UNIVERSITY OF GLASGOW
(Institute of Chemistry)

Application of Irreversible Thermodynamics to Transport Processes in Binary Electrolyte Solutions

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(Ph.D. Thesis)

July, 1971.

GLASGOW SCOTLAND

To

My Uncle

H. C.

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ACKNOWLEDGMENT

It gives me a great pleasure to thank my research supervisor, Dr. R. Paterson, for assigning me this work, his sincere guidance and useful timely discussions during the course of these investigations and helping me in the preparation of this thesis.

I am thankful to Dr. H. S. Dunsmore for taking interest in my practical work and writing some of the major computer programmes required for mathematical analysis of the experimental results.

I am also thankful to Professor J. M. Robertson for providing me the necessary laboratory facilities and financial assistance in the form of a student demonstratorship.

My thanks are also due to the head of the computing department for letting me attend a short course in Algol computing language; to J. Walker for preparing the computer data tapes and assisting me in the setting up of the experimental equipment; to the glass blowers for constructing the conductance and diffusion cells; to the electronics work shop for lending me the Wayne Kerr Oscillator and to my colleagues, J. Anderson and R. Cameron, for correcting a part of the thesis.

Finally I must also thank my sister, Miss Neelam Jalota, for the laborious typing of this manuscript.

ABSTRACT

Theory of irreversible thermodynamics has been applied to isothermal transport processes in binary electrolyte solutions. Relations are presented which express the commonly measureable transport quantities in terms of Onsager transport L_{ik} and inverse frictional R_{ik} coefficients. Relations for L_{ik} and R_{ik} coefficients are presented in terms of the experimental quantities, t_i, Λ and D_v.

Equivalent conductances of rubidium and caesium chlorides and diffusion coefficients of rubidium chloride have been measured in the concentration range 0-3M. These have been combined with the remaining transport, activity and density data which existed in the literature and the L_{ik} and R_{ik} coefficients obtained. Literature from 1930 to 1970 has been surveyed for transport numbers, equivalent conductances, diffusion and activity coefficients for 1:1, 1:2, 2:1 and 2:2 electrolyte solutions in aqueous media. Results, for twenty eight systems for which data was also complete, have been calculated as a basis of comparison.

The relative sizes of these coefficients have been discussed in terms of ion solvation and water structure. An interpretation of the physical significance of frictional coefficients is developed for completely dissociated as well as associated 1:1 electrolytes. Association in alkali metal chlorides, potassium and silver nitrate solutions has been studied by the conductance theories of Pitts and Fuoss. Abnormalities in rubidium-chloride and caesium-chloride interactions have been ascribed to ion association and the true interionic friction coefficients calculated and compared with those for the completely dissociated alkali metal chlorides. The correction reduces the inter-

ionic friction from its apparent value calculated on a stoicheiometric basis and places the salts in a rational order. The significance of q_{12}, the degree of coupling between mobile species, has been developed as a suitable parameter for comparison of a variety of electrolytes of different valence types.

Nomenclature

A	Anion in chapter 2; a coefficient of empirical fit in eqn(5.12) and (6.13).
A_i	Affinity of chemical reaction.
a_0, a_i	Coefficients of empirical fits.
B	A coefficient of empirical fit in eqns (5.12) and (6.13).
cma, cmb	Mean concentrations.
C	Cation in chapter 2.
C_p	Capacitance.
c_i	Molar concentration of ion i.
d	Density.
$\overline{D}(t)$	Concentration average diffusion coefficient.
$\overline{D}$	Integral diffusion coefficient.
D, D_v	Volume fixed differential diffusion coefficient.
D^0	Diffusion coefficient at infinite dilution.
D_0	Solvent fixed differential diffusion coefficient.
dS	Total change of entropy.
d_eS	Change of entropy due to interactions with the exterior.
d_iS	Internal production of entropy.
fa, fb	Vacuum correction factors for salt and solutions.
F	Faraday of electricity.
F_{ik}	Fraction of the force applied on i which is opposed by friction with k.

q_{12}	Degree of coupling between species 1 and 2.
q_{i0}	Degree of coupling between species i and solvent.
R_{ik}, R_{i0}	Coefficients of friction between species i and k and, i and solvent.
R_p, R_T	Apparent and true resistances of solutions.
r_i	Stoicheiometric coefficient of ion i.
r	Sum of stoicheiometric coefficients.
s_v	Local entropy density per unit volume.
S	Entropy in chapter 2 and ionic strength in chapter 6.
T	Absolute temperature.
t_i^h	Hittorf transport number.
t_i^c	e.m.f. transport number.
t_i	Transport number.
t, t_r	Time of a diffusion run.
V	Volume.
v_i	Velocity of species i in liters /cm^{2}sec.
$\overline{v}_i$	Velocity of species i in cm/sec.
W	Frequency of alternating current.
W_b	Molecular weight of solute.
X	Thermodynamic force.
X_i	Thermodynamic force on species i.
x	Distance in cm.

$f_{\pm}$	Stoicheiometric activity coefficients.
I	Current density.
i	Numbers.
J_s	Flow of entropy.
$\mathrm{div}\ J_s$	Divergence of entropy.
$J(t)$	Flux of solute at time t.
J_i	Flow of species i.
J_i^0	Flow of i relative to solvent.
j_i	Flow of free ions i.
J_{ch}	Flow of chemical reaction.
K_a	Association constant.
k	Numbers.
L	Thermodynamic diffusion coefficient.
l	Diffusion path.
L_{ii}	Intrinsic mobilities of species i.
L_{ik}	Coefficient of interaction of mobilities of i with k.
m	Molality.
N	Normality.
n	Numbers.
M	Molarity.
M_0	Molecular weight of solvent.
q	Transport of heat.

x_i	Thermodynamic force on free ions i.
x_{ik}	Coefficient of kinetic friction between species i and k.
y	Mean molar activity coefficient.
Z_i	Valency of ion i.
0	Solvent.
1	Cations.
2	Anions.
ς	Cell constant in conductance measurements.
α	Degree of dissociation.
β	Cell constant in the diffusion experiment.
σ	Rate of entropy production.
Φ	Dissipation function.
λ_i^0	Limiting conductivity of ions i.
Λ	Equivalent conductance.
$\tilde{\mu}_i$	Electrochemical potential of species i.
μ_i	Chemical potential of species i.
μ_{ik}	Chemical potential of neutral electrolyte or ion pair.
ϕ	Electrical potential.
γ	Mean molal activity coefficient.
κ	Specific conductivity.
η	Coefficient of viscosity.
$\varsigma'_+, \varsigma'_-$	Surface density of water around an ion i.

CHAPTER 1

Introduction

In electrolyte solutions transport of charge and mass takes place if an electrical potential is applied to the solution or if a concentration gradient exists in it. Considerable effort has been put on the elucidation of these processes from the original investigations of Kohlrausch(1879)[1], Arrhenius (1887)[2] and Van't Hoff (1887)[3] upto the notable work of Debye and Hückel(1923)[4] and Onsager(1931)[5]. The molecular theories of electrolytic conductance and diffusion are based on the laws of interionic attraction and the concept of ionic atmosphere. These theories successfully account for the observed transport quantities in dilute solutions where long range coulombic forces alone are of importance and where other influences such as intermolecular and short range repulsive forces between ions may be negligible. In concentrated solutions however specific effects become significant, flow of an ion is affected by the presence of similar and counter ions. As concentration increases the dielectric constant changes in the vicinity of an ion and there are specific and changing interactions between ions and solvent molecules. For these reasons theoretical equations for diffusion and conductance are limited to a very narrow range of concentration which for 1:1 electrolytes is upto 0.01M and still lower for higher valence type electrolytes. Fuoss and coworkers[6] and Pitts[7] have recently tried to extend the concentration limit of their theoretical conductance equations by taking into account short range interionic effects.

Their treatment is valid only upto $\simeq$ 0.05M in solutions of completely dissociated 1:1 electrolytes. This concentration limit is further reduced in the case of associated electrolytes and a solvent of low dielectric constant.

An alternative phenomenological approach to the problem has been developed over the last few decades. It is based on the phenomenon of coupling between two or more processes in a transport experiment. In electrolyte conductance, for example, the two processes taking place are the simultaneous flows of cations and anions in the opposite directions under a gradient of electrical potential. The force acting on a species affects the flow of the second and vice-versa. This, the phenomenon of coupling, was first rationalised by Lord Kelvin(1854)[8] in a study of the thermoelectric effect. Rigorous treatment was given by Onsager(1931)[5] who developed the theory of irreversible thermodynamics later to be expanded and generalised by Meixner[9], Casimir[10] and Prigogine[11]. The complete formulation of the subject is most adequately treated in a number of treatises[12,13,14,15].

The theory of irreversible thermodynamics has been specifically applied to isothermal transport processes in electrolyte solutions by Miller[16] and in a slightly different but equivalent form by Newman[17]. The complete picture of the theory as presented by Miller can be applied directly to experimentally measureable transport properties and the application leads to a general description which is valid in any range of concentration. The transport processes are described by phenomenological coefficients which specifically measure the kinetic interactions between ion and ion, and ion and solvent. The concentration dependence of the transport properties like conductance, transport numbers and diffusion coefficients are well described in terms of these phenomenological coefficients which are therefore more fundamental than the transport properties themselves and a knowledge of these coefficients gives better in-sight into the transport processes irrespective of the concentration range.

The interpretation of the transport processes in terms of the phenomenological coefficients is qualitative and therefore becomes more meaningful when a closely related series of electrolytes are considered. One such series is that of alkali metal chlorides. Miller[16a] collected literature data for conductance, transport numbers and diffusion coefficients in aqueous solutions of lithium, sodium and potassium chlorides in the concentration range 0-3M, applied his relations and obtained the phenomenological coefficients. These transport data were not complete for rubidium and caesium chlorides. Equivalent conductances of both and diffusion coefficients of rubidium chloride alone were lacking. These have been measured and presented in this thesis to complete the irreversible thermodynamic analysis of the whole alkali metal chloride series and make a comparison of the changing trends of the magnitudes of phenomenological coefficients when atomic size of the cations in this closely graded series increases regularly from lithium to caesium while the anion remains the same and to find an explanation for the highest values of conductance, transport numbers and diffusion coefficients in solutions of rubidium chloride while this electrolyte lies below caesium chloride in the series.

The theory of irreversible thermodynamic analysis is presented in chapter 2 where it is shown that only three transport quantities, t_i, Λ and D_v, are required to explain the transport processes in binary electrolyte solutions. There are two formalisms in which the phenomenological equations are described. The first is that of direct transport L_{ik} coefficients and the second is that of inverse frictional R_{ik} coefficients.

A detailed literature survey from 1930 onwards was made to collect the transport quantities for 1:1, 1:2, 2:1 and 2:2 binary electrolyte solutions and obtain the phenomenological coefficients for these systems as a basis of comparison with those of the alkali metal chlorides. This is described in chapter 3. The experimental procedures for the measurements of diffusion coefficients and conductances are described in chapters 4 and 5. In chapter 5 ion association in 1:1 electrolyte solutions has been studied using the conductance theories of Fuoss & Pitts and the results of calculations of the complete thermodynamic data for rubidium and caesium chlorides are presented in chapter 6 and the physical significance of the phenomenological coefficients, L_{ik} and R_{ik}, developed. The results of calculations for all other systems are presented in appendix 1. Seven computer programmes were written in Algol language for miscellaneous and repetitive calculations. These are described in appendix 2.

CHAPTER 2

Theory of Irreversible Thermodynamics as Applied to Transport Processes in Binary Electrolyte Solutions.

2.1 Entropy Production in an Irreversible Process: Systems undergoing irreversible processes may be divided into macroscopically small local subsystems. If each subsystem is considered to be at local equilibrium then the laws of classical thermodynamics are valid. If perturbations from equilibrium are not large, the change of entropy of the systems in the irreversible process is given by

$$dS = d_eS + d_iS \qquad (2.1)$$

where d_eS is the flow of entropy due to interactions with the exterior and d_iS is the production of entropy inside the system. d_iS is zero for a reversible process but is always positive if changes occur irreversibly.

For an isolated system in which neither energy nor matter can be exchanged,

$$d_eS = 0 \qquad (2.2)$$

and the entropy production is given by

$$dS = d_iS \geq 0 \qquad (2.3)$$

If two irreversible processes, 1 and 2, occur in an isolated system then

$$dS = d_iS^1 + d_iS^2 \geq 0 \qquad (2.4)$$

Applying eqns(2.2) and (2.3), it is postulated that

$$d_iS^1 \geq 0 \text{ and } d_iS^2 \geq 0 \qquad (2.5)$$

A physical situation in which $d_iS^1 < 0$ and $d_iS^2 < 0$ is excluded That is, in every macroscopic region of the system the entropy production is positive.

In coupled chemical reactions, however, if two simultaneous reactions, 1 and 2, occur, then it is possible that the rate of entropy production in 1, d_iS^1/dt, is positive and in 2, d_iS^2/dt, is negative provided their sum is positive. The reactions are then coupled, reaction, 1, proceeding spontaneously and driving the second against its natural or spontaneous tendency. Such thermodynamic coupling is an essential feature of living systems involved in active transport[18].

2.2 <u>The rate of Entropy Production and the Dissipation Function:</u> The rate of entropy production for a system, d_iS/dt, may be considered to be the sum of contributions from all volume elements so that

$$\frac{d_iS}{dt} = \int_V \sigma \, dV \qquad (2.6)$$

Where σ is the local rate of production of entropy per unit volume, V.

From eqn(2.1), the rate of change of entropy is

$$\frac{dS}{dt} = \frac{d_eS}{dt} + \frac{d_iS}{dt} \qquad (2.7)$$

The total entropy of a system, S, may be defined in terms of the local entropy density (entropy per unit volume), S_V, by[20a]

$$S = \int_V S_V dV \qquad (2.8)$$

The change in total entropy with time becomes

$$\frac{dS}{dt} = \int_V \frac{\partial s_v}{\partial t}\, dV \qquad (2.9)$$

$\frac{d_eS}{dt}$ is related to the flow of entropy, J_s, by

$$\frac{d_eS}{dt} = - \int_V \mathrm{div}\, J_s\, dV \qquad (2.10)$$

Substituting eqns(2.6), (2.9) and (2.10) in eqn(2.7), we obtain

$$\int_V \frac{\partial s_v}{\partial t}\, dV = - \int_V \mathrm{div}\, J_s\, dV + \int_V \sigma\, dV \qquad (2.11)$$

Eqn(2.11) describes the total rate of change of entropy with time. For any local change it becomes

$$\frac{\partial s_v}{\partial t} = - \mathrm{div}\, J_s + \sigma \qquad (2.12)$$

The rate of change in local entropy is therefore equal to the entropy produced, σ, plus the entropy flow term, $-\mathrm{div}\, J_s$.

The necessary conditions for a state of equilibrium are that

$$\frac{\partial s_v}{\partial t} = 0 \text{ and } \mathrm{div}\, J_s = 0 \qquad (2.13)$$

and therefore from eqn(2.12),

$$\sigma = 0 \qquad (2.14)$$

For a system in steady state, however,

$$\frac{\partial S_v}{\partial t} = \Phi$$

and $$\operatorname{div} J_s = \sigma \qquad (2.15)$$

For a continuous system, the entropy production, σ, is given by the relationship[19],

$$\sigma = \left(\frac{J_s}{T}\right) \operatorname{grad}\ (-T) + \sum_{i=1}^{n} \left(\frac{J_i}{T}\right) \operatorname{grad}\ (-\tilde{\mu}_i) + J_{ch} \cdot \left(\frac{A_i}{T}\right) \qquad (2.16)$$

where J_s, J_i and J_{ch} are the flow of heat, matter and chemical reaction (rate) multiplied by their conjugate driving forces, defined by the negative gradients of the temperature, T, electrochemical potential, $\tilde{\mu}_i$, and the affinity of chemical reaction, A_i, respectively.

σ may be replaced by the dissipation function, $\Phi = T\sigma$. It has the dimensions of energy per unit time and is a measure of the rate of local dissipation of free energy. Relation (2.16) may be reformulated as

$$\Phi = T\sigma = J_s \operatorname{grad}\ (-T) + \sum_{i=1}^{n} J_i \operatorname{grad}\ (-\tilde{\mu}_i) + J_{ch} \cdot A_i > 0 \qquad (2.17)$$

For isothermal transport processes in electrolyte solutions in which no chemical reactions take place, the dissipation function, Φ, is given by the second term on the right hand side of eqn(2.17) and defined as the sum of products of conjugate flows and forces. For a system consisting of a neutral solvent, 0, and n solute species, the dissipation function is

$$\Phi = T\sigma = \sum_{i=1}^{n} J_i X_i \qquad (2.18)$$

where J_i is the mass-fixed flow of species, i, in moles/cm^2 sec, and X_i is the thermodynamic force in joules/ mole cm.

2.3 Frames of Reference for Flows: The definition of flows presented in eqn(2.18) is given in terms of an arbitrary frame of reference. It has been shown[20], however, that any frame of reference may be chosen. The choice depends on the purpose of study. The transport equations for binary electrolytes become intuitively more accessible if the solvent fixed rather than, for example, the volume fixed or molar average velocity frame of reference is used. Relations exist for the conversion from one frame of reference into another[21,22a,23,24].

For a binary electrolyte solution consisting of cation, 1, anion, 2, of valencies Z_1 and Z_2 respectively and solvent, 0, eqn(2,18) becomes

$$\Phi = J_1X_1 + J_2X_2 + J_0X_0 \qquad (2.19)$$

where X_i are the gradients of electrochemical potentials so that

$$X_i = -\frac{\partial \tilde{\mu}_i}{\partial x} = -\left(\frac{\partial \mu_i}{\partial x} + Z_i F \frac{\partial \phi}{\partial x}\right) \qquad (2.20)$$

where x is the distance parameter, $\frac{\partial \mu i}{\partial x}$ and $\frac{\partial \phi}{\partial x}$ are the gradients of chemical and electrical potentials.

The Gibbs-Duhem equation states that

$$n_1 d\tilde{\mu}_1 + n_2 d\tilde{\mu}_2 + n_0 d\tilde{\mu}_0 = 0 \qquad (2.21)$$

Dividing eqn(2.21) by the volume, V, and differentiating with respect to x, we obtain

$$c_1X_1 + c_2X_2 + c_0X_0 = 0 \tag{2.22}$$

Where $c_i = n_i/V$, are the concentrations per unit volume. Eqn(2.22) shows that the forces on 1, 2 and 0 are not independent. Eliminating X_0 from eqn(2.19) and (2.22), the dissipation function becomes

$$\Phi = (J_1 - \frac{J_0c_1}{c_0})X_1 + (J_2 - \frac{J_0c_2}{c_0})X_2 \tag{2.23}$$

The flow, J_i, is given by the product of concentration, c_i, and velocity, v_i, of the species, i, so that

$$J_i = c_iv_i \tag{2.24}$$

In these terms, $(J_i - J_0c_i/c_0)$ of eqn(2.23) is defined as $c_i \times (v_i - v_0)$. It is therefore the flow of species, i, relative to solvent, 0, and is given the symbol J_i^0 so that

$$J_i^0 = c_i(v_i - v_0) \tag{2.25}$$

The dissipation function may therefore be represented in terms of two flows and two forces, J_1^0, J_2^0 and X_1, X_2 respectively;

$$\Phi = J_1^0X_1 + J_2^0X_2 \tag{2.26}$$

2.4 The Phenomenological Equations and the Onsager Reciprocal Relations: In situations where a system deviates only slightly from equilibrium, linear phenomenological equations may be written relating the flow of a species, i, to all other forces so that for an n+1 component system,

$$J_i = \sum_{k=0}^{n} L_{ik}X_k \qquad i=0,1,2,3\ldots n \tag{2.27}$$

The terms L_{ik} are the phenomenological coefficients and are independent of the forces.

For a one flow-one force system, the phenomenological equation is

$$J_i = L_{ii}X_i \tag{2.28}$$

In this simple situation, the flow of i is proportional to the force X_i. The magnitude of L_{ii} is a specific measure of the mobility of the species and from the general definition of a force equation, one may obtain, under solely electrical or activity gradients, expressions which correspond to the simple laws of Ohm and Fick. In systems of two components, of which a binary electrolyte solution, on solvent fixed frame of reference, is an example,

$$\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 \\ J_2 &= L_{21}X_1 + L_{22}X_2 \end{aligned} \tag{2.29}$$

The direct coefficients, L_{11} and L_{22}, remain but, in addition, the L_{12}* measure the degree to which a flow of species, 1, is affected by a force on species, 2. The coefficients, L_{12} and L_{21}, are the cross or coupling coefficients. Using the principle of microscopic reversibility, Onsager[5] has shown

* and L_{21}

that close to equilibrium

$$L_{12} = L_{21} \qquad (2.30)$$

In the generalised form eqn(2.30) may be written as

$$L_{ik} = L_{ki} \quad i,k=0,1,2,3,\ldots n \qquad (2.31)$$

These are called Onsager Reciprocal Relations(ORR) and were shown to hold under statistical mechanical models[5]. To characterise a system of n forces and n flows, n^2 such coefficients would be required but under ORR they are reduced to $\frac{1}{2}n(n+1)$. Thus for a two component system, only three such coefficients, L_{11}, L_{12}(equal to L_{21}) and L_{22}, are required. In all cases the cross coefficients are constrained by the inequalities

$$L_{ii}L_{kk} \geq (L_{ik})^2 \qquad (2.32)$$

that is, the direct coefficients must be positive but the cross coefficients may either be positive or negative.

In binary electrolyte solutions, the direct coefficients, L_{ii}, are the transport or mobility coefficients and measure the mobility which an ion would have if there were no interactions with the oppositely charged ions. L_{ik} mean the mobility interaction coefficients and directly determine the cation-anion kinetic coupling. Both the direct, L_{ii}, and cross L_{ik}, coefficients are dependent on the frame of reference. Thus, on the solvent fixed frame of reference they have contributions from the solvent as well.

2.5 Inverse form of Phenomenological Equations - The Frictional Coefficients: An alternative representation of phenomenological coefficients has the form

$$X_i = \sum_{k=0}^{n} R_{ik} J_k \qquad i=0,1,2,3,\dots n \qquad (2.33)$$

in which the Onsager reciprocal relations hold, that is

$$R_{ik} = R_{ik} \qquad (2.34)$$

Eqn(2.33) expresses the force, X_i, as a linear function of all the flows. The direct coefficients, R_{ii}, determine the extent of friction between similar ions while the cross coefficients, R_{ik}, determine the friction between counter ions. Both the R_{ii} and R_{ik} coefficients have the dimentions of force per unit flow.

For binary electrolyte solutions on solvent fixed frame of reference for flows, eqn(2.33) reduces to

$$\begin{aligned} X_1 &= R_{11}J_1 + R_{12}J_2 \\ X_2 &= R_{21}J_1 + R_{22}J_2 \qquad (2.35) \end{aligned}$$

in which $R_{12} = R_{21}$ by ORR. Eqn(2.35) is the analogue of eqn (2.29) which is in terms of L_{ik} $(i,k = 1,2)$ coefficients.

Since neither the X_i nor the J_i are independent, the R_{ik} are not unique. However, under an arbitrary assumption

$$\sum_{k=0}^{n} c_k R_{ik} = 0 \qquad i=0,1,2,3,\dots n \qquad (2.36)$$

the R_{ik} become uniquely defined^{25}. Moreover, with this assumption, the R_{ik} become reference frame independent[22b] and additional frictional coefficients, R_{i0}, can be obtained, which specifically measure the friction between an ion and the solvent.

For a three component system eqn(2.36) becomes

$$c_0R_{i0} + c_1R_{i1} + c_2R_{i2} = 0$$

$$\text{or } c_0R_{i0} = -(c_1R_{i1} + c_2R_{i2}) \qquad i=0,1,2 \qquad (2.37)$$

The coefficients, R_{ii} and R_{ik} $(i,k = 1,2)$, may be obtained by matrix inversion of the L_{ii} and L_{ik} coefficients, which on substitution in eqn(2.37) give $c_0R_{i0}(i = 1,2)$. The $c_0R_{i0}(i=1,2)$ may then be used to obtain $c_0R_{i0}(i = 0)$.

2.6 Experimentally Measureable Transport Properties of Binary Electrolytes in Terms of Phenomenological Coefficients[15a]:

Consider a binary electrolyte, $C_{r_1}A_{r_2}$, in a neutral solvent, 0, which dissociates as

$$C_{r_1}A_{r_2} = r_1C^{Z_1} + r_2A^{Z_2} \qquad (2.38)$$

r_1 and r_2 are the stoichiometric coefficients of dissociation of cations, C, and anions, A of valencies Z_1 and Z_2 respectively.

Chemical potential of the electrolyte, μ_{12}, is equal to the sum of the chemical potentials of ions i.e.,

$$\mu_{12} = r_1\mu_1 + r_2\mu_2 \qquad (2.39)$$

and from the condition of electroneutrality, we have

$$Z_1r_1 + Z_2r_2 = 0 \tag{2.40}$$

The phenomenological equations on solvent fixed frame of reference are given by eqns(2.29) and the forces X_i by eqn(2.20).

To obtain numerical values of the four L_{ik} coefficients of eqns(2.29), four independent experimental quantities are needed and the four suitable ones are the conductance, Λ, volume fixed diffusion coefficient, Dv, Hittorf transport number, t^h and the e.m.f. transport number, t^c. Because of Onsager reciprocal relations, the cross coefficients are identical i.e. $L_{12} = L_{21}$. Therefore only three independent quantities are required. (It will be shown that the two transport numbers, t^h and t^c, become identical under the condition of ORR).

We, however, derive expressions for all the four quantities, Λ, t^h, t^c and Dv in terms of L_{ik} coefficients.

2.6.1 <u>Conductance</u>: By Ohm's law, current density, I, is given by

$$I = \kappa(-\partial\phi/\partial x) \tag{2.41}$$

where κ is the specific conductivity. By definition, equivalent conductivity, Λ, becomes

$$\Lambda = (10^3/N).I/(-\partial\phi/\partial x) \tag{2.42}$$

where N is the equivalent concentration.

In terms of flows, J_i, I becomes

$$I = (Z_1 J_1 + Z_2 J_2)F \qquad (2.43)$$

and the forces X_i are given by

$$X_i = -Z_i F \partial\phi/\partial x \qquad i=1,2 \qquad (2.44)$$

The gradients of chemical potentials, μ_i, of the ions are zero at uniform concentration.

An expression for equivalent conductivity, Λ, is obtained from equations (2.29), (2.42), (2.43) and (2.44);

$$\Lambda = (10^3 F^2/N)(Z_1^2 L_{11} + Z_1 Z_2 (L_{12} + L_{21}) + Z_2^2 L_{22}) \qquad (2.45)$$

At infinite dilution, the cross coefficients L_{ik} are zero and so

$$\Lambda^0 = (10^3 F^2/N)(Z_1^2 L_{11}^0 + Z_2^2 L_{22}^0) = \lambda_1^0 + \lambda_2^0 \qquad (2.46)$$

where λ_1^0 and λ_2^0 are equivalent conductivities of cations and anions at infinite dilution. At finite concentrations, L_{ik} are positive and increase rapidly as concentration increases.

Λ is measured on an apparatus-fixed frame of reference but it may be easily shown[26] that it is independent of the frame of reference.

2.6.2 Hittorf Transport Numbers: Hittorf transport number, t_i^h, is defined as the fraction of the current carried by the ith ion relative to solvent in a solution of uniform concentration. In terms of flow, J_i, t_i^h can be represented as

$$t_i^h = Z_iFJ_i/I = Z_iFJ_i/(Z_1J_1 + Z_2J_2)F \qquad (2.47)$$

Substitution of equations (2.29), (2.43) and (2.44) in (2.47) leads

$$t_1^h = (Z_1^2L_{11} + Z_1Z_2L_{12})/\alpha \qquad (2.48)$$

$$\text{where } \alpha = Z_1^2L_{11} + Z_1Z_2(L_{12} + L_{21}) + Z_2^2\,L_{22} \qquad (2.49)$$

and t_i^h is the cationic transport number.

2.6.3 E.m.f. Transport Numbers: An electrochemical cell, having identical electrodes but which has a varying composition, may be represented as

$$Ag/AgNO_3(c_1) \;\vdots\; AgNO_3(c_2)/Ag$$

where $c_2 > c_1$. In this system diffusion would occur and owing to different ion mobilities a charge separation would take place. After a short time[27], powerful coulombic forces speed up the slow moving ions and slow down the fast moving ones so that no electric current flows through the solution. Thus

$$I = (Z_1J_1 + Z_2J_2)F = 0 \qquad (2.50)$$

In this situation, gradient of chemical potentials, $\partial\mu_i/\partial x$, and the gradient of electrical potential, $\partial\phi/\partial x$, are non-zero.

Substituting equations (2.29) and (2.20) in eqn(2.50),

$$-F\,\partial\phi/\partial x = (t_1^c/Z_1).\partial\mu_1/\partial x_1 + (t_2^c/Z_2).\partial\mu_2/\partial x \qquad (2.51)$$

where $t_1^c/Z_1 = (Z_1L_{11} + Z_2L_{21})/\alpha$

and $t_2^c/Z_2 = (Z_2L_{22} + Z_1L_{12})/\alpha \qquad (2.52)$

where α is as defined in eqn(2.49) and t_i^c are the e.m.f. transport numbers of the ions i.

Comparis~~i~~on of Hittorf and e.m.f. transport numbers, defined in equations(2.48) and (2.52) shows that they are equal only if $L_{12} = L_{21}$ and so only if the ORR are obeyed. Experimental measurements of a number of systems[28,29] show no difference in the Hittorf and e.m.f. transport numbers and so the ORR are justified.

2.6.4 Isothermal Diffusion: Diffusion occurs under a concentration gradient of salt and therefore $\partial\mu_{12}/\partial x$ is not zero and no electrical current flows so that from equations (2.40) and (2.50),

$$J_1/r_1 = J_2/r_2 = J \qquad (2.53)$$

Eqn(2.53) shows that the cationic and anionic motions are coupled and the two ions move together in the proportion present in the neutral salt molecule and so J is the solvent fixed flow of electrolyte as a whole.

The diffusion coefficient for a binary system is described[16a] by

$$J = \frac{J_1}{r_1} = -(D_0/1000)\partial c/\partial x = -L\partial\mu_{12}/\partial x \qquad (2.54)$$

where D_0 is the solvent fixed diffusion coefficient in cm^2/sec and L is the thermodynamic diffusion coefficient in $moles^2/joules\ cm\ sec$. Eqn(2.54) may be rewritten as

$$-(D_0/1000)\partial c/\partial x = -L\partial\mu_{12}/\partial c . \partial c/\partial x$$

so that $$L = D_0/(1000 . \partial\mu_{12}/\partial c) \qquad (2.55)$$

but $$\partial\mu_{12}/\partial c = (1 + cd\ln y/dc)RTr/c \qquad (2.56)$$

where $$r = r_1 + r_2$$

and y is the mean molar activity coefficient. Substituting equations (2.55) and (2.56) in eqn(2.54), we get

$$J=J_1/r_1 = -(\partial\mu_{12}/\partial x).D_0.c/1000Rtr(1 + cd\ln y/dc) \qquad (2.57)$$

From eqn(2.29) for J_1 and the equations (2.20), (2.39), (2.50) and (2.51), we obtain

$$J=J_1/r_1=(\partial\mu_{12}/\partial x)(Z_1Z_2/r_1r_2)(L_{11}L_{22}-L_{12}L_{21})/\alpha \qquad (2.58)$$

Comparing equations (2.57) and (2.58), we get

$$D_0 = -1000RTr(1 + cd\ln y/dc)/c)$$

$$\times(Z_1Z_2/r_1r_2)((L_{11}L_{22}-L_{12}L_{21})/\alpha \qquad (2.59)$$

In the literature, volume fixed diffusion coefficient, D_v, and mean molal activity coefficient, γ, are reported. Transformations from one frame of reference into another exist.[22,23b,24] It may be shown[30] that

$$D_0/(1 + c\,d\ln y/dc) = D_v/(1 + m\,d\ln\gamma/dm) \qquad (2.60)$$

where m is the molality of the solution.
Substituting eqn(2.60) in eqn(2.59), we get

$$D_v=-1000RTrZ_1Z_2(1+m\,d\ln\gamma/dm)(L_{11}L_{22}-L_{12}L_{21})/r_1r_2c\alpha \quad (2.61)$$

where α is as defined in eqn(2.49).

Equations (2.45), (2.48), (2.52) and (2.61) are derived for the four measureable transport quantities. These four equations can be solved simultaneously to obtain L_{ik} in terms of these quantities. The resulting equation is

$$L_{ik}/N=t_i^h t_k^c\Lambda/10^3F^2Z_iZ_k+r_ir_kD_v/10^3RTrr_1Z_1(1+m\,d\ln\gamma/dm) \quad (2.62)$$

Equation (2.62) holds for any neutral solvent and applies to both weak and strong electrolytes. If ORR are assumed then $t_i^c = t_i^h$ and eqn(2.62) becomes

$$L_{ik}/N = t_it_k\Lambda/10^3F^2Z_iZ_k$$

$$+ r_ir_kD_v/10^3RTrZ_1(1 + m\,d\ln\gamma/dm) \qquad (2.63)$$

From eqn(2.63), the three phenomenological coefficients, L_{11}, L_{12}(equal to L_{21}) and L_{22} may be obtained.

If F is the coulombs/equivalent, R in joules/mole deg., and D_v in cm^2/sec., the units of L_{ik} are in mole^2/joule cm sec.

2.7 Expressions for R_{ik}: The coefficients, R_{ik}, are obtained by the matrix inversion of the L_{ik}. For a binary system, the R_{ik} are given by

$$R_{11} = \frac{L_{22}}{L}$$

$$R_{12} = -\frac{L_{21}}{L}$$

$$R_{21} = -\frac{L_{21}}{L}$$

and

$$R_{22} = \frac{L_{11}}{L} \qquad (2.64)$$

where

$$L = \begin{vmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{vmatrix} = L_{11}L_{22} - L_{12}L_{21} \qquad (2.65)$$

Substituting L_{11}/N, L_{12}/N, L_{21}/N and L_{22}/N in the right hand side of expression(2.64), we directly obtain NR_{11}, NR_{12}, NR_{21} and NR_{22} respectively.

The coefficients, R_{i0}, are obtained from R_{ik} using the relations as defined in eqn(2.37);

$$R_{10} = -(r_1R_{11} + r_2R_{12})c/c_0$$

$$R_{20} = -(r_1R_{12} + r_2R_{22})c/c_0$$

$$R_{00} = -(r_1R_{10} + r_2R_{20})c/c_0 \qquad (2.66)$$

in which c_0 is the solvent concentration given by

$$c_0 = 1000\,{}^{c}/_{m}M_0 \qquad (2.67)$$

where M_0 is the molecular weight of the solvent.

The coefficients, R_{ik}, can also be derived directly in terms of the transport quantities using phenomenological equations (2.35). The procedure is the same as described for L_{ik} coefficients. The resulting expressions are

$$NR_{11} = (10^3F^2Z_1^2/\Lambda) - (Z_1Z_2/r_1r_2)(t_2^2/Z_2^2).M^1$$

$$NR_{12} = (10^3F^2Z_1Z_2/\Lambda) + (Z_1Z_2/r_1r_2)(t_2t_1/Z_2Z_1).M^1$$

$$NR_{22} = (10^3F^2Z_2^2/\Lambda) - (Z_1Z_2/r_1r_2)(t_1^2/Z_1^2).M^1 \qquad (2.68)$$

where $M^1 = 10^3RTr\ r_1Z_1(1+m\mathrm{dln}\gamma/\mathrm{dm})/D_v$

$$c_0R_{10} = -10^3RTrt_2(1+m\mathrm{dln}\gamma/\mathrm{dm})/r_1D_v$$

$$c_0R_{20} = -10^3RTrt_1(1+m\mathrm{dln}\gamma/\mathrm{dm})/r_2D_v$$

$$R_{00}/N = (c/Nc_0^2)10^3RTr(1+m\mathrm{dln}\gamma/\mathrm{dm})/D_v \qquad (2.69)$$

The units of R_{ik} coefficients are joule cm sec.mole^{-2}.

2.8 Influence of Ion Pairing on Phenomenological Coefficients: The presence of ion pairs in binary electrolytes has been recognised over the last fifty years or so and it is of interest to examine the thermodynamic analysis where the neutral ion pair may be present. Eqn(2.35) is defined for a completely dissociated electrolyte. If a neutral species, 3, exists in addition to cations, 1, and anions 2, then on the solvent fixed frame of reference the phenomenological equantions are

$$x_i = r_{i1}j_1 + r_{i2}j_2 + r_{i3}j_3 \qquad i=1,2,3 \qquad (2.70)$$

where x_i are the thermodynamic forces and j_i are the conjugate flows for the free species i. r_{ik} are the Onsager frictional coefficients. If the electrolyte is a symmetrical salt, the stoicheiometric coefficients of ionisation, r_1 and r_2, are equal to unity and eqn(2.39) becomes

$$\mu_1 + \mu_2 = \mu_3$$

where μ_3 is the chemical potential of the ion pair. In terms of forces

$$x_1 + x_2 = x_3 \qquad (2.71)$$

Substituting eqn(2.70) in eqn(2.71) and comparing the coefficients of j_i, we get

$$r_{i1} + r_{i2} = r_{i3} \qquad (2.72)$$

By ORR,

$$r_{12} = r_{21},\ r_{13} = r_{31} \text{ and } r_{23} = r_{32} \qquad (2.73)$$

From equations (2.70) and (2.72) for i = 1,2, we get

$$x_i = r_{i1}(j_1+j_3)+r_{i2}(j_2 + j_3) \qquad i=1,2 \qquad (2.74)$$

Since J_i is the total flow of species i, therefore

$$J_i = j_i + j_3 \qquad i = 1,2$$

Eqn(2.74) becomes

$$x_i = r_{i1}J_1 + r_{i2}J_2 \qquad i=1,2 \qquad (2.75)$$

Using purely binary approach for the same system the phenomenological equations are

$$X_i = R_{i1}J_1 + r_{i2}J_2 \qquad i=1,2 \qquad (2.76)$$

The equations (2.75) and (2.76) are identical in all circumstances. The measured flows, J_i, would be (j_i+j_3) e.g., in electrical conductivity the current density, I, is given by

$$I = (Z_1j_1 + Z_2j_2)F = (Z_1J_1 + Z_2J_2)F \qquad (2.77)$$

This shows that either ionic or net flows may be used.

The transport number, t_i, however, equals Z_iJ_iF/I and the observed flow, e.g., in the Hittorf measurement, is the net flow, J_i. Thus the stoicheiometric coefficient, R_{ik}, equals the specific coefficient, r_{ik}.

CHAPTER 3

A Survey of Transport Properties of Binary Electrolyte Solutions and Selection of a System for Experimental Study:

The theory of irreversible thermodynamics developed in chapter 2 shows that at least three measureable transport properties and activity coefficients are required to characterise an electrolyte system completely in terms of Onsager transport, L_{ik} and inverse frictional, R_{ik}, coefficients. These properties are conductance, transport numbers and diffusion. In the alkali halide series literature data were complete for lithium, sodium and potassium chlorides in the concentration range 0-3M. Miller[16a] collected these and applied his theoretical analysis to obtain the L_{ik} and R_{ik} coefficients.

The remaining chlorides of the alkali metal series, those of rubidium and caesium, were therefore of considerable interest. It was therefore decided to survey the existing literature for their transport data and to obtain experimentally those which are required for a complete analysis.

It was found that in concentrated solutions conductance and diffusion data for rubidium chloride and conductance data alone for caesium chloride were lacking. In the dilute region, $c < 0.25M$, the conductance and transport numbers data for both and diffusion data for rubidium chloride were not available. It was therefore necessary to measure the electrical conductance of both (rubidium and caesium chlorides) and diffusion coefficients of rubidium chloride for the whole range of concentration, 0-3M. The experimental measurements are described in chapters 4 and 5.

In dilute solutions, $c < 0.25$, only transport numbers are left to be measured and with their availability, the whole transport data for the concentration range, 0-3M, would be complete.

For the literature survey we searched the chemical abstracts for references from 1930 onwards and consulted the data compiled in standard texts[a,b,c] and reviews[d,e,f,g].

Our literature survey coincided with that of Chapman and Newman[h] who collected from the literature all the available transport data for sixty one binary electrolytes. Out

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a) H.S. Harned and B.B. Owen 'Physical Chemistry of Electrolyte Solutions', 3rd Ed., N.Y., Reinhold Publishing Corp., 1957.

b) R.A. Robinson and R.H. Stokes, 'Electrolyte Solutions', 2nd Ed., London, Butterworths Sci. Publications, 1959.

c) R. Parsons 'Handbook of Electrochemical Constants', London, Butterworths Sci. Publications, 1959.

d) A. Eucken, Ed. Landolt - Bornstein. 'Zahlenwerte und Funktionen aus Physik, Chimie, Astronomie', Geophysik und Technik, 6th ed., vol. 2, part 7. Berlin: Springer - Verlag, 1960.

e) E.W. Washburn Ed. International Critical Tables of Numerical data, Physics, Chemistry and Technology. New York, McGraw - Hill Book Co., Inc., 1926.

f) E.A. Kaimakov and N.L. Varshavskaya. 'Measurement of Transport numbers in Aqueous Solutions of Electrolytes'. Uspekhi Khimii, 1966, 35, 201-288.*

g) J. Timmerman, 'The Physico - Chemical Constants of Binary Systems in Concentrated Solutions', New York, Interscience Publishers Inc., 1960.

* Russ. Chem. Rev., Feb. 1966, P.89-101(English).

of these, data were partially complete for twenty eight systems. Phenomenological coefficients for these systems were calculated. The results are given in appendix-1.

In table 3.1 we present a list of missing transport and activity data for aqueous solutions of 1:1, 1:2, 2:1 and 2:2 electrolytes. <u>All</u> means data is missing for the whole range of concentration, 0-3M, and - denotes data is complete. The concentrations are in moles per litre and the temperature is 25°C unless otherwise mentioned.

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h. T.W. Chapman and J. Newman, 'A compilation of Selected Thermodynamic and Transport Properties of Binary Electrolytes in aqueous solutions', UCRL - 17767, AEC contract W - 7405-eng - 48, University of California, Lawrence Radiation Laboratory, Berkeley, California.

Table 3.1

Transport data that has not been measured experimentally for 1:1, 1:2, 2:1 and 2:2 Electrolytes

Electrolyte		Λ	t_+	D_v	γ
Chlorides	H^+, Li^+, Na^+, K^+	–	–	–	–
	Rb^+	all	< 0.25	> 0.01	–
	Cs^+	> 0.007	< 0.25	–	–
	NH_4^+	–	> 0.2	< 0.1	–
Bromides	H^+	–	all	all	–
	Li^+	all	all	–	–
	Na^+	–	all	–	–
	K^+	–	> 1.0	–	–
	Rb^+	–	all	all	–
	Cs^+	all	all	all	–
Iodides	H^+	> 0.1	> 0.1	all	–
	Li^+	all	all	all	–
	Na^+	–	all	–	–
	K^+	–	> 1.0	–	–
	Rb^+, Cs^+	all	all	all	–
Hydroxides	Li^+	–	all	all	–
	Na^+	–	> 1.0	> 2.0	–
	K^+	–	> 0.1	all	–
	Rb^+	all	all	all	all
	Cs^+	all	all	all	> 1.0

Table 3.1 continued.

Electrolyte		Λ	t_+	D_v	γ
Nitrates	H^+	-	-	0.45	-
	Li^+	-	all	-	-
	Na^+	-	all*	-	-
	K^+	-	>0.1	>0.1	-
	Rb^+	all	all	all	<0.1
	Cs^+	all	all	$>.014$	-
	NH_4^+	-	<0.1 & >0.2	-	-
Chlorates	H^+	all	all	all	all
	Li^+	-	all	-	-
	Na^+	-	all	-	-
	K^+, Rb^+, Cs^+	all	all	all	-
Perchlorates	H^+	>1.0	-	all	-
	Li^+	-	all	all	-
	Na^+	-	all**	-	-
	K^+	all	all	all	-
	Rb	all	all	all	-
	Cs^+	all	all	all	-

* Except at 1,2 and 4M.

** except at 1M.

Table 3.1 continued.

Electrolyte		Λ	t_+	D_v	γ
Fluorides	H^+	all	-	all	-
	Li^+	all	all	all	-
	Na^+	all	-	all	-
	K^+, Rb^+, Cs^+	all	all	all	-
Chlorides	Zn^{++}	all	-	all	-
	Mg^{++}	-	all	all	-
	Cd^{++}	<0.05	-	>0.2	-
Bromides	Zn^{++}	all	-	all	-
	Mg^{++}	all	all	all	-
	Cd^{++}	all	-	0.2	-
Iodides	Zn^{++}	all	-	all	-
	Mg^{++}	all	all	all	-
	Cd^{++}	-	all	$<\cdot01$ & >1.2	-
Sulfates	H^+	-	-	-	-
	Li^+	>0.7	-	>0.005	-
	Na^+	>0.1	>0.1	>1.0	-
	K^+	>0.5	>0.5	>0.5	>0.5
	Rb^+	all	all	all	<0.1
	Cs^+	all	all	>0.005	<0.1

Table 3.1 continued.

Electrolytes		Λ	t_+	D_v	γ
Sulfates	Zn^{++}	all	-	>0.01	-
	Mg^{++}	all	all	all	-
	Cd^{++}	>1.0	-	>0.5	-
	Cu^{++}	-	>0.5	>0.1	-
	Ni^{++}	>1.0	all	all	-
	Mn^{++}	>1.0	all	all	-
KCl	0°	>1M	<0.01	<0.1	< .05
	18°	>1M	<0.01	<0.1	< .05
	35°	<1.0M	<0.01	<0.1	< .05
	50°	<1.0M	<0.01	<0.1	< .05

CHAPTER 4

Measurement of Diffusivity

4.1 Experimental methods applied to the study of diffusivity in electrolyte solutions: We report here briefly the various methods which have been applied to the study of diffusivity in electrolyte solutions. Technical details of these methods are not discussed since a through review on the subject is available.[31]

4.1.1 Conductometric Method: This method involves the measurement of conductances of solutions as diffusion proceeds with time. Its application is limited to dilute solutions only, up to 0.01M for 1:1 and 0.005M for 2:2, 2:1 and 1:2 electrolytes. The achieved accuracy is ± 0.1 to 0.2%.

4.1.2 Gouy Interferometric Method: This is an absolute method and involves the measurement of interference fringes obtained on photographic plates when a beam of monochromatic light is passed through a cell in which a concentration gradient exists. It has been applied to 1:1 electrolytes only upto an accuracy of ± 0.1 to 0.2%. The method gives integral diffusion coefficients.

4.1.3 Rayleigh Interferometric Method: The principle involved in this method is the same as that of the Gouy method except that the photographic system is incorporated with a cylinderical lens. It gives differential diffusion coefficients directly and therefore is preferable to the Gouy method. It has been applied to 1:1 electrolytes only.

4.1.4 Stokes Diaphragm Cell Method: This is a relative method. The cells need to be calibrated with a standard electrolyte diffusion coefficients for which are known from absolute measurements. Only those electrolytes which are similar in nature to the standard electrolyte can be studied by this method. The method has been successfully applied to 1:1 electrolytes to an accuracy of 0.1 to 0.2%. The only other systems studied by this method are sodium and copper sulfates[32,33] to an accuracy of 1 to 5%.

4.1.5 Photometric Method: This method works on the principle of absorption of light by a diffusing electrolyte coloured solutions. The only system studied is copper sulfate[34] to 2% accuracy.

4.1.6 Diffraction Micro Method: The principle involved is the diffraction of light when it passes through a solution each layer of which acts as a prism. It has been applied to the study of cadmium chloride[35a], cadmium sulfate[35b] and lead nitrate[35b] solutions. The accuracy attained is 1 to 3%.

4.1.7 Porous Frit Method: A porous plate is soaked in an electrolyte solution and then it is dipped in a bath of solvent or a solution of lower concentration. The diffusion coefficients obtained are with respect to the cell fixed frame of reference. The method is useful in the study of weak and complexing electrolytes. It has been applied to the study of zinc sulfate(0.03-0.25M)[36] and cadmium iodide (0.01-1.0M)[37] to an accuracy of 1-2%.

4.1.8 Selection of a method for the study of Diffusivity in Rubidium Chloride Solutions: The above study of the various methods for the determination of diffusion coefficients shows that the high precision methods have been applied to 1:1 electrolytes only. In the light of this survey one of the absolute methods or the diaphragm cell method seemed to be the most appropriate for the diffusivity study of rubidium chloride solutions. For the present work the diaphragm cell method was chosen for the following reasons:

a) Rubidium chloride falls between potassium and caesium chlorides in the alkali chloride series and the nature of these salts is similar.

b) The cells could be calibrated with potassium chloride solutions, the diffusion data for which was available in the literature from absolute measurements.

c) Reproducibility of 0.1 to 0.2% could be easily approached.

d) Diffusion data for Rubidium chloride was required in the concentrated solutions only and this method was applicable for concentrations above 0.05M.

e) The method was appropriate in cases where diffusion coefficients did not change rapidly with concentration and this condition was fulfilled by 1:1 electrolytes.

f) Large volumes of solutions were available for concentration analysis.

4.2 The Diaphragm Cell Method: The diaphragm cell technique was first introduced by Northrop and Anson[38] in 1929 and later modified by a number of workers[39,40,41,42,43]. It has its present standing due to the work of the Stokes[44]. The theoretical and experimental aspects of the method are reviewed by Robinson and Stokes[45].

In this method diffusion of solute takes place through a porous diaphragm separating two compartments containing solutions of different concentrations which are maintained uniform by mechanical stirring. The concentration changes take place sufficiently slowly so that a pseudo steady state* may be assumed to prevail in the capillary pores of the diaphragm. Barnes[46] has shown that this assumption does not lead to an appreciable error if the volumes of the solutions in the two compartments are sufficiently large compared with the space in the diaphragm. In this situation diffusion coefficient may be obtained from the Fick's law

$$J(t) = D(-\frac{\partial c}{\partial x}) \qquad (4.1)$$

where J(t)**is the flux at time, t, D is the differential diffusion coefficient defined as the amount in moles of the solute diffusing through unit area of cross-section per unit time per unit concentration difference and $\frac{\partial c}{\partial x}$ is the concentration gradient. Negative sign shows decrease in concentration as diffusion proceeds.

Some inherent disadvantages from which this method suffered is its earlier stage of improvement have now been largely overcome. These disadvantages and their remedies are as follows:

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* Theoretically a steady state of flux and concentration distribution are reached[31] only if the concentrations at the ends of the capilliary pores of the diaphragm are maintained constant. These boundary conditions are not realised in diaphragm cell method because the concentrations at the ends of the capilliaries of the diaphragm change continuously.

a) Disturbance due to viberation and temperature fluctuations: These are eliminated by careful design and further reduced by confining the diffusion process to the capilliary pores only.

b) Stagnant layers on the diaphragm: These are avoided by stirring the solutions in the two compartments continuously.

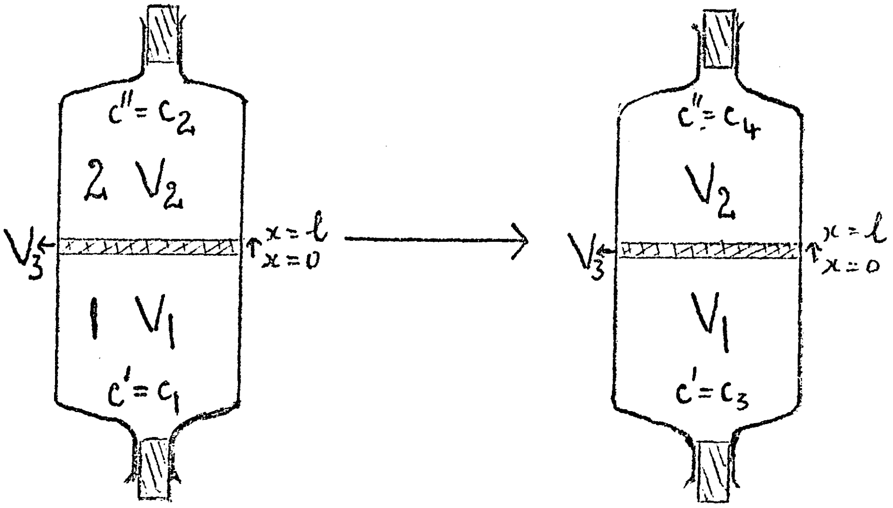
c) Streaming effects: These are avoided by putting the denser solutions in the lower compartment and keeping the cell diaphragm to within ±1-2° of the horizontal.

d) Surface transport effects: With dilute solutions the mobility of particles in the double layer on the capillary pores is enhanced and adsoption also takes place giving rise to anomalously high diffusion coefficients. This has been overcome by limiting the lower concentration to 0.05M above which no surface transport effects are appreciable and make negligible contribution to the total transport.

4.2.1 Theoretical Considerations: Let V_1, V_2, and V_3 be the volumes of the lower compartment, 1, upper compartment, 2, and the diaphragm of the cell as shown in figure41; A and ℓ be the effective area of cross-section and vertical length of the diaphragm pores respectively; c_1 and c_2 be the concentrations of the solutions in the compartments, 1 and 2, at time t equal to zero, and, c_3 and c_4 be the concentrations of the solutions in the compartments, 1 and 2, after a time t_r in seconds, of the diffusion experiment.

** flux J(t) is assumed to be constant over a short time interval so that eqn(4.1) holds.

Figure 4.1



Initial, $t = 0$ Final, $t = t_r$

In the Steady State situation the amount of solute entering the diaphragm at any time, t, is the same as the amount leaving the diaphragm i.e., the flux J(t) is constant. Denoting the concentrations in the compartments, 1 and 2, to be c' and c'' at time, t, the rate of change of concentration is given by

$$\frac{dc'}{dt} = -\frac{A}{V_1} J(t) \tag{4.2}$$

and

$$\frac{dc''}{dt} = \frac{A}{V_2} J(t) \tag{4.3}$$

Subtracting eqn(4.3) from eqn(4.2), we obtain

$$\frac{d(c'-c'')}{dt} = -A\left(\frac{1}{V_1} + \frac{1}{V_2}\right) J(t) \tag{4.4}$$

Let $\bar{D}(t)$ be the average diffusion coefficient over the concentration range c' to c'' prevailing at time, t, then it is defined as

$$\bar{D}(t) = \frac{1}{c'-c''}\int_{c''}^{c'} D\,dc = \frac{1}{c'-c''}\int_{c''}^{c'} D(\frac{\partial c}{\partial x})\partial x \qquad (4.5)$$

Substitution of eqn(4.1) in eqn(4.5) and integration over the path x=0 to x=l gives

$$J(t) = -(c'-c'')\bar{D}(t)/\ell \qquad (4.6)$$

Combining eqns(4.4) and (4.6) and re-arranging we get

$$-\frac{d\ln(c'-c'')}{dt} = \frac{A}{\ell}(\frac{1}{V_1} + \frac{1}{V_2})\bar{D}(t) \qquad (4.7)$$

At the end of the experiment of duration t_r seconds, c' changes from c_1 to c_3 and c'' changes from c_2 to c_4. On integration of eqn(4.7) between these limits we obtain

$$\ln\frac{c_1-c_2}{c_3-c_4} = \frac{A}{\ell}(\frac{1}{V_1} + \frac{1}{V_2})\int_{t=0}^{t=t_r}\bar{D}(t)dt \qquad (4.8)$$

Now $\bar{D}(t)$ is already a concentration average diffusion coefficient, so, introducing $\bar{D}$ as a concentration and time average diffusion coefficient, we have

$$\bar{D} = \frac{1}{t_r}\int_{t=0}^{t=t}\bar{D}(t)dt \qquad (4.9)$$

Substitution of eqn(4.9) in eqn(4.8) gives

$$\bar{D}\beta = \frac{1}{t_r}\ln\frac{c_1-c_2}{c_3-c_4} \qquad (4.10)$$

where $$\beta = \frac{A}{\ell}\left(\frac{1}{V_1} + \frac{1}{V_2}\right) \tag{4.11}$$

The constant parameter, β, depends on the dimens-ions of the cell and therefore is known as cell constant. It is determined by calibration of the cell using an electrolyte for which D is precisely known from absolute measurements. Potassium chloride is used for this purpose. $\bar{D}$ is obtained from a set of D values as follows:

It has been shown[42] that a negligible error is introduced if, instead of using the exact relationship (4.9), we treat the integrand as having a constant value equal to that when the concentrations c' and c'' are halfway between their initial and final values. $\bar{D}$ is then related to D by

$$\bar{D} = \frac{1}{(cma-cmb)}\int_{cmb}^{cma} D\,dc \tag{4.12}$$

where $cma = (c_1+c_3)/2$ and $cmb = (c_2+c_4)/2$ (4.13)

A quantity $\bar{D}^{o}(c)$ is defined as the average D over the concentration range 0 to c, therefore

$$\bar{D}^{o}(c) = \frac{1}{c}\int_{0}^{c} D\,dc \tag{4.14}$$

From eqn(4.12) and (4.14), it may be shown that

$$\bar{D} = \frac{1}{(cma-cmb)}(cma.\bar{D}^{o}(cma)-cmb.\bar{D}^{o}(cmb)) \tag{4.15}$$

Using eqn(4.14), the quantity $\overline{D}^{o}(c)$ for potassium chloride solutions have been computed by Stokes[44] from absolute measurements of D. For a set of mean concentrations cma and cmb, of a diffusion run, $\overline{D}^{o}$(cma) and $\overline{D}^{o}$(cmb) are obtained using an empirical fit* between c and $\overline{D}^{o}(c)$. These are then substituted in eqn(4.15). $\overline{D}$, thus obtained, is further used in eqn(4.10) which gives the numerical magnitude of β.

After calibrating the cell for a particular concentration combination, the diffusion experiment is repeated with the test electrolyte for approximately the same concentration combination and duration. Using the experimental values of the concentrations, c_1, c_2, c_3 and c_4, time, t_r, and the cell constant, β, in eqn(4.10), the concentration and time average diffusion experiment (or the integral diffusion coefficient), $\overline{D}$, is obtained.

4.2.2 Computation of D from $\overline{D}$: An nth degree empirical relationship between D and $\sqrt{c}$ is chosen;

$$D = D^{o} + \int_{i=1}^{i=n} a_i(\sqrt{c})^{i} \qquad (4.16)$$

where a_i are the constants of the empirical fit. D^{o} is the Nernst limiting value of D at zero concentration and may be obtained from ionic conductances at infinite dilution.

Using the relationship(4.16), eqn(4.12) may be integrated between the limits cmb and cma and eqn(4.17) is obtained.

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* Coefficients of this fit and all the subsequent fitted equations are given in table A1 of the appendix 1.

$$\overline{D}(cma-cmb) = \left[D^o c + \sum_{i=0}^{i=n} \frac{a_i c^{(i/2+1)}}{(i/2+1)}\right]_{cmb}^{cma} \qquad (4.17)$$

For a diffusion run, cma, cmb and $\overline{D}$ are known from the experiment, D^o is known theoretically; their substitution in eqn(4.17) reduces it to a numerical expression involving the constant, a_i. To obtain these n constants, n relationships(involving a_i) are required.

4.2.3 The Diaphragm Cells: Two sintered glass discs of diameters 40mm and 50mm, having porosity four and sealed in pyrex glass tubes, were obtained commercially for the construction of the cells. The open ends of the tubes were terminated in B-24(f) and B-14(f) joints and the volumes of the compartments were so adjusted that magnetic stirrers could be easily slipped into and taken out of the cells. The dimensions and schematic diagram of the cells are given in table 4.1 and figure 4.2a.

This cell design is that of Stokes[44] and has been used mostly for diffusivity experiments at a constant temperature. Yeh and Wills[47] and Sanni and Hutchison[48] have modified the cell so that it can be filled automatically and the design of the latter workers allows for the expansion of the experimental solutions so that the diffusion runs can be made at higher temperatures and it also allows for the volume changes on mixing.

4.2.4 The Stoppers: Stoppers for the cell ends, shown in figure 4.2b, were made of B-24(M) and B-14(M) joints which had 2mm capillaries in them. The B-24(M) joint was joined to a B-7(f) joint while the B-14(M) was sealed to a B-7(f) through a high vacuum quality (Teflon) tap.

4.2.5 <u>The Magnetic Stirrers:</u> Two soft iron wires of lengths 35mm and 45mm were sealed in thin glass tubes. The thickness of the wires and the glass tubes were so adjusted that one stirrer of each set would just sink and the other would just float in the experimental solutions. These are shown in figure 4.2c.

4.2.6 <u>The Magnetic Stirring Device:</u> The stirring mechanism is shown in figure 4.3. Two horse-shoe magnets, M, obtained commercially, were fixed at the ends of two brass screws, S, which passed through the vertical arms of the brass plate assembly, B. The screw fittings allowed a fine adjustments of the magnets. The motor and gear system were adjusted to give a constant stirring speed of 55 r.p.m. The north pole of one magnet faced the south pole of the other.

In the original device of Stokes[44] the stirrers just touched the two sides of the diaphragm. We found that in our system the diaphragm started wearing* off with time. This difficulty was overcome by keeping the stirrers at a distance of 2-3mm from the diaphragm surface. This

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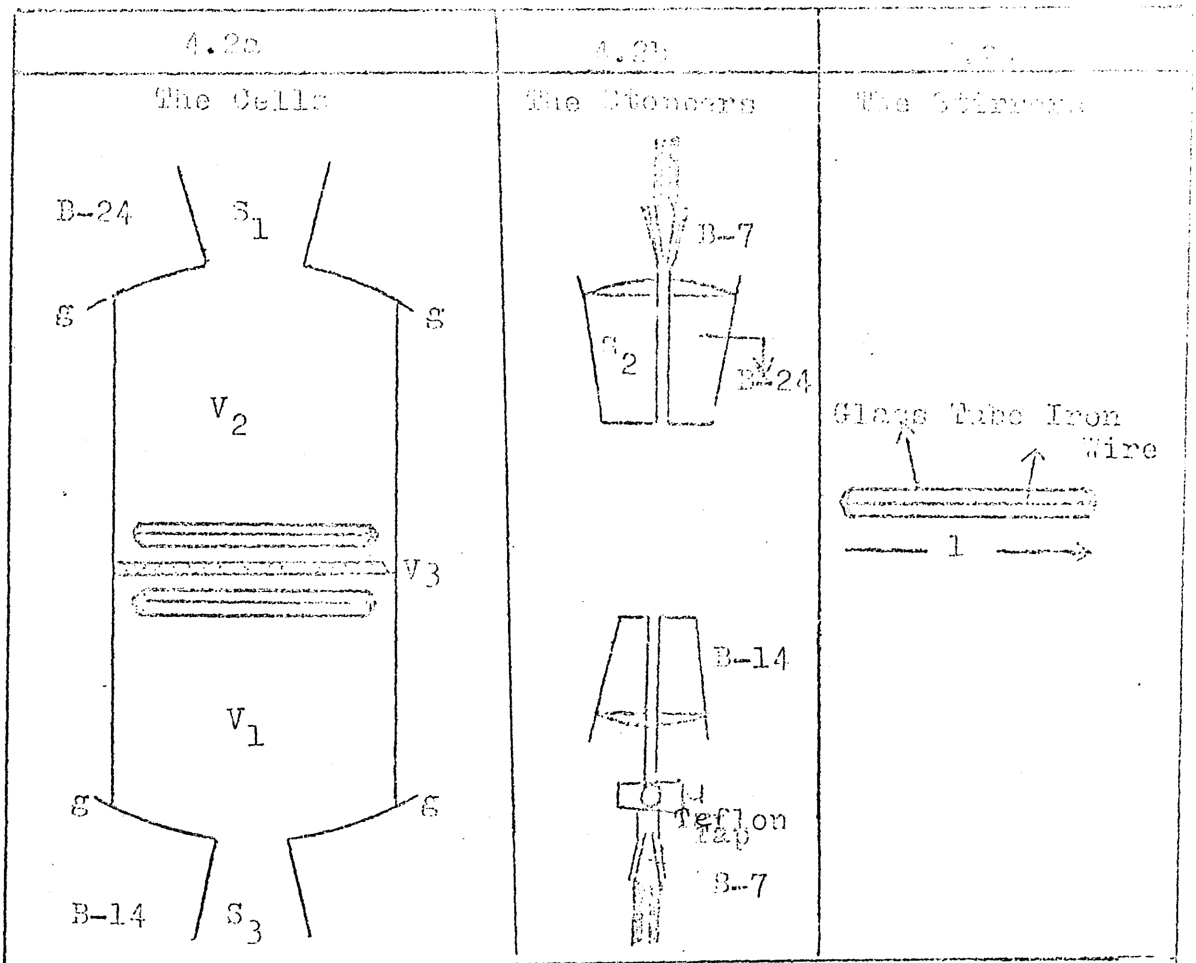
* Janz and coworkers[49] encountered the same difficulty and avoided it by performing periodic calibrations and used a graph of cell constant as a function of the working life of the diaphragm.

Figure 4.2



4.2a The Cells

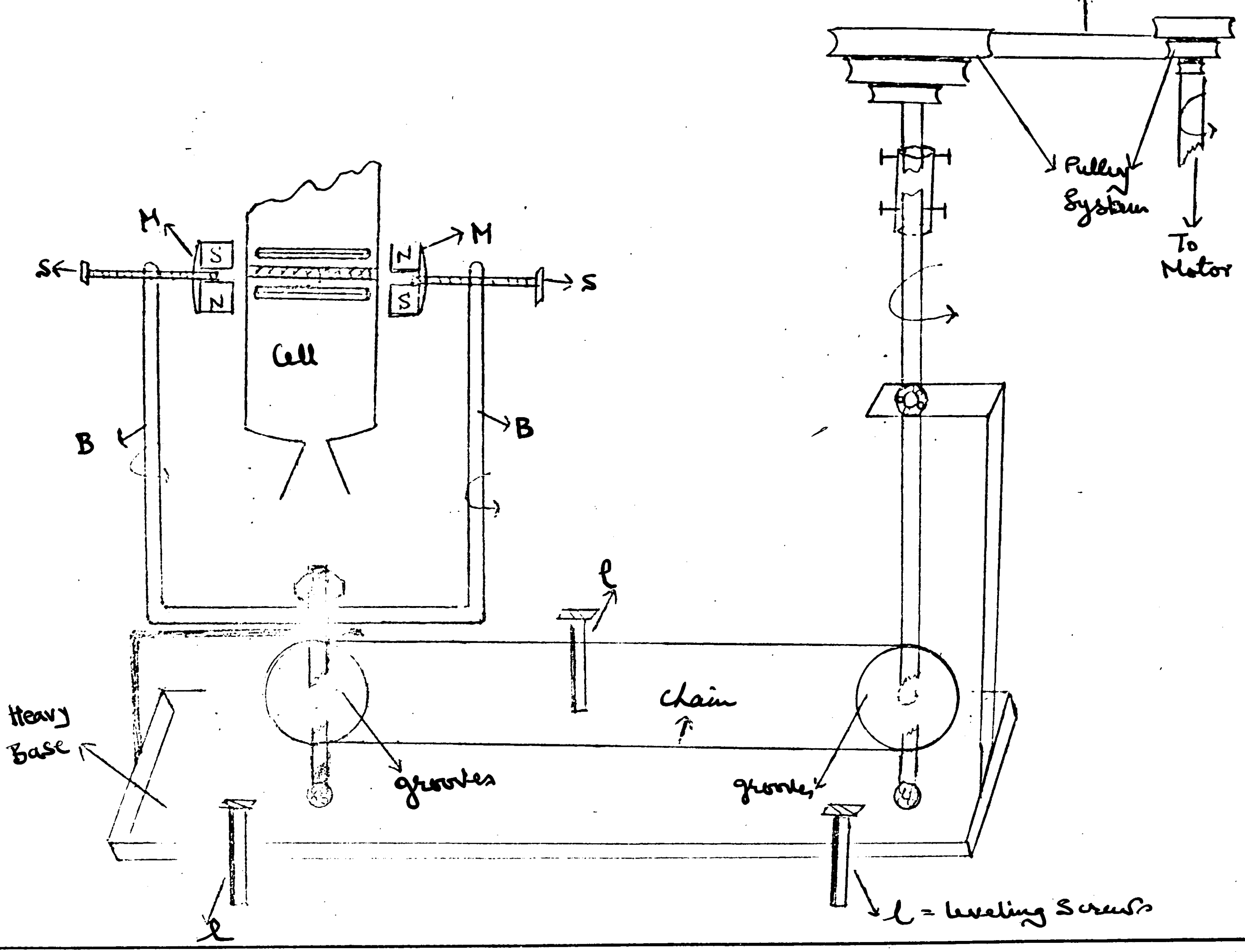
4.2b The Stoppers

4.2c The Stirrers

Table-4.1

Cell Dimensions.		Cell-1	Cell-2
Volume of Compartment 1	V_1	95.36	53.11
" " " 2	V_2	109.83	60.58
Volume of Diaphragm	V_3	3.57	1.76
$(V_2+V_3/2)/(V_1+V_3/2)$	V	1.146	1.138
Diameter of Diaphragm	D	50mm	40mm
Thickness of Diaphragm	x	5mm	2.5mm
Length of Stirrers	l	47mm	37mm

Figure 4.3


chain
Pulley System
To Motor
M
M
S
S
N
N
S
S
N
Cell
B
B
l
chain
Heavy Base
grooves
grooves
l
l = leveling Screws

procedure was standardised for all experimental runs. Test measurements with caesium chloride solutions showed that the results were in perfect agreement with the literature values . This method of stirring was therefore deemed satisfactory.

4.2.7 Determination of Volumes, V_1 V_2 and V_3: The volumes, V_1, V_2 and V_3 of the cell compartments and the diaphragm pores, figure 4.2a, were determined by weighing the cell a) completely filled with water b) with water removed from compartment, 1, c) with water also removed from compartment, 2, and d) when it was dry. All the fillings and weighings were made with the stirrers inserted in both the compartments of the cells.

4.2.8 Filling of the Cell and the Diffusion Run: The cell was cleaned vertically. Degassed concentrated solution was poured into the compartment, 2, figure 4.2a, allowed to flow through the diaphragm capillaries under vacuum. The cell was then inverted. The uppermost compartment (now 1) was filled with the concentrated solution and stoppered. The cell was then re-inverted. The compartment, 2, was half filled with the same solution and stoppered.

A thin film of high vacuum quality Apiezon grease was applied to all the joints and the stirrers were always in their respective compartments.

The cell was then clamped between the magnets of the stirring device fitted in a water thermostat maintained at $25^0 \pm 0.005^0$. The concentrated solution in the compartment, 2, was replaced by degassed dilute solution and stirring started.

After two and a half hours of preliminary diffusion the solution of compartment, 2, was carefully withdrawn in a 100ml pipette which already had in it $\simeq$ 10ml of the dilute solution. The cell was rinsed twice and finally filled with the mixed solution and stoppered. The stirring and the timer were started immediately. This minimised the zero time error*

*The Zero Time Error: In Stokes original method, the building up of a steady state is achieved by preliminary diffusion of some hours and then the solution in compartment, 2, is replaced by the fresh original solution and the diffusion is taken to begin from this time onwards.

If the actual concentration of the solution after preliminary run be c_2^1 and that of the freshly added solution be c_2, then clearly, $c_2^1 > c_2$. The Steady State however corresponds to c_2^1 and not to c_2 which is usually considered. The error thus caused is suggested by Francesconi[51] to be the zero time error.

It is proposed[51] that the zero time error can be removed if after preliminary diffusion of known duration, say t_p seconds, the contents of the upper compartment are analysed to determine concentration c_2^1 and then another run is made with the same fresh solution and the zero time is taken exactly after t_p seconds without changing the solutions. The concentration, c_2^1, would then be the zero time concentration.

Our approach to minimise the zero time error was different. Since the volume of solution, c_2^1, was around 60ml and that of c_2 was $\approx$ 10ml, the concentration of the mixture was very near to c_2^1.

When the diffusion had taken place for a known time, the stirring was stopped and the solution was withdrawn from the upper compartment. The cell was taken out of the thermostat, dried externally and solution then withdrawn from compartment, 1. All the solutions were then analysed as described below.

4.3 Determination of Concentrations by Conductometric Method Involving Calculations by Successive Approximations:

Polynomials (4.18) and (4.19) were curve fitted* between measured specific conductivities, κ , and known concentrations c, and between c and equivalent conductivities, Λ , respectively for $c < 0.1M$.

$$c = a_o + \sum_{i=1}^{n} a_i(\kappa \cdot 10^3)^i \qquad (4.18)$$

$$\Lambda = a_o + \sum_{i=1}^{n} a_i c^i \qquad (4.19)$$

A weighed sample of each solution was diluted to $c < 0.1M$. Its specific conductance was measured and subs-

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*Coefficients a_o and a_i are given in tableA1 of appendix 1.

tituted in eqn(4.18). The value of c thus obtained was used in eqn(4.19). The Λ given by eqn(4.19) was substituted in the relationship

$$c = \kappa . 10^3 / \Lambda \qquad (4.20)$$

and a better value of c was obtained. The eqn(4.19) and the relationship(4.20) were then used in turn till a value of c was approached, which was within ± 0.02% of that given by any further cycle of approximations.

The concentrations of the concentrated solutions were calculated from that of the dilute solutions using the density equations

$$m/c^{*} = a_o + \sum_{i=1}^{n} a_i c^i \qquad (4.21)$$

$$c/m = a_o + \sum_{i=1}^{n} a_i m^i \qquad (4.22)$$

Vacuum corrections were applied for all weights.

Volumetric titerations were also made against standardised silver nitrate solutions and the concentrations obtained were within ± 0.2% of the conductometric values, which are considered to be the more accurate.

4.3.1 Determination of Concentration, c_1: Concentrations c_2, c_3 and c_4 of a diffusion experiment were obtained by the method described above. The original concentration, c_1, could not be measured because it changed during the

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* Coefficients are given in table A1 of appendix 1.

preliminary diffusion run. It could, however, be calculated from c_2, c_3 and c_4 and the volumes of the compartments and the diaphragm pores, at the end of the experiment since the total amount of solute in the system remained constant. The small amount of solute in the diaphragm was assumed to be half at the concentration of the compartment, 1, and half at the compartment, 2; c_1 was then given by

$$c_1 = c_3 + (c_4 - c_2)(V_2 + V_3/2)/(V_1 + V_3/2) \qquad (4.23)$$

4.4. Results of Diffusion Measurements

4.4.1 Cell Calibration with Potassium Chloride Solutions:

For cell calibrations seven diffusion runs were made using potassium chloride solutions over the concentration range 0.01-3.0M. A computer programme* was written, which calculated concentrations from experimental conductances measured before and after each run. The results are presented in table 4.2. The cell constant obtained from various runs remained constant with in ±0.1% upto 1M but then it increased slightly with concentration. The increase was within the experimental error and the mean value was 0.4487±0.2%.

4.4.2 Diffusion Measurements with Caesium Chloride Solutions:

The results of measurements with caesium chloride solutions are presented in table 4.3. To compare these results with the literature differential diffusion coefficients, the latter were converted into integral form

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* given in appendix 2;

Table-4.2

Diffusion runs for Potassium Chloride Solutions.

Cell	Cell-1	Cell-1	Cell-2	Cell-2	Cell-2	Cell-2	Cell-2
Runs	1	2	3	4	5	6	7
c_1	0.09721	0.47045	0.46563	0.94668	0.93214	1.8866	2.99423
c_2	0.0	0.10690	0.0	0.11802	0.16925	0.4193	0.64528
c_3	0.07722	0.3060	0.27927	0.61391	0.62569	1.2895	2.04053
c_4	0.01745	0.17658	0.16375	0.41041	0.43851	0.9440	1.48325
cma	0.08721	0.43053	0.37245	0.78030	0.77891	1.58803	2.5174
cmb	0.00873	0.14174	0.08188	0.26422	0.30388	0.68165	1.0643
$\bar{D}_1$	1.87120	1.8399	1.8396	1.8542	1.85550	1.90487	1.9756
$t_{1/2}10^{5}$	1.568	1.733	1.692	1.692	1.692	1.692	1.692
B	0.1666	0.1662	.44786	.44756	.44754	.44868	0.44952

Time, $t_{1/2}$, is in seconds.

Table-4.3

Diffusion runs for Caesium chloride solutions.

Run	8	9	10
c_1	.0566	.1109	.5050
c_2	.0000	.0000	.0754
c_3	.0466	.0869	.4098
c_4	.0088	.0210	.1585
cma	.0516	.0989	.4574
cmb	.0042	.0105	.1169
β	.1664	.1164	.1664
$t_h 10^{-5}$	1.242	1.640	1.737
$\overline{D}_i$ (Obs.)	1.926	1.903	1.858
$\overline{D}_i$ (Calc.)	1.925	1.898	1.856

Table-4.4

Diffusion runs for Rubidium chloride solutions.

Run	a	b	c	d	e	f	g	h
Cell	1	2	2	2	2	2	2	2
c_1	0.0977	0.9199	1.6446	1.8937	3.3425	3.5273	3.2779	3.2277
c_2	0.0000	0.1116	0.1760	0.7471	0.9382	0.7932	0.9655	1.5549
c_3	0.0765	0.5938	1.0416	1.4150	2.3425	2.3878	2.2885	2.5098
c_4	0.0181	0.3981	0.7058	1.1677	1.8169	1.7944	1.8348	2.1857
cma	0.0868	0.7569	1.343	1.654	2.843	2.958	2.783	2.869
cmb	0.009	0.255	0.441	0.957	1.378	1.294	1.400	1.870
β	0.1664	0.4475	0.4487	0.4487	0.4495	0.4495	0.4495	0.4495
$t_h 10^{-5}$	1.594	1.692	1.705	1.716	1.620	1.624	1.728	1.695
$\bar{D}_i$	1.9184	1.8729	1.9286	1.9924	2.0882	2.0932	2.0967	2.1539

Table–4·5

Experimental and calculated differential diffusion coefficients for Rubidium chloride Solutions.

C	D Experimental	D Calculated	% Deviation	D Literature
0.0	–	2.051	–	2.051
.005	–	1.994	+.03	1.995
.01	1.973	1.974	–.07	1.973
.05	1.911	1.910	+.06	
.1	1.879	1.879	+.02	
.2	1.856	1.857	–.02	
.5	1.869	1.870	–.05	
1.0	1.945	1.944	+.06	
1.5	2.023	2.023	–.02	
2.0	2.100	2.100	+.07	
2.5	2.173	2.173	+.03	
2.87	2.226	2.226	–.01	
3.0	2.245	2.245	+.02	

and then compared with the experimental integral diffusion coefficients. A third degree polynomial (4.16) was fitted between D and $\sqrt{c}$ by a least squares treatment and the coefficients of the fit were substituted in the expression (4.17). The value of $\bar{D}$ corresponding to each set of cma and cmb were then calculated. The experimental values were within ±0.1-0.2% of those obtained from the theoretical fit.

4.4.3 Diffusion Measurements With Rubidium Chloride Solutions: Experimental results are given in table 4.4 inwhich the letters a to h denote the number of diffusion runs made. A fourth degree dependence of D on $\sqrt{c}$ was used in eqn(4.16). Substitution of the literature value of D^o(equal to 2.051) and the values of cma, cmb and $\bar{D}$ for each of the runs, a,b,c,d,e and h, in the expression(4.17) gave six relations among the constants a_1, a_2, a_3 and a_4 of the fit, eqn(4.16). These relations were solved simultaneously using a 4 × 4 determinant. The computer programme is described in the appendix 2. Three combinations of four out of six relations could be obtained to cover the whole range 0.01 to 3.0M. The values of D obtained were within a) ± 0.1% upto 1.5M b) ± 0.2% upto 2.7M and c) ± 0.5% at 3.0M.

Finally the fourth degree polynomial(4.16) was fitted between $\sqrt{c}$ and the mean experimental D for the experimental range of concentration 0.01-3.0M and the resulting equation extrapolated to obtain D for $c < 0.01M$. The calculated results were better than 0.1% of the literature values.[52] Table 4.5 summarises the results.

CHAPTER 5

Measurement of Conductance

5.1 Historic Developements: After the extensive study of the design of conductance cells by Jones and Bollinger[53] in 1931, the theoretical and experimental aspects were reviewed by Shedlovsky[54] in 1960. A few modifications have taken place in the measurement techniques for dilute as well as concentrated solutions. Kay and coworkers[55] devised a salt cup dispensing system without exposing the contents of the cell to the atmosphere and Mysels[56] developed a dough-nut cell for concentrated solutions, in which the same solution could be diluted a number of times. King[57] has introduced a compact cell design for measurements at high temperatures and pressures. Guint[58] has reported work on conductivity of binary mixtures of electrolytes in aqueous solutions. The complete situation of conductance up to 1967 was reviewed, with 248 references, by Barthel[59] with particular reference to measurements in non-aqueous solvents. Since then a number of papers have been contributed by Fuoss and coworkers[6a-e] for the extension of the original Fuoss and Onsager[60] conductance equation which is now valid upto 0.1M concentrations.

For the measurement of conductances of rubidium and caesium chlorides in aqueous solutions for concentrations from 0.01 to 3.0M, we have used Jones and Bollinger[53] type cells incorporating the modifications suggested by later workers, which would be described in the subsequent sections which now follow.

5.2 Conductances of Rubidium and Caesium Chloride Solutions

5.2.1 Conductivity Water: Ordinary distilled water was redistilled thrice, first over acidic potassium dichromate, then over alkaline potassium permanganate and finally distilled as such into a 15-litre pyrex aspirator. Three 5 litre round-bottomed flasks, heated electrically, were used for distillation. Steam coming out of a flask was made to pass through 55"-high vertical glass columns packed with glass beads before it was condensed into the next appropriate flask. The aspirator was fitted with a Teflon tap at the bottom and Teflon bung with two holes, at the top. The holes in the bung carried glass tubes, one for distilled water and other for sucking in cleaned air passed through Sofnolite. The purified water thus obtained had a specific conductance of 1×10^{-6} and after degassing 0.1 to 0.2×10^{-6}.

5.2.2 Purification of Nitrogen: Unpurified cylinder nitrogen was passed through concentrated sulfuric acid and sodium hydroxide solutions, two tubes packed with sofnolite and glass wool and finally twice through conductivity water. The bottles used were of 200ml capacity and were fitted with B-24 gas heads which in turn were fitted at the bottom with sintered glass discs of porosity 4. The gas issuing out of these discs was in the form of bubbles so that it could come into maximum contact with the purifying solutions. The degassing apparatus is shown in figure 5.3.

5.2.3 Crystallisation of Analar Potassium Chloride from Conductivity Water:

B.D.H. AnalaR ootassium chloride was dissolved in conductivity water till the solution was saturated. The saturated solution was filtered hot under vacuum using a porous glass filtering funnel fitted into a 2-litre conical filtering flask with B-24 standard joint.

The conical flask containing the saturated solution was cooled by surrounding it with finely ground ice. The crystals appeared instantaneously. The mother liquor was poured off into another conical flask and preserved. The crystals were transferred to a 2-litre beaker and conductivity water was added in small amounts so that on heating again the solution could remain saturated at $\approx 100^{\circ}$. This solution was again cooled rapidly using ice as before.

The crystals thus obtained were dried in an oven at 130°C in Pyrex glass drying dishes for 24 hours. The drying crystals were cooled in a desiccator over silica gel for an hour or so and then ground in an agate mortar in small amounts. The ground salt was further dried in an oven at 130° for 3 days and then stored in a desiccator over silica gel.

5.2.4 Alcoholic Precipitation of Potassiun Chloride:

To the mother liquor obtained from the second crystallisation from conductivity water, an equal amount of 98% absolute alcohol[61] was added. The precipitated salt was filtered and washed with small amounts of 50% alcohol. The drying and grinding precess was the same as for crystallisation from conductivity water. The dried, ground salt was in the form of powder. It was also stored in a desiccator over silica gel.

5.2.5 *Purification of Rubidium Chloride:* 99.8% laboratory reagent grade rubidium chloride supplied by B.D.H. and Koch-light company was crystallised from conductivity water. The salt was recovered from the mother liquor by alcoholic precipitation using the same procedure as for potassium chloride.

5.2.6 *AnalaR and Spectro-scopic Caesium Chlorides:* About 200 grams of AnalaR and 20g of Spec-pure caesium chloride salts were ground in an agate mortar. The powdered salts were dried as such in platinum drying dishes and used without further purification. There was no difference in conductances of solutions made from AnalaR or Spec-pure salts. The measured conductivities were within the precision of measurement for solutions of the same concentration.

5.2.7 *The Glass Apparatus:* For preparing experimental solution, 100ml and 250ml Pyrex Quick-Fit flasks with B-24 stoppers were used. These flasks and other pyrex glass apparatus were first soaked in Pyroneg detergent solution for 3-4 days and then washed with chromic acid and nitric acid. Finally they were steamed (steam of conductivity water) for 10 to 15 minutes (for each flask and the uncalibrated glass apparatus).

After steaming, the glass apparatus was rinsed with conductivity water and AnalaR acetone, and then dried by compressed air issuing under pressure after passing through silica gel and glass wool to remove moisture and dust.

The apparatus, flasks in particular, were not dried in an oven so that the air in them is kept at room temperature and humidity because otherwise if air in a flask is dry and a few ml of a concentrated solution are added to it a little evaporation is likely, which results in a change of true concentration of the solution[62].

The flasks dried over air were found to have the same weights within 0.0002 grams after repeating the process of cleaning. All the flasks with stoppers were numbered using a diamond scratching knife so that using the same flask and stopper, their weights could be compared and reproduced.

5.2.8 <u>Constant Temperature Bath</u>: A temperature of 25° ± 0.002° was obtained using a toluene mercury coiled glass thermo-regulator in a light-weight transformer oil tank. The oil was heated by a 40 watt electric bulb and cooled by circulating tap water in the tank using a coiled copper pipe immersed in the tank. thorough mixing of the oil was affected by an electric motor stirrer. The rates of heating cooling and stirring were regulated in such a way that temperature variation was within ± 0.002°.

An E-Mil TOT IMM standard thermometer model K14047 calibrated to N.P.L. standards was used for temperature measurements. It was not considered necessary to calibrate this thermometer further because the solutions of electrolytes under study have the same temperature coefficient as those of potassium chloride, which is used for cell calibrations. A constant error of a few hundredths of a degree would largely be compensated[63] by a corresponding change in the conductivity of the standard.

5.2.9 Conductivity Bridge: A digital autobalance precision bridge B-331 manufactured by Wayne Kerr Co., Ltd., was used for conductance measurements. This autobalance bridge displayed capacitance and conductance simultaneously on two meters. An accuracy of 0.01% was attained by operating six pushbutton decades, three for capacitance and three for conductance. The instrument incorporated a special circuit, called "lead elliminator", which completely eliminated error in resistance caused by the use of long connecting leads. The bridge operated at a frequency of 1591.55 H_z.

For conductance measurements at other frequencies ranging from 500 to 4000 cycles per second, external sources of frequency and detection were used. The signal generator was a Wayne Kerr oscillator, model AF S121. The external detector model 96016 of Standard Telephone Company, was recommended by the Wayne Kerr Co, for use with their bridge. With this detector we found that it was difficult to make conductande measurements better than ± 1%. No reason could be found for the insensivity of the instrument. It might have been due to miscellaneous electrical circuits in the laboratory. We, however, managed to get a detector** of the General Radio Company* and this was sensitive enough for measurements with the bridge accuracy of 0.05%(with the external source and detector).

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* Kindly lent to us by Dr. T.R. Foord of the department of Electrical Engineering, University of Glasgow.

** type 1232-A

5.2.10 Conductivity Cells: The design of conductance cells, shown in figure 5.1, is the work of Jones and Bollinger who made an extensive study of cell design to remove the shunt effect and polarisation errors. The shunt effect, which is due to high capacitances, is avoided by keeping contact tubes widely separated and the filling tubes apart. The polarisation is avoided by platinising the electrodes and using alternating current.

Four pyrex cells of cell constants 35.807, 87.140, 92.900 and 172.20, were used to cover the whole range of concentration . The diameter of each electrode was ≃ 1.6mm. Dimensions of the filling and the contact tubes were the same in all cases but the length of the narrow portion of each cell were varied to obtain different cell constants. The approximate dimensions of the cells are shown in table 5.1. To obtain a lower cell constant the length of the narrow portion between the electrodes was decreased and the diameter was increased.

The filling tubes were incorporated[62] with bulbs in the centre. This facilitated rinsing of the cells. The contact tubes were filled with mercury but before filling, the glass platinum joint was further sealed inside the contact tube with the Araldite powder, which hardened on heating and subsequent cooling. Copper rods of two mm diameter were used to make contact with bridge leads for the cell of cell constant 35.807 while platinum rods were used for cells of high cell constants. Copper rods had to be cleaned with dilute hydrochloric acid from time to time to remove the oxide layer which built up slowly and reduced contact.

Table 5.1

Approximate dimensions in centimeters of the conductance cells.

Dimensions	Cells			
	1	2	3	4
l	7	12	12	12
I.D.l.	0.6	0.4	0.4	0.2
h	10	15	16	15
D	1.6	1.6	1.4	1.4
m	3	3	3	3
n	14	14	14	14
I.D.n.	.3	.3	.3	.3
p	9	9	9	9
I.D.p.	0.5	0.5	0.5	0.5
q	1.5	1.5	1.5	1.5
I.D.q.	1	1	1	1

l= length of the narrow portion between the electrodes; I.D.l= diameter of the capillary tubes between the electrodes; h= distance between the electrodes; D= diameter of each electrode; m= horizontal length of the filling tube; n= vertical length of the filling tubes; I.D.n= internal dimeter of the filling tubes; p= vertical length of the filling tubes; I.D.p= internal diameter of the filling tubes; q= diameter of the bulb in the filling tube; I.D.q= internal diameter of the bulb.

Figure 5.1

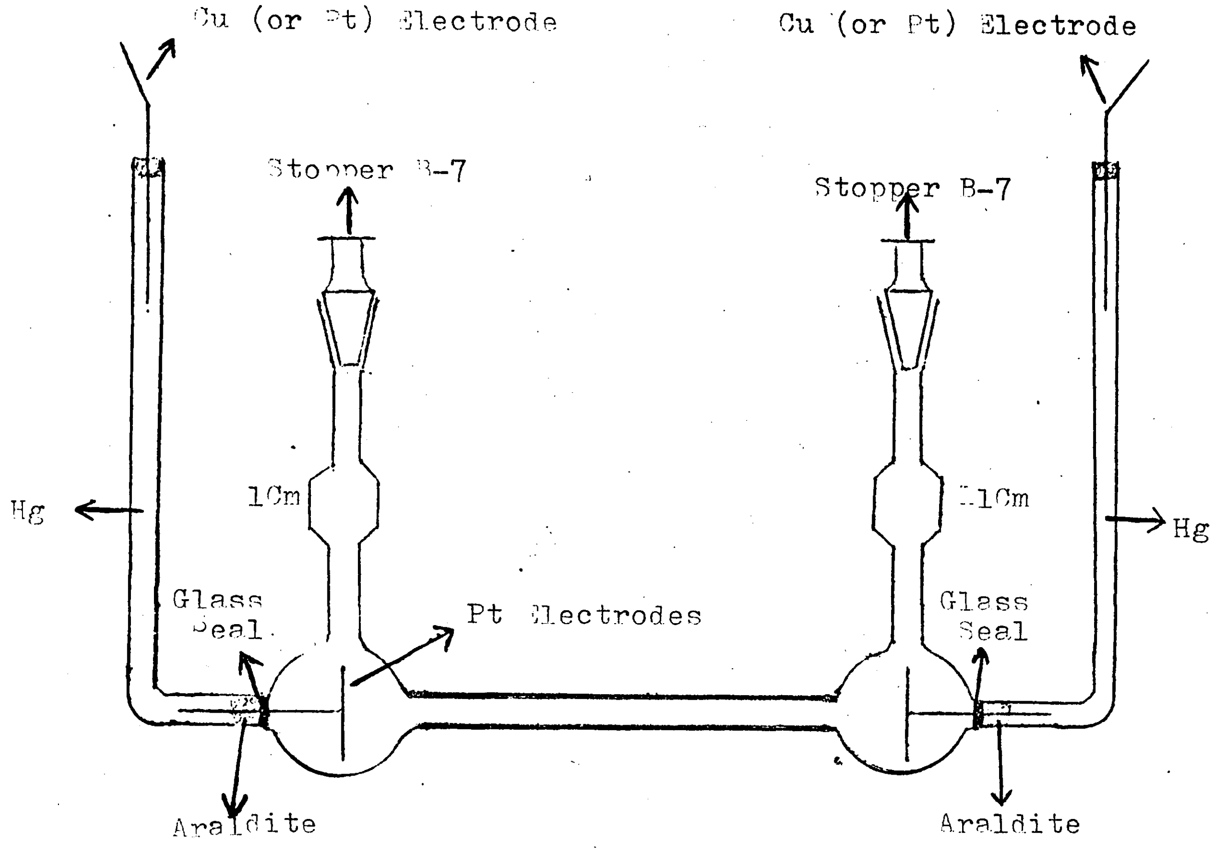
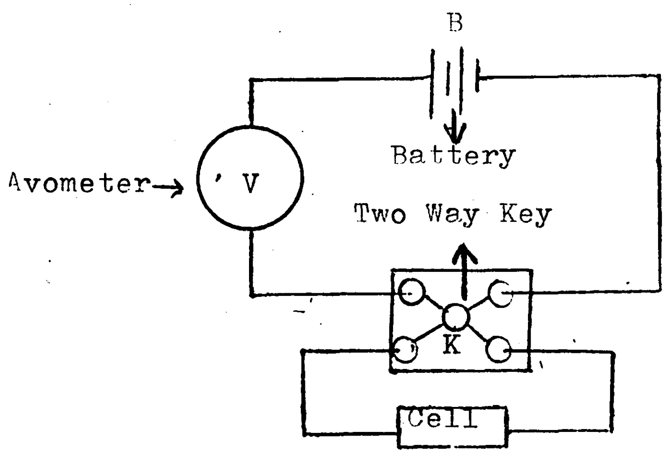


Figure 5.2



5.2.11 Platinisation of Cell Electrodes: For platinisation, again the instructions of Jones and Bollinger[53] were followed. The platinisation solution consisted of 0.025M hydrochloric acid, 0.3% platinic chloride and 0.025% lead acetate. Six coulombs of electricity per square centimeter of the electrode area were passed. The polarity was altered after every ten seconds and the platinising current required was 10mA per cm^2. The electrical circuit is shown in figure 5.2 in which K is the two way key and B is the Battery. Avometer, V, indicated current. After platinisation, cells were washed with distilled water and were always kept filled with it.

5.2.12 Cell Calibration: For cell calibration, 1.0, 0.1 and 0.01 demal solutions of potassium chloride were prepared as recommended by Jones and Bradshaw[64]. 1D* solution was prepared by direct weighing and 0.1 and 0.01D solutions were prepared by dilutions of the 1D solutions. Demal solutions are independent of the atomic weight of the standard electrolyte. Amounts of KCl required for 1000g of the solutions are given in table 5.2 along with their corresponding specific conductances.

5.2.13 Preparation of Demal Solutions: For a 1D solution, approximately 7g of KCl were weighed to 4 places of decimals. This weight was converted into vacuum weight by applying the vacuum correction factor[65], f, which is obtained using

$$f = 1 + 0.0012(1/d - 1/8) \qquad (5.1)$$

---

* D stands for Demal.

Table 5.2

Preparation of Demal solutions.

Demal	g of KCl per 1000g of soln. in vac.	Vac. Correction for solution	Specific conductance
.01	0.745263	1.00105	0.0014087
.1	7.41913	1.00105	0.012856
1.0	71.1352	1.0010	0.111342

Table 5.3

Vacuum correction factors for salt and solutions.

Electrolyte	Mol.wt.	Vacuum Correction for		
		Salt, fa	Solution fb	
			$c < .1$	$c > .1$
KCl	74.56	1.000455	1.00105	1.001
RbCl	120.92	1.000300	1.00105	1.001
CsCl	168.36	1.0001500	1.00105	1.001

where d is density of the salt or solution and for salt this is equal to 1.000455. From this, the weight of the solution required in vacuum was calculated, which on division by vacuum correction factor for solution gave the weight of solution required in air. A little less than the required amount of conductivity water was added to the flask containing the salt and final weight was made by adding water drop by drop. Solutions of ± 0.01% accuracy could be easily prepared by this method. ≈ 10ml of 1D solution were weighed in another flask and diluted to obtain 0.1D solution. 0.01D solution was similar~~x~~ly obtained by dilution of 0.1D solution.

5.2.14 Conductance Measurements: Cell-1 (with lowest cell constant) was calibrated with 0.01 and 0.1D solutions while all other cells were calibtrated with 0.1 and 1D solutions. The cells were rinsed four times with 10ml samples of the stock solutions. After filling the tube, the standard joint (of the filling tube) was dried with filter paper and stoppered. No air bubbles were left trapped in the solution in the cell.

The cells were then thermostated in the oil thermostat for 15 to 20 minutes before conductance measurements were made. The measured conductances remained stationary with time within the accuracy of measurements. The cells were removed from the thermostat, stoppers were removed and the solutions were stirred by tilting the cells slightly. The stoppers were replaced and the conductances were measured once more. No change was observed in the measured conductances showing that adsorption effects were absent.

The specific conductance of water was added to the specific conductances of the demal solutions and the cell constants were then calculated using the relationship

$$\rho \upsilon = \kappa \qquad (5.2)$$

where ρ is the cell constant, υ is the observed conductivity and κ is the total specific conductivity of the solution.

For confirmation of the cell constants, 0.01, 0.1, 1, 2 and 3 molar solutions of NaCl and KCl were prepared, their conductances were measured and the equivalent conductances calculated using the relationship

$$\Lambda = \kappa \cdot 10^3/c$$

The calculated values were in agreement within ± 0.02% of the literature[66] results.

5.2.15 Preparation of RbCl and CsCl Solutions: The equations (5.3) and (5.4),

$$c/m = a_o + \sum_{i=1}^{2} a_i m^i \qquad (5.3)$$

$$m/c = a_o + \sum_{i=1}^{2} a_i c^i \qquad (5.4)$$

were used to calculate molar concentrations, c, from molalities m and vice versa. Coefficients, a_o and a_i of relationship (5.3) were obtained from Harned and Owen[67] and the coefficients of relationship (5.4) were obtained by a least squares, fit between m/c and c. These coefficients are given in table A1, appendix 1, along with the values for KCl solutions. The relationships (5.3) and (5.4) are applicable upto 4M concentrations. For CsCl solutions, the equation

$$d = 0.99707 + 0.12933c - 0.002166c^{3/2} \qquad (5.5)$$

was available[68], and was used to calculate molalities, m, using the relationship

$$m = c/(d-0.001.c.W_b) \qquad (5.6)$$

where W_b is the molecular weight of the salt and d is the density of the solution in gram per ml.

Solutions were prepared at approximate molalities as well as molalities corresponding to exact concentrations. For preparation of solutions at exact concentrations, if Wa is the apparent weight of the salt in air then the apparent weight of the solution required in air, Wy, is given by relationship

$$Wy = Wa \times (1+1000/Wb.m) \times fa/fb \qquad (5.7)$$

where fa and fb are the vacuum corrections for the salt and the solution respectively. The numerical magnitudes of W_b, fa and fb are given in table 5.3. Relationship (5.7) may also be rewritten as

$$Wy = Wa.Y \qquad (5.8)$$

where $$Y = (1+1000/Wb.m)fa/fb \qquad (5.9)$$

An approximate amount of salt was weighed and multiplied by the factor, Y and the apparent weight of the solution required in air was thus calculated. A little less than the calculated amount of conductivity water was added and the final weight was made by adding water drop by drop as mentioned earlier for preparation of demal solutions.

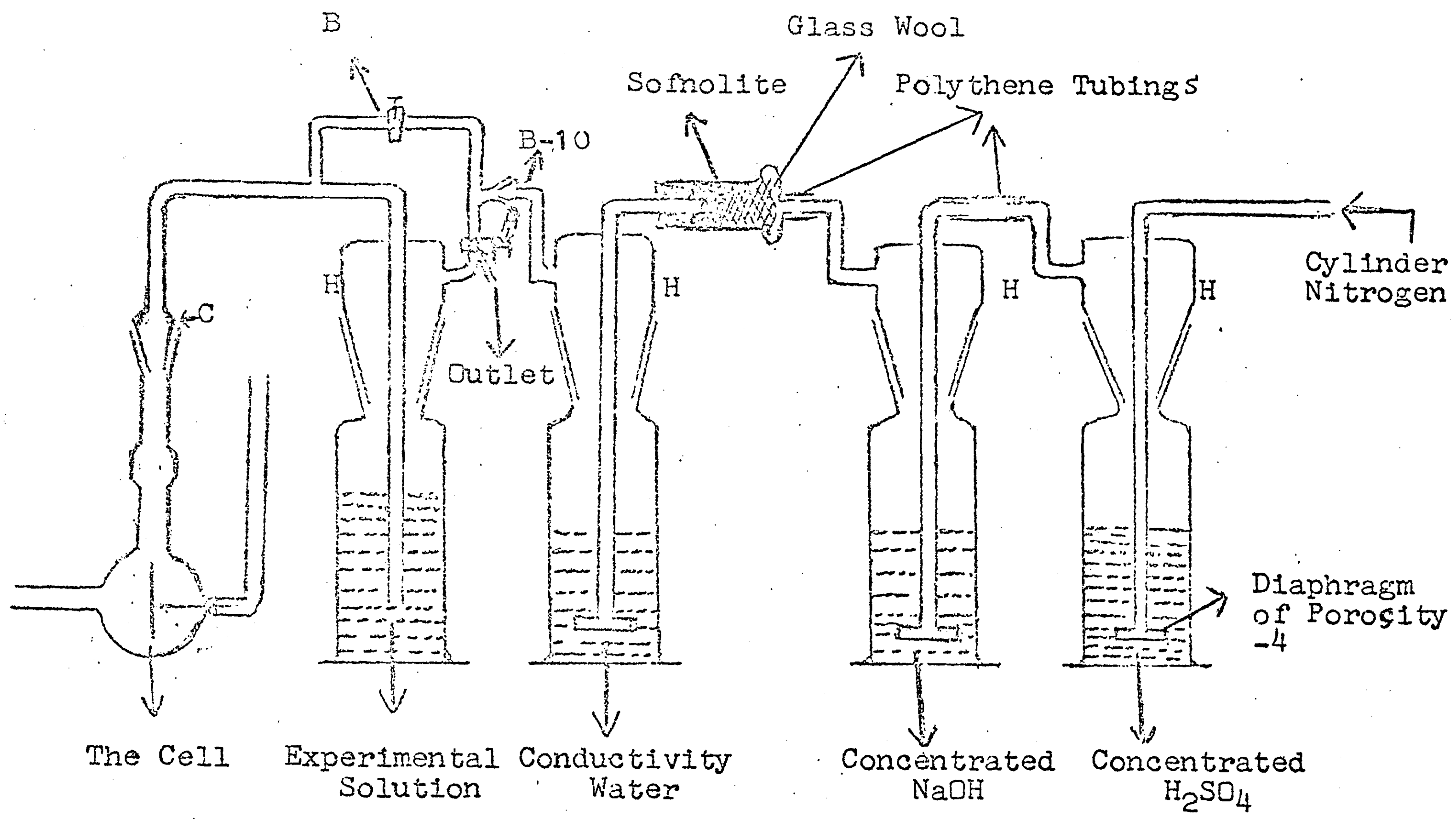
Solutions were also prepared at approximate molalities and the exact concentrations calculated using relationship (5.3).

5.2.16 <u>Degassing of dilute solutions and filling of cells for conductance measurements</u>: Conductances of all solutions above 0.1M were measured without degassing while for all solutions below 0.1M, conductances were measured before and after degassing with purified nitrogen. Specific conductances of undegassed and degassed conductance water were subtracted from the observed specific conductances of the solutions. For $c > 0.01$, no appreciable difference was found in calculated equivalent conductances by both the methods. The degassing and filling apparatus is shown in figure 5.3 in which A is a three way tap, B is a two way tap, and H is the gas head.

Firstly, outlet C of the gas head is closed, B is opened while A is closed from the side of the B-10 joint and open to the atmosphere. This way the gas after passing through the solution issued out to the atmosphere through the outlet in tap A.

Figure 53

Degassing and Cell Filling Apparatus



After degassing of the solutions, the outlet C of the gas head was opened and fitted into the inlet C of the cell. Nitrogen gas, instead of passing through the solution escaped through the cell, thereby creating its own atmosphere in it. This was allowed to take place for 1-2 minutes. After that, tap B was closed and tap A was closed to the atmosphere and open to the solution side. The gas passed straight through A and created a pressure on the solution thereby making it rise up to the gas head tube dipping in it. The solution then started filling the cell through the inlet C. The stopper D was opened to let the gas escape while the solution was entering the cell. Bubbles left in cell were removed by shaking and tilting the cell slightly. When the level in the second filling tube rose nearly to the required mark, the tap A was closed and outlet of the gas head was taken out of the cell and stoppers were immediately placed in the filling tube C, as well as in D. The cell was then ready for conductance measurements.

5.2.17 Frequency Dependence of Conductance: Frequency dependence of conductance is given by Jones and Bollinger's[53] relationship

$$R_p = R_t - R_t^2 . R_p . W^2 . C_p^2 \quad \text{or} \quad R_p = R_t - R \qquad (5.10)$$

where R_p is the apparent resistance, R_t is the true resistance, and W and C_p are the angular frequency and capacitance respectively. If R_t is taken to be roughly equal to R_p, eqn(5.10) becomes

$$R_p = R_t - R_t^3 . W^2 . C_p^2 \qquad (5.11)$$

For all the cells and the whole range of concentration from 0 to 3M, R_p was between 500 and 50,000 ohms and C_p was of the order of $\approx 10^{-12}$ farads. For frequencies, 1000 to 4000 H_z, substitution of W, R_p and C_p in eqn(5.11) shows that the error, $R = R_t^3 . W^2 . C_p^2$, is negligibly small. Its magnitude is much less than 0.01% and the change cannot be observed on the instrument. In theory it is clear that the measured or apparent resistance is the true resistance. In practice, the measurements were first made at bridge frequency and then using an external frequency source and detector in the range 1000 to 4000 H_z for 0.01, 0.1, 1.0 and 3.0M solutions and no visible change was observed within ± 0.05%, (which is the bridge accuracy for external source and detector). The most recent account of dependence of conductance on frequency has been given by Hoover[69].

5.3 Results of Conductance Measurements

5.3.1 Conductance Measurements in Dilute Solutions

Table 5.4 summarises the results both for rubidium chloride and caesium chloride for concentrations less than 0.1M.

Table 5.4

Results of conductance measurements in dilute solutions.

RbCl				CsCl			
c	Λ	c	Λ	c	Λ	c	Λ
.007	146.34	.04	138.11	.01	144.52	.06000	134.63
.008	145.91	.05	136.75	.013888	143.09	.07000	133.51
.01	145.07	.055	136.19	.015133	142.71	.07837	132.66
.0103	144.98	.0633	135.28	.019998	141.32	.08	132.52
.013	143.96	.065	135.09	.028255	139.40	.08926	131.69
.015	143.30	.07	134.59	.03	139.01	.09	131.67
.017	142.77	.075	134.15	.04	137.32	.0929	131.38
.019	142.23	.0828	133.43	.04784	136.12	.098	131.04
.02	141.98	.09	132.87	.049997	135.81	.100	130.84
.03	139.77	.10	132.14	.05	135.80	.100	130.85

Conductance measurements in concentrated solutions

Results are summarised in table-5.5

Table-5.5

Results of conductance measurements in concentrated solutions.

RbCl				CsCl			
c	Λ	c	Λ	c	Λ	c	Λ
.10	132.14	1.0	115.23	.10	130.84	1.0	113.10
.20	127.17	1.5	112.06	.20	125.43	1.5	109.86
.25	125.45	2.0	109.34	.35	120.06	2.0	107.20
.30	124.09	2.5	106.67	.50	118.30	2.5	104.52
.50	120.35	3.0	103.98	.70	115.73	3.0	101.63
.70	117.77			.85	114.33		

5.4 Analysis of Conductance Measurements in Dilute Solutions - A Study of Ion Association:

5.4.1 Fuoss Analysis: During the past three years Fuoss and co-workers[6a-e] have published extensions of the original Fuoss-Onsager conductance equation[60] and applied the extended equation to data for sodium and potassium chlorides, caesium bromide and iodide, potassium nitrate and silver nitrate. The experimental data were first analysed using the implicit equation

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec\ln c + Ac + Bc^{3/2} \qquad (5.12)$$

in which S and E are theoretical parameters and A and B constants of empirical fit. Equation (5.12) is valid upto 0.1M concentration and successfully reproduces the experimental data within the precision of measurements. A computer programme was devised which reproduced the Λ_0, A and B values reported for sodium and potassium chlorides[6b,c]. The experimental data for rubidium and caesium chlorides were then processed. The values of dielectric constant and viscosity of water were taken as 78.54 and 0.008903 (poise) at 25°C and the resulting equation for rubidium and caesium chlorides were

$$\Lambda = 154.01 - 96.000\sqrt{c} + 26.60\, c\ln c + 207.7c - 195.1c^{3/2} \qquad (5.13)$$

$$\Lambda = 153.58 - 95.000\sqrt{c} + 26.31\, c\ln c + 190.4c - 171.6c^{3/2} \qquad (5.14)$$

The equivalent conductances for caesium chloride in the range $c < 0.01M$, calculated from equation (5.14) were in agreement, to within 0.03%, with those obtained by Swan and Evans[70] who, using the original Fuoss-Onsager equation obtained a Λ_0 value for caesium chloride of 153.61 ± 0.02, which is in agreement with equation (5.14). The A and B values obtained for caesium chloride, equation (5.14), are similar to those for caesium bromide and iodide[6c] and the order is $CsCl < CsBr < CsI$.

Equations (5.13) and (5.14) for 1:1 salts in the concentration range 0.01 to 0.1M give satisfactory values of Λ_0 when terms in $c^{3/2}$ are retained[6a-c,71-73].

Using this concentration range improves experimental accuracy and so is preferable to using concentrations < 0.01M.

For solutions where ion association is present Fuoss and Hsia[6a] first used the explicit equation

$$\Lambda = \alpha(\Lambda_0 - \Delta\Lambda)(1 + \Delta X/X)/(1 + 3\phi/2), \tag{5.15}$$

where α is the degree of dissociation, $\Delta\Lambda$ and $\Delta X/X$ contributions from electrophoretic and relaxation effects respectively and ϕ is a function of the ion-size parameter $\mathring{a}$. Equation (5.15) may be solved as a three parameter equation to give self-consistent values of Λ_0, a^o and K_a, the association constant. The latter is derived from values, using activity coefficients from the Debye-Hückel limiting law. Although the values for distance of closest approach are large, 5-6A°, equation (5.15) adequately represented data for sodium and potassium chlorides and caesium bromide and iodide up to 0.1M. MacKenzie and Fuoss[6e], however, found that with potassium and silver nitrates in water and in aqueous dioxane, where the amount of association is comparatively large, the value of K_a obtained was relatively insensitive to the values of a^o chosen. They then treated equation (5.15) as a two parameter equation and calculated K_a from the best fit of a^o.

A detailed computer programme (No.158) of this treatment was kindly supplied by Professor Fuoss[74] and was used to process experimental data for rubidium and caesium chlorides and to recalculate results for other alkali salts. The distance parameter a^o is obtained from the association constant, K_a, using the relationships

$$K_a = (4\pi N\beta^3/6000)F(b) \qquad (5.16)$$

where $$F(b) = E_p(b) - (e^b/b)(1 + \frac{1}{b}) + 2.435 \qquad (5.17)$$

and $$a^o = \beta/b \qquad (5.18)$$

Activity coefficients, $f_\pm$, are calculated using the expression

$$-\ln f_\pm = \tau/(1 + \tau) \qquad (5.19)$$

where $$\tau = \beta\kappa/2 \qquad (5.20)$$

Relations between N, β, a^o, b, τ and κ are given in an earlier publication[75]. A limit has also been set to the maximum concentration such that $c(max) < 10^{-7}.D^3$ where D is the bulk dielectric constant. For aqueous solutions $c(max) \leq 0.05M$ and as association increases this limit decreases further.

Table 5.6

Results for Rubidium Chloride data using the Fuoss analysis.

c	Λ_{calc}	$\Lambda_{calc}-\Lambda_{obs}$	α	$f_{\pm}^2$
.008	145.908	-.002	.9982	.8272
.010	145.066	-.004	.9978	.8109
.0103	144.945	-.035	.9977	.8085
.013	143.980	+.020	.9972	.7901
.015	143.337	+.037	.9968	.7782
.017	142.757	-.013	.9964	.7674
.020	142.218	-.012	.9961	.7576
.020	141.964	-.016	.9959	.7528
.03	139.802	+.032	.9942	.7141
.04	138.131	+.021	.9926	.6847
.05	136.758	+.008	.9911	.6610
.055	136.224	+.034	.9904	.6507

Table 5.7

Results for Caesium Chloride data using the Fuoss analysis

C	Λ_{calc}	$\Lambda_{calc}-\Lambda_{obs}$	α	$f_{\pm}^2$
.010000	144.500	− .020	.99671	.81093
.013888	143.093	+ .003	.99558	.78480
.015133	142.691	− .019	.99524	.77757
.019998	141.299	− .021	.99392	.75299
.028255	139.390	− .010	.99182	.72026
.029991	139.041	+ .001	.99139	.71438
.030000	139.039	+ .029	.99139	.71435
.039991	137.320	+ .000	.98890	.68300
.047836	136.109	− .011	.98730	.66622
.049997	135.815	+ .005	.98683	.66150
.050000	135.814	+ .004	.98683	.66149

α is the degree of dissociation and $f_{\pm}^2$ is the square of the mean activity coefficient.

The results for rubidium and caesium chlorides are given in table 5.6 and 5.7. Table 5.8 summarises calculations for other alkali halides and potassium and silver nitrates. Including in this table are the Λ_o values obtained from equation (5.12). These are larger by 0.08 and 0.05 conductance units for rubidium and caesium chlorides and similarly for sodium and potassium chlorides and caesium bromide. In the sequence of salts from sodium chloride to silver nitrate the ion size parameter a^o, decreases as association constants, K_a, increase. The values for K_a for sodium and potassium chlorides are 0.17 with uncertainty of ±0.12 so that, as expected, the association is barely significant. The association constants for rubidium and caesium halides are significant but smaller than for potassium and silver nitrates. The values of association constant, Ka, for rubidium and caesium chlorides are .275± .083 and .409 ± .061 respectively. For caesium chloride Ka is identical with that for caesium bromide and compares well with an early estimate by Davies[76] of ≃ 0.4, measured at 18°C.

5.4.2 Corresponding Conductances: In a recent paper Guggenheim[77] has used the conductance equations of Pitts[7] to calculate the conductance with an electrolyte would have in the absence of ion association. The principle is one of corresponding conductances, in which the desired equivalent conductance, Λ, is calculated using data for two standard 1:1 salts which were considered to be completely dissociated. It is shown that for a given value of concentration, c,

$$\frac{\Lambda^1 - \Lambda}{\Lambda^1 - \Lambda^2} = \frac{\Lambda_0^1 - \Lambda_0}{\Lambda_0^1 - \Lambda_0^2} = r \quad (c, \text{ constant}) \tag{5.21}$$

where r is the constant defined by the Λ_0 values and therefore independent of concentration. Superscripts 1 and 2 denote the standard salts. In the original paper these salts were potassium and lithium chlorides, but in this work sodium and lithium chlorides were used in order to include potassium chloride, as in the Fuoss treatment given above. (For self-consistency the degree of dissociation is again given the symbol α, where δ was used in the original paper). The value of α is calculated as the ratio Λ_{obs}/Λ, calculated from equation (2.21). The results are shown in table 5.9 and fig. 5.4. The degrees of dissociation present at specific concentrations are closely similar for both treatments and the agreement between them is never worste than 0.5%, although in all cases the Fuoss estimate is the lower and extrapolates to a value which corresponds to Davies[78] estimate of α for CsCl at 0.1M. To compare association constants the Fuoss activity expression, equ.(5.19), has been used and the results given in table 5.8. Once more the agreement for the alkali halides is excellent and within the uncertainty of the K_a values obtained by each method. The corresponding conductance method does however give lower values for potassium and silver nitrates and each method shows that association in potassium chloride is negligible or zero.

The agreement between those two independent approaches is, therefore, excellent.

Table 5.8

Results for Λo, a^o and Ka using programme 158 of Fuoss for literature data on other salts.

Electrolyte	Implicit Equation (1)	Fuoss Programme			Guggenheim Method
	Λ_o	Λ_o	a^o	K_a	$K_a(g)$
NaCℓ	126.61	126.58	5.233	.168 ± 0.124	0
KCℓ	149.96	149.92	5.223	.172 ± .120	0
RbCl	154.01	153.93	4.947	.275 ± .083	.24 ± .13
CsI	154.19	154.30	4.851	.311 ± 0.042	.28 ± .10
CsBr	155.35	155.31	4.597	.409 ± 0.061	.40 ± .13
CsCℓ	153.58	153.53	4.598	.409 ± .051	.40 ± .10
KNO_3	-	145.00	3.726	.784 ± .044	.66 ± .05
$AgNO_3$	-	133.41	3.509	.875 ± .101	.70 ± .05

($K_a(g)$ is the association constant calculated using Guggenheim's degree of dissociation, α^*, and Fuoss's activity coefficient, f±, over the range .01 to .05 M).

*using NaCℓ or LiCℓ as standards instead of LiCℓ and KCℓ as standards.

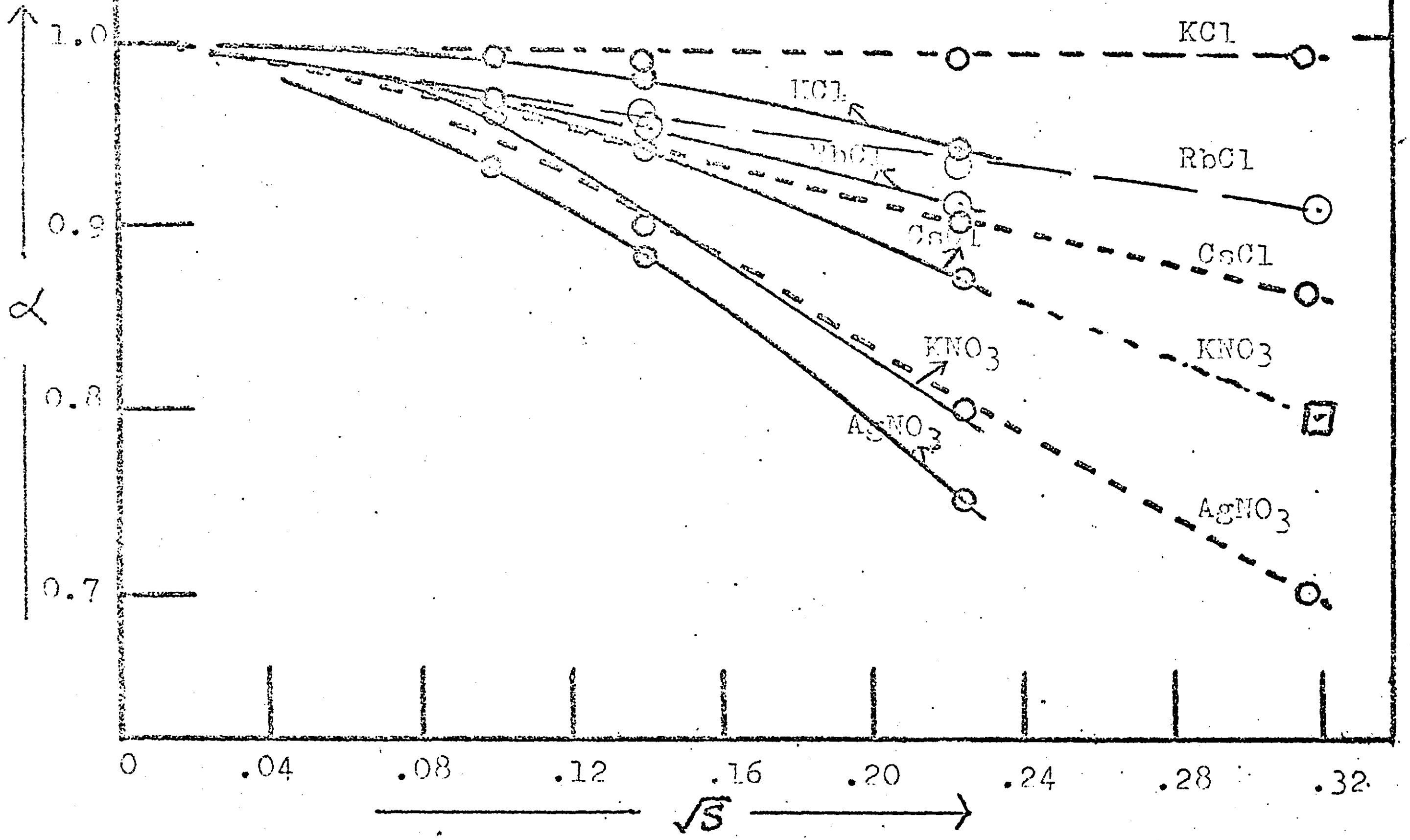
Table 5.9

Degree of dissociation, α, from Guggenheim's method of corresponding conductances (α_g) and from Fuoss programme (α_F).

	c	.01	.02	.05	.10
KCl	α_g	.9986	.9987	.9990	.9993
	α_F	.9986	.9976	.9942	–
RbCl	α_g	.9970	.9958	.9946	.9935
	α_F	.9978	.9959	.9911	–
CsCl	α_g	.9960	.9940	.9900	.9960
	α_F	.9967	.9939	.9868	–
KNO_3	α_g	.9963	.9895	.9806	.9680
	α_F	.9934	.9885	.9753	–
$AgNO_3$	α_g	.9976	.9900	.9780	.9620
	α_F	.9930	.9872	.9725	–

Figure 5.4

Degree of Dissociation, α, vs $S^{\frac{1}{2}}$



CHAPTER 6

Results and Discussion of the Irreversible Thermodynamic Analysis

The experimental results obtained for the electrical conductances of rubidium and caesium chlorides together with the diffusion data for rubidium chloride complete the parameters required for an irreversible thermodynamic analysis of these salts in the concentration range 0.25-3.0M. Transport numbers for both salts were obtained from Tamas, Kaposi and Scheiber[79] in this concentration range. These authors found their data to fit the empirical equations of Jones and Dole[80],

$$t_1(\text{RbCl}) = 1.5060/(1 + 0.005461\sqrt{c}) - 1 \qquad (6.1)$$

$$t_1(\text{CsCl}) = 1.5084/(1 + 0.01059\sqrt{c}) - 1 \qquad (6.2)$$

to an accuracy of 0.1%. Literature values of the volume fixed diffusion coefficient, D_V, for caesium chloride were obtained from Lyons and Riley[81]. To convert these (and the experimental results for rubidium chloride obtained in this thesis) to the solvent fixed frame of reference it was necessary to evaluate the activity correction term, $(1+m\,d\ln\gamma/dm)$, eqn(2.60), over the full concentration range. For this purpose a fourth degree empirical fit was obtained between $\ln\gamma$ and $\ln m$;

$$\ln\gamma = a_0 + \sum_{i=1}^{4} a_i(\ln m)^i. \qquad (6.3)$$

The coefficients a_0 to a_4 for both salts (and also for potassium chloride for check calculations), given in table 6.1, reproduced $\ln\gamma$ values to an accuracy of ±0.1% over the range 0.1-4.0 molal. The values of the function $(1+m d\ln\gamma/dm)$ given in tables 6.2 and 6.3 were obtained from eqn(6.3) on differentiation.

Using the theory discussed in chapter 2 a computer programme was written (appendix 2) which reproduced Miller's calculated data for the chlorides of lithium, sodium, potassium and hydrogen to ±0.1%. The complete sets of transport data for concentrations in the range 0.25 to 3.0 molar for rubidium and caesium chlorides were processed for calculations of the phenomenological coefficients, L_{ik} and R_{ik}. The computer read c, m, t_+, Λ, D_v and $(1 + m d\ln\gamma/dm)$ from the data tape and first calculated the transport coefficients, L_{ik} from eqn(2.63). The inverse frictional coefficients, R_{ik}, were then calculated from L_{ik} by their matrix inversion using eqn(2.64). The ion-solvent frictional coefficients, R_{i0}, were calculated using eqn(2.66) which involved all the three transport properties and the activity correction term. These coefficients could also be obtained using eqn(2.69) which involved transport numbers, diffusion coefficients and the activity term and for R_{00} diffusion coefficients and the activity correction term only. This does not mean that conductance and/or transport numbers are extranous parameters in eqn(2.66), for obtaining the coefficients R_{i0} and R_{00}. It can be seen on expansion that the eqn(2.66) reduces to eqn(2.69). The results for rubidium and caesium chlorides are presented in tables 6.2 and 6.3. Calculations were also carried out for (continued) all other binary systems, for which data were completely or partially available. These results are given in appendix 1.

The formalism of irreversible thermodynamics is justified on two counts. Firstly it allows a meaningful analysis of transport data in the concentration regions far in excess of the applicability of the existing microscopic theories and provides discrete coefficients which define specifically the mobility of ions, L_{ii}, and the coupling between species, L_{ik}. Since the flows are defined relative to a solvent fixed frame of reference all mobility coefficients contain contributions from the frame of reference interactions. It is however apparent that the mobility coefficients are of more fundamental importance than any directly measured parameters such as electrical conductivity or transport numbers, eqns(2.45) and (2.47).

Table 6.1

Coefficients of 4th degree fit, eqn(6.3), between lnm & lnγ.

Coefficients	KCl	RbCl	CsCl
a_0	$-5.0506_{10}{-1}$	$-5.3938_{10}{-1}$	$-6.0912_{10}{-1}$
a_1	$-9.7880_{10}{-2}$	$-1.1367_{10}{-1}$	$-1.5190_{10}{-1}$
a_2	$+2.2020_{10}{-2}$	$+1.8618_{10}{-2}$	$+1.5806_{10}{-2}$
a_3	$+1.4247_{10}{-2}$	$+1.2206_{10}{-2}$	$+1.3164_{10}{-2}$
a_4	$+2.6918_{10}{-3}$	$+2.0989_{10}{-3}$	$+2.0116_{10}{-3}$

To obtain a deeper understanding of electrolyte transport in concentrated media an examination of the variations of these coefficients with concentration is necessary. The interpretation of such coefficients is qualitative and therefore most soundly based when a series of closely related salts are compared.

In the present series of investigations on rubidium and caesium chlorides the remaining alkali metal chlorides provided this background for comparison. The experimental salts contain the largest cations of the series with largest mobilities and are the only salts of this series for which ion association might be expected (chapter 5).

In this analysis, the mobility or L-coefficients and frictional or R-coefficients have been calculated. These two sets are mathematically equivalent but each has merits for interpretation. The mobility coefficients give relationships which are formally more similar to classical equations; for example equivalent conductivity, Λ , where the simple Onsager equation

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

may be compared with eqn(2.45);

$$\Lambda = \left(Z_1^2\frac{L_{11}}{N} + Z_2^2\frac{L_{22}}{N}\right)10^3F^2 + \left(Z_1Z_2\frac{2L_{12}}{N}\right).10^3F^2.$$

The first term in each equation is a function solely of ion mobilities and the second term contains contributions from the cation-anion interaction.

The friction or R-coefficients are more akin to an electrical or mechanical resistance and have the advantage of being independent of the frame of reference. The coupling coefficient, R_{i0}, between ion and water may be isolated and examined. This formalism is largely favoured by workers in the field of membrane transport and the friction analogy, discussed below, has been developed by Spiegler[83], Katchalsky and others.[19,84]

6.1 The Mobility Coefficients: The phenomenological equations for a binary electrolyte solution containing cation, 1, valency, Z_1, anion, 2, valency Z_2, and water, 0, are given by the expression(2.29) where J_i is the flux of ion, i, relative to the solvent. A thermodynamic force on species, i, is defined by the gradient of electrochemical potential (-grad $\tilde{\mu}_i$) and therefore is the force on one mole of species, i; the flow, however, is largely proportional to the concentration of species. This concentration difference is defined and the variation of these parameters with concentration reflects the changes due to the environmental variation. The analogy is that between the use of specific conductivity and equivalent conductivity, Λ , as a basis of comparison of electrolytes at varying concentrations.

6.1.1 The Coefficients, L_{11}/N and L_{22}/N: The L_{ii}/N is an intrinsic mobility, that is, the mobility an ion would have if there were no interactions with the oppositely charged ions. It includes a large obstruction contribution due to lattice exchange, smaller effects such as coulombic interactions with the other i-type ion, solvation and the

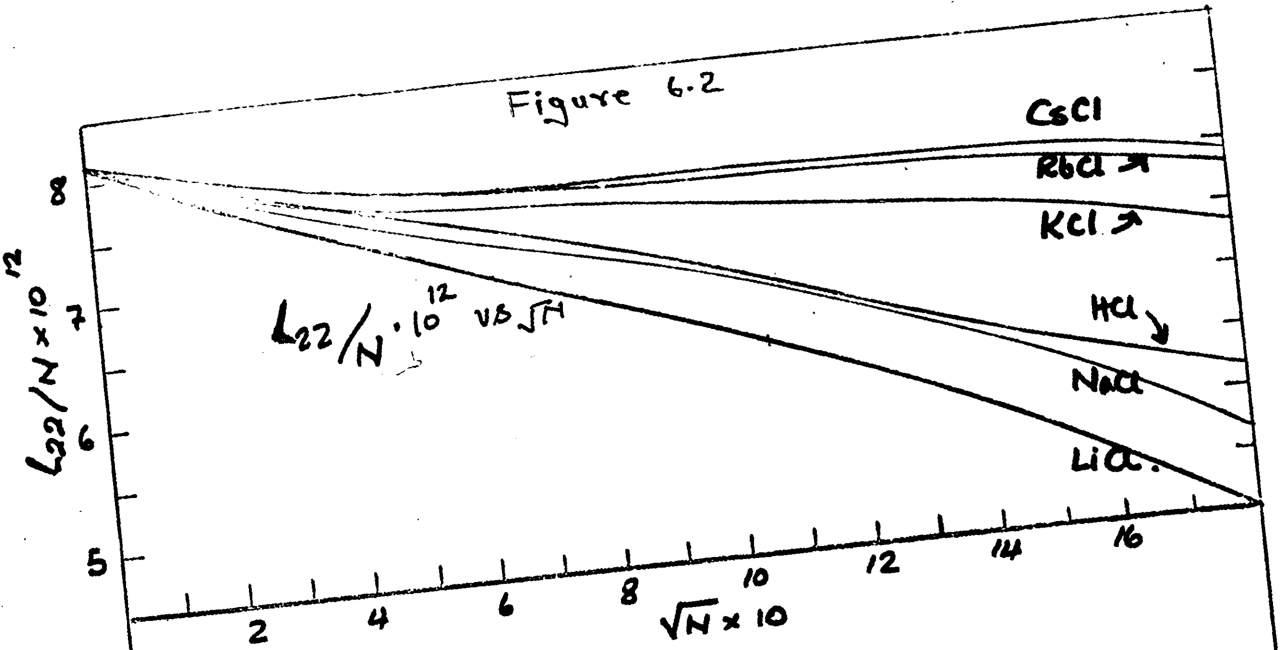


Figure 6.2

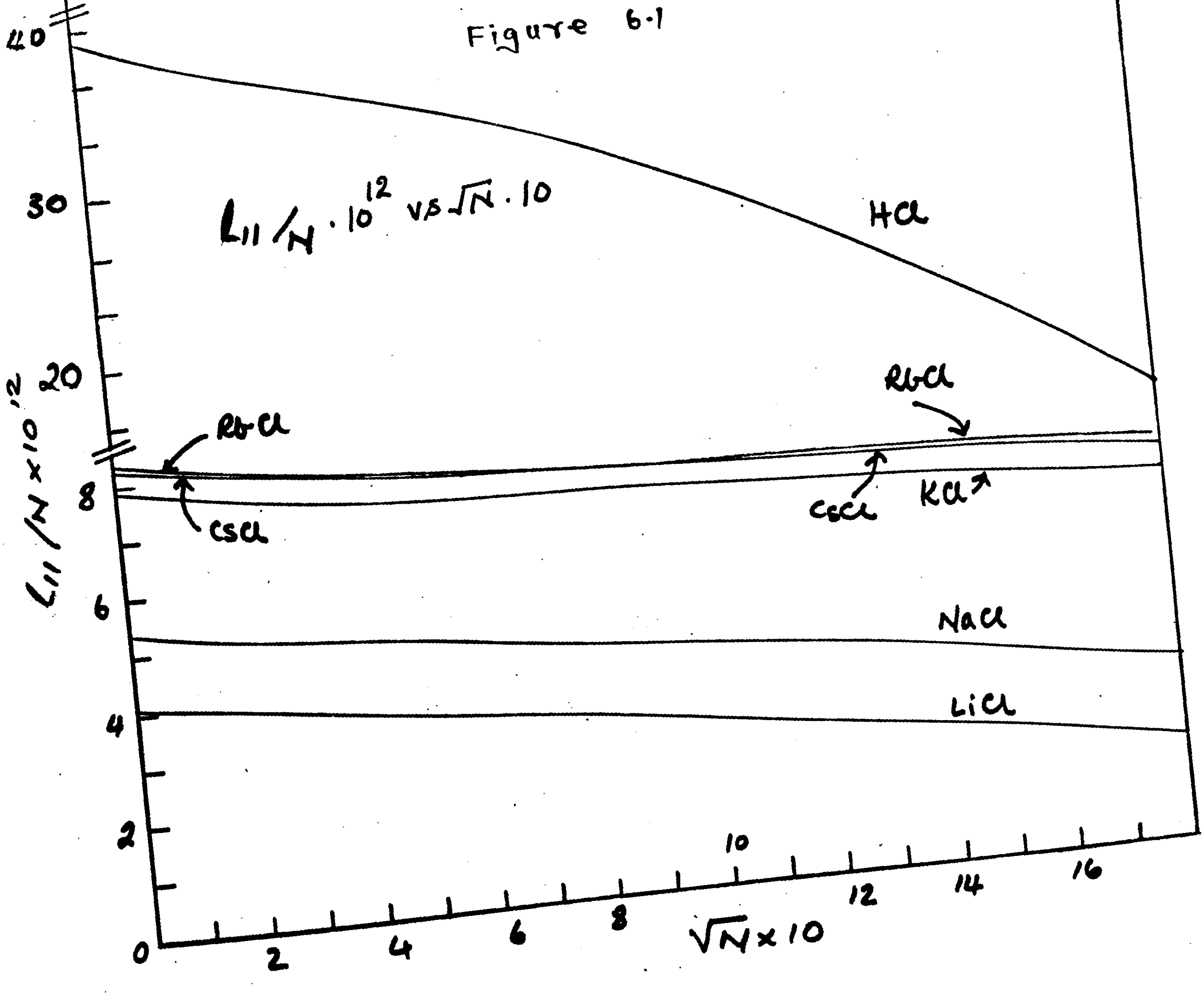


Figure 6.1

frame of reference interactions with the solvent. The cationic and anionic mobility coefficients, L_{11}/N and L_{22}/N, are plotted in figures 6.1 and 6.2 against the square root of ionic strength, S, where S is given by

$$S = N(Z_1 - Z_2)/2 \qquad (6.4)$$

The observed trend of the intrinsic mobilities, L_{ii}/N, may be tentatively explained on the basis of the accumulated evidence[85, 86, 87] of water structure and the effects of electrolytes on that structure. The mobility coefficient, L_{11}/N, is largest for Rb^+ ion showing that this ion has the highest mobility in the alkali metal chloride series. For Rb^+, Cs^+ and K^+ ions the values lie parallel and very close to each other and are the least affected with change in concentration. In the case of more solvated Na^+ and Li^+ ions the coefficients, L_{11}/N, decrease with concentration showing that the most solvated Li^+ ion has the least mobility.

The mobility coefficients, L_{22}/N, plotted in figure 6.2, provide a basis for the comparision of the Cl^- ion mobility in a variety of salt solutions of different concentrations. At finite concentrations it depends upon the nature of the salt. As the concentration tends towards zero, L_{22}/N values converge to a common point in accord with Kohlrausch's law of independent mobilities at infinite dilution. At a finite concentration the L_{22}/N coefficients are in the increasing order of the atomic numbers of the cations. That is,

$$LiCl < NaCl < Kcl < RbCl < CsCl$$

Table-6.2

RUBIDIUM CHLORIDE

c	m	Eqv Cond	t+	D(v)	1+mdlnGamm/dm
0.0000	0.000000	154.16	0.5045	2.0510	1.0000
0.1000	0.100640	132.11	0.5032 *	1.8730	0.8923
0.2500	0.252870	125.45	0.5019	1.8540	0.8790
0.5000	0.510100	120.36	0.5002	1.8700	0.8764
0.7000	0.718950	117.77	0.4992	1.8980	0.8796
1.0000	1.038340	115.23	0.4978	1.9440	0.8885
1.5000	1.586400	112.06	0.4960	2.0240	0.9104
2.0000	2.156400	109.34	0.4945	2.1000	0.9381
3.0000	3.371300	103.97	0.4919	2.2450	1.0050

Sqrt S ×10	l11/N 10+12	l12/N 10+12	l22/N 10+12	F12	Q12
0.0000	8.3511	0.0000	8.2021	0.0000	0.0000
3.1623	7.8403	0.7005	7.7495	0.1649	0.0899
5.0000	7.6485	0.8862	7.5973	0.2083	0.1163
7.0711	7.5382	1.0722	7.5330	0.2491	0.1423
8.3666	7.5045	1.1903	7.5248	0.2735	0.1584
10.0000	7.4801	1.3194	7.5345	0.2990	0.1758
12.2474	7.4453	1.4757	7.5416	0.3291	0.1969
14.1421	7.3870	1.5799	7.5161	0.3499	0.2120
17.3205	7.2077	1.7149	7.3886	0.3806	0.2350

Sqrt S ×10	NR11 10-11	-NR12 10-11	NR22 10-11	Q10	Q20
0.0000	1.1974	0.0000	1.2192	0.7039	0.7103
3.1623	1.2858	0.1162	1.3009	0.6722	0.6769
5.0000	1.3254	0.1546	1.3343	0.6633	0.6661
7.0711	1.3540	0.1927	1.3549	0.6547	0.6550
8.3666	1.3668	0.2162	1.3631	0.6493	0.6481
10.0000	1.3795	0.2416	1.3695	0.6436	0.6403
12.2474	1.3973	0.2734	1.3795	0.6367	0.6306
14.1421	1.4175	0.2980	1.3931	0.6319	0.6235
17.3205	1.4685	0.3408	1.4325	0.6246	0.6123

Sqrt S ×10	-R10 10-9	-R20 10-9	-COR10 10-11	-COR20 10-11	ROO/N 10-7
0.0000	2.1638	2.2031	1.1974	1.2192	7.8909
3.1623	2.1205	2.1479	1.1696	1.1847	7.7387
5.0000	2.1333	2.1496	1.1708	1.1797	7.8044
7.0711	2.1343	2.1360	1.1613	1.1622	7.8483
8.3666	2.1289	2.1221	1.1506	1.1469	7.8656
10.0000	2.1286	2.1099	1.1379	1.1280	7.9284
12.2474	2.1413	2.1073	1.1239	1.1061	8.0948
14.1421	2.1745	2.1272	1.1195	1.0951	8.3555
17.3205	2.2829	2.2101	1.1276	1.0917	9.0959

*Transport number at 0.1M is interpolated.

Table-6.3

CAESIUM CHLORIDE

c	m	Eqv Cond	t+	D(v)$_{10}$5	1+mxdlnGama/dm
0.0000	0.000000	153.63	0.5030	2.0440	1.0000
0.1000	0.100700	130.85	0.5020*	1.8710	0.8884
0.2500	0.253300	123.70	0.5005	1.8550	0.8587
0.5000	0.519900	118.30	0.4972	1.8600	0.8421
0.7000	0.722800	115.73	0.4952	1.8710	0.8414
1.0000	1.046100	113.10	0.4926	1.9020	0.8492
1.5000	1.604800	109.86	0.4891	1.9600	0.8725
2.0000	2.190500	107.20	0.4861	2.0290	0.9011
3.0000	3.452400	101.63	0.4812	2.1750	0.9648

Sqrt S x10	l11/N $_{10}$+12	l12/N $_{10}$+12	l22/N $_{10}$+12	F12	Q12
0.0000	8.2976	0.0000	8.1986	0.0000	0.0000
3.1623	7.7896	0.7348	7.7334	0.1730	0.0947
5.0000	7.6854	1.0360	7.6721	0.2378	0.1349
7.0711	7.5962	1.2790	7.6673	0.2871	0.1676
8.3666	7.5334	1.3783	7.6527	0.3073	0.1815
10.0000	7.4653	1.4817	7.6451	0.3280	0.1961
12.2474	7.3538	1.5829	7.6110	0.3493	0.2116
14.1421	7.2624	1.6657	7.5825	0.3668	0.2245
17.3205	7.0747	1.8223	7.4851	0.4007	0.2504

Sqrt S x10	NR11 $_{10}$-11	-NR12 $_{10}$-11	NR22 $_{10}$-11	Q10	Q20
0.0000	1.2052	0.0000	1.2197	0.7050	0.7092
3.1623	1.2954	0.1231	1.3048	0.6713	0.6743
5.0000	1.3253	0.1790	1.3276	0.6573	0.6581
7.0711	1.3545	0.2259	1.3419	0.6472	0.6430
8.3666	1.3727	0.2472	1.3513	0.6433	0.6361
10.0000	1.3931	0.2700	1.3604	0.6396	0.6234
12.2474	1.4236	0.2961	1.3755	0.6361	0.6195
14.1421	1.4500	0.3185	1.3888	0.6332	0.6121
17.3205	1.5081	0.3671	1.4254	0.6265	0.5977

Sqrt S x10	-R10 $_{10}$-9	-R20 $_{10}$-9	-COR10 $_{10}$-11	-COR20 $_{10}$-11	ROO/N $_{10}$-7
0.0000	2.1777	2.2040	1.2052	1.2197	7.9179
3.1623	2.1267	2.1438	1.1723	1.1817	7.7471
5.0000	2.0924	2.0966	1.1463	1.1486	7.6459
7.0711	2.1140	2.0905	1.1286	1.1160	7.8758
8.3666	2.0935	2.0537	1.1254	1.1040	7.7146
10.0000	2.1166	2.0548	1.1231	1.0904	7.8612
12.2474	2.1731	2.0804	1.1275	1.0794	8.1981
14.1421	2.2325	2.1117	1.1315	1.0703	8.5716
17.3205	2.3653	2.1939	1.1409	1.0582	9.4519

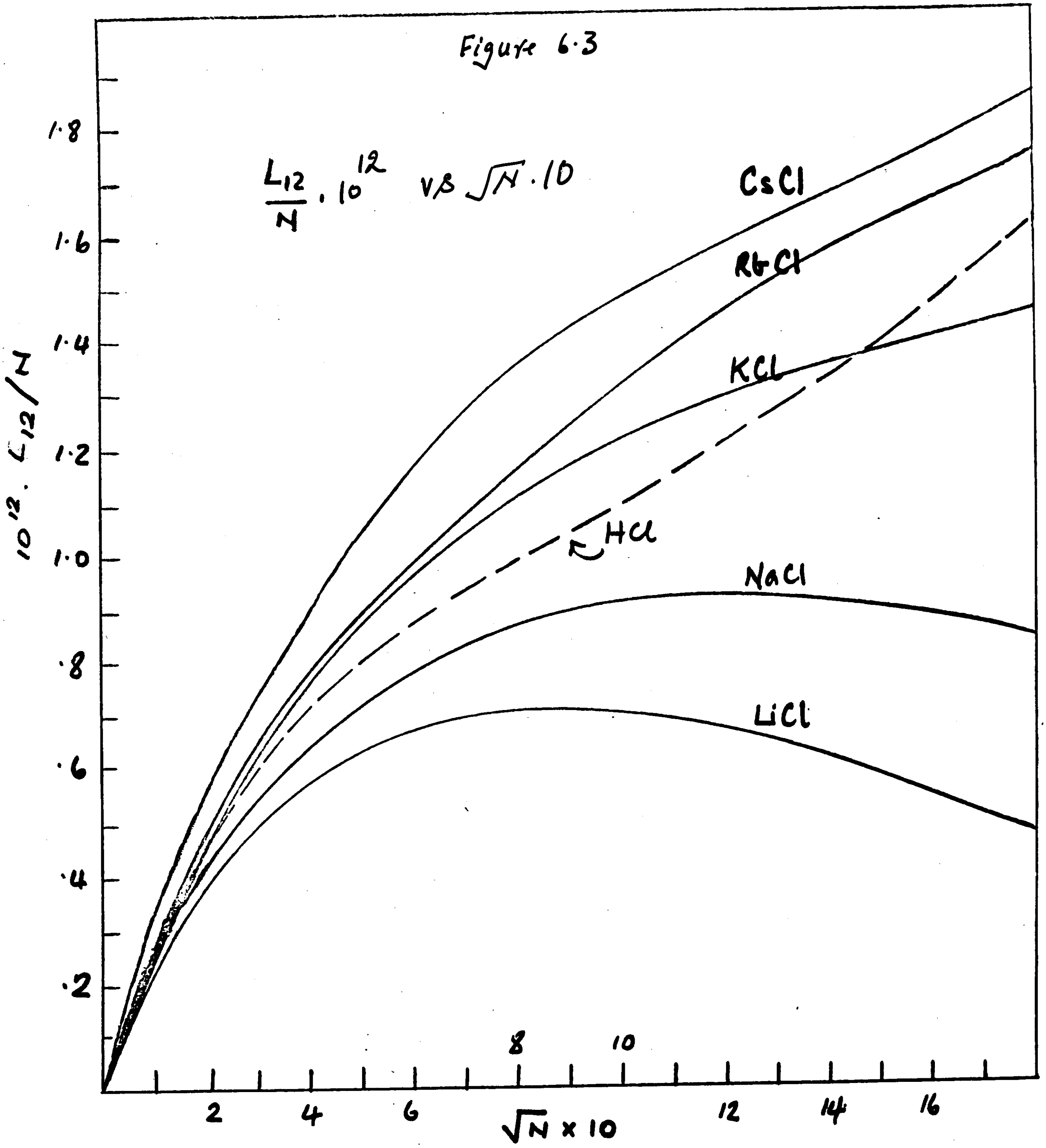
* Transport number at 0.1M is interpolated.

Since the intrinsic mobility of an ion does not depend upon the effect of the counter ion, the above order may be explained in terms of the state of the solvent structure in the presence of different cations. The solvent order producing cations, Li^+ and Na^+, increase the water structure and thereby decrease the mobility of the Cl^- ions. The solvent order destroying ions, K^+, Rb^+ and Cs^+, on the other hand, decrease the resistance of the solvent medium to ionic flow and cause an increase in the mobility of the chloride ion. On the basis of this hypothesis the sequence of the Cl^- ion mobility would be essentially in the same order as that of the cations as is observed in figure 6.1.

In the alkali metal chlorides, RbCl falls between KCl and CsCl but its equivalent conductance, transport numbers and diffusion coefficients, lie above that of CsCl. That is, they are the highest in the whole series. The largest magnitudes of the intrinsic mobility of Rb^+ ion, L_{11}/N, provides an indication to the cause of this anomalous behaviour. Since the intrinsic mobility of an ion depends upon the state of the solvent, the latter is offering the least resistance to the flow of Rb^+ ion, and so explains the order of the transport properties.

6.1.2 <u>The Cross Coefficient, L_{12}/N</u>: The cross or interaction coefficient, L_{12}/N, plotted in figure 6.3, directly represents the cation and anion interaction. Because it is a solvent fixed coefficient there is some solvent contribution. It is zero at zero concentration as there are no interactions when the ions are infinitely separated

Figure 6.3


$\frac{L_{12}}{N} \cdot 10^{12}$ vs $\sqrt{N} \cdot 10$
$10^{12} \cdot L_{12}/N$
1·8
1·6
1·4
1·2
1·0
·8
·6
·4
·2
CsCl
RbCl
KCl
HCl
NaCl
LiCl
2
4
6
8
10
12
14
16
$\sqrt{N} \times 10$

and increase rapidly with concentration. At higher concentrations, L_{12}/N goes through maxima for LiCl and NaCl but increases continuously for KCl, RbCl and CsCl, the values at a particular concentration being largest for CsCl and smallest for LiCl. The highest intrinsic mobility of Rb^+, shown by L_{11}/N coefficients, does not alter the order of L_{12}/N.

The largest interaction of Cs^+ and Cl^- compared to that of Li^+ and Cl^- might well occur if the Li^+ ion were properly screened by its largest solvation sheath which would increase the distance of closest approach and hence decrease the average coulombic force between them. On the other hand the effect of the larger solvation sheath around Li^+ ion would be to orientate solvent more rigidly and subject it to partial dielectric constant around the ion and enhance the coulombic interaction between Li^+ and Cl^- ions. If, however, this model is acceptable, the distance effect would have to be substantially larger in order to explain the sequence. The decrease in L_{12}/N for NaCl and LiCl at higher concentration is again based on this model (of distance effect) which decreases the cation and anion interaction per unit concentration.

Stokes[83] has suggested that L_{12}/N might reflect incipient ion association because of increased coulombic interactions due to decrease in hydration as we go from Li^+ to Cs^+. If this were the case then incipient ion association would be maximum for CsCl and least for LiCl. This, however, is also the order of the intrinsic mobilities of the cations which, in turn, are determined by ion-solvent interactions. This is more clearly brought out by the L_{12}/N values for HCl, HNO_3 and NaOH which are very high indeed. Stoke's model therefore does not provide a clear picture od ion-association. Kedem and Caplan[89] have defined a new parameter q_{12} as a better measure of the degree of coupling between species 1 and 2 in a two component system. q_{12} is explained in the section 6.3.

6.2 The Frictional Coefficients: The phenomenological eqns(2.33) represents relations between the forces, X_i, and their conjugate flows, J_i, in terms of the frictional coefficients, R_{ik}. This inverse description of transport by frictional coefficients provides an alternative and complementary representation. It is theoretically less well defined because of the assumption, $\sum_{k=0}^{n} c_k R_{ik}=0$ $i=0,1,2$; eqn(2.26). The advantages are that the frictional coefficients become independent of the frame of reference[90] and additional frictional coefficients, R_{i0}, which measure friction between ion and solvent, are obtained. On solvent fixed frame of reference the phenomenological eqns(2.35) may be re-written as

$$X_i = R_{ii}J_i + R_{ik}J_k \qquad (6.5)$$

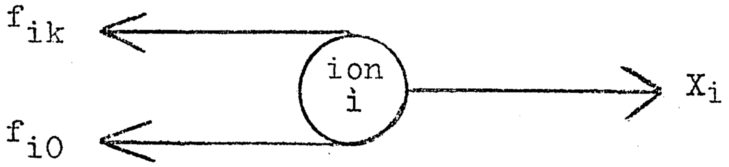
From eqns(2.36) and (6.5), R_{ii} may be eliminated to yield

$$X_i = -R_{ik}(J_i - J_k)-(c_0/c_i)R_{i0}J_i \qquad (6.6)$$

Each term on the right hand side has the dimensions of a thermodynamic force and represent the frictional interactions of species i and k, and i and solvent. This is essencially the mechanistic interpretation of Spiegler[83] who considered a force, X_i, to be balanced exactly by the sum of all the frictional forces, f_{ik}, figure 6.4, such that eqn(6.7) holds;

Figure 6.4

Equilibrium between a force X_i applied on an ion i, and the frictional forces, f_{ik} and f_{i0}.



$$X_i = \sum_{\substack{k=0\\k\neq i}}^{n} f_{ik} = \sum_{\substack{k=0\\k\neq i}}^{n} -x_{ik}(v_i - v_k) \qquad (6.7)$$

where x_{ik} is the coefficient of kinetic friction and $(v_i - v_k)$ is the velocity of i relative to k. Also the relative flow $(J_i - J_k)$ is given by

$$(J_i - J_k) = c_k(v_i - v_k) \qquad (6.8)$$

From eqns(6.6),(6.7) and (6.8) we obtain

$$-x_{ik} = c_k R_{ik} \qquad i,k=0,1,2;i\neq k; \qquad (6.9)$$

For completely dissociated 1:1 salts, $c_1 = c_2 = N$, therefore ion-ion friction is represented by

$$-x_{12} = NR_{12} = -x_{21} = NR_{21} \tag{6.10}$$

That is, the coefficient, $-NR_{12}$, represents the coefficient of kinetic friction, x_{12}.

For a three component system eqn(2.37) may be rewritten as

$$c_i R_{ii} = -\sum_{i=0\neq k}^{n} c_k R_{ik} \tag{6.11}$$

From eqns(6.9) and (6.11) we get

$$c_i R_{ii} = \sum_{i=0\neq k}^{n} x_{ik} \tag{6.12}$$

The term $c_i R_{ii}$ is therefore the sum of the frictional coefficients between one mole of species i and all other species k in one litre of the solution. On this basis the R_{ii} coefficients assume lesser importance than the coefficients, R_{ik}, $i \neq k$. As for example the value of $NR_{11}(c_i=N)$ for RbCl, figure 6.5, is minimum because c_0R_{10}, figure 6.7, is minimum and the order of NR_{11} coefficients is the same as that of c_0R_{10}. The relative difference in magnitude depends upon the value of NR_{12} at that concentration. In the same way the behaviour of NR_{22} coefficients, figure 6.6, depends upon that of c_0R_{20} and NR_{12}. Further, the coefficient, R_{00}/N, figure 6.9, is simply a summation of the coefficients, R_{10} and R_{20}, eqn(2.66). Therefore the transport processes in electrolyte solutions are better understood if we study the nature of the coefficients, c_0R_{i0} and c_kR_{ik}.

Figure 6.5

$NR_{11} \cdot 10^{-11}$ vs $\sqrt{N}$

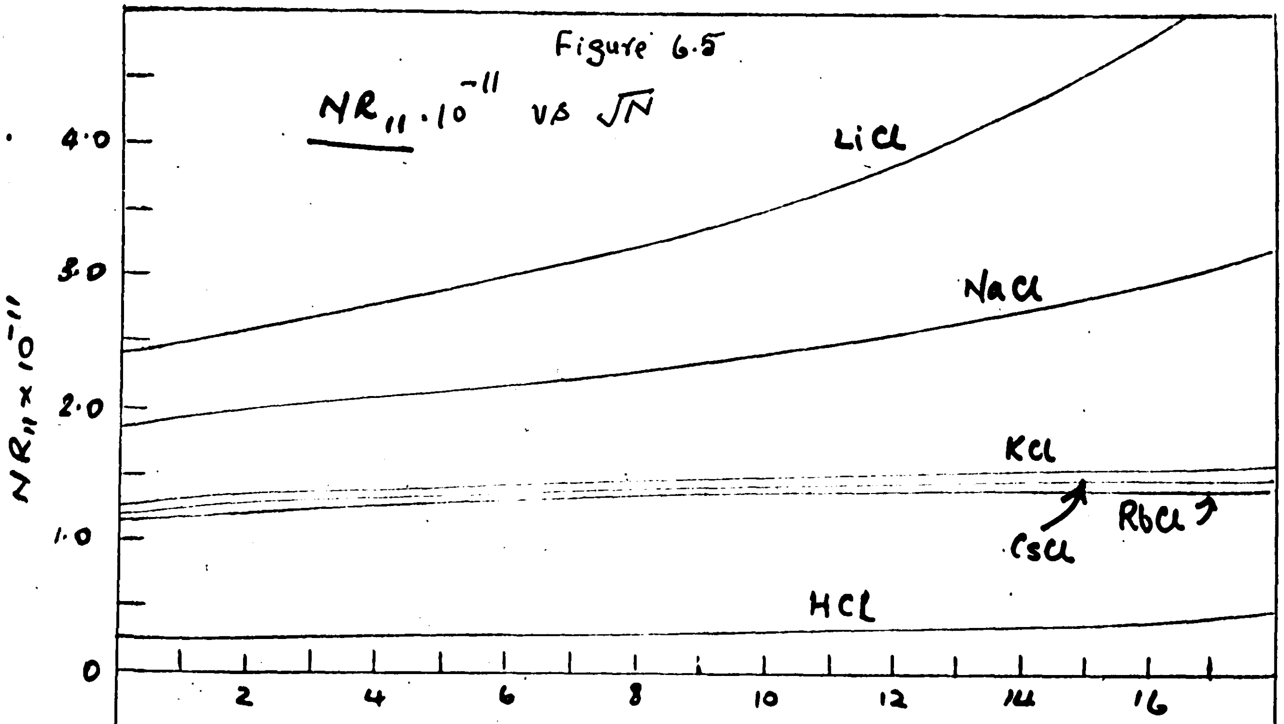
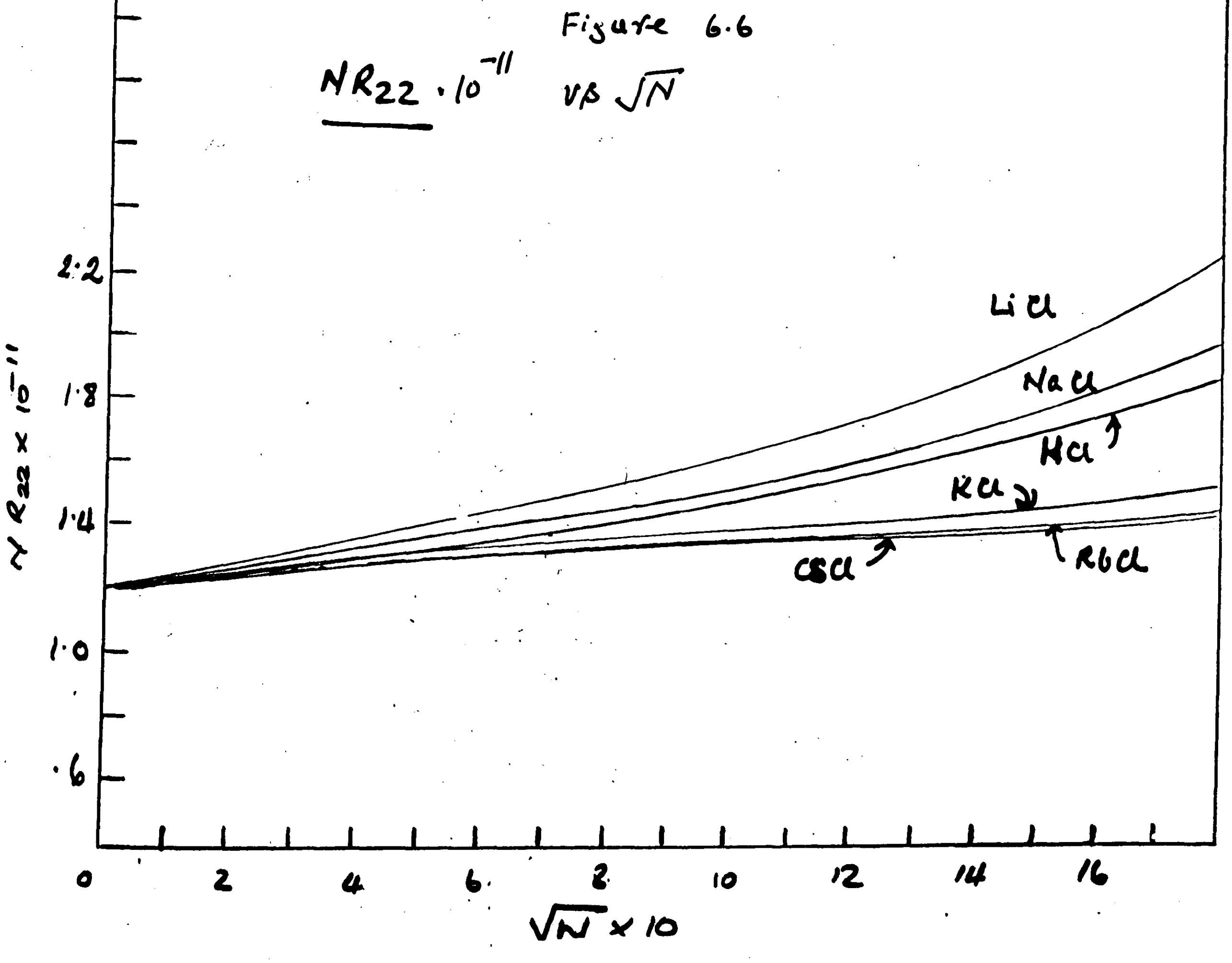


Figure 6.6

$NR_{22} \cdot 10^{-11}$ vs $\sqrt{N}$



6.2.1 The Coefficients, $-c_0R_{10}$ and $-c_0R_{20}$: The coefficients $-c_0R_{10}$ and $-c_0R_{20}$ are plotted in figures 6.7 and 6.8 respectively. They represent friction between one gram ion, i, and the surrounding solvent per litre of the solution.

The coefficient, $-c_0R_{10}$, is the least for RbCl and largest for LiCl. At infinite dilution it has distinct values for each cation. As concentration increases* continuously for NaCl and LiCl. This may be explained in terms of the tendency of the solvent, water, to solvate the ions. Li^+ and Na^+ ions are highly solvated and as concentration increases more and more water molecules are removed from the solution in the process of hydration. This is why $-c_0R_{10}$ increases continuously for these ions. K^+, Cs^+ and Rb^+ ions are the least solvated and therefore $-c_0R_{10}$ for these ions is virtually constant. The lowest value of $-c_0R_{10}$ for RbCl shows that the solvent is offering the least resistance to the motion of Rb^+ ion and for this reason, the transport properties like equivalent conductance, transport numbers and diffusion coefficients, for RbCl, are the highest in the alkali metal chloride series.

The anion frictional coefficient, $-c_0R_{20}$, decreases continuously for RbCl and CsCl while for KCl, NaCl and LiCl it passes through minima and then increases. Since the anion is the same, $-c_0R_{20}$ converge to the same point at infinite dilution. At finite concentrations the magnitude of $-c_0R_{20}$ depends upon the structural interactions of the ions with the solvent. In dilute solutions the order is

$$LiCl < NaCl < Kcl < (RbCl?) < (CsCl?).$$

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* $-c_0R_{10}$ increases

Figure 6.7

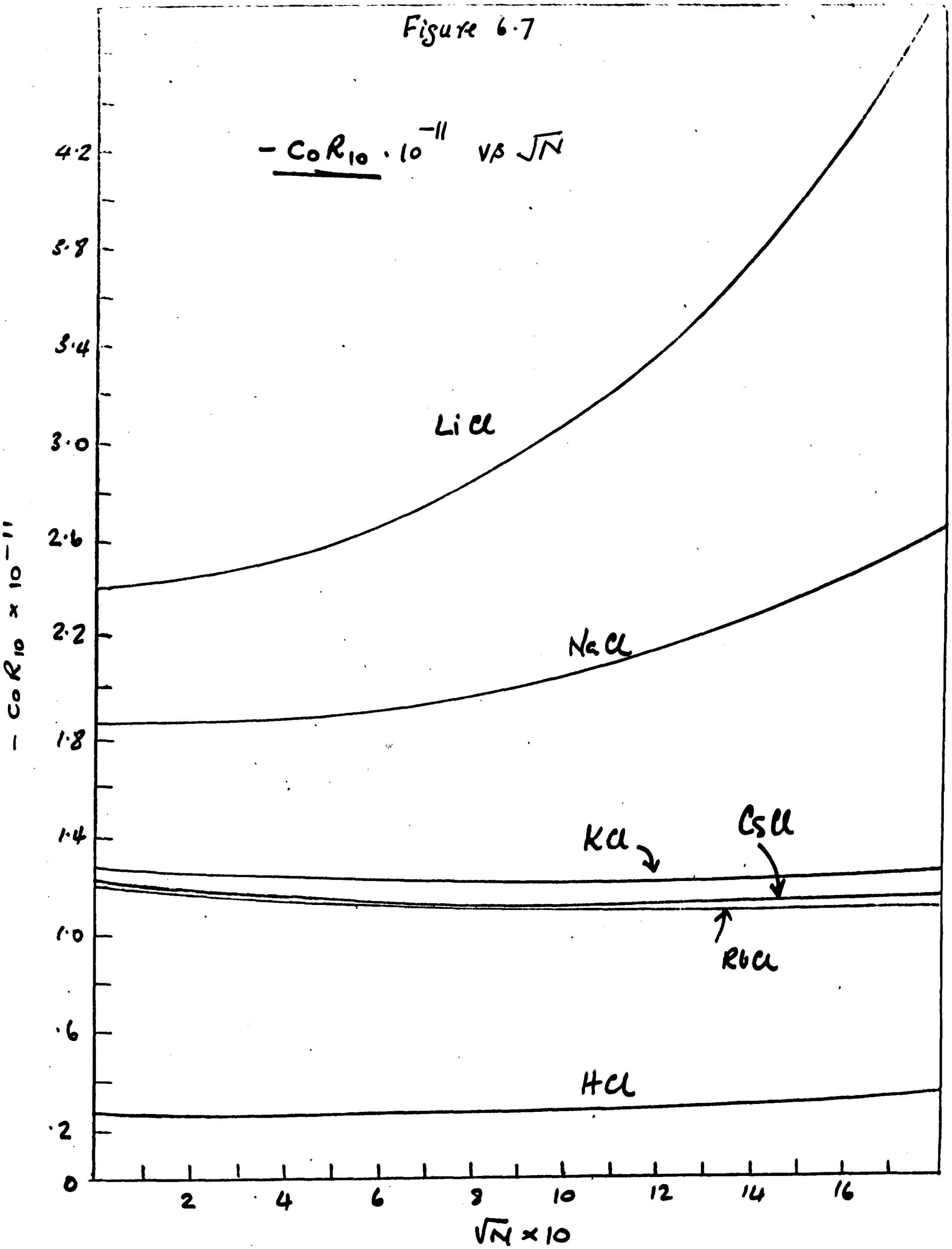
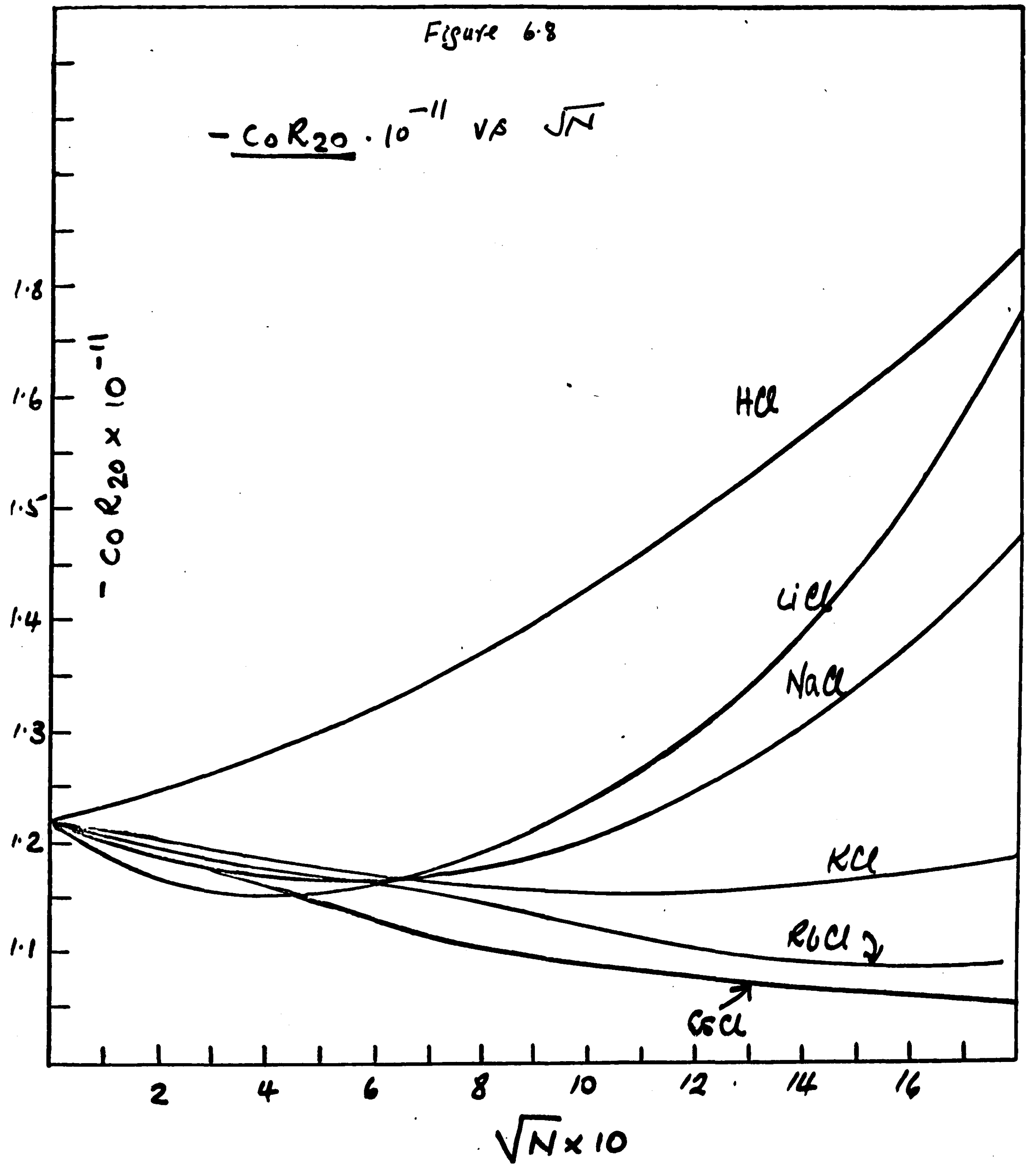

$-C_oR_{10} \cdot 10^{-11}$ vs $\sqrt{N}$
LiCl
NaCl
KCl
CsCl
RbCl
HCl
4·2
3·8
3·4
3·0
2·6
2·2
1·8
1·4
1·0
·6
·2
0
2
4
6
8
10
12
14
16
$-C_oR_{10} \times 10^{-11}$
$\sqrt{N} \times 10$

Figure 6·8


$-\underline{C_0 R_{20}} \cdot 10^{-11}$ vs $\sqrt{N}$
$-C_0 R_{20} \times 10^{-11}$
1·8
1·6
1·5
1·4
1·3
1·2
1·1
2
4
6
8
10
12
14
16
$\sqrt{N} \times 10$
HCl
LiCl
NaCl
KCl
RbCl
CsCl

There is an inversion at ≈ 0.4M and the final order is

$LiCl > NaCl > KCl > RbCl > CsCl$

This behaviour may be explained if we examine the state of the solvent in the vicinity of an ion. According to Gurney's[85] concepts, Li^+ and Na^+ ions are solvent order producing. They enhance the structure of the solvent and increase the ion-solvent friction. On the other hand, the ions, K^+, Rb^+, Cs^+ and Cl^-, are solvent order destroying. They loosen the structure of the solvent and decrease the ion-solvent friction. In dilute solutions of LiCl, the ions are far apart and the order destroying tendency of the Cl^- ion is dominant in controlling the behaviour of $-c_0R_{20}$ and therefore the anion-solvent friction decreases initially. As concentration increases the order producing tendency of the Li^+ ion becomes effective and the Cl^- ion moves through a more structured solvent. The motion of the anion is conditioned by the order producing or order destroying tendency of the cations. Therefore in concentrated solutions the order of $-c_0R_{20}$ is the same as that of $-c_0R_{10}$.

The conditioning of the motion of the Cl^- ion by the solvent order producing and order destroying tendencies of the cations is supported by the behaviour of $-c_0R_{10}$ and $-c_0R_{20}$ coefficients in HCl, HNO_3 and NaOH solutions. The results for HNO_3 and NaOH are given in appendix 1. The coefficients, $-c_0R_{10}$, for HCl and HNO_3, and $-c_0R_{20}$ for NaOH, plotted in figures 6.7 and 6.8, are very small as compared to those of the alkali metal cations, fig.6.7, and the Cl^- ion, fig.6.8. This reflects the unique transport mechanism of the H^+ and OH^- ions. However, these ions are polarising and highly order producing in their effect upon the solvent. This is reflected in the increasing values of $-c_0R_{20}$ for HCl and HNO_3 and of $-c_0R_{10}$ for NaOH as concentration increases. The curves of $-c_0R_{20}$ for HCl and HNO_3 lie above that of LiCl, figure 6.8, and the curve of $-c_0R_{10}$ for NaOH lies above that of NaCl, figure 6.7. The anion plays the same role in figure 6.8 as the H^+ ion does in figure 6.7. At infinite dilution $-c_0R_{10}$ for NaOH is the same as that of NaCl showing that the order producing nature of the OH^- ion and order destroying nature of Cl^- ion have little effect upon the structure of the solvent in the vicinity of the cation, Na^+.

That the solvent is highly structured in solutions of HCl is supported by the work of Sulovkin[91] who has reported the surface densities of H_2O molecules in the first coordination layer of the cations and anions, $\int_{+}^{1}$ and $\int_{-}^{1}$. The values, calculated from the stoicheiometric activity coefficients, are given in table 6.4. It may be seen that $\int_{+}^{1}$ for H^+ is closer to that of Li^+ ion and $\int_{-}^{1}$ in HCl is higher than that for the alkali metal ions showing that the solvent around Cl^- ion in HCl is more structured than in the other halides.

Table 6.4

Surface densities of water in the first coordination layer of cations and anions.

		H^+	Li^+	Na^+	K^+	Rb^+	Cs^+
Cations	$\int_{+}^{1}$	0.060	0.065	0.053	0.043	0.040	0.036
Anions	$\int_{-}^{1}$	0.043	0.035	0.035	0.035	0.035	0.035

The order of coefficients, $-c_0R_{10}$ and $-c_0R_{20}$, in dilute solutions may be correlated with B-coefficients of viscosity introduced by Jones and Dole[92] through the eqn(6.13).

$$\eta = \eta_0(1 + A\sqrt{c} + B\,c) \tag{6.13}$$

Gurney[85] has assigned numerical values of B-coefficients to individual ions and to the electrolyte as a whole in dilute solutions of alkali metal chlorides. These are reproduced in table 6.5.

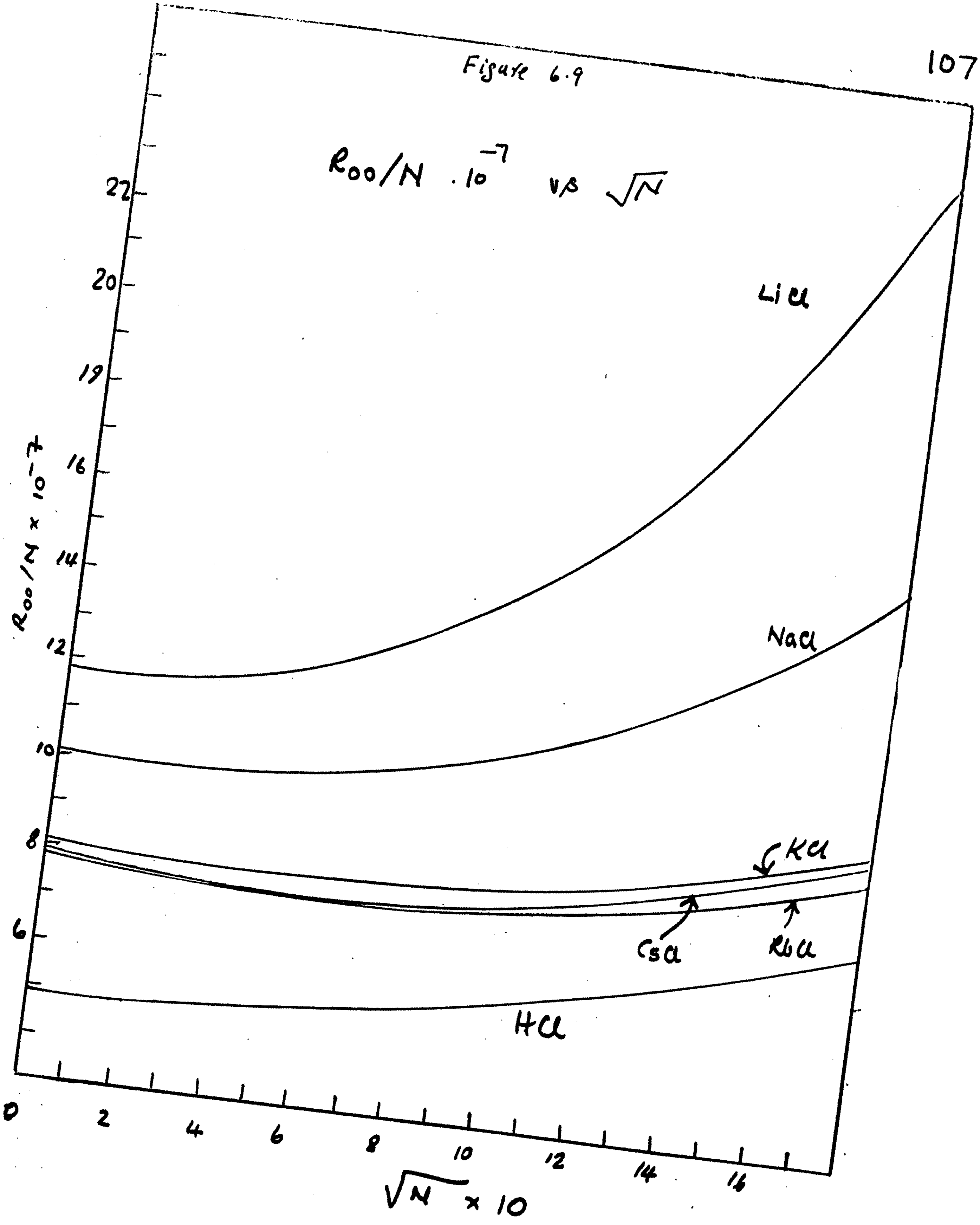
Table 6.5

B-coefficients of viscosity.

	B-coefficients		
	electrolyte	+ve ion	-ve ion
LiCl	+0.139	+0.147	-0.007
NaCl	+0.079	+0.086	-0.007
KCl	-0.014	-0.007	-0.007
RbCl	-0.037	-0.029	-0.007
CsCl	-0.050	-0.042	-0.007

A -ve B-coefficient for an ion implies that the ion is order destroying and a +ve B-coefficient means that the ion is order producing. In this sense Cl^-, K^+, Rb^+ and Cs^+ ions are solvent order destroying and Li^+ and Na^+ are order producing.

Figure 6.9

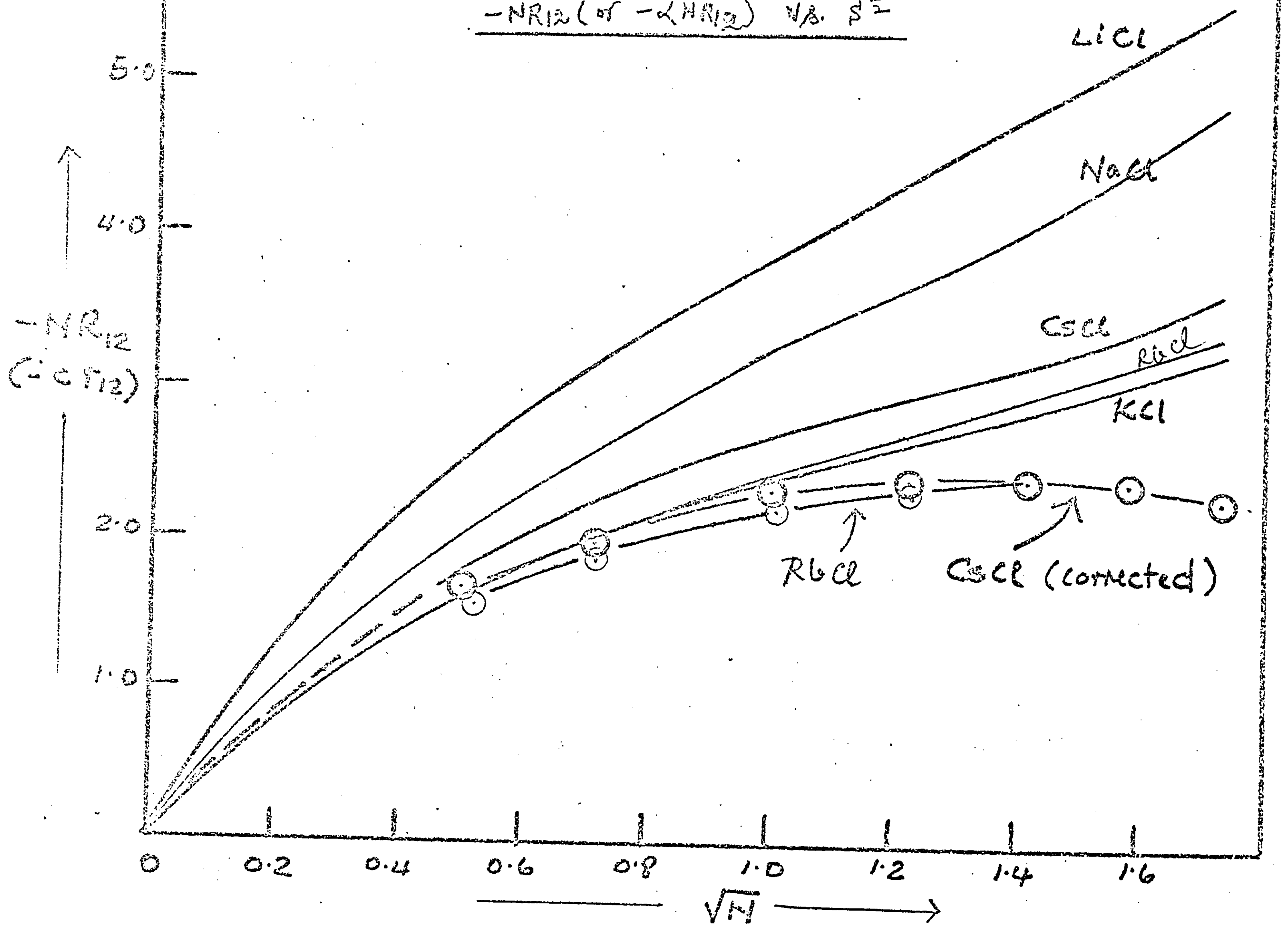

$R_{00}/N \cdot 10^{-7}$ vs $\sqrt{N}$
22
20
19
16
14
12
10
8
6
$R_{00}/N \times 10^{-7}$
0
2
4
6
8
10
12
14
16
$\sqrt{N} \times 10$
LiCl
NaCl
KCl
CsCl
RbCl
HCl

The B-coefficients represent contributions from co-spheres of individual ions and in dilute solutions they are independent and additive. Since in aqueous solutions water molecules make the co-spheres of ions and the coefficients, $-c_0R_{10}$ and $-c_0R_{20}$, add up to give the function, R_{00}/N, it is of interest to compare the overall B-coefficients of the electrolytes with the function, R_{00}/N, plotted in figure 6.9. In solutions of KCl, RbCl and CsCl the effect of -ve overall B-coefficient is that the solvent is loosening its structure and this leads to continuous decrease in the total friction between the ions and solvent. This is shown by the decreasing trends of the curves for these salts. In the solutions of LiCl and NaCl the overall B-coefficients are +ve. R_{00}/N for these salts increases continuously with concentration.

6.2.2 *The Coefficient, $-NR_{12}$*: In figure 6.10, $-NR_{12}$ is plotted vs.$\sqrt{S}$. It is a smoothly increasing curve with zero intercept at infinite dilution. The representation of the cation-anion friction by the frictional coefficient, $-NR_{12}$, is supported by its equality with the coefficient of kinetic friction, x_{12} eqn(6.10). The latter, as it is the frictional coefficient between one gram ion, 1, and all the ions, 2, in one litre of the solution, must tend to zero as $c_1=c_2$ tends to zero. Two features are apparent: a) lithium chloride has the greatest frictional coefficient in the series whereas its coupling of flows, as measured by L_{12}/N, is the least, b) unlike the direct frictional coefficients, NR_{ii}, which are in the inverse order of their corresponding ion mobility coefficients,

Figure 6.10

$-NR_{12}$ (or $-\alpha NR_{12}$) vs. $S^{\frac{1}{2}}$



L_{ii}/N, the cross coefficients, $-NR_{12}$, do not invert. The curves for rubidium and caesium chlorides lie between those of sodium and potassium chlorides. According to the expected order, they should have been below that of potassium chloride. The magnitude of $-NR_{12}$ for these two salts appears to be enhanced and shows that there is an additional factor which increases the friction between the cations and anions. The cations of these salts, Rb^+ and Cs^+, are the heaviest in the alkali metal series. They are therefore most likely to ion-pairing which may be of the type discussed by Gurney[35] between order destroying ions, Rb^+ and Cl^-, and Cs^+ & Cl^-. From an early conductance work at 18°C Davies[32] obtained PK_α value of 0.4 for CsCl, where K_α is the association constant. Effect of ion association on the frictional coefficient, $-NR_{12}$, is therefore of great importance.

The influence of ion association on the phenomenological coefficients was studied in chapter 2, section(2.9) where it was shown that the phenomenological coefficients, R_{ik}, obtained from the formal analysis of transport data, apply to both strong and weak electrolytes. The mechanistic interpretation of Spiegler[33], discussed in section 6.2, showed that it is the function $c_k R_{ik}$ which determines the friction between cations and anions. The magnitude of this function depends upon the concentration of species, k, in the solution. For completely dissociated 1:1 salts, $c_i = c_k = N$, and therefore $-NR_{12}=x_{12}$ representation of the cation-anion friction holds, but for systems in which association takes place $c_k \neq N$ and so $x_{ik} \neq NR_{ik}$. If α is the degree of dissociation then $c_k = \alpha N$ and therefore

$$+x_{ik} = -\alpha NR_{ik} = -c_k r_{ik} \qquad (6.14)$$

It is the function, $-\alpha NR_{ik}$, that determines the interionic frictional interaction. The degree of dissociation α may be obtained by studying ion association using currently available theories[6,7] of conductance in electrolyte solutions.

Ion association for alkali metal chlorides was studied in chapter 5, using the experimental conductance data for RbCl and CsCl and the literature conductance data for the other salts. Association constant, Ka, table 5.8, was found to be negligible for lithium, sodium and potassium chlorides while for rubidium and caesium chlorides its numerical values were 0.275±0.083 and 0.409±0.061 respectively. Using these values of Ka and the relationship[93]

$$\alpha = 1 - N(f_{\pm})^2 Ka \qquad (6.15)$$

where $f_{\pm}$ is the stoichoiometric activity coefficient, an estimation of the degree of dissociation, α, was made. $f_{\pm}$ was obtained from the mean molal activity coefficient, γ, using the relationship[93]

$$f_{\pm} = 0.997\gamma m/c \qquad (6.16)$$

The results of calculations are given in table 6.6 alongwith the calculated values of the function $-\alpha NR_{12}$.

In figure 6.10, dotted curves represent $-\alpha NR_{12}$ for rubidium and caesium chlorides.

For lithium, sodium and potassium chlorides, $\alpha = 1$, and therefore

$$-\alpha NR_{12} = -NR_{12} \qquad (6.17)$$

Table 6.6

Calculated values of degree of dissociation, α, and $-\alpha NR_{12}$ using Ka=0.275 for RbCl and 0.409 for CsCl.[12]

Concentration c	RbCl			CsCl		
	$\gamma_{\pm}$	α	$-\alpha NR_{12}$	$\gamma_{\pm}$	α	$-\alpha NR_{12}$
.25	.688	.967	.150	.672	.953	.170
.5	.633	.943	.182	.603	.920	.208
.7	.606	.926	.200	.572	.901	.223
1.0	.580	.901	.218	.540	.870	.235
1.5	.556	.858	.235	.508	.820	.243
2.0	.543	.813	.242	.491	.765	.244
2.5	.537	.761	.243	.480	.705	.241
3.0	.536	.703	.240	.476	.634	.233

Between one and two molar concentrations the sequence of $-\alpha NR_{12}$ is

$$\mathrm{RbCl} < \mathrm{CsCl} < \mathrm{KCl} < \mathrm{NaCl} < \mathrm{LiCl}$$

Above two molar, $-\alpha NR_{12}$ for RbCl and CsCl overlap and there is no difference in their magnitudes because of large uncertainties in Ka and hence in α .

Below 1M concentration the curve for RbCl is virtually coincident with that of KCl and for CsCl it lies a little above. Unfortunately accurate transport number data below 0.25M does not exist, so no accurate estimate of $-\alpha NR_{12}$ can be made in dilute solutions.

6.2.3 Fraction of a force applied on ion, 1, which is opposed by its friction with the ion, 2, F_{12}:

For a solutions containing cations, 1, and anions, 2, eqn(6.6) may be re-written as:

$$X_1 = -R_{10}(J_1-J_2)-(c_0/c_1)R_{10}J_1 \qquad (6.18a)$$

$$X_2 = -R_{21}(J_2-J_1)-(c_0/c_2)R_{20}J_2 \qquad (6.18b)$$

From eqns(6.18a and b) it is obvious that the applied force, X_i, is exactly balanced by the sum of two opposing forces. Substituting an applied electric force, $X_i = Z_i F(\frac{-\partial\phi}{\partial x})$, in eqn(6.18), we get:

$$1 = F_{12} + F_{10} = \frac{-R_{12}N\Lambda}{10^3F^2} + \frac{-c_0R_{10}t_1N\Lambda}{c_1 . 10^3F^2} \qquad (6.19a)$$

$$1 = F_{21} + F_{20} = \frac{-R_{21}N\Lambda}{10^3F^2} + \frac{-c_0R_{20}t_2N\Lambda}{c_2.10^3F^2} \qquad (6.19b)$$

Where $F_{12}(=F_{21})$ is the fraction of the force applied on ion, 1, which is opposed by its friction with the ion,2. F_{i0} is the fraction of the force applied on ion, i=1,2 which is opposed by its friction with the solvent, 0. F_{10} equals F_{20} from the identity:

$$R_{20}t_2 = R_{10}t_1 \qquad (6.20)$$

(This result is derived from the inverse description of the transport numbers as

$$t_1 = R_{20}/(R_{10} + R_{20}) \qquad (6.21a)$$

$$t_2 = R_{10}/(R_{20} + R_{10}) \qquad (6.21b))$$.

Eqns(6.18) and (6.19) may be re-written as

$$F_{12} = \frac{-R_{12}N\Lambda}{10^3F^2} = -\frac{R_{12}(J_1-J_2)}{X_1} \qquad (6.22a)$$

$$F_{i0} = \frac{-c_0R_{i0}t_iN\Lambda}{c_i10^3F^2} = \frac{-c_0R_{i0}J_i}{c_iX_i} \qquad (6.22b)$$

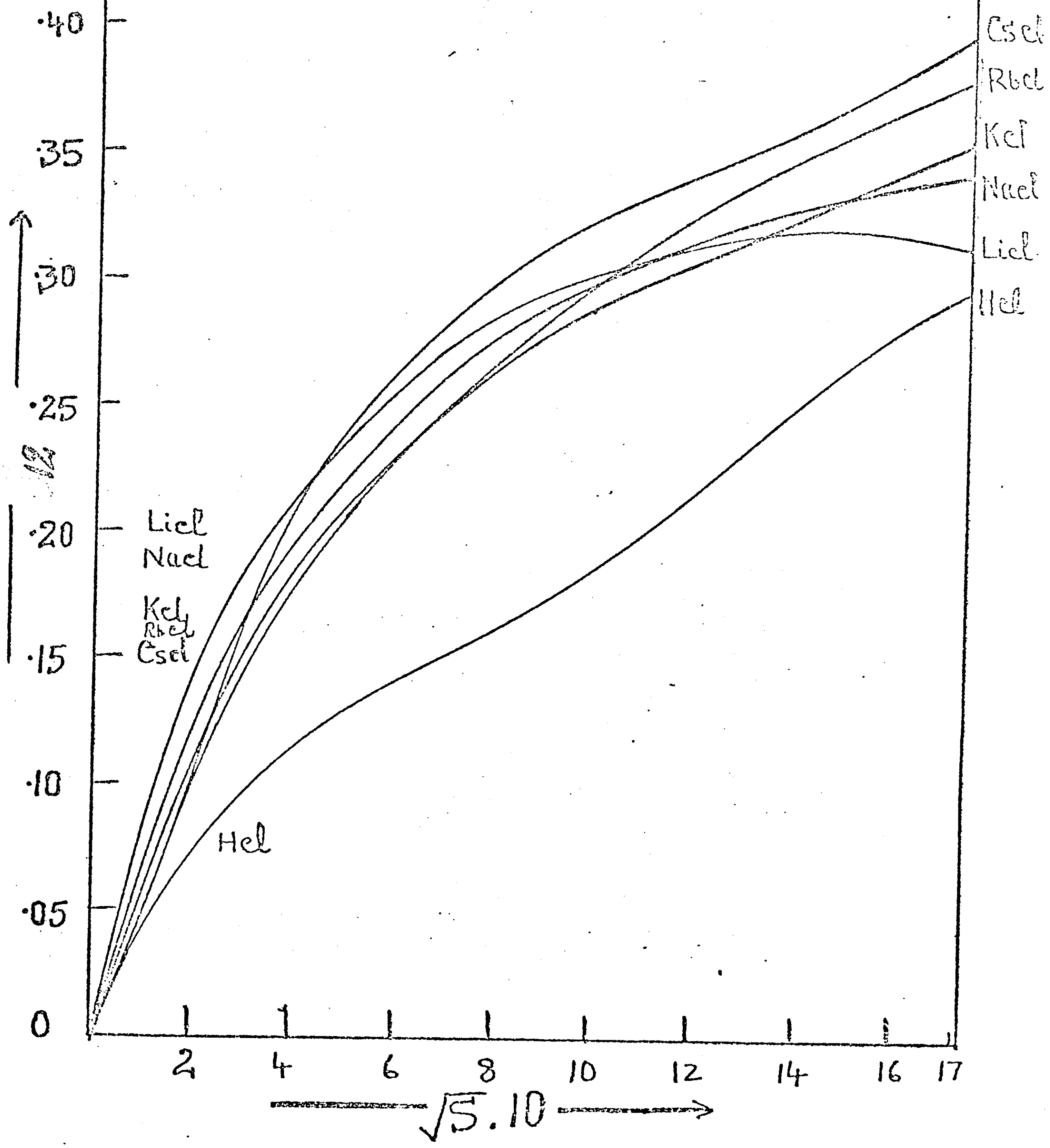
The forces and flows may be replaced by the identities

$$X_i = Z_iF(-\partial\phi/\partial x) \text{ and } J_i = c_iv_i$$

where the velocity, v_i, is in litres/cm^2 sec. For an applied electric gradient of one volt, $(-\partial\phi/\partial x=1)$, in eqns(6.22), we obtain

Figure 6.11

ℓ_{12} VS $\sqrt{S}$



$$\Lambda = (\bar{v}_1 - \bar{v}_2)F/Z_1 \qquad (6.23a)$$

and

$$t_i\Lambda = \bar{v}_i F/Z_i \qquad (6.23b)$$

where $\bar{v}_i$ (cm/sec) is the mobility of the ion i under unit electric gradient and is defined as $10^3 v_i/(-\partial\phi/\partial x)$. For cations $Z_1 = +1$ and anions $Z_2 = -1$, therefore,

$$\Lambda = (\bar{v}_1 - \bar{v}_2)F \qquad (6.24a)$$

$$t_1\Lambda = \bar{v}_1 F \qquad (6.24b)$$

$$t_2\Lambda = \bar{v}_2 F \qquad (6.24c)$$

These expressions (6.24) define the relative mobilities and individual mobilities of ions in more classical terms.

In figure 6.11, values of F_{12} are plotted. As concentration tends to zero, F_{12} tends to zero and $F_{10}(=F_{20})$ to unity. An applied force on an ion at infinite dilution is totally balanced by its friction with the solvent. In dilute solutions the order of F_{12} is:

$$\text{LiCl} > \text{NaCl} > \text{KCl} > (\text{RbCl?}) > (\text{CsCl?}).$$

The ion-ion friction amounts to 10% of the total at $\simeq 0.05$M. In the range of comparison, CsCl has the largest value of F_{12} which amounts to 40.15% of the applied force at 3M. In the range 0.25-3M there is a series of cross-overs until the final order is:

$$\text{CsCl} > \text{RbCl} > \text{KCl} > \text{NaCl} > \text{LiCl}$$

The coupling of flows as measured by the mobility coefficient, L_{12}, might be expected to be a function of F_{12} and a mobility term. By expansion eqn(6.22a) may be expressed in terms of L-coefficients;

$$F_{12}=L_{12}(L_{11}-2L_{12}+L_{22})/(L_{11}L_{22}-L_{12}^2)=L_{12}/L$$

or $$L_{12} = F_{12} \cdot L \tag{6.25}$$

Where $L = (L_{11}L_{22}-L_{12}^2)/(L_{11}-2L_{12}+L_{22})$ is the thermodynamic diffusion coefficient as defined in eqn(2.55). The sequence of the coupling of flows through the salt series may therefore be explained by variations of F_{12} and L. In dilute solutions where F_{12} values are in the reverse sequence, it is the value of L (conditioned mainly by L_{11}) which controls the sequence of L_{12}. The product $F_{12}.L_{11}/N$ vs. $\sqrt{S}$ is closely similar in form to L_{12}/N and places the salts in their 'correct' order over the full concentration range. The magnitude of F_{12} is not in itself a guide to probable ion associations since it may be increased as much by disordering of water as by direct increase in ion-ion interaction. It does, together with $-NR_{12}$, provide a view of coupling phenomena complementary to the L_{12}/N coefficients.

6.3 The Degrees of Coupling, q_{12}, q_{10} and q_{20}: The coupling of flows as measured by the coefficient L_{12}/N depends upon the mobility of the ions. The greater the mobility coefficients L_{ii}/N the higher would be the magnitude of L_{12}/N and vice versa. This may easily be seen from a comparis~~i~~on of L_{ii}/N and L_{12}/N values of CsCl and LiCl at the extreme ends of the alkali metal chloride series. For a large number of 1:2, 2:1 and 2:2 electrolytes, appendix 1, the mobility coefficients L_{ii}/N are lower then those of the alkali metal chlorides. Consequently the coupling coefficients L_{12}/N are lower but in most of these systems the extent of cation-anion coupling is very high. Therefore the coefficient L_{12}/N is not a good measure of the coupling phenomena when a large number of systems are compared.

In chapter 2, it was shown that the mobility coefficients were constrained by the inequality, eqn(2.32), which for a two component system becomes:

$$L_{12}^2 \leq L_{11} \cdot L_{22} \qquad (6.27)$$

Kedem and Caplan[89] have introduced a dimension-less parameter, q, such that

$$q_{12} = L_{12}/\sqrt{L_{11} \cdot L_{22}} \qquad (6.28)$$

q_{12} is defined as the degree of coupling between species 1 and 2 and is a measure of the inequality, eqn(6.27). In terms of R-coefficients q_{12} may be written as

$$q_{12} = -R_{12}/\sqrt{R_{11} \cdot R_{22}} \qquad (6.29)$$

For binary electrolyte solutions where there are no coupled chemical reactions* q_{12} is restricted by the condition

$$0 \leq q_{12} \leq 1 \qquad (6.30)$$

The nearer the absolute value of q is to unity slighter the dependence of j on x where j and x are given by

$$j = J_1/J_2 \text{ and } x = X_1/X_2 \qquad (6.31)$$

That is, a high value of q_{12} indicates tight coupling between the two processes. For $q_{12} = 0$, j is proportional to x; then the two processes are independent of each other and each flow is proportional to each force without any influence from the other force. q_{12}, is, thus, a basis of comparison of different processes.

Since the frictional coefficient formalism gives us additional parameters, R_{10}, R_{20} and R_{00}, we may define the degrees of coupling between ions and solvent, that is,

$$q_{10} = -R_{10}/\sqrt{R_{11}R_{00}} \qquad (6.32)$$

$$q_{20} = -R_{20}/\sqrt{R_{22}R_{00}} \qquad (6.33)$$

q_{10} and q_{20} are also restricted by the conditions, eqns (6.34) and (6.35).

---

* q_{12} can be -ve (in coupled chemical reactions) if L_{12} becomes -ve. For example, the flow of a solute through a membrane may drag another solute along the same direction ($L_{12} > 0$) or tend to push it back($L_{12} < 0$).

$$0 \leqslant q_{10} \leqslant 1 \qquad (6.34)$$

$$0 \leqslant q_{20} \leqslant 1 \qquad (6.35)$$

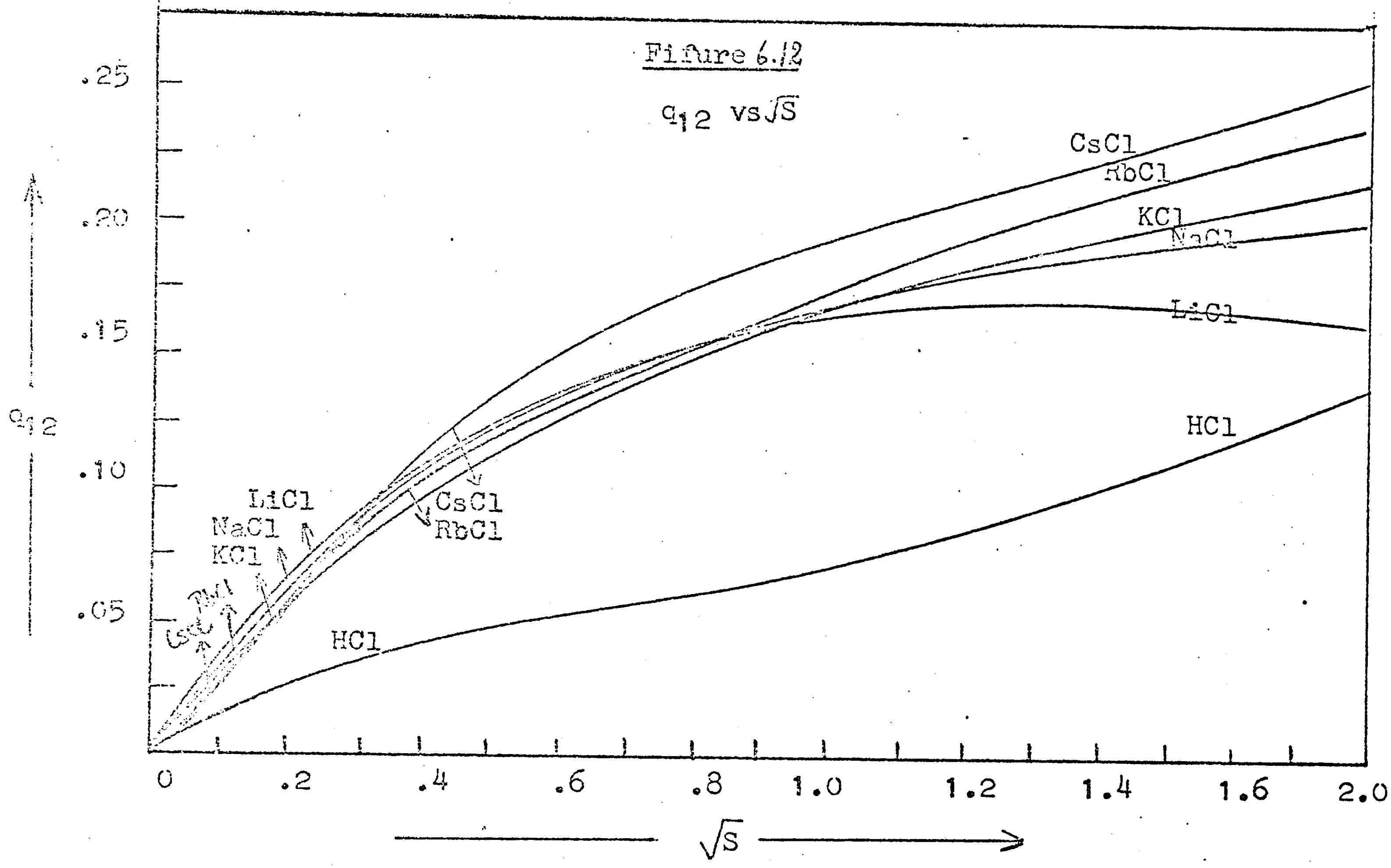
q_{12} for alkali metal chlorides is plotted in figure 6.12. Its concentration dependence is similar to that of F_{12} (figure 6.11). The degree of coupling between cations and solvent, q_{10}, plotted in figure 6.13, is the highest for LiCl showing that Li^+ ion is the most coupled with the solvent in accord with its hydrated nature. The coupling between Cl^- ion and solvent, as measured by q_{20}, figure 6.14, is complementary to that of q_{10}. At infinite dilution q_{20} has different values for each salt because by definition, it has contributions from the cationic mobilities. This may easily be seen by expansion of eqns(6.32) and (6.33) which leads to eqns(6.36) and (6.37);

$$q_{10} = (L_{22} - L_{12})/(L_{22}(L_{22} - 2L_{12} + L_{11}))^{\frac{1}{2}} \qquad (6.36)$$

$$q20 = (L_{11} - L_{21})/(L_{11}(L_{11} - 2L_{21} + L_{22}))^{\frac{1}{2}} \qquad (6.37)$$

The importance of q_{12} becomes more apparent when we compare the transport processes in a variety of salt solutions. Plotted in figure 6.15 are the q_{12} values for various other systems (results in appendix 1). From alkali metal chlorides we have plotted q_{12}^{*} of NaCl for comparision purposes. For 1:1 acids and bases coupling between cations and anions is the least and therefore q_{12} for HNO_3, HCl and NaOH are the lowest. On the other hand the sulfates of Cu^{++}, Zn^{++} and Cd^{++} are known to be the most coupled with these cations and hence q_{12} for these systems are the highest.

* q_{12} of NaCl



Fifure 6.12

q_{12} vs $\sqrt{S}$

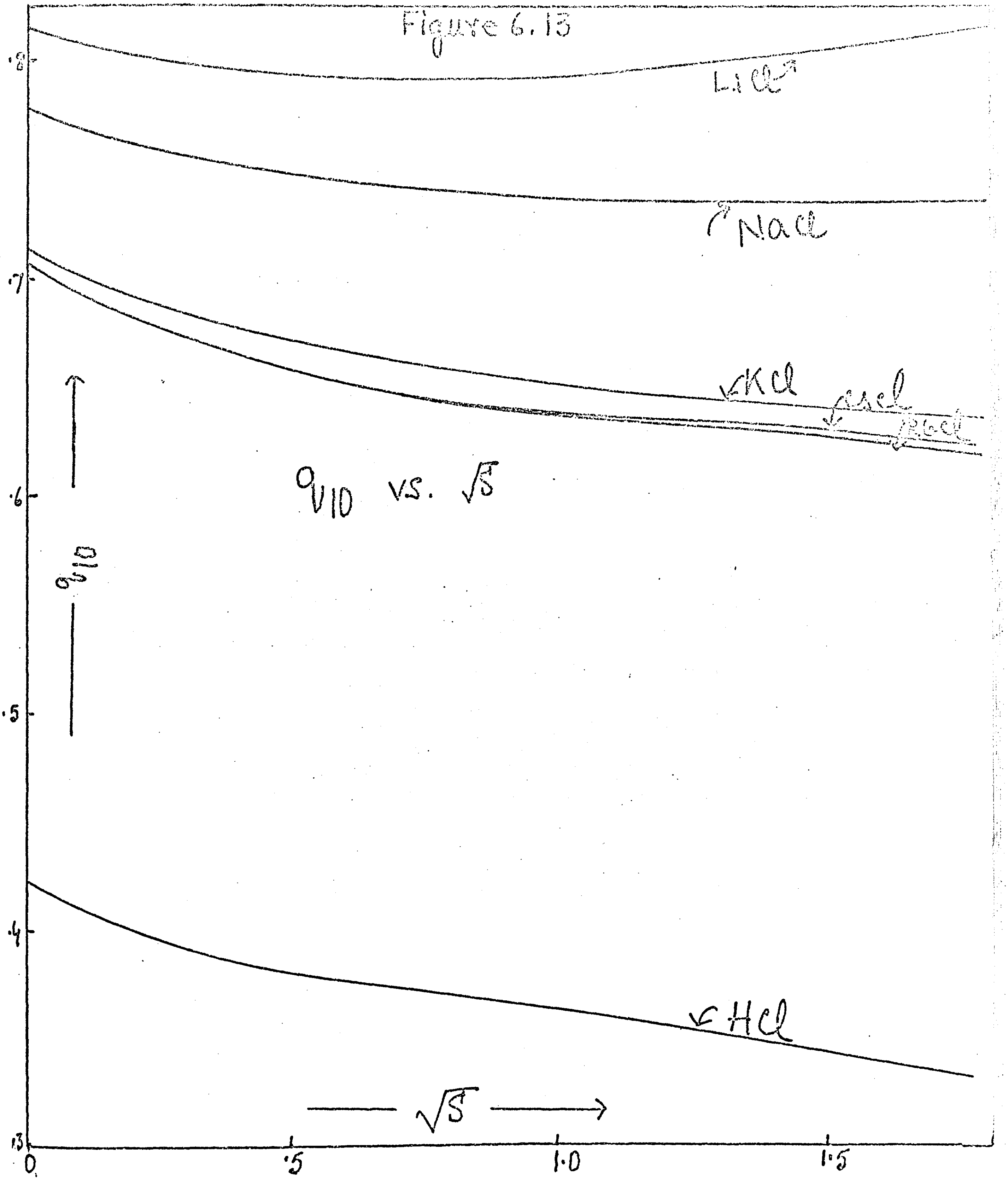
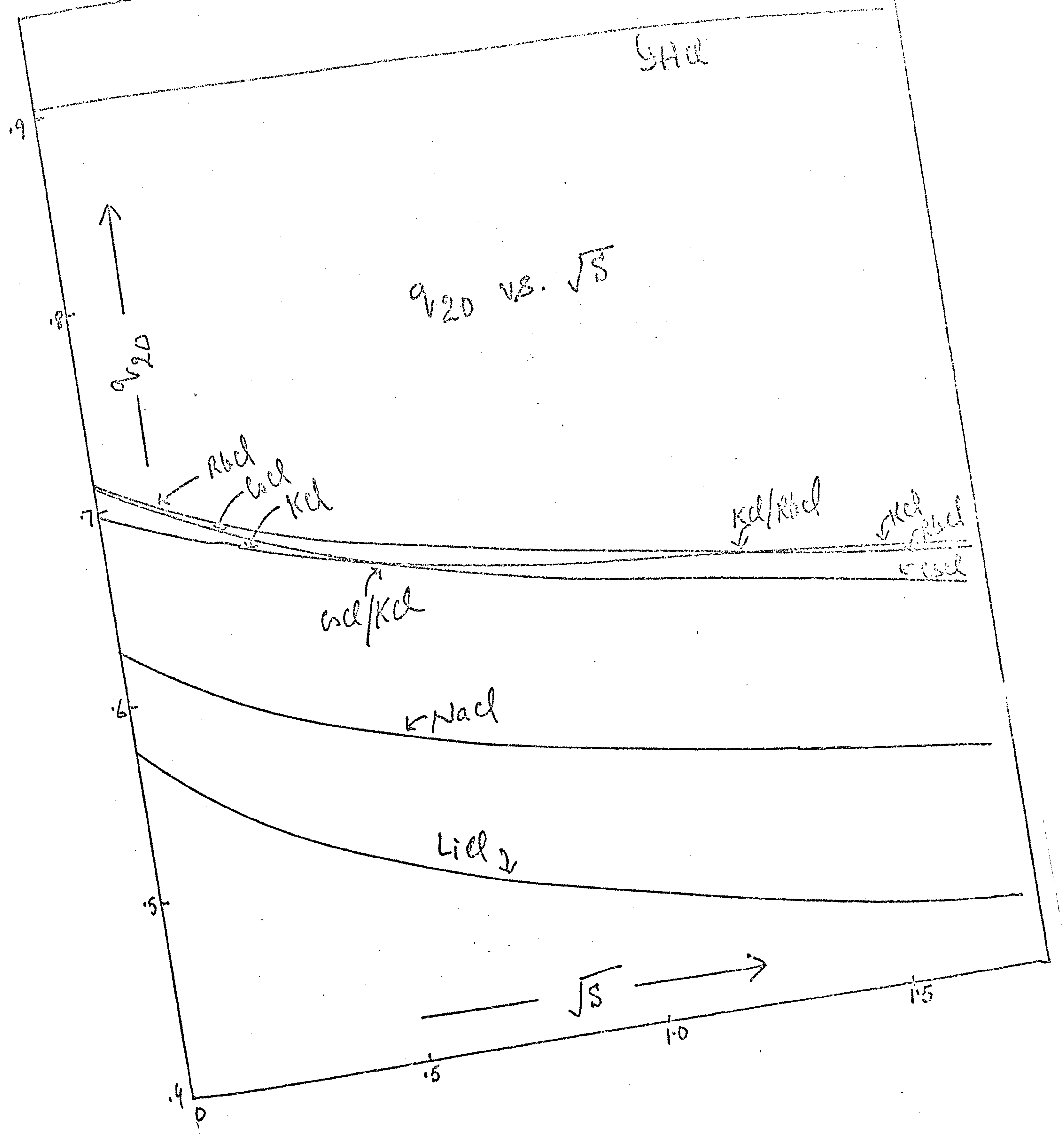


Figure 6.13

LiCl
NaCl
KCl
CsCl
RbCl
HCl
q_{v10} vs. $\sqrt{S}$
q_{v10}
$\sqrt{S}$
·8
·7
·6
·5
·4
·3
0
·5
1·0
1·5

Figure 6.14


GHCl
q_{20} vs. $\sqrt{S}$
q_{20}
RbCl
CsCl
KCl
KCl/RbCl
KCl
RbCl
CsCl
CsCl/KCl
NaCl
LiCl
$\sqrt{S}$
.9
.8
.7
.6
.5
.4
0
.5
1.0
1.5

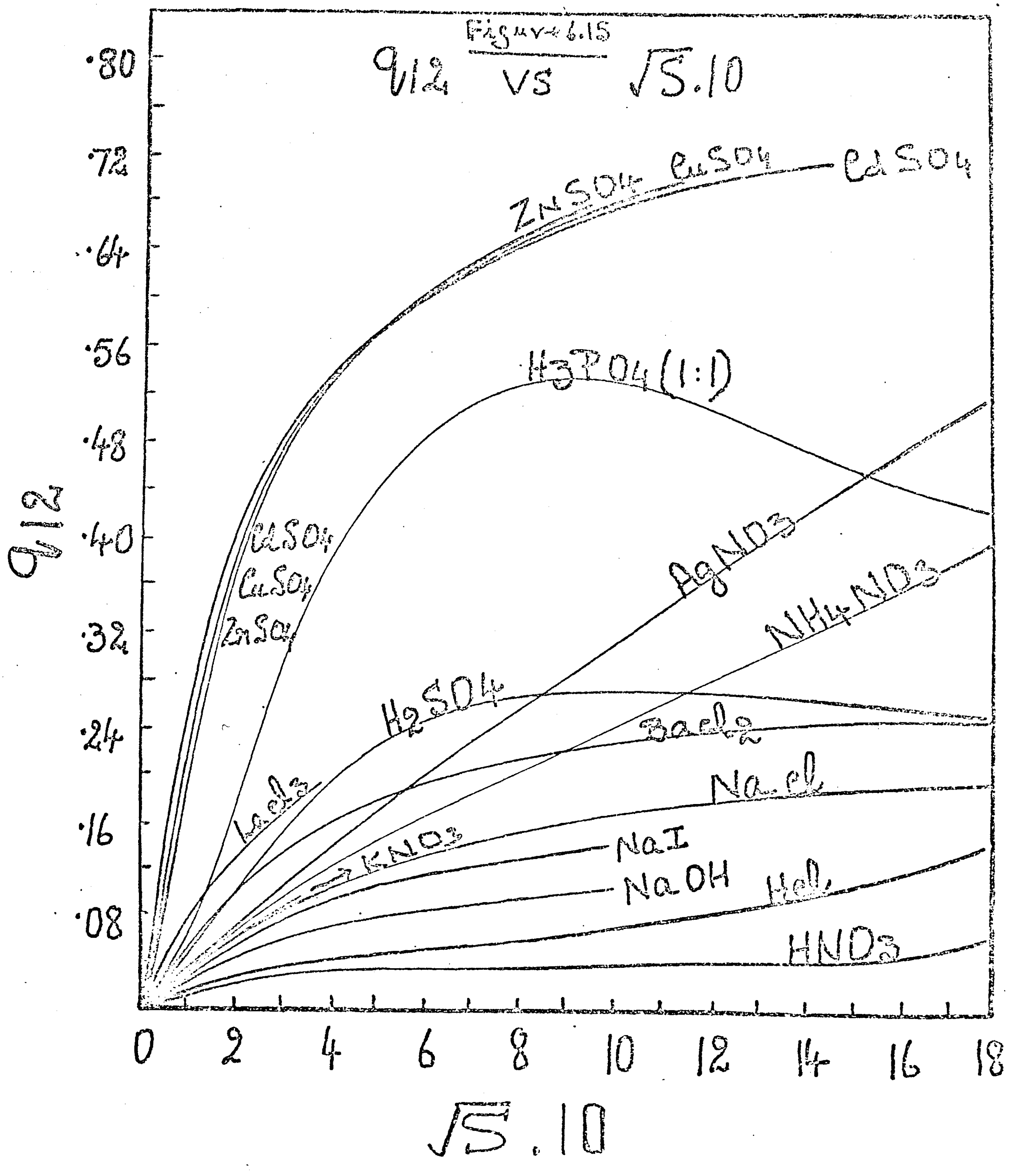


Figure 6.15

q_{12} VS $\sqrt{S}.10$
·80
·72
·64
·56
·48
·40
·32
·24
·16
·08
q_{12}
0
2
4
6
8
10
12
14
16
18
$\sqrt{S}.10$
ZnSO4 CuSO4
CdSO4
CdSO4
CuSO4
ZnSO4
H3PO4 (1:1)
AgNO3
NH4NO3
H2SO4
BaCl2
LaCl3
NaCl
KNO3
NaI
NaOH
HCl
HNO3

6.4 *Conclusions:* Irreversible thermodynamics provides a general macroscopic frame work which can be applied to irreversible processes no matter how complex they may be. It describes the transport processes in terms of linear transport L_{ik} and inverse frictional R_{ik} coefficients. These coefficients are more fundamental than the commonly measured quantities, Λ, t_i and D_v and give better insight into the interionic effects. The $L_{ik} (i \neq k)$ coefficients measure the degree to which a thermodynamic force applied on an ion i affects the flow of ions k and the coefficients L_{ii} represent the mobility an ion i would have if there were no interactions with the oppositely charged ion. In the inverse description, the coefficient $R_{ik} (i,k=0,1,2)$ measure the frictional interactions between ions and ions, and ions and solvent. The R_{ik} formalism for a transport process is in many ways better than the L_{ik} formalism because the former is independent of the frame of reference and additional ion-solvent interaction coefficients are obtained as discrete terms.

The application of the theory to solutions is novel and, in consequence, the prediction of experimentally measureable transport quantities is unlikely to be achieved in the near future. The number of salts for which data now exists in a reasonable range of concentration is very limited. Never the less, the potentialities for practical applications of these results is becoming apparent. Miller[166] has shown by a semi-empirical method that the transport properties of any arbitrary mixture of electrolytes may be calculated with good accuracy from complete sets of binary data. Unpublished results of Paterson et al.[95] have shown that the conductances of ternary and quaternary mixtures in the concentration range 0-3M may be calculated within an accuracy of ±0.2%. Extension of this to practical applications in industry is quite obvious but at this time an insufficient number of salt systems has been investigated. The experimental measurements, reported in this thesis, for conductances of RbCl and CsCl and diffusion coefficients for RbCl complete the transport data for the alkali metal chloride series for its own sake and for a study of the thermodynamic analysis.

Appendix 1

Reported here are the references of the transport, activity and density data collected from the literature for all those systems for which the data was complete and the phenomenological coefficients were calculated.

The coefficients, a_0 and a_i, of the empirical fits used in chapters 4 and 5, are presented in table A1.

The coefficients of the empirical fits used for obtaining molalities from concentrations are given in table A2 and those for obtaining the activity term, $(1 + m\,d\ln\gamma/dm)$, between γ and m, are given in tables A3 and A4. Those of table A3 are taken from reference 17 of this appendix.

Results of calculations of the thermodynamic analysis for all the systems are given in tables A5 to A 32. For rubidium and caesium chloride systems the results are given in chapter 6, tables 6.2 and 6.3 respectively.

Appendix 1 continued

Sources of Data

Potassium Chloride at $0^{\circ}C$ degree

c-m: Obtained graphically from m/c vs c curve using density data of ICT(1929).

Λ: From 'Landolt-Bornstein(1960)'[1]. Data available only upto 1 molar concentration.

t_+: From .01 to .05 molar by m.b. method of Steel(1965)[2] and from .01 to 3.5 molar using e.m.f. data of Caramazza et al., (1960)[3].

D_v: Also from Caramazza et al, (1960)[3] for .1 to 2.7 molar concentration. Values at lower concentrations are extrapolated.

m-r: Again from Caramazza (1960)[4] for .05 to 3.5 molal solutions.

Potassium Chloride at $18^{\circ}C$

c-m: Using density data compiled in Timmerman's Physico-chemical Constants of Binary Systems[5] (1960).

Λ, t_+, D_v and m-γ: As for Potassium Chloride at zero degree from references 1,3 and 4.

Potassium Chloride at $35^{\circ}C$

c-m: Using density data of Firth and Tyrell (1962) for 0.1 to 4 molar and of Kaminsky (1957)[8] for .001 to .5 molar.

Λ: For .0005 to 0.01 molar from Benson and Gordon (1945) and for 1 to 4.5 molar from Suryanarayana et al(1958)[10]. For range .05-1 molar data is not available and has been interpolated.

t_+, D_v and m-γ: As for Potassium Chloride at zero degree from references 3 and 4.

Potassium Chloride at 50°C

c–m: Using density data compiled in Timmerman's Phisico-chemical Constants of Binary Systems[5] (1960).

Λ: For .01 to 4.4 molar from Chambers(1958)[11].

t_+, D_v amd m–γ: As for Potassium Chloride at zero degree from references 3 and 4.

(Temperature for the following systems is 25°C)

Potassium Chloride
Sodium Chloride
Lithium Chloride
Hydrochloric Acid
Calcium Chloride
Barium Chloride
Lanthanum Chloride

For all these systems the valuable compilation of data by Miller(1966)[6] for c–m, Λ, t_+, Dv and m–γ has been fully used without any alterations.

Caesium Chloride

c–m: From $c/m = d_0 - am + bm^2$, the coefficients a and b are reported in Harned and Owen(1958)[33] page 725.

Λ: From Paterson et al(1969)[31] for .1 to 3.0 molar.

t_+: Tamas et.al(1966) for .25 to 3.0 molar.

D_v and m–γ: From data compilations of Robinson and Stokes (1959)[40].

No transference data is available for $c < 0.25$.

Rubidium Chloride

c–m, m–γ and t_+ as for CsCl.

Λ and D_v: Reported in this thesis, chapters 5 and 4.

Sodium Hydroxide

c-m: From ICT(1929) density data using equation $m/c = a + b(c) + c(c)^2$. The coefficients are given in table A2. Values of m/c decrease continously from the value of 1.003 (for H_2O m/c = 1.003) for dilute solution to 1.00045 for 1 molar solution, showing that the volume of solution decreases on dissolution of the electrolyte.

Λ: For .001 to .04 molar from Marsh and Stokes(1964)[12] and for .065 to 12.5 molar from Darken et al.(1942)[13].

t_+: For .01 to 1.0 molar compiled in a review by Ksimakov and Varshavskaya(1966)[14] but actual measurements were made before 1929 by e.m.f. method.

D_v: From Fary's thesis (1966)[17a]. This reference is collected from reference 17.

m-γ: From activity data compiled in Parson's Hand Book of Electrochemical Constants (1959)[15].

Nitric Acid

c-m: As for Sodium Hydroxide.

Λ: For .01 to .2 molar from Landolt-Bornstein(1960)[1] and for .2 to 3.5 molar from Haase et al.(1965)[16].

D_v: From Chapman's thesis(1967)[17] for .4 to 3.0 molar by Rayleigh Interferometric technique. At lower concentrations values are extrapolated.

t_+: For .01 to .10 molar from Prue and Covington[18] (1957) and for 0.1 to 3.5 molar from Haase et al(1964)[19].

m-γ: As for Sodium Hydroxide.

Ammonium Nitrate

c-m: Using density data of Campbell et al.(1959)[20] for .01 to .10 molar and (1950)[21] for 1 to 6 molar.

Λ: For .01 to 1.0 molar from Campbell et. al. (1959)[20] and above 1.0 molar from Wishaw and Stokes (1954)[22].

D_v: From Wishaw and Stokes (1954)[22].

t_+: At 0.1 molar from MacInnes and Cowperth-waite (1927) and at 0.2 molar from Milios and Newman (1968)[24]. At all other concentrations values are assumed to be the same as for .1 and .2 molar.

m-γ: From differentiation of the empirical equation $\ln\gamma = \frac{a\sqrt{m}}{(1+\sqrt{m})} + bm + cm^{3/2} + dm^2 + em^{5/2} + fm^3$.

The coefficients a, b, c, d, e and f were primarily obtained from Chapman's thesis (1967)[17] and are reported in table A3.* Actual activity coefficient values are compiled in Parsons (1959)[15] and Robinsons Stokes (1959)[40].

Potassium Nitrate

c-m: Using density data of Jones and Tolley (1933)[25].

Λ: From data of Shedlovsky (1932)[26].

t_+: For .01 to .2 from Longsworth (1935)[27], for 1.0 from Sukhotin et al. (1969)[28] and for 0.1 molar from MacInnes and Cowperthwaite (1927)[23].

D_v: From .001 to .01 molar from Harned and Hudson (1951)[29] by conductometric method and for .04 to 0.1 from Gokhshtein[30] to an accuracy of 1-3%.

m-γ: From data compiled in Parsons (1959)[15].

Potassium Bromide

c-m: From ICT (1929) density data and also from Harned and Owen[33].

Λ: From Jones and Bickfcrd (1934)[34] and also from Benson and Gordon (1945)[35].

* coefficients g_i of table A3 are the same as the coefficients a, b, c, d, e and f.

t_+: Upto 0.2 molar from Longsworth(1935)[37] by m.b. method. At 1.0 molar from e.m.f. data of ICT(1929)[38]. For 0.5 molar, the values are assumed to be 0.490. This assumption is made because t_+ for KBr lies in the vicinity of 0.500 for the whole range of concentration and for the calculations of L_{12} and R_{12}, the product, $(t_+)\times(t_-)$, remains within 0.1% e.g., 0.50 × 0.50 = 0.2500 and 0.490 × 0.510 = 0.2499.
D_v and m-γ: From data compiled in Robinson and Stokes[40].

Potassium Iodide

c-m, D_v and γ: As for Potassium Bromide.
Λ: From Chambers(1958)[36].
t_+: Upto 0.2 molar from Longsworth(1935)[37] by m.b. method. For 0.5 to 3 molar, t_+ is assumed to be 0.490 as for Potassium Bromide. The product $t_+ \cdot t_-$ does not alter significantly when t_+ lies in the vicinity of 0.500.

Sodium Iodide

c-m, D_v and γ: As for Potassium Bromide.
Λ: From Aston et al.(1933)[41].
t_+: At 0.2 and 1.0 molar from Ray et al.(1958).[42] At infinite dilution from limiting conductances and at .01, .05 and .50 from interpolation of the other data.

Density data for all, KCl, KBr, KI and NaI is also available in Lengyel et al.(1964)[39].

Silver Nitrate

c-m: As for Potassium Bromide and also from Campbell et al (1959)[43].
Λ: From Shedlovsky(1932)[26] and Campbell et al.(1959)[44].

D_v: For .002 to .006 molar from Harned(1951)[45] and from Lakshminarayana(1966)[45a] for 0.1 to 3.5 molar. For .01 and .05 molar, the values are interpolated. Data is also reported by Firth(1962)[46] but it is not compareable with the above two sets of data and hence it is not used.

t_+^*: From Haase et.al.(1964)[19] for 0.1 to 2.0. From Newman et.al(1968)[24] for 0.1 molar and also from Campbell and Singh (1959)[44].

m-γ: As for Ammonium Nitrate.

Ammonium Chloride

c-m: Using density data of Jones and Talley(1953)[25].

Λ: At 0, 0.1 to 5.0 molar from Wishaw and Stokes(1954)[22]. For $c < 0.1$ from Longsworth (1935)[27].

t_+: From Longsworth(1935)[27] for .01 - .2 molar. No data is available for $c > 0.2$ molar.

D_v: From Stokes et.al(1953)[52] for .1 to 5.0 molar by Gouy method. No diffusion data is available for $c < 0.1$ molar.

m-γ: As for Silver Nitrate.

Phosphoric Acid (1:1)

c-m: From density data of Mason and Culvern(1949)[53].

Λ: From Mason and Culvern[53].

t_+: Obtained graphically from the combined plot of the data of Kerker et.al.(1960)[55] for 0.008 to 0.044, of Sahay (1963)[54] for .1 to 3.8 molar and also of Kudra et.al(1964)[56].

D_v: From Edward and Huffman(1959)[57] for .036 to 16.0 molar.

$1+m\,d\ln\gamma/dm$: From Elmore et al.(1946)[58] for the whole range, the values given as such, $H_3PO_4 \rightarrow H^+ + H_2PO_4^-$ is treated as 1:1 acid.

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* t_+ has been reported for .05 to 14M by M.J. Pikal and D.G.Miller, J.Phys. Chem., 74(6), 1377(1970).

Sodium Sulfate

c-m: Obtained from density equation, $d = .99707 + 0.13061c - 0.01212c^{3/2}$, of Harned and Blake(1951)[59] .

Λ: Originally reported in Maclnnes and Longsworth[60] and data compiled in Harned and Owen[33].

t_+: For .005 to 0.1 molar from Longsworth(1935)[61] . For $c < .005$, the values are extrapolated graphically according to the recommendations of Longsworth[61] such that the limiting slope was +ve and the curve had a maximum near $N = 0.001$, where N is the normality.

D_v: For 0.001 to 0.005 molar fron Harned and Blake(1951)[59] by conductometric method. For .1 to 0.1 molar data is available from Vinograd and McBain(1941)[62] to an accuracy of 5% and it has not been used because of too much uncertainty.

m-γ: From compilations of R.Parsons(1959)[15].

Potassium Sulfate

c-m: From density data of Jones and Colvin(1940)[63].

Λ: From Fedoroff(1941)[64] for .0002 to 1.3N; Data is also available from Jenkins and Monk(1950)[65] for .0001 to .001N, from Indelli(1953)[66] for .004 to 0.8N, from Crews(1934)[67] for .001 to .1N and from Hartley and Donaldson(1937)[68] for .000025 to .0025N.

t_+: From Hartley and Donaldson(1937)[68].

D_v: From Mullin and Nienow(1964)[69] for .01 to .65 molar to an accuracy of ±2%.

m-γ: As for Sodium Sulfate.

Sulfuric Acid

c-m: Using ICT(1929) density data.

Λ: For .05 to .10 molar from data of Hlasko and Salit(1935)[70] For .5 to 5.0 molar, calculated graphically using mass fraction vs conductivity data of Roughton(1951)[71].
t_+: Obtained graphically from e.m.f. data of Hamer(1935)[72].
D_v: For .01 to 1.0 obtained graphically from data of Gordon et.al.(1940)[73] and for $c > 1.0$ from Savino et al(1962)[74].
m-$\sqrt{}$: As for Sodium Sulfate from R.Parsons(1959)[15].

Copper Sulfate

c-m: From ICT(1929) density data. m/c is found to decrease from 1.003 upto 0.1 molar concentration showing the decrease in apparent volume of solution on dissolution of the electrolyte.
Λ: From Fedorff(1941)[75] for 0.0 to 1.0 molar and from Owen and Gurry(1938)[76] for 0.0 to 0.1 molar.
t_+: For .125 to .513 molar from Fritz and Fuget(1958)[77] by e.m.f. method to an accuracy of ± 0.001 transference units. Data at lower concentrations is extrapolated graphically from the regular trend of the curve obtained.
D_v: For 0.003 to 0.35 molar from Eversole et.al.(1942)[78] by photometric method to an accuracy of 1 to 3%. For .35 to 1.4 molar from Emanel et.al(1963)[79] to an agreement of ± 5% with the above data.
m-$\sqrt{}$: From R.Pasons(1959)[15].

Zinc Sulfate

c-m: For ICT(1929) density data and also from Purser and Stokes(1951)[80]. Similar to the behaviours of Sodium Hydroxide and Copper Sulfate, the ratio m/c decreases continuously upto .25 molar concentration.

Λ: Upto .005 molar from Owen and Gurry(1938)[76] and from .025 to .25 from Demassiense et.al.(1941)[81].

t_+: For 0.0 to .05 from Dye et al.(1960)[82] by m.b. method, data fitted the equation $t_+ = .3892 - .0633\sqrt{N}$. At 0.25 molar from e.m.f. data of Walton(1949)[83], Purser and Stokes (1951)[80] and Lang(1954)[84]. At 0.1 molar, the value is interpolated from the e.m.f. data at .25 molar and m.b. method data for $c < .05$.

D_v: For .001 to .005 molar from conductometric method of Harned and Hudson(1951)[85]. For .03 to .25 molar from Wall and Wendt(1958)[86] to an accuracy of ± 1%.

m-γ: From R.Parsons(1959)[15].

Cadmium Sulfate

c-m: As for Copper Sulfate.

Λ: From Demassieux et.al.,(1941)[88].

t_+: From Lang and King(1954)[89] by e.m.f. method.

D_v: For .05 to .50 molar from Longworth(1959)[90]. This data has extrapolated for values in dilute solutions.

m-γ: As for Copper Sulfate and Zinc Sulfate.

Cadmium Iodide

c-m: As for Cadmium Sulfate.

t_+: From m.b. data of Sahay[91] (1959) for .005 to .05 molar concentration.

D_0 and $1+cd\mathrm{Ln}y^{*}/dc$: From Porous Frit method of Garland and Tong (1965)[92] w.r.t. solvent fixed frame of reference to an accuracy of 1-2%. Values of activity term have also been reported in this paper as such.

Λ: $\lambda^0_+(\mathrm{cd}^{++})$ has been taken to be that of $\lambda^0_+(\mathrm{Mg}^{++}) = 53.05$.

For .5, 1 and 2 molar solutions conductances are reported by Rysselberghe et al.(1937)[93] but at these concentrations no transference data is available.

* y is the molar activity coefficient.

For .001 to .1 from equation, $\Lambda = 77(1-2.02\sqrt{c}+1.38c)$, reported in Parsons(1959)[15]. Original data were published in 1922.

Table-A1

Coefficients of the equations, $Y = a_o + \sum_{i=1}^{n} a_i x^i$ (n = 1,2,3,4).

Electrolyte	c	y	x	a_o	a_1	a_2	a_3	a_4
KCl	.01-.10	10^3c	10^3K	-0.2504	+7.1566	+0.0655	-0.0014	$9.467 .10^{-3}$
	.01-.10	Λ	10^2c	+144.47	-3.6404	+0.3537	-0.0145	-
	0.0-4.0	m/c	c	+1.0031	+0.0280	+0.0018	-	-
	0.0-4.0	c/m	m	+0.9970	-0.0284	+0.0003	-	-
RbCl	.01-.30	lnc	$\ln K'$*	-4.9861	+1.0227	$+6.8655 .10^{-3}$	$-1.5673 .10^{-4}$	-
	.01-.30	$\ln \Lambda$	lnc	+4.7413	$-7.0856 .10^{-2}$	$-3.3057 .10^{-3}$	$+2.1576 .10^{-4}$	-
	0.0-4.0	m/c	c	1.0031	+0.0324	+0.0026	-	-
	0.0-4.0	c/m	m	0.9970	-0.0331	+0.0004	-	-
	0.0-3.0	D	c	2.0511**	-.87108	+1.1979	-.52778	$9.4668 .10^{-2}$
CsCl	.01-.10	c	K'*	$-2.5718 .10^{-4}$	$+6.9911 .10^{-3}$	$+6.9085 .10^{-5}$	$-1.3626 .10^{-6}$	-
	.01-.10	Λ	c	+148.00	$-3.9577 .10^{+2}$	$+3.7859 .10^{+3}$	$-1.5520 .10^{+4}$	-
	0.0-4.0	m/c	c	+1.0032	+0.0390	+0.0035	-	-
	0.0-4.0	c/m	m	+0.9970	-0.0400	+0.0008	-	-
KCl	.001-.01	$\bar{D}^0c$	c	+1.983	$-1.040 .10^{+1}$	$+9.786 .10^{+2}$	$-3.922 .10^{+4}$	-
	.01-0.1	"	"	+1.959	$-2.410 .10^{0}$	$+2.734 .10^{+1}$	$-1.185 .10^{+2}$	-
	0.1-0.5	"	"	+1.902	$-0.364 .10^{0}$	$+0.825 .10^{0}$	$-0.625 .10^{+0}$	-
	0.5-3.9	"	"	+1.843	$+3.602 .10^{-4}$	$+1.869 .10^{-2}$	$-2.175 .10^{-3}$	-

* $K' = 10^3.K$ where K is the specific conductivity.

** $a_o = D^o$ where D^o is the diffusion coefficient at infinite dilution.

Table- A2

Coefficients of the equations, $y = a_o + \sum_{i=1}^{n} a_i . x^i$, where y=m/c and x=c. Density vs. weight percent data of the International Critical Tables were used to calculate concentrations, c, molalities, m, and m/c term. For all the other systems(not mentioned in this table) concentrations were obtained graphically or densities vs. concentrations were available as such.

Electrolyte	Concn. Range	a_o	a_1	a_2
NaOH	.014-1.040	1.00290	-3.4955(-3)	1.0496(-3)
KBr	.084-3.170	1.00290	3.4737(-2)	2.3763(-3)
KI	.060-1.084	1.00294	4.5949(-2)	3.4143(-3)
H_2SO_4	.102-3.140	1.00256	3.4557(-2)	3.2080(-3)
H_2SO_4	3.400-6.300	1.02630	2.0788(-2)	5.2239(-3)
$AgNO_3$	.012-3.460	1.00284	2.9793(-2)	2.3081(-3)
HNO_3	.160-4.000	1.00315	2.9125(-2)	1.4400(-3)
CdI_2	.056-2.230	0.99760	6.6650(-2)	2.8767(-3)

Numbers in brackets show powers of ten, for example, $1.0493(-3) = 1.0493\ 10^{-3}$.

Table- A3

For the electrolytes in this table the activity term, $(1 + md \ln \gamma / dm)$, was obtained by differentiation of the polynomial:

$$\ln \gamma = \frac{g_1\sqrt{m}}{1+\sqrt{m}} + g_2 m + g_3 m^{3/2} + g_4 m^2 + g_5 m^{5/2} + g_6 m^3 .$$

Electrolyte	g_1	g_2	g_3	g_4	g_5	g_6
KBr	-1.140	.2145	-0.2412	.1533	-.04504	.005012
KI	-1.145	.4003	-0.5188	.3637	-.12030	.014930
NaI	-1.140	.3677	-0.0193	-.2085	.15530	-.032000
NH_4Cl	-1.131	.1496	-0.1783	.1219	-.03860	.004476
$AgNO_3$	-1.153	-.3534	0.0858	-.0010	-.001776	.000148
NH_4NO_3	-1.226	-.0381	-0.0607	.0322	-.005961	.000390

Table A4

Coefficients of the equation, $\ln\gamma = a_0 + \sum_{i=1}^{n} a_i (\ln m)^i$, where n is the degree of the equation, a_0 and a_i are the coefficients of the fit.

Coefficients	m=.05-3.5	.05-4	.05-4	.05-4
	KCl at 0°	KCl at 18°	KCl at 35°	KCl at 50°
a_0	-5.28707(-1)	-5.0805(-1)	-5.0512(-1)	-5.0948(-1)
a_1	-1.22559(-1)	-1.0053(-1)	-9.1003(-2)	-8.8319(-2)
a_2	1.54403(-2)	1.8990(-2)	2.1244(-2)	2.0255(-2)
a_3	1.59028(-2)	1.3294(-2)	1.2372(-2)	1.1763(-2)
a_4	4.50708(-3)	3.5910(-3)	3.2582(-3)	3.6956(-3)
a_5	4.54551(-4)	4.1407(-4)	4.0918(-4)	5.6608(-4)
	m= 0.1-1.6	.001-.3	.002-.3	.001-.01
	NaOH	KNO_3	CsCl	Na_2SO_4
a_0	-3.8651(-1)	-8.1786(-1)	-5.9679(-1)	-1.4808(0)
a_1	8.7567(-3)	-3.4923(-1)	-1.3813(-1)	-3.4714(-1)
a_2	3.2728(-2)	-7.3225(-2)	1.5374(-2)	-1.3835(-2)
a_3	-3.2106(-2)	-9.7083(-3)	8.7582(-3)	3.0145(-3)
a_4	-3.3073(-2)	-7.8148(-4)	9.1794(-4)	3.4586(-4)
a_5	-7.7928(-3)	-2.8177(-5)	2.2209(-5)	1.0859(-5)
	m= .001-.05	.02-.4	.001-.2	.1-1.0
	K_2SO_4	K_2SO_4	H_2SO_4	H_2SO_4
a_0	-2.4361(0)	-1.6664(0)	-1.6913(0)	-2.0257(0)
a_1	-1.1193(0)	-5.9577(-1)	3.2729(-1)	-1.5475(-1)
a_2	-2.4389(-1)	-2.2904(-1)	3.8058(-1)	1.8605(-1)
a_3	-2.5996(-2)	-9.8829(-2)	9.6416(-2)	1.0715(-1)
a_4	-7.7955(-4)	-2.3105(-2)	1.0986(-2)	3.2387(-2)
a_5	3.6499(-5)	-2.0587(-3)	4.8493(-4)	3.8222(-3)

Table-A4 continued.

Coefficients	m= 1.0-6.0	.001-.8	.3-3.0	.005-.8
	H_2SO_4	HNO_3	HNO_3	NaOH
a_0	-2.0255(0)	-3.2000(-1)	-3.2272(-1)	-3.8274(-1)
a_1	-1.9356(-1)	7.0185(-2)	+5.4871(-2)	+5.1601(-2)
a_2	2.5073(-1)	1.0829(-1)	+7.7705(-2)	+1.8454(-1)
a_3	-1.8553(-1)	4.4450(-2)	+2.0173(-2)	+1.7821(-1)
a_4	2.1543(-1)	1.0171(-2)	+2.3687(-2)	+9.5656(-2)
a_5	-5.1169(-2)	1.2989(-3)	+2.6596(-2)	+2.6940(-2)
a_6	-	8.1642(-5)	-5.8247(-3)	+3.7449(-3)
a_7	-	1.7948(-6)	-1.0556(-2)	2.0335(-4)

	m=.001-8	.001-8	.001-8
	$CuSO_4$	$CuSO_4$	$CdSO_4$
a_0	-3.1921(0)	-3.1519(0)	-3.2231(0)
a_1	-7.5369(-1)	-5.2594(-1)	-6.8241(-1)
a_2	-4.3260(-1)	+5.5390(-2)	-1.6584(-1)
a_3	-4.2101(-1)	+3.0313(-2)	-1.3154(-1)
a_4	-1.9701(-1)	+3.4167(-3)	-5.7390(-2)
a_5	-4.6107(-2)	-4.5125(-4)	-1.2589(-2)
a_6	-5.2544(-3)	-1.3294(-4)	-1.3556(-3)
a_7	-2.3158(-4)	-8.0988(-6)	-5.6888(-5)

Table-A5

Potassium Chloride at zero degree

c	m	Eqv Cond	t+	D(v)10 5	1+mxd lnGama/dm
0.0000	0.000000	81.70	0.4980	0.9960	1.0000
0.0500	0.050065	73.90	0.4890	0.9320	0.9114
0.1000	0.100260	71.50	0.4880	0.9240	0.9030
0.5000	0.506600	66.60	0.4870	0.9290	0.8733
1.0000	1.026900	65.23	0.4870	0.9620	0.8783

Sqrt S x10	111/N 10+12	112/N 10+12	122/N 10+12	F12	Q12
0.0000	4.3690	0.0000	4.4041	0.0000	0.0000
2.2361	4.1494	0.2682	4.3240	0.1191	0.0633
3.1623	4.0817	0.3342	4.2660	0.1483	0.0801
7.0711	4.0386	0.5551	4.2246	0.2370	0.1344
10.0000	4.0731	0.6613	4.2552	0.2742	0.1588

Sqrt S x10	NR11 10-11	-NR12 10-11	NR22 10-11	Q10	Q20
0.0000	2.2888	0.0000	2.2706	0.7085	0.7057
2.2361	2.4197	0.1501	2.3220	0.6923	0.6763
3.1623	2.4658	0.1932	2.3593	0.6869	0.6694
7.0711	2.5217	0.3314	2.4107	0.6675	0.6481
10.0000	2.5187	0.3914	2.4109	0.6582	0.6387

Sqrt S x10	-R10 10-9	-R20 10-9	-CCR10 10-11	-CCR20 10-11	R00/N 10-7
0.0000	4.1359	4.1030	2.2888	2.2706	14.8876
2.2361	4.0941	3.9178	2.2696	2.1719	14.4521
3.1623	4.1048	3.9124	2.2726	2.1661	14.4804
7.0711	3.9979	3.7953	2.1903	2.0793	14.2249
10.0000	3.9354	3.7359	2.1273	2.0195	14.1917

Table-A6

Potassium Chloride at 18 degree

c	m	Eqv Cond	t+	D(v)105	1+mxdlnGama/dm
0.0000	0.000000	129.87	0.4919	1.6870	1.0000
1.0000	1.030570	98.15	0.4860	1.6010	0.9006
2.0000	2.128610	92.40	0.4850	1.6970	0.9578
3.0000	3.304250	88.63	0.4850	1.8020	1.0306

Sqrt S x10	111/N 10+12	112/N 10+12	122/N 10+12	F12	Q12
0.0000	6.8588	0.0000	7.0847	0.0000	0.0000
10.0000	6.1610	1.0378	6.4561	0.2827	0.1646
14.1421	5.9932	1.1801	6.2909	0.3225	0.1922
17.3205	5.8499	1.2332	6.1355	0.3415	0.2058

Sqrt S x10	NR11 10-11	-NR12 10-11	NR22 10-11	Q10	Q20
0.0000	1.4580	0.0000	1.4115	0.7128	0.7014
10.0000	1.6683	0.2682	1.5920	0.6568	0.6357
14.1421	1.7326	0.3250	1.6506	0.6468	0.6241
17.3205	1.7851	0.3588	1.7020	0.6415	0.6187

Sqrt S x10	-R10 10-9	-R20 10-9	-CCR10 10-11	-CCR20 10-11	R00/N 10-7
0.0000	2.6346	2.5506	1.4580	1.4115	9.3695
10.0000	2.5994	2.4578	1.4001	1.3238	9.3891
14.1421	2.6987	2.5415	1.4075	1.3255	10.0474
17.3205	2.8300	2.6652	1.4263	1.3432	10.9036

Table-A7

Potassium Chloride at 35 degree

c	m	Eqv Cond	t+	D(v)10 5	1+mxd lnGama/dm
0.0000	0.000000	180.27	0.4889	2.4780	1.0000
1.0000	1.036440	132.28	0.4840	2.3430	0.9106
1.5000	1.579680	126.29	0.4830	2.4020	0.9375
2.0000	2.141600	121.74	0.4830	2.4600	0.9693
2.5000	2.723610	117.79	0.4830	2.5160	1.0040
3.0000	3.327340	113.64	0.4830	2.5710	1.0406
3.5000	3.954180	108.61	0.4820	2.6250	1.0787

Sqrt S x10	l11/N 10+12	l12/N 10+12	l22/N 10+12	F12	Q12
0.0000	9.4639	0.0000	9.8937	0.0000	0.0000
10.0000	8.3497	1.4735	8.8043	0.2934	0.1719
12.2474	8.1646	1.6133	8.6258	0.3226	0.1922
14.1421	8.0033	1.6881	8.4479	0.3408	0.2053
15.8114	7.8420	1.7317	8.2722	0.3541	0.2150
17.3205	7.6692	1.7741	8.0842	0.3679	0.2253
18.7083	7.4593	1.8368	7.8792	0.3868	0.2396

Sqrt S x10	NR11 10-11	-NR12 10-11	NR22 10-11	Q10	Q20
0.0000	1.0566	0.0000	1.0107	0.7149	0.6992
10.0000	1.2341	0.2065	1.1704	0.6555	0.6313
12.2474	1.2718	0.2379	1.2038	0.6483	0.6225
14.1421	1.3045	0.2607	1.2358	0.6432	0.6174
15.8114	1.3370	0.2799	1.2675	0.6394	0.6135
17.3205	1.3737	0.3015	1.3031	0.6352	0.6093
18.7083	1.4223	0.3316	1.3465	0.6303	0.6028

Sqrt S x10	-R10 10-9	-R20 10-9	-CCR10 10-11	-CCR20 10-11	R00/N 10-7
0.0000	1.9094	1.8264	1.0566	1.0107	6.7505
10.0000	1.9186	1.7996	1.0276	0.9638	6.9425
12.2474	1.9616	1.8326	1.0339	0.9659	7.1982
14.1421	2.0135	1.8811	1.0438	0.9752	7.5130
15.8114	2.0747	1.9383	1.0571	0.9876	7.8760
17.3205	2.1423	2.0014	1.0722	1.0017	8.2795
18.7083	2.2199	2.0656	1.0907	1.0149	8.7221

Table-A8

Potassium Chloride at 50 degree

c	m	Eqv Cond	t+	D(v)⏨5	1+mxdlnGama/dm
0.0000	0.000000	228.26	0.4860	3.2890	1.0000
0.0500	0.050212	197.00	0.4840	3.1190	0.9372
0.1000	0.100561	194.59	0.4840	3.0750	0.9045
0.5000	0.508756	174.14	0.4830	3.0180	0.8965
1.0000	1.033760	161.57	0.4830	3.0720	0.9131
2.0000	2.138560	149.92	0.4830	3.2160	0.9703
3.0000	3.323140	137.69	0.4820	3.3360	1.0430

Sqrt S x10	111/N ⏨+12	112/N ⏨+12	122/N ⏨+12	F12	Q12
0.0000	11.9114	0.0000	12.5978	0.0000	0.0000
2.2361	11.1499	0.9095	11.8270	0.1468	0.0792
3.1623	11.2227	1.1075	11.8914	0.1750	0.0959
7.0711	10.6282	1.5948	11.2641	0.2545	0.1458
10.0000	10.3094	1.9280	10.8994	0.3079	0.1819
14.1421	9.9246	2.1476	10.4721	0.3482	0.2107
17.3205	9.3881	2.2603	9.9205	0.3797	0.2342

Sqrt S x10	NR11 ⏨-11	-NR12 ⏨-11	NR22 ⏨-11	Q10	Q20
0.0000	0.8395	0.0000	0.7938	0.7169	0.6971
2.2361	0.9025	0.0694	0.8509	0.6902	0.6667
3.1623	0.8993	0.0838	0.8487	0.6841	0.6605
7.0711	0.9613	0.1361	0.9070	0.6662	0.6407
10.0000	1.0032	0.1775	0.9489	0.6523	0.6266
14.1421	1.0544	0.2162	0.9993	0.6411	0.6152
17.3205	1.1270	0.2568	1.0665	0.6324	0.6049

Sqrt S x10	-R10 ⏨-9	-R20 ⏨-9	-COR10 ⏨-11	-COR20 ⏨-11	R00/N ⏨-7
0.0000	1.5170	1.4344	0.8395	0.7938	5.3332
2.2361	1.5072	1.4138	0.8331	0.7815	5.2845
3.1623	1.4775	1.3859	0.8156	0.7650	5.1872
7.0711	1.5127	1.4132	0.8252	0.7709	5.3632
10.0000	1.5378	1.4366	0.8257	0.7714	5.5392
14.1421	1.6145	1.5084	0.8382	0.7830	6.0157
17.3205	1.7366	1.6159	0.8702	0.8097	6.6900

Table-A9

Potassium Chloride at 25 degree

c	m	Eqv Cond	t+	D(v) $_{10}$5	1+mxd lnGama/dm
0.0000	0.000000	149.86	0.4905	1.9930	1.0000
0.0010	0.001003	146.95	0.4904	1.9640	0.9829
0.0100	0.010030	141.27	0.4902	1.9150	0.9540
0.0500	0.050200	133.37	0.4899	1.8640	0.9209
0.1000	0.100600	128.96	0.4897	1.8470	0.9066
0.5000	0.508800	117.27	0.4887	1.8500	0.8915
1.0000	1.033000	111.87	0.4880	1.8920	0.9051
2.0000	2.133000	105.23	0.4870	1.9990	0.9632
3.0000	3.310000	99.46	0.4862	2.1120	1.0370

Sqrt S x10	111/N $_{10}$+12	112/N $_{10}$+12	122/N $_{10}$+12	F12	Q12
0.0000	7.8924	0.0000	8.1982	0.0000	0.0000
0.3162	7.8261	0.0863	8.1291	0.0214	0.0108
1.0000	7.6949	0.2573	7.9923	0.0635	0.0328
2.2361	7.5206	0.5032	7.8100	0.1233	0.0657
3.1623	7.4308	0.6482	7.7161	0.1577	0.0856
7.0711	7.1938	1.0387	7.4784	0.2481	0.1416
10.0000	7.0778	1.2145	7.3661	0.2880	0.1682
14.1421	6.8667	1.3627	7.1605	0.3255	0.1943
17.3205	6.6332	1.4396	6.9281	0.3504	0.2124

Sqrt S x10	NR11 $_{10}$-11	-NR12 $_{10}$-11	NR22 $_{10}$-11	Q10	Q20
0.0000	1.2670	0.0000	1.2198	0.7138	0.7004
0.3162	1.2779	0.0136	1.2303	0.7101	0.6964
1.0000	1.3010	0.0419	1.2526	0.7024	0.6883
2.2361	1.3354	0.0861	1.2860	0.6908	0.6761
3.1623	1.3557	0.1139	1.3056	0.6837	0.6686
7.0711	1.4185	0.1970	1.3645	0.6635	0.6466
10.0000	1.4540	0.2397	1.3971	0.6539	0.6358
14.1421	1.5135	0.2880	1.4514	0.6445	0.6248
17.3205	1.5788	0.3281	1.5116	0.6380	0.6170

Sqrt S x10	-R10 $_{10}$-9	-R20 $_{10}$-9	-CCR10 $_{10}$-11	-CCR20 $_{10}$-11	R00/N $_{10}$-7
0.0000	2.2895	2.2041	1.2670	1.2198	8.1201
0.3162	2.2846	2.1985	1.2644	1.2167	8.1005
1.0000	2.2750	2.1876	1.2591	1.2107	8.0635
2.2361	2.2598	2.1703	1.2494	1.1999	8.0127
3.1623	2.2505	2.1597	1.2418	1.1917	7.9926
7.0711	2.2393	2.1403	1.2215	1.1675	8.0287
10.0000	2.2597	2.1538	1.2143	1.1574	8.2133
14.1421	2.3545	2.2351	1.2255	1.1633	8.8180
17.3205	2.4860	2.3524	1.2507	1.1835	9.6170

Table-A10

SODIUM CHLORIDE

c	m	Eqv Cond	t+	D(v) 10 5	1+mxd lnGama/dm
0.0000	0.000000	126.45	0.3962	1.6110	1.0000
0.0010	0.001003	123.70	0.3947	1.5870	0.9830
0.0100	0.010030	118.51	0.3918	1.5470	0.9553
0.0500	0.050200	111.06	0.3873	1.5030	0.9265
0.1000	0.100500	106.74	0.3853	1.4850	0.9164
0.5000	0.506200	93.62	0.3753	1.4740	0.9297
1.0000	1.022200	85.76	0.3691	1.4840	0.9795
2.0000	2.085900	74.71	0.3615	1.5180	1.1080
3.0000	3.196600	65.57	0.3561	1.5640	1.2760

Sqrt S x10	111/N 10+12	112/N 10+12	122/N 10+12	F12	Q12
0.0000	5.3814	0.0000	8.2008	0.0000	0.0000
0.3162	5.3262	0.0824	8.1241	0.0253	0.0125
1.0000	5.2203	0.2334	7.9747	0.0715	0.0362
2.2361	5.0660	0.4404	7.7427	0.1346	0.0703
3.1623	4.9705	0.5535	7.6004	0.1693	0.0900
7.0711	4.6142	0.8406	7.1219	0.2629	0.1466
10.0000	4.3108	0.9112	6.7222	0.2982	0.1693
14.1421	3.8121	0.9114	6.0347	0.3298	0.1900
17.3205	3.3654	0.8576	5.3921	0.3469	0.2013

Sqrt S x10	NR11 10-11	-NR12 10-11	NR22 10-11	Q10	Q20
0.0000	1.8583	0.0000	1.2194	0.7770	0.6295
0.3162	1.8778	0.0190	1.2311	0.7741	0.6234
1.0000	1.9181	0.0561	1.2556	0.7684	0.6118
2.2361	1.9837	0.1128	1.2980	0.7599	0.5951
3.1623	2.0283	0.1477	1.3265	0.7549	0.5851
7.0711	2.2148	0.2614	1.4350	0.7423	0.5540
10.0000	2.3882	0.3237	1.5315	0.7385	0.5395
14.1421	2.7215	0.4110	1.7192	0.7363	0.5245
17.3205	3.0970	0.4926	1.9329	0.7359	0.5151

Sqrt S x10	-R10 10-9	-R20 10-9	-COR10 10-11	-COR20 10-11	ROO/N 10-7
0.0000	3.3579	2.2035	1.8583	1.2194	10.0493
0.3162	3.3586	2.1900	1.8588	1.2120	10.0259
1.0000	3.3644	2.1673	1.8620	1.1995	9.9953
2.2361	3.3839	2.1436	1.8709	1.1851	9.9976
3.1623	3.4048	2.1342	1.8806	1.1788	10.0285
7.0711	3.5627	2.1404	1.9534	1.1735	10.4014
10.0000	3.8017	2.2241	2.0645	1.2078	11.0965
14.1421	4.3411	2.4578	2.3105	1.3081	12.7743
17.3205	4.9993	2.7648	2.6044	1.4403	14.9036

Table-A11

LITHIUM CHLORIDE

c	m	Eqv Cond	t+	D(v)105	1+mxd lnGamma/dm
0.0000	0.000000	115.03	0.3363	1.3660	1.0000
0.0010	0.001003	112.37	0.3339	1.3440	0.9832
0.0100	0.010030	107.28	0.3288	1.3120	0.9570
0.0500	0.050200	100.13	0.3211	1.2800	0.9350
0.1000	0.100500	95.86	0.3168	1.2680	0.9332
0.5000	0.506000	81.40	0.2992	1.2720	1.0128
1.0000	1.021500	72.90	0.2864	1.3020	1.1418
2.0000	2.084700	61.80	0.2688	1.3690	1.4332
3.0000	3.196900	52.80	0.2563	1.4260	1.8191

Sqrt S x10	l11/N 10+12	l12/N 10+12	l22/N 10+12	F12	Q12
0.0000	4.1526	0.0000	8.1974	0.0000	0.0000
0.3162	4.1028	0.0731	8.1120	0.0265	0.0127
1.0000	4.0110	0.2225	7.9561	0.0805	0.0394
2.2361	3.8702	0.4170	7.7180	0.1510	0.0763
3.1623	3.7740	0.5124	7.5463	0.1870	0.0960
7.0711	3.3159	0.7002	6.8269	0.2764	0.1472
10.0000	2.9423	0.6999	6.2871	0.3043	0.1627
14.1421	2.4063	0.6222	5.4754	0.3229	0.1714
17.3205	1.9537	0.5003	4.7177	0.3164	0.1648

Sqrt S x10	NR11 10-11	-NR12 10-11	NR22 10-11	Q10	Q20
0.0000	2.4081	0.0000	1.2199	0.8147	0.5799
0.3162	2.4377	0.0220	1.2329	0.8125	0.5727
1.0000	2.4970	0.0698	1.2589	0.8077	0.5573
2.2361	2.5990	0.1404	1.3033	0.8014	0.5353
3.1623	2.6743	0.1816	1.3375	0.7980	0.5232
7.0711	3.0825	0.3162	1.4972	0.7930	0.4858
10.0000	3.4911	0.3887	1.6338	0.7963	0.4672
14.1421	4.2815	0.4865	1.8816	0.8051	0.4464
17.3205	5.2613	0.5580	2.1789	0.8154	0.4367

Sqrt S x10	-R10 10-9	-R20 10-9	-COR10 10-11	-COR20 10-11	R00/N 10-7
0.0000	4.3515	2.2044	2.4081	1.2199	11.8464
0.3162	4.3651	2.1881	2.4158	1.2110	11.8410
1.0000	4.3857	2.1484	2.4272	1.1890	11.8066
2.2361	4.4468	2.1032	2.4586	1.1628	11.8471
3.1623	4.5131	2.0927	2.4927	1.1559	11.9600
7.0711	5.0434	2.1532	2.7663	1.1811	13.1202
10.0000	5.7093	2.2914	3.1025	1.2452	14.7231
14.1421	7.1263	2.6197	3.7950	1.3951	18.3010
17.3205	9.0293	3.1117	4.7034	1.6209	23.3075

Table-A12

HYDROCHLORIC ACID

c	m	Eqv Cond	t+	D(v)$_{10}$5	1+mxd lnGama/dm
0.0000	0.000000	426.50	0.8210	3.3360	1.0000
0.0010	0.001003	421.46	0.8224	3.2760	0.9833
0.0100	0.010030	412.02	0.8251	3.1820	0.9576
0.0500	0.050200	399.12	0.8292	3.0840	0.9375
0.1000	0.100500	391.34	0.8314	3.0560	0.9380
0.5000	0.506200	360.86	0.8376	3.1840	1.0337
1.0000	1.022400	332.31	0.8407	3.4530	1.1853
2.0000	2.086300	281.66	0.8429	4.0450	1.5218
3.0000	3.196000	237.74	0.8430	4.6430	1.8944

Sqrt S x10	l11/N $_{10}$+12	l12/N $_{10}$+12	l22/N $_{10}$+12	F12	Q12
0.0000	37.6045	0.0000	8.1967	0.0000	0.0000
0.3162	37.3350	0.1089	8.1480	0.0162	0.0062
1.0000	36.8285	0.3167	8.0562	0.0472	0.0184
2.2361	36.1088	0.5644	7.8859	0.0851	0.0334
3.1623	35.6241	0.6801	7.7664	0.1035	0.0409
7.0711	33.4037	0.9411	7.2352	0.1515	0.0605
10.0000	31.1013	1.0964	6.7819	0.1866	0.0755
14.1421	26.8539	1.3557	6.1081	0.2529	0.1059
17.3205	23.0891	1.5643	5.5731	0.3164	0.1379

Sqrt S x10	NR11 $_{10}$-11	-NR12 $_{10}$-11	NR22 $_{10}$-11	Q10	Q20
0.0000	0.2659	0.0000	1.2200	0.4230	0.9061
0.3162	0.2679	0.0036	1.2273	0.4186	0.9055
1.0000	0.2716	0.0107	1.2417	0.4099	0.9044
2.2361	0.2773	0.0198	1.2695	0.3982	0.9035
3.1623	0.2812	0.0246	1.2898	0.3922	0.9031
7.0711	0.3005	0.0391	1.3872	0.3759	0.9022
10.0000	0.3234	0.0523	1.4830	0.3654	0.9006
14.1421	0.3766	0.0836	1.6557	0.3496	0.8946
17.3205	0.4415	0.1239	1.8291	0.3361	0.8865

Sqrt S x10	-R10 $_{10}$-9	-R20 $_{10}$-9	-COR10 $_{10}$-11	-COR20 $_{10}$-11	R00/N $_{10}$-7
0.0000	0.4805	2.2045	0.2659	1.2200	4.8519
0.3162	0.4775	2.2112	0.2643	1.2238	4.8583
1.0000	0.4715	2.2243	0.2609	1.2310	4.8711
2.2361	0.4656	2.2603	0.2574	1.2497	4.9302
3.1623	0.4645	2.2905	0.2566	1.2651	4.9880
7.0711	0.4767	2.4588	0.2614	1.3481	5.3539
10.0000	0.4993	2.6351	0.2711	1.4307	5.7732
14.1421	0.5506	2.9544	0.2930	1.5721	6.5868
17.3205	0.6095	3.2726	0.3176	1.7052	7.4505

Table-A13

CALCIUM CHLORIDE

c	m	Eqv Cond	t+	D(v)10 5	1+md lnGamma/dm
0.0000	0.000000	135.85	0.4380	1.3350	1.0000
0.0001	0.000100	133.30	0.4363	1.3100	0.9808
0.0005	0.000502	130.31	0.4342	1.2840	0.9600
0.0010	0.001003	128.20	0.4326	1.2670	0.9463
0.0050	0.005015	120.38	0.4264	1.2120	0.9019
0.0100	0.010035	115.66	0.4220	1.1860	0.8798
0.0500	0.050200	102.46	0.4059	1.1380	0.8440

Sqrt S x10	l11/N 10+12	l12/N 10+12	l22/N 10+12	F12	Q12
0.0000	1.5974	0.0000	8.1987	0.0000	0.0000
0.1732	1.5794	0.0356	8.1413	0.0396	0.0099
0.3873	1.5589	0.0794	8.0775	0.0883	0.0224
0.5477	1.5444	0.1106	8.0337	0.1229	0.0314
1.2247	1.4912	0.2260	7.8680	0.2501	0.0660
1.7321	1.4594	0.2978	7.7755	0.3285	0.0884
3.8730	1.3598	0.4863	7.5103	0.5364	0.1522

Sqrt S x10	NR11 10-11	-NR12 10-11	NR22 10-11	Q10	Q20
0.0000	6.2603	0.0000	1.2197	0.7497	0.6618
0.1732	6.3323	0.0277	1.2284	0.7475	0.6568
0.3873	6.4179	0.0631	1.2386	0.7448	0.6505
0.5477	6.4814	0.0892	1.2460	0.7428	0.6458
1.2247	6.7353	0.1934	1.2765	0.7353	0.6278
1.7321	6.9061	0.2645	1.2962	0.7306	0.6156
3.8730	7.5282	0.4875	1.3631	0.7191	0.5773

Sqrt S x10	-R10 10-9	-R20 10-9	-CCR10 10-11	-CCR20 10-11	R00/N 10-7
0.0000	5.6561	2.2040	3.1301	1.2197	9.0930
0.1732	5.6710	2.1947	3.1385	1.2146	9.0890
0.3873	5.6842	2.1811	3.1458	1.2071	9.0764
0.5477	5.6943	2.1708	3.1514	1.2014	9.0669
1.2247	5.7354	2.1318	3.1742	1.1798	9.0336
1.7321	5.7643	2.1043	3.1885	1.1640	9.0144
3.8730	5.9264	2.0245	3.2766	1.1193	9.0214

Table-A14

BARIUM CHLORIDE

c	m	Eqv Cond	t+	D(v) $_{10}$5	1+md lnGa m±/dm
0.0000	0.000000	139.98	0.4546	1.3850	1.0000
0.0010	0.001003	132.11	0.4483	1.3200	0.9457
0.0050	0.005015	123.93	0.4419	1.2670	0.8998
0.0100	0.010035	119.03	0.4381	1.2390	0.8759
0.0500	0.050200	105.19	0.4249	1.1780	0.8295
0.1000	0.100600	98.56	0.4162	1.1600	0.8252
0.2000	0.201600	91.55	0.4036	1.1500	0.8415
0.5000	0.507600	80.50	0.3793	1.1610	0.9264
1.0000	1.027900	68.90	0.3527	1.1790	1.0980

Sqrt S x10	111/N $_{10}$+12	112/N $_{10}$+12	122/N $_{10}$+12	F12	Q12
0.0000	1.7080	0.0000	8.1969	0.0000	0.0000
0.5477	1.6514	0.1223	8.0726	0.1303	0.0335
1.2247	1.5965	0.2522	7.9328	0.2664	0.0709
1.7321	1.5645	0.3287	7.8406	0.3456	0.0938
3.8730	1.4648	0.5294	7.5559	0.5544	0.1591
5.4772	1.4036	0.6043	7.3884	0.6394	0.1877
7.7460	1.3193	0.6543	7.1728	0.7121	0.2127
12.2474	1.1536	0.6675	6.7015	0.7922	0.2401
17.3205	0.9521	0.5992	5.9884	0.8300	0.2509

Sqrt S x10	NR11 $_{10}$-11	-NR12 $_{10}$-11	NR22 $_{10}$-11	Q10	Q20
0.0000	5.8549	0.0000	1.2200	0.7385	0.6742
0.5477	6.0624	0.0919	1.2402	0.7314	0.6570
1.2247	6.2952	0.2001	1.2670	0.7229	0.6380
1.7321	6.4486	0.2703	1.2867	0.7175	0.6262
3.8730	7.0044	0.4907	1.3578	0.7032	0.5900
5.4772	7.3848	0.6040	1.4029	0.6988	0.5715
7.7460	7.9392	0.7242	1.4602	0.6983	0.5509
12.2474	9.1987	0.9163	1.5835	0.7050	0.5192
17.3205	11.2090	1.1216	1.7821	0.7196	0.4916

Sqrt S x10	-R10 $_{10}$-9	-R20 $_{10}$-9	-COR10 $_{10}$-11	-COR20 $_{10}$-11	R00/N $_{10}$-7
0.0000	5.2899	2.2045	2.9275	1.2200	8.7630
0.5477	5.3111	2.1578	2.9393	1.1942	8.6973
1.2247	5.3258	2.1085	2.9475	1.1669	8.6214
1.7321	5.3402	2.0818	2.9540	1.1516	8.5906
3.8730	5.4469	2.0122	3.0115	1.1125	8.5653
5.4772	5.5971	1.9951	3.0884	1.1009	8.6876
7.7460	5.8932	1.9941	3.2453	1.0981	8.9718
12.2474	6.7360	2.0581	3.6831	1.1253	9.9237
17.3205	8.3013	2.2616	4.4829	1.2213	11.8739

Table-A15

LANTHANUM CHLORIDE

c	m	Eqv Cond	t+	D(v)105	1+mxd lnGama/dm
0.0000	0.000000	145.95	0.4769	1.2920	1.0000
0.0001	0.000100	141.05	0.4739	1.2460	0.9609
0.0005	0.000502	135.16	0.4705	1.2020	0.9218
0.0010	0.001003	131.13	0.4681	1.1750	0.8980
0.0050	0.005015	118.10	0.4598	1.1010	0.8303
0.0100	0.010035	111.26	0.4541	1.0690	0.8007
0.0250	0.025100	101.98	0.4430	1.0230	0.7672

Sqrt S x10	l11/N 10+12	l12/N 10+12	l22/N 10+12	F12	Q12
0.0000	0.8305	0.0000	8.1984	0.0000	0.0000
0.2449	0.8139	0.0488	8.1163	0.1120	0.0190
0.5477	0.7954	0.1096	8.0153	0.2501	0.0434
0.7746	0.7828	0.1508	7.9434	0.3428	0.0605
1.7321	0.7437	0.2872	7.7135	0.6442	0.1199
2.4495	0.7226	0.3591	7.6005	0.8001	0.1532
3.8730	0.6871	0.4439	7.4325	0.9904	0.1964

Sqrt S x10	NR11 10-11	-NR12 10-11	NR22 10-11	Q10	Q20
0.0000	12.0415	0.0000	1.2198	0.7233	0.6906
0.2449	12.2903	0.0739	1.2325	0.7188	0.6815
0.5477	12.5956	0.1723	1.2500	0.7126	0.6700
0.7746	12.8221	0.2434	1.2635	0.7082	0.6618
1.7321	13.6416	0.5079	1.3153	0.6927	0.6329
2.4495	14.1714	0.6695	1.3473	0.6845	0.6155
3.8730	15.1381	0.9042	1.3994	0.6762	0.5896

Sqrt S x10	-R10 10-9	-R20 10-9	-CCR10 10-11	-CCR20 10-11	R00/N 10-7
0.0000	7.2530	2.2041	4.0138	1.2198	8.3515
0.2449	7.2689	2.1826	4.0228	1.2079	8.3217
0.5477	7.2751	2.1548	4.0263	1.1925	8.2753
0.7746	7.2830	2.1365	4.0306	1.1824	8.2469
1.7321	7.2986	2.0708	4.0393	1.1460	8.1377
2.4495	7.3293	2.0323	4.0542	1.1242	8.0906
3.8730	7.4914	1.9860	4.1418	1.0980	8.1087

Table-A16

Sodium Hydroxide

c	m	Eqv Cond	t+	D(v)$_{10}5$	1+mxdlnGama/dm
0.0000	0.000000	248.40	0.2020	2.1270	1.0000
0.0100	0.010029	238.47	0.2030	2.0460	0.9423
0.0500	0.050136	227.80	0.1890	1.9660	0.9133
0.1000	0.100256	221.17	0.1830	1.9190	0.9095
0.2000	0.200449	212.93	0.1770	1.8660	0.9333
0.5000	0.500702	197.12	0.1690	1.7950	0.9529
1.0000	1.000450	177.71	0.1630	1.7440	1.0088

Sqrt S x10	111/N $_{10}+12$	112/N $_{10}+12$	122/N $_{10}+12$	F12	Q12
0.0000	5.3789	0.0000	21.2793	0.0000	0.0000
1.0000	5.4351	0.2359	20.6486	0.0539	0.0223
2.2361	5.2160	0.5919	20.4338	0.1363	0.0573
3.1623	5.0515	0.7045	20.1114	0.1655	0.0699
4.4721	4.7493	0.7015	19.5227	0.1740	0.0729
7.0711	4.4043	0.8264	18.4194	0.2175	0.0918
10.0000	3.9942	0.8832	16.8583	0.2533	0.1076

Sqrt S x10	NR11 $_{10}-11$	-NR12 $_{10}-11$	NR22 $_{10}-11$	Q10	Q20
0.0000	1.8591	0.0000	0.4699	0.8934	0.4492
1.0000	1.8408	0.0210	0.4845	0.8876	0.4407
2.2361	1.9235	0.0557	0.4910	0.8874	0.4093
3.1623	1.9893	0.0697	0.4997	0.8879	0.3968
4.4721	2.1168	0.0761	0.5150	0.8907	0.3884
7.0711	2.2898	0.1027	0.5475	0.8909	0.3705
10.0000	2.5330	0.1327	0.6001	0.8906	0.3563

Sqrt S x10	-R10 $_{10}-9$	-R20 $_{10}-9$	-COR10 $_{10}-11$	-COR20 $_{10}-11$	ROO/N $_{10}-7$
0.0000	3.3594	0.8492	1.8591	0.4699	7.6049
1.0000	3.2878	0.8374	1.8198	0.4635	7.4532
2.2361	3.3740	0.7863	1.8678	0.4353	7.5151
3.1623	3.4671	0.7766	1.9197	0.4300	7.6646
4.4721	3.6846	0.7924	2.0407	0.4389	8.0835
7.0711	3.9455	0.8024	2.1871	0.4448	8.5653
10.0000	4.3260	0.8425	2.4003	0.4674	9.3152

Table-A17

Nitric Acid

c	m	Eqv Cond	t+	D(v)10 5	1+mxd lnGamma/dm
0.0000	0.000000	420.50	0.8300	3.1580	1.0000
0.0100	0.010033	406.00	0.8392	3.0030	0.9534
0.0500	0.050225	393.30	0.8393	2.8810	0.9382
0.1000	0.100607	385.00	0.8392	2.8290	0.9345
0.5000	0.509035	356.80	0.8368	2.8500	0.9735
1.0000	1.033720	341.72	0.8332	2.9780	1.0601
2.0000	2.134320	280.13	0.8201	3.1620	1.2699
2.5000	2.712400	256.03	0.8139	3.2320	1.3887
3.0000	3.310470	234.79	0.8079	3.3060	1.4599

Sqrt S x10	l11/N 10+12	l12/N 10+12	l22/N 10+12	F12	Q12
0.0000	37.4822	0.0000	7.6752	0.0000	0.0000
1.0000	37.0624	0.4692	7.4809	0.0739	0.0282
2.2361	35.9495	0.4968	7.2849	0.0802	0.0307
3.1623	35.2269	0.5265	7.1755	0.0862	0.0331
7.0711	32.7386	0.6719	6.9258	0.1138	0.0446
10.0000	31.1450	0.5657	6.6875	0.0998	0.0392
14.1421	25.2574	0.5837	5.9962	0.1162	0.0474
15.8114	22.9100	0.5295	5.6468	0.1128	0.0466
17.3205	21.0268	0.6542	5.4983	0.1432	0.0608

Sqrt S x10	NR11 10-11	-NR12 10-11	NR22 10-11	Q10	Q20
0.0000	0.2668	0.0000	1.3029	0.4123	0.9111
1.0000	0.2700	0.0169	1.3378	0.3882	0.9103
2.2361	0.2784	0.0190	1.3740	0.3870	0.9098
3.1623	0.2842	0.0209	1.3952	0.3860	0.9092
7.0711	0.3061	0.0297	1.4467	0.3839	0.9053
10.0000	0.3216	0.0272	1.4976	0.3908	0.9045
14.1421	0.3968	0.0386	1.6715	0.4030	0.8951
15.8114	0.4374	0.0410	1.7748	0.4107	0.8917
17.3205	0.4774	0.0568	1.8255	0.4114	0.8847

Sqrt S x10	-R10 10-9	-R20 10-9	-COR10 10-11	-COR20 10-11	R00/N 10-7
0.0000	0.4821	2.3544	0.2668	1.3029	5.1255
1.0000	0.4575	2.3874	0.2531	1.3209	5.1419
2.2361	0.4695	2.4520	0.2594	1.3550	5.2868
3.1623	0.4773	2.4909	0.2633	1.3743	5.3796
7.0711	0.5069	2.5990	0.2764	1.4171	5.6963
10.0000	0.5482	2.7383	0.2944	1.4704	6.1203
14.1421	0.6886	3.1392	0.3582	1.6329	7.3589
15.8114	0.7748	3.3887	0.3964	1.7337	8.1378
17.3205	0.8360	3.5161	0.4206	1.7687	8.6517

Table-A18

Ammonium Nitrate

c	m	Eqv Cond	t+	D(v)$_{10}$5	1+mxdlnGamma/dm
0.0000	0.000000	145.00	0.5070	1.9280	1.0000
0.0100	0.010034	136.20	0.5130	1.8720	0.9488
0.0500	0.050266	128.00	0.5130	1.8170	0.9055
0.1000	0.100770	122.70	0.5130	1.7690	0.8817
0.2000	0.203180	117.00	0.5140	1.7490	0.8549
0.5000	0.514000	108.60	0.5140	1.7240	0.8115
1.0000	1.051400	101.43	0.5140	1.6900	0.7638
2.0000	2.223950	91.76	0.5140	1.6330	0.6869
3.0000	3.531700	84.07	0.5140	1.5780	0.6262

Sqrt S x10	111/N $_{10}$+12	112/N $_{10}$+12	122/N $_{10}$+12	F12	Q12
0.0000	7.8920	0.0000	7.6740	0.0000	0.0000
1.0000	7.8294	0.3252	7.4491	0.0817	0.0426
2.2361	7.6654	0.6130	7.3080	0.1515	0.0819
3.1623	7.5151	0.7547	7.1724	0.1865	0.1028
4.4721	7.4465	0.9877	7.0947	0.2393	0.1359
7.0711	7.3667	1.3716	7.0402	0.3201	0.1905
10.0000	7.3411	1.7418	7.0361	0.3903	0.2424
14.1421	7.3990	2.3335	7.1231	0.4866	0.3214
17.3205	7.4685	2.8275	7.2156	0.5563	0.3852

Sqrt S x10	NR11 $_{10}$-11	-NR12 $_{10}$-11	NR22 $_{10}$-11	Q10	Q20
0.0000	1.2671	0.0000	1.3031	0.7021	0.7120
1.0000	1.2796	0.0559	1.3449	0.6824	0.7012
2.2361	1.3134	0.1102	1.3776	0.6679	0.6870
3.1623	1.3449	0.1415	1.4091	0.6601	0.6793
4.4721	1.3682	0.1905	1.4360	0.6468	0.6677
7.0711	1.4085	0.2744	1.4739	0.6256	0.6468
10.0000	1.4472	0.3582	1.5099	0.6047	0.6261
14.1421	1.5073	0.4938	1.5656	0.5717	0.5932
17.3205	1.5722	0.6161	1.6273	0.5437	0.5652

Sqrt S x10	-R10 $_{10}$-9	-R20 $_{10}$-9	-COR10 $_{10}$-11	-COR20 $_{10}$-11	ROO/N $_{10}$-7
0.0000	2.2897	2.3547	1.2671	1.3031	8.3924
1.0000	2.2120	2.3301	1.2237	1.2890	8.2103
2.2361	2.1791	2.2954	1.2032	1.2674	8.1037
3.1623	2.1846	2.3012	1.2034	1.2676	8.1433
4.4721	2.1554	2.2795	1.1777	1.2456	8.1165
7.0711	2.1003	2.2213	1.1341	1.1995	8.0035
10.0000	2.0626	2.1814	1.0889	1.1517	8.0384
14.1421	2.0302	2.1472	1.0135	1.0719	8.3684
17.3205	2.0277	2.1446	0.9561	1.0112	8.8486

Ammonium Nitrate-----CONTINUED-----

c	m	Eqv Cond	t+	D(v)10 5	1+md lnGama/dm
4.0000	5.006260	76.97	0.5140	1.5240	0.5809
5.0000	6.683150	70.09	0.5140	1.4720	0.5500
6.0000	8.610800	63.36	0.5140	1.4210	0.5270

Sqrt S x10	111/N 10+12	112/N 10+12	122/N 10+12	F12	Q12
20.0000	7.4759	3.2268	7.2444	0.6098	0.4385
22.3607	7.3873	3.5180	7.1765	0.6517	0.4832
24.4949	7.2367	3.7390	7.0462	0.6875	0.5236

Sqrt S x10	NR11 10-11	-NR12 10-11	NR22 10-11	Q10	Q20
20.0000	1.6560	0.7376	1.7089	0.5192	0.5405
22.3607	1.7659	0.8657	1.8178	0.4978	0.5189
24.4949	1.9038	1.0102	1.9553	0.4776	0.4984

Sqrt S x10	-R10 10-9	-R20 10-9	-COR10 10-11	-COR20 10-11	R00/N 10-7
20.0000	2.0707	2.1900	0.9184	0.9713	9.6065
22.3607	2.1678	2.2927	0.9003	0.9521	10.7404
24.4949	2.3102	2.4433	0.8936	0.9450	12.2898

Table-A19

Potassium Nitrate

c	m	Eqv Cond	t+	D(v) 10^{5}	1 +mxd lnGama/dm
0.0000	0.000000	144.92	0.5072	1.9230	1.0000
0.0010	0.001003	141.80	0.5076	1.8990	0.9822
0.0050	0.005016	138.44	0.5081	1.8660	0.9630
0.0100	0.010033	135.78	0.5084	1.8460	0.9494
0.0200	0.020074	132.37	0.5087	1.8240	0.9320
0.0500	0.050244	126.27	0.5093	1.7470	0.9006
0.1000	0.100683	120.36	0.5103	1.5030	0.8674

Sqrt S ×10	l11/N 10^{+12}	l12/N 10^{+12}	l22/N 10^{+12}	F12	Q12
0.0000	7.8930	0.0000	7.6688	0.0000	0.0000
0.3162	7.8239	0.0934	7.5924	0.0239	0.0121
0.7071	7.7471	0.1923	7.5062	0.0492	0.0252
1.0000	7.6913	0.2773	7.4463	0.0707	0.0366
1.4142	7.6265	0.3945	7.3792	0.0999	0.0526
2.2361	7.4305	0.5236	7.1782	0.1338	0.0717
3.1623	6.8614	0.2648	6.5951	0.0758	0.0394

Sqrt S ×10	NR11 10^{-11}	-NR12 10^{-11}	NR22 10^{-11}	Q10	Q20
0.0000	1.2670	0.0000	1.3040	0.7020	0.7122
0.3162	1.2783	0.0157	1.3173	0.6974	0.7082
0.7071	1.2916	0.0331	1.3331	0.6923	0.7039
1.0000	1.3019	0.0485	1.3448	0.6880	0.7001
1.4142	1.3148	0.0703	1.3589	0.6819	0.6945
2.2361	1.3528	0.0987	1.4003	0.6745	0.6881
3.1623	1.4597	0.0586	1.5186	0.6856	0.7004

Sqrt S ×10	-R10 10^{-9}	-R20 10^{-9}	-COR10 10^{-11}	-COR20 10^{-11}	ROO/N 10^{-7}
0.0000	2.2894	2.3563	1.2670	1.3040	8.3947
0.3162	2.2814	2.3518	1.2626	1.3016	8.3718
0.7071	2.2743	2.3492	1.2585	1.3000	8.3553
1.0000	2.2655	2.3429	1.2534	1.2963	8.3296
1.4142	2.2504	2.3301	1.2446	1.2886	8.2821
2.2361	2.2703	2.3563	1.2541	1.3016	8.3755
3.1623	2.5414	2.6483	1.4011	1.4600	9.4137

Table-A20

Potassium Bromide

c	m	Eqv Cond	t+	D(v)$_{10}$5	1+mxdlnGama/dm
0.0000	0.000000	151.80	0.4847	2.0160	1.0000
0.0500	0.050233	135.44	0.4831	1.8920	0.9222
0.1000	0.100638	131.19	0.4833	1.8740	0.9086
0.2000	0.201988	126.59	0.4841	1.8700	0.8991
0.5000	0.510440	120.35	0.4845	1.8850	0.8999
1.0000	1.040030	115.44	0.4850	1.9750	0.9213
2.0000	2.163540	109.37	0.4900	2.1230	0.9876
3.0000	3.385510	103.55	0.4900	2.2800	1.0654

Sqrt S x10	l11/N $_{10}$+12	l12/N $_{10}$+12	l22/N $_{10}$+12	F12	Q12
0.0000	7.8967	0.0000	8.3956	0.0000	0.0000
2.2361	7.5332	0.5058	8.0249	0.1222	0.0651
3.1623	7.4514	0.6417	7.9220	0.1542	0.0835
4.4721	7.3815	0.7997	7.8138	0.1906	0.1053
7.0711	7.2593	0.9968	7.6600	0.2359	0.1337
10.0000	7.2405	1.2273	7.6124	0.2838	0.1653
14.1421	7.1564	1.4006	7.3913	0.3230	0.1926
17.3205	6.9869	1.5374	7.2093	0.3562	0.2166

Sqrt S x10	NR11 $_{10}$-11	-NR12 $_{10}$-11	NR22 $_{10}$-11	Q10	Q20
0.0000	1.2664	0.0000	1.1911	0.7179	0.6962
2.2361	1.3331	0.0840	1.2514	0.6959	0.6713
3.1623	1.3515	0.1095	1.2712	0.6891	0.6646
4.4721	1.3699	0.1402	1.2941	0.6805	0.6570
7.0711	1.4026	0.1825	1.3292	0.6696	0.6465
10.0000	1.4199	0.2289	1.3505	0.6572	0.6347
14.1421	1.4512	0.2750	1.4051	0.6429	0.6278
17.3205	1.5017	0.3202	1.4554	0.6334	0.6182

Sqrt S x10	-R10 $_{10}$-9	-R20 $_{10}$-9	-COR10 $_{10}$-11	-COR20 $_{10}$-11	ROO/N $_{10}$-7
0.0000	2.2883	2.1523	1.2664	1.1911	8.0242
2.2361	2.2607	2.1129	1.2491	1.1674	7.9156
3.1623	2.2517	2.1062	1.2420	1.1617	7.9008
4.4721	2.2374	2.0995	1.2297	1.1539	7.8904
7.0711	2.2439	2.1089	1.2201	1.1467	8.0053
10.0000	2.2315	2.1015	1.1910	1.1216	8.1184
14.1421	2.2922	2.2023	1.1762	1.1301	8.7588
17.3205	2.4019	2.3077	1.1815	1.1351	9.5747

Table-A21

Potassium Iodide

c	m	Eqv Cond	t+	D(v)10 5	1+mxdlnGama/dm
0.0000	0.000000	150.38	0.4892	1.9990	1.0000
0.0100	0.010034	142.18	0.4884	1.9290	0.9559
0.0500	0.050262	134.97	0.4882	1.8910	0.9274
0.1000	0.100756	131.11	0.4883	1.8650	0.9172
0.2000	0.202456	126.89	0.4887	1.8590	0.9123
0.5000	0.513380	121.58	0.4900	1.9550	0.9210
1.0000	1.052310	117.61	0.4900	2.0650	0.9541
2.0000	2.216730	112.30	0.4900	2.2540	1.0433
3.0000	3.515720	106.47	0.4900	2.4400	1.1146

Sqrt S x10	l11/N 10+12	l12/N 10+12	l22/N 10+12	F12	Q12
0.0000	7.8974	0.0000	8.2462	0.0000	0.0000
1.0000	7.7130	0.2550	8.0672	0.0626	0.0323
2.2361	7.5679	0.4910	7.9100	0.1194	0.0635
3.1623	7.4590	0.5831	7.7885	0.1422	0.0765
4.4721	7.3650	0.7049	7.6730	0.1715	0.0938
7.0711	7.4168	1.0185	7.6780	0.2379	0.1350
10.0000	7.3985	1.2091	7.6511	0.2770	0.1607
14.1421	7.2537	1.3437	7.4949	0.3084	0.1822
17.3205	7.1612	1.5581	7.3899	0.3528	0.2142

Sqrt S x10	NR11 10-11	-NR12 10-11	NR22 10-11	Q10	Q20
0.0000	1.2662	0.0000	1.2127	0.7147	0.6994
1.0000	1.2979	0.0410	1.2409	0.7039	0.6872
2.2361	1.3267	0.0823	1.2693	0.6928	0.6757
3.1623	1.3486	0.1010	1.2915	0.6880	0.6709
4.4721	1.3698	0.1259	1.3148	0.6814	0.6648
7.0711	1.3733	0.1822	1.3266	0.6651	0.6502
10.0000	1.3875	0.2193	1.3416	0.6553	0.6403
14.1421	1.4260	0.2557	1.3801	0.6470	0.6318
17.3205	1.4635	0.3086	1.4183	0.6344	0.6192

Sqrt S x10	-R10 10-9	-R20 10-9	-COR10 10-11	-COR20 10-11	R00/N 10-7
0.0000	2.2881	2.1913	1.2662	1.2127	8.0943
1.0000	2.2719	2.1689	1.2569	1.1999	8.0273
2.2361	2.2535	2.1496	1.2444	1.1870	7.9737
3.1623	2.2645	2.1610	1.2476	1.1905	8.0329
4.4721	2.2685	2.1683	1.2440	1.1890	8.0910
7.0711	2.2032	2.1168	1.1911	1.1444	7.9909
10.0000	2.2146	2.1278	1.1682	1.1224	8.2320
14.1421	2.3368	2.2451	1.1703	1.1244	9.1488
17.3205	2.4384	2.3428	1.1550	1.1097	10.0939

Table-A22

Sodium Iodide

c	m	Eqv Cond	t+	D(v) $_{10}$5	1+mxd lnGamma/dm
0.0000	0.000000	126.94	0.3947	1.6160	1.0000
0.0100	0.010033	119.24	0.3882	1.5700	0.9565
0.0500	0.050231	112.79	0.3850	1.5270	0.9320
0.1000	0.100633	108.78	0.3837	1.5200	0.9288
0.2000	0.201973	104.98	0.3827	1.5320	0.9390
0.5000	0.510501	98.83	0.3828	1.5800	0.9890
1.0000	1.041080	92.53	0.3840	1.6620	1.0787

Sqrt S x10	111/N $_{10}$+12	112/N $_{10}$+12	122/N $_{10}$+12	F12	Q12
0.0000	5.3836	0.0000	8.2548	0.0000	0.0000
1.0000	5.2408	0.2693	8.1043	0.0813	0.0413
2.2361	5.1004	0.4366	7.8866	0.1321	0.0688
3.1623	5.0211	0.5383	7.7385	0.1631	0.0864
4.4721	4.9423	0.6273	7.5874	0.1906	0.1024
7.0711	4.7778	0.7146	7.2659	0.2218	0.1213
10.0000	4.5732	0.7571	6.8788	0.2436	0.1350

Sqrt S x10	NR11 $_{10}$-11	-NR12 $_{10}$-11	NR22 $_{10}$-11	Q10	Q20
0.0000	1.8575	0.0000	1.2114	0.7780	0.6283
1.0000	1.9114	0.0635	1.2360	0.7691	0.6068
2.2361	1.9700	0.1091	1.2740	0.7622	0.5933
3.1623	2.0066	0.1396	1.3019	0.7573	0.5853
4.4721	2.0448	0.1691	1.3320	0.7525	0.5780
7.0711	2.1242	0.2089	1.3968	0.7460	0.5706
10.0000	2.2272	0.2451	1.4807	0.7404	0.5661

Sqrt S x10	-R10 $_{10}$-9	-R20 $_{10}$-9	-COR10 $_{10}$-11	-COR20 $_{10}$-11	R00/N $_{10}$-7
0.0000	3.3565	2.1890	1.8575	1.2114	10.0208
1.0000	3.3399	2.1192	1.8479	1.1725	9.8671
2.2361	3.3679	2.1084	1.8609	1.1650	9.9111
3.1623	3.3847	2.1073	1.8670	1.1624	9.9564
4.4721	3.4125	2.1156	1.8758	1.1629	10.0572
7.0711	3.5229	2.1850	1.9153	1.1879	10.4987
10.0000	3.7174	2.3174	1.9821	1.2356	11.3183

Table-A23

SILVER NITRATE

c	m	Eqv Cond	t+	D(v)e5	1+mdlnGam/dm
0.0000	0.000000	133.32	0.4643	1.7680	1.0000
0.0010	0.001003	130.49	0.4644	1.7380	0.9817
0.0100	0.010032	124.23	0.4648	1.6980	0.9475
0.0500	0.050221	115.16	0.4673	1.6230	0.8995
0.1000	0.100582	109.05	0.4684	1.5880	0.8677
0.2000	0.201770	101.73	0.4702	1.5730	0.8223
0.5000	0.509079	89.48	0.4769	1.4230	0.7207
1.0000	1.034629	77.92	0.4886	1.2690	0.6160
1.5000	1.578291	70.05	0.5002	1.1320	0.5392

Sqrt S x10	111/N e+12	112/N e+12	122/N e+12	F12	Q12
0.0000	6.6530	0.0000	7.6753	0.0000	0.0000
0.3162	6.5936	0.0851	7.5914	0.0238	0.0120
1.0000	6.4899	0.2584	7.4338	0.0719	0.0372
2.2361	6.3444	0.5647	7.1533	0.1550	0.0838
3.1623	6.2611	0.7752	7.0013	0.2100	0.1171
4.4721	6.2741	1.1368	6.9253	0.2946	0.1725
7.0711	6.1355	1.5524	6.5795	0.3930	0.2443
10.0000	6.1532	2.0643	6.3440	0.4968	0.3304
12.2474	6.1171	2.3538	6.1140	0.5558	0.3849

Sqrt S x10	NR11 e-11	-NR12 e-11	NR22 e-11	Q10	Q20
0.0000	1.5031	0.0000	1.3029	0.7319	0.6814
0.3162	1.5168	0.0170	1.3175	0.7277	0.6771
1.0000	1.5430	0.0536	1.3471	0.7187	0.6681
2.2361	1.5873	0.1253	1.4078	0.7005	0.6525
3.1623	1.6194	0.1793	1.4481	0.6876	0.6406
4.4721	1.6427	0.2696	1.4882	0.6655	0.6205
7.0711	1.7333	0.4090	1.6164	0.6322	0.5969
10.0000	1.8243	0.5936	1.7694	0.5874	0.5698
12.2474	1.9191	0.7388	1.9200	0.5544	0.5547

Sqrt S x10	-R10 e-9	-R20 e-9	-CCR10 e-11	-CCR20 e-11	R00/N e-7
0.0000	2.7157	2.3540	1.5031	1.3029	9.1595
0.3162	2.7100	2.3498	1.4998	1.3005	9.1423
1.0000	2.6917	2.3376	1.4894	1.2934	9.0894
2.2361	2.6455	2.3207	1.4620	1.2825	8.9860
3.1623	2.6094	2.2991	1.4401	1.2689	8.8941
4.4721	2.4955	2.2147	1.3731	1.2186	8.5605
7.0711	2.4292	2.2146	1.3244	1.2074	8.5177
10.0000	2.2939	2.1916	1.2307	1.1758	8.3605
12.2474	2.2372	2.2390	1.1803	1.1812	8.4847

c	m	Eqv Cond	t+	D(v)D5	1+mdlnGam/dm
2.0000	2.141649	64.07	0.5116	1.0130	0.4764
2.5000	2.726504	59.27	0.5223	0.9130	0.4209
3.0000	3.334111	55.20	0.5327	0.8300	0.3724
4.0000	4.626510	48.57	0.5513	0.7100	0.3171
5.0000	6.035367	43.22	0.5668	0.6270	0.2870
6.0000	7.580735	38.72	0.5801	0.5540	0.2715
7.0000	9.287392	34.26	0.5932	0.5160	0.2655
8.0000	11.186621	31.25	0.6059	0.4870	0.2721
9.0000	13.314200	28.07	0.6222	0.4650	0.2895

Sqrt S x10	l11/N D+12	l12/N D+12	l22/N D+12	F12	Q12
14.1421	6.0901	2.5697	5.9305	0.5991	0.4276
15.8114	6.1119	2.7871	5.8280	0.6370	0.4670
17.3205	6.1780	3.0199	5.7903	0.6717	0.5049
20.0000	6.1018	3.2260	5.5666	0.7143	0.5535
22.3607	5.8953	3.2666	5.2798	0.7413	0.5855
24.4949	5.5896	3.1772	4.9234	0.7583	0.6057
26.4575	5.2150	3.0323	4.5291	0.7735	0.6239
28.2843	4.8423	2.8087	4.1314	0.7780	0.6280
30.0000	4.4070	2.5312	3.6702	0.7813	0.6294

Sqrt S x10	NR11 D-11	-NR12 D-11	NR22 D-11	Q10	Q20
14.1421	2.0094	0.8707	2.0635	0.5261	0.5438
15.8114	2.0925	1.0007	2.1944	0.4992	0.5330
17.3205	2.1725	1.1330	2.3180	0.4728	0.5218
20.0000	2.3628	1.3693	2.5900	0.4344	0.5097
22.3607	2.5811	1.5970	2.8821	0.4067	0.5025
24.4949	2.8255	1.8234	3.2078	0.3859	0.5004
26.4575	3.1399	2.1022	3.6153	0.3667	0.4983
28.2843	3.4097	2.3181	3.9964	0.3552	0.5044
30.0000	3.7576	2.5915	4.5119	0.3424	0.5146

Sqrt S x10	-R10 D-9	-R20 D-9	-CCR10 D-11	-CCR20 D-11	R00/N D-7
14.1421	2.1967	2.3010	1.1387	1.1920	8.6765
15.8114	2.1451	2.3453	1.0918	1.1937	8.8223
17.3205	2.0811	2.3724	1.0394	1.1849	8.9165
20.0000	2.0700	2.5434	0.9935	1.2207	9.6124
22.3607	2.1402	2.7945	0.9842	1.2851	10.7306
24.4949	2.2809	3.1511	1.0021	1.3844	12.3639
26.4575	2.4803	3.6168	1.0377	1.5132	14.5730
28.2843	2.7499	4.2278	1.0916	1.6783	17.5776
30.0000	3.1077	5.1181	1.1661	1.9204	21.9222

Table-A24

Ammonium Chloride

c	m	Eqv Cond	t+	D(v) $_{10}$5	1+mxd lnGama/dm
0.0000	0.000000	149.90	0.4907	1.9940	1.0000
0.1000	0.100660	128.80	0.4907	1.8380	0.9053
0.2000	0.200246	123.80	0.4911	1.8360	0.8934

Sqrt S x10	111/N $_{10}$+12	112/N $_{10}$+12	122/N $_{10}$+12	F12	Q12
0.0000	7.8986	0.0000	8.1980	0.0000	0.0000
3.1623	7.4261	0.6381	7.6834	0.1558	0.0845
4.4721	7.3520	0.8223	7.5887	0.1984	0.1101

Sqrt S x10	NR11 $_{10}$-11	-NR12 $_{10}$-11	NR22 $_{10}$-11	Q10	Q20
0.0000	1.2660	0.0000	1.2198	0.7137	0.7005
3.1623	1.3563	0.1126	1.3109	0.6834	0.6697
4.4721	1.3769	0.1492	1.3339	0.6736	0.6604

Sqrt S x10	-R10 $_{10}$-9	-R20 $_{10}$-9	-COR10 $_{10}$-11	-COR20 $_{10}$-11	ROO/N $_{10}$-7
0.0000	2.2877	2.2042	1.2660	1.2198	8.1169
3.1623	2.2552	2.1728	1.2436	1.1982	8.0298
4.4721	2.2144	2.1369	1.2277	1.1847	7.8485

Table-A25

Phosphoric Acid

c	m	Eqv Cond	t+	D(v) $_{10}5$	1 +mxd lnGam± /dm
0.0000	0.000000	383.86	0.8950	1.9200	1.0000
0.0100	0.009998	223.00	0.9010	1.1650	0.8888
0.1000	0.100725	104.05	0.9100	0.9440	0.6823
0.5000	0.513347	64.71	0.9100	0.8530	0.4825
1.0000	1.051857	60.15	0.9160	0.8300	0.4881
2.0000	2.213614	58.31	0.9240	0.8130	0.6461
3.0000	3.506721	54.07	0.9280	0.8030	0.8174
4.0000	4.957244	48.95	0.9300	0.7970	0.9654
5.0000	6.599789	43.52	0.9320	0.7830	1.0916

Sqrt S ×10	111/N $_{10}+12$	112/N $_{10}+12$	122/N $_{10}+12$	F12	Q12
0.0000	36.8966	0.0000	4.3273	0.0000	0.0000
1.0000	22.0869	0.5076	2.8787	0.1920	0.0637
3.1623	12.0448	1.8755	2.8813	0.6720	0.3184
7.0711	9.3212	2.9968	3.6223	0.8404	0.5157
10.0000	8.8504	2.9329	3.4756	0.8551	0.5288
14.1421	7.3850	2.0984	2.5743	0.8267	0.4657
17.3205	6.9826	1.5935	2.0117	0.8042	0.4252
20.0000	6.2123	1.3230	1.6910	0.7945	0.4082
22.3607	5.5069	1.1506	1.4685	0.7953	0.4046

Sqrt S ×10	NR11 $_{10}-11$	-NR12 $_{10}-11$	NR22 $_{10}-11$	Q10	Q20
0.0000	0.2710	0.0000	2.3109	0.3240	0.9461
1.0000	0.4546	0.0802	3.4880	0.2856	0.9382
3.1623	0.9239	0.6014	3.8621	0.1772	0.8765
7.0711	1.4616	1.2092	3.7611	0.1247	0.7858
10.0000	1.5685	1.3236	3.9942	0.1145	0.7826
14.1421	1.6195	1.3201	4.9606	0.1185	0.8235
17.3205	1.7482	1.3848	6.0680	0.1223	0.8463
20.0000	1.9315	1.5112	7.0960	0.1234	0.8555
22.3607	2.1714	1.7014	8.1430	0.1213	0.8586

Sqrt S ×10	-R10 $_{10}-9$	-R20 $_{10}-9$	-COR10 $_{10}-11$	-COR20 $_{10}-11$	ROO/N $_{10}-7$
0.0000	0.4897	4.1752	0.2710	2.3109	8.4282
1.0000	0.6744	6.1379	0.3744	3.4078	12.2696
3.1623	0.5852	5.9169	0.3225	3.2608	11.7984
7.0711	0.4668	4.7200	0.2524	2.5519	9.5934
10.0000	0.4641	5.0605	0.2449	2.6706	10.4686
14.1421	0.5970	7.2558	0.2994	3.6405	15.6638
17.3205	0.7651	9.3618	0.3634	4.6832	22.3781
20.0000	0.9385	12.4687	0.4204	5.5848	29.9332
22.3607	1.1176	15.3175	0.4700	6.4416	39.0810

Phosphoric Acid ----continued -----

c	m	Eqv Cond	t+	D(v)10 5	1+mxd lnGama/dm
6.0000	8.479367	38.07	0.9360	0.7590	1.2048
7.0000	10.667479	32.79	0.9420	0.7250	1.3167
8.0000	13.240649	27.78	0.9500	0.6800	1.4437
10.0000	19.976029	18.89	0.9740	0.6260	1.8793
12.0000	30.310685	11.81	1.0140	0.3830	3.1599

Sqrt S x10	l11/N 10+12	l12/N 10+12	l22/N 10+12	F12	Q12
24.4949	4.8529	1.0258	1.2875	0.8072	0.4104
26.4575	4.2357	0.9182	1.1225	0.8268	0.4211
28.2843	3.6428	0.8084	0.9575	0.8508	0.4328
31.6228	2.5966	0.6205	0.6733	0.9235	0.4693
34.6410	1.5487	0.2625	0.2447	1.0737	0.4264

Sqrt S x10	NR11 10-11	-NR12 10-11	NR22 10-11	Q10	Q20
24.4949	2.4780	1.9743	9.3402	0.1141	0.8592
26.4575	2.8698	2.3476	10.8292	0.1027	0.8589
28.2843	3.3780	2.8517	12.8509	0.0883	0.8598
31.6228	4.9391	4.5521	19.0484	0.0451	0.8610
34.6410	7.8919	8.4646	49.9397	-0.0319	0.9177

Sqrt S x10	-R10 10-9	-R20 10-9	-CCR10 10-11	-CCR20 10-11	R00/N 10-7
24.4949	1.2823	18.7530	0.5036	7.3659	51.0083
26.4575	1.4337	23.2848	0.5222	8.4815	67.8609
28.2843	1.5692	29.8140	0.5263	9.9992	93.5729
31.6228	1.3926	52.1674	0.3870	14.4962	192.7451
34.6410	-2.6057	188.7279	-0.5726	41.4751	846.9288

Table-A26

Sodium Sulfate

c	m	Eqv Cond	t+	D(v)$_{10}$5	1+m×dlnGama/dm
0.0000	0.000000	129.90	0.3860	1.2300	1.0000
0.0030	0.003009	116.01	0.3856	1.1470	0.9093
0.0050	0.005015	112.44	0.3848	1.1230	0.8902

Sqrt S ×10	l11/N $_{10}$+12	l12/N $_{10}$+12	l22/N $_{10}$+12	F12	Q12
0.0000	5.3867	0.0000	2.1419	0.0000	0.0000
0.9487	5.2451	0.2203	2.0240	0.2598	0.0676
1.2247	5.1809	0.2670	1.9908	0.3148	0.0831

Sqrt S ×10	NR11 $_{10}$-11	-NR12 $_{10}$-11	NR22 $_{10}$-11	Q10	Q20
0.0000	1.8564	0.0000	4.6687	0.7836	0.6213
0.9487	1.9153	0.2085	4.9635	0.7622	0.5943
1.2247	1.9436	0.2607	5.0580	0.7576	0.5875

Sqrt S ×10	-R10 $_{10}$-9	-R20 $_{10}$-9	-COR10 $_{10}$-11	-COR20 $_{10}$-11	R00/N $_{10}$-7
0.0000	3.3545	4.2182	1.8564	2.3344	9.8728
0.9487	3.2724	4.1075	1.8111	2.2732	9.6239
1.2247	3.2764	4.0987	1.8133	2.2683	9.6231

Table-A27

Potassium Sulfate

c	m	Eqv Cond	t+	D(v)$_{10}$5	1+mxdlnGama/dm
0.0000	0.000000	153.53	0.4788	1.5290	1.0000
0.0100	0.010033	127.50	0.4848	1.3300	0.8596
0.0250	0.025100	117.75	0.4870	1.2820	0.8008
0.0500	0.050233	109.25	0.4890	1.2280	0.7711
0.1000	0.100653	101.15	0.4910	1.1840	0.7256
0.2500	0.253140	89.60	0.4909	1.0850	0.6769

Sqrt S x10	l11/N $_{10}$+12	l12/N $_{10}$+12	l22/N $_{10}$+12	F12	Q12
0.0000	7.8923	0.0000	2.1479	0.0000	0.0000
1.7321	7.3796	0.3705	1.9490	0.3561	0.0977
2.7386	7.3049	0.5730	1.9084	0.5324	0.1535
3.8730	7.0888	0.6755	1.8367	0.6309	0.1872
5.4772	7.0075	0.8367	1.8008	0.7627	0.2356
8.6603	6.6299	0.9530	1.7013	0.8842	0.2837

Sqrt S x10	NR11 $_{10}$-11	-NR12 $_{10}$-11	NR22 $_{10}$-11	Q10	Q20
0.0000	1.2671	0.0000	4.6558	0.7219	0.6919
1.7321	1.3681	0.2601	5.1803	0.6828	0.6604
2.7386	1.4020	0.4210	5.3663	0.6603	0.6408
3.8730	1.4619	0.5377	5.6422	0.6458	0.6291
5.4772	1.5109	0.7020	5.8794	0.6251	0.6113
8.6603	1.6404	0.9189	6.3927	0.6054	0.5914

Sqrt S x10	-R10 $_{10}$-9	-R20 $_{10}$-9	-COR10 $_{10}$-11	-COR20 $_{10}$-11	ROO/N $_{10}$-7
0.0000	2.2896	4.2065	1.2671	2.3279	7.9378
1.7321	2.2378	4.2115	1.2381	2.3301	7.8507
2.7386	2.1551	4.0917	1.1915	2.2622	7.5982
3.8730	2.1593	4.1328	1.1931	2.2834	7.6481
5.4772	2.1031	4.0575	1.1598	2.2377	7.4921
8.6603	2.1542	4.1544	1.1810	2.2775	7.7186

Table-A28

Sulfuric Acid

c	m	Eqv Cond	t+	D(v)10 5	1+mxdlnGama/dm
0.0000	0.000000	429.80	0.8138	2.6000	1.0000
0.0500	0.050215	290.00	0.8190	1.8640	0.6566
0.1000	0.100605	255.00	0.8190	1.8280	0.6400
0.5000	0.510320	214.00	0.8170	1.8180	0.7049
1.0000	1.040330	199.80	0.8070	1.9680	0.8254
2.0000	2.169020	166.00	0.7910	2.2640	1.1691
3.0000	3.405330	132.80	0.7700	2.5900	1.5930
4.0000	4.772200	102.80	0.7490	2.7980	1.9432
5.0000	6.304220	78.40	0.7220	2.8980	2.5168

Sqrt S x10	l11/N 10+12	l12/N 10+12	l22/N 10+12	F12	Q12
0.0000	37.5636	0.0000	2.1482	0.0000	0.0000
3.8730	28.5267	1.5090	2.1638	0.7905	0.1921
5.4772	26.0521	1.8109	2.1447	0.9430	0.2423
12.2474	22.2778	1.7500	1.9265	1.0092	0.2671
17.3205	20.3874	1.5351	1.8029	0.9576	0.2532
24.4949	16.3632	1.1304	1.4967	0.8682	0.2284
30.0000	12.8291	0.9234	1.2818	0.8447	0.2277
34.6410	10.0664	0.8984	1.1420	0.9280	0.2650
38.7298	7.4861	0.7034	0.9369	0.9085	0.2656

Sqrt S x10	NR11 10-11	-NR12 10-11	NR22 10-11	Q10	Q20
0.0000	0.2662	0.0000	4.6550	0.4315	0.9021
3.8730	0.3640	0.2538	4.7984	0.3434	0.8558
5.4772	0.4078	0.3443	4.9533	0.3234	0.8397
12.2474	0.4834	0.4391	5.5896	0.3160	0.8298
17.3205	0.5241	0.4462	5.9264	0.3329	0.8279
24.4949	0.6448	0.4870	7.0489	0.3607	0.8257
30.0000	0.8221	0.5922	8.2282	0.3836	0.8119
34.6410	1.0684	0.8405	9.4176	0.3902	0.7844
38.7298	1.4372	1.0790	11.4836	0.4167	0.7657

Sqrt S x10	-R10 10-9	-R20 10-9	-CCR10 10-11	-CCR20 10-11	R00/N 10-7
0.0000	0.4811	4.2058	0.2662	2.3275	4.6692
3.8730	0.4289	3.8815	0.2371	2.1454	4.2873
5.4772	0.4270	3.8646	0.2356	2.1323	4.2761
12.2474	0.4851	4.3314	0.2638	2.3557	4.8740
17.3205	0.5641	4.7172	0.3010	2.5170	5.4775
24.4949	0.7840	5.9345	0.4013	3.0375	7.3290
30.0000	1.0756	7.2019	0.5260	3.5219	9.5631
34.6410	1.3931	8.3140	0.6482	3.8683	11.9287
38.7298	2.0390	10.5913	0.8977	4.6629	16.6601

Table-A29

Copper Sulfate

c	m	Eqv Cond	t+	D(v)$_{10}$5	1+m×dlnGama/dm
0.0000	0.000000	133.60	0.4030	0.8540	1.0000
0.0010	0.001003	108.30	0.3990	0.7860	0.8060
0.0100	0.010028	72.25	0.3905	0.6810	0.6260
0.0500	0.050138	50.58	0.3740	0.5920	0.5150
0.1000	0.100275	43.60	0.3602	0.5630	0.4680
0.2000	0.200566	38.20	0.3390	0.5340	0.4420
0.3500	0.351120	32.20	0.3110	0.5050	0.4340
0.5000	0.501925	29.00	0.3040	0.4820	0.4340

Sqrt S ×10	111/N $_{10}$+12	112/N $_{10}$+12	122/N $_{10}$+12	F12	Q12
0.0000	1.4439	0.0000	2.1398	0.0000	0.0000
0.6325	1.4465	0.2862	2.0338	1.1640	0.1669
2.0000	1.3930	0.6354	1.8178	2.3167	0.3993
4.4721	1.3493	0.8414	1.6915	2.9030	0.5569
6.3246	1.3652	0.9435	1.6925	3.1105	0.6207
8.9443	1.3363	0.9886	1.6666	3.2455	0.6625
11.8322	1.2572	0.9883	1.5840	3.3685	0.7003
14.1421	1.1920	0.9553	1.4973	3.4116	0.7151

Sqrt S ×10	NR11 $_{10}$-11	-NR12 $_{10}$-11	NR22 $_{10}$-11	Q10	Q20
0.0000	6.9257	0.0000	4.6733	0.7727	0.6347
0.6325	7.1115	1.0008	5.0576	0.7186	0.5657
2.0000	8.5408	2.9855	6.5447	0.6296	0.4608
4.4721	10.7435	5.3438	8.5698	0.5609	0.3752
6.3246	11.9160	6.6426	9.6115	0.5321	0.3336
8.9443	13.3355	7.9106	10.6928	0.5185	0.2970
11.8322	15.6115	9.7404	12.3905	0.5090	0.2579
14.1421	17.1674	10.9536	13.6677	0.5019	0.2457

Sqrt S ×10	-R10 $_{10}$-9	-R20 $_{10}$-9	-COR10 $_{10}$-11	-COR20 $_{10}$-11	ROO/N $_{10}$-7
0.0000	6.2574	4.2223	3.4629	2.3367	9.4685
0.6325	5.5207	3.6652	3.0554	2.0284	8.2990
2.0000	5.0179	3.2149	2.7776	1.7796	7.4365
4.4721	4.8771	2.9138	2.6998	1.6130	7.0371
6.3246	4.7630	2.6815	2.6367	1.4844	6.7241
8.9443	4.9003	2.5131	2.7124	1.3911	6.6965
11.8322	5.3054	2.3947	2.9356	1.3251	6.9580
14.1421	5.6186	2.4541	3.1069	1.3570	7.2995

Table-A30

Zinc Sulfate

c	m	Eqv Cond	t+	D(v)10 5	1+mxdlnGama/dm
0.0000	0.000000	132.82	0.3892	0.8486	1.0000
0.0010	0.001003	108.00	0.3865	0.7480	0.8236
0.0020	0.002006	98.75	0.3853	0.7330	0.7801
0.0030	0.003009	92.76	0.3844	0.7240	0.7487
0.0050	0.005015	84.91	0.3830	0.7050	0.7053
0.0250	0.025070	60.75	0.3751	0.6870	0.6009
0.0500	0.050135	52.50	0.3692	0.6640	0.5605
0.1000	0.100260	45.00	0.3610	0.6310	0.5138
0.2500	0.250665	36.30	0.3500	0.5740	0.4540

Sqrt S x10	111/N 10+12	112/N 10+12	122/N 10+12	F12	Q12
0.0000	1.3961	0.0000	2.1863	0.0000	0.0000
0.6325	1.3492	0.2284	2.0074	0.9973	0.1388
0.8944	1.3413	0.3197	1.9495	1.3493	0.1977
1.0954	1.3433	0.3859	1.9191	1.5827	0.2403
1.4142	1.3425	0.4694	1.8760	1.8623	0.2957
3.1623	1.3826	0.7707	1.7900	2.6736	0.4899
4.4721	1.3869	0.8665	1.7557	2.9009	0.5553
6.3246	1.3961	0.9599	1.7320	3.0999	0.6173
10.0000	1.3945	1.0534	1.6869	3.3044	0.6868

Sqrt S x10	NR11 10-11	-NR12 10-11	NR22 10-11	Q10	Q20
0.0000	7.1630	0.0000	4.5739	0.7812	0.6243
0.6325	7.5576	0.8598	5.0793	0.7374	0.5666
0.8944	7.7588	1.2722	5.3381	0.7169	0.5417
1.0954	7.9008	1.5887	5.5301	0.7013	0.5234
1.4142	8.1625	2.0422	5.8413	0.6802	0.4991
3.1623	9.5173	4.0978	7.3509	0.5965	0.4074
4.4721	10.4244	5.1448	8.2349	0.5652	0.3722
6.3246	11.5730	6.4139	9.3285	0.5337	0.3358
10.0000	13.5734	8.4758	11.2206	0.4941	0.2926

Sqrt S x10	-R10 10-9	-R20 10-9	-COR10 10-11	-COR20 10-11	ROO/N 10-7
0.0000	6.4718	4.1325	3.5815	2.2869	9.5810
0.6325	6.0512	3.8122	3.3489	2.1098	8.9111
0.8944	5.8597	3.6729	3.2433	2.0329	8.6114
1.0954	5.7021	3.5606	3.1560	1.9707	8.3675
1.4142	5.5289	3.4320	3.0602	1.8996	8.0949
3.1623	4.8953	2.9384	2.7098	1.6265	7.0760
4.4721	4.7685	2.7909	2.6398	1.5451	6.8275
6.3246	4.6591	2.6321	2.5795	1.4573	6.5847
10.0000	4.6038	2.4790	2.5488	1.3724	6.3968

Table-A31

Cadmium Sulfate

c	m	Eqv Cond	t+	D(v)$_{10}$5	1+m×dlnGama/dm
0.0000	0.000000	118.01	0.3984	0.8630	1.0000
0.0010	0.001003	105.50	0.3840	0.8080	0.7896
0.0050	0.005015	81.90	0.3840	0.7500	0.6880
0.0100	0.010030	70.30	0.3840	0.7140	0.6338
0.0500	0.050164	48.75	0.3840	0.6000	0.5461
0.1000	0.100386	41.70	0.3690	0.5600	0.4889
0.2000	0.201025	34.62	0.3380	0.5100	0.4445
0.2500	0.251445	33.70	0.3280	0.4920	0.4367
0.5000	0.504750	27.00	0.2950	0.4320	0.4207

Sqrt S ×10	111/N $_{10}$+12	112/N $_{10}$+12	122/N $_{10}$+12	F12	Q12
0.0000	1.3733	0.0000	2.0172	0.0000	0.0000
0.6325	1.4497	0.3620	2.1069	1.4030	0.2071
1.4142	1.4237	0.5793	1.9339	2.1075	0.3491
2.0000	1.4145	0.6897	1.8524	2.4281	0.4261
4.4721	1.3011	0.7985	1.6048	2.8823	0.5526
6.3246	1.3077	0.8945	1.6010	3.0973	0.6182
8.9443	1.2634	0.9492	1.5645	3.2810	0.6751
10.0000	1.2336	0.9368	1.5449	3.2979	0.6786
14.1421	1.0987	0.8849	1.3960	3.4177	0.7145

Sqrt S ×10	NR11 $_{10}$-11	-NR12 $_{10}$-11	NR22 $_{10}$-11	Q10	Q20
0.0000	7.2817	0.0000	4.9575	0.7713	0.6364
0.6325	7.2069	1.2382	4.9590	0.7143	0.5368
1.4142	7.9988	2.3959	5.8887	0.6569	0.4772
2.0000	8.6376	3.2159	6.5956	0.6218	0.4436
4.4721	11.0641	5.5050	8.9704	0.5563	0.3852
6.3246	12.3780	6.9158	10.1100	0.5277	0.3414
8.9443	14.5451	8.8242	11.7451	0.5103	0.2899
10.0000	15.0258	9.1117	11.9983	0.5143	0.2809
14.1421	18.5932	11.7857	14.6342	0.5081	0.2396

Sqrt S ×10	-R10 $_{10}$-9	-R20 $_{10}$-9	-COR10 $_{10}$-11	-COR20 $_{10}$-11	ROO/N $_{10}$-7
0.0000	6.5790	4.4791	3.6409	2.4787	9.9910
0.6325	5.3925	3.3615	2.9844	1.8604	7.9088
1.4142	5.0620	3.1555	2.8014	1.7464	7.4241
2.0000	4.8983	3.0535	2.7109	1.6899	7.1840
4.4721	5.0238	3.1317	2.7796	1.7327	7.3702
6.3246	4.9391	2.8883	2.7311	1.5971	7.0777
8.9443	5.1795	2.6445	2.8605	1.4605	7.0836
10.0000	5.3580	2.6152	2.9571	1.4433	7.2233
14.1421	6.1900	2.5902	3.4037	1.4242	7.9839

Table-A32

CADMIUM IODIDE

c	m	Eqv Cond	t+	D(v)10 5	1+mxd lnGama/dm
0.0000	0.000000	129.80	0.4083	0.9130	1.0000
0.0050	0.005015	66.54	0.4504	0.8760	0.6500
0.0100	0.010032	63.00	0.4477	0.8720	0.5800
0.0250	0.025104	55.06	0.4148	0.8640	0.4950
0.0500	0.050250	47.53	0.3208	0.8500	0.4350

Sqrt S x10	l11/N 10+12	l12/N 10+12	l22/N 10+12	F12	Q12
0.0000	1.1949	0.0000	7.3362	0.0000	0.0000
1.2247	1.2686	0.9278	5.7832	1.0239	0.3425
1.7321	1.3499	1.1852	6.1074	1.1725	0.4128
2.7386	1.4279	1.6294	6.7194	1.3884	0.5260
3.8730	1.4451	2.0715	7.6101	1.5767	0.6246

Sqrt S x10	NR11 10-11	-NR12 10-11	NR22 10-11	Q10	Q20
0.0000	8.3691	0.0000	1.3631	0.7781	0.6281
1.2247	8.9307	1.4327	1.9590	0.6110	0.5345
1.7321	8.9293	1.7328	1.9736	0.5813	0.5012
2.7386	9.6823	2.3479	2.0576	0.5490	0.4221
3.8730	11.3471	3.0887	2.1548	0.5563	0.3015

Sqrt S x10	-R10 10-9	-R20 10-9	-COR10 10-11	-COR20 10-11	R00/N 10-7
0.0000	7.5615	2.4631	4.1845	1.3631	11.2826
1.2247	5.4797	2.2453	3.0326	1.2426	9.0077
1.7321	4.9371	2.0010	2.7318	1.1072	8.0778
2.7386	4.5102	1.5985	2.4932	0.8836	6.9711
3.8730	4.6799	1.1052	2.5848	0.6104	6.2375

Appendix 2

For analysis of the experimental data and where repeated calculations were involved we wrote a few computer programmes in Algol language and manipulated them on the computer KDF9. A brief description of these programmes is given below.

The programme 1 analysed the conductance data for the solution of the Fuoss implicit equation in $c^{3/2}$ while the programme 2 solved the data for the dissociation constant, K_a, and the ion size parameter, a_0, using the Fuoss explicit equation. The programme 2 was kindly applied to us by Professor R.M.Fuoss. Originally it was in Fortran language that we translated it into Algol.

The programme 3 was designed to analyse data obtained from salt diffusion experiments. It calculated concentrations of the solutions from measured specific conductances by the conductometric method of analysis and then the cell constant and the integral diffusion coefficient.

For the conversion of integral into differential diffusion coefficients we needed a programme for the solution of simultaneous equations. This was applied to us by Mr. R.E. Moran of the department of Astronomy of this university. In this programme the simultaneous equations were solved by the method of determinants.

The programme 5, used for curve fitting by the method of least squares, belonged to Dr. M. Gibson of the computing department of this university and was available in the computing library. It was particularily used for fitting 4th or 5th degree equations between molality and activity coefficients. The coefficients of the fits, thus obtained were used in differentiations of the equations to obtain the activity term, $(1+m\,d\ln\gamma/dm)$. This is described in the programme 6.

The calculations of the L-coefficients from the experimental transport data and their subsequent matrix inversion for obtaining the R-coefficients are described in the programme 7.

Each of the programme starts with a comment heading which gives a brief discription of calculations and is followed by intructions for and a specimen of the data input.

PROGRAMME 1

```
BE2592000MPU+1030062JPSP→
begin   comment  This program calculates function
y=A+Bxsqrt C OF THE Fuoss Empirical conductance
equation in C to the power 3/2 and then fits stra-
ight line between y and sqrt C
gama is the degree of dissociation in this program;
 real  alfa, beta, ea, eb, sya, syb, l, g, sx, sy,
       sxy,sx2, sy2, m, x, z, me, xa, za, dd, s, e;
integer f, n, i; open(20);  open(70);
        copytext(20, 70, [;]); f:=format([-nddd.dddc]);
     alfa:=read(20); beta:=read(20);
     ea:=read(20); eb:=read(20);
again: copytext(20, 70, [;]);   l:=read(20);  g:=read(20);
     n:=read(20); sya:=1.0; sx:=sx2:=0.0;

     begin array  c, rc, fc, yc, gama, d, dc,y[1:n];
           for i:=1 step 1 until n do begin
           c[i]:=read(20);  d[i]:=read(20); gama[i]:=
           read(20); c[i]:=c[i]×gama[i];
           d[i]:=d[i]/gama[i]; rc[i]:=sqrt(c[i]);
            fc[i]:= c[i]×ln(c[i])×0.4342;
           sx:=sx + rc[i];  sx2:= sx2 + rc[i]↑2;  end;
           m:= n×sx2-sx↑2;
   repeat: me:= sya; dd:=l; s:=alfa×dd+beta; e:=ea×dd- eb;
           sy:=sxy:=sy2:=0.0; for i:=1 step 1 until n do
           begin y[i]:=(d[i]-dd+s×rc[i] -e×fc[i])/c[i];
           sy  := sy + y[i];
            sxy  := sxy + rc[i] × y[i];
            sy2  := sy2 + y[i]↑2  end;
            x:=(n×sxy-sx×sy)/m;  z:=(sx2×sy-sx×sxy)/m;
            sy:= 0.0; for i:=1 step 1 until n do begin
              yc[i]:= x×rc[i]+z;
           dc[i]:=dd-s×rc[i] +e×fc[i]+ yc[i]×c[i]; end;
           for i:= 1step 1untiln do
            sy:=sy+(d[i]-dc[i])↑2;
           sya:= sqrt(sy/(n-2)); if sya<me then begin
           xa:=x; za:=z; l:=l+g; goto repeat end else
           begin  writetext(70,[[c]LAMBDAO[7s]=*]);
            write(70, f, l-g);
           writetext(70,[SLOPE[8s]=*]); write(70, f,xa);
           writetext(70,[INTERCEPT[4s]=*]);
             write(70,f,za);
           writetext(70,[MEAN-ERROR-IN-LAMBDA[4s]=*]);
           write(70,f, me);
          writetext(70,[MEAN*ERROR*IN*INTERCEPT*=*]);
           for i:=1step 1 until n do
           sy:= sy+(y[i]-xa×rc[i]-za)↑2;
           syb:=sqrt(sy/(n-2)); write(70,f, syb); end;
   end;    n:=read(20); if n=1 then goto again;
           close(20); close(70);
end→
```

Instructions for data input for program DD25520

```
[cc] Name [cc];
alfa; beta; ea; eb;          (theoretical parameters)
[cc] Heading[cc]:

l;                           (approximate equiv. conductivity)
g;                           (increment in equiv. conductivity)
k;                           (no. of increments in g)
n;                           (no. of sets of C and equiv. cond.)

C;  equiv. cond.; gama;      (n  actual sets of C     equiv. cond.
                                                      and gama)
```

(where gama is the degree of dissociation)

```
1;    or   0;→               ( 1; for repeating calculations on
                                another  set, in this case goto
                                [cc]Heading[c]: or 0;→ for finish)
```

Specimen input instructions

```
S*JALOTA[cc];
0.2297;  60.62;  0.531;  20.525;

[2c]conductance*data*for*RbCl[cc] Impirical*fit*[cc]:

153.99; .01; 12; 20;

.00800; 145.912; 1;
.01000; 145.068; 1;
.01031; 144.977; 1;
.01300; 143.955; 1;
.01500; 143.300; 1;
.01700; 142.766; 1;
.01897; 142.234; 1;
.02000; 141.975; 1;
.03000; 139.770; 1;
.04000; 138.108; 1;
.05000; 136.750; 1;
.05500; 136.189; 1;
.06330; 135.278; 1;
.06500; 135.092; 1;
.07000; 134.592; 1;
.07500; 134.146; 1;
.08280; 133.428; 1;
.09000; 132.872; 1;
.10000; 132.130; 1;
.10000; 132.140; 0;→
 0;→
```

Programme 2

comment Fuoss program for solving Fuoss explicit equation and calculating dissociation constant, Ka, and the ion size parameter, ao, from the input data of concentration and equivalent conductivity;

```
Specimen data input        Instructions for data input


M                            (means program is on magnetic tape)
 DD0101200KF4+1 0jee62←PSU→ (binary program and job number)

[5c]s *jalota[cc]
rbc I*data[cc];              (name and heading)

12;                          (no. of sets of c and equiv. cond.)
78.54;                       (dielectric constant for solvent)
 .008903;                     (coefficient of viscisity of solvent)
298.16;                      (absolute temperature)
154.0;                       (approximate value of limiting
                                equiv. cond.)
6;                           (approximate value of ionsize
                              parameter)

.00800; 145.912;             (12 sets of c and equiv. cond.)
 .01000; 145.068;
.01031; 144.977;
.01300; 143.955;
.01500; 143.300;
.01700; 142.766;
.01897; 142.234;
.02000; 141.975;
.03000; 139 770;
.04000; 138.108;
.05000; 136.750;
.05500; 136.189; 0;→             (0;→ for finish)
```

Programme 3

```
ED255DF00WFU-H C300622FST→

begin  comment This program calculates concentrations
for a diffusion run by the conductometric method of analysis,
calibrates the cell for cell constant with a standard salt
and then calculates integral diffusion coefficient for an
 unknown salt;
integer l,n,i,f,j,r,s;
real  v,k,t,C1,C2,C3,C4,C,di,dm,dmb,cm,cv,ci,wx,wy,wb,wg,m;
open(20);     open(70);
copytext(20,70, [;]);f:= format([-ndd.ddd₁₀dd]);
again:     n:= read(20);     r:= read(20);
begin array a, b[1:n], p,q[1:3];

real procedure C(k);value k;real k;begin  real st, lamia, CC;
CC:=0.0;  if r=6 then k:=ln(k); for i:=1 step 1 until n do
CC:= CC+ a[i]×k↑(i-1); rep: st:=CC;          lamda:= 0.0;
for i:=1 step 1 until n do  lamia:= lamia+ b[i]×CC↑(i-1);
if r=6 then CC:=k-lamia else CC  := k/lamia;
if r=6 then begin if abs((exp(st)-exp(CC))/exp(CC))
>0.0003 then goto rep  end else   begin
if abs((st-CC)/CC) > 0.0003 then goto rep  end;
if r=6 then CC  := exp(CC);      if s=15 then  begin  m:= 0.0;
for j:= 1 step 1 until  3 do    m:= m + p[j]×CC↑(j-1);
m:= m×CC;  wg  := m×wb×wy/(1000+m×wb);
m  := wg×1000/(wb×(wx-wg));
CC:=0.0; for  j:= 1  step 1  until 3 do CC:= CC+ q[j]×m↑(j-1);
 CC  := m×CC          end;       C:= CC   end C;

real procedure d(c); value c; real c;  begin
if c≤.01 then d:= 1.9834 - 10.4036×c  + 970.602×c↑2-39220.0×c↑3;
 if c>.01 and c≤.1 then d:= 1.9590 - 2.4101×c  + 27.3377×c↑2
 - 118.482×c↑3;
if c>.1 and c≤.5 then d:= 1.90175 -0.36375×c   + 0.825×c↑2
  - 0.625×c↑3;
if c>.5 and c<3.9 then d:=  1.84273 +0.000360167×c  +0.0186942
×c↑2 -0.0021745×c↑3; end d;


for i:= 1 step 1 until n do   a[i]  := read(20);
 for i:= 1 step 1 until n do   b[i]  := read(20);
s := read(20); if s=15 then begin
 wb:=read(20);  for j:= 1 step 1  until 3 do p[j]:=read(20);
for j:= 1 step 1 until 3 do q[j]:=read(20);  end;
```

```
repeat:     copytext(20, 70, [;]);   v:=read(20);
  s:= read(20); if s=15 then begin wx:=read(20);
 wy:=read(20) end;
k:= read(20); if k= 0.0 then C2:=0.0 else C2 := C(k);
s := read(20); if s=15 then begin  wx:=read(20); wy:=read(20) end;
 k:= read(20); C3:= C(k);
s :=read(20);  if s=15 then begin  wx:=read(20); wy:=read(20) end;
k:= read(20);   C4:= C(k);

t:=read(20);   l:=read(20); C1 := C3+ (C4-C2)×v;
c ma:=  (C1+C3)/2;    c mb:= (C2+C4)/2;

writetext(70, [ c ma *= ]);   write(70, f, cma);
writetext(70, [ c mb *= ]);   write(70, f, cmb);
 writetext(70, [ C1 *= ] );    write(70, f, C1  );
writetext(70, [ C2 *= ] );    write(70, f, C2  );
writetext(70, [ C3 *= ] );    write(70, f, C3  );
 writetext(70, [ C4 *= ] );    write(70, f, C4  );
writetext(70, [ C1 -C2 *=*]);  write(70, f, C1 -C2);
writetext(70,[ C3 -C4 *=*]);   write(70, f, C3 -C4);

ci:=(C1 -C2)/(C3 -C4);  writetext(70, [c1 -C2/C3 -C4  *=* ] );
 write(70, f, ci );
writetext( 70, [betaxdo *=* ]);   write(70, f, ln(ci)×₁₀5/t);

if l=7 then  begin c:= cma; dma:= d(c);
writetext(70, [dma *=*]); write(70, f, dma);
c :=cmb; dmb:= d(c); writetext(70, [dmb *=*]);
 write(70, f, dmb);
di:= (cma×dma-cmb×dmb)/(cma-cmb); writetext(70, [doi *=*]);
write(70, f, di);  writetext(70, [beta *=*]);
write(70, f, ln(ci)×₁₀5/(t×di) ); end;  l:= read(20);
if l=1 then goto repeat else if l=2 then goto again  end;
close(20);    close(70);     end→
```

Instructions for data input for programme 3.

Name[cc];

n;	(number of the coefficients of the eqn fitted between a) concentration as a function of specific conductivity and b) equiv. conductivity as a function of concentration)
r;	(r=6 if natural logrithms are usedin the above equations)
a[i];	(n coefficients of eqn between concentration and specific conductivity)
b[i];	(n coefficients of eqn between equiv. conductivity and concentration)
s;	(s=0 if the solutions are not diluted otherwise s=15. If s=15 then also punch wa, p[i] and q[i])
wa;	(molecular weight of the salt)
p[i];	(coefficients of eqn between m/c and c)
q[i];	(coefficients of eqn between c/m and m)
[c]Heading[c]:	(name of the salt)
v;	volume parameter for the cell given by (v2+v3/2)/(v1+v3/2))
s;	(s=15 if solution 2 is diluted otherwise s=0. If s=15 then also punch wx and wy)
wx;	(weight of the concentrated solution)
wy;	(weight of the dilute solution 2)
k;	(specific conductivity of solution 2)
s; wx; wy;	(for solution 3)
k;	(specific conductivity of solution 3)
s; wx; wy;	(for solution 4)
k;	(specific conductivity of solution 4)
t;	(time in seconds for a diffusion run)
1;	(1=7 for cell calibration with KCl otherwise 1=0)
1;	(1=1 if calculations are to be done for anothe diffusion run but with the same salt, in this case goto [c] Heading[c]: 1= 2 if calculations are to be done for another electrolyte, in this case goto n; 1=0 for finish)

Specimen data input for programme 3.

```
S*Jalota[2c];
4;  6;
-4.95916;  +1.02152;  +0.0074681;  -0.00024766;
+4.71746;  -0.0699613;  -0.00301695;  +0.00025442;
0;
[cc]run21*****.5/H20****kcl**cell**40mm[cc]:

1.1381;
0; 0.0;   0; 33.977;  0; 20.558;
1.692⏨5; 7; 2;

4; 6;
-4.9861;  +1.0227;  +6.8654⏨-3; -1.5673⏨-4;
4.7413;   -7.0856⏨-2; -3.3057⏨-3; +2.1576⏨-4;

15; 120.92;
1.0031; 0.0324; 0.00262;
 0.9970; -0.0331; 0.0004;
[cc]run*22****4/.65****rubedium*chloride[cc]:

1.1381;
15; 11.687; 107.521; 10.850;
15; 8.505; 106.798; 20.613;
15; 8.661; 107.777; 16.477;
 1.6236⏨5; 0; 1;

[cccc]run*23**4/1.0**rubedium*chloride*cell*40*mm[c]:

1.1381;
15; 8.781; 108.444; 9.5054;
 15; 12.493; 104.597; 29.931;
15; 10.144; 97.134; 21.390;
 1.62⏨5; 0; 0;→
```

Programme 4

comment This is a program for the solution of linear equations by the method of determinants;

(program available from Dr. H.S. Dunsmore)

Instructions for data input

```
m;                              (number of sets to be calculated)
n; n;                           (numbers for n:n determinant)
1;                              (punch as such)
 5n-11;                         (punch as such)

n11; n22; ......; s1;           (n11 ..... are the coefficients
                                 of the first row and s1 is the
                                  constant of the first row)
n21; n22;.......; s2;           (as above but for the 2nd row)
-      -          -
-      -          -
-      -          -
n(nn)  -          s(n)           (for the nth row)
->                              (punch arrow for ending the
                                 program otherwise goto n; n;)
```

Specimen input data

```
2;
4; 4; 1; 5n-11;
0.21191; 0.04795; 0.01138; 0.00280; -0.1326;
0.70356; 0.50586; 0.37097; 0.27690; -0.1781;
1.13930; 1.30589; 1.50563; 1.74582; -0.0586;
1.44511; 2.11003; 3.11139; 4.63104; +0.0372;

4; 4; 1; 5n-11;
0.21191; 0.04795; 0.01138; 0.00280; -0.1326;
0.70356; 0.50586; 0.37097; 0.27690; -0.1781;
0.93384; 0.89200; 0.86965; 0.86347; -0.1224;
1.44511; 2.11003; 3.11139; 4.63104; +0.0372;->
```

Programme 5

```
comment M. Gibsons program for curve fitting by
        the method of least squares;

Specimen input data                    Instructions for data input

M                                      (program is on magnetic tape)
DD062L100KP4+103C062JFSU→              (program and job number)
39;                                    (a no. greater than double the
                                        no. of data sets of x and y)
5;                                     (degree of the equation to be
                                        fitted)
2;                                     (no. of equations to be fitted)
12;                                    (no. of data sets of x and y)
-1;                                    (reads x and y in pairs)

0.07071;  1.9950;                       (12 sets of x and y)
0.10000;  1.9730;
0.2236;   1.9107;
0.3162;   1.8790;
0.4472;   1.8563;
1.0000;   1.9450;
1.2247;   2.0230;
1.4142;   2.1000;
1.5811;   2.1730;
1.6432;   2.2010;
1.6941;   2.2260;
1.7321;   2.2450;
1;                                     (leave as such)
0;                                     (leave as such)
5; 5;                                   ( two numbers as the degree
                                          of equation )
1;                                     (if 1 then eqn is fitted
                                         between x and y but if 4
                                         then eqn is fitted between
                                         ln x and ln y)
1; 0;                                  (leave as such)

0; 0; 0;                               (leave as such)

[cc]S*JALOTA[cc]sqrt*CONCN*
 Vs* DIFFERENTIAL*DIFF*
 COEFFT*FOR*RbC1*5th*DEGREE
  *FIT[cc];
                                        (name and heading, put → after ;
                                        if no more eqn is to be fitted
                                        otherwise goto no. of data sets
                                        of x and y)

19;-1;                                  (data for fitting second eqn)
0.1; .770;
0.2; .718;
0.3; .688;
0.4; .666;
```

Programme 6

```
RD255DCCVPU-H(S00(2EESP→
begin  comment  This program calculates 1+Md ln gama/dM
                from 5th or lower degree fit between
                ln M and  ln gama;
         real  DY,  B,  m,  C,x,  D,E,  F;
integer  i,  n,  f ;
 open(20);  open(70);
again:   copytext(20,70,[;] );
 B:=read(20); C:=read(20);D:=read(20);E:=read(20);
 F:=read(20);  f:=format([nss-d.dddd₁₀-nd]);
 writetext(70,[ [c4s]MOLALITY[6s]DIFFL-COEFF[c]]);
 n:=read(20);  for i:=1 step 1  until n do
 begin  m:=read(20); x:=ln(m);
DY:= 1.0+B+2×C×x  +3×D×x↑2+4×E×x↑3+5×F×x↑4;
write(70,f,m); write(70,f,DY); newline(70,1);
 end;  n:=read(20);   if n = 1 then goto again ;
close(20);  close(70);
 end→
```

Instructions for data input

[cc] Name and heading [cc]:

B; C; D; E; F;	(2nd, 3rd, 4th and 5th and 6th coefficients of the 5th degree equation. If the degree is lower then put zeros for the last coefficients)
n;	(no. of sets to be calculated)
m;	(n number of molalities, m, at which 1+Md ln gama/dM is to be calculated)
1; OR 0;→	(1 for repeating the calculations, in this case goto [cc] Name and heading [cc]: 0;→ is for finish)

Specimen data input

```
S-JALOTA[cc]kcl[cc]:
 -1.01247₁₀-1;  1.05577₁₀-2; 4.64480₁₀-3; 3.64775₁₀-4; 0.0;
5;
.0502; .1006; .2017; .5088; .7166;
 1;

[cc]rbcl[cc]:

-1.17226₁₀-1; 9.30198₁₀-3; 4.80871₁₀-3; 3.77023₁₀-4; 0.0;
 6;
.10064; .20195; .25287; .30396; .5101; .71895;
0;→
```

```
0.5; .649;
0.6; .637;
0.7; .626;
0.8; .618;
0.9; .610;
1.0; .604;
1.2; .593;
1.4; .586;
1.6; .580;
1.8; .576;
2.0; .573;
2.5; .569;
3.0; .569;
3.5; .572;
4.0; .577;
1;
0; 5; 5;
4; 1; 0;
0; 0; 0;
[cc]molality *vs *activity *coefficient *for *kcl[cc]
eqn is fitted between ln m and ln gama[cc];→
```

PROGRAMME 7

```
DD2552A00WPU+1030062JPSP->
begin   comment  This program reads n sets of concn,
        molality/density, eqivalent conductivity,
        transport numbers, diffusion coefficients
        and activity term and it then calculates
        Onsager L and R coefficients and three degrees
        of coupling and outputs the results in tabular
        form;
           integer r, r1, r2, n, z, z1, z2, f, md, i, DV;
     real     R, F, T, M, q;

open(20);          DV:=read(20);             open(DV);
 f:=format([-nddd.dddd]);  copytext(20, DV, [;;]);
repeat: R:=read(20);  F:=read(20);  T:=read(20);
again:  copytext(20, DV, [:]);
        M:=read(20);  r1:=read(20);  r2:=read(20);
 z1:=read(20);            z2:=read(20);  r:=r1+r2;
   z:=read(20);  n:=read(20);  md:=read(20);
begin array c, d, m, t1, lda, D, l11, l22, l12, R11,
     R22, R12, R10, R20, R00, F12, x, y, act [1:n];
for i:= 1 step 1 until n do begin
c[i]:=read(20);   d[i]:=read(20); lda[i]:=read(20);
t1[i]:=read(20);   D[i]:=read(20);   act[i]:=read(20)
end;
q:=10↑8×R×T×r×r1×z1;
for i := 1 step 1 until n do  begin
x[i]:=D[i]/(q×act[i]);  y[i]:=lda[i]/(1000×F↑2);
if md = 3 then m[i] := d[i] else
 m[i]:=c[i]/(d[i]-0.001×c[i]×M);

l11[i]:=y[i]×t1[i]↑2/z1↑2+r1↑2×x[i];
if c[i]=0.0 then l12[i]:=0.0 else
 l12[i]:=y[i]×t1[i]×(1-t1[i])/(z1×z2) + r1×r2×x[i];
l22[i]:=y[i]×(1-t1[i])↑2/z2↑2+r2↑2×x[i];
x[i]:=l11[i]×l22[i]-l12[i]↑2;
R11[i]:=l22[i]/x[i];
R12[i]:=-l12[i]/x[i];    F12[i]:=-R12[i]×y[i];
R22[i]:=l11[i]/x[i];
if md = 3 then  begin  if c[i] = 0.0 then x[i] :=0.01807/z
 else x[i] := 18.015×m[i]/( 1000 × z × c[i]) end
             else   x[i]:= 18.015/(z×(1000×d[i]-M×c[i]));
R10[i]:=-(r1×R11[i]+r2×R12[i])×x[i];
R20[i]:=-(r1×R12[i]+r2×R22[i])×x[i];
R00[i]:=-(r1×R10[i]+r2×R20[i])×x[i]     end;     test(0);

writetext(DV, [ [11s]c[8s]m[7s]Eqv*Cond[6s]t+[5s]D(v)n5[s]
                        1+m×dlnGama/dm[2c]]);
for i:=1 step 1 until n do begin
space(DV, 5);
 write(DV, f, c[i] );
  write(DV, format([ndd.dddddd]), m[i]);
   write(DV, format([-ssnddd.dd]), lda[i]);
    write(DV, f, t1[i]);
     write(DV, f, D[i]);
      write(DV, f, act[i]); newline(DV, 1); end;
```

```
writetext( DV, [ [2c9s]Sqrt*S[4s]l11/N[5s]l12/N
            [5s]l22/N[6s]F12[7s]Q12[c10s]
            ×10[7s]₁₀+12[6s]₁₀+12[6s]₁₀+12[2c] ] );

for i := 1 step 1 until n do begin

space(DV, 5);
 write(DV, f, 10×sqrt( z × c[i] × ( z1 - z2 )/2) );
  write(DV, f, l11[i] × ₁₀12 );
   write(DV, f, l12[i]×₁₀12 );
    write(DV, f, l22[i]×₁₀12 );
     write(DV, f, F12[i]);
      write(DV, f, l12[i]/ sqrt( l11[i]×l22[i] ) );
       newline(DV, 1);  end;

writetext( DV, [ [2c9s]Sqrt*S[4s]NR11[6s]-NR12[5s]
           NR22[7s] Q10[7s]Q20[c10s]×10[6s]₁₀-11
          [7s]₁₀-11  [5s]₁₀-11[2c] ] );

for i := 1 step 1 until n do begin


space(DV,5);
 write(DV, f, 10× sqrt( z × c[i] × (z1-z2)/2 ) );
  write(DV, f, R11[i]×₁₀-11 );
   write(DV, f, -R12[i]×₁₀-11 );
    write(DV, f,  R22[i]×₁₀-11 );
     write(DV, f, -R10[i]/sqrt( R11[i]×R00[i] ) );
      write(DV, f, -R20[i]/sqrt(R22[i]×R00[i]) );
       newline(DV, 1);  end;



writetext( DV, [ [2c9s]Sqrt*S[4s]-R10[6s]
-R20[6s]-COR10[4s]-COR20[4s]R00/N[c10s]
  ×10[7s]₁₀-9[7s]₁₀-9[6s]₁₀-11[6s]₁₀-11[8s]₁₀-7[2c] ] );

for i:= 1 step 1 until n do begin


space(DV,5);
 write(DV, f, 10× sqrt( z× c[i] × (z1-z2)/2 ) );
  write(DV, f, -₁₀-9×R10[i] );  write(DV, f, -₁₀-9×R20[i] );
   write(DV, f, -₁₀-11 ×R10[i]/(z× x[i]) );
    write(DV, f, -₁₀-11 × R20[i]/ (z×x[i]) );
     write(DV, f, R00[i]×₁₀-7 );  newline(DV, 1);
end   end;      n:=read(20);
if n = 1 then goto again else if n=2 then goto repeat;
close(20);   close(DV);
end→
```

Specimen Data Input for Programme 7

```
70;
S*Jalota[4c];;
8.314;  96493;  298.15;
[p6c 93] Rubidium* Chloride[2c]:
120.92;  1;  1;  +1;  -1;  1;  10;  [illegible];

0.00;   0.00000;  154.16;  0.5045;  2.051;  1.0000;
0.10;   0.10064;  132.11;  0.5032;  1.879;  0.8923;
0.25;   0.25287;  125.45;  0.5019;  1.854;  0.8790;

0.50;   0.51010;  120.36;  0.5002;  1.870;  0.8764;
0.70;   0.71895;  117.77;  0.4992;  1.898;  0.8796;
1.00;   1.03834;  115.23;  0.4978;  1.944;  0.8885;
1.50;   1.58640;  112.06;  0.4960;  2.024;  0.9104;
2.00;   2.15640;  109.34;  0.4945;  2.100;  0.9381;
2.50;   2.75040;  106.67;  0.4931;  2.173;  0.9700;
3.00;   3.37130;  103.97;  0.4919;  2.245;  1.0050;
1;
[p6c 93]rubidium*chloride[2c]:
120.92; 1; 1; +1; -1; 1; 9; 3;
0.00;   0.00000;  154.16;  0.5045;  2.051;  1.0000;
0.10;   0.10064;  132.11;  0.5032;  1.879;  0.8923;
0.25;   0.25287;  125.45;  0.5019;  1.854;  0.8790;

0.50;   0.51010;  120.36;  0.5002;  1.870;  0.8764;

0.70;   0.71895;  117.77;  0.4992;  1.898;  0.8796;
1.00;   1.03834;  115.23;  0.4978;  1.944;  0.8885;
1.50;   1.58640;  112.06;  0.4960;  2.024;  0.9104;
2.00;   2.15640;  109.34;  0.4945;  2.100;  0.9381;
3.00;   3.37130;  103.97;  0.4919;  2.245;  1.0050;
0;→
```

References for Chapters 1-6

1. F.W.Kohlrausch, Ann. Phys., 1879, 6, 1.
2. S. Arrheni~~o~~us, a) Z. Phys. Chem., 1887, 1, 631;
   b) Phil. Mag., 1888, 26, 81.
3. J.H.Van't Hoff, Z. Physik, Chem., 1887, 1, 481.
4. P. Debye and E. Hückel, Physik. Z., 1923, 24, 305.
5. L. Onsager, a) Phys. Rev., 1931, 37, 405;
   b) Phys. Rev., 1931, 38, 2265.

6a. R.M.Fuoss and K.L.Hsia, Proc. Nat. Acad. Sci., U.S., 1967, 57, 1550.
 b. Y.C.Chiu and R.M.Fuoss, J. Phys. Chem., 1968, 72, 4123.
 c. K.L.Hsia and R.M.Fuoss, J. Amer. Chem. Soc., 1968, 90, 3055.
 d. R.M.Fuoss, Rev. Pure and Appl.Chem., 1968, 18, 125.
 e. I.D.McKenzie and R.M. Fuoss, J. Phys. Chem., 1969, 73, 1951.

7a. E. Pitts, Proc. Roy. Soc., A, 1953, 217, 43.
 b. E. Pitts, B.E. Tabor and J. Daly, Trans. Faraday Soc., 1969, 65, 849.

8. W. Thomson (Lord Kelvin), a) Proc. Roy. Soc. Edinburgh, 1854, 3, 225; b) Trans. Roy. Soc. Edinburgh, 1857, 21, 123.
9. J. Meixner, a) Ann. Physik, 1941, 39, 333;
   b) 1942, 41, 409;
   c) 1943, 43, 244.
10. H.B.G. Casimir, Rev. Mod. Phys., 1945, 17, 343.
11. I. Prigogine. Etude Thermodynamique des Phenomenes Irreversibles, Dunod, Paris and Desoer, Liege, 1947.
12. S. R. De-Groot and P. Mazur, Non-Equilibrium Thermodynamics, North Holland, Amsterdam, 1962.
13. D.D.Fitts, Non-Equilibrium Thermodynamics, McGraw-Hills, New York, 1962.
14. R. Haase, Thermodynamik der Irreversiblen Prozesse, Dietrich Steinkopff, Darmstadt, W.Germany, 1963.

15. I. Prigogine, Introduction to Irreversible Thermodynamics, 3rd Ed., Interscience, New York, 1967.

16. D.G. Miller, a) J. Phys. Chem., 1966, 70, 2639;
b) J. Phys. Chem., 1967, 71, 616;
c) J. Phys. Chem., 1967, 71, 3588.

17. J. Newman, 'Transport Processes in Electrolyte Solutions', in 'Advances in Electrochemistry and Electrochemical Engineering; Editor, C.W. Tobias, Interscience Publishers, London, 1967, 5, P. 87-135.

18. R. Paterson, 'Irreversible Thermodynamics as Applied to Biological Systems; chapter 5, in 'Membrane Metabolism and Ion Transport; Editor, E.E. Bitter, Johnwiley and Sons, N. Y., 1970, P. 128.

19. A. Katchalsky and P. Curran, 'Non Equilibrium Thermodynamics in Biophysics; Harvard Univ. Press, Cambridge, 1965, a) P.66; b) P.80.

20. Ref. 12, P.43-45.

21. G.J.Hooyman, Physica, 1956, 22, 751.

22. J.G.Kirkwood, R.L.Baldwin, P.J. Dunlop, L.J. Gosting and G. Kegeles, J.Chem. Phys., 1960, 33, a)1505; b) 37.

23. L. A. Woolf, D. G. Miller and L. J. Gosting, J. Amer. Chem. Soc., 1962, 84, 317.

24. K. Micka, Berichte der Bunsengesellschaft, 1968, 72, Nr 1, 60.

25. Ref. 16a, P.2652.

26. Appendix 1 of Ref. 16a.

27. D.R.Hafemann, J.Phys. Chem., 1965, 69, 4226.

28. D.G.Miller, Chem. Rev., 1960, 60, 15.

29. M.J. Pikal and D.G. Miller, J. Phys.Chem.,1970,74, 1337.

30. Appendix 2 of reference 16a.

31. A. L. Geddes and R.B. Pontius,'Determination of Diffusivity' in 'Techniques of Organic Chemistry' Ed. A. Weissberger, Physical Methods of Organic Analysis, Interscience Pub. Co., N. Y., 1960, 3rd Edition, 1(2), P. 896-1004.

32. J.R.Vinograd and J.W McBain, J. Amer.Chem.Soc., 1941,63,2008.
33. Emanuel and Olander, J. Chem.Engg. Data, 1963,8, 31.
34. W.G Eversole et.al., J. Phys. Chem., a) 1937, 41, 663;
b) 1942, 46, 370.
35. Y.P. Gokhshtein, Zhur. Fiz. Khim., a) 1954, 28, 1417;
b) 1952, 26, 224.
36. F.T. Wall and R.Wendt, J. Phys.Chem., 1958, 62, 1581.
37. C.W. Garland and S. Tong, J. Phys. Chem., 1965, 69, 1781.
38. J. H. Northrop and M. L. Anson, J. Gen. Physiol.,1929,12,543.
39. H.Mouquin and W.H.Cathcart, J.Amer.Chem. Soc., 1935,57,1791.
40. J.W.McBain and C.R.Dawson, Proc. Roy.Soc., 1935,148A,32.
41. G.S.Hartley and D.F.Runnicles, Proc.Roy.Soc., 1938,168A,401.
42. A.R.Gordon, Ann.N.Y.Acad. Sci., 1945, 46, 285.
43. K.J.Mysels and J.W. McBain, J.Coll.Sci., 1948, 3, 45.
44. R.H.Stokes, J.Amer. Chem.Soc., a) 1950, 72, 763;
b) 1951, 73, 3527.
45. R.A.Robinson and R.H.Stokes, 'Electrolyte Solutions', Butterworths Sci. Publications, London, 1959, P.253.
46. C.Barnes, Physics, 1934, 5, 4.
47. H.S. Yeh and G.B. Wills, J.Chem. Engg.Data, 1970, 15, 187.
48. S.A. Sanni and H.P. Hutchison, J.Sci.Inst.(J.Physics E), 1968, 1, Ser. 3, 1101.
49. G.J. Janz et.al., J.Phys. Chem., 1966, 70, 536.
50. H.S. Harned et al., J.Amer. Chem. Soc., 1954, 76, 4219.
51. R. Francesconi, Ing. Chem.Ital., 1970, 6, 72.
52. H.S.Harned and H. Blander, J.Amer. Chem. Soc.,1953,75,2853.
53. G. Jones and G.M. Bollinger, J.Amer.Chem.Soc.,1931,53(1),411.
54. T. Shedlovsky, 'Conductivity' in Ref. 31, 1(4), P.3011.
55. R.L. Kay et al., J.Phys.Chem., 1965, 69, 2420;1967,71,3925.
56. K.J. Mysels, J.Phys. Chem., 1961, 65, 1081.
57. E. King, J. Sci.Instrum., 1969, 2, 59.
58. J. Quint, C. R. Acad.Sci., 1969, C, 268, 2153.

59. J. Barthel, Angew Chem. Int. Ed. Engl., 1968, 7(4), 260.
60. R.M. Fuoss and L. Onsager, J.Phys. Chem., 1957, 61, 668.
61. H.M. Daggett, E.J. Bair and C.A. Kraus, J.Amer.Chem.Soc., 1951, 73, 799.
62. R.H.Stokes, J. Phys. Chem., 1961, 65, 1242.
63. Ref. 45, P. 87.
64. G. Jones and D.M. Bradshaw, J.Amer.Chem.Soc., 1933, 55, 1780.
65. A. Vogel, 'A Text Book of Quantitative Analysis' Longmans, 3rd Edition, 1961, P.154.

66. J.F.Chambers, J.M.Stokes and R.H.Stokes, J.Phys.Chem., 1956, 60, 985.
67. H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolyte Solutions', 3rd Edn., Reinhold Publishing Corp., N. Y., 1958, P.725.
68. A. R. Gordon, J. Chem. Phys., 1937, 5, 522.
69. T.B. Hoover, J. Phys.Chem., 1970, 74(13), 2667.
70. C. G. Swan and D.F.Evans, J.Amer.Chem.Soc., 1966, 88, 383.
71. J.C.Justice, J. Chim.Phys., 1968, 65, 353.
72. J.C.Justice, J. Chim. Phys., 1969, 66, 1193.
73. R. Fernandez-Prini, Trans. Faraday Soc., 1969, 65, 3311.
74. Private Communication with Prof. R.M.Fuoss, 1969.
75. R.M. Fuoss and L. Onsager, Proc.Nat.Acad.Sci.,U.S., 1967, 57, 1550.
76. C.W. Davies, Trans. Faraday Soc., 1927, 23, 351.
77. E.A. Guggenheim, Trans. Faraday Soc., 1969, 65, 2474.
78. C.W. Davies, 'Ion Association', Butterworths(London), 1962, P.40-41.
79. J. Tamas, O. Kaposi and P. Scheiber, Magyer Kem Folyoirat, 1966, 72, 362.
80. G. Jones and M. Dole, J. Amer. Chem. Soc., 1929, 51, 1073.

81. P.A.Lyons and J.F.Riley, J. Amer.Chem.Soc.,1954,76, 5216.
82. Ref. 45, P.495.
83. K.S.Spiegler, Trans. Faraday Soc., 1958, 54, 1409.
84. O. Kedem and A. Katchalsky, J. Gen. Physiol., 1961,45,143.
85. R.W.Gurney, 'Ionic Processes in Solutions', McGraw-Hill, N.York, 1953.
86. O. Ya Samoilov, 'The Structure of Aqueous Solutions of Electrolytes and of Hydrated Ions. IZD-VO AN SSSR,MOSKOW,1957.
87. J. Lee Kavanau, 'Water and Solute-Water Interactions', Holden-Day, Inc., London, 1964.
88. Ref. 16a, P.2650.
89a.O. Kedem and S.R.Kaplan, Trans.Faraday Soc., 1965,61,1997;
b.S.R. Caplan, J. Theoret. Biol., 1966, 10, 209.
90. Ref. 16a, P.2652.
91. A.S.Sulovkin, Zhurnal Strukturnoi Khimii, 1968,9(2),305.
92. G.Jones and M.Dole, J.Amer.Chem.Soc., 1929, 51, 2950.
93. Ref. 78, P.36-37.
94. Ref. 16a, eqn(38).
95. R. Paterson, J. Anderson and I. Hamilton, B.Sc. Thesis, The University, Glasgow W.2., 1970.

References for Appendix 1

1. A. Eucken, Ed. Landolt-Bornstein, 'Zahlenwerte Und Funktionen aus Physik, Chimie, Astronomie', Geophysik Und Technik, 6th Ed., 2(7), Berlin: Springer-Verlag,1960.
2. Steel, J. Phys. Chem., 1965, 69, 3208.
3. Vitagliano and Caramazza, Gaz. Chim.Ital.,1960,90,1730.
4. Caramazza, Gaz. Chim. Ital., 1960, 90, 1721.
5. Timmermans, 'The Physico-Chemical Constants of Binary Systems in Concentrated Solutions', N. Y., Int. Sci., Pub., Inc., 1960.
6. D.G. Miller, J.Phys. Chem., 1966, 70(8), 2639.
7. Firth and Tyrrell, J. Chem. Soc.,A, 1962, 2042.
8. Kaminsky, Z. Physik. Chem., N.F., 1957, 12, 206.
9. Benson and Gordon, J.Phys. Chem., 1945, 13, 473.
10. Suryanarayana et al., Acta Chim.Acad.Sci.Hung.,1958,17,327.
11. Chambers, J.Phys. Chem., 1958, 62, 1136.
12. Marsh and Stokes, Aus. J. Chem., 1964, 17, 740.
13. Darken et al., J.Amer.Chem.Soc., 1942, 64, 621.
14. Kaimakov and Varshavskaya, Russ. J.Phys.Chem.,1966,2,89-105.
15. R. Parsons, 'Hand Book of Electrochemical Constants, Butterworths, London, 1959.
16. Haase et al., Z.Physik. Chem., N.F., 1965, 46, 129.
17. Chapman, Ph.D. Thesis, University of California, UCRL-17768, 1967.

17a. Fary, Ph.D Thesis, Institute of Paper Chemistry, 1966 (this reference is collected from ref. 17).

18. Prue and Covington, J.Chem. Soc., A, 1957, 1567.
19. Haase et al., Z. Phys. Chem., N.F., 1964, 42, 32.
20. Campbell et al., Can. J.Chem., 1959, 37, 1288.
21. Campbell et al., Can. J. Res., 1950, 28B, 161.
22. Wishaw and Stokes, J.Amer. Chem. Soc., 1954, 76, 2065.

References for Appendix 1 continued.....

23. MacInnes and Cowperthwaite, Trans. Faraday Soc.,1927,23,400.
24. Milios and Newman, University of California, UCRL-18105,1968.
25. Jones and Talley, J.Amer. Chem. Soc., 1933, 55, 624.
26. Shedlovsky, J.Amer. Chem. Soc., 1932, 54, 1411.
27. Longsworth, J.Amer. Chem. Soc., 1935, 57, 1185.
28. Sukhotin et al., Electrokhimiya, 1969, 5, 114.
29. Harned and Hudson, J.Amer. Chem. Soc., 1951, 73, 652.
30. Gokhshtein, Z.Fiz. Khim, 1952, 26, 224.
31. Dunsmore, Jalota and Paterson, J.Chem.Soc.,A, 1969, 1061.
32. Tamas, Kaposi and Scheiber, Magyar Kem Folyoirat, 1966,72,362.
33. Harned and Owen, 'The Physical Chemistry of Electrolyte Solutions', 3rd Ed., Reinhold Pub. Corp., N.Y., 1958.
34. Jones and Bickford, J.Amer. Chem.Soc., 1934, 56, 602.
35. Benson and Gordon, J.Phys. Chem., 1945, 13,473.
36. Chamber, J.Phys. Chem., 1958, 62, 1136.
37. Longsworth, J.Amer. Chem. Soc., 1935, 57, 1185.
38. Internation Critical Tables, 1929, 6, P.310.
39. Lengyel, Tamas, Giber and Holderith, Mag. Kem Folyoirat, 1964, 70, 66.
40. Robinson and Stokes, 'Electrolyte Solutions', Butterworths, London, 1959.
41. Aston et al., J.Amer. Chem. Soc., 1933, 55, 3067.
42. Ray et al., J.Amer. Chem. Soc., 1958, 80, 1029.
43. Campbell and Friesen, Can. J. Chem., 1959, 37, 1288.
44. Campbell and Singh, Can. J. Chem., 1959, 1959.
45. Harned, J.Amer Chem. Soc., 1951, 3292;
45a. Lakshminarayana, J.Phys. Chem., 1966, 536.
46. Firth et al., J.Chem.Soc., A, 1962, 2042.
47. Spiro et al., Trans. Faraday Soc., 1952, 263.
48. Haase, Z.Phys. Chem., 1962, 375.
49. Longsworth, Chem. Rev., 1932, 171.
50. Haase et al., Z.Phys. Chem., 1964, 42, 32.

References for Appendix 1 continued...

51. Campbell and Singh, Can. J. Chem., 1959, 37, 1959.
52. Hall, Wishaw and Stokes, J.Amer. Chem. Soc., 1953, 75, 1556.
53. Mason and Culvern, J.Amer. Chem. Soc., 1949, 71, 2387.
54. Sahay, Ind. J. Chem., 1963, 1, 103.
55. Kerker et al., Trans. Faraday Soc., 1960, 56, 1039.
56. Kundra et al., Zh. Neorg. Khim., 1964, 9, 2454.
57. Edward and Huffman, J. Phys. Chem., 1959, 63, 1830.
58. Elmore et al., J.Amer. Chem. Soc., 1946, 68, 2528.
59. Harned and Blake, J. Amer. Chem. Soc., 1951, 73, 2448.
60. MacInnes and Longsworth, 'Principles of Electrochemistry', Reinhold Publishing Corp., N.Y. , 1939, P.339.
61. Longsworth, J.Amer. Chem. Soc., 1935, 57, 1185.
62. Vinograd and McBain, J. Amer. Chem. Soc., 1941, 63, 2008.
63. Jones and Colvin, J.Amer. Chem. Soc., 1940, 62, 338.
64.* Feddorff, Ann. Dechimie, Ser.11, 1941, 16, 154.
65. Jenkins and Monk, J.Amer. Chem. Soc., 1950, 72, 2695.
66. Indelli, Ricerca Sci., 1953, 23, 2258.
67. Crews, Proc. Phys. Soc.(London), 1934, 46, 764.
68. Hartley and Donaldson, Trans. Faraday Soc., 1937, 33, 457.
69. Mullin and Nienow, J.Chem. Engg. Data, 1964, 9, 526.
70. Hlasko and Salit, Bull. Int.Acad. Polonoise, A, 1935, 189.
71. Roughton, J. Applied Chem.(London), 1951, 1, Suppl. Issue No. 2, S 141.
72. Hamer, J. Amer. Chem. Soc., 1935, 57, 662.
73. Gordon et al., J.Chem. Phys., 1940, 423.
74. Savino and Vitagliano, Ric. Sci. Rend.Sez., A2, 1962, 341.
75.* Fedoroff, Ann. Dechimie, 1941, Ser. 11, 16, 154.
76. Owen and Gurry, J.Amer.Chem.Soc., 1938, 60, 3074.
77. Fritz and Fuget, J. Phys. Chem., 1958, 62, 303.
78. Eversole et al., J.Phys. Chem., 1942, 46, 370.
79. Emannel et al., J.Chem. Engg. Data, 1963, 8, 31.
80. Purser and Stokes, J.Amer. Chem. Soc., 1951, 73, 5650.

* These references are the same.

References for Appendix 1 continued...

81.* Demassieuse et al., Ann. De Chim., 1941, 16, 215.

82. Dye et al., J.Amer, Chem. Soc., 1960, 82, 315.

83. Walton, J.Amer. Chem. Soc., 1949, 71, 576.

84. Lang et al., J.Amer. Chem. Soc., 1954, 76, 4716.

85. Purser et al., J.Amer. Chem. Soc., 1951, 73, 5650.

86. Wall and Wendt, J.Phys. Chem., 1958, 62, 1581.

87. Bray, J.Amer. Chem. Soc., 1927, 49, 2372.

88.* Demassieux et al., Ann. De Chim., 1941, Ser.11, 16, 215.

89. Lang and King, J.Amer. Chem. Soc., 1954, 76, 4716.

90. Longsworth, 'Structure of Electrolyte Solutions', Ed. Hamer, John Wiley and Sons, Inc., N.Y.? 1959, P. 183.

91. Sahay, J. Sci. Industr. Res., 1959, 18B, 235.

92. Garland and Tong, J.Phys. Chem., 1965, 69(5), 1718.

93. Rysselberghe et al., J.Amer. Chem. Soc., 1937, 59, 336.

* These references are the same.