

THERMOGRAVITATIONAL SEPARATION IN
SOLUTIONS OF ELECTROLYTES

A DISSERTATION PRESENTED FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY
AT THE UNIVERSITY OF CAMBRIDGE

by

MRS. RAJALAKSHMI HEYROVSKÁ,
B.Sc.(Mysore), M.Sc.(I.I.Sc.),
(formerly MISS RAJALAKSHMI NATARAJAN)
GIRTON COLLEGE,
CAMBRIDGE.

THE BOARD OF GRADUATE STUDIES
APPROVED THIS DISSERTATION
FOR THE Ph. D. DEGREE ON 19 FEB 1970

PREFACE

This dissertation describes the research work carried out independently by me in the Department of Physical Chemistry of the University of Cambridge, England. It has not been submitted either in part or in full for the award of any degree or diploma of any other University. References have been given wherever information from literature has been incorporated.

I wish to express my gratitude to Dr.J.N.Agar for kindly suggesting the problem and supervising the research work. My sincere thanks are due to Prof.R.G.W.Norrish for granting me admission into the Department of Physical Chemistry and for his interest in the work. Acknowledgment is also due to the Association of Commonwealth Universities for the award of a Commonwealth Scholarship from October 1964 till September 1967.

I am grateful to the authorities of the Indian Institute of Science, Bangalore, for sanctioning lien on my post of Senior Research Assistant in the Department of Inorganic and Physical Chemistry during the period of my research studies at Cambridge.

Rajalakshmi Heyrovská.

April, 1969.

(Sd.) Rajalakshmi Heyrovská.

THERMOGRAVITATIONAL SEPARATION
IN SOLUTIONS OF ELECTROLYTES

C O N T E N T S

| CHAPTER <u>No.</u> | | PAGE <u>No.</u> |
|-----------------------|--|--------------------|
| | PREFACE | |
| | SYNOPSIS. | 1 |
| I | GENERAL INTRODUCTION. | 4 |
| II | THEORY OF Soret SEPARATION AND OF THE CLUSIUS-DICKEL COLUMN. | 12 |
| III | DESIGN AND CONSTRUCTION OF THE COLUMN AND MEASUREMENT OF CONCENTRA- TION CHANGE. PART A: PRELIMINARY EXPERIMENTS. | 27 |
| IV | DESIGN AND CONSTRUCTION OF THE COLUMN AND MEASUREMENT OF CONCENTRATION CHANGE. PART B: THE ALL-GLASS COLUMN. | 49 |
| V | COMPARISON OF PERFORMANCE OF THE COLUMN WITH THEORY : SEPARATION OF 1:1 ELECTROLYTES. | 61 |
| VI | EFFECT OF INITIAL CONCENTRATION ON SEPARATION: (i) POTASSIUM CHLORIDE AND (ii) CADMIUM SULPHATE. | 82 |
| VII | STUDIES OF WEAK ACIDS: (i) ACETIC, (ii) PROPIONIC AND (iii) n-BUTYRIC ACIDS. | 90 |
| VIII | GENERAL CONCLUSIONS. | 101 |
| | REFERENCES | 105 |

SYNOPSIS.

Clusius and Dickel invented the thermogravitational column in the year 1938 for the separation of mixtures of gases; they subsequently demonstrated its application to liquid solutions as well. The theory of the method was developed a few years later and has been further elaborated by more recent authors. Although some aspects of the theory have been compared with experiment, information about the agreement of the observed thermogravitational separation with those predicted by theory is far from complete. Owing to the several approximations introduced into the theory, some discrepancy is to be expected between theory and experiment.

Until recently, a satisfactory test of the theory was not possible because few, if any, reliable values for certain parameters appearing in the theory (Soret coefficients and thermal diffusion coefficients) existed. But these parameters are now available for many dilute aqueous solutions of electrolytes, thereby enabling prosecution of the present work on thermogravitational separation and the comparison of the performance of the column with that predicted by theory.

The first part of the work was to construct a simple column of materials (i.e. glass) resistant to common chemicals. This makes metal tubes unsatisfactory. An all-glass column without reservoirs was constructed for this purpose and calibration experiments were carried out using dilute aqueous solutions of several 1:1 electrolytes of known Soret coefficients by other methods. The change in concentration was followed by conductimetric methods, based on an adaptation of

the resistance ratio method previously used by Agar and Turner for studying the Soret effect in static cells. Short glass columns of the concentric cylindrical types were used, the annular spacing being of the order of 1 mm. Platinum ring electrodes were fitted at the top and bottom, the lower and the "centre-tap" electrodes being sealed into the column.

The changes in the concentration of the electrolyte solutions were followed as a function of time and were found to approach the steady state exponentially. The steady state separations were plotted against the thermal diffusion coefficients calculated as the product of the Soret and diffusion coefficients available in the literature. The graph was found to be a straight line, thereby, confirming the linearity predicted by theory. However, the slope of the straight line was less than the value expected by theory. But the discrepancy does not seem excessive in view of the approximations in deducing the theoretical equations. The linear graph could therefore be used as the calibration curve for the determination of the thermal diffusion coefficients of substances for which the values have not ^{been} determined before. The Soret coefficients and heats of transport of substances with known activity coefficients could also be determined.

In order to test the performance of the column as well as the validity of the theory over a range of concentrations, experiments were conducted on several concentrations of potassium chloride and cadmium sulphate solutions for both of which Soret coefficients have been determined previously over a range of concentrations by the "pure Soret" and e.m.f. methods. The results have been compared with those in the lite-

rature. In the concentration region studied, there is no evidence for the existence of a minimum in the Soret coefficient vs concentration curves as expected by previous research workers. The influence of the "forgotten effect" has also been investigated in concentrated solutions of cadmium sulphate.

Having thus found encouragement in the thermogravimetric method for the determination of thermal diffusion coefficients of electrolyte solutions, studies of weak acids were undertaken since no data are available in the literature on their thermal diffusion properties. Separations of acetic, propionic and n-butyric acids have been measured over a wide range of concentrations. Their Soret coefficients and heats of transport have been evaluated from the experimentally determined thermal diffusion coefficients and their isothermal diffusion coefficients available in the literature. The concentration dependence of ^{the} heats of transport of the three acids has been investigated.

CHAPTER I.

GENERAL INTRODUCTION.

Thermal diffusion is the phenomenon of preferential movement of the solute and solvent molecules relative to each other caused by the application of a temperature gradient to a solution of uniform composition. Provided there is no convective mixing, relative migration of the components occurs until a time-invariant concentration gradient is established. When the temperature gradient is removed, the components gradually migrate back to their original mixed state. This phenomenon was discovered in 1856, by Ludwig ¹ and later more systematically investigated by Soret ² in 1879. Soret minimized convective mixing in the vertical cylindrical columns of solution he used, by maintaining the upper end hotter than the lower end. In condensed phases, thermal diffusion has since been referred to as the Soret effect. The magnitude of the Soret effect is usually expressed in terms of the Soret coefficient, defined as the fractional change in concentration produced by a unit temperature difference. The mathematical expressions will be given later.

The inverse phenomenon was demonstrated in 1872 by Dufour ³ in a mixture of gases. This "Dufour effect" is the production of a temperature gradient when two gases mixed in two different proportions are allowed to diffuse into each other. But this effect is very small in liquids on account of the dissipation of heat due to their high thermal conductivities. Waldman ⁴, in his extensive studies on gases, refers to the Dufour effect as the "diffusion-thermo-effect".

In spite of the paucity of the data available at that time, van't Hoff ⁵ was the first to suggest an explanation for the Soret effect. According to him, the concentration gradient was established in such a way that at the steady state, the osmotic pressure was uniform throughout the solution. While testing this hypothesis by extensive experiments, more light was thrown on the subject by Arrhenius ⁶ and later by Scarpa ⁷. Although the results do not appear to be quantitatively reliable, they emphasized the dependence of the magnitude of Soret effect on the nature of the solute and solvent, a fact which is in contradiction to the theory proposed by van't Hoff.

Meanwhile, an interesting relation between Soret effect and thermoelectric effects in electrolytic conductors was pointed out by Nernst ⁸.

The production of electrolytic thermoelectric current had been observed by Andrews ⁹ and Faraday ¹⁰. Andrews demonstrated the existence of the thermo-e.m.f. by using two unequally heated platinum electrodes dipped in molten borax and sodium carbonate. Faraday observed the thermoelectric current in several metal/aqueous solutions/^{systems} by maintaining identical electrodes at different temperatures. Faraday speculated that the energy for the flow of current must come from the effect of temperature on the "intensity of chemical affinity". This speculation - the contribution of the temperature coefficient of the metal/solution potential to the thermo e.m.f. - was confirmed by the work of Wild ¹¹ on non-isothermal cells. He used well-defined reversible electrodes such as Cu/CuSO_4 and Zn/ZnSO_4 .

Nernst suggested that in a non-isothermal system, since the nature of the medium is non-uniform, the motion of the ions is governed by forces $k_i \frac{dT}{dx}$, in addition to the gradients of osmotic pressure and electrical potential. He pointed out that both the Soret effect and thermal diffusion potentials are related to the factors k_i , which are specific properties of the ions.

Since in a non-isothermal cell, the temperature gradient would be expected to produce a concentration difference between the electrodes, Podszus¹² predicted that this ought to gradually change the initial thermo e.m.f. corresponding to uniform composition of the solution, till a steady value determined by Soret equilibrium is reached. However, it was detected experimentally only forty years later¹³. Eastman's work¹⁴ was a significant step towards a better understanding of the thermodynamic principles of the non-isothermal cells.

Around this period, by the year 1930, significant advances in the experimental technique and measurement of the Soret coefficient had been made by Tanner¹⁵. A formal theoretical approach was worked out by Eastman¹⁶ and Wagner¹⁷.

Between 1925 and 1933 the electrolytic Peltier heat analogous to the Peltier heat of metals (inverse Seebeck effect) was also successfully measured by Lange and others¹⁸. Their measurements were accurate and remain the best in the field. The e.m.f. of a thermo-cell can be calculated from the measured electrolytic Peltier heat by using a relation similar to Kelvin's equation connecting the corresponding effects in metals¹⁹.

A detailed account of the development of researches on non-isothermal cells can be found in Tyrrell's book ²⁰. While the latter was the first to detect experimentally the change in the thermoelectric power of a thermocell as the Soret equilibrium is established ¹³, quantitative studies were made by Chanu ²¹ who used a silver-silver chloride electrode system. Agar and Breck ²² used amalgam electrodes, which had the advantage of excellent stability.

While convective mixing is the biggest disturbing factor in obtaining considerable separations due to the Soret effect, Clusius and Dickel ²³ invented in 1938, an ingenious method of utilizing the very same convective currents to produce a much larger degree of separation of the components of a mixture, thereby making possible the industrial application of thermal diffusion. They accomplished this by establishing a horizontal temperature gradient in a mixture of gases contained in a long vertical tube, axially heated by passing an electric current through a wire. Due to thermal diffusion, the lighter molecules drifted towards the central hot wire and were carried upwards by the convective currents whereas at the colder walls of the tube the heavier molecules were carried downwards, eventually setting up a vertical concentration gradient.

If this process were to go on without any opposition, complete separation of the components could be achieved very easily. However, it is unfortunate that in a closed apparatus, the upward and downward convection currents produce circulation in the vertical plane and hence re-mixing occurs. Also, the development of a concentration gradient is opposed

by ordinary diffusion. The initial rate of separation is thus reduced in course of time until the competing effects bring it to a steady state. The magnitude of the separation at the steady state depends, therefore, solely on the magnitude of the three competing processes, viz., diffusion due to thermal gradient, convective mixing and ordinary diffusion. The last two factors can be minimized by suitably choosing the geometrical dimensions of the apparatus and also the temperature conditions ²⁴.

In order to achieve much higher degrees of separation, multistage columns have been used in the case of certain gases ²⁵. Metal spacers have also been found to improve the performance ²⁶.

The thermogravitational technique was soon applied to liquid mixtures as well ^{27,28}, though the degree of separation was much smaller than in the case of gases. Most of the columns used are of either parallel plate or cylindrical type with or without reservoirs. In certain organic liquid mixtures, glass-wool packing ^{29,30} has increased the degree of separation.

The method has found application in certain gaseous isotope mixtures ³¹, organic liquid mixtures ^{20,32} and also fractionation of polymers ^{33,34}. Solutions of electrolytes and non-electrolytes in aqueous and non-aqueous media have also been studied.

Among the types of apparatus used for liquids, to mention a few, are : columns without reservoirs with withdrawal ports along the length designed by Jones and Millberger ³⁵; a semi-micro column by Thompson et al. ³⁶; parallel plate columns by de Groot²⁴, Prigogine et al.³⁷ and Alexander³⁸; coaxial cylindrical columns

by Murin and Popov ³⁹, Hirota ⁴⁰, Hiby and Wirtz ⁴¹ and Horne and Bearman ⁴². Korsching ⁴³ has used a co-axial column with provision for continuous addition of solvent into the lower reservoir and removal of the same from the upper reservoir. A flow type thermogravitational column^s with a centre feed has also been used ⁴⁴. The effect of gravitational field on the operation of the column has been studied by Tilvis ⁴⁵ and by Farber and Libby ⁴⁶. The latter authors found linear increases in both the equilibrium separations and the rates of separation of gaseous mixtures with increasing centrifugal force up to a certain maximum value. Above this rate of rotation, both the rate and the equilibrium separations fell rapidly.

In the year 1952, a modification of the thermogravitational technique was suggested by Baranowski and Demichowicz ⁴⁷. Their apparatus consists of a vertical capillary tube cooled on the outside by circulating water and heated along the central axis by passing an alternating electric current through the solution. This is known as electrogravitational separation by electro-thermo-diffusion. This method has also been applied to parallel plate columns ⁴⁸. But the ^{method} is restricted to electrically conducting solutions.

During the thermogravitational and electrogravitational separations of those mixtures whose components have widely differing partial specific volumes, an inversion in the direction of separation has been observed. This phenomenon has been termed "l'effet oublie" (the forgotten effect) by de Groot and others ^{24,49}, since the variation of density with changes in concentration during the separation had been

§ The theory of a flow system between two coaxial cylinders has been worked out recently by Neumann¹⁰⁷.

"ignored" in deriving the theoretical equations. But the theory of the forgotten effect is yet uncertain ^{37,42,50}.

The theoretical treatment of ^{the} thermogravitational separation has been attempted by several investigators. But the comparison of the theory with the experimental performance has remained difficult owing to (i) the lack of a satisfactory method of determining the concentration change "in situ" without disturbing the separation process, (ii) the need for accurate data on Soret and isothermal diffusion coefficients and (iii) the limitations of the theory due to simplifying assumptions required to make the mathematical problems tractable. The influence of the geometry of the apparatus and temperature conditions on the separations has been verified qualitatively by experiments ²⁴.

As regards the data on Soret coefficients, after the work of Tanner ¹⁵ in 1927 who determined the Soret coefficients for a number of electrolytes using the optical method, it was only after 1950 that more work appeared on the pure Soret effect in electrolyte solutions. Optical methods were used by Korsching ⁵¹, Longworth ⁵², Chanu and Lenoble ⁵³ and again by Tanner ⁵⁴. Alexander ⁵⁵, and Saxton, Dougherty and Drickamer ⁵⁶ have used the diaphragm cell technique originally due to Riehl ⁵⁷, for the determination of Soret coefficients; but they were not practicable for dilute electrolyte solutions. The Thomaes' ⁵⁸ flow cell which has recently been used by Butler and Turner ⁵⁹ has not yet been used for electrolyte solutions except in test runs. For dilute electrolyte solutions, Chipman ⁶⁰ devised in 1926, a conductimetric method and was able to calculate the Soret coefficients from the

changes in conductivities at the top and bottom ends of a pure Soret cell, measured by a pair of platinized-platinum electrodes at each extremity of the cell. In 1958, a different version of the conductimetric method called the "resistance ratio" technique was invented by Agar and Turner ^{61,62,63}. In this method, the change in the ratio of the resistances of the top half to bottom half in a pure Soret cell during the separation was measured as a function of time and these changes were related to the Soret coefficient of the electrolyte solution under investigation. This method has enabled accurate determination of the Soret coefficients for many electrolyte solutions.

The availability of more accurate data on the Soret coefficients of electrolyte solutions have made possible the present researches on thermogravitational separation described in this thesis. The theoretical and experimental aspects of the Clusius-Dickel column will be discussed in detail in later chapters.

CHAPTER II.

THEORY OF SORET SEPARATION AND OF THE CLUSIUS-DICKEL COLUMN.

The Soret coefficient.

The Soret effect in solution was first expressed mathematically by Soret ⁶⁴ by introducing an additional term in the Fick's First Law equation for isothermal diffusion. In the case of a one-dimensional system, in which the temperature and concentration gradients existed together, provided there is no convection, the equation is of the form,

$$J = -E \frac{\partial T}{\partial x} - D \frac{\partial c}{\partial x} \quad (1)$$

where J = the net flux of solute in moles per unit area per unit time due to the combined effect of thermal and ordinary diffusions,

D = isothermal diffusion coefficient expressed as sq.cm. per sec.,

$\frac{\partial c}{\partial x}$ = concentration gradient in moles per c.c. per cm.,

E = a constant denoting the flux of solute in moles per unit area per unit time when a unit temperature gradient is maintained across the solution, and

$\frac{\partial T}{\partial x}$ = the temperature gradient in degrees per cm.

In the steady state, which is also known as "Soret Equilibrium", the rate of separation due to thermal diffusion is assumed to be equal to the rate of mixing due to ordinary diffusion,

$$J = 0, \text{ and } \left[\frac{dc}{dT} \right]_{st} = - \frac{E}{D} = \text{const.} \quad (2)$$

However, since $\left[\frac{dc}{dT} \right]_{st}$ was found to be approximately proportional to c , an improved equation,

$$J = - D \frac{dc}{dx} - D' c \frac{dT}{dx} \quad (3)$$

was suggested ²⁰, where D' (expressed in sq.cm.per sec. per degree) is called the "Thermal diffusion coefficient".

In the steady state, $J = 0$ and equation (3) may be re-written as

$$- \frac{D'}{D} = \left[\frac{1}{c} \frac{dc}{dT} \right]_{st} \quad (4)$$

However, this description is unsatisfactory, because owing to thermal expansion/contraction (at the beginning of the experiment) $\frac{dc}{dT}$ has a non-zero value even in the absence of thermal diffusion. A better description is obtained ⁶¹ if we replace the concentration c in moles/lit. by the molality m . For the steady state, we then have

$$\left[\frac{1}{m} \left(\frac{dm}{dT} \right) \right]_{st} = - \sigma \quad (5)$$

or

$$(\text{grad } \ln m)_{st} = - \sigma \text{ grad } T \quad (6)$$

which defines the Soret coefficient (units : per degree).

The negative sign in the above equation enables one to express the Soret coefficient as a positive fraction for most of the electrolytes in aqueous solutions, where the migration of the electrolyte is in the direction of heat flow. The opposite sign is used for the migration of the solute up the

temperature gradient. The value of the Soret coefficient is of the order of $10^{-3} \text{ }^{\circ}\text{C}^{-1}$ for many electrolytes in aqueous solution and it increases with increasing temperature. It is also a function of the concentration of the solute.

Since the numerical values of the diffusion coefficients have been shown to depend on the frame of reference ⁶⁵, the Fick frame defined by the following equation,

$$J_1^F V_1 + J_0^F V_0 = 0 \quad (7)$$

is usually adopted, where V_1 and V_0 are the partial molar volumes of the solute and solvent respectively and J_1^F and J_0^F are the corresponding fluxes.

This frame of reference is fixed by the geometry of the apparatus and is therefore useful in diffusion experiments where there is no bulk flow of the solution relative to the apparatus, assuming all other forms of volume changes are negligible.

Thermodynamics of the process.

The thermodynamic aspects of thermal diffusion has been reviewed and discussed recently by Agar in several articles ^{61, 66, 67}. The following brief account introduces certain essential features of his treatment ⁶⁷.

The system under consideration is supposed to be enclosed in a cylindrical tube of unit cross-sectional area divided into two parts (which may be as large as we please) by a reference plane 00 as shown in Figure 1.

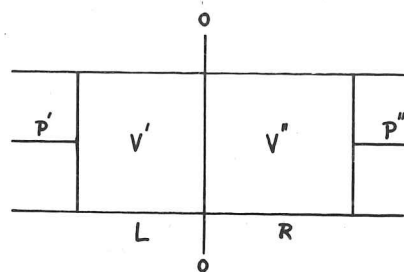


FIG. 1.

The system can lose or gain energy in the form of P-V work by the two movable pistons at the ends. The walls of the container are impermeable to heat and matter. The properties of the system in the two sections L and R are defined by single and double primes respectively.

If one mole of a component 'i' is made to migrate across the plane 00 from L to R under following conditions,

(a) there is no net amount of any other component crossing the reference plane,

(b) the pressure at any point in the system is maintained unaltered, and

(c) the temperature at any point in the system is also left unaltered,

then the increase of entropy in the region R is " s_i ", the partial molar entropy of i. In such a case, the decrease in entropy of L is also s_i leaving the net exchange of heat with the surroundings zero, provided the process is carried out reversibly.

(a) and (b) can be satisfied by acting on the components

with suitably chosen forces and at the same time moving the reference plane relative to the containing vessel. Condition (c) can be satisfied by transferring or extracting heat to or from the surroundings.

During the above process of migration of one mole of component "i" from left to right, an amount of entropy \hat{S}_i must be transferred to a reservoir from R, in the form of "heat of transport" \hat{Q}_i , in order to satisfy conditions (a), (b) and (c) for the system on the R side of the reference plane 00.

Hence the actual "transported entropy" by one mole of "i" across the reference plane from L to R is given by

$$\bar{S}_i = \hat{S}_i + s_i \quad (8)$$

The "heat of transport" \hat{Q}_i is related to \hat{S}_i , by the usual relation

$$\hat{S}_i = \hat{Q}_i/T \quad (9)$$

where T is the absolute temperature at the reference plane.

The above equations thus give the amount of heat transferred from L to R by ^{the} migration of 1 mole of i under isothermal conditions. If the system is not isothermal there will of course be an additional heat flow across 00 due to the temperature gradient at this point.

It has been shown ^{67,68} that for Soret equilibrium,

$$\begin{aligned} \sigma &= -\left(\frac{d \ln m}{dT}\right)_{st} = \frac{\nu_1 \hat{S}_1 + \nu_2 \hat{S}_2}{(\nu_1 + \nu_2) RT [1 + (\partial \ln \gamma_{\pm} / \partial \ln m)]_T} = \\ &= \frac{\hat{S}}{B} = \frac{\hat{Q}}{TB} \end{aligned} \quad (10)$$

where ν_1 and ν_2 are numbers of ions of type '1' and '2',

γ_{\pm} is the mean molal activity coefficient, $\hat{S} = \nu_1 \hat{S}_1 + \nu_2 \hat{S}_2$ is the molal entropy of transport and \hat{Q} is the molal heat of transport.

Since 'B' can be calculated from the known values of γ_{\pm} and σ can be obtained from experiments, the molal entropy of transport and hence the molal heat of transport, \hat{Q} , can be calculated for the substance under investigation.

The theory of the Clusius-Dickel column.

The theory of thermogravitational separation was developed by Furry, Jones and Onsager⁶⁹, Debye⁷⁰, de Groot²⁴, Bardeen⁷¹, Korsching⁴³ and many others⁷²⁻⁷⁵. More recently, Home and Bearman⁴² and Korschinsky and Emery⁵⁰ have developed theories incorporating the forgotten effect into their equations. These will be outlined later.

General theory of Furry, Jones and Onsager as outlined by Tyrrell²⁰.

Considering an apparatus in the form of a rectangular parallelepiped, which encloses a binary solution, the geometry of the apparatus is fixed by the reference axes with their origin at the base of the cooled surface. Let 'a' be the slit width, 'b' and 'h' the width and height of the parallel plates. Let $0 < x < a$, $0 < y < h$ and $0 < z < b$ (Fig.2).

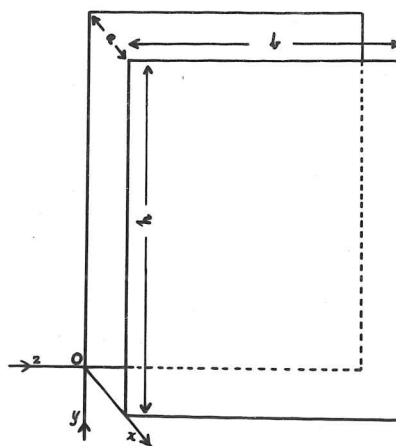


FIG. 2

Ordinary and thermal diffusion occur along the x-axis, ordinary diffusion and convective flow along the y-axis and no flow along the z-axis.

Assuming a mass-fixed frame of reference, the fluxes can be written as

$$J_x = -D\rho\left(-\frac{\partial w}{\partial x} + \sigma w(1-w)\frac{\partial T}{\partial x}\right) \quad (11)$$

$$J_y = -D\rho\left(\partial w / \partial y\right) + v(x)\rho w \quad (12)$$

$$\text{and } J_z = 0 \quad (13)$$

where $v(x)$ is the velocity of convection in cm. sec.^{-1} ,

w is the mass fraction of the solute,

ρ is the density of the solution,

τ is the temperature difference between the hot and cold surfaces,

and σ is the Soret coefficient defined here as $\frac{1}{w(1-w)} \times \left(\frac{dw}{dT}\right)_{st}$.

At the steady state, the equation of continuity

$$-\frac{\partial}{\partial t}(w\rho) = -\text{div } J = 0 \quad (14)$$

The velocity of convection $v(x)$ is assumed to be zero at $x = 0$ and a . Its value for any other value of x , $0 < x < a$ is obtained by solving the three hydrodynamic equations,

$$\partial p / \partial x = 0 \quad (15)$$

$$\partial p / \partial y + g\rho = \eta \partial^2 v / \partial x^2 \quad (16)$$

$$\partial p / \partial z = 0 \quad (17)$$

for laminar flow parallel to the y -axis, where p is the pressure at any point, η the viscosity of the solution and 'g' the acceleration due to gravity.

The above equations can be combined and written as

$$a^2 g \, d\rho / d\xi = d/d\xi \left(\eta \partial^2 v / \partial \xi^2 \right) \quad (18)$$

where $\xi = x/a$, and the new boundary conditions are

$$v(0) = v(1) = 0 \quad (19)$$

Also since the volume is conserved

$$\int_0^1 v(\xi) d\xi = 0 \quad (20)$$

The two main assumptions introduced for the solution of the above equation for the steady state are

- (1) η is independent of ξ and hence of temperature and concentration, and
- (2) $d\rho/d\xi$ is independent of ξ .

Since

$$\begin{aligned} d\rho/d\xi &= \frac{\partial \rho}{\partial T} \cdot \frac{dT}{d\xi} + \frac{\partial \rho}{\partial w} \frac{dw}{dT} \frac{dT}{d\xi} \\ &= -\beta \rho \tau + \tau \frac{\partial \rho}{\partial w} [-\sigma w(1-w)] \\ &= -\beta \rho \tau - \sigma \tau w(1-w) \partial \rho / \partial w \quad (21)^* \end{aligned}$$

- * 1. Assuming a uniform temperature gradient, $dT/d\xi$ has been replaced by $\tau = \text{constant}$.
2. The equality $dw/d\xi = -\sigma w(1-w) dT/d\xi$ need not be true in general.

(where $\beta = -1/\rho \cdot \partial \rho / \partial T$ is the coefficient of thermal dilatation)

this assumption means that β , w , σ and D are independent of ξ and that $\partial \rho / \partial w$ is independent of w and hence ρ is a linear function of w .

It has been shown by de Groot ²⁴ that even if there be a marked dependence of viscosity on temperature, the final error due to assumption (1) is small.

The solution of equation (18) thus reduces to

$$v(\xi) = - \frac{ga^2}{6\eta} \frac{d\rho}{d\xi} \xi \left(\xi - \frac{1}{2} \right) (\xi - 1) \quad (22)$$

It is a curve vanishing at $\xi = 0, \frac{1}{2}$ and 1 and having extreme values of $\mp \frac{ga^2}{128\eta} \frac{d\rho}{d\xi}$ at $\xi = \frac{2}{4}$ & $\frac{3}{4}$ respectively.

The total mass flux of solute m^* , in the vertical direction is given by

$$m^* = ab \int_0^1 J_y d\xi \quad (23)$$

where ab = cross-sectional area of the apparatus.

$$\text{Or, } m^* = ab \int_0^1 \left(-D\rho \frac{\partial w}{\partial y} + v(\xi) \rho w \right) d\xi \quad (24)$$

This total flux can be divided into two parts m_d and m_c being due to the diffusion in the y -direction and the flow due to convection respectively.

The flux due to the convection m_c works out to be

$$m_c = -K \partial / \partial y (\rho w) - H \rho w (1 - w) \quad (25)$$

where

$$H = -(\sigma \tau g / 6! \eta) ba^3 d\rho / d\xi \quad (26)$$

and $K = 1/9! (g/\eta \cdot d\rho/d\xi)^2 a^7 b/D$ (27)

The vertical diffusion flow, m_d comes out as

$$m_d = -\rho Dab (\partial w / \partial y) = -\rho K_d (\partial w / \partial y) \quad (28)$$

Assuming in addition that ρ is independent of y ,

$$m^* = -\rho [Hw(1-w) + K^* \partial w / \partial y] \quad (29)$$

where $K^* = K + K_d$. Since the ratio K_d/K is of the order of $a^{-6} \times 10^{-9}$, K_d need to be considered only for very small slit widths or very small $(d\rho/d\xi)$ (i.e. very small temperature difference).

For columns without reservoirs, Bardeen ⁷¹ has obtained the following final equations *

$$\frac{w_u}{w_o} = -\frac{2A^* \exp(-2A^*)}{\exp(-2A^*) - 1} + \exp(-A^*) \sum_{j=1}^{\infty} b_j (-1)^j \exp\left(-\frac{t}{\theta_j}\right) \quad (30)$$

and $\frac{w_l}{w_o} = \frac{-2A^*}{\exp(-2A^*) - 1} + \sum_{j=1}^{\infty} b_j \exp(-t/\theta_j) \quad (31)$

where assuming $d\rho/d\xi = -\beta\rho\tau$ (32)

$$A^* = Hh/2K^* = -252 D'h/(\beta\rho g/\eta)a^4 \quad (33)$$

$$b_j = \frac{-4j^2 \pi^2}{A^{*3}} \left[\frac{1 - (-1)^j \exp A^*}{(1 + j^2 \pi^2/A^{*2})^2} \right] \quad (34)$$

and $\theta_j = \frac{2abh}{A^* H (1 + j^2 \pi^2/A^{*2})} \quad (35)$

In the steady state, when $t = \infty$,

$$\left(\frac{w_u}{w_o} \right)_{t=\infty} = \frac{-2A^*}{1 - \exp 2A^*} \quad (36)$$

$$\left(\frac{w_l}{w_o} \right)_{t=\infty} = \frac{-2A^*}{\exp(-2A^*) - 1} \quad (37)$$

* w_u and w_l are mass fractions at the upper and lower ends, respectively, and w_o is the initial mass fraction.

$$\text{and } (w_u/w_l)_{t=\infty} = \exp(-2A^*) \quad (38)$$

When A^* is sufficiently small, $\exp(-A^*)$ can be replaced by $(1 - A^*)$ and

$$\frac{w_u}{w_l} = 1 - 2A^* \left[1 - \frac{8}{\pi^2} \sum_{q=0}^{\infty} \frac{\exp - \frac{(2q+1)^2 t}{\theta}}{(2q+1)^2} \right] \quad (39)$$

and θ has a single value,

$$\theta = 2 abh/A^* H (1 + \pi^2/A^{*2}) \quad (40)$$

θ is called the "characteristic time" and it determines the rate of approach to steady state.

$$\text{At } t = \infty \quad (w_u/w_l)_{\infty} = 1 - 2A^* \quad (41)$$

$$\text{and at } t = 0, \quad w_u/w_l = 1 \quad (42)$$

For small values of t/θ , equation (39) can be abbreviated to

$$\frac{w_u}{w_l} = 1 - 4H \left(\frac{t}{\pi ab K^*} \right)^{1/2} \quad (43)$$

The last expression enables the calculation of the thermal diffusion coefficient from the initial slope of a plot of w_u/w_l vs. $t^{1/2}$, if the mutual diffusion coefficient is known. When A^* is sufficiently small, it can be determined by using equation (41) for steady state separation. Hence D' can be calculated using equation (33).

For a column with reservoirs, the steady state equation for small values of A^* also reduces to

$$\left(\frac{w_u}{w_l} \right)_{\infty} = 1 - 2A^* \quad (41)$$

Whereas the initial rate of separation is greater for a column without reservoirs as can be seen by comparing equation (43) with the one below :

$$\frac{w_u}{w_1} = 1 - \frac{2t}{(V/H + t)} \approx 1 - \frac{2Ht}{V} \quad (44)$$

where V is the volume of the reservoir.

Hence/^{the} initial changes in concentration occur more rapidly in columns without reservoirs. It must be noted that in both cases, the initial rate is independent of the height of the column. This has been confirmed experimentally ²⁸.

Equations obtained by Horne and Bearman ⁴²

The equation for the thermal diffusion factor, α , obtained by Horne and Bearman who include the forgotten effect F in their derivation, for the steady state in the cylindrical column is :

$$\alpha_1 = \frac{AB (T^{\beta}/w_1 w_2) \Delta w_1}{(1 - F)} \quad (45)$$

where

$$F = (5/16)AB \left(\frac{\bar{V}_2 - \bar{V}_1}{\bar{V}} \right) \Delta w_1 \quad (46)$$

$$A = 2g (2\chi r_o)^4 / 504 h$$

$$B = \rho / \eta D$$

D = experimental mutual diffusion coefficient

h = vertical distance between the reservoirs

$$\chi = \frac{1}{2} \ln \left(\frac{r_1}{r_2} \right), \quad r_o = (r_1 r_2)^{1/2}$$

[If a is small compared with r_1 and r_2 , $(2 \chi_{r_0}) \approx a \equiv (r_1 - r_2)$]

α_1 = thermal diffusion factor ($-T\sigma$, σ =Soret coefficient)

w_1, w_2 = mass fractions of components 1 and 2 respectively

Δw_1 = difference between the steady state composition of the top reservoir and the initial composition

\bar{v}_1, \bar{v}_2 = partial specific volumes of components 1 and 2

\bar{v} = total specific volume

$$\beta = (1/\bar{v}) \left(\partial \bar{v} / \partial T \right)_{p, w_1} = - \frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_{p, w_1}; \quad \rho = \frac{1}{\bar{v}}$$

on comparing the above equation for F with those obtained earlier, it can be shown that in the following equation obtained by de Groot ²⁴

$$d\rho/d\xi = - \tau (\beta \rho + q \sigma w (1 - w) \partial \rho / \partial w) \quad (47)$$

q gets the value $5/16$ instead of the variable value $1 - 0.3$ given by de Groot according as the annular spacing is small or large.

For dilute electrolyte solutions, the value of F is very small (less than 0.1% for 0.01m solutions) and hence can be omitted without serious error.

As can be seen from the above equations, the forgotten effect directly affects the convective velocity. For a given mixture, the first term in equation (47) varies much less rapidly with composition than the second term. Since the forgotten effect depends on the difference between the partial specific volumes of the two components, it will be negligible for an approximately ideal mixture having components of similar densities. As an illustration, can be cited Prigogine's³⁷

They reported that
experiments on binary organic mixtures. ~~The~~ mixture tetra-
bromoethane-tetrachloroethane, when separated in a thermogra-
vitational column undergoes a complete inversion in the di-
rection of separation of the components. *(but see below)*.

Recent work on the forgotten effect.

Korschinsky and Emery ⁵⁰ have recently discussed the theo-
retical aspect of the forgotten effect. According to them,
the forgotten effect influences only the approach to the
steady state but neither increases nor decreases the steady
state separation. Also, the forgotten effect should produce
inversion in the direction of separation within about a minu-
te after the start of the experiment. In those cases where
the more dense component is known to diffuse to the hot wall,
they maintain that the variation of density with concentrat-
ion is too small to cause reversal in the direction of flow
of the components. The influence of forgotten effect on the
transient behaviour is larger the smaller the plate spacing.

In order to verify the experiments on concentration re-
versals reported in the literature, they have tried to dupli-
cate the experiments of Jones and Millberger ³⁵ on 50% to-
luene-cyclohexane and of Prigogine et al. ³⁷ on the system
1,1,2,2-tetrachloroethane-1,1,2,2-tetrabromoethane and also
on bromobenzene-carbontetrachloride. But in all these cases,
Korschinsky and Emery did not observe any concentration re-
versal. So they conclude that the concentration reversals re-
ported in the literature are not caused by the forgotten ef-
fect but by imperfections in their experimental work. *of*
Prigogine et al.

Turner, Butler and Story ⁷⁶ using the flow-cell technique for the determination of concentration changes due to thermal diffusion in the carbon tetrachloride - cyclohexane system, have confirmed Korschinsky and Emery's views that the forgotten effect does not influence the steady state separation. Their results agree better with those obtained by Horne and Bearman ⁴² when ~~Horne and Bearman's~~ correction for the forgotten effect ~~is omitted~~.

Horne and Bearman ⁷⁷ have since re-checked their steady state equations and have traced their error as due to prematurely tailoring off their Taylor's series expansion for the density. Retention of higher terms gave the following equation

$$\alpha_1 = \frac{(2X_{r_0})^4 g \rho \beta \bar{T}^2 \Delta w_1}{504 w_1 w_2 \eta Dh [1 - (152/143) (F/25)]} \quad (48)$$

and hence the denominator is more nearly equal to unity than in their earlier ⁴² equation (45).

CHAPTER III.

DESIGN AND CONSTRUCTION OF THE COLUMN AND MEASUREMENT OF CONCENTRATION CHANGE. PART A: PRELIMINARY EXPERIMENTS.

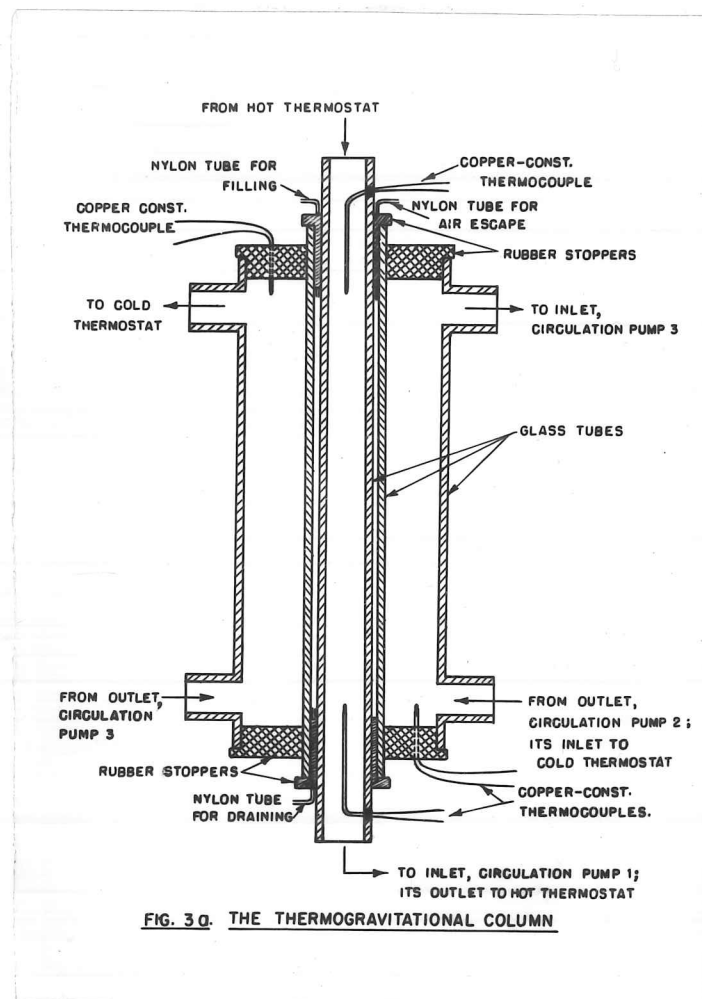
Outline of the method.

The apparatus consists of three concentric cylindrical glass tubes (Fig.3a). Thermostated hot water is circulated through the innermost tube and cold water from another thermostat is circulated between the middle and the outermost tubes. The spacing between the innermost and the middle tube is of the order of one millimetre. The solution under study is injected into this annular space. The concentration changes occurring in the column of solution due to a temperature difference imposed across the solution are measured by a suitable method.

Temperature control and measurement.

The temperatures of the hot and cold thermostats were controlled by electronic relays through mercury-toluene regulators to $\pm 0.02^\circ\text{C}$.

Three circulation pumps were used for circulating the thermostated water from the hot and cold thermostats as shown in Fig.3a. The temperature difference between the hot and cold jackets at the top and bottom ends of the column as well as the mean temperature along the length of the column were maintained as uniform as possible by the method of circulation illustrated in Fig.3a. Circulation pump 1 circulates hot water through the ^{most} inner tube from the hot thermostat and pump 2 circulates cold water through the outer jacket from the cold ther-



mostat. The pump 3 serves as a stirrer for the outer jacket and circulates the water from the top of the jacket to the bottom so as to equalize the temperature of the water in the jacket from top to bottom. The measured rate of circulation of pump 1 was 420 gallons per hour and those of the two pumps on the cold jacket were 160 gallons per hour each.

Copper-Constantan thermocouples were used to measure the temperature of the circulating water at the top and the bottom ends of the column. All the Constantan ends were soldered together (Fig. 3b) so that only one junction could be used for reference. All junctions were coated with cellulose cement (Radio Spares) so as to electrically insulate them from the circulating water. The lengths of the free copper ends of the thermocouples were so chosen that they could be connected to the terminals of the Potentiometer without introducing connecting leads or switches, thereby avoiding stray e.m.f.'s.

A Tinsley potentiometer, in conjunction with a lamp and scale galvanometer, was used for measuring the thermo-e.m.f. The reference junction was maintained at 0°C by immersing in a mixture of broken ice and water.

The effective temperature drop across the solution in the annular space was determined as follows :

Fig. 3c represents a cross-section of the apparatus. r_0 , r_1 , r_2 and r_3 represent the radii and t_0 , t_1 , t_2 and t_3 , the corresponding temperatures.

If an amount of heat ' q ' flows across a slab of thickness dr , and thermal conductivity k in unit time, it produces a temperature drop dt , according to the following equation

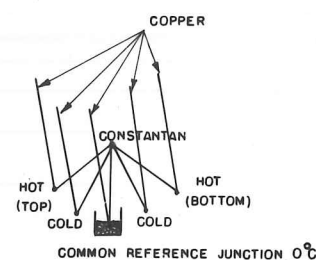


FIG. 3b. THE THERMOCOUPLES

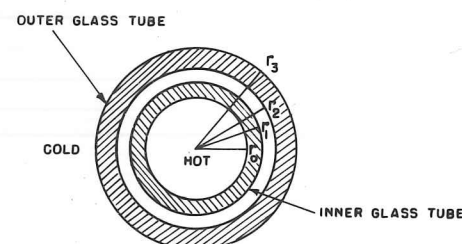


FIG. 3c. CROSS-SECTION OF THE COLUMN

$$q = -kA \frac{dt}{dr} \quad (49)$$

where A is the cross sectional area. In the case of a cylindrical tube, $A = 2 \pi r h$, where h is the length of the cylinder and r the radius.

Referring to Fig.3c, the total heat 'q' flowing per sec. from the surface at t_0 to that at t_1 is given by

$$q \int_{r_0}^{r_1} \frac{dr}{r} = - \left[2 \pi h \cdot k \int_{t_0}^{t_1} dt \right] \quad (50)$$

$$\text{or} \quad q \ln \frac{r_1}{r_0} = -2 \pi h k (t_1 - t_0) \quad (51)$$

$$\text{or} \quad (t_1 - t_0) = - (q/2 \pi h k) \ln r_1/r_0 \quad (52)$$

It follows from this relation that, for a steady state

$$(t_0 - t_1) : (t_1 - t_2) : (t_2 - t_3) = \frac{\ln r_1/r_0}{k_{\text{glass}}} : \frac{\ln r_2/r_1}{k_{\text{solution}}} : \frac{\ln r_3/r_2}{k_{\text{glass}}} \quad (53)$$

Assuming $k_{\text{glass}} = 0.002$ and $k_{\text{water}} = k_{\text{solution}} = 0.0014 \text{ cal cm}^{-1} \cdot \text{sec}^{-1} \cdot \text{deg}^{-1}$ and referring to Fig.3c, for the following set of values for the radii, $r_0 = 0.60 \text{ cm}$, $r_1 = 0.78 \text{ cm}$, $r_2 = 0.90 \text{ cm}$ and $r_3 = 1.10 \text{ cm}$, the ratio

$$(t_0 - t_1) : (t_1 - t_2) : (t_2 - t_3) \equiv 6.42 : 5.00 : 4.92 \quad (54)$$

For a temperature difference $(t_1 - t_2) = 5^\circ\text{C}$, $(t_0 - t_3)$ must be $6.42 + 5.00 + 4.92 = 16.34^\circ\text{C}$.

In order to fix the values of t_0 and t_3 in such a way that the mean temperature of the solution is 25.0°C and the

difference $(t_0 - t_3) = 16.34^\circ\text{C}$ the mean temperature of the solution was assumed as a rough approximation to be $(t_1 + t_2)/2 = 25.0^\circ\text{C}$. Since $(t_1 - t_2) = 5.0^\circ\text{C}$, t_1 and t_2 get the values 27.5°C and 22.5°C respectively. Knowing t_1 and t_2 , t_0 and t_3 could be calculated from the above equation (54)

$$t_0 = 27.5 + 6.42 = 33.92^\circ\text{C}$$

$$\text{and } t_3 = 22.5 - 4.92 = 17.58^\circ\text{C}$$

Having thus a rough idea of t_0 and t_3 , the mean temperature of the solution was experimentally set at 25.0°C by the following experiment.

~~The mean temperature of the solution in the column was determined by experiment as follows :~~

The solution in the column was maintained isothermal successively at three different temperatures, say, 20, 25, and 30°C by circulating water from the same thermostat through the inner and outer jackets. The total electrical resistance of the solution was measured under isothermal conditions by introducing two stout/^{platinized}platinum rings at the top and bottom ends of the annular space, the leads being taken out through the thin rubber stoppers at the ends. The solution chosen was 0.01M HCl. A graph of resistance vs. temperature was drawn for use as a reference curve for the next part of the experiment.

The hot and cold jackets were now maintained at $t_0 = 33.92^\circ$ and $t_3 = 17.58^\circ\text{C}$ respectively and the total resistance of the solution was measured. From the graph of temperature vs. resistance the mean temperature could be read. Since the assumption $t_m = (t_1 + t_2)/2$ is only a rough approximation, t_0 and t_3 needed slight adjustments (maintaining

$t_0 - t_3 = 16.34^\circ$) till the measured mean temperature was exactly 25.0°C . The t_0 and t_3 temperatures thus found were 34.05°C and 17.71°C respectively.

Measurement of temperature changes between the thermostats and the inlets and outlets at the hot and cold jackets necessitated the maintenance of the two thermostats at 34.06°C and 17.35°C respectively. While the hot thermostat showed a variation of $\pm 0.05^\circ$ during the circulation of water, the cold one had a larger variation of $\pm 0.1^\circ$. But the variations in the temperatures of the circulating water through the hot and cold jackets were such that the mean temperature across the solution (determined by measuring the total resistance) was constant to $\pm 0.05^\circ$.

The above calculation of the temperature difference is not very precise since k_{glass} may not be exactly 0.002. An error of ± 0.0005 in the value of k_{glass} causes a variation in $(t_1 - t_2)$ from 4.1° to 5.8° . The convective/^{heat}transfer across the annulus is likely to increase the effective thermal conductivity of the solution, thereby the temperature drop across the solution will become smaller. Also the surfaces of the glass tubes in contact with the circulating water may not be exactly at the temperatures t_0 and t_3 of the circulating water in the cold and hot jackets.

In the absence of an experimental method of determining the precise temperature drop across the solution in the annulus, the calculation by the above method gives us a fair estimation of the temperature difference.

Description of the columns used and the methods of determination of the changes in the concentration of the solution in the column.

Column : Two concentric pyrex glass tubes.

Determination of concentration change by indicator titrations.

The initial experiments were carried out in 1 meter long pyrex glass columns with ^amillimeter annular spacing. The top and bottom ends were closed by rubber tubes ground to fit the annular space (Fig.3a). Two small holes were bored through the rubber stopper at the top for filling and air-escape and one through the lower stopper for draining or withdrawing the solution. Thin nylon tubings were used for the purpose. Water from the same thermostat was circulated through both the inner and outer jackets. The column was then filled with the solution. 0.01M NaCl and 0.01M NaOH were used in the initial experiments. The temperature of one of the jackets was then changed by circulating water from the other thermostat. The temperature difference across the solution was about 20°C. After a definite interval of time, say 10 hours about 5 ml. samples were withdrawn from the top and the bottom ends respectively and their concentrations determined by titration using indicators.

For the above experiment, say in the case of 0.01M NaCl ($D' = D \sigma = 2.52 \times 10^{-8}$) ⁷⁸, θ has the value 50 hours (eqn 40). At the end of 10 hours, the expected separation $w_u/w_l = 0.97$ (eqn.43). In terms of the titre values, 5 ml. of the solution from the top and bottom ends of the column,

should give an equivalent of 4.85 and 5.15 ml. of 0.01M AgNO_3 . The observed values were 4.95 and 5.05 ml. respectively. Thus a definite increase in concentration was found at the lower end of the column and a corresponding decrease in concentration at the upper end. However, the observed changes were much less than the expected.

Column : Two concentric pyrex glass tubes.

Determination of concentration change by electrometric titrations.

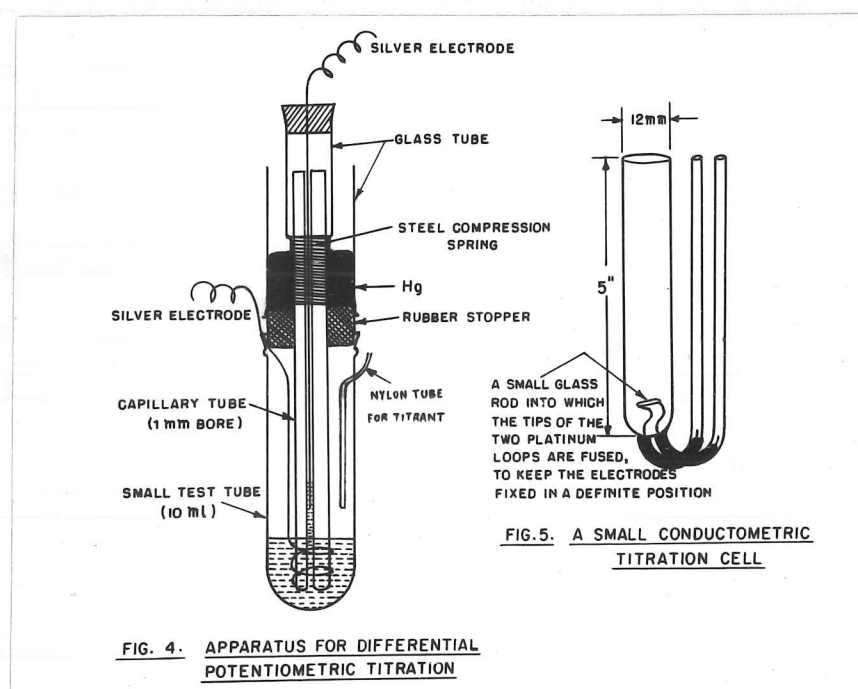
Since the indicator titration method was not accurate enough for these small concentration changes, in subsequent experiments, the concentration changes in NaCl solution were determined by the differential potentiometric titration ⁷⁹ using Ag/AgCl electrodes (Fig.4) and those of NaOH, by conductometric titration in a cell constructed specially for the purpose for small volumes of solution (Fig.5).

The results were obviously better than those obtained by the indicator titrations in that the end points were sharp. The observed titre volumes were again 4.95 and 5.05 ml. respectively for the top and bottom 5 ml. of 0.01M NaCl solution at the end of 10 hours in the column of the above dimensions.

Column : Pyrex outer tube and stainless steel inner tube.

Determination of concentration change by electrometric titrations.

In another experiment on 0.01M NaCl, a column of stainless steel inner tube and glass outer tube (annular space : 0.12



cm. and height: 97.0 cm) was used in order to increase the effective temperature drop across the solution and thereby decrease θ to reduce the time of approach to steady state. For a temperature difference of 50° , θ works out as 2 hours. The expected steady state separation according to equation (41), $(w_u/w_l)_{\infty} = 0.8$.

At the end of 59 hours, the experiment was stopped by switching off the circulation pumps and three successive 5 ml. portions from the top and three similar portions from below were titrated against standard AgNO_3 solution. (5 ml. of original NaCl solution \equiv 3.40 ml. standard AgNO_3 solution.) The observed titre values in order from the top were : 3.25, 3.35, 3.45; 3.45, 3.50 and 3.55 ml. AgNO_3 respectively. The expected titre values for the top and bottom portions of the solution are 3.05 and 3.75 ml standard AgNO_3 respectively, - observed change, 43% lower than the expected change.

In the above column, 0.8M NaOH solution was then subjected to thermogravitational separation, for which θ works out as 1.5 hours. At the end of 25.5 hours, about 1.5 ml. of the solution was withdrawn from each of the extrem~~e~~ ends of the column and 1 ml. of each was titrated against standard HCl solution in the conductimetric cell. The volumes of HCl required were 2.15 and 3.10^{ml.}/respectively, while 1 ml. of the original NaOH needed 2.65 ml. The separation process was continued further although the height of the solution in the column was less than it was before. At the end of 57 hours, the experiment was stopped and 1 ml. samples from the top and bottom gave titre values of 2.20 and 3.10 ml. of HCl respectively, thereby indicating the attainment of steady state al-

ready at the end of 25.5 hours. The expected value of $(w_u/w_l)_\infty = 0.37$ ($\sigma_{\text{NaOH}} = 12.5$)¹⁵ and the expected titre values for the steady state are 1.45 and 3.85 ml. standard HCl respectively; - observed change is 42% lower than the expected change.

In the above experiments, although the observed separations are about 40% less than the expected values, the important feature of the results was that the concentration changes at equal distances on either side of the centre of the column were equal but opposite in sign. This eliminates the necessity of measuring the concentration changes at both ends of the column. Therefore, in the following experiments, only the concentration changes occurring at the top end of the column were measured.

The poor agreement of the observed and expected concentration changes in the above experiments was perhaps mainly because of the inevitable non-uniformity of the annular spacing over the length of 1 meter (the steady state separation depends on the fourth power of the spacing) of even the best selected tubings for these preliminary experiments. Another drawback was that samples of solution had to be withdrawn from the column for analysis externally. This caused disturbance of the vertical concentration profile while withdrawing out of the column and also reduced the height of the solution in the annular space, thereby altering the conditions of the subsequent separation process. Thus, during one run, the concentration changes occurring at different intervals of time could not be determined without altering the length of the column of solution.

Column : Two concentric pyrex glass tubes.

Determination of concentration change by conductimetric method

In order to maintain the same height of the solution in the column during the whole experiment, pipette-type microconductivity cells (Fig.6) were introduced so that the conductivity of the solution could be measured at definite intervals of time and the solution dropped back into the column. In the previous experiments, since slight corrosion was suspected on the surface of the stainless steel tube, only glass tubes were used for all the following experiments.

As shown in the Fig.6, two almost identical conductivity cells A and B of 0.9 ml. capacity each and with provision for circulation of the thermostated water were constructed. The two cells were clamped above the top of the column, one of them was always kept filled with the original solution with which the column was filled. This served as the comparison cell. Into the other cell the solution from the top of the column was periodically (at exact intervals of 5 or 10 mins. initially and at longer intervals as the separation approached the steady state) sucked in and the conductivity determined (temperature controlled by the thermostated water circulating through the jackets of the two cells A and B at 20 gallons per hour). The solution was then dropped back into the column. It must be mentioned that the cell had to be rinsed thrice with the solution from the top of the column (the rinsings were dropped back into the column) before taking the conductivity readings.

As an illustration of the type of results obtained, the data obtained for 0.01M HCl in a column with 0.17 cm. annular spacing and 87.5 cm. height with a temperature difference of 5° at a mean temperature of 25°C have been tabulated.

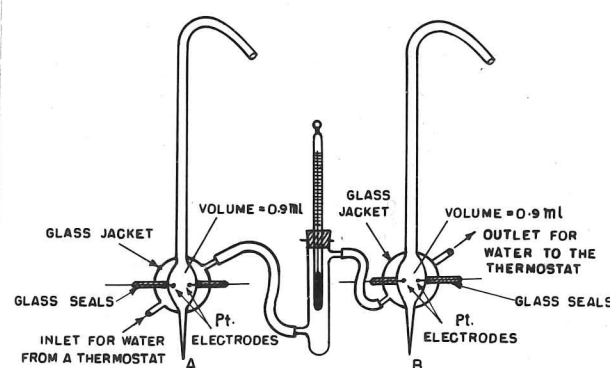


FIG. 6. TWIN PIPETTE - TYPE MICRO-CONDUCTIVITY CELLS.

Table I.

Separation of 0.01M HCl; Resistance (ohms) in cells A and B

| Time | R_A | R_B | Duration (mins.) |
|------------|---------------|-------|----------------------------------|
| 2.57 p.m. | 579.8 | 555.4 | 0 |
| 3.10 | 592.2 | 555.4 | 13 |
| 3.20 | 598.3 | 555.4 | 23 |
| 3.30 | 600.2 | 555.4 | 33 |
| 3.45 | 606.1 | 555.5 | 48 |
| 4.00 | 612.5 | 555.5 | 63 |
| 4.30 | 617.6 | 555.4 | 93 |
| 5.00 | 622.2 | 555.4 | 123 |
| 5.30 | 629.8 | 555.4 | 153 |
| 6.00 | 631.4 | 555.4 | 183 |
| 7.05 | 636.5 | 555.4 | 248 |
| 10.25 | 652.8 | 555.4 | 448 |
| 10.10 a.m. | 652.5 | 555.4 | 19 ^h .13 ^m |
| 12.13 p.m. | 653.5 | 555.4 | 21 ^h .16 ^m |
| 12.17 p.m. | pumps stopped | | |

The steady state separation expected for 0.01M HCl ($D = 3.2 \times 10^{-5} \text{ cm}^2.\text{sec}^{-1}$)⁸⁰ and ($\sigma = 9.00 \times 10^{-3} \text{ deg}^{-1}$)⁷⁸ under the above conditions is $(w_u/w_1)_\infty = 0.58$, which ought to give a change in the resistance, R_A from 579.8 to 732 ohms at steady state, whereas the observed value is 48% of the expected change. On the other hand, using the value $D' = 21.0 \times 10^{-8} \text{ cm}^2.\text{sec}^{-1}.\text{deg}^{-1}$ obtained with the all-glass column (p. 72), the above resistance change (12.5%), corresponds to 67% of the expected value (19%).

The interesting aspect of the above experiment is the approach to the steady state. The table below shows what percentage of the final steady state resistance change is covered at various times after the start of the experiment.

T a b l e II.

The approach to steady state; 0.01M HCl

| Time (hrs.) | 1 | 2 | 3 | 4 | 5 | 6 | 7.5 |
|--|----|----|----|----|----|----|-----|
| % of resis. change at steady state | 45 | 60 | 75 | 83 | 90 | 95 | 100 |

Nearly half the steady state separation occurs in the first hour; the separation then gradually levels off attaining the steady state value in less than 10 hours ($\theta = 5$ hours, from eqn.40).

Column : Shorter glass tubes.

Determination of concentration change by conductimetric method.

In order to get better agreement of the observed and expected separation, it was thought that reducing the height of the column from one meter to about 20 cm. would minimize the effect of non-uniform annular spacing⁵⁰ on the percentage separation (eqns 33 and 41).

Experiments were therefore conducted in a shorter column of 15.8 cm. height and 0.17 cm. annular spacing, the temperature conditions remaining the same.

The steady state for 0.01M HCl was attained within one

hour ($\theta = 10$ min.) and the observed change was 60% of the expected $(w_u/w_l)_\infty = 0.9$. This result was quite encouraging, but there still remained one more snag which had to be overcome - that of disturbing the separation process while sucking the solution into the conductivity cell and dropping it back. Also, since the cell had to be rinsed many times before taking a measurement, the precise value of the instantaneous concentration at any instant could not be obtained.

Column : Short concentric glass tubes.

Determination of concentration change by the "resistance ratio" method.

With all the experience gathered in the above preliminary experiments, it was finally decided to introduce two platinized-platinum ring electrodes at the top and bottom ends of the annular space and measure the ratio of the resistance of the solution in the upper half to that in the lower half of the column by introducing a centre-tap electrode. This technique of measuring concentration changes was first devised and used in these laboratories ^{61,62,63} for static Soret cells with ^{vertical} temperature difference. The experiments described in the following pages will show that this method was equally successful in the case of ^{the} thermogravitational column as well, in spite of the existence of non-uniform temperature across the solution in the column.

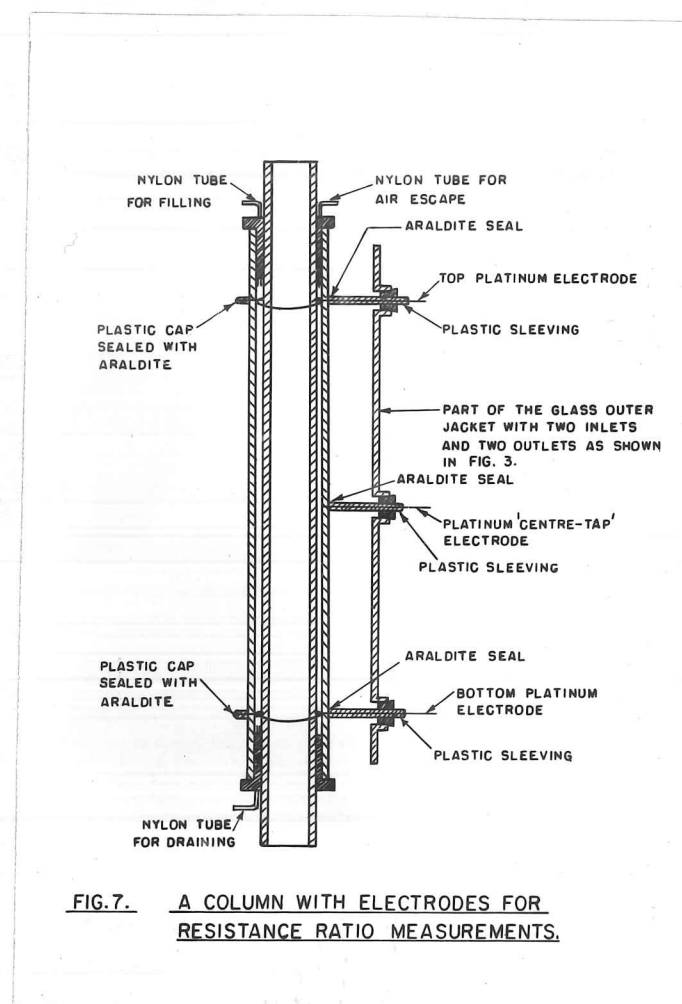
Preliminary experiments in this series were carried out on several short columns of about 15-20 cms. height made of glass tubes with precision inner diameters and of annular

spacings 0.17, 0.12 and 0.10 cm.

Construction of the column.

In the first experiment, a column of 20 cm. height (between the stoppers) and 0.17 cm. annular spacing was used (Fig. 7). Two platinum rings formed the end electrodes. A tiny bead at one end of a platinum wire formed the centre-tap electrode. The distance between the top and bottom electrodes was 17 cm. The two leads of each of the end ring electrodes were taken out horizontally through the wall of the outer glass tube of the annular space, since the rubber stoppers enclosing the annular space were too thin to bore holes and take the leads through them. The second lead of each ring electrode served only to fix the rings firmly. A pair of holes of 1 mm. diameter were carefully made in the wall of ^{the} outer glass tube at either end and another one exactly midway between the top and the bottom holes, by means of a heated tungsten wire, without causing much deformation in the glass tube. The central electrode was carefully adjusted not to protrude beyond the inner wall of the outer tube. All the leads were covered with plastic insulation sleeveings and sealed on to the outer surface of the glass tube with "Araldite". These leads were taken out through the glass wall of ^{the} outer jacket through three corresponding holes fitted with small rubber stoppers as shown in Fig. 7.

The rubber stoppers at the ends were removed and the column was cleaned with chromic acid followed by distilled water. The electrodes in the column were coated with platinum black by the usual method ⁸¹. The column was once again clean-



ed thoroughly with distilled water and finally with conductivity water.

Measurement of the resistance ratio.

The ratio of the resistance of the top half to the bottom half of the solution (in future referred to as the resistance ratio) was measured by the Wheatstone bridge technique using a Wagner earth for the balance, as shown in Fig.8. The bridge was fed from a 1 kcs. oscillator through a screened transformer. A cathode-ray oscilloscope was used to detect the off-balance signal amplified by an amplifier.

The two halves of the solution resistances were balanced against two 4-decade boxes, R_u and R_l , each of 10000 ohms maximum resistance. The Wagner arm consisted of two decade boxes W_u and W_l of 1000 ohms each and a 15-ohm rheostat, W_f for fine adjustment. The floating terminal of the rheostat, which formed the centre of the Wagner arm, was permanently connected to the earth end of the detector. The other end of the detector (Y-plates) was connected to either E or F through a single pole double throw switch S_D . The reference wave was fed to the X-plates of the C.R.O. from the same 1 kcs. oscillator feeding the bridge. The excess capacitance on either the upper or lower half of the solution resistance was balanced by the variable condensers C_W and C_R , one end of each of which was permanently connected to the centre of the Wagner and resistance arms respectively. The other end of each was connected to either the upper or lower end of the bridge through the s.p.d.t. switches S_W and S_R .

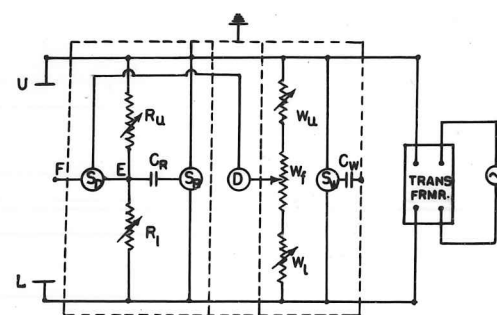


FIG. 8. WHEATSTONE-BRIDGE WITH WAGNER EARTH

The resistance ratio was then measured as follows :

Step (1).

The detector was first connected to the centre-tap and the solution resistances were balanced against the Wagner arm by adjusting the resistances W_u , W_f and W_l and the capacitance C_W connected across the upper or lower side of the Wagner arm, by means of switch S_W .

Step (2).

The detector was then connected to the resistance arm through the switch S_D and the resistances and capacitance on the Wagner arm were balanced by adjusting R_u , R_l and C_R , the switch S_R being used as necessary.

Step (3).

Step (1) was repeated and the resistances and capacitance on the Wagner arm were re-adjusted. This was then followed by Step (2).

This procedure was repeated till the bridge components needed no re-adjustments.

y_t , the index of concentration change.

In the above method of measurement, R_u and R_l were always so adjusted as to keep their sum constant at, say, $(R_u + R_l) = 10000$ ohms. This enabled one to obtain the ratio $\frac{2 y_t}{10^4} = \frac{(R_u - R_l)_t}{R_u + R_l}$ and hence $2 y_t = (R_u - R_l)_t$ directly from the bridge readings.

Since $\frac{1}{2} y_t$ is a measure of the resistance changes as a consequence of the concentration changes in the top half and

bottom half of the column of solution, $\frac{1}{4} y_t$ can be considered to represent the changes occurring at $\frac{1}{4}$ and $\frac{3}{4}$ of the column height.

Hence the concentration changes occurring at the top and bottom ends of the column can be assumed to be

$$4 y_t = 2 (R_u - R_l)_t \quad (55)$$

(This assumption has been verified in a later experiment; see p. 65).

Relation between y_t and concentration change.

Since R_u and R_l correspond to the concentrations c_u and c_l at the upper and lower half of the column, they can be related by the definition of equivalent conductivity Λ :

$$K_{sp} = \frac{L}{AR} = \frac{\Lambda [c]}{1000} \quad (56)$$

where K_{sp} is the specific conductivity of the solution, L is the distance between the electrodes, A the cross-sectional area of the electrodes which enclose the solution, R the resistance of the solution and $[c]$, the concentration in equiv. per liter.

$$\text{Hence } R_u \propto \left(\frac{1}{\Lambda [c]} \right)_u ; R_l \propto \left(\frac{1}{\Lambda [c]} \right)_l \text{ and } \frac{R_u}{R_l} = \frac{(\Lambda [c])_l}{(\Lambda [c])_u} = \frac{(\Lambda c)_l}{(\Lambda c)_u}, \text{ where } c \text{ is the molar concentration.}$$

$(\Lambda c)_l / (\Lambda c)_u$ can be equated to c_l / c_u since the concentration changes involved are small. For example, in the case of 0.01M HCl, where one expects a large change in c_u / c_l from unity on account of its high $D' = 29 \times 10^{-8}$ ⁷⁸ (6% change in concentration at steady state according to eqn (41), for a column of 17 cm. height and 0.17 cm. annulus at 25°C), the

following values of Λc at 25° were obtained from a graph of Λ vs. c (data taken from Landolt-Börnstein ⁸²) for a 20% change in concentration. At $c_1 = 0.008$, $c_2 = 0.010$, and $c_3 = 0.012M$, $\Lambda_1 c_1 = 3.29$, $\Lambda_2 c_2 = 4.11$ and $\Lambda_3 c_3 = 4.92$ respectively. Hence $\frac{\Lambda_2 c_2}{\Lambda_1 c_1} = 0.125 = \frac{c_2}{c_1}$ and $\frac{\Lambda_3 c_3}{\Lambda_2 c_2} = 0.120 = \frac{c_3}{c_2}$.

Therefore, $\left(\frac{R_u}{R_l}\right)_t = \left(\frac{c_1}{c_u}\right)_t$ for small changes in concentration.

Hence, A^* can be calculated from the steady state eqn. (38), (the Horne and Bearman expression for the steady state, eqn.(48) for cylindrical column reduces to the flat cell expressions (eqn.41) since $(2Xr_0) = a = r_1 - r_2$ in the present experiment, the radii r_1 and r_2 being 0.95 and 0.78 cm. respectively), using the measured value of y_∞ (i.e. y_t at steady state) thus :

$$\frac{4 y_\infty}{10^4} = 2 \left(\frac{R_u - R_l}{R_u + R_l} \right)_\infty = 2 \left(\frac{c_1 - c_u}{c_u + c_1} \right)_\infty = \left(\frac{w_l - w_u}{w_u + w_l} \right)_\infty = \frac{1 - e^{-2A^*}}{1 + e^{-2A^*}} \quad (57)$$

$$\text{or } y_\infty = -2500 \tanh A^* \quad (58)$$

For small values of A^* , $\tanh A^* = A^*$, and hence

$$y_\infty = -2500 A^* \quad (59)$$

from which A^* and hence D' can be calculated from the steady state value of y_∞ .

* A more accurate expression is given on p.70.

Procedure of the experiment.

The hot and cold jackets had to be maintained at 34.05°C and 17.7°C for a column of cross-sectional data as given on p. 29, according to the calculations described on page 31, for getting a mean temperature of 25.0°C and a temperature difference across the solution of 5.0°C .

Before filling the column with the solution under study, the column was maintained under isothermal conditions by circulating water from the same thermostat through both the inner and outer jackets. The column was then filled with the solution and the isothermal resistance ratio was measured. The constancy of this ratio was checked over a period of about 20 minutes. The solution was then subjected to the temperature difference and y_t was measured as a function of time.

0.01M LiCl solution was used for the first experiment to check the stability of the resistance ratio under a temperature difference, since its Soret coefficient is very nearly zero.

This was then followed by measurements on several 0.01M solutions of 1:1 electrolytes, for which the Soret coefficients and the diffusion coefficients are known by other methods, so that the separation obtained by these experiments could be compared with the values expected according to equation (58).

The separation obtained in these experiments were about 40% lower than the values calculated according to equation (58). More details of calculation are omitted here since they will be described at length in a later chapter.

The difficulties encountered in the above experiments.

Apart from the theoretical limitations of the equation (38), it was thought that the results could be improved by shifting the end electrodes as far towards the stoppers as possible. Also it was decided to drill holes through the glass walls by an ultrasonic drill instead of using the tungsten wire method, so as to avoid deformations in the glass tubes during the latter procedure.

The other main difficulties encountered in these preliminary experiments were :

(1) Very often after the calibration experiments which used to take about a week, the solution started leaking through the holes where the leads were sealed on to the glass tube, giving rise to electrical leakage and hence irreproducibility of the experiments.

(2) Before filling with different solutions, the rubber stoppers at the ends had to be removed for cleaning them and the column. In order to take care not to break the leads of the electrodes, the column had to be disconnected from the circulation pumps. To avoid these difficulties, in subsequent experiments, the electrode leads were taken out through the end rubber stoppers fitting the cold jackets. Only the lead from the centre-tap electrode was taken out through the wall of the outer jacket.

Eventually the rubber annular stoppers were replaced by polythene stoppers which were carefully ground for the purpose. The lower stopper was sealed into the annular space with "Araldite". The leads of the end ring electrodes were taken out through holes bored in the polythene stoppers, thereby

isolating them from the circulating water. This set-up enabled one to leave the apparatus undisturbed while cleaning the column by just sliding up the polythene stopper at the top. The leads were sealed from the outside into the holes in the polythene stoppers with a drop of "Araldite" so that they could be removed or inserted into the annular space along with the electrodes. This enabled one to maintain a constant electrode to electrode distance in the column. As in the case of the rubber stoppers, two holes through the upper stoppers were bored for filling and air escape and one through the lower stopper for draining or filling the solution.

Unfortunately, after a certain number of runs, the temperature difference produced cracks in the glass tube around the stoppers. Hence the stoppers had to be removed and resealed in a fresh pyrex glass column. Columns of different annular spacings were also used for these experiments.

Column for measuring the separation as a function of height :

A set of experiments was carried out in a short column having nine probe-electrodes and two large ring electrodes at the ends, to find out the dependence of separation on the height of the column.

The apparatus which can be seen in Fig.9 was similar to the one shown in Fig.7 except that nine probe-electrodes were sealed with "Araldite" into the outer tube through holes drilled at regular intervals by a supersonic drill. The distances of the electrodes in cm. from the ring electrode at the top are given below.

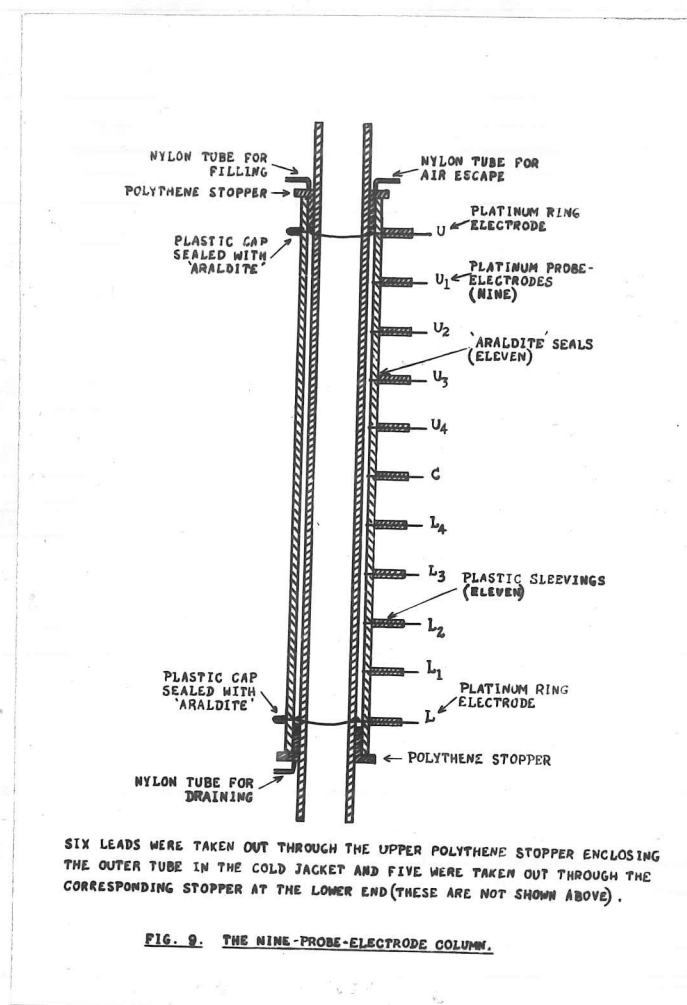
Table III.

The spacings (in cm) of the electrodes: the nine-probe-electrode column.

| Top ring elec- trode (U) | U ₁ | U ₂ | U ₃ | U ₄ | C | L ₄ | L ₃ | L ₂ | L ₁ | Lower ring electrode (L) | |
|--------------------------------------|----------------|----------------|----------------|----------------|------|----------------|----------------|----------------|----------------|--------------------------------|-------|
| | 0.00 | 2.12 | 3.98 | 6.00 | 8.04 | 10.20 | 12.38 | 14.46 | 16.52 | 18.74 | 20.50 |

The annular space was 0.097 cm., the temperature drop across the solution and the mean temperature were 5° and 25°C respectively. The resistance ratio was measured as in the case of the center-tap electrode columns - keeping the total resistance between the top (U) and bottom (L) ring electrodes constant on the bridge at 10000 ohms. The detector Y-plate was connected to the nine-probe-electrodes in succession from top to bottom. The constancy of the resistance ratio at each of the nine-probe-electrodes was tested by using 0.01m solution of LiCl, NaCl, KCl and HCl at isothermal conditions and under a temperature gradient in the case of 0.01m LiCl. Since these resistance ratios must be proportional to the spacings of the probe-electrodes, they are compared in a separate table taking into consideration the measured distance of 20.50 cm. between U and L, the top and bottom ring electrodes.

The thermogravitational separation as a function of the height of the solution in the column was measured for 0.01m HCl solution. All the results are given in Chapter V.



CHAPTER IV.

DESIGN AND CONSTRUCTION OF THE COLUMN AND MEASUREMENT OF CONCENTRATION CHANGE. PART B: THE ALL-GLASS COLUMN.

The all-glass column.

In view of the many difficulties encountered so far in the design of the column it was decided to completely dispense with the problem of stoppers and glue-sealing of the centre-tap electrode. An all-glass column was, therefore, constructed as described below from precision inner bore pyrex glass tubings. This column turned out to be more satisfactory than any other column constructed so far both regards reproducibility of the experiments and higher percentage separation.

The column is of 18.0 cms height and 0.125 cm. annular spacing. The top and bottom electrodes (A and B) (Fig.10a) are rings made of 1 mm. diameter platinum wire. A 24 s.w.g. platinum wire was used for the central electrode (C). Fig.10a represents a diagram of this apparatus.

The lower end of the outer glass tube was carefully fused on to the inner tube so that the distortion of the annular space at the joint did not proceed beyond about 1 cm. The lead of the bottom electrode was sealed (L) into the annular space through a tungsten extension. A small outlet (M) for draining the column was also made. The centre tap electrode (C) was also sealed (K) into the outer glass tube at exactly 9.0 cms above the lower ring electrode (B). These two glass seals (K,L) were made with extreme care so as to leave the

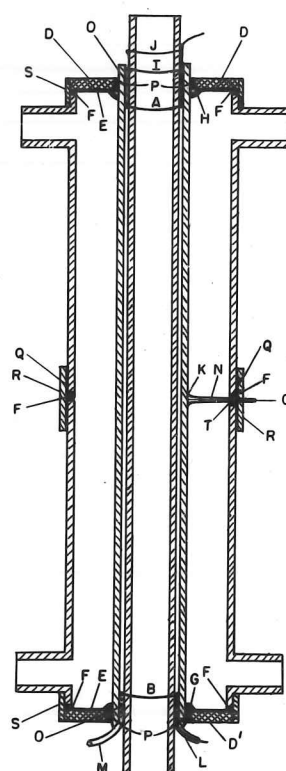


FIG. 10 a. THE ALL-GLASS COLUMN

annular space between the top and bottom ring electrodes as uniform as the precision glass tubings permitted. The bottom and the centre-tap electrodes thus fixed the height of the lower of half of the column. The top end of the column was left open so that the upper electrode (A) could be introduced into the annular space and the lead fastened by a firm rubber-band (J) onto the inner tube. The height of this electrode could be adjusted till the isothermal resistance ratio was exactly unity. A P.T.F.E. O-ring (I) ground to the appropriate size was used to close the upper end of the column to prevent evaporation of the solution in the column. The lower electrode was so sealed that the ring was above the slight distortion produced at the glass seal. This dead space was minimized by filling it with a platinum gauze cylinder (O). For purposes of symmetry, a similar one was used above the top electrode as well. The dead space at either end makes a bit of a reservoir at each end, but the effect is assumed to be negligible.

The jacket outfit for circulation of thermostated water.

This column was fitted into the outer jacket as described below, in such a way as to enable one to dismantle or assemble it without much difficulty.

The outer jacket (Fig.10a) was a 48 mm. glass tube horizontally split approximately in half as shown, so that a small groove (T) of about 2 mm. length could be made in one half for taking the central lead out. Small washers (F) were cut out of a rubber sheet and were stuck on the rims of the split

ends of the jacket, so that on assembling together, they would form a liquid-tight seal.

The column was enclosed in this jacket by means of two metal caps (D,D') on either end of the jacket as follows :

Two brass discs of $1/8"$ thickness and of the outer diameter of the jacket, were cut so as to exactly sit on top of the ends of the jacket. Holes (W) (Fig.10b) of diameter $1/2$ mm. in excess of the outer diameter of the outer glass tube of the column were made at the centres of the two circular metal discs. Three more holes (U) of $1/8"$ diameter were made in each of them (Fig.10b) for fixing the metal caps on either end of the jacket, by means of three vertical rods(V), passing inside the jacket. The metal cap D' for the lower end of the jacket was split along a diameter since the column with the central and lower two glass projections could not be introduced through the hole in the brass cap. Two rubber discs (E) of the same diameter as the metal caps were ^{cut} out of a cycle tube. Three 1 mm. holes were made in them corresponding to the $1/8"$ holes in the metal caps for the vertical rods, so that these holes made a liquid-tight fitting on the rods. A small central hole was made in each for introducing the column, and so as to fit the outer glass tube firmly. Small thin strips of rubber sheet were sealed to both the rims of the inner hole in order to act as washers (P) between the glass and metal. One end of each of the three vertical rods was screwed into the upper metal cap (D) and locked with nuts (not shown in the diagram) so that all three were liquid tight. Small rubber rings (F) (Fig.10a) were cut out of the cycle tube rubber so

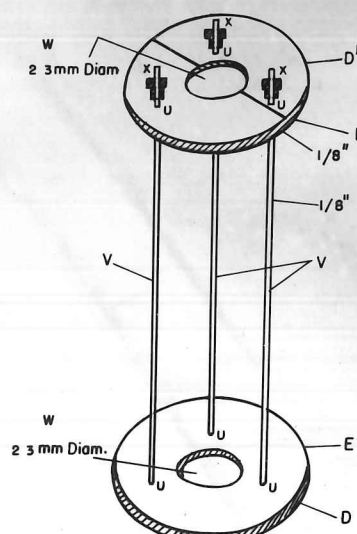


FIG. 10b. THE METAL CAPS AND THE FIXING RODS

as to form washers between the metal and ^{the} glass at the rim of the cold jacket. These washers were sealed to the glass by silicone rubber. A short length of rubber tube was cut of from the neck of a balloon. Half the length was sleeved on a brass cylindrical ring (H) (Fig.10a) of the same inner diameter as the central hole in the metal cap. The other half acted as a tight seal between the outer glass tube of the column and the metal ring. This ring was sealed on to the lower side of the upper metal cap (D). The rubber disc was then passed down the three metal rods on top, of the metal ring, so that the upper end of the column could be passed through the rubber and then the metal discs. The upper side of the column was thus fitted into one half of the jacket.

Keeping this assembly fixed upside down as in Fig.10b on a suitable stand, the lower half of the jacket was assembled as follows : The other rubber disc E was sleeved on the three vertical rods and the column by stretching the holes. A tight fitting rubber O-ring (G) (Fig.10a) was then slid on the outer glass tube of the column above the rubber disc. The lower half of the jacket was then placed in position. The split metal caps were now placed on top and the lower and upper metal caps were held together at either end of the whole jacket by tightening the knurled head brass nuts (X) on the vertical rods at the split metal cap end. The rubber washers (F) at the centre of the jacket made the latter liquid tight. To hold these halves in position, a short length of the cycle tube was stretched and fitted over the same (Q) (Fig.10a). For the sake of extra security, an aluminium cylindrical clamp

(R) (Fig.10a) was also fastened. The little groove (T) through which the insulated lead (N) of the central electrode was taken out, was sealed with silicone rubber. In order to prevent the metal caps at either end from sliding laterally, two small copper cylindrical rings (S) (Fig.10a), the inner diameters of which were equal to the outer diameter of the cold jacket and the metal cap, were fitted at either end so as to hold the latter two together. The assembly after turning upside down was ready for use. A photograph of the assembled apparatus can be seen in the next page.

Before use the column was cleaned with chromic acid and the electrodes were platinized as described on page 40.

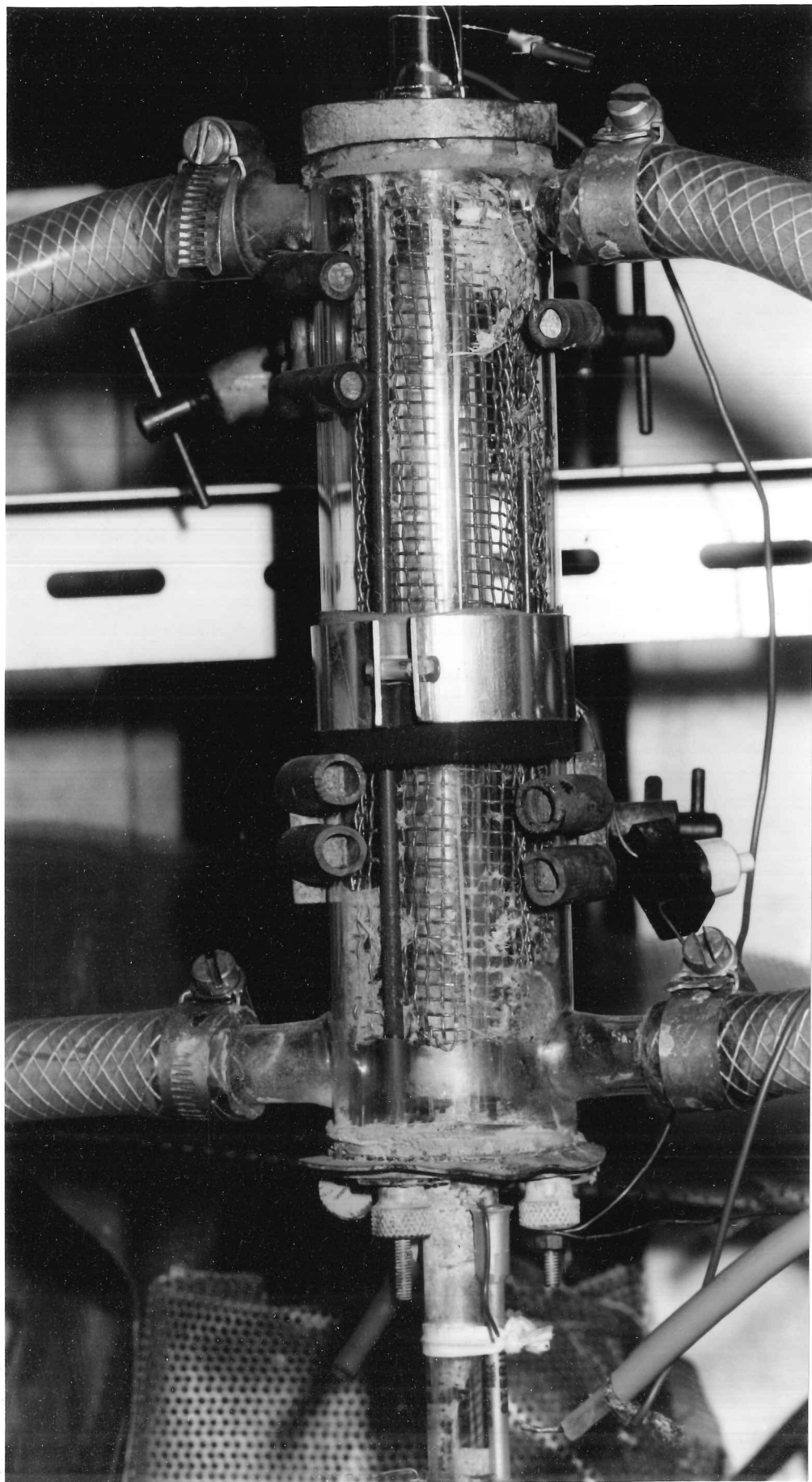
Electrical resistance measurements.

The resistance ratio and the derived quantity y_t were measured by a Wheatstone bridge as described on p.41.

The double ellipse bridge balance display.

To increase the sensitivity of the null-balance method, a double ellipse method described recently by Clothier ⁸³ was used.

In this method the same single ellipse bridge balance circuit described on page 41 was used; but the single ellipse could be split into two ellipses by adding a square wave to the sinusoidal horizontal input to the C.R.O. The square wave was obtained also from the same oscillator which generated the sine wave. By suitably adjusting the frequency and amplitude of the square wave, two identical ellipses could



Photograph I

be obtained side by side on the screen of the oscilloscope, in place of the more usual single ellipse. These ellipses were then closed to two parallel straight lines by balancing the out-of-phase capacitance. The resistances were then adjusted to make them collinear. The collinearity of the two lines can be judged more easily than the horizontality of the line in a single ellipse method, by making a small separation of the two adjacent tips very distinct. Also, a small out-of-balance resistance causes these tips to move in opposite directions and hence the displacement from collinearity is doubled.

Wagner balance method found unnecessary.

Finally one more idea in the technique of measurement of the resistance ratio was tested experimentally :

Since there is always the fear that there might be a slight electrical leakage to earth through the circulating water via the insulation at the centre-tap electrode, it was thought that one could earth the latter itself and dispense with the Wagner arm. The resistance ratio could then be measured straightaway by balancing the same on two resistance boxes.

To test this experimentally, y_t was measured during the entire course of an experiment by both the methods : one, by the usually Wagner balance when the centre-tap is not directly earthed; and the other, with the centre-tap earthed and the column shielded by an earthed copper gauze immersed in the cold jacket, but without the Wagner arm. This was done by using two way switches at appropriate places. This experiment was repeated several times and it was found that y_t measured

by these two methods always differed by a constant small fraction which was the same from the beginning to the end of the course of an experiment.

Some values of resistance measurements during thermogravimational separation are given below for illustration.

T a b l e IV.

Bridge balance resistance with and without Wagner arm.

Electrolyte : 0.01M KCl; $R_u + R_l = 10000$ ohms.

| | (i) | (ii) | |
|---|--|----------------|-----------------------------|
| | Cell centre earth- ed, Wagner arm eliminated | Wagner balance | Diffe- rence (i)-(ii) |
| Isothermal resistance reading on box R_u : | 5021 | 5009 | 12 |
| Resistance reading after 1 hour with temperature difference : | 5030 | 5018 | 12 |

T a b l e V.

Bridge balance resistance with and without Wagner arm.

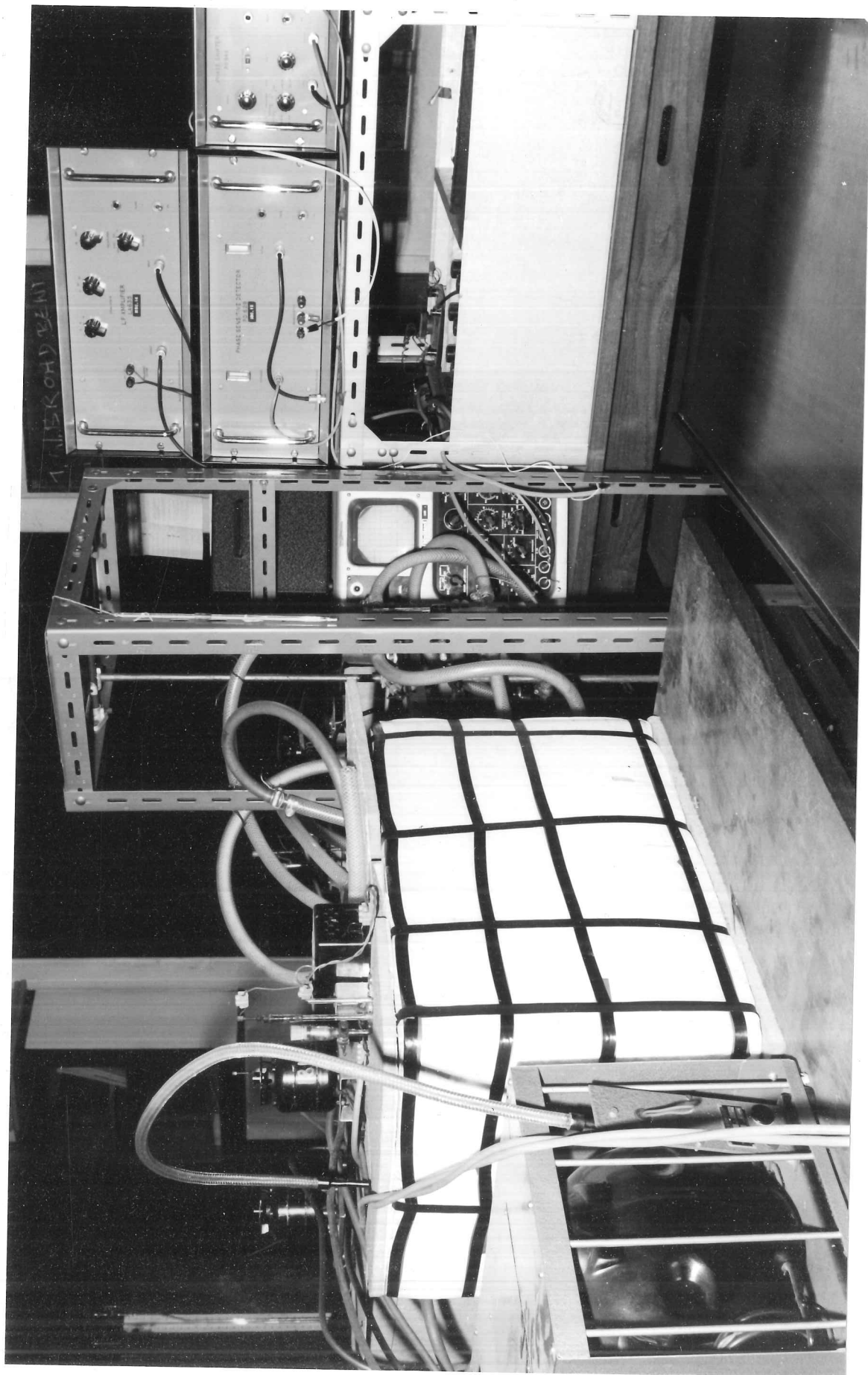
Electrolyte : 0.01M RbCl; $R_u + R_l = 10000$ ohms.

| | (i) | (ii) | |
|---|--|----------------|-----------------------------|
| | Cell centre earth- ed, Wagner arm eliminated | Wagner balance | Diffe- rence (i)-(ii) |
| Isothermal resistance reading on box R_u : | 5006 | 4994 | 12 |
| Resistance reading R_u after 2 hrs. with temperature differ.: | 5052 | 5038 | 12 |
| Steady state reading on box R_u : | 5063 | 5050.5 | 12.5 |

Since in all these experiments one is interested only in the difference between the initial and final values of R_u , the Wagner balance method was found unnecessary. The number of components on the bridge side is, thereby, reduced to only two 4-decade resistance boxes (R_u and R_l) (see Fig.8) and one 150 pF. variable condenser (C_R). Care was taken to see that the centre-tap was earthed properly and the whole column shielded by the earthed copper gauze (see Photograph I.) immersed in the cold jacket.

The bridge network and determination of V_t .

This bridge assembly is shown in the Photograph II. opposite. The offbalance voltage between the centre-tap and the centre of the two decade boxes, R_u and R_l was amplified by a low frequency amplifier and fed to the Y-plates of a cathode-ray oscilloscope. The reference wave was fed to the X-plates through a "phase shifter" from the same 1 kcs. oscillator that fed the bridge. The phase shifter consists of a variable R-C coupling network, which enables the reference wave to be corrected in phase by an amount appropriate to the bridge conditions. This is done by initially getting a null-balance on the C.R.O. by adjusting the two resistances R_u and R_l and the capacitance C_R in parallel with them. The bridge was then deliberately put out of balance by increasing or decreasing the resistance on one of the arms. The ellipse thereby produced was then collapsed to a straight line by adjusting the phase shifter. This adjustment was needed only once - while measuring the initial isothermal ratio. No re-adjustment was



Photograph II

needed during the subsequent course of the experiment. The tilted straight line was then brought back to the horizontal by balancing the resistance R_u and R_l , keeping their sum constant at 10000 ohms. y_t was then calculated as $\frac{R_u - R_l}{2}$ (eqn.55).

Scope of using a recorder for following the course of the separation process.

It may be mentioned at this stage that the off-balance signal from the L.F amplifier can be fed into a "phase-sensitive detector" which compares it with the reference signal coming through the "phase shifter" and gives a rectified output that can be recorded by a potentiometric recorder. In this way one could record the entire course of the separation process as a function of time by using an appropriate potentiometric recorder.

Experimental measurements.

In this column, since the height of the upper electrode could be altered, the initial isothermal resistance ratio R_u/R_l was always adjusted to be exactly unity as follows : The resistances of the upper and lower halves of the solution (for an arbitrary position of the top ring electrode in the column) were first balanced (a) against decade boxes R_u and R_l and then (b) against R_l and R_u respectively by reversing the leads at the upper and lower electrodes. The mean values of the two resistance readings for each of the upper and lower half of the solution were calculated. The upper elec-

trode was then lowered or raised till this mean was exactly 5000 ohm (since $R_u + R_l = 10000$ ohms). The difference between the two resistance readings (a) and (b) say for the upper half solution. When their mean is 5000 ohms was noted down.

For example, in the case of 0.01 M RbCl, the isothermal resistance values on R_u and R_l were as follows : [resistance of the lower half of the solution = (10000 - resistance of the upper half of the solution)] .

T a b l e VI.

The isothermal resistances R_u and R_l ; 0.01M RbCl.

| | (a) | (b) | Mean resistance $\frac{(a) + (b)}{2}$ |
|-----------------------|----------------|----------------|--|
| Upper half solution : | 5012 (R_u) | 5072 (R_l) | 5042 (i) |
| Lower half solution : | 4988 (R_l) | 4928 (R_u) | 4958 (ii) |

The upper electrode was then lowered slightly till the means (i) and (ii) were exactly 5000 each. The resistance readings were :

| | (a) | (b) | Mean Resistance $\frac{(a) + (b)}{2}$ |
|-----------------------|----------------|----------------|--|
| Upper half solution : | 4970 (R_u) | 5030 (R_l) | 5000 (i) |
| Lower half solution : | 5030 (R_l) | 4970 (R_u) | 5000 (ii) |

The resistances of the upper half of the solution measured by (a) and (b) differ by 60 ohms and so also the lower half. This difference of ± 30 ohms of (a) and (b) from the

mean persisted even on using the Wagner balance method. During the entire course of an experiment this difference was checked periodically and was found to be constant.

For instance, in the above experiment on RbCl, the isothermal resistance values (a) 4970 and (b) 5030 of the upper half of solution changed to 5031 and 5091 respectively at steady state. Thus the difference $5031 - 4970 = 5091 - 5030 = 61$. Therefore the mean 5000 changes to 5061.

Since the above difference was a constant during the entire course of an experiment, one had only to note it down while adjusting the initial isothermal resistance ratio to unity. It was then sufficient to record the resistance readings of one of the two resistance boxes, say, R_u , during any experiment. This constant difference between the resistance readings (a) and (b) is perhaps due to some unsymmetry in the electrical field distribution around the centre-tap electrode.

The experiments on the thermogravitational separation of all the electrolyte solutions mentioned in the subsequent chapters were repeated and were found to be reproducible. The values of y_t were plotted as a function of time. All the separation curves were exponential with respect to time, leveling off in the course of two hours. This enabled one to do at least two experiments every day.

AnalaR grade chemicals were used whenever available. Otherwise, the best available grades were used.

Standard solutions of salts were prepared in volumetric flasks by weighing the required amounts of the solid substances, and dissolving them in conductivity water ($\rho > 3$

megohms. cm).

All the acids used were prepared by diluting concentrated A.R. acids and were standardized by titration against standard carbonate-free sodium hydroxide solution.

C H A P T E R V.

COMPARISON OF PERFORMANCE OF THE COLUMN WITH THEORY :
SEPARATION OF 1:1 ELECTROLYTES.

Before presenting the results of the all-glass column, the separation obtained as a function of the height of the solution in the column measured using the nine-probe-electrode column is presented below.

Concentration change as a function of height in the nine-
-probe-electrode column.

Table VII below gives the set of resistance readings on box R_u (which are proportional to the resistance of the solution between the top ring electrode U and the probe-electrode concerned, when the total resistance of the solution between the top and bottom ring electrodes, U and L, is referred to a constant bridge resistance of 10^4 ohms distributed on the two decade boxes R_u and R_l such that $R_u + R_l = 10000$ ohms) obtained for 0.01M LiCl solution at isothermal conditions.

In Table VIII are presented the resistance readings obtained when a temperature difference of 5°C was applied across the LiCl solution (whose Soret coefficient is around zero) at a mean temperature of 25°C .

T a b l e VII.

0.01m LiCl at isothermal conditions (17.38°C).

| Probe-electrode | Time (p.m.) | R_u (ohms) | Time (p.m.) | R_u (ohms) |
|-----------------|-------------|--------------|-------------|--------------|
| U_1 | 4.55 | 1015 | 5.37 | 1015 |
| U_2 | 4.57 | 1981 | 5.40 | 1981 |
| U_3 | 5.00 | 2974 | 5.43 | 2972 |
| U_4 | 5.05 | 3987 | 5.46 | 3986 |
| C | 5.10 | 5026 | 5.48 | 5026 |
| L_4 | 5.15 | 6098 | 5.50 | 6099 |
| L_3 | 5.18 | 7104 | 5.53 | 7105 |
| L_2 | 5.21 | 8126 | 5.56 | 8127 |
| L_1 | 5.26 | 9140 | 5.59 | 9140 |

T a b l e VIII.

0.01m LiCl; temperature difference : 5°C; mean temperature: 25°C

| Probe-electrode | Time (p.m.) | R_u (ohms) | Time (p.m.) | R_u (ohms) |
|-----------------|-------------|--------------|-------------|--------------|
| U_1 | 6.45 | 1021 | 10.03 | 1021 |
| U_2 | 6.50 | 1989 | 10.00 | 1989 |
| U_3 | 6.55 | 2979 | 9.58 | 2973 |
| U_4 | 6.58 | 3985 | 9.54 | 3983 |
| C | 7.02 | 5018 | 9.51 | 5017 |
| L_4 | 7.05 | 6085 | 9.48 | 6083 |
| L_3 | 7.09 | 7090 | 9.45 | 7088 |
| L_2 | 7.11 | 8117 | 9.42 | 8115 |
| L_1 | 7.15 | 9138 | 9.37 | 9135 |

The constancy of the resistance readings with time in both the above tables indicates the absence of electrical and liquid leakage in the column.

The isothermal readings for 0.01m LiCl are compiled below with those obtained in the case of 0.01m NaCl, KCl and HCl solutions.

T a b l e IX.

Balancing resistance readings, R_u , at isothermal conditions (17.38°C) for 0.01m electrolyte solutions.

| Probe-electrode | LiCl | NaCl | KCl | HCl | Average |
|-----------------|------|------|------|------|---------|
| U_1 | 1015 | 1031 | 1017 | 1035 | 1025 |
| U_2 | 1981 | 2003 | 1990 | 2019 | 1998 |
| U_3 | 2972 | 2996 | 2984 | 3007 | 2990 |
| U_4 | 3986 | 4004 | 3988 | 4000 | 3994 |
| C | 5026 | 5039 | 5020 | 5016 | 5025 |
| L_4 | 6099 | 6107 | 6084 | 6067 | 6089 |
| L_3 | 7105 | 7110 | 7087 | 7058 | 7090 |
| L_2 | 8127 | 8132 | 8112 | 8087 | 8115 |
| L_1 | 9140 | 9139 | 9129 | 9120 | 9132 |

Since the above average isothermal resistance values must be proportional to the spacings of the probe-electrodes along the column, they are compared below with the measured distances presented in Table III. In the table below, the average values of the least column in Table IX have been multiplied by the factor $20.5/10^4$ where 20.5 cm. is the distance between

U and L (Fig.9).

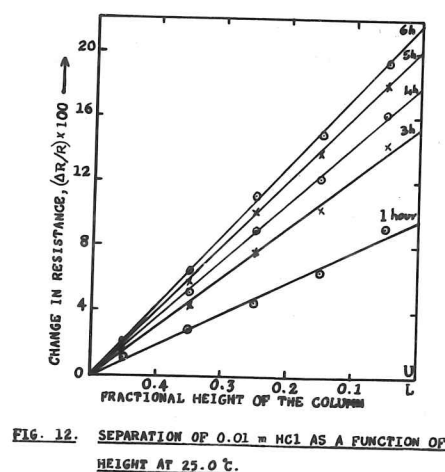
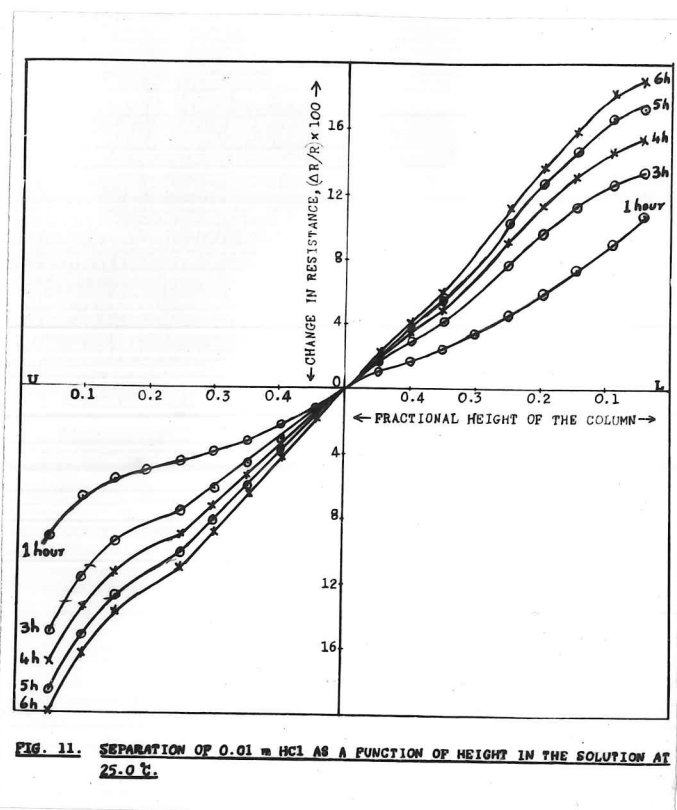
T a b l e X.

Comparison of the ratio of the average isothermal resistance
with the measured spacing.

| Electrodes | Measured distance (cm) | Calculated from elec- trical resistance (cm) |
|----------------|---------------------------|--|
| U | 0.00 | 0.00 |
| U ₁ | 2.12 | 2.10 |
| U ₂ | 3.98 | 4.00 |
| U ₃ | 6.00 | 6.13 |
| U ₄ | 8.04 | 8.19 |
| C | 10.20 | 10.30 |
| L ₄ | 12.38 | 12.48 |
| L ₃ | 14.46 | 14.53 |
| L ₂ | 16.52 | 16.63 |
| L ₁ | 18.74 | 18.72 |
| L | 20.50 | 20.50 |

Thus the agreement of the calculated and measured spacings seems to be good.

The separation of 0.01M HCl solution was measured as a function of height. A set of graphs of resistance readings vs. time was plotted for each of the probe-electrodes. From these graphs, the instantaneous resistance reading at any time at different heights could be obtained. It has been assumed that the resistance R_u measured at any probe-electrode, say U_1 ,



corresponds to concentration changes occurring at a height midway between U and U_1 . The percentage resistance change calculated as 100 (resistance reading at any time-isothermal resistance readings) \div isothermal resistance reading was then plotted as a function of height. These curves representing the concentration change at different heights and at different times after the start of the experiment can be seen for 0.01M HCl in Fig.11. U and L represent the top and bottom ring electrodes and O the mid-point between the two ring electrodes. The distance between the latter is divided into ten equal units. The middle regions of the curves are linear whereas the ends of the curves seem to reflect the convective stirring at the closed ends of the column.

These curves have been replotted in Fig.12 taking the mean of the percentage separation at equal distances on either side of the centre of the column. Fig.12 thus shows that the percentage separation increases linearly from the centre towards the extremities of the column. The important point that emerges out of this experiment is that the separation measured at the central electrode C, which corresponds to the concentration change occurring at a fractional height of 0.25 from either end of the column, is half the change at the ends at all times as seen by extrapolation of the straight lines to zero fractional height.

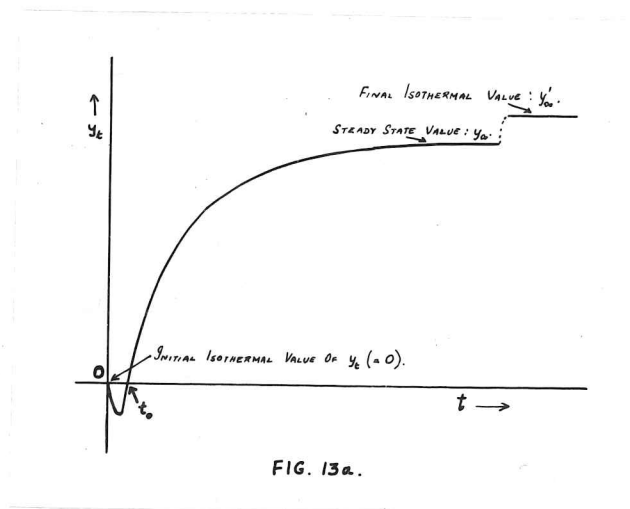
The column could not be used for more than the preliminary few experiments on 0.01M solutions of sodium and potassium chlorides since leakage at the electrodes once again was a difficult factor to control. These results have therefore not

been presented.

Results obtained with the centre-tap all-glass column :

The all-glass column described on pp.49-53 and represented in Fig.10a was used for all the results presented in the following pages. Aqueous solutions of 1:1 electrolytes of known diffusion and Soret coefficients were first used for separation in order to check the theoretical equation (41) for the thermogravitational column without reservoirs.

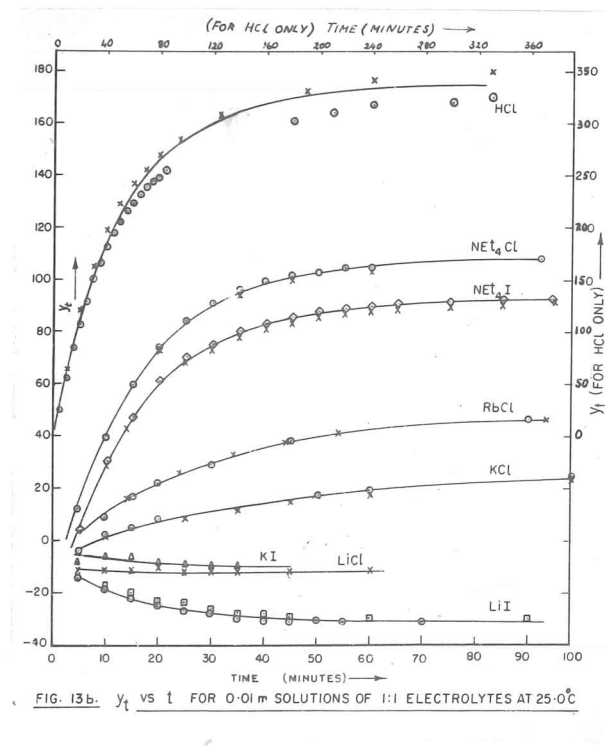
The shape of a typical separation curve is presented below (Fig.13a). The origin represents the point when the temperature difference is just switched on after the initial isothermal state, usually at the lower temperature. The curve exhibits an initial decrease in y_t which then passes through a minimum and then follows an exponential course reaching the steady state in the course of about two hours. The minimum value of y_t of about 9 always occurs within two minutes after switching on the temperature difference. This minimum is probably due to the decrease in the resistance of the solution/ⁱⁿ the top half caused by the rise of the hot solution along the hot wall immediately after the temperature difference is switched on, which causes the average temperature of the upper half of the column to rise slightly above that of the lower half. A similar observation has been reported ⁶² for experiments on pure Soret cells. But this temperature effect in the column, though similar in principle, is much smaller than in pure Soret cells. After the establishment of the steady state, when the temperature difference was reduced to zero by circulation



of water from the same thermostat through both the jackets, the vertical concentration profile was not destroyed; on the other hand, the steady state value of y_t increased by exactly the same amount as the initial decrease at the beginning of the experiment. This observation seems to support the idea of the temperature effect on the resistance at the initial minimum. The value of y'_{∞} (for calculation of D') was therefore taken as the difference between the initial isothermal value of y_t (i.e. $y_t = 0$) and the final isothermal value, y'_{∞} , which was usually the steady state value of $y_{\infty} + 9$ or occasionally $y_{\infty} + 10$.

It is interesting to note here that the vertical concentration difference at steady state persists even after cutting off the temperature difference. This fact could perhaps be used for the measurement of isothermal diffusion coefficient.

All the results are presented in the form of graphs of y_t as a function of time (Fig. 13b). The solutions chosen were 0.01m LiCl, KCl, RbCl, NEt_4Cl , HCl, LiI and KI. The range of



diffusion and Soret coefficients covered were from $1.155 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$ for NET_4Cl to $3.2 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$ for HCl and from 0.02×10^{-3} per degree for LiCl to 9.00×10^{-3} per degree for HCl respectively. Fig. 13b. also shows the separation curve for NET_4I for which only the diffusion coefficient can be calculated from theoretical equations. This substance was chosen to illustrate the calculation of thermal diffusion coefficient from the thermogravitational separation curves.

All the separation curves were found to obey the following exponential equation,

$$y_t = y_\infty [1 - \exp(-\alpha(t - t_0))] \quad (60)$$

where t_0 is the time taken for y_t to become zero after passing through the initial minimum, y_∞ is the steady state value and α is ^{a function of} the curvature of the plots.

The equation can also be taken in the form,

$$(y_t - y_0) = (y_\infty - y_0) (1 - e^{-\alpha t}) \quad (61)$$

where y_0 is the interpolated value of y_t at $t = 0$ in the imaginary case of no initial minimum. Since we are not concerned with the initial correction taken in the form of either y_0 or t_0 for the calculation of the thermal diffusion coefficient, equation (60) was chosen for the convenience of graphical calculation of y_∞ and α , and the initial correction t_0 .

The graphical calculation of the constants y_∞ , α , and t_0 are carried out as follows, as in the case of kinetic reactions of the first order ⁸⁴.

Step (i).

Since at time t'

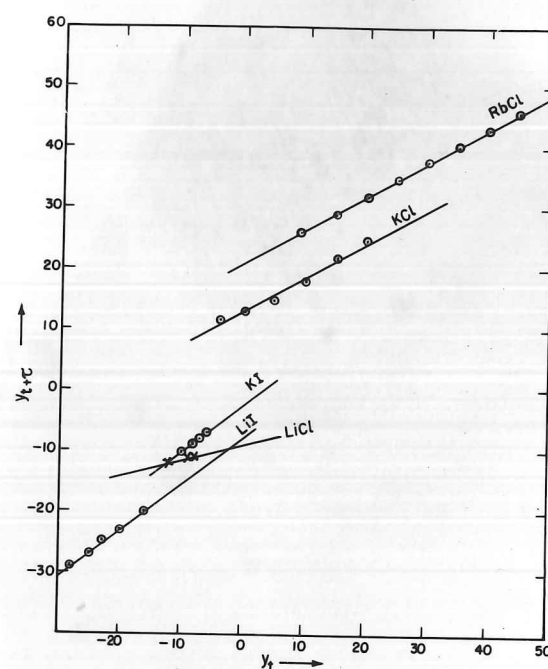


FIG. 14. $y_{t+\tau}$ vs y_t FOR 0.01m SOLUTIONS OF ELECTROLYTES AT 25.0°C

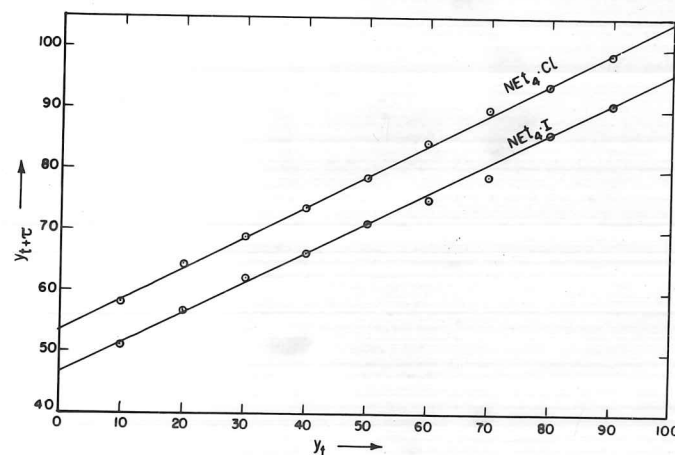


FIG. 15. $y_{t+\tau}$ vs y_t FOR 0.01m SOLUTIONS OF NET_4Cl AND NET_4I AT 25.0°C

$$y_\infty - y_t = y_\infty \exp(-\alpha(t - t_0)) \quad (60')$$

at time $t + \tau$,

$$y_\infty - y_{t+\tau} = (y_\infty - y_t) e^{-\alpha\tau} \quad (62)$$

or

$$y_{t+\tau} = y_\infty (1 - e^{-\alpha\tau}) + y_t e^{-\alpha\tau} \quad (62)$$

If we choose a constant time interval τ , then a plot of $y_{t+\tau}$ vs. y_t must give a straight line with slope $e^{-\alpha\tau}$ and intercept $y_\infty (1 - e^{-\alpha\tau})$ at $y_t = 0$. Hence α and y_∞ can be calculated.

Choice of τ :

Let $y_{t+\tau} = y_\infty / n$ when $y_t = 0$.

Then $e^{-\alpha\tau} = 1 - 1/n$ from equation (62).

When $y_{t+\tau} = y_\infty / 4$, $n = 4$, $e^{-\alpha\tau} = 3/4$; $\tau = 1/2 \ln 4/3 = t_{1/4}$

When $y_{t+\tau} = y_\infty / 2$, $n = 2$, $e^{-\alpha\tau} = 1/2$; $\tau = 1/2 \ln 2 = t_{1/2}$

When $y_{t+\tau} = (3/4)y_\infty$, $n = 4/3$, $e^{-\alpha\tau} = 1/4$; $\tau = 1/2 \ln 4 = t_{3/4}$.

Since (i) τ will be maintained constant,

(ii) it is better to have large number of points on the graph ($\therefore n \neq$)

and (iii) $e^{-\alpha\tau}$ has to be appreciably < 1 ($\therefore n \neq$),

τ was chosen to be very nearly $t_{1/2}$.

Graphs 14 - 16 represent the $y_{t+\tau}$ vs. y_t plots for all the electrolytes presented in Fig. 13b.

Step (ii).

For the determination of t_0 , the time when the experimental curve crosses $y_t = 0$, the values of α and y_∞ were used in the equation written in the form,

$$\ln(y_\infty - y_t) = \ln y_\infty + \alpha t_0 - \alpha t \quad (63)$$

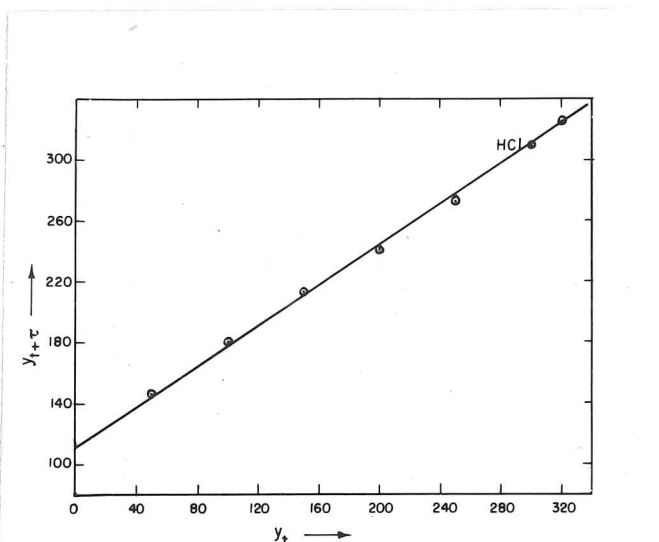


FIG. 16. $y_{t+\tau}$ vs y_t FOR 0.01 m SOLUTION OF HCl AT 25.0°C

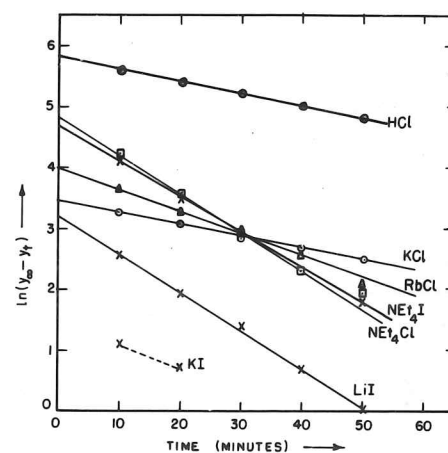


FIG. 17. $\ln(y_{\infty} - y_t)$ vs t FOR 0.01 m SOLUTIONS OF 1:1 ELECTROLYTES

and $\ln(y_{\infty} - y_t)$ was plotted against t , t_0 was calculated from the intercept and from the slope α was again obtained, its value being the same as that obtained in step (i). Fig. 17 shows the linear dependence of $\ln(y_{\infty} - y_t)$ on t .

Step (iii).

These values of y_{∞} , α and t_0 were used in equation (60), and the curves passing through the experimental points were drawn.

N.B. - Steps (i) and (ii) obviously need calculation of the slopes and intercepts by the least square method. The small error involved in not doing so shows up in step (iii). This was corrected by a minor parallel-shifting of the curves. The values of α , t_0 , and y_{∞} were once again calculated for the best-fitting curves.

All the values are tabulated in Table XI.

It has been shown by Agar and Turner⁶² that the ratio y_t has to be corrected by a factor $b_{01} = (1 + \frac{d \ln \Lambda}{d \ln m})$ for the variation of conductance with concentration during the course of the experiment. The values of y_{∞}' will therefore have to be multiplied by $1/b_{01}$ before finding the value of D' . b_{01} can be found from a graph of $\log \Lambda$ vs. $\log m$ from the conductivity values available in the literature.

The thermal diffusion coefficient, D' , was calculated from the corrected equation (59)

$$y_{\infty}' / b_{01} = -2500 A^* \quad (64)$$

$$A^* = (-252 D' h) / (\beta \rho g / \eta) a^4 \quad (33)$$

where $h = 18.0$ cm, $a = 0.125 \pm 0.005$ cm, $\beta = 2.555 \times 10^{-4}$

deg^{-1} , $\rho = 0.9971 \text{ gm/cm}^3$, $g = 980 \text{ cm/sec}^2$ and $\eta = 0.008949$ poise.

Hence,

$$y_{\infty}' / b_{01} = (1.70 \pm 0.25) \times 10^9 D' \quad (65)$$

Since y_{∞}' / b_{01} is known, D' can be calculated from the above equation (65) or graphically from a straight line of slope 1.7×10^9 passing through the origin, y_{∞}' / b_{01} being the ordinate. Fig. 18a represents the straight line.

The D' obtained from this straight line thus represents the value expected from the theoretical equations containing the geometrical constants of the apparatus (a^4 and h) and the physical properties of the solution (β , ρ and η).

The rather large estimated error of $\pm 0.25 \times 10^9$ in the slope of the straight line 18a is due to the uncertainty in the measured value of the annular space which occurs as the fourth power in the steady state equations (64) and (33).

Equation (60) written in the form,

$$\ln [y_{\infty}' / (y_{\infty}' - y_t)] = \alpha (t - t_0) \quad (66)$$

can also be used to find $(t_{1/2} - t_0)$, corresponding to the half time of a first order reaction,

$$\alpha (t_{1/2} - t_0) = \ln 2 \quad (67)$$

when $y_t = y_{\infty}' / 2$.

All the parameters of the separation curves are collected together in Table XI, along with the values of b_{01} and D' .

T a b l e X I.

Parameters of the separation curves for 0.0100M solutions of 1:1 electrolytes at 25.0°C (experimental data : All-glass column, $h = 18.0$ cm., $a = 0.125$ cm. and $\Delta T = 5.0^\circ\text{C}$)

| | KCl | RbCl | NEt ₄ Cl | HCl | LiCl | NEt ₄ I | LiI | KI |
|---|-------|-------|---------------------|----------------------|-------|----------------------|-------|-------|
| y_∞ | 25 | 48 | 109 | 336 | -12 | 93 | -31 | -10 |
| α (min ⁻¹) | 0.030 | 0.038 | 0.063 | 0.020 | - | 0.062 | 0.064 | - |
| $t_{1/2}$ - t_0 (min.) | 23 | 18 | 11 | 35 | - | 10.5 | 11 | - |
| $b_{ol}^{(62)}$ | 0.972 | 0.971 | 0.969 | 0.97 ⁽⁸²⁾ | 0.969 | 0.97 ⁽⁸²⁾ | 0.969 | 0.975 |
| $10^8 D'$ (cm ² . sec ⁻¹ . deg ⁻¹) | 2.1 | 3.5 | 7.1 | 21.0 | -0.25 | 6.2 | -1.3 | -0.1 |

Discussion.

The steady state separation :

The published Soret and mutual diffusion coefficients of the electrolytes chosen for study are given in Table XII. Their product, the thermal diffusion coefficient, is given in the next row. This will be referred to as D'_{lit} . In the Fig.18, the straight line b shows the graph of the experimental y_∞ / b_{ol} values against D'_{lit} . It is to be noted that the straight line dependence of y_∞ / b_{ol} vs. D'_{lit} confirms for the first time, the linearity of the relation (eqn.64) between the steady

Table XI.

Parameters of the separation curves for 0.0100m solutions of 1:1 electrolytes at 25.0°C (experimental data : All-glass column, $h = 18.0$ cm., $a = 0.125$ cm. and $\Delta T = 5.0^\circ\text{C}$)

| | KCl | RbCl | NEt ₄ Cl | HCl | LiCl | NEt ₄ I | LiI | KI |
|---|-------|-------|---------------------|----------------------|-------|----------------------|-------|-------|
| y_∞ | 25 | 48 | 109 | 336 | -12 | 93 | -31 | -10 |
| α (min ⁻¹) | 0.030 | 0.038 | 0.063 | 0.020 | - | 0.062 | 0.064 | - |
| $t_{1/2}$ | 23 | 18 | 11 | 35 | - | 10.5 | 11 | - |
| $-t_0$ (min.) | | | | | | | | |
| $b_{ol}^{(62)}$ | 0.972 | 0.971 | 0.969 | 0.97 ⁽⁸²⁾ | 0.969 | 0.97 ⁽⁸²⁾ | 0.969 | 0.975 |
| $10^8 D'$ (cm ² . sec ⁻¹ . deg ⁻¹) | 2.1 | 3.5 | 7.1 | 21.0 | -0.25 | 6.2 | -1.3 | -0.1 |

Discussion.

The steady state separation :

The published Soret and mutual diffusion coefficients of the electrolytes chosen for study are given in Table XII. Their product, the thermal diffusion coefficient, is given in the next row. This will be referred to as D'_{lit} . In the Fig.18, the straight line b shows the graph of the experimental y_∞/b_{ol} values against D'_{lit} . It is to be noted that the straight line dependence of y_∞/b_{ol} vs. D'_{lit} confirms for the first time, the linearity of the relation (eqn.64) between the steady

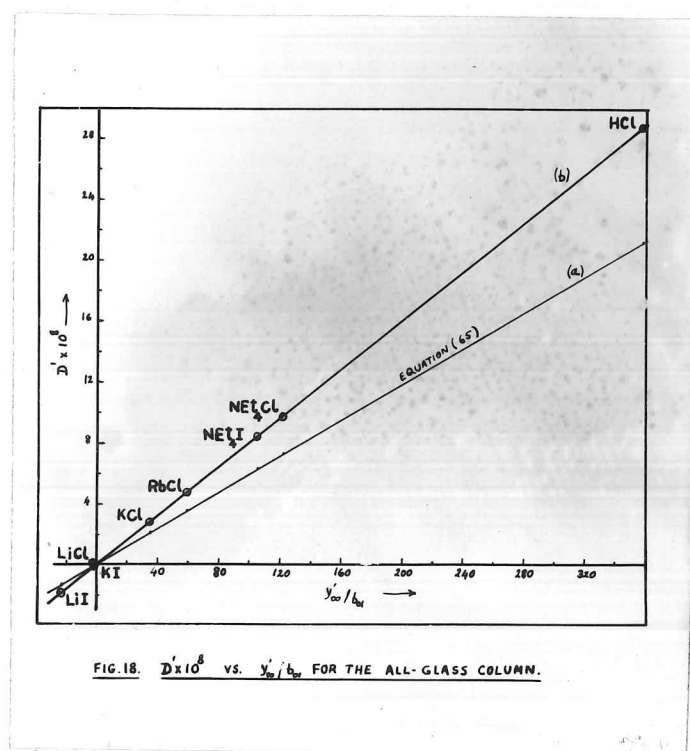


FIG.18. $D' \times 10^8$ vs. y_∞/b_{ol} FOR THE ALL-GLASS COLUMN.

N.B. In the text, y_∞/b_{ol} is the ordinate.

state separation and D' for dilute solutions and for small values of A^* for a thermogravitational column without reservoirs.

T a b l e XII.

Thermal diffusion coefficients of 0.0100M solutions of electrolytes at 25.0°C. (Data from Literature.)

| | KCl | RbCl | NEt ₄ Cl | HCl | LiCl | LiI | KI |
|---|-------|-------|---------------------|---------------------|-------|-------|-------|
| $10^3 \sigma^{-78}$ (deg ⁻¹) | 1.41 | 2.37 | 8.41 | 9.00 | 0.02 | -1.44 | -0.08 |
| $10^5 D^{62}$ (cm ² . sec ⁻¹) | 1.914 | 1.971 | 1.155 | 3.2 ⁽⁸⁰⁾ | 1.311 | 1.315 | 1.920 |
| $10^8 D'_{lit}$ (cm ² . sec ⁻¹ . deg ⁻¹) | 2.70 | 4.67 | 9.71 | 28.80 | 0.026 | -1.89 | -0.15 |

Comparison of the thermal diffusion coefficients obtained by the use of equation (64) and the geometrical constants of the apparatus, with the D'_{lit} values is made by the slopes of the two straight lines in the Fig.18. The slopes of ^{the} lines a and b are 1.70×10^9 and 1.25×10^9 respectively. If we assume the D'_{lit} values as accurate, then it is possible to consider the ratio of the slopes of lines a and b as the calibration factor for the thermogravitational column. This enables one to determine the thermal diffusion coefficient D' of any substance from the straight line Fig.18b from a knowledge of its steady state separation.

The design of the thermogravitational column and the technique of measurement of the concentration changes "in situ" have thus for the first time enabled a comparison of the separations obtained in^a thermogravitational column with those obtained in convectionless pure Soret cells by others. The cause of the actual discrepancy between the experimental D' values and the D'_{lit} values is considered below in the light of the errors that are likely to arise on account of the following reasons :

(1) The approximations involved in the theory during the derivation of the equation for the steady state (eqn.41).

(2) Of the geometrical constants involved in the equation for the steady state separation, the annular space which appears as the fourth power must be accurately known since it is of the order of 0.1 cm. Also the spacing must be uniform throughout the length of the column. Since the precision glass tubings used for the construction of the apparatus had only their inner diameter^s of uniform specified precision, the nonuniformity of the outer diameter of the inner tube contributed mainly to the non-uniformity of the annular space. The average deviation of the annular space from the mean value thus becomes considerable. The value of the annular space was thus found to be 0.125 ± 0.005 cm by weighing conductivity water occupying different heights in the column at 25°C. This gives rise to an error of $\pm 0.25 \times 10^9$ in the slope of the straight line "a" (vide eqn.65) in Fig.18.

The theoretical slope of 1.70×10^9 reduces to the observed slope of 1.25×10^9 for as small an increase as 1/100 cm. in

the measured value of the annular space. The effect of the small irregularities in the non-precision outer diameter of the inner tube on the steady state separation perhaps makes the effective annular space higher than the measured value.

(3) Another factor that might be responsible for the low values of y_{∞} is the fact that the upward and downward convection currents may produce some stirring at the top and bottom closed ends where their directions are reversed. These end effects may be rather important and may affect the separation over a considerable length of the column at either ends. The steady state separation may thus be reduced.

(4) A more accurate experiment on the extent of thermogravitational separation as a function of the height in the column might possibly give a factor of $< 1/2$ for the separation at $1/4$ or $3/4$ height. The separation at the ends may therefore be more than double that at $\frac{1}{4}$ or $3/4$ half height. It is likely that this might be connected with the end effects discussed above.

If we consider the 26% discrepancy between the observed and the literature values of D' as due to equal contributions by (2) and the end effects (3) and (4), then a +0.005 cm. increase in the annular space above the measured value of 0.125 cm. and a 13% reduction in the separation due to the end effects, is sufficient to fill the gap.

The forgotten effect has been shown to have no influence on the steady state separation ⁵⁰ (vide Chapter II.).

In view of the many possible sources of error that can account for the lower experimental values of D' (Table XI.) and

in the context of the lack of existence of a better theory for the thermogravitational separation, the results seem satisfactory.

The straight line, Fig.18b, which is a plot of the experimental y'_{∞} / b_{01} value against the D'_{lit} , can be considered as the calibration graph for the all-glass column.

Thermal diffusion coefficient, Soret coefficient and heat of transport of 0.01M tetraethylammonium iodide at 25.0°C.

Tetraethylammonium iodide was chosen as a demonstrative example, since neither its thermal diffusion coefficient nor its Soret coefficient has yet been determined.

The final isothermal steady state value y'_{∞} was found (Fig.13b) to be $93 + 9 = 102$. When corrected for b_{01} , the value of $y'_{\infty} / b_{01} = 102 / 0.97 = 105$. From the straight line b in Fig. 18, its thermal diffusion coefficient is $8.4 \times 10^{-8} \text{ cm}^2 \cdot \text{sec}^{-1} \cdot \text{deg}^{-1}$.

The heat of transport, \hat{Q} , was then calculated from D' as follows :

The equation for the isothermal diffusion coefficient (ignoring the small electrophoretic term) ⁸⁰,

$$D = \frac{2RT}{F^2} \left(\frac{\lambda_+^0 + \lambda_-^0}{\lambda_+^0 + \lambda_-^0} \right) \left(1 + \frac{d \ln \gamma}{d \ln m} \right) \quad (68)$$

can be combined with equation (10) for the heat of transport,

$$\hat{Q} = \hat{Q}_+ + \hat{Q}_- = 2RT^2 \left(1 + \frac{d \ln \gamma}{d \ln m} \right) \sigma \quad (10)$$

to get the relation between D' and \hat{Q} ,

$$D' = D\sigma = \left(\frac{\hat{Q}}{T}\right) \frac{1}{F^2} \left(\frac{\lambda_+^0 + \lambda_-^0}{\lambda_+^0 + \lambda_-^0}\right) \quad (69)$$

$$\text{or } \hat{Q} = T F^2 \left(\frac{\lambda_+^0 + \lambda_-^0}{\lambda_+^0 + \lambda_-^0}\right) D' \quad (70)$$

where λ_+^0 and λ_-^0 are the limiting ionic conductivities of the cation and the anion respectively.

The limiting ionic conductivities λ_+^0 and λ_-^0 were found to be 32.6 and 74.8 respectively ⁸⁰ for the NEt_4^+ and I^- ions. Using eqn.(70), the value of $\hat{Q} = 2435$ cal/mole was obtained for the heat of transport.

From the activity coefficient data of Lindenbaum and Boyd ⁸⁵, the value of $(1 + d \ln \gamma / d \ln m)$ was found to be 0.975. The Soret coefficient, σ , could then be calculated from eqn.(10) as $71 \times 10^{-3} \text{ deg}^{-1}$.

Comparison with the data in literature:

Agar, Turner and Snowdon have estimated the ionic heats of transport, \hat{Q}_+ and \hat{Q}_- of the NEt_4^+ and the I^- ions in their several articles ^{62,66,67,78}. The average value of their sum, $(\hat{Q}_+ + \hat{Q}_-)_{\text{lit}}$ was found to be 2424 cal/mole, which is in close agreement with the above experimental value, $\hat{Q} = 2435$ cal/mole.

From the \hat{Q}_{lit} value, D'_{lit} and σ_{lit} could be calculated using eqns. (70) and (10) respectively. Thus, $D'_{\text{lit}} = 8.35 \times 10^{-8} \text{ cm}^2 \cdot \text{sec}^{-1} \cdot \text{deg}^{-1}$ and $\sigma_{\text{lit}} = 7.05 \times 10^{-3} \text{ deg}^{-1}$.

Incidentally, since the value of D has not been experimentally determined in the literature, it was calculated from eqn.(69) and was found to be $1.185 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$.

Thus the agreement of the experimental and the literature

values seems good.

Approach to the steady state.

The characteristic time θ , which governs the approach to the steady state, was calculated from the equation (40), which when $A^*{}^2$ is omitted in comparison with π^2 becomes,

$$\theta = 10,080 \left(\frac{h}{\pi a^3} \right)^2 \left(\frac{6\eta}{\beta \rho_g \tau} \right)^2 D \quad (71)$$

But Debye ⁷⁰ gets a smaller numerical coefficient of 7,680.

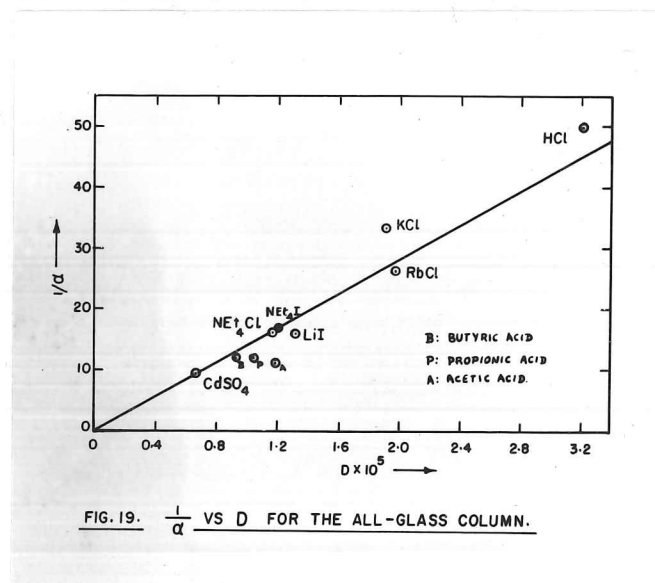
Comparison of equations (39) and (60) shows that $1/\alpha$ must be proportional to θ and hence to D . A plot of $1/\alpha$ vs. D must therefore be a straight line. Fig.19 shows such a graph for the 1:1 electrolytes studied. The graph includes a point corresponding to the data obtained for 0.01m CdSO_4 (Chapter VI). Also points corresponding to the values for 0.01m acetic, propionic and n-butyric acids (Chapter VII) have been incorporated. The values of $1/\alpha$ used in the Figure correspond to concentration changes at 1/4 and 3/4 of the column height and therefore to half the effective length of the column.

The observed straight line confirms the linear dependence of the characteristic time on the diffusion coefficient as required by eqn.(71). The slope of the straight line was found to be 14.0×10^5 . Hirota ⁴⁰ has also observed a linear dependence of θ upon D in a column without reservoirs.

Substitution of the numerical values of the various parameters (p.70; with $h = 18.0$ cm) in the equation for θ gives,

$$\theta = 26.8 \times 10^5 D \text{ mins} \quad (72)$$

and Debye's equation gives



$$\theta = 20.4 \times 10^5 D \text{ min.} \quad (73)$$

Thus the experimental slope is slightly more than half the numerical coefficients of D in equations (72) and (73). $1/\alpha$ must therefore be about $\theta/2$.

In the theoretical equation (71) for θ , since the annular space 'a' appears as the sixth power, θ is very sensitive to errors in 'a'. As in the case of the steady state separations which suggest about +8 % error in 'a', the average calculated value of θ from equations (72) and (73) also demands nearly the same error in 'a' if $1/\alpha$ must be equal to θ .

The effective height of the solution in the column is probably less than the geometrical electrode-to-electrode distance due to the end effects mentioned on p.75. Thus, a 22% reduction in the actual height of the solution (i.e. $h_{\text{effective}} = 0.78 h_{\text{actual}}$) can also explain the observed low values of $1/\alpha$.

As on p.75, if we assume equal contributions from errors arising from both the above two sources, then a 4% increase in 'a' and an 11% reduction in the measured value of 'h' will eliminate the difference between the calculated value of θ and the observed value of $1/\alpha$. It is thus worth noting that the lower experimental values of y_{∞} and θ than the theoretically expected values can both be explained by errors of the same magnitude in 'a' as well as in 'h'.

According to Bardeen's equation (43) for small values of t/θ , the separation depends linearly on $t^{1/2}$. From the slope of the straight line, the Soret coefficient can be calculated. But, in the present set of experiments, such a de-

pendence was not found probably because of the low characteristic times.

Conclusions.

The all-glass column and the measuring circuit for the study of separation of dilute electrolyte solutions have been the first of their kind in many respects which are listed below :

(i) The column is of all-glass design, so that it can be used for electrolyte solutions of all kinds without any fear of contamination by adhesive cements or rubber stoppers. It can be cleaned easily without disconnecting it from the rest of the apparatus. The distance between the end electrodes can always be maintained at the same constant value for all experiments since the centre-tap and the lower electrodes are glass-sealed.

(ii) The resistance ratio method previously used for studying the concentration changes in pure Soret cells ^{62,63} has been successfully adapted for the study of thermogravitational separation. The separation of dilute electrolyte solutions has thus been studied "in situ" in a column without reservoirs.

(iii) The column gives a sufficiently large separation in a short time thereby enabling experiments to be carried out quickly.

(iv) It is worth noting that the separation curves are of exponential form and the linearity of the separation vs. thermal diffusion coefficient predicted by the steady state equation (64) for dilute solutions is confirmed. A comparison

of theory with experiment has been made and it has been possible to compare the results obtained with those obtained for pure Soret cells.

(v) The technique of measurement of concentration changes "in situ" and the design of the column have considerably reduced the discrepancy between theory and experiment found in previous research work.

(vi) It has been shown that Wagner earth is not necessary for the resistance ratio method.

(vii) The design of the circuit enables the use of a potentiometric recorder for the continuous recording of the course of the experiment.

(viii) The use of the method for the determination of D' and hence $\frac{\sigma}{Q}$ and σ has been demonstrated.

CHAPTER VI.

EFFECT OF INITIAL CONCENTRATION ON SEPARATION: (i) POTASSIUM CHLORIDE AND (ii) CADMIUM SULPHATE.

The dependence of thermogravitational separation on the concentration of the electrolyte solution was studied in the case of KCl and CdSO_4 whose diffusion coefficients differ widely from each other. The aim was to compare their Soret coefficients and heats of transport over a wide range of concentration with the available data in the literature obtained by different methods. Studies on KCl were extended from 10^{-4}m . up to 2.0m ., since a comparison of the results obtained by Snowdon and Turner ⁷⁸ at lower concentrations by conductimetric methods with those obtained by Longworth ⁸⁶ and by Channu ⁵³ at higher concentrations by optical methods indicates the presence of a minimum in the plots of Soret coefficient and heat of transport vs. concentration. The measurements on CdSO_4 were made from $4 \times 10^{-4}\text{m}$. up to 0.4m . Comparative data could be obtained from Snowdon and Turner's ⁷⁸ conductimetric methods, from Breck and Agar's ²² measurements with amalgam cells, and Longworth's ⁸⁶ from optical methods. The separations at higher concentrations were measured also to investigate the influence of the "forgotten effect", if any.

Results.

The results are presented in Figs. 20 and 21 for KCl and CdSO_4 respectively. The solid lines are exponential curves fitted by graphical calculations as described on page 68.

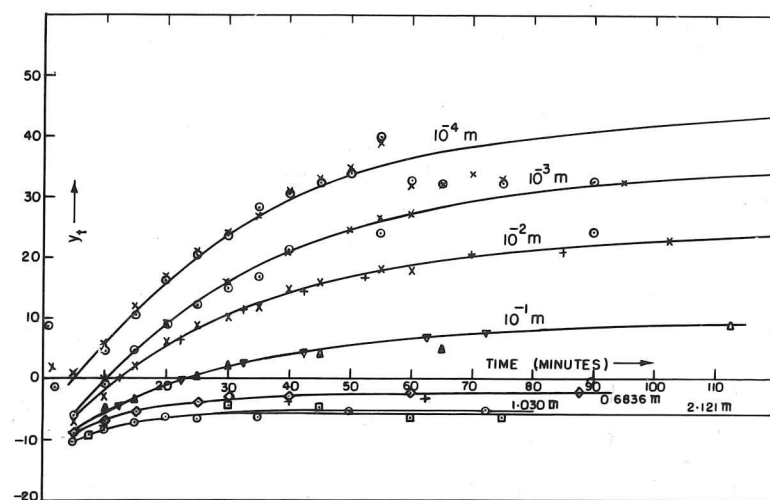


FIG. 20. y_t vs t FOR KCl SOLUTIONS AT 25.0°C

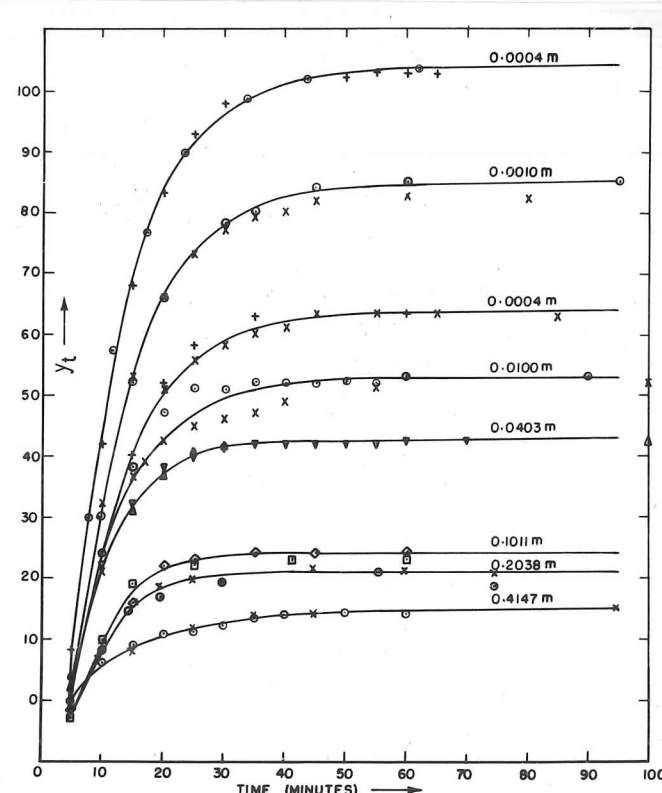


FIG. 21. y_t vs t FOR CdSO_4 SOLUTIONS AT 25.0°C

In the Fig. 20 for KCl, y_t increases exponentially with time upto the steady state, but then levels off at a slightly lower value than indicated by the exponential curve. This deviation at the steady state becomes smaller at higher concentrations. The lower steady state values at the lower concentrations, 10^{-4} m and 10^{-3} m are probably due to convective stirring at the closed ends of the column. On the other hand, the separations for CdSO_4 follow the exponential course from the beginning to the end of the experiment and at all concentrations.

The values of y_∞ , α and $t_{1/2}$, have been tabulated in Tables XIII and XIV, for KCl and CdSO_4 respectively.

The correction factor b_{01} at each concentration was calculated as described on page 70 by a log-log plot of equivalent conductivity vs. concentration. The data for KCl were taken from Robinson and Stokes⁸⁰ and those for CdSO_4 from the International Critical Tables⁸⁷. At concentrations higher than 0.01 m, a further correction was applied to equation (64) for the solution viscosity, η_s , the thermal expansion, β_s , and the density, ρ_s , thus :

$$\left(\frac{y_\infty}{b_{01}} \right)_{\text{corr.}} = \frac{y_\infty}{b_{01}} \cdot \frac{\beta_s \rho_s \eta}{\beta \rho \eta_s} = -2500 A^* \quad (74)$$

where A^* is defined by equation (33) and the parameters β , ρ and η here in (33) refer to water.* The viscosity and density values were taken from standard tables^{88,89}. The factor $(\beta_s \rho_s / \beta \rho) = (\partial \rho_s / \partial T) / (\partial \rho / \partial T)$ was calculated from the density data.

* It has been assumed throughout that in dilute solutions these parameters have the same values as in water.

The values of D' were then read out from the straight line b of Fig.18 corresponding to the corrected values of y_{∞} , i.e. y_{∞}' / b_{01} for the solutions ^{of} 0.01 m and lower concentrations and $(y_{\infty}' / b_{01})_{\text{corr}}$ for the more concentrated solutions. The D' values are presented in Tables XIII & XIV for KCl and CdSO_4 respectively.

T a b l e XIII.

Effect of initial concentration on the separation of aqueous KCl solutions at 25.0°C

| | | | | | | | |
|--|--------|--------|--------|--------|----------|----------|--------|
| m | 0.0001 | 0.0010 | 0.0100 | 0.1000 | 0.6838 | 1.030 | 2.121 |
| y_{∞} | 45 | 35 | 25 | 10^* | $(-2)^*$ | -5.5^* | -5^* |
| α (min. ⁻¹) | 0.030 | 0.030 | 0.030 | 0.030 | 0.030 | (0.03) | (0.03) |
| $t_{1/2} - t_0$ (min.) | 23 | 22.5 | 22.5 | 22.5 | - | - | - |
| b_{01} | 0.995 | 0.992 | 0.972 | 0.950 | 0.934 | 0.920 | 0.914 |
| $10^8 D'$ (cm ² . sec. ⁻¹ . .deg. ⁻¹) | 4.3 | 3.5 | 2.7 | 1.6 | 0.5^a | 0.3 | 0.3 |

* $y_{\infty}' = (y_{\infty} + 100)$; in all other cases; $y_{\infty}' = (y_{\infty} + 9)$

a correction due to β_s, β_s, η_s was -0.1×10^{-8} ; less in other cases.

The diffusion coefficients of different concentrations of KCl have been determined by Gosting ⁹⁰, Harned and Nuttall ⁹¹

T a b l e XIV.

Effect of initial concentration on the separation of aqueous
CdSO₄ solutions at 25.0°C.

| | | | | | | | | |
|--|--------|--------|--------|--------|------------------|------------------|------------------|------------------|
| m | 0.0004 | 0.0010 | 0.0040 | 0.0100 | 0.0403 | 0.1011 | 0.2038 | 0.4147 |
| y _∞ | 104 | 85 | 64 | 53 | 43 | 24 | 21 | 15 |
| (min ⁻¹) | 0.10 | 0.10 | 0.10 | 0.11 | 0.13 | 0.15 | 0.15 | 0.08 |
| t _{1/2} -t ₀ | 7.5 | 7.5 | 7.5 | 6.0 | 5.0 | 5.5 | 5.5 | 8.0 |
| (min.) | | | | | | | | |
| b ₀₁ | 0.95 | 0.875 | 0.80 | 0.775 | 0.775 | 0.775 | 0.775 | 0.775 |
| 10 ⁸ D' | 9.5 | 8.6 | 7.2 | 6.4 | 5.2 ^a | 3.4 ^b | 3.2 ^c | 2.6 ^d |
| (cm ² . .sec ⁻¹ . .deg ⁻¹) | | | | | | | | |

corrections due to β_s , ρ_s and η_s in units of 10⁻⁸ were
(a) -0.1, (b) +0.1, (c) +0.2 and (d) +0.2.

and Longworth⁸⁶. Their data were plotted on a graph from which the diffusion coefficients at corresponding concentrations have been obtained and assembled in Table XV. Data for CdSO₄ were taken from the papers of Agar and Turner⁶², Snowden and Turner⁷⁸ and Longworth⁸⁶. The diffusion coefficients for the various concentrations of CdSO₄ presented in Table XVI were obtained from a similar graph.

Tables XV and XVI show the values of the Soret coefficients calculated as D'/D. The values obtained have been plotted as

a function of \sqrt{m} in Figs. 22 and 23.

Table XV.

Soret coefficients and heats of transport of aqueous KCl solutions at 25.0°C.

| | | | | | | | |
|---|-------|-------|-------|-------|-------|-------|-------|
| \sqrt{m} | 0.010 | 0.032 | 0.100 | 0.317 | 0.827 | 1.015 | 1.459 |
| $10^5 D$ ($\text{cm}^2 \cdot \text{sec}^{-1}$) | 1.975 | 1.963 | 1.915 | 1.851 | 1.861 | 1.89 | 1.99 |
| $10^3 \sigma$ (deg^{-1}) | 2.15 | 1.75 | 1.40 | 0.85 | 0.25 | 0.15 | 0.15 |
| $10^{-5} BT$ ($\text{cal} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$) | 3.51 | 3.48 | 3.35 | 3.19 | 3.14 | 3.18 | 3.37 |
| \hat{Q} ($\text{cal} \cdot \text{mole}^{-1}$) | 765 | 620 | 440 | 275 | 85 | 50 | 50 |

Table XVI.

Soret coefficients and heats of transport of aqueous CdSO_4 solutions at 25.0°C.

| | | | | | | | | |
|--|-------|-------|-------|-------|-------|-------|-------|-------|
| \sqrt{m} | 0.020 | 0.032 | 0.063 | 0.100 | 0.200 | 0.318 | 0.451 | 0.644 |
| $10^5 D$ ($\text{cm}^2 \cdot \text{sec}^{-1}$) | 0.775 | 0.74 | 0.69 | 0.67 | 0.625 | 0.56 | 0.51 | 0.455 |
| $10^3 \sigma$ (deg^{-1}) | 12.3 | 11.65 | 10.45 | 9.55 | 8.3 | 6.05 | 6.25 | 5.7 |
| $10^5 BT$ ($\text{cal} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$) | 3.30 | 2.95 | 2.57 | 2.30 | 1.95 | 1.70 | 1.65 | 1.53 |
| \hat{Q} ($\text{cal} \cdot \text{mole}^{-1}$) | 4050 | 3430 | 2690 | 2200 | 1620 | 1030 | 1035 | 870 |

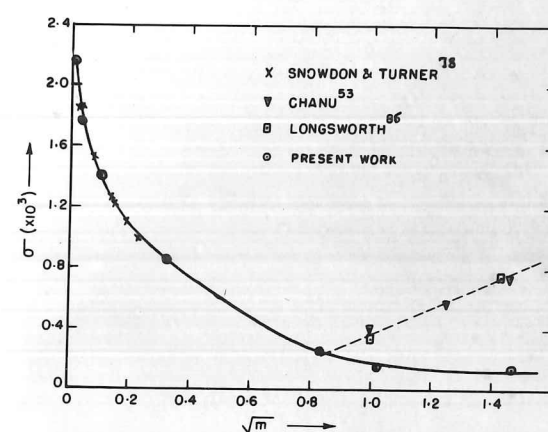


FIG. 22. Soret coefficients for KCl solutions at 25.0°C

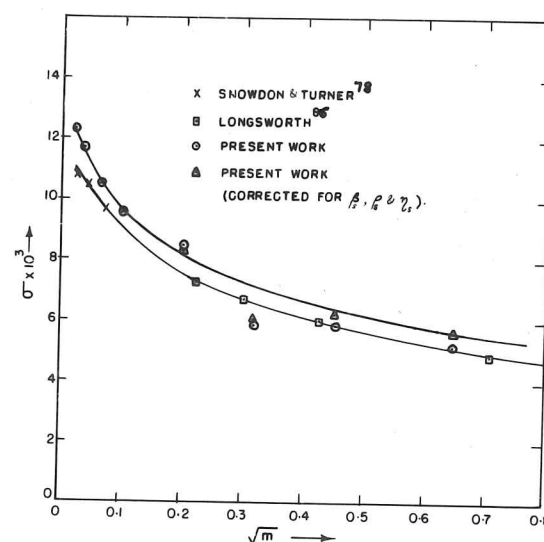


FIG. 23. Soret coefficients for CdSO_4 solutions at 25.0°C

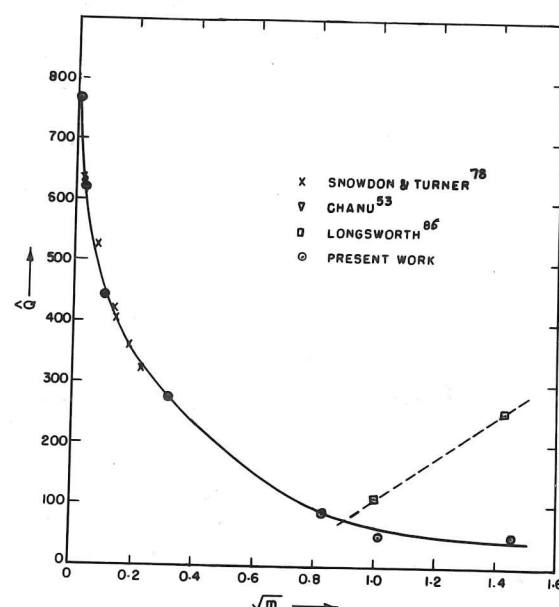


FIG. 24. HEATS OF TRANSPORT FOR KCl SOLUTIONS AT 25.0°C

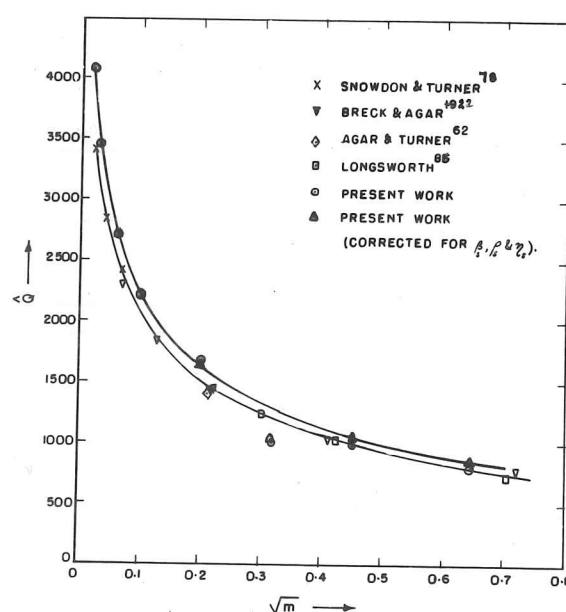


FIG. 25. HEATS OF TRANSPORT FOR CdSO₄ SOLUTIONS AT 25.0°C

The heats of transport were calculated using equation (10). The values of the factor B were determined from the data on activity coefficients available in the literature for KCl⁸⁰ and CdSO₄⁹² from plots of $\log \gamma_{\pm}$ vs. $\log m$. All the values are collected together in Tables XV and XVI for the two electrolytes. Figs. 24 and 25 depict the variation of \hat{Q} with \sqrt{m} .

Discussion.

The results indicate in both cases, a smooth decrease of the Soret coefficients and heats of transport with increasing concentration as has been observed by others.

In Figs. 22 and 24 the corresponding results obtained for KCl in pure Soret cells by Snowdon and Turner using the conductimetric methods and by Longworth and Chanu by the optical methods have also been plotted for comparison. In the concentration region 1 - 4 m, Chanu and Longworth observed an increase in σ and \hat{Q} with increase in concentration. The present experiments did not indicate a variation of this sort upto 2m as can be seen from the two Figs. 22 and 24. On the other hand, at lower concentrations, the values obtained by Snowdon and Turner and by Agar and Turner for KCl solutions are found to fall exactly on the experimental curve. The Soret coefficients and heats of transport of CdSO₄ solutions seem to be slightly higher than those obtained by Snowdon and Turner, by Breck and Agar and by Longworth as can be seen from Figs. 23 and 25. Whether this is due to the forgotten effect, will be discussed later.

The results obtained are seen to confirm the behaviour of

the thermal diffusion of these salts as a function of initial concentration observed by earlier workers except for KCl at higher concentrations. Thermogravitational separation thus ranks as a method additional to the "pure Soret" and "non-isothermal cell" methods for the determination of the Soret coefficient and the heats of transport of electrolytes. Thus it is for the first time that confidence in the method and dependability of the results has been established. The large changes in the resistance ratio have enabled the measurements to be carried out over a wider concentration range than has been attempted earlier by conductimetric methods on pure Soret cells.

Influence of the forgotten effect.

The factor $1/25 \cdot 152/143$ F representing the forgotten effect in the equation (48) for the steady state was calculated from the known parameters in equation (46). $\partial \rho / \partial w$ was obtained from the density values at 25.0°C ⁸⁹. While for KCl it was less than 0.1% in D' even for a 2 m solution, for CdSO_4 it amounted to a correction of only -2% at 0.4 m.

Thus the steady state separation in both cases is not influenced by the forgotten effect thereby supporting Korchinsky and Emery's⁵⁰ views.

Agar^{66,67} has developed a theory for the variation of heat of transport with concentration, which in conjunction with the Debye-Hückel theory predicts the sign and magnitude of the changes of \hat{Q} with dilution in dilute electrolyte solutions. The equations are similar to those derived by Helfand

and Kirkwood⁹³ by statistical methods. He deduces the equations by considering the distribution of heat sources around the moving ion. The approximate limiting law predicts a slope of

$$\left. \begin{aligned} \frac{d\hat{Q}}{dI^{1/2}} &\approx -2100 \text{ cal.mole}^{-3/2}.\text{kg}^{1/2} \text{ for a 1:1 electrolyte} \\ \text{and } &\approx -8400 \text{ cal.mole}^{-3/2}.\text{kg}^{1/2} \text{ for a 2:2 electrolyte.} \end{aligned} \right\} (75)$$

The values predicted by Helfand and Kirkwood are 2565 and 2565 x 4 for 1:1 and 2:2 electrolytes respectively.

The results of Snowden and Turner yield values of -2050 and 14000 for KCl and CdSO₄ respectively. The higher value for CdSO₄ is thought to be due to probable ion-pair formation, whereas the lower value for KCl as due to electrophoretic effects.

A similar calculation of the limiting slopes for KCl and CdSO₄ from Fig.26 gives values of 4.2×10^3 and 20.6×10^3 cal.mole^{-3/2}.kg^{1/2} for the two salts which are both higher than the values predicted by the above limiting laws.

On the other hand, when \hat{Q} is plotted as a function of $m^{1/3}$ (Fig.26), the dilute end of the curve gives the slope $d\hat{Q}/dm^{1/3}$ equal to 2.1×10^3 and 10.3×10^3 cal.mole^{-4/3}.kg^{1/3} for KCl and CdSO₄ solutions respectively. Fig.26 compares the \hat{Q} vs. $m^{1/2}$ and \hat{Q} vs. $m^{1/3}$ graphs for the two compounds in the dilute region. The variation of the heat of transport^{with concentration} of these electrolytes in dilute solutions thus reminds one of the dependence of the logarithm of the activity coefficient on the cube root of concentration⁹⁴.

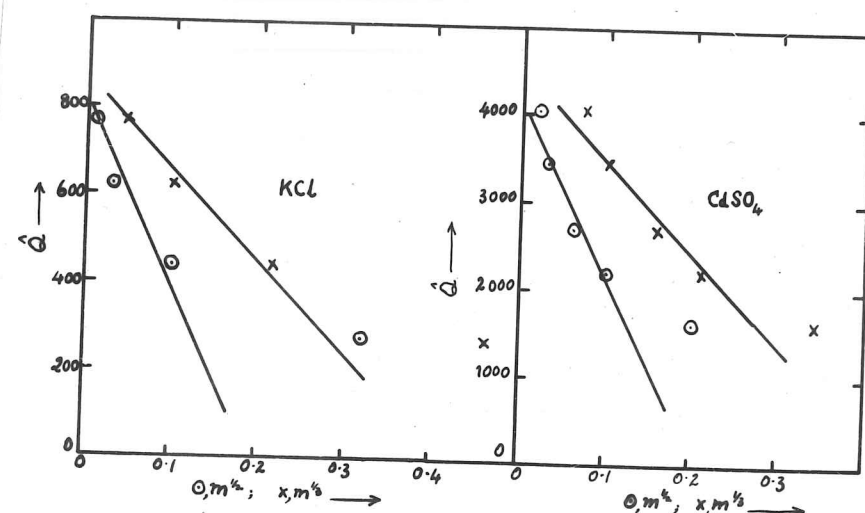


FIG. 26. HEAT OF TRANSPORT VS. $m^{1/2}$ AND $m^{1/3}$ FOR DILUTE KCl AND CdSO₄ SOLUTIONS.

CHAPTER VII.

STUDIES OF WEAK ACIDS : (i) ACETIC, (ii) PROPIONIC AND (iii) n-BUTYRIC ACIDS.

Thermogravitational separations of acetic, propionic and butyric acids were measured in order to determine their thermal diffusion coefficients since no data exist in ^{the} literature on the thermal diffusion of these acids. The isothermal diffusion coefficients of these acids have been determined by Vitagliano and Lyons ⁹⁵ (acetic acid) and Dunn and Stokes ⁹⁶ (propionic and n-butyric acids). The Soret coefficients and hence the heats of transport could therefore be estimated from the experimentally determined thermal diffusion coefficients. The effect of change in concentration on the separation has also been studied for all these acids and their Soret coefficients and heats of transport have been estimated.

Molar stock solutions were prepared by dilution of the AnalaR acids and they were standardized by titration with standard carbonate-free sodium hydroxide solutions using phenolphthalein as indicator. The lower concentrations were prepared by dilution. The molality was calculated from the relation ⁸⁰,

$$m = \frac{c}{d - 0.001cW_B} \quad (76)$$

where d is the density of the solution, c is the molar concentration and W_B is the molecular weight of the solute.

The separation curves were obtained as described earlier. Experiments were always conducted from the lowest to the highest concentration.

Results :

Figs. 27, 28 and 29 show y_t as a function of time for acetic, propionic and n-butyric acids respectively. The solid lines are bestfitting exponential curves passing through the experimental points. All the constants y_∞ , α and $(t_{\frac{1}{2}} - t_0)$ were calculated graphically as before.

b_{01} values were estimated from log-log plots of conductivity vs. concentration. The conductivity data for acetic acid were obtained from Mac Innes and Shedlovsky ⁹⁷, for propionic acid from Belcher ⁹⁸ and for n-butyric acid from Saxton and Darken ⁹⁹, all at 25.0°C. y'_∞ / b_{01} was then corrected for β_s , ρ_s and η_s as described on page 82 for CdSO_4 solutions.

The viscosity values were obtained from reference (100) for all the three acids at 25.0°C and the density data for acetic acid were also taken from the same reference. Densities of propionic and butyric acid solutions were available in the International Critical Tables ⁸⁹. After applying these corrections for y'_∞ , the values of D' were read out from the straight line (b) of Fig. 18. All the results are assembled in Tables XVII, XVIII and XIX for acetic, propionic and n-butyric acids respectively.

The values for the diffusion coefficients, D were obtained for the different concentrations from graphs of D vs. m of the data given by Vitagliano and Lyons and by Dunn and Stokes. The Soret coefficients were then calculated as D'/D for all the three acids over the whole concentration region studied. Fig. 30 shows the dependence of σ on \sqrt{m} .

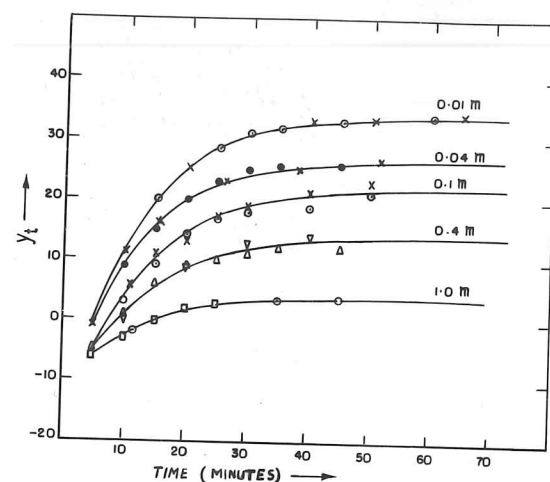


FIG. 27. Y_t vs t FOR ACETIC ACID SOLUTIONS AT 25.0°C

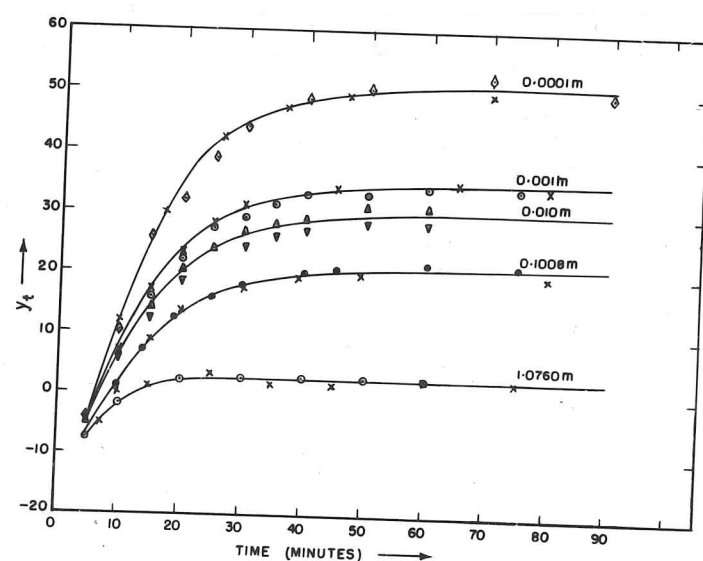


FIG. 28. Y_t vs t FOR PROPIONIC ACID SOLUTIONS AT 25.0°C

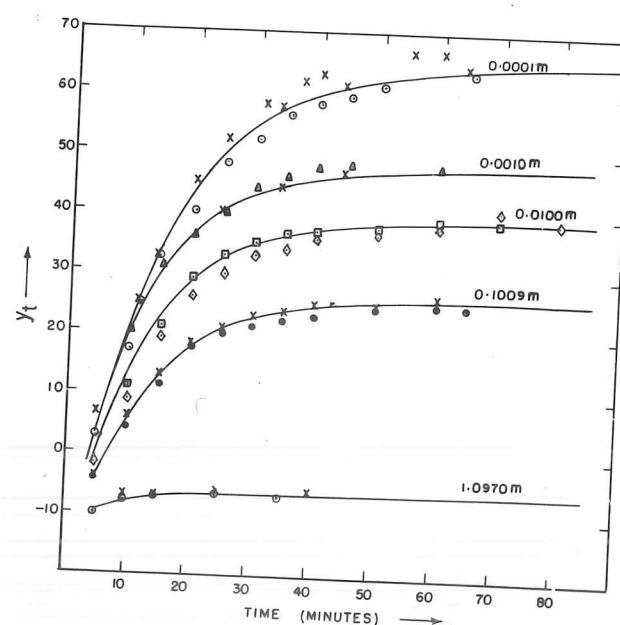


FIG. 29. Y_t vs t FOR BUTYRIC ACID SOLUTIONS AT 25.0°C

TABLE XVII.

Effect of initial concentration on the separation of aqueous Acetic acid solutions at 25.0°C.

| | | | | | |
|---|--------|--------|--------|--------|------------------|
| m | 0.0100 | 0.0401 | 0.1006 | 0.4097 | 1.0580 |
| y_{∞} | 34 | 27 | 22 | 14 | 4 |
| α (min. ⁻¹) | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| $t_{1/2}-t_0$ (min.) | 8.0 | 7.5 | 7.5 | 8.0 | 7.0 |
| b_{01} | 0.52 | 0.52 | 0.52 | 0.52 | 0.5 (approx.) |
| $10^8 D'$ (cm ² .sec ⁻¹ .deg ⁻¹) | 6.6 | 5.5 | 4.7 | 3.4 | 2.4 ^a |

^a correction for β_s , β_s and η_s was $+0.4 \times 10^{-8}$ cm².sec⁻¹.deg⁻¹; negligible at lower concentrations.

TABLE XVIII.

Effect of initial concentration on the separation of aqueous Propionic Acid solutions at 25.0°C.

| | | | | | |
|-----------------------------------|--------|--------|--------|--------|---------|
| m | 0.0001 | 0.0010 | 0.0100 | 0.1018 | 1.0760 |
| y_{∞} | 51 | 35 | 30 | 21 | 2 |
| α (min. ⁻¹) | 0.08 | 0.085 | 0.085 | 0.085 | (0.085) |
| $t_{1/2}-t_0$ (min.) | 8.5 | 8.0 | 8.0 | 8.0 | - |

T A B L E XVIII (contn.)

| | | | | | |
|--|------|-----|-----|------|------------------|
| b_{01} | 0.65 | 0.5 | 0.5 | 0.45 | 0.4 (approx) |
| $10^8 D'$ ($\text{cm}^2 \cdot \text{sec}^{-1} \cdot \text{deg}^{-1}$) | 7.4 | 7.0 | 6.2 | 5.3 | 2.7 ^a |

^a correction for β_s , ρ_s and η_s was $+0.5 \times 10^{-8} \text{ cm}^2 \cdot \text{sec}^{-1} \cdot \text{deg}^{-1}$; negligible at lower concentrations.

T A B L E XIX.

Effect of initial concentration on the separation of aqueous
n-Butyric acid solutions at 25.0°C.

| | | | | | |
|--|--------|--------|--------|--------|------------------|
| m | 0.0001 | 0.0010 | 0.0100 | 0.1009 | 1.0970 |
| y_{∞} | 65 | 48 | 39 | 26 | -6 |
| α (min^{-1}) | 0.07 | 0.09 | 0.085 | 0.085 | (0.085) |
| $t_{1/2} - t_0$ (min.) | 10 | 7.5 | 8.0 | 8.0 | - |
| b_{01} | 0.65 | 0.5 | 0.5 | 0.45 | 0.4 (approx.) |
| $10^8 D'$ ($\text{cm}^2 \cdot \text{sec}^{-1} \cdot \text{deg}^{-1}$) | 9.1 | 9.1 | 7.6 | 6.2 | 0.7 ^a |

^a correction for β_s , ρ_s and η_s was $+0.2 \times 10^{-8} \text{ cm}^2 \cdot \text{sec}^{-1} \cdot \text{deg}^{-1}$; negligible at lower concentrations.

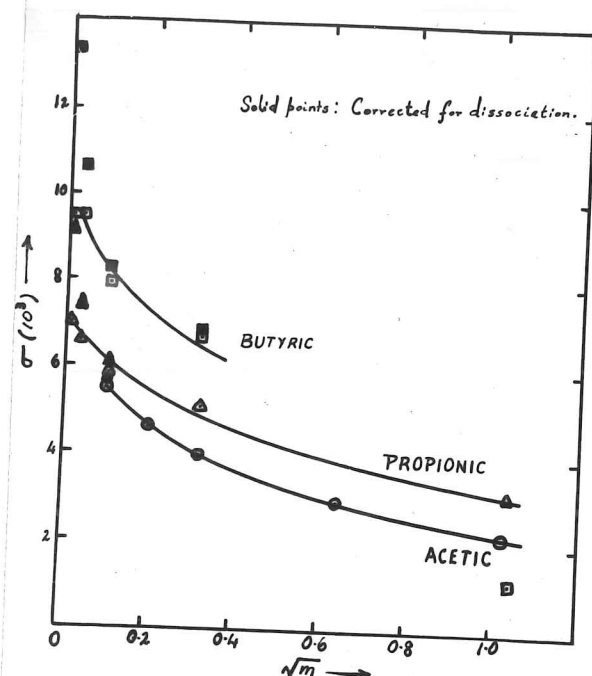


FIG. 30. σ vs \sqrt{m} FOR ACETIC, PROPIONIC AND n -BUTYRIC ACID SOLUTIONS AT 25.0°C.

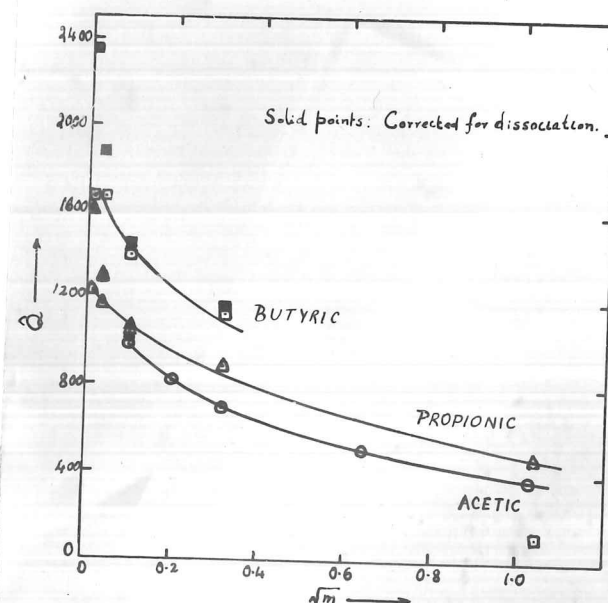


FIG. 31. \hat{Q} vs \sqrt{m} FOR ACETIC, PROPIONIC AND n -BUTYRIC ACID SOLUTIONS AT 25.0°C.

The activity coefficient data of Dunn and Stokes were used for the calculation of \hat{Q} , using eqn.(77) for ^{an}unionized solute,

$$\hat{Q}_{\text{mol}} = \frac{1}{2} (TB\sigma) \quad (77)$$

where B equals $2RT \times (1 + d \ln \gamma / d \ln m)$ as in eqn.(10).

Fig.31 represents the variation of \hat{Q} with \sqrt{m} for the three acids. Tables XX, XXI and XXII contain the numerical data plotted in Figs.30 and 31.

TABLE XX.

Soret coefficients and heats of transport of aqueous Acetic acid solutions at 25.0°C.

| | | | | | |
|---|-------|-------|-------|-------|-------|
| \sqrt{m} | 0.100 | 0.200 | 0.317 | 0.640 | 1.028 |
| $10^5 D$ (cm. ² sec. ⁻¹) | 1.205 | 1.200 | 1.195 | 1.155 | 1.080 |
| $10^3 \sigma$ (deg. ⁻¹) | 5.5 | 4.6 | 3.95 | 2.95 | 2.2 |
| $10^{-5} TB$ (cal.mole ⁻¹ .deg) | 3.53 | 3.52 | 3.50 | 3.44 | 3.32 |
| \hat{Q}_{mol} (cal.mole ⁻¹) | 975 | 810 | 690 | 505 | 365 |

T A B L E XXI.

Soret coefficients and heats of transport of aqueous Propionic acid solutions at 25.0°C.

| | | | | | |
|--|-------|-------|-------|-------|-------|
| \sqrt{m} | 0.010 | 0.032 | 0.100 | 0.317 | 1.037 |
| $10^5 D$ (cm ² .sec. ⁻¹) | 1.06 | 1.06 | 1.06 | 1.04 | 0.855 |
| $10^3 \sigma$ (deg. ⁻¹) | 7.0 | 6.6 | 5.85 | 5.1 | 3.15 |
| $10^5 TB$ (cal.mole ⁻¹ .deg.) | 3.53 | 3.53 | 3.52 | 3.48 | 3.02 |
| \hat{Q}_{mol} (cal.mole ⁻¹) | 1235 | 1165 | 1030 | 885 | 475 |

T A B L E XXII.

Soret coefficients and heats of transport of aqueous n-Butyric acid solutions at 25.0°C.

| | | | | | |
|--|-------|-------|-------|-------|-------|
| \sqrt{m} | 0.010 | 0.032 | 0.100 | 0.318 | 1.047 |
| $10^5 D$ (cm ² .sec. ⁻¹) | 0.96 | 0.96 | 0.955 | 0.925 | 0.615 |
| $10^3 \sigma$ (deg. ⁻¹) | 9.5 | 9.5 | 7.95 | 6.7 | 1.14 |
| $10^5 TB$ (cal.mole ⁻¹ .deg.) | 3.53 | 3.52 | 3.51 | 3.36 | 2.05 |
| \hat{Q}_{mol} (cal.mole ⁻¹) | 1675 | 1670 | 1395 | 1125 | 117 |

Discussion_:

The results obtained indicate that the separation increases with dilution as in the case of strong electrolytes studied previously. No minimum is observed in any of the three cases in the concentration region studied.

The Soret coefficients and heats of transport increase in magnitude as we go from acetic to n-butyric acid (with the exception of 1m n-butyric acid). This is in agreement with the view that an ion which introduces large non-polar groups into water causes increase in the local order on account of its inability to take part in ^{the}electrostatic interactions and form what are usually termed as "icebergs" with the water molecules in the solution, just as the nonpolar groups themselves would do in the absence of the ionic charge ¹⁰¹⁻¹⁰⁴. That the above acids introduce large non-polar groups in weakly dissociated forms into the solution, can be seen from their ionisation constants, K_{HAC} , K_{HPr} and K_{HBu} equal to 1.754×10^{-5} , 1.336×10^{-5} and 1.515×10^{-5} respectively. The increase in the heats of transport of the tetraalkylammonium halides with increasing hydrophobicity of the alkyl groups has been discussed by Agar ^{67,105} and recent experimental results have been reported by Ikeda and Miyoshi ¹⁰⁶ for tetra methyl, ethyl, propyl and n-butyl ammonium halides. Unfortunately, no data on the thermal diffusion of weak acids exists in the literature for comparison.

The concentration dependence of the heat of transport.

The equation (77) considers the acids as neutral molecules in molecular

form. Although this is nearly true for the concentrated solutions, as the dilution increases the degree of dissociation ^{increases} and the observed heat of transport is the sum of the contributions from the ions as well as the undissociated acid. The rise in the heat of transport curves with dilution is probably caused by the increasing ionic contribution since \hat{Q} is large for the ions H^+ , Ac^- , Pr^- and $n-Bu^-$. Agar ⁶⁷ quotes values of 3038, 1230, 1650 and 1940 cal.(g.-ion)⁻¹ respectively for the above ions in 0.01m aqueous solution at 25°C. So, for the hypothetically completely ionized acids at 0.01m, the heats of transport taken as the sum of the ionic values, are 4268, 4688 and 4978 cal.mole⁻¹ for HAc, HPr and HBu acids respectively.

The observed \hat{Q}_{obs} at any concentration can be considered as the sum of \hat{Q}_{undiss} and \hat{Q}_{diss} of the molecular and ionic parts of the acid. Let \hat{Q}_{undiss} be proportional to $B/2 \cdot \sigma(1 - \theta)$ and \hat{Q}_{diss} to $B\sigma\theta$, where θ is the degree of dissociation of the acid. Then

$$\begin{aligned}\hat{Q}_{obs} &= \hat{Q}_{undiss} + \hat{Q}_{diss} \\ &= \frac{TB\sigma}{2} (1 - \theta) + TB\sigma\theta \\ &= \frac{TB\sigma}{2} (1 + \theta) \\ &= \hat{Q}_{mol} (1 + \theta)\end{aligned}\tag{78}$$

At infinite dilution, $\theta = 1$ and hence $(\hat{Q}_{obs})_{\infty} = TB\sigma$.

The values of θ for the three acids were computed from the conductance data ^{80,98}. The values of \hat{Q}_{obs} are compiled in Tables XXIII. - XXV. for the three acids.

T A B L E XXIII.

Correction for dissociation in dilute solutions : \hat{Q}_{obs} for
Acetic acid.

| | | | |
|--|--------|--------|--------|
| m | 0.0100 | 0.0401 | 0.1006 |
| \sqrt{m} | 0.100 | 0.200 | 0.317 |
| θ | 0.040 | 0.022 | 0.013 |
| \hat{Q}_{mol} (cal.mole ⁻¹) | 975 | 810 | 690 |
| \hat{Q}_{obs} (cal.mole ⁻¹) | 1015 | 830 | 700 |

T A B L E XXIV.

Correction for dissociation in dilute solutions : \hat{Q}_{obs} for
Propionic acid.

| | | | | |
|--|--------|--------|--------|--------|
| m | 0.0001 | 0.0010 | 0.0100 | 0.1018 |
| \sqrt{m} | 0.010 | 0.032 | 0.100 | 0.317 |
| θ | 0.30 | 0.11 | 0.036 | 0.012 |
| \hat{Q}_{mol} (cal.mole ⁻¹) | 1235 | 1165 | 1030 | 885 |
| \hat{Q}_{obs} (cal.mole ⁻¹) | 1605 | 1295 | 1065 | 895 |

The \hat{Q}_{obs} values given in the above tables are also plotted in Fig.31. The corresponding Soret coefficients corrected for dissociation can be seen in Fig.30.

At 0.01m, half the mean of the mean ionic values $67, \frac{1}{2} \frac{\hat{Q}_+ + \hat{Q}_-}{2}$

T A B L E XXV.

Correction for dissociation in dilute solutions : \hat{Q}_{obs} for
n-Butyric acid.

| | | | | |
|--|--------|--------|--------|--------|
| m | 0.0001 | 0.0010 | 0.0100 | 0.1009 |
| \sqrt{m} | 0.010 | 0.032 | 0.100 | 0.318 |
| θ | 0.40 | 0.117 | 0.038 | 0.017 |
| \hat{Q}_{mol} (cal.mole ⁻¹) | 1675 | 1670 | 1395 | 1125 |
| \hat{Q}_{obs} (cal.mole ⁻¹) | 2345 | 1865 | 1445 | 1145 |

of the hypothetically completely ionized acetic, propionic and n-butyric acids work out as 1065, 1167 and 1245 cal.mole⁻¹ respectively. The corresponding \hat{Q}_{obs} values are 1015, 1065 and 1445 cal.mole⁻¹. This shows that the \hat{Q}_{obs} values are mainly due to the molecular form of these acids as expected since the dissociation is only of the order of 4% at this concentration. As can be seen in Fig.31 for propionic and n-butyric acids, the increasing deviation of \hat{Q}_{obs} from the molecular value \hat{Q}_{mol} occurs only at higher dilutions owing to the increasing degree of dissociation, since the ions have higher heats of transport.

Approximate values of \hat{Q}_{obs} at infinite dilution can be estimated from the \hat{Q}_{obs} values at 10⁻⁴m for propionic and n-butyric acids. Since the acids are 30 and 40% dissociated at this concentration, $(\hat{Q}_{obs})_{\infty} \approx 1605/0.3 = 5350$ cal.mole⁻¹ for propionic acid and $\approx 2345/0.4 = 5862$ cal.mole⁻¹

for n-butyric acid. The heats of transport for ^{the} theoretically completely ionized propionic and n-butyric acids at 0.01m are 4688 and 4978 cal.mole⁻¹ respectively. Thus the estimated values of $(\hat{Q}_{obs})_{\infty}$ seem reasonable.

Finally, as regards the α values (Tables XVII-XIX), which characterize the approach to the steady state, the data obtained for 0.01m acids are plotted in Fig.19, thereby, further supporting the approximately linear dependence of $1/\alpha$ on the isothermal diffusion coefficient.

The present studies on weak acids have thus provided for the first time data on the thermal diffusion of acetic, propionic and n-butyric acids, and the effect of dilution on their separations.

CHAPTER VIII.

GENERAL CONCLUSIONS.

Thermogravitational separation of aqueous solutions of electrolytes has been studied in a column without reservoirs. An all-glass column was designed and constructed for the purpose. The resistance ratio method of measuring concentration changes "in situ" previously used for static cells has been successfully adapted to the all-glass column for measuring the separation of dilute electrolyte solutions. The movable upper electrode enabled the resistance ratio of the top half to bottom half to be adjusted to unity at isothermal conditions. On the Wheatstone bridge side, the Wagner earth has been found unnecessary for the measurement of the resistance ratio. By suitably incorporating a L.F. amplifier, a phase shifter and a phase sensitive detector, the circuit enables the use of a potentiometric recorder for recording the course of the experiment continuously.

The separation curves were exponential with respect to time. The results for seven 1:1 electrolytes in dilute aqueous solution confirm for the first time the linear dependence of the separation on the thermal diffusion coefficient as predicted by equation (59) for the steady state for a column without reservoirs and for small values of A^* . This is demonstrated in Fig. 18b. Thus it is for the first time that a satisfactory comparison of theory with experiment has been made. The difference in the experimental and theoretical slopes has been discussed in terms of the approximations invol-

ved in the theory, probable errors in the geometrical factors and the end-effects mentioned in Chapter V. In the context of the lack of existence of a better theory for thermogravitational separation the differences do not seem excessive. From the steady state separation the thermal diffusion coefficient of an electrolyte solution can be found out from the calibration graph for the apparatus, Fig.18b. The linear dependence of the characteristic time on the isothermal diffusion coefficient predicted by theory has also been confirmed by experiment. But again the experimental and theoretical slopes differ in magnitude.

The investigations on the effect of dilution on the separation of potassium chloride and cadmium sulphate solutions confirm the previous observation of the decrease in the Soret coefficients and heats of transport with increasing concentration. The existence of a minimum in the curves has not been observed. In the case of KCl solutions the results agree well with those obtained by others using static Soret cells except at high concentrations. But in the case of cadmium sulphate solutions the values of the heats of transport and Soret coefficients seem to lie above the curve obtained by plotting the results of others on pure Soret cells and amalgam cells. The limiting slopes predicted by the theory of Agar and of Helfand and Kirkwood for the variation of the heat of transport with the square root of concentration have been found to be lower than the experimental values in both the cases as in earlier work. However, when the heats of transport values of the dilute solutions are plotted as a

function of $m^{1/3}$, the limiting value of $d\hat{Q}/dm^{1/3}$ is ^{numerically} very nearly equal to that of $d\hat{Q}/dm^{1/2}$ predicted by Agar and ^{by} Helfand and Kirkwood for both potassium chloride and cadmium sulphate solutions, reminding one of the dependence of the logarithm of activity coefficient on the cube root of concentration.

The above research was followed by studies on weak acids for which no data are available on their thermal diffusion coefficients. Acetic, propionic and n-butyric acids were chosen for the study. The Soret coefficients, were calculated from the measured thermal diffusion coefficients using the values of the isothermal diffusion coefficients available in the literature. All the three acids have been studied over a wide range of concentrations. The results indicate that their Soret coefficients and heats of transport increase in magnitude in the order acetic, propionic and n-butyric acids (with the exception of 1m n-butyric acid). This is explained in terms of the increasing "ice-likeness" of water as the size of the non-polar group of the dissolved substance and of the ions of these acids becomes larger. This view is also supported by the increase in the heats of transport of tetraalkylammonium halides with increasing hydrophobicity of the alkyl groups discussed by Agar and by Ikeda and Miyoshi.

Increasing the dilution has been found to increase the heat of transport probably due to the larger contributions from the ions of the acids. But for concentrations, $10^{-2}m$ and higher, the heat of transport is mainly due to the molecular form since the degree of dissociation of these acids is less than 4 percent. Approximate values of the heats of transport at infinite dilution have been estimated for pro-

pionic and n-butyric acids.

The work described in this dissertation has thus placed the thermogravitational technique on a par with other methods for the determination of Soret coefficients and the heats of transport of electrolytes in aqueous solutions. The design of the column and the technique of measuring the concentration changes "in situ" for dilute solutions have^e/considerably narrowed the gap between theory and experiment, thus encouraging further exploitation of this method for the separation of the components of a homogeneous solution and determination of their thermal diffusion coefficients.

UNIVERSITY
LIBRARY
1954

REFERENCES

1. Ludwig, C.,
Sitzber.Akad.Wiss.Wien, 20, 539 (1856).
2. Soret, C.,
Arch.Sci.Phys.Nat.Geneve, 2, 48 (1879).
3. Dufour, L.,
Arch.Sci.Phys.Nat.Geneve 45, 9 (1872); Ann.Phys. 5 28,
490 (1873).
4. Waldman, L.,
Naturwissenschaften, 31, 204 (1943); Z.Physik 121, 501
(1943).
5. Van't Hoff, J.H.,
Z.Physik.Chem.1, 481 (1887).
6. Arrhenius, S.,
Ofvers.Vetensk Akad.Forh.Stockh.2, 61 (1894); (cf. abstracted in Z.Physik.Chem.26, 187 (1898)).
7. Scarpa, O.,
R.C.Accad.Lincei 17, 362 (1908).
8. Nernst, W.,
Wied.Ann.58, supplement to part 8 (1896).
9. Andrews, T.,
Phil.Mag.10, 433 (1837).
10. Faraday, M.,
"Experimental Researches", Everyman, Dent, 1922, p.279.
11. Wild, H.,
Pogg.Ann.103, 353 (1858).

12. Podszus, E.,
Ann.Physik.27, 859 (1908).
13. Tyrrell, H.J. and Hollis, G.,
Trans.Faraday Soc.48, 893 (1952).
14. Eastman, E.D.,
J.Am.Chem.Soc.48, 1482 (1926); 49, 794 (1927).
15. Tanner, C.C.,
Trans.Faraday Soc., 23, 75 (1927).
16. Eastman, E.D.,
J.Am.Chem.Soc.50, 283, 292 (1928).
17. Wagner, C.,
Ann.Physik.(V) 3, 629 (1929); (V) 6, 370 (1930).
18. Lange, E. and Monheim, J.,
Z.Physik.Chem.A 150, 177 (1930);
Lange, E. and Hesse, Th.,
Z.Elektrochem.38, 428 (1932); 39, 374 (1933); J.Am.Chem.
Soc.55, 853 (1933).
19. Thomson, W.,
Mathematical and Physical Papers Vol.I, p.232. Cambridge
University Press, 1882; (first published, 1854).
20. Tyrrell, H.J.V.,
"Diffusion and Heat Flow in Liquids", Butterworths, 1961.
53. Chanu, J. and Lenoble, J.,
J.Chim.Phys.53, 309 (1956).
22. Agar., J.N. and Breck, W.G.,
Trans.Faraday Soc.53, 167, 179 (1957).

23. Clusius, K. and Dickel, G.,
Naturwissenschaften 26, 546 (1938).
24. de Groot, S.R.,
"L'Effet Soret", North Holland, Amsterdam, 1945.
25. Joshi, R.K., Mathur, B.P. and Saxena, S.C.,
J.Chem.Phys.46, 3005 (1967).
26. Onsager, L. and Watson, W.W.,
Phys.Rev.56, 474 (1939).
Donaldson, J. and Watson, W.W.,
Phys.Rev.82, 909 (1951).
27. Clusius, K. and Dickel, G.,
Naturwissenschaften 27, 148 (1939); Z.phys.Chem.B 44,
397, 451 (1939).
28. Korsching, H. and Wirtz, K.,
Naturwissenschaften 27, 110, 267 (1939).
29. Debye, P. and Bueche, A.M.,
p.497, "High Polymer Physics", ed.H.A.Robinson, Remsen
Press, New York, 1948.
Also, "The Collected Papers of P.J.W.Debye", Intersci.,
New York, 1954, p.443.
30. Sullivan, L.J., Ruppell, T.C. and Willingham, C.E.,
Ind.Eng.Chem.47, 208 (1955).
31. Devyatykh, G.G. and Borisov, G.K.,
Russ.J.Phys.Chem.37, 1076 (1963).
32. Thomson, C.J., Coleman, H.J., Ward, C.J. and Rall, H.F.,
Anal.Chem.29, 1601 (1957).
32. Khoo, Y.K.,
Birmingham Univ., Chem. Engr.16, 56 (1965); ¹⁴⁰⁶⁷ (1965) /
cf. C.A.63, /

33. Langhammer, G., Pfenning, H. and Quitsch, K.,
Z.Elektrochem.62, 458 (1958).
34. Kossler, I. and Krauserova, H.,
J.Polymer Sci., Pt.A-I, 4 (6) 1329 (1966).
35. Jones, A.L. and Millberger, E.C.,
Ind.Eng.Chem.45, 2689 (1953).
36. Thompson, C.J., Coleman, H.J., Ward, C.C. and Rall, H.T.,
Anal.Chem.29, 1601 (1957).
37. Prigogine, I., de Brouckere, L. and Amand, R.,
Physica 16, 577 (1950).
38. Alexander, K.F.,
Z.Physik.Chem.(Leipzig) 203, 213 (1954).
39. Murin, A.N. and Popov, D.,
Dokl.Akad.Nauk.SSSR 38, 879 (1953).
40. Hirota, K.,
Bull.Chem.Soc.Japan 16, 475 (1941); J.Chem.Soc.Japan 62,
480 (1941).
41. Hiby, J.W. and Wirtz, K.,
Phys.Z.41, 77 (1940).
42. Horne, F.H. and Bearman, R.J.,
J.Chem.Phys.37, 2842, 2857 (1962); 46, 4128 (1967).
43. Korsching, H.,
Z.Naturforsch.7b, 187 (1952); Naturwissenschaften 32,
220 (1944).
44. Powers, J.E. and Wilke, C.R.,
J.Chem.Phys.27, 1000 (1957).

45. Tilvis, E.,
Soc.Sci.Fennica Commentationes Phys.-Math.13, No.15 (1947).
46. Farber, M. and Libbey, W.E.,
J.Chem.Phys.8, 965 (1940).
47. Baranowski, B. and Demichowicz, J.,
Roczn.Chem.26, 488 (1952); 27, 494 (1953).
Baranowski, B. and Demichowicz, J.,
Bull.Acad.Polon.Sci.Cl.III, 2, 435 (1954);
Baranowski, B.,
Bull.Acad.Polon.Sci.Cl.III, 2, 439 (1954).
48. Murphy, G.W. and Batzer, D.,
J.Electrochem.Soc.99, 520 (1952).
49. de Groot, S.R., Hoogenstraaten, M. and Gorter, C.J.,
Physica 9, 923 (1942); 10, 81 (1943).
50. Korzchinsky, W.J. and Emery, A.H., Jr.,
A.I.Ch.E.J.13 (2) 224 (1967).
51. Korsching, H.,
Z.Naturforsch.10a, 242 (1955).
52. Longworth, L.G.,
J.Phys.Chem.61, 1557 (1957).
21. Chanu, J.,
J.Chim.Phys.55, 733, 743 (1958).
54. Tanner, C.C.,
Trans.Faraday Soc.49, 611 (1953).
55. Alexander, K.F.,
Z.Physik.Chem.(Leipzig) 197, 233 (1951).

56. Saxton, R.L., Dougherty, E.L. and Drickamer, H.G.,
J.Chem.Phys.22, 1166 (1954).
57. Riehl, N.,
Z.Elektrochem.49, 306 (1943).
58. Thomaes, G.,
J.Chim.Phys.53, 407 (1956).
59. Turner, J.C.R.,
Chem.Eng.Sci.17, 95 (1962).
Butler, B.D. and Turner, J.C.R.,
Trans.Faraday Soc., 62, 3114, 3121 (1966).
60. Chipman, J.,
J.Am.Chem.Soc.48, 2577 (1926).
61. Agar, J.N.,
Rev.Pure Appl.Chem.8, No.1 (1958).
62. Agar, J.N. and Turner, J.C.R.,
Proc.Roy.Soc.A 255, 307 (1960).
63. Turner, J.C.R.,
Thesis, Cambridge University, 1955.
64. Soret, C.,
Ann.Chim.Phys.22, 293 (1881).
65. Hartley, G.S. and Crank, J.,
Trans.Faraday Soc.45, 801 (1949).
66. Agar, J.N.,
ch.13 "The Structure of Electrolytic Solutions", ed.W.J.
Hamer, John Wiley, New York, 1959.

67. Agar, J.N.,
ch.2, "Advances in Electrochemistry and Electrochemical Engineering" Vol.3, ed.P.Delahay, Interscience, New York, 1963.
68. Haase, R.,
Z.Physik.Chem.(Frankfurt) 11, 379 (1957).
69. Furry, W.H., Clark Jones, R. and Onsager, L.,
Phys.Rev.55, 1083 (1939).
70. Debye, P.,
Ann.Physik.36, 285 (1939).
71. Bardeen, J.,
Phys.Rev.57, 35 (1940).
72. Davies, R.H. and Kendall, J.T.,
Proc.Intern.Congr,Pure Appl.Chem.London 11, 429 (1947).
73. Murin, A.N.,
Dokl.Akad.Nauk SSSR 41, 291 (1943).
74. Saha, M.N. and Srivastava, B.N.,
"A Treatise on Heat", 4th ed., Allahabad, 1958.
75. Tykodi, R.J.,
"Thermodynamics of Steady States", Macmillan, New York, 1967.
76. Turner, J.C.R., Butler, B.D. and Story, M.J.,
Trans.Faraday Soc.63, 1906 (1967).
77. Horne, F.H. and Bearman, R.J.,
J.Chem.Phys.49, 2457 (1968).

78. Snowdon, P.N. and Turner, J.C.R.,
Trans.Faraday Soc.56, 1409, 1812 (1960).
79. Müller, E.,
"Die Elektrochemische Massanalyse", Th.Steinkopff, Dresden
und Leipzig, 1926.
80. Robinson, R.A. and Stokes, R.H.,
"Electrolytic Solutions", 2nd.edn., 1959.
81. Jones, G. and Bollinger, D.M.,
J.Am.Chem.Soc.57, 280 (1935).
82. Landolt-Börnstein,
Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie,
Geophysik, und Technik, Zweiter Band, 7 Teil, Springer-
-Verlag, Berlin, 1960.
83. Clothier, W.K.,
J.Sci.Instr.43, 264 (1966).
84. Guggenheim, E.A.,
Phil.Mag.2, 538 (1926).
85. Lindenbaum, S. and Boyd, G.E.,
J.Phys.Chem.68, 911 (1964).
86. Longworth, L.G.,
ch.12, "The Structure of Electrolytic Solutions", ed.
W.J.Hamer, John Wiley, New York, 1959.
87. "International Critical Tables", vol.VI,
McGraw-Hill, New York, 1929.
88. D'Ans-Lax,
Taschenbuch für Chemiker und Physiker, Band I., Springer-
-Verlag, Berlin, 1967.

89. "International Critical Tables", vol.III,
McGraw-Hill, New York, 1929.
90. Gosting, L.J.,
J.Am.Chem.Soc.72, 4418 (1950).
91. Harned, H.S. and Nuttall, R.L.,
J.Am.Chem.Soc.69, 736 (1947).
92. Harned, H.S. and Owen, B.B.,
"The Physical Chemistry of Electrolytic Solutions", 3rd
ed., Rheinhold, New York, 1958.
93. Helfand, E. and Kirkwood, J.G.,
J.Chem.Phys.32, 857 (1960).
94. Frank, H.S. and Thompson, P.T.,
ch.8, "The Structure of Electrolytic Solutions", ed.W.J.
Hamer, John Wiley, New York, 1959.
95. Vitagliano, V. and Lyons, P.A.,
J.Am.Chem.Soc.78, 4538 (1956).
96. Dunn, L.A. and Stokes, R.H.,
Australian J.Chem.18, 285 (1965).
97. Mac Innes, D.A. and Th.Shedlovsky,
J.Am.Chem.Soc.54, 1429 (1932).
98. Belcher, D.,
J.Am.Chem.Soc.60, 2744 (1938).
99. Saxton, B. and Darken, L.S.,
J.Am.Chem.Soc.62, 846 (1940).
100. Dykyj, J. and Co.,
Fysikálně-chemické tabulky, SNTL, Praha 1953.

101. Frank, H.S.,
J.Chem.Phys.13, 478 (1945);
Frank, H.S. and Evans, M.W.,
J.Chem.Phys.13, 507 (1945).
102. Gurney, R.W.,
"Ionic Processes in Solution", McGraw-Hill, New York,
1953.
103. Frank, H.S. and Wen-Yang Wen,
Disc.Faraday Soc.24, 133 (1957).
104. Goddard, E.D., Hoeve, E.A.J. and Benson, G.C.,
J.Phys.Chem.61, 593 (1957).
105. Agar, J.N.,
Ann.Rev.phys.Chem.15, 469 (1964).
106. Ikeda, T. and Miyoshi, H.,
J.Phys.Chem.70, 3361 (1966).
107. Neumann, H.P.,
Ber. Bunsenges. physik. Chem.72, 1205,1214 (1968).

