TRANSLATIONAL PROCESSES IN METHANOLIC SOLUTION

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CONTENTS

Abstract

A detailed study has been made of the electrolyte conductance of a series of salts in methanolic solution. The pressure coefficients of the limiting equivalent conductances were evaluated over the range $2 - 25 \times 10^{-4}$ moles $litre^{-1}$, $5 - 45^{\circ}C$ and 1 - 2000 atm. In conjunction with a separate study of the compressibility of methanol, these coefficients were analysed in terms of the Transition State Theory of conductance. The significant variables are temperature and $(\pi + P)$, the sum of the internal and external pressures.

From a consistent representation of the transition state theory three principal parameters were evaluated; (i) the isochoric energy of activation, (ii) the volume of activation and (iii) an entropy term related to, but not equal to, the entropy of activation.

The variation of these activation parameters with volume, temperature and ion-size is discussed and this leads to an improved conception of ionic migration in methanol and presumably other liquids.

The rectilinearity of the isochores is a striking feature of the work and justifies the application of the constant volume principle.

Glossary of Symbols

A^+, A^-, — the pre-exponent in the Transition State Conductance equation for individual ions;

B, — the temperature dependent constant in the Tait equation;

c, — concentration;

C, — the temperature independent constant in the Tait equation;

D, — the pre-exponent in the integrated Arrhenius equation at constant volume;

e_o, — the electronic charge;

E_p, — the energy of activation at constant pressure;

E_v, — the energy of activation at constant volume;

F, — the faraday;

f(v), — function of v;

$f'(v)$, — derivative of f(v);

$\triangle G_o^*$, — the Gibbs free energy of activation; the free energy excess at infinite dilution of one mole of activated ions over one mole of ions in the unactivated state;

$\overline{\triangle G_o^*}$, — the "mean" Gibbs free energy of activation, at infinite dilution, for simultaneous cation and anion conductance;

$\triangle H_o^*$, — the enthalpy of activation; the enthalpy excess, at infinite dilution, of one mole of activated ions over one mole of ions in the unactivated state;

h , Plank's constant;

J_i^o , the flux vector for migrating ions at infinite dilution;

k, the slope in the Kohlrausch equation;

L, the jump distance of the migrating ion;

N, the Avogadro number;

P, p, pressure;

R, the gas constant;

r, distance;

$\underline{r}$, Stokes' radius of an ion;

ΔS_o^*, ΔS_+^*, ΔS_-^*, ΔS_i^*, the entropy of activation of one mole of ion at infinite dilution;

$\overline{\Delta S_o^*}$, the "mean" entropy of activation at infinite dilution for simultaneous cation and anion conductance;

T, temperature, ^oK;

t, temperature, ^oC;

t_i, t_+, t_-, transport number;

ΔU_o^*, ΔU_+^*, ΔU_-^*, ΔU_i^*, the energy of activation at infinite dilution of one mole of ions;

$\overline{\Delta U_o^*}$, the "mean" energy of activation at infinite dilution for simultaneous cation and anion conductance;

V_s, the specific volume of solid methanol;

V, v, specific volume;

ΔV_o^*, ΔV_+^*, ΔV_o^*, ΔV_i^*, volume of activation at infinite dilution of one mole of ions;

$\overline{\Delta V_o^*}$, the "mean" volume of activation at infinite dilution for simultaneous cation and anion transport;

Z_i, valence of ions;

α, coefficient of cubical expansion of the system, i.e. solvent;

β, coefficient of compressibility of the system, i.e. solvent;

η, coefficient of viscosity of the solvent;

κ, specific conductance;

Λ, molar conductance of an electrolyte;

Λ_o, limiting molar conductance of an electrolyte at infinite dilution;

λ_i^o, λ_+^o, λ_-^o limiting ionic conductance;

ϕ, Electrical Field;

π, the internal pressure of the system, i.e. solvent, $(= (\partial U/\partial V)_T)$;

$\underline{\pi}$, the constant (3.1416);

ρ, density.

CHAPTER 1

INTRODUCTION AND THEORY

Contents

1. Introduction

This thesis describes an experimental study of the mechanism of ionic migration in methanolic solution. Ionic migration is one of the several translational parameters which can be used to characterise molecular movement in a liquid system. Its principal advantage over all others is the precision with which it can be determined; but it suffers the disadvantage that it reflects the properties of the ion solvent complex rather than that of the ion itself or the pure solvent.

Methanol was chosen as a good ionizing medium known to be "normal" in the sense that any structural configurations arising from its polar character are not overwhelming and are not evident in the pressure and temperature coefficients of its fluidity (1). A range of simple 1:1 electrolytes was chosen namely, $KClO_4$, Me_4NClO_4, Et_4NClO_4, $n\text{-}Pr_4NClO_4$ and $n\text{-}Bu_4NClO_4$. Firstly because they were known to be completely dissociated and secondly they allowed a systematic study of the effect of ionic radius on the transport parameters to be derived.

2. Theories of Ionic migration

It has been remarked elsewhere (2,3) that virtually all of the extensive investigations of electrolyte conductance have been concerned to study its dependence on ionic concentration either in terms of incomplete dissociation or in terms of interionic attraction theories,

notably those of Onsager (4) and Fuoss and Onsager (5). Very little attention has been paid to the limiting ionic conductance and there is no detailed description of this quantity.

The ionic mobility at infinite dilution is formally defined by the equation

$$J_i^o = - u_i^o \text{ grad. } \phi \quad , \tag{1}$$

in which the effect of all other transport processes is zero, i.e. as enunciated in Kohlrausch's law of independent mobility of ions. Experimentally

$$u_i^o = \frac{1}{F} \left(\frac{1000 \, Kt_i}{c} \right)_{c \rightarrow o} \tag{2}$$

and requires for its determination a range of specific conductances and transport numbers in dilute solution.

The exact evaluation of λ_i^o or u_i^o has been the subject of extensive and detailed experimental and theoretical studies and accurate values have been tabulated for numerous ions mainly in aqueous solution and mainly at 25°C and 1 atm.

On the other hand the interpretation of λ_i^o is at a primitive stage. The earliest notion, and still the commonest starting point of most theories is that of a hard charged sphere moving with a steady velocity through a viscous and dielectric continuum. In terms of Stokes's law this leads to the simple relation

$$u_i^o = \frac{z_i e_o F}{6 \pi \eta r} \quad , \tag{3}$$

and thence to the Walden Rule,

$$u_i^o \eta = \text{constant.} \qquad (4)$$

These sterile relations are highly unsatisfactory and they err in several different ways.

1) They offer at the most a semi-quantitative correlation between λ_i^o and η, as may be seen by inspection of Table 1 (6).

2) They introduce an apparent cause and effect relation between λ_i^o and η which is not real, in the sense that both are determined by the same more fundamental properties.

3) They describe a model which is quite unrealistic. The solvent is not a continuum, the motion of the ion is not steady and no empirical or semi-empirical adjustments of $\underline{r}$ or η are likely to provide a more satisfactory theory.

The migrating ions are minor constituents of a molecular array undergoing Brownian motion upon which is superimposed (at all ordinary voltages) a small bias which immediately causes a net drift of electrical charge. The problem, to describe such a system adequately, will not be easily solved. Much simpler, equilibrium properties of condensed phases still present formidable difficulties and it is clear that until considerably more is known about local order, local properties and local interactions, progress must be slow and uncertain.

Because of this the continuum model cannot be totally abandoned. Its incorporation into the Onsager theory is evidently satisfactory, for dilute solutions at least, and its modification by Fuoss to allow for dielectric relaxation is a useful and stimulating improvement.

Table 1.

The product $\lambda_i^o \eta$ in various solvents at 25°C (6).

Solvent	K^+	Na^+	I^-	CNS^-	Et_4N^+	$Picrate^-$
Water	0.668	0.459	0.686	0.598	0.295	0.269
Methanol	0.292	0.251	0.332	0.327	0.294	0.267
Ethanol	0.267	0.238	0.285	0.28	0.295	0.263
Acetone	0.222	0.217	0.366	0.40	0.294	0.266
Furfural	0.215	0.190	0.424	-	0.293	-
Acetonitrile	0.31	0.28	0.38	0.44	0.294	-
Pyridine	0.27	0.22	0.42	0.45	0.294	-

For large ions, for structureless solvents, for hydrodynamic considerations the continuum theory may even be the best approximation for some years to come; but it is no basis for a better understanding of the mechanism of ionic migration and it will not be considered further here.

There are two more fundamental descriptions of ionic conductance. The first is closely related to the concept of migration by preferred "jumps" over an energy barrier characteristic of the system. An expression for ionic conductance is readily obtained from the transition state theory and a number of detailed treatments have been given (2,3).

That of Polissar (7) describes the activated process as the energy to "escape" from the "cage" of surrounding molecules and his analysis supplies approximate values of many of the parameters of biased Brownian motion. The other theories are less specific in their attitude to the nature of the transition state but they all lead essentially to the same equation (8, 2, 3).

$$\lambda_i^o = \frac{z_i e_o F L^2}{6 h} \exp.\left(-\frac{\Delta G_o^*}{R T}\right) . \qquad (5)$$

The usefulness of this equation depends upon two factors.

1) The correctness of its inherent frequency factor as applied to a dense fluid.

2) The applicability of equilibrium thermodynamics to the free energy of activation.

It is difficult to argue the cases for 1) or 2) without embarking on a detailed statistical mechanical treatment of the entire

problem and such a treatment (9) is likely to lead as we shall see to an entirely different final relationship. We propose, therefore, to accept this application of the transition state theory if only as a means of directed exploration of translational processes. It is extremely valuable in indicating an experimental analysis of λ_i^o which generates several simpler terms more likely to be calculated from first principles than λ_i^o itself. It offers, in its most recent form, a clear relationship between the various properties of a liquid and its density. It suffers ultimately however in that it does not lead directly to these quantities, although in the present work we shall present a detailed thermodynamic description of the activated process. We shall not be able to evaluate any of the terms from more fundamental considerations.

The second principal approach attempts just this. The development of statistical mechanics has led to numerous descriptions of condensed phases, none of them as yet satisfactory. The school of Kirkwood has been particularly active in this direction and recently a series of papers has been published aimed at a realistic statistical treatment of molecular motion and ionic migration (9). The electrical work is regarded as being dissipated against "hard-core collisions" and "soft interactions". The former is purely a property of colliding masses and the subsequent distribution of momentum. The second takes into account the "interactions" between the moving sphere and its surroundings. The final relation has the form,

$$u_i^o = \frac{e_o}{\frac{8}{3} N \sigma^2 g(\sigma) \left[2\pi m m_1 k T / m + m_1 \right]^{\frac{1}{2}} + \zeta} , \qquad (6a)$$

Where $\zeta = \zeta_o^4 / 4 \pi m_1 c^3 \rho_{m_1}$, (6b)

and $\zeta_o^2 = \frac{1}{3} \rho_{m_1} \int \nabla^2 V(R) g(R) d\bar{R}$. (6c)

In equation (6a) σ equals the collision diameter of the ion and a molecule, i.e. $\frac{1}{2} (\sigma_{ion} + \sigma_{molecule})$, m the mass of ion and m_1 the mass of the molecule. N is the number density of the system. $g(\sigma)$ is the pair correlation function. The term in equation (6a) which contains these parameters is from the contribution to the mobility of the hard-core collisions. The friction coefficient, ζ , is an expression of the "soft interactions" between the ion and its environment.

The expression of ζ is shown by equations (6b) and (6c). ρ_{m_1} is the mass density of the fluid. c is the velocity of sound in the fluid. V (R) is the intermolecular pair potential and g (R) is the correlation function. m_1 in equation (6b) and (6c) is the molecular mass.

The basic notion of this theory is that the ion undergoes a hard-core collision with a molecule. After this collision the ion follows a trajectory determined by the rapidly fluctuating field of all the neighbouring molecules. The system relaxes after collision and the trajectory of the ion is regarded as a quasi-random walk. The relaxation time is small compared with the time between hard-core collisions.

This theory predicts within a few per cent the absolute velocity of the ions generated by irradiating the liquid rare gases and had it been published at the outset of this work we might have devoted a larger part of the time to its detailed development and application to more conventional systems. Even so it is unlikely that there would have been any difference in the experimental programme and the lasting features of this research described here, namely the experimental temperature and pressure derivatives of λ_i^o, will have to be taken into account in any subsequent theoretical developments.

3. The application of the Transition State Theory to ionic migration

The free energy of activation defined by equation (5) can be resolved into its thermodynamic components, i.e.

$$\Delta G_o^* = \Delta U_o^* + (P + \pi)\Delta V_o^* + T\Delta S_o^* \quad . \qquad (7)$$

The inclusion of the internal pressure is required for the isolation of ΔU_o^*, the internal energy of activation at constant volume. All of the parameters are local terms, referring to the ion-solvent complex. The ion itself is assumed not to undergo any change during the activated step, and the parameters therefore refer to its interaction with the solvent adjacent to it.

One of the first assumptions made in the application of equation (5) is that the local internal pressure and the local compressibility are the same as those of the pure material. In view of the electrostrictive pressure this type of assumption is probably unwarranted and a further discussion of this difficulty will be given

later.

The ionic jump may well be a co-operative phenomenon in which the shape and density of the cage may change. There may be several equivalent modes of translation in which case ΔG_o^* is the weighted mean of their particular energies of activation.

Whatever the shortcomings of equation (5), it does immediately suggest several ways of evaluating its component terms, i.e. by determining the relationship between λ, T, P and V experimentally.

4. The temperature and pressure derivatives of the Transition State Theory conductance equation

The assumption of Brummer and Hills (2) that the jump distance, L, is a simple function of the intermolecular distance is expressed as follows,

$$L = c' V^{1/3} \quad . \tag{8}$$

c' is an arbitrary constant.

Equation (5) may be expressed in logarithmic form as,

$$\ln \lambda_i^o = A + \frac{2}{3} \ln V - \frac{\Delta G_o^*}{RT} \quad . \tag{9}$$

Where $A = \ln \left[\frac{Z_i \, e_o \, F c'}{6h} \right] = \text{constant.}$

Differentiation of equation (9) with respect to $(\pi + P)$ at constant temperatures gives

$$\left(\frac{\partial \ln \lambda_i^o}{\partial (\pi + P)} \right)_T = \frac{2}{3} \left(\frac{\partial \ln V}{\partial (\pi + P)} \right)_T - \frac{\Delta V_o^*}{RT} \quad . \tag{10}$$

This equation provides the method of determining ΔV_o^* which is used in the analysis of the data.

The temperature derivative of equation (9) is at constant $(\pi + P)$ and is given as

$$\left(\frac{\partial \ln \lambda_i^o}{\partial T}\right)_{(\pi + P)} = \frac{2}{3}\left(\frac{\partial \ln V}{\partial T}\right)_{(\pi + P)} + \frac{\Delta H_o^*}{R T^2} \quad . \qquad (11)$$

Equations (10) and (11) will be used in a later part of the analysis. Equation (11) could be used to determine ΔH_o^* ; however a more satisfactory method is discussed in the next section.

5. The constant volume principle

A number of references (1, 2, 3, 10, 11, 12) have been made in the literature to the significant difference between the activation parameters at constant pressure and constant total volume of the system. The importance of carrying out condensed phase reactions at constant volume was emphasised by Goodeve (13). Constant volume conditions are more important in the liquid state than in the gaseous state because the energy of a condensed system is a marked function of intermolecular distance. Measurement of energies of activation in the liquid state at constant pressure must contain complicating factors due to the change of interaction with altering intermolecular distance.

Experimentally the energies of activation of conductance at constant volume and pressure, E_V and E_P respectively, are defined

as

$$E_V = RT^2\left(\frac{\partial \ln\lambda_i^o}{\partial T}\right)_V \quad , \tag{12}$$

and

$$E_P = RT^2\left(\frac{\partial \ln\lambda_i^o}{\partial T}\right)_P \quad . \tag{13}$$

These are strictly apparent quantities since they are obviously related to ΔH_o^* and ΔU_o^*. The significance of E_V in terms of the transition state theory may be seen from the general analysis of reaction rates of Evans and Polanyi (12), i.e. expressing

$$\lambda = f\ (T, (\pi + P)) \ .$$

$$\left(\frac{\partial \ln\lambda_i^o}{\partial T}\right)_V = \left(\frac{\partial \ln\lambda_i^o}{\partial T}\right)_{(\pi+P)} + \left(\frac{\partial \ln\lambda_i^o}{\partial(\pi+P)}\right)_T \left(\frac{\partial(\pi+P)}{\partial T}\right)_V \ . \tag{14}$$

But

$$\left(\frac{\partial(\pi+P)}{\partial T}\right)_V = -\left(\frac{\partial \ln V}{\partial T}\right)_{(\pi+P)} \Bigg/ \left(\frac{\partial \ln V}{\partial(\pi+P)}\right)_T \ . \tag{15}$$

Substituting in equation (14) for $(\partial(\pi+P)/\partial T)_V$ and multiplying by RT^2 throughout

$$RT^2\left(\frac{\partial \ln\lambda_i^o}{\partial T}\right)_V = RT^2\left(\frac{\partial \ln\lambda_i^o}{\partial T}\right)_{(\pi+P)} - RT^2\left(\frac{\partial \ln\lambda_i^o}{\partial(\pi+P)}\right)_T \left(\frac{\partial \ln V}{\partial T}\right)_{(\pi+P)} \Bigg/ \left(\frac{\partial \ln V}{\partial(\pi+P)}\right)_T \ . \tag{16}$$

Substituting in equation (16) for, $RT^2\,(\partial \ln\lambda_i^o/\partial T)_V$,

$RT^2 \left(\partial \ln \lambda_i^\circ / \partial T\right)_{(\pi + P)}$ and $\left(\partial \ln \lambda_i^\circ / \partial (\pi + P)\right)_T$ from equations (12), (11) and (10) respectively we obtain

$$E_V = \Delta H_o^* + \frac{2}{3} RT^2 \left(\frac{\partial \ln V}{\partial T}\right)_{(\pi + P)} - RT^2 \left[\frac{2}{3}\left(\frac{\partial \ln V}{\partial (\pi + P)}\right)_T - \frac{\Delta V_o^*}{RT}\right]\left(\frac{\partial \ln V}{\partial T}\right)_{(\pi + P)} \Bigg/ \left(\frac{\partial \ln V}{\partial (\pi + P)}\right)_T , \qquad (17)$$

which on simplification provides

$$E_V = \Delta H_o^* - T \Delta V_o^* \left(\frac{\partial (\pi + P)}{\partial T}\right)_V . \qquad (18)$$

Expanding ΔH_o^* in the usual way

$$\Delta H_o^* = \Delta U_o^* + (P + \pi) \Delta V_o^* , \qquad (19)$$

and substituting for ΔH_o^* from equation (19) in equation (18)

$$E_V = \Delta U_o^* + (\pi + P) \Delta V_o^* - T \Delta V_o^* \left(\frac{\partial (\pi + P)}{\partial T}\right)_V . \qquad (20)$$

We recall the definition of π , i.e. $\left(\partial U / \partial V\right)_T$ and note that

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{T} (\pi + P) . \qquad (21)$$

Attention is now drawn to the derivative $\left(\partial P / \partial T\right)_V$. Table (2) gives values of P and T for the solvent methanol at constant volume. The readings are plotted in figure 1. The results shew that within the limit of the experimental error

$$P = a + b T \quad \text{(at constant V)}. \qquad (22)$$

Table 2.

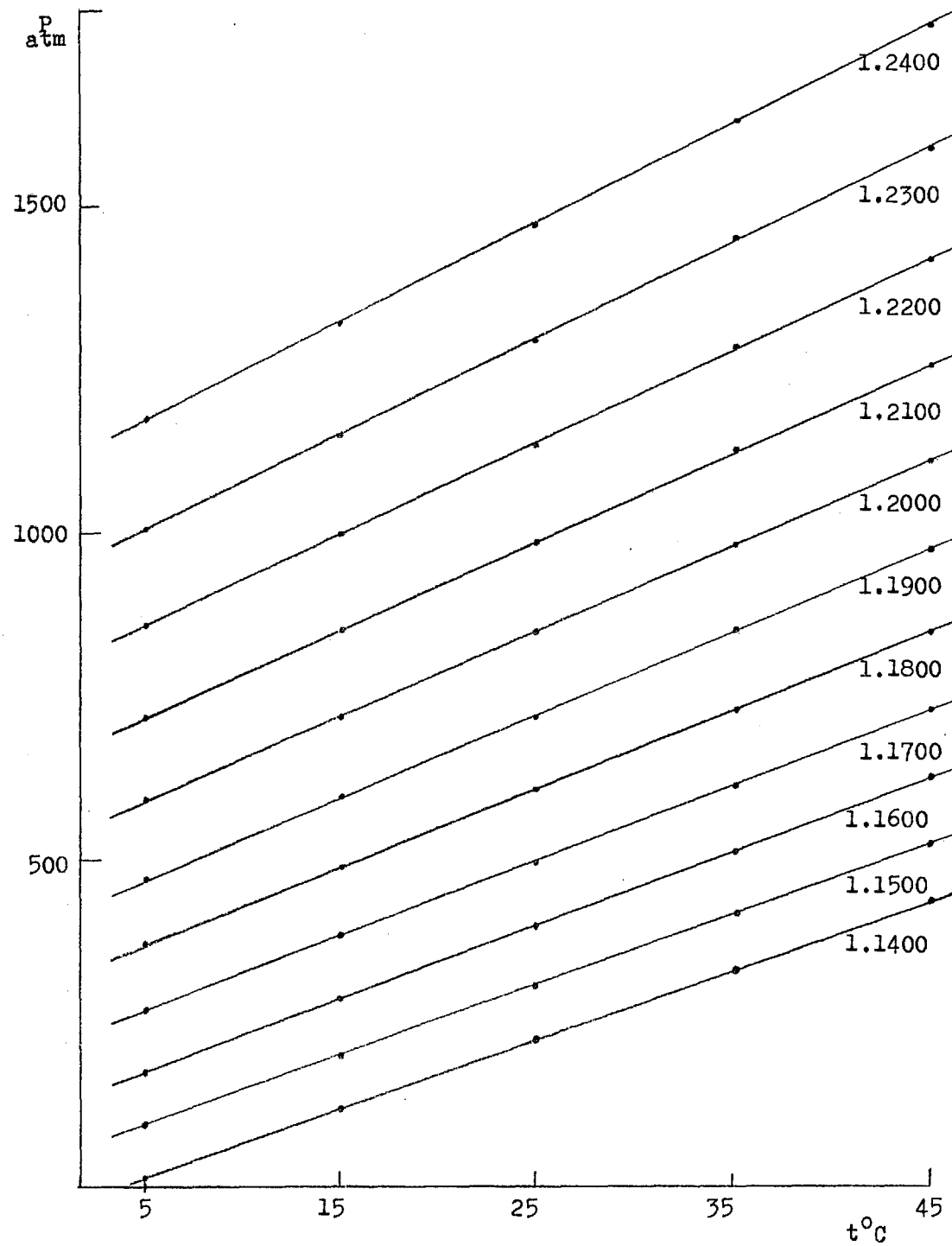
Pressure and temperature data for methanol at constant volume

V ml gm^{-1} \ t	5	15	25	35.14	45
	P_t atms	P_t atms	P_t atms	P_t atms	P_t atms
1.2400	13	118	223	332	434
1.2300	91	198	306	420	525
1.2200	175	286	397	516	623
1.2100	266	381	496	619	730
1.2000	365	484	603	731	846
1.1900	473	596	719	853	972
1.1800	591	717	845	985	1108
1.1700	719	849	982	1129	1255
1.1600	858	993	1130	1284	1415
1.1500	1009	1149	1291	1453	1588
1.1400	1173	1319	1466	1635	1775

Figure 1

P vs. t (at constant volume) for methanol

(V in ml gm^{-1} is given under each isochore)



Where a and b are two arbitrary constants. This conclusion is discussed in detail by Bridgman (14). It is expected that

$$\left(\frac{\partial P}{\partial T}\right)_V = f_1(V) \neq f(T) \quad , \tag{23}$$

at low pressures. However Bridgman reports divergence from this condition at the very high pressures of some of his measurements, which are beyond the range of the present studies.

Integration of the equality of equation (23) gives

$$P = T f_1(V) + f_2(V). \tag{24}$$

At constant volume $f_1(V)$ and $f_2(V)$ are constants, in which case equation (24) is identical with the empirical equation (22).

Differentiating equation (22) gives

$$\left(\frac{\partial P}{\partial T}\right)_V = b \quad .$$

Therefore, on recalling equation (21)

$$(\pi + P) = Tb. \tag{25}$$

Hence,

$$\left(\frac{\partial}{\partial T}\right)_V^{(\pi + P)} = b \quad ,$$

and

$$T\left(\frac{\partial}{\partial T}\right)_V^{(\pi + P)} = Tb. \tag{26}$$

Substituting for $(\pi + P)$ and $T\,(\partial/\partial T)_V\,(\pi + P)$, from equations (25) and (26) respectively, in equation (20) we obtain,

$$E_V = \Delta U_o^* \quad , \tag{27}$$

i.e. $$RT^2 \left(\frac{\partial \ln \lambda_i^o}{\partial T}\right)_V = \Delta U_o^* \quad . \tag{28}$$

If it is assumed that ΔU_o^* is not a function of temperature equation (28) can be integrated to give

$$\ln \lambda_i^o = K - \frac{\Delta U_o^*}{RT} \quad . \tag{29}$$

K is a constant.

This analysis differs in certain details from that of Brummer (15). His treatment was self-consistent but was based on the alternative pressure and temperature derivatives

$$\left(\frac{\partial \ln \lambda_i^o}{\partial P}\right)_T \quad \text{and} \quad \left(\frac{\partial \ln \lambda_i^o}{\partial T}\right)_P \quad ,$$

which clearly lead to different values of ΔV^* and ΔH^*, but not to different values of ΔU_o^*. This is a fortunate consequence of equation (22) and might not be generally true.

6. Energy of activation at constant pressure

It is also interesting to derive a relationship for E_P and hence for the difference between E_P and E_V.

As before,

$$\ln \lambda_i^o = f(P, T) \quad ,$$

and

$$\left(\frac{\partial \ln \lambda_i^o}{\partial T}\right)_V = \left(\frac{\partial \ln \lambda_i^o}{\partial T}\right)_P + \left(\frac{\partial \ln \lambda_i^o}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V . \tag{30}$$

Multiplying throughout by RT^2 and expanding the term $(\partial \ln \lambda_i^o / \partial P)_T$ we obtain

$$E_V = E_P + \left(\frac{\partial \ln \lambda_i^o}{\partial (\pi + P)}\right)_T \left(\frac{\partial (\pi + P)}{\partial \ln V}\right)_T \left(\frac{\partial \ln V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V RT^2 . \tag{31}$$

Recalling equations (10) and (21) to transform $(\partial \ln \lambda_i^o / (\pi + P))_T$ and $(\partial P / \partial T)_V$ respectively, equation (31) becomes

$$E_V = E_P + \left[\frac{2}{3}\left(\frac{\partial \ln V}{\partial (\pi + P)}\right)_T - \frac{\Delta V_o^*}{RT}\right] \left(\frac{\partial (\pi + P)}{\partial \ln V}\right)_T \left(\frac{\partial \ln V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V RT^2 . \tag{32}$$

Substituting $\beta = -\left(\frac{\partial \ln V}{\partial P}\right)_T$ and $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta}$

in equation (32) the simplified result is

$$E_V = E_P - \frac{2}{3} RT^2 \alpha + \Delta V_o^* T \alpha \left(\frac{\partial (\pi + P)}{\partial \ln V}\right)_T . \tag{33}$$

From equation (25),

$$\left(\frac{\partial (\pi + P)}{\partial \ln V}\right)_T = V T f_1'(V), \tag{34}$$

and substituting this result in equation (33) we obtain

$$E_P = E_V + \frac{2}{3} RT^2 \alpha - \Delta V_o^* V T^2 \alpha f_1'(V) , \tag{35}$$

or,

$$E_P = E_V + \frac{2}{3} RT^2 \alpha - \Delta V_o^* T^2 \left(\frac{\partial V}{\partial T}\right)_P f_1'(V) . \tag{36}$$

It is evident from equation (35) or (36) that $\overline{E}_p$ is a complex quantity. The $2/3.\ RT^2\alpha$ term arises from the temperature dependence of the pre-exponent term of equation (5). The right hand term of equation (30) expresses the change in the work done by the ion against its environment with increasing temperature.

7. Entropies of activation

The ~~pre-exponent~~ constant of equation (29) contains two unknown terms, the entropy of activation and the jump distance. Since we have no a priori knowledge of the entropy term the resolution of requires the evaluation of L. This term is open to several interpretations which would lead to varying estimates of its size. The simplest assumption would be that it is the average distance between two methanol molecules,

i.e. $$L = \sqrt[3]{\frac{\overline{V}}{N}} \quad . \qquad (37)$$

Alternatively, if the free volume of the liquid is regarded as discrete molecular holes occupying quasi-lattice sites, L would be the collision diameter of two methanol molecules. The difference between these two extreme values of L is not likely to be large, although the differences between their temperature and pressure derivations could be considerable, and we shall later prefer the value of L given by equation (37). Using this derivation of L values of $\overline{\triangle S_o^*}$ will be presented and this term will be seen to be of over-riding importance.

8. Transport numbers

So far the entire discussion of ionic migration has been concerned with single ionic conductances. In any experimental determination of conductance both cations and anions are involved and the determined quantity is $\Lambda = \lambda_+ + \lambda_-$. The separate ionic conductances then follow from measurements of the corresponding transport numbers. The complete experimental study is therefore a two-stage process.

Unfortunately the determination of transport numbers is both a different and more difficult problem from conductance. It is particularly difficult to determine the pressure coefficient of transport numbers; only in an isolated example (for aqueous HCl and NaCl) has this proved to be possible. From the beginning it was never the intention to include such a study in the present work.

The limitations imposed by this restriction were appreciated at the outset. The conductance Λ is given, in terms of equation (5) by the sum

$$\Lambda = A^+ \exp. - \frac{\Delta G_+^*}{RT} + A^- \exp. - \frac{\Delta G_-^*}{RT} ,$$

from which it follows that

$$\left(\frac{\partial \ln \Lambda}{\partial T}\right) \neq \left(\frac{\partial \ln \lambda_+}{\partial T}\right) \neq \left(\frac{\partial \ln \lambda_-}{\partial T}\right) ,$$

unless $\Delta G_+^* = \Delta G_-^*$. Furthermore, even if the ionic isochores, $\left(\frac{\partial \ln \lambda_+}{\partial (1/T)}\right)_V$ or $\left(\frac{\partial \ln \lambda_-}{\partial (1/T)}\right)_V$, were strictly rectilinear, the resultant total isochore, $\left(\frac{\partial \ln \Lambda}{\partial (1/T)}\right)_V$, clearly need not be, although the deviations will be small if $\Delta G_+^* \approx \Delta G_-^*$. It is therefore

remarkable that the first preliminary result (3) on methanol shewed the total isochore to be linear. The conclusion (15) drawn from this was that $\triangle G_+^*$ must be close to $\triangle G_-^*$. This is in accordance with the intuitive conviction that the activation energy of migration is predominantly a solvent function.

The linearity of the isochores is confirmed in the present work but on the further analysis of the results it became increasingly doubtful whether the apparent equality of $\triangle G_+^*$ and $\triangle G_-^*$ extended to their temperature and pressure derivatives. This uncertainty will only be removed by a corresponding study of transport numbers.

The subsequent chapters of this thesis are concerned to describe the experimental details, secondly the results and their analysis and finally the significance of the derived parameters $\overline{\triangle U}_o^*$, $\overline{\triangle V}_o^*$ and $\overline{\triangle S}_o^*$.

CHAPTER 2

EXPERIMENTAL

Contents

1. Preliminary remarks on the experimental procedure

This work was begun as part of a programme for the extension of the initial study by Brummer and Hills (2,3) into the effect of pressure on electrolytic conductance in a number of different solvents. The investigation here is restricted to a considerably more detailed study of the variation with temperature and pressure of the conductance of methanolic solutions of potassium perchlorate and four tetra-alkyl ammonium perchlorates, viz. methyl, ethyl, n-propyl and n-butyl. In preliminary experiments, following Brummer, the corresponding picrates were used, but it was found that at 35° and 45°C these solutions became discoloured and changed from yellow to dark brown. Furthermore the resistances of these solutions even at 1 atm tended to be less reproducible than those of the perchlorates which were subsequently used and are the basis of all of the measurements recorded later.

The experimental procedure was an extension of that of Brummer and Hills; larger, more effective pressure vessels were used, which allowed the pressure range to be extended to 2000 atm. The pressure vessel heads were fitted with six terminals so that measurements with five high-pressure cells could be carried out simultaneously. This greatly accelerated the collection of a sufficiently large body of conductance data.

In the absence of any published comprehensive compressibility data for methanol it was necessary to measure this property of the solvent at those temperatures used in the conductance work, viz.

5^{o}, 15^{o}, 25^{o}, 35.14^{o} and $45^{o}C$. The concentration range used, 25×10^{-4} to 1×10^{-4} mole litre^{-1}, was sufficiently dilute that no serious error was involved in equating the density of the solution at a particular temperature and pressure to that of pure methanol.

The conductance measurements were based on the determination of the resistance of methanolic solutions of each of the five salts as a function of temperature and concentration at 1 atm pressure and then as a function of pressure at the five temperatures of the experimental range. The specific conductance at a pressure P, (K_p) was calculated from the integral pressure coefficient of resistance of a particular solution initially of concentration c_1, i.e. $(R_p/R_1)_{c_1}$, where R_p is the resistance of the solution at a pressure P in a particular cell and R_1 is the resistance of the solution at 1 atm in the same cell. It follows that

$$(K_p)_{c_p} = (R_p/R_1)^{-1} (K_1)_{c_1} .$$

, is the specific conductance of the solution at 1 atm and c_p is the concentration at P atm as given by the Tait equation for the compressibility of methanol, i.e.

$$c_p = \frac{c_1}{1 - C \ln\left(\frac{B + P}{B + 1}\right)} .$$

Corrections were also made for the distortion of the cell, and the change with pressure of cell constant. Whence the Λ_p, the molar conductance of the solution at pressure P and at concentration

c_p is

$$\Lambda_p = \frac{\kappa_p \, 1000}{c_p} \quad .$$

The following sections describe the apparatus used, the preparation of the materials and finally the experimental procedure.

2. Preparation of materials

Potassium chloride

Analytical grade potassium chloride was recrystallised three times from conductivity water, dried in air at 200°C and finally fused in platinum.

Tetra-methyl ammonium perchlorate (16) was precipitated from 25% aqueous tetra-methyl ammonium hydroxide solution by addition of 60% perchloric acid until the solution remained weakly alkaline. The precipitate was recrystallised four times from conductivity water and dried at 100°C under vacuum.

Tetra-ethyl ammonium perchlorate (17) and tetra n-propyl ammonium perchlorate were prepared in an identical way to the tetra-methyl salt.

Tetra n-butyl ammonium perchlorate was precipitated from 40% aqueous tetra n-butyl ammonium hydroxide solution by 60% perchloric acid as above, but the salt was recrystallised from a water-methanol mixture. After four recrystallisations the salt was dried at 100°C under vacuum.

Potassium perchlorate Laboratory grade $KClO_4$ was recrystallised four times from conductivity water and dried under vacuum at 100°C. A sample was heated to 250°C to test for completeness of drying (18) and there was no further loss in weight.

Purification of methanol

Methanol was rectified by fractionation under an atmosphere of purified nitrogen. The fractionating column was 2 metres long and packed with Fenske helices, the take-off being controlled by means of a mercury-sealed glass tap. The conductivity of the distillate was measured continuously by means of a cell of capacity 50 ml (cell constant, 4.72×10^{-2} cm^{-1}) mounted between the take-off jet and the receivers.

The boiler was charged with 4 litres of "Analar" methanol. Only the middle fraction, of some 1.5 litres, of the distillate was used for the preparation of solutions. The specific conductivity of this fraction was approximately 1×10^{-8} ohm^{-1} cm^{-1}, which compares with the values of $3-5 \times 10^{-8}$ ohm^{-1} cm^{-1} and $2-7 \times 10^{-9}$ ohm^{-1} cm^{-1} of Butler, Schiff and Gordon (19) and Evers and Knox (20) respectively.

It was found that the conductivity of the distillate invariably increased with time and this was attributed to reaction, and perhaps ion exchange, between the alcohol and the Pyrex glass of the storage vessel. There is evidence to the effect that dry alcohol attacks Pyrex glass (21), and this phenomenon was also reported by Steel (22). Evers and Knox (20), however, claim remarkable stability of their alcohol in Pyrex after treatment of the vessels with methanol vapour.

This treatment was also tried in the present research but it did not stabilise the conductivity of the alcohol. Nevertheless the increase in solvent conductance was small after, what seemed to be an "equilibrium value" of 4-8 x 10^{-8} ohm^{-1} cm^{-1} had been reached after about 2 days, subsequent changes represented a negligible uncertainty in the conductance of even the most dilute solution.

The main receiving flask was fitted with an internal stopper which could be operated magnetically so that the alcohol could be transferred from the still to a dry-box containing an atmosphere of dry nitrogen.

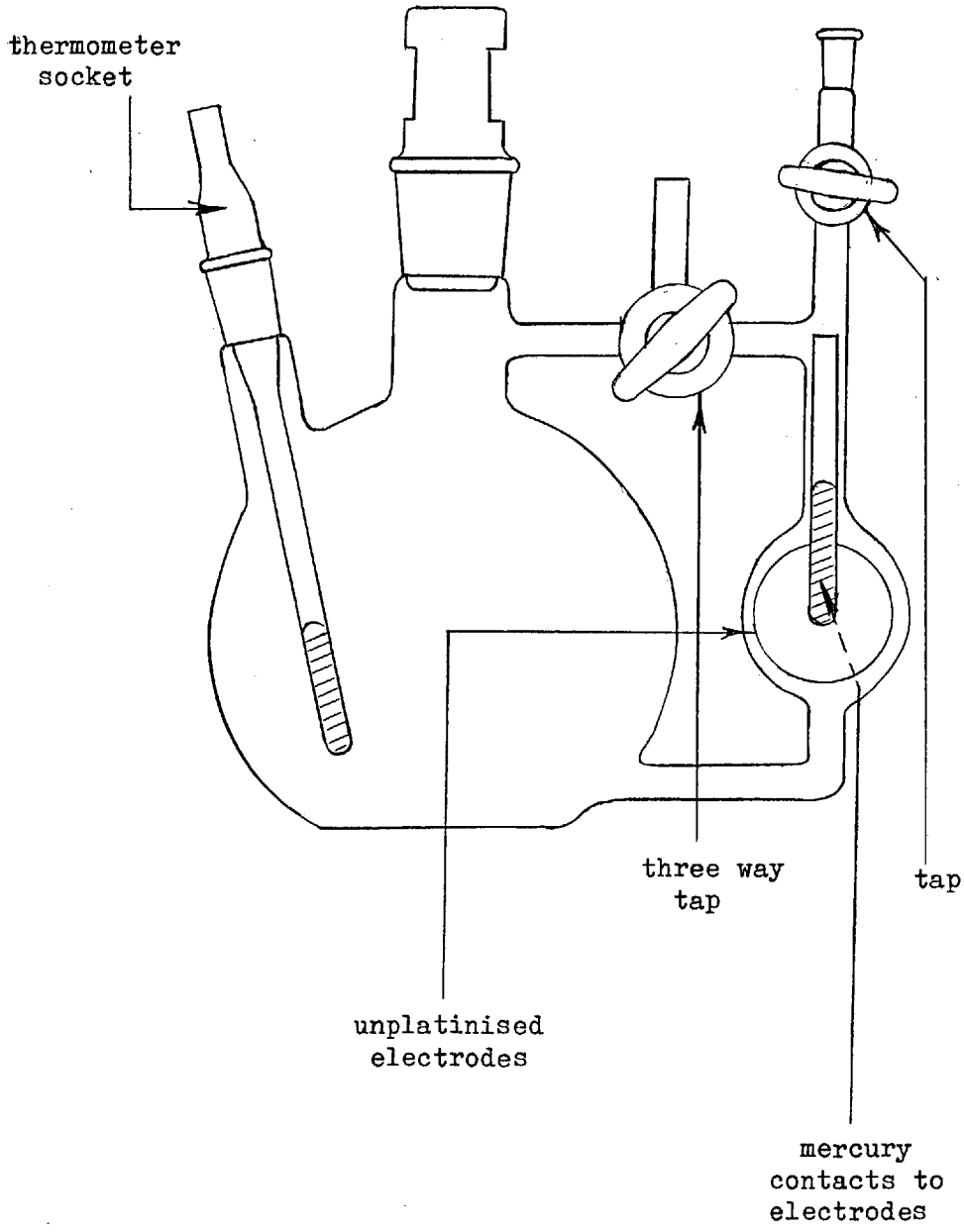
The alcohol was stored in the dry-box in Pyrex glass. Prior to the preparation of solutions the solvent was transferred to a 1 litre flask with an attached conductance cell of constant 5.55 x 10^{-2} cm^{-1} (figure 2). The particular solvent conductances determined in this way were taken as the appropriate solvent corrections for the solutions prepared from the alcohol.

Purification of mercury

The mercury used to isolate the solutions from the oil and to act as a pressure transmitting fluid in the pressure measurements was purified in the way described by Ives and Janz (23). Oily mercury was first cleaned by washing with petrol followed consecutively by ether and alcohol and finally with water before proceeding with the above purification.

Figure 2

The solvent cell (capacity 1 litre)



3. The Apparatus

(a) High Pressure conductance cells

Two sets of high pressure conductance cells were used. They are designated sets A and B, and are illustrated in figure 3. Each set consisted of five cells, the cell constants of which varied from ~ 0.2 to ~ 0.05. The cells were made of Pyrex glass and electrodes of lightly platinised platinum. Platinisation was carried out as indicated by Findlay (24). The construction of cells in set A was slightly different from set B in that the rods of the electrodes in set B were enclosed in glass so that, in the event of the formation of a bubble at 1 atm (particularly at 45°C), the resistance between the electrodes would not be affected. This feature of the construction of the cells was responsible for the difference in pressure distortion characteristics of the two sets of cells.

The cells were filled in the dry-box and sealed by dipping the pipette tips into cups of mercury, which as well as being the pressure transmitting fluid was an effective seal of each system. The combination of cell and mercury cup was transferred from the dry-box and strapped to a rigid mounting fastened to the pressure vessel head.

The rod and ring cell

It has been demonstrated by Ovenden (25) that a cell with the rod and ring electrode system (illustrated in figure 4) has a cell constant which is independent of the small compressions and distortions of the containing envelope likely to be experienced over the pressure range of this work (P_{max} = 2000 atm).

Figure 3

High pressure conductance cells

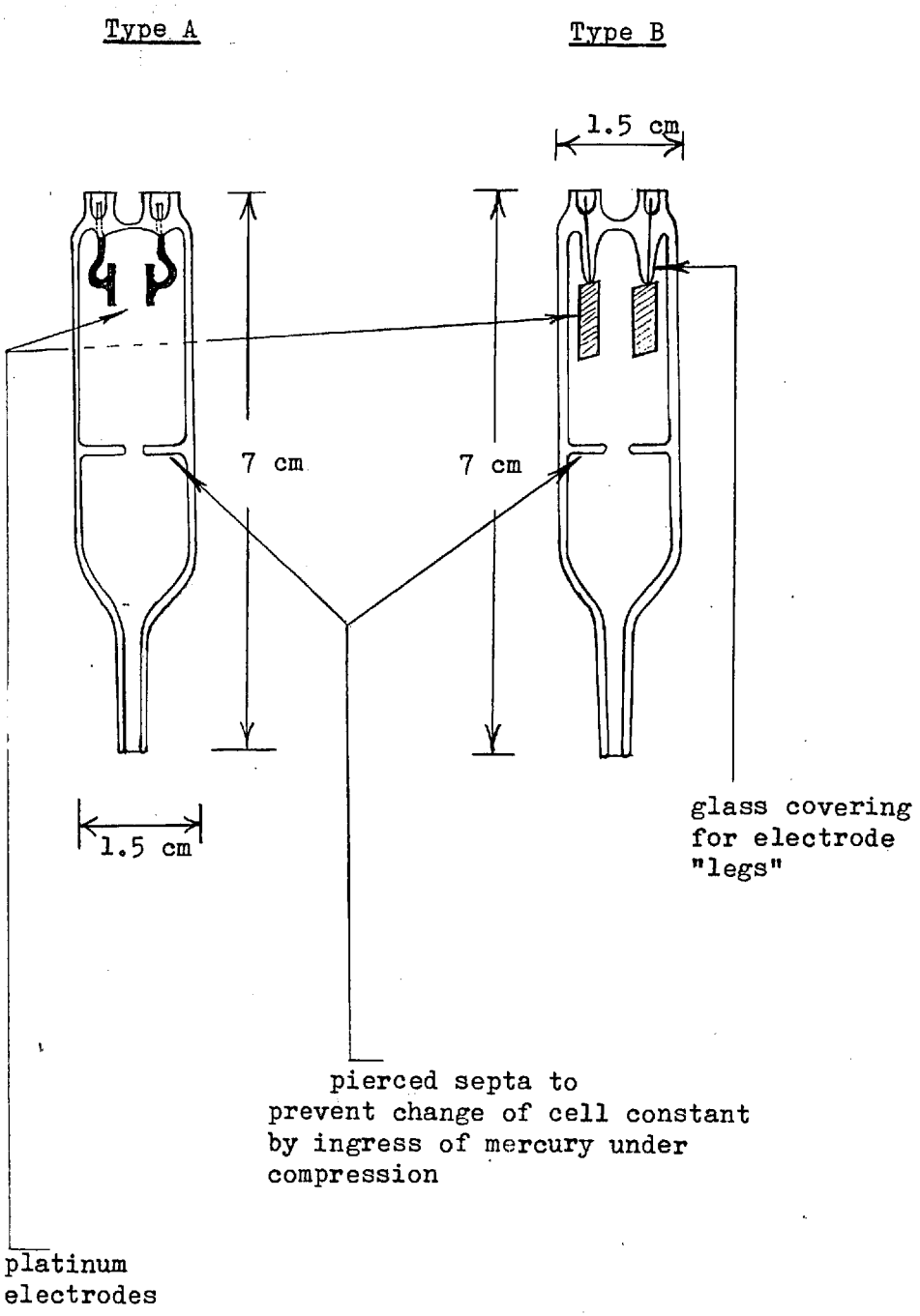
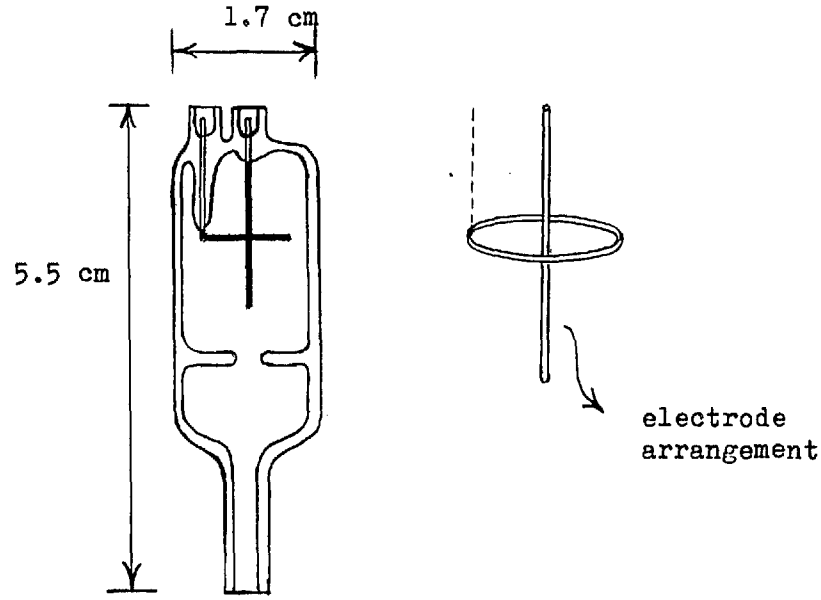


Figure 4

The rod and ring high-pressure conductance cell



This was verified by mounting the electrodes firstly on a rigid and incompressible plug and secondly in a highly deformable P.T.F.E. plug. In both cases the variation with pressure of R_p / R_1 was the same, but very different from that of other non-compensated electrode arrangements.

Calibration of set A and B conductance cells

It was originally proposed to correct the R_p / R_1 values for change of cell constant with pressure by assuming a linear compression of the glass between the electrodes. However, following the above investigation of the rod and ring electrode system a cell utilizing this principle was used to calibrate the ten conductance cells already in use.

These correction factors were expressed as $\frac{(R_p / R_1)_{\text{rod and ring cell}}}{(R_p / R_1)_{\text{cell}}}$ as a function of P. The calibration chart for the cells is given in figure 5, and it was found that the corrections for set A cells were consistent with those based on the original assumption of a linear compression of the glass between the electrodes, i.e. a correction factor of $(1 + 1.0 \times 10^{-6} P)$ (26). Set B cells shewed greater distortions than set A cells, giving both positive and negative correction coefficients. The calibrations of these cells with respect to the rod and ring cell were consistent with an internal calibration carried out initially.

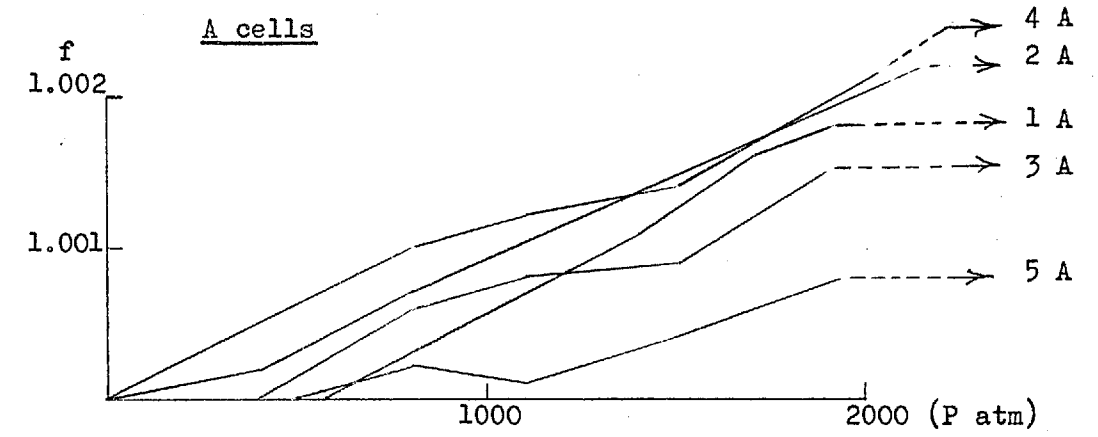
Figure 5

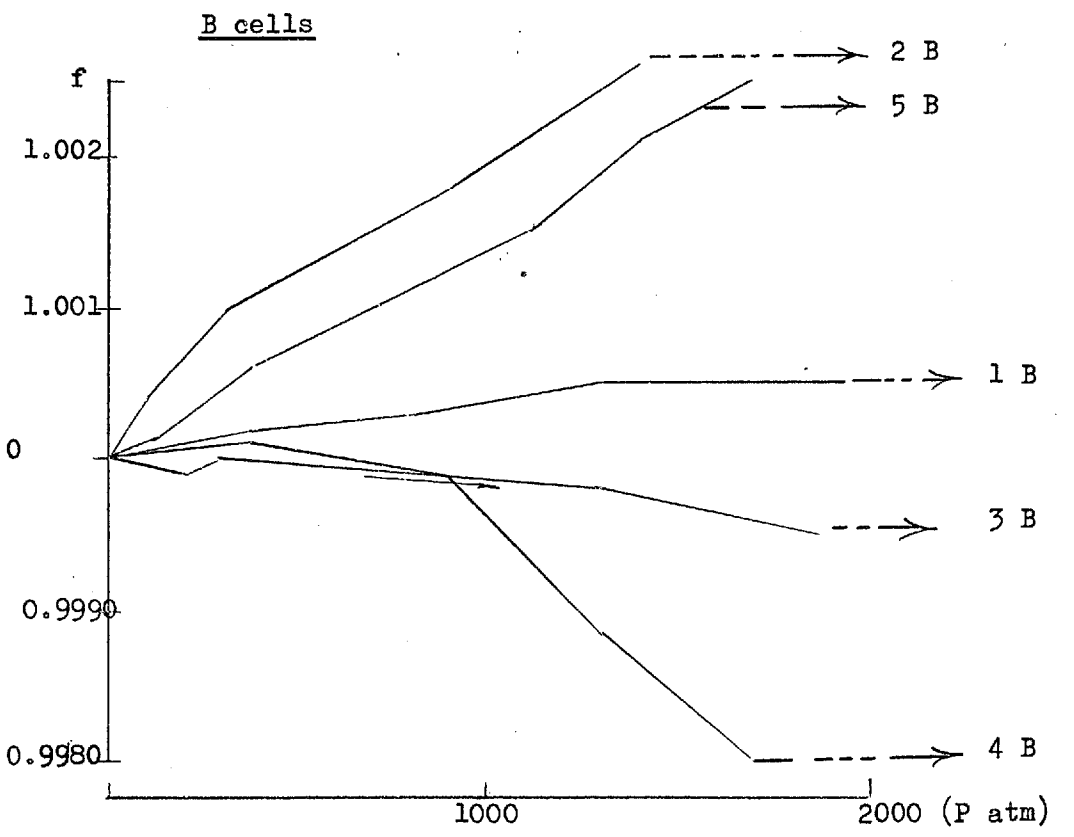
Calibration Chart of high pressure conductance cells

$$f = \frac{(R_p/R_1)_{\text{rod and ring cell}}}{(R_p/R_1)_{\text{cell}}}$$

No 1 cells used for most conc. solution

No 5 cells " " " dilute solution





(b) 1 Atmosphere conductance cells

Preliminary experiments with simple conductance cells consisting of two electrodes in a single small compartment gave resistances which changed with time when filled with solutions of concentration $< 12 \times 10^{-4}$ mole litre^{-1}, the resistance invariably decreasing with time. It was presumed that this was due to desorption of ionic material from the electrodes and to dissolution of the glass.

Three conductance cells were constructed of the Shedlovsky type in which the conductance cell was fused on to a 50 ml conical storage flask (see figure 6). The electrodes were lightly platinised (24). The solution between the electrodes could be renewed by tilting the cell backwards and forwards. The resistance of a dilute solution in the electrode compartment still decreased with time but by tilting the cell the resistance could be brought back to a steady value. This "shaking effect" was also noticed by Prue (27).

The cell constants of the cells were determined using the equation of Fuoss (28) for the conductance of aqueous potassium chloride as a function of concentration. The solution of KCl was made up by weight and converted to concentration using the density relation (29),

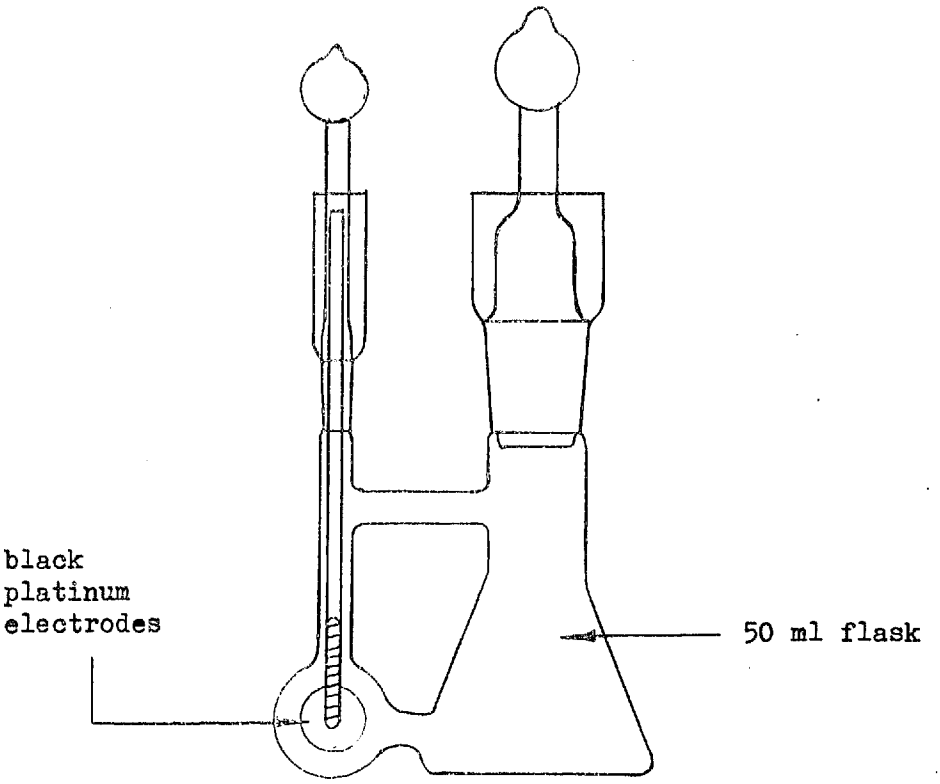
$$\rho^{25^\circ} = 0.9971 + 0.0049\, c \quad .$$

For the present purpose the density obtained by assuming molarity equals molality for c was sufficiently accurate. The potassium chloride was fused in platinum before use and was dissolved in conductance water of known specific conductance.

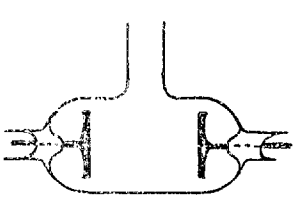
The cell constants of these cells were 0.3932, 0.3851 and 0.5896 cm^{-1}. These values were checked several times during the

Figure 6

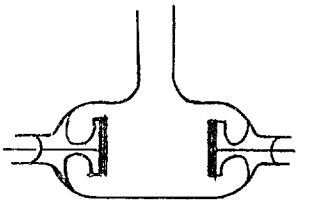
General pattern of 1 atm conductance cells



The two types of platinum electrodes used



conventional rod
and disc electrodes
(1 cell)



Foil supported on
glass "table" with
foil seal to side
arm
(2 cells)

period of use and were found unchanged.

The solvent cell

The methanol was stored prior to the preparation of solutions in another larger conductance cell (see figure 2) which consisted of a 1 litre flask with a conductance cell sealed into a separate side compartment (cell constant 5.55×10^{-2} cm^{-1}). This conductance cell contained large unplatinised electrodes.

(c) Pressure vessels

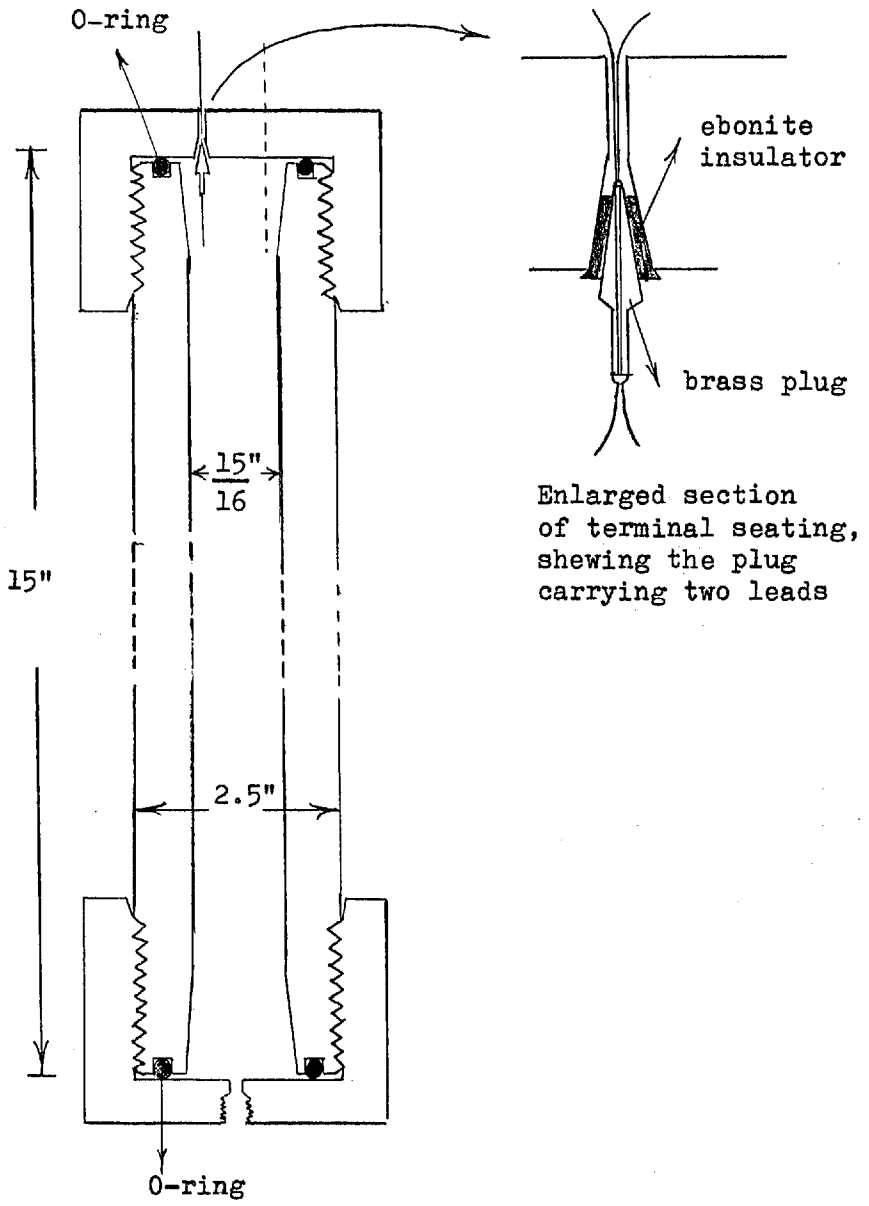
Both were mounted in similar oil thermostats, one of which had an attached refrigeration unit, for the measurements at 5°, 15° and $25^{\circ}C$.

Figures 7 and 8 give details of the dimensions and the construction of the pressure vessels. The second pressure vessel, which operated at the higher temperatures, was manufactured by Pressure Products Ltd., Hatboro, U.S.A. and proved to be very satisfactory. The other pressure vessel was made in the Chemical Engineering Workshops of this college and suffered from a serious defect of design. The simple groove and O-ring closure provided a good pressure-tight seal but the pressure tended to extrude the O-ring between the head and the pressure vessel and when this happened the removal of the head was exceedingly difficult. This problem was partly overcome by inserting a thin copper ring in the external space between the O-ring and the groove, but even so this vessel was never easy to seal and manipulate.

A further disadvantage of this vessel was that it had only four through terminals. To accommodate five cells in the pressure vessel it was necessary to increase the number of terminals to six and this

Figure 7

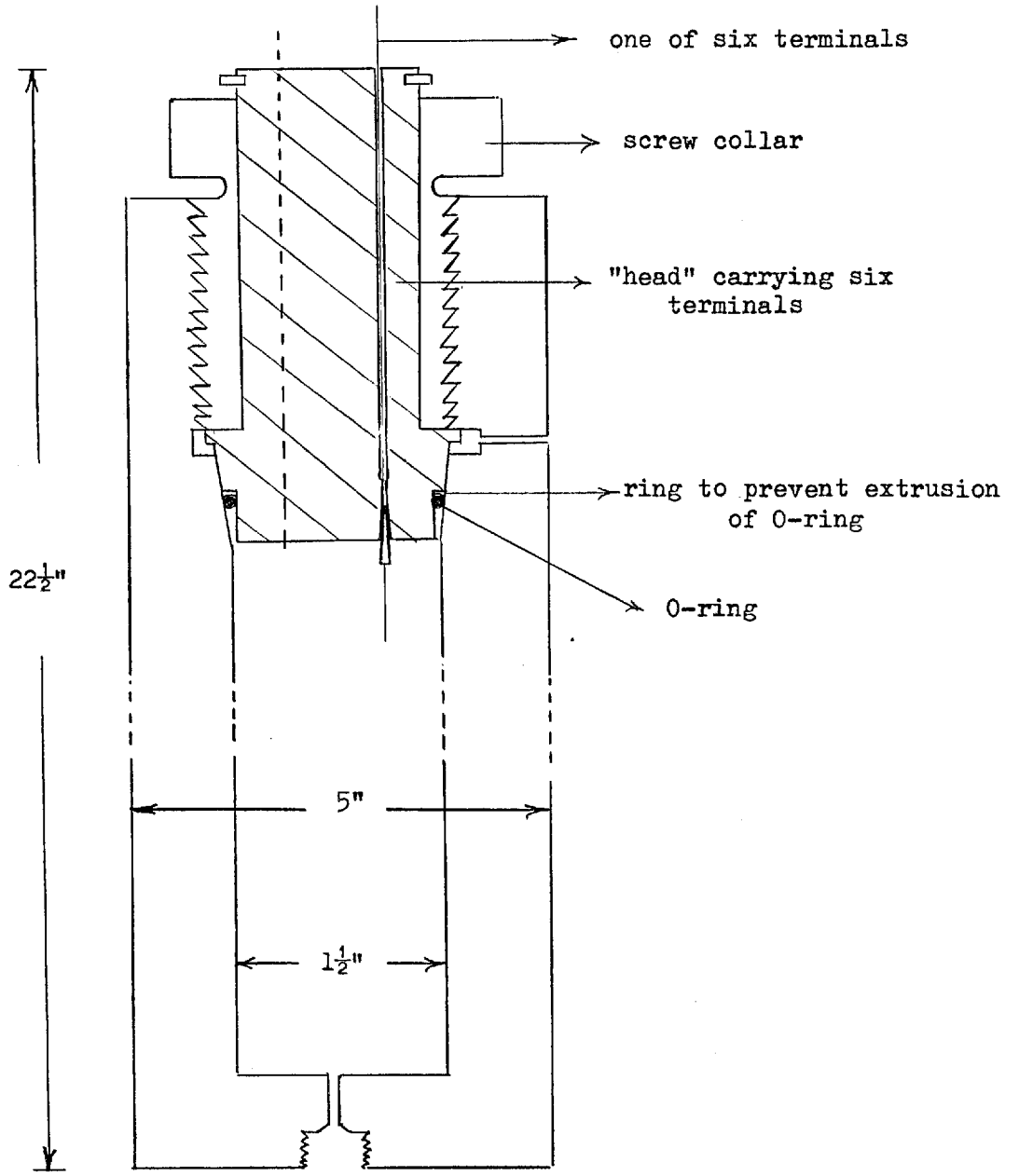
Pressure vessel 1



Enlarged section
of terminal seating,
shewing the plug
carrying two leads

Figure 8

Pressure vessel 2



was done by replacing two of the original stainless steel cones by brass cones which had been drilled straight through with a 1/32" diameter hole. Two S.W.G. 30 enamelled copper wires were then cemented into the hole using Araldite AY105 with hardener HY956 and cured overnight at 70°C.

Ebonite insulators were used in this pressure vessel. The ceramic insulators originally supplied with the pressure vessel were a continual source of trouble since they need very careful machining to ensure a pressure-tight fit. Ebonite, being more plastic, always sealed on the application of pressure but was firm enough to resist extrusion even at 45°C. Generally, however, this pressure vessel operated at 5, 15 and 25°C.

(d) Pressure gauges

Two 10" Bourdon pressure gauges were used, one attached to each pressure vessel. As supplied by Messrs. Budenberg and Co Ltd they had a maximum scale reading of 3000 atm divided in 50 atm intervals. These 50 atm divisions were further subdivided by hand into 10 atm intervals and the flat tip of the pointer was twisted through 90° to give a pointer-end as fine as the thickness of the metal.

Since the manufacturer's calibration indicated differences between readings on rising and falling pressure half-cycles, pressure readings were always taken on a rising scale and as a precaution against sticking the gauges were carefully tapped before taking a reading. The maximum pressure to which a gauge was subjected was 2/3 of the maximum scale reading, i.e. 2000 atm; stressing beyond this point was likely to result in severe hysteresis.

(e) The pressure lines, needle valves and hydraulic pump

The needle valves and high pressure tubing were supplied by AMINCO. (The American Instrument company). The hydraulic pump (Blackhawk, Type P 228) was officially rated to 2,500 atms.

(f) Thermostats

Four thermostats were used. Two were glass-sided of 30 and 20 gallon capacity respectively. Each was filled with Shell Risella 23 oil. These tanks were well stirred with multiple paddles and controlled with mercury-toluene regulators and valve switches linked to 250 watt Robertson heating lamps. The temperature in these thermostats was constant to $\pm$ 0.01°C.

The two pressure vessels were each mounted in a large well insulated metal tank of 40 gallons capacity. The tank containing pressure vessel 2 was used for temperatures 35.14° and 45°C and was also filled with Shell Risella 23 oil. The temperature was likewise controlled by a mercury-toluene regulator and valve switch linked to four heating lamps. The temperature was constant to $\pm$ 0.01°C. The other 40 gallon thermostat was used to maintain the temperatures 5, 15 and 25°C. A cooling coil from a refrigeration unit was permanently immersed in the tank and isolated from the main body of the oil by a metal box. One of the sides of the box could be removed to increase the rate of cooling and was used when changing the temperature of the thermostat. The temperature control on the refrigeration unit was immersed in the coil compartment and operated on the minimum differential of 1.0°C. The balancing heat was provided by four 250 watt Robertson

heating lamps controlled by a mercury-toluene regulator. The temperature of this thermostat was constant to $\pm$ 0.02°C.

(g) Temperature measurement

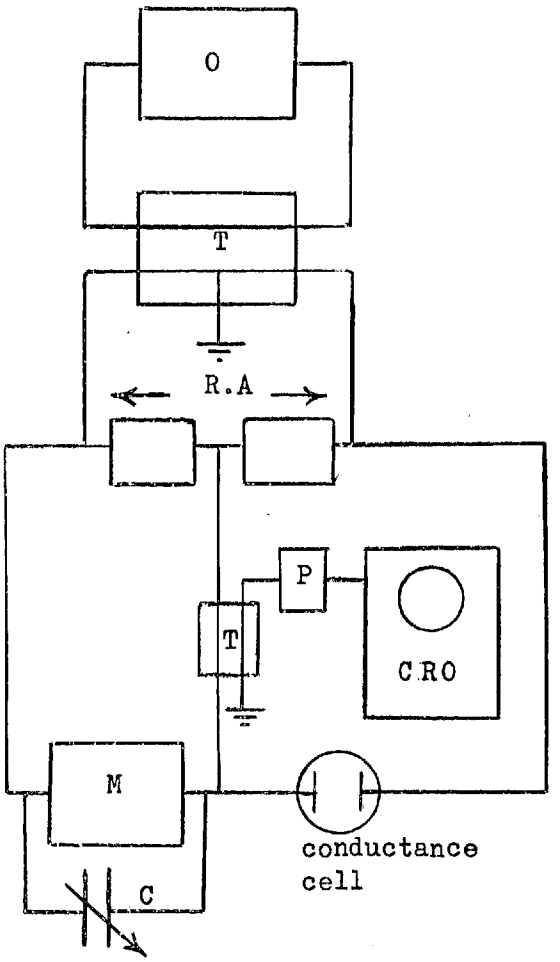
The temperature of the thermostats was measured with a set of mercury in glass thermometers supplied by Messrs. Short and Mason; each covered a range of 10°C and was graduated in intervals of 0.02°C. All had been calibrated recently at the N.P.L. and were internally consistent. At the onset of the work a 35°C thermometer was not available. A setting was taken on a Beckmann thermometer at approximately 35°C, which transpired on later checking with an N.P.L. calibrated thermometer to be 35.14°C.

(h) The conductance bridge

The conductance bridge used was a conventional A.C. Wheatstone bridge. A diagram of the bridge together with a list of components is given in figure 9. The centre of the input transformer to the bridge was earthed to act as a Wagner earth at balance. Coaxial leads were used for all connections and these were made as short as possible. The coaxial screens were all earthed to a common point. The limit of the resistance boxes was specified as accurate to 0.05% and the bridge was sufficiently sensitive to detect 0.1 ohm in 5000. The bridge shewed no frequency dependence over the working range of 1 - 4000 cps. The 10 thousand decade on the measuring box was not non-inductive which made it impossible to correct for frequency dependence of the 1 atm conductance cells if the resistance of the solution in the cell exceeded 9999.9 ohms. In fact the frequency

Figure 9

The conductance bridge



O oscillator. (A.F. Generator, working on 600 ohms output impedance, attenuated to 20 d b.)

T screened balanced transformer

C variable capacitor

CRO cathode ray oscilloscope to detect balance point

RA ratio arm (1:1, 1:10, 1:100, 1:1000)

M measuring decade resistance box range 0.1 - 10^5 ohms, 0.05%

P transistorised variable gain amplifier, maximum gain x 40

dependence of the cells was always very small, i.e. less than 0.1% and was estimated by the method of Jones and Christian (30).

(i) Preparation of solutions

A stock solution was prepared of concentration $\sim 25 \times 10^{-4}$ mole litre^{-1}. A semi-micro balance was used to weigh out the solute and the total weight of the solution was ~ 500 gms. Other solutions were made by weight dilution of this stock solution and in every case the W/W composition was converted to volume concentration in terms of the density of pure methanol (31). All solutions were prepared using a dry-box filled with an atmosphere of dry oxygen-free nitrogen. Weighings were made outside the dry-box using well-stoppered storage flasks.

(j) Cleaning of cells and solution flasks

Initially the storage flasks were cleaned with chromic-sulphuric acid mixture followed by steaming. This procedure gave rise to spurious conductance values at low concentrations, the values being invariably high. This practice was discontinued and instead the flasks were cleaned by "steaming" with methanol vapour. Flasks and cells were inverted over a jet of vapour for ~ 30 minutes and then dried at 70°C overnight. Particular flasks and cells were reserved for solutions of the same concentration.

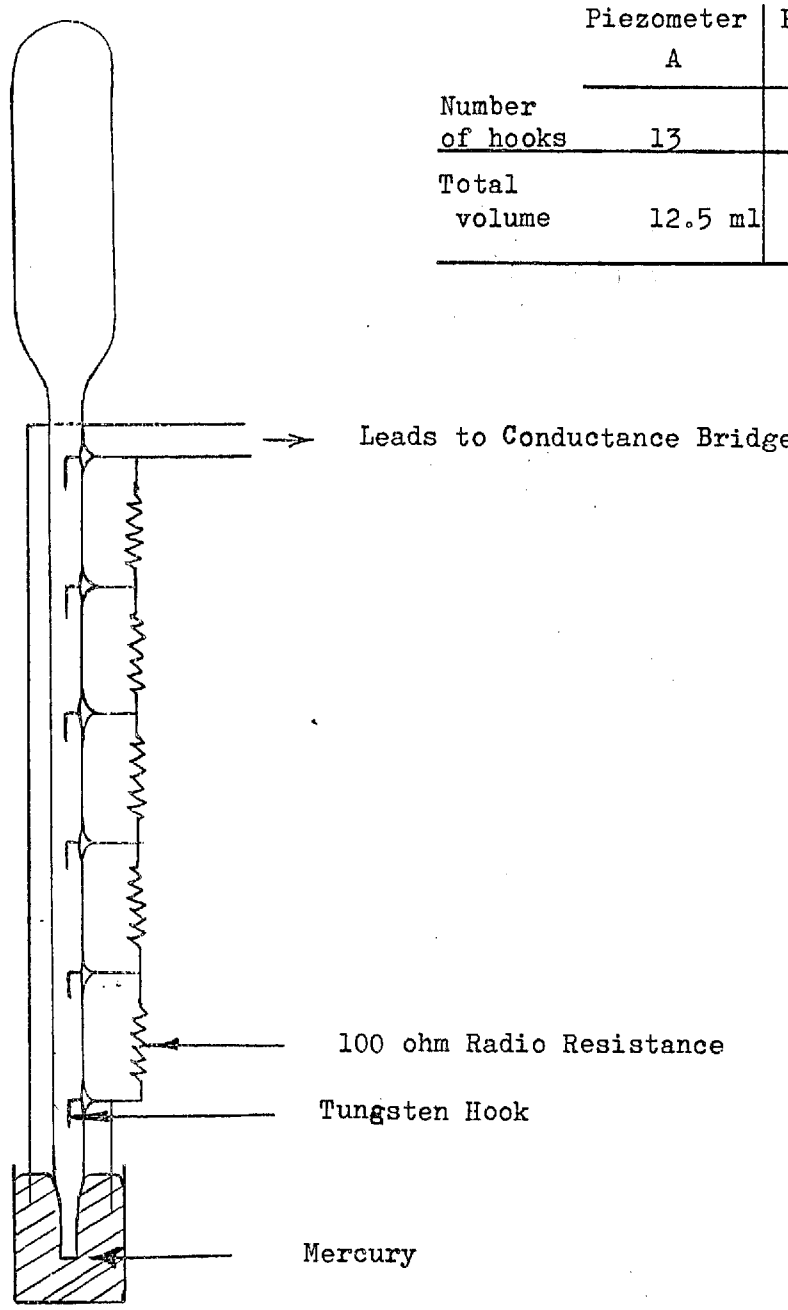
4. The apparatus for the compressibility measurements

The compressibility of methanol was measured from 5°C to 45°C at 10° intervals. Two piezometers (figure 10) were used of the type

Figure 10

Piezometer design

	Piezometer A	Piezometer B
Number of hooks	13	16
Total volume	12.5 ml	18.5 ml



described by Amagat (32) and more recently, by Eduljee, Newitt and Weale (33). The internal diameters of the pressure vessels were different and one of the piezometers, B, could be used only in the larger pressure vessel 2. Piezometer A was smaller and was used in both pressure vessels. The piezometers were made of Pyrex glass with tungsten contacts sealed into the stem. These were cleaned internally by electrolysis in KOH solution. The contacts were shorted externally by small 100 ohm radio resistors silver-soldered between them. The piezometer was filled with alcohol in the dry-box and the tip immersed in a cup of mercury. A platinum wire connected the mercury to the 100 ohm resistance soldered below the lowest contact. Electrical connections were taken from the mercury and the top resistance through the head of the pressure vessel to the conductance bridge. Application of pressure compressed the methanol and forced the mercury up the stem successively shorting out the 100 ohm resistances on reaching the internal contacts. A small correction was made for the compressibility of the glass, i.e. $\sim$ 0.1%, that of the mercury does not enter into the method since the mercury merely acts as a piston.

The piezometers were calibrated by weighing in mercury up to each contact point and finally with the piezometer full of mercury. The ratio of the volume to each contact point to the total volume was obtained. A small correction was made for the fact that in the calibration procedure the meniscus is inverted with respect to the operating position. Piezometer A was also calibrated using ethyl iodide, the compressibility of which has been measured by Amagat (34). The two calibrations were identical to within the experimental error of $\sim$ 0.2%.

At higher temperatures it was convenient to fill the piezometer with liquid at a temperature below that of the determination to ensure that the piezometer is completely filled by subsequent expansion of the liquid. This was less convenient for the temperatures 15°C and 5°C and an alternative technique was adopted for these temperatures. In this case the piezometer was filled at room temperature, which was below 25°C, and then equilibrated in a thermostat at 25°C. After 1 hour to ensure thermal equilibrium the piezometer was inserted in the pressure vessel at the temperature of the particular measurement, 5° or 15°C. The calibration of the piezometer can be corrected for the changed initial volume in terms of the densities of methanol at 25°C and the temperature of the measurement.

5. Description of the Experimental Method

(a) Conductance at 1 atmosphere

The conductances of methanolic solutions of $KClO_4$, Me_4NClO_4, Et_4NClO_4, $n\text{-}Pr_4NClO_4$ and $n\text{-}Bu_4NClO_4$ were measured at the following temperatures, 5°, 15°, 25°, 35.14° and 45°C over the concentration range 1×10^{-4} to 25×10^{-4} mole litre^{-1}. Between eight and sixteen solutions were measured over each range of concentration.

The specific conductances of the solutions were measured in the "flask cells", previously described, 30 - 45 minutes being required for temperature equilibrium to be established. The resistances of the solutions were stable overnight, provided the cells were shaken to renew the solution between the electrodes.

At 35.14° and 45°C the vapour pressure of the solution was

sufficiently high to force out the stoppers of the cells. At these temperatures stoppers were used which carried fine capillary tubes closed by taps. Using these the cell resistance was first measured at 25°C. The cell was then placed in the thermostat at the higher temperature, the tap was opened until thermal equilibrium was reached and then closed. The small loss of vapour was estimated by returning the cell to the 25°C thermostat and determining the new resistance of the solution. To minimise this the cells were almost filled with solution and only sufficient space was left to allow the solution to be mixed by shaking. In this way the correction was reduced to less than 1 part in 1000.

(b) Conductance as a function of Pressure

A small correction was made at each pressure for solvent conductance using the expression,

$$(R_p/R_1)_{corrected} = \frac{(R_p/R_1)_{measured}}{1 + x\left[1 - y\,(R_p/R_1)_{measured}\right]} \quad . \qquad (38)$$

$$x = \frac{K_{(solvent)}}{K_{(solute)}}, \text{ at 1 atm for a solution}$$

$$y = \frac{K_{(solvent,\ at\ pressure\ p)}}{K_{(solvent\ at\ 1\ atm)}} \quad .$$

The parameter "y" as a function of pressure was difficult to measure because the specific conductance of the solvent was so small. It was in fact determined only at 25°C and was assumed to be the same at all other temperatures since the correction was small and significant

for only the most dilute solutions.

It was found that the solvent conductance increased with pressure, presumably because of an increase of the dissociation of the solvent and this is in accordance with the increase with pressure of the dielectric constant (35).

Measurement of conductance under pressure was carried out in the micro-conductance cells already described. Five cells were used simultaneously containing five different concentrations, covering isobarically the concentration range 25×10^{-4} to 2×10^{-4} mole litre^{-1}. This procedure had the advantage that whatever the residual uncertainty in the pressure sensing it could not influence the extrapolation of these conductances to infinite dilution.

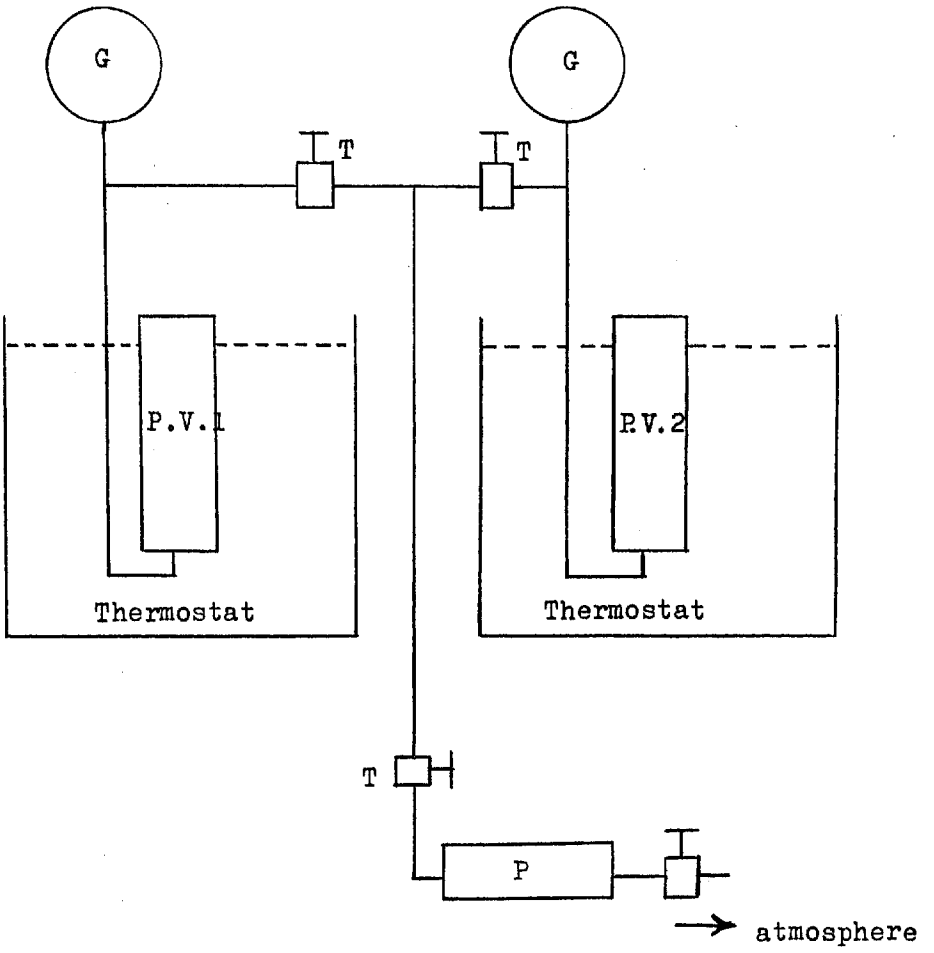
The hydraulic fluid was the thermostat oil, Shell Risella 23 for vessel 2 and Shell Tellus 11 for vessel 1. The pressure lines of the two vessels were linked together and led to the hydraulic pump. A line diagram of the pressure system is shewn in figure 11.

After the pressure vessels had been filled with oil the conductance cells were inserted and the heads then carefully screwed into position. Very little force was needed to produce a pressure seal and pressure vessel 1 needed only to be finger-tight.

With the valve on the hydraulic pump open, the cells in the pressure vessels were at 1 atm pressure. The 1 atm resistances were measured after thermal equilibrium had been established after which the first pressure cycle was begun. After each increment of pressure time was required for the heat of compression to be dissipated, 1 hour for pressure vessel 2 and 35 minutes for vessel 1. The 1 atm resistance

Figure 11

Line diagram of high pressure apparatus



G pressure gauge

T tap

P hydraulic pump

P.V. pressure vessel

values were reproducible to 0.1%.

After each pressure cycle the cells were removed, cleaned and refilled with solution before another pressure cycle at another temperature was commenced.

(c) The compressibility measurements

The mountings in the pressure vessels were changed to accommodate the piezometers. The piezometers were filled with methanol in the dry-box, sealed with mercury, inserted in the pressure vessel and allowed to reach thermal equilibrium. The pressure was then raised from 1 atm until the conductance bridge shewed that the first resistance had been shorted out by contact of the mercury with the first tungsten hook. The pressure was then dropped ~25 atm and the heat of compression allowed to dissipate (~ 30 min). The pressure was then raised slowly until contact was again made with the hook. The pressure was dropped again and a further 10 min allowed for thermal equilibrium. Thus by shortening the intervals the final contact pressure could be determined with a precision of 1 to 5 atm from one run to another.

There was a tendency for bubbles to form in the piezometer at 35.14° and 45°C despite the out-gassing of the alcohol under vacuum and occasionally the alcohol "dropped out" of the piezometers.

CHAPTER 3

RESULTS

Contents

1. Preliminary remarks

Because of the multiplicity of the variables a large number of experimental observations were recorded. Each of the five salts was studied at five different concentrations, five different temperatures and at between sixteen and twenty different pressures. Much of this information was fitted in the course of the analysis to empirical or semi-empirical equations. In terms of these equations interpolated values and various derived functions were obtained. These smoothed data are recorded next and are the basis of the discussion which follows.

Nevertheless it was considered wrong to discard the experimental measurements and these are recorded separately in appendices A, B and C.

The results presented in this chapter are the constants of the interpolation equations, certain smoothed values and derived activation parameters. The analytical procedures by which these were evaluated are also described.

Certain immediately relevant comments are made in this part but a detailed discussion is reserved for the final section of this chapter.

The analysis of Brummer and Hills (2, 3) proceeded with the assumption that Λ_o could be expressed as,

$$\Lambda_o = A V^{\frac{2}{3}} \exp \left(- \frac{\overline{\Delta G}_o^*}{RT} \right) . \qquad (39)$$

A is as defined on page 16.

The activation parameters follow from this equation and are given by,

$$-\frac{\overline{\Delta V}_o^*}{RT} = \left(\frac{\partial \ln \Lambda_o}{\partial(\pi + P)}\right)_T - \frac{2}{3}\left(\frac{\partial \ln V}{\partial(\pi + P)}\right)_T , \qquad (40)$$

and

$$\overline{\Delta U}_o^* = RT^2 \left(\frac{\partial \ln \Lambda_o}{\partial T}\right)_V . \qquad (41)$$

$\overline{\Delta U}_o^*$ in equation 41 is the experimental quantity E_V.

In the absence of transport numbers the present analysis proceeds from the above equations and the significance of these parameters, $\overline{\Delta V}_o^*$ and $\overline{\Delta U}_o^*$, in terms of the individual ionic activation parameters is discussed in the final section of this chapter.

2. The compressibility of methanol

The compressibility data was required for two purposes in the analysis, (a) to provide the density of the solvent as a function of pressure over the experimental temperature range and (b) to provide an estimation of the internal pressure of the solvent. These two uses of the compressibility are considered separately.

a) The density of the solvent

The observed volume changes were fitted to the Tait equation (36),

$$1 - \frac{V_p}{V_1} = C \ln\left(\frac{B + P}{B + 1}\right) . \qquad (42)$$

It is reported by Harned and Owen (37) that the compressibility data of Gibson (38) for methanol fits the Tait equation and the constants B and C are given as 764 atm and 0.09589 respectively. The constant C is normally assumed to be independent of temperature; this is found to be the case for many liquids (37) and it is reasonable to assume that this is also true for methanol.

In theory the simplest method of obtaining the constants B and C from a given set of measurements of compression is through the differentiated form of equation 42, which is

$$\left(\frac{\partial V}{\partial P}\right)_T = - \frac{V_1 C}{B + P} \quad . \tag{43}$$

However, in order to obtain C and B from equation 43, it is necessary to derive values of $(\partial V / \partial P)_T$. This can be done through an interpolation formula or by fitting the original data to a polynomial. In either case a loss of precision is inevitable.

An attempt was made to overcome this problem by selecting values of the constant C and calculating from it the values of B for each of a particular series of measurements. The mean value of B was then taken and together with the original value of C it was possible to evaluate the mean deviations. In principle, further values of B and C could be progressively selected until a minimum mean deviation was obtained. The method is difficult to justify and in any event failed because of the insensitivity of the logrithmic function to small changes in B.

Finally it was decided to accept the value of C provided by

Gibson (37) since his measurements at 25°C were undoubtedly more precise than the present ones and because the mean value of B generated from the present measurements at 25°C, using the value 0.09578 for C, was very close to that of Gibson. The resulting values of B and C are presented in table 3. The deviations from the mean value of B selected in this way were usually less than $\pm$ 5 atm.

Table 3

Constants for the Tait equation

t	5°	15°	25°	35.14°	45°
C	0.09589	0.09589	0.09589	0.09589	0.09589
B	868	810	756	712	660

b) The internal pressure

We recall the thermodynamic expression

$$\pi + P = T \frac{\alpha}{\beta} \quad . \tag{44}$$

The values of α (= 1/V. $(\partial V/\partial T)_P$) were obtained by interpolating the volume at 100 atm intervals over the range 1 - 2000 atm using equation 42. The natural logrithms of these values were then fitted to third order polynomials in T and the corresponding derivatives were obtained at the temperatures 15°, 25° and 35.14°C. The β coefficients were obtained from equation 43. The resulting values of $(\pi + P)$ are shewn in table 4, and are quoted for the restricted

Table 4

Specific volume and (π + P) of methanol as a function of pressure

P atm	15°C		25°C		35.14°C	
	π + P	$V_{ml\ gm^{-1}}$	π + P	$V_{ml\ gm^{-1}}$	π + P	$V_{ml\ gm^{-1}}$
100	3000	1.2424	2979	1.2563	2957	1.2710
200	3124	1.2299	3128	1.2428	3098	1.2567
300	3245	1.2184	3271	1.2307	3234	1.2439
400	3363	1.2080	3408	1.2197	3363	1.2322
500	3478	1.1986	3545	1.2096	3493	1.2216
600	3590	1.1896	3676	1.2003	3619	1.2118
700	3700	1.1814	3781	1.1916	3743	1.2027
800	3806	1.1737	3933	1.1835	3860	1.1943
900	3910	1.1664	4058	1.1758	3980	1.1864
1000	4017	1.1595	4183	1.1687	4097	1.1789
1100	4118	1.1531	4305	1.1620	4211	1.1719
1200	4216	1.1470	4425	1.1556	4319	1.1653
1300	4314	1.1411	4545	1.1495	4427	1.1590
1400	4415	1.1355	4665	1.1437	4538	1.1530
1500	4507	1.1303	4773	1.1395	4643	1.1473
1600	4599	1.1250	4881	1.1329	4748	1.1419
1700	4694	1.1154	4994	1.1279	4849	1.1366
1800	4780	1.1109	5101	1.1230	4951	1.1317
1900	4875	1.1065	5209	1.1182	5047	1.1268

temperature range corresponding to the limits of justifiable differentiation.

3. The conductance measurements

a) The conductance at 1 atm

It was found from analysis of the data that, below concentrations of $\sim 28 \times 10^{-4}$ mole litre^{-1}, all salts investigated obeyed the empirical Kohlrausch equation,

$$\Lambda = \Lambda_o - k\sqrt{c} \quad , \tag{45}$$

at all temperatures. It is questionable whether the intercept at $\sqrt{c} = 0$ is in fact Λ_o and it has frequently been observed that even when ion-pair formation is appreciable and when therefore the interionic basis of the Kohlrausch equation is insufficient, slightly erroneous but still linear extrapolations can be obtained.

For 1:1 electrolytes in methanol there are good grounds for supposing that ion pair formation is small and that the observed linear dependence of Λ on $c^{\frac{1}{2}}$ is a satisfactory basis for evaluating Λ_o. However, it must be admitted that if this were not the case there is quite insufficient supporting data for methanol to allow an adequate exploration of other extrapolation formulae. Furthermore it was never the intention to focus attention on Λ_o itself but rather on its derivatives. It is confidently assumed that any residual ambiguity in these terms arising from an interionic effect is small.

The constantsof equation 45 for all salts at the experimental temperatures are presented in table 5.

Table 5

Constants of the Kohlrausch equation, 45, at 1 atm

	t	5°	15°	25°	35.14°	45°
$KClO_4$	Λ_o	91.51	105.75	121.72	138.84	156.68
	k	235.3	275.7	337.2	397.4	464.6
Me_4NClO_4	Λ_o	105.99	121.48	138.83	157.46	176.49
	k	359.3	407.9	475.8	547.5	618.7
Et_4NClO_4	Λ_o	99.68	114.46	130.62	148.09	166.22
	k	324.8	371.2	430.3	492.9	564.0
$n\text{-}Pr_4NClO_4$	Λ_o	88.32	101.40	116.03	131.92	148.47
	k	300.3	335.4	387.9	443.9	507.0
$n\text{-}Bu_4NClO_4$	Λ_o	83.12	95.46	108.74	123.71	139.26
	k	292.0	326.3	364.4	418.3	474.6

b) The conductance under pressure

The values of R_p/R_1 recorded in appendix A already include a small correction for cell distortion. In order to convert them to molar conductances at recorded pressures or at particular specific volumes it was necessary first to correct for the solvent conductance and then for the change in concentration resulting from the compression.

The solvent correction as calculated by equation 38 contains the function y, which is the ratio of solvent conductance at pressure

P to that at 1 atm. For the purpose of the correction y was expressed as a second order polynomial in P,

$$y = a_1 + a_2P + a_3P^2 \quad . \tag{46}$$

The values of the constants of equation 46 were found to be $a_1 = 1.02$, $a_2 = 4.41 \times 10^{-4}$ and $a_3 = -0.0011 \times 10^{-4}$.

The change in concentration was evaluated in terms of the corresponding Tait equation and the resulting molar conductances were then fitted by least squares to a linear relation in $c^{\frac{1}{2}}$ and finally extrapolated to infinite dilution. This processing of the R_p/R_1 values was carried out in Autocode form on the Pegasus computer of Southampton University and the final values of Λ_o and the slope of the corresponding regression lines are recorded in table 6, (i) to (v).

As a further part of the programme the values of Λ_o were expressed in natural logrithmic form and fitted by least squares to a third order polynomial in P. The constants of these equations are given in table 7. These polynomials were used to interpolate rounded values of $\ln \Lambda_o$ at 100 atm intervals over the range 1 - 1900 atm, and these are recorded in table 8 (i) to (v).

The Tait equation, which was used to calculate the concentration changes under compression, was used again to calculate the pressures corresponding to certain pre-selected specific volumes, which were the same for all temperatures. The values of $\ln \Lambda_o$ corresponding to these pressures were printed out from the programme, and were made the basis of the isochores. This isochoric data is presented in table 9 (i) to (v).

Table 6 (i)

Constants of the Kohlrausch equation, 45, at the experimental pressures and temperatures

$KClO_4$

5°C			15°C			25°C		
P atm	Λ_o	k	P atm	Λ_o	k	P atm	Λ_o	k
1	91.15	235.3	1	105.8	275.7	1	121.7	337.2
145	86.95	214.0	150	100.4	250.2	151	115.5	307.6
253	84.00	201.8	261	96.97	235.4	259	111.7	288.6
368	81.09	189.7	374	93.67	221.5	359	108.5	272.9
479	78.33	178.5	476	90.88	209.5	452	105.3	258.4
614	75.50	167.7	597	87.99	197.7	566	102.2	245.0
724	73.30	160.1	704	85.53	188.7	693	98.91	232.0
849	70.96	152.1	816	83.19	180.3	831	95.65	219.4
973	68.79	144.9	937	80.77	172.3	960	92.76	209.6
1108	66.57	137.7	1075	78.15	162.9	1080	90.27	201.1
1221	64.79	131.7	1187	76.24	157.5	1196	88.02	194.0
1357	62.79	126.1	1298	73.72	129.4	1318	85.72	186.2
1468	61.21	120.7	1427	72.26	144.9	1456	83.29	178.9
1584	59.68	116.3	1532	70.81	142.5	1543	81.82	174.0
1698	58.16	111.8	1676	68.52	132.7	1672	79.64	165.8
1842	56.40	106.8	1787	66.98	128.1	1813	77.42	157.9
1932	55.39	103.9	1854	66.03	125.6	1928	75.67	152.5
			1927	65.11	123.2			

Table 6 (i) (continued)

Constants of the Kohlrausch equation, 45, at the experimental pressures and temperatures

$KClO_4$

35.14°C			45°C		
P atm	Λ_o	k	P atm	Λ_o	k
1	138.8	397.4	1	156.7	464.6
138	132.4	362.6	120	150.2	428.3
199	129.7	350.6	175	147.4	413.0
322	124.9	325.4	280	142.6	387.1
410	121.7	311.6	386	138.2	364.6
528	117.9	292.2	453	135.5	351.8
594	115.9	285.1	585	130.9	330.1
746	111.7	266.2	677	127.8	316.2
940	106.6	245.7	792	124.4	300.8
961	106.0	244.6	880	121.8	290.4
1156	101.6	226.6	963	119.5	281.1
1366	97.12	211.1	1078	116.5	269.2
1603	92.74	199.6	1193	113.7	258.5
1716	90.77	193.4	1311	110.96	246.6
1904	87.59	183.7	1429	108.4	238.3
			1527	106.0	224.5
			1644	104.0	223.2
			1750	102.1	219.3
			1852	100.1	213.0
			1929	98.68	206.6

Table 6 (ii)

Constants of the Kohlrausch equation, 45, at the experimental pressures and temperatures

Me_4NClO_4

5°C			15°C			25°C		
P atm	Λ_o	k	P atm	Λ_o	k	P atm	Λ_o	k
1	106.0	359.3	1	121.5	407.9	1	138.8	475.8
139	100.3	324.9	139	115.3	370.0	130	132.1	432.4
263	96.35	302.8	242	111.3	347.7	252	126.6	399.7
393	92.26	280.8	341	107.6	327.6	358	122.4	377.2
535	88.15	260.0	446	104.1	310.4	458	118.4	354.2
581	87.06	256.3	544	101.1	294.0	566	114.8	336.7
698	83.88	238.8	650	97.96	278.8	681	111.0	316.8
848	80.34	223.0	771	94.72	264.3	801	107.6	301.6
926	78.89	219.7	921	90.95	247.4	917	104.3	285.4
1018	76.68	207.2	1032	88.25	236.1	1022	101.5	274.1
1186	73.35	193.3	1141	85.83	226.5	1122	99.08	265.6
1336	70.60	182.9	1251	83.53	217.8	1226	96.54	253.2
1472	68.23	174.1	1389	80.79	207.3	1347	93.85	242.1
1613	65.91	166.2	1481	79.02	200.8	1466	91.29	232.4
1744	63.88	158.8	1595	77.08	197.8	1588	88.74	224.5
1852	62.39	156.2	1760	74.13	185.9	1697	86.53	215.6
1944	61.09	153.1	1875	72.29	182.8	1795	84.67	209.0
			1973	70.73	176.9	1917	82.42	199.5
						1983	81.30	196.4

Table 6 (ii) continued)

Constants of the Kohlrausch equation, 45, at the experimental pressures and temperatures

Me_4NClO_4

35.14°C			45°C		
P atm	Λ_o	k	P atm	Λ_o	k
1	157.5	547.5	1	176.5	618.7
136	149.6	496.9	109	169.5	574.6
256	143.6	462.1	179	165.1	549.0
374	138.5	438.2	289	159.3	515.1
489	133.6	411.8	380	154.6	489.0
618	128.9	388.6	486	149.7	462.8
742	124.6	369.0	575	145.9	440.9
866	120.6	349.7	683	141.6	421.6
992	116.8	333.3	797	137.5	400.0
1141	112.5	308.4	888	134.2	385.0
1354	107.0	284.6	994	130.7	368.2
1464	104.3	274.0	1092	127.6	353.7
1568	102.0	265.0	1190	124.7	342.0
1692	99.27	254.8	1288	121.9	330.5
1812	96.74	245.4	1392	119.2	318.7
1905	94.90	239.0	1500	116.4	308.4
1980	93.42	233.5	1599	113.9	297.7
			1692	111.7	290.4
			1821	108.7	278.4

Table 6 (iii)

Constants of the Kohlrausch equation, 45, at the experimental pressures and temperatures

Et_4NClO_4

5°C			15°C			25°C		
P atm	Λ_o	k	P atm	Λ_o	k	P atm	Λ_o	k
1	99.68	324.8	1	114.5	371.2	1	130.6	430.3
132	94.59	298.4	132	108.6	339.8	131	124.0	393.7
246	90.70	279.7	268	103.4	313.8	246	118.8	368.1
372	86.82	261.2	392	99.03	292.1	362	114.3	345.0
624	79.95	230.8	500	95.51	275.6	460	110.5	326.9
755	76.89	218.0	623	91.97	259.9	572	106.8	310.0
871	74.27	207.9	756	88.41	243.8	696	102.9	293.1
993	71.72	197.8	878	85.41	232.6	806	99.93	280.7
1122	69.27	188.8	928	84.23	226.2	929	96.54	266.5
1238	67.13	180.9	1014	82.27	221.1	1049	83.45	254.8
1289	66.30	178.0	1134	79.61	208.8	1169	90.76	244.6
1383	64.63	172.1	1267	76.96	199.9	1294	87.93	234.3
1483	63.13	166.9	1362	75.20	194.4	1407	85.53	225.9
1594	61.25	159.9	1408	74.26	190.6	1515	83.43	218.4
1833	57.75	149.0	1533	72.12	183.5	1617	81.43	211.3
			1618	70.71	180.0	1742	79.14	203.1
			1714	69.01	173.0	1853	77.16	196.4
			1811	67.59	169.8	1962	75.35	190.0
			1888	66.28	164.1			
			1956	65.34	162.1			

Table 6 (iii) (continued)

Constants of the Kohlrausch equation, 45, at the experimental pressures and temperatures

Et_4NClO_4

35.14°C			45°C		
P atm	Λ_o	k	P atm	Λ_o	k
1	148.1	492.9	1	166.2	564.0
126	140.7	447.6	129	157.8	516.8
243	134.9	420.7	233	152.3	485.9
326	131.1	400.3	331	146.6	456.3
441	126.2	376.2	541	137.2	408.8
534	122.6	359.7	629	133.6	393.1
654	118.3	340.1	718	130.3	377.2
741	115.6	327.0	831	126.4	361.2
869	111.5	310.5	931	123.0	345.1
966	108.6	297.8	1046	119.5	332.0
1090	105.3	285.7	1142	116.7	320.9
1184	102.8	274.8	1234	114.1	309.9
1312	99.61	263.5	1362	110.7	297.2
1391	97.87	256.7	1459	108.3	288.0
1510	95.14	247.5	1582	105.3	277.9
1603	93.11	240.5	1698	102.7	268.1
1684	91.45	235.9	1802	100.5	260.4
1804	89.45	235.6	1908	98.18	253.3
1917	86.84	220.0			

Table 6 (iv)

Constants of the Kohlrausch equation, 45, at the experimental pressures and temperatures

$n\text{-}Pr_4NClO_4$

5°C			15°C			25°C		
P atm	Λ_o	k	P atm	Λ_o	k	P atm	Λ_o	k
1	88.32	300.3	1	101.4	335.4	1	116.0	387.9
141	83.52	275.3	137	95.91	304.3	139	109.8	352.8
252	80.14	257.6	244	92.12	284.8	243	105.6	331.9
366	76.95	240.8	361	88.47	266.1	359	101.5	311.0
460	74.38	228.0	474	84.83	240.0	459	98.03	293.6
598	71.11	210.5	591	82.02	234.6	565	94.88	278.8
714	68.54	199.1	723	78.78	219.4	685	91.50	263.2
855	65.73	186.4	864	75.65	206.1	807	88.52	250.7
952	63.87	178.6	992	72.92	195.0	916	85.90	242.2
1075	61.72	170.0	1103	70.82	186.7	1025	83.40	231.3
1169	60.19	164.0	1225	68.58	177.9	1136	81.05	220.9
1284	58.34	157.1	1354	66.30	168.8	1249	78.79	212.8
1382	56.83	151.2	1474	64.39	162.1	1393	75.77	195.5
1531	54.75	143.9	1622	62.09	153.7	1510	73.69	187.4
1644	53.17	137.8	1754	60.16	146.8	1603	72.08	181.5
1748	51.82	132.5	1869	58.54	141.4	1746	69.80	174.4
1839	50.67	128.6				1851	68.11	168.5
1922	49.66	124.9				1946	66.57	160.3

Table 6 (iv) (continued)

Constants of the Kohlrausch equation, 45, at the experimental pressures and temperatures

$n\text{-}Pr_4NClO_4$

35.14°C			45°C		
P atm	Λ_o	k	P atm	Λ_o	k
1	131.9	443.9	1	148.5	507.0
125	125.4	407.3	105	142.3	472.0
230	120.5	379.3	211	136.4	439.3
329	116.2	357.0	309	131.5	408.9
419	112.8	340.1	429	126.4	386.7
533	108.8	321.2	523	122.6	365.1
629	105.8	305.7	632	118.8	348.7
746	102.4	290.1	713	116.1	336.1
832	99.96	281.8	837	112.2	318.0
934	97.06	267.1	914	109.6	303.3
1033	94.67	258.7	1036	106.5	293.6
1129	92.32	248.7	1115	104.2	282.5
1275	89.07	233.9	1338	98.93	263.1
1386	86.68	224.0	1459	96.17	251.8
1498	84.45	215.9	1535	94.60	247.6
1692	80.83	202.3	1687	91.60	234.5
1674	81.16	202.1	1751	90.45	234.0
1794	79.11	196.4	1841	88.56	224.5
			1918	87.07	218.9

Table 6 (v)

Constants of the Kohlrausch equation, 45, at the experimental pressures and temperatures

$n\text{-}Bu_4NClO_4$

5°C			15°C			25°C		
P atm	Λ_o	k	P atm	Λ_o	k	P atm	Λ_o	k
1	83.12	292.0	1	95.46	326.3	1	108.7	364.4
134	78.77	267.5	141	90.24	297.3	142	102.6	329.4
250	75.43	249.5	246	86.84	279.4	253	98.48	307.3
356	72.68	235.3	363	82.98	251.7	371	94.65	287.7
462	69.97	221.4	472	80.25	245.5	487	91.01	269.8
596	67.07	206.4	616	77.06	232.3	616	87.37	250.7
671	65.64	203.7	735	74.29	222.0	753	84.17	238.7
794	63.34	192.9	993	69.04	197.8	892	80.97	225.2
922	61.02	182.1	1134	66.58	188.1	1005	78.56	215.6
1039	58.99	173.8	1262	64.39	178.7	1096	76.45	207.3
1176	56.91	165.3	1505	60.70	165.1	1227	74.27	198.9
1303	54.97	157.1	1617	59.09	159.2	1332	72.37	191.6
1440	53.06	149.9	1716	57.91	159.1	1443	70.62	185.1
1572	51.41	145.7	1834	56.37	153.7	1517	69.28	179.7
1704	49.69	137.7	1929	55.13	148.9	1649	67.19	172.0
1803	48.45	131.4				1767	65.40	165.0
1934	46.93	125.3				1870	63.92	159.8
						1976	62.47	155.2

Table 6 (v) (continued)

Constants of the Kohlrausch equation, 45, at the experimental pressures and temperatures

$n\text{-}Bu_4NClO_4$

35.14°C			45°C		
P atm	Λ_o	k	P atm	Λ_o	k
1	123.7	418.3	1	139.3	474.6
131	117.3	382.8	130	132.0	433.3
205	114.1	366.4	251	126.1	400.4
			316	123.2	386.0
417	106.0	323.1	435	118.4	360.8
542	102.0	304.5	529	115.2	349.4
623	99.60	294.5	635	111.5	326.5
761	95.94	277.7	745	108.3	313.6
832	93.95	269.0	834	105.6	300.0
942	91.24	257.1	944	102.6	288.4
1030	89.20	249.4	1140	97.56	267.7
1157	86.38	237.0	1191	96.46	262.4
1248	84.57	230.8	1365	92.62	247.2
1349	82.59	222.6	1576	88.35	231.6
1427	80.61	202.2	1645	87.07	227.1
1526	79.21	210.8	1784	84.50	218.1
1625	77.54	203.9	1897	82.55	211.1
1713	76.05	198.4			
1820	74.32	192.3			
1908	72.87	186.9			

Table 7

Constants for the polynomial equation describing $\ln \Lambda_o$ as a function of pressure at constant temperature.

$$(\ln \Lambda_o)_t = a_t + b_t P + c_t P^2 + d_t P^3 .$$

n is the decimal scale factor for the corresponding horizontal row.

t		n	$KClO_4$	Me_4NClO_4	Et_4NClO_4	$n\text{-}Pr_4NClO_4$	$n\text{-}Bu_4NClO_4$
5°	a_t	0	4.5158	4.6615	4.6017	4.4813	4.4198
	b_t	-4	-3.5278	-3.7173	-4.0092	-4.0924	-4.0731
	c_t	-8	7.4389	6.4529	8.7325	8.7053	9.5029
	d_t	-11	-1.3687	-0.9687	-1.6929	-1.5717	-1.9312
15°	a_t	0	4.6604	4.7991	4.7395	4.6184	4.5575
	b_t	-4	-3.4772	-3.7544	-3.9870	-4.1130	-4.0234
	c_t	-8	7.5896	7.8451	8.7866	9.9694	9.4349
	d_t	-11	-1.3498	-1.3717	-1.5653	-1.9768	-1.7158
25°	a_t	0	4.8015	4.9323	4.8714	4.7528	4.6879
	b_t	-4	-3.5331	-3.7911	-3.9869	-4.0148	-4.0867
	c_t	-8	9.0693	8.9510	9.5693	9.6843	10.512
	d_t	-11	-1.8381	-1.7394	-1.8070	-1.9095	-2.0404
35.14°	a_t	0	4.9325	5.0576	4.9964	4.8810	4.8163
	b_t	-4	-3.5010	-3.6564	-3.9715	-4.0915	-4.0082
	c_t	-8	8.9071	7.9098	9.7547	10.786	10.080
	d_t	-11	-1.6925	-1.3825	-1.8257	-2.1624	-1.8753
45°	a_t	0	5.0529	5.1727	5.1121	4.9997	4.9348
	b_t	-4	-3.5319	-3.7955	-4.0391	-4.1827	-4.1120
	c_t	-8	9.1515	9.6842	10.623	11.701	11.424
	d_t	-11	-1.6803	-1.9045	-2.0441	-2.2852	-2.2509

Table 8 (i)

The Isobaric data

$KClO_4$

P x 10^{-2} atm \ t	5°	15°	25°	35.14°	45°
	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$
1	4.4812	4.6264	4.7670	4.8984	5.0185
2	4.4481	4.5938	4.7343	4.8659	4.9858
3	4.4163	4.5626	4.7031	4.8350	4.9547
4	4.3857	4.5326	4.6735	4.8056	4.9252
5	4.3563	4.5039	4.6452	4.7776	4.8971
6	4.3279	4.4762	4.6181	4.7508	4.8703
7	4.3006	4.4496	4.5923	4.7253	4.8447
8	4.2742	4.4239	4.5674	4.7007	4.8203
9	4.2486	4.3991	4.5435	4.6772	4.7969
10	4.2237	4.3751	4.5205	4.6545	4.7744
11	4.1995	4.3518	4.4981	4.6326	4.7528
12	4.1759	4.3292	4.4763	4.6114	4.7318
13	4.1528	4.3070	4.4550	4.5907	4.7115
14	4.1301	4.2854	4.4341	4.5705	4.6917
15	4.1078	4.2641	4.4135	4.5506	4.6723
16	4.0638	4.2431	4.3930	4.5310	4.6532
17	4.0420	4.2224	4.3726	4.5116	4.6344
18	4.0202	4.2017	4.3521	4.4922	4.6157
19	3.9983	4.1812	4.3315	4.4728	4.5970

Table 8 (ii)

The Isobaric data

Me_4NClO_4

t / P x 10^{-2} atm	5°	15°	25°	35.14°	45°
	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$
1	4.6250	4.7623	4.8952	5.0218	5.1357
2	4.5896	4.7271	4.8599	4.9875	5.1006
3	4.5556	4.6932	4.8261	4.9546	5.0671
4	4.5226	4.6606	4.7938	4.9231	5.0352
5	4.4906	4.6293	4.7629	4.8928	5.0048
6	4.4596	4.5991	4.7333	4.8637	4.9758
7	4.4296	4.5700	4.7048	4.8356	4.9480
8	4.4005	4.5420	4.6774	4.8086	4.9213
9	4.3722	4.5148	4.6509	4.7825	4.8957
10	4.3447	4.4884	4.6253	4.7572	4.8710
11	4.3178	4.4628	4.6004	4.7327	4.8471
12	4.2916	4.4379	4.5762	4.7088	4.8238
13	4.2661	4.4135	4.5525	4.6855	4.8012
14	4.2410	4.3896	4.5292	4.6628	4.7789
15	4.2164	4.3662	4.5063	4.6404	4.7570
16	4.1923	4.3431	4.4836	4.6184	4.7354
17	4.1685	4.3202	4.4610	4.5967	4.7138
18	4.1450	4.2975	4.3842	4.5751	4.6923
19	4.1218	4.2749	4.4158	4.5536	4.6706

Table 8 (iii)

The Isobaric data

Et_4NClO_4

P x 10^{-2} atm \ t	5°	15°	25°	35.14°	45°
	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$
1	4.5624	4.7005	4.8325	4.9576	5.0728
2	4.5249	4.6632	4.7953	4.9207	5.0354
3	4.4888	4.6274	4.7599	4.8855	5.0000
4	4.4542	4.5931	4.7261	4.8520	4.9662
5	4.4209	4.5602	4.6937	4.8199	4.9342
6	4.3889	4.5285	4.6627	4.7893	4.9036
7	4.3580	4.4981	4.6330	4.7599	4.8744
8	4.3282	4.4688	4.6044	4.7317	4.8465
9	4.2992	4.4404	4.5769	4.7047	4.8197
10	4.2712	4.4130	4.5503	4.6785	4.7940
11	4.2438	4.3864	4.5246	4.6533	4.7692
12	4.2171	4.3605	4.4995	4.6287	4.7451
13	4.1909	4.3353	4.4751	4.6048	4.7217
14	4.1651	4.3106	4.4512	4.5815	4.6988
15	4.1397	4.2863	4.4277	4.5585	4.6763
16	4.1144	4.2624	4.4044	4.5359	4.6541
17	4.0893	4.2387	4.3814	4.5134	4.6321
18	4.0642	4.2152	4.3584	4.4911	4.6101
19	4.0391	4.1918	4.3354	4.4687	4.5880

Table 8 (iv)

The Isobaric data

$n\text{-}Pr_4NClO_4$

t / P x 10^{-2} atm	5°	15°	25°	35.14°	45°
	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$
1	4.4413	4.5783	4.7136	4.8411	4.9590
2	4.4028	4.5400	4.6762	4.8033	4.9206
3	4.3660	4.5035	4.6405	4.7673	4.8842
4	4.3306	4.4686	4.6065	4.7332	4.8497
5	4.2965	4.4352	4.5739	4.7006	4.8170
6	4.2637	4.4033	4.5426	4.6696	4.7859
7	4.2321	4.3726	4.5127	4.6400	4.7564
8	4.2016	4.3431	4.4838	4.6116	4.7283
9	4.1721	4.3146	4.4560	4.5843	4.7014
10	4.1434	4.2871	4.4291	4.5580	4.6756
11	4.1156	4.2603	4.4029	4.5326	4.6508
12	4.0884	4.2343	4.3775	4.5079	4.6268
13	4.0619	4.2088	4.3526	4.4838	4.6035
14	4.0359	4.1838	4.3281	4.4602	4.5808
15	4.0103	4.1591	4.3040	4.4369	4.5585
16	3.9850	4.1346	4.2801	4.4139	4.5364
17	3.9600	4.1102	4.2563	4.3909	4.5145
18	3.9351	4.0858	4.2325	4.3678	4.4927
19	3.9102	4.0613	4.2086	4.3446	4.4707

Table 8 (v)

The Isobaric data

$n\text{-}Bu_4NClO_4$

t / P x 10^{-2} atm	5°	15°	25°	35.14°	45°
	$\ln\Lambda_o$	$\ln\Lambda_o$	$\ln\Lambda_o$	$\ln\Lambda_o$	$\ln\Lambda_o$
1	4.3800	4.5182	4.6481	4.7772	4.8948
2	4.3420	4.4807	4.6103	4.7400	4.8569
3	4.3056	4.4448	4.5743	4.7046	4.8211
4	4.2708	4.4106	4.5400	4.6709	4.7871
5	4.2375	4.3778	4.5073	4.6387	4.7549
6	4.2054	4.3464	4.4762	4.6080	4.7243
7	4.1746	4.3162	4.4464	4.5787	4.6952
8	4.1449	4.2872	4.4178	4.5505	4.6674
9	4.1161	4.2593	4.3904	4.5235	4.6408
10	4.0882	4.2324	4.3640	4.4975	4.6153
11	4.0610	4.2063	4.3385	4.4724	4.5907
12	4.0345	4.1809	4.3137	4.4480	4.5669
13	4.0085	4.1562	4.2895	4.4244	4.5438
14	3.9828	4.1321	4.2659	4.4012	4.5212
15	3.9575	4.1084	4.2426	4.3785	4.4990
16	3.9323	4.0850	4.2196	4.3562	4.4771
17	3.9071	4.0619	4.1968	4.3341	4.4553
18	3.8819	4.0389	4.1739	4.3120	4.4335
19	3.8565	4.0160	4.1510	4.2900	4.4115

Table 9 (i)

The Isochoric data

$KClO_4$

t / V ml gm^{-1}	5°	15°	25°	35.14°	45°
	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$
1.2400	4.5111	4.6204	4.7271	4.8255	4.9156
1.2300	4.4844	4.5943	4.7013	4.7999	4.8903
1.2200	4.4564	4.5670	4.6743	4.7734	4.8642
1.2100	4.4270	4.5384	4.6464	4.7459	4.9372
1.2000	4.3962	4.5085	4.6175	4.7174	4.8094
1.1900	4.3640	4.4774	4.5876	4.6881	4.7807
1.1800	4.3305	4.4451	4.5566	4.6578	4.7511
1.1700	4.2956	4.4116	4.5246	4.6265	4.7206
1.1600	4.2593	4.3768	4.4915	4.5940	4.6888
1.1500	4.2215	4.3406	4.4569	4.5600	4.6556
1.1400	4.1822	4.3029	4.4204	4.5242	4.6204

Table 9 (ii)

The Isochoric data

Me_4NClO_4

t / V ml gm^{-1}	5°	15°	25°	35.14°	45°
	$\ln\Lambda_o$	$\ln\Lambda_o$	$\ln\Lambda_o$	$\ln\Lambda_o$	$\ln\Lambda_o$
1.2400	4.6566	4.7558	4.8521	4.9444	5.0248
1.2300	4.6284	4.7276	4.8241	4.9169	4.9975
1.2200	4.5986	4.6979	4.7948	4.8882	4.9691
1.2100	4.5671	4.6668	4.7643	4.8582	4.9400
1.2000	4.5339	4.6343	4.7325	4.8270	4.9094
1.1900	4.4990	4.6004	4.6996	4.7946	4.8779
1.1800	4.4624	4.5651	4.6654	4.7608	4.8453
1.1700	4.4241	4.5284	4.6299	4.7258	4.8113
1.1600	4.3841	4.4902	4.5930	4.6892	4.7757
1.1500	4.3423	4.4505	4.5545	4.6510	4.7381
1.1400	4.2986	4.[illegible]90	4.5140	4.6107	4.6977

Table 9 (iii)

The Isochoric data

Et_4NClO_4

$ml^{V}gm^{-1}$ \ t	5°	15°	25°	35.14°	45°
	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$
1.2400	4.5963	4.6936	4.7874	4.8747	4.9553
1.2300	4.5661	4.6637	4.7581	4.8454	4.9265
1.2200	4.5343	4.6324	4.7274	4.8151	4.8966
1.2100	4.5009	4.5996	4.6956	4.7836	4.8658
1.2000	4.4661	4.5655	4.6625	4.7509	4.8340
1.1900	4.4297	4.5299	4.6282	4.7172	4.8012
1.1800	4.3918	4.4930	4.5926	4.6823	4.7673
1.1700	4.3524	4.4546	4.5559	4.6461	4.7321
1.1600	4.3114	4.4149	4.5177	4.6086	4.6955
1.1500	4.2687	4.3736	4.4781	4.5694	4.6569
1.1400	4.2242	4.3306	4.4365	4.5280	4.6156

Table 9 (iv)

The Isochoric data

$n\text{-}Pr_4NClO_4$

V ml gm^{-1} \ t	5°	15°	25°	35.14°	45°
	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$	$\ln \Lambda_o$
1.2400	4.4759	4.5712	4.6680	4.7563	4.8385
1.2300	4.4450	4.5406	4.6384	4.7265	4.8092
1.2200	4.4125	4.5086	4.6075	4.6957	4.7789
1.2100	4.3784	4.4752	4.5753	4.6638	4.7477
1.2000	4.3427	4.4406	4.5419	4.6309	4.7157
1.1900	4.3055	4.4046	4.5072	4.5969	4.6828
1.1800	4.2667	4.3674	4.4712	4.5618	4.6478
1.1700	4.2264	4.3289	4.4339	4.5255	4.6139
1.1600	4.1845	4.2889	4.3952	4.4876	4.5775
1.1500	4.1409	4.2474	4.3547	4.4479	4.5392
1.1400	4.0956	4.2041	4.3120	4.4058	4.4981

Table 9 (v)

The Isochoric data

$n\text{-}Bu_4NClO_4$

V ml gm^{-1} \ t	5°	15°	25°	35.14°	45°
	$\ln\Lambda_o$	$\ln\Lambda_o$	$\ln\Lambda_o$	$\ln\Lambda_o$	$\ln\Lambda_o$
1.2400	4.4144	4.5112	4.6020	4.6937	4.7761
1.2300	4.3837	4.4812	4.5721	4.6643	4.7472
1.2200	4.3515	4.4498	4.5410	4.6338	4.7173
1.2100	4.3178	4.4171	4.5088	4.6023	4.6866
1.2000	4.2828	4.3830	4.4754	4.5697	4.6550
1.1900	4.2462	4.3477	4.4410	4.5360	4.6224
1.1800	4.2083	4.3111	4.4054	4.5012	4.5888
1.1700	4.1690	4.2733	4.3688	4.4653	4.5541
1.1600	4.1282	4.2342	4.3309	4.4281	4.5180
1.1500	4.0858	4.1937	4.2916	4.3893	4.4798
1.1400	4.0415	4.1516	4.2504	4.3484	4.4390

4. The derived functions

a) The isochores

$\ln \Lambda_o$ as obtained from the isochoric data (table 9) was plotted against 1/T. A typical result is shewn in figure 12. The deviations of the points from linearity were small and non-systematic as evidenced by a least squares analysis for the best linear fit.

The integration of equation 41, assuming $\overline{\Delta U}_o^* \neq f(T)$ gives

$$\ln \Lambda_o = D - \frac{\overline{\Delta U}_o^*}{RT} \quad . \tag{47}$$

D is an integration constant and the slope of the isochore is given by $\overline{\Delta U}_o^* / R$. Values of $\overline{\Delta U}_o^*$, or alternatively E_v, and D are given in tables 10 and 11 and are plotted as functions of V in figures 13 and 14 respectively.

b) The volumes of activation

The data from tables 4 and 8 were combined to express ln V and $\ln \Lambda_o$ as third order polynomials in $(\pi + P)$, from which were obtained the derivatives at specified values of $(\pi + P)$. These derivatives were used to derive the corresponding values of $\overline{\Delta V}_o^*$ as indicated by equation 40. These values of $\overline{\Delta V}_o^*$ are presented in table 12 (i to iii) and illustrated in figure 15.

c) The entropies of activation

The simple assumption of equation 37 was utilised together with the data of the previous sections to calculate $\overline{\Delta S}_o^*$. The results are contained in table 13 and are illustrated in figure 16.

Table 10

Energies of activation at constant volume (E_V) at infinite dilution

V ml gm^{-1}	$KClO_4$ E_V cal	Me_4NClO_4 E_V cal	Et_4NClO_4 E_V cal	$n\text{-}Pr_4NClO_4$ E_V cal	$n\text{-}Bu_4NClO_4$ E_V cal
1.2417	1778	1617	1576	1598	1587
1.2400	1782	1626	1580	1599	1591
1.2300	1787	1630	1586	1606	1598
1.2200	1796	1637	1596	1616	1608
1.2100	1807	1646	1606	1629	1621
1.2000	1819	1658	1619	1645	1635
1.1900	1835	1672	1635	1664	1652
1.1800	1852	1689	1652	1685	1671
1.1700	1872	1707	1671	1707	1690
1.1600	1892	1726	1690	1730	1710
1.1500	1912	1744	1708	1752	1728
1.1400	1930	1758	1723	1769	1742
1.1300	1956	1783	1741	1772	1745
1.1200	1992	1806	1790	1805	1764

Table 11

The integration constant, D, from equation 47 as a function of volume

V ml gm^{-1}	$KClO_4$	Me_4NClO_4	Et_4NClO_4	$n\text{-}Pr_4NClO_4$	$n\text{-}Bu_4NClO_4$
	D	D	D	D	D
1.2400	7.734	7.596	7.453	7.367	7.291
1.2300	—	—	7.435	—	—
1.2200	7.705	7.558	—	7.335	7.259
1.2100	7.695	7.544	7.405	7.324	7.248
1.2000	7.687	7.532	7.394	7.317	7.240
1.1900	7.683	7.523	7.386	7.314	7.233
1.1800	7.681	7.517	7.380	7.313	7.229
1.1700	7.681	7.512	7.375	7.313	7.225
1.1600	7.682	7.506	7.369	7.314	7.220
1.1500	7.680	7.497	7.359	7.309	7.211
1.1400	7.674	7.479	7.341	7.296	7.193

Table 12 (i)

Volumes of activation $(\overline{\Delta V}^*)$ as functions of V and $(\pi + P)$ at 15°C.

V ml gm^{-1}	$(\pi + P)$ atm	$KClO_4$ $\overline{\Delta V}^*_o$ ml $mole^{-1}$	Me_4NClO_4 $\overline{\Delta V}^*_o$ ml $mole^{-1}$	Et_4NClO_4 $\overline{\Delta V}^*_o$ ml $mole^{-1}$	$n\text{-}Pr_5NClO_4$ $\overline{\Delta V}^*_o$ ml $mole^{-1}$	$n\text{-}Bu_4NClO_4$ $\overline{\Delta V}^*_o$ ml $mole^{-1}$
1.2424	3000	4.36	4.84	5.25	5.51	5.33
1.2230	3200	4.26	4.76	4.89	5.26	5.14
1.2046	3400	4.18	4.69	5.01	5.10	4.99
1.1884	3600	4.12	4.62	4.93	4.97	4.87
1.1737	3800	4.08	4.61	4.87	4.89	4.78
1.1603	4000	4.06	4.60	4.82	4.85	4.71
1.1480	4200	4.06	4.60	4.81	4.86	4.68
1.1362	4400	4.08	4.61	4.81	4.91	4.68
1.1251	4600	4.11	4.64	4.84	5.01	4.71
1.1146	4800	4.17	4.69	4.89	5.16	4.77

Table 12 (ii)

Volumes of activation as functions of V and $(\pi + P)$ at 25°C.

V ml gm^{-1}	$(\pi + P)$ atm	$KClO_4$ $\overline{\Delta V}^*_o$ ml $mole^{-1}$	Me_4NClO_4 $\overline{\Delta V}^*_o$ ml $mole^{-1}$	Et_4NClO_4 $\overline{\Delta V}^*_o$ ml $mole^{-1}$	$n\text{-}Pr_4NClO_4$ $\overline{\Delta V}^*_o$ ml $mole^{-1}$	$n\text{-}Bu_4NClO_4$ $\overline{\Delta V}^*_o$ ml $mole^{-1}$
1.2546	3000	3.88	4.29	4.60	4.65	4.75
1.2368	3200	3.70	4.14	4.42	4.47	4.54
1.2200	3400	3.56	4.02	4.28	4.33	4.35
1.2052	3600	3.43	3.91	4.15	4.20	4.18
1.1913	3800	3.36	3.84	4.06	4.08	4.06
1.1790	4000	3.31	3.79	4.00	4.50	3.98
1.1673	4200	3.29	3.77	3.96	4.01	3.91
1.1568	4400	3.29	3.79	3.93	4.03	3.89
1.1469	4600	3.32	3.82	3.94	4.06	3.90

Table 12 (iii)

Volumes of activation as functions of V and $(\pi + P)$ at 35.14°C.

V ml gm^{-1}	$(\pi + P)$ atm	$KClO_4$ $\overline{\Delta V}_o^*$ ml $mole^{-1}$	Me_4NClO_4 $\overline{\Delta V}_o^*$ ml $mole^{-1}$	Et_4NClO_4 $\overline{\Delta V}_o^*$ ml $mole^{-1}$	n-Pr_4NClO_4 $\overline{\Delta V}_o^*$ ml $mole^{-1}$	n-Bu_4NClO_4 $\overline{\Delta V}_o^*$ ml $mole^{-1}$
1.2660	3000	3.94	4.24	4.75	4.95	4.80
1.2470	3200	3.81	4.19	4.60	4.74	4.66
1.2289	3400	3.70	4.14	4.48	4.57	4.53
1.2125	3600	3.62	4.11	4.38	4.44	4.43
1.1978	3800	3.56	4.08	4.31	4.35	4.34
1.1845	4000	3.52	4.07	4.26	4.29	4.27
1.1722	4200	3.51	4.08	4.24	4.28	4.22
1.1609	4400	3.51	4.09	4.24	4.30	4.19
1.1500	4600	3.54	4.12	4.27	4.36	4.17
1.1389	4800	3.60	4.16	4.33	4.46	4.18
1.1291	5000	3.68	4.21	4.41	4.60	4.20

Table 13

Entropies of activation at 25°C

V ml gm^{-1}	$KClO_4$ $\overline{\Delta S_o^*}$ cal $mole^{-1}$ deg^{-1}	Me_4NClO_4 $\overline{\Delta S_o^*}$ cal $mole^{-1}$ deg^{-1}	Et_4NClO_4 $\overline{\Delta S_o^*}$ cal $mole^{-1}$ deg^{-1}	$n\text{-}Pr_4NClO_4$ $\overline{\Delta S_o^*}$ cal $mole^{-1}$ deg^{-1}	$n\text{-}Bu_4NClO_4$ $\overline{\Delta S_o^*}$ cal $mole^{-1}$ deg^{-1}
1.2400	9.61	9.44	9.23	9.07	8.94
1.2200	—	9.43	—	9.07	8.92
1.2100	9.61	9.43	9.24	9.09	8.93
1.2000	9.62	9.45	9.25	9.11	8.94
1.1900	9.65	9.48	9.28	9.15	8.96
1.1800	9.69	9.51	9.31	9.20	8.99
1.1700	9.74	9.56	9.41	9.25	9.03
1.1600	9.80	9.62	9.43	9.33	9.08
1.1500	9.85	9.65	—	9.37	9.11
1.1400					

d) The isobars

The isobars were constructed by plotting $\ln\Lambda_o$ (at constant pressure, see table 8) against 1/T. The apparent complexity of E_p is not reflected to any large extent in the isobars (see figure 17). There is visible evidence of a slight curvative and the least squares analysis for linearity indicated a greater total deviation than for the isochores. The slopes of the isobars are greater than those of the isochores; the corresponding E_p values are shewn in table 14.

Table 14

Energies of activation at constant pressure (E_p) at infinite dilution

P atm	$KClO_4$ E_p cal	Me_4NClO_4 E_p cal	Et_4NClO_4 E_p cal	$n\text{-}Pr_4NClO_4$ E_p cal	$n\text{-}Bu_4NClO_4$ E_p cal
200	2368	2253	2247	2282	2265
300	2371	2257	2250	2284	2267
400	2380	2263	2254	2289	2271
600	2389	2279	2267	2303	2283
800	2406	2299	2284	2323	2298
1000	2427	2323	2304	2347	2318
1200	2451	2347	2327	2373	2340
1400	2476	2371	2352	2401	2365
1600	2502	2393	2378	2429	2391
1800	2528	2412	2404	2455	2419

Figure 12

Isochores for $KClO_4$

$\ln \Lambda_o$ vs. 1/T at constant volume

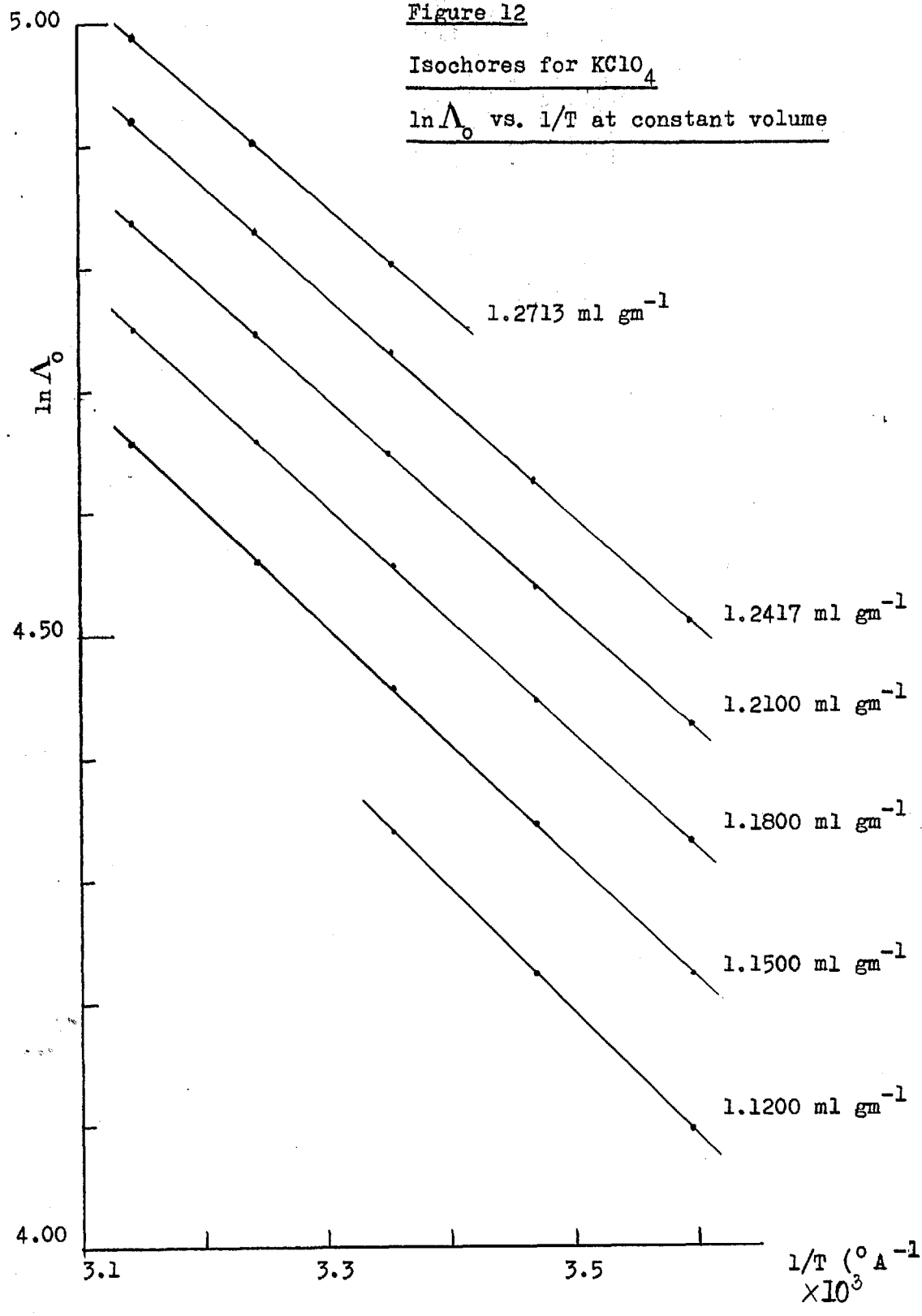


Figure 13

E_V vs. specific volume

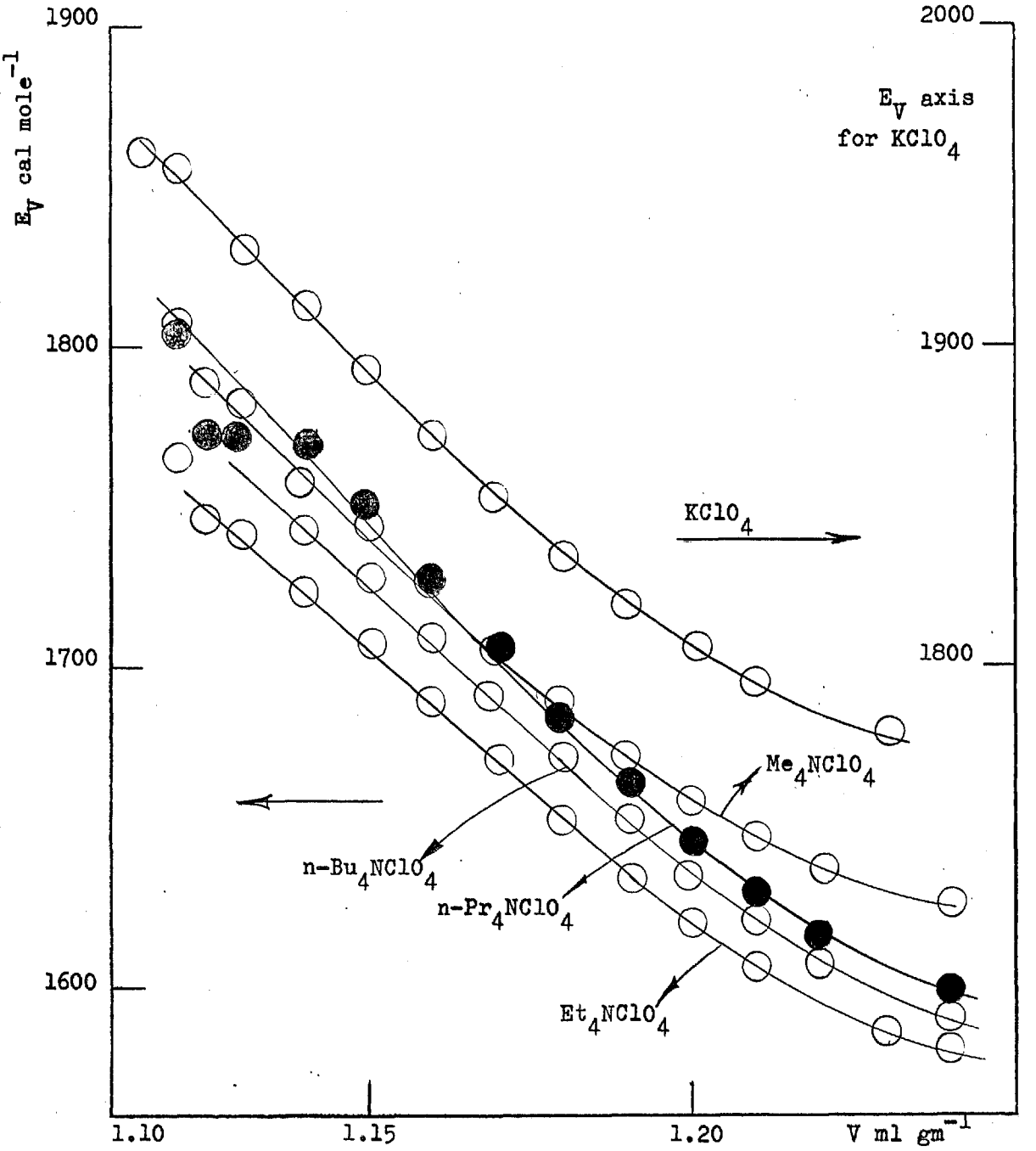


Figure 14

D (Integration constant of eqn 41) vs. V

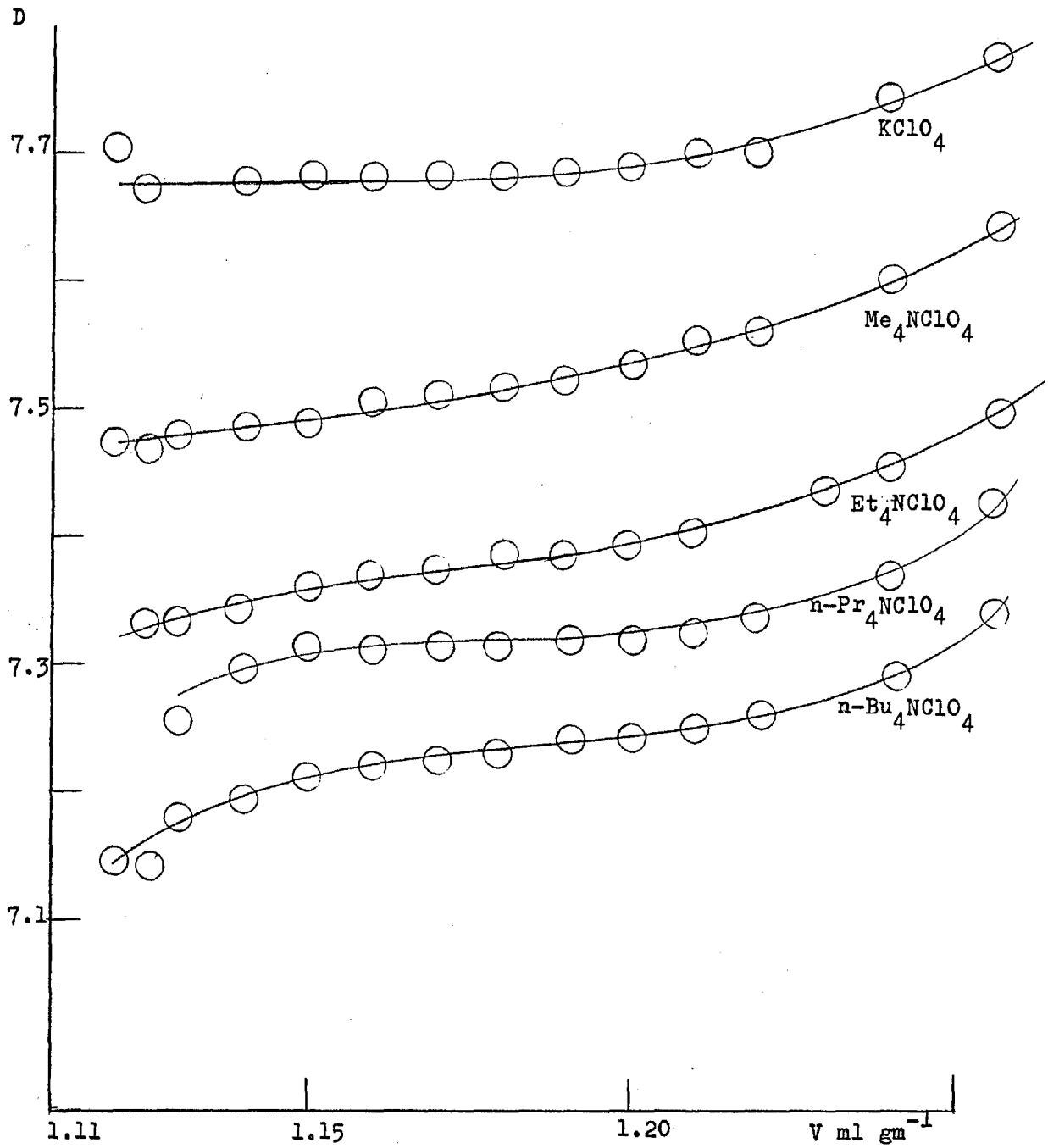


Figure 15

$\overline{\Delta V_o^*}$ vs. V at 25°C

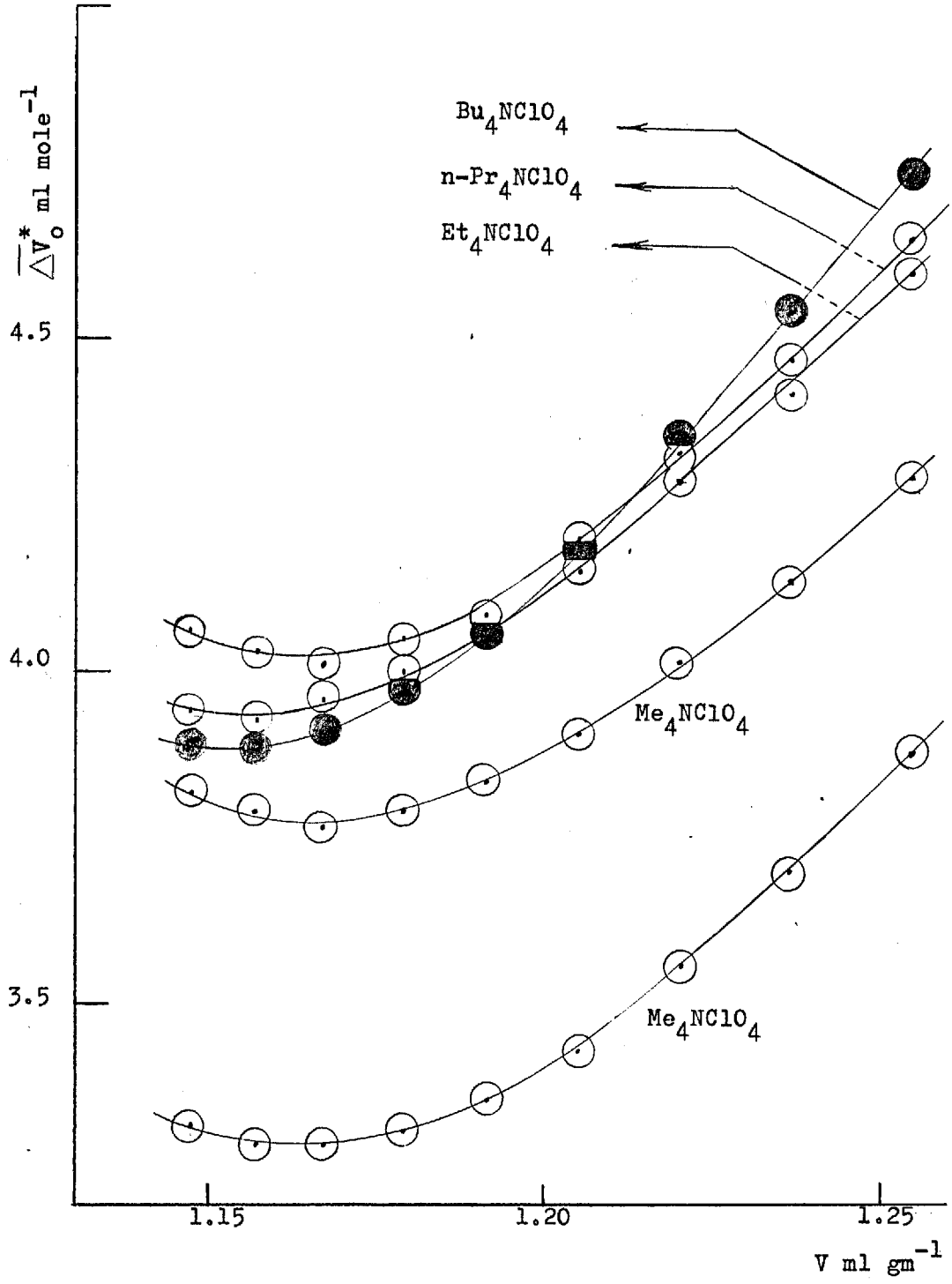


Figure 16

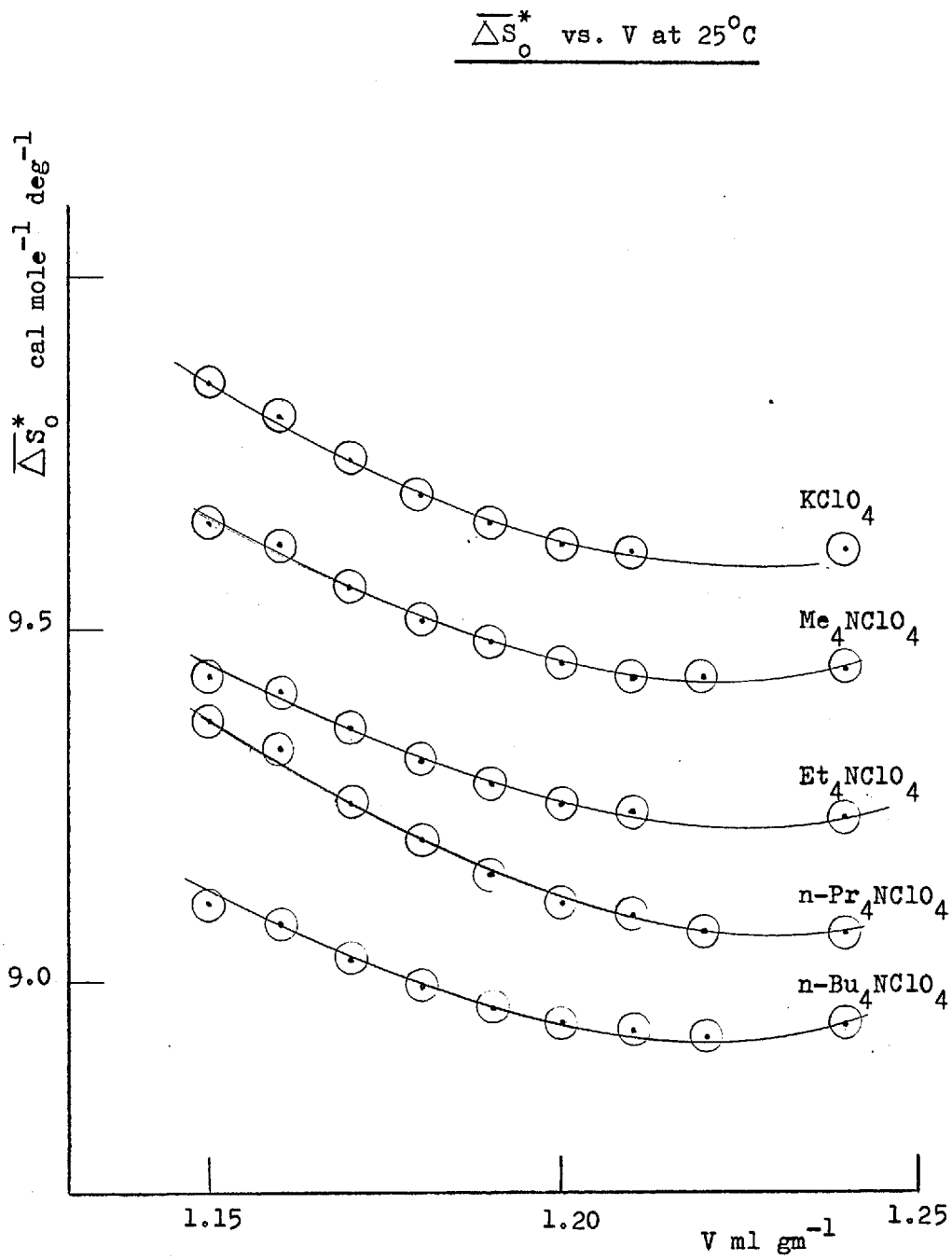
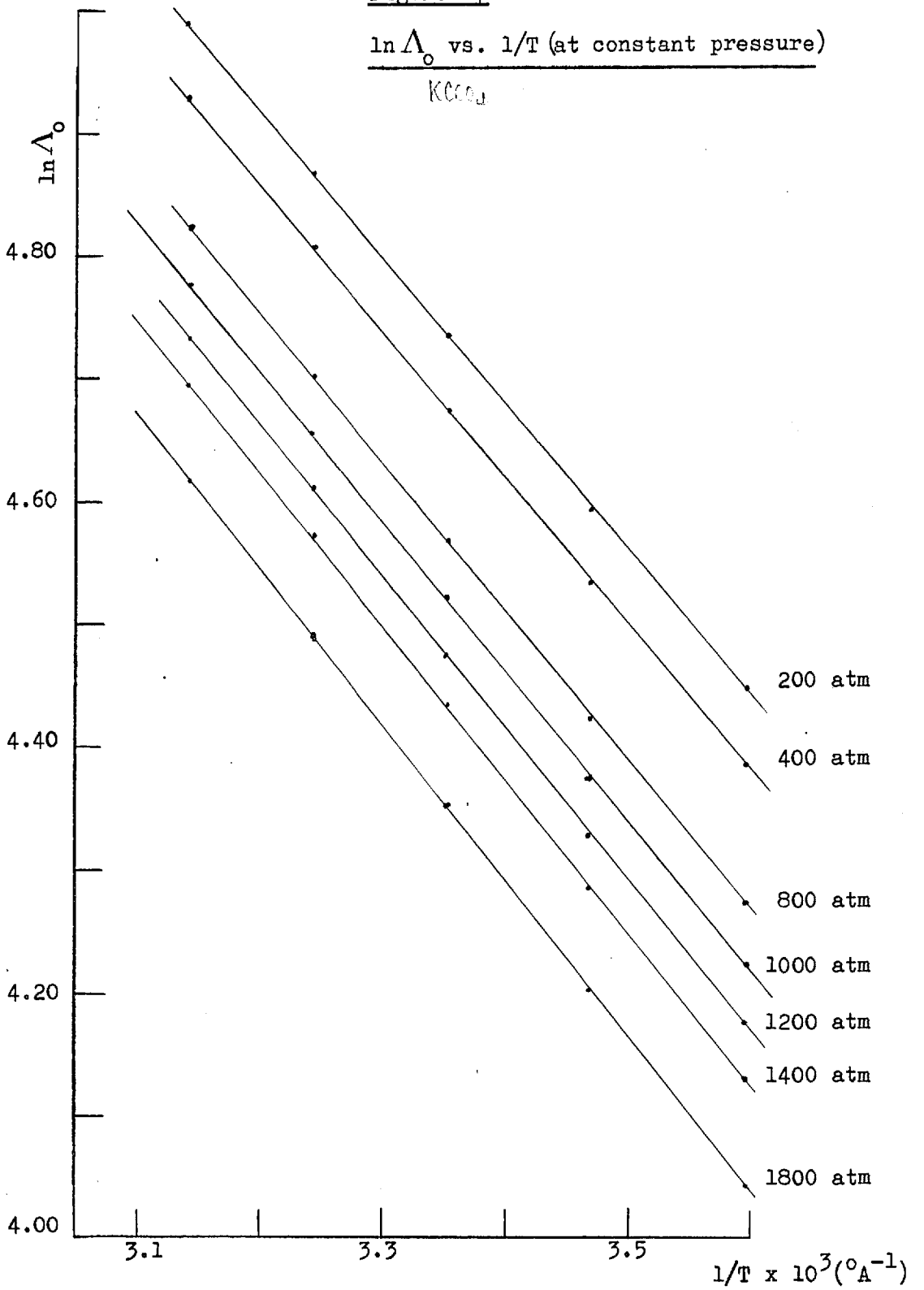

$\overline{\Delta S}_o^*$ vs. V at 25°C
$\overline{\Delta S}_o^*$ cal mole^{-1} deg^{-1}
9.5
9.0
KClO$_4$
Me$_4$NClO$_4$
Et$_4$NClO$_4$
n-Pr$_4$NClO$_4$
n-Bu$_4$NClO$_4$
1.15
1.20
1.25
V ml gm^{-1}

Figure 17

$\ln \Lambda_o$ vs. 1/T (at constant pressure)

KCO$_3$



CHAPTER 4

DISCUSSION

Contents

Discussion

Before attempting the interpretation of the experimental "average" activation parameters, tabulated above, two related aspects of them must be made clear, i.e. (1) their precise relationship to the corresponding ionic quantities and (2) the extent to which they can consequently be used to describe the migration of ions in solution.

It was pointed out earlier that a persistent ambiguity in this research arises from the lack of corresponding transport numbers. It will be shewn that the "average" activation parameters $\overline{\Delta U}_o^*$, $\overline{\Delta V}_o^*$ and, to a lesser extent, $\overline{\Delta S}_o^*$ are quite simply related to the individual ionic parameters and that many of the features of the ionic properties are apparent in the "average" properties.

(a) The significance of the experimental activation parameters (contained in equation 39)

E_V is the experimental isochoric energy of activation which we have related in equation 41 to $\overline{\Delta U}_o^*$, the "average" parameter arising from both cation and anion. Recalling equation 41,

$$R T^2 \left(\frac{\partial \ln \Lambda_o}{\partial T} \right)_V = \overline{\Delta U}_o^* = E_V \quad . \qquad (41)$$

$$E_V = RT^2 \left(\frac{\partial \ln (\lambda_+^o + \lambda_-^o)}{\partial T} \right)_V ,$$

$$= \frac{RT^2}{(\lambda_+^o + \lambda_-^o)} \left(\frac{\partial (\lambda_+^o + \lambda_-^o)}{\partial T} \right)_V ,$$

$$= \frac{RT^2}{\Lambda_o} \left[\lambda_+ \left(\frac{\partial \ln \lambda_+^o}{\partial T} \right)_V + \lambda_- \left(\frac{\partial \ln \lambda_-^o}{\partial T} \right)_V \right] ,$$

$$= RT^2 \left[t_+ \left(\frac{\partial \ln \lambda_+^o}{\partial T} \right)_V + t_- \left(\frac{\partial \ln \lambda_-^o}{\partial T} \right)_V \right] .$$

Thus it follows from equation 28 that,

$$\overline{\Delta U}_o^* = t^+ \Delta U_+^* + t^- \Delta U_-^* . \qquad (48)$$

By applying a similar argument to equation 40 and equation 10 it can be shewn that,

$$\overline{\Delta V}_o^* = t_+ \Delta V_+^* + t_- \Delta V_-^* . \qquad (49)$$

Finally by applying to equations 39 and 9 the thermodynamic relationship

$$-\Delta S = \left(\frac{\partial \Delta G}{\partial T} \right)_P ,$$

it can be shewn that

$$\overline{\Delta S}_o^* = t_+ \Delta S_+^* + t_- \Delta S_-^* + R \ln \Lambda_o - R(t_+ \ln \lambda_+^o + t_- \ln \lambda_-^o) \qquad (50)$$

The equalities 48, 49 and 50 shew that $\overline{\triangle U_o^*}$ and $\overline{\triangle V_o^*}$ are compounded of the individual ionic parameters in a simple way. $\overline{\triangle S_o^*}$, however, is a more complicated function of the individual parameters and of the corresponding λ_i values and it will be more difficult to attach definite significance to this term.

(b) The energies of activation

The primary feature of all the isochores is their linearity (figure 12). This is regarded as the justification of the constant volume principle. The temperature independence of both the isochoric exponent and preexponent are a substantial justification of the correctness of the form of the transition state conductance equation.

There is a large difference between E_p and E_v (tables 14 and 10). This difference was anticipated in the introduction and it is a consistent feature of all other studies. It emphasises the more complex nature of E_p and it is likely that in many systems where E_p is apparently a function of T that this arises out of the additional terms of equation 35.

$\overline{\triangle U_o^*}$ as well as being a relatively unambiguous parameter is also that most accurately determined in the present set of measurements. The linearity of the isochores requires that $\overline{\triangle U_o^*}$ is not a function of temperature and the integration of equation 41 is carried out on this basis. Because of the compound nature of $\overline{\triangle U_o^*}$ ($= t_+ \triangle U_+^* + t_- \triangle U_-^*$) it does not follow that the individual components are separately independent. We note that because

$\left(\frac{\partial t_-}{\partial T}\right) = -\left(\frac{\partial t_+}{\partial T}\right)$ and if the $\triangle U_+^*$ and $\triangle U_-^*$ terms are close, the sum $(t_+\triangle U_+^* + t_-\triangle U_-^*)$ cannot vary markedly with temperature unless in fact, $\triangle U_+^*$ and $\triangle U_-^*$ are very different or are themselves very temperature dependent. In view of the conformity of all of these systems, varying from $KClO_4$ to n-Bu_4NClO_4, it would seem that $\triangle U_+^*$ and $\triangle U_-^*$ are not widely different and that they are not temperature dependent.

Whereas $\overline{\triangle U}_o^*$ is not a function of temperature, it is very much a function of density, or specific volume, of the system (figure 13). It is likely that $\triangle U_+^*$ and $\triangle U_-^*$ are similarly dependent on volume although the exact shape of the individual relationship cannot be ascertained. The only certain feature of the $\triangle U_i^*$ values is that they increase with decreasing specific volume. This is the direct consequence of the corresponding change of the "free volume" of the system, $V - V_s$.

It is considered that the composition of $\triangle U_o^*$ in terms of $t_i\triangle U_i^*$ tends to obscure any "fine structure" in its variation with volume. Values of $\triangle U_+^*$ and $\triangle U_-^*$ at $V = 1.2400$ ml gm^{-1} are presented in table 15. They were calculated with the values of t_+ and t_- at 25°C and 1 atm on the assumption that, because the transport numbers of Me_4N^+ and ClO_4^- are approximately equal their energies of activation are equal. This is obviously a dubious assumption considering the possible effect of $\triangle S_i^*$ on the mobility of the ion.

Table 15

	t_+	t_-	$\triangle U_+^*$	$\triangle U_-^*$
$KClO_4$	0.43	0.57	1990	1626
Me_4NClO_4	0.50	0.50	1626	1626
Et_4NClO_4	0.47	0.53	1530	1626
$n\text{-}Pr_4NClO_4$	0.40	0.60	1550	1626
$n\text{-}Bu_4NClO_4$	0.36	0.64	1530	1626

It can be seen from table 15 that the values of $\triangle U_+^*$ are not grossly different from those of $\overline{\triangle U_o^*}$. With the exception of Et_4N^+ there is apparent asymptotic fall of $\triangle U_+^*$ from K^+ to $n\text{-}Bu_4N^+$. The low value of Et_4N^+ in relation to the other ions cannot be accounted for completely by the experimental error though it could easily arise from the inapplicability of the original assumption. It is thought that this decay of $\triangle U_i^*$ from K^+ (the smallest ion) to $n\text{-}Bu_4N^+$ (the largest ion) is a realistic feature of the variation of $\triangle U_i^*$ with ion size.

The $\triangle U_i^*$ is considered to arise from the movement of the ion in the mutual field, $F_i^n(r)$, of the ion and its n surrounding solvent molecules,

$$\triangle U_i^* = \int_{\text{initial state}}^{\text{transition state}} F_i^n(R)\, dr \quad . \qquad (51)$$

This term, $\triangle U_i^*$, does not contain any contribution from "expansion work" which has been accounted for by $(\pi + P)\triangle V_i^*$; it is

generated by the change in intermolecular and interionic distance with corresponding changes in mutual interaction potential.

There is a suggestion from figure 13 that the relation between E_v and V is an exponential one. Certainly it is to be expected that as $(V - V_s) \rightarrow 0$, $E_v \longrightarrow \infty$ since ion migration in the solid phase, other than by defect mechanism, cannot take place.

The similarity of the E_v values, particularly for the alkyl ammonium salts, strongly suggests that they have a common basis, i.e. solvent - solvent interactions. It would be expected that E_v for $n\text{-}Bu_4NClO_4$ which shews minimal specific ion character would be close to E_v for the viscosity of methanol, and this is found to be the case (1).

A significant contribution to $\triangle U_i^*$, which would be contained in equation 51 is likely to be from dipole relaxation. (This would make integral 51 time dependent to be strictly accurate.) This phenomenon, similar to the Onsager time of relaxation effect, has already been used by Fuoss to correct the Stokes' law relation for dielectric relaxation. A similar concept is visualised here except that a microscopic or molecular re-orientation is a more realistic model than that of a continuum. Qualitatively they are the same and it need only be noted that the effect increases with increasing field strength and with increasing dielectric constant. The larger values of $\overline{\triangle U_o^*}$ for potassium perchlorate are at least partially the result of this effect and the asymptotic fall of $\overline{\triangle U_o^*}$ from Me_4NClO_4 ——→ Bu_4NClO_4 is in accordance with the dechay of this term.

$\overline{\triangle U_o^*}$ for $KClO_4$ is, therefore, higher because of its greater polarizing power which increases both the time-invariant potential energy contribution and the time dependent relaxation effect.

(c) Entropy of activation

At this stage it should be recalled that the sequence of $\overline{\triangle U_o^*}$ is not that of the Λ_o values.

$KClO_4$ which has the highest $\overline{\triangle U_o^*}$ value has a much higher conductance than $n\text{-}Bu_4NClO_4$. The compensating factor has to be found in the entropy term since $(\pi + P)\,\overline{\triangle V_o^*}$ is neither large enough nor sufficiently discriminating.

$\overline{\triangle S_o^*}$, the experimental entropy of activation has been expressed in terms of its separate ionic constituents in equation 50. The term involving R, Λ, λ_i and t_i for the present series of salts can have a maximum value of $\sim$1.5 and decreases with decreasing Λ. It is impossible in the present work to evaluate this term and thus the entropies recorded in table 13 and plotted in figure 16 are useful only in that they indicate the magnitude of the entropy of activation. It is notable that $KClO_4$ has the highest entropy of activation, which is consistent with the idea of greater structural changes involved in the formation of its transition state. This more than compensates for the higher value of E_v. This entropy term $\overline{\triangle S_o^*}$ is contained together with $(\pi + P)\overline{\triangle V_o^*}$ in the isochoric intercept D (see table 11 and figure 14). The sequence of D values is identical with that of the $\overline{\triangle S_o^*}$. The direction of change is reversed because of the increasing value of $(\pi + P)\,\overline{\triangle V_o^*}$ with increasing pressure.

(d) The volume of activation

The experimental volume of activation $\overline{\Delta V_o^*}$ is composed of $t_i \Delta V_i^*$ terms as shewn in equation 49. Values of $\overline{\Delta V_o^*}$ are plotted in figure 15. The curves exhibit minima and it is interesting that, with the exception of n-Bu_4NClO_4, the larger ions have larger volumes of activation. It is evident that the size of the ion bears some relation to its volume of activation, i.e. increasing with increasing ion size. The effect, however, is small and again indicates a common basis for the migration of all ions, namely solvent displacement during the act of translation.

It is possible to explain the discrepancy of the n-Bu_4NClO_4 curve in relation to those of the other ions in figure 15 in terms of equation 49. The transport number t_- would allow a relatively larger contribution from the ion with the smaller volume of activation. It is impossible to substantiate this in the absence of the appropriate transport numbers.

Recalling equation 49 for ease of reference,

$$\overline{\Delta V_o^*} = t_+ \Delta V_+^* + t_- \Delta V_-^* \quad . \tag{49}$$

Differentiating with respect to V at constant T gives,

$$\left(\frac{\partial \overline{\Delta V_o^*}}{\partial V}\right)_T = t_+ \left(\frac{\partial \Delta V_+^*}{\partial V}\right)_T + \Delta V_+^* \left(\frac{\partial t_+}{\partial V}\right)_T + t_- \left(\frac{\partial \Delta V_-^*}{\partial V}\right)_T + \Delta V_-^* \left(\frac{\partial t_-}{\partial V}\right)_T \quad . \tag{52}$$

But,

$$\left(\frac{\partial t^+}{\partial V}\right)_T = -\left(\frac{\partial t^-}{\partial V}\right)_T \quad . \tag{53}$$

Substituting the result of equation 53 in equation 52 and rearranging,

$$\left(\frac{\partial \overline{\Delta V}_o^*}{\partial V}\right)_T = \left(\frac{\partial \Delta V_+^*}{\partial V}\right)_T + t^- \left[\left(\frac{\partial \Delta V_-^*}{\partial V}\right)_T - \left(\frac{\partial \Delta V_+^*}{\partial V}\right)_T\right]$$

$$+ \left(\frac{\partial t^+}{\partial V}\right)_T (\Delta V_+^* - \Delta V_-^*) \quad . \tag{54}$$

If we assume that ΔV_i^* is purely a solvent property then,

$$\left(\frac{\partial \Delta V_-^*}{\partial V}\right)_T = \left(\frac{\partial \Delta V_+^*}{\partial V}\right)_T \quad ,$$

and equation 54 becomes,

$$\left(\frac{\partial \overline{\Delta V}_o^*}{\partial V}\right)_T = \left(\frac{\partial \Delta V_+^*}{\partial V}\right)_T + \left(\frac{\partial t^+}{\partial V}\right)_T (\Delta V_+^* - \Delta V_-^*). \tag{55}$$

At the minimum as exhibited in figure 15,

$$\left(\frac{\partial \overline{\Delta V}_o^*}{\partial V}\right)_T = 0 \quad . \tag{56}$$

ΔV_i^* is a decreasing function of V and therefore $(\partial \Delta V_+^* / \partial V)_T$ is a negative quantity. Since it would be expected that, at least for the larger ions, $(\Delta V_+^* - \Delta V_-^*)$ is a positive quantity, in order that the condition 56 be satisfied $\left(\frac{\partial t^+}{\partial V}\right)_T$ must be positive.

Hence it is predicted that the transport number of the positive ion will have a positive pressure coefficient.

The temperature dependence of the volume of activation as shewn in table 12 is irregular. This is probably due to the assumption that the solvent function π was sufficiently accurate for the purpose of obtaining $\overline{\triangle V_o^*}$. The electrostriction at the surface of the ion would suggest that this assumption is unwarranted but in the present stage of development of the theory there is insufficient quantitative information on which to base an alternative formulation of this term.

(e) Conclusion

The activation parameters give in a qualitative sense a satisfactory account of the factors determining ionic migration in methanol. Further quantitative progress waits on many developments, the most immediate of which is the determination of transport numbers. They are not likely to alter radically any of the findings presented here but they will allow a more detailed examination of the data. This problem is in hand and is proving to be difficult.

The general conclusions of this research corroborate the importance and relevance of the constant volume principle. The separation of potential energy and kinetic energy in any description of an equilibrium or non-equilibrium system is regarded as an essential step in the analysis of data relating to condensed phases.

The results recorded here represent a substantial enlargement of the body of conductance data as a function of T and V and they have

permitted the elimination of interionic effects. The range of salts, albeit small, has indicated the type of variation arising out of changing ion-size. The modification of the analysis in terms of $(\pi + P)$ leads to greater consistency between the observed pressure coefficients and the parameters of the transition state theory. The values of $\triangle V_o^*$ now have a clearer significance.

The accepted implication that ion migration is largely determined by the properties of the solvent has been given a more detailed expression. If these parameters for $n\text{-}Bu_4N^+$ are approaching the limit of "total solvent dependence", then the activation energy of conductance will be close to that for viscosity. It follows that if,

$$\lambda_i^o = A_1 \exp - \left(\frac{\triangle G_\lambda^*}{RT} \right) , \tag{57}$$

$$\eta = A_2 \exp + \left(\frac{\triangle G_\eta^*}{RT} \right) , \tag{58}$$

$$\text{and} \quad \triangle G_\lambda^* = \triangle G_\eta^* , \tag{59}$$

$$\text{then} \quad \eta \lambda = A_1 A_2 . \tag{60}$$

A_1 and A_2 are temperature independent constants and $\triangle G_\lambda^*$ and $\triangle G_\eta^*$ are the free energies of activation of conductance and viscosity, respectively. It follows that equation 60 is the expression of Walden's Rule, and it can be seen from inspection of table 1 that it is obeyed by $n\text{-}Bu_4NClO_4$.

To the extension of this type of research there may be added a number of other related problems hitherto only touched upon. A similar analysis may be attempted of the viscosity of electrolyte solutions, the compressibilities, their dielectric constants and related relaxation phenomena. Each of these would constitute a research programme in itself but are unavoidable if a sufficiently detailed account of the ion-solvent complex is to be given.

There is also much exciting progress to be made in bridging the gap between statistical mechanical theory and these various observations. There is scope here for new theoretical developments and especially for quantitatively significant microscopic parameters on which to base them. It was as a contribution to this aspect that the present work was conceived and carried out.

APPENDIX A

Experimental values of R_p / R_1 (corrected for cell distortion) as functions of concentration and pressure.

$KClO_4$, $t = 5^{\circ}C$.

$c_t \times 10^4$ mole litre^{-1}	25.25	15.478	9.914	7.130	4.0730
$\kappa_t \times 10^8$ (MeOH) ohm^{-1} cm^{-1}	8.7	8.7	8.7	8.7	8.7
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
145	1.0315	1.0329	1.0333	1.0343	1.0347
253	1.0543	1.0564	1.0573	1.0587	1.0591
368	1.0782	1.0813	1.0827	1.0844	1.0850
479	1.1033	1.1074	1.1096	1.1113	1.1121
614	1.1305	1.1357	1.1385	1.1402	1.1413
724	1.1539	1.1597	1.1630	1.1645	1.1661
849	1.1805	1.1871	1.1909	1.1924	1.1942
973	1.2068	1.2142	1.2185	1.2200	1.2220
1108	1.2357	1.2435	1.2484	1.2502	1.2523
1221	1.2602	1.2687	1.2738	1.2760	1.2784
1357	1.2903	1.2990	1.3046	1.3070	1.3096
1468	1.3143	1.3238	1.3298	1.3326	1.3353
1584	1.3397	1.3497	1.3561	1.3590	1.3618
1698	1.3664	1.3768	1.3838	1.3870	1.3897
1842	1.3989	1.4097	1.4176	1.4209	1.4237
1932	1.4181	1.4294	1.4377	1.4410	1.4439

$KClO_4$, $t = 15^{\circ}C$.

$c_t \times 10^4$ mole litre^{-1}	24.96	15.300	9.799	7.048	4.026
$K_t \times 10^8$(MeOH) ohm^{-1} cm^{-1}	0.99	0.99	0.99	0.99	0.99
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
150	1.0305	1.0322	1.0326	1.0331	1.0340
261	1.0523	1.0549	1.0560	1.0565	1.0577
374	1.0755	1.0789	1.0805	1.0812	1.0829
476	1.0961	1.1004	1.1026	1.1033	1.1056
597	1.1186	1.1241	1.1269	1.1276	1.1301
704	1.1400	1.1462	1.1494	1.1501	1.1530
816	1.1613	1.1682	1.1718	1.1726	1.1756
937	1.1854	1.1933	1.1962	1.1979	1.2013
1075	1.2124	1.2212	1.2260	1.2269	1.2299
1187	1.2343	1.2435	1.2481	1.2491	1.2528
1298	1.2429	1.2666	1.2715	1.2728	1.2766
1427	1.2832	1.2936	1.2989	1.3003	1.3044
1532	1.3034	1.3144	1.3198	1.3215	1.3238
1676	1.3335	1.3451	1.3513	1.3534	1.3580
1787	1.3563	1.3685	1.3752	1.3771	1.3821
1854	1.3714	1.3833	1.3906	1.3927	1.3976
1927	1.3863	1.3983	1.4059	1.4081	1.4130

$KClO_4$, t = 25°C.

$c_t \times 10^4$ mole litre^{-1}	24.67	15.118	9.683	6.964	3.978
$K_t \times 10^7$ (MeOH) ohm^{-1} cm^{-1}	1.1	1.1	1.1	1.1	1.1
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
151	1.0302	1.0317	1.0325	1.0326	1.0332
259	1.0499	1.0523	1.0538	1.0544	1.0552
359	1.0680	1.0713	1.0734	1.0743	1.0754
452	1.0870	1.0913	1.0940	1.0952	1.0965
566	1.1075	1.1125	1.1158	1.1173	1.1188
693	1.1307	1.1367	1.1407	1.1422	1.1437
831	1.1554	1.1623	1.1669	1.1687	1.1702
960	1.1800	1.1874	1.1925	1.1944	1.1960
1080	1.2024	1.2102	1.2160	1.2180	1.2194
1196	1.2240	1.2321	1.2381	1.2401	1.2421
1318	1.2471	1.2555	1.2620	1.2642	1.2665
1456	1.2735	1.2822	1.2891	1.2915	1.2939
1543	1.2895	1.2987	1.3061	1.3087	1.3107
1672	1.3140	1.3244	1.3321	1.3350	1.3375
1813	1.3407	1.3515	1.3603	1.3634	1.3662
1928	1.3633	1.3749	1.3843	1.3873	1.3901

$KClO_4$, t = 35.14°C.

$c_t \times 10^4$ mole litre^{-1}	24.37	14.932	9.564	6.878	3.929
$\kappa_t \times 10^7$ (MeOH) ohm^{-1} cm^{-1}	1.22	1.22	1.22	1.22	1.22
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
138	1.0250	1.0263	1.0271	1.0279	1.0285
199	1.0378	1.0392	1.0411	1.0416	1.0420
322	1.0589	1.0617	1.0639	1.0651	1.0664
410	1.0763	1.0794	1.0825	1.0836	1.0850
528	1.0954	1.0998	1.1029	1.1047	1.1072
594	1.1079	1.1121	1.1162	1.1176	1.1200
746	1.1322	1.1377	1.1420	1.1441	1.1472
940	1.1673	1.1737	1.1790	1.1818	1.1850
961	1.1715	1.1780	1.1835	1.1863	1.1890
1156	1.2043	1.2121	1.2180	1.2216	1.2250
1366	1.2415	1.2500	1.2617	1.2607	1.2639
1603	1.2849	1.2939	1.3023	1.3060	1.3083
1716	1.3048	1.3141	1.3231	1.3267	1.3292
1904	1.3391	1.3493	1.3587	1.3629	1.3651

$KClO_4$, t = 45°C.

$c_t \times 10^4$ mole litre^{-1}	24.07	14.751	9.448	6.795	3.881
$\kappa_t \times 10^7$ (MeOH) ohm^{-1} cm^{-1}	1.28	1.28	1.28	1.28	1.28
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
120	1.0214	1.0227	1.0235	1.0240	1.0246
175	1.0317	1.0335	1.0348	1.0355	1.0363
280	1.0495	1.0524	1.0547	1.0555	1.0568
386	1.0678	1.0716	1.0745	1.0756	1.0776
453	1.0798	1.0841	1.0873	1.0887	1.0910
585	1.1015	1.1065	1.1107	1.1124	1.1151
677	1.1170	1.1230	1.1275	1.1295	1.1323
792	1.1346	1.1410	1.1463	1.1488	1.1518
880	1.1504	1.1574	1.1629	1.1660	1.1687
963	1.1643	1.1715	1.1776	1.1807	1.1838
1078	1.1830	1.1909	1.1973	1.2010	1.2041
1193	1.2019	1.2103	1.2173	1.2210	1.2246
1311	1.2208	1.2302	1.2374	1.2418	1.2457
1429	1.2407	1.2503	1.2579	1.2626	1.2666
1527	1.2573	1.2674	1.2754	1.2801	1.2879
1644	1.2758	1.2866	1.2950	1.2998	1.3043
1750	1.2945	1.3050	1.3144	1.3186	1.3226
1852	1.3121	1.3233	1.3328	1.3373	1.3414
1929	1.3247	1.3369	1.3461	1.3515	1.3558

Me_4NClO_4 , t = 5°C.

$c_t \times 10^4$ mole litre^{-1}	20.98	16.093	9.339	3.899	2.118
$K_t \times 10^7$(MeOH) ohm^{-1} cm^{-1}	0.87	0.94	0.96	0.98	0.94
p atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
139	1.0342	1.0358	1.0369	1.0385	1.0391
263	1.0601	1.0624	1.0645	1.0669	1.0681
393	1.0902	1.0935	1.0967	1.1000	1.1017
535	1.1235	1.1280	1.1323	1.1365	1.1388
581	1.1342	1.1387	1.1430	1.1466	1.1497
698	1.1622	1.1679	1.1736	1.1786	1.1815
848	1.1982	1.2047	1.2113	1.2174	1.2203
926	1.2156	1.2221	1.2289	1.2339	1.2374
1018	1.2390	1.2465	1.2543	1.2614	1.2642
1186	1.2797	1.2880	1.2970	1.3051	1.3079
1336	1.3172	1.3263	1.3357	1.3450	1.3474
1472	1.3521	1.3614	1.3721	1.3819	1.3841
1613	1.3892	1.3990	1.4109	1.4210	1.4226
1744	1.4231	1.4332	1.4461	1.4570	1.4584
1852	1.4520	1.4631	1.4755	1.4847	1.4875
1944	1.4780	1.4892	1.5022	1.5127	1.5122

Me_4NClO_4 , t = 15°C

$c_t \times 10^4$ mole litre^{-1}	20.74	15.908	9.232	3.854	2.093
$\kappa_t \times 10^7$ (MeOH) ohm^{-1} cm^{-1}	1.0	1.08	1.10	1.12	1.08
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
139	1.0304	1.0313	1.0326	1.0346	1.0347
242	1.0533	1.0547	1.0569	1.0598	1.0601
341	1.0755	1.0776	1.0807	1.0844	1.0850
446	1.0993	1.1011	1.1054	1.1099	1.1104
544	1.1200	1.1230	1.1281	1.1332	1.1339
650	1.1437	1.1471	1.1535	1.1590	1.1598
771	1.1703	1.1740	1.1814	1.1877	1.1882
921	1.2036	1.2079	1.2167	1.2238	1.2241
1032	1.2300	1.2345	1.2444	1.2521	1.2521
1141	1.2554	1.2595	1.2707	1.2788	1.2787
1251	1.2808	1.2852	1.2969	1.3056	1.3054
1389	1.3128	1.3175	1.3304	1.3393	1.3393
1481	1.3351	1.3397	1.3533	1.3630	1.3624
1595	1.3632	1.3693	1.3814	1.3914	1.3893
1760	1.4037	1.4100	1.4238	1.4346	1.4327
1875	1.4365	1.4393	1.4540	1.4653	1.4629
1973	1.4603	1.4636	1.4792	1.4907	1.4883

Me_4NClO_4 , t = 25°C

$c_t \times 10^4$ mole litre^{-1}	20.49	15.719	9.122	3.808	1.895
$\kappa_t \times 10^7$ (MeOH) ohm^{-1} cm^{-1}	1.11	1.20	1.23	1.25	1.40
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
130	1.0277	1.0288	1.0298	1.0316	1.0325
252	1.0537	1.0557	1.0577	1.0607	1.0622
358	1.0757	1.0784	1.0812	1.0852	1.0864
458	1.0975	1.1009	1.1043	1.1094	1.1117
566	1.1190	1.1233	1.1273	1.1332	1.1351
681	1.1435	1.1484	1.1532	1.1601	1.1626
801	1.1683	1.1736	1.1791	1.1870	1.1888
917	1.1928	1.1988	1.2048	1.2136	1.2162
1022	1.2158	1.2222	1.2289	1.2385	1.2403
1122	1.2369	1.2446	1.2508	1.2610	1.2624
1226	1.2593	1.2664	1.2741	1.2852	1.2870
1347	1.2849	1.2924	1.3007	1.3124	1.3146
1466	1.3110	1.3188	1.3278	1.3403	1.3421
1588	1.3410	1.3491	1.3564	1.3710	1.3728
1697	1.3661	1.3746	1.3820	1.3982	1.3997
1795	1.3887	1.3976	1.4057	1.4222	1.4235
1917	1.4164	1.4259	1.4343	1.4519	1.4541
1983	1.4317	1.4414	1.4502	1.4681	1.4695

Me_4NClO_4 , t = 35.14°C.

$t \times 10^4$ mole litre^{-1}	20.24	15.526	9.011	3.762	1.8719
$K_t \times 10^7$ (MeOH) ohm^{-1} cm^{-1}	1.23	1.33	1.37	1.39	1.55
p atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
136	1.0278	1.0287	1.0302	1.0317	1.0324
256	1.0520	1.0541	1.0567	1.0593	1.0596
374	1.0759	1.0790	1.0825	1.0860	1.0843
489	1.0999	1.1035	1.1082	1.1124	1.1109
618	1.1254	1.1299	1.1355	1.1404	1.1384
742	1.1507	1.1553	1.1622	1.1676	1.1651
866	1.1759	1.1807	1.1887	1.1948	1.1923
992	1.2020	1.2069	1.2158	1.2224	1.2199
1141	1.2313	1.2379	1.2466	1.2541	1.2554
1354	1.2750	1.2823	1.2925	1.3008	1.3027
1464	1.2980	1.3055	1.3162	1.3253	1.3271
1568	1.3195	1.3272	1.3385	1.3479	1.3499
1692	1.3465	1.3544	1.3665	1.3764	1.3783
1812	1.3727	1.3808	1.3939	1.4041	1.4059
1905	1.3926	1.4010	1.4147	1.4250	1.4268
1980	1.4090	1.4179	1.4321	1.4426	1.4443

Me_4NClO_4 , t = 45°C.

$c_t \times 10^4$ mole litre^{-1}	27.50	22.98	13.900	7.284	3.485
$\kappa_t \times 10^8$ (MeOH) ohm^{-1} cm^{-1}	7.41	7.6	8.0	8.2	8.4
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
109	1.0202	1.0213	1.0226	1.0238	1.0242
179	1.0350	1.0359	1.0382	1.0399	1.0413
289	1.0549	1.0566	1.0599	1.0626	1.0647
380	1.0728	1.0752	1.0791	1.0826	1.0856
486	1.0935	1.0961	1.1014	1.1056	1.1090
575	1.1097	1.1126	1.1190	1.1238	1.1283
683	1.1312	1.1343	1.1412	1.1472	1.1514
797	1.1511	1.1544	1.1622	1.1692	1.1745
888	1.1696	1.1730	1.1818	1.1894	1.1947
994	1.1895	1.1932	1.2028	1.2112	1.2172
1092	1.2082	1.2110	1.2225	1.2308	1.2380
1190	1.2273	1.2311	1.2423	1.2519	1.2588
1288	1.2466	1.2495	1.2630	1.2724	1.2793
1392	1.2659	1.2701	1.2828	1.2936	1.3011
1500	1.2881	1.2915	1.3063	1.3169	1.3243
1599	1.3071	1.3117	1.3256	1.3379	1.3459
1692	1.3263	1.3298	1.3461	1.3575	1.3656
1821	1.3523	1.3574	1.3725	1.3863	1.3945

Et_4NClO_4 , t = 5°C.

$c_t \times 10^4$ mole litre^{-1}	28.10	16.794	12.895	9.334	2.266
$K_t \times 10^8$(MeOH) ohm^{-1} cm^{-1}	3.7	4.9	3.2	5.7	2.6
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
132	1.0342	1.0358	1.0359	1.0370	1.0381
246	1.0632	1.0659	1.0665	1.0681	1.0700
372	1.0947	1.0987	1.0998	1.1021	1.1047
624	1.1595	1.1660	1.1683	1.1712	1.1753
755	1.1921	1.1997	1.2025	1.2060	1.2105
871	1.2233	1.2317	1.2351	1.2389	1.2436
993	1.2552	1.2647	1.2685	1.2727	1.2779
1122	1.2884	1.2990	1.3032	1.3079	1.3130
1238	1.3195	1.3309	1.3355	1.3406	1.3461
1289	1.3320	1.3437	1.3484	1.3537	1.3592
1383	1.3587	1.3711	1.3763	1.3818	1.3874
1483	1.3833	1.3962	1.4019	1.4077	1.4133
1594	1.4165	1.4301	1.4358	1.4418	1.4491
1833	1.4850	1.5003	1.5076	1.5136	1.5203

Et_4NClO_4 , t = 15°C.

$c_t \times 10^4$ mole litre^{-1}	27.78	16.601	12.746	9.226	6.531
$\kappa_t \times 10^8$ (MeOH) ohm^{-1} cm^{-1}	4.21	5.6	3.7	6.5	3.5
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
132	1.0331	1.0344	1.0349	1.0358	1.0364
268	1.0662	1.0684	1.0694	1.0712	1.0723
392	1.0963	1.0993	1.1010	1.1037	1.1051
500	1.1232	1.1271	1.1295	1.1324	1.1343
623	1.1524	1.1574	1.1602	1.1634	1.1657
756	1.1838	1.1898	1.1932	1.1968	1.1999
878	1.2141	1.2208	1.2247	1.2284	1.2315
928	1.2249	1.2320	1.2364	1.2401	1.2441
1014	1.2482	1.2558	1.2600	1.2641	1.2671
1134	1.2766	1.2863	1.2901	1.2954	1.2985
1267	1.3100	1.3202	1.3243	1.3297	1.3333
1362	1.3340	1.3438	1.3491	1.3537	1.3580
1408	1.3462	1.3574	1.3618	1.3673	1.3712
1533	1.3768	1.3884	1.3932	1.3988	1.4031
1618	1.3995	1.4104	1.4166	1.4213	1.4258
1714	1.4249	1.4373	1.4430	1.4487	1.4534
1811	1.4501	1.4618	1.4689	1.4735	1.4784
1888	1.4708	1.4843	1.4907	1.4961	1.5015
1956	1.4890	1.5014	1.5093	1.5139	1.5194

Et_4NClO_4 , t = 25°C

$c_t \times 10^4$ mole litre^{-1}	27.45	16.404	12.600	9.117	4.029
$K_t \times 10^8$ (MeOH) ohm^{-1} cm^{-1}	4.7	6.2	4.1	7.2	7.9
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
131	1.0314	1.0330	1.0333	1.0345	1.0352
246	1.0590	1.0618	1.0623	1.0643	1.0654
362	1.0847	1.0885	1.0897	1.0922	1.0939
460	1.1092	1.1141	1.1155	1.1186	1.1207
572	1.1343	1.1402	1.1420	1.1455	1.1480
695	1.1636	1.1703	1.1727	1.1766	1.1794
806	1.1871	1.1946	1.1971	1.2016	1.2045
929	1.2162	1.2246	1.2275	1.2327	1.2357
1049	1.2453	1.2546	1.2577	1.2634	1.2664
1169	1.2718	1.2820	1.2849	1.2911	1.2945
1294	1.3021	1.3131	1.3160	1.3231	1.3263
1407	1.3294	1.3414	1.3441	1.3516	1.3550
1515	1.3545	1.3670	1.3698	1.3777	1.3814
1617	1.3798	1.3924	1.3960	1.4041	1.4079
1742	1.4099	1.4231	1.4273	1.4357	1.4397
1853	1.4378	1.4516	1.4558	1.4648	1.4690
1962	1.4642	1.4782	1.4835	1.4925	1.4969

Et_4NClO_4 , t = 35.14°C.

$c_t \times 10^4$ mole litre^{-1}	24.98	15.757	9.300	6.519	4.224
$\kappa_t \times 10^8$ (MeOH) ohm^{-1} cm^{-1}	6.5	6.7	6.3	4.7	5.3
p atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
126	1.0293	1.0304	1.0316	1.0322	1.0344
243	1.0564	1.0585	1.0607	1.0618	1.0628
326	1.0751	1.0781	1.0806	1.0823	1.0838
441	1.1011	1.1050	1.1082	1.1103	1.1125
534	1.1223	1.1265	1.1309	1.1328	1.1352
654	1.1492	1.1543	1.1591	1.1615	1.1645
741	1.1667	1.1721	1.1779	1.1805	1.1836
869	1.1963	1.2026	1.2091	1.2119	1.2150
966	1.2175	1.2246	1.2315	1.2349	1.2381
1090	1.2456	1.2529	1.2609	1.2638	1.2674
1184	1.2665	1.2749	1.2829	1.2866	1.2903
1312	1.2961	1.3048	1.3139	1.3174	1.3212
1391	1.3124	1.3216	1.3309	1.3347	1.3387
1510	1.3410	1.3502	1.3605	1.3645	1.3682
1603	1.3630	1.3729	1.3834	1.3872	1.3916
1684	1.3827	1.3923	1.4039	1.4071	1.4113
1804	1.4103	1.4205	1.4326	1.4357	1.4343
1917	1.4384	1.4493	1.4619	1.4653	1.4700

Et_4NClO_4 , t = 45°C

$c_t \times 10^4$ mole litre^{-1}	24.68	15.565	9.186	6.440	4.174
$K_t \times 10^8$ (MeOH) ohm^{-1} cm^{-1}	6.8	7.0	6.6	4.9	5.5
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
129	1.0301	1.0312	1.0330	1.0328	1.0334
223	1.0510	1.0530	1.0555	1.0561	1.0570
331	1.0757	1.0786	1.0819	1.0828	1.0843
541	1.1209	1.1253	1.1303	1.1318	1.1341
629	1.1402	1.1452	1.1510	1.1523	1.1548
718	1.1586	1.1641	1.1705	1.1724	1.1749
831	1.1835	1.1892	1.1963	1.1984	1.2011
931	1.2046	1.2114	1.2190	1.2218	1.2244
1046	1.2293	1.2365	1.2448	1.2475	1.2502
1142	1.2506	1.2585	1.2653	1.2701	1.2731
1234	1.2702	1.2785	1.2875	1.2911	1.2939
1362	1.2973	1.3064	1.3164	1.3196	1.3226
1459	1.3186	1.3280	1.3385	1.3419	1.3452
1582	1.3460	1.3561	1.3670	1.3705	1.3738
1698	1.3705	1.3814	1.3922	1.3963	1.4002
1802	1.3932	1.4044	1.4163	1.4199	1.4239
1908	—	1.4307	1.4433	1.4466	1.4505

$n\text{-}Pr_4NClO_4$, t = 5°C.

$c_t \times 10^4$ mole litre^{-1}	25.86	16.286	8.438	3.043	1.3689
$\kappa_t \times 10^7$ (MeOH) ohm^{-1} cm^{-1}	0.78	0.81	0.84	0.86	0.87
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
141	1.0370	1.0386	1.0397	1.0402	1.0404
252	1.0654	1.0682	1.0700	1.0723	1.0712
366	1.0943	1.0982	1.1010	1.1041	1.1036
460	1.1201	1.1249	1.1287	1.1321	1.1322
598	1.1539	1.1600	1.1652	1.1682	1.1720
714	1.1843	1.1923	1.1978	1.2011	1.2053
855	1.2204	1.2284	1.2361	1.2397	1.2443
952	1.2464	1.2551	1.2636	1.2676	1.2722
1075	1.2784	1.2878	1.2973	1.3017	1.3061
1169	1.3027	1.3127	1.3227	1.3271	1.3320
1284	1.3340	1.3456	1.3555	1.3605	1.3652
1382	1.3608	1.3731	1.3837	1.3889	1.3940
1531	1.4008	1.4135	1.4255	1.4306	1.4356
1644	1.4325	1.4461	1.4594	1.4648	1.4695
1748	1.4609	1.4755	1.4898	1.4954	1.5002
1839	1.4871	1.5021	1.5172	1.5228	1.5277
1922	1.5107	1.5264	1.5424	1.5480	1.5529

$n\text{-}Pr_4NClO_4$, $t = 15^{\circ}C$.

$c_t \times 10^4$ mole litre^{-1}	25.56	16.100	8.341	3.008	1.3531
$\kappa_t \times 10^7$(MeOH) ohm^{-1} cm^{-1}	0.88	0.92	0.96	0.98	1.0
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
137	1.0346	1.0363	1.0375	1.0390	1.0394
244	1.0618	1.0641	1.0664	1.0688	1.0694
361	1.0896	1.0933	1.0966	1.0998	1.1004
474	1.1119	1.1241	1.1283	1.1323	1.1330
591	1.1457	1.1514	1.1570	1.1616	1.1626
723	1.1774	1.1843	1.1911	1.1964	1.1977
864	1.2118	1.2194	1.2272	1.2334	1.2346
992	1.2445	1.2528	1.2617	1.2684	1.2696
1103	1.2712	1.2799	1.2896	1.2969	1.2979
1225	1.3015	1.3111	1.3215	1.3294	1.3304
1354	1.3342	1.3446	1.3564	1.3647	1.3657
1474	1.3646	1.3750	1.3875	1.3964	1.3974
1622	1.4027	1.4142	1.4279	1.4371	1.4379
1754	1.4368	1.4490	1.4639	1.4734	1.4742
1869	1.4678	1.4806	1.4965	1.5060	1.5069

$n\text{-}Pr_4NClO_4$, t = 25°C.

$c_t \times 10^4$ mole litre^{-1}	25.26	15.907	8.242	2.972	1.3371
$\kappa_t \times 10^7$ (MeOH) ohm^{-1} cm^{-1}	0.98	1.03	1.07	1.09	1.11
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
139	1.0338	1.0352	1.0368	1.0376	1.0382
243	1.0591	1.0611	1.0639	1.0647	1.0661
359	1.0860	1.0890	1.0930	1.0941	1.0960
459	1.1113	1.1150	1.1201	1.1220	1.1238
565	1.1354	1.1400	1.1461	1.1481	1.1502
685	1.1634	1.1688	1.1760	1.1785	1.1807
807	1.1904	1.1962	1.2045	1.2071	1.2092
916	1.2163	1.2223	1.2315	1.2345	1.2363
1025	1.2431	1.2498	1.2597	1.2630	1.2634
1136	1.2686	1.2749	1.2862	1.2899	1.2911
1249	1.2962	1.3022	1.3140	1.3179	1.3196
1393	1.3288	1.3382	1.3498	1.3566	1.3603
1510	1.3558	1.3662	1.3788	1.3862	1.3891
1603	1.3784	1.3890	1.4028	1.4104	1.4129
1746	1.4135	1.4242	1.4394	1.4470	1.4485
1851	1.4403	1.4511	1.4675	1.4752	1.4768
1946	1.4637	1.4745	1.4919	1.4994	1.5061

$n\text{-}Pr_4NClO_4$, t = 35.14°C.

$c_t \times 10^4$ mole litre^{-1}	24.95	15.712	8.141	2.9354	1.3207
$\kappa_t \times 10^7$ (MeOH) ohm^{-1} cm^{-1}	1.09	1.14	1.19	1.21	1.23
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
125	1.0305	1.0314	1.0330	1.0338	1.0342
230	1.0552	1.0569	1.0601	1.0617	1.0625
329	1.0790	1.0816	1.0855	1.0878	1.0894
419	1.0994	1.1028	1.1073	1.1106	1.1117
533	1.1257	1.1294	1.1354	1.1388	1.1403
629	1.1458	1.1504	1.1566	1.1610	1.1633
746	1.1707	1.1761	1.1830	1.1879	1.1906
832	1.1913	1.1967	1.2047	1.2102	1.2105
934	1.2146	1.2209	1.2299	1.2358	1.2375
1033	1.2367	1.2432	1.2530	1.2593	1.2597
1129	1.2589	1.2655	1.2762	1.2825	1.2840
1275	1.2898	1.2981	1.3095	1.3170	1.3185
1386	1.3149	1.3239	1.3360	1.3436	1.3463
1498	1.3403	1.3499	1.3625	1.3709	1.3729
1674	1.3785	1.3901	1.4026	1.4132	1.4152
1692	1.3840	1.3949	1.4084	1.4178	1.4197
1794	1.4064	1.4180	1.4314	1.4419	1.4431

$n\text{-}Pr_4NClO_4$, t = 45°C.

$c_t \times 10^4$ mole litre^{-1}	24.65	15.521	8.0421	2.900	1.3046
$\kappa_t \times 10^7$ (MeOH) ohm^{-1} cm^{-1}	1.14	1.19	1.24	1.26	1.29
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
105	1.0243	1.0252	1.0266	1.0274	1.0271
211	1.0504	1.0524	1.0548	1.0566	1.0566
309	1.0726	1.0753	1.0790	1.0817	1.0837
429	1.0998	1.1039	1.1081	1.1114	1.1122
523	1.1209	1.1248	1.1308	1.1349	1.1365
632	1.1436	1.1490	1.1549	1.1598	1.1608
713	1.1612	1.1664	1.1737	1.1792	1.1797
837	1.1875	1.1940	1.2015	1.2077	1.2087
914	1.2049	1.2113	1.2200	1.2264	1.2302
1036	1.2301	1.2375	1.2468	1.2537	1.2545
1115	1.2480	1.2555	1.2654	1.2728	1.2752
1338	1.2953	1.3040	1.3154	1.3235	1.3242
1459	1.3214	1.3312	1.3429	1.3515	1.3528
1535	1.3386	1.3479	1.3604	1.3697	1.3689
1687	1.3683	1.3792	1.3922	1.4016	1.4028
1751	1.3840	1.3943	1.4077	1.4179	1.4151
1841	1.4042	1.4152	1.4293	1.4395	1.4396
1918	1.4219	1.4338	1.4477	1.4587	1.4587

$n\text{-}Bu_4NClO_4$, $t = 5^{\circ}C$.

$c_t \times 10^4$ mole litre^{-1}	25.43	17.252	12.286	9.207	3.890
$K_t \times 10^8$(MeOH) ohm^{-1} cm^{-1}	3.4	3.3	3.3	3.4	3.4
P atm	R_p / R_1	R_p / R_1	R_p / R_1	R_p / R_1	R_p / R_1
134	1.0348	1.0362	1.0367	1.0375	1.0386
250	1.0644	1.0670	1.0682	1.0691	1.0714
356	1.0910	1.0945	1.0964	1.0973	1.1006
462	1.1198	1.1244	1.1269	1.1282	1.1323
596	1.1516	1.1577	1.1614	1.1626	1.1678
671	1.1731	1.1787	1.1819	1.1836	1.1878
794	1.2029	1.2093	1.2132	1.2150	1.2201
922	1.2350	1.2427	1.2477	1.2494	1.2551
1039	1.2668	1.2754	1.2809	1.2827	1.2889
1176	1.3011	1.3104	1.3167	1.3183	1.3254
1303	1.3352	1.3454	1.3528	1.3543	1.3620
1440	1.3723	1.3832	1.3911	1.3927	1.4011
1572	1.4079	1.4241	1.4272	1.4289	1.4383
1704	1.4452	1.4571	1.4659	1.4677	1.4777
1803	1.4708	1.4846	1.4944	1.4965	1.5071
1934	1.5072	1.5222	1.5332	1.5355	1.5464

$n\text{-}Bu_4NClO_4$, t = 15°C.

$c_t \times 10^4$ mole litre^{-1}	25.13	17.053	12.144	9.101	3.846
$\kappa_t \times 10^8$ (MeOH) ohm^{-1} cm^{-1}	3.9	3.8	3.7	3.9	3.9
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
141	1.0353	1.0369	1.0374	1.0385	1.0392
246	1.0609	1.0635	1.0646	1.0662	1.0673
363	1.0888	1.0925	1.0942	1.0963	1.1029
472	1.1171	1.1219	1.1241	1.1266	1.1295
616	1.1484	1.1545	1.1573	1.1600	1.1623
735	1.1791	1.1894	1.1896	1.1924	1.1952
886	1.2154	1.2236	1.2273	1.2305	1.2339
993	1.2422	1.2513	1.2555	1.2590	1.2628
1134	1.2755	1.2857	1.2902	1.2943	1.2980
1262	1.3064	1.3179	1.3230	1.3274	1.3316
1396	1.3396	1.3519	1.3574	1.3622	1.3666
1505	1.3664	1.3790	1.3848	1.3899	1.3946
1617	1.3948	1.4079	1.4144	1.4198	1.4245
1716	1.4227	1.4346	1.4402	1.4462	1.4492
1834	1.4527	1.4652	1.4722	1.4779	1.4804
1929	1.4775	1.4909	1.4983	1.5043	1.5068

$n\text{-}Bu_4NClO_4$, $t = 25^{\circ}C$.

$c_t \times 10^4$ mole litre^{-1}	24.83	16.851	12.000	8.993	3.800
$\kappa_t \times 10^8$ (MeOH) ohm^{-1} cm^{-1}	4.4	4.2	4.2	4.4	4.4
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
142	1.0354	1.0368	1.0377	1.0387	1.0398
253	1.0618	1.0641	1.0658	1.0672	1.0692
371	1.0886	1.0917	1.0942	1.0962	1.0987
616	1.1460	1.1509	1.1542	1.1622	1.1615
753	1.1768	1.1824	1.1871	1.1903	1.1948
892	1.2092	1.2154	1.2207	1.2245	1.2295
1005	1.2357	1.2423	1.2481	1.2523	1.2576
1227	1.2870	1.2945	1.3010	1.3061	1.3121
1332	1.3119	1.3197	1.3270	1.3320	1.3386
1443	1.3353	1.3438	1.3512	1.3565	1.3634
1517	1.3544	1.3630	1.3712	1.3766	1.3840
1649	1.3861	1.3950	1.4043	1.4097	1.4177
1767	1.4140	1.4235	1.4339	1.4392	1.4478
1870	1.4391	1.4487	1.4599	1.4651	1.4744
1976	1.4652	1.4750	1.4866	1.4919	1.5017

$n\text{-}Bu_4NClO_4$, t = 35.14°C.

$c_t \times 10^4$ mole litre^{-1}	24.53	16.64	11.853	8.883	3.754
$\kappa_t \times 10^8$ (MeOH) ohm^{-1} cm^{-1}	4.8	4.7	4.6	4.8	4.8
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
131	1.0316	1.0327	1.0336	1.0340	1.0352
205	1.0503	1.0515	1.0531	1.0536	1.0553
340	1.0808	1.0834	1.0854	1.0864	1.0894
417	1.0987	1.1017	1.1043	1.1057	1.1095
542	1.1263	1.1302	1.1335	1.1347	1.1395
623	1.1451	1.1487	1.1528	1.1540	1.1591
761	1.1734	1.1780	1.1822	1.1839	1.1900
832	1.1908	1.1954	1.2003	1.2024	1.2085
942	1.2147	1.2202	1.2254	1.2276	1.2345
1030	1.2348	1.2401	1.2460	1.2485	1.2553
1157	1.2623	1.2689	1.2748	1.2775	1.2856
1248	1.2825	1.2887	1.2956	1.2982	1.3062
1349	1.3039	1.3112	1.3179	1.3207	1.3296
1427	1.3125	1.3297	1.3368	1.3408	1.3490
1526	1.3457	1.3532	1.3611	1.3639	1.3731
1625	1.3663	1.3745	1.3819	1.3860	1.3954
1713	1.3863	1.3947	1.4026	1.4067	1.4166
1820	1.4104	1.4194	1.4273	1.4319	1.4421
1908	1.4314	1.4412	1.4491	1.4541	1.4646

$n\text{-}Bu_4NClO_4$, $t = 45^{\circ}C$.

$c_t \times 10^4$ mole litre^{-1}	24.23	16.442	11.709	8.775	3.708
$K_t \times 10^8$(MeOH) ohm^{-1} cm^{-1}	5.1	4.9	4.8	5.1	5.1
P atm	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1	R_p/R_1
130	1.0313	1.0323	1.0333	1.0337	1.0350
251	1.0594	1.0616	1.0631	1.0642	1.0666
435	1.1013	1.1046	1.1072	1.1089	1.1129
635	1.1433	1.1482	1.1512	1.1539	1.1595
834	1.1854	1.1910	1.1918	1.1985	1.2050
316	1.0740	1.0767	1.0785	1.0798	1.0827
529	1.1211	1.1251	1.1282	1.1300	1.1329
745	1.1658	1.1706	1.1747	1.1772	1.1830
944	1.2092	1.2151	1.2200	1.2233	1.2299
1047	1.2311	1.2377	1.2427	1.2465	1.2536
1140	1.2520	1.2587	1.2643	1.2682	1.2758
1191	1.2609	1.2682	1.2735	1.2780	1.2859
1365	1.2976	1.3057	1.3118	1.3167	1.3251
1576	1.3431	1.3519	1.3587	1.3639	1.3732
1645	1.3587	1.3643	1.3747	1.3789	1.3886
1784	1.3884	1.3980	1.4054	1.4108	1.4210
1897	1.4127	1.4228	1.4305	1.4361	1.4468

APPENDIX B

The measurements of compression of methanol at temperatures 5° 15° 25° 35.14° and $45^{\circ}C$ as a function of pressure.

V_p/V_1 is corrected for the compression of the glass piezometer.

Piezometer A

t = 5°C.

Series (A) 1	
P atm	V_p/V_1
1	1.0000
231	0.9778
390	0.9650
569	0.9520
743	0.9414
968	0.9284
1207	0.9155
1538	0.9024
1840	0.8907

Series (A) 2	
P atm	V_p/V_1
1	1.0000
231	0.9778
390	0.9650
570	0.9520
743	0.9414
967	0.9284
1207	0.9155
—	0.9024
1839	0.8907

t = 15°C.

Series (A) 3	
P atm	V_p/V_1
1	1.0000
204	0.9788
349	0.9661
504	0.9543
684	0.9418
905	0.9289
—	0.9184
1355	0.9057
1626	0.8930

Series (A) 4	
P atm	V_p/V_1
1	1.0000
199	0.9788
347	0.9661
495	0.9543
677	0.9418
888	0.9289
1086	0.9186
1346	0.9057
1618	0.8930
2001	0.8802

Series (A) 5	
P atm	V_p/V_1
1	1.0000
214	0.9780
351	0.9661
514	0.9533
702	0.9405
880	0.9301
1118	0.9171
1355	0.9044
1802	0.8914

Piezometer A

t = 25°C.

Series (A) 6	
P atm	V_p/V_1
1	1.0000
197	0.9788
328	0.9662
467	0.9544
639	0.9419
835	0.9291
1023	0.9188
1261	0.9060
1514	0.8933
1864	0.8805

Series (A) 7	
P atm	V_p/V_1
1	1.0000
187	0.9789
328	0.9662
465	0.9544
638	0.9419
836	0.9291
1022	0.9188
1264	0.9060
1514	0.8933
1864	0.8805

t = 35.14°C.

Series (A) 8	
P atm	V_p/V_1
1	1.0000
176	0.9789
317	0.9662
433	0.9545
594	0.9420
784	0.9292
948	0.9190
1172	0.9062
1412	0.8936
1748	0.8809

Series (A) 9	
P atm	V_p/V_1
1	1.0000
176	0.9789
305	0.9662
431	0.9545
594	0.9420
785	0.9292
950	0.9190
1172	0.9062
1412	0.8936
1748	0.8809

Piezometer A

$t = 45^{\circ}C.$

Series (A) 10	
P atm	V_p/V_1
1	1.0000
162	0.9789
284	0.9663
404	0.9545
551	0.9421
729	0.9294
883	0.9192
1094	0.9064
1308	0.8939
1624	0.8812
1889	0.8698

Series (A) 11	
P atm	V_p/V_1
1	1.0000
163	0.9789
288	0.9663
404	0.9545
552	0.9421
727	0.9294
881	0.9192
1091	0.9064
1308	0.8939
1619	0.8812
1889	0.8698

Piezometer B

t = 25°C

t = 35.14°C

Series (B) 1		Series (B) 2		Series (B) 3		Series (B) 4	
P atm	V_p/V_1	P atm	V_p/V_1	P atm	V_p/V_1	P atm	V_p/V_1
1	1.0000	1	1.0000	1	1.0000	1	1.0000
138	0.9831	139	0.9831	140	0.9831	138	0.9831
232	0.9736	227	0.9736	226	0.9736	228	0.9736
338	0.9645	324	0.9645	325	0.9645	324	0.9645
453	0.9547	432	0.9547	431	0.9547	431	0.9547
557	0.9473	521	0.9474	522	0.9474	522	0.9474
681	0.9387	642	0.9388	642	0.9388	638	0.9388
953	0.9216	904	0.9218	905	0.9218	897	0.9218
1082	0.9145	1021	0.9146	1023	0.9146	1069	0.9146
1255	0.9056	1184	0.9057	1187	0.9057	1184	0.9057
1466	0.8960	1383	0.8963	1385	0.8963	1382	0.8963
1668	0.8879	1555	0.8882	1563	0.8882	1551	0.8882
1868	0.8799	1759	0.8802	1764	0.8802	1753	0.8802

Piezometer B

$t = 45^{\circ}C.$

Series (B) 5		Series (B) 6		Series (B) 7	
P atm	V_p/V_1	P atm	V_p/V_1	P atm	V_p/V_1
1	1.0000	1	1.0000	1	1.0000
127	0.9831	128	0.9831	127	0.9831
210	0.9737	210	0.9737	207	0.9737
297	0.9646	297	0.9646	294	0.9646
403	0.9548	402	0.9548	396	0.9548
482	0.9475	482	0.9475	482	0.9475
595	0.9389	597	0.9389	592	0.9389
841	0.9220	835	0.9220	838	0.9220
952	0.9148	948	0.9148	947	0.9148
1109	0.9059	1116	0.9059	1106	0.9059
1277	0.8966	1275	0.8966	1275	0.8966
1462	0.8885	1450	0.8885	1450	0.8885
1639	0.8805	1635	0.8805	1630	0.8805
1875	0.8706	1875	0.8706	1873	0.8706

APPENDIX C

The conductance data at 1 atm

Λ as a function of $\sqrt{c}$

$KClO_4$

5°C		15°C		25°C		35.14°C		45°C	
Λ $ohm^{-1}\ cm^2\ mole^{-1}$	$\sqrt{c}$ $mole^{\frac{1}{2}}$ x 10^2	Λ $ohm^{-1}\ cm^2\ mole^{-1}$	$\sqrt{c}$ $mole^{\frac{1}{2}}$ x 10^2	Λ $ohm^{-1}\ cm^2\ mole^{-1}$	$\sqrt{c}$ $mole^{\frac{1}{2}}$ x 10^2	Λ $ohm^{-1}\ cm^2\ mole^{-1}$	$\sqrt{c}$ $mole^{\frac{1}{2}}$ x 10^2	Λ $ohm^{-1}\ cm^2\ mole^{-1}$	$\sqrt{c}$ $mole^{\frac{1}{2}}$ x 10^2
		91.14	5.346	103.93	5.313	119.70	4.766	132.44	5.252
78.95	5.376	91.71	5.072	104.71	5.041	120.15	4.726	134.39	4.757
79.49	5.101	92.60	4.783	105.46	4.814	122.39	4.165	134.87	4.699
80.13	4.814	93.27	4.496	105.90	4.701	123.18	3.922	137.54	4.141
80.82	4.524	94.24	4.213	106.60	4.470	124.76	3.553	138.52	3.897
81.54	4.238	94.42	4.066	107.65	4.188	126.83	3.075	140.22	3.532
81.73	4.089	95.85	3.596	108.00	4.041	126.89	2.980	142.61	3.058
82.85	3.617	97.21	3.069	108.46	3.945	129.23	2.401	142.77	2.962
84.44	3.106	98.19	2.747	109.57	3.574	130.94	1.961	145.41	2.387
84.08	3.085	98.24	2.710	111.41	3.093	131.11	1.961	147.68	1.949
84.95	2.762	99.68	2.247	111.30	3.051			147.78	1.949
84.95	2.727			111.56	2.997				
85.89	2.439			112.45	2.730				
86.32	2.261			112.51	2.694				
				114.33	2.234				
				115.10	1.972				
				116.09	1.689				

Λ as a function of $\sqrt{c}$

Me_4NClO_4

5°C		15°C		25°C		35.14°C		45°C	
Λ	$\sqrt{c}$	Λ	$\sqrt{c}$	Λ	$\sqrt{c}$	Λ	$\sqrt{c}$	Λ	$\sqrt{c}$
$ohm^{-1}\ cm^2\ mole^{-1}$	$mole^{\frac{1}{2}}\ x\ 10^2$	$ohm^{-1}\ cm^2\ mole^{-1}$	$mole^{\frac{1}{2}}\ x\ 10^2$	$ohm^{-1}\ cm^2\ mole^{-1}$	$mole^{\frac{1}{2}}\ x\ 10^2$	$ohm^{-1}\ cm^2\ mole^{-1}$	$mole^{\frac{1}{2}}\ x\ 10^2$	$ohm^{-1}\ cm^2\ mole^{-1}$	$mole^{\frac{1}{2}}\ x\ 10^2$
86.64	5.372	99.79	5.341	113.72	5.308	128.75	5.280	144.14	5.248
88.36	4.911	101.67	4.883	116.79	4.625	131.24	4.826	146.99	4.797
89.12	4.680	102.51	4.652	119.54	4.046	132.23	4.598	148.13	4.570
91.14	4.094	104.96	4.071	120.81	3.775	135.23	4.026	151.53	4.001
92.11	3.820	106.86	3.602	121.74	3.579	137.88	3.558	154.53	3.536
92.87	3.622	108.68	3.154	123.81	3.135	140.29	3.116	157.21	3.097
94.46	3.256	108.96	2.767	125.80	2.732	142.56	2.717	159.74	2.700
95.98	2.765	113.16	2.103	128.96	2.090	146.12	2.078	163.78	2.066
98.10	2.115	114.29	1.901	129.92	1.890	147.22	1.879	165.07	1.868
99.10	1.912								

Λ as a function of $\sqrt{c}$

Et_4NClO_4

5°C		15°C		25°C		35.14°C		45°C	
Λ	$\sqrt{c}$	Λ	$\sqrt{c}$	Λ	$\sqrt{c}$	Λ	$\sqrt{c}$	Λ	$\sqrt{c}$
$ohm^{-1}\ cm^2\ mole^{-1}$	$mole^{\frac{1}{2}}\ x\ 10^2$	$ohm^{-1}\ cm^2\ mole^{-1}$	$mole^{\frac{1}{2}}\ x\ 10^2$	$ohm^{-1}\ cm^2\ mole^{-1}$	$mole^{\frac{1}{2}}\ x\ 10^2$	$ohm^{-1}\ cm^2\ mole^{-1}$	$mole^{\frac{1}{2}}\ x.10^2$	$ohm^{-1}\ cm^2\ mole^{-1}$	mol- x 1
83.22	5.088	95.82	5.060	109.20	5.029	123.69	4.999	141.50	4.414
84.96	4.521	97.74	4.495	111.38	4.469	126.18	4.441	143.91	3.946
86.50	4.041	99.44	4.017	113.31	3.993	128.35	3.970	146.93	3.397
88.34	3.479	101.54	3.459	115.71	3.438	131.10	3.418	149.03	3.032
91.27	2.599	102.92	3.086	117.27	3.069	132.87	3.050	151.95	2.539
92.85	2.092	104.91	2.585	119.60	2.569	135.50	2.553	154.77	2.044
94.85	1.496	106.85	2.080	124.20	1.478	138.01	2.056	158.12	1.443
		108.93	1.488	124.42	1.461	140.77	1.470		
		108.99	1.470	126.37	1.010	141.11	1.452		

Λ as a function of $\sqrt{c}$

$n\text{-}Pr_4NClO_4$

5°C		15°C		25°C		35.14°C		45°C	
Λ ohm^{-1} cm^2 mole^{-1}	$\sqrt{c}$ mole$^{\frac{1}{2}}$ x 10^2	Λ ohm^{-1} cm^2 mole^{-1}	$\sqrt{c}$ mole$^{\frac{1}{2}}$ x 10^2	Λ ohm^{-1} cm^2 mole^{-1}	$\sqrt{c}$ mole$^{\frac{1}{2}}$ x 10^2	Λ ohm^{-1} cm^2 mole^{-1}	$\sqrt{c}$ mole$^{\frac{1}{2}}$ x 10^2	Λ ohm^{-1} cm^2 mole^{-1}	$\sqrt{c}$ mole$^{\frac{1}{2}}$ x 10^2
73.04	5.099	84.45	5.070	96.54	5.040	109.77	5.012	123.34	4.981
74.45	4.632	86.00	4.605	98.37	4.579	111.76	4.552	125.60	4.525
74.48	4.587	86.01	4.561	98.37	4.533	111.79	4.509	125.68	4.482
76.04	4.075	87.83	4.052	100.39	4.029	114.06	4.055	128.20	3.981
77.65	3.560	89.57	3.540	102.40	3.518	116.36	3.501	130.82	3.479
78.92	3.083	91.07	3.065	104.16	3.047	118.32	3.029	133.02	3.012
80.93	2.554	92.17	2.718	105.29	2.702	119.87	2.687	134.83	2.671
82.18	2.000	92.97	2.540	106.28	2.524	120.80	2.510	135.97	2.496
		94.78	1.988	108.37	1.992	123.32	1.967	138.60	1.956
				110.42	1.472	125.46	1.464	141.14	1.455

Λ as a function of $\sqrt{c}$

$n\text{-}Bu_4NClO_4$

5°C		15°C		25°C		35.14°C		45°C	
Λ	$\sqrt{c}$	Λ	$\sqrt{c}$	Λ	$\sqrt{c}$	Λ	$\sqrt{c}$	Λ	$\sqrt{c}$
$ohm^{-1}\ cm^2\ mole^{-1}$	$mole^{\frac{1}{2}} \times 10^2$	$ohm^{-1}\ cm^2\ mole^{-1}$	$mole^{\frac{1}{2}} \times 10^2$	$ohm^{-1}\ cm^2\ mole^{-1}$	$mole^{\frac{1}{2}} \times 10^2$	$ohm^{-1}\ cm^2\ mole^{-1}$	$mole^{\frac{1}{2}} \times 10^2$	$ohm^{-1}\ cm^2\ mole^{-1}$	$mole^{\frac{1}{2}} \times 10^2$
66.71	5.680	77.14	5.647	88.36	5.613	102.91	4.970	115.80	4.940
68.36	5.060	80.06	4.720	90.42	5.000	106.05	4.222	119.04	4.261
69.20	4.747	80.66	4.499	91.66	4.692	106.90	4.022	120.30	3.998
69.08	4.747	81.14	4.407	92.34	4.499	110.22	3.225	123.58	3.304
71.21	4.096	82.29	4.039	93.91	4.047	111.39	2.952	125.33	2.934
72.86	3.468	83.70	3.591	95.82	3.568	112.88	2.590	127.40	2.501
77.39	2.000	84.13	3.448	96.28	3.428				
		85.59	2.995	97.35	3.137				
		86.34	2.831	97.87	2.969				
		88.06	2.226	97.90	2.978				
		89.08	1.991	100.73	2.212				
		89.50	1.853	101.16	2.065				

REFERENCES

1. Jobling, A., Lawrence, A.S.C., J. Chem. Phys., 1952, 20, 1296.

2. Brummer, S. B., Hills, G. J., Trans. Faraday Soc., 1961, 57, 1816.

3. Brummer, S. B., Hills, G. J., ibid., 1961, 57, 1823.

4. Onsager, L., Phys. Z., 1927, 28, 277.

5. Fuoss, R. M., Onsager, L., J. Phys. Chem., 1957, 61, 668.

6. Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolyte Solutions", (Rheinhold, N.Y., 3rd Edition), page 284.

7. Polissar, M. J., J. Chem. Phys., 1938, 6, 833.

8. Glasstone, S., Laidler, K.J., Eyring, H., "The Theory of Rate Processes", (McGraw-Hill, N.Y., 1941)

9. Allnatt, A. R., Rice, S. A., J. Chem. Phys., 1961, 34, 2156.

   Rice, S. A., Allnatt, A. R., J. Chem. Phys., 1961, 34, 2144.

   Davis, H. T., Rice, S. A., Meyer, L., J. Chem. Phys., 1962, 37, 947.

   Davis, H. T., Rice, S. A., Meyer, L., J. Chem. Phys., 1962, 37, 1521.

10. Newitt, D. M., Wassermann, A., J. Chem. Soc., 1940, 735.

11. Collins, F. C., J. Chem. Phys., 1957, 26, 398.

12. Evans, M. G., Polanyi, M., Trans. Faraday Soc., 1935, 31, 875.

13. Goodeve, C. F., ibid., 1938, 34, 155.

14. Bridgman, P. W.,
"The Physics of High Pressure,"
(G. Bell and Sons Ltd., 1949) page 138.

15. Brummer, S. B., Ph.D. Thesis, University of London, 1960.

16. Walden, P., Ulich, H., Busch, G.,
Z. Physik. Chem., 1926, 123, 442.

17. Walden, P., Ulich, H., Busch, G.,
Z. Physik. Chem., 1926, 123, 442.

18. Frazer, J. E., Hartley, H.,
Proc. Roy. Soc., 1925, A109, 351.

19. Butler, J. B., Shiff, H. I., Gordon, A.R.,
J. Chem. Phys., 1951, 19, 752.

20. Evers, E. C., Knox, A. G.,
J. Amer. Chem. Soc., 1951, 75, 1739.

21. Porter, R. P., J. Phys. Chem., 1957, 61, 1260.

22. Steele, H., Ph. D. Thesis, Univ. New England, N.S.W, 1960.

23. Ives, D. J. G., Janz, G. J.,
"Reference electrodes; theory and practice"
(Academic Press, N. Y. and London, 1961),
page 133.

24. Findlay, A., "Practical Physical Chemistry",
(Longmans, London, 8th Edition), page 206.

25. Ovenden, P., Private communication.

26. International Critical Tables
(McGraw-Hill, 1931), Vol. II, 93.

27. Prue, J. E., Sherrington, P. J.,
Trans. Faraday Soc., 1961, 57, 1795.

28. Lind, J. E., Zwolenik, J. J., Fuoss, R. M.,
J. Amer. Chem. Soc., 1959, 81, 1557.

29. Findlay, A., "Practical Physical Chemistry",
(Longmans, London, 8th Edition), page 210.

30. Jones, G., Christian, S. M.,
J. Amer. Chem. Soc., 1935, 57, 272.

31. International Critical Tables,
(McGraw-Hill, 1931), Vol. 3, 27.

32. Amagat, M. E.-H., Ann. Chim. Phys., 1893, 29, 505.

33. Eduljee, H. E., Newitt, D. M., Weale, K, E.,
J. Chem. Soc., 1951, 3086.

34. Amagat, M. E.-H., Ann. Chim. Phys., 1893, 29, 505.

35. Hamann, S. D., Strauss, W.,
Discuss. Faraday Soc., 1956, 22, 70.

36. Tait, P. G.,
"Physics and Chemistry of the Voyage of H.M.S. Challenger",
(H.M.Stationery Office 1888), Vol. 2, part IV.

37. Harned, H. S., Owen, B. B.,
"The Physical Chemistry of Electrolyte Solutions",
(Rheinhold, N. Y., 3rd Edition), page 379.

38. Gibson, R. E., J. Amer. Chem. Soc., 1935, 57, 1551.

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