

KINETICS OF INORGANIC REACTIONS IN MIXED SOLVENTS

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CHAPTER 1

INTRODUCTION

The aim of this study was to investigate the role of mixed aqueous solvents in the kinetics of chemical reactions in order to probe possible relationships between rates of reaction and the properties of the mixture.

The importance of solvent structure on the behaviour of a chemical reaction was realised as early as 1890 by Menschutkin¹. The problem is, as it was then, to determine how the structure of the solvent can best be expressed in a quantitative manner. For many years rates of reaction were related to physical parameters such as dielectric constant, dipole moment and refractive index. The success of these treatments was not outstanding and led to the development of the so called 'polarity' of the solvent², solvent Y values³, X values⁴, Z values⁵, and E_T values⁶. These parameters have been reasonably successful at relating solvent effects on particular reactions. For example, solvent Y values have been used to correlate the solvent effects on mechanistically related reactions. They have also been used to help in mechanistic studies e.g. the solvolysis of halides of phosphorus⁷. Solvent Y values have been less successful in correlating data for reactions in mixed aqueous media.

In a study of solvent effects on a reaction, the latter must satisfy certain requirements in order to be suitable. These requirements are as follows:-

- 1) The reaction must be sufficiently sensitive to changes in solvent that detectable changes in reaction rates can be measured.

2) The reaction must proceed at a convenient rate for which techniques are available.

3) The mechanism of the reaction must be well established.

Reactions that were initially thought to meet these requirements were:-

a) The hydrolysis of cis-dichlorobis (ethylenediamine) Cobalt(III) chloride to cis-dihydroxobis-(ethylenediamine) Cobalt(III) chloride. This is a two step process and the solvent may affect both steps.

b) Aquation of substituted 1,10-phenanthroline iron(II) chloride complexes. The rates of aquation of these complexes, particularly the $5NO_2$ complex, are sensitive solvent. In addition, the mechanism of the reaction has been carefully studied.

c) Ligand substitution at the square planar complex chloro (diethylenetriamine) platinum(II) chloride. In this complex the solvent can interact with the metal atom from either side of the plane of the molecule. Also during ligand substitution the solvent may interact with the leaving group i.e. chloride.

d) Ligand substitution at chloro (N,N,N',N' - tetraethyldiethylenetriamine) palladium (II) chloride. Models of this complex have indicated that the ethyl groups are arranged such that they lie above and below the palladium atom. Thus the solvent effects on the leaving of the chloride can be monitored.

e) Finally, a different type of substitution reaction, that between Nickel (II) or Cobalt (II) with the ligand pyridine-2-azo-p-dimethyl aniline (pada). This reaction involves the substitution of solvent molecules in the primary solvation layer around the metal atom with the ligand, pada. The rate of this substitution is too rapid to be measured by conventional techniques but can be easily determined using a stopped-flow or temperature jump apparatus.

In the mixed solvent systems used in this study, water was one component. Water is one of the most interesting solvents and is important in biological systems. The co-solvents were chosen to produce the widest spread of behaviour of the mixed solvents. The solvent systems chosen were hydrogen peroxide + water, acetonitrile + water, acetone + water, dimethyl sulphoxide + water and glycerol + water.

CHAPTER 2

AQUEOUS MIXTURES

1. Introduction

When considering the properties of aqueous mixtures it is inevitable that to understand them fully the nature of water itself must be first considered. After a suitable description of liquid water is found progress can then be made in understanding aqueous mixtures.

A useful approach to the study of aqueous mixtures is through their thermodynamic properties which provide useful insights into the nature of solute -solvent interactions.

2. Water

The investigations on the structure of water are very extensive but they have not yet led to a complete understanding of this liquid. Several models have been suggested for the structure of water which explain some properties more or less adequately. No experimental proof unequivocally supports the acceptance of one of the suggested models and eliminates all the others. Some models have been found that are in agreement with a group of properties. No simple model explains all of the properties of water and aqueous solutions, although in recent years considerable progress has been made.

3. Structure of Liquid Water

Water has several properties which differ from those of 'normal' liquids, the best known being the increase of density on melting and the further increase of density as the temperature is raised to 277K. The heat capacity of

liquid water is almost twice that of ice; the thermal expansion coefficient of water increases with increasing pressure in the 273-318K temperature range (in general the thermal expansion coefficient decreases with increasing pressure); over the same temperature range the compressibility of water decreases with increasing pressure between 273 and 298K, the dielectric constant and self-diffusion rates of water also change anomalously with pressure. The large heat of evaporation coupled with large positive entropy change indicate that water is a highly associated liquid with a high degree of order.

a) Theories Based on the Structure of Ice

Bernal and Fowler¹ tried to reproduce X-ray diffraction measurements by comparing different arrangements of water molecules. They put forward the proposal that each water molecule was surrounded by 4 other water molecules at the corners of a tetrahedron. They considered water to be homogeneous at all temperatures and that the change in properties of water was due to a gradual change in its structure from basically an ice-like structure through a quartz like structure, to a more closely packed structure then an open quartz structure.

Bernal² in later years published a modification of this theory. Again the co-ordination number of water is 4 but the water molecules forming predominantly 5-membered rings.

These rings are then arranged in ordered groups.

Other X-ray diffraction investigations by Morgan and Warren³, Brady et al⁴ and Danford and Levey⁵ seem to confirm the existence of short-range order which resembles a modification of the structure of ice. This structure breaks down with increasing temperature.

b) Bent Hydrogen Bond Model

Pople⁶ assumed that all water molecules in the liquid are hydrogen bonded to 4 other water molecules but the hydrogen bonds can be bent and stretched to produce irregular and varied networks.

This theory assumes that there are no broken hydrogen bonds. Infra-red and Raman spectroscopic investigations have been carried out on water to determine the ratio of hydrogen bonds present and the fraction of the molecules bound to one, two, three or four of its neighbours. Due to the difficulty of interpreting the spectra contradictory conclusions are drawn by different researchers.

Raman work by Wall and Hornig⁷ and infra-red work on water by Falk and Ford⁸ suggest there are no broken bonds. However the Raman work carried out by Walrafen⁹ indicates that there are broken hydrogen bonds and their number increases with temperature.

Buijs and Choppin¹⁰ in their study of the infra-red spectrum of water conclude that 42 per cent of the hydrogen

bonds are broken on the melting of ice. Luck¹¹, however, interprets the infra-red absorption to show that the majority of hydrogen bonds break only above the normal boiling point.

From these studies it seems that a better understanding of the nature of hydrogen bonding in water is required.

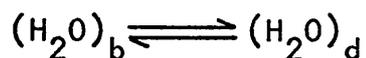
c) Flickering Cluster Model

Frank and Wen¹² proposed the idea of clusters of water molecules that were made and broken up on a fast time scale, $\sim 10^{-11}$ s, to explain the properties of water. They put forward the idea that formation and rupture of hydrogen bonds is a co-operative process i.e. if two water molecules are attached to each other by a hydrogen bond, a third molecule joins this more readily than it would a monomeric molecule and this process continues leading to the formation of clusters. Similarly if a water molecule leaves a cluster then this will facilitate its break down. The result is, therefore, 'flickering clusters'. Between the clusters are monomeric water molecules. Nemethy and Scheraga¹³ carried out a statistical thermodynamic calculation on this model to obtain cluster size and ratio of monomeric water to cluster water. This calculation has come under criticism from various workers.

Symons¹⁴ in his paper on water refutes the idea of co-operative break-down of clusters in water to produce water molecules.

d) Model chosen for this work

For this work the structure of water is discussed in terms of the following equilibrium: ¹⁵



$(H_2O)_b$ describes water molecules hydrogen bonded to each other, in a low density ("bulky water") state. The other species $(H_2O)_d$ is non hydrogen bonded and therefore will allow shorter O-O distances ("dense water"). This model has been chosen as it seems to be able to explain the effect of solutes on water more clearly than the other models. Raman spectra⁹, X-ray diffraction studies⁵ and simulated Raman spectra⁹ seem to support this model. Frank suggests that $(H_2O)_b$ has a structure similar to ice - 1h and $(H_2O)_d$ describes water molecules in voids in the "lattice". This model is thus a mixture model, comprising of guest and host. The life time of $(H_2O)_b$ is around 10^{-11} s as estimated from dielectric, ultrasonic and n.m.r. relaxation times.

4. Thermodynamic Properties of Liquid Mixtures

An insight into interactions in aqueous mixtures can be obtained from the molar excess thermodynamic quantities. An excess thermodynamic function is defined as the difference per mole between the value of a function in a given mixture

and that in an ideal mixture at the same composition and the same temperature and pressure.

An ideal mixture can be defined as a liquid mixture for which the chemical potential of each component can be described by the equation ¹⁶

$$\mu_i (P, T, x) = \mu_i^\ominus (P, T) + RT \ln x_i$$

x_i = mole fraction of component i

μ_i^\ominus = chemical potential of pure i

For a real solution the chemical potential is given by the equation -

$$\mu_i (P, T, x) = \mu_i^\ominus (P, T) + RT \ln a$$

a = activity = $x_i f_i$ f_i = activity coefficient such that $f_i \rightarrow 1$ as $x_i \rightarrow 1$.

To calculate the excess thermodynamic functions of mixing for a binary mixture, the ideal thermodynamic function is subtracted from that for the real. For example, in the case of the Gibbs free energy for the mixing of n_1 moles of component 1 and n_2 moles of component 2, we have

$$G(\text{ideal}) = n_1(\mu_1^\ominus + RT \ln x_1) + n_2(\mu_2^\ominus + RT \ln x_2)$$

$$G(\text{real}) = n_1(\mu_1^\ominus + RT \ln x_1 f_1) + n_2(\mu_2^\ominus + RT \ln x_2 f_2)$$

$$G^E = \frac{[G(\text{real}) - G(\text{ideal})]}{(n_1 + n_2)} = x_1 RT \ln x_1 f_1 + x_2 RT \ln x_2 f_2$$

Then it follows that the excess molar enthalpy, H^E , and the molar entropy S^E are related by

$$G^E = H^E - TS^E$$

The enthalpy of mixing for the mixture equals H^E because the enthalpy of mixing of an ideal mixture is zero.

Aqueous mixtures can be classified into two main groups according to the relative magnitudes of the excess enthalpy of mixing H^E and the entropy of mixing TS^E . If $|TS^E| > |H^E|$ and $G^E > 0$ then the mixture is said to be 'Typically Aqueous'; if $|H^E| > |TS^E|$ then the mixture is said to be 'Typically Non Aqueous',¹⁷.

5. Typically Aqueous

In these mixtures the solution thermodynamics are dominated by a large negative entropy of mixing and a positive excess Gibbs free energy. For these co-solvents there is a pronounced concentration dependence of all physical properties in the very dilute solution range. The thermodynamic behaviour exhibited by this solute is only found in aqueous systems; hence their name. Solutes which exhibit this type of behaviour include monohydric alcohols, acetone and amines.

Hydrocarbons exhibit typically aqueous behaviour. These apolar solutes have large negative entropies of solution¹⁸ and a small negative enthalpy of solution. Thus they are insoluble due to the dominant entropy change.

To explain the excess thermodynamic quantities for the hydrocarbons Frank and Evans¹⁹ suggest that the presence of

Plot of H^E Against Mole Fraction for t-Butyl Alcohol +
Water (a Typically Aqueous System)

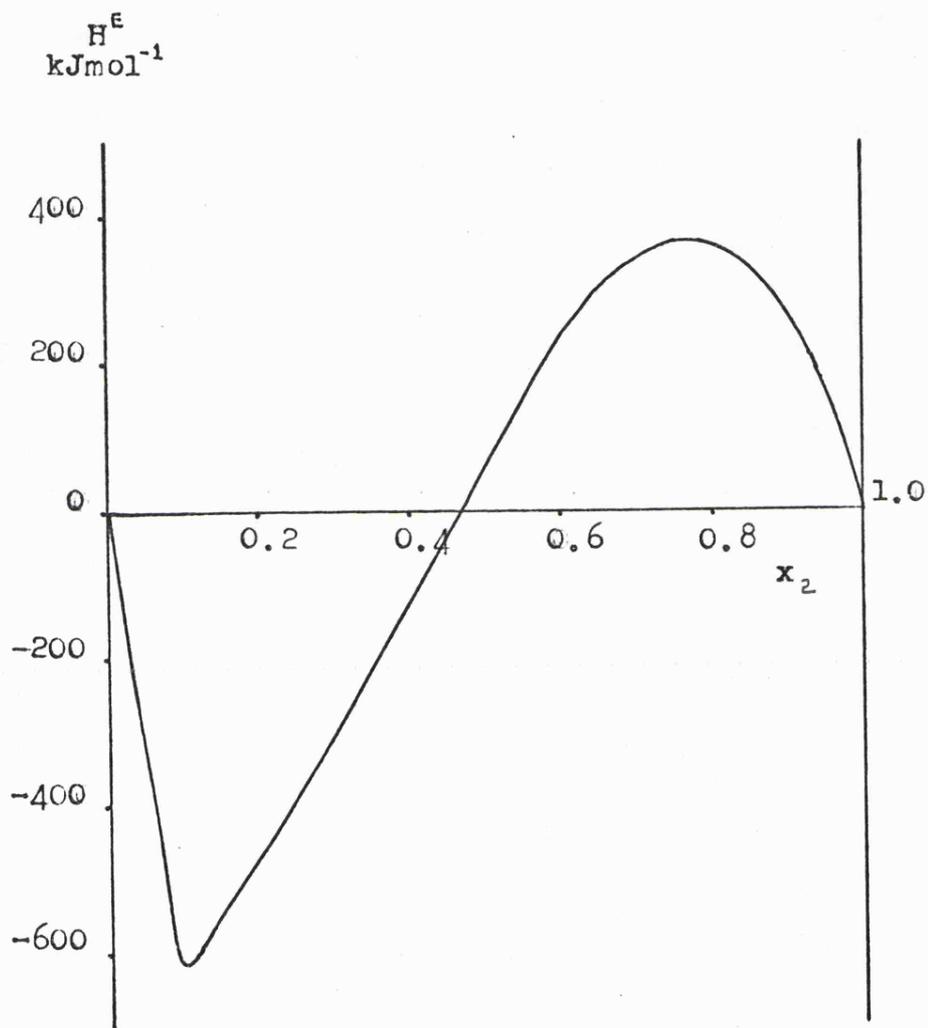


FIGURE 2-1

the apolar molecule causes the order of water around it to increase, building up an 'iceberg' around itself by enhancing water-water interactions. Alternatively the hydrocarbon could be said to move the equilibrium of water in favour of $(\text{H}_2\text{O})_b$

Various theoretical studies of aqueous solutions of apolar solvents have been reported. The key feature of all calculations is the extent to which the solute affects the solvent. Frank and Reid²⁰ point out that the maximum in solubility of apolar solutes in water occurs at roughly the same solute radius as required for maximum stability of the clathrate hydrate.

Alcohols are one of the most studied solutes in this class. Their thermodynamic behaviour has been reviewed by Frank and Ives²¹. These mixtures have a positive G^E and the plot of H^E against mole fraction is typically S-shaped (figure 2-1) At low alcohol mole fraction (x_2) $H^E < 0$ but as x_2 is increased H^E goes through a minimum. In some cases, when x_2 is further increased, H^E goes through an endothermic maximum. The actual shape of $H^E(x_2)$ curve depends on the shape and size of the alkyl group and the temperature. The excess molar heat capacity C_p^E has a positive maximum at low x_2 .

For dilute solutions of alcohols there is a similarity between their thermodynamic properties and those for the

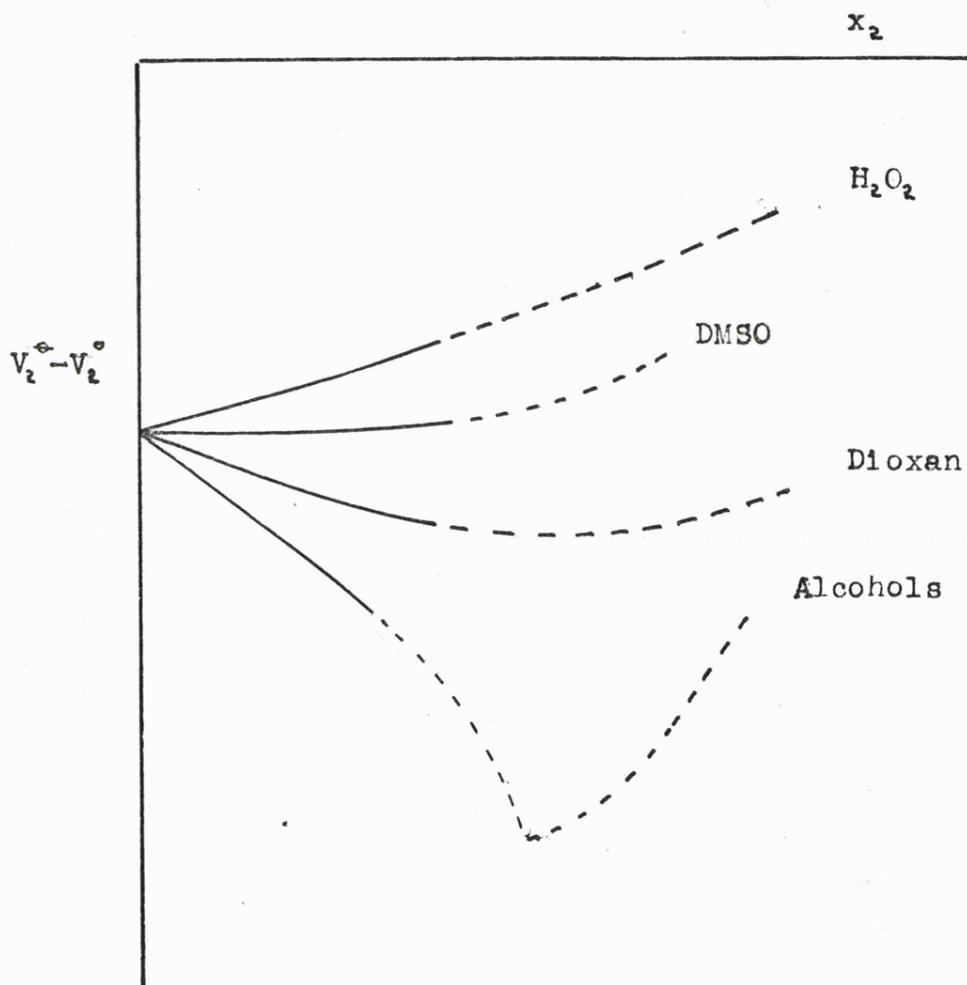
Different Types of Partial Molar Volume Behaviour

FIGURE 2-2

alkanes. The enthalpy, Gibbs free energy and entropy show a similar trend. Alcohols are sometimes referred to as 'solubilised hydrocarbons',^{17(b)}. However, a recent paper by Oakes²² draws attention to the importance of the hydrogen bonds between alcohol and water.

The dependence of the partial molar volume on concentration (figure 2-2)^{17(a)} shows that three types of behaviour can be identified.

1) a negative slope, i.e. $dV_2/dx_2 < 0$, is an indication of long range co-operative 'structure making'

2) a zero slope combined with the knowledge that $V_2^\ominus - V_2^\circ$ is negative signifies no co-operative structural effects.

3) a positive slope indicates structure breaking effects.

For alcohols $dV_2/dx_2 < 0$ ^{17(a)} at low mole fractions and this is taken to indicate that the alcohol exerts a 'structure making' effect. The structure of the aqueous solutions can be described in terms of effectively cooling²³ the water or in terms of a clathrate arrangement of water molecules²⁴. Proponents of the clathrate model argue that when alcohol is added to water the system remains homogeneous due to alcohol-water hydrogen bonding. Of greater significance is the enhancement of water-water interactions around the alkyl-group, the resulting structure resembling a clathrate hydrate.

TABLE 2-A

Solute	* x_2	** x_2
Ethanol	0.09	0.20
Isopropyl Alcohol	0.06	0.18
t-Butyl Alcohol	0.04	0.10
Acetone	0.06	0.35

As the amount of alcohol is increased the co-spheres of enhanced water structure around the alcohol overlap and mutually enhance the water structure. This continues until, at a mole fraction, x_2^* , there is insufficient water to maintain this clathrate structure. The value of x_2^* is dependent on the size and shape of the alcohol. After this point, as the mole fraction of alcohol is increased the water tries to maintain a three dimensional hydrogen-bonded network which causes local concentration fluctuations, the effect maximising at a mole fraction x_2^{**} . In the table 2-A some examples of x_2^* and x_2^{**} are given. At the mole fraction x_2^{**} the system has the greatest tendency to phase separate and this mole fraction approximately coincides with the minimum in H^E . Both x_2^* and x_2^{**} are dependent on co-solvent and temperature.

Evidence for the structuring effect is available from several experimental sources.

Ultrasonic Absorption

Ultrasonic absorption of aqueous mixtures containing t-butyl alcohol²⁴ or n-propyl alcohol shows a maximum which correlates with x_2^{**} . At low mole fraction there is little change in absorption but at x_2^* there is a sudden rise. These observations are explained in terms of the model described previously. The alcohol at first fits into the clathrate cavities in the water and therefore has little effect on the sound absorption but when these sites have all been filled

(i.e. $x_2 = x_2^*$) then changes will be brought about in the water hence altering its sound absorption. The maximum near x_2^{**} corresponds to a situation where the concentration fluctuations are extensive, the system being close to phase separation.

N.M.R.

N.M.R. relaxation¹⁹ studies have shown that in dilute solutions of typically aqueous solutes, e.g. alcohols, an increase in the solute concentration is accompanied by a general slowing down of the diffusional motions of water. However, the rotation of the solute molecules is hardly affected and resembles that which is found in the vapour state. These observations are consistent with the idea that the solute is accommodated into the voids of water.

Neutron Scattering

This technique has been applied²³ to t-butyl alcohol mixtures. The addition of t-butyl alcohol has a marked effect on the spectrum of water. The discrete structure disappears and is replaced by a broad intense scattering maximum. The effect was explained by proposing that the water had taken up the properties of a supercooled liquid i.e. a glassberg, when small amounts of alcohol had been added.

Heats of Mixing at 298 K for (a) Acetonitrile + Carbon Tetrachloride and (b) Acetonitrile + Water

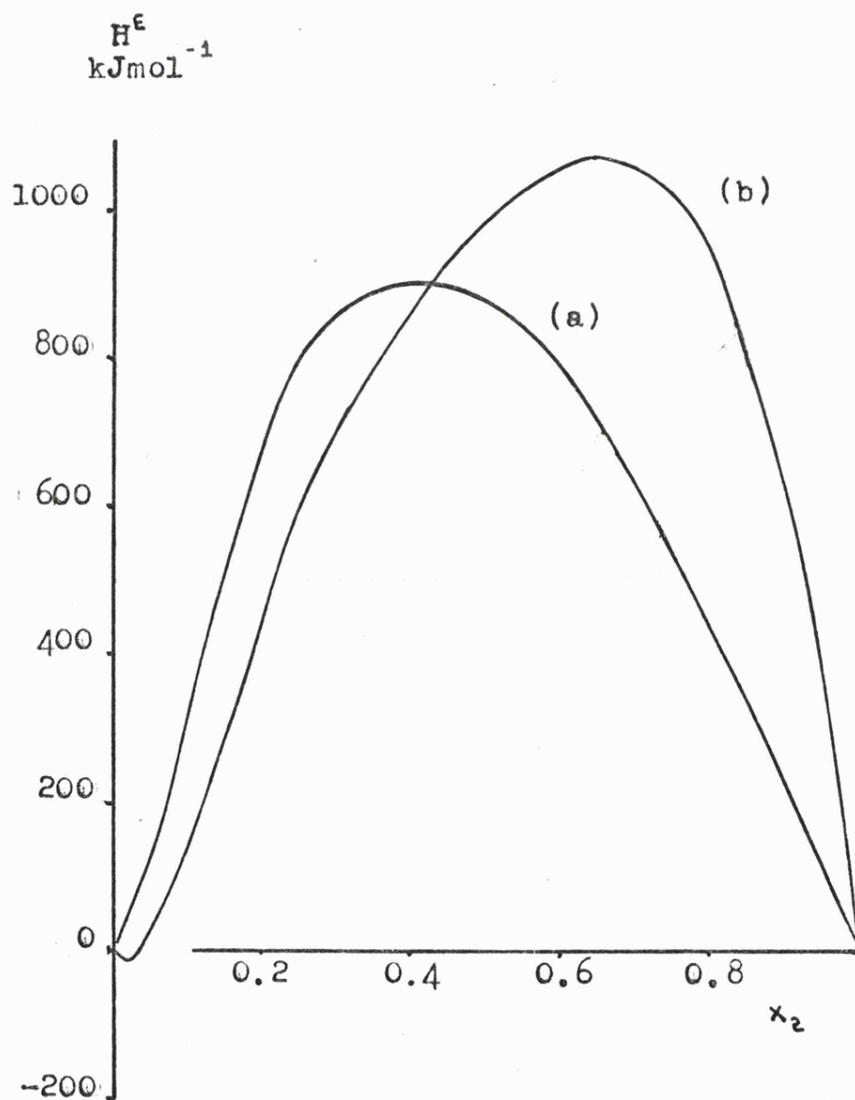


FIGURE 2-3

6. Typically Non-Aqueous

The properties of this group resemble non-aqueous systems e.g. carbon tetrachloride and methyl alcohol with respect to their excess thermodynamic properties (figure 2-3) i.e. the sign and magnitude of G^E are determined by H^E . Solutes which give rise to this behaviour are often poly-functional e.g. hydrogen peroxide and glycerol. For aqueous mixtures containing such co-solvents there is a specific interaction between their polar groups and water i.e. they are hydrophilic. Little is known about these co-solvents as they do not show such varied or dramatic effects as are exhibited by the alcohols.

Typically non-aqueous mixtures can be sub-divided into two groups -

a) mixtures where G^E is positive (TNAP)

e.g. acetonitrile + water

b) mixtures where G^E is negative (TNAN) e.g. Hydrogen

Peroxide + water; Dimethyl sulphoxide + water

a) TNAP Mixtures

The only common co-solvent which falls into this category is acetonitrile. Ultrasonic and spectroscopic²⁵ studies have been carried out to investigate the structure of this mixture. The enthalpy of mixing of acetonitrile and water was compared to the properties of methyl alcohol + carbon tetrachloride i.e. the mixing of an 'inert' component and a highly polar component. The results of the study

Excess Thermodynamic Parameters for Hydrogen-Peroxide +
Water at 298 K

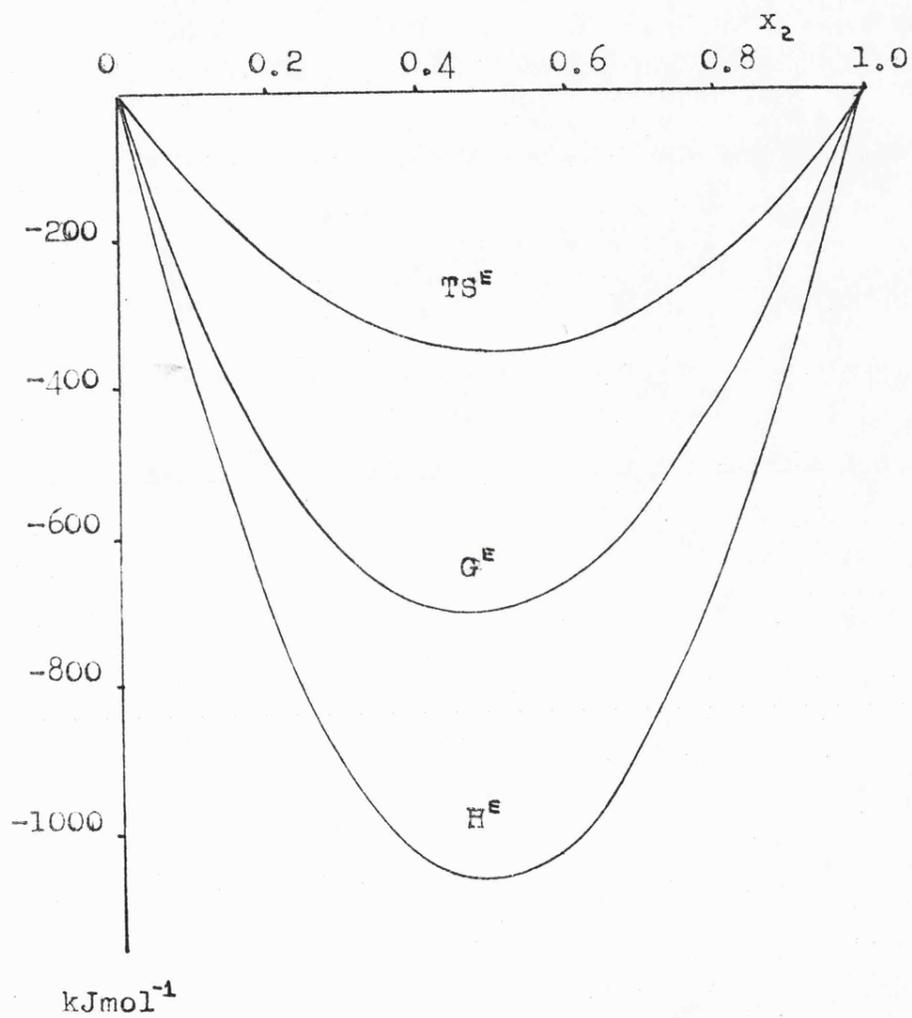


FIGURE 2-4

suggest that there is a continuous breakdown of the water structure as x_2 increases.

(b) TNAN Mixtures

These mixtures have $G^E < 0$ and a small S^E ; which corresponds to an increase in order in the solution (figure 2-4). For these types of mixtures intercomponent association occurs between the co-solvent and water.

The association between water and hydrogen peroxide was shown in a study of the basicity of the solvent mixture²⁶. N.M.R. studies²⁷ on dimethyl sulphoxide (DMSO) and water indicated there was a strong intercomponent association between DMSO and water. A maximum in relaxation²⁸ time at a mole fraction of DMSO $x_2 = 0.65$ was thought to be caused by a 2:1 H₂O: DMSO associated species.

Thermodynamic studies of DMSO + water²⁹ show that there is a positive deviation from ideality which again strongly suggests association between the two components.

Viscosity and density have maximum deviation from a ratio of 2 moles of H₂O to 1 mole DMSO. The results show there is a greater degree of association in H₂O - DMSO mixtures than in water alone.

For TNAN mixtures the water structure is again broken but unlike TNAP mixtures this results from interaction between the co-solvent and water.

CHAPTER 3

REACTION KINETICS

1. The Arrhenius Law

In 1889 Arrhenius proposed that the dependence of a rate constant on temperature should conform to an equation similar to that for the corresponding dependence of an equilibrium constant (van't Hoff equation)

$$\text{i.e. } \frac{d \ln k}{dT} = \frac{E_{\text{exp}}}{RT^2} \quad 3 - 1$$

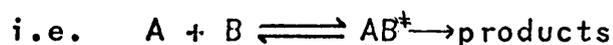
where E_{exp} is the activation energy for the reaction. This equation has been found to be obeyed with high accuracy for all types of chemical reactions over small temperature ranges.

2. Transition State Theory

Transition state theory¹ assumes that a reaction passes through a high energy intermediate state or activated complex. This complex is regarded as being situated at the top of an energy barrier lying between the initial and final states. The rate of the reaction is, therefore, controlled by the rate at which the complex travels over the top of the barrier.

3. Derivation of Transition State Thermodynamic Parameters

Consider, for example, the simple case of two molecules coming together to give a product -



If the activated complex, AB^* , is in equilibrium with the reactants, then the equilibrium constant for the formation of the complex is given by the following equation -

$$K^* = \frac{[AB^*]}{[A][B]} \quad 3 - 2$$

From which the concentration of the activated complex is

$$[AB^\ddagger] = K^\ddagger [A] [B] \quad 3 - 3$$

The rate of the reaction is dependent on the concentration of the activated complex and the rate at which it decomposes. The activated complex will break up when one of its modes of vibration is converted into a translational motion i.e. what was formerly one of the bonds of the complex is simply the line of centres between separating fragments. The frequency of decomposition, ν , is equal to E/h where E is the average energy of the vibration that leads to breakdown of the complex. At temperature, T , this vibration, a thoroughly excited vibration, has a classical energy $E = kT$. Thus the frequency of decomposition is given by :-

$$\nu = \frac{kT}{h} \quad 3 - 4$$

The rate of reaction can be expressed as:-

$$-\frac{d[A]}{dt} = k_1 [A][B] = K [A][B] \frac{kT}{h} \quad 3 - 5$$

Thus the rate constant is:-

$$k_1 = \frac{kT}{h} K \quad 3 - 6$$

Equation 3 - 6 can be used to introduce thermodynamic parameters, by using the relationship between the equilibrium constant and the change in the Gibbs free energy in equation 3 - 6

$$\text{i.e. } \Delta G^\ddagger = -RT \ln K^\ddagger \quad 3 - 7$$

substituting for K^\ddagger in equation 3 - 6

$$k_1 = \frac{kT}{h} e^{\frac{-\Delta G^\ddagger}{RT}} \quad 3 - 8$$

ΔG^\ddagger is the difference between the Gibbs free energy of the activated complex and that of the reactants when all are in their standard states. Equation 3 - 8 can be used to introduce further thermodynamic parameters as:-

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad 3 - 9$$

The rate constant can now be expressed as

$$k_1 = \frac{kT}{h} \exp\left[\frac{\Delta S^\ddagger}{R}\right] \exp\left[\frac{-\Delta H^\ddagger}{RT}\right] \quad 3 - 10$$

From equation 3 - 10 it can be seen that the temperature dependence of the rate constant, k_1 , will enable the activation enthalpy, ΔH^\ddagger , to be calculated. If the rate constant is measured over a large temperature range then the temperature dependence of ΔH^\ddagger needs to be considered i.e. ΔC_p^\ddagger , $\frac{d\Delta H^\ddagger}{dT}$, and possibly $d\Delta C_p^\ddagger/dT^{2,3}$. Indeed ΔC_p^\ddagger has proved to be of considerable interest in organic solvolysis reactions⁴.

4. Effect of Solvent on Reaction Rates

a) Empirical Relationships describing the Effect of Solvent on Kinetics

These equations are the so called linear free energy relationships and have been developed largely by the organic chemists. The aim was to produce a quantity which is characteristic of the solvent. Perhaps the best known of these equations is the one developed by Grunwald and Winstein⁵ who derived solvent 'Y values'. These equations measured the ionising power of the solvent.

These relationships were reasonably successful as they are concerned with the Gibbs free energy of activation, ΔG^\ddagger , which is a 'well behaved' function. In contrast the enthalpy, ΔH^\ddagger , and entropy, ΔS^\ddagger , are not 'well behaved' and show much more complex behaviour. Thus, if relationships based on ΔH^\ddagger or ΔS^\ddagger had been attempted, correlations would not have been so readily obtained.

b) Effect of Solvent Structure on Rates of Chemical Reactions

The first studies in this field were in the realm of organic chemistry. Winstein and Fainberg⁶, as well as others, showed that the Gibbs free energy of activation for hydrolysis reactions varied monotonically with solvent composition of aqueous binary mixtures. However, the enthalpy and entropy of activation showed extremum behaviour as a function of solvent composition. For example, the behaviour of ΔH^\ddagger with mole fraction for the solvolysis of t-butyl chloride and for ester hydrolysis show extrema in ΔH^\ddagger in aqueous rich mixtures⁴. These extrema have been correlated with extrema in the enthalpies of solution for solutes in these mixtures.

The influence of solvent structure on inorganic reaction kinetics has not been studied in as much detail. Caldin⁷ has used the solvent structure to interpret solvent effects on the rate of ligand substitution at nickel (II). Caldin in his interpretation of solvent effect uses the Frank and Wen⁸ model for the solvated ion. Briefly in this model, an ion is surrounded by three regions:- the solvent next to the ion

which is highly ordered; next to this is a disordered region and finally the bulk solvent. The rate of solvent exchange is governed by, in Caldin's terms, the 'stiffness' or 'looseness' of the solvent. For the reaction to occur a solvent or ligand molecule must break away from the ion, travel through the disordered region and into the bulk solvent. The ease with which the ligand or solvent is incorporated into the bulk solvent will depend on the 'stiffness' of the solvent. The stiffness of the solvent is compared with the enthalpy of vapourisation and its fluidity. A linear correlation was found between the enthalpy of activation for 2, 2' - bipyridyl substitution at nickel (11) relative to that for solvent exchange, $\Delta\Delta H^\ddagger$, in various solvents and the heat of vapourisation.

Coetzee⁹ has also interpreted his results for the solvent dependence of ligand substitution kinetics of nickel(11) in a similar manner. He agreed with Caldin that the structure of the solvent is important and "the solvent effect on rates mirrors the rhythm of molecular reorganisation of the liquid". However, Mackeller and Rorabacher¹⁰ interpret their results for the solvent dependence of the rate of reaction between nickel(11) and ammonia in methyl alcohol-water mixtures in terms of changes in composition of the inner solvation sphere.

Recently Bennetto¹¹ has tried to correlate the rate of reaction on nickel(11) with pyridine-2-azodimethylaniline in various pure solvents with the heat of evaporation.

and with solvent fluidity. However, he did not achieve as good a correlation as that obtained for the reaction between nickel(II) with 2,2'-bipyridyl.

5. Analysis of Activation Parameters

A useful approach when studying the variation in activation parameters, ΔX^\ddagger , in various solvents is to adopt the kinetic parameters for the reaction in water as a reference. The difference in ΔX^\ddagger between that in water and that in the binary solvent mixture can be calculated and the change represented by $\delta_m \Delta X^\ddagger$, where δ_m is the solvent operator

$$\delta_m \Delta X^\ddagger = \Delta X^\ddagger (x_2) - \Delta X^\ddagger (x_2=0)$$

The variation in ΔX^\ddagger is the result of several factors. The properties of both the initial state and final state will vary with mole fraction of co-solvent, x_2 , but not necessarily in the same manner. The change in solute properties (reactant or transition state) can be brought about by direct co-solvent solute interactions or by the co-solvent causing variations in water - water interactions which in turn modify solute-water interactions.

In order to interpret the activation parameters it is necessary to separate the solvent effects on the transition state and the initial state. The solvent effect on the transition state, $\delta_m \Delta X^\ddagger$, is impossible to measure due to the nature of the transition state. However, the solvent effects

on the initial state can sometimes be measured. Arnett et al.¹³ devised a method for measuring the enthalpy of solution for reacting substances, before any appreciable reaction had occurred. The enthalpy of solvation of the initial state, ΔH_3° , was obtained. The activation enthalpy, ΔH^\ddagger , can then be obtained in the normal way. The enthalpy of solvation of the transition state can be obtained. The activation energy, ΔH^\ddagger , can then be obtained in the normal way. The enthalpy of solvation of the transition state can be obtained by the difference -

$$\Delta H_t = \Delta H^\ddagger + \Delta H_3^\circ$$

If it is not possible to measure values for actual reactants it is often possible to draw tentative conclusions from measuring the transfer quantities for similar solutes. This technique was used in the analysis of solvent effects on the solvolysis of alkyl halides, which are in general hydrophobic solutes, using the solubilities of hydrocarbons and other gases in pure solvent¹⁴.

6. Correlation Between Rate of Reaction and Thermodynamic Parameters

A classification of liquid mixtures has been outlined in Chapter 2. If this classification is used, then a pattern can be identified between the variation of the rate constant, for some reactions, in a solvent mixture with the class of the mixture¹⁵. For example, in the S_N1 solvolysis

of organic halides and aquation of Co(II) amines¹⁶ or ammine halide complexes, the rate decreases when TA non-aqueous component is added. The rate also decreases when TNAP co-solvent acetonitrile is added and when the TNAN co-solvent DMSO is added^{17,18}. However, for TNAN co-solvent hydrogen peroxide the rate increases¹⁹.

A similar pattern has been recognised for the variation of the rate of aquation of tris (5NO₂ - 1,10-phenanthroline) iron(II) in various mixed solvents²⁰. In TA mixtures the rate of aquation increases markedly with increasing x_2 , in TNAN mixture acetonitrile + water there is a less dramatic increase in rate. However, the rate in formic acid decreases with increasing x_2 . The tris (4,7-dimethyl-1,10-phenanthroline) iron(II) does not show this variation of reaction rate, the rate of aquation decreases with increasing concentration of the co-solvent for all classes¹⁹.

There also appears to be a correlation between G^E for the binary mixture and the trend in $\delta_m \Delta G^\ddagger$ ¹⁵. For the hydrolysis of t-butyl chloride $\delta_m \Delta G^\ddagger$ at a fixed mole fraction increases as G^E increases in TA aqueous rich mixtures. The TNAP solvent acetonitrile complies with this pattern but not however water + DMSO mixtures. The reaction of nickel(II) with 2,2'-bipyridyl²¹ in methanol, ethanol and t-butyl alcohol aqueous mixtures appears to show a correlation between $\delta_m \Delta G^\ddagger$ and G^E .

The (5NO₂-1,10-phenanthroline) iron(II) complex displays

the opposite type of behaviour to that of t-butyl chloride i.e. ΔG^\ddagger decreases as G^E increases when TA co-solvents are added. The different behaviour of the rate of aquation of the $5NO_2$ iron complex and the hydrolysis of t-butyl chloride with solvent mixture can be explained in terms of the different nature of the initial and transition states of the two reactants. For the hydrolysis of t-butyl chloride there is a hydrophobic initial state and a hydrophilic transition state but for the $5NO_2$ iron complex the initial state is hydrophilic and the final state is more hydrophilic²².

Thus the solvent structure has been shown to play an important role in determining the rate of reaction. The basic problem has been how best to represent the structure of the solvent as the reacting molecule experiences it. The excess thermodynamic functions appear to be able to give a good indication of such structure.

CHAPTER 4

ENDOSTATIC ANALYSIS

1. Introduction

The variation of kinetic parameters with composition for reactions in mixed aqueous solvents is often very complex¹. As outlined in Chapter 2 the excess thermodynamic functions provide useful information about the structure of mixed aqueous solvents. Indeed there appears to be a qualitative link between $\delta_m \Delta G^\ddagger$ and the excess Gibbs free energy G^E for some reactions² in mixed aqueous solvents. A more quantitative approach of relating excess thermodynamic quantities and derived activation parameters, ΔX^\ddagger , has been put forward by Grunwald³. Grunwald applied the method to analyse the activation parameters for the solvolysis of t-butyl chloride in ethanol + water mixtures. This analysis has been applied to the kinetics of aquation of tris(5NO₂-1,10-phenanthroline) iron(II) with some interesting results (Chapter 7). This chapter summarises the background to the theory.

2. Solutes in Binary Solvent Mixtures

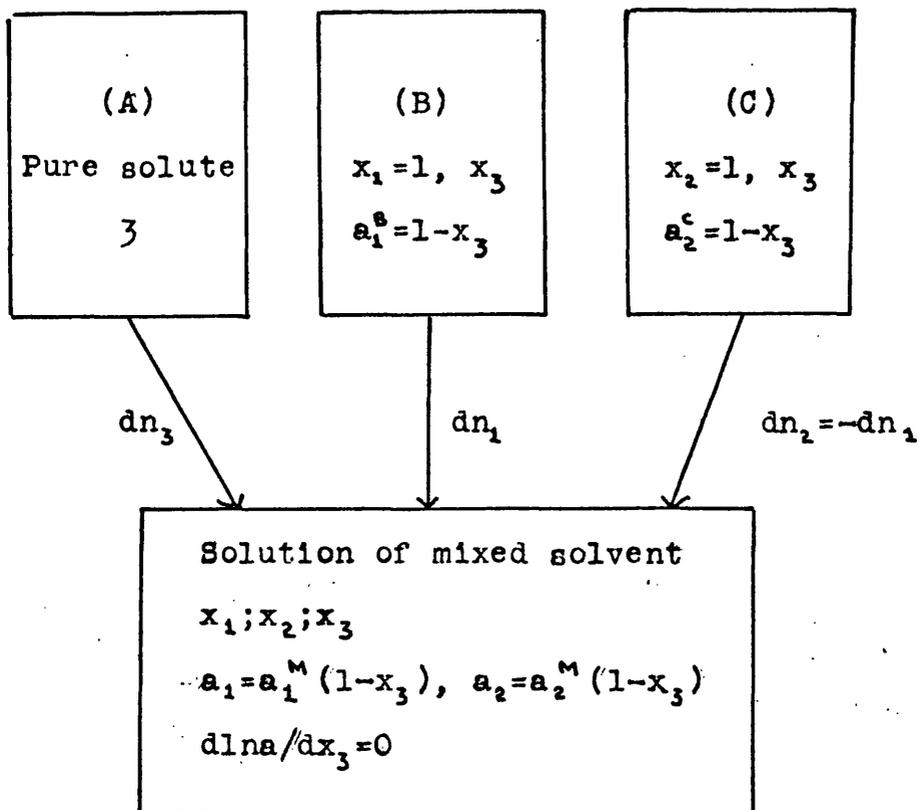
When a solute is added to a mixed solvent, marked changes in the properties of the components can occur. In thermodynamic terms, the solute will significantly alter the activities of the two solvent components⁴. The effect, therefore, of adding the solute to a binary mixture is complex and the properties of the solvent components differ from those in the binary mixture. Thus the properties of the simple

binary mixture cannot be readily used to interpret kinetic data for reactions in mixtures. Grunwald suggests that by comparing systems at constant activity rather than constant composition the situation may be easier to understand. Grunwald in his paper reminds us of the simple system comprising a mixed solvent containing a solute separated by a semi-permeable membrane from the mixed solvent at the same composition. When osmotic equilibrium is reached then it is the activity and not the composition of the solvent that is equal⁵ on either side of the membrane. A more 'natural' way, therefore, for dealing with binary solvents might be at constant activity rather than constant composition. The problem, of course, is how to realise such a situation. The next section outlines the method for converting conventional thermodynamic quantities to comparable values at constant activity.

In order to distinguish conventional thermodynamic quantities from corresponding ones calculated at constant activity the term endostatic will be used for the ones calculated at constant activity (endo=internally static=staying constant).

3. Endostatic Conditions

As stated previously the most important condition is that the activities of the two solvent components are kept constant i.e. the ratio a_1/a_2 is constant ($a_1 = x_1 f_1, a_2 = x_2 f_2$). For brevity this ratio will be given the symbol α .



Endostatic addition of solute to a solution in a
mixed solvent

FIGURE 4-1

When a solute is added at constant activity then Scatchard⁵ has shown that the solute behaves ideally i.e. it obeys Raoult's Law.

If a solute is added to a binary solvent then it is obviously necessary to allow the composition of the two solvent components to vary. For ease of calculation the total number of moles of solvent ($n_1 + n_2$) is kept constant.

4. Endostatic Thermodynamic Functions

Figure 4 - 1 gives the process for defining endostatic molar functions. It comprises the simultaneous transfer of dn_3 moles of pure solute, dn_1 moles of solvent 1 and dn_2 ($= -dn_1$) of component 2 to the binary solvent.

For the endostatic transfer of dn_3 moles of pure solute the total change in any thermodynamic quantity is given by

$$\begin{aligned} \text{Total change in } X_3 &= dX_S - dX_A - dX_B - dX_C \\ &= dn_3 [X_{\alpha 3} - X_3^\circ] \quad 4 - 1 \end{aligned}$$

X_3° = extensive property of pure 3

$X_{\alpha 3}$ = endostatic partial molar function in the mixed solvent or for the transfer of dn_3 moles

$$X_{\alpha 3} - X_3^\circ = \left[\frac{\partial (X_3 - X_A - X_B - X_C)}{\partial n_3} \right]_{\alpha, (n_1 + n_2)} \quad 4 - 2$$

5. Definition of Functions Used

The standard state of a component of a mixed solvent is taken to be the pure component symbol X° .

For the solute the reference state is a hypothetical solution of unit mole fraction

$$\text{i.e. } \mu_3 = \mu_3^\circ + RT \ln x_3 f_3 \quad \text{where } f_3 \rightarrow 1 \text{ as } x_3 \rightarrow 0$$

4 - 3

Here μ_3° is a function of solvent composition.

\bar{X}_1 and \bar{X}_2 will be used to denote partial molar quantities in the mixture. $\bar{X}_1 - \bar{X}_1^\circ$, are relative partial molar quantities. The differentials required for equation 4 - 2 are as follows -

$$dX_3 = \bar{X}_1 dn_1 + \bar{X}_2 dn_2 + X_3 dn_3 \quad 4 - 4$$

$$dX_A = X_3^\circ dn_3 \quad 4 - 5$$

$$dX_B = \bar{X}_1(B) dn_1 \quad 4 - 6$$

$$dX_C = \bar{X}_2(C) dn_2 \quad 4 - 7$$

suffixes represent the source.

Substituting these equations into equation 4 - 1

$$X_{\alpha 3} - X_3^\circ = \left[(\bar{X}_3 - X_3^\circ) dn_3 + (\bar{X}_1 - \bar{X}_1(B)) dn_1 + (\bar{X}_2 - \bar{X}_2(B)) dn_2 \right]$$

4 - 8

$$\text{But } dn_1 = -dn_2$$

Therefore

$$X_{\alpha 3} = X_3 + \left[(\bar{X}_1 - \bar{X}_1(B)) - (\bar{X}_2 - \bar{X}_2(B)) \right] \left[\frac{\partial n_1}{\partial n_3} \right]_{\alpha, n_1+n_2}$$

4 - 9

The difference in the partial molar quantities, $\bar{X}_1 - \bar{X}_1(B)$ is required. We consider first the simplest case of the chemical potential.

$$\text{In B} \quad \mu_1(B) = \mu_1^\circ + RT \ln (1 - x_3) \quad 4 - 10(a)$$

$$\text{In solution} \quad \mu_1(s) = \mu_1^\circ + RT \ln a_1(s) (1-x_3) \quad 4 - 10(b)$$

$$\text{Therefore} \quad \mu_1(s) - \mu_1(B) = RT \ln a_1(s) \quad 4 - 11$$

$$\text{i.e. the difference between } \mu_1(s) - \mu_1(B) = \delta \mu_1 \quad 4 - 12$$

$\delta \mu_1$ = relative chemical potential.

It can also be shown that the difference in the other partial molar quantities is the relative partial molar quantity.

Equation 4 - 9 can therefore now be expressed as

$$X_{\alpha 3} = X_3^\circ + (\delta \bar{X}_1 - \delta \bar{X}_2) \left[\frac{\partial n_1}{\partial n_3} \right]_{\alpha, n_1+n_2} \quad 4 - 13$$

where $\delta \bar{X}_1$ = relative partial molar quantity.

In order to evaluate equation 4 - 13 the differential dn_1/dn_3 is required. This differential cannot be calculated directly but requires two stages.

The first stage makes use of the equation defining the mole fractions x_1 and x_3 i.e.

$$x_1 = \frac{n_1}{n_1 + n_2} \quad x_3 = \frac{n_3}{n_1 + n_2 + n_3} \quad 4 - 14$$

Differentiation of these equations at constant α and $n_1 + n_2$ followed by multiplication gives:-

$$\left[\frac{\partial n_1}{\partial n_3} \right]_{\alpha, n_1 + n_2} = (1 - x_3)^2 \left[\frac{\partial x_1}{\partial x_3} \right]_{\alpha} \quad 4 - 15$$

The next problem is to evaluate $\partial x_1 / \partial x_3$. It is convenient to introduce $\ln \alpha$ in place of α and thereby convert the differential, as expressed in equation 4 - 16

$$\left[\frac{\partial x_1}{\partial x_3} \right]_{\alpha} = \left[\frac{\partial x_1}{\partial x_3} \right]_{1n\alpha} = - \frac{(\partial \ln \alpha / \partial x_3) x_1}{(\partial \ln \alpha / \partial x_1) x_3} \quad 4 - 16$$

The quantity $(\partial \ln \alpha / \partial x_1)_{x_3}$ can be calculated by using the following relationships.

$$\frac{\partial \mu_3}{\partial n_1} = \frac{\partial \mu_1}{\partial n_3} \quad \frac{\partial \mu_2}{\partial n_3} = \frac{\partial \mu_3}{\partial n_2} \quad 4 - 17$$

The chemical potential of each component is then treated as a function of two variables x_1 and x_3 . Partial differentiation of chemical potential results in the following equations:-

$$\frac{\partial \mu_3}{\partial n_1} = \frac{\partial \mu_3}{\partial x_1} \left[\frac{x_1}{n_1+n_2} \right] + \frac{\partial \mu_3}{\partial x_3} \left[\frac{x_3}{n_1+n_2+n_3} \right] \quad 4 - 18$$

$$\frac{\partial \mu_1}{\partial n_3} = \frac{\partial \mu_1}{\partial x_3} \left[\frac{1 - x_3}{n_1+n_2+n_3} \right] \quad 4 - 19$$

$$\frac{\partial \mu_2}{\partial n_3} = \frac{\partial \mu_1}{\partial x_3} \left[\frac{1 - x_3}{n_1+n_2+n_3} \right] \quad 4 - 20$$

$$\frac{\partial \mu_3}{\partial n_2} = - \frac{\partial \mu_3}{\partial x_1} \left[\frac{x_1}{n_1+n_2} \right] - \frac{\partial \mu_3}{\partial x_3} \left[\frac{x_2}{n_1+n_2+n_3} \right] \quad 4 - 21$$

By using the relationships given in 4 - 17 and subtracting, we obtain -

$$\frac{\partial (\mu_1 - \mu_2)}{\partial x_3} = \frac{1}{(1-x_3)^2} \frac{\partial \mu_3}{\partial x_1} \quad 4 - 22$$

since $\mu_1 = \mu_1^\circ + RT \ln a_1$

and $\mu_2 = \mu_2^\circ + RT \ln a_2$

then $\mu_1 - \mu_2 = \mu_1^\circ - \mu_2^\circ + RT \ln \alpha \quad 4 - 23$

By differentiating 4-23 and equating with 4-22 the required differential is obtained 4-24 -

$$RT \frac{d \ln \alpha}{dx_3} = \frac{1}{(1-x_3)^2} \frac{\partial \mu_3}{\partial x_1} \quad 4 - 24$$

If this equation together with 4-16 are substituted into 4-13 then we have

$$X_{\alpha 3} = X_3^{\circ} - (\delta \bar{X}_1 - \delta \bar{X}_2) \frac{(\partial \mu_3^{\circ} / dx_1)}{(RT d \ln \alpha / dx_1)_{x_3}} \quad 4 - 25$$

This equation expresses an endostatic thermodynamic parameter in terms of quantities that are either measurable or calculable.

6. Expressions Relating Conventional and Endostatic Thermodynamic Parameters

Consider firstly the case of the Gibbs free energy.

By combining equations 4-11, 4-12, 4-16 and 4-24, we obtain

$$\mu_{\alpha 3}^{\circ} = \mu_3^{\circ} - (\ln \alpha) (\partial \mu_3 / \partial x_1) / (\partial \ln \alpha / \partial x_1) \quad 4 - 26$$

Other thermodynamic functions can be calculated from 4 -25.

Endostatic activation parameters are obtained by writing the endostatic equation for the reactant and the activated complex, and then subtracting, which gives the following expressions for $\Delta G_{\alpha}^{\ddagger}$ and $\Delta H_{\alpha}^{\ddagger}$

$$\Delta G_{\alpha}^{\ddagger} = \Delta G^{\ddagger} - (\ln \alpha) \cdot (d \Delta G^{\ddagger} / dx_1) / (d \ln \alpha / dx_1) \quad 4 - 27$$

$$\Delta H_{\alpha}^{\ddagger} = \Delta H^{\ddagger} - (H_1^E - H_2^E) - (\partial \Delta G^{\ddagger} / dx_1) / RT d \ln \alpha / dx_1 \quad 4 - 28$$

The endostatic entropy of activation can be found by using the equation:-

$$\Delta G_{\alpha}^{\ddagger} = \Delta H_{\alpha}^{\ddagger} - T \Delta S_{\alpha}^{\ddagger} \quad - 4 - 29$$

Thus endostatic activation parameters can be calculated from conventional ΔG^\ddagger quantities.

7. Calculation of Parameters Required for Endostatic Calculation

Activation parameters were initially calculated in the usual manner (Chapter 6). In all the equations for endostatic values the differential of the activation Gibbs free energy with respect to the mole fraction x_1 is required. A small BASIC programme was written to calculate this quantity using a simple running parabola procedure. The programme used the first three points fitted them to a parabola and calculated the slope at the middle point. The programme then dropped the first point and used the fourth to calculate the slope at the third point, the programme working along the curve finding the slope at each point.

The values of $\ln \alpha$ and $d \ln \alpha / dx_1$ were obtained by differentiating the excess Gibbs free energy with respect to x_1

$$G^E = RT (x_1 \ln f_1 + x_2 \ln f_2) \quad 4 - 30$$

$$\frac{dG^E}{dx_1} = RT \ln \frac{f_1}{f_2}$$

Therefore

$$\ln \alpha = \frac{1}{RT} \frac{dG^E}{dx_1} + \ln \frac{x_1}{x_2} \quad 4 - 31$$

$$\frac{d \ln \alpha}{dx_1} = \frac{1}{RT} \frac{d^2 G^E}{dx_1^2} + \frac{1}{x_1 x_2} \quad 4 - 32$$

The values of G^E are normally obtained from vapour pressure data. These data can then be fitted to an algebraic equation, the Guggenheim Scatchard equation⁶.

$$G^E = x_1(1-x_1) \sum_{i=1}^i A_i (1-2x_1)^{i-1} \quad 4 - 33$$

An ALGOL programme (MARY A) was written to fit published values of G^E . The number of coefficients, n_1 was increased until the standard deviation between calculated and input values of G^E was a minimum. Using these coefficients it was possible to calculate G^E at the required values of x_1 and also to calculate the quantities $\ln \alpha$ and $d \ln \alpha / dx$. In order to evaluate equations 4-31 and 4-32 the first and second differential of G^E with respect to x_1 are required. These can be calculated from the differentials of equation 4-33 with respect to x_1 and the A_i coefficients calculated in the G^E fit. The differentials of equation 4-33 are :-

$$dG^E/dx_1 = (1-2x_1) \sum_{i=1}^i A_i (1-2x_1)^{i-1} - x_1(1-x_1) \sum_{i=1}^i 2A_i (i-1) (1-2x_1)^{i-2} \quad 4 - 34$$

$$\begin{aligned} d^2G^E/dx_1^2 &= 4x_1(1-x_1) \sum_{i=1}^i A_i (i-1) (i-2) (1-2x_1)^{i-3} \\ &\quad - 4(1-2x_1) \sum_{i=1}^i A_i (i-1) (1-2x_1)^{i-2} \\ &\quad - 2 \sum_{i=1}^i A_i (1-2x_1)^{i-1} \end{aligned} \quad 4 - 35$$

A small BASIC programme was written to evaluate the equations 4-34 and 4-35.

The remaining parameters required are the partial molar quantities. These are calculated by differentiating the required excess function with respect to the mole fraction x_1 .

For the case of the excess enthalpy:-

$$H^E = (1-x_1) \bar{H}_2 + x_1 \bar{H}_1 \quad 4 - 36$$

$$\frac{\partial H^E}{\partial x_1} = (1-x_1) \frac{\partial \bar{H}_2}{\partial x_2} - \bar{H}_2 + x_1 \frac{\partial \bar{H}_1}{\partial x_1} + \bar{H}_1$$

But from the Gibbs-Duhem Equation

$$(1-x_1) \frac{d\bar{H}_2}{dx_1} + x_1 \frac{d\bar{H}_1}{dx_1} = 0$$

Equation then becomes

$$\frac{\partial H^E}{\partial x_1} = \bar{H}_1 - \bar{H}_2 \quad 4 - 37$$

To evaluate $\partial H^E / \partial x_1$ literature values of H^E are fitted to the Guggenheim-Scatchard equation

$$H^E = x_1(1-x_1) \sum_{i=1}^i A_i (1-2x_1)^{i-1} \quad 4 - 38$$

This equation is then differentiated and the values of A_i found previously are used to calculate its value at the required mole fractions.

8. Importance of Endostatic Approach

This approach of analysing kinetic data has succeeded in combining two sets of information, the kinetic data as expressed in terms of activation parameters and the thermodynamic behaviour of the mixed solvent. Moreover this information is combined in a quantitative manner.

CHAPTER 5

EXPERIMENTAL

1. Introduction

This chapter is concerned with the preparation of the complexes used in these studies, together with the construction and operation of the apparatus.

Due to the differences in the rate constants of the reactions used two separate techniques were employed. Conventional spectrophotometry was used to study reactions with half-lives of the order of 10 seconds up to a number of hours. The other technique was used to study 'fast reactions' i.e. reactions with half-lives of the order 10^{-3} seconds. Due to the different nature of these two methods they will be described independently in the following sections.

2. Spectrophotometry Kinetics - Basic Principles

The rate of any chemical reaction is defined as the rate of disappearance of a reactant or the rate of appearance of a product. The change of concentration can be monitored spectrophotometrically because the absorbance of a solution varies directly with concentration as given by Beer's Law

$$A = c l \epsilon$$

where A = absorbance c = concentration
 l = path length ϵ = extinction coefficient

By following the dependence of the absorbance of the reaction mixture on time, the rate of change of concentration of one of the constituents can be determined and from this information the rate constant calculated.

For each reaction investigated a suitable wavelength at which to follow the reaction had to be chosen. The spectrum of the reactants was taken over the whole ultra-violet and visible range covered by the spectrophotometer. The spectrum was then taken at regular time intervals. Hence the wavelength at which the maximum change in absorbance occurred was found. This procedure was carried out in all solvents used to check that the reaction went to completion and also that the products of the reaction were unchanged by the solvent.

3. Fast Reactions

The bulk of the work in this part of the investigations was carried out on a stopped-flow apparatus (Applied Photo-physics, designed by P Moore). A small amount of work was undertaken using the temperature jump apparatus at the University of Kent with the help of Dr. D. Hague.

(a) Principles of the Stopped-flow Method

In this technique two reactant solutions are rapidly mixed by a specially designed mixing chamber. The mixed solutions flow down a tube and then the flow is suddenly stopped (within one or two milliseconds). The reaction is then followed by measuring the absorbance of a fixed element of the stopped mixed solution. The response signal from the photo-multiplier can then be applied to a storage cathode ray oscilloscope. By suitable adjustment of the time base on the oscilloscope a curve representing the extent of

reaction against time can be displayed on the screen from which the half-life of the reaction can be measured.

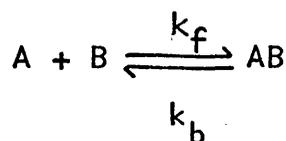
(b) Principles of the Temperature-Jump Technique

The temperature jump technique of following fast reactions is a relaxation technique. The system is allowed to come to equilibrium and is then disturbed by a sudden rise in temperature. If this change is made sufficiently rapidly there is a time lag during which the system approaches the new equilibrium position. This time lag is related to the rate constants for the forward and back reactions. The response depends on the standard enthalpy change, ΔH^\ominus , for the reaction according to the following equation

$$\frac{d \ln K}{dT} = \frac{\Delta H^\ominus}{RT^2}$$

The rate of response in terms of a relaxation time which is related to the rate parameters.

For example consider the reaction



The rate of reaction can be described by

$$\frac{d [AB]}{dt} = -\frac{d [A]}{dt} = -\frac{d [B]}{dt} = k_f [A] [B] - k_b [AB]$$

If the reaction is allowed to equilibrate and is then disturbed by a sudden change in temperature then the concentration of the components as the reaction proceeds can be described by the following equations -

$$[A] = [A_e] + \Delta[A]$$

$$[B] = [B_e] + \Delta[B]$$

$$[AB] = [AB_e] + \Delta[AB]$$

subscript e designates equilibrium concentrations

Δ 's are the deviation from the equilibrium concentrations.

A quantity ΔC is defined such that

$$\Delta C = \Delta[AB] = -\Delta[A] = -\Delta[B]$$

$$\text{then } \frac{-d\Delta C}{dt} = (k_f([A_e] + [B_e]) + k_b)\Delta C - k_f[A_e][B_e] + k_b[AB_e] - k_f[\Delta C]^2$$

$$\text{as } \frac{k_f}{k_b} = \frac{[AB_e]}{[A_e][B_e]}$$

If ΔC is small the $[\Delta C]^2$ can be ignored

$$\frac{d\Delta C}{dt} = -(k_f([A_e] + [B_e]) + k_b)\Delta C$$

Integrating

$$\ln \frac{\Delta C_0}{\Delta C} = [(k_f([A_e] + [B_e]) + k_b)t]$$

The relaxation time, τ , is defined as the time at which the distance from equilibrium to $1/e$ of the initial concentration

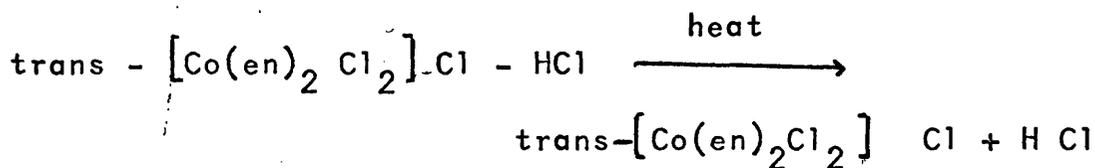
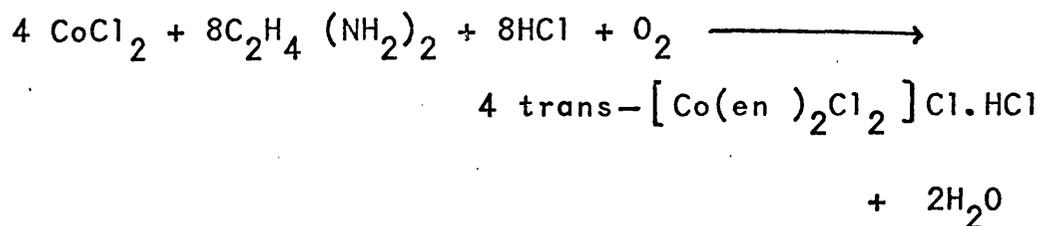
$$\text{therefore } \tau = \frac{1}{k_f([A_e] + [B_e]) + k_b}$$

4. Experimental Details

(a) Preparation of Complexes

(i) cis - Dichlorobis (ethylenediamine) Cobalt(III) was prepared as described in the literature¹.

The preparation involves the transformation of the analogous trans complex which is formed according to the following equations:-



en = ethylenediamine

An excess of 10% solution of ethylenediamine was added to a 3M solution of Cobalt chloride. A vigorous stream of air was drawn through the solution for 10 to 12 hours. Concentrated hydrochloric acid was added and the solution was evaporated on a steam bath until a crust was formed. The solution was allowed to cool and bright green crystals of the hydrochloride slowly formed which were filtered, washed with alcohol and dried in an oven at 110°C overnight. The crystals crumbled to give dark green powder of trans - $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$.

Conversion to the cis form was accomplished by evaporating a neutral solution of the trans form to dryness on a steam bath. This was repeated twice to try to ensure complete conversion. However, it was found later that 100% conversion was not obtained and therefore gave rise to irregularities in the kinetics of aqutation.

(ii) Tris (5-nitro-1,10-phenanthroline) iron(II) was prepared in solution by adding a stoichiometric amount of ligand to a freshly prepared aqueous solution of iron(II) sulphate. The purity of the product was checked by determining the rate of aquation which was found to agree with published data and also by checking for the persistence of first-order kinetics over numerous half-lives.

(iii) Chloro(diethylenetriamine) platinum(II) chloride was prepared as described by previous workers². The synthesis involved several stages; preparation of platinum(II) iodide monohydrate followed by the conversion to (iododiethylenetriamine) platinum(II) iodide and conversion of the iodo complex to the chloro complex.

Platinum iodide monohydrate was made by adding potassium iodide to a solution of sodium tetrachloroplatinate (II). Platinum iodide was formed as a dark grey precipitate with a metallic sheen. The precipitate was filtered, washed with water, dried and weighed. The platinum iodide was made into a thick paste with water. A stoichiometric quantity of diethylenetriamine (dien) was added, the paste becoming dry and turning an orange /brown colour. The mixture was heated on a water bath for several hours. Any unreacted platinum iodide was removed by adding water at 90°C in which it is soluble but the dien complex is not. The hot mixture was filtered and allowed to cool. Yellow crystals of (iododiethylenetriamine) platinum(II) iodide were formed.

These crystals were filtered, washed with water and dried in vacuo over potassium hydroxide for 2 hours. The product was weighed.

To convert to the corresponding chloro complex, the iodo complex, 1.1g, was dissolved in 50mls of water to which 1.9g of silver nitrate in 1.5mls of 6M Hydrochloric acid were added. This mixture was stirred in the dark for 48 hours. The liquid was filtered. The clear yellow filtrate was evaporated to ca 5ml on a steam bath. On cooling, in an ice-bath bright yellow crystals of the chloro complex slowly formed. The crystals were filtered, washed with acetone and dried in vacuo for 1hr over potassium hydroxide. A second crop of crystals were obtained by dilution of the filtrate with acetone.

(iv) Chloro (N,N,N",N" - tetraethyldiethylenetriamine) palladium(II) chloride was prepared by a previously described method³. The synthesis involved mixing 2g of palladium(II) chloride with 5ml of concentrated acid followed by 15ml of water. The mixture was stirred at room temperature until the palladium chloride dissolved forming a deep red/orange solution. The solution was filtered and 2ml of N,N,N",N" tetra ethyldiethylenetriamine (Et₄dien) was slowly added to a stirred filtrate. As the amine was added an orange precipitate was formed. After all the Et₄dien had been added the mixture was heated on a steam bath for about 10 minutes during which time the solid dissolved to

form an orange solution. Lithium chloride (2g) was then added followed by evaporation of the solution to 15ml on a steam bath. On cooling a yellow solid was formed. This was filtered washed with ether and left to dry overnight.

The purity of the product was checked by monitoring the spectral changes during the reaction of the complex with iodide ion at 298K and then comparing with the published spectra³. Excellent agreement was obtained.

(b) Solvent

All solvents used were highest quality reagent grade. All solutions were made up by weight except for hydrogen peroxide solutions. Hydrogen peroxide solutions were made up by volume. The concentration of the hydrogen peroxide was determined by standard sodium thiosulphate and iodide titration as described by Vogel⁴.

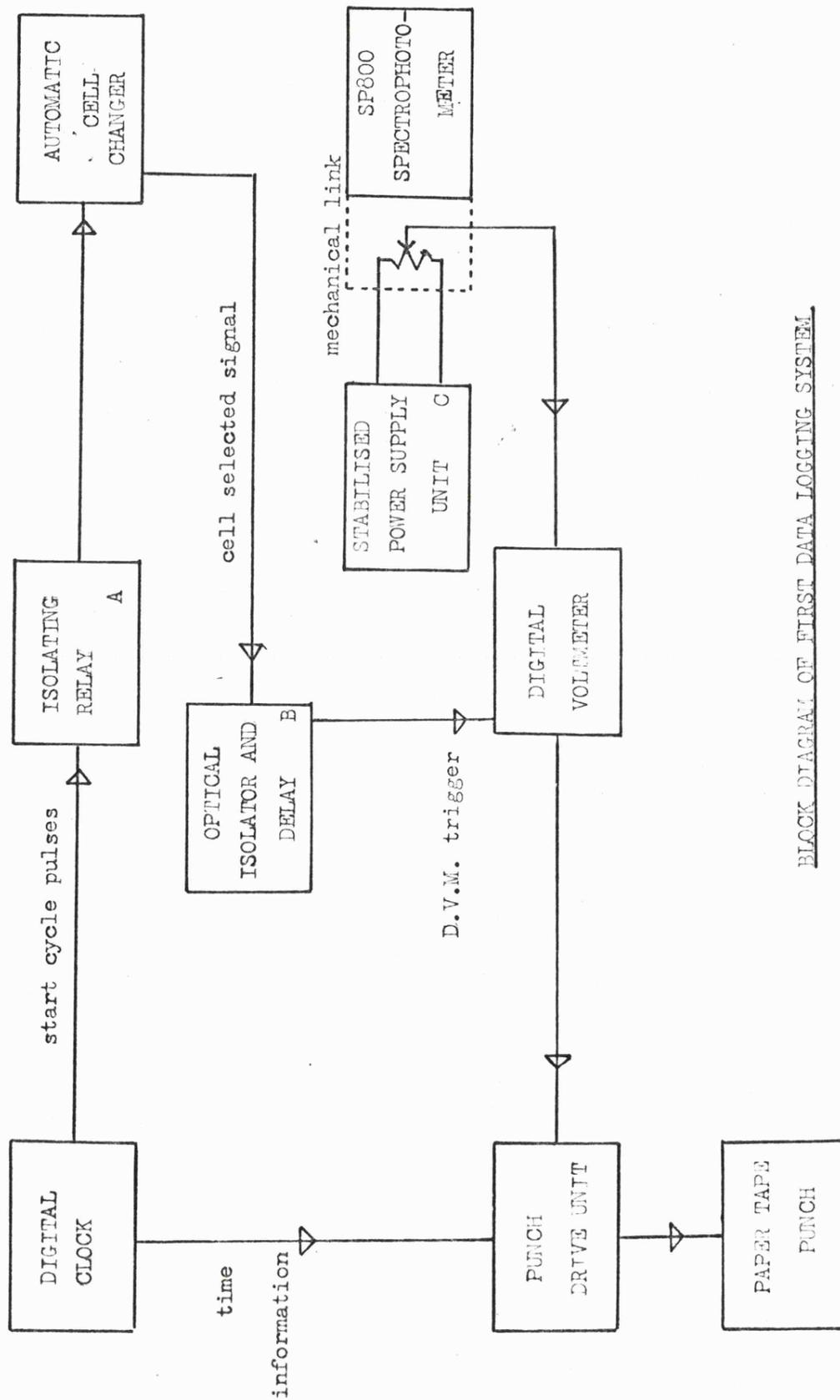
5. Experimental Details of Spectrophotometry Kinetics

(a) Spectra

All kinetic measurements were undertaken on a Unicam SP800 spectrophotometer fitted with a cell change unit SP125. The cell block was thermostated by pumping water through the cell holder from a thermostated tank.

(b) Data Logging

It was decided that for ease of calculation and for greater accuracy the SP800 should be linked to a data logging system. The first system was made up from pieces of equipment



BLOCK DIAGRAM OF FIRST DATA LOGGING SYSTEM.

FIGURE 5-1

that had been in the department for a number of years. Due to their age and neglect in previous years, this initial set up proved very unreliable. Thus about half-way through this study a new data logging system was purchased. The two systems will be described separately.

(i) First Data Logging System

A Solartron D.V.M. (LM14202) was joined to a digital clock (LU 14636), a data logging unit and an Addo punch. To connect the data logging equipment to the SP800 an 'electronic black box' was designed by Mr. Clemenson of this department.

There were a number of problems with this equipment. One major problem was electrical interference between the cell change unit of the SP800 and the punch drive unit which caused the system to record spurious readings. To overcome this problem optical isolators were used in the electronic circuit combining the two.

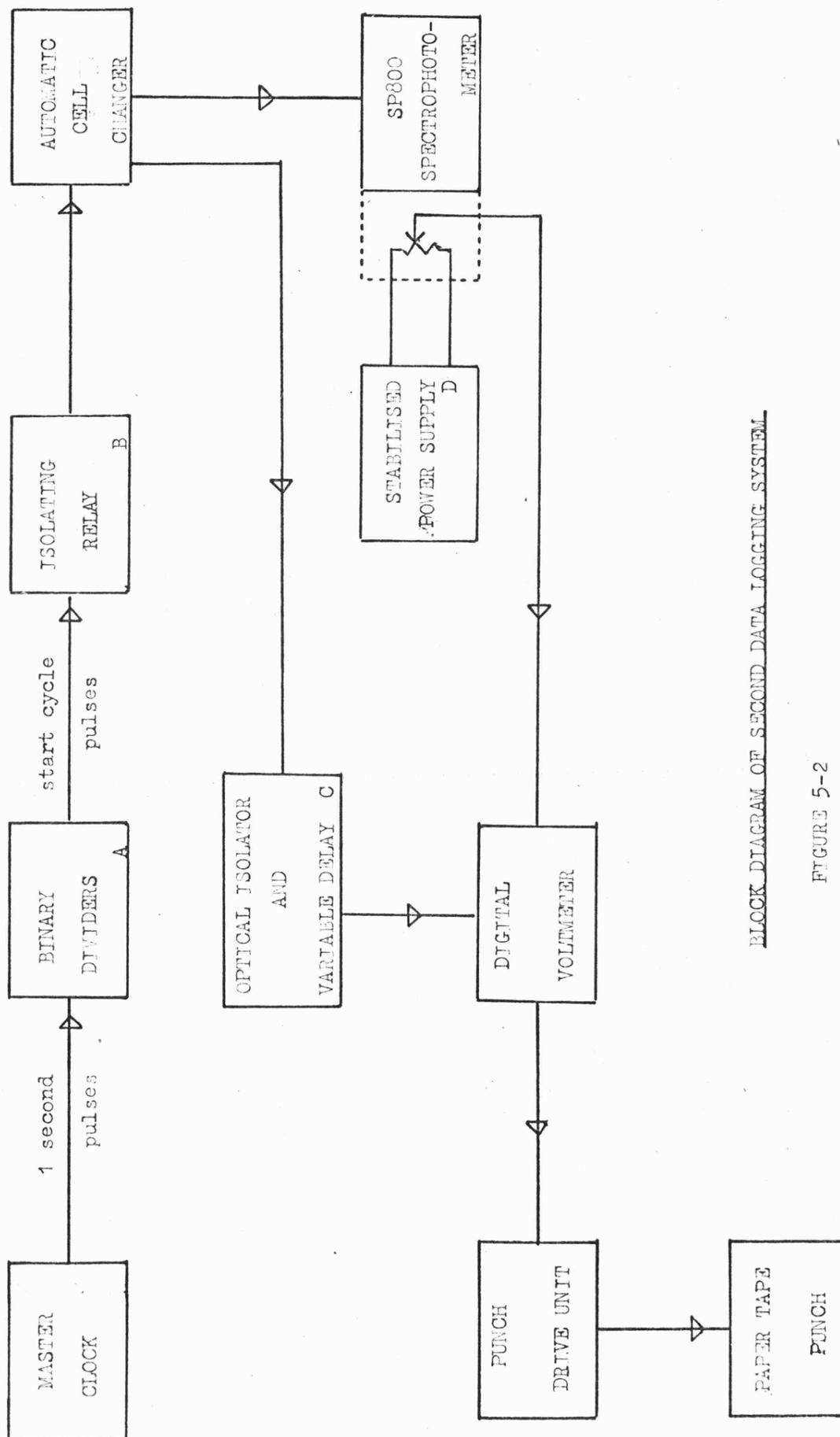
Figure 5 - 1 is a block diagram of the system. Blocks A, B and C made up the interface unit. The required time interval was set on the digital clock. At preset time intervals the clock provided a signal, via an isolating relay, to the cell change unit, on the SP800, which initiated a cycle. Simultaneously the clock provided the punch drive unit with time information which was punched onto the paper tape. The cell change unit then selected each cell in turn in the SP800 and provided a command signal for the

digital voltmeter via an optical isolator and delay (to allow the absorbance reading to stabilise) to read the absorbance signal. The absorbance signal was taken from a variable potentiometer which was connected to the recording pen. The voltage obtained from the potentiometer depended on the pen position and therefore the absorbance. The voltage reading on the D.V.M. was fed to the punch via the punch drive unit. In this way the absorbance of all four cells was recorded on the punched tape. The tape produced was therefore made up of a series of blocks of readings consisting of time followed by the absorbance readings of the four cells.

There were a number of problems with this set up which prompted the purchase of the second system. The Solatron D.V.M. used a standard cell to measure voltages but the actual voltage drifted from the specified voltage. On a kinetic run lasting for several hours this drift was found to be quite large.

The time intervals available on the digital clock were very limited i.e. 1 minute, 10 mins., 1 hour and 10 hrs. A more flexible system was obviously required.

A time delay between selecting the cell and recording the absorbance was produced by the electronic interface unit. This time interval was set by the circuit and therefore difficult to change. This time interval was important as if it was too short a reading was taken before the pen had stabilised or if it was too long the pen was moving again.



BLOCK DIAGRAM OF SECOND DATA LOGGING SYSTEM

FIGURE 5-2

Due to difficulties in determining the optimum time lag in the design of a second system a variable time delay was incorporated into the circuit.

The major criticism of this old arrangement was the unreliability of the Solatron digital voltameter. The frequent breakdowns were a cause of much frustration.

(ii) Second Data Logging System

This system, a very much improved version of the first system, incorporated a Solatron D.V.M. (220), a Solatron Recorder Drive Unit (A295) and a Facit high speed punch. There was no internal clock on the D.V.M.; an Advance Time Unit was therefore used. An interface unit was designed to avoid the faults of the old system.

A block diagram of the data logging system is given in Figure 5 - 2. Blocks A, B, C and D make up the interface unit. The Timer unit supplied 1 second pulses to binary dividers in the interface unit. Time intervals were therefore available in powers of 2, the range being 2^0 to 2^{12} seconds. The required time interval was set on the interface unit. The binary dividers combined the pulses until the required time interval was reached. A signal was then sent to the automatic cell changer as before. The absorbance of each of the four cells was recorded on the punch tape as in the previous system.

In this arrangement the time was not recorded on the tape, only the absorbance readings were recorded.

Readings could be taken at quite short time intervals and hence reasonably fast reactions could be followed i.e. reactions with half-lives of the order of 10 seconds. The time taken to record the absorbance readings of all four cells was 32 seconds. Hence four cells could not be used to follow fast reactions. However absorbance readings of only one cell could be taken, a facility for this being built into the system. A switch on the interface unit by-passed the cell selection circuits.

(b) Experimental Procedure

Preliminary Spectra were recorded to determine a suitable wavelength at which to follow the reaction, and also a suitable time interval between readings. Also the spectra checked that the correct products were formed and that isobestic points were unaltered.

The temperature of the thermostated cell block in the SP800 was measured using a copper-constantan thermocouple.

For all complexes except cis-dichlorobis (ethylenediamine) cobalt chloride, stock solutions in water were prepared. The concentration of the stock solution was such that 0.5ml was required in a 10mm cell (total volume 3ml) to produce a solution with an absorbance in the region 1.2 - 1.6 when mixed with the mixed solvent. The stock solutions were brought up to the correct temperature by placing them in the thermostat tank that provided the water to the cell block of the SP800. The mixed solvents (2.5mls in each cell) were measured out into the cells by means of a graduated pipette.

The procedure for a normal kinetic run was as follows:-

- 1) The Unicam SP800 was set to operate at fixed wavelength.
 - 2) The wavelength was set to the pre-determined value.
 - 3) The link motor in the SP800 was disconnected. Normally on fixed wavelength scanning the table moves from right to left and then stops when the table reaches the end of the scan. This is not required as it would stop the experiment prematurely.
 - 4) The automatic cell change was activated by setting the cell change switch to "Auto" and the programmes switch to the "on" position (If one cell was being used, only one cell switch was put in the "on" position). The cell block was always set so cell 1 was being sampled.
 - 5) A variable resistor was adjusted by means of a control marked 'set O.D.' so that the readings of the 'absorbance' as read by the D.V.M. varied from 0 to 20,000 corresponding to absorbance readings of 0 to 2.0. This was achieved by manually moving the pen to an absorbance of 1.0 and adjusting the variable resistor so that the reading on the D.V.M. was 10,000. The pen was then moved to zero absorbance to check that the reading on the D.V.M. was also zero; if not, the variable resistance was adjusted again.
 - 6) The required time interval was set on the interface unit.
 - 7) The recorder drive unit was set for external sampling.
- The number of readings per line recorded on the punch tape

was set to the number of cells being used; this was useful when the tape was edited which was occasionally necessary.

8) The punch was switched on and a length of clear tape run out. The number of cells and time interval were punched onto the tape by means of the recorder drive unit (The recorder drive unit has a manual punch unit).

9) Then 2.5mls (usually) of mixed solvent were pipetted into eight 10mm ultra-violet cells, four reference, four sample. Then 0.5mls of water put in each reference cell. The cells were put into the cell block and allowed to thermostat for about 15 minutes.

10) The required amount of stock solution was added to the sample cells (usually 0.5ml).

11) Initiation of the kinetic run was achieved by turning the switch on the pen carriage to 'scan' and moving the 'set run' switch on the interface unit to the run position. Once started the automatic cell changer was triggered to move position to cell 2. The cell remains in position for 5 seconds in which time an absorbance reading was taken. The absorbance of the remaining three cells was recorded in a similar manner. Once the fourth reading was taken the system waited for the set time interval to be reached when the next start cycle pulse was sent out.

12) The system was allowed to run for at least three half-lives.

13) At the end of the run the system was stopped by turning

the switch on the pen carriage to "Stop" and putting the switch on the interface unit to "Set".

14) A stop code for the computer, 99999, was then punched on the end of the tape. Some clear tape was run out and the tape torn off. This tape was passed directly into the computer to be analysed.

6. Fast Reactions

The bulk of this work was carried out on a stopped-flow apparatus designed by P. Moore (University of Warwick). A small amount of work was undertaken using a temperature-jump apparatus at the University of Kent with the assistance of Dr. D. Hague.

The reaction studied on the stopped-flow apparatus was the formation of nickel(II) pyridine-2-azo-p-dimethyl aniline from nickel nitrate solution and pada solution. The reaction of cobalt(II) and pada was used in the temperature jump study.

7. The Stopped-Flow Apparatus

A diagram of the stopped-flow apparatus is given in figure 5 - 3. The reagents were introduced into the driving syringes D_1 and D_2 by means of R_1 and R_2 using valves V_1 and V_5 . To mix the two solutions valves V_2 and V_4 were opened and then the piston drive unit was pushed manually so that the reagent passed through the mixer, M, into the observation chamber (figure 5 - 4); also into the

Stopped Flow Apparatus

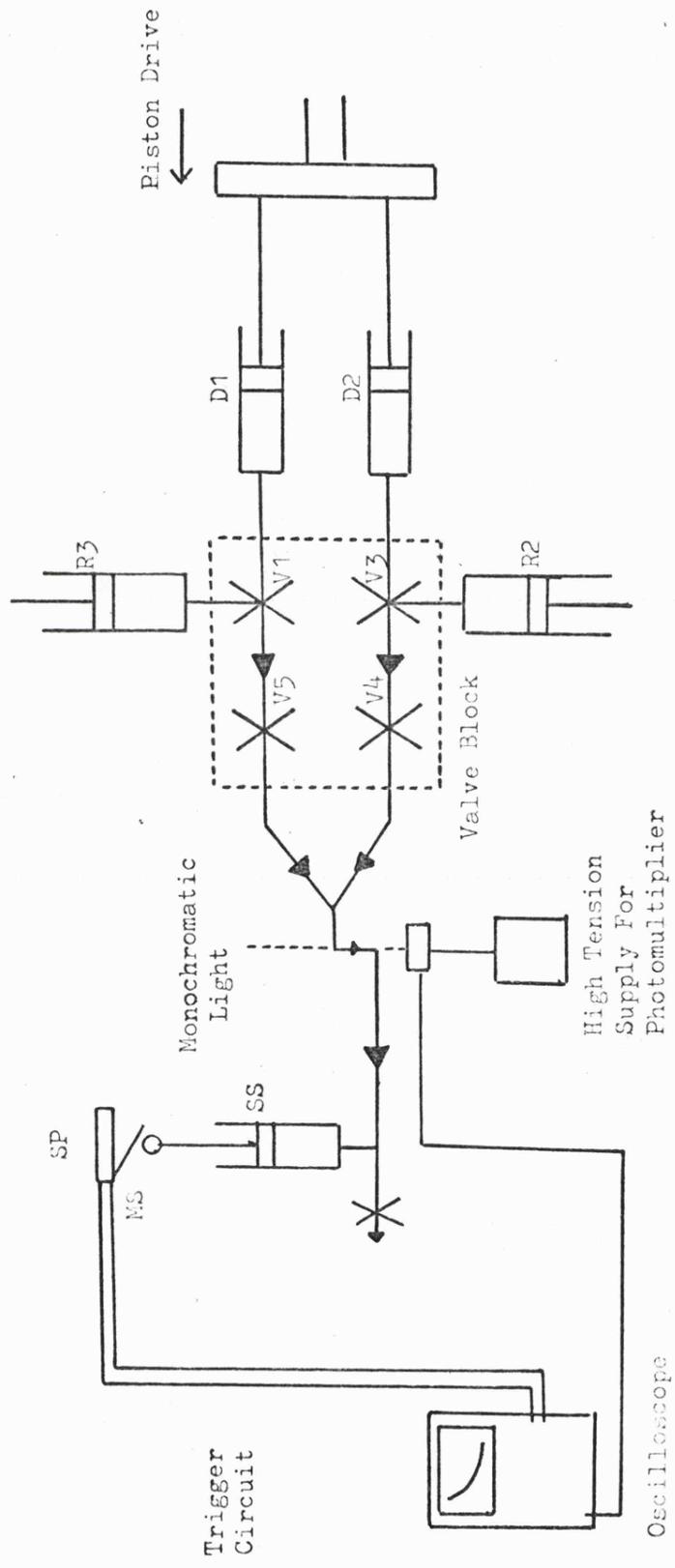


FIGURE 5-3

Observation Tube Arrangement

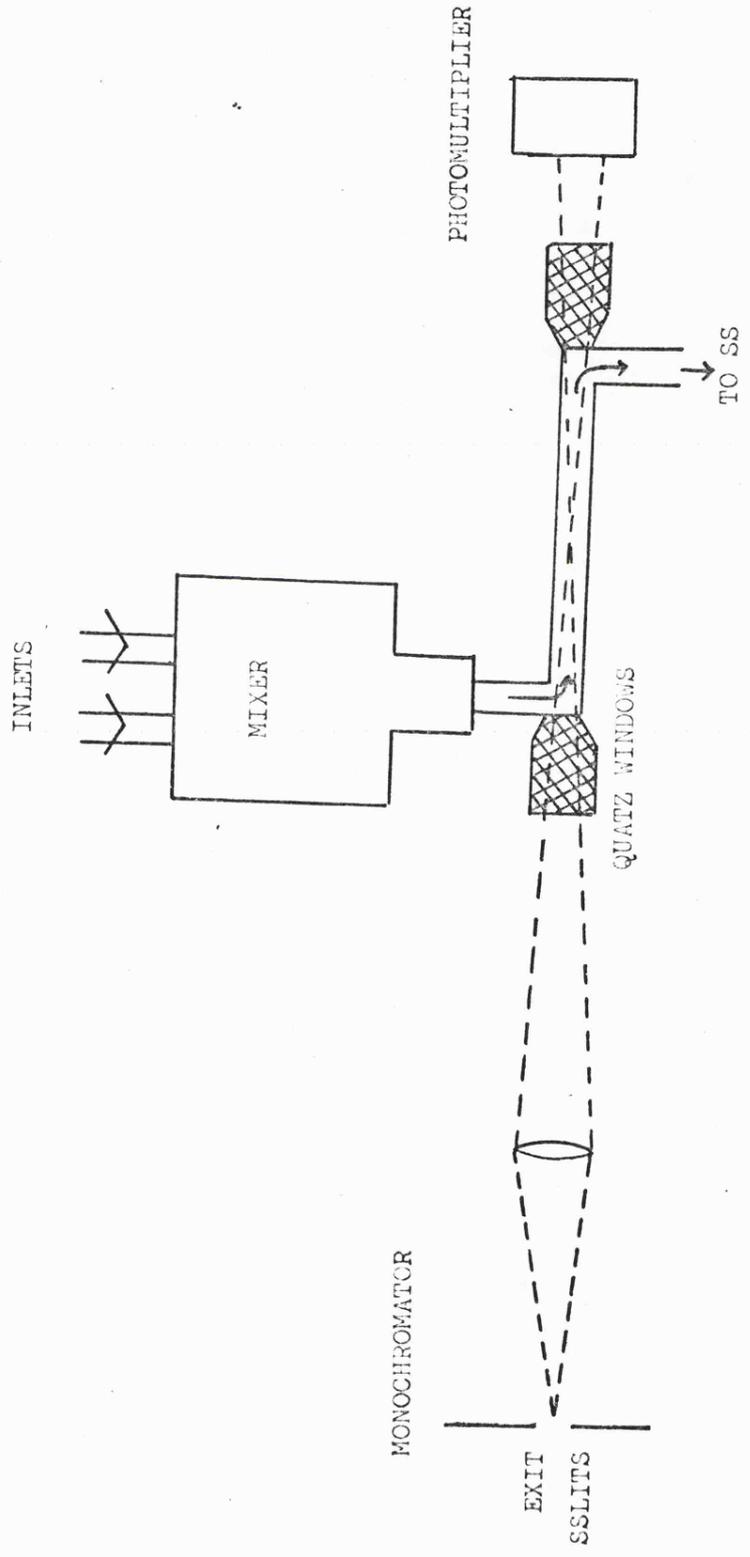


FIGURE 5-4

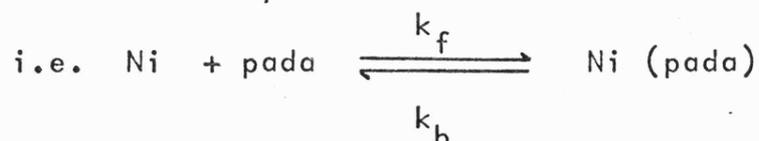
2ml stopping syringe (S.S.). The flow was abruptly stopped by allowing the plunger of the stopping syringe to impinge onto a stopping plate (S.P.). At the same time a microswitch (M.S.) sent a pulse to the external trigger of a recording oscilloscope.

A monitoring light beam was focused onto the centre of the observation tube; the transmitted light was detected continuously by a photomultiplier. The output was fed to the Y plates of an oscilloscope. The voltage (V), from the photomultiplier, was directly proportional to the intensity of the light transmitted from the observation tube.

The monochromatic light was supplied from a SP 500 spectrophotometer and the output of the photomultiplier was connected to an oscilloscope.

8. Requirements of the Reaction

Using the stopped-flow system, the reaction between the nickel(II) ion and pada was studied. This is a simple formation reaction;



The rate constant for this reaction is given by the following expression (which can be derived in an analogous way to that used in the example for the temperature jump method).

$$k = k_f ([Ni(11)] + [pada]) + k_b$$

where k = overall rate constant

k_f = rate of forward reaction

k_b = rate of backward reaction

If the concentration of pada is small compared to that of the nickel(11) then the expression simplifies to -

$$k = k_f [Ni(11)] + k_b$$

To obtain both k_b and k_f , the rate constant must be determined at several concentrations of nickel(11). If these rate constants are then plotted against concentration of nickel, the slope of this graph is k_f and the intercept is k_b .

At a given concentration of nickel(11) ions the reaction obeys simple first order kinetics. The rate constant can therefore be determined from the half-life.

$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

where $t_{\frac{1}{2}}$ = half-life

k = rate constant

9. General Experimental Procedures

Stock solutions of nickel nitrate ($\sim 1 \times 10^{-2}M$) and pada ($\sim 1.5 \times 10^{-4}M$) were made up in 500ml quantities. The solution of pada was buffered by adding a few drops of collidine (2,4,6 - trimethylpyridine) to this stock solution. This prevented protonation but, because of the

2 methyl groups does not complex with the nickel(II). Nickel nitrate was standardised by titration against disodium ethylenediaminetetraacetate (EDTA).

The pada solution used in the reactions was half the concentration of the stock solution, the latter being diluted with the required amount of co-solvent and water. Nickel solutions were made up to the required Nickel concentration and co-solvent concentration.

The visible spectra of both reactants and products were recorded on the SP800 in order to find suitable wavelengths at which to monitor this reaction. The wavelength was 550n.m.

The stopped-flow apparatus valve block and observation tube were thermostated by circulating water from a thermostat tank.

The trigger circuit was set up as shown in figure 5 - 3. The trig level and stability of the oscilloscope had to be carefully adjusted so that when the microswitch was closed the oscilloscope was triggered. At the beginning of a series of reactions, the time base of the oscilloscope was set to a suitable guessed value, usually about 50ms. The line position was then adjusted to a suitable position of the screen i.e. near to the bottom of the screen if the amount of light absorbed was expected to increase.

The slits of the SP500 were set so that, sufficient light was detected by the photomultiplier. If the intensity was too great, however, the line on the oscilloscope was

too broad.

The operation of the stopped-flow apparatus has been described previously. Each operation of the apparatus produces a trace on the oscilloscope. The first trace was normally unusable as the guessed time base was probably not correct. An infinity reading could be obtained by triggering the circuit again whilst the sample was still in the observation chamber. The half-life for the reaction could then be easily measured from the curve.

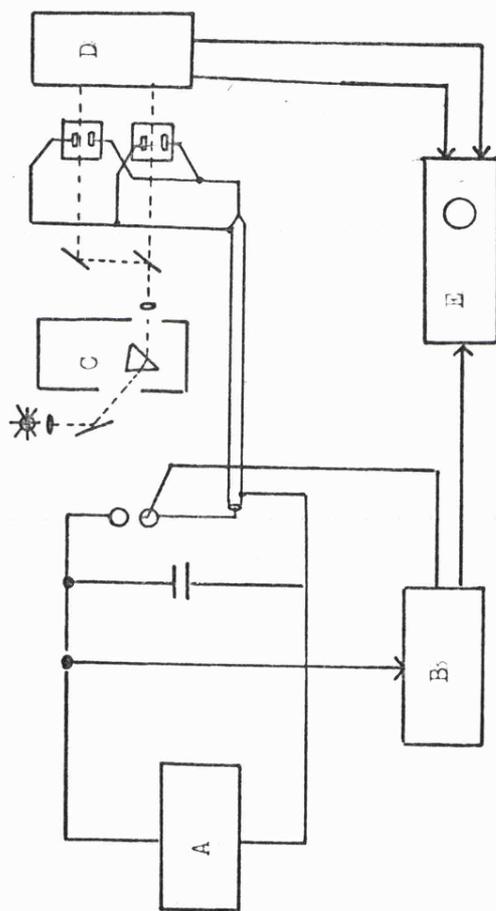
10. Temperature-jump Apparatus

The temperature jump apparatus, built in Göttingen (Germany), is drawn schematically in figure 5 - 5. The sudden rise in temperature was produced by the discharge of a capacitor which had previously been charged to a few thousand volts. The relaxation of the system back to equilibrium was recorded on a storage oscilloscope, the traces being then photographed. The relaxation times were then determined by projecting the photographs onto graph paper and then recording times and absorbances. These were analysed by a basic computer programme to obtain relaxation times.

11. Experimental Procedure

The formation of cobalt(II) pada was followed by this technique, as the reaction is too fast to be followed by

Temperature Jump Apparatus



A H.T. generator; B, H.T. measurement and triggering; C, monochromator; D, photomultipliers and pre-amplifiers; E, differential amplifier and oscilloscope.

FIGURE 5-5

stopped-flow. PADA stock solution was made by dissolving 1.5×10^{-4} M of pada in 2mls of AR methanol (it is slow to dissolve in water) then diluting this to 500mls with water.

A few drops of collidine were added to the solution.

Cobalt nitrate stock solutions ($\sim 10^{-2}$ M) was standardised using disodium EDTA.

Solutions were prepared in 25 ml quantities, the ionic strength being kept constant at 0.3M using sodium nitrate. The concentration of the cobalt(II) was varied from 10^{-3} M to 4×10^{-3} M.

CHAPTER 6

ANALYSIS OF KINETIC DATA

1. Rate of a Reaction

The rate of a chemical reaction is the rate of change of concentration ^{of the components} which make up the reaction i.e. it is the rate of decrease of concentration of the reactants or the rate of increase of concentration of the products.

The variation of the rate of a reaction with concentration of reacting substances can often be indicated by stating the order of the reaction. Often the rate of a reaction is proportional to the a th power of the concentration of one reactant A_1 to the b th power of concentration of B

$$\text{i.e. Rate} = k c_A^a c_B^b \quad k = \text{rate constant} \quad 6 - 1$$

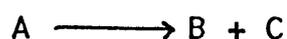
The overall order n is then given by the sum of the powers -

$$\text{i.e. } n = a + b \dots\dots \quad 6 - 2$$

2. First-Order Reactions

A first order reaction is one where the rate of reaction only depends on the concentration of one component.

Consider, for example, the simple case of the following reaction



$$\text{Then } \frac{-dA}{dt} = k [A] \quad 6 - 3$$

If the initial concentration of A is a_0 and after a time t x moles of A have decomposed, then the remaining concentration of A is $a_0 - x$ and x moles of B and C will

have been produced. The rate of formation of B or C is thus dx/dt and for a first-order reaction this is proportional to the instantaneous concentration of A, so that

$$\frac{dx}{dt} = k_1 (a_0 - x) \quad 6 - 4$$

Integrating equation 6 - 4 gives

$$k = \frac{1}{t} \ln \frac{a_0}{a_0 - x} \quad 6 - 5$$

Reactions for which the rate depends on the concentration of two or more components can be made to obey first order kinetics by having one component present in much lower concentration than the others. This will result in the rate being dependant only on the concentration of the component which is not in excess and therefore the rate will obey equation 6 - 4.

3. Analysis of Data from a First Order Reaction

Data for any chemical reaction are usually in the form of a series of measurements of some physical property (which is linearly related to concentration) at various times. Often, as in this study the physical property used is the absorbance.

An analysis to determine first order rate constants was devised by P. Moore¹. This analysis was used because of its great flexibility. It does not require that initial or final concentration are known nor does it require constant time intervals (cf the Guggenheim Method).

This method makes use of the following relationship:-

$$\ln \left[\frac{(A_t - A_\infty)}{(A_0 - A_\infty)} \right] = -kt \quad 6 - 6$$

where A_t , A_∞ and A_0 are the values of A at $t = t$, ∞ and 0 respectively.

Equation 6 - 6 can be rearranged to express the absorbance A at any time t in terms of A_∞ , k and A_0 .

$$A_t = A_\infty (1 - e^{-kt}) + A_0 e^{-kt} \quad 6 - 7$$

The absorbance A can be treated as a parameter dependant on the three variables A_∞ , A_0 and k . The three variables A_∞ , A_0 and k can be found by solving equation 6 - 7 by an iterative non-linear least squares procedure.

In mathematical notation the absorbance A at a time t can be expressed as

$$A_t = A(A_\infty, A_0, k) \quad 6 - 8$$

Differentiating 6 - 8 gives

$$\delta A_t = \left[\frac{\partial A}{\partial A_\infty} \right]_{A_0, k} \delta A_\infty + \left[\frac{\partial A}{\partial A_0} \right]_{A_\infty, k} \delta A_0 + \left[\frac{\partial A}{\partial k} \right]_{A_0, A_\infty} \delta k \quad 6 - 9$$

For the best values of A_∞ , A_0 and k the difference between the left and right hand sides of equation 6-9 should be a minimum when summed over all points taken i.e. -

$$\sum_{i=1}^N \left[dA_t - \frac{\partial A}{\partial A_\infty} \delta A_\infty - \frac{\partial A}{\partial A_0} \delta A_0 - \frac{\partial A}{\partial k} \delta k \right]^2 = \text{minimum} \quad 6 - 10$$

δ = partial differential i.e. all other variables are kept constant.

In order to find the minimum in expression 6-10 the partial derivatives with respect to A_0 , A_∞ and k are required. These partial derivatives are then equated to

zero and give rise to the so called normal equations of the least squares method.

$$\sum_{i=1}^N \left[\frac{\partial A}{\partial k} \right]^2 \delta k + \sum_{i=1}^N \left[\frac{\partial A}{\partial k} \right] \left[\frac{\partial A}{\partial A_{\infty}} \right] \delta A_{\infty} + \sum_{i=1}^N \left[\frac{\partial A}{\partial k} \right] \left[\frac{\partial A}{\partial A_0} \right] \delta A_0 = \sum_{i=1}^N E_i \left[\frac{\partial A}{\partial k} \right]$$

6 - 11

$$\sum_{i=1}^N \left[\frac{\partial A}{\partial k} \right] \left[\frac{\partial A}{\partial A_{\infty}} \right] \delta k + \sum_{i=1}^N \left[\frac{\partial A}{\partial A_{\infty}} \right]^2 \delta A_{\infty} + \sum_{i=1}^N \left[\frac{\partial A}{\partial A_0} \right] \left[\frac{\partial A}{\partial A_{\infty}} \right] \delta A_0 = \sum_{i=1}^N E_i \left[\frac{\partial A}{\partial A_{\infty}} \right]$$

6 - 12

$$\sum_{i=1}^N \left[\frac{\partial A}{\partial k} \right] \left[\frac{\partial A}{\partial A_0} \right] \delta k + \sum_{i=1}^N \left[\frac{\partial A}{\partial A_{\infty}} \right] \left[\frac{\partial A}{\partial A_0} \right] \delta A_{\infty} + \sum_{i=1}^N \left[\frac{\partial A}{\partial A_0} \right]^2 \delta A_0 = \sum_{i=1}^N E_i \left[\frac{\partial A}{\partial A_0} \right]$$

6 - 13

E_i is the difference between the observed absorbance and that calculated from equation 6-7 using estimated values for the unknown parameters; N is the total number of observations.

The three equations 6-11 to 6-13 together with the partial derivatives of equation 6-7 can be solved to give values for δk , δA_0 and δA_{∞} . The estimated values of k , P_0 and P_{∞} are then altered as in equation 6-14.

$$k \text{ (improved)} = k \text{ (previous)} + \delta k \quad 6 - 14$$

The initial estimates for A_0 , A_{∞} and k are determined as follows -

$$A_0 = \text{First absorbance reading} \quad 6 - 15$$

$$k = \frac{2}{(\text{Time of last observation})} \quad 6 - 16$$

$$A_{\infty} = 1.25 \times (\text{last observation}) - 0.25 A_0 \quad 6 - 17$$

The values of the three parameters A_{∞} , A_0 and k are adjusted until $\sum_{i=1}^N E_i^2$ is a minimum, which is taken to

be reached when $\sum_{i=1}^N E_i^2 < 10^{-6}$.

4. Computation

The basis for the computer programme (ALGOL) was Forwin which was a programme written by P. Moore. This programme was modified and developed to meet our requirements. A listing is given in appendix 2 (Rogue). As explained in chapter 5 the data produced from our kinetic studies were printed out on punched tape. Each tape consisted of a total of N sets of absorbance readings of n_c cells (n_c varied from 1 to 4) at preset time intervals. This information was read into a n_c by N array. Each column, which contains the information for one cell, was then analysed separately.

It was found necessary to have a special procedure to locate the end of the tape. The ordinary stop code used for paper tape was insufficient for our computer. If this was used the computer still demanded more information on paper tape. Therefore, at the end of each tape '99999' was punched and a procedure was designed to locate this number.

The analysis calculated the rate constant and its standard deviation, together with the infinity reading A_∞ and initial reading A_0 .

5. Series First Order Reaction

Series first order reactions are reactions of the type



The concentration of components A, B and C at any time t can be found from the following differential equations.

$$\frac{dA}{dt} = -k_1 A \quad 6 - 19$$

$$\frac{dB}{dt} = k_1 A - k_2 B \quad 6 - 20$$

$$\frac{dC}{dt} = k_2 B \quad 6 - 21$$

Integration of 6-19 produces an expression for A

$$A = A_o e^{-k_1 t} \quad 6 - 22$$

where A_o is the initial concentration of A.

Substitution of equation 6-22 into 6-20 followed by integration leads to equation 6-23

$$B = \frac{A_o k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad 6 - 23$$

The relationship for C can be found by using the following equation which follows from the mass balance of the system.

$$\frac{dA}{dt} + \frac{dB}{dt} + \frac{dC}{dt} = 0 \quad 6 - 24$$

Then using the expression for A and B

$$C = A_o \left[1 + \frac{1}{k_1 + k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right] \quad 6 - 25$$

6. Analysis of Spectroscopic Data from series first order reactions

A method of analysing spectroscopic data for a series first order reaction has been devised by P. Moore². The analysis is similar to the one developed for the first-order reaction.

The absorbance of a solution at any time t at a given wavelength (a length l cm) is given by

$$D = \epsilon_A [A] + \epsilon_B [B] + \epsilon_C [C] \quad 6 - 26$$

Where ϵ_A , ϵ_B and ϵ_C are the molar extinction coefficients of A, B and C respectively. An expression relating the absorbances D and the two rate constant k_1 and k_2 can be obtained by substituting equation 6 - 22 and 6 - 25 into 6 - 26.

$$D/A_0 = (\epsilon_A - \epsilon_C) e^{-k_1 t} + \frac{k_1}{(k_1 - k_2)} (\epsilon_A - \epsilon_C) (e^{-k_2 t} - e^{-k_1 t}) + \epsilon_C \quad 6 - 27$$

Values of ϵ_A and ϵ_C can normally be measured. However a value for ϵ_B is often very difficult to obtain. The absorbance is therefore treated as depending on three parameters ϵ_B , k_1 and k_2 .

The calculation is then very similar to that described for the first order reaction case. The analysis is carried out by an iterative non-linear least squares procedure. The three normal equations are given below -

$$\sum_{i=1}^N \left[\frac{\partial D}{\partial k_1} \right]^2 \delta k_1 + \sum_{i=1}^N \left[\frac{\partial D}{\partial k_1} \right] \left[\frac{\partial D}{\partial k_2} \right] \delta k_2 + \sum_{i=1}^N \left[\frac{\partial D}{\partial k_1} \right] \left[\frac{\partial D}{\partial \epsilon_B} \right] \delta \epsilon_B =$$

$$\sum_{i=1}^N \left[\frac{\partial D}{\partial k_1} \right] \Delta_i \quad 6 - 28$$

$$\sum_{i=1}^N \left[\frac{\partial D}{\partial k_1} \right] \left[\frac{\partial D}{\partial k_2} \right] \delta k_1 + \sum_{i=1}^N \left[\frac{\partial D}{\partial k_2} \right]^2 \delta k_2 + \sum_{i=1}^N \left[\frac{\partial D}{\partial k_2} \right] \left[\frac{\partial D}{\partial \epsilon_B} \right] \delta \epsilon_B =$$

$$\sum_{i=1}^N \left[\frac{\partial D}{\partial k_2} \right] \Delta_i \quad 6 - 29$$

$$\sum_{i=1}^N \left[\frac{\partial D}{\partial k_1} \right] \left[\frac{\partial D}{\partial \epsilon_B} \right] \delta k_1 + \sum_{i=1}^N \left[\frac{\partial D}{\partial k_2} \right] \left[\frac{\partial D}{\partial \epsilon_B} \right] \delta k_2 + \sum_{i=1}^N \left[\frac{\partial D}{\partial \epsilon_B} \right]^2 \delta \epsilon_B =$$

$$\sum_{i=1}^N \left[\frac{\partial D}{\partial \epsilon_B} \right] \Delta_i \quad 6 - 30$$

Δ_i is the difference between the calculated absorbance as found from equation 6 - 26 using approximate values of ϵ_B , k_1 and k_2 and the measured absorbance. The approximate values of k_1 , ϵ_B and k_2 are then altered by using the calculated values of δk_1 , δk_2 and $\delta \epsilon_B$.

$$k_1(\text{improved}) = k_1(\text{previous}) + \delta k_1 \quad 6 - 31$$

If the values of k_1 and k_2 are close then the analysis needs to be modified, because equation 6 - 27 contains terms in $(k_1 - k_2)$ which become very small and therefore make the equation indeterminate. In order to remove this expression from the equation the substitution $R = \frac{k_1}{k_1 - k_2}$ is made. Equation 2 - 26 then becomes -

$$D = (\epsilon_A - \epsilon_C) e^{-k_1 t} + (\epsilon_B - \epsilon_C) e^{-k_1 t} (e^{k_1 R t} - 1) / R + \epsilon_C$$

6 - 32

then $e^{k_1 R t}$ can be expressed as a series neglecting all terms

larger than R^4 .

$$D = (\epsilon_A - \epsilon_C) e^{-k_1 t} + (\epsilon_B - \epsilon_C) e^{-k_1 t} \left(k_1 t + R k_1^2 t^2 / 2 + R^2 k_1^3 t^3 / 6 + R^3 k_1^4 t^4 / 24 \right) + \epsilon_C$$

6 - 33

Moore found that this substitution was only necessary if $R \leq 0.01$.

An ALGOL programme (TIGER Appendix 2) was written to analyse spectroscopic data from a series first order reaction. The data were fed into the programme in the form of absorbances and times together with the concentration of starting material for a number of cells (usually 1 to 4). The analysis required estimates of k_1, k_2 and ϵ_B also the values of the extinction coefficients of reactant and product. The estimates of k_1, k_2 and ϵ_B can be made from preliminary investigations of the system involved. It proved important that good estimates are made for these values, otherwise the correction term became very large; which could produce negative rate constants.

In order to obtain a good value for k_1 sufficient data are required to define the first stage of the reaction. The analysis, in fact, requires good data for both stages of the reaction, as the method can not produce an estimate for one rate constant and a good value for the other. This requirement leads to restrictions on the temperature range that can be used to study a reaction.

TABLE 6-A

Rate constants for the Reaction of Rhenium Pentacarbonyl Halides
with Cyanide Ion in Aqueous Methanol.

Re(CO) ₅ I	First Stage				Second Stage				
	10 ² k _{obs} /s ⁻¹				k ₁₂ /dm ³ mol ⁻¹ s ⁻¹	10 ⁴ k _{obs} /s ⁻¹		10 ⁴ k ₂₁ /s ⁻¹	
T/K	10 ² [KCN]/mol dm ⁻³					1.0	1.5	2.0	
293.2	-	-	1.09	1.40	0.55	-	-	1.07	
298.2	1.17	1.81	2.8	2.8	1.14	1.02	1.35	1.75	0.29
303.3	2.1	3.5	4.4	5.1	2.00	1.48	1.94	2.4	0.45
308.1	2.5	4.9	6.7	10.3	4.99	2.4	2.9	3.9	0.66

The data from the series first order reaction chosen in this study were found to be unsuitable for this programme due primarily to the large difference between the rate constants for the two steps. The programme has, however, proved a useful tool for the department. For example, it was used to analyse the kinetics of the following two stage reaction³, the results of which are given in Table 6-A



7. Calculation of Activation Parameters

Definitions of activation parameters are given in chapter 3. The method used for calculating these parameters was based on the analysis suggested by Clarke and Glew⁴. The programme (Tempan Appendix 2) has been described previously⁵.

Briefly the analysis extended the well known equation (6 - 34) relating the rate constant to the activation parameters to a more extended form by using additional temperature variables

$$R \ln k = \Delta S^\ddagger - \frac{\Delta H^\ddagger}{T} \quad 6 - 34$$

The method fits the data about a reference temperature, B, which is usually taken to be the mid-point of the experimental temperature range used. A least squares procedure is used to fit N experimental measurements of k to various forms of the following equation -

$$R \ln k = b_0 + b_1 u_1 + b_2 u_2 + b_3 u_3 + b_4 u_4 + b_5 u_5 \quad 6 - 35$$

$$\text{where } b_0 = \Delta G_B^\ddagger / B \quad b_1 = \Delta H_B^\ddagger / B \quad b_2 = \Delta C_{pB}^\ddagger \quad b_3 = \frac{B}{2} \frac{d \Delta C_{pB}^\ddagger}{dT}$$

$$b_4 = \left[\frac{\theta^2}{6} \right] \left[\frac{d^2 \Delta C_p \theta}{dT^2} \right] \quad b_5 = \left[\frac{\theta^3}{24} \right] \left[\frac{d^3 \Delta C_p \theta}{dT^3} \right]$$

The variable u_1 to u_5 are dependant on powers of the ratio $\frac{T - \theta}{\theta}$. Depending on the temperature range used varying numbers of coefficients, 1 to 6, may be required to produce the best fit for the experimental data.

8. Parameters Required for Endostatic Calculation

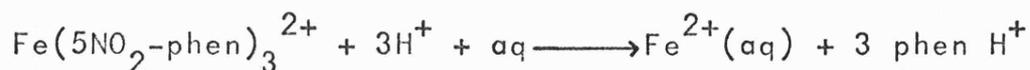
The differential $d\Delta G^\ddagger/dx$ is required for the endostatic calculation. This was calculated as was $d^2\Delta G^\ddagger/dx^2$ using the method explained in chapter 3.

CHAPTER 7

RESULTS

1. Results for the aquation of Tris (5-nitro-1,10-phenanthroline) iron(II) cation

The aquation of this complex can be represented by the following equation



In aqueous solution the complex forms an equilibrium between the complex and $\text{Fe}^{2+}(\text{aq})$. In order for the reaction to proceed to completion a scavenger for the outgoing phen must be added. This can be H^+ ions, as expressed in the equation, but both nickel(II) ¹ and hydrogen peroxide are effective scavengers.

(a) Acetonitrile + Water

Acetonitrile was chosen as a co-solvent as it forms a TNAP mixture (chapter 2) with water and therefore complements the previous studies of $\text{Fe}(\text{5NO}_2\text{ phen})_3^{2+}$ in t-butyl alcohol and ethanol + water mixtures.

All solvent mixtures were made up by weight using Analar acetonitrile to a specified mole fraction and the required amount of concentrated sulphuric acid to produce a 0.5M solution. The hydrolysis of $\text{Fe}(\text{5NO}_2\text{ phen})_3^{2+}$ was followed at four different concentrations of acetonitrile each at six different temperatures. The rate constants are given in Appendix 1 but they are also plotted in figure 7-1. The highest mole fraction of acetonitrile was $x_2 = 0.28$. At higher concentrations the reaction reached equilibrium.

The graph (figure 7-1) of rate constant against mole

First - order Rate Constants for Aquation of Tris-(5-nitro-1,10-phenanthroline)iron(II) in Acetonitrile + Water

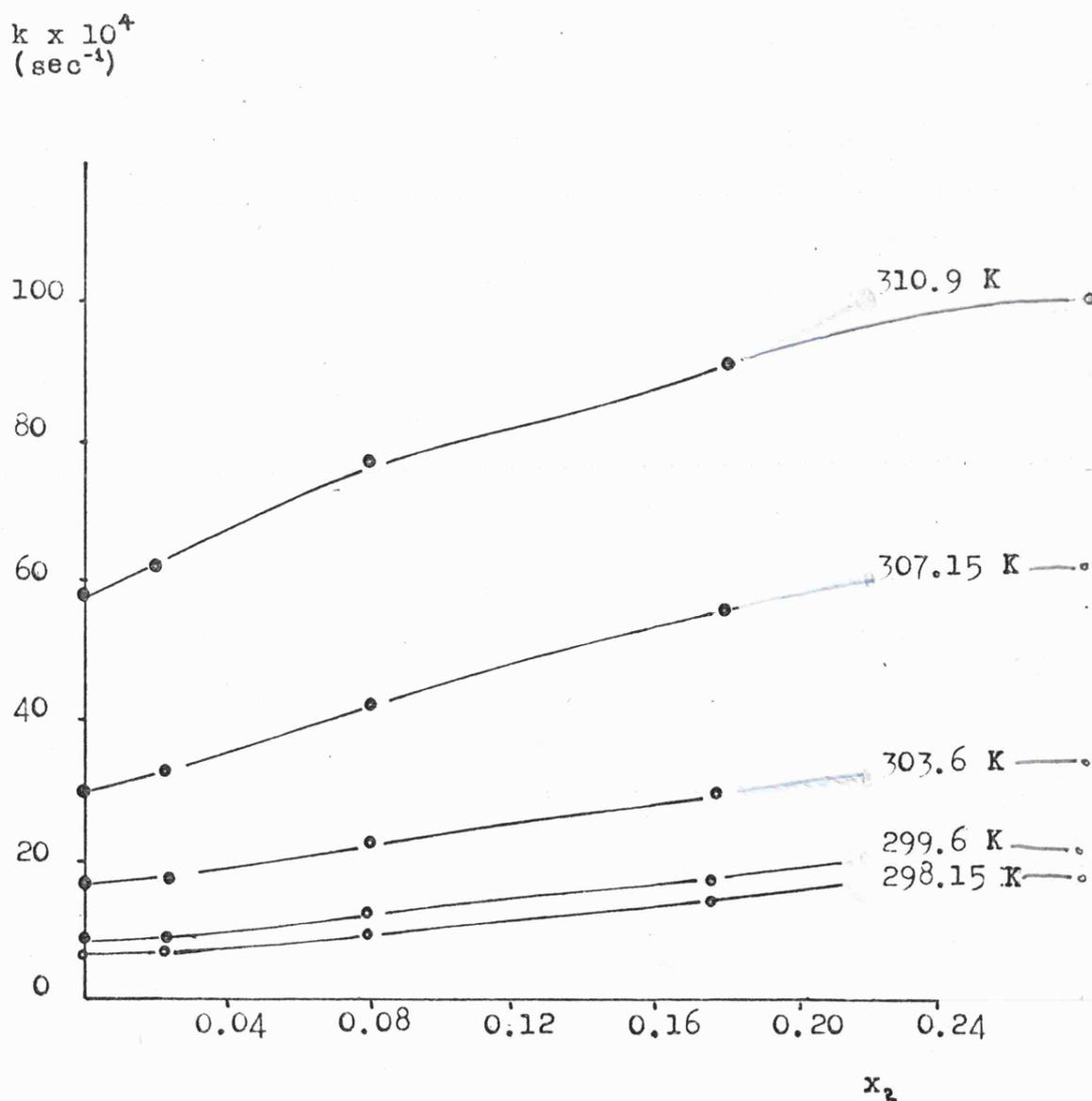


FIGURE 7-1

TABLE 7-A

Activation Parameters for Acetonitrile + Water
Mixtures at 298.2 K

x_2	ΔG^\ddagger /kJmol ⁻¹	ΔH^\ddagger /kJmol ⁻¹	$T\Delta S^\ddagger$ /kJmol ⁻¹
0.0	91.5	120	28.5
0.02	91.0	124. <u>+1.2</u>	33.0
0.08	90.4	119.8 <u>+3</u>	29.4
0.18	89.4	115.8 <u>+2.8</u>	26.5
0.28	88.9	110.0 <u>+4</u>	21.1

Activation Parameters for the Aquation of Tris-(5-nitro-1,10-phenanthroline)iron(II) in Acetonitrile + Water

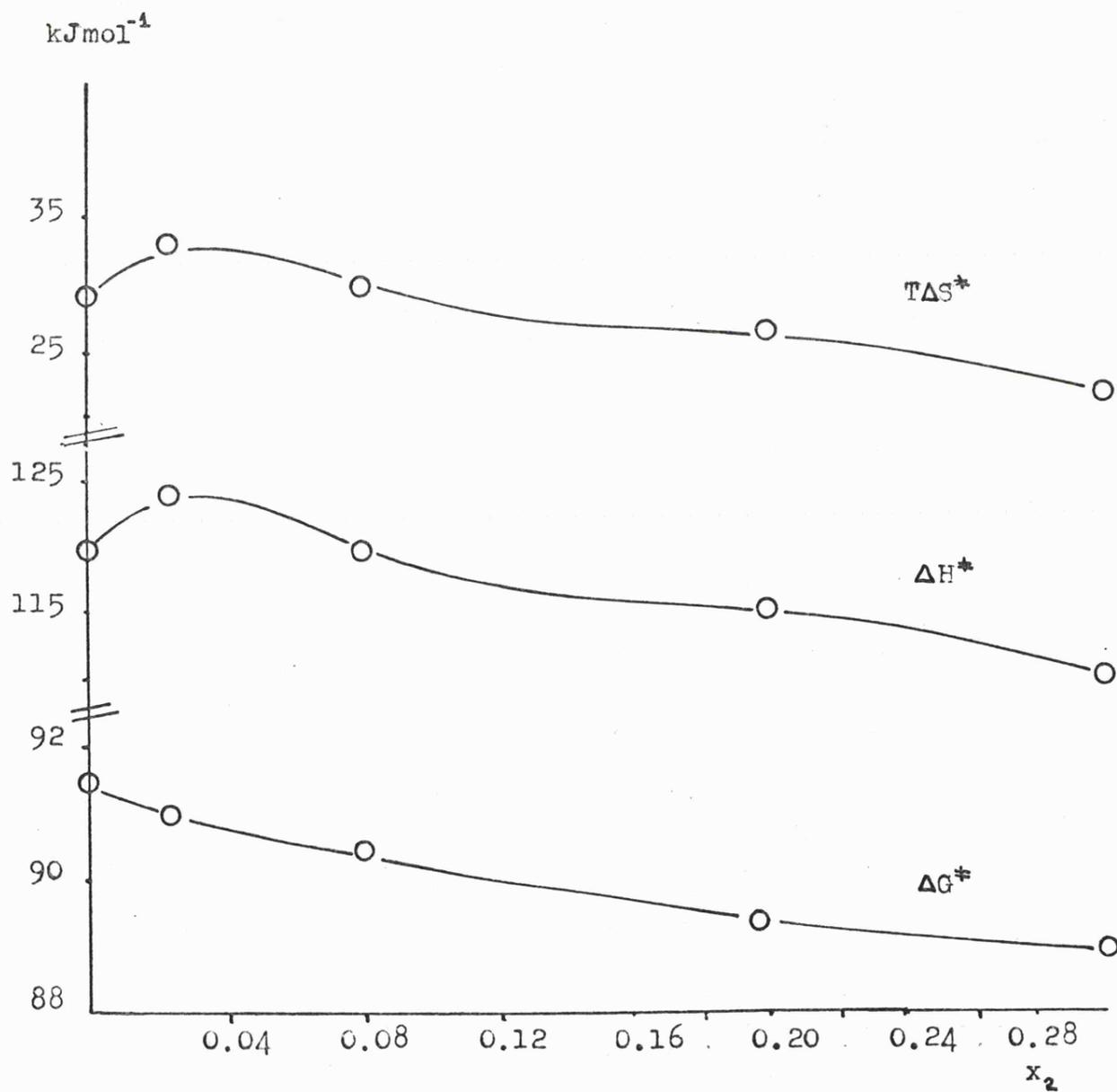


FIGURE 7-2

fraction of acetonitrile shows that the rate of hydrolysis of the 5NO_2 complex varies smoothly with increase in concentration of acetonitrile. These rate data were used to calculate the activation parameters ΔH^\ddagger , $T\Delta S^\ddagger$, and ΔG^\ddagger (chapter 6). These parameters are given in Table 7-A and also in figure 7-2.

(b) Hydrogen Peroxide + Water

Hydrogen peroxide is a rather unusual co-solvent as it is an inorganic co-solvent. In hydrogen peroxide + water mixtures the presence of hydrogen ions is not necessary. Hydrogen peroxide is a scavenger for the out going phen. Thus any change in the rate of hydrolysis of the 5NO_2 complex is due only to the effect of the solvent and not on the solvent mixture + acid. Although this is, of course, useful it does present difficulties when making comparisons with other data. Also the rate constant at a mole fraction hydrogen peroxide, $x_2 = 0$, is impossible to obtain.

Various hydrogen peroxide + water mixtures were made up by volume. The concentration of each mixture was determined by standard iodine-thiosulphate titration. Titrations were also periodically carried out on the stock solutions to check for any decomposition of hydrogen peroxide.

Problems were experienced due to the hydrogen peroxide decomposing in the reaction cell. This was especially marked above room temperature. For this reason the maximum temperature used for this solvent mixture was 306 K. Bubbles of oxygen produced from the decomposition would occlude to

First-order Rate Constants, k , for Aquation of Tris-
(5-nitro-1,10-phenanthroline)iron(II) in Hydrogen Peroxide
+ Water

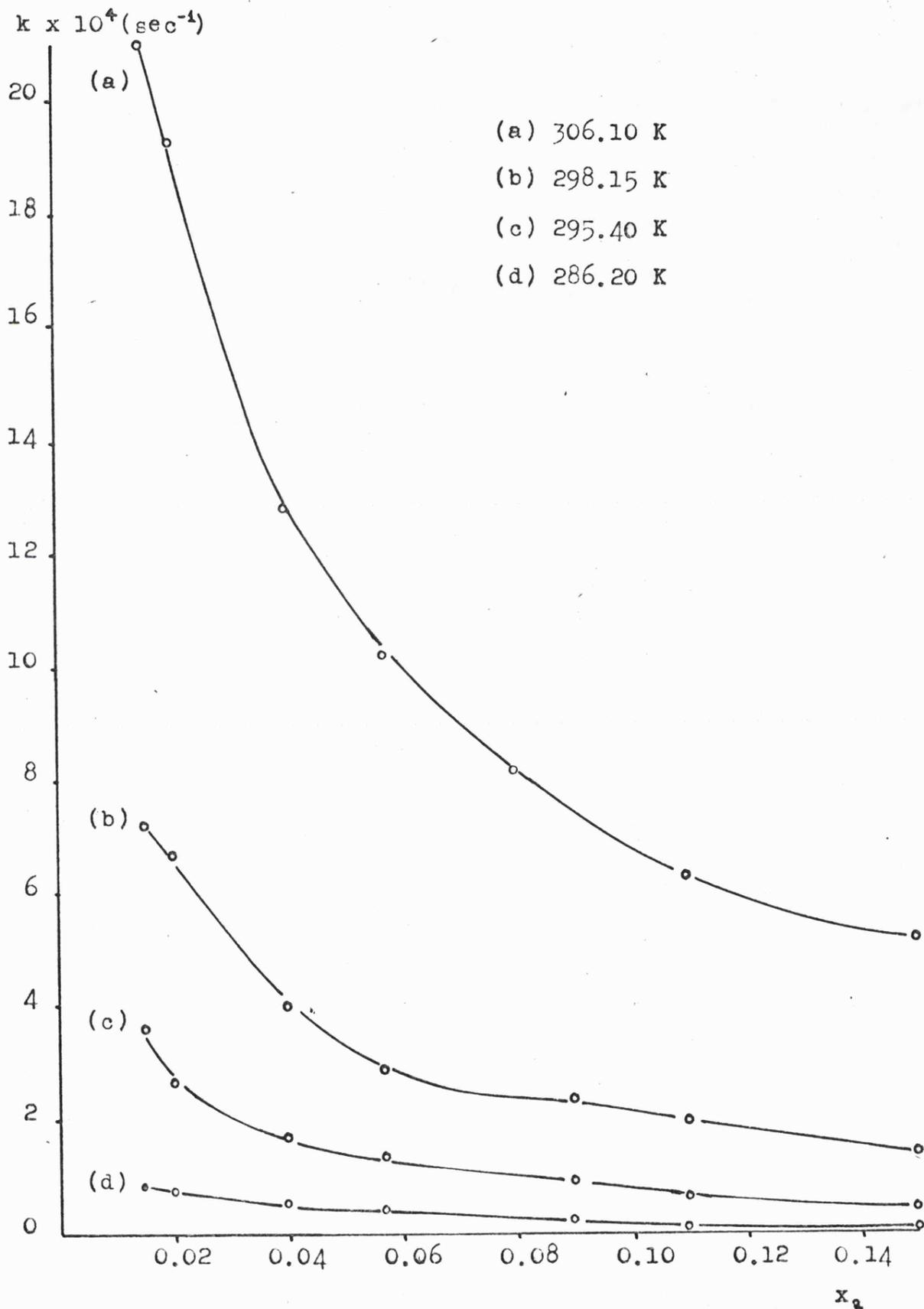


FIGURE 7-3

TABLE 7-B

Activation Parameters for Hydrogen Peroxide + Water
Mixtures at 298.2 K.

x_2	ΔG^\ddagger /kJmol ⁻¹	ΔH^\ddagger /kJmol ⁻¹	$T\Delta S^\ddagger$ /kJmol ⁻¹
0.015	90.96	114 ± 2	23
0.020	91.12	115 ± 3	24
0.040	91.43	118 ± 3	26
0.057	92.16	122 ± 3	29
0.090	93.48	132 ± 4	38
0.110	94.14	141 ± 4	47
0.150	95.02	146 ± 5	51

Activation Parameters for the Aquation of Tris-(5-nitro-1,10-phenanthroline)iron(II) in Hydrogen Peroxide + Water
 The Points at $x = 0, \square$, Denote Values for Acid

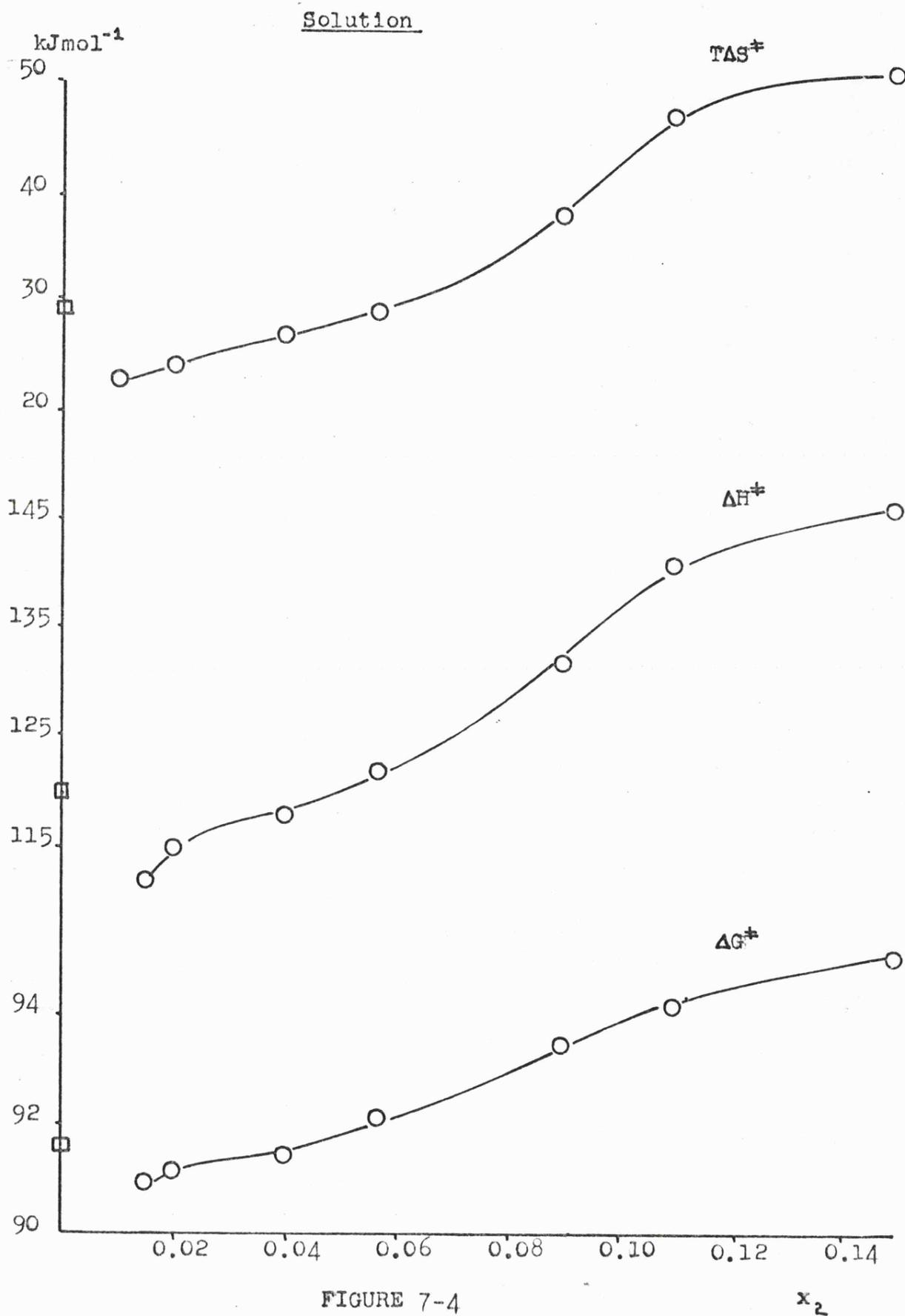


FIGURE 7-4

 x_2

the cell walls and therefore give rise to spurious readings of optical density. Provision for these readings was made in the computer programme (ROGUE). This was achieved by ignoring in the calculations, obviously low readings of optical density as compared to the previous recorded readings.

The rate of hydrolysis of the 5NO_2 complex was studied in seven different hydrogen peroxide + water mixtures each at four different temperatures. The rate constants are given in Appendix 1 and plotted in figure 7-3. An interesting point about these data, is that the rate constant at very low hydrogen peroxide concentrations is, in fact, larger than the rate of hydrolysis in water + acid at the same temperature. This is despite the overall trend for rate constant to fall with increasing concentration of hydrogen peroxide.

Activation parameters were calculated from the rate data and are given in Table 7-B and in figure 7-4.

(c) Glycerol + Water Mixtures

Glycerol + water, like hydrogen peroxide + water is a TNAN solvent mixture.

Analar glycerol was used to make up all mixtures, each of which was made up by weight to a specified mole fraction, and concentrated H_2SO_4 was added to produce a 0.5M solution in H_2SO_4 . The aquation of the 5NO_2 complex was followed at five concentrations of glycerol each at 5 different temperatures. The rate constants are given in Appendix 1 and plotted in figure 7-5. The graph of rate constant against mole fraction

First - order Rate Constants, k , for Aquation of Tris-
(5-nitro-1,10-phenanthroline)iron(II) in Glycerol + Water.

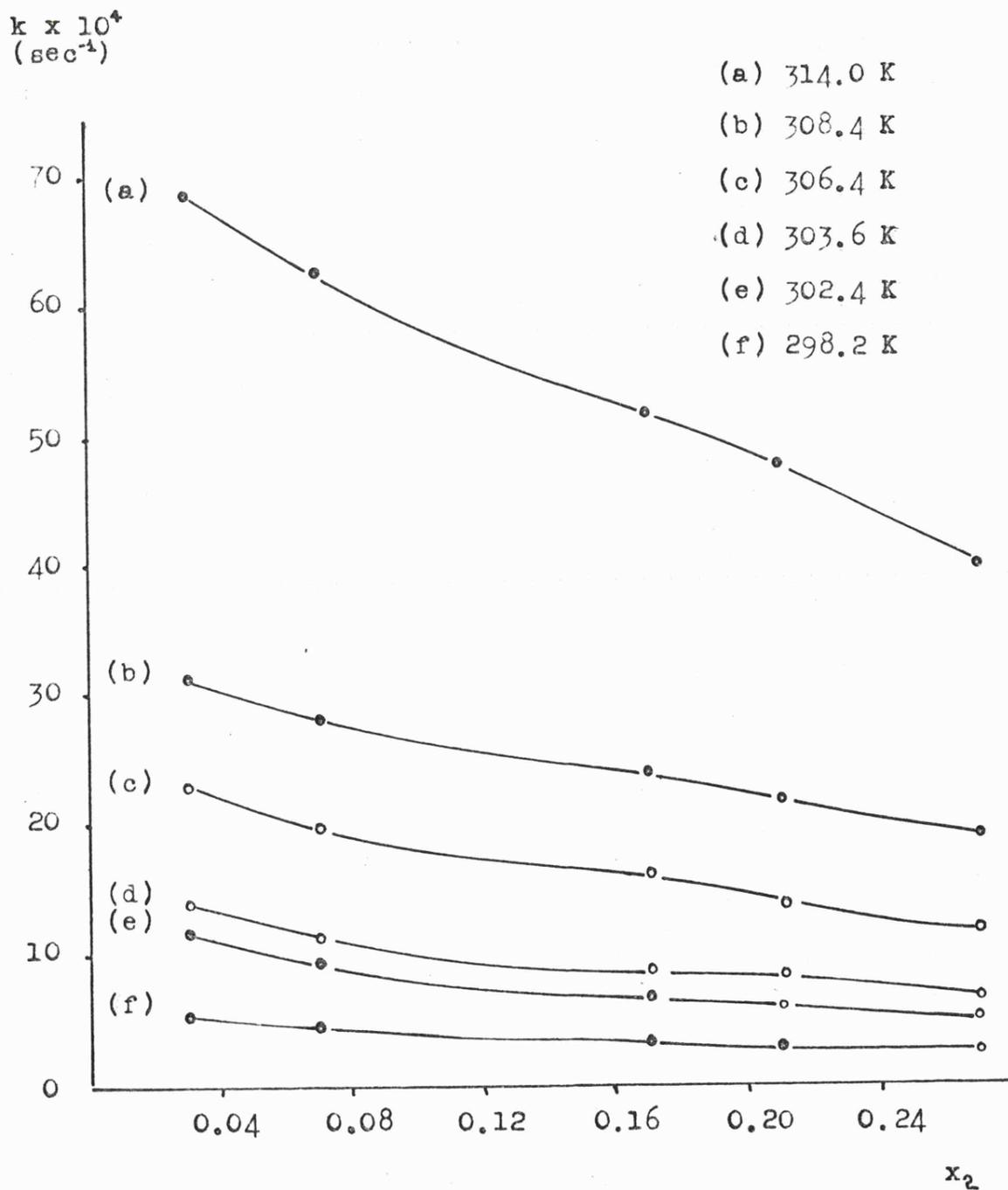


FIGURE 7-5

TABLE 7-C

Activation Parameters for Glycerol + Water Mixtures
at 298.2 K

x_2	ΔG^\ddagger /kJmol ⁻¹	ΔH^\ddagger /kJmol ⁻¹	$T\Delta S^\ddagger$ /kJmol ⁻¹
0.03	91.76	118.4 ± 2.5	26.6
0.07	92.11	126.3 ± 3.0	34.2
0.17	92.89	136.8 ± 2.8	44.0
0.21	93.27	136.8 ± 3.0	43.6
0.27	93.72	138.8 ± 4.0	45.1

Activation Parameters for the Aquation of Tris-(5-nitro-1,10-phenanthroline)iron(II) in Glycerol + Water

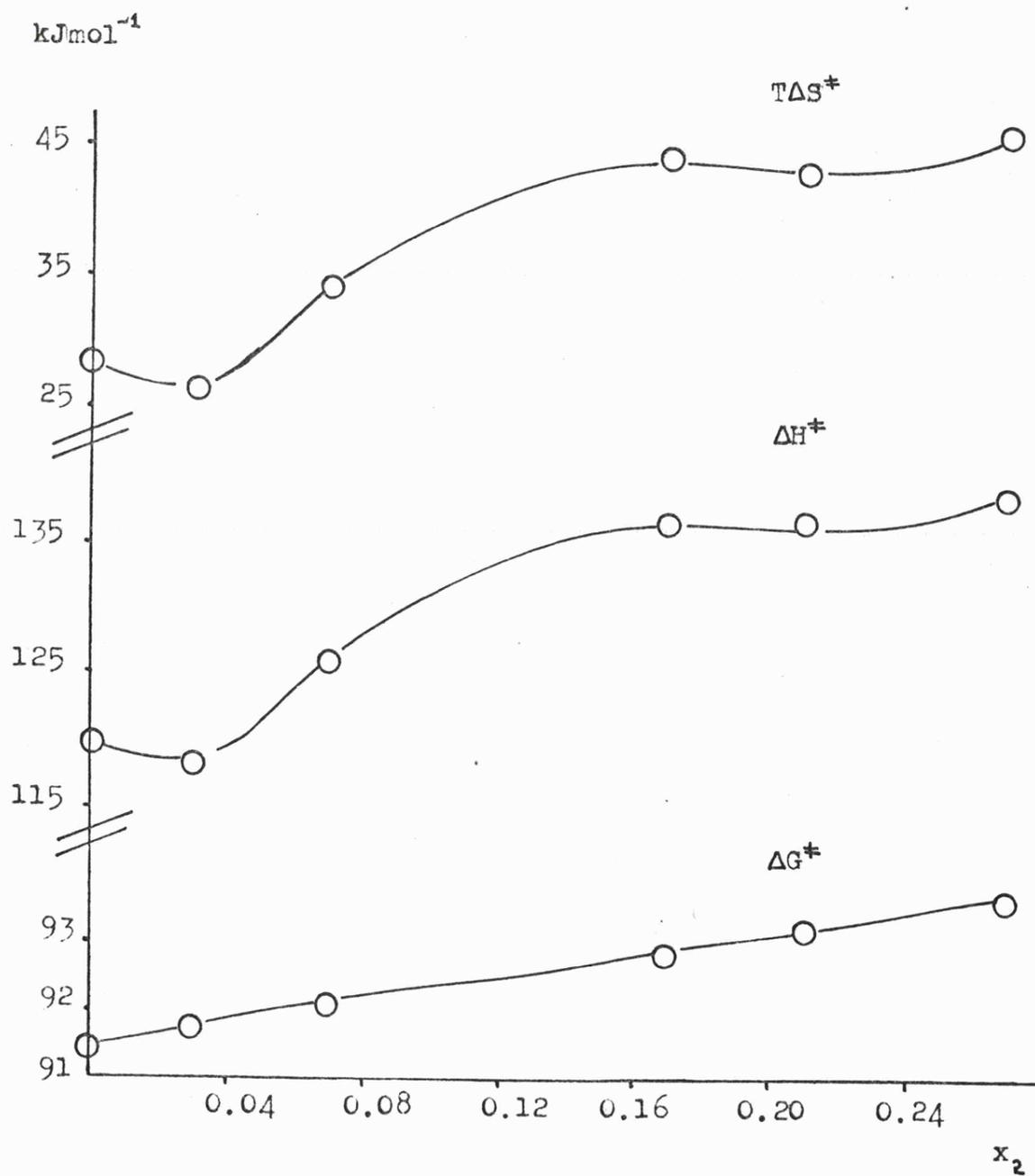


FIGURE 7-6

of glycerol shows that there is a very small variation of the rate constant with mole fraction of glycerol. The activation parameters, Table 7-C and figure 7-6, show a rather more complex dependence on x_2 than that of the rate constants themselves.

The only difficulty encountered with this solvent mixture was in mixing the stock solution of the 5NO_2 complex with the glycerol + water mixtures. For the more concentrated mixtures the mixing took a few seconds (30 sec. to 1 min.). Therefore the first few readings of absorbance were ignored by the computer programme.

(d) Acetone + Water Mixtures

This solvent mixture was chosen because of its close similarity to t-butyl alcohol + water mixtures with respect to thermodynamic parameters. The hydrolysis of the 5NO_2 iron complex in t-butyl alcohol + water² mixtures has been studied previously. There is extensive thermodynamic information about both solvent mixtures hence they were chosen for the endostatic analysis.

BDH Analar acetone was used to make up all solutions, all of which were made up by weight to a known mole fraction and sufficient concentrated H_2SO_4 was added to produce a 0.5M solution. Eight different mole fractions of acetone were studied each at four temperatures. The rate data are given in the appendix but they are also plotted in figure 7-7.

First-order Rate Constants, k , for Aquation of Tris-
(5-nitro-1,10-phenanthroline)iron(II) in Acetone +
Water

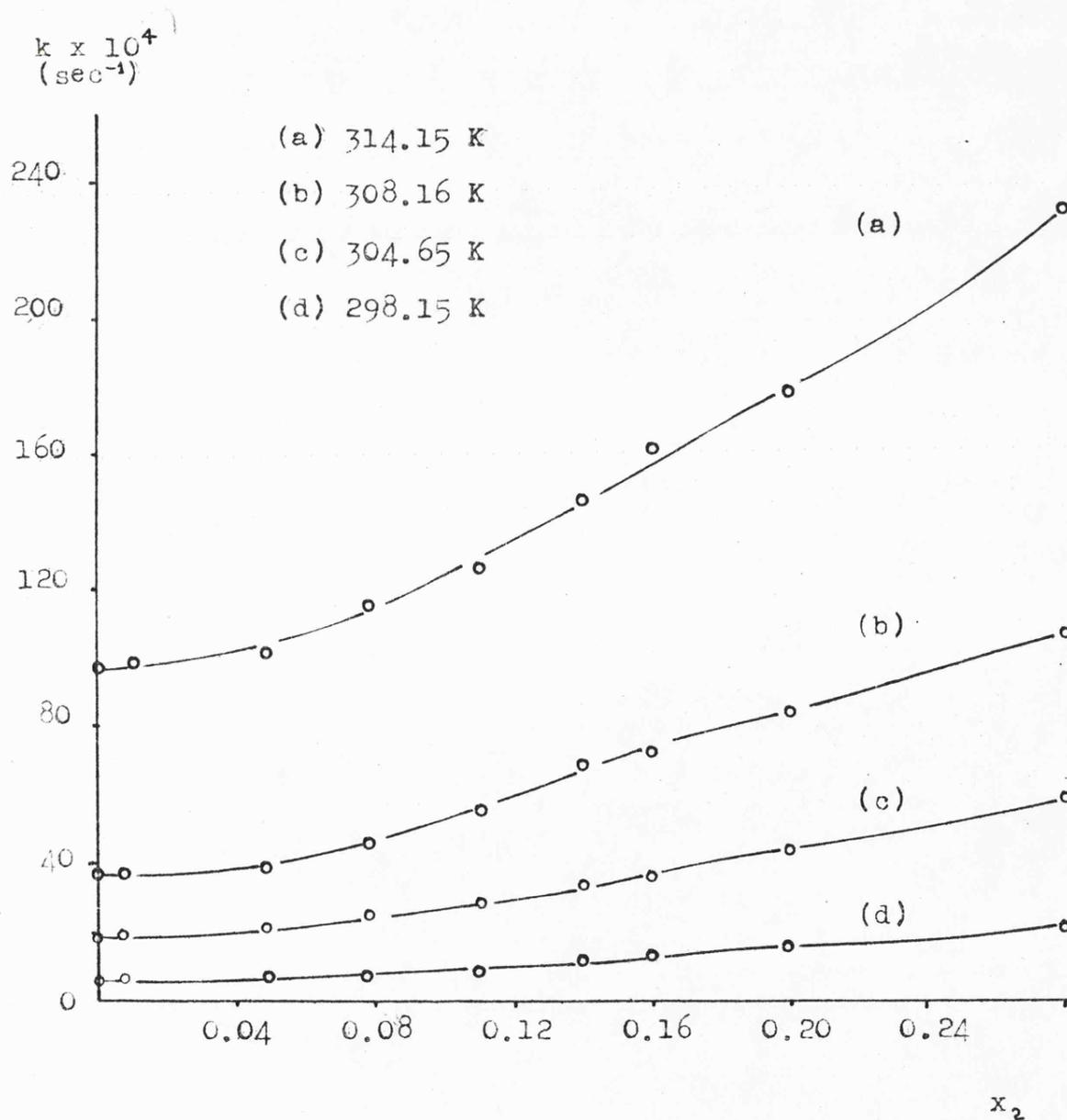


FIGURE 7-7

TABLE 7-D

Activation Parameters For Acetone + Water Mixtures
at 298 K

x_2	ΔG^\ddagger /kJmol ⁻¹	ΔH^\ddagger /kJmol ⁻¹	$T\Delta S^\ddagger$ /kJmol ⁻¹
.007	91.12	122.6 ± 1.12	31.4
.048	90.97	121.9 ± 2.8	30.6
.078	90.59	116.6 ± 2.4	26.0
.110	90.21	115.5 ± 1.9	25.3
.140	89.87	113.5 ± 1.1	23.6
.160	89.63	112.0 ± 2.8	22.4
.200	89.02	108.2 ± 4.0	18.2
.280	88.20	102.0 ± 3.2	13.8

Activation Parameters for the Aquation of Tris-(5-nitro-1,10-phenanthroline)iron(II) in Acetone + Water

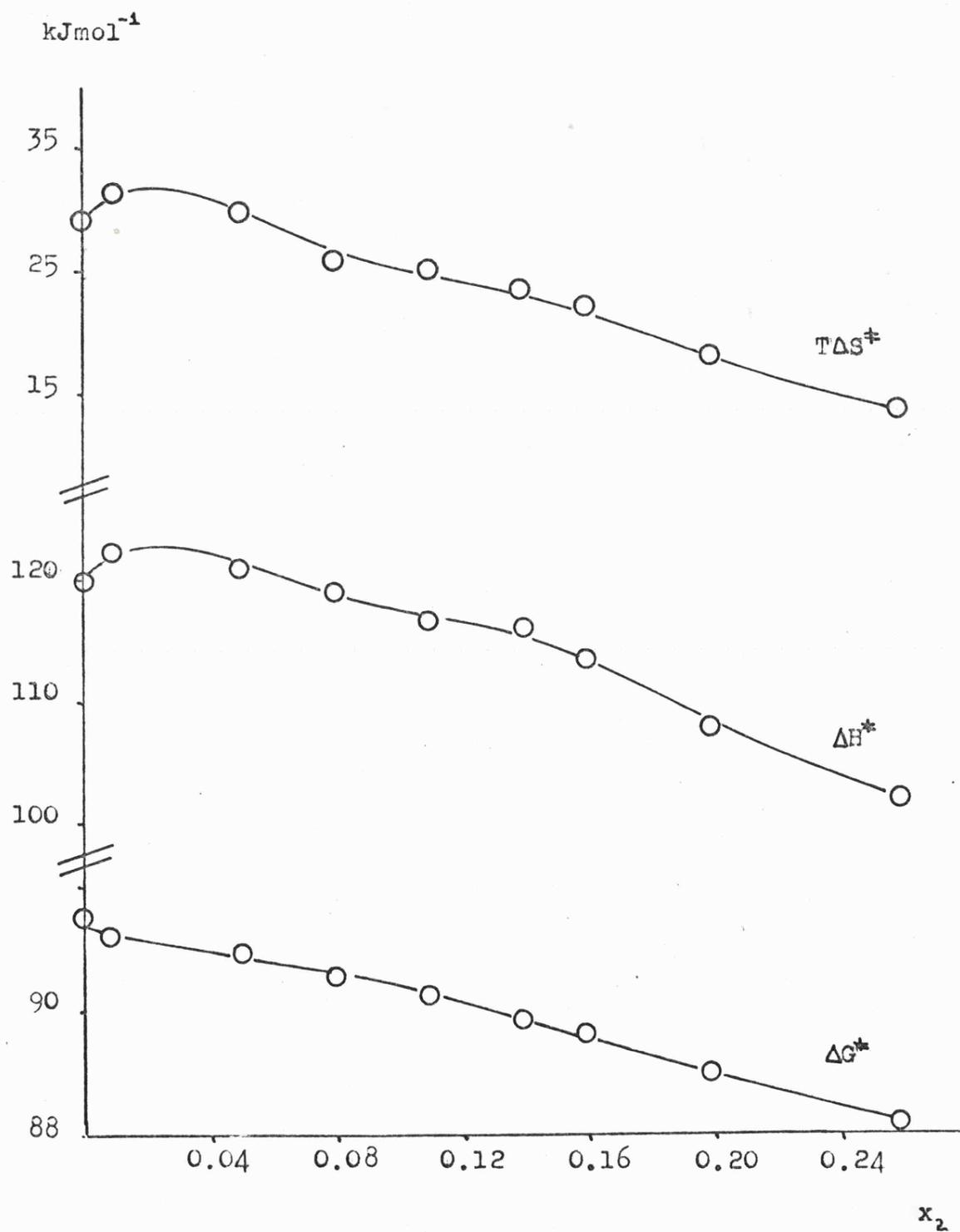


FIGURE 7-8

TABLE 7-E

Endostatic Activation Parameters for Acetone + Water and the Parameters Required in Their Calculation

(a) Gibbs Free Energy of Activation

x_2	ΔG^\ddagger /kJmol ⁻¹	$d\Delta G^\ddagger/dx_1$	$\ln \alpha$	$d \ln \alpha / dx_1$	ΔG^\ddagger /kJmol ⁻¹
0.007	91.21	-0.734	141.9	136.9	91.06
0.048	90.97	9.788	21.29	18.31	90.08
0.078	90.59	12.284	14.12	11.65	89.19
0.110	90.21	11.458	10.73	8.64	88.86
0.140	89.87	11.867	8.70	6.88	88.50
0.160	89.63	13.35	7.60	5.94	88.17
0.200	89.02	13.58	5.71	4.34	87.07
0.280	88.20	-	4.58	2.01	-

TABLE 7-E (cont.)

(b) Activation Enthalpy and Entropy

x_2	ΔH^\ddagger /kJmol ⁻¹	\bar{H}_1	\bar{H}_2	ΔH^\ddagger /kJmol ⁻¹	$T\Delta S^\ddagger$ /kJmol ⁻¹	$T\Delta S_\alpha^\ddagger$ /kJmol ⁻¹
0.007	122.6	-4.5	-371167.7	121.9	31.4	30.1
0.048	121.9	-166.25	-28478.1	115.8	30.6	25.7
0.078	116.6	-357.27	-23747.1	106.6	26.0	17.4
0.110	115.5	-559.65	-19864.6	105.2	25.3	16.3
0.140	113.5	-717.38	-17024.7	102.2	23.6	13.7
0.160	112.0	-800.64	-15434.6	98.8	22.4	5.6
0.200	108.2	-922.4	-12718.2	93.4	18.2	6.3
0.280	102.0	-109.12	-8180.1	-	13.8	-

TABLE 7-F
 Endostatic Activation Parameters for t-Butyl Alcohol + Water and the Parameters Required in their Calculation

x_2	ΔG^\ddagger /kJmol ⁻¹	$d\Delta G^\ddagger/dx_1$	$\ln \alpha$	$d \ln \alpha / dx_1$	ΔG^\ddagger /kJmol ⁻¹
0.01	91.839	10.136	2.809	90.43	91.62
0.023	91.881	5.021	1.396	35.23	91.72
0.035	91.110	17.895	1.068	19.71	90.46
0.055	91.200	17.832	0.789	9.89	90.46
0.075	91.000	11.888	0.642	5.60	90.09
0.09	90.750	15.666	0.576	3.79	89.95
0.10	90.600	7.182	0.544	2.96	90.22
0.105	90.584	18.104	0.532	2.62	90.207
0.125	90.165	15.341	0.495	1.64	89.19

(a) Gibbs Free Energy of Activation

TABLE 7-F (cont.)

(b) Activation Enthalpy and Entropy

x_2	ΔH^\ddagger /kJmol ⁻¹	\bar{H}_1	\bar{H}_2	ΔH^\ddagger /kJmol ⁻¹	$T\Delta S^\ddagger$ /kJmol ⁻¹	$T\Delta S^\ddagger$ /kJmol ⁻¹
0.01	120.49	-12.742	-12656.39	120.01	28.6	28.5
0.023	121.33	-58.378	-9908.927	120.89	29.4	29.2
0.035	120.08	-127.620	-7597.091	118.25	29.0	28.2
0.055	112.54	-266.94	-4671.204	110.87	21.3	21.1
0.075	109.2	-418.67	-2528.92	108.45	18.2	18.9
0.090	106.5	-529.152	-1336.188	105.09	15.7	16.9
0.100	105.5	-598.68	-704.288	105.49	14.9	16.4
0.105	105.01	-630.68	-431.269	105.17	14.4	18.7
0.125	99.16	-746.3	-416.39	99.42	9.6	13.1

Comparison of Conventional and Endostatic Activation
Gibbs Free Energy, ΔG^\ddagger and ΔG_α^\ddagger , at 298.2 K as a
Function of Mole Fraction of Acetone.

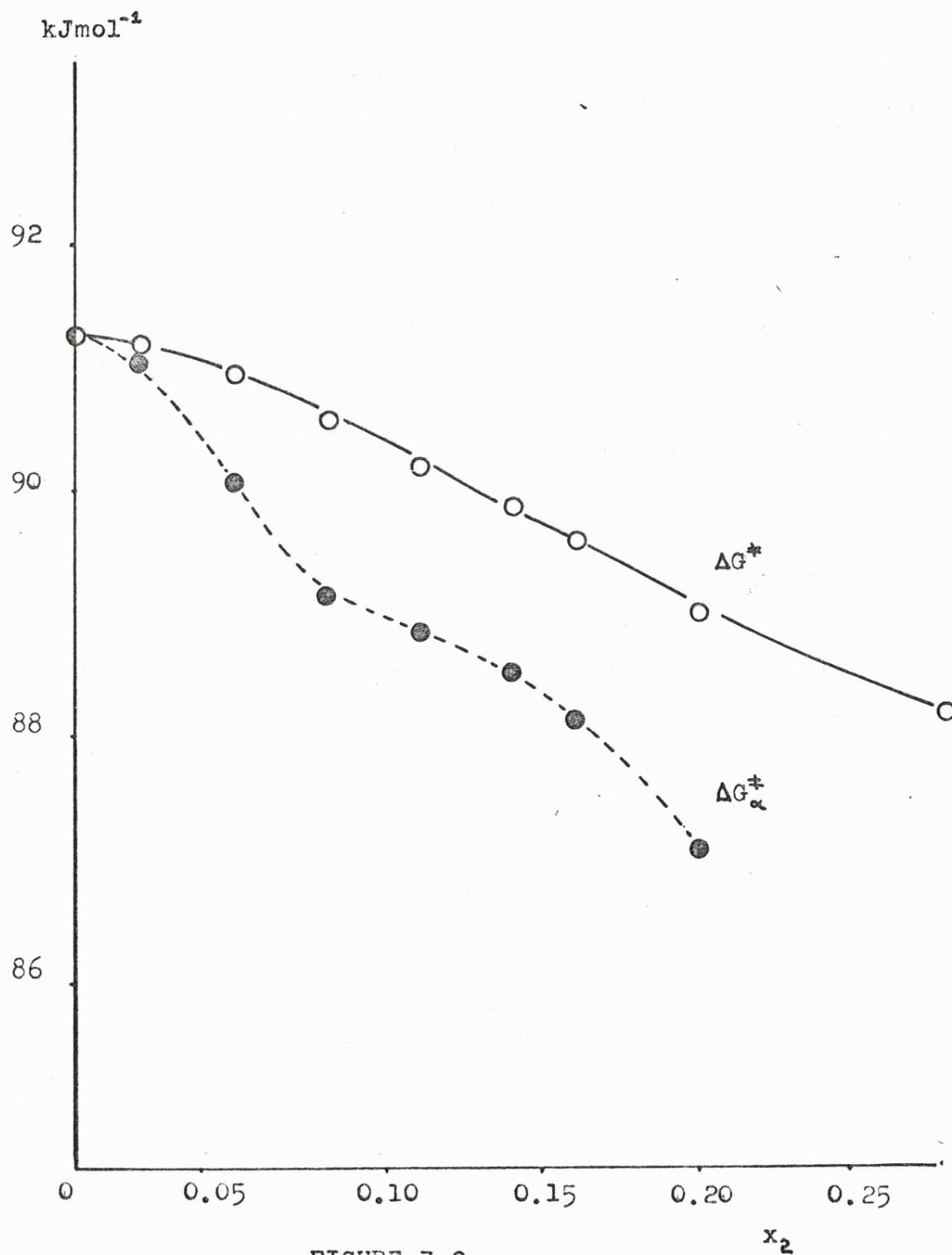


FIGURE 7-9

Comparison of Conventional and Endostatic Activation
Enthalpy and Entropy at 298.2 K as a Function of Mole
Fraction of Acetone

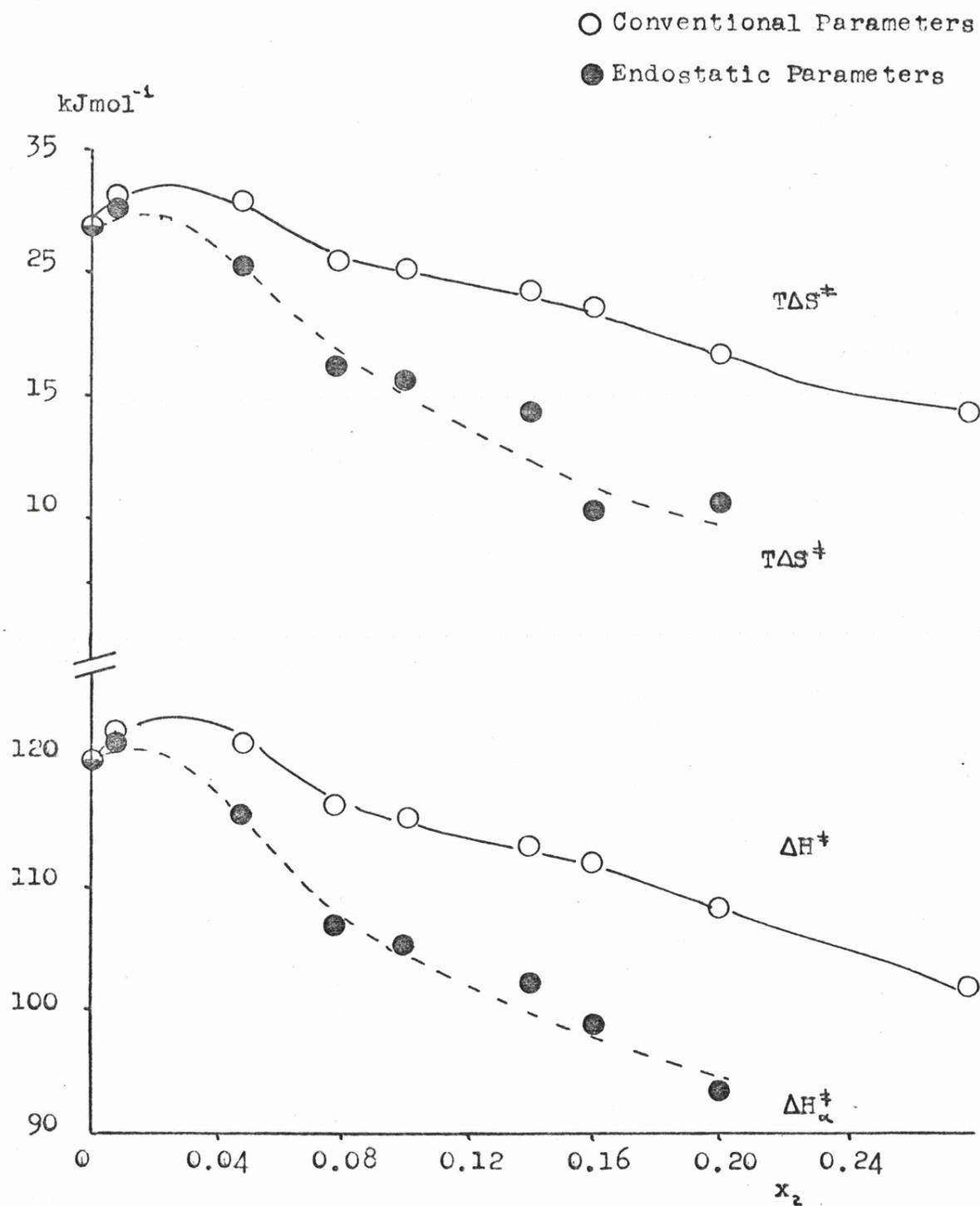


FIGURE 7-10

Comparison of Conventional and Endostatic Activation
Gibbs Free Energy, ΔG^\ddagger and ΔG_α^\ddagger , at 289.2 K as a
Function of Mole Fraction of t-Butyl Alcohol.

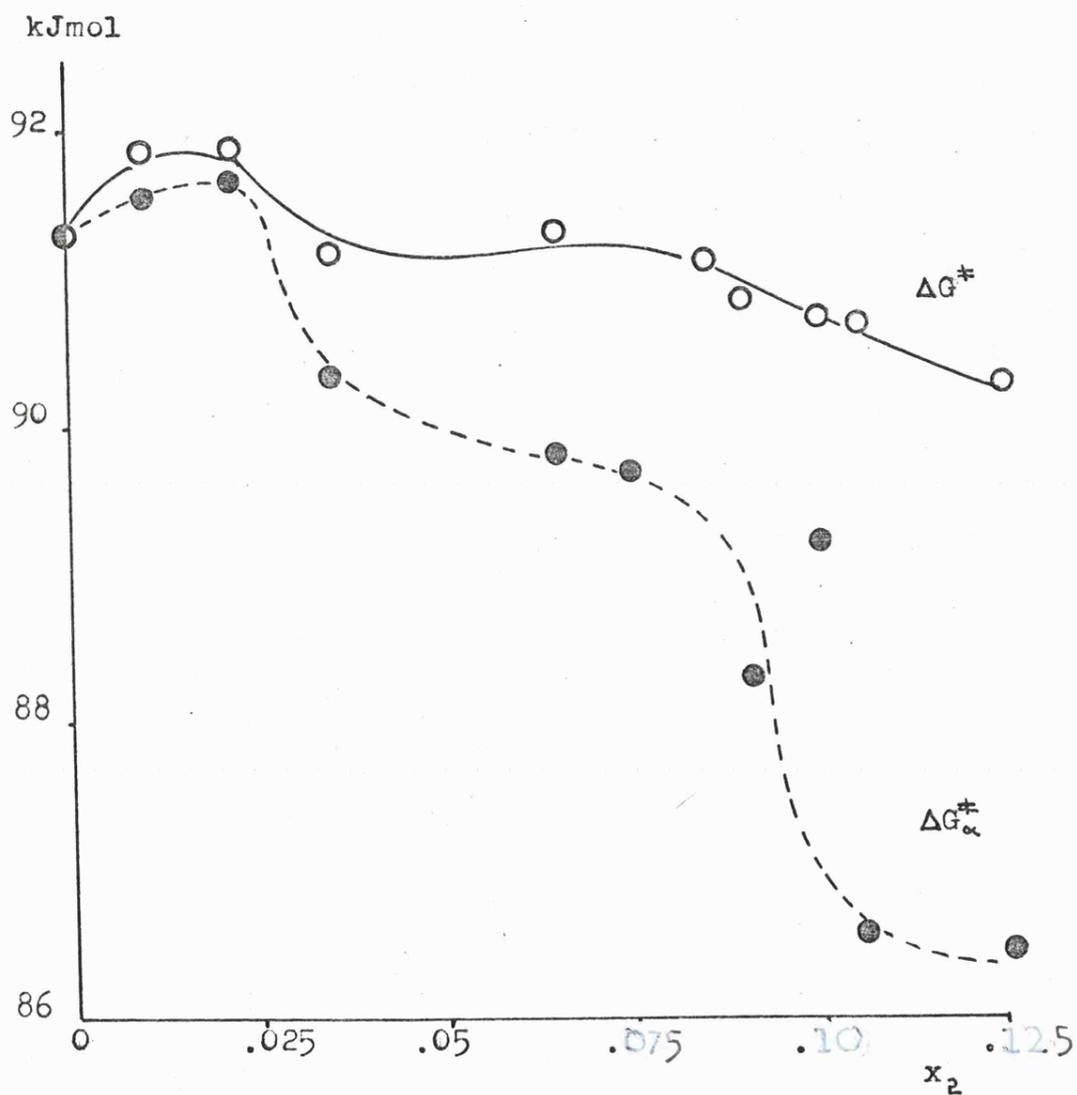


FIGURE 7-11

Comparison of Conventional and Endostatic Activation
Enthalpy and Entropy at 298.2 K as a Function of Mole
Fraction of t-Butyl Alcohol.

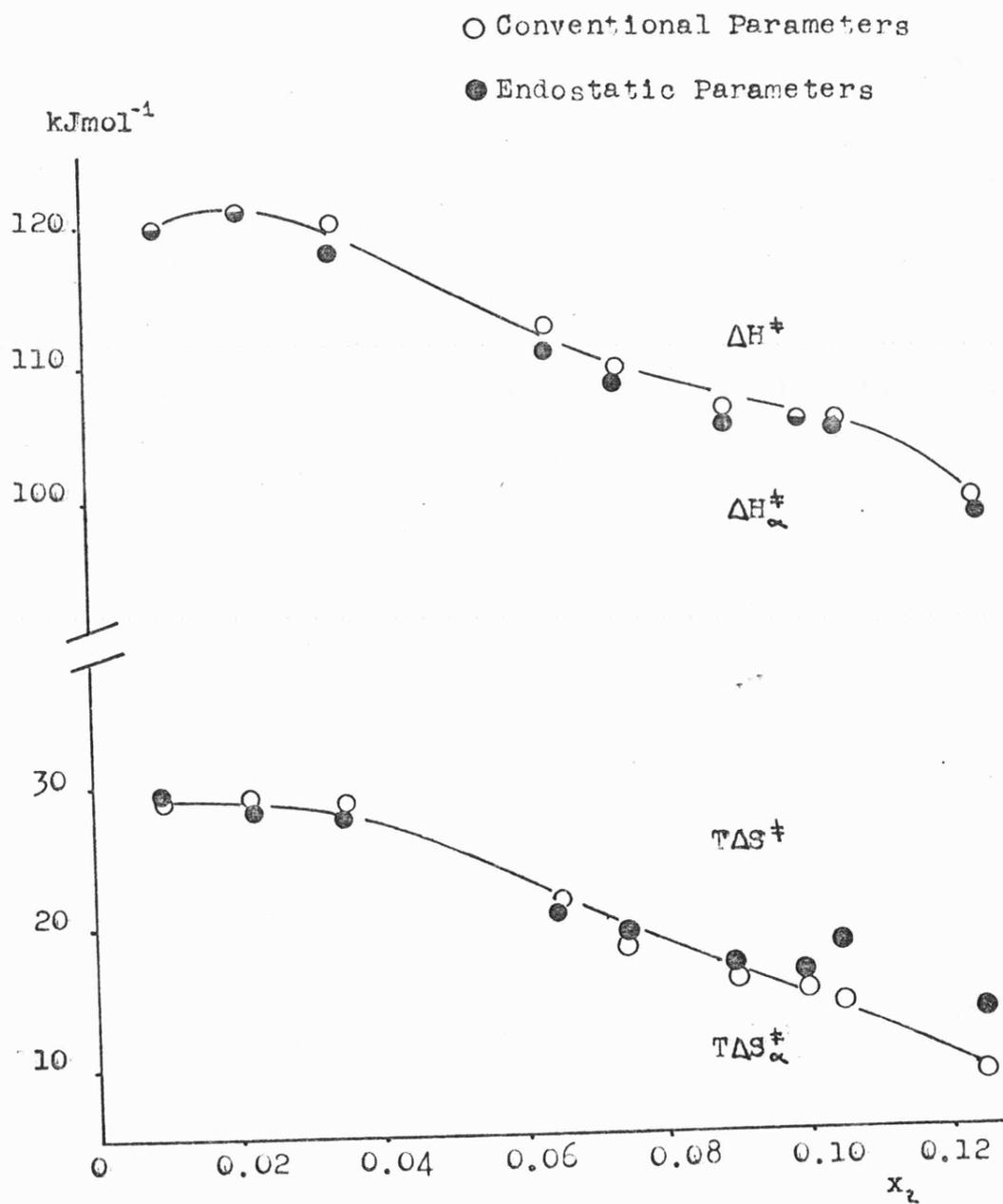


FIGURE 7-12

The variation in rate with concentration of acetone is very similar to the variation obtained for t-butyl alcohol and water mixtures. Both co-solvents only have an appreciable effect on the rate constant after the mole fraction x_2^* (chapter 2). The rate data were used to calculate activation parameters (Table 7-D and Figure 7-8).

An endostatic analysis on the rate data for both acetone + water and t-butyl alcohol + water was performed as described in Chapter 4. Thermodynamic parameters required were obtained from the literature. The set of data given by Ken'tamaa et al³ was used for t-butyl alcohol + water mixtures. The parameters obtained by Blandamer and Waddington⁴ in their analysis of vapour pressure⁵ and enthalpy of mixing data⁶ were used for acetone + water mixtures. The values of the important parameters calculated in this analysis together with the endostatic activation parameters are given in Tables 7-E and 7-F for the two solvent systems. The endostatic activation parameters are also drawn in figures 7-9 to 7-12.

2. Reaction between Nickel(II) and PADA

This reaction was followed using the stopped flow technique as discussed previously (chapter 5) and results in the formation of a 1:1 complex which has an intense purple colour

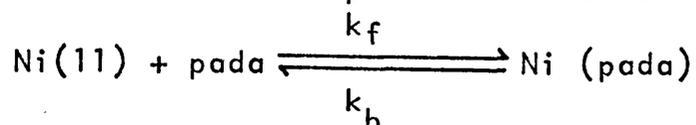


TABLE 7-G

Formation Rate Constants for Nickel + PADA at 298 K

Cosolvent	x_2	k_f /dm ³ mol ⁻¹ s ⁻¹
	0	814.3
acetonitrile	.038	721.24
	.186	663.09
dimethyl sulphoxide	.059	907.4
	.144	1367.7

The Dependence of Observed First-Order Rate Constant on
Nickel Concentration for Ni(II) + pada at 298 K in aqueous
Solution.

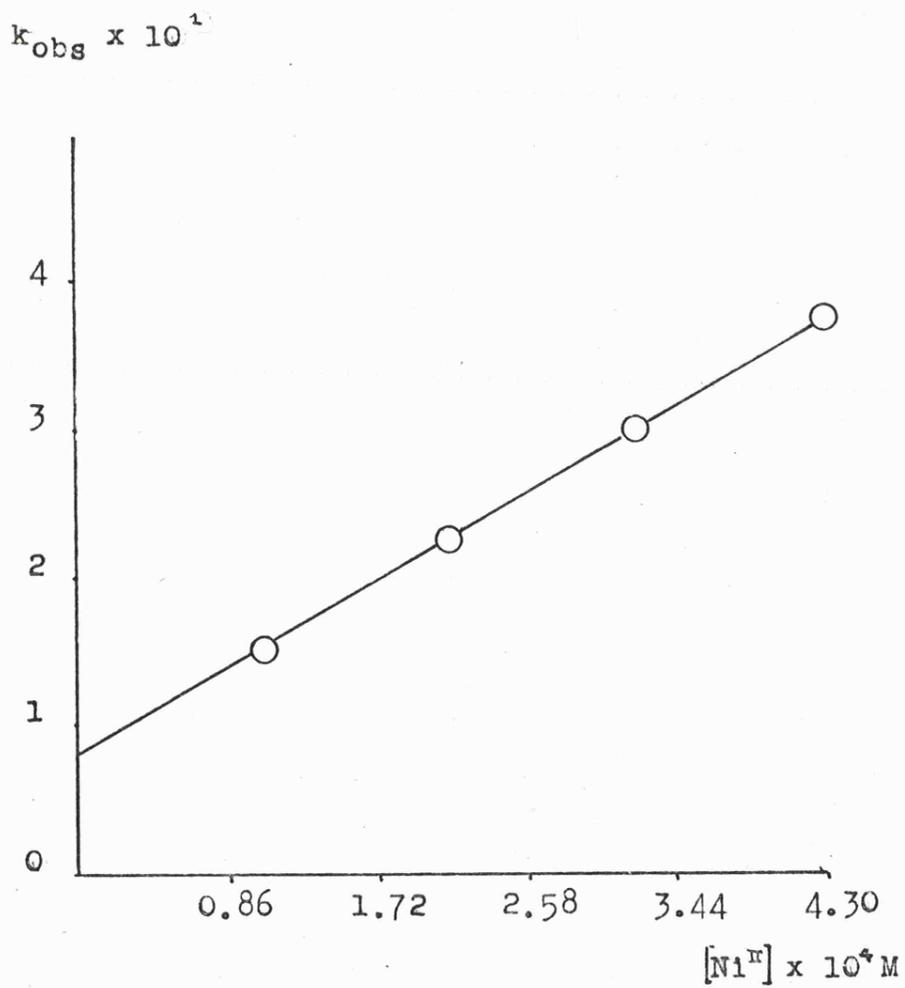


FIGURE 7-13

The Dependence of Observed First-Order Rate Constant on
Nickel Concentration for Ni(II) + pada at 298 K in
Acetonitrile + Water.

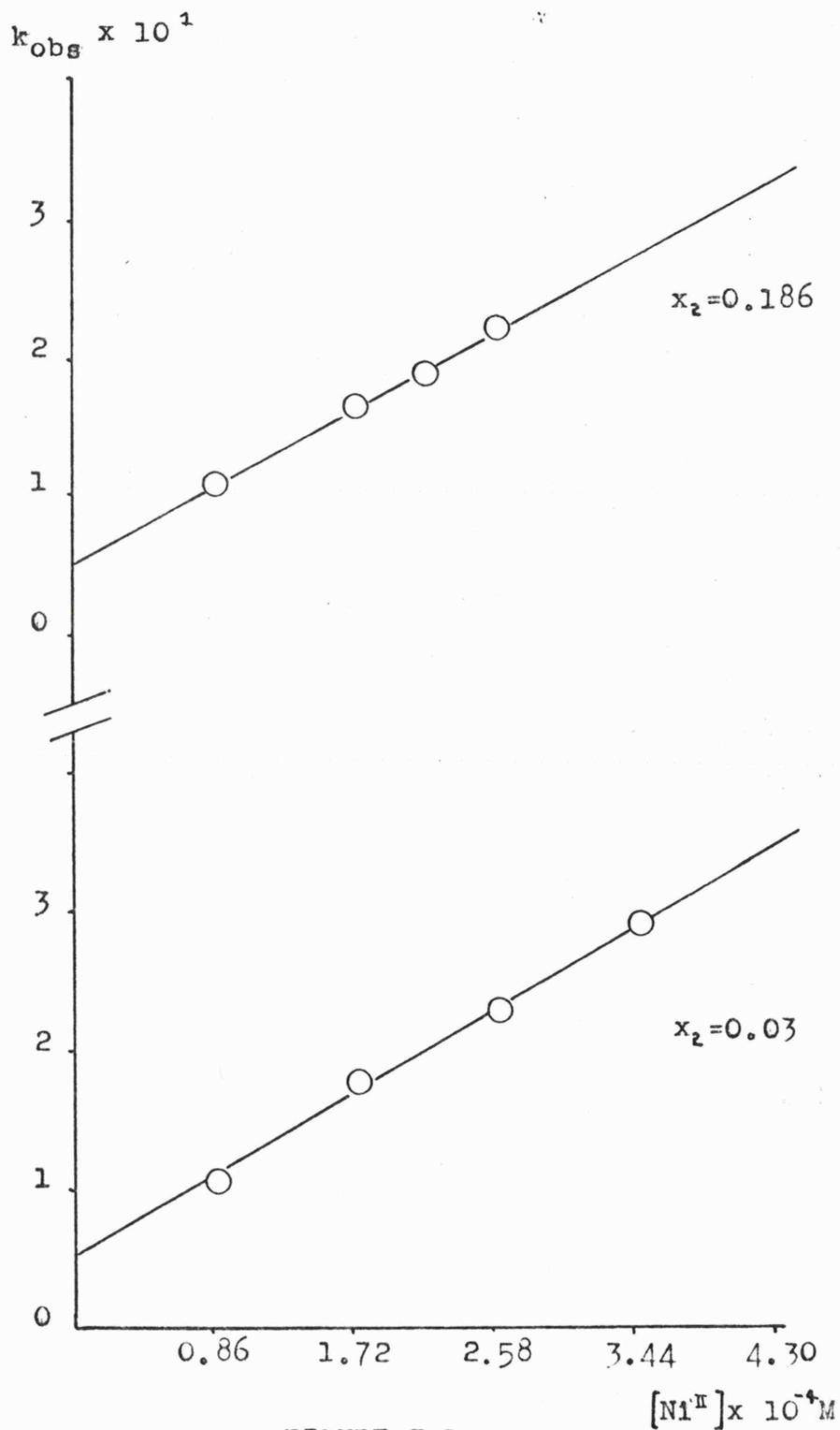


FIGURE 7-14

The Dependence of Observed First-Order Rate Constants on
Nickel Concentration for Ni(II) + pada at 298 K in
DMSO + Water.

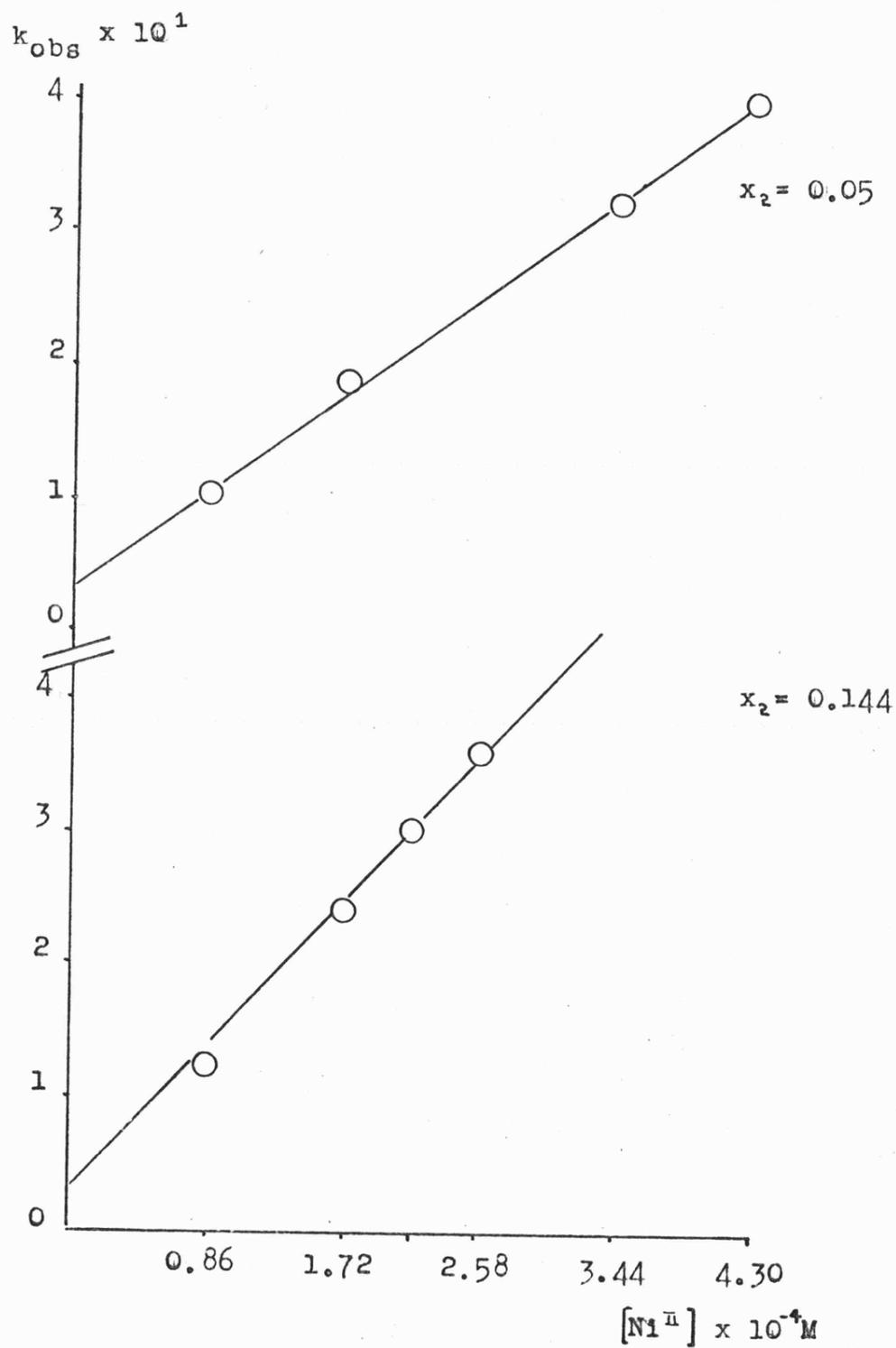


FIGURE 7-15

Stock solutions of nickel nitrate (0.017M) and pada ($3 \times 10^{-5} \text{M}$) were prepared as previously described. The concentrations are such that first order conditions were obtained in all reaction mixtures.

The reaction follows the rate equation -

$$\text{rate} = k_f + k_b [\text{Ni}^{II}]$$

Hence by determining the rate of reaction at several concentrations of nickel(II) the two rate constants can be obtained by plotting observed first-order rate constants against nickel(II) concentration.

All measurements were carried out at 298K. The values of k_f and k_b were determined in water and were found to agree with previous published data.

	k_f /dm ³ mol ⁻¹ s ⁻¹	k_b /s ⁻¹
This work	814.3	.08
Previous work ⁷	890	.1

The rate constant k_b was subject to a large error as its value is found from the intercept of the graph observed first order rate constant against Ni(II) concentration and only a small change in slope produces a large error in the intercept.

The reaction was then studied in acetonitrile + water and DMSO + water mixtures the results are given in Table 7-G and in figures 7-13 to 7-15. Unfortunately both glycerol + water and hydrogen peroxide + water mixtures could not be used in this apparatus. Glycerol + water mixtures have a

high viscosity and are therefore unsuitable. Hydrogen peroxide + water decomposes to give bubbles of oxygen which therefore make the mixture unsuitable. The two co-solvents acetonitrile and DMSO were chosen to complement the data for this reaction⁸ and also there is thermodynamic information available for these two solvent systems.

From the results given in Table 7-G it can be seen that acetonitrile retards the formation of the complex whereas DMSO accelerates its formation.

3. Cobalt + PADA

A tentative study was undertaken using the reaction between cobalt(II) and pada. This reaction is thought to proceed by a very similar mechanism to that for the reaction between nickel(II) and pada. This reaction was followed using a temperature jump technique (carried out at the University of Kent with the assistance of Dr. D. Hague). The reaction was studied in glycerol + water to complement the range of solvents used. Hydrogen peroxide + water mixtures are, of course, unsuitable for the temperature jump technique.

Stock solutions of pada (1.5×10^{-4} M) and cobalt nitrate (10^{-2} M) were made up as described earlier. In all reaction mixtures the metal ion was always in large excess relative to the pada solution. Therefore first order conditions were obtained.

Solutions for the kinetic runs were prepared in 25ml graduated flasks and the ionic strength was maintained by

Dependence of the Relaxation Time, τ , on Cobalt
Concentration for Co(II) + pada in (a) aqueous solution
and (b) Glycerol + Water at 298 K

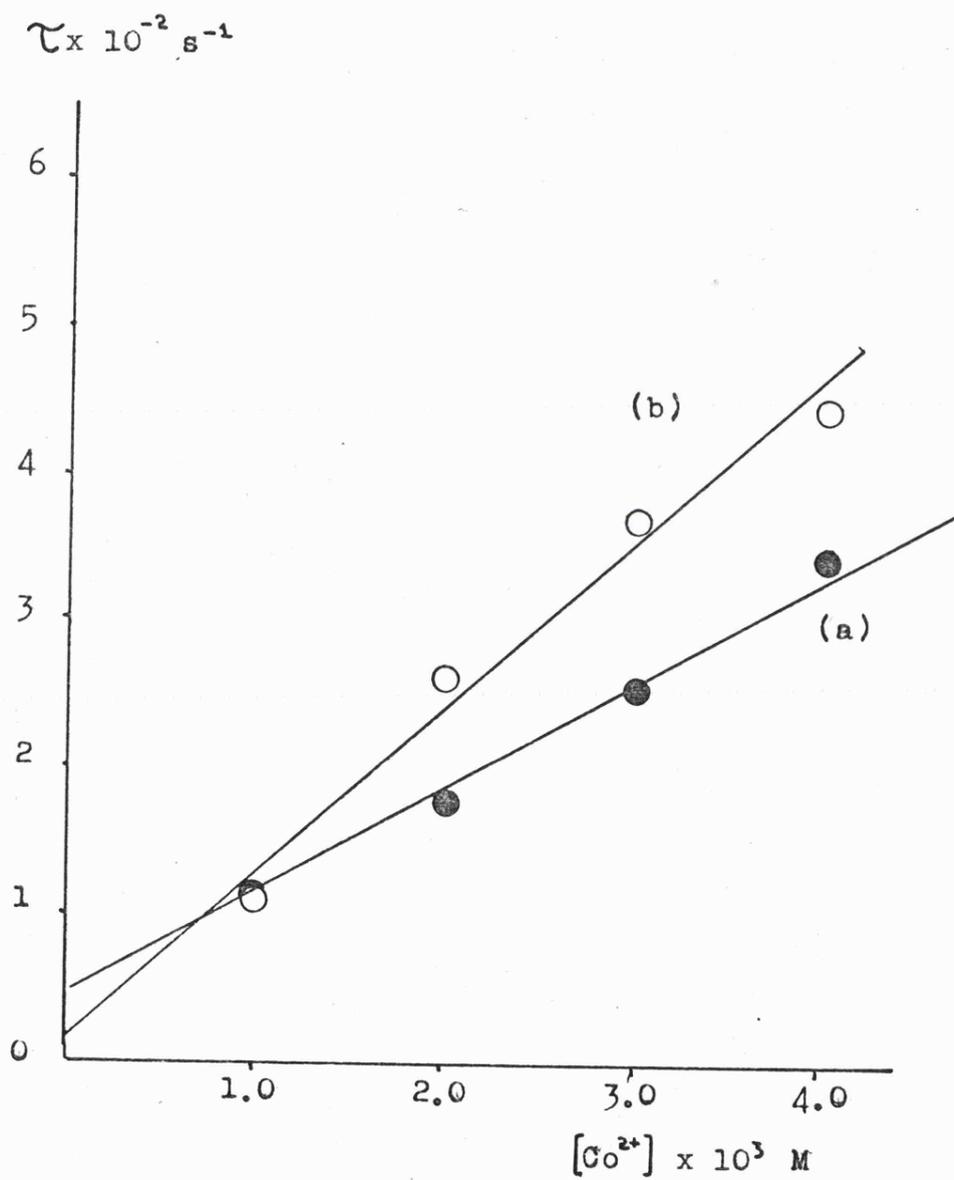


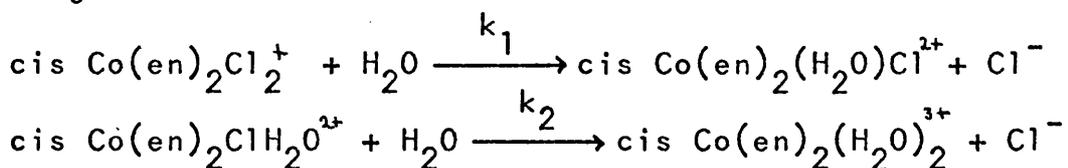
FIGURE 7-16

adding 5mls of sodium nitrate (1.5M) to each flask and 5mls of glycerol were added to each flask. These solutions were used to fill the cell of the temperature jump apparatus. The cell had two specially shaped electrodes⁹ which have been designed to produce a near-uniform field. The cell was allowed to thermostat. The temperature was recorded by means of a thermocouple. The capacitor was charged to such a voltage (the apparatus having been previously calibrated) that the temperature was raised by 2K to 298K. The traces produced on the storage oscilloscope were photographed.

The rate constant was calculated by enlarging the photograph and measuring values of time and light transmitted. These were then computed to obtain the relaxation time (τ). The graph of k against concentration of cobalt(III) is given in 7-16. Also given in the diagram are the corresponding values for the reaction in water¹⁰. From figure 7-16 it can be seen that glycerol accelerated the rate of formation of the complex.

4. Aquation of cis Dichlorobisethylenediamine Cobalt(III)

cis - Dichlorobisethylenediamine Cobalt(III) in acid solution forms bisaquobisethylenediamine Cobalt(III) in two stages as follows -



It was originally hoped that both rate constants k_1 and k_2 could be obtained. A computer programme was written to analyse absorption data (chapter 6) for a series first order reaction but difficulties in the analysis were encountered. These can be summed as follows.

(a) The preparation of this complex involved converting the trans complex to the corresponding cis complex by evaporation of the former to dryness. The kinetic results obtained indicated that there was still some unconverted trans complex in the cis. Hence there were parallel first order reactions occurring.

(b) The second stage was very much slower than the first stage. Due to these difficulties no further work was undertaken on this complex.

5. Chlorodiethylenetriamine Platinum(II) Chloride

The reaction studied can be represented by the following equation -



where $\text{Y}^- = \text{I}^-$ or Br^- .

The rate law, which applies to many square planar complexes, is given by ¹¹

$$\text{Rate} = \left[k_1 + k_2 [\text{Y}] \right] [\text{Pt}(\text{dien})\text{X}]$$

where k_1 and k_2 are first and second order rate constants respectively.

All kinetic runs were carried out at constant ionic strength, $I = 0.1$. The concentration of reagent Y was

greatly in excess of the complex concentration in order to maintain first order conditions.

The reaction of the complex both with the iodide and the bromide ion had an induction period. Initially it was thought that this could be due to impurities in the diethylenediamine used in the preparation of the complex. A purity check was carried out by means of a C^{13} n.m.r. (carried out at the University of Warwick thanks to P. Moore).

The induction period may stem from the formation of a 5 co-ordinate intermediate which has a relatively short lifetime. The intermediate could not be isolated. If an intermediate is formed then it will have an absorption spectra. The absorption at different wavelengths will then be modified by different amounts. Therefore if an intermediate is formed the calculated rate of substitution will vary with wavelength. The rate constants were calculated at six different wavelengths for the reaction between the complex and I^- at 293K.

λ /cm ⁻¹	$k \times 10^4$ /s ⁻¹
38,500	3.7
37,500	3.0
36,500	2.3
35,500	3.3
34,500	5.1
33,500	5.1

The fact that the rate did vary with wavelength indicated that a 5 co-ordinate intermediate was formed.

The existence of an intermediate has been observed for the reaction between NO_2^- and $\text{cis Pt}(\text{NH}_3)_2 \text{Cl}_2$. The intermediate showed up spectrophotometrically¹². A 5 co-ordinate intermediate was suggested ~~by~~ *by Gray*¹³ in forming the aquo complex ~~of~~ *of* $\text{Pt}(\text{dien})\text{X}$.

The fact that this reaction had an induction period made it an unsuitable probe reaction and it was therefore studied no further.

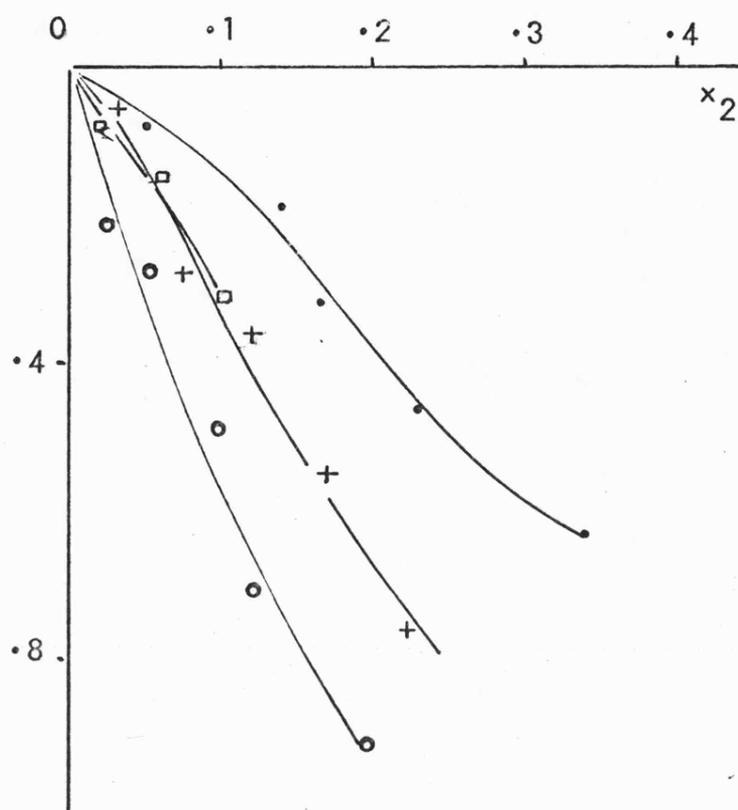
6. Ligand Substitution at Sterically Hindered Palladium(II)

Complex

The complex used was $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]^+$ where $\text{Et}_4\text{dien} = \text{N},\text{N},\text{N}',\text{N}'\text{-tetraethylethylenetriamine}$. The spectra and rate constant for the complex between $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]^+$ ($8 \times 10^{-4}\text{M}$) and iodide ($8 \times 10^{-2}\text{M}$) were found to be in good agreement with previously reported data¹⁴. The rate constant for this reaction was found to be $k = 2.08 \times 10^{-3}\text{s}^{-1}$ and for the previous study $k = 1.9 \times 10^{-3}\text{s}^{-1}$.

This reaction was studied in acetonitrile + water mixtures; with increase in mole fraction of acetonitrile isobestic points on the spectra were changed. At mole fractions above $x_2 = 0.1$ there was no isobestic point, suggesting that a 5 co-ordinate intermediate was formed, as occurs in pure acetonitrile¹⁵.

Dependence of k/k_0 for the Reaction of $\text{Pd}(\text{Et}_4\text{dien})\text{Cl}^+ + \text{I}^-$
 on Mole Fraction of Co-solvent.



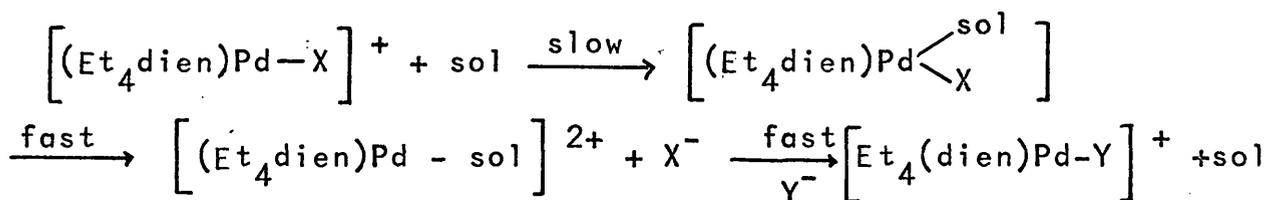
	Co-solvent	Reference	Temperature
□	Acetonitrile	This Work	293 K
•	Methanol	18	303 K
▽	Ethanol	18	303 K
○	Acetone	18	303 K

FIGURE 7-17

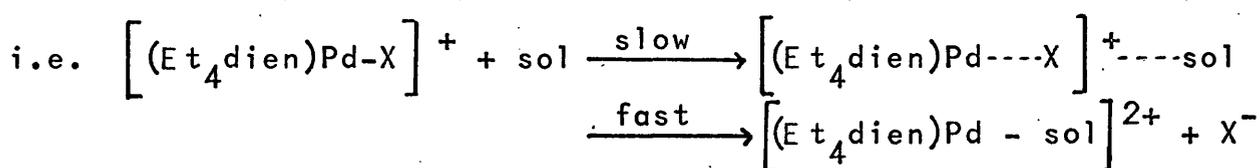
The results together with previous data are given in figure 7-17.

Molecular models of this complex showed¹⁶ that the two axial positions of palladium are blocked by two ethyl groups that are bound to the terminal nitrogen atoms of the ligand. From n.m.r. data it was shown that the ability to displace the axial ethyl groups and interact with the palladium decreases in the order $\text{H}_2\text{O} > \text{CH}_3\text{OH} > \text{C}_2\text{H}_5\text{OH} > \text{DMSO} > \text{CH}_2\text{Cl}_2$.

Activation parameters indicate that there are probably two different mechanisms by which the complex can react. One that is thought to occur in aqueous and alcohol solutions is an associative mechanism



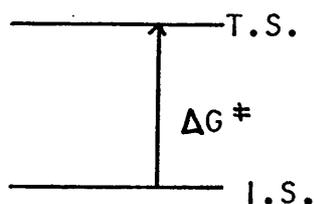
In aprotic solvents such as DMSO and DMF the reaction is thought to proceed by a dissociative interchange mechanism



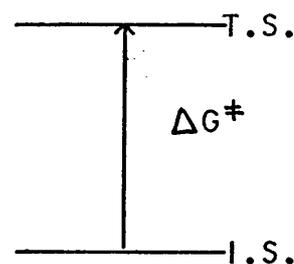
The pattern for the variation in rate constant is very similar to that obtained for the hydrolysis of t-butyl chloride in various mixed aqueous solvents. It is unfortunate that the reaction of $\text{Pd}(\text{Et}_4\text{dien})\text{Cl}$ with I^- could not be followed in hydrogen peroxide + water mixtures as this would confirm the pattern (hydrogen peroxide oxidises iodide to iodine); this suggests that the mechanism for the two are

similar. This indicates that the pathway for the substitution reactions is predominantly dissociative in character as is the hydrolysis of t-butyl chloride¹⁷. The decrease in rate on the addition of alcohols to water in the hydrolysis of t-butyl chloride is rationalised in terms of variation of solvation of the initial state (I.S.) and transition state (T.S.). The initial state of the hydrolysis of t-butyl chloride is predominantly hydrophobic; the addition of alcohols therefore leads to increased solvation and hence stabilisation of the initial state and thus an increase in ΔG^\ddagger .

i.e.



in water



in aqueous alcohols

For $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]^+$ complex the initial state will be more hydrophobic than the transition state; as the large Et_4dien molecule will undergo hydrophobic interaction with the water. In the transition state the Cl^- ion is leaving and will therefore have more charge associated with it hence will be more hydrophilic than the initial state. This is an analogous situation to that of t-butyl chloride and opposite to the aquation of the tris phenanthroline iron(II) complexes.

CHAPTER 8

DISCUSSION

1. Aquation of Tris (1,10-phenanthroline) iron(II) Complexes

The reaction in aqueous solution is represented by the following equation



Loss of the first ligand from the tris complex is the rate determining step. Aquation rates have been shown to be independent of the pH; the ligand is protonated after the rate determining severance from the iron¹. Other scavengers have been used for the outgoing phen; nickel(II) or hydrogen peroxide are both effective². The mechanism has been debated for some years. The $(\text{Fe phen}_3)^{2+}$ is a 1st Row d^6 low spin complex. Comparison with cobalt(III) complexes, leads one to expect it to react via a dissociative mechanism³. However, rate laws and activation parameters for the reaction of many complexes of $\text{Fe}(\text{phen})_3^{2+}$ indicate bimolecular attack by cyanide and by hydroxide⁴. It has been proposed⁵ that in the cases of both cyanide and of hydroxide the attack of the incoming nucleophile occurs at the phen ring rather than at the iron atom.

The reactivity patterns for the aquation of $\text{Fe}(\text{5NO}_2 \text{ phen})_3^{2+}$ and $\text{Fe}(\text{4,7 dimethyl phen})_3^{2+}$ can be rationalised by their different degrees of S_N2 character. The nitro group of the $\text{5NO}_2 \text{ phen}$ is strongly electron withdrawing and will therefore make the iron more susceptible to nucleophilic attack than the dimethyl complex. This explanation appeared to rationalise the experimental information on the mixed solvent work. The rate of aquation of the 5NO_2 iron complex

is accelerated by those co-solvents that break up the structure of water and which therefore increase the availability of water to react with the complex (e.g. t-butyl alcohol + water, ethanol + water). The rate of aquation decreases for the co-solvents that interact with water and therefore reduce its availability to react with the complex. However the results can be equally well explained in terms of changes in solvation of initial state and transition state in a dissociative mechanism.

Volume of activation studies of tris (1,10-phenanthroline) iron(II) complexes have been carried out⁶ to probe the mechanism. The volumes of activation for aquation of the complexes in aqueous solution were as follows -

	$\Delta V^\ddagger \text{ cm}^3 \text{ mol}^{-1}$
phen H	15 ± 0.4
5NO_2	17.9 ± 0.3
4,7- dimethyl	11.6 ± 0.6

These are all large positive values which indicate that all these reactions are dissociative in character. These values compare well with those obtained for water exchange by a presumed Id mechanism (Id = dissociative interchange) at trans $[\text{Co}(\text{en})_2(\text{OH}_2)_2]^{3+}$ for which $\Delta V^\ddagger = +13.1$ to $14.3 \text{ cm}^3 \text{ mol}^{-1}$ at 298K (value dependent on pH)⁷. These volumes of activation together with inspection of molecular models of the $(\text{phen})_3 \text{ Fe}$ complexes led workers to conclude that the most probable mode of dissociation is the simultaneous stretching of both Fe - N bonds of the bidentate chelate.

The transition state, therefore, has two stretched Fe-N bonds. The effect of added salts on the aquation of the 5NO_2 iron complex has been studied⁸ and the results were also explained in terms of a dissociative mechanism. Assuming that the two Fe-N bonds are stretched then in the transition state more of the hydrophobic phen is exposed to the solvent than in the initial state. If a hydrophobic co-solvent is added then the transition state will be better solvated than in pure water and therefore the reaction will be more rapid than in pure water.

The results for each of the solvent mixtures in which the aquation of the 5NO_2 iron complex was studied will be discussed separately below.

2. Acetonitrile + Water

The addition of acetonitrile enhanced the rate of aquation at all mole fractions studied. Before the effect on the rate of aquation is discussed the nature of the mixed solvent will be considered. Acetonitrile is a TNAP co-solvent (chapter 2) due to the fact that it does not possess either an oxygen atom or a polar hydrogen and it can not hydrogen bond with water. Excess volume V^E , studies on water + acetonitrile were used to calculate the partial molar volumes. When the partial molar volumes for acetonitrile are plotted against mole fraction the graph shows no minimum, unlike that of the monohydric alcohols (chapter 2). The

effect of acetonitrile on the infra-red absorption of HOD is very different from the effect of t-butyl alcohol. The latter systems show an isobestic point in the near I.R. and it is thought that the change in spectra is due to a change in the equilibrium between H_2O free and H_2O hydrogen bonded. Acetonitrile mixtures, however, have no tendency to show a comparable isobestic point. It therefore, must have a different effect to that of t-butyl alcohol on the structure of water.

The excess molar enthalpy, H^E , for acetonitrile + water shows a trend similar⁹ to that for the H^E data expected for a polar solvent mixing with an inert solute. The conclusion drawn from the behaviour of acetonitrile + water mixtures is that acetonitrile has a depolymerising effect on water i.e. it breaks up the hydrogen bonded network in liquid water. This conclusion was also arrived at using an electrolytic study¹⁰. Several kinetic studies have been undertaken in acetonitrile + water mixtures; ΔH^\ddagger is greater in acetonitrile + water mixtures than in water for the hydrolysis of dimethylsulphanyl chloride¹¹, the hydrolysis of t-butyl chloride¹², the rate of solvolysis of organic halides¹³ and the aquation of Cobalt(III) ammine or ammine halide complexes¹⁴. The decrease in the rate constant for solvolysis of organic halides has been explained in terms of differences in solvation of the initial and transition states. The initial state is hydrophobic and will be stabilised by the addition of an organic co-solvent.

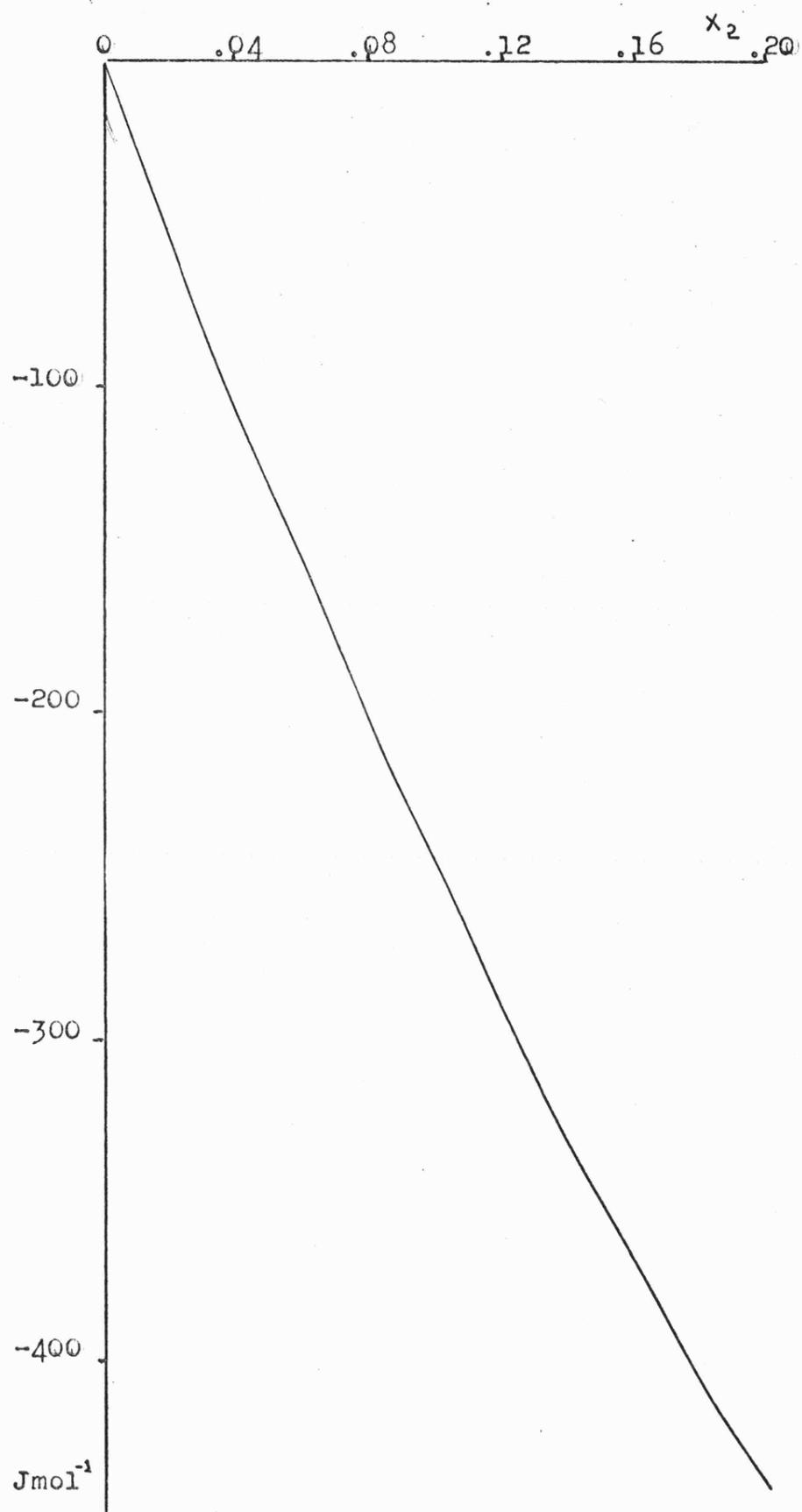
G^E For glycerol + Water Mixtures

FIGURE 8-1

The rate equation of $\text{Fe}(\text{5NO}_2 \text{ phen})_3^{2+}$ in acetonitrile + water mixtures was greater than the rate of aquation in water at all concentrations studied i.e. ΔG^\ddagger was decreased. If the reaction proceeds by the dissociative mechanism discussed earlier then the transition state will be more hydrophobic than the initial state. The addition of acetonitrile will, being an organic co-solvent, solvate the transition state better than water which will result in a stabilisation of the transition state and thus to a decrease in ΔG^\ddagger .

3. Glycerol + water

Glycerol + water is a polyfunctional solvent and therefore falls into the category of TNA co-solvent. Glycerol + water is in this group because each glycerol has 3 hydroxyl groups which can undergo extensive hydrogen bonding with water and with other glycerol molecules (hence its high viscosity). Unfortunately there is little thermodynamic information on this system. The excess Gibbs free energy, figure 8-1, was calculated from some early work by Scatchard¹⁵ on osmotic coefficients by means of an ALGOL programme SUNNY (Appendix 2); unfortunately these data only reached a mole fraction of $x_2=0.2$. No other thermodynamic information could be found on this system. The excess Gibbs free energy G^E is negative indicating association between glycerol and water, the association presumably occurring by hydrogen bonding between the three OH group on glycerol and the water.

The other excess thermodynamic functions, H^E , V^E etc. have not yet been determined. The structure of pure glycerol is thought to involve hydrogen-bonded collinear chains which are hydrogen bonded laterally thus giving rise to a three dimensional structure.

The structure of glycerol + water mixtures was compared¹⁷ to the structure of methanol + water mixtures due to similar effects on the transference number of H^+ in water/HCl mixtures. From this study it was suggested that glycerol depolymerises water and becomes embedded into the water structure. Around the alcohol, increased hydrogen bonding will occur and the effect maximises at 10 - 30 % (w/w) glycerol.

There have been few kinetic studies undertaken in aqueous glycerol. Rates of solvolysis of benzyl chloride in glycerol-water mixtures have been determined¹⁸.

The rate of solvolysis decreased with increase in concentration of glycerol and had a minimum at about 40 vol % of glycerol. There was a shallow minimum in ΔH^\ddagger (as opposed to a very large minimum with t-butyl alcohol).

Caldin¹⁹ has carried out kinetic studies on ligand substitution of nickel(II) and other metal(II) ions in pure glycerol. The results of this investigation showed that in pure glycerol the dominant factor in the energetics was the structure of glycerol. This was shown by similar rates for several different metal (II) ions with different ligands and with a large increase in ΔH^\ddagger for the reactions as compared to that in water.

The rate of aquation of the 5NO_2 iron complex was decreased by the addition of glycerol. The effect on ΔG^\ddagger can again be explained in terms of changes in solvation of the transition state. Glycerol is a hydrophilic co-solvent and therefore can not stabilise the transition state. The glycerol interacts with water and will therefore cause a break down of water structure and possibly give rise to a more structured network. This will presumably make it more difficult for the bulky phen ring to leave, thus ΔG^\ddagger was increased in glycerol + water mixtures.

The activation parameters $T\Delta S^\ddagger$ and ΔH^\ddagger were calculated for the mixtures used. There is a very shallow minimum in ΔH^\ddagger at ca. 0.03mf (figure 7-6) which is similar to the results of previous work. This shallow minimum could indicate that glycerol at low mole fraction has a depolymerising effect on water. Due to its large size and three hydroxyl groups it will interfere with some of the hydrogen bonds in water. Hydrogen bonding is a co-operative process (chapter 2), therefore the presence of glycerol initially leads to a break down in water structure making it easier for the phen to leave and thus causing a decrease in ΔH^\ddagger . But as the amount of glycerol is increased the solvent becomes more structured making it more difficult for the phen to leave and thus causing ΔH^\ddagger to increase.

4. Hydrogen Peroxide + Water

Aqueous Hydrogen peroxide is a unique binary system. Hydrogen peroxide is one of the few inorganic co-solvents; it has a high dipole moment and the difference in dielectric constant between water and hydrogen peroxide is so small that they can be considered isodielectric²⁰. Hence in hydrogen peroxide mixtures the effect of permittivity on reactivity will be minimised. Thus the effect of solvent structural effects on the reactivity can be clearly observed.

Due to its close chemical similarity with water it will hydrogen bond with water. A water molecule has 2 bonding protons and 2 acceptor sites whereas hydrogen peroxide has 2 bonding protons and 4 acceptor sites.

All excess thermodynamic properties have been determined and are drawn in figure 2-4. The thermodynamic behaviour is very different from that of the alcohols. There is only a small change in entropy of mixing and a large change in enthalpy which is a good indication of intercomponent association. This association is reflected in the change of acidity of hydrogen peroxide molecules and the basicity of water molecules²¹, both of which change very rapidly with composition of the solvent. In an equimolar mixture of the two ligands the basicity is 1/360th that of water and the acidity about 1/40th that of hydrogen peroxide.

Few kinetic or other studies have been undertaken in this solvent mixture. The enthalpy of transfer of sodium chloride from water to aqueous hydrogen peroxide at 298K has

been determined²². In this study it was concluded that hydrogen peroxide had a similar effect to that of urea on the structure of water i.e. it is a structure breaker. An n.m.r. study of alkali metal halides in hydrogen peroxide + water mixtures investigated the change of composition of the solvation shell around the alkali metal ions in water + hydrogen peroxide mixtures²³.

Hydrogen peroxide + water mixtures offer one unique advantage over other binary aqueous solvent systems for the study of the kinetics of aquation of the tris (5NO₂ phen) Fe(II) cation as hydrogen peroxide can act as scavenger for the released ligand²⁴ as well as co-solvent for the reaction. Normally an extra component needs to be added to the reaction mixture to act as scavenger for the released ligand which could cause perturbations of the inter solvent and intra solute interactions especially when it is necessary to use a large concentration of acid. Hence the kinetics of aquation of these iron(II) complexes can be studied in hydrogen peroxide + water without any other reagent.

Overall the rate constant, for both the 5NO₂ iron complex and the 4,7 dimethyl ion complex, decreases with increasing hydrogen peroxide concentration. The Gibbs free energy of activation increases continuously as the mole fraction increases from $x_2 = 0.015$ to 0.15 for the 5NO₂ iron complex. There was a 10-fold change in the rate constant which is similar to the change produced by other aqueous organic solvent mixtures²⁵, despite the small variation in dielectric constant.

The change in aquation rate was presumably due to changes in initial state and transition state solvation.

Extrapolation of the trend of aquation rate constants for mole fractions 0.15 to 0.015 hydrogen peroxide back to pure water produces a rate constant markedly greater than that reported for aquation in acid aqueous solution; indeed rate constants for aquation in low mole fraction ($x_2 < 0.015$) of hydrogen peroxide were also greater than that for acid aqueous medium. This fact seems to suggest an extremum at low mole fraction of hydrogen peroxide but this in fact may not be the case as the ionic strength in acid + water and for hydrogen peroxide + water will be somewhat different. The trend in rate constant for hydrogen peroxide + water mixtures all containing sulphuric acid was one of continuous decrease²⁶.

The reason for the difference is hard to rationalise. Although possible in the case of the 5NO_2 iron complex, the same rationalisation does not hold for other substituted 1,10-phenanthroline and 2,2'-bipyridyl complexes. The ratio of rate constant extrapolated from hydrogen peroxide + water mixtures to those for aqueous acid vary from ca 0.8 to ca 1.1 with no pattern in the substituents nature.

The activation parameters ΔH^\ddagger and $T \Delta S^\ddagger$, like ΔG^\ddagger , show a continuous trend with variation in composition with no evidence for extrema within the hydrogen peroxide mole fraction range 0.015 to 0.15. This lack of extrema for the TNAN co-solvent contrasts with the typically aqueous systems. In the latter cases, as for example alcohol + water systems, there

are marked extrema at relatively low mole fraction of organic co-solvent.

The activation parameters ΔH^\ddagger and $T\Delta S^\ddagger$ for the aquation of the 5NO_2 iron complex show considerable compensation to give a less rapidly varying ΔG^\ddagger . In this respect hydrogen peroxide + water mixtures show similar behaviour to TA mixed solvent systems.

The decrease in rate constant must arise from an increase in ΔG^\ddagger caused by differences in solvation of the initial and transition states. The chemical potential of transfer for some ions from water to hydrogen peroxide + water mixtures is negative ²⁷ which shows the process is favourable. Hence the ionic solutes will be more solvated in hydrogen peroxide mixtures than in water. The 5NO_2 ion complex will therefore be better solvated in hydrogen peroxide + water than in water and thus the chemical potential of the initial state will be lowered. The effect on the hydrophobic transition state will be small. The activation Gibbs free energy ΔG^\ddagger will therefore be increased. The enthalpy of activation increases reflecting the increase in solvation of the initial state, as the phen ring will experience more difficulty in expanding the more solvated the complex ion. There is an increase in entropy which fits in with the transition state of the 5NO_2 phen ring being loosely attached to the iron.

Comparison of H^E for (a) t-Butyl Alcohol + Water
and (b) Acetone + Water.

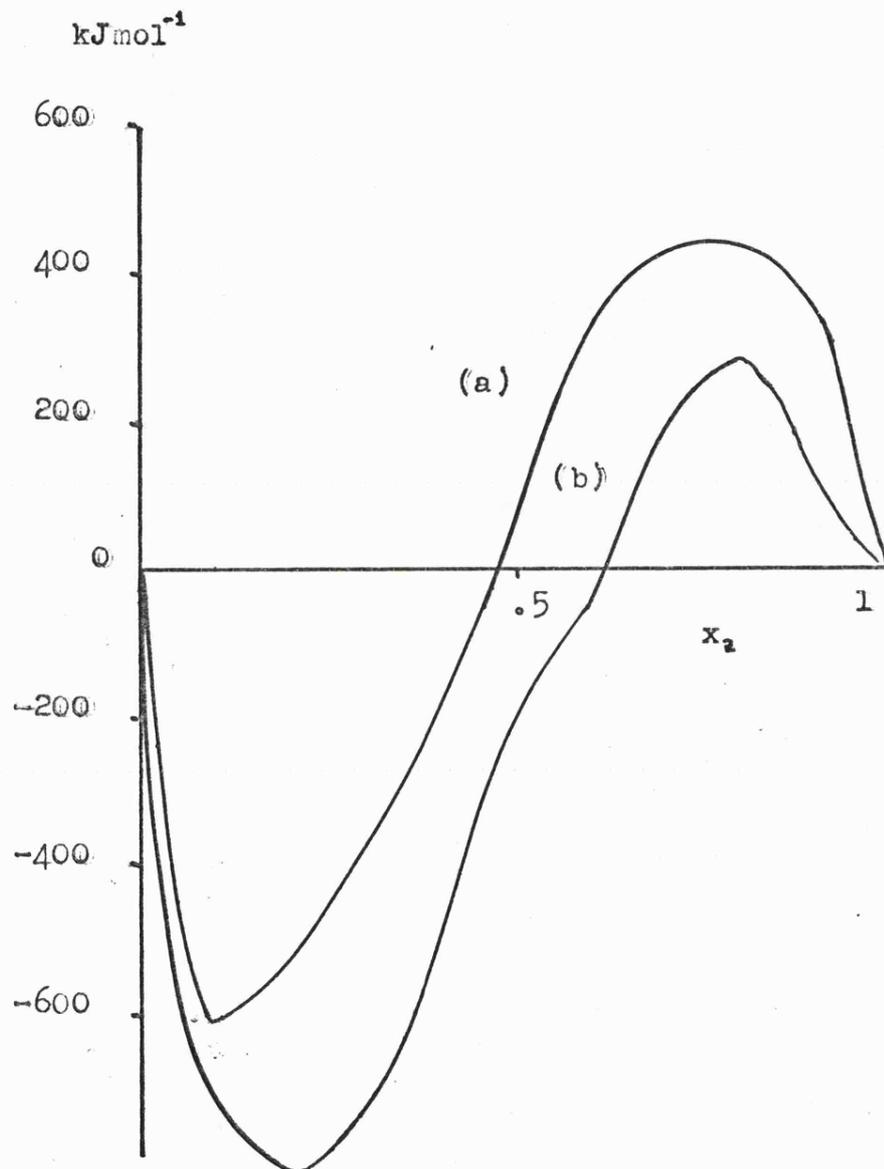


FIGURE 8-2

5. Acetone + Water

Acetone + water mixtures behave similarly to alcohol + water mixtures. This is reflected in the values for the excess thermodynamic properties, the H^E curves for acetone + water and t-butyl alcohol + water are very similar (figure 8-2). Hence acetone + water is a TA mixture. Acetone enhances the structure of water at low mole fractions, this effect maximises at $x_2 = 0.06$ (x_2^*) after which acetone has a structure breaking effect which maximises at $x_2 = 0.35$ (x_2^{**}). Acetone + water mixtures exhibit similar properties to those of the alcohols but in a less dramatic way than say t-butyl alcohol.

Acetone itself is a relatively structureless liquid, its dielectric constant is less than that of water. It has an oxygen atom and can therefore partake in hydrogen bonding with water. Acetone + water mixtures have not been as well studied as alcohol + water mixtures. The enthalpies of transfer of H^+ and OH^- into acetone have been determined²⁸. The chemical potential of transfer for the solvated proton²⁹ was determined. This was then used to calculate the values for other single ions; a slight curvature was found in the curve of mole fraction of acetone vs $\Delta G_t^\circ(Cl^-)$ and $\Delta G_t^\circ(H^+)$ at $x_2 \geq 0.1$ i.e. at x_2^* . The kinetics of the aquation of penta-amminechlororuthenium (III) dichloride and cis-dichloro-bis(ethylenediamine) ruthenium (III) chloride hydrate³⁰ have been studied in several mixed water organic

solvents including acetone + water. This study found a good fit of the rate data to the Grunwald - Winstein relationship³¹

$$\log k/k_0 = mY$$

and used this to help in a mechanistic study of the reaction. For the aquation of cis-dichlorobis (ethylenediamine) Cobalt(III) in mixed aqueous solvents, including acetone, the rate data fit the Grunwald-Winstein equation.

The rate constant for the hydrolysis of tris (5NO₂-1, 10-phenanthroline) iron(III) cation plotted against mole fraction of acetone is given in figure 7-7. At low mole fractions of acetone $x_2 = 0$ to 0.1, acetone has very little effect on the rate of hydrolysis; in more concentrated solutions ($x_2 > 0.1$) the rate of aquation varies more rapidly. This behaviour is similar to that observed in t-butyl alcohol + water mixtures³². Unfortunately unlike the case for t-butyl alcohol mixtures the mole fraction corresponding to x_2^{**} ($x_2 = 0.35$) for acetone could not be studied as aquation of the complex does not go to completion at high organic mole fractions. The activation parameters for acetone + water mixtures and t-butyl alcohol mixtures were used to calculate endostatic activation parameters and are discussed below.

6 Endostatic Analysis

The analysis (chapter 4) requires good thermodynamic parameters. Two important quantities $d \ln \alpha / dx_1$, and $\ln \alpha$, are derived from derivatives of G^E with respect to x_1 (equation 4-27 and 4-29) hence putting a heavy burden on the reliability of the G^E data. Indeed the second differential cannot be calculated with absolute confidence from published G^E data in all cases. However, some tests can be applied for thermodynamic consistency, for example³³ if $d \ln (f_1/f_2) / dx_1$ is negative then $d \ln \alpha / dx_1$ must be positive. Grunwald and Effio reported that this test fails for the data they used for the t-butyl alcohol + water mixtures, although for the data used in this analysis this criterion is satisfied for the water rich mixtures over the range for which the kinetic data are available. It is a annoying feature of this analysis that ΔG^\ddagger for a reaction can be more readily determined than G^E , the latter requiring for example careful determination of vapour pressures. Alternatively H^E for the mixtures can be directly measured using calorimetry whereas ΔH^\ddagger requires kinetic data over a range of temperatures.

If, as argued previously, the primary step of a quation is the simultaneous stretching of the Fe-N bonds resulting in a more hydrophobic transition state, the reaction will be sensitive to changes in water structure as this will

affect ^{differences in} the hydrophobic interactions between the initial state and transition state. Addition of acetone or t-butyl alcohol has a dramatic effect on the structure of water and therefore it would be expected that these changes would be reflected in ΔG^\ddagger . The effect of acetone or t-butyl alcohol is determined by their concentration, initially both co-solvents have a structuring effect on water up to x_2 ($x_2^* = 0.1$ for acetone $x_2^* = 0.04$ for t-butyl alcohol). For $x_2 > x_2^*$, the co-solvents have a structure breaking effect which maximises at x_2^{**} ($x_2^{**} = 0.35$ for acetone $x_2^{**} = 0.1$ for t-butyl alcohol).

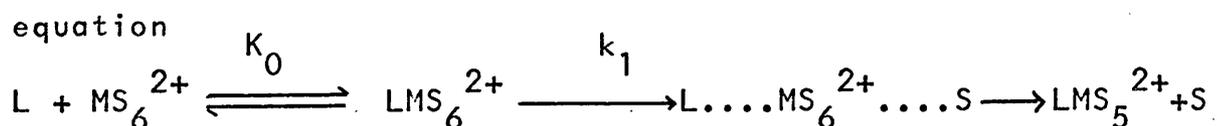
Despite the dramatic changes in the properties and structures of these aqueous mixtures in the water rich range, ΔG^\ddagger for the reaction in these aqueous mixtures gradually decreases as x_2 increases. This behaviour stems from compensation³⁴ between changes in solvent dependence of ΔH^\ddagger and $T\Delta S^\ddagger$.

The solvent dependences of the activation Gibbs free energy (ΔG_α^\ddagger), figures 7-9 and 7-11, provide some clear indication of the changes in mixture organisation near the mole fractions discussed above. In particular the pattern observed for $\delta_m \Delta G^\ddagger$ in the t-butyl alcohol + water mixtures shows in a striking way the importance of changes in the solvent structure in the $x_2 > 0.04$ and 0.1 regions. Thus the endostatic quantity ΔG_α^\ddagger is more sensitive to solvent than

ΔG^\ddagger for the aquation of the iron complex and for the aquation of t-butyl chloride³³. Since the latter reaction is dissociative the similarity of pattern is in agreement with the proposal that the aquation of the iron complex occurs by a dissociative mechanism. Interpretation of the related dependence of ΔH_α^\ddagger and $T \Delta S_\alpha^\ddagger$ on solvent composition is not clear cut. The difference between the two curves is small.

7. Fast Reactions

Both reactions that were followed by fast reaction techniques were ligand substitution reactions. A scheme for the mechanism of substitution was put forward by Eigen and Wilkins³⁵ which can be summarised by the following



where L = pada

M = Co^{II} or Ni^{II}

S = Solvent Molecule

K_0 = equilibrium constant

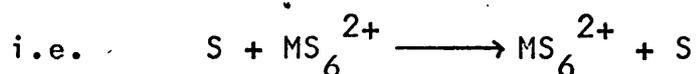
for first step

k_1 = rate constant for

second process

Thus there is rapid formation of an outer sphere complex, followed by the rate determining formation of an inner sphere

complex. The rate constant k_1 is assumed to be equal to that of the first order rate constant for solvent exchange, k_{ex}

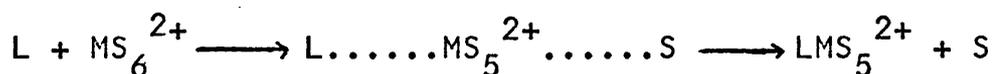


The rate of ligand substitution is given by the following expression (under the normal experimental conditions of excess ligand)-

$$k_L = K_o k_1 \quad \text{where } k_L = \text{rate of ligand substitution}$$

or $k_L = K_o k_{ex}$ replacing k_1 by k_{ex} .

A similar mechanism was put forward by Langford and Gray³⁶ which was-



This scheme does not consider the formation of an outer sphere complex.

Caldin and Bennetto³⁷ tested this mechanism by calculating K_o and using values of k_{ex} which had been determined by n.m.r. for water and several non-aqueous solvents³⁸.

The value of K_o was calculated using the theoretical relationship-

$$K_o = \frac{4 \pi N a^3}{3 \cdot 10^3} e^{-U(a)/kT}$$

$$N = \text{Avogadro's } N^e$$

a = centre to centre distance of closest approach of the solvated metal and the ligand.

$$\text{where } U(a) = \frac{Z_1 Z_2 e^2}{Da} - \frac{Z_1 Z_2 e^2 k}{D(1+k_a)}$$

For neutral ligands such as pada $U(a) = 0$.

If a value of $a = 5\text{\AA}$, which is considered to be a reasonable approximation, is used for the distance of closest approach then $K_o = 0.1^{39}$. This value of K_o , together with experimentally determined values of k_L , were used to calculate k_{ex} using the following relationship-

$$k_{ex} = \frac{k_L}{K_o}$$

For ligand substitution reactions at Ni(II), it was found that k_L/K_o agreed with k_{ex} to within a factor of 10 for many ligands. However, the model does predict little change with charge on the ligand whereas there is a 40-fold variation in rate for L^{2-} ligands, 5-fold for L^- and 20-fold for neutral ligands.

The mechanism was further tested by Caldin³⁷ by using the fact that $k_L/K_o k_{ex}$ should be approximately equal to 1 or some constant value in a particular solvent for a variety of ligands. This was found to hold for water and for methanol, but varied 200-fold when the solvent was changed from acetonitrile to DMSO. Overall the highest and lowest values of the ratio differed by a factor of about 10^4 . Also the differences in activation enthalpies between ligand substitution and solvent exchange should be approximately zero but varies from -20kJ mol^{-1} to $+20\text{kJ mol}^{-1}$.

An approximate linear relationship was found between the logarithm of the ratio of $k_L/0.1 \times k_{ex}(n)$ and the heat of evaporation of the solvent (ΔH_{evap}) and also between $\log n$

and the fluidity (density/viscosity) of the solvent. There was also a fair correlation between the difference in activation enthalpies between ligand substitution and solvent exchange. To explain these correlations Caldin, as discussed in Chapter 3, uses the Frank and Wen model of the solvated ion.

Caldin has therefore introduced the important feature of solvent structure into the discussion of the mechanism and solvent effects on the rate of ligand substitution. Further work in this field⁴⁰ with the substitution reactions of Ni(II) with pyridine, 2,2'-bipyridine, 1,10-phenanthroline, and 2,2',2''-terpyridine in acetonitrile and DMSO shows a link between solvent structure and variation in reaction rate.

More recent work on the reaction between Ni(II) and pada again concluded that the solvent structure plays an important part in ligand substitution⁴¹. A fair correlation was obtained between ΔH_{evap} and the ratio of rates but this was not as good as that obtained for the previous work. Solvent structure was found to be the dominant factor in the kinetics of the reaction between pada and Co^{II} , Ni^{II} , Zn^{II} and Cu^{II} in glycerol⁴².

The reaction of Ni(II) with pada was studied in DMSO + water mixtures and in acetonitrile + water mixtures and the results will be discussed in terms of the Eigen-Wilkins mechanism below.

DMSO has a negative excess Gibbs free energy and also has a negative excess enthalpy (hence is a TNAN co-solvent) which indicates there is strong interaction between DMSO and H_2O

Dependence of k/k_0 for some Ligand Substitution Reactions
 at Nickel(II) on Mole Fraction of Co-solvent

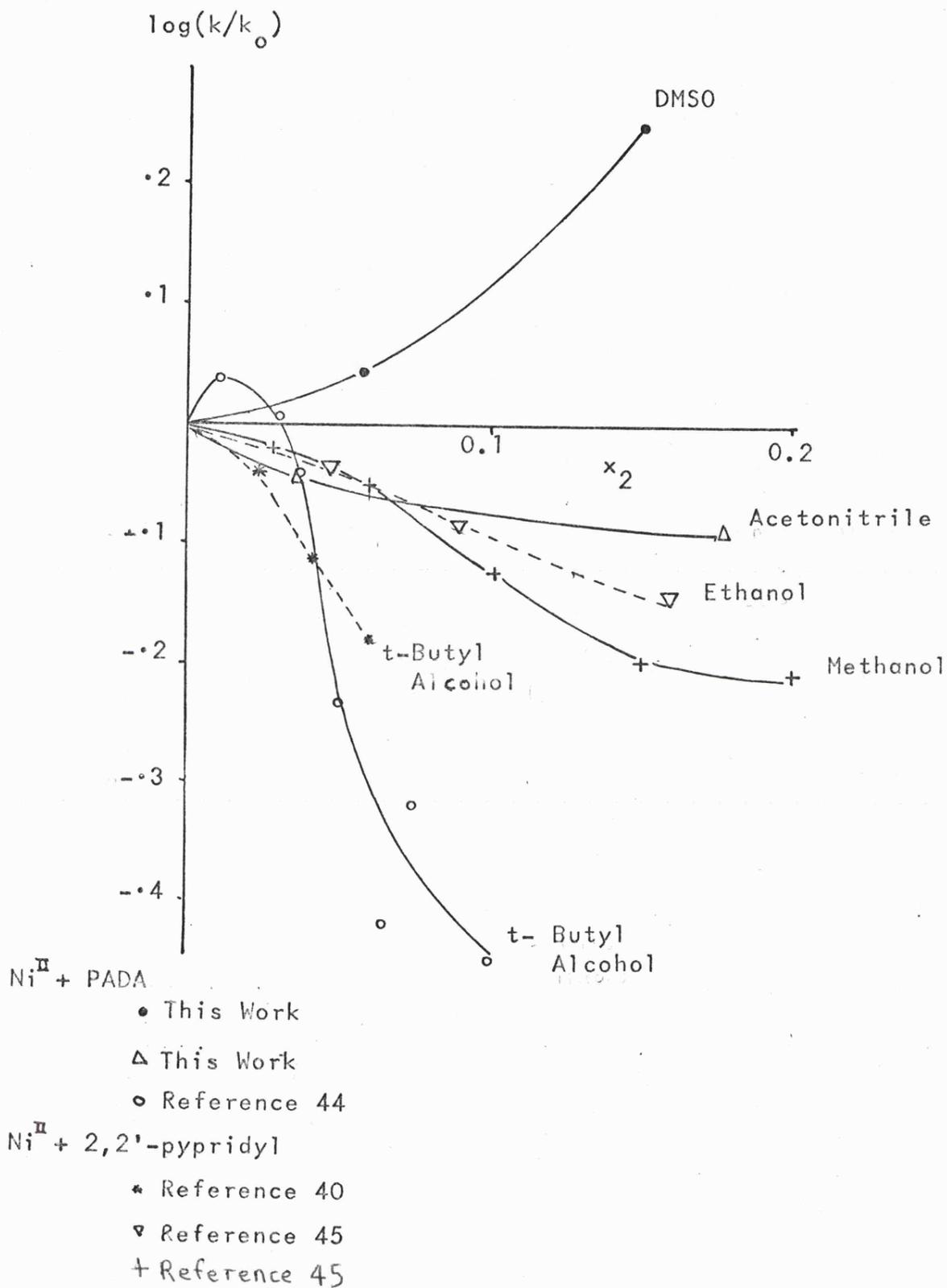


FIGURE 8-3

and that there is a greater degree of association in water + DMSO mixtures than in water alone. DMSO can hydrogen bond with water due to its oxygen atom. Volume change on mixing together with viscosity data and enthalpies of mixing suggest that water and DMSO form a 2:1 associated complex⁴³. The result therefore of adding DMSO to water is a breakdown of water structure but a more tightly bound structure replaces water's own structure.

The nature of acetonitrile + water mixtures has been discussed previously. Briefly acetonitrile + water is a TNAP mixture i.e. acetonitrile breaks down water-water interactions but there is no interaction between water and acetonitrile.

The two solvents have opposite effects on the rate of reaction between nickel(II) and pada due presumably to their different effect on the structure of water. The reaction proceeds in two main stages and therefore the effect of the solvent structure can influence either stage or both of the reaction.

Figure 8-3 gives the results of this study together with previously published data for ligand substitutions at Ni(II). From the diagram it can be seen that TNAN co-solvent and the TA co-solvents t-butyl alcohol, ethyl alcohol and methyl alcohol (except for low mole fractions of t-butyl alcohol for the reaction between Ni(II) and pada) decrease the rate of substitution. DMSO a TNAP co-solvent increases the rate of

substitution. From these data it appears that an increase in the amount of disorder in the solvent causes a decrease in the rate of substitution.

These solvent effects can be explained in two ways. One is to consider the solvation of the initial and transition states and the other is to consider changes in the solvent structure. Firstly, with reference to the solvation of the initial and transition states, the ligands used are all large organic molecules and are hydrophobic. The addition of organic co-solvents to solutions of the ligands will presumably result in a decrease in their chemical potential. If μ^{\ominus} (ligand) decreases, this will result in an increase in ΔG^{\ddagger} .

With reference to structures of the various solvent mixtures, the Eigen-Wilkins mechanism for ligand substitution proposes that the rate determining step is loss of a solvent molecule from the solvation shell of nickel(II). Thus any change in solvent structure that will assist in this step will enhance the rate of reaction. DMSO interacts strongly with water; its presence as a co-solvent could therefore help pull off a water molecule. Likewise, at low mole fractions of t-butyl alcohol, the structured water could help pull off a solvent molecule. In unstructured solvents the solvated molecules of solvent will not have this assistance to leave and thus the rate will be less than that in water.

In order to decide if changes in solvation of the pda or other ligand molecule can explain the pattern of rates in the various mixed solvents, the solubilities of the ligands

in the mixed solvents need to be determined. It would also be interesting to have the rate of ligand substitution in hydrogen peroxide + water to compare with the DMSO results.

The rate of ligand substitution between cobalt and pada was enhanced in the low mole fraction of glycerol used. Glycerol, as discussed earlier, breaks down water's own structure but interacts with water forming a more structured solvent. Assuming cobalt(II) reacts with pada via the same mechanism as that for ligand substitution at nickel(II), then the structured glycerol + water can assist in the loss of the solvent molecule from cobalt(II) resulting in an increase in rate.

Conclusion

The understanding of the nature of mixed solvents is fundamental to interpreting solvent effects on reaction kinetics. This study has indicated how useful the consideration of the excess thermodynamic properties of the mixed solvents is in rationalising their effects on reaction kinetics. The most useful thermodynamic function appears to be G^E for prediction and rationalisation of kinetic results.

Also there appears to be a quantitative link between the excess thermodynamic functions and the activation parameters, as shown in the endostatic analysis. Endostatic

parameters, particularly ΔG_{\ddagger} , show up the effect of solvent structure on reaction rates.

In all studies of solvent effects on reaction rates well understood reactions are required, otherwise the problem becomes too complex. The reaction of nickel(II) + pda showed up the difficulties in interpreting solvent effects due to uncertainties in the mechanism. Good thermodynamic data for the mixed solvents are essential but, unfortunately, are not always available.

APPENDIX 1

Mean first-order rate constants, k, for the aquation of the tris-(5-nitro-1,10-phenanthroline)iron(II) cation in:-

x	298.15 K	299.60 K	303.60 K	307.5 K	310.9 K
0.00	6.2	8.5	16.5	29.8	57.5
0.02	7.2	8.7	17.0	32.7	61.0
0.08	9.5	12.7	22.4	42.0	76.0
0.18	14.5	17.5	29.5	55.7	91.0
0.28	17.5	20.2	32.0	60.0	101.0

(b) Hydrogen Peroxide + Water

x_2	$k \times 10^3 \text{ s}^{-1}$			
	286.2 K	295.4 K	298.2 K	306.1 K
0.008	-	-	8.6	-
0.015	0.84	3.6	7.2	21.0
0.020	0.75	2.7	6.7	19.3
0.034	-	-	6.4	-
0.040	0.54	1.7	5.9	12.8
0.047	-	-	5.5	-
0.057	0.45	1.4	4.4	10.5
0.090	0.21	0.92	2.6	8.2
0.11	0.13	0.66	2.0	6.5
0.150	0.09	0.42	1.4	5.2

(c) Glycerol + Water

x	298.2 K	302.4 K	303.6 K	306.4 K	308.4 K	314 K
0.03	5.5	12.0	14.2	23.2	31.5	69.0
0.07	4.8	9.9	11.2	20.2	28.2	63.0
0.17	3.5	7.0	9.0	16.4	24.0	52.0
0.21	3.0	6.0	8.2	14.0	23.0	48.0
0.27	2.5	5.1	6.6	12.0	19.0	40.0

(d). Acetone + Water

x:	298.15 K	$k \times 10^3 \text{ s}^{-1}$	304.65 K	308.16 K	314.15 K
0.007	0.63	1.94	3.7	8.8	
0.048	0.66	2.12	3.9	10.1	
0.078	0.69	2.42	4.6	11.5	
0.110	0.82	2.78	5.5	12.6	
0.140	0.95	3.3	6.8	14.6	
0.160	1.19	3.5	7.2	16.1	
0.20	1.59	4.4	8.4	17.8	
0.28	2.15	6.0	10.6	23.2	

APPENDIX 2

```
&JOB; CH001050MARY;MJB16;
SWOP
BATCH
```

```
&ALGOL;
LIBRARY
ALGOL
```

```
&LIST;
```

```
1 MARYA;
2 "BEGIN"
3 "INTEGER" I,J,N,K,W;
4 "READ" N;
5 "BEGIN"
6 "COMMENT" N IS NO. OF DATA POINTS INCLUDING X=0 AND X=1 -
7 X IS MOLE FRACTION OF WATER;
8 "ARRAY" X,XE(1:N);
```

```
&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"
107 S:=S+(A(I)*B(I)*K);
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 XC[I]:=XC[I];=0;
117 "READ" XC[I], XE[I];
118 "PRINT" SAMELINE, SCALED(9), I, 'S3', XC[I], 'S3', XE[I];
119 "END";
120 "END";
121
122 "PROCEDURE" FIT(X, XE, N, K);
123 "INTEGER" N, K;
124 "ARRAY" X, XE;
125 "BEGIN"
126 "INTEGER" I, J;
127 "ARRAY" Y1, Z, Y, U, X1, X2, DEV, XC[1:N], P, PIC[1:K], C, BC[1:K, 1:K], AC[1:K, 1
128 "REAL" RMS, STD, DIFF, Q;
129 "FOR" I:=1 "STEP" 1 "UNTIL" N "DO" "BEGIN"
130 ZE[I]:= 1-2*XC[I];
131 YC[I]:= XC[I]*(1-XC[I]);
132 UC[I]:= YC[I]*XE[I];
133 YI[I]:= YC[I]*YC[I];
134 "END";
135 "FOR" I:= 1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
136 BC[I, 1]:=0;
137 "FOR" J:= 1 "STEP" 1 "UNTIL" K "DO"
138 AC[I, J]:=0;
139 "END";
140 "PRINT" 'L' FORM MATRIX';
141 "FOR" I:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
142 BC[I, 1]:=SUMPROD(U, Z, I-1, N);
143 "FOR" J:=1 "STEP" 1 "UNTIL" K "DO"
144 AC[I, J]:=SUMPROD(Y1, Z, I+J-2, N);
145 "END";
146 "PRINT" 'L' MATRIX SET UP';
147 UNSYMDÉT(K, 2, 0, -37, A, RMS, I, C, FAIL);
148 UNSYMSOL(K, 1, A, C, B);
149 "PRINT" 'L5' OUTPUT-NUMBER OF COEFFICIENTS=', SAMELINE, SCALED(3)
150 "PRINT" 'L' PARAMETERS',
151 "FOR" I:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
152 "PRINT" 'L' COEFFICIENT,', SAMELINE, SCALED(2), I, 'S3'=',
153 SAMELINE, SCALED(9), BC[I, 1];
154 "END"; DIFF:=0;
155 "PRINT" 'L' COMPARISON OF INPUT + OUTPUT', 'L';
156 "FOR" I:=1 "STEP" 1 "UNTIL" N "DO" "BEGIN"
157 "FOR" J:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
158 PC[J]:= BC[J, 1]*ZC[I]†(J-1);
159 "END";
160 Q:= SUM(P, 1, K);
161 XCC[I]:=YC[I]*Q;
162 DIFF:=(XC[I]-XCC[I])*(XC[I]-XCC[I])+DIFF;
163 "PRINT" 'L', SAMELINE, SCALED(9), I, 'S2', XE[I], 'S2', XCC[I];
164 "END";
165 RMS:= SQRT(DIFF/N);
166 STD:= SQRT(RMS*RMS*N/(N-K));
167 "PRINT" 'L' ERRORS ON XE FITTING', 'L' RMS DEVIATION=',
168 SAMELINE, SCALED(9), RMS, 'L' STANDARD DEVIATION=',
169 SAMELINE, SCALED(9), STD;
170 FAIL;
171 "END";

```

```
172 HEAD;  
173 W:=N-2;  
174 "FOR" I:=1 "STEP" 1 "UNTIL" W "DO" "BEGIN"  
175 FIT(X,XE,N,I);  
176 "END";  
177 "END";  
178 "END";  
600 MC  
1590 CODE  
2190 TOTAL
```

```
&RUN;  
MARYA  
DBO
```

```
&JOB; CH001050ROGU;MJB16;
```

```
&ALGOL;
LIBRARY
ALGOL
```

```
&LIST;
```

```

1  ROGUE;
2  "BEGIN"
3  "INTEGER" I, J, W, JA, TE, M, FJ, WW, V,
4  VV, CONT, K, NC;
5  "REAL" TS, TNEW, DIFF, TH, TM,
6  TC, DUMMY;
7  READER(1); "READ" NC, TS; "BEGIN"
8  "ARRAY" TC[1:1500], GC[1:NC, 1:1500], TF, PE[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" HELL;
14 FJ:=FJ+1; TTFJ[1:TC[I]]:=GC[M, I];
15 HELL;
16 "END"; "PRINT" ('L' NUMBER OF POINTS=), SAMELINE,
17 SCALED(9), FJ; "END" SETUP;
18
19 "PROCEDURE" INVMX(B);
20 "ARRAY" B; "BEGIN" "REAL" MAX, EPS;
21 "INTEGER" SS, L, V, Z, R;
22 R:=3; EPS:=2*(10*(1-37));
23 "BEGIN" "INTEGER" "ARRAY" RR, BR[1:R];
24 "FOR" SS:=1 "STEP" 1 "UNTIL" R "DO" "BEGIN"
25 MAX:=0;
26 "FOR" L:=1 "STEP" 1 "UNTIL" R "DO" "BEGIN"
27 "FOR" V:=1 "STEP" 1 "UNTIL" SS=1 "DO"
28 "IF" C=BR[V] "THEN" "GOTO" L1;
29 "IF" ABS(MAX)-ABS(B[L, 1])>LE "0" "THEN" "BEGIN"
30 BRESS[1:V]:=B[L, 1]; "END";
31 L1: "END";
32 "IF" ABS(MAX)<EPS "THEN" "BEGIN"
33 "PRINT" ('L' INVMX ERROR) STOP; "END"; V:=BRESS[1];
34 "FOR" C:=1 "STEP" 1 "UNTIL" R "DO"
35 B[C, R+1]:= "IF" C=V "THEN" 1 "ELSE" 0;
36 "FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
37 BC[V, C]:=BC[V, C+1]/MAX;
38 "FOR" L:=1 "STEP" 1 "UNTIL" R "DO" "BEGIN" MAX:=B[C, 1];
39 "IF" C=NE "V" "THEN" "FOR" Z:=1 "STEP" 1 "UNTIL" R "DO"
40 B[C, Z]:=B[C, Z+1]*MAX*BC[V, Z]; "END"; "END";
41 "FOR" Z:=1 "STEP" 1 "UNTIL" R "DO" RR[Z]:=Z;
42 "FOR" Z:=1 "STEP" 1 "UNTIL" R=1 "DO" "BEGIN"
43 "IF" BRESS=RR[Z] "THEN" "GOTO" LOOP "ELSE"
44 "FOR" L:=Z+1 "STEP" 1 "UNTIL" R "DO"
```

```

45 "IF"RREL=BRZ"THEN"GOTO"SWOP;
46 SWOP:"FOR"V:=1"STEP"1"UNTIL"R"DO"BEGIN"
47 MAX:=B[Z,V];
48 B[Z,V]:=B[L,V];B[L,V]:=MAX;"END";
49 RREL:=RR[Z];
50 COOP:"END";
51 "FOR"Z:=1"STEP"1"UNTIL"R=1"DO"BEGIN"
52 "FOR"L:=Z"STEP"1"UNTIL"R"DO"
53 "IF"RREL=Z"THEN"BEGIN"
54 "IF"Z=L"THEN"GOTO"OUT;
55 "FOR"V:=1"STEP"1"UNTIL"R"DO"BEGIN"
56 MAX:=B[V,Z];B[V,Z]:=B[V,L];B[V,L]:=MAX;"END";
57 BREL:=BR[Z];"END";OUT:"END";
58 "END";"END"INVMX;
59
60 "REAL"PROCEDURE"PGALC(PINF,KK,TT,PPQ);
61 "REAL"RPINF,KK,TT,PPQ;"BEGIN"REAL"SSS;
62 SSS:=EXP(-KK*TT);PGALC:=PRINF*(1-SSS)+PPQ*SSS;"END";
63
64 "PROCEDURE"FORWIN(LABEL,N,T,P);
65 "INTEGER"LABEL,N;"ARRAY" T,P;"BEGIN"
66 "ARRAY"EE[1:3],A[1:4,1:4]"BOOLEAN"OK;
67 "INTEGER" I,J,CYCLE,S;
68 "REAL"RINF,PQ,K,DPOK,DPDINF,DPOP,DPDK,DPDPO,
69 DELC,DELINF,DELPD,TF,SDEL,DELTA,SSDEL;
70 STK,STINF,STRO,S,INC,LARGET;
71 "PRINT" 'L'FIRST ORDER REACTIONZ';
72 "PRINT" 'L'RUN NUMBER=',SAMELINE,SCALED(9),
73 LABEL;
74 "PRINT" 'L'POINT','S5'TIME','S5'OBSERVED';
75 CYCLE:=0;SSDEL:=.50;INC:=LARGET:=0;
76 "FOR" I:=1"STEP"1"UNTIL"N"DO"BEGIN"
77 "IF" I=1"THEN"BEGIN"PO:=PEI;
78 "IF"TCI>.20"THEN"INC:=TCI;"END";
79 "IF"TCI<INC"THEN"BEGIN"PO:=PCI;INC:=TCI;"END";
80 "IF"TCI>LARGET"THEN"BEGIN"SI:=I;LARGET:=TCI;"END";
81 "END";K:=2/LARGET;RINF:=1.25*P(SI)=0.25*PO;
82 "IF"INC>-.20"THEN"BEGIN"
83 "FOR" I:=1"STEP"1"UNTIL"N"DO"TCI:=TCI-INC;
84 "END";"PRINT" 'L'CYCLE RATE CONSTANT INFINITY';
85 "PRINT" SAMELINE, 'S6'ZERO', 'S7'NEW SUM', 'S5'OLD SUM', 'L'
86 "PRINT" 'S7'SECONDS(-1)', 'S6'READING';
87 E[1]:=E[1];E[2]:=E[2];E[3]:=SDEL:=0;
88 "FOR" I:=1"STEP"1"UNTIL"3"DO"
89 "FOR" J:=1"STEP"1"UNTIL"3"DO"A[I,J]:=0;
90 "FOR" I:=1"STEP"1"UNTIL"N"DO"BEGIN"
91 S:=EXP(-K*TCI);DPDK:=TCI*S*(PINF=PO);
92 DRDINF:=1-S;DPDPO:=S;
93 A[1,1]:=A[1,1]+DPDK*DPDK;
94 A[2,2]:=A[2,2]+DPDINF*DPDINF;
95 A[3,3]:=A[3,3]+DPDPO*DPDPO;
96 A[1,2]:=A[2,1]:=A[1,2]+DPDK*DRDINF;
97 A[1,3]:=A[3,1]:=A[1,3]+DPDK*DPDPO;
98 A[2,3]:=A[3,2]:=A[2,3]+DPDINF*DPDPO;
99 DELTA:=PEI-PCALC(RINF,K,TCI,PO);
100 SDEL:=SDEL+DELTA*DELTA;
101 E[1]:=E[1]+DELTA*DRDK;
102 E[2]:=E[2]+DELTA*DRDINF;
103 E[3]:=E[3]+DELTA*DRDPO;
104 "END";"IF"CYCLE=0"THEN"PRINT"

```

```

105  'L', SAMELINE, SCALED(9), CYCLE, 'S5', K,
106  'S3', PINF, 'S2', PO, 'S3', SDEL,
107  'S3', 'S3', 'L' "ELSE" "PRINT" SAMELINE, SCALED(9),
108  CYCLE, 'S3', K, 'S3', PINF, 'S2', PO,
109  'S2', SDEL, 'L';
110  INVMX(A);
111  "FOR" I:=1 "STEP" 1 "UNTIL" 3 "DO"
112  "FOR" J:=1 "STEP" 1 "UNTIL" 3 "DO" "BEGIN"
113  "IF" J<I "THEN" A[I, J]:=A[J, I]; "END";
114  DELK:=A[1, 1]*E[1]+A[1, 2]*E[2]+A[1, 3]*E[3];
115  DELINF:=A[2, 1]*E[1]+A[2, 2]*E[2]+A[2, 3]*E[3];
116  DELPO:=A[3, 1]*E[1]+A[3, 2]*E[2]+A[3, 3]*E[3];
117  CYCLE:=CYCLE+1;
118  "IF" ABS(SDEL-SSDEL)"LE" 6 "THEN" "GOTO" EXIT;
119  "IF" SDEL<SSDEL "THEN" "BEGIN" STK:=K; STINF:=PINF;
120  STPO:=PO; SSDEL:=SDEL; "END"; K:=K+DELK;
121  PINF:=DELINF+PINF; PO:=PO+DELPO;
122  "IF" CYCLE=51 "THEN"
123  "PRINT" 'L' 50 CYCLES COMPLETED, 'L';
124  "IF" CYCLE=51 "THEN" "GOTO" EXIT; "GOTO" L1; EXIT;
125  "PRINT" 'L2' POINT, 'S5', 'S' TIME, 'S8' CALCULATED,
126  SAMELINE, 'S6' ERROR, 'L';
127  "PRINT" SAMELINE, 'S8' (SECONDS), 'S5' READING,
128  SAMELINE, 'S5' READING, 'S6' IN READING, 'L2';
129  "FOR" I:=1 "STEP" 1 "UNTIL" N "DO" "BEGIN"
130  S:=PCALC(STINF, STK, TC[I], STPO);
131  "PRINT" DIGITS(2), SAMELINE, 'S4', SCALED(9), TC[I]+INC,
132  'S4', PEI, 'S4', S, 'S4', PEI-S, 'L';
133  "END"; "PRINT" 'L2' ESD(OBSERVATION=), SAMELINE,
134  SCALED(5), Sqrt(SSDEL/(N-3));
135  "PRINT" 'L', 'S9' RATE CONSTANT=, SAMELINE,
136  SCALED(9), STK, 'S5', 'S' SECONDS(-1);
137  "PRINT" 'L' ESD(RATE CONSTANT)=, SAMELINE, SCALED(9),
138  Sqrt(AE1, 1)*SSDEL/(N-3), 'S' SECONDS(=1);
139  "PRINT" 'L' CALC INF READING=, SAMELINE,
140  SCALED(9), STINF;
141  "PRINT" 'L' ESD(INFINITY)=, SAMELINE, SCALED(9),
142  Sqrt(AE2, 2)*SSDEL/(N-3), 'L2';
143  FINISH; "END" FORWIN;
144
145  "PROCEDURE" RUNEND(FRED); "LABEL" FRED; "BEGIN"
146  "IF" GEJ, I]=99999 "THEN" "BEGIN" K:=I-1;
147  "PRINT" 'L2' NUMBER OF POINTS=, SAMELINE, SCALED(9), K;
148  "GOTO" FRED; "END"; "END";
149
150  V:=10;
151  "PRINT" 'F' ANALYSIS FOR RATE DATA FROM SPECTRA';
152  "PRINT" 'L' UNIVERSITY OF LEICESTER***M; J. BLANDAMER';
153  IE:=0; "PRINT" 'L' SYSTEM, "BEGIN"
154  "PRINT" 'L' NUMBER OF CELLS=, SAMELINE, SCALED(9),
155  NC, 'L' TS=, SAMELINE, SCALED(9), TS; "BEGIN"
156  I:=0; BAKER: I:=I+1; TC[I]:=TS*I; CHARLIE:
157  "FOR" J:= 1 "STEP" 1 "UNTIL" NC "DO" "BEGIN"
158  DAD:
159  "READ" GEJ, I];
160  RUNEND(FRED);
161  "IF" GEJ, I]<200 "THEN" "GOTO" DAD;
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;
    610 MC
    1812 CODE
    2422 TOTAL
```

```
&RUN;
ROGUE
DRO
```

```

JOB;CH001050MJB;
SNCP
BATCH

```

```

&ALGOL;
LIBRARY
ALGOL

```

```

&LIST;

```

```

1  TIGER;
2  "BEGIN"
3  "INTEGER" I,J,W,
4  JA,TE,
5  WW,VV,CONT,V,
6  K,NC;
7  "REAL" TS,TNEW,DIFF,TH,TM,
8  SA,SB,SC,QD,
9  R,
10 TC,DUMMY,EXB,SEK1,SEK2,SEEB;
11 "ARRAY" T[1:1000],G[1:10,1:1000],
12 DK1,DK2,DEB,A0,K1G,
13 K2G,EBG[1:10],
14 K1,K2,EB[1:51],
15 EC,EA,
16 DDK1R,DDDR,DDEBR,P,DCALC,DELTA,
17 DDELTA,
18 DDK1,DDK2,DDEB[1:1000],
19 C,A[1:3,1:3],B[1:4,1:4];
20
21
22 "PROCEDURE" MXCOPY(B,A);
23 "ARRAY" A,B;
24 "BEGIN"
25 "INTEGER" Q,S;
26 "FOR" Q:=1 "STEP" 1 "UNTIL" W "DO"
27 "FOR" S:=1 "STEP" 1 "UNTIL" W "DO"
28 B[Q,S]:= A[Q,S];
29 "END" MXCOPY;
30 "PROCEDURE" INVIX(B);
31 "ARRAY" B;
32 "BEGIN"
33 "REAL" MAX, EPS;
34 "INTEGER" SS,L,V,Z,R;
35 R:=W;
36 EPS:=2.0*10-37;
37 "BEGIN"
38 "INTEGER" "ARRAY" RR,BR[1:R];
39 "FOR" SS:=1 "STEP" 1 "UNTIL" R "DO"
40 "BEGIN"
41 MAX:=0;
42 "FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
43 "BEGIN"
44 "FOR" V:=1 "STEP" 1 "UNTIL" SS-1 "DO"

```

```
45 "IF" L=BR[V] "THEN" "GOTO" L1;
46 "IF" ABS(MAX)-ABS(B[L,1])
47 "LE" 0 "THEN"
48 "BEGIN"
49 BR[SS]:=L;
50 MAX:= B[L,1];
51 "END";
52 L1: "END";
53 "IF" ABS(MAX)<EPS "THEN"
54 "BEGIN"
55 "PRINT" 'L\ INVMX ERROR';
56 STOP;
57 "END";
58 V:= BR[SS];
59 "FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
60 B[L,R+1]:="IF"L=V "THEN" 1 "ELSE" 0;
61 "FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
62 B[V,L]:=B[V,L+1]/MAX;
63 "FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
64 "BEGIN"
65 MAX:= B[L,1];
66 "IF" L "NE" V "THEN" "FOR" Z:=1 "STEP" 1 "UNTIL" R "DO"
67 B[L,Z]:= B[L,Z+1]-MAX*B[V,Z]
68 "END"
69 "END";
70 "FOR" Z:=1 "STEP" 1 "UNTIL" R "DO"
71 RR[Z]:=Z;
72 "FOR" Z:=1 "STEP" 1 "UNTIL" R-1 "DO"
73 "BEGIN"

74 "IF" BR[Z]=RR[Z] "THEN" "GOTO" LOOP "ELSE"
75 "FOR" L:= Z+1 "STEP" 1 "UNTIL" R "DO"
76 "IF" RR[L]= BR[Z] "THEN" "GOTO" SWOP;
77 SWOP: "FOR" V:=1 "STEP" 1 "UNTIL" R "DO"
78 "BEGIN"
79 MAX:=B[Z,V];
80 B[Z,V]:=B[L,V];
81 B[L,V]:=MAX
82 "END";
83 RR[L]:=RR[Z];
84 LOOP:"END";
85 "FOR" Z:=1 "STEP" 1 "UNTIL" R-1 "DO"
86 "BEGIN"
87 "FOR" L:=Z "STEP" 1 "UNTIL" R "DO"
88 "IF" BR[L]=Z "THEN"
89 "BEGIN"
90 "IF" Z=L "THEN" "GOTO" OUT
91 ;
92 "FOR" V:=1 "STEP" 1 "UNTIL" R "DO"
93 "BEGIN"
94 MAX:=B[V,Z];
95 B[V,Z]:=B[V,L];
96 B[V,L]:=MAX
97 "END";
98 BR[L]:=BR[Z]
99 "END";
100 OUT: "END"
101 "END";
102 "END" INVMX;
103 "PROCEDURE" MXPROD (C,A,B);
104 "ARRAY" A,B,C;
```

```

105 "BEGIN"
106 "INTEGER" I,J,K;
107 "FOR" I:=1 "STEP" 1 "UNTIL" W "DO"
108 "FOR" J:=1 "STEP" 1 "UNTIL" W "DO"
109 "BEGIN"
110 C[I,J]:=0;
111 "FOR" K:=1 "STEP" 1 "UNTIL" W "DO"
112 C[I,J]:=C[I,J]+A[I,K]*B[K,J];
113 "END";
114 "END" MXPROD;
115 "PROCEDURE" PRINTMX(C,N);
116 "INTEGER" N;
117 "ARRAY" C;
118 "BEGIN"
119 "INTEGER" I,J,K,L,M,MM;
120 "INTEGER" "ARRAY" LIM[0:7];
121 FREEPOINT (11); DIGITS(3);
122 I:=N "DIV" 9;
123 LIM[0]:=N-9*I;
124 K:=0;
125 "FOR" J:=1 "STEP" 1 "UNTIL" I "DO" LIM[J]:=9;
126 "FOR" J:=I "STEP" -1 "UNTIL" 0 "DO"
127 "BEGIN"
128 "PRINT" 'L',S6;
129 "IF" LIM[J]>0 "THEN" "BEGIN"
130 "FOR" L:=1 "STEP" 1 "UNTIL" LIM[J] "DO"
131 "PRINT" SAMELINE,DIGITS(7),L+K,'S5';
132 "FOR" M:=1 "STEP" 1 "UNTIL" N "DO"
133 "BEGIN"
134 "PRINT" 'L',SAMELINE,DIGITS(2),'S3',M;
135 "FOR" MM:=K+1 "STEP" 1 "UNTIL" K+LIM[J] "DO"
136 "PRINT" SAMELINE,SCALED(9),C[M,MM];
137 "END";
138 K:=K+9; "PRINT" 'L';
139 "END" ;
140 "END";
141 "END" PRINTMX;
142
143 "PROCEDURE" MXSET;
144 "BEGIN"
145 "COMMENT" R>0.01;
146 "FOR" I:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
147 "IF" T[I]=0 "THEN" "GOTO" POOLE;
148 DDK1[I]:=((E[C[W]-E[C[W]])/(K1[W]-K2[W])+2)*((K1[W]-K2[W])*
149 (EXP(-K2[W]*T[I])-EXP(-K1[W]*T[I])+K1[W]*T[I]*EXP(-K1[W]*T[I]))
150 -K1[W]*(EXP(-K2[W]*T[I])-EXP(-K1[W]*T[I]))))
151 -T[I]*(E[C[W]-E[C[W]])*EXP(-K1[W]*T[I]);
152 DDK2[I]:=((K1[W]*(E[C[W]-E[C[W]])/((K1[W]-K2[W])+2))
153 *((EXP(-K2[W]*T[I])-EXP(-K1[W]*T[I])-(K1[W]-K2[W])*T[I]
154 *EXP(-K2[W]*T[I])));
155 DDEB[I]:=K1[W]*(EXP(-K2[W]*T[I])-EXP(-K1[W]*T[I])-
156 EXP(-K1[W]*T[I]))/(K1[W]-K2[W]);
157 POOLE:"END";"END"MXSET;
158
159 "PROCEDURE" MXSETUP;
160 "BEGIN"
161 "COMMENT" R<0.01;
162 "FOR" I:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
163 "IF" T[I]=0 "THEN" "GOTO" SOTON;
164 R:=(K1[W]-K2[W])/K1[W];
165 DDK1R[I]:=(EXP(-K1[W]*T[I]))*(E[C[W]-E[C[W]])*(T[I]+R*K1[W]*T[I]);

```

```

165 ((R+3*K1[W]+3*T[I]+4)/6)
166 -T[I]*((K1[W]*T[I])+
167 ((R*K1[W]+2*T[I]+2)/2)
168 +((R+2*K1[W]+3*T[I]+3)/6)
169 +((R+3*K1[W]+4*T[I]+4)/24))
170 -T[I]*(EXP(-K1[W]*T[I]))*(EACW]-ECCW]);
171 DDDR[C]:=(EBCW]-ECCW])*(EXP(-K1[W]*T[I]))*(((K1[W]+2*T[I]+2)/2)
172 +((R*K1[W]+3*T[I]+3)/3)
173 +((R*K1[W]+4*T[I]+4)/8));
174 DDK1[I]:=DDK1R[I]+(DDDR[C]*K2[W]/K1[W]+2);
175 DDK2[I]:=DDDR[C]*(-1/K1[W]);
176 DDEB[C]:=(EXP(-K1[W]*T[I]))*(K1[W]*T[I]+((R*K1[W]+2*T[I]+2)/2)
177 +((R+2*K1[W]+3*T[I]+3)/6)
178 +((R+3*K1[W]+4*T[I]+4)/24));
179 SOTON:"END";"END";
180 "PROCEDURE"MXMAKE;
181 "BEGIN"
182 "FOR" I:=1"STEP"1"UNTIL"3"DO"
183 "FOR" J:=1 "STEP" 1 "UNTIL" 3 "DO"
184 A[I,J]:=0;
185 "FOR" I:=1"STEP"1"UNTIL"K"DO""BEGIN"
186 A[1,1]:=A[1,1]+((DDK1[I])+2);
187 A[1,2]:=A[1,2]+(DDK1[2]*DDK2[I]);
188 A[1,3]:=A[1,3]+(DDK1[I]*DDEB[C]);
189 A[2,2]:= A[2,2]+((DDK2[I])+2);
190 A[2,3]:=A[2,3]+(DDK2[I]*DDEB[C]);
191 A[3,3]:=A[3,3]+((DDEB[C])+2);
192 LONDON:"END";
193 A[2,1]:=A[1,2];
194 A[3,1]:=A[1,3];
195 A[3,2]:=A[2,3];
196 "END";

197 "PROCEDURE"COLUMN;
198 "BEGIN"
199 SA:=SB:=SC:=0;
200 "FOR" I:=1"STEP" 1"UNTIL" K"DO""BEGIN"
201 "IF" T[I]=0"THEN""GOTO"NEWYORK;
202 DCALC[C]:=(EACW]-ECCW])*EXP(-K1[W]*T[I])-(((EBCW]-ECCW])*
203 K1[W]*(EXP(-K2[W]*T[I])-EXP(-K1[W]*T[I])))/(K1[W]-K2[W]))+ECCW]
204 DELTAD[C]:=P[C]-DCALC[C];
205 SA:=SA+DELTAD[C]*DDK1[I];
206 SB:=SB+DELTAD[C]*DDK2[I];
207 SC:=SC+DELTAD[C]*DDEB[C];
208 NEWYORK:"END";"END";
209 "PROCEDURE"TIME;
210 "BEGIN"
211 "FOR" I:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
212 TC:=T[I];
213 TH:=ENTIER(TC/100);
214 TM:=TC-(100*TH);
215 TH:=60*TH;
216 TM:=TM+TH;
217 T[I]:=60*TH;
218 "END";
219 "END"TIME;
220
221 "PROCEDURE"TIMECHECK(BAKER);"LABEL"BAKER;
222 "BEGIN"
223 "IF" I>1 "THEN" "BEGIN"
224 V:=I-1;

```

```

225 "IF" TC[I]=TC[V]+TS "THEN" "GOTO" ABLE;
226 "PRINT" 'L' TIMEOUT*I=', SAMELINE, SCALED(9), I;
227 "READ" DUMMY; "GOTO" BAKER;
228 ABLE:
229 "END"
230 "END" TIMECHECK;
231
232 "PROCEDURE" RUNEND(FRED); "LABEL" FRED;
233 "BEGIN"
234 "IF" TC[I] < 1 "THEN" "BEGIN"
235 K:=I-1;

236 "PRINT" 'L2' NUMBER OF POINTS =', SAMELINE, SCALED(9), K; "GOT
237 "END" "END"; FRED;
238
239 "PROCEDURE" ADJUST(CHARLIE); "LABEL" CHARLIE;
240 "BEGIN"
241 "FOR" W:=J "STEP" 1 "UNTIL" NC "DO" GC[W, I]:=0;
242 WW:=I-1;
243 "FOR" W:=J "STEP" -1 "UNTIL" 1 "DO" "BEGIN"
244 "IF" GC[W, WW]=TC[I]-TS "THEN"
245 "GOTO" VICTOR; GC[W, WW]:=0; "END"; VICTOR:
246 "PRINT" 'L' A OUT OF SEQUENCE*I=',
247 SAMELINE, SCALED(9), I;
248 I:=I+1;
249 TC[I]:= TNEW; "GOTO" CHARLIE; "END";
250
251
252
253
254
255 "PROCEDURE" SCANOUT;
256 "BEGIN"
257 "PRINT" 'L' ABSORBANCE OUT OF SEQUENCE', SAMELINE,
258 SCALED(9), I, 'S8', J;
259 "END";
260
261 "PROCEDURE" CHECK;
262 "BEGIN"
263 "COMMENT" IF CONT=1, BAND GROWS BUT IF CONT=0
264 BAND DECAYS;
265 "IF" CONT=1 "THEN" "BEGIN"
266 "FOR" I:=1 "STEP" 1 "UNTIL" NC "DO"
267 "BEGIN"
268 "FOR" J:=2 "STEP" 1 "UNTIL" K "DO" "BEGIN"
269 JA:=J-1;
270 "IF" G[I, JA]=0 "THEN" "GOTO" MEXICO;
271 DIFF:=G[I, J]+(G[I, J]/10);
272 "IF" DIFF<G[I, J] "THEN" "BEGIN"
273 G[I, J]:=0;
274 TE:=TE+1;
275 SCANOUT;
276 "END";
277 MEXICO:
278 "END";
279 "END";
280 "END";
281 "IF" CONT=0 "THEN" "BEGIN"
282 "FOR" I:=1 "STEP" 1 "UNTIL" NC "DO" "BEGIN"
283 "FOR" J:=2 "STEP" 1 "UNTIL" K "DO"
284 "BEGIN"

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```

285 JA:=J-1;
286 "IF" GC[I,JA]=0 "THEN" "GOTO" BRAZIL;
287 DIFF:=G[C,I,J]-(G[C,I,J]/10);
288 "IF" DIFF>G[C,I,JA] "THEN" "BEGIN"
289 G[C,I,J]:=0;
290 TE:=TE+1;
291 SCANOUT;
292 "END";
293 BRAZIL:
294 "END" "END" "END" "END";
295
296 "PRINT" 'F ANALYSIS FOR RATE DATA FROM SPECTRA';
297 "PRINT" 'L UNIVERSITY OF LEICESTER***M.J.BLANDAMER';
298 "PRINT" 'L DATA FROM TAPE +CARDS';
299 TE:=0;
300 "PRINT" 'L SYSTEM';
301 "PRINT" 'L4';
302 "BEGIN"
303 "INTEGER" I,J,W,WW,
304 V,K,NC;
305 "REAL" TS,TNEW,DUMMY;
306 "ARRAY" TC[1:1000],G[1:10,1:1000];
307 "READ" NC;
308 "READ" TS;
309 "READ" CONT;
310 "PRINT" 'L NO CELLS=',SAMELINE,SCALED(9),NC;
311 "PRINT" 'L TS=',SAMELINE,SCALED(9),TS;
312 "BEGIN"
313 I:=1;
314 READER(1);
315 BAKER:
316 "PRINT" 'L TAPE NOW INPUT';
317 "READ" TC[I]; TNEW:=TC[I]+TS;
318 "PRINT" 'L ',SAMELINE,SCALED(9),I,'S5',TC[I];
319 CHARLIE:
320 RUNEND(FRED);
321 TIMECHECK(BAKER);
322 "FOR" J:=1 "STEP" 1 "UNTIL" NC "DO" "BEGIN"
323 "READ" GC[J,I];
324 "PRINT" SAMELINE,SCALED(9),'S5',J,'S3',I,'S3',GC[J,I];
325 "IF" GC[J,I]=TNEW "THEN" ADJUST(CHARLIE);
326 "END";
327 I:=I+1;
328 "GOTO" BAKER;
329 "END";
330 FRED:
331 "PRINT" 'L TAPE SUMMARY';
332 "FOR" I:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
333 "PRINT" SAMELINE,SCALED(9),TC[I],'S3';
334 "FOR" W:=1 "STEP" 1 "UNTIL" NC "DO" "BEGIN"
335 "PRINT" SAMELINE,SCALED(9),GC[W,I];
336 "END";
337 "PRINT" 'L';
338 "END";
339 "END";
340 CHECK;
341 TIME;
342 "COMMENT" INPUT K READINGS FOR NC CELLS;
343 READER(6);
344 "FOR" W:=1 "STEP" 1 "UNTIL" NC "DO" "BEGIN"

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```

345 "READ" A0[W], K1[G[W], K2[G[W], EB[G[W], EA[W], EC[W];
346 "COMMENT" G MEANS GUESSED****
347 ****A0, EA, EC, ARE KNOWN;
348 "PRINT" 'L5' ANALYSIS OF DATA FOR CELL= ', SAMELINE, SCALED(9), W;
349 K1[W]:=K1[G[W];
350 "PRINT" 'L' GUESSED K1= ', SAMELINE, SCALED(9), K1[W];
351 K2[W]:=K2[G[W];
352 EB[W]:=EB[G[W];
353 "FOR" I:=1"STEP"1"UNTIL"K"DO"
354 PC[I]:=GEH, I]/A0[W];
355 "PRINT" 'L' CYCLE STARTED**NUMBER= ', SAMELINE, SCALED(9), W;
356 "FOR" V:=1"STEP"1"UNTIL"50"DO" "BEGIN"
357 "PRINT" 'L2' CYCLE NUMBER= ', SAMELINE, SCALED(9), V;
358 R:=(K1[W]-K2[W])/K1[W];
359 EXB:=EB[W];
360 "IF" R=0.01"THEN"MXSETUP;
361 "IF" R>0.01"THEN"MXSET;
362 "IF" R<0.01"THEN"MXSETUP;
363 MXMAKE;
364 "PRINT" 'L' MXSETUP ', 'L';
365 MXCOPY(A, B);
366 "PRINT" 'L' MATRIX A ', 'L';
367 PRINTMX(A, 3);
368 "PRINT" 'L' MATRIX B ', 'L';
369 INVMX(B);
370 MXPROD(C, A, B);
371 "PRINT" 'L' MATRIX C ', 'L';
372 PRINTMX(C, 3);
373 COLUMN;
374 "PRINY" 'L' COLUMN IS SET UP ', 'L';
375 "PRINT" 'L' MX PROCEDURES COMPLETE';
376 DK1[W]:=SA*B[1, 1]+SB*B[1, 2]+SC*B[1, 3];
377 DK2[W]:=SA*B[2, 1]+SB*B[2, 2]+SC*B[2, 3];
378 DEB[W]:=SA*B[3, 1]+SB*B[3, 2]+SC*B[3, 3];
379 VV:=W+1;
380 K1[VV]:=K1[W]+DK1[W];
381 K2[VV]:=K2[W]+DK2[W];
382 EB[VV]:=EB[W]+DEB[W];
383 "PRINT" 'L' CYCLE NUMBER = ', SAMELINE, SCALED(9), V;
384 "PRINT" 'L' ESTIMATED K1= ', SAMELINE, SCALED(9), K1[VV];
385 "PRINT" 'L' ESTIMATED K2= ', SAMELINE, SCALED(9), K2[VV];
386 "PRINT" 'L' EST EXT COEF OF B= ', SAMELINE, SCALED(9), EB[VV];
387 "IF" V=50"THEN" "BEGIN"
388 "PRINT" 'L' 50 CYCLES 50 OUT';
389 "GOTO" PETER; "END";
390 "IF" ABS((K1[W]-K1[VV])*100/K1[W])<0.01"THEN" "GOTO" PETER;
391 "END"; PETER;
392 "PRINT" 'L2' ANALYSIS COMPLETE';
393 "PRINT" 'L2' CALCULATED K1= ', SAMELINE, SCALED(9), K1[W];
394 "PRINT" 'L2' CALCULATED K2= ', SAMELINE, SCALED(9), K2[W];
395 "PRINT" 'L2' CALCULATED EXB= ', SAMELINE, SCALED(9), EB[W];
396 "COMMENT" NOW CALCULATE STANDARD ERRORS;
397 QD:=0;
398 "FOR" I:=1"STEP"1"UNTIL"K"DO" "BEGIN"
399 "IF" TC[I]=0"THEN" "GOTO" LEEDS;
400 QD:=QD+((DDELTA[I])^2);
401 LEEDS: "END";
402 SEK1:=SQRT((B[1, 1]*QD)/(K-3));
403 SEK2:=SQRT((B[2, 2]*QD)/(K-3));
404 SEEB:=SQRT((B[3, 3]*QD)/(K-3));

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```
405 "PRINT"'L3'STANDARD ERROR ON K1=',SAMELINE,SCALED(9),SEK1;  
406 "PRINT"'L3'STANDARD ERROR ON K2=',SAMELINE,SCALED(9),SEK2;  
407 "PRINT"'L3'STANDARD EPROR ON EB=',SAMELINE,SCALED(9),SEEB;  
408 "END";  
409 "PRINT"'L'CHANGE';  
410 "END";  
      878      MC  
      3406     CODE  
      4284     TOTAL
```

```
&END;  
TIME = 0001 28  
A
```

```
&JOB;CH001050TEMP;HJB16;
```

```
&ALGOL;
LIBRARY
ALGOL
```

```
&LIST;
```

```

1  TEMPAN;
2  "BEGIN"
3  "INTEGER" I,N,M,Q,S,Z,ZZ,ZZZ,ZZZZ,V,W;
4  "REAL" THETA,DTHETA,USA,USB,USC,USD,USE,USSA,USSB,USSC,USSD,
5  BO,DGT,KRCALC,
6  USSE,UAM,UBM,UCM,UDM,UEM,YM,SA,SB,SC,SD,SE,BA,BB,BC,BD,BE,YCA
7  QD,DF,DGTHETA,TEMP,DTEMP,USAT,XTEMP,USBT,USCT,USDT,USET,USSAT
8  USSCT,USSDT,USSET,UAT,UBT,UCT,UDT,UET,KRCALT,DSTHETA,DHTHETA,
9  DDCPTHETA,DDDCPTHETA,DDDDCPHETA,VARBA,VARBB,VARBC,VARBD,VARB
10 DKR,LDKR,
11 VARDG,VARDH,VARCP,VARDCP,VARDS,VARDDCP,VARDDDCP,DHT,
12 DCPT,DST,D1CPT,D2CPT,D3CPT,KRCAL,KRTHETA;
13 Q:=S:=5;
14 "READ" N;
15 "READ" THETA;
16 "READ" DTEMP;
17 "READ"Z;
18 "READ" ZZ;
19 "READ" ZZZ;
20 "READ" ZZZZ;
21 "BEGIN"
22 "ARRAY" KR,KG,KRC,
23 YC,
24 KGCAL,X,Y,YCALC,T,UA,UB,UC,UD,UE[1:N],A[1:Q,1:S],
25 B[1:Q+1,1:S+1],C[1:Q,1:S];
26 "READ" DTHETA;
27 "PRINT" 'F', CLARKE AND GLEW ANALYSIS OF RATE DATA AND DERIV
28 OF PSEUDO THERMODYNAMIC FUNCTIONS';
29 "PRINT" 'L**M:J.BLANDAMER***UNIVERSITY OF LEICEISTER';
30 "PRINT" 'L2', SYSTEM';
31 "PRINT" 'L2', THETA= 'SAMELINE,SCALED(9),THETA;
32 "PRINT" 'L2', TEMPERATURE RANGE FOR MEASURED RATE CONSTANTS=
33 "FOR" I:=1 "STEP" 1"UNTIL" N "DO"
34 "BEGIN"
35 "READ" KR[I], TC[I];
36 "END";
37 "FOR"Q:=1"STEP"1"UNTIL"5"DO"
38 "FOR"S:=1"STEP"1"UNTIL"5"DO"
39 B[Q,S]:=0;
40 START;
41 "IF" Z=0 "THEN" "BEGIN"
42 ZZ:= ZZZ:= ZZZZ :=0;
43 W:=1;
44 "PRINT" 'L2', ANALYSIS USING TWO CONSTANT EQUATION';
45 "GOTO" DAN;
```

```

46 "END";
47 "IF" ZZ=0 "THEN" "BEGIN"
48 ZZZ:= ZZZZ:=0;
49 W:=2;
50 "PRINT" 'L2', ANALYSIS USING THREE CONSTANT EQUATION';
51 "GOTO" DAN;
52 "END";
53 "IF" ZZZ=0 "THEN" "BEGIN"
54 ZZZZ:=0;
55 W:=3;
56 "PRINT" 'L2', ANALYSIS USING FOUR CONSTANT EQUATION';
57 "GOTO" DAN;
58 "END";
59 "IF" ZZZZ=0 "THEN" "BEGIN"
60 W:=4;
61 "PRINT" 'L2', ANALYSIS USING FIVE CONSTANT EQUATION';
62 "GOTO" DAN;
63 "END";
64 "IF" ZZZZ=1 "THEN" "BEGIN"
65 W:=5;
66 "PRINT" 'L2', ANALYSIS USING SIX CONSTANTS';
67 "GOTO" DAN;
68 "END";
69 DAN;
70 "FOR" I:=1 "STEP" 1 "UNTIL" N "DO"
71 "BEGIN"
72 KG[I]:= (KRC[I]/TC[I])*(6.626196/(1.380622*10+11));
73 Y[I]:= 8.31434*LN(KG[I]);
74 X[I]:= (TC[I]-THETA)/THETA;
75 "END";
76 "FOR" i:=1 "STEP" 1 "UNTIL" N"DO"
77 "BEGIN"
78 USSA:=0;
79 USSB:=0;
80 USSC:=0;
81 USSD:=0;
82 USSE:=0;
83 V:=0;
84 JIL;V:=V+1;
85 USA:=((-X[I])+(V-1));
86 USSA:= USSA+USA;
87 "IF" ABS (USA/USSA)>1.-12 "THEN" "GOTO" JIL "ELSE"
88 UAC[I]:= X[I]*USSA;
89 V:=0;
90 "IF" Z=0 "THEN" "BEGIN"
91 UBC[I]:= UCC[I]:= UDC[I]:= UEC[I]:=0;
92 "GOTO" PETE;
93 "END";
94 LIZ;V:=V+1;
95 USB:=((-X[I])+(V-1))*(V/(V+1));
96 USSB:= USSB+USB;
97 "IF" ABS(USB/USSB)>1.-12 "THEN" "GOTO" LIZ "ELSE"
98 UBC[I]:= USSB*(X[I]+2);
99 V:=0;
100 "IF" ZZ=0 "THEN" "BEGIN"
101 UCC[I]:= UDC[I]:= UEC[I]:=0;
102 "GOTO" PETE;
103 "END";
104 MIK;V:=V+1;
105 USC:= ((-X[I])+(V-1))*(V/(V+2));

```

```

106  USSC:= USSC+ USC;
107  "IF" ABS(USC/USSC)>1.-12 "THEN" "GOTO" MIK "ELSE"
108  UCCI:= USSC*(X[I]+3);
109  V:=0;
110  "IF" ZZZ=0 "THEN" "BEGIN"
111  UDCI:= UE[I];=0;
112  "GOTO" PETE;
113  "END";
114  MAR;V:=V+1;
115  USD:= ((-X[I])+(V-1))*(V/(V+3));
116  USSD:= USSD+USD;
117  "IF" ABS(USD/USSD)>1.-12 "THEN" "GOTO" MAR "ELSE"
118  UDCI:=USSD*(X[I]+4);
119  V:=0;
120  "IF" ZZZZ=0 "THEN" "BEGIN"
121  UEI:=0;
122  "GOTO" PETE;
123  "END";
124  BRI;V:=V+1;
125  USE:= ((-X[I])+(V-1))*(V/(V+4));
126  USSE:= USSF+USE;
127  "IF" ABS(USE/USSE)>1.-12 "THEN" "GOTO" BRI "ELSE"
128  UEI:=USSE*(X[I]+5);
129  PETE;
130  "END";
131  UAM:=0;
132  UBM:= 0;
133  UCM:=0;
134  UDM:=0;
135  UEM:=0;
136  YM:=0;
137  "FOR" I:=1 "STEP" 1 "UNTIL" N"DO"
138  "BEGIN"
139  UAM:= UAM+UAEI;
140  UBM:= UBM+UBEI;
141  UCM:= UCM+ UCCI;
142  UDM:= UDM+UDEI;
143  UEM:= UEM+ UEI;
144  YM:= YM+ YEI;
145  "END";
146  UAM:= UAM/N;
147  UBM:= UBM/N;
148  UCM:= UCM/N;
149  UDM:= UDM/N;
150  UEM:= UEM/N;
151  YM:= YM/N;
152  "BEGIN"
153  "FOR" Q:=1 "STEP" 1 "UNTIL" 5 "DO"
154  "FOR" S:=1 "STEP" 1 "UNTIL" 5 "DO"
155  A[Q,S]:=0;
156  "END";
157  "FOR" I:=1 "STEP" 1 "UNTIL" N "DO"
158  "BEGIN"
159  A[1,1]:= A[1,1]+((UAEI-UAM)+2);
160  A[1,2]:= A[1,2] +((UBEI-UBM)*(UAEI-UAM));
161  A[1,3]:= A[1,3] +((UCCI-UCM)*(UAEI-UAM));
162  A[1,4]:= A[1,4] +((UDEI-UDM)*(UAEI-UAM));
163  A[1,5]:= A[1,5] +((UEI-UEM)*(UAEI-UAM));
164  A[2,2]:= A[2,2] +((UBEI-UBM)+2);
165  A[2,3]:= A[2,3] +((UBEI-UBM)*(UCCI-UCM));

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166 A[2,4]:= A[2,4] + ((UB[I]-UBM)*(UD[I]-UDM));
167 A[2,5] := A[2,5] + ((UB[I]-UBM)*(UE[I]-UEM));
168 A[3,3] := A[3,3] + ((UC[I]-UCM)*2);
169 A[3,4] := A[3,4] + ((UC[I]-UCM)*(UD[I]-UDM));
170 A[3,5] := A[3,5] + ((UC[I]-UCM)*(UE[I]-UEM));
171 A[4,4] := A[4,4] + ((UD[I]-UDM)*2);
172 A[4,5] := A[4,5] + ((UD[I]-UDM)*(UE[I]-UEM));
173 A[5,5] := A[5,5] + ((UE[I]-UEM)*2);
174 "END";
175 A[2,1]:= A[1,2];
176 A[3,1]:= A[1,3];
177 A[4,1]:= A[1,4];
178 A[4,2]:= A[2,4];
179 A[3,2]:= A[2,3];
180 A[4,3]:= A[3,4];
181 A[5,1]:= A[1,5];
182 A[5,2]:= A[2,5];
183 A[5,3]:= A[3,5];
184 A[5,4]:= A[4,5];
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 + ((UAC[I]-UAM)*(Y[I]-YM));
193 SB:= SB + ((UB[I]-UBM)*(Y[I]-YM));
194 SC:= SC + ((UC[I]-UCM)*(Y[I]-YM));
195 SD:= SD + ((UD[I]-UDM)*(Y[I]-YM));
196 SE:= SE + ((UE[I]-UEM)*(Y[I]-YM));
197 "END";
198 "PRINT" 'L',SAMELINE,SCALED(9),SA,'S2',SB,'S2',SC,
199 'S2',SD,'S2',SE;
200 "BEGIN"
201 "PROCEDURE" MXCOPY(B,A);
202 "ARRAY" A,B;
203 "BEGIN"
204 "INTEGER" Q,S;
205 "FOR"Q:=1"STEP"1"UNTIL"W"DO"
206 "FOR"S:=1"STEP"1"UNTIL"W"DO"
207 B[Q,S]:= A[Q,S];
208 "END" MXCOPY;
209 "PROCEDURE" INVMX(B);
210 "ARRAY" B;
211 "BEGIN"
212 "REAL" MAX, EPS;
213 "INTEGER" SS,L,V,Z,R;
214 R:=W;
215 EPS:=2.0*10-37;
216 "BEGIN"
217 "INTEGER" "ARRAY" RR,BR[1;R];
218 "FOR" SS:=1 "STEP" 1 "UNTIL" R "DO"
219 "BEGIN"
220 MAX:=0;
221 "FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
222 "BEGIN"
223 "FOR" V:=1 "STEP" 1 "UNTIL" SS-1 "DO"
224 "IF" L=BR[V] "THEN" "GOTO" L1;
225 "IF" ABS(MAX)-ABS(B[L,1])

```

```

226 "LE" 0 "THEN"
227 "BEGIN"
228 BR[SS]:=L;
229 MAX:= B[L,1];
230 "END";
231 L1; "END";
232 "IF" ABS(MAX) < EPS "THEN"
233 "BEGIN"
234 "PRINT" 'L INVMX ERROR';
235 STOP;
236 "END";
237 V:= BR[SS];
238 "FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
239 B[L,R+1]:="IF" L=V "THEN" 1 "ELSE" 0;
240 "FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
241 B[V,L]:=B[V,L+1]/MAX;
242 "FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
243 "BEGIN"
244 MAX:= B[L,1];
245 "IF" L "NE" V "THEN" "FOR" Z:=1 "STEP" 1 "UNTIL" R "DO"
246 B[L,Z]:= B[L,Z+1]-MAX*B[V,Z]
247 "END"
248 "END";
249 "FOR" Z:=1 "STEP" 1 "UNTIL" R "DO"
250 RR[Z]:=Z;
251 "FOR" Z:=1 "STEP" 1 "UNTIL" R-1 "DO"
252 "BEGIN"
253 "IF" BR[Z]=RR[Z] "THEN" "GOTO" LOOP "ELSE"
254 "FOR" L:= Z+1 "STEP" 1 "UNTIL" R "DO"
255 "IF" RR[L]= BR[Z] "THEN" "GOTO" SWOP;
256 SWOP: "FOR" V:=1 "STEP" 1 "UNTIL" R "DO"
257 "BEGIN"
258 MAX:=B[Z,V];
259 B[Z,V]:=B[L,V];
260 B[L,V]:=MAX
261 "END";
262 RR[L]:=RR[Z];
263 LOOP:"END";
264 "FOR" Z:=1 "STEP" 1 "UNTIL" R-1 "DO"
265 "BEGIN"
266 "FOR" L:=Z "STEP" 1 "UNTIL" R "DO"
267 "IF" BR[L]=Z "THEN"
268 "BEGIN"
269 "IF" Z=L "THEN" "GOTO" OUT
270 ;
271 "FOR" V:=1 "STEP" 1 "UNTIL" R "DO"
272 "BEGIN"
273 MAX:=B[V,Z];
274 B[V,Z]:=B[V,L];
275 B[V,L]:=MAX
276 "END";
277 BR[L]:=BR[Z]
278 "END";
279 OUT: "END"
280 "END";
281 "END" INVMX;
282 "BEGIN"
283 MXCOPY (B,A);
284 INVMX (B);
285 "END";

```

```

286 BA:=B[1,1]*SA+B[1,2]*SB+B[1,3]*SC+B[1,4]*SD+B[1,5]*SE;
287 BB:=B[2,1]*SA+B[2,2]*SB+B[2,3]*SC+B[2,4]*SD+B[2,5]*SE;
288 BC:=B[3,1]*SA+B[3,2]*SB+B[3,3]*SC+B[3,4]*SD+B[3,5]*SE;
289 BD:= B[4,1]*SA + B[4,2]*SB + B[4,3]*SC + B[4,4]*SD + B[4,5]
290 *SE;
291 BE:= B[5,1]*SA + B[5,2]*SB + B[5,3]*SC +B[5,4]*SD
292 + B[5,5]*SE;
293 BO:= YM-(BA*UAM)-(BB*UBM)-(BC*UCM)-(BD*UDM)-(BE*UEM);
294 "PRINT" 'L2' BO:=', SAMELINE, SCALED(9), BO;
295 "PRINT" 'L2' BA=', SAMELINE, SCALED(9), BA;
296 "PRINT" 'L2' BB=', SAMELINE, SCALED(9), BB;
297 "PRINT" 'L2' BC=', SAMELINE, SCALED(9), BC;
298 "PRINT" 'L2' BD=', SAMELINE, SCALED(9), BD;
299 "PRINT" 'L2' BE=', SAMELINE, SCALED(9), BE;
300 "PRINT" 'L2' YM=', SAMELINE, SCALED(9), YM;
301 "PRINT" 'L' CALCULATED CD RATE CONSTANTS', 'L';
302 QD:=0;
303 "FOR" I:=1 "STEP" 1 "UNTIL" N "DO"
304 "BEGIN"
305 YC[I]:= BO + (BA*UAC[I]) + (BB*UBC[I]) + (BC*UC[I])
306 + (BD*UDC[I]) + (BE*UEC[I]);
307 QD:=QD+((Y[I]-YC[I])^2);
308 KRCC[I]:=(T[I]*(1.380622e11)/6.626196)*EXP(YC[I]/8.31434);
309 DKR:=(KRCC[I]/KRC[I]);
310 LDKR:=(LN(DKR))/(2.3026);
311 "PRINT" SAMELINE, SCALED(6), T[I], 'S4', KRC[I], 'S4',
312 KRCC[I], 'S4', Y[I], 'S4', DKR, 'S4', LDKR, 'L';
313 "END";
314 "PRINT" 'L' RESIDUAL SUM OF SQUARES Q(RLNK)
315 ABOUT REGRESSION FOR N OBSERVED VALUES OF RLNK=',
316 SAMELINE, SCALED(9), QD;
317 "PRINT" 'L' NUMBER OF DATA POINTS =', SAMELINE, SCALED(9), N;
318 "IF" Z=0 "THEN" "BEGIN"
319 DF:=N-2;
320 "PRINT" 'L' DEGREES OF FREEDOM=', SAMELINE, SCALED(9), DF;
321 QD:=QD/(N-2);
322 "GOTO" JESS;
323 "END";
324 "IF" ZZ=0 "THEN" "BEGIN"
325 DF:=N-3;
326 "PRINT" 'L' DEGREES OF FREEDOM=',
327 SAMELINE, SCALED(9), DF;
328 QD:=QD/(N-3);
329 "GOTO" JESS;
330 "END";
331 "IF" ZZZ=0 "THEN" "BEGIN"
332 DF:=N-4;
333 "PRINT" 'L' DEGREES OF FREEDOM=',
334 SAMELINE, SCALED(9), DF;
335 QD:=QD/(N-4);
336 "GOTO" JESS;
337 "END";
338 "IF" ZZZZ=0 "THEN" "BEGIN"
339 DF:=N-5;
340 "PRINT" 'L' DEGREES OF FREEDOM=', SAMELINE, SCALED(9), DF;
341 QD:=QD/(N-5);
342 "GOTO" JESS;
343 "END";
344 "IF" ZZZZ=1 "THEN" "BEGIN"
345 DF:=N-6;

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```

346 "PRINT" 'L'DEGREES OF FREEDOM=',SAME LINE ,SCALED(9),DF;
347 QD:=QD/(N-6);
348 "GOTO" JESS;
349 "END";
350 JESS:
351 "PRINT" 'L'RESIDUAL MEAN SQUARE ERROR=',
352 SAMELINE,SCALED(9),QD;
353 QD:=SQRT(QD);
354 "PRINT" 'L'STANDARD ERROR SIGMA ON A SINGLE
355 OBSERVED RLNK=',SAMELINE,SCALED(9),QD;
356 DGTHETA:=-THETA*BO;
357 VARDG:= QD*THETA*SQRT(1/4);
358 KRTHETA:=EXP(-DGTHETA/(8.31434*THETA))*((THETA*1.3806226.62(196)11)/β)
359 "PRINT" 'L'DELTA G AT THETA=',SAMELINE,SCALED(9),DGTHETA;
360 "PRINT" 'S3'SE=',SAMELINE,SCALED(9),VARDG;
361 DHTHETA:= THETA *BA;
362 VARDH:= QD*THETA*SQRT(B[1,1]);
363 "PRINT" 'L'DELTA H AT THETA =',SAMELINE,SCALED(9),DHTHETA;
364 "PRINT" 'S3'SE=',SAMELINE,SCALED(9),VARDH;
365 "PRINT" 'L'RATE CONSTANT AT THETA=', SAMELINE,
366 SCALED(9),KRTHETA;
367 DSTHETA:= (DHTHETA-DGTHETA)/THETA;
368 "PRINT" 'L'DELTA S AT THETA =',SAMELINE,SCALED(9),DSTHETA;
369 "IF" Z=0 "THEN" "GOTO" ANN;
370 DCPHETA:= BB;
371 VARDCP:= QD*SQRT(B[2,2]);
372 "PRINT" 'L3'DELTA CP AT THETA =', SAMELINE,
373 SCALED(9),DCPHETA,'S3'SE=',SAMELINE,SCALED(9),VARDCP;
374 "IF" ZZ=0 "THEN" "GOTO" ANN;
375 DDCPHETA:= (2/THETA)*(BC);
376 VARDDC:= QD*(2/THETA)*SQRT(B[3,3]);
377 "PRINT" 'L'DDELTA CP AT THETA =',SAMELINE,SCALED(9),DDCPHET
378 SE=',SAMELINE,SCALED(9),VARDDC;
379 "IF" ZZZ=0 "THEN" "GOTO" ANN;
380 DDDCPHETA:= (6/(THETA+2))*BD;
381 VARDDDC:= QD*(6/(THETA+2))*SQRT(B[4,4]);
382 "PRINT" 'L'D2DELTA CP AT THETA=',SAMELINE,SCALED(9),
383 DDDCPHETA,'S3'SE=',SAMELINE,SCALED(9),VARDDDC;
384 "IF" ZZZZ=0 "THEN" "GOTO" ANN;
385 DDDDCPHETA:= (24/(THETA+3))*BE;
386 VARDDDDC:=(24/(THETA+3)*SQRT(B[5,5]));
387 "PRINT" 'L'D3DELTA CP AT THETA =',SAMELINE,SCALED(9),
388 DDDDCPHETA,'S3'SE=',SAMELINE, SCALED(9),VARDDDDC;
389 ANN:
390 TEMP:= 273.15;
391 "PRINT" 'L'CALC TD PARAM AT FIXED TEMP INT';
392 NEW;"PRINT" 'L'TEMPERATURE=',SAMELINE,
393 SCALED(9), TEMP;
394 XTEMP:= (TEMP-THETA)/THETA;
395 USSA:=0;
396 USSB:=0;
397 USSC:=0;
398 USSD:=0;
399 USSE:=0;
400 V:=0;
401 AT;V:=V+1;
402 USA:=(-XTEMP)^(V-1);
403 USSA:= USSA+USA;
404 "IF" ABS(USA/USSA)>10-12 "THEN" "GOTO" AT "ELSE"
405 UAT:= XTEMP*USSA;

```

```

406 V:=0;
407 "IF" Z=0 "THEN" "GOTO" IAN;
408 BT:=V:=V+1;
409 USB:= ((-XTEMP)+(V-1))*(V/(V+1));
410 USSB:= USSB+ USB;
411 "IF" ABS(USB/USSB)>1.0-12 "THEN" "GOTO" BT "ELSE"
412 UBT:= USSB*((XTEMP)+2);
413 V:=0;
414 "IF" ZZ=0 "THEN" "GOTO" IAN;
415 CT:=V:=V+1;
416 USC:= ((-XTEMP)+(V-1))*(V/(V+2));
417 USSC:= USSC+USC;
418 "IF" ABS(USC/USSC)>1.0-12 "THEN" "GOTO" CT "ELSE"
419 UCT:= USSC*(XTEMP+3);
420 V:=0;
421 "IF" ZZZ=0 "THEN" "GOTO" IAN;
422 DT:=V:=V+1;
423 USD:= ((-XTEMP)+(V-1))*(V/(V+3));
424 USSD:= USSD+ USD;
425 "IF" ABS(USD/USSD)>1.0-12 "THEN" "GOTO" DT "ELSE"
426 UDT:= USSD*(XTEMP+4);
427 V:=0;
428 "IF" ZZZZ=0 "THEN" "GOTO" IAN;
429 ET:=V:=V+1;
430 USE:= ((-XTEMP)+(V-1))*(V/(V+4));
431 USSE:= USSE + USE;
432 "IF" ABS(USE/USSE)>1.0-12 "THEN" "GOTO" ET "ELSE"
433 UET:= USSE*(XTEMP+5);
434 IAN;
435 "IF" W=4 "THEN" "BEGIN"
436 BE:=0;
437 UET:=UEN:=0;B[1,5]:=B[2,5]:=B[3,5]:=B[4,5]:=B[5,5]:=0;
438 B[5,1]:=B[5,2]:=B[5,3]:=B[5,4]:=B[5,5]:=0;
439 "END";
440 "IF" W=3 "THEN" "BEGIN"
441 BE:=BD:=0;
442 B[1,5]:=B[2,5]:=B[3,5]:=B[4,5]:=B[5,5]:=0;
443 B[1,4]:=B[2,4]:=B[3,4]:=B[4,4]:=0;
444 B[5,1]:=B[5,2]:=B[5,3]:=B[5,4]:=0;
445 B[4,1]:=B[4,2]:=B[4,3]:=0;
446 "END";
447 "IF" W=2 "THEN" "BEGIN"
448 BE:=BD:=BC:=0;
449 B[1,5]:=B[2,5]:=B[3,5]:=B[4,5]:=B[5,5]:=0;
450 B[1,4]:=B[2,4]:=B[3,4]:=B[4,4]:=0;
451 B[5,1]:=B[5,2]:=B[5,3]:=B[5,4]:=0;
452 B[4,1]:=B[4,2]:=B[4,3]:=0;
453 B[1,3]:=B[2,3]:=B[3,3]:=0;
454 B[3,1]:=B[3,2]:=0;
455 "END";
456 "IF" W=1 "THEN" "BEGIN"
457 BE:=BD:=BC:=BB:=0;
458 B[1,5]:=B[2,5]:=B[3,5]:=B[4,5]:=B[5,5]:=0;
459 B[1,4]:=B[2,4]:=B[3,4]:=B[4,4]:=0;
460 B[5,1]:=B[5,2]:=B[5,3]:=B[5,4]:=0;
461 B[4,1]:=B[4,2]:=B[4,3]:=0;
462 B[1,3]:=B[2,3]:=B[3,3]:=0;
463 B[3,1]:=B[3,2]:=B[1,2]:=B[2,2]:=B[2,1]:=0;
464 "END";
465 DGT:= -TEMP*(YM+BA*(UAT-UAM)+BB*(UBT-UBM)

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```

466 +BC*(UCT-UCM) + BD*(UDT-UDM) +BE*(UET-UEM));
467 VARDG:= QD*(-TEMP)*SQRT((1/N)+B[1,1]*((UAT-UAM)†2)
468 +2*B[1,2]*(UAT-UAM)*(URT-UBM)+B[2,2]*((URT-UBM)†2)
469 +2*B[1,3]*(UAT-UAM)*(UCT-UCM)+2*B[2,3]*(UBT-UBM)*(UCT-UCM)uBm)
470 +B[3,3]*((UCT-UCM)†2)+2*B[1,4]*(UAT-UAM)*(UDT-UDM)+2*B[2,4]*(UE
471 *(UDT-UDM)+2*B[3,4]*(UCT-UCM)*(UDT-UDM)+B[4,4]*((UDT-UDM)†2)
472 +2*B[1,5]*(UAT-UAM)*(UET-UEM)+2*B[2,5]*(UBT-UBM)*(UET-UEM)
473 +2*B[3,5]*(UCT-UCM)*(UET-UEM)+2*B[4,5]*(UDT-UDM)*(UET-UEM)
474 +B[5,5]*((UET-UEM)†2));
475 KRCALC:= EXP(-DGT/(8.31434*TEMP))*TEMP*(1.380622*10†11)/6.62619
476 "PRINT" 'L'RATE CONSTANT=',SAMELINE,
477 SCALED(9), KRCALC;
478 LDKR:=(LN(KRCALC))/2.3026;
479 "PRINT" 'L'LOG KR=',SAMELINE, SCALED(9), LDKR;
480 "PRINT" 'L'DELTA G AT TEMP=',SAMELINE, SCALED(9), DGT;
481 "PRINT" SAMELINE, 'S3'SE=',SAMELINE, SCALED(9), VARDG;
482 DHT:= THETA*(BA+BB*XTEMP+BC*(XTEMP†2)+BD*(XTEMP†3)
483 +BE*(XTEMP†4));
484 VARDH:= QD*THETA*SQRT(B[1,1]+2*B[1,2]*XTEMP+B[2,2]
485 *(XTEMP†2)+2*B[1,3]*(XTEMP†2)+2*B[2,3]*(XTEMP†3)+
486 B[3,3]*(XTEMP†4)+2*B[1,4]*(XTEMP†3)
487 +2*B[2,4]*(XTEMP†4)+2*B[3,4]*(XTEMP†5)
488 +B[4,4]*(XTEMP†6)+2*B[1,5]*(XTEMP†4)
489 +2*B[2,5]*(XTEMP†5)+2*B[3,5]*(XTEMP†6)
490 +2*B[4,5]*(XTEMP†7)+B[5,5]*(XTEMP†8));
491 DST:= (DHT-DGT)/TEMP;
492 "PRINT" 'L'DELTA H AT TEMP=',SAMELINE, SCALED(9),
493 DHT, 'S3'SE=',SAMELINE, SCALED(9), VARDH;
494 "PRINT" 'L' DELTA S AT TEMP=', SAMELINE, SCALED(9), DST;
495 "IF" Z=0 "THEN" "GOTO" WIL;
496 DCPT:= (BB+2*XTEMP*BC+3*(XTEMP†2)*BD+4*(XTEMP†3)*BE);
497 VARCP:= QD*SQRT(B[2,2]+2*B[2,3]*2*XTEMP+B[3,3]*4*(XTEMP†2)
498 +2*B[2,4]*3*(XTEMP†2)+2*B[3,4]*6*(XTEMP†3)
499 +B[4,4]*9*(XTEMP†4)+B[2,5]*8*(XTEMP†3)
500 +2*B[3,5]*8*(XTEMP†4)+2*B[4,5]*12*(XTEMP†5)+B[5,5]*16*(XTEMP†6))
501 "PRINT" 'L'DELTA CP AT TEMP=',SAMELINE, SCALED(9),
502 DCPT, 'S3'SE=',SAMELINE, SCALED(9), VARCP;
503 "IF" ZZ=0 "THEN" "GOTO" WIL;
504 D1CPT:= (2/THETA)*(BC+BD*3*XTEMP+BE*6*(XTEMP†2));
505 VARDDCP:= (2*QD/THETA)*SQRT(B[3,3]+2*B[3,4]*3*XTEMP
506 +B[4,4]*9*(XTEMP†2)+2*B[3,5]*6*(XTEMP†2)+2*B[4,5]
507 *18*(XTEMP†3)+B[5,5]*36*(XTEMP†4));
508 "PRINT" 'L'DDELTA CP=',SAMELINE, SCALED(9),
509 D1CPT, 'S3'SE=',SAMELINE, SCALED(9), VARDDCP;
510 "IF" ZZZ=0 "THEN" "GOTO" WIL;
511 D2CPT:= (6/(THETA)†2)*(BD+4*XTEMP*BE);
512 VARDDDCP:= (QD*6/(THETA†2))*SQRT(B[4,4]
513 +8*B[4,5]*XTEMP+B[5,5]*16*(XTEMP†2));
514 "PRINT" 'L'D2DELTA CP=',SAMELINE, SCALED(9),
515 D2CPT, 'S3'SE=',SAMELINE, SCALED(9), VARDDDCPT;
516 "IF" ZZZZ=0 "THEN" "GOTO" WIL;
517 D3CPT:= (24/(THETA†3))*BE;
518 VARDDDDCP:= (QD)*(24/(THETA†3))*SQRT(B[5,5]);
519 "PRINT" 'L'D3DELTA CP =',SAMELINE, SCALED(9),
520 D3CPT, 'S3'SE=',SAMELINE, SCALED(9), VARDDDDCP;
521 WIL;
522 TEMP:=TEMP+DTEMP;
523 "IF" TEMP<371.15 "THEN" "GOTO" NEW "ELSE"
524 "IF" ZZZZ=1 "THEN" "BEGIN"
525 ZZZZ:=0;

```

```
526 "GOTO" START;  
527 "END";  
528 "IF" ZZZ=1 "THEN" "BEGIN"  
529 ZZZ:=0;  
530 "GOTO" START;  
531 "END";  
532 "IF" ZZ=1 "THEN" "BEGIN"  
533 ZZ:=0;  
534 "GOTO" START;  
535 "END";  
536 "IF" Z=1 "THEN" "BEGIN"  
537 Z:=0;  
538 "GOTO" START;  
539 "END";  
540 "PRINT" 'L2' CALCULATION COMPLETE FOR A GIVEN THETA ;  
541 THETA:= THETA + DTHETA;  
542 "IF" THETA <353 "THEN" "GOTO" START "ELSE"  
543 "END";  
544 "PRINT" 'L3' END OF GLEN TYPE ANALYSIS';  
545 "END";  
546 "END";  
836 MC  
4732 CODE  
5568 TOTAL
```

```
&RUN;  
TEMPAN  
DR0
```

```
&JOB:CH001050SUNN;MJB16;
```

```
&ALGOL;
LIBRARY
ALGOL
```

```
&LIST;
```

```
1  SUNNY;
2  "BEGIN"
3  "INTEGER" I,J,K,U,V,N,Z;
4  "READ" U;
5  "COMMENT" U IS NUMBER OF DATA POINTS;
6  "BEGIN"
7  "ARRAY" M,P,QE,X1,X2,LF1,LF2[1:N];
8  A,B,C[1:40,1:40],DEV[1:N];
9  "REAL" HW,T,R,NS,RMS,PRED,DIFF;
```

```
&UNLIST;
```

```
ITEM INSERTED
ITEM INSERTED
```

```
&LIST;
```

```
88
89
90
91  "REAL" "PROCEDURE" SUMPROD(A,B,K,N);
92  "INTEGER" N,K;
93  "ARRAY" A,B;
94  "BEGIN"
95  "INTEGER" I;
96  "REAL" S;
97  S:=0;
98  "FOR" I:=1 "STEP" 1 "UNTIL" N"DO"
99  S:=S+A[I]*(B[I]*(K-1));
100 SUMPROD:=S;
101 "END";
102
103
104 "REAL" "PROCEDURE" SUM(A,K,N);
105 "INTEGER" K,N;
106 "ARRAY" A;
107 "BEGIN"
108 "INTEGER" I;
109 "REAL" S;
110 S:=0;
111 "FOR" I:=1 "STEP" 1 "UNTIL" N"DO"
112 S:=S+(A[I]*K);
```

```

113 SUM:=S;
114 "END";
115
116
117
118
119 "PROCEDURE" HEAD;
120 "BEGIN"
121 "PRINT" 'F' CALCULATION OF GE FROM OSMOTIC COEFF';
122 'L' M, J, BLANDAMER, 'I' INPUT DATA FOR SYSTEM***';
123 "FOR" I:=1 "STEP" 1 "UNTIL" N "DO" "BEGIN"
124 "READ" HC[I];
125 "READ" PC[I];
126 "END";
127 MW:= 18.015;
128 R:=8.31434;
129 T:=298.15;
130 NS:=(10+3)/MW;
131 "FOR" I:=1 "STEP" 1 "UNTIL" N "DO" "BEGIN"
132 X2[I]:=H[I]/(HC[I]+NS);
133 X1[I]:= 1-X2[I];
134 LF1[I]:=- (PC[I]*HC[I]/NS)-LN(X1[I]);
135 "PRINT" 'I', SAMELINE, SCALED(9), 'S' I=', I, 'S' PHI=',
136 PC[I], 'S' X1=', X1[I], 'S' X2=', X2[I],
137 'S' LNF1=', LF1[I];
138 "END";
139 "END" HEAD;
140
141
142
143
144 "PROCEDURE" FIT(K);
145 "INTEGER" K;
146 "BEGIN"
147 "FOR" I:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
148 BC[I,1]:=SUMPROB(LF1,X2,I+2,N);
149 "FOR" J:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
150 AC[I,J]:=SUM(X2,I+J+2,N);
151 "END";
152 "END";
153 UNSYMDDET(K,2.0,-37,A,RMS,I,C,FAIL);
154 UNSYMSOL( K,1,A,C,B);
155 "PRINT" 'L' COEFFICIENTS';
156 "FOR" I:=1 "STEP" 1 "UNTIL" K "DO" "BEGIN"
157 "PRINT" 'I' A-COEFFICIENT=', SAMELINE, SCALED(9), 'S' I=', I,
158 'S10', BC[I,1];
159 "END";
160 "PRINT" 'I' COMPARISON OF INPUT + OUTPUT';
161 DIFF:=0;
162 "FOR" I:=1 "STEP" 1 "UNTIL" N "DO" "BEGIN"
163 PRED:=0;
164 "FOR" Z:=1 "STEP" 1 "UNTIL" K "DO"
165 PRED:=PRED+(BC[Z,1]*X2[I]+(Z+1));
166 DEVL[I]:=LF1[I]-PRED;
167 "PRINT" 'I', SAMELINE, SCALED(9), 'S' LNF1=', LF1[I],
168 'S' PRED=', PRED;
169 DIFF:=DIFF+(DEVL[I]+2);
170 "END";
171 DIFF:=SQRT(DIFF/(N-K));
172 "PRINT" 'L' STANDARD DEVIATION =', SAMELINE, SCALED(9), DIFF;

```

```

173 "END";
174
175
176
177 "PROCEDURE" EXCES(K);
178 "INTEGER" K;
179 "BEGIN"
180 "REAL" U,Q,D,H;
181 "PRINT" (' \ EXCESS FUNCTION \);
182 "FOR" I:=1 "STEP" 1 "UNTIL" N "DO" "BEGIN"
183 U:=Q:=D:=H:=0;
184 "FOR" J:=3 "STEP" 1 "UNTIL" K "DO" "BEGIN"
185 Z:=J-2;
186 U:=U+B[Z,1]*X2[I]+(J-1);
187 Q:=Q+B[Z,1];
188 D:=D+(((J-1)/(J-2))*R[Z,1]*X2[I]+(J-2));
189 H:=H+(((J-1)/(J-2))*R[Z,1]);
190 "END";
191 LF2[I]:=U-Q-D+4;
192 GE[I]:=(X1[I]*LF1[I]+(X2[I]*LF2[I]));
193 GE[I]:=R*T*GE[I];
194 "PRINT" (' \ \, SAMELINE, SCALED(9), 'S' I= \, I,
195 'S' X2= \, X2[I], 'S' LNF1= \, LF1[I],
196 'S' LNF2= \, LF2[I],
197 'S' GE= \, GE[I];
198 "END";
199 "END" EXCES;
200
201
202
203 HEAD;
204 "FOR" K:=1 "STEP" 1 "UNTIL" 20 "DO" "BEGIN"
205 "PRINT" (' \L4\ NUMBER OF PARAMETERS = \, SAMELINE, SCALED (9), K
206 FIT (K);
207 V:=K+2;
208 EXCES(V);
209 FAIL;
210 "END";
211 "END";
212 "END";
632 MC
1662 CODE
2294 TOTAL

```

```
&END;
```

```

RESULT = A
CPU TIME =0000 16.104
REAL TIME =0000 28
SLAVE SIZE = 51712
CARDS READ = 0141
PRINT LINES= 0167
DISC TRANS = 0131

```

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ABSTRACT



Rate constants for some inorganic reactions in mixed aqueous solutions were determined spectrophotometrically. The rate of aquation of the tris-(5-nitro-1,10-phenanthroline)iron(II) cation was determined in acetonitrile + water, hydrogen peroxide + water, glycerol + water and acetone + water. From the rate data thermodynamic activation parameters were calculated. The results were discussed in terms of the thermodynamic properties and structure of the aqueous mixtures. The rate data for acetone + water and t-butyl alcohol + water mixtures (data for this mixture were obtained from previously published work) have been analysed to obtain kinetic activation parameters for reaction in corresponding mixtures where the ratio of activities of the two solvent components is constant i.e. under endostatic conditions. A method is described for calculating endostatic activation parameters from kinetic data and molar thermodynamic excess functions for the binary mixture. The results of these calculations are discussed in the light of the known properties and structures of the solvent mixtures. The solvent dependence of the activation Gibbs free energy $\Delta G_{\omega}^{\ddagger}$ calculated under endostatic conditions for the aquation of the iron complex reflect changes in solvent structure more markedly than the conventional activation

activation parameter ΔG^\ddagger calculated from transition state theory. The rate of ligand substitution at chloro-(N,N,N',N'-tetraethyldiethylenetriamine) palladium(II) chloride was measured in acetonitrile + water mixtures. Rate constants were obtained for the reaction between nickel(II) and pyridine-2-azo-p-dimethyl aniline (pada) in dimethyl sulphoxide + water; also for cobalt(II) and pada in glycerol + water. These results were interpreted in terms of the structures of the mixed solvents.