A PIEZOKINETIC STUDY OF THE SOLVOLYSES OF BENZYL CHLORIDES

by

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PREFACE

The object of the work described in this thesis was to study the use of volumes of activation as a tool in the investigation of the mechanisms of solvolysis reactions. The compounds under investigation are benzyl chloride and several _para_-substituted benzyl chlorides. The solvolytic media chosen were acetone-water mixtures. A study has been made of the substituent dependence of the volumes of activation and the solvent dependence of the volumes of activation. The parameters $(\delta \Delta V^{*}/\delta P)_T$ were also calculated and the partial molar volumes of _p_-methyl benzyl chloride in solvent mixtures of different acetone composition were also measured. An attempt has been made to discuss the mechanistic implications of these results.

The candidate owes a great deal to his research director Professor K.J. Laidler, and wishes to express his gratitude for his kind and generous help in every respect.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Rate constants for the solvolysis of benzyl chloride, p-methyl benzyl chloride, p-nitro benzyl chloride and p-chloro benzyl chloride were determined at four pressures at 50°C in an acetone-water mixture containing 0.1407 mole fraction acetone. Rate constants for the solvolysis of p-methyl benzyl chloride in four acetone-water mixtures were also determined at four pressures at 50°C. The partial molar volumes of this latter compound were determined in these same acetone-water mixtures at 25°C. The $\log_{10}k$-pressure data were fitted to polynomials of the first or second order and the volumes of activation and the parameters $(\delta \Delta V^*/\delta P)_T$ were calculated.

It was found that the volumes of activation were all negative and varied with substituent in the order $p\text{-CH}_3 > \text{H} > p\text{-Cl} > p\text{-NO}_2$ and the parameters $(\delta \Delta V^*/\delta P)_T$ were zero or positive, varying in the order $p\text{-NO}_2 > p\text{-Cl} > \text{H} > p\text{-CH}_3$. Several effects which could produce this behavior were explored but it was not possible to assign these reactions to either the extreme S_N1 or S_N2 categories on the basis of these results.

It was also found that the volumes of activation for the solvolysis of p-methyl benzyl chloride in different acetone-water mixtures passed through a minimum when plotted against solvent composition. The partial molar volume of p-methyl benzyl chloride passed through a maximum as a function of solvent composition. This suggested that the minimum in the volumes of activation arose at least in part from a maximum in the partial molar volumes of the reactants.

A linear correlation between the entropies and volumes of activation is observed. This is discussed in terms of simple dielectric theory.

CHAPTER I

Introduction

Part I Studies of Chemical Reactions at High Pressures

(a) General

Solvolytic reactions are amongst the most thoroughly studied of chemical reactions. However, there remain several unresolved problems associated with the mechanism of these reactions and the indispensable role of the solvent in these processes, especially in aqueous organic mixtures. Recent advances in piezochemical studies of chemical reactions in the liquid phase have been very fruitful in throwing light on both of these aspects. The present study was undertaken with this in mind; it involves measurements of the pressure coefficients of the logarithms of the rate constants for the solvolysis of benzyl chloride and substituted benzyl chlorides in acetone-water mixtures.

(b) Some Aspects of High Pressure Studies of Chemical Reactions in the Liquid Phase

In the present chapter an exhaustive review of the rather extensive field of piezochemistry will not be attempted. Fortunately several reviews have been recently published and the reader is referred to the work of Hamann[1,2], Bradley[3], Gonikberg[4] and Whalley[5]. The latter review is concerned mainly with the mechanistic implications of high-pressure reaction-rate studies. The author, however, will attempt to review aspects of this field pertinent to the present study.

The earliest report of high-pressure studies on the rate of a chemical reaction in the liquid phase was made by Bertholet and

Pean de Saint Gilles[6]. It was shown that pressures of 50 to 100 atmospheres had no detectable effect on the rate of esterification of acetic acid by ethanol. Later work by Roentgen[7] and Stern[8] on the acid-catalyzed inversion of sucrose at 500 atmospheres indicated that in the presence of strong acids pressure had an adverse effect on the rate of inversion, whereas when weak acids were present, pressure accelerated the process. Rothmund[9], and Tamann and Bogojawlensky[10] showed that the rates of solvolysis of esters in neutral solution and acid and base catalyzed solvolysis reactions were increased at 500 atmospheres. It was also found that reactions catalyzed by weak acids and bases were affected by pressure to a greater extent than those catalyzed by strong acids and bases.

Improved equipment design permitted Cohen and his co-workers[11,12,13,14] to extend the pressure range to 1500 atmospheres. They established that changes in the rates of chemical reactions with increased pressure arose from two effects;

(1) Increasing the pressure resulted in a decrease in the volume of the reaction mixture, which in turn increased the concentration of the reactants. The resulting increase in the rate was found to be small compared to the profound changes in rate brought about by changes of pressure in the gas phase.

(2) Increasing the pressure altered the rate constants themselves, resulting in a change of reaction rate. The change in the rate constant was also found to depend on the reaction being studied.

In the nineteen thirties the extensive work of Bridgman[15] resulted in the design of equipment suitable for reaction-rate studies, and extended the range of pressures which could be used to 12,000 atmospheres. Using these new techniques Perrin and co-workers[16,17,18,19] studied the rates of a number of reactions. Perrin[19] showed that the reactions studied could be classified into three categories according to their frequency factors and the effect of pressure on their rates, as follows:

(1) "Slow" reactions - These were bimolecular reactions with very small frequency factors; they were markedly accelerated by pressure.

(2) "Normal" reactions - These were bimolecular reactions with normal frequency factors; they were slightly accelerated by pressure.

(3) Unimolecular reactions - These were slightly retarded by pressure (only one example was given).

In more recent times the design of equipment has permitted a considerably wider range of static pressures and temperatures. A notable achievement utilizing these advanced designs has been the synthesis of diamonds from other forms of carbon[20].

Developments of a theoretical nature regarding the effect of pressure on reaction rates have kept pace with developments in equipment design.

Very early Planck[21] showed thermodynamically that the equilibrium constant K of a reaction of the form

$$A + B + \text{-------} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + D + \text{-------}$$

was related to the pressure P at constant temperature by the expression

$$(\delta \log_e K/\delta P)_T = - \Delta V/RT \qquad (1.1)$$

where ΔV is the difference between the partial molar volumes of reactants and products. Van't Hoff[22] arrived at the same formula and also proposed that as the equilibrium constant was related to the rate constants k_1 and k_2 of the forward and reverse reactions respectively by the relationship

$$K = k_1/k_2 \ , \tag{1.2}$$

the expression (1.1) could be divided into two other expressions by the relationship

$$(\delta \log_e k_1/\delta P)_T - (\delta \log_e k_2/\delta P)_T = -(\Delta V_1 - \Delta V_2)/RT \ . \tag{1.3}$$

However no particular significance was accorded the quantities ΔV_1 and ΔV_2 until the development of the activated-complex theory[23]. Moesveld[24] however established that, in general, plots of the logarithm of the rate constant against pressure were not linear. He found that data could be best fitted to polynomials of the second degree.

Evans and Polanyi[25] suggested on the basis of the activated-complex theory that the rate of change of the logarithm of the rate constant with pressure at constant temperature was directly proportional to the difference between the sum of the partial molar volumes of the reactants, $\sum_g \overline{V}_g$, and the partial molar volume of the activated complex, $\overline{V}_t$, or;

$$(\delta \log_e k/\delta P)_T = -\Delta V^*/RT \ , \tag{1.4}$$

where $$\Delta V^* = \overline{V}_t - \sum_g \overline{V}_g \ . \tag{1.5}$$

ΔV^* was called the volume of activation. To facilitate the discussion of this activation parameter on a molecular level, it was suggested that ΔV^* might also be divided in another manner into two terms:

$$\Delta V^* = \Delta V_1{}^* + \Delta V_2{}^* \ . \tag{1.6}$$

ΔV_1^* is the contribution to ΔV^* due to changes in the volumes occupied by the reactant molecules during the activation process, and ΔV_2^* is the contribution to ΔV^* due to changes in the organization of solvent molecules about the reactant molecules while forming the activated complex.

Considerable effort has been spent in measuring and estimating the relative contributions of ΔV_1^* and ΔV_2^* to the volumes of activation of different reactions. Although these efforts have not been successful quantitatively, several phenomena making important contributions to both terms have been identified. These have been discussed by Whalley[5a]. In our present study it is expected that contributions to ΔV_1^* due to bond stretching and bond forming, and contributions to ΔV_2^* due to electrostriction, may be important. Consequently some of the work associated with the experimental and theoretical estimations of ΔV_1^* and ΔV_2^* in these terms will be considered.

The contributions to ΔV_1^* due to bond forming and bond breaking have been estimated from theoretical considerations in two ways. Stearn and Eyring[26] have considered the reactant molecules in solution as occupying a volume within which they are free to move without collision with other solvent molecules and which is maintained because of the motion of the reactant molecules. Restriction of this motion in the process of bond formation results in a reduction of the volume occupied by the species. The resultant effect is a constriction of the whole system. For similar reasons bond breaking results in a net increase in volume. For a unimolecular reaction in which bond breaking is occurring they derived the relationship

$$\Delta V_1{}^* = 0.1\, l^* V/(\sum_i l_i + r_1 + r_2 + 1) \quad , \tag{1.7}$$

and for a bimolecular reaction in which bond breaking and bond forming are taking place they derived the relationship

$$\Delta V_1{}^* = -l^* \sum V/(\sum_i l_i + \sum_j r_j + 2) \quad . \tag{1.8}$$

The l_i's are the bond lengths taken in the direction of the reaction; the r_j's are covalent or ionic radii, and the V's are the molar volumes of the reactants. The molar volumes of the reactants are assumed not to change on solution. When applied to reactions where large changes in polarity are not expected in the activation process, good agreement was observed between experiment and theory. Buchanan and Hamann[27] have shown however that agreement between theory and experiment, when large differences between the polarity of the reactants and transition state are to be expected, is probably fortuitous. The above theory does not take into account electrostriction of solvent. It was found by Hamann and his co-workers[27,28,29,30] and Burris and Laidler[31] that in these cases increased pressure affects the free energy of hydration of strongly solvated species, resulting in a change of reaction rate (see below).

Hamann[2a] has suggested the following method of estimating ΔV_1^*. The volume increase due to partial bond breaking, ΔV^*_{1B}, is considered to be equal to the volume of a cylinder whose length, δl is the difference between the bond distance in reactant and transition state of the bond which is breaking and whose cross-sectional area is the arithmetic mean of the cross-sectional areas of the separating atoms, i.e.

$$\Delta V^*_{1B} = (r_A^2 + r_B^2)\ \delta 1/2. \qquad (1.9)$$

The volume decrease due to partial bond formation, ΔV^*_{1F}, is considered to be equal to the volume of a cylinder whose length, δ 1, is the difference between the sum of the van der Waals radii of the atoms between which bond formation is taking place and the bond distance between these atoms, in the activated state. The cross-sectional area of the cylinder is considered to be the same as above. The relationship then becomes

$$\Delta V^*_{1F} = - (r_A^2 + r_B^2)\ (r_A + r_B - 1 - \delta 1)/2. \qquad (1.10)$$

In equations (1.9) and (1.10)r_A and r_B are the van der Waals radii of the atoms between which the bond is breaking or forming.

The estimate of ΔV^*_1 from either of the above methods is quite crude. In addition to other difficulties, the calculated values depend strongly on the choice of the partial covalent bond distance in the activated state. Hamann[2a] has shown that potential-energy-surface calculations of several reactions indicate that there is a considerable variation in the degree of bond stretching which can occur in the activation processes. Calculations using reasonable values of the activated-state partial-covalent-bond distance leads to magnitudes of ΔV^*_1 which compare favorably with the results of studies of reactions where large changes in polarity do not occur.[2a]

The importance of ΔV^*_2 in ionogenic reactions has been established from studies of chemical equilibria and reaction rates by

Hamann and co-workers[27,28,29,30] and Laidler and co-workers [31,32,33]. Perrin's[19] classification was also recognized to be based on the differences in polarity between reactants and activated state. A more complete classification along these lines has been given by Hamann[1].

In order to estimate ΔV_2^*, reliance has been placed on the Born[34] and Kirkwood[35] models for calculating the free energy of charging a conducting sphere in a medium of static dielectric constant D. In each of these cases the reactant or activated complex is considered to occupy a spherical cavity in the solvent of fixed dimensions, and within this sphere centers of charge are distributed at known positions (shapes other than spheres have been successfully treated although the latter shape is mathematically the simplest case[36]).

ΔV_2^* for a reaction of the type

$$A\text{-}B \longrightarrow \overset{\delta+}{A}\text{---}\overset{\delta-}{B} \longrightarrow \text{Products} \quad ,$$

has been given by Heydtmann and co-workers[37] in terms of the Kirkwood expression by the relationship

$$\Delta V_2^* = N(\mu^2/r^3 - \mu_*^2/r_*^3)\ \delta[(D-1)/(2D+1)]/\delta P + \delta\phi/\delta P \ , \qquad (1.11)$$

where N is Avogadros number; μ and r represent the dipole moment and radius of the reactant molecules; μ_* and r_* are the same quantities for the activated complex; D is the static dielectric constant of the medium; and ϕ is a term containing expressions for other polar interactions which for purposes of their study was considered negligible. It has also been assumed in this expression that $1/r(\delta r/\delta P)_T = 0$. This assumption has been recently discussed by Whalley[38].

Heydtmann and co-workers[37] have tested this relationship from studies of Menschutkin reactions in different solvents and non-aqueous mixtures. They showed that plots of $\delta[(D-1)/(2D+1)]/\delta P$ versus ΔV^* were linear in many cases. In solvents where specific interaction between the solvent and reactant molecules or activated complexes are expected, deviations from the usual straight line were observed.

David and Hamann[39] have also shown that dielectric theory is useful in predicting trends within a given series of reactions in the same solvent. The volumes of activation for the ethanolysis of ethyl halides in ethanol solution become more negative as the halide atom is changed from iodine to bromine to chlorine. This is the expected order of increase of field intensity about these partially ionic species, and the observation was taken as an indication of the high polarity of the activated complexes for these reactions.

Equation (1.11) also predicts that reactions characterized by large differences in polarity between reactants and activated complex will have volumes of activation which are strongly dependent on solvent change. Brower[40] has confirmed this conclusion. He found that in reactions where ions were created or destroyed the variation of the volume of activation with solvent change resembled in magnitude and kind the variation of the partial molar volumes of electrolytes in the same solvents.

The use of the Kirkwood expression in correlating volumes of activation in different solvents has many shortcomings especially in aqueous organic mixtures. These will be explored in Chapter 2 of this thesis. One of the difficulties is that in order to calculate ΔV_2^* from first principles one must have a knowledge of the charge distribution within an activated complex. Several workers have chosen reasonable charge distributions within molecules, and have estimated ΔV_2^* to be of the order 10 to 30 cm^3 per mole when the change in polarity between reactants and activated complex is 1 electrostatic unit. This is to be compared with an estimate of 26 cm^3 per mole by Couture and Laidler[41] from an empirical correlation of the partial molar volumes of ions.

(c) Formal Derivation of the Volume Parameters of Chemical Reactions from Piezokinetic Studies and Density Measurements of Solutions of Reactants

Both the collision theory and activated-complex theory of chemical reactions may be used as a starting point for deriving the volume parameters of a chemical reaction. The latter theory has however been found to be the most convenient and easily visualized means of discussing ΔV^*. This is, in part, due to the fact that this theory focuses attention on a species of higher energy, intermediate between the reactants and products of an elementary reaction. Furthermore, we may talk about partially formed or partially broken bonds in the activated complex. In any case, the activated-complex theory and collision theory have been shown to give essentially equivalent results[42].

From the point of view of the activated-complex theory, in a general reaction

$$aA + bB + \cdots \longrightarrow X^{*} \longrightarrow mM + nN + \cdots ,$$

the molecules A and B are considered to proceed to products M and N through a molecular species X^* of maximum potential energy. The rate of formation of products is proportional to the concentration of activated species X^* , and the species A, B and X^* are considered to be in equilibrium with one another at any time during the reaction. Allowing for the fact that one of the vibrational degrees of freedom is very loose in the activated complex, the rate constant for the forward direction in the above reaction can be divided into kinetic and thermodynamic terms, i.e.

$$k = \kappa \, \underline{k} \, T \, K^{*}/ h \quad , \qquad (1.12)$$

where k is the specific rate constant, $\underline{k}$ is the Boltzmann constant, h is Planck's constant and κ is the "transmission coefficient". (A statistical factor may also be involved, as recently discussed by Bishop and Laidler[43]). The "transmission coefficient" is usually close to unity for most reactions, and following Eyring[26] we will assume that it is independent of pressure and temperature. K^* is defined as:

$$K^{*} = [X^{*}] / [A]^{a} [B]^{b} \qquad (1.13)$$

Differentiating equation (1.12) with respect to pressure at constant temperature we obtain the relationship

$$(\delta \log_e k/\delta P)_T = (\delta \log_e K^{*}/\delta P)_T \quad . \qquad (1.14)$$

The chemical potential of any species in the reaction mixture is given by

$$\mu_A = \mu_A^o + RT \log_e a_A \quad , \qquad (1.15)$$

where μ_A^o is the chemical potential of the standard state, which for convenience in the present work is chosen to be the infinitely dilute solution; a_A is the activity of species A which in the dilute solutions used in this work is considered to be equal to the molar concentration of A. In order for the reactants and activated complex to be in equilibrium with one another the chemical potential of the activated state must be equal to the sum of the chemical potentials of the reactants. Therefore

$$RT \log_e K^* = RT \log_e [X^*]/[A]^a[B]^b = a\mu_A^o + b\mu_B^o + \text{----} - \mu_X^o{}^*. \qquad (1.16)$$

The concentration scale usually used in kinetic measurements is the molar scale. Consequently, differentiating equation (1.16) with respect to pressure at constant temperature we obtain the relationship

$$(\delta\, RT \log_e K^*/\delta P)_T = (a\overline{V}_A^o + b\overline{V}_B^o + \text{---} - \overline{V}_X^o{}^*) + (1-a-b\text{---})\, \beta_s RT$$

$$= -\Delta V^* + (1-a-b\text{----})\, \beta_s RT\ , \qquad (1.17)$$

where the $\overline{V}_j^o$'s are the partial molar volumes of the respective solute species in their standard states. They are related to the chemical potential of any species "J" in its standard state by the relationship

$$(\delta\, \mu_J^o/\delta P)_T = \overline{V}_j^o \quad . \qquad (1.18)$$

β_s is the isothermal compressibility of the solution in which the reaction is taking place. It is defined at any pressure by

$$\beta_s = -\, 1/V_s(\delta V_s/\delta P)_T\ . \qquad (1.19)$$

V_s is the volume of the solution at pressure P. The term in β_s arises because of the choice of concentration units. The term in equation (1.17) involving the compressibility is zero in the present study, as the reactions being studied are first order. This term however can amount to a considerable correction in reactions of higher order. ΔV^*, the volume of activation, is then the excess of the partial molar volume of the activated complex over that of the sum of the partial molar volumes of the reactants, all in their standard states.

Substitution of equation (1.17) into equation (1.14) gives the following relationship between the specific rate constant k and the volume of activation:

$$(\delta\ RT \log_e k/\delta P)_T = -\Delta V^*. \tag{1.20}$$

In order to understand changes in ΔV^* with the change of some other variable it is helpful to have some knowledge of the manner in which $\overline{V}_t$ and $\overline{V}_g$ change. By the very nature of the activated complex it is impossible to directly measure the partial molar volume of this species. However, given a method which can quickly measure the density of a solution of reactant accurately, the partial molar volumes of the reactants can be measured as a function of solute concentration and extrapolated to infinite dilution. A study using a method whereby the volume of a solution can be measured accurately and quickly after addition of solute molecules has recently been reported by Golinkin[44]. It will be shown in Chapters 3 and 4 that a method utilizing density measurements of solutions of reactants can be used to accomplish this work. The relationship between solution density and reactant partial molar volume may be developed as follows.

It is well known that extensive properties of a system, e.g., volume, entropy, free energy etc., are functions of physical variables such as pressure, temperature and also the quantities of the different components. In the case of a solution at constant temperature and pressure, the total volume V of the system may be written differentially in terms of the contributions from the different constituents as:

$$dV = (\delta V/\delta n_1)_{T,P}\ dn_1 + (\delta V/\delta n_2)_{T,P}\ dn_2 + (\delta V/\delta n_3)_{T,P}\ dn_3 + \text{---}$$
$$\text{--} + (\delta V/\delta n_i)_{T,P}\ dn_i + \quad , \qquad (1.21)$$

where n_i is the number of moles of constituent i. The term $(\delta V/\delta n_i)_{T,P}$ is called the partial specific, partial molar, or partial molal volume depending on the units in which n is expressed and is usually denoted by the symbol $\overline{V}_i$. The partial volume quantity $\overline{V}_i$ may be considered as the increase in volume of the solution when one mole of constituent i is added to such a large volume of solution that the composition of the solution remains effectively unchanged.

In the present work the partial molar volumes of p-methyl benzyl chloride are measured in a series of acetone-water mixtures of differing composition. The method chosen to measure the partial molar volume in each solvent is to measure the density of a series of solutions over a range of solute concentrations. As the number of moles of acetone and water remain constant for each series of density readings, the following approach to the measurements can be made. The apparent partial molar volume ϕ_o is defined by the equation

$$\phi_o = (V - n\, V_1^o)/n_2 \qquad (1.22)$$

where V_1^o is the molar volume of the solvent, defined in this case as the sum of the volumes of acetone and water in a given mixture divided by the sum of the numbers of moles of acetone and water in that mixture. n is the sum of the number of moles of acetone and water in the solvent mixture being studied. V is the volume of the solution and n_2 is the number of moles of solute. The quantity ϕ_o is related to the partial molar volume $\overline{V}_2$, as is the ratio of finite increments to the corresponding differential coefficient. If the concentration of the solution $c = n_2/V$ is expressed in moles per litre, equation (1.22) may be written as

$$\phi_o = 1000(d_o - d)/cd_o + M_2/d_o \ , \qquad (1.23)$$

where d_o is the density of the pure solvent, d is the density of the solution and M_2 is the molecular weight of the solute.

It can also be seen from equation (1.23) that

$$V = n_2\phi_o + n\,\overline{V}_1^o \qquad (1.24)$$

and consequently the partial molar volume of the solute at any concentration may be obtained from

$$\overline{V}_2 = (\delta V/\delta n_2)_{n,T,P} = \phi_o + n_2(\delta \phi_o/\delta n_2) \qquad (1.25)$$

This shows that at infinite dilution, i.e., $n_2 \longrightarrow 0$, the partial molar volume becomes identical with the apparent partial molar volume.

Knowing the partial molar volumes of the reactants, a full analysis of ΔV^* data is possible in terms of the partial molar volumes of the reactants and activated complex. Hence any variations of ΔV^* with change in solvent composition or substituent may be considered in terms of changes in the partial molar volumes of the reactants and activated complex.

Part II Some Aspects of Solvolytic Reaction Mechanisms and the Mechanism of the Solvolysis of Benzyl Chloride in Aqueous Organic Mixtures

(a) General

Several general reviews have been written recently on solvolytic reactions[45,46] and most textbooks on physical organic chemistry include some discussion of this subject[47,48]. To review this work at this point is therefore inappropriate. There are however some areas of controversy, as has been indicated in Part I of this chapter, which have direct bearing on the present work and should be considered. Moreover, as the solvolysis reactions of benzyl chloride and substituted benzyl chlorides have been studied frequently, these reactions will be used to illustrate the problems wherever possible. Finally a brief summary of the work which has led us to our present understanding of the mechanisms of these latter reactions will be presented.

(b) Mechanisms of Solvolytic Reactions

Solvolytic reactions are examples of nucleophilic substitution reactions, which are characterised by the fact that the electrons in the bond to be broken remain associated with the departing group, X, while a new bond is formed by co-ordination of the nucleophile, Y, with the substrate:

$$Y: \quad + \quad C : X \;\text{———}\; Y : C \quad + \quad :X$$

(The dots represent electrons)

There is no restriction on the charges on the substrate or nucleophile provided that the electron displacements occur in the above manner. Thus the following process is a nucleophilic substitution:

$$RCl + H_2O \longrightarrow ROH + H^+ + Cl^-$$

These reactions have been discussed in terms of two mechanisms[49]; (a) the so-called S_N1 mechanism and (b) the S_N2 mechanism. The first of these mechanisms is characterised by a slow reversible endothermic fission of the C-X bond followed by a fast exothermic recombination step involving the nucleophile Y. The large activation energy required for the gas phase heterolysis of the C-X bond is reduced to accessible values in solution by solvation of the polar activated complex[50]. This is illustrated by the following scheme:

$$R\text{-}CH_2\text{-}X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R\text{-}CH_2^+ + X^-$$

$$R\text{-}CH_2^+ + Y^- \xrightarrow{k_2} R\text{-}CH_2\text{-}Y$$

On the assumption that the $R\text{-}CH_2^+$ concentration reaches a steady state, the rate of formation of products is given in terms of the $R\text{-}CH_2\text{-}X$, Y^- and X^- concentrations by

$$d[R\text{-}CH_2\text{-}Y]/dt = k_1k_2[R\text{-}CH_2\text{-}X][Y^-]/(k_{-1}[X^-] + k_2[Y^-]). \qquad (1.26)$$

This rate is equal to $k_1[R\text{-}CH_2\text{-}X]$ if $k_2[Y^-] \gg k_{-1}[X^-]$. Mechanism S_N1 is known to operate in the solvolysis of tert-butyl chloride in aqueous acetone.[51]

The S_N2 mechanism involves the fission of the C-X bond at the same time as the new bond C-Y is formed, i.e.

$$Y^- + R\text{-}CH_2\text{-}X \xrightarrow{k_3} R\text{-}CH_2\text{-}Y + X^-$$

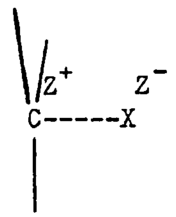
The rate of formation of products in terms of the concentration of $R\text{-}CH_2\text{-}X$ and Y^- is given by

$$d[R\text{-}CH_2\text{-}Y]/dt = k_3[R\text{-}CH_2\text{-}X][Y^-], \qquad (1{\cdot}27)$$

which is equal to $k_4[R\text{-}CH_2\text{-}X]$ if the concentration of Y^- is very large compared to that of $R\text{-}CH_2\text{-}X$ ($k_4 = k_3[Y^-]$). This is usually the situation in studies of solvolysis reactions. In this case two molecules undergo covalency change on passage from the initial state to the activated complex. An example of a reaction by this mechanism is that of the solvolysis of methyl bromide in aqueous ethanol.[50]

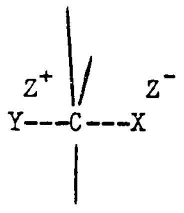
Typical activated complexes for S_N1 and S_N2 reactions are given below

(a)



S_N1

(b)

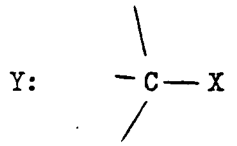


S_N2

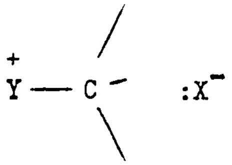
Hinshelwood, Laidler and Timm[52] recognised very early that the S_N1 activated complex is just a special case of the S_N2 activated complex; the activated complexes of different reactions occurring by this latter mechanism were considered to differ in the degree of charge development and in the degrees of bond stretching and bond formation. Consequently, a continuous series of S_N2 activated complexes, qualitatively similar but quantitatively different, was envisaged. Several more recent discussions along these lines have been given[53,54] and many of the results of studies varying the groups Y, $R\text{-}CH_2\text{-}$ and X as well as solvent conditions may be readily understood in these terms. Some of these conclusions with regard to benzyl chloride solvolysis will be considered below.

From what has been said above,it can be concluded that a region of transition from mechanism S_N2 to S_N1 is expected to exist. This region has frequently been referred to as the borderline region. The precise nature of the reaction path in this region is of considerable interest to the present study as the solvolysis of benzyl chloride is frequently discussed in these terms. Two alternatives have been proposed for the nature of the reaction path in this region. Firstly all individual acts may proceed through a single reaction path. The activated complex is regarded as a resonance hybrid of all the following three canonical forms[55]

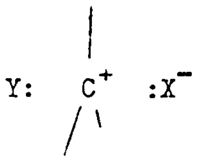
(I)



(II)



(III)



The greater the contribution from structure (III) relative to (II), the more S_N1-like the activated complex. The second alternative is that a variety of reaction paths are available, some of which involve contributions from structure (II) while others do not. Hence it is possible for a reaction to occur by the concurrent operation of mechanisms S_N1 and S_N2. So far, no unambiguous experimental evidence in favour of either of these alternatives is available for solvolytic reactions although both possibilities have been proposed[56,57,58,59,60]. However, evidence for the concurrent operation of mechanisms S_N1 and S_N2 has been obtained for reactions where more powerful nucleophiles other than solvent molecules have been present[56,61,62].

(c) Methods used for the Recognition of Mechanism in Solvolytic Reactions

In solvolytic reactions, where the solvent water is usually present in large excess, the usual methods of determining the order of the reaction with respect to water concentration are not available. Indirect methods must be employed in order to obtain information about the mechanism. Several methods are available, namely,

(i) Structural changes in the group R,
(ii) Systematic variations in the nucleophile Y,
(iii) Following the stereochemical course of the substitution,
(iv) The effect of electrolyte additions and solvent changes on the rate of reaction,
(v) The study of the activation parameters of these

reactions, and more recently the measurement of the ratio of the heat capacity of activation, ΔC_p^*, to the entropy of activation, ΔS^*.

The present study is to investigate the potential use of the volume of activation of chemical reactions in this connection.

(d) Activation Parameters and the Enthalpy - Entropy Compensation Effect

The simple discussion of activation parameters in terms of mechanism is open to some question. The problem of a meaningful discussion of such results in these terms has been considered many times and is discussed in some detail by Grunwald and Leffler[63]. The problem may be illustrated using previous studies of benzyl chloride solvolysis.

The data of Tommila and his co-workers[54] for the solvolysis of benzyl chlorides in acetone-water mixtures show clearly that, with change of solvent composition, the entropies and enthalpies of activation for the solvolysis of benzyl chloride in acetone-water mixtures show extremum behaviour. The free energies of activation do not show such behaviour but increase with increasing acetone concentration. This is an example of the entropy - enthalpy compensation effect (not complete in this case). This phenomena has been observed several times and is in many cases responsible for the observation of linear free energy relationships.

The behaviour of the free energy of activation is apparently simple and changes in the free energy function with systematic variation in reaction conditions have been interpreted simply in terms of reaction mechanism and changes in the properties of the activated complex. Laidler[53] has shown that the variation of the free energies of activation for the solvolysis of benzyl chloride with dielectric constant in acetone - water mixtures is consistent with the activated complex of the reaction being S_N1-like in the region of high dielectric constant but S_N2-like in the region of low dielectric constant. Tommila and co-workers[54] have shown that the variation of the free energies of activation of benzyl chloride solvolysis with change in substituent in a mixture of constant composition is consistent with the p-nitro benzyl chloride activated complex being more S_N2-like than the p-methyl benzyl chloride activated complex. As the dielectric constant of the mixture decreases the S_N2 character of the p-nitro benzyl chloride activated complex becomes more distinct from that of the p-methyl benzyl chloride activated complex, which is still somewhat S_N1 in character.

The extremum behaviour of the other activation parameters is frequently ascribed to specific solvent effects. Studies by Hyne and co-workers[64,65,66] have shown that the entropies, enthalpies and volumes of activation for the solvolysis of benzyl chloride and substituted benzyl chlorides in ethanol - water mixtures display extrema as a function of solvent composition. Moreover it has been shown that the positions of the extrema for each of the activation parameters do not generally coincide on the solvent composition axis. The positions of the extrema were also shown to shift on the solvent composition axis with change of substituent and with change of the position of substitution on the aromatic ring. Furthermore recent experiments by Hyne and Golinkin[67] and Arnett et al.[68] have shown that in many cases this extremum behaviour in the activation parameters is due in large measure to extremum behaviour in the partial thermodynamic function of the reactant with change in solvent composition. Further discussion of these latter observations will be deferred to Chapter 2 but it is apparent that trends in activation parameters with systematic variations in reaction conditions must be interpreted cautiously in terms of simple reaction mechanism.

An approach to the discussion of the present results will be made utilizing the following suggestions made by Laidler[69] based on the results of measurements of the heats of dissociation and free energies of dissociation of some organic acids in aqueous solution[70,71,72,73] and other theoretical considerations:

(1) Purely polar effects arising from inductive and mesomeric influences are considered to affect ΔH^* but not ΔS^*, ΔV^* and ΔC_p^*. They therefore have no effect on $T\Delta S^*$ or $P\Delta V^*$ but affect ΔH^* and ΔG^* in an exactly parallel manner. Polar effects on ΔH^* are additive. Hence if polar effects were involved alone, both ΔH^* and ΔG^* would be additive and linear-free-energy relationships would be observed. This has been assumed to be the case by Dewar and Sampson[74] in their theoretical treatment of alkyl halide

solvolysis reactions.

(2) Steric effects, such as those arising from the interference between an ortho substituent and the functional ionizing group, are considered to affect ΔH^*, ΔS^*, ΔV^* and ΔC_p^*. They therefore affect ΔG^*, ΔH^*, ΔS^* and ΔV^* in a complicated manner. As a result there is a loss of additivity, and the relationship between the free energies in different series may not be linear.

Under certain circumstances there is an approximate compensation between the changes in ΔH^* and $T\Delta S^*$, so that the influence on ΔG^* is fairly small. Additivity relationships and linear free-energy relationships are therefore still found in ΔG^*, but additivity is lost in ΔV^*, ΔH^* and $T\Delta S^*$.

(3) Solvent effects arising from solvent-solute interactions, and specific solvent interactions between solvent and parts of the reacting molecules, are also considered to change ΔH^*, ΔS^* and ΔV^*. As with steric effects, compensating changes in ΔH^* and $T\Delta S^*$ may occur. These solvent effects do not necessarily destroy the additivity or free-energy relationship in ΔG^*, but may destroy the additivity as far as ΔH^*, ΔV^* and $T\Delta S^*$ are concerned.

Hepler and co-workers[75,76] have given a clear-cut quantitative discussion of the data of Chen and Laidler[77] and Papée _et al._[71] in terms such as these.

Baliga and Whalley[78] have proposed that the constant-volume activation parameters are more easily understood than the constant-pressure parameters which have been discussed above.

(e) The Mechanism of Solvolysis of the Benzyl Chlorides

In an earlier section (Part IIb) it has been pointed out that there is no sharp dividing line between an S_N1 and S_N2 mechanism, the S_N1 mechanism being essentially the limiting case of an S_N2 mechanism. As a result, many reactions exhibit some behaviour which, if considered on the basis of a sharp division between S_N1 and S_N2 mechanisms, would suggest an S_N1 mechanism, and at the same time exhibit other behaviour suggesting an S_N2 mechanism. This appears particularly true of benzyl chloride solvolysis, for which it is impossible to interpret all the results in terms of either an extreme S_N1 or an extreme S_N2 mechanism. The mechanism is therefore an intermediate one. In the present section the experimental evidence on benzyl chloride hydrolysis is briefly summarized, whether the behaviour points towards an extreme S_N1 or an extreme S_N2 mechanism.

Evidence that seems to point towards S_N1 behaviour is as follows:

(1) Bennett and Jones[79], Olivier[80] and Tommila and co-workers[54] found that the order of reactivity with para-substituents is

$$\underline{p}\text{-}CH_3 > H > \underline{p}\text{-}Cl > \underline{p}\text{-}NO_2 \ .$$

This is the order of ease of ionization of the C-Cl bond, so that this evidence is consistent with S_N1 behaviour (see, however, point 2' below). Bensley and Kohnstam[81] similarly found that α-chlorination increases reactivity, a result which also points to S_N1 behaviour.

(2) Charleton and Hughes[82] studied the effect of

successive o-methylation on the rate of benzyl chloride solvolysis, and they found that the presence of a single o-methyl group increases the rate to a similar extent to p-methylation, and that the substitution of a second o-methyl group gave a rate increase of the same magnitude as that observed after the first methylation. There appears therefore to be little steric interference of the reaction, a result which points towards an S_N1 mechanism.

(3) The rate of reaction is reduced by the addition of chloride ion salts but accelerated by the addition of non-common ion salts[83]. This behaviour suggests the operation of a common ion effect. This is also consistent with an S_N1 mechanism, for which the initial equilibrium

$$RCl \rightleftharpoons R^+ + Cl^-$$

is shifted to the left by the addition of chloride ions. This observation however must be treated with some reserve because of the very complex nature of salt solutions of aqueous organic mixtures (see for example Coburn et al.[84] and Jackson[85]).

(4) Roberts and Hammett[86] have studied the effect of added mercury salts on the solvolysis of benzyl chloride in aqueous dioxane mixtures. They observed, during the course of the reaction, the development of a transient yellow colour ascribed to complex formation between the carbonium ion, formed by dissociation of the benzyl chloride, and the mercury ions.

(5) Hill and Fry[87] studied the Cl_{37} and Cl_{35} isotope effects on the rates of solvolysis of a series of substituted benzyl chlorides,

finding the k_{35}/k_{37} ratio to be the same for all of the compounds studied. Furthermore, they argue that the ratio observed is that expected for a purely S_N1 mechanism. However, Thornton[88] has cast some doubt on their conclusion that the mechanisms are purely S_N1, on the grounds that strong solvation effects may be influencing the chlorine isotope ratios.

The following evidence points away from a pure S_N1 mechanism, and suggests an intermediate mechanism with some marked S_N2 characteristics:

(1') Olivier and Weber[89], Beste and Hammett[83] and Tommila and co-workers[54] found that the addition of hydroxide ion leads to a considerable increase in the rates of a number of benzyl chloride hydrolyses. These results indicate that an S_N2 reaction occurs in the presence of OH^- ions. They provide no direct evidence that hydrolysis by water molecules is S_N2, but are not inconsistent with this[56,61,62,].

(2') Bensley and Kohnstam pointed out that the substituent effects (point 1 above) are associated with changes in the entropy of activation ΔS^* rather than in ΔH^*. If the mechanisms were purely S_N1 the effect would be largely on ΔH^*.

(3') Bensley and Kohnstam measured the ratio $\Delta C_p^*/\Delta S^*$ for the solvolysis of benzyl chloride in different solvent mixtures, and found the ratio to be independent of the solvent. The ratio is lower than for reactions whose mechanisms were largely S_N1 (e.g. the solvolysis of $C_6H_5CHCl_2$ and $C_6H_5CCl_3$), so that Kohnstam concluded that benzyl chloride did not react by a purely S_N1 mechanism[91]. Some additional discussion of these measurements is given by Robertson and Scott[92] and Cowie et al.[93].

(4') Bensley and Kohnstam[81] also found that α-chlorination does not increase the rate of benzyl chloride solvolysis as much as does α-chlorination of benzylidine chloride ($C_6H_5CHCl_2$). The solvolysis of benzylidine chloride has most of the characteristics of a largely S_N1 reaction, so that Bensley and Kohnstam conclude that the solvolysis of benzyl chloride is not purely S_N1.

(5') Tommila and co-workers[54] showed that the sensitivity of the rate constants of different substituted benzyl chlorides to change of solvent composition in acetone - water mixtures is in the order

$$\underline{p}\text{-CH}_3 > \text{H} > \underline{p}\text{-Cl} > \underline{p}\text{-NO}_2$$

In more aqueous mixtures the rates are higher with $\underline{p}$-CH_3 than with $\underline{p}$-NO_2, and as the mixture is made less aqueous the $\underline{p}$-CH_3 rates are reduced more than the $\underline{p}$-NO_2 rates. These results cannot be explained on the basis of a pure S_N1 or a pure S_N2 mechanism, but only if the change in solvent is bringing about a change of mechanism. The solvolyses will have more S_N1 character in the case of $\underline{p}$-CH_3 and the more aqueous mixtures; making the solvent less aqueous will make the hydrolysis of p-methyl benzyl chloride less S_N1-like. The hydrolysis of p-nitro benzyl chloride is already more S_N2-like, and the solvent effect is less. In the limit, when the water concentration is low, one would expect the mechanisms to show extreme

S_N2 behaviour, and the p-NO_2 compound to hydrolyse more rapidly than the p-CH_3 compound[53].

Bensley and Kohnstam[90] have also noted that the solvent effects on the benzyl chloride solvolyses are intermediate between those on the solvolysis of t-butyl chloride, which is S_N1, and those on the solvolysis of ethyl bromide, which is S_N2. This also suggests that the benzyl chloride solvolysis occurs by an intermediate mechanism.

The evidence reviewed above makes it clear that benzyl chloride solvolysis cannot be interpreted in terms of its being an extreme S_N1 mechanism, or an extreme S_N2 mechanism. An intermediate type mechanism must occur as mentioned previously, with a shift in the importance of the S_N1 and S_N2 components as the conditions are varied.

CHAPTER 2

Properties of the Acetone-Water System and their Importance in Determining the Magnitudes of Activation Parameters

(a) General

For many reactions in aqueous organic mixtures it is found that plotting log k against (D-1)/2D+1) results in a straight line. However in many instances this relationship is not observed and the Kirkwood expression is not valid especially when reaction rates in different solvent mixtures of various dielectric constants are compared. More serious discrepancies also appear. Feakins and Watson[94] and Grunwald and co-workers[95] have found that dielectric theory incorrectly predicts the variation of the free energies of hydration of anions and cations with change in solvent composition.

The use of bulk dielectric constants in correlating reaction rate constants may be questioned on other grounds. It has been found that the bulk dielectric constant of a substance is a strong function of electrical field[96]. Moreover it has been shown that a large part of the free energy of charging a sphere (assumed to be a model of an ion in solution) in a liquid is made up by bringing the charge through this region of the ionic field[96]. It is this region in the immediate vicinity of a reactant molecule or activated complex which is kinetically significant. The use of the bulk dielectric constant is therefore questionable in such correlations. The situation is even more complex in solvent mixtures due to the possibility that a reactant or activated complex may be solvated mostly by one of the components of the liquid mixtures, a phenomenon known as selective solvation[97]. The solvent composition in the immediate vicinity of the ion is then quite different from that in the bulk solvent and should have quite different dielectric properties.

Considerable interest has been shown recently in the study of the properties of aqueous organic mixtures and their solutions. Some speculation as to the kinetic significance of these results has also arisen. It is with this in mind that the following review of acetone-water properties is given. This was aided considerably by reviews written by Bobtelsky and co-workers[98] and Franks and Ives[99] for aqueous ethanol mixtures. As in the latter work considerable weight is also attached to recent structural theories of liquids, as considerable success has been met in the understanding of the properties of liquids, water in particular, using this approach and there is ample indication that the properties of aqueous organic mixtures, at least in the region of high water content, can be understood in these terms.

(b) Properties of Water

The anomalous properties of water, (a) maximum density at 4°C, (b) high dielectric constant, (c) high heat capacity, (d) high viscosity, (e) high thermal conductivity and (f) high critical temperature, etc. together with its differences from deuterium oxide, have received considerable attention in recent years in efforts to understand the intermolecular forces which bind water molecules together. The initial structural model of water was presented in a paper by Bernal and Fowler[100]. Since this time considerable numbers of structural models for the water system have been considered, many of which have considerable aspects to recommend them.

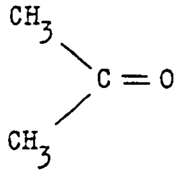
The essential features of these models are; (1) Each distinguishes two types of water in equilibrium with one another. There are ordered regions of low density which have been described as "flickering clusters"[101], broken down clathrate cages[102] or some other pseudo-crystalline configuration. There are also less ordered regions, of higher density, containing non-hydrogen bonded water molecules which interact with one another by strong dipole-dipole and London forces. As the temperature rises the proportion of water of the latter type increases. (2) This ordering is considered to be short in range in order to preserve molecular disorder which would be expected to prevail in the liquid state. (3) This short-range ordering is due to hydrogen bonding between water molecules. (4) Frank and Wen[101] have suggested that this hydrogen bonding tends to extend itself through the solvent with a suitable, localized low-energy fluctuation and is disrupted in turn by a suitable high energy fluctuation ("flickering cluster" model mentioned above). (5) Other models proposed differ in the nature of the structure of the close-packed water, the arrangement of the hydrogen bonds in the open structured component, the number of hydrogen bonds formed by one water molecule, the nature of the structure set up by the energy fluctuation, and the ease with which hydrogen bonds are broken.

Bernal and Fowler[100] have also pointed out from viscosity data that some ions have the effect of tightening the existing water structure, whereas other ions have the effect of loosening it. This early description enters more recent work where "structure-promotion" and "structure-breaking" properties are attributed to ions. Frank and Evans[103] have pointed out that the anomalous high partial-molar heat capacity for the salt $(\underline{n}\text{-}C_4H_9)_4$ NBr and the entropies of solution of uncharged solute molecules would indicate that these molecules stabilize the open structure of water. In the case of the salt the extra ice-like character of the water is caused by the cation. It effectively breaks down with increase in temperature with the absorption of extra heat. Both of these observations may be of considerable significance in terms of aqueous acetone solutions and the effect which ionic species will have on these mixtures.

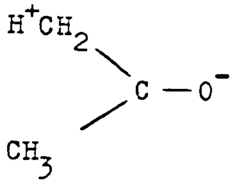
(c) Properties of Acetone

For water and alcohols, hydrogen bonding appears to be the primary contributor to intermolecular attraction and in large measure determines the properties and short-range structural components of these liquids.[100] However, hydrogen bonding in acetone, an aprotic solvent, is not expected to make a large contribution to the properties of liquid acetone unless the enol form of the ketone becomes an important component in the acetone being studied (Adams and Laidler[104] have shown that this is unlikely). Comparison of acetone with other liquid systems suggests that the predominating orienting forces in acetone are expected to be dipole-dipole and London force interactions, superimposed upon which will be the steric requirements of the methyl groups attached to the carbonyl groups.

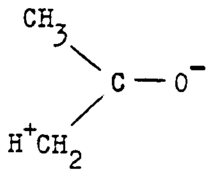
The high vapour pressure, low viscosity, low boiling point and other properties of liquid acetone suggest that these interactions are much weaker than those which arise from hydrogen-bonding, but evidence has been found which suggests that acetone molecules undergo temperature-dependent association in the liquid state. The very high dipole moment of acetone, 2.75D[105], has been interpreted as being due to hyperconjugation[105] and it has been suggested that resonance structures of the form



I



II



III

make contributions to the properties of acetone molecules. This would result in enhanced dipole-dipole interactions which could lead to the existence of some common mode of co-association of acetone molecules, which in turn could lead to cooperative reinforcement of dipole fields[99]. Such enhancement of dielectric constant is expressed by the Kirkwood correlation parameter g,[106] which exceeds unity (1.21)[107] (g = 1 only for "normal" liquids devoid of directional short range association forces). It has been pointed out by Franks and Ives[99] that this situation can arise in two ways. A relatively stable association complex may be formed, long-lived enough to be oriented by the low frequency field used to measure static bulk dielectric constants. Water however shows only one very short dielectric relaxation time[108] and contains no long-lived orienting complex. In this case the high correlation parameter has been explained as being due to the enhancement of polarity of the molecules by the dynamic association in which they are taking part.

With "normal" liquids such as CCl_4, the heat capacity at constant volume C_v increases when the liquid is compressed at constant temperature. It has been found by Adams and Laidler[104] that this is indeed the case for acetone. The slopes of the graphs of C_v against molal volume become less negative as the volume is increased, but at the lowest temperatures the slopes are much less negative over the entire volume range than is the case with normal liquids. This behavior is consistent with there being, particularly at lower temperatures, some associative interactions leading to ordering within the liquid system. This ordering was attributed by Adams and Laidler to dipole-dipole interactions superimposed upon which are the packing patterns favored by the shape of these molecules.

The understanding of the properties of the pure liquids which go to make up binary mixtures is of course very important as the thermodynamic properties of these mixtures will contain terms due to the breakdown of intermolecular interactions in the pure phases. It is apparent that the nature of the association in water and that in acetone are quite different, and it is of interest to see if these interactions persist even when small amounts of one of these liquids are added to the other and what effect these will have on activation parameters of chemical reactions in these regions. It is also worth noting that any conclusions concerning binary aqueous organic mixtures will be tentative, pending a better understanding of the properties of pure liquids.

(d) Acetone-Water Properties

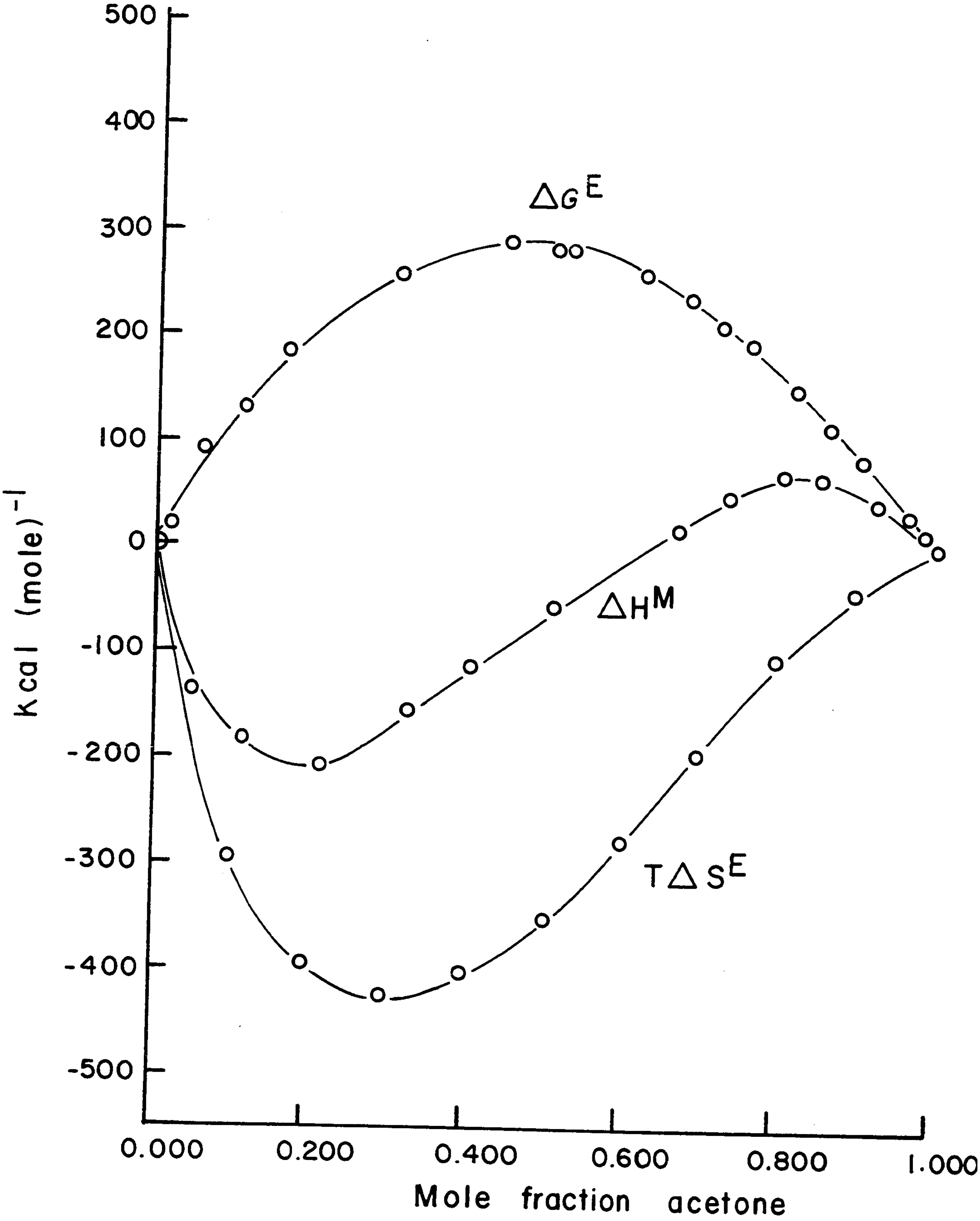
The acetone-water system and other aqueous ketone systems do not appear to have undergone the same intensive study which has been given to aqueous alcohol mixtures. However, similarities between the properties of the acetone-water system and the alcohol-water systems do appear, and several discussions of specific properties of acetone-water mixtures have been made in terms similar to those of alcohol-water mixtures (see below). It is the purpose of this section to interrelate the properties of the above systems in order to relate kinetic parameters in the two systems. This comparison is greatly facilitated by the review of Franks and Ives[99] on the properties of aqueous alcohol mixtures.

(i) Thermodynamic Properties

The terms in the function $\Delta G^E = \Delta H^M - T\Delta S^E$ (discussed by Rowlinson[109]) for the system acetone-water are plotted as a function of acetone mole fraction ($X_{(CH_3)_2CO}$) in Figure 1. The calculation of the $T\Delta S^E$ term by difference must be commented on. The ΔG^E data available from Brungis et al.[110] were made from vapour composition measurements at the boiling points of the mixtures and consequently involve a range of temperatures. However, as these workers point out (see also data plotted in review by Franks and Ives[99]), the ΔG^E curve changes very little with temperature. With this limitation, the

Figure 1

Plots of the excess thermodynamic functions of mixing of the system acetone-water as functions of acetone concentration.


500
400
300
200
100
0
-100
-200
-300
-400
-500
Kcal (mole)$^{-1}$
ΔG^E
ΔH^M
$T\Delta S^E$
0.000
0.200
0.400
0.600
0.800
1.000
Mole fraction acetone

data of Mobius[111] for the heats of mixing, ΔH^M, at 20°C are taken and used to calculate the excess entropy term. Heats of mixing at other temperatures have been measured by Sandonnini[112], Drinkard and Kivelson[113], Kister and Waldman[114] and Nicholson[115]. Reference will be made to this work, but no graphs will be presented.

The excess Gibbs free energy of mixing is positive over the whole concentration range and nearly symmetrical about $X_{(CH_3)_2CO} = 0.50$. It is a function of an enthalpy term which above $X_{(CH_3)_2CO} = 0.60$ is positive and below $X_{(CH_3)_2CO} = 0.60$ is negative, and a negative entropy. The relative magnitudes of $T\Delta S^E$ and ΔH^M show that it is $T\Delta S^E$ which determines the nature of the deviations from Raoult's Law, so that whether a mixture is formed with take up or loss of heat it shows positive deviations from ideality. Given the near constancy of the $\Delta G^E - X_{(CH_3)_2CO}$ curve, the ΔH^M values of the above references indicate that with changing temperature the $T\Delta S^E - X_{(CH_3)_2CO}$ curve changes very little as compared to the $\Delta H^M - X_{(CH_3)_2CO}$ curve, which undergoes considerable changes with temperature. The cross-over point on the mole fraction axis is a function of temperature, shifting to the high water concentration region with increase in temperature. The sizes of the extrema on either side of the cross-over point are also very strong functions of temperature.

The above situation compares with the case for alcohol-water and dioxane-water mixtures[99]. Caution must however attend the interpretation of these data, for at best the excess functions are the result of the difference of two much larger terms, i.e., the energy required to break down the acetone and water interactions in the pure phases, and energy released with association between the acetone and water molecules in the mixture. Franks and Ives[99] have shown that the general disposition of the excess function is consistent with the operation of these two major energy changes and the breakdown and formation of hydrogen bonds in these systems. They also showed, by comparison of the excess energy function of several alcohol-water mixtures, that other interactions were involved and that other interaction mechanisms may be more important at different positions on the mole-fraction axis. For example, in the region of high water concentration, heat capacity data[116], activity coefficient data[117], and variation of the maxima of the ΔH^M data for different alcohol-water mixtures in the high water region, suggest that this is essentially an aqueous region where the water structure is maintained even though organic molecules are being added. Such data for acetone are not available for comparison. However other properties of acetone-water mixtures are consistent with this contention.

A very interesting observation in this connection is the variation with acetone concentration of the partial molar enthalpy of acetone and water in acetone-water mixtures at 20°C observed by Mobius[111]. Above $X_{H_2O} = 0.70$ the partial molar enthalpy of acetone becomes very negative but levels off becoming positive below $X_{H_2O} = 0.75$. This is consistent with the hypothesis that the high water region is essentially an aqueous region, and will be discussed further in this chapter with similar observations of the variation of the partial molar volumes of acetone and water in acetone-water mixtures.

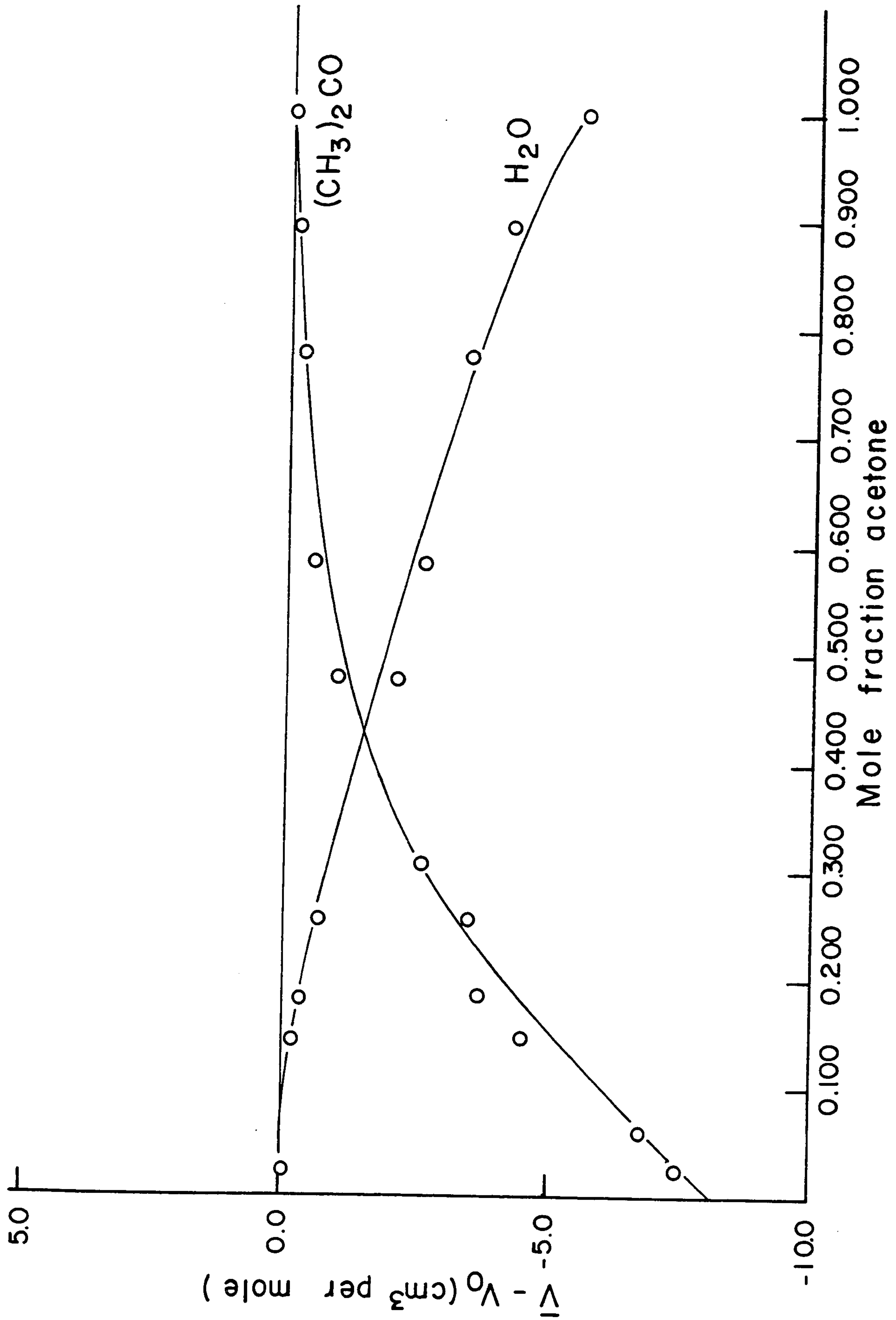
(ii) Pressure-Volume-Temperature Relations

Acetone and water mix with volume contraction over the whole range of concentration at 25°C. The excess volumes of mixing from the data of Fort and Moore[118] go through a pronounced minimum at $X_{(CH_3)_2CO} = 0.40$. On initial investigation this might be indicative of strong intermolecular attraction. However, more detailed examination indicates many more complexities to explain. The partial molar volume-mole fraction isotherm at 25°C calculated from the density data of McAllister and Thomas[119] and Howard and McAllister[120] is shown in Figure 2. The partial molar volumes of acetone undergo larger changes than that of water and the variations are similar to those observed for the variations of the partial molar enthalpies calculated by Mobius[111], although the variation of the partial molar enthalpy of acetone over that of water is proportionately much larger than in the partial molar volumes. This behavior is similar to the dioxane-water and hydrogen peroxide-water cases. However, in the case of the ethanol-water system at 25°C the partial molar volume of ethanol goes through a remarkable minimum at $X_{H_2O} = 0.80$.

Again the interpretation of these data must be attended with some caution. Franks and Ives[99] in the ethanol-water case at high water concentrations (the region of interest in this study) support the view that the changes described in the previous paragraph may best be viewed from the angle of alcohol contraction (and water expansion) which stem from some structural

Figure 2

Plots of the excess of the partial molar volumes of water and acetone in acetone-water mixtures over the molar volume of each compound as a function of acetone concentration at 25°C.


(CH3)2CO
H2O
5.0
0.0
-5.0
-10.0
V̄ - V0 (cm3 per mole)
0.100
0.200
0.300
0.400
0.500
0.600
0.700
0.800
0.900
1.000
Mole fraction acetone

feature of water which is adversely affected by temperature. Evidence was cited by comparison of the abnormally low partial molar volumes of alcohols in the high aqueous region with similar abnormally low partial molar volumes of hydrocarbons in water[121]. Similar arguments can be constructed for the acetone-water case.

Adiabatic compressibilities of acetone-water mixtures are also available at 25°C[118]. They increase monotonically with increasing X_{H_2O} but at the high water end of the mole fraction scale there is a tendency to level off. This observation may also be interpreted in terms of the essentially aqueous nature of short-range structural configurations set up between water molecules in this composition region, which resist compression.

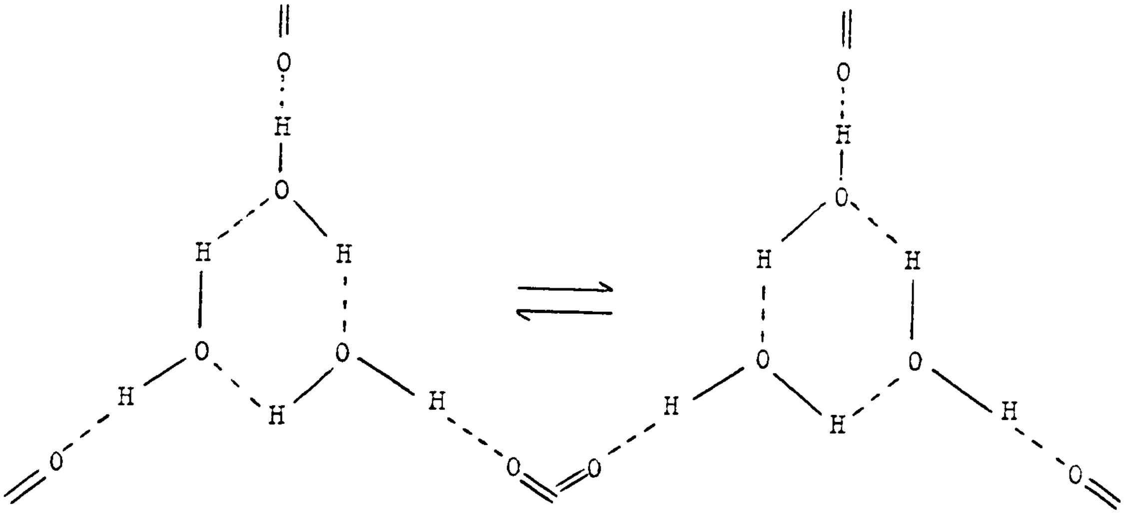
(iii) Spectroscopic Properties

Drinkard and Kivelson[113] have studied the spectral properties of acetone and dimethyl sulfoxide mixtures with methanol, ethyl ether and water. On the simple hypothesis that the major contribution to the heats of mixing and spectral shifts in these mixtures was the formation and breakdown of hydrogen bonds, correlations between these two properties were investigated. No simple correlations were found, and the authors have suggested that other phenomena, which do not appear to be directly reflected in the spectral properties, make considerable contributions to the heats of mixing. The very great importance of hydrogen bonding between molecules in these mixtures was however established.

The ultra-violet spectra of acetone-water mixtures are difficult to interpret. The spectra showed an intense continuous absorption beginning at about 3400Å at 25°C for mixtures of methanol, ethyl ether and water with acetone. In the case of water a shoulder appeared at 2800Å which varied in intensity with changing water concentration.

Infra-red spectroscopy is also of limited use in the study of acetone-water mixtures because of the very complex interactions, covering a wide and continuous range of energies, which give rise to wide, unresolvable absorption bands. In the region of low water concentration the intensity of absorption of the OH stretching frequency band was intense and wide and the peak frequencies could be determined to within 15.0 to 20.0 cm^{-1} [113]. The results are not unequivocal but for water concentrations corresponding to $X_{H_2O} < 0.30$ there appeared to be a definite shift of the -OH stretching band to lower frequencies with increasing water concentration. This shift is attributed to increased hydrogen bonding[100]. As will be seen, these results tend to confirm the N.M.R. spectra results that water forms stronger hydrogen bonds with other water molecules than with acetone. This has also been suggested by Persianova and Tarasov[122] and Shakparanov and Akadov[123] from other non-spectral evidence.

N.M.R. spectra show that the water proton shift moves to lower field with increase in water concentration, whereas the methyl proton shift is almost independent of solvent. It has been shown[124] that such behavior is indicative of a decrease in the average degree of hydrogen bonding in the liquid mixture. Drinkard and Kivelson[113] conclude that this is evidence that hydrogen bonding between water molecules is preferred energetically. Holmes et al.[125] have studied the rate of hydrogen transfer from acetone to water and vice versa in dilute water solution. This kinetic evidence suggests the existence of structures of the form



This is in line with suggestions, in the case of alcohol-water mixtures in the same solvent composition region, that "centrosymmetrical association favoring the peripheral presentation of alkyl groups to the remainder of the solution is a dominant feature of the properties of such mixtures in this composition region"[99].

(iv) Dielectric and Mechanical Properties

The bulk dielectric constants of solvent mixtures are usually smooth functions of solvent composition. Apparently the low frequency fields used to measure this property do not detect any specific short range interactions in the bulk phase but present an average "picture" of all the solvent interactions. This is the case in acetone-water mixtures where the dielectric constant becomes smaller with increasing acetone concentration[123].

The results of dielectric relaxation-time studies of acetone-water mixtures are more enlightening, however. Shakparanov and Akadov[123] summarize their results as follows:

(1) The relaxation times τ for the reorientation of the solvent molecules from their equilibrium positions in the electric field to their positions of equilibrium in the absence of this field pass through a maximum at $X_{(CH_3)_2CO} = 0.20$. The heights of the maxima but not their position on the mole fraction axis are strong functions of temperature. The ratio τ_{mix}/τ_{H_2O} does not depend on temperature in the interval $0 < X_{(CH_3)_2CO} < 0.40$ but tends to increase when $X_{(CH_3)_2CO} > 0.40$.

(2) The distribution parameter α[105], which characterizes the width of the interval of possible τ values and thence mechanisms of relaxation, is small at concentrations $X_{H_2O} > 0.80$; τ is larger when $X_{H_2O} < 0.80$ and passes through a maximum at $X_{H_2O} = 0.40$. The position of the maximum on the solvent composition axis is not a function of temperature. However as the temperature increases α decreases sharply, indicating the greater importance of thermal relaxation mechanisms.

(3) The enthalpy of activation for the relaxation process at 20°C passes through a maximum in the region $0.95 < X_{H_2O} < 0.90$. The entropy of activation for relaxation is positive when $X_{H_2O} > 0.10$ but at higher concentrations it is negative.

Shakparanov and Akadov[123] interpreted these results in the high water concentration region in terms of the essentially aqueous nature of this region. The addition of acetone, it was argued, merely filled up the spaces in the open-structured component of water. This is in line with previous suggestions of Samoilov and Bushlaev[126].

Viscosity measurements[120] show similar behavior to dielectric relaxation time measurements, i.e., a maximum on the mole fraction axis at $X_{(CH_3)_2CO} = 0.20$ where height, but not position on the mole-fraction axis, is a strong function of temperature. Such behavior may also be interpreted in terms of a structure promotion in water due to hydrogen bonding which resists the flow process, or a filling up of the free volume in the open structure of water, which would have a similar effect. In terms of activated complex theory[23], the calculated activation energy for viscous flow also passes through a maximum at the same point on the mole fraction axis, $X_{(CH_3)_2CO} = 0.20$, indicating that at this point the flow process is most sensitive to temperature. The activation energy for viscous flow has been interpreted in terms of the ease with which holes can be created within the liquid system such that a molecule, part of a molecule, or molecule complex may move into a new position of equilibrium[127].

It is difficult to decide in this case why the energy of activation for viscous flow is a maximum at $X_{(CH_3)_2CO} = 0.20$ on the basis of the existing evidence. The energy term may increase for at least three reasons; (1) The increase in structural component of the water system, (2) the filling up of available holes within the water system by acetone molecules, and (3) the formation of new acetone-water complexes such that the species moving through the solution would be larger than in the case of pure water. Any of these phenomena if they were operative would lead to an increase in viscosity with addition of small amounts of acetone to water.

(e) Ions and Non-Polar Molecules in Aqueous Organic Mixtures

Small ions in water have been envisaged by Frank and Wen[101] as follows. Because of the strength of ion-dipole interactions, ions cause a breakdown of the water structure in their immediate vicinity. The water molecules firmly attracted to an ion in this region forms what is known as the hydration shell. (The situation of water molecules in this region is frequently compared with that in ice[128]). The region may be further subdivided into two zones. The inner one is called the primary hydration shell, and in it water molecules are associated with the ion with loss of rotational and vibrational freedom. For univalent ions, this shell usually contains four water molecules. The outer zone is called the secondary hydration shell; a water molecule in this zone retains some translational freedom but has lost its rotational freedom owing to dielectric orientation by the electric field. The orientation effect of the field is spherically symmetrical. Around a positive ion the water molecules are oriented with the oxygen atoms inward and hydrogen atoms **outward** (vice-versa for a negative ion). Immediately outside the hydration shell there exists a region where water molecules retain an abnormally high degree of disorder.

Beyond this zone is the ordinary water structure.

Small non-polar molecules also cause solvent ordering of water molecules in their immediate vicinity. The situation about these molecules is somewhat different from that about ions. It was suggested by Frank and Evans[103] that a microscopic "iceberg" of water molecules, somewhat like a cage, is built up about non-polar molecules. Other evidence for such enhanced structure is also convincing, and the structural units have been referred to as gas hydrates or clathrate complexes[102]. The forces involved in "iceberg" formation probably consist of dipole-induced dipole interactions, London dispersion forces, and repulsive forces if the non-polar molecule comes too close to the water molecules.

The importance of the above conclusions to the present study is clear. In the region of acetone-water composition which is essentially aqueous in character, the situation about the reactants and activated complexes is expected to be similar to that described above. An additional consideration in the present study will be the possibility of selective solvation of the non-polar reactants by acetone molecules and highly polar activated complexes by water molecules[97]. This will be considered further in Chapter 5.

The extensive work on the measurement of the partial molar heats of solution of salts and non-electrolytes in aqueous ethanol mixtures by Arnett and co-workers[68,129,130,131,132] and Bobtelsky and co-workers[98] may be summarized as follows:

(1) Sharp inflections of the partial molar heats of solution of salts and non-electrolytes in aqueous alcohol mixtures always display endothermic maxima as a function of solvent

composition relative to the partial molar heats of solution in water[68,129].

(2) The heights of these maxima depend on; (a) the nature of the cosolvent; the greater the ratio of hydrocarbon chains to polar end groups or the more foreign the properties of the cosolvent from that of water, the greater the maxima for all the solutes studied and the closer the position of the maxima to pure water on the mole fraction axis at a given temperature. At 25°C aqueous methanol mixtures show a small maxima at $X_{H_2O} = 0.70$ while t-butanol gives a larger maxima close to $X_{H_2O} = 0.90$ for the same solutes[129]. (b) the relative number of polar groups to non-polar alkyl or aryl groups in the solute; the greater the ratio of non-polar groups to polar groups in the solute species, the greater the maximum[129]. (c) the charge on the solute molecule; the greater the charge on the solute molecule the smaller the maximum. Salts give smaller maxima than do non-electrolytes of the same size. The results of the above work may be compared with measurements of the partial molar heats of solution of alkali halides in acetone-water mixtures by Bushlaev and Samoilov[126], where endothermic maxima on the solvent composition axis are also observed.[129]

The partial molar volumes of benzyl chloride in different aqueous alcohol mixtures has recently been reported by Golinkin[44]. The partial molar volumes were found to display maxima on the solvent composition axis in each aqueous alcohol system studied. The heights of the maxima increased as the cosolvent was changed in the order CH_3OH < C_2H_5OH < C_3H_7OH < t-C_4H_9OH. The positions of the maxima also tended towards pure water in the same order, the t-C_4H_9OH being the closest.

Bateman[133,134] has reported the measurement of the apparent partial molar volumes of barium chloride and strontium chloride in ethanol-water mixtures. The data indicate that, in both cases, the calculated partial molar volumes show a maximum with changing solvent composition. The interpretation of these data is quite complex and uncertain because of the relatively high concentrations of the solutions whose densities were measured. In each case ion pairs or undissociated species are undoubtedly present and contribute to the curvature of the plots of apparent partial molar volume against the square root of the molar concentration of solute.

(f) Relationship of Properties of Solvent Mixtures and their Solutions to the Magnitude of Activation Parameters

The properties of solutions in aqueous organic mixtures may be understood qualitatively in terms of current ideas of solvation phenomena in pure water and the suggested structural models of aqueous organic mixtures. (Chapter 5). The important kinetic aspect of this work, however, is that both non-polar and highly polar species display similar behavior in their properties, albeit perhaps for different reasons. As this is the case, many of the results which have been reported on the extremum behavior of activation parameters in aqueous organic reactions may be the result of extremum behavior in the partial thermodynamic quantities of the activated complexes or reactants.

The relationship between the partial molar heat of a reactant, $\bar{H}_r$, to its partial molar heat of solution, $\Delta\bar{H}_s$, and the enthalpy of activation, ΔH^*, is shown by the following Born-Haber cycle:

$$\begin{tikzcd}
\mathrm{R{-}X}\ (g) \arrow[r, "\Delta H^*_g"] & \overset{\delta^+}{\mathrm{R}}\text{-----}\overset{\delta^-}{\mathrm{X}}\ (g) \arrow[dd, "\Delta\bar{H}^*_s"'] \\
\mathrm{R{-}X}\ (l) \arrow[u, "\Delta H_v"] \arrow[d, "\Delta\bar{H}_s"'] & \\
\mathrm{R{-}X}\ (s) \arrow[r, "\Delta H^*"'] & \overset{\delta^+}{\mathrm{R}}\text{-----}\overset{\delta^-}{\mathrm{X}}\ (s)
\end{tikzcd}$$

where ΔH_v is the heat of vaporization of R—X, $\Delta\bar{H}^*_s$ is the partial molar heat of solution of the activated complex and ΔH^*_g is the hypothetical enthalpy of activation for the partial ionization of RX in the gas phase. The letters g, l, and s refer to the gaseous liquid and solution states respectively.

It is readily seen then that

$$\Delta H^* + \Delta\bar{H}_s = \Delta H_v + \Delta H^*_g + \Delta\bar{H}^*_x \qquad (2.1)$$

Similar relationships may be derived for the entropies and free energies of activation. The volume of activation as shown above is merely the difference between the partial molar volumes of the activated complex and reactants. The latter quantity may be measured directly.

It is clear from what has been said above that the partial thermodynamic properties of reactants and activated complexes in aqueous organic mixtures cannot be expected to vary in the same manner with changing solvent composition especially in ionogenic reactions. Arnett and co-workers[68] have reported the measurement of the partial molar heats of solution of t-butyl chloride in different aqueous organic mixtures. It was found that the endothermic maxima observed in the solvolysis of this compound in ethanol-water mixtures are accounted for by variations in the heats of solution of the reactant with change in solvent composition change, and not by changes in this function for the activated complexes. Golinkin et al.[67] have also reported that the minima observed in the volumes of activation for the solvolysis of benzyl chloride in different alcohol water mixtures are due primarily to pronounced maxima observed in the partial molar volumes of the reactants. The calculated partial molar volumes of the polar activated complexes also display maxima with changing solvent composition but these are not as large as those observed for the non-polar reactants.

(g) Empirical Parameters of Solvent Polarity

The further understanding of activation parameters by the above method to the point of permitting an estimate of reaction rate constants or their variation with solvent, necessitates a full knowledge of the sum of all the molecular interactions between solvent and solute species of which a given solvent system is capable. This includes a knowledge of intermolecular coulombic, directional inductive, dispersion, charge-transfer and hydrogen bonding forces, etc., on a molecular level. This knowledge is at present not available and even if it were there is some doubt that it could be used for the above purpose (e.g. see Hudson[135]).

An empirical approach to this problem has been made using linear free-energy relationships. One essentially works backwards from the effect of the solvent on a solvent-dependent standard process (the rate of a chemical reaction; the absorption of light by a solvatochromic dye) in order to define a "polarity" parameter of the solvent. Correlation between this defined parameter and the free energy changes of other similar processes defines for this process a "sensitivity" parameter which is characteristic of the new process. It is tacitly assumed in such correlations that the intermolecular forces that contribute to the free energy changes in the standard process are of the same kind as those in the reactions being correlated. This is probably not true in a large number of cases as is demonstrated by the failures of these relationships under certain conditions, and conclusions as to the solvation of any organic molecules based on these approaches appear to be very restricted. Some of the defined solvent parameters which have been found useful are (1) Y - values[136] (2) X - values[137] (3) Ω - values[138] (4) Z - values[139] (5) E_T - values[140] (6) R- and S- values[141].

CHAPTER 3

Experimental

Part I Volume of Activation Measurements

(a) General

Schematic diagrams of the apparatus and important parts of the apparatus used in these experiments are shown in Figures 3 to 5. The apparatus is similar to one used by Koskikallio and Whalley[142]. It was designed such that samples of reaction mixtures could be withdrawn from the reaction vessel quickly, and without appreciable change in the bomb pressure.

(b) The Pressure Vessel and Pressure Generating Equipment

A thick-walled steel cup (machined at the Canadian Research and Development Establishment, Valcartier, P.Q.) provided with a tight fitting, o-ring sealed plug and a screw cap, was connected by 1/4 in. outside diameter (O.D.) stainless steel tubing (304 ss) to a calibrated 20,000 p.s.i.g. Bourdon tube gauge (Acragage, Milford, Conn.) and an electric, hydraulic compressor (American Instrument Co., model number 46-2245). The cavity of the pressure vessel was of about 300 ml. capacity and could be sealed off from the rest of the apparatus by closing valves V_1, V_2, V_3 and BV_1 (see Figure 3). The gauges were readable to ± 20 p.s.i.g. and it was found that a pressure of 15,000 p.s.i.g. could be maintained for one week without a noticeable change in pressure. In order to achieve this, special care had to be taken with the machining of the ends of the tubing where metal-to-metal seals were to be made.

Figure 3

Schematic diagram of hydrostatic system.

EHP, electric hydraulic pump; CV, check valve; V30, 30,000 p.s.i.g. valve; 3BC, 3-way block connector (30,000 p.s.i.g.); R, oil resevoir; G20, 20,000 p.s.i.g. gauge; HP30, hand operated pump (30,000 p.s.i.g.); RV, reaction vessel; BV30, 30,000 p.s.i.g. 2-way block valve (stems a and b close off the sample inlet system (S.I.) and sample outlet system (S.O.) respectively); FV30, flow control valve (30,000 p.s.i.g.).

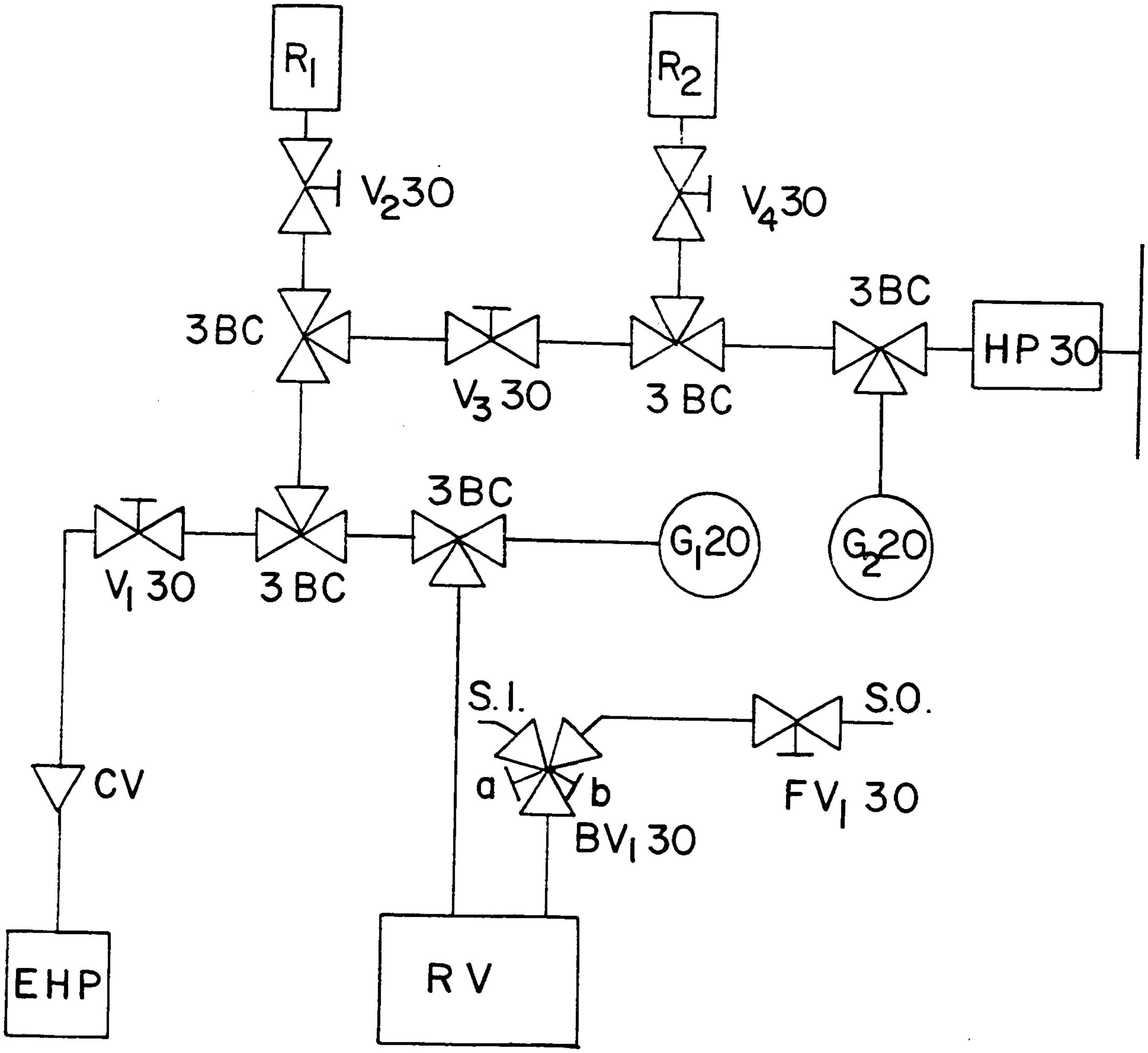

R1
R2
V2 30
V4 30
3BC
V3 30
3 BC
3BC
HP 30
3BC
V1 30
3 BC
G1 20
G2 20
S.I.
S.O.
a
b
CV
BV1 30
FV1 30
EHP
RV

Figure 4

Pressure vessel assembly showing schematically the reaction vessel, inlet system and outlet system.

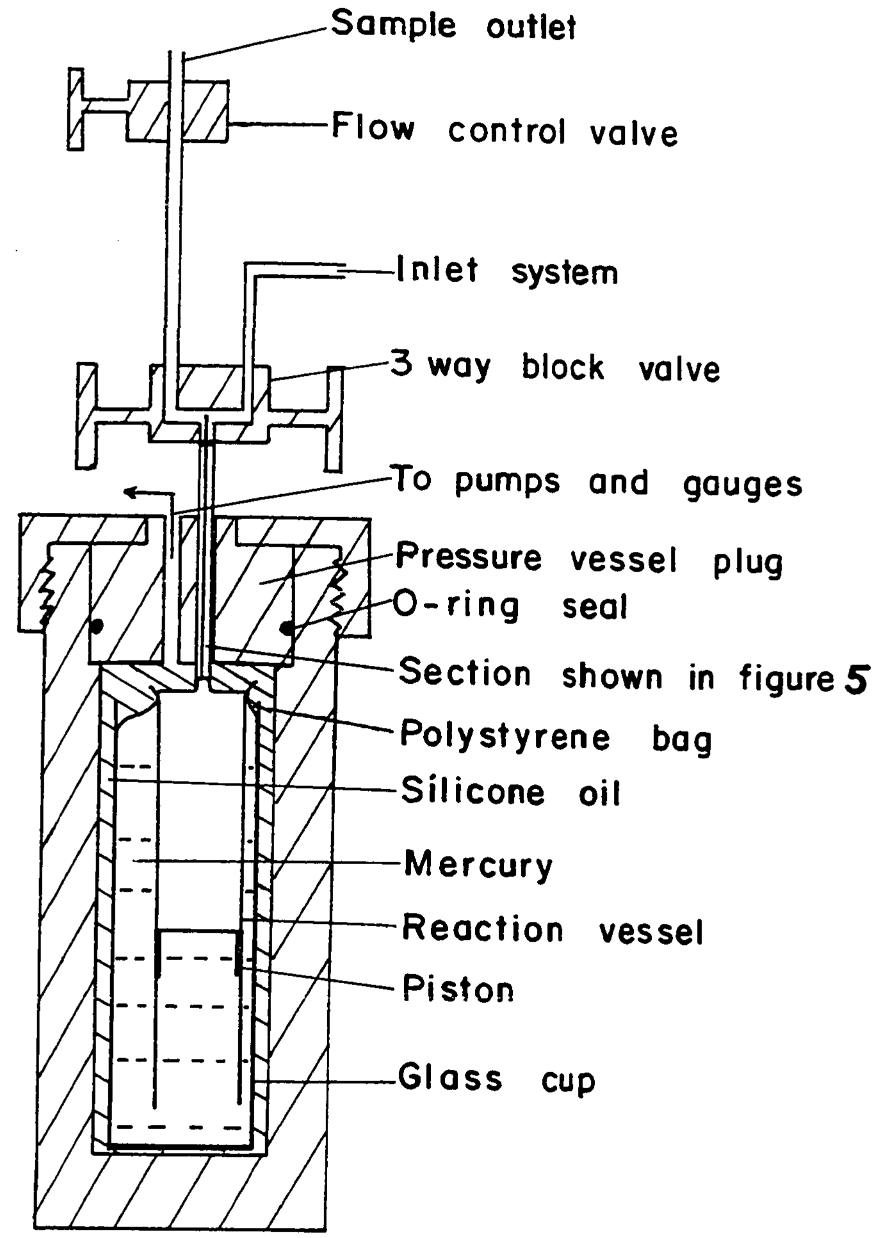
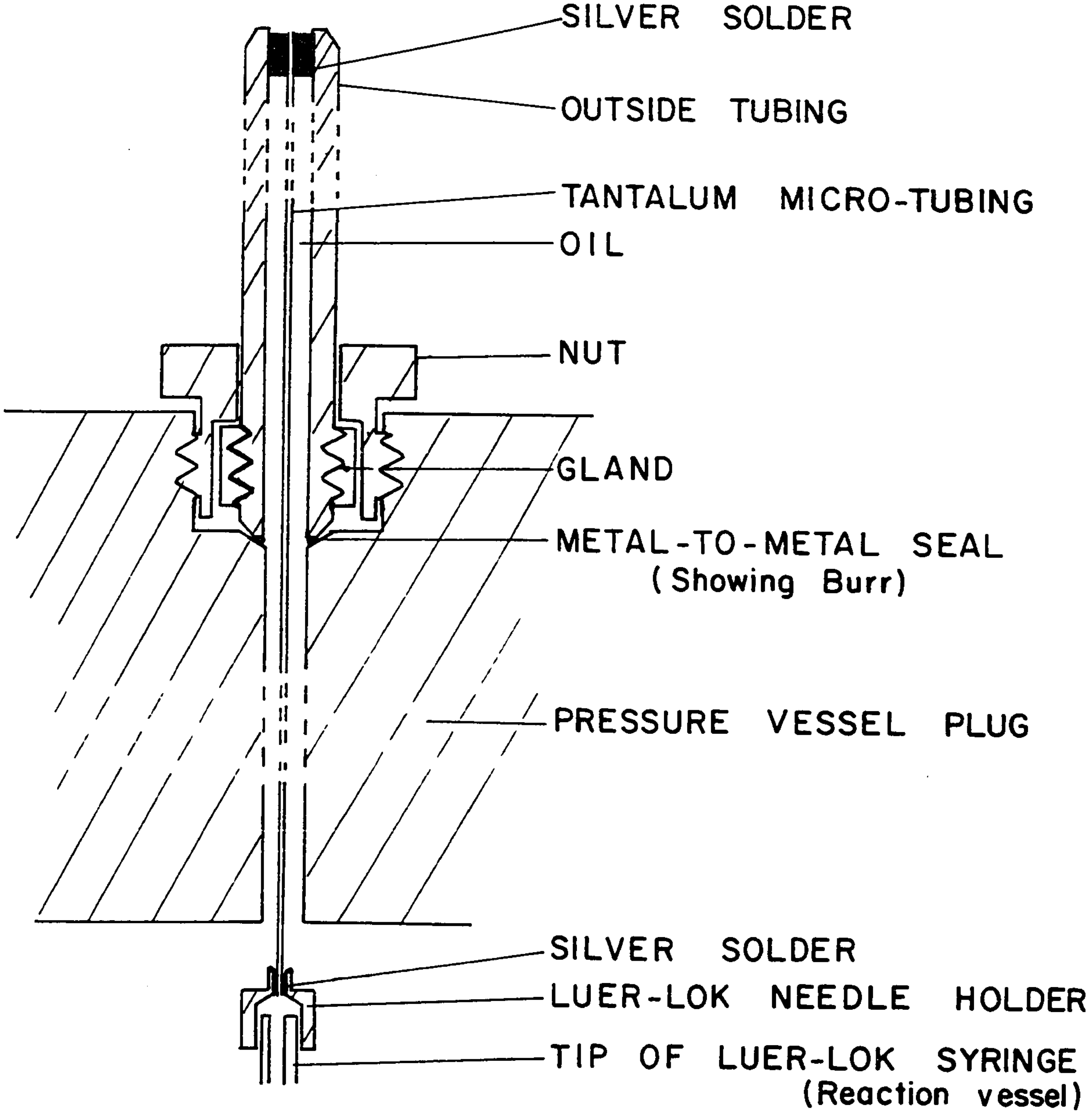

Sample outlet
Flow control valve
Inlet system
3 way block valve
To pumps and gauges
Pressure vessel plug
O-ring seal
Section shown in figure 5
Polystyrene bag
Silicone oil
Mercury
Reaction vessel
Piston
Glass cup

Figure 5

Tantalum micro-tubing arrangement.


SILVER SOLDER
OUTSIDE TUBING
TANTALUM MICRO-TUBING
OIL
NUT
GLAND
METAL-TO-METAL SEAL
(Showing Burr)
PRESSURE VESSEL PLUG
SILVER SOLDER
LUER-LOK NEEDLE HOLDER
TIP OF LUER-LOK SYRINGE
(Reaction vessel)

All the tubing ends were coned using a lathe. The coning on the tube ends were made first and then the end of the tube was machined flat. To finish the coning a final fine cut was made along the cone. This left a small metal burr. This metal burr apparently acted as an o-ring when the metal-to-metal seal was made and tended to fill in any imperfections on the surfaces of the valves at the seal and thus preventing leakage. A gland-nut seal of the type used in the present work is shown in Figure 5.

A 10 ml., manually-operated pressure pump (HP 30) was isolated from the rest of the apparatus by valve V_3 and provided with its own calibrated pressure gauge (20,000 p.s.i.g.) and oil reservoir. With valves V_3 and V_1 open, the pressure in the system could therefore be raised to the approximate experimental pressure, and then the required experimental reading could be set accurately by fine adjustments with the hand pump. Also when samples were taken, valve V_3 could be opened and, as a sample flowed out of the reaction vessel through valve BV_1b, the volume of the system could be reduced with the hand pump and constant pressure maintained.

(c) Reaction Vessel and Assembly Procedure

The reaction vessel was a 100 ml. Luer-Lok syringe. The pressure was transmitted to the reaction mixture with a tight fitting piston made by cutting the original syringe piston to a length of 1 in. In order to assemble the apparatus, a glass cup lined with a flexible polystyrene bag was filled with triple-distilled mercury. The syringe with its piston inserted was placed into the mercury with Luer-Lok up. The bag was tightly wired about the syringe, and the syringe was then connected to a Luer-Lck needle head. The needle head had been previously silver-soldered to a piece of tantalum micro-tubing (O.D. .016 in.) which was mounted as shown in Figures 4 and 5. The tubing passed through the central hole bored in the bomb plug and through a piece of 1/4 in. O.D. stainless steel tubing, and was internally silver soldered at the coned end of this tubing, where it connected to the two-way block valve (BV_1). The outside tubing thus formed a regular gland-nut seal with the bomb plug and with the two-way block valve (BV_1). Oil was then placed in the pressure vessel cavity and the above assembly was lifted and placed as one unit into the cavity. The sealing plug was fitted into place and tightly seated, and the cap of the pressure vessel was screwed snugly into place. The two-way block valve was screwed on tightly, and the whole pressure vessel assembly was placed in the constant temperature bath. The tubing from the pressure pumps and gauges was then attached to the pressure vessel at the point shown in Figure 3.

(d) Constant Temperature Bath

The constant temperature bath was a 30 gallon metal tank made by cutting off the head of a commercial 45 gallon acetone drum. The outside of the bath was wrapped several times with aluminium foil paper, and then wrapped several times with asbestos paper. This was secured in place by wrapping the whole bath with asbestos tape and painting over the outside of the wrapping with liquid glass. The bath was mounted in place on a wooden stand.

The pressure vessel was placed in the center of the bath. Two Gallenkamp induction motors, provided with large stirring blades, placed on either side of the pressure vessel at 180° to each other, were used to stir the bath oil (Esso-Diol N-35). A 1000 watt heating element was placed in the bath as a heat source and cooling took place by heat loss from the bath into the laboratory. Temperature control was maintained by placing a mercury thermoregulator in the oil close to the heating coil. This arrangement gave maximum sensitivity in controlling the bath temperature. The temperature used in all these experiments was 50.00°C. It was measured by a mercury-in-glass thermometer which had been calibrated at the Division of Applied Physics of the National Research Council of Canada. Variations in temperature were measured on a Beckmann thermometer, and the temperature was found to be constant within ±0.025°C over long periods of time. The pressure vessel and the oil bath were thermostatted while reaction mixtures were being made up outside the apparatus.

(e) Preparation of Reaction Mixtures and Insertion of the Mixture into the Reaction Vessel

Reaction mixtures of known acetone and water concentrations and known benzyl chloride concentrations were made up by pipetting together water and an acetone solution of benzyl chloride of known concentration. The benzyl chloride solution in acetone was made up by weighing a specific amount of benzyl chloride into a volumetric flask and making the solution up to volume by adding acetone. This solution was freshly prepared before each run. Both the benzyl chloride solution and the water were thermostatted in a bath at 20.00 ± 0.02°C. This permitted aqueous acetone solutions to be made up to ±0.0002 mole fraction. The vessel into which the liquids were pipetted was a 50 ml. syringe whose outlet had been closed with a teflon plug. After pipetting, the syringe piston was inserted, the mixture was thoroughly shaken to ensure homogeneity, the teflon plug was removed, and the reaction mixture was forced into the reaction vessel with valves V_2 and BV_1a open. The pressure for the particular run was then established as described previously. The whole operation of pipetting and mixing the reagents, forcing the reaction mixture into the reaction vessel and establishing the required pressure, took about five minutes.

The sample inlet system consisted of a bent 4 in. piece of 1/4 in. O.D. stainless steel tubing, coned and threaded at one end. The coned end was attached to a two-way block needle valve (BV_1) as shown in Figure 4. Around the unconed end was tightly fitted a 2 in. length of polyethylene tubing. The outlet of the syringe used to make up the reaction mixtures could be placed very tightly into the open end of this tubing and, with valve BV_1a open, the reaction mixture could be forced into the reaction vessel.

(f) Sampling Technique and Sample Analysis

The sampling system (see Figure 4) consisted of a flow-control valve FV30 connected to the two-way block valve as shown in Figure 3. The valve BV_1b was opened very carefully and the flow valve was left closed. The flow valve was then carefully opened until the sample flowed drop-by-drop through a delivery tube into a 20 ml beaker, the pressure being maintained constant as described above. The first few drops of the sample were discarded and then a 5 ml. aliquot of the solution was pipetted out; the reaction was quenched by pipetting the sample into an Erlenmeyer flask which was cooled in an ice bath. The acid produced during the reaction was then titrated with a standardized barium hydroxide solution (0.01N) using cresol red as the indicator[53]. The whole sampling operation took about 1 min. After each sample was taken, the sampling system was detached from the apparatus. It was cleaned and dried and then replaced.

(g) Preparation of Reagents

The benzyl chloride and substituted benzyl chlorides used in this work were all purchased from the Fisher Chemical Co. as reagent grade chemicals. The benzyl chloride, p-methyl benzyl chloride and p-chloro benzyl chloride were then dried over anhydrous calcium chloride and doubly-distilled under vacuum. The distillation column used was 22 inches in length, packed with glass helices and wrapped in asbestos tape. In each distillation three fractions were taken; the middle fraction from the first distillation was taken and redistilled. The middle fraction of this second distillation (done periodically as needed) was then used in the experiments. The p-nitro benzyl chloride was purified by triple recrystallization from ethanol[54]. The refractive index was taken for the liquid reagents and they compared favorably with values found in the literature. The boiling points, melting points and other physical data for each of these compounds are compared with the literature values in Table 1.

The solvents acetone and water used to make up the acetone-water mixtures were also of highest purity. The acetone was high purity spectral-grade acetone purchased from the Baker Chemical Co. and was used directly without any further purification being attempted. The water used was doubly distilled (Barnstead tin-lined still). It was always taken freshly from the distillate of the still while warm and was cooled under the protection of a soda-lime tube to prevent the absorption of carbon dioxide.

The barium hydroxide solution used in titrations was made up under a nitrogen atmosphere, from a standard solution purchased from the Fisher Chemical Co. The burette used throughout the work was an automatic 5 ml. capacity micro-burette. The barium hydroxide solution, made up in water freed from carbon dioxide, was stored in a reservoir at the top of the burette, under carbon dioxide-free nitrogen in order to prevent barium carbonate formation. This solution was standardized before and after each run to check for any change in concentration. The indicator used in the standardization was potassium hydrogen phthalate.

TABLE 1

Physical Data for Reagents

COMPOUND	Exp. B.P. °C	Lit. B.P. °C	Melting Pt. °C	Lit. Melting Pt. °C	Refractive Index	Lit. Refractive Index
Benzyl Chloride	58.2-58.5 12 mm	56 10 mm			1.5410 26.0°C	1.5417 15°C
Para-Nitro-Benzyl Chloride			73.0 - 73.5	72.5 - 73.0		
Para-Chloro-Benzyl Chloride	78.5-78.6 5.2 mm	99.5 16 mm				
Para-Methyl-Benzyl Chloride	88.5-88.7 15.1 mm 92.1-92.5 19.9 mm	89 17 mm			1.5312 26.0°C	

Part II Partial Molar Volume Measurements

(a) General

It was shown in Chapter I of this thesis that the partial molar volumes of benzyl chloride and substituted benzyl chlorides in acetone-water mixtures could be obtained by measuring the densities of their solutions. The method used in this work utilizes a differential buoyancy technique where the difference in weight of two weighted buoys of known volume, immersed in liquid of known density, is measured, followed by the measurement of the difference in weight of the two buoys when one is immersed in a solution of unknown density and the other in the above liquid of known density. The density of the unknown solution can then be found using Archimedes principle from the volumes of the buoys, the known density of the standard liquid (water in this case) and the two weight differences. The apparatus used was one constructed and used by Conway *et al.*[143] for the measurement of the densities of dilute solutions of tetraalkyl ammonium halides in water and methanol. These workers found that this method yielded results of excellent precision (recorded density measurements with uncertainty in the sixth place from the decimal point). The apparatus had been modified slightly by exchanging an equal arm manual balance for an Oertling automatic balance of the same precision.

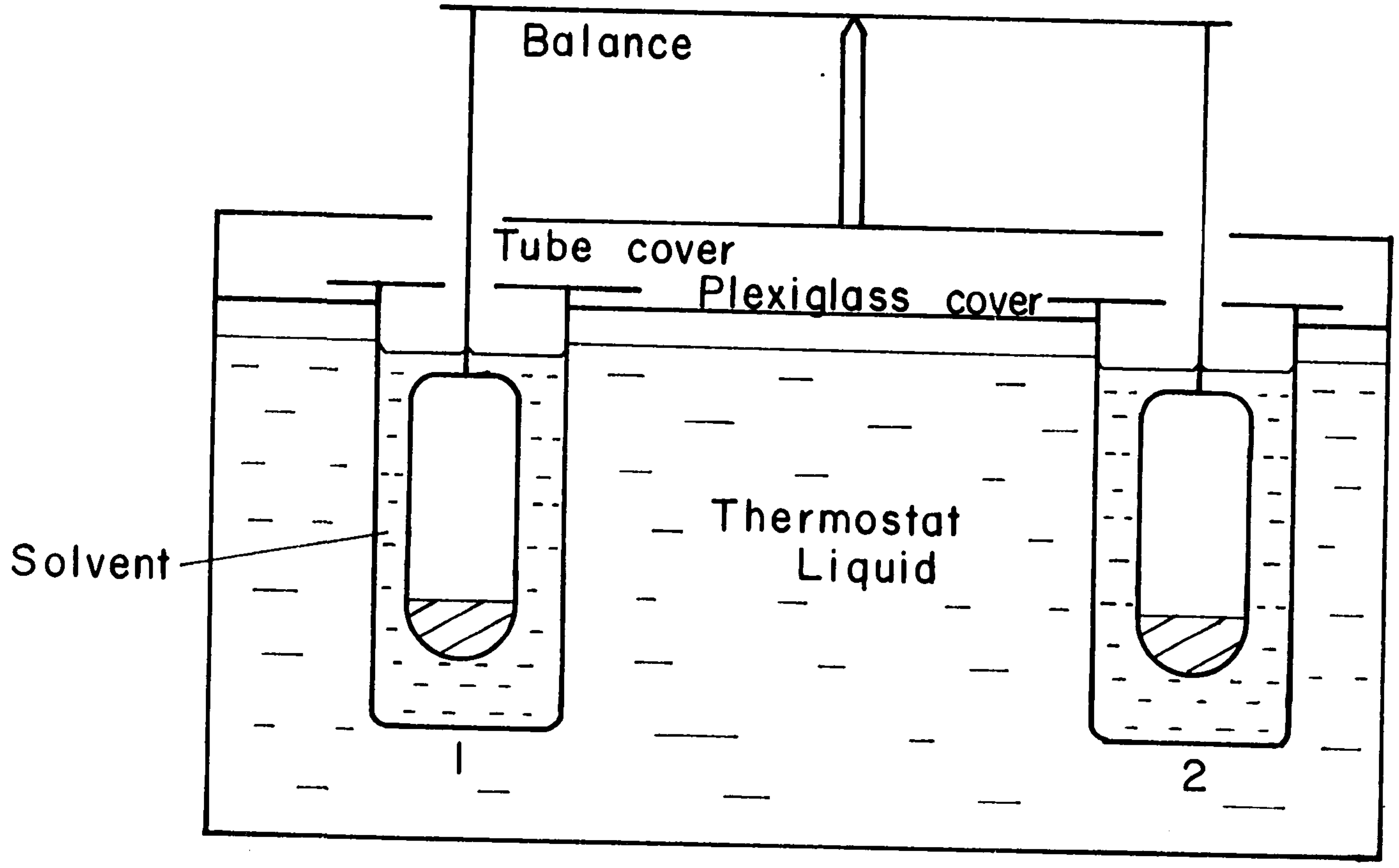
(b) Description of Apparatus

A schematic diagram of the essential parts of the apparatus is shown in Figure 6. The exact dimensions and discussion of its construction are given by Verrall[137]. The general principles and operating procedure used in making density measurements using this technique are obvious from the diagram. The Oertling balance used in the weight measurements had a sensitivity of ±0.1 mg. The pyrex containers in which the liquids were contained were usually filled such that they would contain about 250 ml. of liquid in each container. The pyrex glass buoys were weighted with mercury and provided with a glass hook such that they could be connected to the balance pans by suspension wires. The lower parts of these suspension wires were made of fine tungsten (0.0015-0.002 in. diameter) and the upper parts of the wires were made of fine gold alloy chains. When the solutions had been made up and the buoys had been connected to the balance pans, plexiglass covers were placed over the pyrex vessel openings in order to minimize evaporation. The volumes of the bulbs were determined by comparing the weight of each in air with their weight in water (applying buoyancy corrections to the value in air). They had an apparent specific gravity of 1.12 and a volume of approximately 120 cm^3.

The pyrex tubes in which the solutions were contained were immersed in a well-stirred water thermostat provided with an annular window and heated by means of a partially immersed electric light bulb. Temperature control was maintained by a large mercury thermoregulator, and the whole bath was contained in a thermostatted room, the temperature of which fluctuated by about 1°C. The approximate temperature of the room was 22°C and all solutions were made up and operations outside the thermostat bath were performed in

Figure 6

Schematic diagram of differential buoyancy apparatus.



DIFFERENTIAL BUOYANCY APPARATUS

this room. Because of problems encountered with evaporation from the acetone-water mixture it was necessary using this apparatus to thermostat the bath at 25°C. This was disappointing as the results obtained are not directly comparable with the volumes of activation, which have been measured at 50°C, but should lead to some indication of the way in which $\overline{V}_g$ varies with solvent composition.

(c) Experimental Procedure

Stock solutions of acetone and water were made up by adding x L. of acetone to (5-x) L. of water. This was stored under pressure of nitrogen in a bath thermostatted at approximately 25°C. Samples of the benzyl halide to be studied were weighed into a weighing bottle and flushed into a 250 ml. volumetric flask using the acetone-water solvent. The flask was stoppered and sealed and the solution was thermostatted in a 25°C bath for 15 min. The solution was then poured into one of the clean dry solution containers of the density apparatus, plugged and thermostatted for another 10 min. Then the buoys were connected to the balance, and weighings were begun. The standard solvent used throughout this work was double distilled water which had been boiled to expel dissolved gases and then cooled while stoppered. It is usual in the use of this apparatus to measure the weight difference when one buoy is immersed in the solvent and the other is immersed in a solution made up in this solvent. It was decided in this work that because of the fleeting nature of acetone vapours above acetone-water mixtures it would be best to measure the weight difference when one buoy was immersed in water and one buoy was immersed in solution. It is then found that the balance reading changes as a function of time, owing to evaporation of acetone and water from the mixtures. Consequently in order to obtain a balance difference reading at zero time it was necessary to follow this reading for about 3/4 hr. taking measurements every 5 min. A graph of balance reading versus time was made and extrapolated to time zero in order to get the correct weight difference. Another problem encountered was the fact that making up the solutions and thermostatting them resulted in acetone evaporation. Consequently this process was also timed in order that every solution should undergo the same experimental treatment. Also, when the density of the solvent was measured the same procedure used in making up solutions was followed.

Other precautions taken in the use of this equipment are as follows:

(a) The suspension wires and buoys were cleaned using the method of Verrall[144] and after each density determination they were well rinsed with acetone and dried in a stream of nitrogen.

(b) The position of the buoys in the liquid-containing vessels was carefully checked to avoid sticking to the walls. This was done periodically by adding a small weight to the balance. Any sticking resulted in considerable delay in balance response.

(c) Air bubbles sometimes adhered to the surface of the buoys. This also was checked for and corrected whenever it was found, as this effect would tend to upset the accurate weight difference reading.

(d) The temperature of the bath was continuously checked using a calibrated mercury-in-glass thermometer (12 in. scale for a 6°C change). The temperature was found to be maintained to ±0.01°C, and there was no detectable temperature fluctuation from one solvent vessel to the other.

(e) Care was also taken to fill the liquid containers to the same point each time and to gauge the amount added so that approximately the same amount of tungsten wire was covered by solution in each case. This minimized errors due to the change in weight difference due to liquid displacement by the wires.

Using the above method, and scrupulously following the above precautions, measurements of the weight differences of the two buoys were made, (a) when water was contained in the two measuring vessels, (b) when water was contained in vessel 1 and solvent in vessel 2, and (c) when water was contained in vessel 1 and solutions in vessel 2. A buoy was always immersed in the same vessel for each measurement. Consequently the density of the unknown solvent and solutions were calculated from the volume of buoy 2, (120.380 ± 0.001 cm^3) the density of water, (0.997048 gm per cm^3 at 25°C) and the weight differences which could be estimated to 3 decimal places after extrapolation. Usually the density of 4-5 solutions were measured (limits to the concentration range which could be studied were set by solubility and balance sensitivity). The densities of solvent and solutions were then used to calculate the apparent partial molar volumes of the solute in the various solvents, as shown in Chapter I. These were reproducible to

±1.0 cm^3 per mole using p-methyl benzyl chloride in 60% water solutions. The partial molar volumes of the solutes were calculated by plotting graphs of apparent partial molar volume versus concentration. The extrapolated value at zero concentration was the partial molar volume of the species. This was known to approximately ± 2 cm^3 per mole from a least squares treatment of the experimental data.

(d) Preparation of Materials

The materials used in the experiments described in this section were prepared in the same manner as in Part I. Special precautions were taken in the case of water when cooling it. It was exposed to the air for as short a time as possible in order to minimize the possibility of bubble formation during the measurement of the densities of the solutions.

CHAPTER 4

Results and Analysis

(a) Kinetic Measurements

As described in Chapter 3, the method chosen to follow the rate of formation of products was a standard volumetric method. The concentration of water in each reaction mixture was also very large compared with the substrate concentration and consequently the reaction was pseudo-first order.

The rate expression for the pseudo-first order reaction is

$$- da/dt = ka \ , \tag{4.1}$$

where a is the concentration of benzyl chloride or substituted benzyl chloride at time t. The rate constants, k, for each of the reactions studied, together with the least-mean-square deviations were calculated by the usual methods using the well-known integrated form of the above expression

$$k = (2.303/t)\log_{10}[a_o/(a_o-x)] \ , \tag{4.2}$$

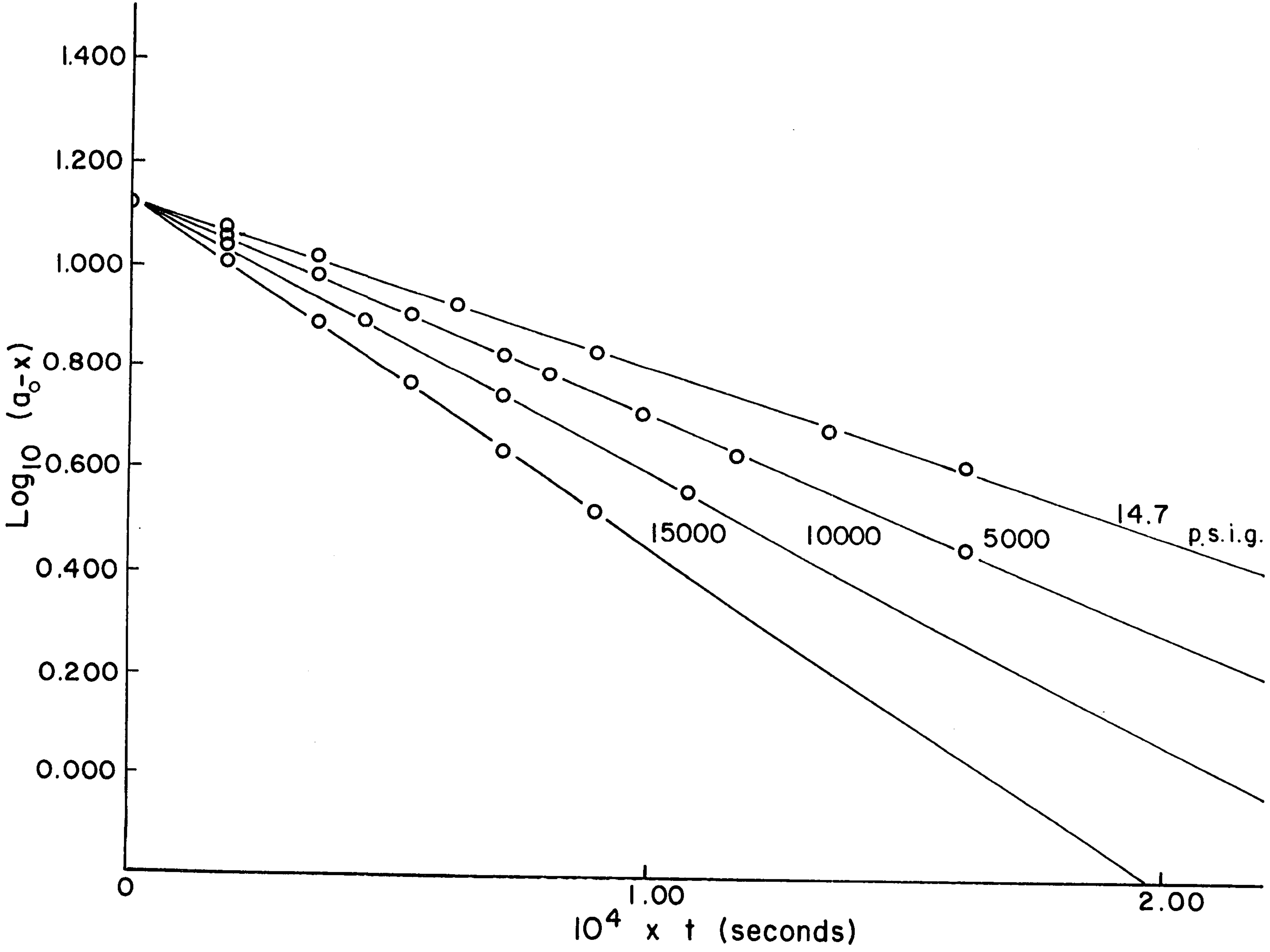
where x is the concentration of reactant which has reacted at time t and a_o is the initial concentration of reactant. The latter quantity was calculated in the following manner. The reaction mixture was made up by pipetting the required amount of water into a known volume of solution of reactant in acetone whose concentration was known accurately. The solutions were thermostatted at 20.00 ± 0.02°C when being made up. The exact concentration of benzyl chloride in a reaction mixture was then calculated from the density-temperature-composition data of Howard and McAllister[120].

In each run at least five samples were taken for titration and the rate constants reported are usually the result of duplicate and in some cases triplicate runs. The time-course plots for the results of one series of runs at four pressures for the reactant p-methyl benzyl chloride in the acetone-water mixture containing $X_{(CH_3)_2CO} = 0.1407$ are shown in Figure 7. The rate constants for each of the compounds studied in the above acetone-water mixture are given in Table 2 together with their least-mean-square deviations. The rate constants for the solvolysis of p-methyl benzyl chloride in acetone-water mixtures of different composition together with their least-mean-square deviations are given in Table 3. The maximum least-mean-square deviation quoted in these tables is about 3% of the value of the rate constant. This is the usual value reported for such aliquot methods of measuring reaction rates.

There do not appear to be any data at atmospheric pressure, in acetone-water mixtures, for the compositions used in this work, with which these data may be compared. The results of Tommila and co-workers[54] at 50°C in acetone-water mixtures are not directly comparable with our data because of differences in the method used to make up the reaction mixtures. Beste and Hammett[83] have also found that differences in the concentration of reactant used lead to differences in the rate constants measured. Given the above restrictions, the present data at one atmosphere pressure

Figure 7

Plots of $\log_{10}(a_o-x)$ against time for the solvolysis of p-methyl benzyl chloride in the acetone-water mixture containing 0.1407 mole fraction acetone at 50.00°C.



1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
Log$_{10}$ (a$_o$-x)
0
1.00
2.00
10^4 x t (seconds)
14.7 p.s.i.g.
5000
10000
15000

Table 2

Rate constants for the solvolysis of benzyl chloride and substituted benzyl chlorides at various pressures at 50.00°C in an acetone-water mixture containing 0.1407 mole fraction acetone .

Substituent	10^6 x k (sec^{-1})			
	Pressure (p.s.i.g.)			
	14.7	5000	10,000	15,000
p - Methyl	75.8±0.8	96.8±0.09	121±4.0	155±4.0
H	7.18±0.07	9.58±0.06	12.2±0.2	15.8±0.3
p - Chloro	3.76±0.06	4.99±0.09	6.47±0.06	8.45±0.03
p - Nitro	0.537±0.009	0.708±0.004	0.901±0.016	1.096±0.004

Table 3

Rate constants for the solvolysis of p-methyl benzyl chloride at various pressures at 50.00^{o}C in different acetone-water mixtures .

Solvent Composition (Mole Fraction Acetone)	10^{6} x k $(sec)^{-1}$ Pressure (p.s.i.g.)			
	14.7	5000	10,000	15,000
0.1407	75.8±0.8	96.8±0.9	121±4.0	155±4.0
0.1972	22.7±0.1	30.5±0.3	39.3±0.2	49.3±0.4
0.2692	7.61±0.01	10.11±0.01	12.80±0.02	16.00±0.02
0.4955	0.552±0.008	0.714±0.012	0.917±0.009	1.184±0.008

compare favorably with those of Tommila and co-workers[54].

(b) Volume of Activation Measurements

The logarithms of the rate constants are plotted as a function of pressure, for the compounds and solvent mixtures studied, in Figures 8 to 14. It is seen that in general these graphs are not linear, indicating, as could be expected from measurements of the compressibility of pure liquids,[145] that the partial molar volumes of the reactants and activated complexes depend on pressure in different ways. Such a situation arises frequently in the study of other activation parameters of chemical reactions (e.g., see Hyne and Robertson[146]) and presents a problem where it is necessary to estimate these parameters accurately in order to establish the reality of small differences such as the ones expected in the present work. Several different methods for estimating ΔV^* have been used and, in some cases, differences in the values of ΔV^* calculated have arisen. This has given rise to some controversy.

The most common approach to this problem is the use of standard graphical methods for the measurement of the slope of a tangent to a curve at a given point. This however does not permit, in general, an estimate of the precision of the results. In cases where the graphs of log k against pressure are linear within experimental error as in the results of Burris and Laidler[31] the usual least-mean-square methods give a value for the slope and an estimate of its precision. Another partly graphical method used by Whalley[5] utilizes the well known method[147] of estimating the tangent to a quadratic curve whose curvature is quite small.

Figure 8

A plot of $\log_{10}$ k against pressure for the solvolysis of p-methyl benzyl chloride in the acetone-water mixture containing 0·1407 mole fraction acetone at 50.00°C.

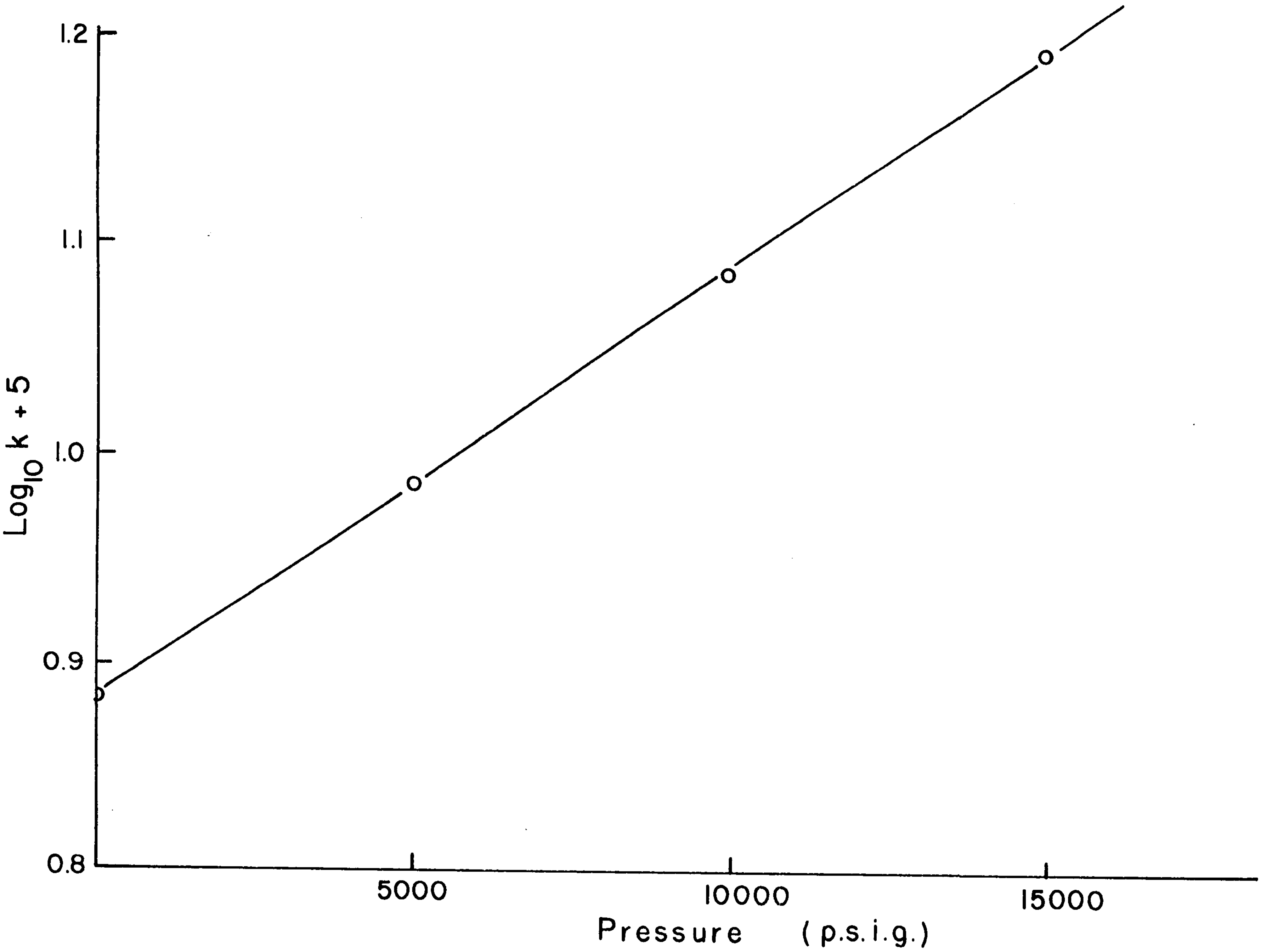

1.2
1.1
1.0
0.9
0.8
$\text{Log}_{10}\, k + 5$
5000
10000
15000
Pressure (p.s.i.g.)

Figure 9

A plot of $\log_{10} k$ against pressure for the solvolysis of benzyl chloride in the acetone-water mixture containing 0.1407 mole fraction acetone at 50.00°C.

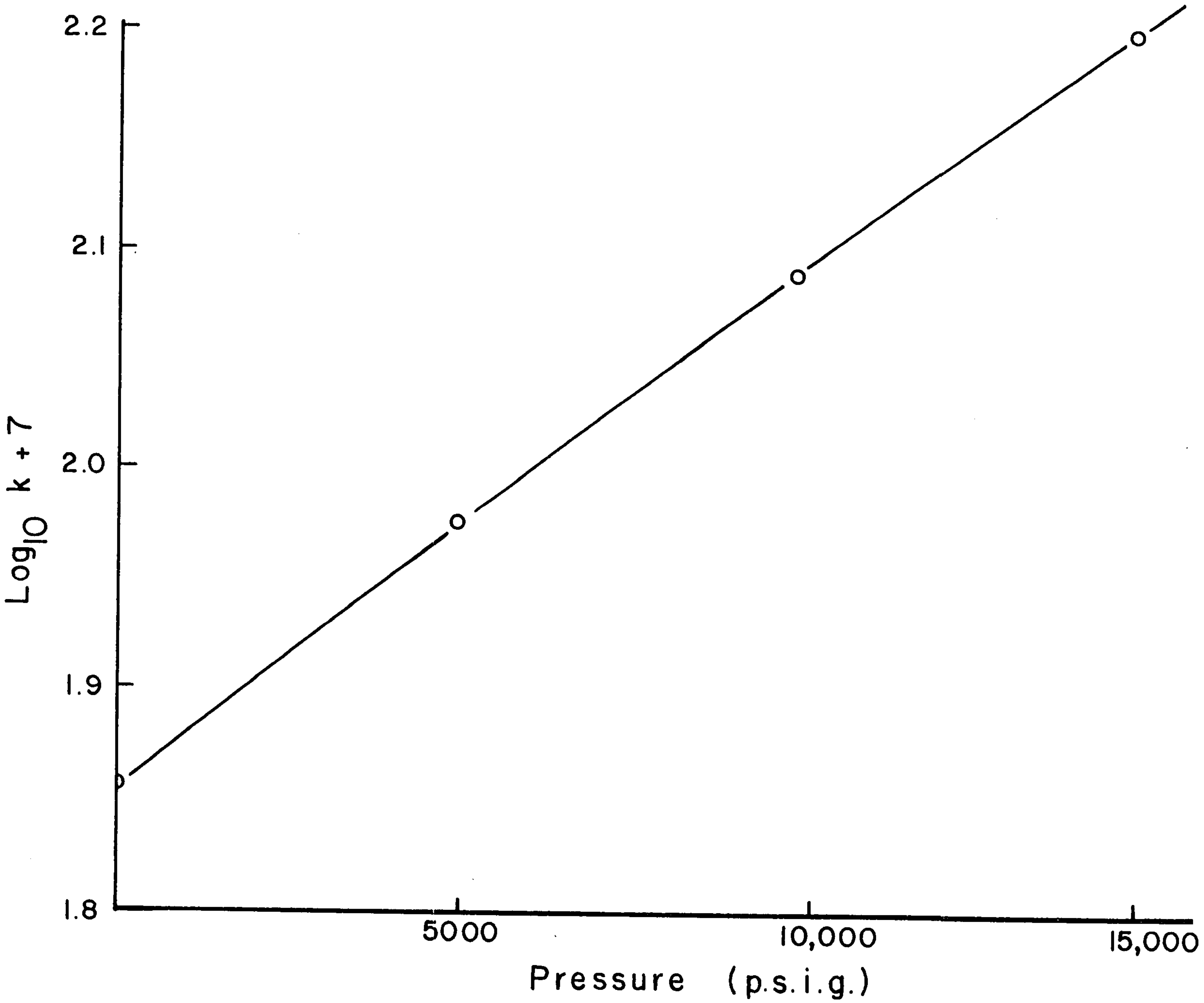

2.2
2.1
2.0
1.9
1.8
Log$_{10}$ k + 7
5000
10,000
15,000
Pressure (p.s.i.g.)

Figure 10

A plot of $\log_{10}$ k against pressure for the solvolysis of p-chloro benzyl chloride in the acetone-water mixture containing 0.1407 mole fraction acetone at 50.00°C.

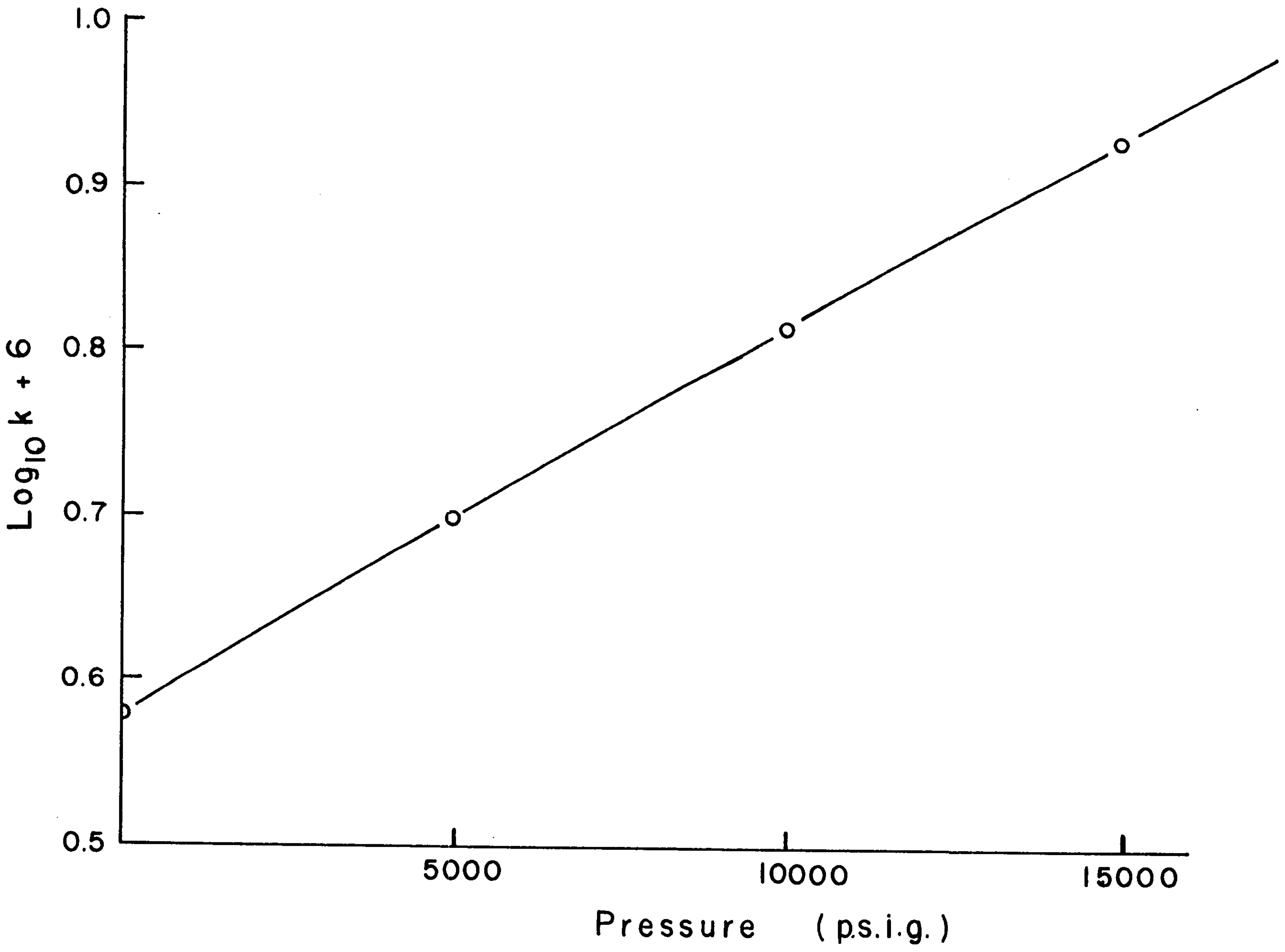

1.0
0.9
0.8
0.7
0.6
0.5
$Log_{10} k + 6$
5000
10000
15000
Pressure (p.s.i.g.)

Figure 11

A plot of $\log_{10}$ k against pressure
for the solvolysis of p-nitro benzyl chloride
in the acetone-water mixture containing 0.1407
mole fraction acetone at 50.00°C.

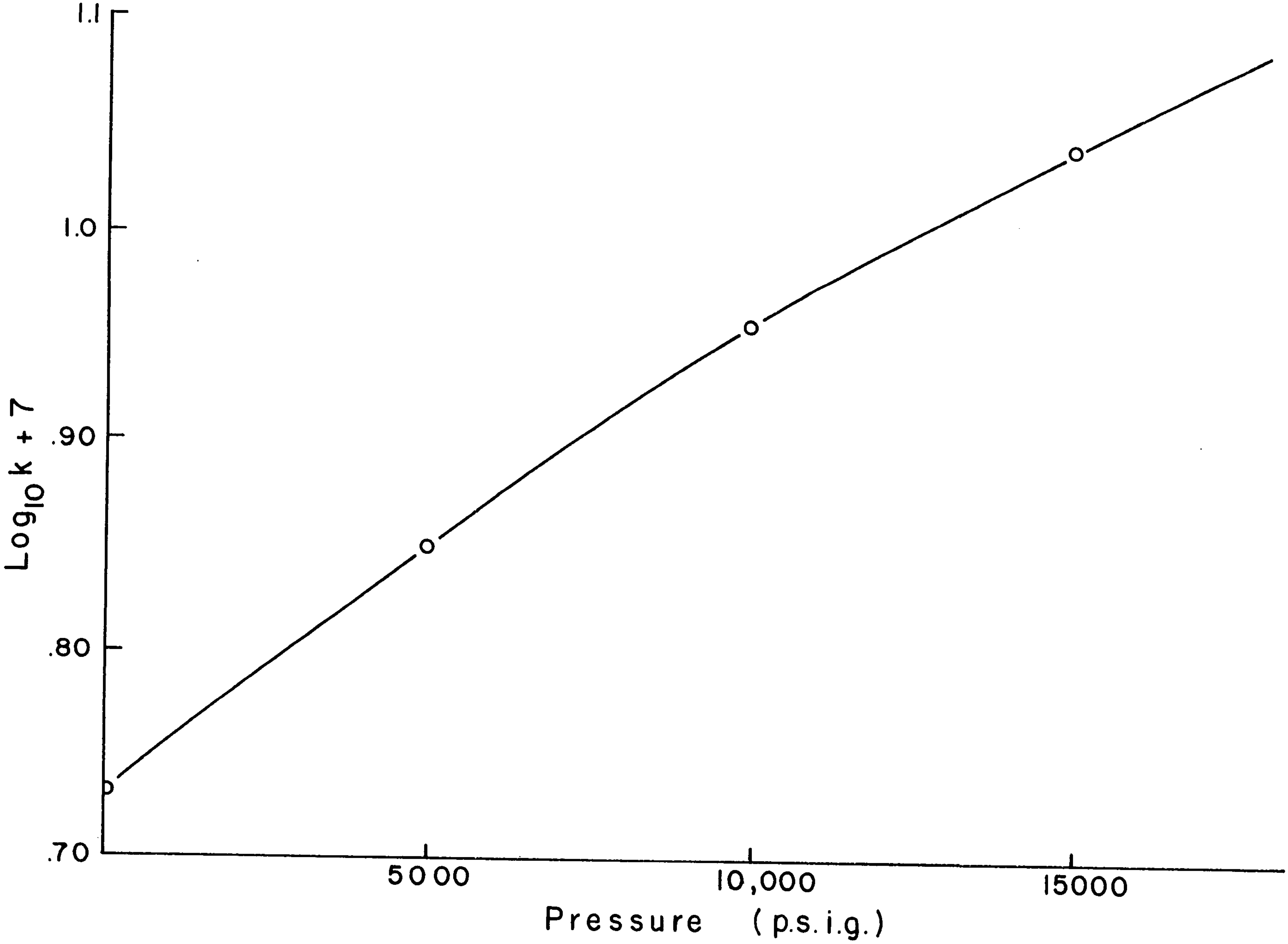
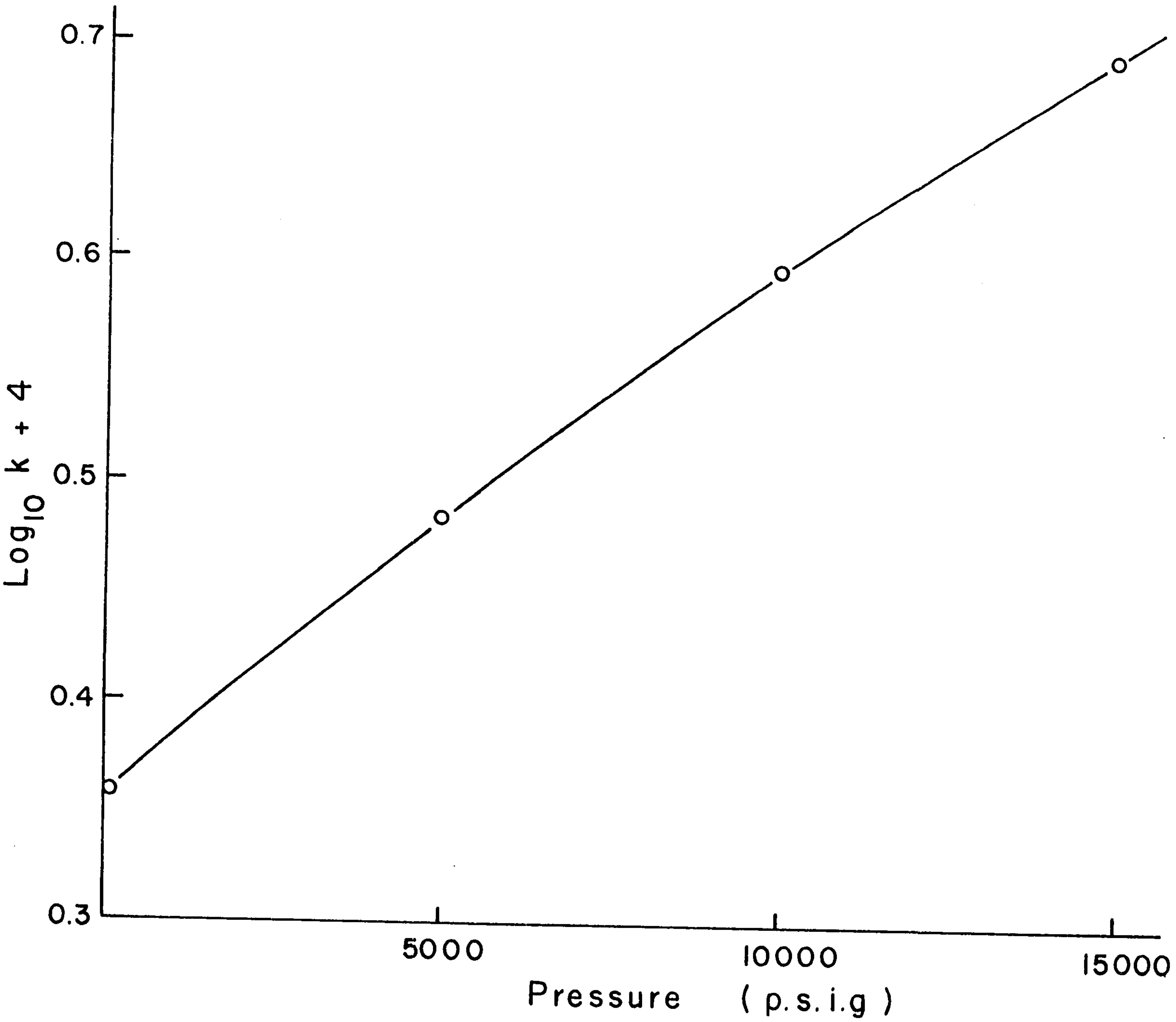

1.1
1.0
.90
.80
.70
Log$_{10}$k + 7
5000
10,000
15000
Pressure (p.s.i.g.)

Figure 12

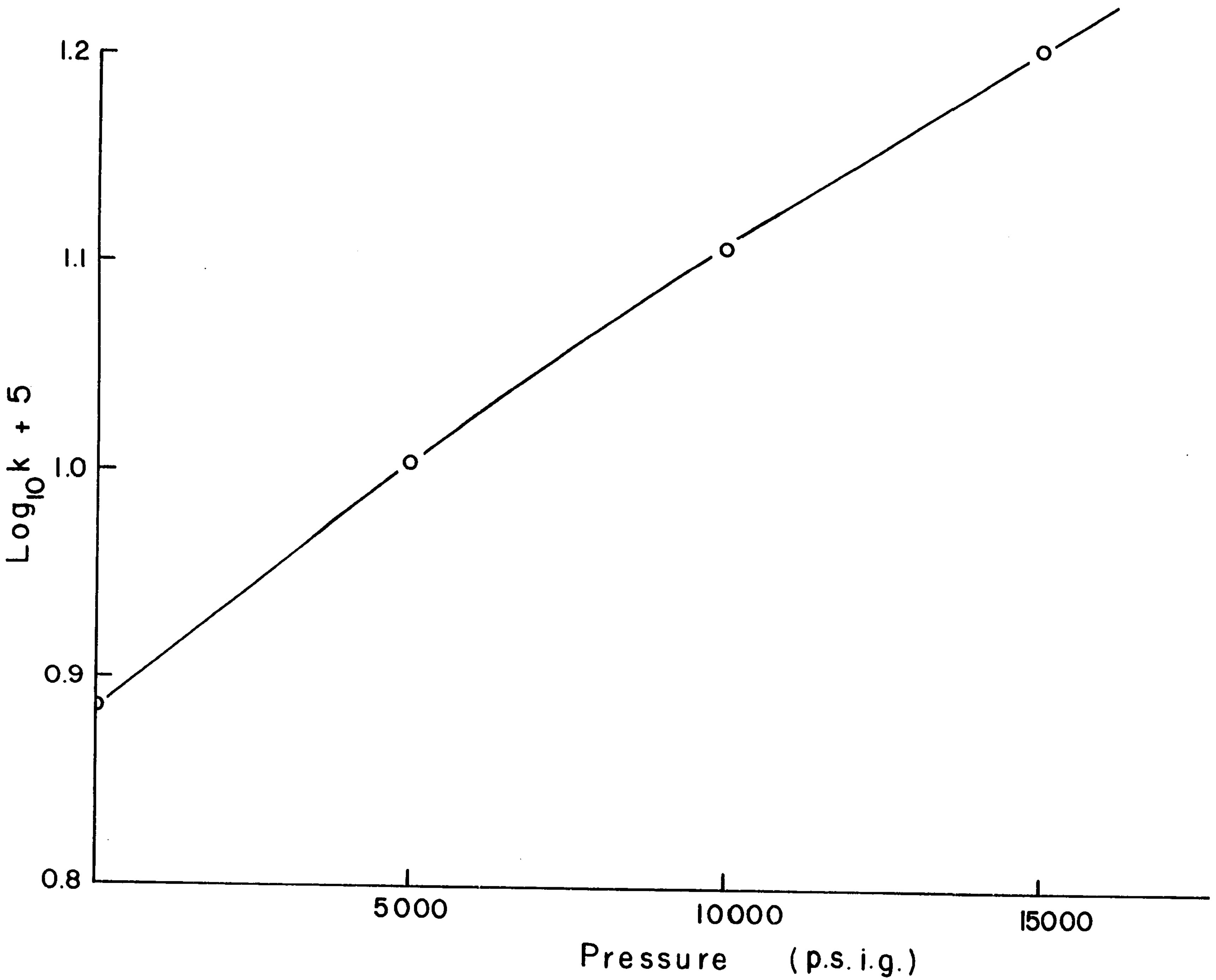
A plot of $\log_{10}$ k against pressure
for the solvolysis of p-methyl benzyl chloride
in the acetone-water mixture containing 0.1972
mole fraction acetone at 50.00°C.



0.7
0.6
0.5
0.4
0.3
$\mathrm{Log}_{10}\,k + 4$
5000
10000
15000
Pressure (p.s.i.g)

Figure 13

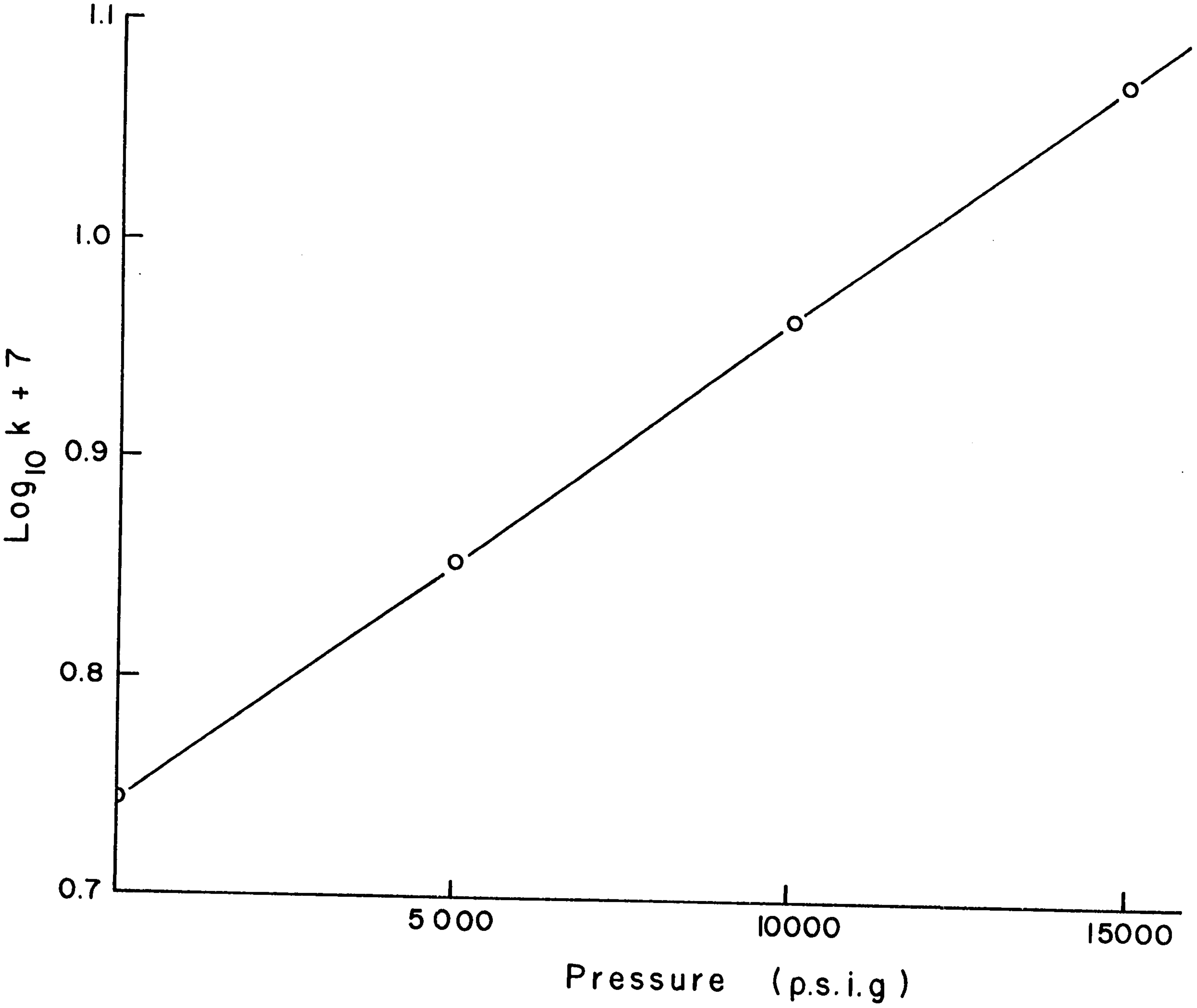
A plot of $\log_{10}$ k against pressure for the solvolysis of p-methyl benzyl chloride in the acetone-water mixture containing 0.2692 mole fraction acetone at 50.0°C.



1.2
1.1
1.0
0.9
0.8
$\mathrm{Log}_{10}k + 5$
5000
10000
15000
Pressure (p.s.i.g.)

Figure 14

A plot of $\log_{10} k$ against pressure for the solvolysis of p-methyl benzyl chloride in the acetone-water mixture containing 0.4955 mole fraction acetone at 50.00°C.


1.1
1.0
0.9
0.8
0.7
$\mathrm{Log}_{10}\,k + 7$
5000
10000
15000
Pressure (p.s.i.g)

It consists of measuring the integral slope between consecutive points and plotting the result against the median pressure of the interval over which the slope was taken. Extrapolation to zero pressure gives an estimate of the tangent to the curve at this point. The assumption that the $\log_{10} k$ - pressure curve is best represented by a polynomial of second degree will be discussed later.

Most controversy has arisen over the approach of Benson and Berson[148] to the estimate of ΔV^*. They suggested that the variation with pressure of the partial molar volumes of a species in solution might be represented by the Tait equation[149]

$$(\delta \overline{V}/\delta P)_T = A/(B+P) \quad , \tag{4.3}$$

where A and B are empirical parameters. This equation has been found to represent the variation of the volumes of pure liquids with pressure with excellent precision[145]. Expressing the partial molar volumes of reactants and activated complex in terms of this equation, they arrived at an expression of the form

$$(\log_e k_p/k_o)/P = C + DP^{0.532} \quad , \tag{4.4}$$

where D is a complex expression containing ΔV^*. It was argued by Benson and Berson[148] that, because of changes in the activity coefficients of ions or ionic species with pressure, this equation could not be used in reactions where such species are important. They applied it to several free radical reactions. The equation was first used to obtain ΔV^* for the dimerization of isoprene and led to a value of -36.5 cm^3 per mole, whereas Walling and Peisach[150], using a standard graphical technique, had obtained a value of -24.3 cm^3 per mole. Walling and Peisach[150] had concluded that the activated complex for this reaction was non-cyclic. Benson and Berson[148] however argued, on the basis of their treatment of the results, that such a conclusion was not justified. Walling and Tanner[151] later criticized the Benson and Berson equation from thermodynamic arguments. It has also been criticized by Hamann[2b] on the grounds that at high pressures it unrealistically predicts negative volumes of activation, and that the activated complex is assumed to obey the same kind of equation of state as stable molecules. This Hamann feels is an unjustified assumption. Hyne, Golinkin and Laidlaw[66] fitted their data of the rate constants for the solvolysis of benzyl chloride as a function of pressure to the above equation, and found a reasonable fit.

Hyne and co-workers[66] have, however, concluded that their data were best fitted by a polynomial of the second order

$$\log_e k = a + bP + cP^2 \; . \qquad (4.5)$$

Walling and Tanner[151] found that their results were best fitted by a polynomial of the third order. Because of these findings, and also because this method permits the estimation of the curvature of the present graphs as well as permitting an estimation of the least-mean-square deviation of both ΔV^* and $(\delta \, \Delta V^*/\delta \, P)_T$, this method was used in the present work.

The data were fitted by the least-squares method outlined by Hildebrand[152] using the I.B.M. 320 computer to a linear polynomial and a quadratic polynomial. In order to decide which was the best fit, a variance parameter was defined in terms of the number of points N and the particular polynomial by

$$\sigma^2 = \frac{1}{N}\sum_i d_i^2 = \frac{1}{N}\sum_i (a+bx_i+cx_i^2+ --- -y_i)^2. \qquad (4.6)$$

The polynomial used to represent the data was chosen when this parameter became greater in going to the polynomial of higher degree. It was found that the data for the solvolysis of p-methyl benzyl chloride in the acetone-water mixtures containing $X_{(CH_3)_2CO} = 0.1407$ and $X_{(CH_3)_2CO} = 0.4955$ were best represented by a polynomial of the first degree. The remaining data were best fitted by polynomials of the second degree. The values of ΔV^* calculated from the coefficient of pressure to the first power are given in Tables 4 and 5.

The least-mean-square deviation in ΔV^* was found from the variance parameter σ^2 by the expression

$$\sigma_b^2 = \sum_i (\delta I/\delta y_i)\ \sigma^2 , \qquad (4.7)$$

where I is the least-mean-square expression for the coefficient, b, of P. It is assumed that the pressure is known with much less uncertainty than $\log_e k$. σ_b^2, the variance in the coefficient of P, is a measure of the precision to which ΔV^* can be determined from the present data. The calculated least-mean-square deviations in the volumes of activation are also included in Tables 4 and 5. The calculated least-mean-square deviations indicate that the trends observed in ΔV^* are not the result of experimental uncertainty.

There do not appear to be any data with which the present results can be compared. They are similar in magnitude to the results of Hyne and co-workers[66] for the volumes of activation for the solvolysis of benzyl chloride in alcohol-water mixtures.

(c) The Parameter $(\delta \Delta V^*/\delta P)_T$

In those cases where the data are best fitted by a polynomial of the second degree, the parameter $(\delta \Delta V^*/\delta P)_T$ was calculated from the coefficient of P^2. The results are given in Tables 6 and 7.

The least-mean-square deviation, σ_c^2, in this parameter was calculated from the expression

$$\sigma_c^2 = \sum_i (\delta J/\delta Y_i)\, \sigma^2 , \qquad (4.8)$$

where J is the least-mean-square expression for the coefficient of P^2. The results of this calculation are shown also in Tables 6 and 7. As expected the calculated deviations in $(\delta \Delta V^*/\delta P)_T$ are known much less accurately than the values of ΔV^*. However the differences between the parameters for different reactions lie outside the calculated deviations.

Table 4

Volumes of activation for the solvolysis of benzyl chloride and substituted benzyl chlorides at 50.00°C in an acetone-water mixture containing 0.1407 mole fraction acetone .

Substituent	$-\Delta V^*$ (cm^3 $mole^{-1}$)
p - Methyl	18.5±0.1
H	21.4±0.8
p - Chloro	21.8±0.1
p - Nitro	23.3±0.2

Table 5

Volumes of activation for the solvolysis of *p*-methyl benzyl chloride at 50.00°C in different acetone-water mixtures.

Solvent Composition (Mole Fraction Acetone)	$-\Delta V^*$ $cm^3\ (mole)^{-1}$
0.1407	18.5 ± 0.1
0.1972	24.0 ± 1.0
0.2692	22.8 ± 0.2
0.4955	20.0 ± 0.2

Table 6

The parameters $(\delta \Delta V^{*}/\delta P)_T$ for the solvolysis of benzyl chloride and substituted benzyl chlorides at 50.00°C in an acetone-water mixture containing 0.1407 mole fraction acetone.

Substituent	$10^3 \times (\delta \Delta V^{*}/\delta P)_T$ (cm^3 (p.s.i.g.)$^{-1}$ mole^{-1})
p - Methyl	- (a)
H	0.1±0.1
p - Chloro	0.21±0.07
p - Nitro	1.1±0.4

(a) Best fit to the data was a linear polynomial. $(\delta \Delta V^{*}/\delta P)_T \doteqdot 0$

Table 7

The parameters $(\delta\ \Delta V^*/\delta\ P)_T$ for the solvolysis of p-methyl benzyl chloride at 50.00°C in different acetone-water mixtures.

Solvent Composition (Mole Fraction Acetone)	$10^3 \times (\delta\ \Delta V^*/\delta\ P)_T$ $cm^3\ (p.s.i.g.)^{-1}\ mole^{-1}$
0.1407	- (a)
0.1972	1.0±0.3
0.2692	0.86±0.05
0.4955	- (a)

(a) Best fit to the data was a linear polynomial $(\delta\ \Delta V^*/\delta\ P)_T \doteqdot 0$

(d) The Partial Molar Volumes of p-Methyl Benzyl Chloride in Different Acetone-Water Mixtures

The formulation used to calculate the apparent partial molar volumes of p-methyl benzyl chloride in acetone-water mixtures from density measurements of solutions has been given in Chapter 1. The method of measuring the densities of the solutions using a differential buoyancy apparatus was outlined in Chapter 3. A problem associated with acetone evaporation was also described in Chapter 3. A typical time-course plot of balance reading versus time for a 0.06000 molar p-methyl benzyl chloride solution in an acetone-water mixture containing 0.4955 mole fraction acetone is shown in Figure 15. Extrapolation of these graphs to zero time gave values for the weight differences used to calculate the densities of the solutions with uncertainty in the fourth decimal place. This uncertainty permitted the calculation of the densities to five significant figures and the estimation of the apparent partial molar volumes to three significant figures.

The densities of solutions of p-methyl benzyl chloride in acetone-water mixtures of known acetone and water composition, the apparent partial molar volumes of this compound in these mixtures, and the extrapolated values of the partial molar volumes, together with their least-mean-square deviations are given in Table 8. The concentration range over which the densities of solutions were measured was determined by the solubility of the compound in the reaction mixture and the response of the balance. The ability to reproduce the densities of the solvents was checked several times,

Figure 15

A typical time-course plot of balance reading versus time for the acetone-water mixture containing 0.4955 mole fraction acetone and 0.06000 molar *p*-methyl benzyl chloride at 25.00°C.

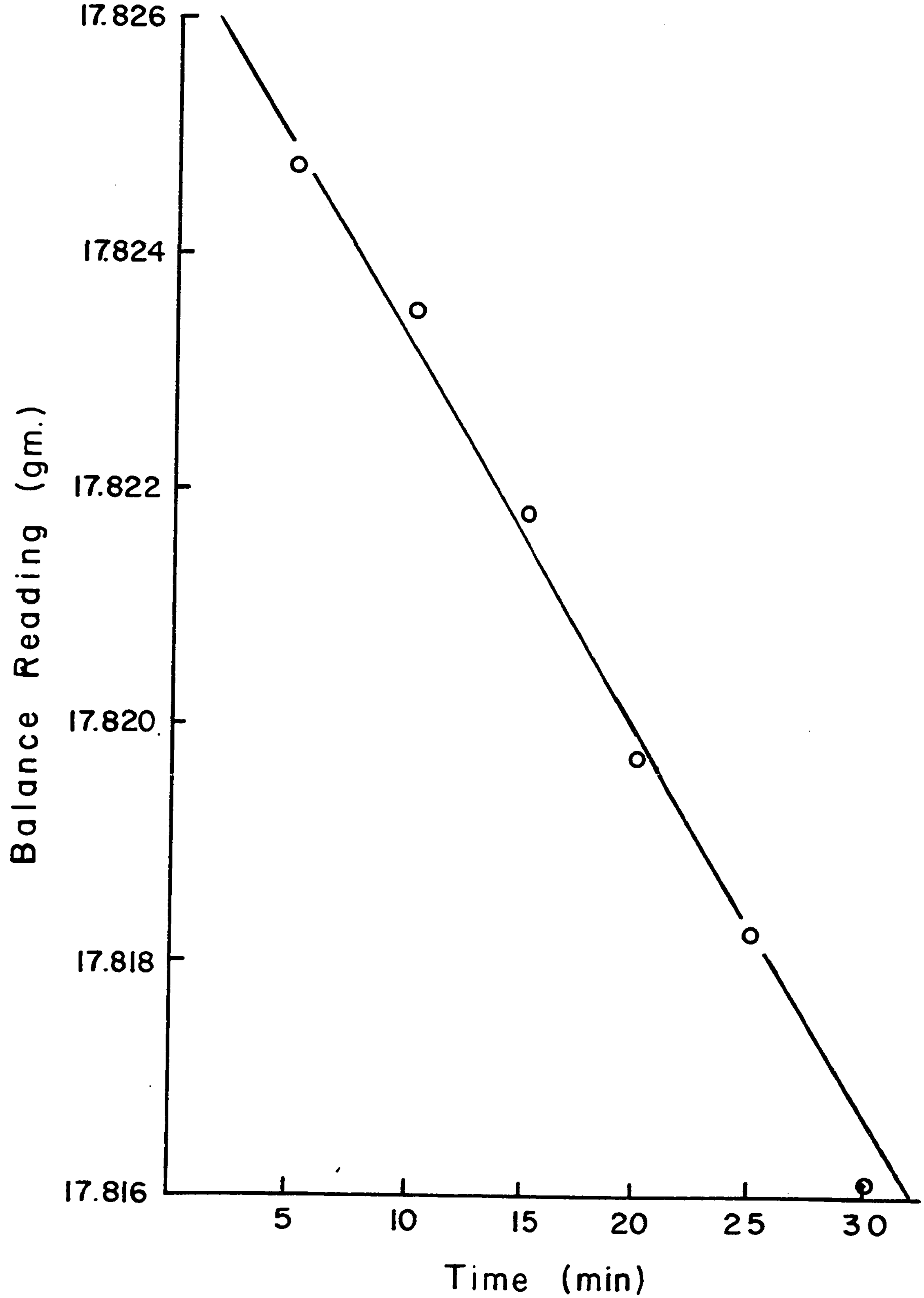

17.826
17.824
17.822
17.820
17.818
17.816
Balance Reading (gm.)
5
10
15
20
25
30
Time (min)

Table 8

Densities, apparent partial molar volumes, and extrapolated partial molar volumes of p-methyl benzyl chloride in various acetone-water mixtures.

Temperature = 25.00±0.01°C

Mole Fraction Acetone in Solvent	Concentration of Solute moles $(\text{liter})^{-1}$	Density of Solution gm. cm^{-3}	Apparent Partial Molar Volume $\text{cm}^3\ (\text{mole})^{-1}$	Extrapolated Partial Molar Volume $\text{cm}^3\ (\text{mole})^{-1}$
0.4955	0	0.85445		125±2
"	0.02984	0.85533	130	
"	0.04003	0.85558	131	
"	0.04200	0.85562	132	
"	0.04971	0.85580	132	
"	0.06000	0.85596	135	
0.2692	0	0.90712		145±2
"	0.01991	0.90734	143	
"	0.02977	0.90746	142	
"	0.03972	0.90761	141	
"	0.04499	0.90774	140	
"	0.04978	0.90778	140	

Table 8 (Continued)

Mole Fraction Acetone in Solvent	Concentration of Solute moles $(\text{liter})^{-1}$	Density of Solution gm. cm^{-3}	Apparent Partial Molar Volume $\text{cm}^3\ (\text{mole})^{-1}$	Extrapolated Partial Molar Volume $\text{cm}^3\ (\text{mole})^{-1}$
0.1972	0	0.92891		137±2
"	0.01977	0.92912	139	
"	0.02973	0.92923	139	
"	0.03971	0.92927	141	
"	0.04984	0.92937	141	
0.1407	0	0.94649		128±2
"	0.01927	0.94681	131	
"	0.02000	0.94682	130	
"	0.02030	0.94682	131	
"	0.02135	0.94681	132	

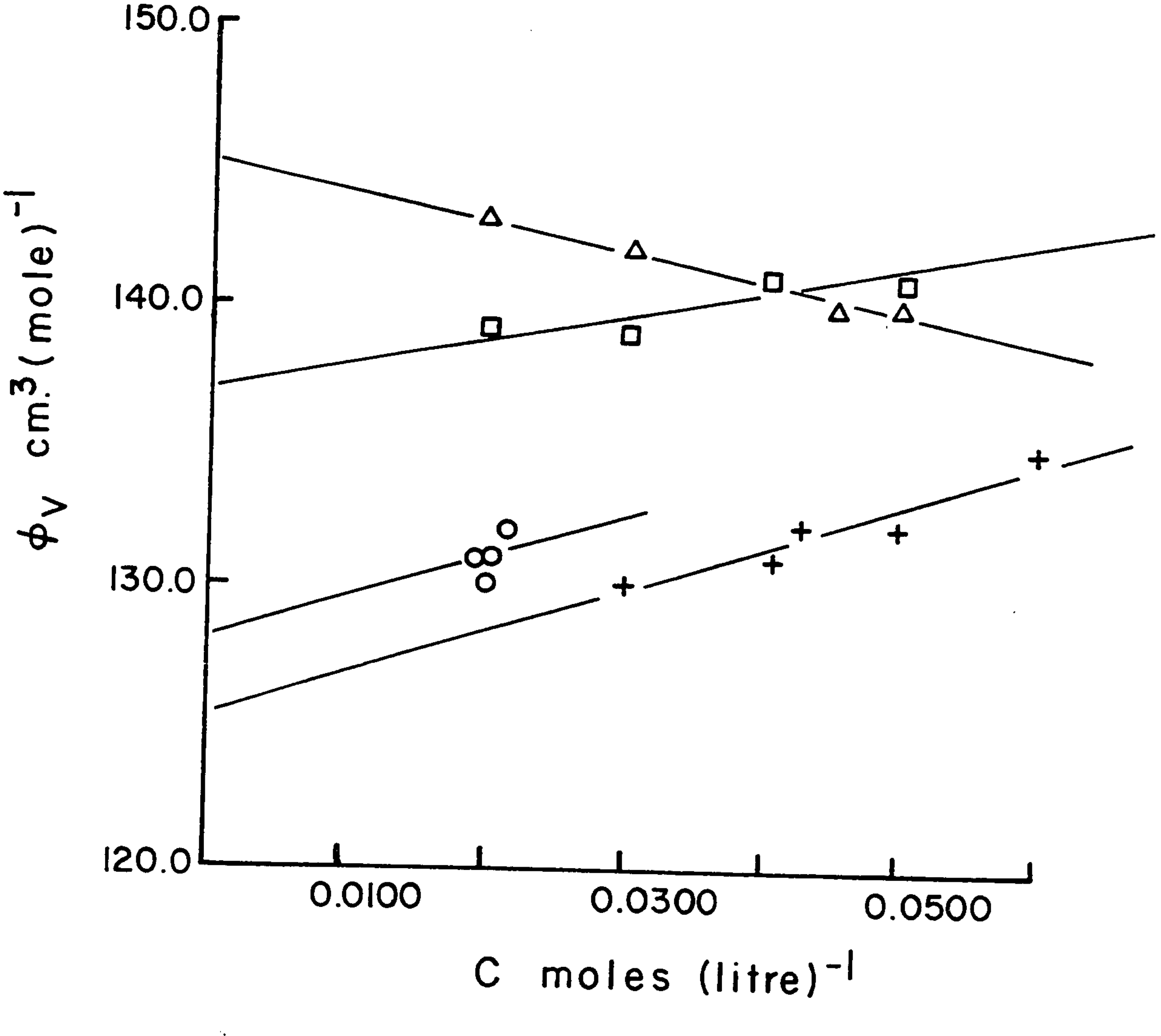
and the necessity of measuring the apparent partial molar volumes of p-methyl benzyl chloride in the mixture containing 0.1407 mole fraction acetone over a very small range of concentration, indicated that the apparent partial molar volumes could be estimated to better than 1 cm^3 per mole. The apparent partial molar volumes are plotted as a function of p-methyl benzyl chloride concentration in each solvent mixture in Figure 16. The usual least-mean-square treatment of these data indicated that the standard deviations in the acetone-water mixtures containing 0.1972, 0.2692 and 0.4955 mole fraction acetone were about 2 cm^3 per mole. The extrapolation in the case of the acetone-water mixture containing 0.1407 mole fraction acetone was made on the basis of the slope of the 0.4955 mole fraction mixture.

There appear to be no data in the literature with which to compare the present data. A similar maximum in the partial molar volumes in aqueous-alcohol mixtures has been reported by Golinkin *et al.*[67] for the partial molar volumes of benzyl chloride.

Figure 16

A plot of apparent partial molar volume of p-methyl benzyl chloride against concentration in various acetone-water mixtures at 25.00°C.

Δ	0.2692 mole fraction acetone
□	0.1972 mole fraction acetone
○	0.1407 mole fraction acetone
+	0.4955 mole fraction acetone


150.0
140.0
130.0
120.0
ϕ_V cm.^{3}(mole)$^{-1}$
0.0100
0.0300
0.0500
C moles (litre)$^{-1}$

CHAPTER 5

Discussion

Part I The Volumes of Activation

(a) Electrostriction and the Sign of ΔV^*.

It is seen from Tables 4 and 5 that the volumes of activation for all the reactions studied are large and negative. It was shown that such behaviour is to be expected in ionogenic reactions where solvent electrostriction about the activated complex plays an important role in the activation process. The present observations therefore support previous conclusions regarding the highly polar character of the activated complexes in the solvolysis of benzyl chloride and substituted benzyl chlorides[54].

The question now arises as to whether the signs and magnitudes of these parameters will be helpful in determining the extent of S_N1 and S_N2 character of the activated complexes of these reactions. Data from other neutral solvolysis reactions whose mechanisms are well established would be helpful but unfortunately these data are not plentiful. Furthermore it is difficult to draw conclusions from them because of the different solvents used in the various studies, and the different degrees of bond making and breaking in the activated complexes of the various reactions. Because of this, the available volumes of activation for neutral solvolysis reactions cover a wide range of values and it is not clear from the results whether there is a boundary line which divides the volumes of activation for purely S_N1 reactions from those for purely S_N2 reactions.

Buchanan and Hamann[27] have measured the volumes of activation for the S_N1 solvolysis of t-butyl chloride in 80 per cent aqueous ethanol and report a value of -21 ml per mole. David and Hamann[29] have measured the volume of activation for the S_N2 solvolysis of ethyl bromide in the same solvent mixture and report a value of -15 ml per mole. The reported uncertainties in these results however make it difficult to draw conclusions. The change in leaving group, X, from chlorine to bromine will also affect the magnitudes of the volumes of activation because of changes in atomic size.

It should be noted here that surveys of the literature on the entropies of activation of reactions whose mechanisms are well established have shown that the entropies of activation of bimolecular reactions such as S_N2 solvolyses are usually somewhat more negative than those of unimolecular reactions such as S_N1 solvolyses[153,154]. In part III of this chapter it will be shown that in solvents of the same composition a linear relationship between the electrostatic contributions to the volumes of activation and entropies of activation is to be expected. It might therefore be concluded that the volumes of activation of reactions whose mechanism is S_N2 might be expected to be somewhat more negative than those which are S_N1.

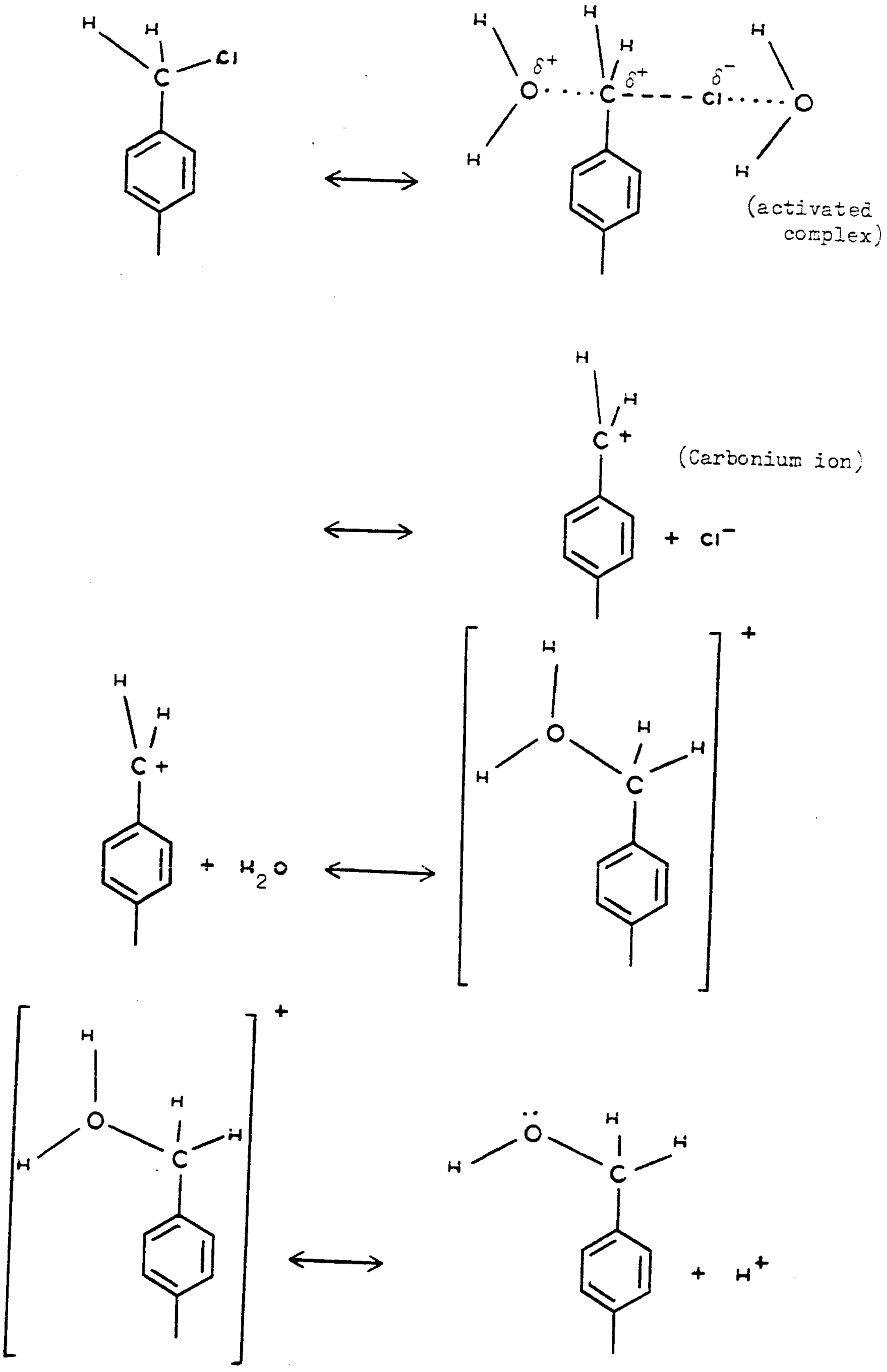
Consideration of the mechanisms and activated complexes of solvolytic reactions does not help to distinguish between purely S_N1 or S_N2 solvolytic reactions on the basis of their volumes of activation. Three essentially different simple mechanisms can be recognised[54,81,87]. They are illustrated in Figure 17 using the

Figure 17

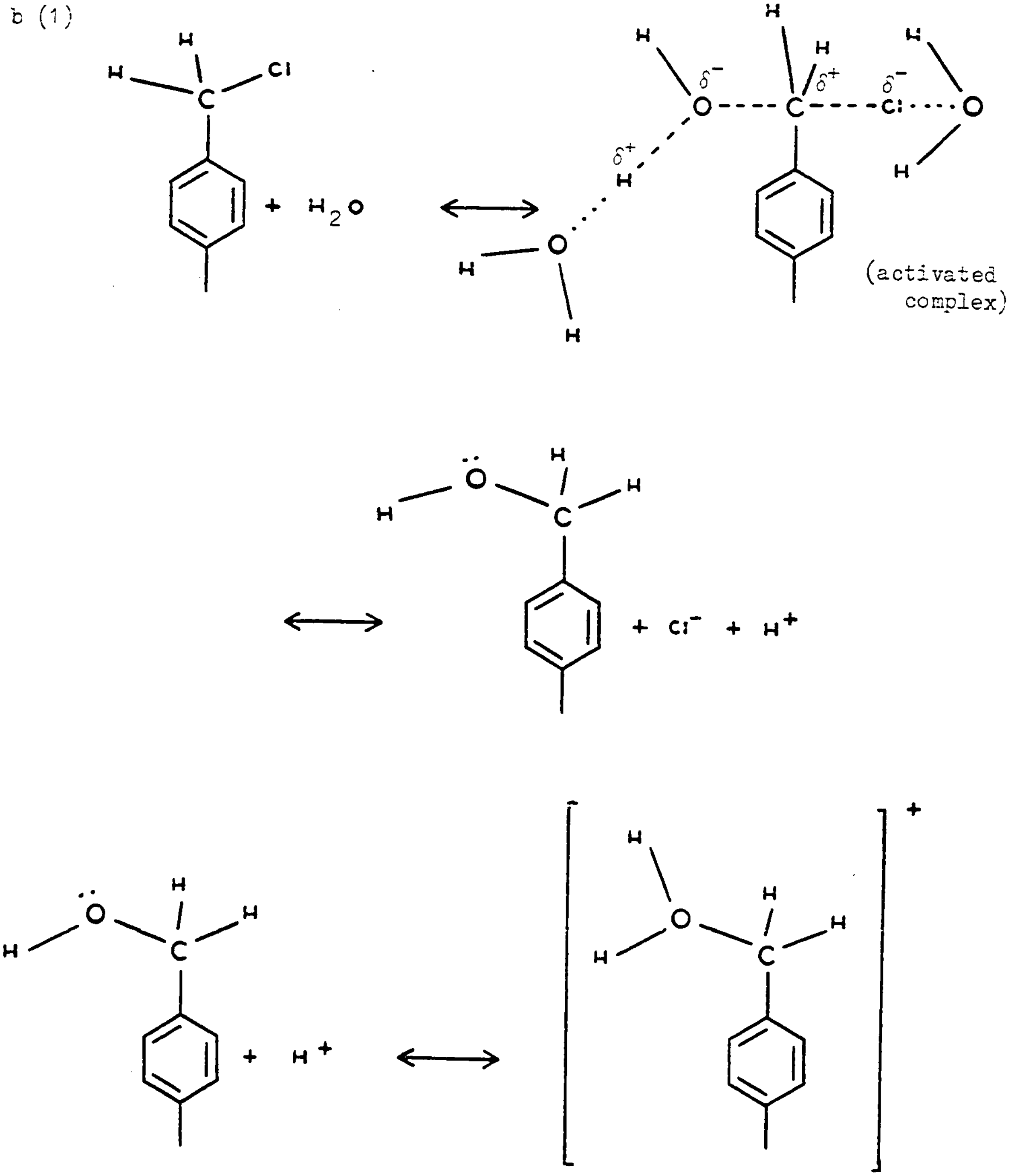
Three mechanistic schemes for the solvolysis of benzyl chloride. (Consistent with the data of Tommila and co-workers[54], Bensley and Kohnstam[81], and Fry and Hill[87]) (.......represents a coulombic interaction and ------- represents a partial covalent bond*)

Note. * It must be remembered that coulombic interactions are not directed interactions as are bonding interactions. This might be implied by the symbol ..... . It is used here to help distinguish between the extreme S_N1 and S_N2 reaction mechanisms.

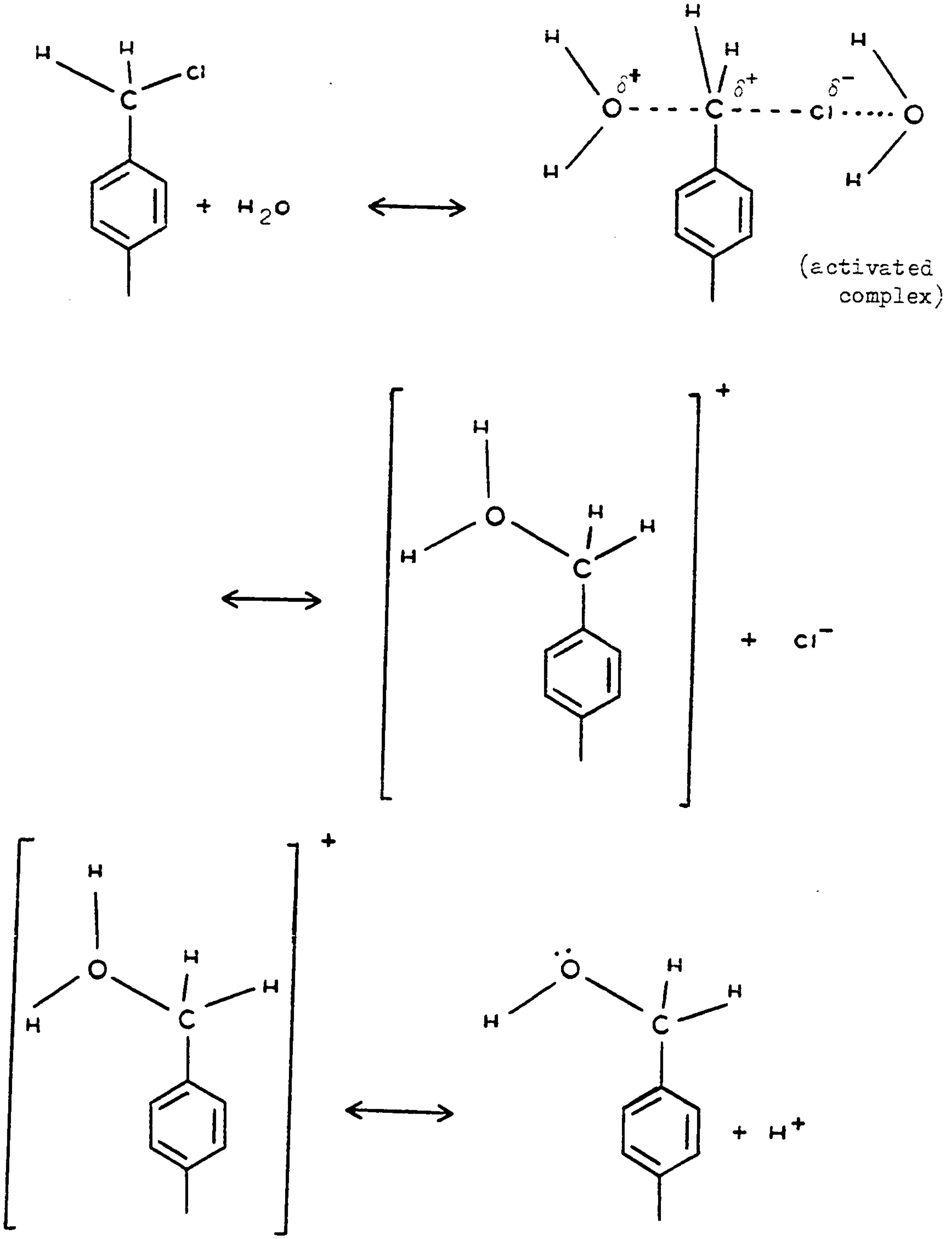
a



b (1)



b (2)


H
H
Cl
C
+ H₂O
H
H
H
H
H
δ+
δ+
δ−
O
C
Cl
O
H
H
(activated complex)
H
O
H
C
H
H
+
+ Cl⁻
H
O
H
C
H
H
+
O
H
C
H
H
+ H⁺

benzyl chloride molecule as the reactant. Each of these mechanistic schemes have been proposed at one time or another for the solvolysis of benzyl chloride.

The three mechanisms differ primarily in the number of covalency changes which are taking place in the activated complexes. There is only <u>one</u> covalency change taking place in the slow step of the S_N1 mechanism, that of the breaking of the α-carbon to chlorine bond. In addition to this, the S_N2 activated complexes involve covalency changes in a water molecule of the solvent. In case b(1) a partial covalent bond has formed between an oxygen atom of a water molecule, and an oxygen to hydrogen bond in this same water molecule has begun to break. In case b(2), although a partial covalent bond is formed between an oxygen atom and the α-carbon atom of the substrate molecule in the activated complex, no partial breaking of an oxygen to hydrogen bond has occurred.

The formation of a partial covalent bond in the activated complex is accompanied by charge development at the atoms between which the bonds are being formed or broken due to transfer of electrons between these atoms. Consequently the activated complex of reaction b(1), in which two bonds are being broken and one bond is being formed, is expected to be more polar than the remaining two activated complexes, and on this account to have a more negative volume of activation. The difference between the volumes of activation to be expected from mechanisms a or b(2) is very difficult to assess. Whalley and Koskikallio[155] have found that the volumes of activation of A-1 and A-2 reactions are a useful criterion of mechanism.

The latter reaction mechanism has been shown to give a more negative volume of activation. The primary difference between the activated complexes of the slow steps of these reactions was considered to be the incorporation of a water molecule into the A-2 activated complex, and not in the A-1 case. The presence of a water molecule partially bound to the substrate molecule also distinguishes mechanism a from b (2). Consequently, on this view one might expect the volumes of activation of a reaction such as b(2) to be more negative than that of reaction a. However, in the above reactions the charge developed in the S_N2 activated complex is most probably spread over a larger volume, which should reduce the degree of solvent electrostriction to be expected from that found in the S_N1 case. This compensatory behavior makes it more difficult to estimate _a priori_ the difference between the volumes of activation to be expected from mechanisms a and b (2).

It must be concluded from what has been said above that, in the absence of more experimental ΔV^* values for neutral solvolysis reactions, it is difficult to assess what magnitudes of this parameter are to be expected for the extreme S_N1 and S_N2 reactions, although the latter part of our discussion suggests that the volume of activation for the S_N2 reaction might be expected to be more negative than that of the S_N1 reaction. It may be concluded also that the negative signs of the volumes of activation confirm previous conclusions regarding the high polarity of the activated complexes of these neutral solvolysis reactions and the importance of solvent electrostriction in the activation process.

(b) The Variation of ΔV^{*} with Substituent in a Solvent Mixture of Constant Composition

It is seen from Table 4 that the volumes of activation diminish (i.e. become more negative) in the series

$$\underline{p}\text{-CH}_3 > \text{H} > \underline{p}\text{-Cl} > \underline{p}\text{-NO}_2$$

the value being -18.5 cm^3 per mole for p-methyl and -23.3 cm^3 per mole for p-nitro. The present section is concerned with the interpretation of these results from a mechanistic point of view. In view of the inherent complexities of the situation, the mechanism not being simple, it is unfortunately not possible to arrive at firm conclusions about the significance of these results. Various possible factors will be suggested, with special reference to the values for p-methyl and p-nitro.

It will be convenient, in discussing these results, to consider first two extreme and over-simplified situations in order to see what effects would be expected in these cases. These are:

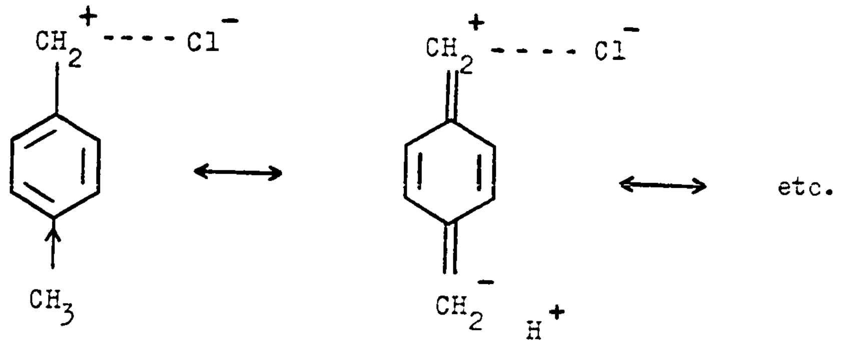
Case I. The reactions all occur by extreme S_N1 mechanisms.

Case II. p-methyl benzyl chloride is hydrolyzed by an extreme S_N1 mechanism, p-nitro benzyl chloride by an extreme S_N2 mechanism.

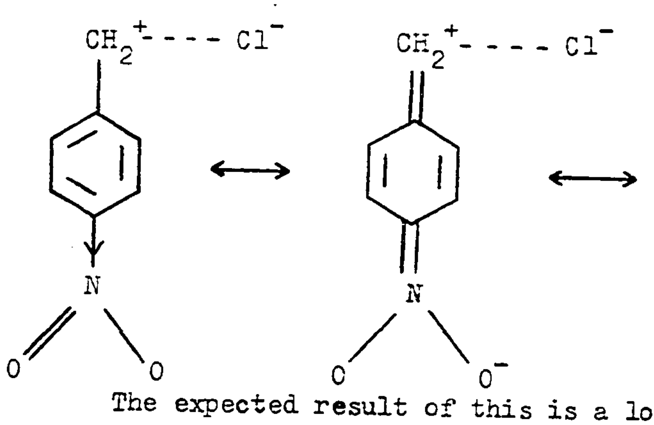
In the light of the discussion in Section e, Part II of Chapter 1, it is realized that neither of these simple possibilities is consistent with all of the evidence. The true situation appears to be represented by

Case III. All the reactions occur by S_N2 mechanisms, the p-methyl reaction having relatively more S_N1 character and the p-nitro compound relatively more S_N2 character.

Case I implies that the activated complexes in all of the reactions correspond to essentially complete ionization of the C-Cl bond. The chlorine atom will bear a full negative charge and the remainder of the molecule a full positive charge. However, the charge distribution on the benzene ring will be different in the case of the p-methyl and p-nitro compounds because of the effects of the substituents. The methyl group, because of its inductive and resonance effects, will tend to reduce the positive charge at the α-carbon atom, so that there will be a smearing of the positive charge over the p-methyl benzyl ion and thus effectively reducing the electrostatic field strength about the activated complex:



The nitro group, on the other hand, tends to draw electrons to itself for similar reasons, and will therefore bring about no reduction of positive charge on the α-carbon atom and consequently no reduction in the intensity of the electrostatic field about the nascent benzyl carbonium ion in the activated complex:



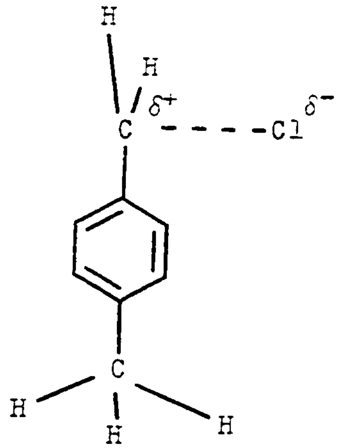
The expected result of this is a lower (more negative) volume of activation for the p-nitro compound, because of greater solvent electrostriction brought about by the full positive charge on the α-carbon atom. The spreading of the charge in the p-methyl case will reduce the solvent electrostriction. The volumes of activation for the S_N1 solvolysis of several substituted benzenediazonium ions in aqueous solution

$$RN_2^+ + 2H_2O \text{ ——— } ROH + N_2 + H_3O^+$$

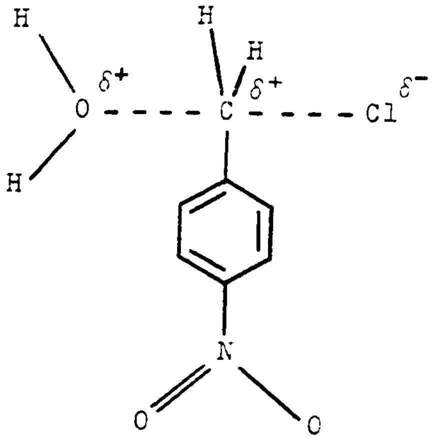
measured by Brower[156] have been interpreted in a manner similar to that given above[5b]. On the basis of this hypothesis the solvent effects on the volume of activation are expected to predominate (ΔV_2^*); structural effects will be essentially independant of the substituent although, with a reduction of the charge on the α-carbon atom, the C-Cl distance in the p-methyl benzyl chloride case is expected to be greater than in the p-nitro benzyl chloride case. Consequently ΔV_1^* for the latter reaction should be less than ΔV_1^* for the former. Therefore structural effects would predict the same trend in the volume of activation.

The deductions for this case are in accord with the facts. Although the mechanisms are not extreme S_N1 mechanisms it seems likely that the affects discussed here actually play some part, and that "charge-smearing" is relevant to the observed volumes of activation.

Case II is more difficult to assess because of lack of information about the magnitudes of volumes of activation for reactions occurring by S_N1 and S_N2 mechanisms (cf. Section a of Chapter 5). On this view the activated state for the hydrolysis of the p-methyl compound would be



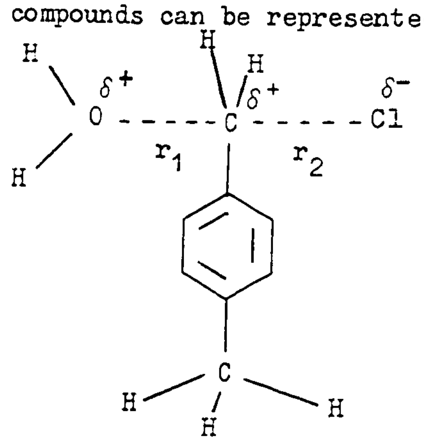
That for the p-nitro compound would be



This explanation might lead to the effects observed, since there is a suggestion (cf. Section (a) of Chapter 5) that volumes of activation may, other things being equal, be lower (more negative for reactions occurring by an S_N2 mechanism than for S_N1 reactions. Certainly the structural effects are in the right direction, the S_N2 activated complex having a partial covalent bond formed between a water molecule and the α-carbon atom. The solvent electrostriction effects might tend to counteract this to some extent, but will not be large especially in view of the charge smearing brought about by the p-methyl group.

Case III, that the mechanism is more S_N1-like for the p-methyl compound and more S_N2-like for the p-nitro compound, is probably the true situation. Both of the effects considered under Cases I and II will play a part here.

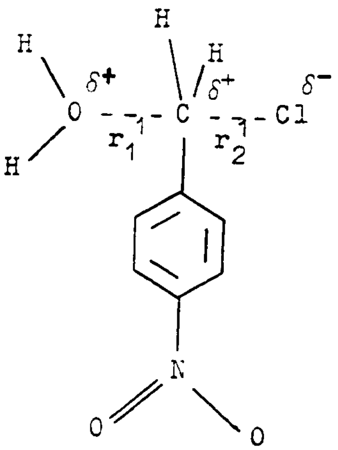
The activated complexes for the p-methyl and p-nitro compounds can be represented as



and

$r_1 > r_1^1$

$r_2 > r_2^1$



The most important effects are now:

(1) As in Case I there will be a greater charge smearing in the p-methyl compound, so that there will be less electrostriction of solvent.

(2) As in Case II, the activated complex will be more compact in the p-nitro compound. This is due to the shorter α-carbon to chlorine

and α-carbon to oxygen distances in this activated complex than in the others. That this effect is qualitatively reasonable and predicts the observed trend in the volumes of activation may be seen from the following calculations. They are based on the procedure used by Hamann to estimate the contribution to the volume of activation from such structural effects (cf. Part Ib, Chapter 1).

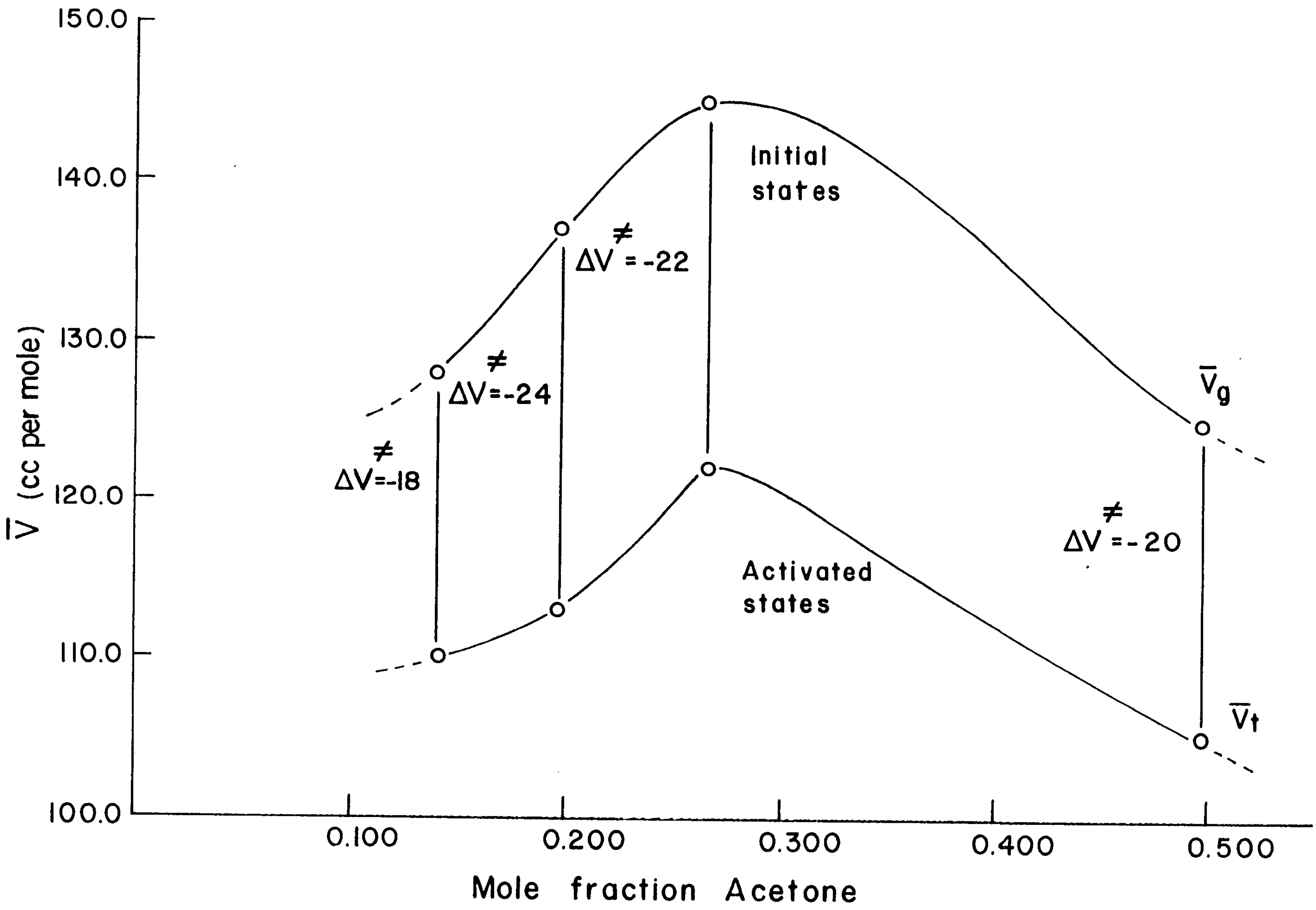
Initially, it will be assumed that the difference between the volumes of activation for the p-methyl and p-nitro reactions is due only to a difference in the α-carbon to chlorine distance in the activated complexes of the two reactions (this distance in the p-methyl activated complex being greater). The van der Waals radii of the carbon and chlorine atoms are taken to be 2.0 Å and 1.8 Å[157] respectively. Equation (1.16) shows that the measured volume of activation difference for the p-methyl and p-nitro reactions of 4.8 cm^3 per mole requires that the difference in the above-mentioned bond lengths in the activated complexes be approximately .4 Å. On the assumption that the α-carbon to chlorine bond distance in the p-nitro activated complex is 10 to 20 per cent greater than the same distance in the reactants, (cf. Stearn and Eyring[158]), the α-carbon to chlorine bond distance in the p-methyl activated complex is 32 to 42 per cent greater than this distance in the reactant molecule (1.765 Å). Such a figure does not seem unreasonable, in that bond extensions of 100 per cent have been calculated from potential-energy surfaces.[2a] In any event, the decreasing α-carbon to oxygen distance in the activated complexes (smallest distance in the p-nitro reaction) have not been considered in the above calculations. If this were taken into account much smaller bond extensions would be required to explain the differences in the volumes of activation. This behavior would indeed be favoured from an energetic point of view.

(c) The Volumes of Activation for the Solvolysis of p-Methyl Benzyl Chloride as a Function of Solvent Composition.

The results given in Table 5 for the solvent dependence of the volumes of activation of p-methyl benzyl chloride in acetone-water mixtures show that the values pass through a distinct minimum as a function of solvent composition. The partial molar volume measurements of p-methyl benzyl chloride made at 25°C (Table 8) in acetone-water mixtures of the same composition show that this function passes through a maximum in the same region of solvent composition as the volumes of activation pass through a minimum (the $\overline{V}_g$ maximum is displaced to a higher acetone mole fraction than the minimum in ΔV^*, due probably to the lower temperature of measurement). This behavior suggests that the minimum in ΔV^* arises at least in part from a maximum in $\overline{V}_g$. If it is assumed that the $\overline{V}_g$'s are not strong functions of temperature the partial molar volumes of the activated complexes of the above reactions may be calculated. The results are plotted in Figure 18. They show that the height of the maximum in $\overline{V}_t$ is not as great as that for $\overline{V}_g$. These observations are in agreement

Figure 18

Plots of the partial molar volumes of the reactants and activated complexes for the solvolysis of *p*-methyl benzyl chloride in different acetone-water mixtures.


$\bar{V}$ (cc per mole)
150.0
140.0
130.0
120.0
110.0
100.0
0.100
0.200
0.300
0.400
0.500
Mole fraction Acetone
Initial states
Activated states
$\Delta V^{\neq}=-18$
$\Delta V^{\neq}=-24$
$\Delta V^{\neq}=-22$
$\Delta V^{\neq}=-20$
$\bar{V}_g$
$\bar{V}_t$

with those made by Arnett and co-workers[68] who studied enthalpies of activation, and by Hyne et al.[67] who studied volumes of activation. They found that the maximum in the respective partial thermodynamic quantities for an ionic species, such as the activated complex of the present reaction, was smaller in height than a similar maximum observed for a non-polar species such as the reactants in the present study.

This behavior is very difficult to understand owing to the very complex nature of aqueous organic mixtures. As discussed in Chapter 2 it would appear that the region of high water content is essentially aqueous in nature, with acetone molecules merely occupying spaces in the less dense component of the water system. This behavior persists until sufficient acetone is added to cause a concerted breakdown of the water structure.

Currently accepted theories of the solvation of non-polar molecules in water would suggest that p-methyl benzyl chloride molecules would also be expected to fit into the less dense component of the water structure in a manner similar to the acetone molecules. Consequently an abnormally low partial molar volume is expected for both compounds. As the acetone concentration increases a fraction of the less dense component is filled up, leaving less space into which the substrate molecule may fit. Consequently an increase in the partial molar volume of the substrate is expected. This behavior would be expected to persist until the breakdown of the water structure. Beyond this point the decrease in the partial molar volume of the substrate would be understood if selective solvation of this species by acetone molecules occurred and became the predominant solvation mechanism.[97] Again an abnormally low partial molar volume would be observed. Indeed the selective solvation of the substrate molecules may be important over the whole range of solvent composition, its effect in lowering the partial molar volume of the substrate molecules being the most important solvation mechanism in the region of high acetone content. This latter contention could only be demonstrated by further density measurements on solutions in aqueous-organic mixtures.

The maximum in the partial molar volumes of the highly polar activated complex is more difficult to understand. The strength of the ion-dipole interactions between the activated complex and solvent in the highly aqueous region is apparently strong enough to result in the breakdown of the less dense open-structured component of the water, with the result that there are fewer spaces into which the added acetone molecules may fit. This would explain the increasing partial molar volume of the activated complex in the high aqueous region. With the total breakdown of the water structure on the addition of sufficient acetone the usual electrostriction of solvent about the activated complex will explain the abnormally low partial molar volume observed in this composition region.

The above discussion suggests very strongly that properties of the reactant molecules in solution and, in particular, solvation phenomena associated with solvent molecules in the immediate vicinity of these species, play a large role in determining the energetics of solvolysis of benzyl chloride and substituted benzyl chlorides. This possibility will be examined further in terms of the significance of the volumes of activation from the standpoint of their mechanisms.

PART II The Parameter $(\delta \Delta V^*/\delta P)_T$

(a) General

Experimental techniques of sufficient precision to measure with some degree of accuracy the parameter $(\delta \Delta V^*/\delta P)_T$ have only recently been developed. This parameter will be useful in checking the conclusions drawn from measurements of volumes of activation, in the same way that the measurement of heat capacities of activation have helped with our understanding of enthalpies of activation. The general disposition of $\log_e k$ - pressure data suggests that the parameter is usually zero or positive, indicating that the reactants are as compressible, or more compressible than the activated complexes. Recently some examples of negative values have been observed[66,159]. Further comments on these latter observations will be given in the Appendix.

From the definition of the volume of activation

$$\Delta V^* = \bar{V}_t - \bar{V}_g \quad ,$$

an expression for $(\delta \Delta V^*/\delta P)_T$ in terms of $\bar{V}_t$ and $\bar{V}_g$ can be derived, i.e.,

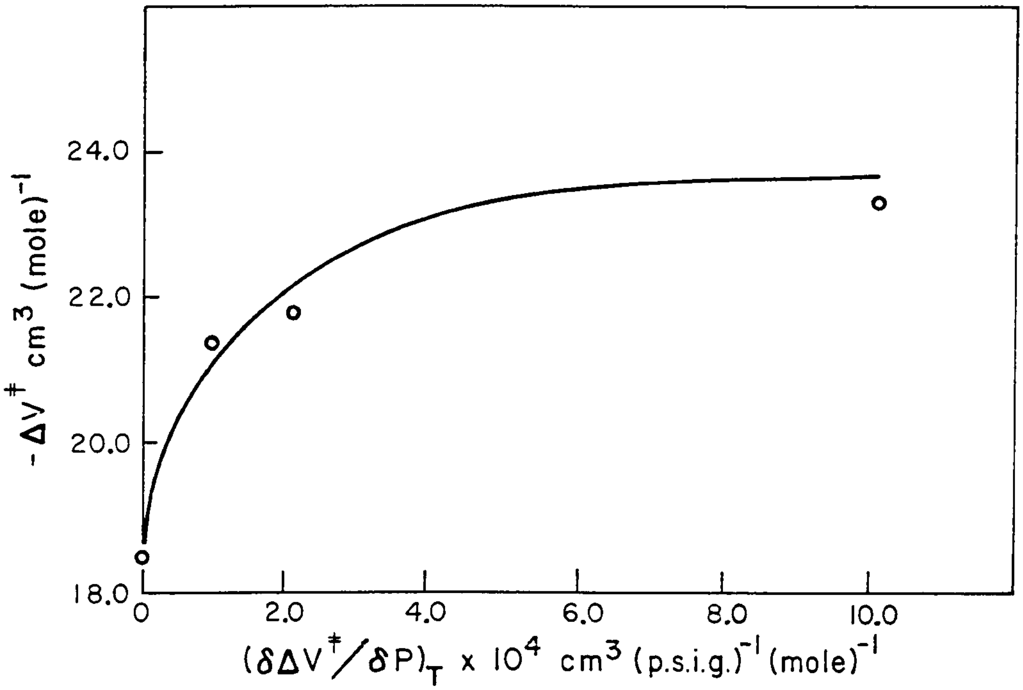
$$(\delta \Delta V^*/\delta P)_T = (\delta \bar{V}_t/\delta P)_T - (\delta \bar{V}_g/\delta P)_T . \qquad (5.1)$$

In view of the very small amount of data in the literature on the isothermal compressions of solutions of ions and non-polar molecules, it is difficult to interpret the present data in other than the simplest terms. It might be expected, by analogy with the pure liquid case, that the more strongly a molecular system is held together the more resistant it will be to compression, and vice-versa. Consequently, the greater the degree of solvent electrostriction about a molecular species, the greater the resistance of that system to compression will be; also the weaker the partial covalent bonds in the activated complex the more easily will the system be compressed. The observation that the parameters $(\delta\ \Delta V^*/\delta\ P)_T$ for ionogenic reactions are usually positive may be understood in the above terms. Solvation of non-polar species is usually the result of weak dipole-dipole and dispersion-force interactions, which are much weaker than ion-dipole interactions which characterize solvation of highly polar species[107]. On the above view, the reactant-solvent system would be much more sensitive to compression than the activated complex-solvent system because of the greater polarity of the latter species. Consequently a positive curvature is usually observed. Negative curvature has only as yet been observed in water as solvent and probably reflects the strength of solvent species surrounding non-polar species when dissolved in this liquid (see Appendix).

A plot of ΔV^* versus $(\delta\ \Delta V^*/\delta\ P)_T$ (shown in Figure 19) for the various substituted benzyl chlorides appears to bear out this conclusion as will be seen in the following section. Although the relationship between these two parameters is not linear, a distinct negative correlation exists. The more negative is ΔV^* the greater is the difference between $(\delta\ \overline{V}_t/\delta\ P)_T$ and $(\delta\ \overline{V}_g/\delta\ P)_T$, this being due to the more compact p-nitro benzyl chloride activated complex. (see Part Ib, Chapter 5).

Figure 19

A plot of ΔV^* against $(\delta\ \Delta V^*/\delta\ P)_T$ for the various substituted benzyl chlorides in the acetone-water mixture containing 0.1407 mole fraction acetone.



24.0
22.0
20.0
18.0
0
2.0
4.0
6.0
8.0
10.0
$-\Delta V^{\ddagger}$ cm^3 (mole)$^{-1}$
$(\delta \Delta V^{\ddagger}/\delta P)_T \times 10^4$ cm^3 (p.s.i.g.)$^{-1}$ (mole)$^{-1}$

(b) Mechanistic Implications of the Variation of $(\delta\,\Delta V^*/\delta\,P)_T$ with Substituent.

The results quoted in Table 6 show that the parameter $(\delta\,\Delta V^*/\delta\,P)_T$ increases in the order p-CH_3 < H < p-Cl < p-NO_2. Since the terms $(\delta\,\overline{V}/\delta\,P)_T$ are always negative, this behavior would be observed in three possible ways, two of which are illustrated schematically in Figure 20. They are;

(1) If $(\delta\,\overline{V}_t/\delta\,P)_T$ decreases in the order p-CH_3 < H < p-Cl < p-NO_2 and $(\delta\,\overline{V}_g/\delta\,P)_T$ remains essentially constant. The p-methyl and p-nitro benzyl chloride cases are chosen in Figure 20a for illustration. The change with increasing pressure in the partial molar volume of the p-nitro activated complex is seen to be much less than the change in the partial molar volume of the p-methyl activated complex.

(2) If $(\delta\,\overline{V}_g/\delta\,P)_T$ increased in the order p-CH_3 > H > p-Cl > p-NO_2 and $(\delta\,\overline{V}_t/\delta\,P)_T$ remains essentially constant. This case is illustrated in Figure 20b, using the same cases as above. The change in the partial molar volume of the p-nitro benzyl chloride substrate is seen to be much larger than the p-methyl substrate partial molar volume.

(3) If both $(\delta\,\overline{V}_t/\delta\,P)_T$ and $(\delta\,\overline{V}_g/\delta\,P)_T$ vary in a complex manner with change in substituent such as to give the observed changes in $(\delta\,\Delta V^*/\delta\,P)_T$. One would require a considerable amount of additional data to discuss this possibility; at the present time these are not available. Consequently consideration of this case must be deferred.

Figure 20

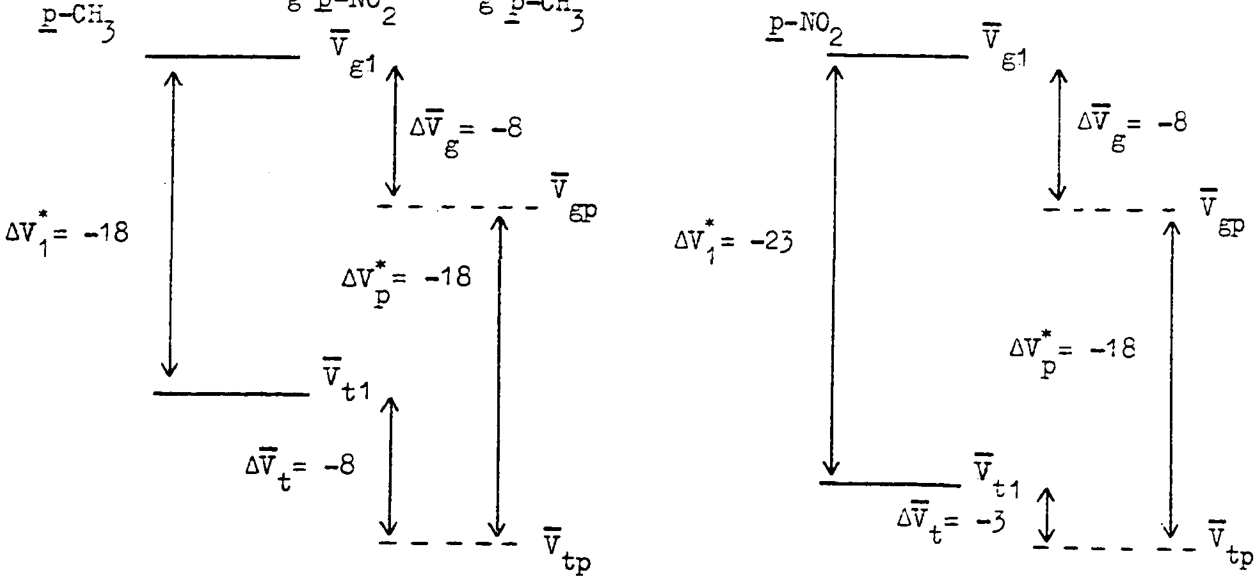
A schematic representation of the relative variations of $\overline{V}_t$ and $\overline{V}_g$ with pressure for p-nitro and p-methyl benzyl chlorides when

$$(a)\quad (\delta \overline{V}_g/\delta P)_{T_{\underline{p}\text{-}NO_2}} = (\delta \overline{V}_g/\delta P)_{T_{\underline{p}\text{-}CH_3}}$$

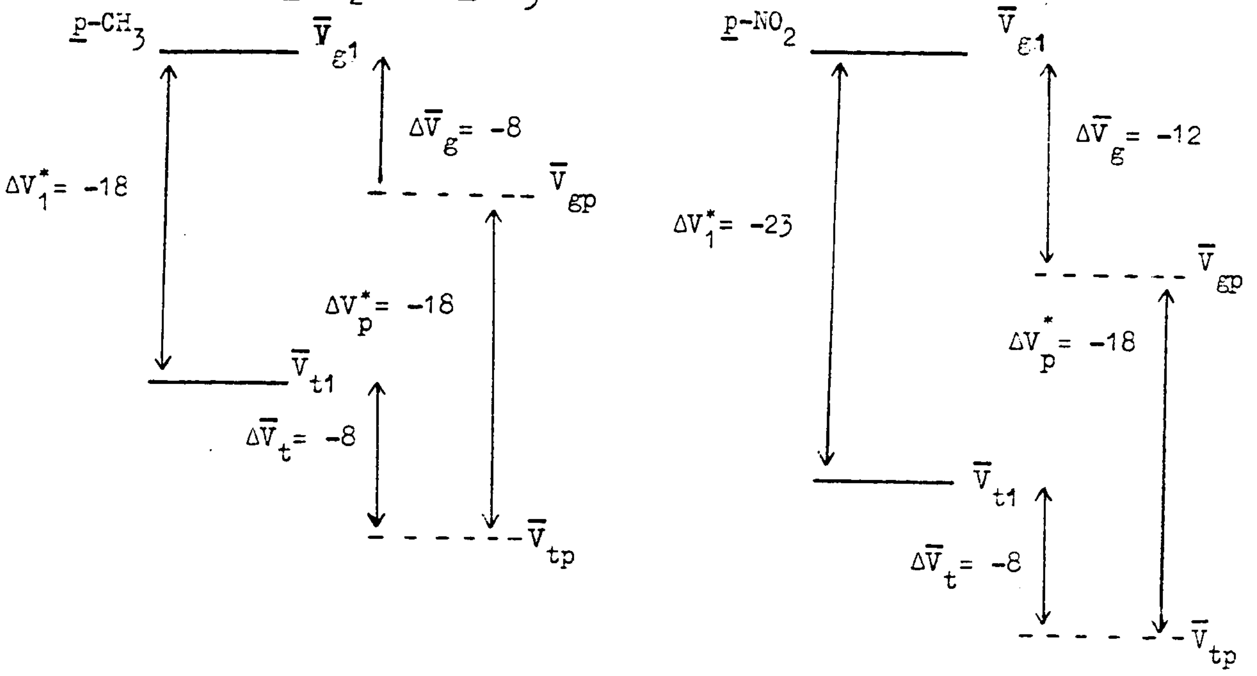
and

$$(b)\quad (\delta \overline{V}_t/\delta P)_{T_{\underline{p}\text{-}NO_2}} = (\delta \overline{V}_t/\delta P)_{T_{\underline{p}\text{-}CH_3}}.$$

a. Case 1. $\Delta\overline{V}_g$ p-NO_2 = $\Delta\overline{V}_g$ p-CH_3



b. Case 2 $\Delta\overline{V}_t$ p-NO_2 = $\Delta\overline{V}_t$ p-CH_3



Case (1) will be considered here, and case (2) will be considered in Section d following. It was shown in Part Ib of this chapter that the degree of covalent bonding in the p-nitro benzyl chloride activated complex, and the difference between the polarity of reactants and activated complexes, are expected to be greater than in the other compounds. For these reasons the forces holding these activated complexes together are greater than in the other cases; $(\delta \overline{V}_{\ddagger}/\delta P)_T$ is much less negative and $(\delta \Delta V^*/\delta P)_T$ is more positive, as is observed. The other compounds may be viewed in a manner similar to that above. Consequently the present results for $(\delta \Delta V^*/\delta P)_T$ confirm our previous conclusions in Part Ib.

(c) The Dependence of $(\delta \Delta V^*/\delta P)_T$ on Solvent Composition

Table 7 shows the values of $(\delta \Delta V^*/\delta P)_T$ as a function of solvent composition for the solvolysis of p-methyl benzyl chloride in solutions of different acetone and water compositions. It is seen that extremum behavior is also observed in this parameter as is generally found in other activation parameters. The parameter displays a maximum at the same point on the solvent composition axis as the volumes of activation display a minimum. For reasons similar to those given in the previous section, this maximum could arise from either a minimum in $(\delta \overline{V}_{\ddagger}/\delta P)_T$ or a maximum in $(\delta \overline{V}_g/\delta P)_T$ or from a more complex variation of both of these quantities. The complexity of the present system, together with the almost complete lack of other data, makes the discussion of the first and last possibilities virtually impossible. In the following section some discussion of the second possibility will be offered in terms of current theories of the solvation of non-polar species in water.

(d) Reconsideration of the Mechanistic Significance of the ΔV^* and $(\delta \Delta V/\delta P)_T$ Data.

The observed minimum in the volumes of activation for the solvolysis of *p*-methyl benzyl chloride in different acetone-water mixtures appears to arise from a large maximum in the partial molar volumes of the reactants and a smaller maximum in the partial molar volumes of the activated complexes. This was discussed in Part Ib of Chapter 5 in terms of peculiar solvation phenomena in aqueous organic mixtures and no reference was made to changes in the structure and charge development in the activated complexes with change in solvent composition. Consideration should also be given to the possibility that changes in ΔV^* and $(\delta \Delta V^*/\delta P)_T$ with substituent arise for similar reasons.

Limited solubility prevented the measurement of the partial molar volumes of the various substituted benzyl chlorides except the *p*-methyl compound, but in any case the discussion of these results in the above terms would be complicated by the necessity of knowing the volumes occupied by the various substituents on the aromatic ring.

However the trend in the parameter $(\delta \Delta V^*/\delta P)_T$ with change in substituent may be discussed qualitatively in the above terms. The situation to be explained is: $(\delta \bar{V}_t/\delta P)_T$ for each of the activated complexes is approximately constant and $(\delta \bar{V}_g/\delta P)_T$ diminishes in the order (*p*-CH_3 > H > *p*-Cl > *p*-NO_2).

The review of acetone-water properties in Chapter 2 suggests that the solvent composition region in which the substituent dependence of ΔV^* and $(\delta\, \Delta V^*/\delta\, P)_T$ was measured (0.1407 mole fraction acetone) is essentially aqueous in nature where the addition of non-polar molecules has the effect of enhancing the open-structured component of the water in the vicinity of the non-polar species. The results of Arnett et al.[68,130] suggest that the less polar the species the greater the degree of structural enhancement in the solvent, other things being equal. Comparison of water and other hydrogen bonded liquids with non-hydrogen bonded liquids also suggests that the stronger this structural enhancement the less sensitive will the system be to compression.

The dipole moments of the various substituted benzyl chlorides increase in the order p-CH_3(0.80D)$^{\neq}$ < H(1.75D) < p-Cl(1.73D) < p-NO_2(3.66D)[160]. The degree of structural enhancement should therefore decrease in this order for the above reasons (i.e. greatest in the p-methyl case). This would then qualitatively explain the trend in $(\delta\, \overline{V}_g/\delta\, P)_T$ above. Unfortunately our present knowledge does not permit us to choose between this latter situation and that described in Part IIb of this Chapter.

$\neq$ Estimated from the dipole moments of p-nitro benzyl chloride, nitrobenzene and toluene.

Part III. Correlations between ΔS^* and ΔV^*.

(a) General

In Figure 21 the volumes of activation for the various benzyl chlorides studied in a mixture of constant composition, are plotted against the entropies of activation for the same conditions of temperature and pressure. The latter data were extrapolated from the work of Tommila and co-workers[54]. The data for the entropies and volumes of activation for the solvolysis of some esters and amides in water, taken from a paper by Chen and Laidler[77], are also plotted. In both cases a linear correlation is obtained (see also reference 75). The slope in the former case is 1.8 ± 0.3 cm^3 °C gm^{-1}. The slope in the latter case is somewhat lower at 1.0 ± 0.4 cm^3 °C gm^{-1}.

Such linear correlations between these and other activation parameters of chemical reactions have been observed frequently and indeed have some basis in theory where the magnitudes of the activation parameters are determined to a large extent by electrostatic interactions. In this part of this thesis an attempt will be made to examine a simplified theoretical treatment of these reactions in terms of the Born expression, along the lines suggested by King[161], in order to ascertain some of the limitations of such correlations.

(b) The Born Expression and the Relationship between ΔV_2^* and ΔS_2^* of Ionogenic Reactions.

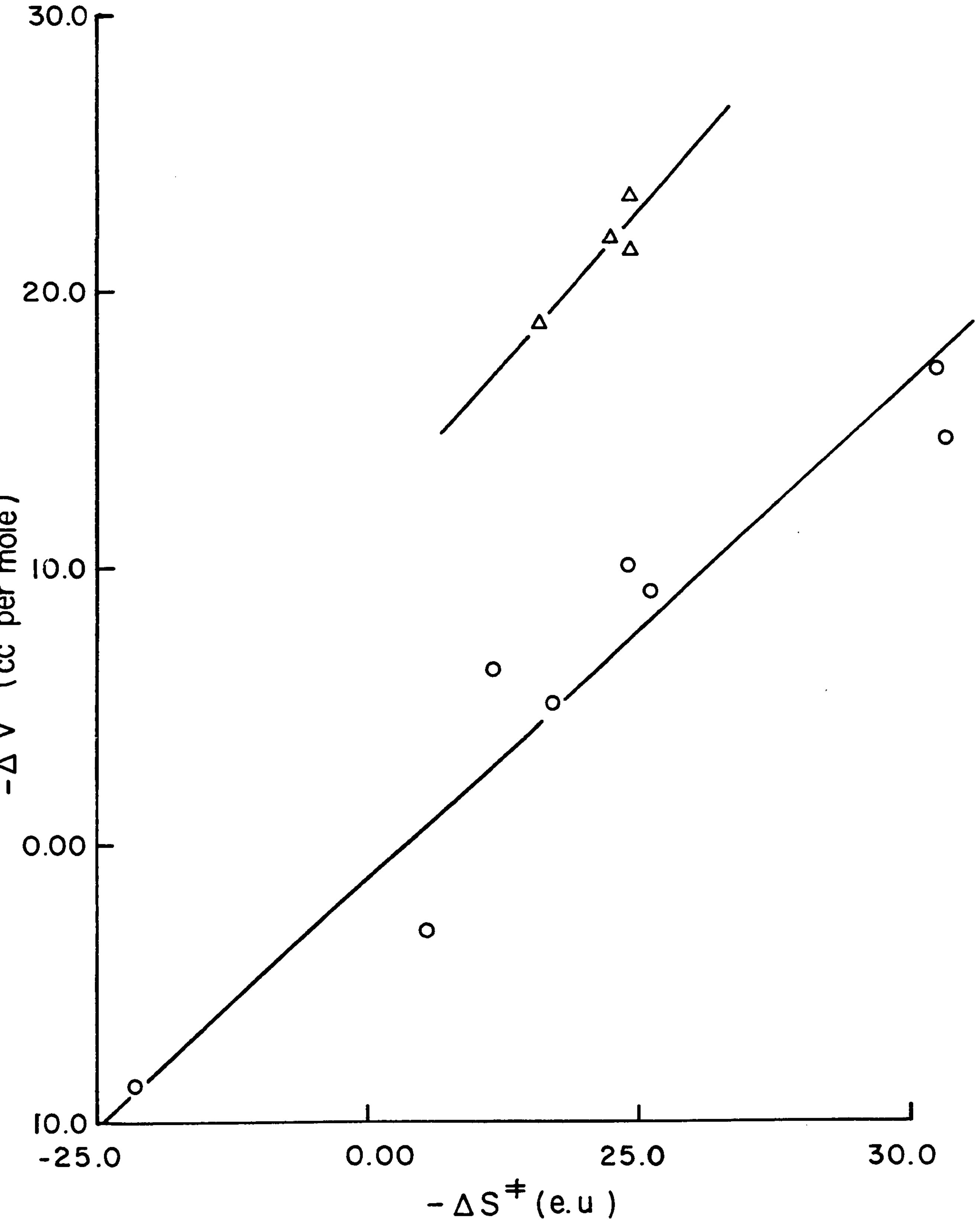
The electrostatic contribution to the free energy of activation of reactions of the form

Figure 21

Correlation between ΔV^* and ΔS^* for various reactions in the liquid phase.

(a) Data for some reactions in water as solvent, taken from a paper by Chen and Laidler[77].

(b) Data from present study for the various substituted benzyl chlorides in the acetone-water mixture containing 0.1407 mole fraction acetone.


30.0
20.0
10.0
0.00
10.0
-25.0
0.00
25.0
30.0
-ΔS ǂ (e.u)
-ΔV ǂ (cc per mole)

$$A - B \longrightarrow [A^{+}{-}{-}{-}{-}B^{-}] \longrightarrow A^{+} + B^{-}$$

in terms of the Born expression, assuming that A and B are highly ionic in character in the activated complex, is given by

$$\Delta G^{*}_{es} = (Ne^{2}/D)\ (\underset{\text{activated complex}}{Z^{2}/r^{*}} - \underset{\text{reactants}}{\sum Z^{2}/r})\ , \tag{5.2}$$

where Z represents the number of charges on the species considered; e is the charge on the electron; r^{*} is the radius of the sphere which the activated complex is considered to occupy and r is the radius of a reactant species. Setting

$$\phi = (\underset{\text{activated complex}}{Z^{2}/r^{*}} - \underset{\text{reactants}}{\sum Z^{2}/r})\ , \tag{5.3}$$

the electrostatic contribution to the entropy of activation is given by

$$(\delta\, \Delta G^{*}_{es}/\delta\, T)_P = \Delta S_2^{*} = Ne^{2}\phi[\delta(1/D)/\delta\, T]_P - (Ne^{2}/D)(\delta\, \phi/\delta\, T)_P \tag{5.4}$$

and the electrostatic contribution to the volume of activation is given by

$$(\delta\, \Delta G^{*}_{es}/\delta\, P)_T = \Delta V_2^{*} = Ne^{2}\phi[\delta(1/D)/\delta\, P)_T - (Ne^{2}/D)(\delta\, \phi/\delta\, P)_T\ . \tag{5.5}$$

It has been found[160] that the following empirical equations relate the dielectric constant of water to its temperature and pressure coefficients in the range of temperature and pressures given to a precision of ± 0.2 and ± 0.3 per cent respectively.

$$D = D_\theta \exp(-T/\theta) \quad 273 \leqslant T \leqslant 323^\circ K$$

at 1 atmosphere and

$$D = D_\pi \exp(P/\pi) \quad 0 < P < 1000 \text{ atmospheres}$$

where $\pi = (1/D)(\delta D/\delta P)_T$ and $\theta = (1/D)(\delta D/\delta T)_P$

Similar relationships have been found for many liquids[1].

Very little is known about the terms $(\delta\phi/\delta P)_T$ and $(\delta\phi/\delta T)_P$ as they involve terms in $(\delta r/\delta P)_T$ and $(\delta r/\delta T)_P$, where r is the radius of the reactant or activated complex. Rough estimates of these effects have been derived from the coefficients of expansion and bulk compressibilities of ionic crystals. However, for purposes of the present argument these terms are usually neglected as being very small. Consequently ϕ and r become adjustable parameters, but in view of the approximations made in the use of the Born model (see Chapter 2) r is only the radius by convention.

Neglecting the terms in ϕ in equations (5.4) and (5.5) a correlation between the electrostatic contributions to the entropies and volumes of activation of a series of reactions in the same solvent, the form

$$\Delta S_2^* = \pi/\theta \quad \Delta V_2^* \qquad (5.6)$$

is predicted. On substituting for π and θ this becomes

$$\Delta S_2^* = (\delta P/\delta T)_V \Delta V_2^*$$

$$= \alpha/\beta \quad \Delta V_2^* \quad , \qquad (5.7)$$

where α and β are the isobaric expansivity and the isothermal compressibility respectively of the solvent.

A relationship similar to that above is predicted from the following Maxwell relationship

$$(\delta \Delta S^*/\delta \Delta V^*)_{T,P} = (\delta P/\delta T)_V \ . \qquad (5.8)$$

The importance of solvent electrostriction in determining the sign and magnitude of ΔV^* and ΔS^* in these reactions suggests that the α and β terms referred to in the above expressions are not those of the bulk solvent but refer primarily to the region of solvent electrostricted about the activated complex of the reaction. Several pieces of evidence point to the fact that the pressure in the immediate vicinity of such an ionic species is extremely high[15] (of the order of 10^4 atmospheres).

Consequently the kinetically derived α and β refer primarily to values at some suitably high pressure[75]. The situation is indeed quite likely to be more complex than this because more than nearest neighbour interactions between reactant and solvent and activated complex and solvent make a contribution to the activation process. The term α/β is probably therefore a weighted average which reflects the contribution of all the solvent to the activation process. This point is extremely important in mixed solvents where solvent sorting is possible.

Another point may also be made. The above treatment predicts that where reactions are done in different solvents or solvent mixtures, a linear relationship between the various ΔV^*'s and ΔS^*'s is not to be expected, as has been suggested[63]. Clearly α/β will in general be completely different from one solvent to the next.

APPENDIX

The Variation of ΔV^* with Pressure

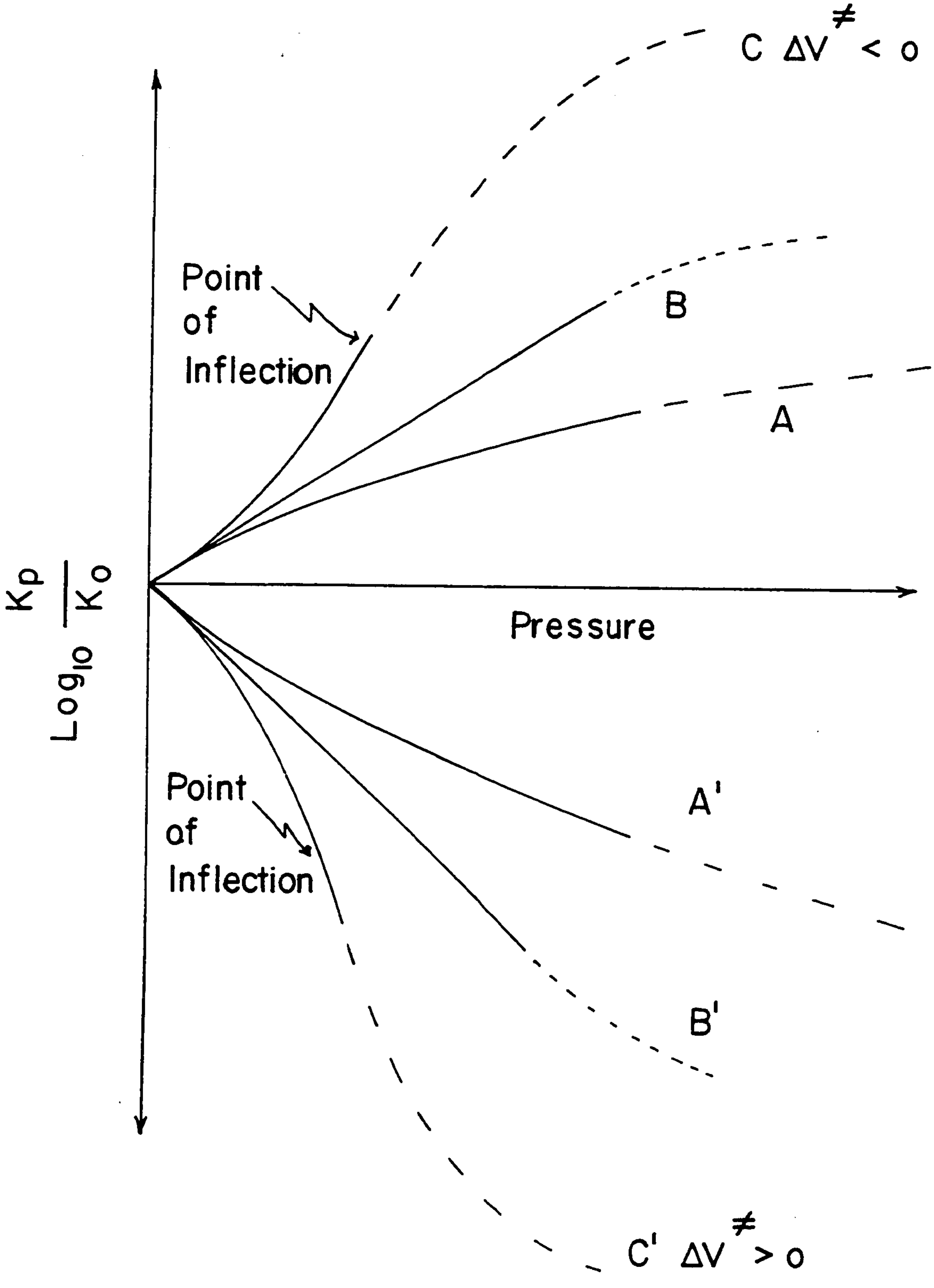
An example of a negative $(\delta\ \Delta V^*/\delta\ P)_T$ parameter has recently been observed by Hyne and co-workers[66] for the solvolysis of benzyl chloride in pure water. This behavior is similar to that observed by Osugi et al.[159] in pressure studies of the dissociation constant for the dissociation of the ion-pair $[Co(NH_3)_6](SO_4)^+$ in water; negative curvature of the $\log_e K$ - pressure data was observed at 20°C and 25°C, whereas at 40°C the more typical positive curvature was observed.

It will be shown that these observations throw some doubt on the procedure of fitting $\log_e k$ - pressure data to polynomials of the second degree. Curves A, B, A' and B' in Figure 22 show the most frequently observed dispositions of $\log_e k$ - pressure data. The behavior shown by the first part of curve C is that described above. The behavior shown by C' does not seem to have been observed as yet. The points of inflection shown on curves C and C' have also not been observed. Their possible existence and position on the pressure axis is the point of present interest.

That they may be expected can be shown in the following manner (curve C will be discussed specifically but a similar argument may be used in the case of curve C'). It will also be assumed throughout the following argument that diffusion of reactants throughout the solution at higher pressures does not affect the

Figure 22

Possible dispositions of $\log_{10}k$ - pressure data from piezokinetic studies of reactions in the liquid phase.


C $\Delta V^{\neq} < 0$
Point of Inflection
B
A
$\log_{10} \frac{K_p}{K_o}$
Pressure
A'
Point of Inflection
B'
C' $\Delta V^{\neq} > 0$

observed rate constant for the reaction. If curve C maintained negative curvature over the whole range of possible pressures, a small increment of pressure at very high pressures would have a very large effect on the rate and the volume of activation would become larger in magnitude, indicating that the partial molar volumes of the reactants diverge from one another with increasing pressure. This is just the opposite behavior to that expected. From behavior in pure liquids,and in solutions, the partial molar volumes of both the reactants and activated complexes are expected to decrease with increasing pressure, and the derivatives $(\delta \bar{V}_t/\delta P)_T$ and $(\delta \bar{V}_g/\delta P)_T$ are expected to tend towards zero as the pressure increases. (The form of the Tait equation[149] predicts such behavior). Consequently at higher pressures the parameter $(\delta \Delta V^*/\delta P)_T$ is expected to tend towards zero with increasing pressure, or ΔV^* should tend towards a constant value. There must therefore be a point of inflection along the pressure axis. The fact that in the region of lower pressure negative curvature is observed must reflect a different dependence on pressure of the partial molar volumes of the reactants and activated complexes, the latter decreasing more with pressure than the former in the low pressure region.

The position of the point of inflection is also of some importance and is related to the functional dependence of the partial molar volumes of the reactants and activated complexes on pressure; these are probably quite different from one another as the latter species is quite polar but the former species is non-polar.

It may be noted that up to the present time the above behavior has only been found where pure water has been the solvent medium. The many anomalies of properties of ordinary water have already been commented upon. Of particular importance in the present case is the ability of non-polar molecules to stabilize the open-structured component of water. The negative curvature in the region of lower pressure apparently reflects the strength of these interactions as compared with the usually more compact polar activated complex. The position of the point of inflection indicates the position on the pressure axis where the two species have equal compressions.

The proposed fall-off of the $\log_e k$ - pressure data may also be understood by analogy with the pure liquid case. Pressure is expected to affect the activated complexes and reactants in a similar way, the effect of pressure in the low pressure region being to compress the reactant solvent system and activated complex solvent system so as to achieve the degree of closest molecular packing.[4] The difference between the partial molar volumes of the reactants and activated complex is then expected to be small and to reflect volume changes caused by bond-breaking, bond-making and configurational changes. Hence the $\log_e k$ - pressure curves shown in Figure 22 tend to fall off at higher pressures.

In summary it might be concluded that in cases where positive curvature is found for $\log_e k$ - pressure data, some caution should be exercised in fitting data to polynomials of the second degree. This anomalous behavior as far as water is concerned appears to be a reflection of the peculiar properties of this substance as a solvent, and in the case of benzyl chloride solvolysis a reflection of the "structure making" interactions between this non-polar reactant and the water molecules.

CLAIMS TO ORIGINAL RESEARCH

(1) The volumes of activation for the solvolysis of p-methyl, p-chloro and p-nitro benzyl chloride and benzyl chloride have been measured in an acetone-water mixture of constant composition.

(2) The volumes of activation for the solvolysis of p-methyl benzyl chloride in four different acetone-water mixtures have been measured.

(3) The partial molar volumes of p-methyl benzyl chloride in four different acetone-water mixtures have been measured.

(4) The parameters $(\delta \Delta V^{*}/\delta P)_T$ have been calculated for each set of $\log_{10}k$-pressure data obtained.

(5) The results have been discussed in terms of the mechanisms of these reactions, and several phenomena contributing to changes in the measured activation parameters have been explored.

(6) The significance of a negative correlation between ΔV^{*} and $(\delta \Delta V^{*}/\delta P)_T$ for the solvolysis of the various substituted benzyl chlorides is discussed.

(7) A correlation between ΔS^{*} and ΔV^{*} for the substituted benzyl chlorides has been found.

(8) A theoretical treatment which predicts such a correlation between ΔS^{*} and ΔV^{*} for ionogenic reactions has been discussed and the limitations of such correlations have been explored in terms of this treatment.

REFERENCES

(1) Hamann, S.D., "Physico-Chemical Effects of Pressure", Scientific Publications, London, England, (1957).

(2) Hamann, S.D., In "High Pressure Physics and Chemistry", Vol.2, R.S. Bradley ed., Academic Press Inc., Ltd., London, England, (1963), Chapters 7 and 8 (a) pp. 166-171 (b) pp.179-182.

(3) Bradley, R.S., "High Pressure Physics and Chemistry", Vol.1 and 2, Academic Press Inc. Ltd., London, England, (1963).

(4) Gonikberg, M.G., "Chemical Equilibria and Reaction Rates at High Pressures", Israel Program for Scientific Translations Ltd., Jerusalem, Israel, (1963).

(5) Whalley, E., In "Advances in Physical Chemistry", Vol.2, V.Gold ed., Academic Press Inc., New York, N.Y. (1964) (a) pp. 108-114 (b) pp. 117-118.

(6) Bertholet, M., and Pean de Saint Gilles, L., Annes. Chim. (Phys.), 36, 231 (1862).

(7) Roentgen, W.C., Ann. Phys. Lpz., 45, 98 (1892).

(8) Stern, O., ibid, 59, 659 (1896).

(9) Rothmund, V., Z. Phys. Chem., 20, 168 (1896).

(10) Tamann, G., and Bogojawlensky, A., ibid, 23, 13 (1897).

(11) Cohen, E., and deBoer, R.B., ibid, 84, 13 (1911).

(12) Cohen, E., and Kaiser, H.F.G., ibid, 89, 338 (1915)

(13) Cohen, E., and Valeton, A.M., ibid, 92, 443 (1917)

(14) Cohen, E., "Physico-Chemical Metamorphoses and some Problems in Piezochemistry", McGraw-Hill, New York, N.Y., (1926).

(15) Bridgman, P.W., "The Physics of High Pressure", G. Bell and Sons Ltd., London, England (1958).

(16) Gibson, R.O., Fawcett, E.W., and Perrin, M.W., Proc. Roy. Soc., 150A, 223 (1935).

(17) Williams, E.W., Perrin, M.W., and Gibson, R.O., ibid, 154A, 684 (1936).

(18) Perrin, M.W., and Williams, E.W., ibid, 159A, 162 (1937).

(19) Perrin, M.W., Trans. Faraday Soc., 34, 144 (1938).

(20) Bundy, F.P., Hall, H.T., Strong, H.M. and Wentorf, R.H., Nature, 176, 51 (1955).

(21) Planck, M., Ann. Phys. Chem., 32, 462 (1887).

(22) van't Hoff, J.H., "Vorlesungen über Theoretische und Physicalische Chemie", Vol. 1, 236 (1961).

(23) Glasstone, S., Laidler, K.J., and Eyring, H., "Theory of Rate Processes", McGraw-Hill, New York, N.Y. (1941).

(24) Moesveld, A.L. Th., Z. Phys. Chem., 103, 486 (1922).

(25) Evans, M.G. and Polanyi, M., Trans.Faraday Soc., 31, 875 (1935).

(26) Stearn, A.E. and Eyring, H., Chem.Rev., 29, 509 (1941).

(27) Buchanan, J. and Hamann, S.D., Trans.Faraday Soc., 49, 1425 (1953).

(28) Hamann, S.D. and Strauss, W., ibid, 51, 1684 (1955).

(29) David, H.G. and Hamann, S.D., ibid, 50, 1188 (1954).

(30) Hamann, S.D. and Teplitzky, D.R., Disc. Faraday Soc. 22, 114 (1956).

(31) Burris, C.T. and Laidler K.J., ibid, 51, 1497 (1955).

(32) Couture, A.M. and Laidler, K.J., Can.J.Chem., 55, 207 (1957).

(33) Chen, D.T.Y. and Laidler, K.J., Trans.Faraday Soc., 54, 1026 (1958).

(34) Born, M., Z. Phys., 1, 45 (1920).

(35) Kirkwood, J.G., J. Chem. Phys., 2, 351 (1934).

(36) (a) Westheimer, F.H., and Kirkwood, J.G., J. Chem. Phys., 6, 513 (1938). (b) Sarmousakis, J.N., J. Chem. Phys., 12, 277 (1944).

(37) Heydtmann, Von H., Schmidt, A.P., and Hartmann, H., Berichte, 70, 444 (1966).

(38) Whalley, E., J. Chem. Phys., 38, 1400 (1963).

(39) David, H.G., and Hamann, S.D., Disc. Faraday Soc., 22, 119 (1956).

(40) Brower, K.R., J. Am. Chem. Soc., 85, 1401 (1963).

(41) Couture, A.M., and Laidler, K.J., Can. J. Chem., 55, 207 (1957).

(42) Hinshelwood, C.N., J. Chem. Soc., 629 (1937).

(43) Bishop, D., and Laidler, K.J., J. Chem. Phys., 42, 1688 (1965).

(44) Golinkin, H.S., Ph.D. Thesis, University of Alberta, Calgary (1966).

(45) Streitwieser Jr., A., "Solvolytic Displacement Reactions", McGraw-Hill Book Co. Inc. New York, N.Y. (1962).

(46) Thornton, E.R., "Solvolysis Mechanisms", Ronald Press, New York, N.Y. (1964).

(47) Gould, E.S., "Mechanism and Structure in Organic Chemistry" Cornell University Press, Ithica, N.Y. (1953), Chapter 8.

(48) Hine, J., "Physical Organic Chemistry", 2nd ed., McGraw-Hill Book Co. Inc. New York, N.Y. (1962), Chapter 6.

(49) Gleave, J.L., Hughes, E.D., and Ingold, C.K., J. Chem. Soc., 236 (1935).

(50) Hughes, E.D., and Ingold, C.K., J. Chem. Soc., 244 (1935).

(51) Hughes, E.D., J. Chem. Soc., 255 (1935).

(52) Hinshelwood, C.N., Laidler, K.J. and Timm, E.W., J. Chem. Soc., 848 (1939).

(53) Laidler, K.J., Suomen Kemistilehte, A33, 44 (1960).

(54) Tommila, E., Paakkala, E., Virtanen, U.K., Erva, A. and Varila, S., Ann. Acad. Sci. Fenn., A11, 91 (1959).

(55) Grunwald, E., Jones, H.W., and Winstein, S., J. Am. Chem. Soc., 73, 2700 (1951).

(56) Weiner, H., and Sheen, R.A., J. Am. Chem. Soc., 84, 3599 (1962).

(57) Hughes, E.D., and de la Mare, P.B.D., J. Chem. Soc., 845 (1956).

(58) Bird, M.L., Hughes, E.D., and Ingold, C.K., J. Chem. Soc., 634 (1954).

(59) Grunwald, E. and Winstein, S., J. Am. Chem. Soc., 73, 2700 (1951).

(60) Bown, D.E., Mosely, R.B., and Swain, G.G., J. Am. Chem. Soc., 77, 3731 (1955).

(61) Casapieri, P., and Swart, E.R., J. Chem. Soc., 1254 (1963).

(62) Gold, V., J. Chem. Soc., 4633 (1956).

(63) Grunwald, E. and Leffler, J.E., "Rates and Equilibrium of Organic Reactions", John Wiley and Sons, Inc., New York, N.Y. (1963), pp. 342-402.

(64) Hyne, J.B., and Wills, R., J. Am. Chem. Soc., 85, 3650 (1963).

(65) Hyne, J.B., Wills, R., and Wonkka, R.E., J. Am. Chem. Soc., 84, 2914 (1962).

(66) Hyne, J.B., Golinkin, H.S., and Laidlaw, W.G., J. Am. Chem. Soc., 88, 2104 (1966).

(67) Golinkin, H.S., Lee, I., and Hyne, J.B., J. Am. Chem. Soc., 89, 1307 (1967).

(68) Arnett, E.M. Bentrude, W.G., Burke, J.J., and Duggleby, P.McC., J. Am. Chem. Soc., 87, 1541 (1965).

(69) Laidler, K.J., Trans. Faraday Soc., 55, 1725 (1959).

(70) Mortimer, C.T., and Laidler, K.J., ibid, 55, 1731 (1959).

(71) Papée, H.M., Canady, W.J., Zawidski, T.W., and Laidler, K.J., ibid, 55, 1734 (1959).

(72) Zawidski, T.W., Papée, H.M., Canady, W.J., and Laidler, K.J., ibid, 55, 1738 (1959).

(73) Zawidski, T.W., Papée, H.M., and Laidler, K.J., ibid, 55, 1743 (1959).

(74) Dewar, M.J.S., and Sampson, R.J., J. Chem. Soc., 2789 (1956).

(75) Hepler, L.G., J. Phys. Chem., 69, 965 (1965).

(76) Hepler, L.G., and O'Hara, W.F., J. Phys. Chem., 65, 811 (1961).

(77) Chen, D.T.Y., and Laidler, K.J., Trans. Faraday Soc. 58, 480 (1962).

(78) Baliga, B.T. and Whalley, E., Can. J. Chem., 42, 1019 (1964).

(79) Bennett, G.M., and Jones B., J. Chem. Soc., 1815 (1935).

(80) Olivier, S.C.J., Rec. Trav. Chim., 49, 697 (1930).

(81) Bensley, B., and Kohnstam, G., J. Chem. Soc., 4747 (1957).

(82) Charleton, J.C. and Hughes, E.D., J. Chem. Soc., 850 (1956).

(83) Beste, G.W., and Hammett, L.P., J. Am. Chem. Soc., 62, 2481 (1940).

(84) Coburn, W.C., Grunwald, E., and Marshall, H.P., J. Am. Chem. Soc., 75, 5735 (1953).

(85) Jackson, E., Ph.D. Thesis, University of Durham, 1966.

(86) Roberts, I., and Hammett, L.P., J. Am. Chem. Soc., 59, 1063 (1937).

(87) Hill, J.W., and Fry, A., J. Am. Chem. Soc., 84, 2763 (1962).

(88) Thornton, E.R. "Solvolysis Mechanisms", Ronald Press, New York, N.Y. (1964), p.206.

(89) Olivier, S.C.J., and Weber, A.P. Rec. Trav. Chim., 53, 869 (1934).

(90) Bensley, B. and Kohnstam, G., J. Chem. Soc., 287 (1956).

(91) Kohnstam, G., In "The Transition State", Special Publication The Chemical Society, Burlington House, London, W.1. (1962), pp. 179-195.

(92) Robertson, R.E., and Scott, J.M.W., J. Chem. Soc., 1596 (1961).

(93) Cowie, G.R. Fitches, H.J.M., and Kohnstam, G., J. Chem. Soc., 1585 (1963).

(94) Feakins, D. and Watson, P., J. Chem. Soc., 4734 (1963).

(95) Grunwald, E., Baughman, G. and Kohnstam, G., J. Am. Chem. Soc., 82, 5801 (1960).

(96) Laidler, K.J.,and Pegis, C., Proc. Roy. Soc., Vol. 241A, 80 (1957).

(97) (a) Hyne, J.B., J. Am. Chem. Soc., 82, 5129 (1960);

(b) Long, F.A., and McDevit, W.F., Chem.Reviews, 51, 119 (1952).

(98) (a) Bobtelsky, M. and Larisch, R.D., J. Chem. Soc., 3612 (1932);

(b) Bobtelsky, M., ibid, 3615 (1932);

(c) Bobtelsky, M. and Cohn, F., Z. Anorg. Chem., 210, 225 (1933).

(99) Franks, F., and Ives, D.J.G., Quart. Rev., 20, 1 (1966).

(100) Bernal, J.D., and Fowler, R.H., J. Chem. Phys., 1, 515 (1933).

(101) Frank, H.S., and Wen, W.Y., Disc. Faraday Soc., 24, 133 (1957).

(102) Glew, D.N., Nature, 201, 922 (1964).

(103) Frank, H.S. and Evans, M.W., J. Chem. Phys., 13, 507 (1945).

(104) Adams, W.A., and Laidler, K.J., Can. J. Chem., 45, 123 (1967).

(105) Smyth, C.P., "Dielectric Behaviour and Structure", McGraw-Hill Book Co. Inc., New York, N.Y. (1955), (a) pp. 290-291.

(106) Kirkwood, J.G., J. Chem. Phys., 1, 971 (1939).

(107) Hildebrand, J.H., and Scott, R.L. "The Solubility of Non-electrolytes", 3 ed., Reinhold Publishing Corp., New York, N.Y. (1950).

(108) Magat, M., "Hydrogen Bonding" ed. D. Hadzi and H.W. Thompson, Pergamon Press, London (1959).

(109) Rowlinson, J.S., "Liquids and Liquid Mixtures", Butterworths Scientific Publications, London (1959).

(110) Brungis, A.S., and Bogart, M.J.P., Ind. Eng. Chem., 35, 255 (1943).

(111) Mobius, Von H.H., J. für Pract. Chem., 2, 95 (1955).

(112) Sandonnini, L. (a) Atti.Acad.Licei (6), 1, 448 (1925);

(b) Gazz. Chim. Ital. 55, 921 (1925).

Quoted in International Critical Tables.

(113) Drinkard, W., and Kivelson, D., J. Am. Chem. Soc., 62, 1494 (1958).

(114) Kister, A.T. and Waldman, D.C., J. Am. Chem. Soc., 62, 245 (1958).

(115) Nicholson, D.E., J. Chem. Eng. Data, 5, 309 (1960).

(116) Katayama, T., Chem. Eng. (Japan) 26, 361 (1962).

(117) Knight, W.S., Diss. Abs., 24, 993 (1963).

(118) Ford, R.J. and Moore, W.R., Trans.Faraday Soc., 61, 2102 (1965).

(119) Thomas, K.T. and McAllister, R.A., J. Am. Inst. Chem. Eng., 3, (2), 161 (1957).

(120) Howard, K.S., and McAllister, R.A., J. Am. Inst. Chem. Eng., 4, 416 (1958).

(121) (a) Gjaldback, J.A. and Hildebrand, J.H., J. Am. Chem. Soc., 72, 1077 (1950).

(b) Masterton, W.L., J. Chem. Phys., 22, 1830 (1954).

(122) Persianova, I.V. and Tarasov, U.U., Izvest. Vysshikh. Ucleb. Zaved. Khim. I. Khim Teckhnol, 3, (1), 4 (1960).

(123) Shakparanov, M. and Akadov, Ya. Yu., J. Struct. Chem. (USSR), 6, 21 (1965).

(124) Huggins, C.M., Pimental, G.C. and Shoolery, J.N., J. Chem. Phys., 23, 1244 (1955).

(125) Holmes, J.R., Kivelson, D. and Drinkard, W.C., J. Am. Chem. Soc., 84, 4677 (1962).

(126) Samoilov, O. Ya. and Bushlaev, M.N., J. Struct. Chem. (U.S.S.R.) , 4, 502 (1963).

(127) Bondi, I., J. Chem. Phys., 15, 527 (1947).

(128) Frost, A.A., and Pearson, R.G., "Kinetics and Mechanism" 2nd ed., John Wiley & Sons Inc., New York, N.Y. (1961), p.134.

(129) Arnett, E.M. and McKelvey, D.R., J. Am. Chem. Soc., 87, 1393 (1965).

(130) Arnett, E.M., "Correlation of Kinetic, Thermodynamic and Spectral Behaviour in Highly Aqueous Binary Solvents", Symposium on Physico-Chemical Processes at Bradford Institute, Bradford, England, May, 1966 (in Press).

(131) Arnett, E.M. and McKelvey, D.R., Record Chem. Progress, 26, 185 (1965).

(132) Arnett, E.M. McKelvey, D.R. and Hafford, D., J. Am. Chem. Soc., 88, 3140, 3142 (1966).

(133) Bateman, R.L., J. Am. Chem. Soc., 74, 5516 (1952).

(134) Bateman, R.L., ibid, 71, 2291 (1949).

(135) Hudson, R.F., J. Chem. Soc., (Phys. Org.) B, 761 (1966).

(136) (a) Grunwald, E. and Winstein, S., J. Am. Chem. Soc., 70, 846 (1948).

(b) Winstein, S., Grunwald, E. and Jones, H.W. ibid, 73, 2700 (1956).

(c) Fainberg, A.H. and Winstein, S. ibid, 78, 2770 (1956).

(137) Köbrich, G., Angew. Chem., Internat. Edit., 1, 382 (1962).

(138) Berson, J.A., Hamlet, Z. and Mueller, W.A., J. Am. Chem. Soc., 84, 297 (1962).

(139) Kosower, E.M., J. Am. Chem. Soc., 80, 3253 (1958).

(140) Dimroth, K., Reichardt, C., Siepmann, T., and Bohlmann, F., Liebigs Ann. Chem., 661, 1 (1963).

(141) Brownstein, S., Can. J. Chem., 38, 1590 (1960).

(142) Koskikallio, J., and Whalley, E., Trans. Faraday Soc., 55, 809 (1959).

(143) Conway, B.E., Verrall, R.E. and Desnoyes, J.E., Trans. Faraday Soc., 62, 2738 (1966).

(144) Verrall, R.E., Ph.D. Thesis, University of Ottawa, (1966).

(145) Gibson, R.E. and Kincaid, J.F., J. Am. Chem. Soc., 60, 511 (1938).

(146) Hyne, J.B., and Robertson, R.E., Can. J. Chem., 33, 1544 (1955).

(147) Mellor, J.W. "Higher Mathematics for Students of Chemistry and Physics", Dover Publications Inc., New York, N.Y. (1955) Chap. 3.

(148) Benson, S.W. and Berson, J.A., J. Am. Chem. Soc., 84, 152 (1962).

(149) Tait, P.G., "Physics and Chemistry of the Voyage of H.M.S. Challenger", Vol. II, Part IV (1888).

(150) Walling, C., and Peisach, J., J. Am. Chem. Soc., 80, 5819 (1958).

(151) Walling, C. and Tanner, D.D., ibid, 85, 612 (1963).

(152) Hildebrand, F.B., "Introduction to Numerical Analysis", McGraw-Hill, New York, N.Y. (1956).

(153) Gold, V. and Jefferson, E.G., J. Chem. Soc., 1409 (1953).

(154) Brown, O.A. and Hudson, R.F., J.Chem. Soc., 3352 (1953).

(155) Koskikallio, J. and Whalley, E., Can. J. Chem., 37, 783, 788 (1959).

(156) Brower, H.R., J. Am. Chem. Soc., 82, 4535 (1960).

(157) Pauling, L., "Nature of the Chemical Bond", Cornell University Press, New York, N.Y. (1960).

(158) Stearn, A.E., and Eyring, H., J. Chem. Phys., 3, 778 (1935)

(159) Osugi, J., Shimizu, K., and Takizawa, H., Rev. Phys. Chem. Japan, 33, 1 (1963).

(160) McClellan, A.L., "Tables of Experimental Dipole Moments", W.H. Freeman and Co., London (1963).

(161) King, E.J., International Encyclopedia of Physical Chemistry and Chemical Physics, Topic 25 : Equilibrium Properties of Electrolyte Solutions, Vol. 4, Acid-Base Equilibrium, Pergamon Press, New York, N.Y. (1965).