I]:=G[I]*10(-(2));
"IF" RA=7 "THEN" G[I]:=G[I]*10(-(1));
"IF" RA>7 "THEN" "BEGIN"
G[I]:=0;
"PRINT" '"L'RA>7-TAPE ERROR AT I=',
SAMEINE;SCAPE(9),',',S4''',T[I];
TE:=TE+1;
"END";
"IF" I>N "THEN" "BEGIN"
V:=I-N;
CHECK(NUT);
"END";
"IF" I>(2*N) "THEN" "BEGIN"
V:=I-2*N;
CHECK(NUT);
"END";
ROBIN;
NUT;
SELECT;
MIKE:
"FOR" M:=1 "STEP" 1 "UNTIL" N "DO"
"BEGIN"
"PRINT" '"L'TEMPERATURE='',SAMEINE,
SCAPED(9),T[M];
SETUP;
FORIN(M,FJ,TT,P);
"END";
"END";
"END";
END;
MC
TOTAL
TIME = 0001 20
Listing of STEVE.

AL501;  "BEGIN"
L01;  "INTEGER" \[;\] J, W, JA, TE, QQ, M, FJ, WW, V, VV, CONT, K, NC;
"REAL" TS, TNEW, DIFF, TH, TM, TC, DUMMY;
"ARRAY" T[1:1500], G[1:4, 1:1500];
"PROCEDURE" SETUP;
"BEGIN"
FJ := 0;
"FOR" I := 1 "STEP" 1 "UNTIL" K "DO"
"BEGIN"
FJ := FJ + 1;
"IF" T[I] = 0 "THEN" "BEGIN"
FJ := FJ - 1;
"GOTO" PARIS;
"END";
T[I] := T[I];
"IF" GL[I] = 0 "THEN" "BEGIN"
FJ := FJ - 1;
"GOTO" PARIS;
"END";
PC[FJ] := G[M, I];
PARIS;
"END";
"PRINT" 'NUMBER OF POINTS=', SAMELINE, SCALED(9), FJ;
"PROCEDURE" INVGMX(B);

Lines 59-130 of HOPE.

"REAL" "PROCEDURE" PCALC(PPIINF, KK, TT, PPO);
Lines 134-139 of HOPE.

"PROCEDURE" FORWIN(LABEL, N, T, P);
Lines 142-263 of HOPE.
"PROCEDURE "TIME;\nBEGIN\nIF TC[I]=0 THEN QQ:=QQ+1;\nTC[I]:=TC[I]+QQ=2400;\nTC:=TC[I];\nTH:=ENTER(TC/100);\nTM:=TC-(100*TH);\nTH:=0*TH;\nTM:=TM+TH;\nTC[I]:=60*TM;\nTC[I]:=TC[I]-3540;\n"END" "TIME;\n\n"PROCEDURE "RUN-END(FRED);"LABEL "FRED;\nBEGIN\nIF T[I]<0 THEN "BEGIN\nK:=I-1;\nPRINT ''L2' NUMBER OF POINTS < ', SAMELINE, SCALED(9), K; "GOTO" FRED;\n"END" "END;\n\n"PROCEDURE "TIMECHECK;\nBEGIN\nIF I>1 THEN "BEGIN\nV:=I-1;\nIF TC[I]=T[V]+TS "THEN" "GOTO" ABLE;\nPRINT ''L TIMEOUT*=', SAMELINE, SCALED(9); I;\nTC[I]:=0;\nFOR JA:=1"STEP"1"UNTIL"NC"DO" (\nG[V,1]:=0;\nDIFF:=T[V]+2*TS;\nI:=I+1;\nMIAMI;\nRUN-END(FRED);\nTIME;\nIF TC[I]=DIFF "THEN" "GOTO" USA;\nGOTO"MIAMI;\nUSA;\nPRINT''L'' SAMELINE, SCALED(9), I, ''55'', TC[I]; ABLE;\nEND" "END" TIMECHECK;\n\n"PROCEDURE "ADJUST(CHARLIE);"LABEL "CHARLIE;\nBEGIN\nFOR W:=J "STEP" 1 "UNTIL," NC "DO" G[W,1]:=0;\nWW:=1-1;\nFOR W:=J "STEP" -1 "UNTIL" 1 "DO" "BEGIN\nIF G[W,WW]=TC[I]-TS "THEN\nGOTO" VICTOR; GLW,WW:=0; "END" VICTOR;\nPRINT ''L' OUT OF SEQUENCE *I=', SAMELINE, SCALED(9), I;\nI:=I+1;\nT[C,1]:=TNEW;"GOTO"CHARLIE;"END;\n\n"PROCEDURE "SCANOUT;\nBEGIN\nPRINT ''L'\'ABSORBANCE OUT OF SEQUENCE', SAMELINE, SCALED(9), I, ''S6'', J;\nEND;"
"PROCEDURE" CHECK;
"BEGIN"
"FOR" I:=1 "STEP" 1 "UNTIL" NC "DO"
"BEGIN"
"FOR" J:=2 "STEP" 1 "UNTIL" K "DO" "BEGIN"
JA:=J-1;
"IF" G[I,JA]=0 "THEN" "GOTO" MEXICO;
DIFF:=ABS(G[I,J]-G[I,JA]);
"IF" DIFF>50 "THEN" "BEGIN"
G[I,J]:=0;
TE:=TE+1;
SCANOUT;
"END";
MEXICO:
"END";
"END";
"END";
"PRINT" '"ANALYSIS FOR RATE DATA FROM SPECTRA';
"PRINT" '"L'UNIVERSITY OF LEICESTER***M, J, BLANDAMER';
"PRINT" '"L 'DATA FROM TAPE +CARDS';
"PRINT" '"L'SYSTEM';
"PRINT" '"L"';
"BEGIN"
READ NC;
"READ" NS;
"PRINT" '"L'NO. CELLS=',SAMELINE,SCALED(9),NC;
"PRINT" '"L'TS=',SAMELINE,SCALED(9),TS;
"BEGIN"
M I := 0;
READER (1);
"PRINT" '"L'TAPE NOW INPUT';
BAKER:
I:=I+1;
"READ" T[I];
TIME:
TNEW:=T[I]+TS;
CHARLIE:
RUNEND(FRED);
TIMECHECK:
"FOR" J:=1 "STEP" 1 "UNTIL" NC "DO" "BEGIN"
"READ" G[J,I];
"IF" G[J,I]=TNEW "THEN" ADJUST(CHARLIE);
"END";
"GOTO" BAKER;
"END";
FRED:
"PRINT" '"L'TAPE SUMMARY';
"FOR" I:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
"PRINT" SAMELINE,SCALED(9),T[I], '"SS'';
"FOR" W:=1 "STEP" 1 "UNTIL" NC "DO" "BEGIN"
"PRINT" SAMELINE,SCALED(9),G[W,I];
"END";
"PRINT" '"L'';
"END";
"END";
CHECK;
"COMMENT" INPUT K READINGS FOR NC CELLS;
"FOR" M:=1 "STEP" 1 "UNTIL" NC "DO"
"BEGIN"
SETUP;
FORWIN(M.FJ,TT,P);
"END";
"END" STEVE;
MC
CODE
TOTAL
Listing of ROGUE.

1 ROGUE;
2 "BEGIN"
3 "INTEGER" I,J,N,J,N,TE,M,F,J,WW,V,
4 VV,CONT,K,NC;
5 "REAL" TS,TH,DIFF,TH,TM,
6 TC,DUMMY;
7 READER(1);"READ" NC,TS;"BEGIN"
8 "ARRAY" T[1:1500],G[1:NC,1:1500],TT,PCI[1:1500];
9
10 "PROCEDURE" SETUP;
11 "BEGIN" FJ:=0;
12 "FOR" I:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
13 "IF" I<4 "THEN" "GOTO" HELC;
14 FJ:=FJ+1; T[I,FJ]:=T[I]; P[FJ]:=G[M,I];
15 HELC:
16 "END"; "PRINT" ("NUMBER OF POINTS=",SAMELINE,
17 SCALED(9),FJ; "END"SETUP;
18
19 "PROCEDURE" INVMX(Q);

Lines 59-130 of HOPE.

60 "REAL","PROCEDURE" PGACL(PPINF,KK,TT,PPQ);

Lines 134-139 of HOPE.

64 "PROCEDURE" FOR4IN(LAREL,N,T,P);

Lines 142-243 of HOPE.
144 "PROCEDURE"RUNEND(FRED);"LABEL"FRED;"BEGIN"
145 "IF"GCJ,11=9999"THEN""BEGIN"K:=I-1;
146 "PRINT""L2'NUMBER OF POINTS=',SAMELINE,SCALED(9),K;
147 "GOTO"FRED;"END";"END"
148
149 V:=10;
150 "PRINT""F'ANALYSIS FOR RATE DATA FROM SPECTRA'
151 "PRINT""L'UNIVERSITY OF LEICESTER**M.J.BEANAMER'
152 TE:=0;"PRINT""L'SYSTEM'""BEGIN"
153 NC,'NUMBER OF CELLS=',SAMELINE,SCALED(9),
154 "PRINT""L'TS='SAMELINE,SCALED(9),TS;"BEGIN"
155 I:=0;BAKER:I:=I+1;TC1:=TS+1;CHARLIE;
156 "FOR"J:=1"STEP"1"UNTIL"NC"DO""BEGIN"
157 v:=v+10;
158 "END"
159 "READ"GCJ'I1;
160 RUNEND(FRED);
161 "IF"GCJ,I1<200"THEN""GOTO"DAR;
162 "IF"I>v"THEN""BEGIN"
163 V:=V+10;
164 "END"
165 "END";"GOTO"BAKER;"END";FRED;
166 "END";
167 "FOR"M:=1"STEP"1"UNTIL"NC"DO""BEGIN"SETUP;
168 FORWIN(M,FJ,TT,P);"END";"END";"END"ROGUE;
169 MC
1712 CODE
2422 TOTAL

&RUN
ROGUE
DHO
Listing of PDP 11 program.

5 CLOSE3
6 OPEN"KB:"ASFILE3
8 REM K-ORS CALCULATION FOR J.O.C.
10 DIMX(30),Y(30)
11 LET S1=0:LET S2=0:LET S3=0:LET S4=0
12 LET D=0
13 PRINT "UNIT TIME VALUE=";
14 INPUT #3,Q
15 PRINT "NO. OF POINTS=";
16 INPUT #3,N
18 FOR I=1 TO N
19 LET X(I)=I
21 PRINT"Y(";I")=";
22 INPUT #3,Y(I)
23 NEXT I
24 PRINT"RANGE OF INF +STEP=";
25 INPUT P,R,O
27 FOR W=P TO R STEP O
29 PRINT "INF=";W
30 FOR I=1 TO N
32 LET X=X(I)
33 LET Y=Y(I)
35 LETY=LOG(Y-W)
36 LETS1=S1+X
37 LET S2=S2+Y
38 LET S3=S3+X*Y
39 LET S4=S4+X*X
40 NEXT I
41 LETC=1/(N*S4-S1*S1)
42 LETA=(N*S3-S1*S2)*C
43 LETR=(S1+S2-S1*S3)*C
44 FOR I=1 TO N
45 LET D2=A*X(I)+B-LOG(Y(I)-W)
46 LET D=0+D2*D2
47 NEXT I
48 LETD=0*C/(N-2)
49 PRINT"RATE CONSTANT=",A/Q
50 PRINT "STANDARD ERROR=",SQR(N*D)/Q
51 PRINT "Z ERROR=",SQR(N*D)/(1-A)*100
52 LET S1=0:LET S2=0:LET S3=0:LET S4=0:LET D=0
53 NEXT W
54 REM FINITE RANGE!!!!!
55 GOTO24
56 STOP

READY
Listing of TEMPAN.

1 TEMPAN:
2 "BEGIN"
3 "INTEGER" I,N,M,O,S,Z,ZZZ,ZZZZ,V,W;
4 "REAL" THEA,DTHEA,AUSA,USA,SUSA,SUSB,USA,SUSB,USSSU,USSSU,
5 BO,DP,KRTHCA;
6 USSE,USNE,USNE,USIE,USNE,USNE,USNE,USIE,USNE,USNE,USIE,
7 USIE,USIE,USIE,USIE,USIE,USIE,USIE,USIE,USIE,USIE,USIE,
8 USIE,USIE,USIE,USIE,USIE,USIE,USIE,USIE,USIE,USIE,USIE,
9 CONS,CONS,CONS,CONS,CONS,CONS,CONS,CONS,CONS,CONS,CONS,
10 UKR,LUKB;
11 RVAR,VARDH,VARDCP,VARDDCP,VARD,RVARDCP,VARDD,RVARDCP,DHR,
12 DCP,TST,DCPT,DCP,TST,DCPT,KRCA,KRTHCA;
13 Q=0.5=5;
14 "READ" N;
15 "READ" THEA;
16 "READ" DAT;
17 "READ" Z;
18 "READ" ZZZ;
19 "READ" ZZ;
20 "READ" ZZ;
21 "BEGIN"
22 "ARRAY" KI,KG,KRC,
23 YC,
24 KGCA,KY,CALC,TA,UA,UE,UO,UE(1:N),AI(1:0,1:S),
25 BCI:0.1:1,5+1,CI:0.1:51;
26 "READ" DTHEA;
27 "PRINT" "'F ', CLARKE AND GLEW ANALYSIS OF RATE DATA AND DERIVATION"
28 OF PSEUDO THERMODYNAMIC FUNCTIONS';
29 "PRINT" "'L2', SYSTEM';
30 "PRINT" "'L2', TEMPERATURE RANGE FOR MEASURED RATE CONSTANTS= ';
31 "FOR" I:=1 "STEP" 1 "UNTIL" N "DO"
32 "BEGIN"
33 "READ" KRC(I), T(I);
34 "END"
35 "PRINT" "'L2', ANALYSIS USING TWO CONSTANT EQUATION';
36 "GOTO" DAN;
37 "END"
38 "IF" ZZ=0 "THEN" "BEGIN"
39 ZZZ:= ZZ; ZZZ:= Z;
40 W:=1;
W:=2;
"PRINT" '12', ANALYSIS USING THREE CONSTANT EQUATION';
"GOTO" DAN;
"END";
"IF" ZZZ=0 "THEN" "BEGIN"
ZZZ:=0;
W:=3;
"PRINT" '12', ANALYSIS USING FOUR CONSTANT EQUATION';
"GOTO" DAN;
"END";
"IF" ZZZ=0 "THEN" "BEGIN"
ZZ:=4;
W:=5;
"PRINT" '12', ANALYSIS USING FIVE CONSTANT EQUATION';
"GOTO" DAN;
"END";
"IF" ZZZ=1 "THEN" "BEGIN"
W:=5;
"PRINT" '12', ANALYSIS USING SIX CONSTANTS';
"GOTO" DAN;
"END";
DAN:
"FOR" i:=1 "STEP" 1 "UNTIL" N "DO"
"BEGIN"
KGE[I]:=(KRE[I]/T[I])*(6.626196/(1.380622*10**11));
Y[C]:=0.31434*LH(KGL[I]);
X[C]:=T[C]*THETA/THETA;
"END";
"FOR" i:=1 "STEP" 1 "UNTIL" N "DO"
"BEGIN"
USSA:=0;
USR:=0;
USSC:=0;
USD:=0;
USE:=0;
V:=0;
JIL:=V:=V+1;
USA:=(-X[C][I]+(V-1))*(V/(V+1));
USSA:=USSA+USA;
"IF" ABS(USA/USSA)>1**-12 "THEN" "GOTO" JIL "ELSE"
USC[I]:=X[C][I]*USSA;
V:=0;
"IF" Z=0 "THEN" "BEGIN"
UCC[I]:=USC[I]:=001.13:=UEC[I]:=0;
"GOTO" PETE;
"END";
LIZ:=V:=V+1;
USB:=((-X[C][I]+(V-1)))*(V/(V+1));
USB:=USB+USB;
"IF" ABS(USB/USB)>1**-12 "THEN" "GOTO" LIZ "ELSE"
UB[C][I]:=USB*(X[C][I]*2);
V:=0;
"IF" ZZ=0 "THEN" "BEGIN"
UC[I]:=001:=UEC[I]:=0;
"GOTO" PETE;
"END";
MII:=V:=V+1;
USC:=((-X[C][I]+(V-1)))*(V/(V+2));
USC:=USC+USC;
"IF" ABS(USC/USC)>1**-12 "THEN" "GOTO" MIK "ELSE"
UCC[I]:=USC*(X[C][I]*3);
V:=0;
"IF" ZZZ=0 "THEN" "BEGIN"
UEC[I]:=UEC[I]:=0;
"GOTO" PETE;
"END";
MAR: V := V + 1;
USD := ((-XI) * (V-1)) * (V/(V+3));
USD := USD + USD;
IF "ABS(USD/US)// > 1 then "GOTO" MAR "ELSE"
UC[I] := 0; USD := (XI) * (X[I]+4);
V := 0;
"IF" ZL := 0 "THEN" "BEGIN"
MAR[1] := 0;
"GOTO" PETE;
"END";
BRI: V := V + 1;
USC := ((-XI) * (V-1)) * (V/(V+4));
USD := USD + USL;
IF "ABS(US2/US3) > 1 then "GOTO" BRI "ELSE"
UC[I] := (US2 + US3);
"BEGIN";
IF "A" = "G" then "ENDIF"
MAR[I] := 0; X := X[I] + 1;
"IF" ZS := 0 "THEN " "IF"
MAR[1] := 0; "ENDIF"
"FOR" I := 1 "STEP" 1 "UNTIL" N "DO"
"BEGIN"
UAM := UAM * UC[I];
UMN := UMN * UD[I];
UCN := UCM + UC[I];
UDM := UDM + UD[I];
UEM := UEM + UE[I];
YM := YM + YL[I];
"ENDIF"
UAM := UAM / N;
UMN := UMN / N;
UCN := UCN / N;
UDM := UDM / N;
UEM := UEM / N;
YM := YM / N;
"BEGIN"
UAM := UAM / N;
UMN := UMN / N;
UCN := UCM / N;
UDM := UDM / N;
UEM := UEM / N;
YM := YM / N;
"FOR" I := 1 "STEP" 1 "UNTIL" N "DO"
"BEGIN"
A[I, 1] := AL, 1 + ((UL1-UAM) + 2);
A[I, 2] := AL, 2 + ((UL2-UAM) + (UL1-UAM));
A[I, 3] := AL, 3 + ((UL2-UAM) + (UL1-UAM));
AL, 4 := AL, 4 + ((UL2-UAM) + (UL1-UAM));
AL, 5 := AL, 5 + ((UL2-UAM) + (UL1-UAM));
AL, 6 := AL, 6 + ((UL2-UAM) + (UL1-UAM));
AL, 7 := AL, 7 + ((UL2-UAM) + (UL1-UAM));
AL, 8 := AL, 8 + ((UL2-UAM) + (UL1-UAM));
AL, 9 := AL, 9 + ((UL2-UAM) + (UL1-UAM));
ALA := AL1,1 + ((UL1-UAM) + 2);
AL2, 1 := AL2, 1 + ((UL1-UAM) + 2);
AL2, 2 := AL2, 2 + ((UL2-UAM) + (UL1-UAM));
AL2, 3 := AL2, 3 + ((UL2-UAM) + (UL1-UAM));
AL2, 4 := AL2, 4 + ((UL2-UAM) + (UL1-UAM));
AL2, 5 := AL2, 5 + ((UL2-UAM) + (UL1-UAM));
AL2, 6 := AL2, 6 + ((UL2-UAM) + (UL1-UAM));
AL2, 7 := AL2, 7 + ((UL2-UAM) + (UL1-UAM));
AL2, 8 := AL2, 8 + ((UL2-UAM) + (UL1-UAM));
AL2, 9 := AL2, 9 + ((UL2-UAM) + (UL1-UAM));
AL3, 1 := AL3, 1 + ((UL1-UAM) + 2);
AL3, 2 := AL3, 2 + ((UL1-UAM) + 2);
AL3, 3 := AL3, 3 + ((UL1-UAM) + (UL1-UAM));
AL3, 4 := AL3, 4 + ((UL1-UAM) + (UL1-UAM));
AL3, 5 := AL3, 5 + ((UL1-UAM) + (UL1-UAM));
AL3, 6 := AL3, 6 + ((UL1-UAM) + (UL1-UAM));
AL3, 7 := AL3, 7 + ((UL1-UAM) + (UL1-UAM));
AL3, 8 := AL3, 8 + ((UL1-UAM) + (UL1-UAM));
AL3, 9 := AL3, 9 + ((UL1-UAM) + (UL1-UAM));
AL4, 1 := AL4, 1 + ((UL1-UAM) + (UL1-UAM));
AL4, 2 := AL4, 2 + ((UL1-UAM) + (UL1-UAM));
AL4, 3 := AL4, 3 + ((UL1-UAM) + (UL1-UAM));
AL4, 4 := AL4, 4 + ((UL1-UAM) + (UL1-UAM));
AL4, 5 := AL4, 5 + ((UL1-UAM) + (UL1-UAM));
AL4, 6 := AL4, 6 + ((UL1-UAM) + (UL1-UAM));
AL4, 7 := AL4, 7 + ((UL1-UAM) + (UL1-UAM));
AL4, 8 := AL4, 8 + ((UL1-UAM) + (UL1-UAM));
AL4, 9 := AL4, 9 + ((UL1-UAM) + (UL1-UAM));
AL5, 1 := AL5, 1 + ((UL1-UAM) + 2);
AL5, 2 := AL5, 2 + ((UL1-UAM) + 2);
AL5, 3 := AL5, 3 + ((UL1-UAM) + (UL1-UAM));
AL5, 4 := AL5, 4 + ((UL1-UAM) + (UL1-UAM));
AL5, 5 := AL5, 5 + ((UL1-UAM) + (UL1-UAM));
AL5, 6 := AL5, 6 + ((UL1-UAM) + (UL1-UAM));
AL5, 7 := AL5, 7 + ((UL1-UAM) + (UL1-UAM));
AL5, 8 := AL5, 8 + ((UL1-UAM) + (UL1-UAM));
AL5, 9 := AL5, 9 + ((UL1-UAM) + (UL1-UAM));
"END";
AC[1, 1] := AC[1, 2];
AC[1, 2] := AC[1, 3];
177 \[ A[4,1] := A[1,4]; \]
178 \[ A[4,2] := A[2,4]; \]
179 \[ A[4,3] := A[3,4]; \]
181 \[ A[5,1] := A[1,5]; \]
185 \[ SA := 0; \]
186 \[ SB := 0; \]
187 \[ SC := 0; \]
188 \[ SD := 0; \]
189 \[ SE := 0; \]
190 "FOR" I := 1 "STEP" 1 "UNTIL" N "DO";
191 "BEGIN";
192 SA := SA + (UAI - UAM) * (Y[i] - YM));
193 SB := SB + (UCl - UCM) * (Y[i] - YM));
194 SC := SC + (UCl - UCM) * (Y[i] - YM));
195 SD := SD + (UCl - UCM) * (Y[i] - YM));
196 SE := SE + (UCl - UCM) * (Y[i] - YM));
197 "END";
198 "PRINT" ""L",SAMELINE,SCALER(9),SA,""S2",""S6,""S2",""S6;""SE;";
199 ""S2",""S6,""S2",""S6;""SE;
200 "BEGIN";
201 "PROcedures" MXCOPY(B,A);
202 "PROcedures" INVMx(X);
203 "BEGIN";
204 MXCOPY(B,A);
205 INVMX(A);
206 "END";
212 BA := BA - (BA * UAM) - (BB * UCM) - (BC * UCM) - (BD * UCM) - (BE * UCM);
213 BB := BB - (BA * UAM) - (BB * UCM) - (BC * UCM) - (BD * UCM) - (BE * UCM);
214 BC := BC - (BA * UAM) - (BB * UCM) - (BC * UCM) - (BD * UCM) - (BE * UCM);
215 BD := BD - (BA * UAM) - (BB * UCM) - (BC * UCM) - (BD * UCM) - (BE * UCM);
216 BE := BE - (BA * UAM) - (BB * UCM) - (BC * UCM) - (BD * UCM) - (BE * UCM);
217 "PRINT" ""L",SAMELINE,SCALER(9),BA;
218 "PRINT" ""L",SAMELINE,SCALER(9),BB;
219 "PRINT" ""L",SAMELINE,SCALER(9),BC;
220 "PRINT" ""L",SAMELINE,SCALER(9),BD;
221 "PRINT" ""L",SAMELINE,SCALER(9),BE;
222 "PRINT" ""L",SAMELINE,SCALER(9),Y[i];
223 "PRINT" ""L",SAMELINE,SCALER(9),Y[i];
224 "PRINT" ""L",SAMELINE,SCALER(9),Y[i];
225 "PRINT" ""L",SAMELINE,SCALER(9),Y[i];
226 "PRINT" "L",CALCULATED RATE CONSTANTS,""L";";
227 "END";
228 "FOR" I := 1 "STEP" 1 "UNTIL" N "DO";
229 "BEGIN";
230 YC[i] := B0 + (BA * UAM) + (BB * UCM) + (BC * UCM) + (BA + UCM)
231 + (BC * UCM) + (BD * UCM) + (BE * UCM);
232 QD := 0; (+YC[i] - YC[i] + 2);
233 KRC[i] := ((YC[i] - YC[i]) + 6.526196) * EXP(YC[i] / 3.1434);
234 DCR := ((KRC[i] / KRC[i]));
235 "PRINT" SAMELINE,SCALER(9),T[i],""S4",KPC[i],""S4",KPC[i],""S4",Y[i],""S4",KR,""S4",LDRK,""L";
236 "END";
237 "PRINT" "L",RESIDUAL SUM OF SQUARES O(RLNK);
238 "BEGIN";
239 ABOUT REGRESSION FOR N OBSERVED VALUES OF RLINK=.
240 SAMELINE,SCALER(9),QD;
"PRINT" "L'NUMBER OF DATA POINTS = '', SAMELINE, SCALED(9), N;
"IF" Z=0 "THEN" "BEGIN"
IF N-2:
"PRINT" "L'DEGREES OF FREEDOM= '', SAMELINE, SCALED(9), DF;
QU=QU/(N-2);
"GOTO" JES;
"END";
"IF" ZZ=0 "THEN" "BEGIN"
IF N-3:
"PRINT" "L'DEGREES OF FREEDOM= '', SAMELINE, SCALED(9), DF;
QU=QU/(N-3);
"GOTO" JES;
"END";
"IF" ZZ=0 "THEN" "BEGIN"
IF N-4:
"PRINT" "L'DEGREES OF FREEDOM= '', SAMELINE, SCALED(9), DF;
QU=QU/(N-4);
"GOTO" JES;
"END";
"IF" ZZ=0 "THEN" "BEGIN"
IF N-5:
"PRINT" "L'DEGREES OF FREEDOM= '', SAMELINE, SCALED(9), DF;
QU=QU/(N-5);
"GOTO" JES;
"END";
"IF" ZZ=0 "THEN" "BEGIN"
"PRINT" "L'RESIDENTIAL S.D.Span square = ERROR = '', SAMELINE, SCALED(9), QU;
VARPC=VARPC/SORT(1/N);
"PRINT" "L'STANDARD ERROR SIGMA ON A SINGLE OBSERVED BLOCK= '', SAMELINE, SCALED(9), QU;
"PRINT" "L'OBSERVED ERROR = '', SAMELINE, SCALED(9), QU;
"GTHETA-=THETA^-90;
VAR=VAR/THETA=SORT(1/N);
KTHETA=E^((GTHETA/4.319368*THETA))-((THETA^1.380622a11)/0.52619);
"PRINT" "L'DELTAS AT THETA= '', SAMELINE, SCALED(9), GTHETA;
"PRINT" "L'SIM''GA'' S= '', SAMELINE, SCALED(9), VARKRA;
"PRINT" "L'RATE CONSTANT AT THETA= '', SAMELINE, SCALED(9), KTHETA;
NTHETA=(GTHETA-GTHETA)/THETA;
"PRINT" "L'DELTAS AT THETA= '', SAMELINE, SCALED(9), NTHETA;
"IF" Z=0 "THEN" "GOTO" ANN;
DCPTheta=A6;
VARDCP=VARDCP/SORT(12,2,1);
"PRINT" "L'DELTAS AT THETA= '', SAMELINE, SCALED(9), DCPTheta, ''S3'' S='', SAMELINE, SCALED(9), VARDCP;
"IF" ZZ=0 "THEN" "GOTO" ANN;
DDCPTheta=(2/THETA)^(BC);
VARDCP=VARDCP/SORT(BC,3);
"PRINT" "L'DELTAS AT THETA= '', SAMELINE, SCALED(9), DDCPTheta, ''S3'' S='', SAMELINE, SCALED(9), VARDDCP;
"IF" ZZ=0 "THEN" "GOTO" ANN;
DDDCPTheta=(6/THETA*2)^BD;
VARDDDC := QD*(6/(THETA+2))*SQRT(8[4,4]);

"PRINT" ""UDELTACP AT THETA=,SAMELINE,Scaled(9),VARDDDC;"

DOPCPHETA := "S3" := SAMELINE.Scaled(9),VARDDDC;

"IF" "THETA<0.5" "THEN" "GOT0" ANN;

DOPCPHETA := (24/(THETA+3))*UE;

VARDDDC := (24/(THETA+3))*SQRT(8[5,5]);

"PRINT" "UDELTACP AT THETA=,SAMELINE,Scaled(9),VARDDDC;"

ANN :=

"TEMP := 273.15;"

"PRINT" "'CALC TO PARAM AT FIXED TEMP INT;"

NEW."PRINT" "'I TEMPERATURE='SAMELINE,""SCAL""(9),""TEMP;"

XTEMP := (TEMP-THETA)/THETA;

USSA := 0;

ÚSSS := 0;

ÚSSD := 0;

ÍSE := 0;

V := 0;

"IF" "Z<=0" "THEN" "GOT0" IAN;

ÚT := V := V + 1;

"IF" "ABS(US/US>1)=""1-12""THEN" "GOT0" AT "ELSE"

UAT := XTEMP*ÚSSA;

Ú := 0;

Ú := 0;

Ú := 0;

"IF" "Z<=0" "THEN" "GOT0" IAN;

ÚT := V := V + 1;

"IF" "ABS(US/US>1)=""1-12""THEN" "GOT0" BT "ELSE"

ÚNT := ÚSB*((XTEMP+2);

Ú := 0;

"IF" "Z<=0" "THEN" "GOT0" IAN;

ÚT := V := V + 1;

"IF" "ABS(US/US>1)=""1-12""THEN" "GOT0" CT "ELSE"

ÚCT := ÚSC*((XTEMP+3);

Ú := 0;

Ú := 0;

Ú := 0;

"IF" "Z<=0" "THEN" "GOT0" IAN;

ÚT := V := V + 1;

"IF" "ABS(US/US>1)=""1-12""THEN" "GOT0" DT "ELSE"

ÚDT := ÚSD*((XTEMP+4);

Ú := 0;

Ú := 0;

Ú := 0;

"IF" "Z<=0" "THEN" "GOT0" IAN;

ÚT := V := V + 1;

"IF" "ABS(US/US>1)=""1-12""THEN" "GOT0" DT "ELSE"

ÚDT := ÚSD*((XTEMP+4);

Ú := 0;

Ú := 0;

Ú := 0;

"IF" "Z<=0" "THEN" "GOT0" IAN;

ÚT := V := V + 1;

"IF" "ABS(US/US>1)=""1-12""THEN" "GOT0" DT "ELSE"

ÚDT := ÚSD*((XTEMP+4);

Ú := 0;

Ú := 0;

Ú := 0;

"IF" "Z<=0" "THEN" "GOT0" IAN;

ÚT := V := V + 1;

"IF" "ABS(US/US>1)=""1-12""THEN" "GOT0" DT "ELSE"

ÚDT := ÚSD*((XTEMP+4);

Ú := 0;

Ú := 0;

Ú := 0;

"IF" "Z<=0" "THEN" "GOT0" IAN;

ÚT := V := V + 1;

"IF" "ABS(US/US>1)=""1-12""THEN" "GOT0" DT "ELSE"

ÚDT := ÚSD*((XTEMP+4);

Ú := 0;

Ú := 0;

Ú := 0;

"IF" "Z<=0" "THEN" "GOT0" IAN;

ÚT := V := V + 1;

"IF" "ABS(US/US>1)=""1-12""THEN" "GOT0" DT "ELSE"

ÚDT := ÚSD*((XTEMP+4);

Ú := 0;

Ú := 0;

Ú := 0;

"IF" "Z<=0" "THEN" "GOT0" IAN;

ÚT := V := V + 1;

"IF" "ABS(US/US>1)=""1-12""THEN" "GOT0" DT "ELSE"

ÚDT := ÚSD*((XTEMP+4);

Ú := 0;

Ú := 0;

Ú := 0;

"IF" "Z<=0" "THEN" "GOT0" IAN;

ÚT := V := V + 1;

"IF" "ABS(US/US>1)=""1-12""THEN" "GOT0" DT "ELSE"

ÚDT := ÚSD*((XTEMP+4);

Ú := 0;

Ú := 0;

Ú := 0;

"IF" "Z<=0" "THEN" "GOT0" IAN;

ÚT := V := V + 1;

"IF" "ABS(US/US>1)=""1-12""THEN" "GOT0" DT "ELSE"

ÚDT := ÚSD*((XTEMP+4);

Ú := 0;
507 DIQCT,'"S?SE=',SAMELINE,SC?ELED(9),VAR0DCP;
  600 IF"ZZZ=0"THEN"GOTO"WIL;
  611 DIQCT:=(6/(THETA+2))=(BD+XTMP*BE));
  612 VAR0DCP:=(QD)*6/(THETA+2)*SQR(BL4,4)
  613 +B*5(4,5)*XTMP*BL5516*(XTMP+2));
  614 "PRINT""L'D2DELI A C P='SAMELI,SCA LED(9),
  615 DIQCT,'"S?SE=',SAMELINE,SCA LED(9),V A R 0DCP;
  616 IF"ZZZ=0"THEN"GOTO"WIL;
  617 DIQCT:=(24/(THETA+3))=BE;
  618 V A R O D C P : = (Q D ) * ( 2 4 / ( T H E T A + 3 ) ) * S Q R ( P L 5 , 5 1 ) ;
  619 "PRINT""L'D2UETACP='SAMELI,SCALED(9),
  620 DIQCT,'"S?SE=',SAMELINE,SCA LED(9),VAR0DCP;
  621 WIL;
  622 TMP:=TMP*UTMP;
  623 "IF"TEMP<371.15"THEN"GOTO"NEW"ELSE"
  624 "IF"ZZZ=1"THEN"BEGIN"
  625 ZZZ:=0;
  626 "GOTO"START;
  627 "END";
  628 "IF"ZZZ=1"THEN"BEGIN"
  629 ZZZ:=0;
  630 "GOTO"START;
  631 "END";
  632 "IF"Z=1"THEN"BEGIN"
  633 Z:=0;
  634 "GOTO"START;
  635 "END";
  636 "IF"Z=1"THEN"BEGIN"
  637 Z:=0;
  638 "GOTO"START;
  639 "END";
  640 "PRINT""L2 CALCULATION COMPLETE FOR A GIVEN THETA"
  641 THETA:=THETA+DTHETA;
  642 "IF"THETA<353"THEN"GOTO"START"ELSE"
  643 "END";
  644 "PRINT""L3 END OF CLEW TYPE ANALYSIS";
  645 "END";
  646 "END";
  836 MC
  4732 CONE
  5568 TOTAL

*LOAD;TEMPAN,EG;DC;1;ALGOL;
TEMPAN

*RUN;
DR20
Listing of XEFIT.

&J01; CH01050MARY; M916;

&ALGOL;
LIRIARY
ALGOL
XEFIT

&UNLIST;
ITEM INSERTED
ITEM INSERTED

&LIST;
87 "REAL" "PROCEDURE" SUM(A,K,N);
88 "VALUE" K;
89 "INTEGER" N,K;
90 "REAL" "ARRAY" A;
91 "BEGIN" "INTEGER" I;
92 "REAL" S;
93 S:=0;
94 "FOR" I:=1 "STEP" 1 "UNTIL" N "DO"
95 S:=S+A[I]+K;
96 SUM:=S;
97 "END";
98 "REAL" "PROCEDURE" SUMPROD(A,B,K,N);
99 "VALUE" K;
100 "INTEGER" N,K;
101 "REAL" "ARRAY" A,B;
102 "BEGIN"
103 "INTEGER" I;
104 "REAL" S;
105 S:=0;
106 "FOR" I:=1 "STEP" 1 "UNTIL" N "DO"
108 SUMPROD:=S;
109 "END";
110 "PROCEDURE" HEAD;
111 "BEGIN"
112 "PRINT" "F" "ANALYSIS OF EXCESS FUNCTIONS", "L" M.J. BLANDAMER",
113 "L" X IS MOLE FRACTION OF WATER",
114 "L" NUMBER OF DATA POINTS", SAMELINE, SCALED (4),N;
115 "FOR" I:=1 "STEP" 1 "UNTIL" N "DO" "BEGIN"
116 X[I]:=X[EL1];=0;
117 "READ" X[EL1],X[EL2];
118 "PRINT" SAMELINE, SCALED (9), I,"S3",X[I],"S3",X[EL1];
119 "END";
120 "END";
121 "PROCEDURE" FIT(X,XE,N,K);" INTEGER" N,K;
122 "ARRAY" X,XE;
"BEGIN"

"INTEGER" I,J;

"ARRAY" Y1,Y2,Y3,U,X1,X2,DEV,XC[1:N],P,P1[1:K],C,C1[1:K],1,K1[1:K],A[1:K,1:K]

"REAL" RMS,STD,DIFF,0;

"FOR" I:=1 "STEP" 1 "UNTIL" N "DO" "BEGIN"
  Z[I]:=-1-2*X1[I];
  Y[I]:=X[I]*(1-X[I]);
  U[I]:=Y[I]*X[I];
  Y[I]:=Y[I]*Y[I];
  "END";

"FOR" I:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
  B1[I]:=0;
  "END";

"FOR" J:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
  AC[I,J]:=0;
  "END";

"PRINT" "L FORM MATRIX";

"FOR" I:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
  D1[I]:=SUMPROD(U,Z,I-1,N);
  "END";

"PRINT" "L PARAMETERS";

"FOR" I:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
  PRINT "L COEFFICIENT I SAMELINE,SCALED(3),K;"
  "END";

"PRINT" "L OUTPUT-NUMBER OF COEFFICIENTS"; "SAMELINE;SCALED(3),K;"

"PRINT" "L COMPARISON OF INPUT + OUTPUT";

"FOR" I:=1 "STEP" 1 "UNTIL" N "DO" "BEGIN"
  RMS:=SORT(DIFF/N);
  STD:=SORT(RMS*RMS*N/(N-K));
  "PRINT" "L ERRORS ON XE FITTING";
  "L STANDARD DEVIATION="; SAMELINE,SCALED(9),STD;
  "SAMELINE;SCALED(9),STD;
  "END";

"END";

171 "END";

172 "END";

173 "END";

174 "FOR" I:=1 "STEP" 1 "UNTIL" W "DO" "BEGIN"
  FIT(X,X,E,N,1);
  "END";

177 "END";

178 "END";

600 MC

1590 CODE

2190 TOTAL
Listing of H2O2.

\$OR:CH0010501JU;
SNAP
BATCH

\$ALGOL;
LIBRARY
ALGOL

&LIST;

1 H2O2;
2 "BEGIN"
3 "REAL" DMDG,DMUT,DMUI,KX2,KX0,R,TEMP,NA,PI,EO,UDIX2,UDIX0,
4 UDX2,UDTX0,ERX2,ERX0,AIX0,AIX2,ATX0,ATX2,KTK,ERX0UT,ERX2UT,
5 TBL,RD,RR,
6 QI,QT,
7 A,B,C,D,DMHT,DMHI;
8 "INTEGER" I,J,K,W;
9 "PROCEDURE" RATERATIO;
10 "BEGIN"
11 DMDG:=DMUT-DMUI;
12 KTK:=EXP(-DMDG/(R*TEMP));
13 "IF" KTK<1.1 "THEN" "GOTO" CAT;
14 "IF" KTK>2 "THEN" "BEGIN"
15 I:=I+1; "GOTO" DOG; "END";
16 "PRINT" 'M2' MEDIUM EFFECT ON INITIAL STATE= ',SAMELINE,SCALED(9)
17 DMUI;
18 "PRINT" SAMELINE,'S2' MEDIUM EFFECT ON TRANSITION STATE= ',
19 SAMELINE,SCALED (9),DMUT;
20 "PRINT" 'M M' MEDIUM EFFECT ON DELTA G= ',SAMELINE,SCALED (9),KTK;
21 "END";
22 "PROCEDURE" DELTAH;
23 "BEGIN"
24 "REAL" DH;
25 DH:=DMHT-DMHI;
26 "PRINT" 'L' DELTA M ON TRANS STATE= ',SAMELINE,
27 scaled (9),DMHT;
28 "PRINT" SAMELINE,'S2' DELTA M ON INIT STATE= ',SAMELINE,
29 scaled (9),DMHI;
30 "PRINT" 'L' CHANGE IN DELTA H= ',SAMELINE,SCALED (9),DH;
31 "END";
32 "PROCFUN.RE" FNTTRANS;
33 "BEGIN"
34 "REAL" DH;
35 DMHT:=-TEMP*2*;
36 (NA*(UDTX2+2))A/(4*PI*EO*(TEMP+2)*(ATX2+3))
37 -(NA*(UDTX2+2)+B/(TEMP+4*PI*EO*(ATX2+3))
38 -(NA*(UDTX0+2)+C/((TEMP+2)*4*PI*EO*(ATX0+3))
39 +(NA*(UDTX0+2)+D/(TEMP+4*PI*EO*(ATX0+3)))
40 );
"PROCEDURE" ENTHIN;
"BEGIN"
TH := TEMP + 2;

(NA*(UDTX2/2)/(4*PI*E0*(ATX2/3)))

-((ERX2-1)/(ERX2+2))+(NA*(UDTX0)/(4*PI*E0*(ATX0/3)));

"END";

"PROCEDURE" DELTAMINIT;
"BEGIN"

DNTH := -(NA*(UDTX2/(4*PI*E0*(ATX2/3)))

1*(ERX2+2))+(NA*(UDTX0)/(4*PI*E0*(ATX0/3)));

"END";

"PROCEDURE" DELTHTRANS;
"BEGIN"

DNTH := -(NA*(UDTX2/(4*PI*E0*(ATX2/3)))

-((ERX2-1)/(ERX2+2))+(NA*(UDTX0)/(4*PI*E0*(ATX0/3)));

"END";

PI := 3.14159;
NA := 0.02171*10^23;
R := 3.14134;
E0 := 8.85418*10^-12;
TEMP := 298.15;
"PRINT" "Kirkwood ANALYSIS FOR H2O2-H2O MIXTURES";
"PRINT" "Dielectric PROPERTIES";
"PRINT" "SAMELINE, SCALED (9), S' ERX0= ',ERX0,'S3' ERX0DT= '

ERX0DT,'S5' ERX2= ',ERX2,'S2' ERX2DT= ',ERX2DT;

Q1 := UDIX0/(3.335*10^-30);
"PRINT" "Dipole MOMENT OF INITIAL STATE= ',SAMELINE,

SCALED (9), Q1;
ATX0 := 1.319*10^-10;

"FOR" I := 1 "STEP" 1 "UNTIL" 50 "DO" "BEGIN"

DO;

"PRINT" "Radii OF INITIAL STATE= ',SAMELINE,

SCALED (9), AIX0;

ATX0 := ATX0 + 0.2*10^-10;

"PRINT" "L' RADIUS OF TRANSITION STATE= ',SAMELINE,

SCALED (9),ATX0;

Q1 := UDIX0/(3.335*10^-30);

"PRINT" "Dipole MOMENT OF TRANSITION STATE= ',SAMELINE,

SCALED (9), Q1;

ATX0 := ATX0;

AIX0 := AIX0;

"FOR" J := 2 "STEP" 2 "UNTIL" 50 "DO" "BEGIN"

UDTX0 := UDIX0 + (UDTX0*J);

QT := UDXT0/(3.335*10^-30);

"PRINT" "Dipole MOMENT OF TRANSITION STATE= ',SAMELINE,

SCALED (9), QT;

THL := UDTH0*0.335/1.602;
"PRINT" SAMELINE;SCALED(9),"S'RRz'.RR;
"PRINT" SAMELINE;SCALED(9),"S'RD='RD';
"COMMENT" ASSUMING SIZE AND DIPOLE MOMENT OF INITIAL STATE ARE INDEPENDENT OF SOLVENT;
UDTX2:=UDTX0; UDI2:=UDI0;
DELTAMINIT;
DELTMTRANS;
RATERATIO;
ENTHIN;
ENTHTRANS;
DELTAH;
CAT:
"PRINT" ''L'';
"END";
"END";
"END";
MC
1510 TOTAL

&PUN;
H202
DRO
Listing of BONGO.

\&JOP;CH001050.MJR;
SWOP
BATCH

\&ALGOL;
LIBRARY ALGOL

\&LIST;

1 BONGO;
2 "BEGIN"
3 "INTEGER" I,N,J,K,V,W;
4 "REAL" AA,BB,CC,Y,M,S1,S2,S3,EC,DT;
5 "PROCEDURE" MXCOPY(B,A,W);
6 "INTEGER" W;
7 "ARRAY" A,B;
8 "BEGIN"
9 "INTEGER" Q,S;
10 "FOR" Q:=1 "STEP" 1 "UNTIL" W "DO"
11 "FOR" S:=1 "STEP" 1 "UNTIL" W "DO"
12 BEG,SJ:=ALQ,SJ;
13 "END" MXCOPY:
14 "PROCEDURE" INVMX(B,W);
15 "INTEGER" W;
16 "ARRAY" B;
17 "BEGIN"
18 "REAL" MAX, EPS;
19 "INTEGER" SS,L,V,Z,R;
20 R:=W;
21 EPS:=2,0^37;
22 "BEGIN"
23 "INTEGER" "ARRAY" RR,BR[I,R];
24 "FOR" SS:=1 "STEP" 1 "UNTIL" R "DO"
25 "BEGIN"
26 "FOR" V:=1 "STEP" 1 "UNTIL" SS-1 "DO"
27 "IF" L=BR[V] "THEN" "GOTO" L1;
28 "IF" ABS(MAX)-ABS(B[L,1]) "THEN"
29 "END"
30 "BEGIN"
31 "REAL" RR[SS]:L;
32 MAX:=B[L,1];
33 "END";
34 L1: "END";
35 "IF" ABS(MAX)<EPS "THEN"
36 "BEGIN"
37 "PRINT" "L INV MX ERROR";
38 STOP;
4  "EMU";
5  V := U[3];
6  "FOR" L := 1 "STEP" 1 "UNTIL" R "DO"
7  B[L, R+1] := IF L = V "THEN" 1 "ELSE" 0;
8  "FOR" L := 1 "STEP" 1 "UNTIL" R "DO"
9  BL, LJ := BL, I+1]/MAX;
10 "FOR" L := 1 "STEP" 1 "UNTIL" R "DO"
11 "BEGIN"
12 MAX := BL, I;
13 "IF" L < N "THEN" "FOR" Z := 1 "STEP" 1 "UNTIL" R "DO"
15 "END"
16 "END";
17 "FOR" Z := 1 "STEP" 1 "UNTIL" R "DO"
18 PHZ := Z;
19 "FOR" Z := 1 "STEP" 1 "UNTIL" R-1 "DO"
20 "BEGIN"
21 "IF" BL, Z = RR, Z "THEN" "GOTO" LOOP "ELSE"
22 "FOR" L := Z+1 "STEP" 1 "UNTIL" R "DO"
23 "IF" RR, L = BR, Z "THEN" "GOTO" SWAP;
24 SWAP: "FOR" V := 1 "STEP" 1 "UNTIL" R "DO"
25 "BEGIN"
26 MAX := BL, Z, V;
28 P[L, V] := MAX
29 ;
30 "END";
31 RRL, I := RR, Z;
32 LOOP: "END";
33 "FOR" Z := 1 "STEP" 1 "UNTIL" R-1 "DO"
34 "BEGIN"
35 "FOR" L := Z "STEP" 1 "UNTIL" R "DO"
36 "IF" BL, L = BR, Z "THEN"
37 "BEGIN"
38 "IF" Z = L "THEN" "GOTO" OUT;
39 "FOR" V := 1 "STEP" 1 "UNTIL" R "DO"
40 "BEGIN"
41 MAX := BL, V, Z;
42 BL, V, Z := BL, V, I;
43 BL, LJ := MAX
44 ;
45 "END";
46 BR, L := BR, Z;
47 ;
48 "END";
49 "OUT: "END";
50 "END";
51 "END" INVMX;
52 "PROCLODEPE" MPXPROD(C, A, B, W);
53 "INTEGER" W;
54 "ARRAY" A, B, C;
55 "BEGIN"
56 "INTEGER" I, J, K;
57 "FOR" I := 1 "STEP" 1 "UNTIL" W "DO"
58 "FOR" J := 1 "STEP" 1 "UNTIL" W "DO"
59 "BEGIN"
60 C[I, J] := 0;
61 "FOR" K := 1 "STEP" 1 "UNTIL" W "DO"
63 "END";
"END" MXPGRD;

"PROCEDURE" PRINTMX(C,N);
"INTEGER" N;
"ARRAY" C;
"BEGIN"
"INTEGER" I,J,K,L,H,MM;
"INTEGER" "ARRAY" LIM[0:7];
FREEPOINT (11); DIGITS(3);
I:=N "DIV" 9;
LIM[0]:=N-9*I;
K:=0;
"FOR" J:=1 "STEP" 1 "UNTIL" I "DO" LIM[J]:=9;
"FOR" J:=1 "STEP" -1 "UNTIL" 0 "DO"
"BEGIN"
"PRINT" ""L",""S6";";
"IF" LIM[J] >0 "THEN" "BEGIN"
"FOR" L:=1 "STEP" 1 "UNTIL" LIM[J] "DO"
"PRINT" SAMELINE,DIGITS (7),L+K,""S5";";
"FOR" M:=1 "STEP" 1 "UNTIL" N "DO"
"BEGIN"
"PRINT" ""L",SAMELINE,"S3";";
"END";
K:=K+9; "PRINT" ""L";";
"END";
"END" PRINTMX;

"READ" N;
M:=N+1;
"PRINT" "F, ANALYSIS OF DIELECTRIC DATA";
"PRINT" "L, SYSTEM*** H2O2 + H2O";
"READ" X;
"PRINT" "L, HOLE FRACTION OF H2O2 =",SAMELINE,SCALED(9),X;
"BEGIN"
"FOR" I:=1 "STEP" 1 "UNTIL" N "DO" "BEGIN"
"READ" ERIJ,TC[I];
TK[I]:=TC[I]+273.15;
"PRINT" ""L",SAMELINE,SCALE(9),TC[I],""S4",TK[I],""S4",ER[I];
"END";
"FOR" I:=1 "STEP" 1 "UNTIL" 4 "DO"
"FOR" J:=1 "STEP" 1 "UNTIL" 4 "DO"
AL1,13,:=NC[1,13];
AL2,3,:=AL1,3J+TC[1,3];
AL3,3,:=AL3,3J*(TC[1,3]) 2;
AL4,3,:=AL4,3J*(TC[1,3]) 3;
AL5,3,:=AL5,3J*(TC[1,3]) 4;
S1:=S1+ERJ;
S2:=S2+ERJ*TC[1,3];
S3:=S3+ERJ*TC[1,3]*TC[1,3];
"END";
AC1,1J,:=AC1,1J+TC[1,3];
AC2,1J,:=AC2,1J+TC[1,3];
AC2,2J,:=AC2,2J+TC[1,3];
AC3,3,:=AC3,3J+TC[1,3];
AC4,3,:=AC4,3J;
BB := B[2,1]*S1 + B[2,2]*S2 + B[2,3]*S3;
CC := B[3,1]*S1 + B[3,2]*S2 + B[3,3]*S3;
"PRINT" "'I.2' COEFFICIENTS';
"PRINT" "'I. AA := 'SAMELINE, SCALED(9), AA;
"PRINT" "'I. BB := 'SAMELINE, SCALED(9), BB;
"PRINT" "'I. CC := 'SAMELINE, SCALED(9), CC;
"FOR" I := 1 "STEP" 1 "UNTIL" N "DO" "BEGIN"
ECLI := AA + BB*TC[I] + CC*(TC[I] + 2);
"PRINT" "'I. S3', SCLINE, SCALED(9), TC[I], 'S3', TC[I],
S3', ER[C[I], 'S3', ER[C[I];
"END";
"PRINT" "'I. AT T=298.15K----CALCULATED';
EC := AA + (25*60) + (625*CC);
"PRINT" "'I. DIELECTRIC CONSTANT= 'SAMELINE, SCALED(9), EC;
DT := BB + (50*CC);
"PRINT" "'I. TEMPERATURE COEFFICIENT= 'SAMELINE, SCALED(9), DT
"END";
"END";
MC
CODE
TOTAL

&RUN;
RONGD
DRO
Appendix 3
Rate Constants for $t$-BuCl solvolysis in $\text{H}_2\text{O}_{2}$/WATER Mixtures.

1) 0.03 mole fraction

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>273.59K</th>
<th>278.26K</th>
<th>283.22K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^3k$</td>
<td>1.02789</td>
<td>2.15414</td>
<td>4.59100</td>
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<tr>
<td>1.02592</td>
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<td>4.58289</td>
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<tr>
<td>1.02583</td>
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Rate Constants for t-BuCl solvolysis in PVP/WATER mixtures.

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Rate of tris(5-nitro-1,10-phenanthroline)iron(II) aquation in PVP/WATER mixtures, at 308K.

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Rates of tris(5-nitro-1,10-phenanthroline) iron (II) aquation in aqueous sols. and gels.

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3) **0.2% agar gel.**

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4) **289.41K**

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<th>2% Gelatin gel.</th>
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Rates of cyanide reaction with tris(5-methyl-1,10-phenanthroline) iron (II) in agar sols. and gels.

1) Water only

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2) 0.1% agar sol.

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3) 0.2% agar gel.

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Rate Constants for tBuCl solvolysis in UREA/WATER mixtures

1) tBuCl/Water only

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2) tBuCl/1 mol. dm$^{-3}$ Urea

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<table>
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3) \textbf{tBuCl/2 mol. dm}^{-3} \textbf{Urea}

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<th>(10^3k)</th>
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4) \textbf{tBuCl/3 mol. dm}^{-3} \textbf{Urea}

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<th>(10^3k)</th>
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5) \( \text{tBuCl/4 mol. dm}^{-3} \text{ Urea} \)

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6) \( \text{tBuCl/6 mol. dm}^{-3} \text{ Urea} \)

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Rate Constants for t-BuCl solvolysis in GLYCEROL/WATER mixtures.

1) 0.01 mole fraction

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2) 0.025 mole fraction

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### 0.025 mol fraction (cont.)

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4) 0.075 mole fraction  

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### Rate Constants for tBuCl solvolysis in PROPANE-1,2-DIOL/WATER Mixtures

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Rate constants for tBuCl solvolysis in 
PROPANE-1,3-DIOL/WATER Mixtures

1) 0.025 mole fraction

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2) **0.05 mole fraction**

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"Kinetics in Aqueous Systems"

Abstract:

The available literature concerning water and aqueous solutions of non-electrolytes has been briefly reviewed, and an introduction to the present understanding of the gel state given. Thermodynamic properties of binary liquid mixtures have been examined, with particular emphasis being laid on the solubility of volatile substrates in such systems. Kinetics of reactions have been studied in binary aqueous media, against the theoretical background of this solubility analysis. The apparatus for two different techniques of kinetic measurement (conductivity and spectroscopy) have been described in detail, as well as methods for analysing the resulting data, based on computer calculations for rate constants and activation parameters. Experimental results for the solvolysis of t-butyl chloride in aqueous hydrogen peroxide, polyvinylpyrrolidone, urea, glycerol, propane-1,2-diol and propane-1,3-diol are given and discussed, along with results for the aquation and substitution reactions of tris(1,10-phenanthroline) complexes of iron(II) in aqueous polyvinylpyrrolidone and aqueous sols and gels. Appendices include further work on gelling agents, computer programs, and tables of experimental rate constants.