A STUDY OF DIFFUSION RATES
IN POROUS MEDIA

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JAMES STEWART

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PREFACE

In the first year of this research the rates of extraction of mannitol from various species of seaweed were investigated.

A bench-scale unit for the flow of solvents through a bed of seaweed, confined between two porous discs, was developed permitting variation of solvent temperature and rate of flow. It was hoped to apply the results obtained to the full development of a pilot-plant scale counter-current unit, which had been initially developed at the Institute of Seaweed Research (Inveresk, Musselburgh, Scotland) and had been redesigned and rebuilt by the author.

Difficulty in obtaining the necessary supplies of the correct species of seaweed caused the reluctant abandonment of this work.

It was decided to continue work on certain aspects of the mass transfer of concentrated electrolytic solutions to and from porous media[1].

SUMMARY

The object of this research was to investigate the mass transfer of electrolytic solutions to and from porous media at temperatures of 20, 30, 40 and 50°C.

This was done by immersing previously impregnated earthenware slabs (approximate dimensions - 1" x 1.5" x 0.25") in a moving stream of liquid and allowing absorption or desorption of the solute to proceed for measured intervals of time.

The sources of possible errors in the experimental results have been discussed and the accuracy of the experimental technique estimated at ± 3-4 per cent.

It was found that the mass transfer was in accordance with Fick's law and that values of $\bar{D}$, the integral diffusion coefficient, could be estimated from semi-log plots of the fraction of solute absorbed or desorbed against t, time.

The derived values of $\bar{D}$ were related to temperature T, using the correlation suggested by Taylor (J.Chem.Phys., 1938, 6, 331)

namely $D = A \exp. (-Q/RT)$

where Q = an activation energy.

A = a constant.

Activation energies were calculated for both absorption and desorption to and from the porous media. For any

one solute these were found to be dependent upon the physical properties of the media, and for any one medium they were found to be dependent upon the physical properties of the solute.

The values for $\bar{D}$ were found to be smaller than the corresponding diffusion coefficients for diffusion in free solution. The relationship between this apparent reduction in diffusivity and the physical properties of both the porous media and the solutes has been discussed for the absorption and desorption of N. solutions of KCl, HCl and LiCl to and from five porous media of varying physical properties.

The apparent reduction appears to be dependent on the internal structure of the porous media and to a lesser extent on the size of the diffusing ions.

A comparison has been made of rates of absorption and desorption. This has shown that the physical properties of the porous media have no bearing upon which process is the quicker. It appears that the variation of the diffusivity of the solute in free solution with increase in concentration is the controlling factor.

Investigation into the effect of initial solute concentration for the diffusion of N. and 2N. solutions of KCl, HCl, LiCl, HNO_3, KNO_3 and KAc to and from one porous medium has shown that the rates of absorption and descrption vary with increasing concentration in the same manner as do the diffusivities of the solutes in free solution.

A statistical analysis was carried out on the values of $\bar{D}$ for the absorption and desorption of N. solutions of KCl, HCl and LiCl to and from five porous media at temperatures of 20, 30, 40 and 50°C. This showed that although the diffusion coefficients for mass transfer to and from porous media are dependent upon the physical build-up of the media, the process taking place, and the temperature at which the process is taking place, they are not dependent upon functions of the same combinations of these variables.

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1. INTRODUCTION.

1.1. Preface

The mass transfer of concentrated electrolytic solutions to and from porous media touches several well developed research fields viz., diffusion in free solution, diffusion of electrolytic solutions, and diffusion in porous media.

The following introduction is divided into three parts,

(1) A brief historical introduction to diffusion in free solution.

(2) A summary of the more recent ideas and theories of diffusion in electrolytic solutions.

(3) A detailed account of the mass transfer of solutions to and from porous media.

1.2. Diffusion in free solution.

In 1855 Fick[2] laid the foundation for a mathematical development of diffusion processes by enunciating what is now known as Fick's First Law of Diffusion. This states that the quantity of substance which diffuses through a given area in a given time is proportional to the difference between the concentrations of two areas infinitely near to each other. Mathematically this may be written;

$$\frac{dm}{dt} = - D A \frac{dc}{dx}$$

This law can be expanded to give an expression for the rate of accumulation of a diffusing substance at any point in a medium, viz;

$$\frac{c}{t} = D \left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right] \quad \ldots\ldots\ldots(2)$$

This is generally known as Fick's Second Law.

The necessary assumption of equations 1 and 2 is that the diffusion coefficient is constant. It is now well established that diffusivity varies with concentration and although some solutions have been proposed for equation 3, where account is taken of a variable diffusivity, their application is extremely difficult and has not gained prominence

$$\frac{\partial c}{\partial t} = - \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Detailed mathematical treatments of diffusion have been given by Barrer[3], Jost[4], Crank[5], and Bird[6].

As the basic theory of diffusion is analogous to that of heat transfer in solids, extensive treatment of the transformations of the fundamental equations are to be found in the relevant textbooks by Carslaw[7], Carslaw and Jaeger[8], and Churchill[9].

Early attempts at correlating diffusion coefficients with the properties of the diffusing substances and their solvents followed two patterns, namely; the application of the existing kinetic theory of gases to diffusion in liquids and the examination of the relationship between viscosity and diffusivity.

The first successful kinetic approach was made by Arnold[10] who deduced an equation for calculating the diffusion coefficient in the form

$$D = \frac{B\sqrt{\frac{1}{M_1} + \frac{1}{M_2}}}{A_1\ A_2\ S^2\sqrt{\eta_2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

where M_1 and M_2 = molecular weights of the solute and solvent

A_1 and A_2 = factors for correction of the association of solute and solvent molecules

B = correction constant for collision rates

S = sum of molecular diameters

η_2 = viscosity of the solvent

He summarised the previous work on diffusion and by using the experimental results available, confirmed the validity of his equation.

Recently Caldwell and Babb[11] have shown that Arnold's equation is applicable to medium concentrations of solute and gives values for diffusivities which agree with experimental values to within 10%.

In 1858 the relationship between viscosity and diffusivity was investigated by Wiedemann[12] who stated that diffusivity was inversely proportional to viscosity.

Later Walden[13] combined this relationship with the fact that diffusivity was known for gases to be inversely proportional to the square root of the density and proposed that $D.\eta.\ M = \text{constant}$ ....(5)

where M = molecular weight of the diffusing substance

η = viscosity

D = diffusion coefficient.

Sutherland[14] and Einstein[15] independently showed that

$D. = \alpha\, k\, T$ ....(6)

where α = mobility factor

k = Boltzmann's constant

T = absolute temperature.

and α can be found from Stokes' law for falling bodies viz.,

$$\alpha = \frac{1}{6\,\pi\,\eta\,r} \qquad \text{........................(7)}$$

where η = viscosity of the system

r = radius of the falling body or the diffusing particle.

The combination of equations 6 and 7 is now commonly known as the Stokes-Einstein law. This has been shown to give good agreement between calculated and experimental values in the restricted case of a large solute molecule diffusing in a medium of smaller solvent molecules.

Eyring and his co-workers[16-21] have also investigated the relativity of diffusivity and viscosity by the application of the kinetic theory of reaction rates.

This work has been summarised by Glasstone, Laidler and Eyring[22]. They considered diffusion as a process in which molecules jump from a given position in the liquid system into one of the adjacent holes available in the liquid structure and deduced that the rate of "jumping" was

$$K = \frac{k\,T}{h} \cdot \frac{f^{*}}{f} \cdot e^{(-\frac{E}{RT})} \qquad \ldots\ldots\ldots\ldots\ldots(8)$$

where K = a specific reaction constant for the moving molecules

E = an activation energy

k = Boltzmann constant

h = Plank constant

T = absolute temperature

f^{*} = a partition function for the activated state

f = a partition function for the normal state.

Now from basic diffusion principles

$$D = \lambda^2 K \qquad \ldots\ldots\ldots\ldots\ldots(9)$$

where λ = the distance between equilibrium positions of the diffusing molecules

$$\therefore \quad D = \frac{\lambda^2\,k\,T}{h} \cdot \frac{f^{*}}{f} \cdot e^{-(\frac{E}{kT})} \ldots\ldots\ldots\ldots\ldots(10)$$

The values of f^* and f can be found by considering that a diffusing molecule whilst in a hole is contained in this position by the neighbouring molecules but that it has complete freedom of motion within the hole. Eyring et al.[16-22] showed that

$$f = \left(\frac{2\,\pi\,m\,k\,T}{h^2}\right)^{3/2} \left[\iiint e^{\left(-\frac{V}{RT}\right)} dx.dy.dz.\right] \quad .....(11)$$

and

$$f^* = \left(\frac{2\,\pi\,m\,k\,T}{h^2}\right) \left[\iiint e^{\left(-\frac{V}{RT}\right)} dx.dy.dz.\right]^{2/3} \quad .....(12)$$

Therefore

$$D = \frac{\lambda^2 k\,T\sqrt{2\,\pi\,m\,K\,T}}{h^2} \left[\iiint e^{\left(-\frac{V}{RT}\right)} dx.dy.dz.\right]^{1/3} \quad ..(13)$$

They also developed an expression for viscosity by the application of reaction-rate theory, viz.

$$\frac{D\eta}{k\,T} = \frac{\lambda_1}{\lambda_2\,\lambda_3} \quad \frac{K_v}{K_d} \quad ....(14)$$

where λ_1 = the perpendicular distance between two neighbouring layers of molecules sliding past one another

λ_2 = the distance between two neighbouring molecules in the direction of motion

λ_3 = the distance between neighbouring molecules in the plane normal to the direction of motion.

K_v = rate constant for the process of viscosity

K_d = rate constant for the process of diffusion

If the rate constant for viscosity and diffusivity are assumed equal this reduces to

$$\frac{D\eta}{k\,T} = \frac{\lambda_1}{\lambda_2\,\lambda_3} \quad ....(15)$$

This equation has been shown to give better agreement between diffusivity and viscosity than the Stokes-Einstein equation when the solvent and solute molecules are of comparable size.

Equation 10 suggests that diffusivity should vary exponentially with the absolute temperature. This has been verified by several workers, namely, Graupner and Winter[23], Partington, Hudson and Bagnall[24], Caldwell and Babb[25], and by Taylor[26] who using the data of Cohen and Bruins[27] showed that D varied with T according to the equation

$$D = A\, e^{(-\frac{E}{RT})} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(16)$$

where E = an activation energy

A = an experimental constant

Christiansen[28] has proposed that

$$D = B\, T^{\frac{1}{2}}.e.^{-(\frac{E}{RT})} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(17)$$

where B = an experimental constant.

Hartley and Crank[29] have shown that for "ideal" solutions

$$D_A = (\frac{RT}{N})(\frac{1}{\sigma_A \eta}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(18)$$

and for "real" solutions under constant volume conditions

$$D_{A.B.} = \frac{RT}{\eta N}\left[1 + \frac{\partial \ln \gamma_A}{\partial \ln N_A}\right]\left[\frac{N_B}{\sigma_A} + \frac{N_A}{\sigma_B}\right] \quad \ldots\ldots\ldots(19)$$

where D_A = diffusion coefficient for component A

$D_{A.B.}$ = mutual diffusion for system of components A and B

T = absolute temperature

N = Avogadro's Number

γ_A and γ_B = activity coefficients of components A and B

N_A and N_B = mole fractions of components A and B

η = viscosity of the system

ζ_A and ζ_B = resistance terms for components A and B

Sandquist and Lyons[30] have deduced that

$$\frac{1}{\zeta_A} = \frac{N.}{RT}\left[D_{O.A.} + k_1 \frac{\Delta\eta_{A.}}{\eta_{O.A.}}\right]\eta_{O.A.} \quad \text{.....(20)}$$

where subscript "O.A." shows that the concentration of component A in the system is zero: (a similar equation is possible for ζ_B).

Values of ζ_A and ζ_B can therefore be calculated for insertion in the Hartley-Crank equation to give an expression for calculating the diffusion coefficients for such systems over the entire concentration range i.e. for $N_A = 0$ to $N_A = 1$.

Prager[31] after the work of Johnson[32] on the relationship between the self diffusion coefficient of two components and their mutual diffusion coefficient, has proposed that self diffusion coefficients should have the same value as mutual diffusion coefficients corrected for solution activity.

Lamm[33] in considering diffusion in a system of three components A, B and isotopically labelled A- denoted A', has developed equations for the self diffusion of component A and for the mutual diffusion coefficient of components A and B viz.

$$D_{A'A'} = D_{AA} = \frac{RT}{\phi_{A'A'}\left[\frac{1}{n_A} + \frac{1}{n_{A'}}\right] + \phi_{AB}\left[\frac{1}{n_A + n_{A'}}\right]} \quad \ldots(21)$$

and $$D_{AB} = \frac{RT}{\phi_{AB}\left[\frac{1}{n_A + n_{A'}} + \frac{}{n_B}\right]} \times \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln N_B}\right) \ldots\ldots(22)$$

where n_A = the molar concentration of component A

ϕ_{AB} = frictional resistance per c.c. between components A and B

D_{AB} = mutual diffusion coefficient for components A and B

γ_B = activity of component B

The absolute theory of diffusion remains somewhat complicated for everyday application to chemical problems and the introduction of empirical factors has resulted in some useful correlations.

Wilke[34] following the work of Taylor[26] on the inter-diffusion of dissimilar molecules and the effect of temperature on the diffusion coefficients proposed that

$$F = \frac{T}{D\eta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(23)$$

where T = absolute temperature

η = viscosity

D = diffusion coefficient

F = a diffusion factor,

and investigated the effects of temperature, solute and solvent properties, and concentration upon F.

He found that F was constant for any given solvent-function of the molal volume of the solute for the diffusion of various solutes into a given solvent. To account for the effect of solvent properties in such systems he introduced a factor

$$\text{where} \quad \phi = \frac{F_S}{F_W} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(24)$$

F_S = the diffusion factor for diffusion of a solute into any solvent.

F_W = the diffusion factor for diffusion of the same solute into water at the same molal volume.

Using these factors he prepared a "Diffusion Factor Chart" from which the diffusion factor F for a solute of known molal volume diffusing into a known solvent could be estimated. If F and the solvent viscosity are known the diffusion coefficient of the solute can be estimated from equation (23).

Schiebel[35] expressed Wilke's correlations by the empirical equation

$$F = 1.22 \times 10^{7} \times \frac{V_A^{1/3}}{1 + \left(\frac{3V_B}{V_A}\right)^{2/3}} \qquad \ldots\ldots(25)$$

where V_A and V_B = mole volumes of components A and B, and suggested that

$$D = 8.2 \times 10^{-8} \, \frac{T}{\eta} \cdot \frac{1 + \left(\frac{3V_B}{V_A}\right)^{2/3}}{V_A^{1/3}} \qquad \ldots\ldots(26)$$

Othmer and Thakar[36] proposed that diffusivity and viscosity are related by the equation

$$\text{Log } D = -\frac{E_d}{E_v} \log \eta + c \qquad \ldots\ldots\ldots\ldots\ldots\ldots(27)$$

where E_d = energy of activation for diffusion

E_v = energy of activation for viscosity.

As $E_d \approx E_v$, logarithmic plots of diffusivity vs viscosity should result in straight lines of slopes equal to minus one.

They found that for a number of systems the slopes of the lines were between -1.07 and -1.15.

They assumed an average slope of -1.1 and proposed that for diffusion of a solute in water

$$D_w \times 10^5 = \frac{14.0}{\eta^{1.1} \; V_m^{0.6}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(28)$$

and for diffusion of the same solute in any solvent

$$D_s \times 10^5 = \frac{14.0}{\eta_w^{1.1 \frac{L_s}{L_w}} . V_m^{0.6} \; \eta_s^{20}} \qquad \ldots\ldots\ldots\ldots\ldots(29)$$

where D_s and D_w = diffusion coefficients in water and solvent

η_w = viscosity of water

η_s^{20} = viscosity of solvent at 20°C.

V_m = molal volume of diffusing substance

L_w = latent heat of vaporisation of water

L_s = latent heat of vaporisation of solvent

Recently Innes and Albright[37] discussed the effect of temperature on liquid diffusion coefficients and showed that

$$D = A T^n e^{-\frac{B}{T}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (30)$$

where A, B and n are constants, gave better agreement between calculated and experimental results than did

$$\frac{D\eta}{T} = F \quad (34)$$

They proposed that diffusion coefficients of any given class of compounds at a given temperature can be estimated from $DV^m = K$ where K and m are constants which depend upon the class of compounds and the solvent in use.

1.3.1. The Diffusion of Electrolytes in Solution

In general two types of diffusion coefficient are of interest in the study of electrolytic solutions, namely; salt-diffusion and self-diffusion.

1.3.1.1 Salt-diffusion

The diffusion coefficient for salt-diffusion gives a measure of the rate of mass transfer of an electrolyte from one solution into another solution of lower concentration.

This diffusion coefficient can be determined experimentally in two ways; either with the electrolyte diffusing from a reservoir with a theoretically constant concentration or from a reservoir whose concentration is continually decreasing as the electrolyte diffuses from it. The former method gives a differential value of the diffusion coefficient, i.e. mass transfer for a specific concentration, and the latter an integral value, i.e. mass transfer for a concentration range.

A summary of the numerous experimental methods available for measuring diffusion coefficients of this type has been given by Longsworth[38].

1.3.1.2 Self-diffusion

The diffusion coefficient for self-diffusion gives a measure of the rate of movement of one type of ion at small concentrations, usually a common ion isotopically labelled, in an electrolytic solution of otherwise constant composition.

Most of the self-diffusion coefficient values found experimentally have been determined by use of either the diaphragm cell method[39-41] or the open-ended capillary method[42-46].

1.3.2. General theory for diffusion in electrolytic solutions.

1.3.2.1 Introduction.

The quantitative theory of electrolytes depends upon two facts, viz:

(i) To a first approximation the properties of electrolytic solutions are additive and functions of the individual ions.

(ii) The deviations from additivity, which increase slowly with increasing concentration, may be explained by the interactions between ions as charged particles and between ions and the solvent molecules. In dilute solutions the effect of solvent molecules is negligible and theories for the properties of ionic solutions can therefore be developed on the basis of general electrostatic principles for charged particles.

1.3.2.2. Salt diffusion of simple electrolytes in dilute solutions

By considering the diffusion of a simple electrolyte dissociating into ν_1, cations and ν_2 anions with Z_1 and Z_2 as respective ionic valencies.

Harned[47] after the method of Onsager and Fuoss[48] has shown that for an 'ideal' solution

$$Do = Dn_{\rightarrow o} = \frac{(\nu_1 + \nu_2)\, w_1\, w_2}{\nu_1\, w_2 + \nu_2\, w_1}\, kT \qquad \ldots\ldots\ldots\ldots(31)$$

where w_1 and w_2 = mobilities of the ions in unit force fields. This is the limiting equation of diffusion originally developed by Nernst[49] valid at infinite dilution of electrolyte. This equation can be extended by considering a 'real' electrolytic solution to give:

$$D = (\nu_1 + \nu_2)\, \frac{M}{n}\, kT\, \left(1 + \frac{n\, \partial \ln y}{\partial n}\right) \qquad \ldots\ldots\ldots\ldots(32)$$

where n = number of mols. of electrolyte per unit volume

y = activity coefficient

T = absolute temperature

Onsager and Fuoss[49] have shown that the mobility term $\frac{M}{n}$ is equal to

$$\frac{M}{n} = 1.0741 \times 10^{-20} \frac{\lambda^{o}_{1} \lambda^{o}_{2}}{\nu_{1}|z_{1}|\Delta^{o}}$$

$$- \frac{(|z_2|\lambda^{o}_{1} - |z_1|\lambda^{o}_{2})^{2}}{|z_1 z_2|(\nu_1 + \nu_2)\Delta^{o2}} \times \frac{3.133 \times 10^{-19}\sqrt{I}}{\eta_{o}(D^{1}T)^{\frac{1}{2}}(1 + ka)}$$

$$+ \left(\frac{z_2^{\,2}\lambda^{o}_{1} + z_1^{\,2}\lambda^{o}_{2}}{\Delta^{o}}\right)^{2} \times \frac{9.304 \times 10^{-13}}{\eta^{o}(D^{1}T)^{2}} C^{2}\phi(ka) \ldots (33)$$

where λ^{o}_{1} and λ^{o}_{2} = limiting equivalent ionic conductances

Δ^{o} = sum of the limiting ionic conductances

D^{1} = dialectric constant for the solvent

η_{o} = viscosity of the solvent

I = ional concentration $\Sigma C_i Z_i^{2}$

k = reciprocal of the radius of the ionic atmosphere

α = the distance parameter of the Debye-Hückel theory

$\phi(ka)$ = the exponential integral function of the Debye-Hückel theory.

Now, in ionic solutions the electrostatic forces tend to bring the ions of opposite sign together while thermal forces act contrariwise. Debye and Hückel[50,51] have shown that these effects lead to the formation of ionic atmospheres whereby each positive ion is surrounded by an atmosphere which contains more negative and less positive ions than the bulk solution. Similarly a negative ion is surrounded by a positive atmosphere.

The action of forces which cause the ions to move, leads to two effects which are subject to quantitative treatment viz.:

(A) The "time of relaxation" effect whereby the applied force causes the central ion to move away from its atmosphere. This ion attracts the lagging atmosphere and causes the original spherical distribution of the ions in the atmosphere to assume an assymetry. The nett. effect is the retardation of the motion of the ion. This effect has been treated by Onsager[52] in his development of an equation for the mobility term in the general diffusion theory.

It should be pointed out however that in the process of diffusion of a simple electrolyte both kinds of ion travel with the same velocity in the same direction and the 'time of relaxation' effect is absent.

(B) The effect due to electrophoresis. This is due to the central ion migrating in one direction and its atmosphere and solvent moving in the opposite direction. This counterwise motion has the effect of retarding the motion of the ion.

From many experimentally determined diffusion coefficients it is now well established that for solutions of simple electrolytes:-

(1) Plots of differential diffusivity vs concentration or square root concentration pass through a minimum value which corresponds closely to the minimum in the activity coefficient function. This confirms the suggestion of Van Rysselberghe[53] that for KCl solutions the differential diffusivity depends mostly on the activity factor.

(2) The values of diffusivity calculated from theoretical equations agree with experimental results only at very low concentrations (e.g. for NaCl $< .01M$) and that the experimental values become increasingly less than the calculated value as the concentration increases.

For concentrated electrolytic solutions a number of effects negligible in dilute solutions become of greater importance e.g. viscosity, ionic hydration or solvation and incomplete dissociation (activity coefficient).

To correct the deviation between experimental results and calculated results for concentrated solutions Onsager and Fuoss suggested that the increase in viscosity with increasing concentration would have an appreciable effect on the mobility term in the theoretical equation and that this effect is approximately inversely proportional to the viscosity of the solution.

Gordon[54] has also suggested an equation for calculating diffusion coefficients which includes the ratio $\frac{\eta_0}{\eta}$ in the mobility term.

Harned and Owen[55] have shown that correction of the theoretical plot for NaCl diffusivities by $\frac{\eta_o}{\eta}$ causes it to approach the experimental values at moderate concentrations but overcorrects in solutions of higher concentrations. More recently, Robinson and Stokes[56] after the method of Hartley and Crank[29] have attempted to compute the diffusion coefficients of electrolytes in concentrated solutions. Their work is theoretically uncertain in several instances, however[57].

1.3.2.3 Self-diffusion of single electrolytes.

The Nernst equation for computing diffusion coefficients of ions at infinite dilution

$$D_i = \frac{RT}{ZF^2} \lambda^o_1 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (34)$$

where λ^o_1 = limiting conductance

Z = charge on the ion

R = gas constant

T = absolute temperature

F = Faraday

has been adapted to self-diffusion by Mills and Kennedy[46]. Gosling and Harned[58] have applied Onsager's[52] limiting equation for the diffusion coefficient of an ion at very small concentrations in a solution of otherwise constant composition, to self-diffusion. This takes the form

$$D_1 = \frac{RT\,\lambda^o_1}{|Z_1|F^2} - \frac{\lambda^o_1|Z_1|\;F}{3N\;D}\;2.7 \times 10^6\sqrt{\frac{4\pi}{DRT}}\;\left[1 - \sqrt{d(w_1)}\right]\;I \quad ..(35)$$

where F = Faredays

R = gas constant

T = abs. temperature

Z_1 = charge on ion '1'

λ^o_1 = limiting conductance of ion '1'

$d(w_1)$ = a factor dependent upon the number and valence types of the ions present, and

$$d(w_1) = \left(\frac{|Z_1|}{|Z_2| + |Z_3|}\right)\left(\frac{|Z_2|\lambda^o_2}{|Z_1|\lambda^o_2 + |Z_2|\lambda^o_1} + \frac{|Z_3|\lambda^o_3}{|Z_1|\,\lambda^o_1 + |Z_3|\,\lambda^o_1}\right) \quad (36)$$

for the diffusion of ion type '1' of low concentration in a solution containing ion types 2 and 3 with $C_2|Z_2| = C_3|Z_3|$. Mills and Kennedy[46] have shown that in solutions of alkali metal halides the self-diffusion coefficient of an iodide ion D_I^* approaches the limiting theoretical value calculated from the Nernst equation.

The values of D_I^* decrease with increasing concentration in a manner which suggests that the bulk viscosity of the solution has an important effect on diffusivity. They also showed that at moderate concentrations $D_I^* \frac{\eta}{\eta_0}$ is almost a linear function of $\sqrt{C}$.

Wang[59] has recently shown that the graph obtained by plotting the ratios of the self diffusion coefficients of sodium and chloride ions in sodium chloride relative to their values in water, against concentration is similar to the graph of $\frac{\eta_o}{\eta}$ vs concentration

where η_o = viscosity of water

η = viscosity of solution

From these self-diffusion results it would appear that viscosity plays an important part in determining the rates at which ions move.

1.3.3. Diffusion in mixed electrolytes.

Following the theory of Nernst, Vinograd and McBain[60] showed that the equation for calculating the diffusivity of any cation is

$$n_+N_+ = \frac{-RT}{F}\ \frac{u_+}{n_+}\left[G_+ - n_+C_+\ \frac{\Sigma u_+\ G_+/n_+ - \Sigma u_-\ G_-/n_-}{\Sigma u_+\ C_+ + \Sigma u_-\ C_-}\right]\ldots\ldots(37)$$

where n = valence of ion

u = mobility of ion

C = concentration of ion

G = concentration gradient of the ion

N = ion flux

and where the diffusing potential for each ion involves both the concentration gradient of the particular ion and the gradient of the electrical potential in the solution. This equation, however, is subject to the limitations that activity coefficients, collision effects and the effects of ion pairs have been ignored. Vinograd and McBain applied this equation to mixtures of $BaCl_2/HCl$ and KCl/HCl and found good agreement between theoretical and experimental results.

Qualitatively their conclusions were:-

(1) The diffusivities of cations present only in small concentrations are increased by the accompanying diffusion of an electrolyte in which the diffusivity of the cation is slower than its anion.

(2) The diffusivity of cations present only in small concentrations is decreased by the accompanying diffusion of an electrolyte in which the cation diffuses faster than its anion.

Dean[61] considered the diffusion of ions in supporting electrolytes and proposed the equation

$$\bar{D} = D_o \left[1 \pm \frac{Z\Delta}{\Delta_s} \quad 1 - \frac{\Delta_o}{\Delta_s} \ln(1 + \frac{\Delta_o}{\Delta_s}) \right] \quad \ldots.(38)$$

where $\Delta = \Sigma u_+ C_+ / Z_+ - \Sigma u_+ C_- / Z_-$ for the diffusing salt

$\Delta_s = \Sigma u_+ C_+ =$ conductivity of the diffusing salt

$\Delta_o = \Sigma u_+ C_+ =$ the conductivity of the supporting electrolyte.

This equation predicts that the effect of the supporting electrolyte will be determined only by its conductivity relative to that of the diffusing salt and will be independent of the relative ionic mobilities of the non-diffusing salt.

The experimental results and those calculated from the equation also showed good agreement despite the fact that the equation is based on approximations.

1.4. Diffusion in porous media

In the earlier work on diffusion from porous media, the media, usually gels, were used solely as a means of providing a sharp boundary between the solution and the solvent, with the assumption that the gel exerted no influence on the diffusion rates.

Studies of diffusion in gelatin were carried out by Graham[62], Beckhold and Zeigler[63], Herzog and Polotsky[64] and of diffusion in agar gels by Voigtlander[65], Beckhold and Zeigler[63], Stiles et al.[66-68], and Fricke[69].

The first extensive investigation of the effect of solid structure on the diffusion process was carried out by Friedman and Kraemer[70], who devised a method of studying the structure of gelatin gels by considering the diffusion of non electrolytes to and from the gel. The diffusion coefficients of these non electrolytes were calculated using an equation, developed by March and Weaver[71] and showed slower diffusion in gels than in water solutions. They suggested that, provided the diffusion took place only through the liquid in the pores of the gel, the slowing down was due to three causes:-

(1) The solid gelatin mechanically blocked part of the area across which diffusion could take place. (This is the "porosity factor" of a later reference[95].)

(2) Since diffusion was taking place through very small capillaries there was a drag on the molecules caused by the proximity of the capillary walls.

(3) The viscosity of the liquid in the gel was different from that of water at the same temperature.

An equation was deduced connecting diffusion coefficients in water and in gels so as to include the radii of the openings in the gel framework. viz:

$$K_w = K_g(1 + 2.4\,\tfrac{r}{R})(1 + \alpha)(1 + \pi) \quad \ldots\ldots\ldots(39)$$

where K_w = diffusion coefficient in water.
K_g = diffusion coefficient in the gel
r = radius of the diffusing particle
R = average radius of the pores
α = a correction factor for viscosity
π = a correction factor for mechanical blocking

This correction for the proximity of the pores to the diffusing particles $(1 + 2.4\,\tfrac{r}{R})$ was obtained from Ladenburg's correction to Stokes' law.

In further investigations on gelatin and agar gels Friedman[72-73] using the same experimental technique, showed that for some ten non-electrolytes the product of the molecular weight and the square of the diffusion coefficient was almost constant - a result specific for molecular diffusion[74]. Friedman and Klemm[75] continued this work by studying the diffusion of methanol and ethanol in gels of cellulose acetate in benzyl alcohol.

The effect of gel concentration on the rates of diffusion of electrolytes in gelatin gels has been studied by Cordier[76,77] who has shown that diffusion coefficients in gels, when extrapolated to zero gel concentration, do not result in values equal to the values in pure water and suggested that this is caused mainly by changes in the gel structure by the presence of the diffusing electrolyte.

Using experimental methods similar to those of Friedman, Cady and Williams[78] studied the diffusion of non electrolytes in wood. They calculated the approximate pore sizes for various species of wood and pointed out that:-

(1) The most significant of the effects of a porous medium on diffusion, as suggested by Friedman, was that of mechanical blocking which is proportional to the fraction of the area unobstructed by the solid structure - denoted A. In order to compare D_S (diffusion coefficient in solution) and D_W (diffusion coefficient in wood) they proposed that D_W should be multiplied by A and that any difference between D_S a and D_W after this correction was due to the other effects suggested by Friedman.

A, had previously been expressed by Buckingham[79] on the basis of observations on the resistance of soils to the diffusion of gases, in terms of, S, the partial pore volume, as $A = S^2$, and also by

Dumaski[80] as $A = 1 - (1 - S)^{2/3}$ ....(40)

Cady and Williams found that this latter relationship reasonably satisfied their experimental results

where $S = 1 - \frac{g}{d}$

g = grms. of wood / bulk c.c.

d = density of the wood.

(2) When the ratio of $\frac{r}{R}$ varied, the following three types of diffusion took place.

(A) Hindered diffusion, in which $\frac{r}{R}$ was not too small to be of significance.

(B) Free diffusion, in which the effective pores were small enough to prevent mixing of the water in the media with the surrounding solution but large enough to allow practically unrestricted diffusion of the solute molecules.

(C) Stirred diffusion, in which the pores were so large that mechanical mixing with the liquid in the pores took place as the solution was stirred.

Boucher, Brier and Osburn[81] investigated the extraction of soybean oil from porous plates using perchlorethylene and carbon tetrachloride - ethylene dichloride mixture as solvents. They concluded that:-

(1) The liquid film resistance was negligible compared with the resistance to diffusion within the solid, within the limits of Re No.14.7 - 20,400.

(2) The extraction process was one of pure molecular

diffusion with the diffusion coefficients being substantially constant for any one temperature and independent of concentration gradient despite the large differences in solute and solvent viscosities.

(3) The diffusion coefficients could be correlated as a function of the product of the viscosities of the solute and solvent.

(4) The values of the diffusion coefficients found were less than would be obtained for the simple interdiffusion of two pure components and that this was due to, the mechanical blocking effect of the solid, the drag on the molecules due to their proximity to the capillary walls, and to the tortuous paths which the diffusing particles would have had to follow within the solid.

Although diffusion theory had been shown to apply to the extraction of soybean oil from porous clay plates Osburn and Katz[82] found that the extraction of oil from soybean flakes did not follow the general diffusion pattern. They expanded the application of diffusion theory to solvent extraction from porous solids to include both the internal and external structure of the solids. They showed that with diffusion taking place simultaneously from two or more different structures, wide variations in the type of theoretical extraction curves were possible and that comparison of extraction data for different materials could be made only when details of the structure of the solid were known.

On this basis extraction curves which seemingly do not fit diffusion theory may be resolved into subsidiary curves each of which follows the requirements of normal diffusion theory, with each curve being representative of a constant diffusion coefficient.

This work was continued by King, Katz and Brier[83] who showed that the experimental extraction curves obtained could not be duplicated by a single theoretical curve for any constant value of diffusion coefficient for a given flake thickness as was the case for the extraction of oil from the porous slabs. They claimed that the structure of the soybean flakes and the distribution of the extractable material in the flakes were responsible for the discrepancy.

It should be noted however that the flakes used by King, Katz and Brier were prepared by a roller mill and were therefore not of a uniform thickness - a condition required by diffusion theory.

Othmer and Agarwal[84], who worked on the extraction of oil from soybeans using commercial hexane containing varying quantities of soybean oil, showed that mass transfer from whole or half beans did not agree with diffusion theory. They found that the rate of extraction was proportional to the 3.5 power of the oil remaining in the flakes at any time and that the extraction rate decreased approximately as the flake thickness raised to the fourth power.

They suggested that extraction was a problem of fluid dynamics and that extraction rates were physically and mathematically defined by the Hougen-Poiseuille law governing viscous fluid flow in capillaries.

It would appear that the method of preparation of the flakes for extraction plays a very important part as to whether or not extraction is by diffusion. That this is true has been shown by Morris and Wakeham[85] in their work on extraction of peanut oil from a section of peanut kernels specially prepared with a microtome, using n-pentane and a mixture of hexanes as solvents.

They showed that after the initial extraction, mass transfer was caused by molecular diffusion and that the rate of diffusion was independent of slice thickness. It was thought that the initial extraction was from the loosely held oil in the ruptured cells and that the cell walls were the main obstacles to extraction.

Recently Antoniali and Turrizioni[86] working on the extraction of peanut oil at various temperatures with benzene as solvent, found that the resistance to mass transfer was mainly that of the cellular membranes. They also found that the energy of activation of the diffusion process was almost equal to the activation energy of the viscous flow of the solvent.

A detailed investigation into the extraction of electrolytes from three types of inert carriers of increasing complexity; single capillaries, tubes containing beds of small glass beads and porous alumina spheres, has been carried out by Piret, Ebel, King and Armstrong[87].

The mass transfer mechanism was found to be diffusional and the results obtained for diffusion rates from the capillary tubes were found to be in close agreement with the corresponding values for the integral diffusion coefficients of the respective solutes measured in free solution. In the case of the more complex carriers the experimental diffusion rates were found to be slower than those in free solution.

In addition to the mechanical blocking, and the drag on the molecules by the proximity of the walls, the porous medium also presents to the diffusing particle a tortuous path which is larger than that suggested by the linear dimension. To account for this they introduced the concept of a pore shape factor K^2, where K is the ratio of the actual to the theoretical extraction time; or for an actual sphere of radius R, KR is the radius of an equivalent idealised sphere whose structure offers no resistance to diffusion.

This concept seems in effect to be better than using an effective diffusivity D which depends both on the solid and solute and is somewhat misleading since it is not the diffusivity which is substantially altered but rather the length of the diffusion path.

The effect of initial solute concentration was investigated and their experimental results showed that this concentration had no effect on the extraction rate.

Some interesting observations on the effect of solute concentration and porous media on diffusion rates have come to light in the development of porous diaphragm diffusion cells.

McBain and Liu[88] using a diffusion cell similar to that developed by Northrop and Anson[89] with diaphragm pores varying between 2-20 x 10^{-4} Å showed that diffusion rates through the diaphragm, when compared with a standard value of KCl in water, were independent of the size of the pores and of the porosity of the diaphragm.

Stokes[41], examining the criticisms which Gordon[90] had made about the diaphragm cell of Harned and Nuttal, experimented with a similar cell having magnetic stirrers. His work on the diffusion of KCl into water showed that for integral diffusion coefficients above 0.05N there was good agreement between the results obtained by this method and those available in literature but that below this concentration the diffusion coefficients became increasingly higher with dilution than those available in literature. This he ascribed to the adsorption of the layers of solute molecules immediately close to the pore walls.

In developing a quick method for finding differential diffusion coefficients, Wall, Grieger and Childers[91] showed that the rate of diffusion of 0.52N.KCl from a porous disc suspended in a bath of solvent was the same as the rate of diffusion of NaCl from the bath into a disc impregnated with water. They therefore claimed that adsorption of solute molecules on the walls of the pores within the solid did not play an important part on the diffusion process.

Mills and Kennedy[46] using isotopic sodium and a diaphragm cell found that there was some residual radioactivity in the capillaries of the diaphragm even after repeated washing. This adsorption was not found with any other ions.

Recently two new methods of investigating pore structure and diffusion processes have been introduced.

(1) Wyllie and Rose[92] have suggested that tortuosity can be derived from the ratio of the specific electrical resistance of a porous medium saturated with a conducting fluid to the specific resistance of the fluid itself. Fatt[93] after the suggestion of Barrer[94] has shown that the tortuosities calculated for sintered glass samples from transient diffusion measurements are equal to the

tortuosities calculated from specific resistance measurements.

(2) In a mathematical paper on the diffusion of gases through pores Petersen[95] has shown that, although the normal empirical method of accounting for low diffusivities is to relate the ratio of effective diffusivity to normal diffusivity, to a function of the product of porosity (which allows for the reduced area of diffusion) and of tortuosity (which allows for the increase in diffusion path length) periodic constrictions in the cross-section of the pore might also reduce the diffusion coefficients.

Crank and Henry[96] have shown mathematically that if the diffusivity of a substance increases uniformly with increasing concentration then absorption into a porous medium is quicker than desorption from the same medium and that when the diffusivity decreases with increasing concentration the reverse is true.

2. EXPERIMENTAL PROGRAMME

Macdonald[1] has investigated the processes of absorption and desorption of N. and 3N. potassium chloride solutions and 0.3M. and 3M. sucrose solutions to and from two types of porous media at temperatures ranging from 20-80°C.

From this work it can be concluded that

(1) The mass transfer to and from the porous media was controlled by molecular diffusion and the values of the integral diffusivities obtained were lower than those for diffusion in free solution.

(2) The diffusivities vary with temperature in accordance with the suggestion of Taylor[26] that

$$D = A \exp. - \frac{Q}{RT}$$

where Q = activation energy

A = constant

R = gas constant

T = absolute temperature.

(3) The diffusivities, and the activation energies calculated from these values, depend upon the concentration of the solution, the physical properties of the solid, and whether diffusion was to or from the porous medium.

(4) The results obtained for 3N. KCl and M. sucrose agree with the theoretical submission of Crank

and Henry[95], concerning the relationship between rates of absorption and desorption and the variation of differential diffusivity in free solution with concentration.

The results for N. KCl appear somewhat anomalous in that at higher experimental temperatures absorption is quicker than desorption whereas at the lower experimental temperatures absorption is slower than desorption (an analogous changeover in diffusion rates was also found for 0.3M. sucrose solutions).

(5) Rates of desorption are substantially independent of initial solute concentration.

On the basis of these results it was decided to continue this work to include a wider range of porous materials and electrolytes with specific investigation into:

(1) The seemingly anomalous behaviour of N. KCl and whether this occurred with other electrolytic solutions

(2) The apparent independence of initial solute concentrations and rates of desorption even although the diffusivity in free solution varies with increase in concentration

(3) The relationship between (a) tortuosity
(b) porosity
(c) ion size

and the decrease in diffusivity, as compared with diffusion in free solution, of solutes diffusing to and from porous slabs.

(4) The effect of the presence of foreign ions on the diffusivities of electrolytic solutions.

3. MATHEMATICAL TREATMENT OF DIFFUSION.

3.1. Introduction

The solution of problems of diffusion has invariably been based in the past on the use of Fick's law. Recently Babbitt[97,98] has pointed out that Fick's law is not generally valid as the fundamental equation of diffusion because in the elementary kinetic derivation of this law the assumption is made that the concentration gradient is constant; such an assumption requires that the mass transfer be linearly related to the gradient and this, of course, is simply Fick's law. It is not legitimate to say that the derivation is a proof of Fick's law since the law has already been assumed.

In the following mathematical treatment therefore Fick's second law will be derived from first principles.

3.2.1. Derivation of Fick's second law.

Consider the flow of a multi component fluid - particularly the ith. component - through a small rectangular element of volume.

The mass of component 'i' in this small element of volume at any time is $\rho_i \ \delta x. \ \delta y. \ \delta z.$

Therefore the rate of change of this mass $= \dfrac{\partial \rho_i}{\partial t} \delta x. \ \delta y. \ \delta z.$ where ρ_i = density of the ith component of fluid at point x.y.z. at any time, t.

This rate of change is caused by

(a) the amount of the ith species flowing in not being equal to the amount flowing out at the same time

(b) any chemical reaction which can take place inside the small volume, producing 'i'.

If V_{x_i} V_{y_i} V_{z_i} are the components of V_i (the velocity of the ith component of fluid at point x.y.z. at time, t) in the directions of the axes then the nett rate of increase of mass across any two opposite faces of the small cubical volume, due to the first effect is

$$\rho_i(x)\, V_{x_i}(x)\ \delta y\ \delta z\ -\ \rho_i(x+\delta x)\, V_{x_i}(x+\delta x)\ \delta y\ \delta z$$

$$= -\left[\frac{\partial}{\partial x}(\rho_i V_{x_i})\right]\delta x\ \delta y\ \delta z\ +\ \delta y\ \delta z\ 0(\delta x^2) \quad \ldots(41)$$

Similar expressions can be found for the flow across other faces of the small volume.

Therefore the nett rate of increase of the ith component due to fluid flow is

$$-\left[\frac{\partial}{\partial x}(\rho_i V_{x_i}) + \frac{\partial}{\partial y}(\rho_i V_{y_i}) + \frac{\partial}{\partial z}(\rho_i V_{z_i})\right]\delta x\ \delta y\ \delta z\ +\ O(\delta x^4) \quad \ldots.(42)$$

and the nett rate of increase of 'i' due to chemical reaction is

$$k_i\, \delta x\, \delta y\, \delta z$$

where k_i = rate of increase of i per unit volume.

Therefore $\frac{\partial \rho_i}{\partial t} \delta x \; \delta y \; \delta z \quad =$

$$-\left[\frac{\partial(\rho_i \, V_{x_i})}{\partial x} + \frac{\partial(\rho_i \, V_{y_i})}{\partial y} + \frac{\partial(\rho_i \, V_{z_i})}{\partial z}\right] \delta x \; \delta y \; \delta z$$

$$+ \; O(\delta x^4) \; + \; k_i(\delta x \, \delta y \, \delta z) \qquad \ldots\ldots\ldots\ldots\ldots\ldots(43)$$

On dividing both sides by $\delta x \; \delta y \; \delta z$ and letting δx, δy and δz tend to zero, equation (43) becomes

$$\frac{\partial \rho_i}{\partial t} = -\left[\frac{\partial(\rho_i \, V_{x_i})}{\partial x} + \frac{\partial(\rho_i \, V_{y_i})}{\partial y} + \frac{\partial(\rho_i \, V_{z_i})}{\partial z}\right] + k_i$$

$$= -\nabla \cdot (\rho_i \; V_i \;) \; + \; k_i \qquad \ldots\ldots\ldots\ldots\ldots\ldots(44)$$

Now if u_i is the velocity of species, 'i', w.r.t. the mass average velocity v

$$u_i = V_i - V$$

$$\therefore \; \frac{\partial \rho_i}{\partial t} = -\nabla \cdot \rho i(u_i + V) \; + \; ki$$

$$= -\nabla \cdot j_i \; - \; \nabla \cdot \; \rho_i \, v \; + \; ki \quad \ldots\ldots(45)$$

where j_i is called the mass flux vector and is the sum of four components. These components are

(1) j_i^{c} the mass flux vector due to a concentration gradient (ordinary diffusion)

(2) j_i^{P} the mass flux vector due to a pressure gradient (pressure diffusion)

(3) j_i^{F} the mass flux vector due to a difference in external forces (forced diffusion)

(4) j_i^{T} the mass flux vector due to a temperature gradient (thermal diffusion)

Expressions for these mass fluxes can be obtained by means of the Onsager relations in the thermodynamics of irreversible processes and the equations of momentum and energy of the previous system.

The main assumptions are that the system is almost in equilibrium and that the fluxes are proportional to the first power of the gradient in the physical properties.

The pressure diffusion contribution to the mass flux is extremely small and can usually be neglected. The forced diffusion term is only important in ionic systems and if gravity is the only external force the term becomes zero. The thermal diffusion (Soret effect) is important only in cases where there are very steep temperature gradients.

3.2.2. Ordinary diffusion in a binary system

For two components A and B we have

$$\frac{\partial \rho_A}{\partial t} = -\nabla \cdot j_A - \nabla \cdot \rho_A V + k_A \qquad \ldots\ldots\ldots(46)$$

For ordinary diffusion in a binary system

$$j_A = \frac{c^2}{\rho RT} M_A M_B D_{AB} \left[x_B \left(\frac{\partial \bar{G}_B}{\partial x_A} \right)_{P.T.} \nabla x_A \right] \ldots(47)$$

where $\bar{G}_B$ = partial molar free energy (chemical potential)

M_A = molecular weight of component A

C = total concentration

x_A = mole fraction of component A

D_{AB} = binary component diffusion coefficient

Using the Gibb-Dukem relation

$$x_A \, d\bar{G}_A + x_B \, d\bar{G}_B = 0 \quad \ldots\ldots\ldots\ldots\ldots(48)$$

and $$\bar{G}_A = G_A^{o}(T) + RT \log a_A \quad \ldots\ldots\ldots\ldots\ldots(49)$$

where a_A is the activity of A

.˚. Equation (47) becomes

$$j_A = \frac{c^2}{\rho} M_A \; M_B \; D_{A.B.} \left(\frac{\partial \log a_A}{\partial \log x_A} \right)_{P,T.} \nabla x_A \quad \ldots(50)$$

Now in dilute liquid systems and for ideal gas mixtures the activity is equal to the mole fraction. Therefore

$$j_A = \frac{c^2}{\rho} M_A \; M_B \; D_{A.B.} \; \nabla x_A \quad \ldots\ldots\ldots\ldots(51)$$

Most diffusion problems are covered by two special cases,

(1) a system of constant mass density

(2) a system of constant molar density

The first refers to dilute liquid solutions at constant temperature and pressure, the second to ideal gases at constant temperature and pressure.

For a system of constant mass density we have

$$\rho = \rho_A + \rho_B = \text{constant} \quad \ldots\ldots\ldots(52)$$

$$x_A = \frac{c_A}{c}$$

$$= \frac{\rho_A}{M_A}$$

$$= \frac{\dfrac{\rho_A}{M_A}}{\dfrac{\rho_A}{M_A} + \dfrac{\rho_B}{M_B}}$$

$$= \frac{\rho_A \; M_B}{\rho_A \, (M_B - M_A) + \rho M_A} \quad \ldots\ldots\ldots\ldots\ldots\ldots(53)$$

$$\text{Therefore } \nabla x_A = \frac{\left[\rho_A(M_B - M_A) + \rho M_A\right]M_B - \rho_A\, M_B(M_B - M_A)}{\left[\rho_A\ (M_B - M_A) \quad + \rho\, M_A\right]^2}\ \nabla\rho_A \qquad \ldots\ldots(54)$$

$$= \frac{\rho.\ M_A.\ M_B.\ \nabla\ \rho_A.}{\left[\rho_A\ M_B\ +\ \rho_B\ \ M_A\right]^2} \qquad \ldots\ldots(55)$$

$$\therefore \quad j_A \ = -\frac{c^2}{\rho}\, M_A\ M_B\ D_{AB}.\frac{\rho\, M_A\ M_B \nabla \rho_A}{\left[\rho_A\ M_B\ +\ \rho_B\ M_A.\right]^2} \qquad \ldots\ldots(56)$$

$$= -\ D_{AB}\nabla\rho_A. \qquad \ldots\ldots\ldots\ldots\ldots\ldots(57)$$

Substituting for j_A in equation (56)

$$\frac{\partial\rho_A}{\partial t} = \nabla.(D_{AB}\ \nabla\rho_A) - \nabla\rho_A.V \ +\ k_A \qquad \ldots\ldots(58)$$

D_{AB} is usually assumed to be independent of position and if there is no chemical reaction $k_A = 0$ and equation (58) becomes

$$\frac{\partial\rho_A}{\partial t} = D_{AB}\ \nabla^2\rho_A \quad - \quad \nabla.(\rho_A.V.) \qquad \ldots\ldots\ldots\ldots(59)$$

For diffusion in dilute non reacting liquid systems which are not flowing, V = 0 and equation (59) becomes

$$\frac{\partial\rho_A}{\partial t} = D_{AB}\ \nabla^2\rho_A$$

$$\text{or} \quad \frac{\partial\, C_A}{\partial t} = D_{AB}\ \nabla^2 C_A \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(60)$$

Equation (60) is generally known as Fick's second law of diffusion.

3.3.1. The solution of Fick's second law for the experimental conditions used for desorption.

$$\frac{1}{D}\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \quad \ldots\ldots\ldots\ldots\ldots(61)$$

The boundary conditions are:-

(1) $C = 0$ for $x = 0, a$; $y = 0, b$; $z = 0, d$ for all values of t

(2) $C = C_o$ at $t = 0$, $0 < x < a$; $0 < y < b$; $0 < z < d$

The method used for solving the equation (61) was the application of a double Fourier Transform in x and y, followed by a Laplace Transform in t.

This gave

$$C = \frac{16\ C_o}{\pi^2} \sum_{p=0}^{\infty}\sum_{q=0}^{\infty} \frac{\exp.-D\pi^2\left[\left(\frac{2p+1}{a}\right)^2 + \left(\frac{2q+1}{b}\right)^2\right]t}{(2p+1)(2q+1)} \sin\frac{(2p+1)\pi x}{a}$$

$$\times \sin\frac{(2q+1)\pi y}{b}\left[1 - \sum_{=0}^{\infty}\left(\operatorname{erfc}\left(\frac{d+2d\delta - z}{2\sqrt{Dt}}\right) - \operatorname{erfc}\left(\frac{2d+2d\delta - z}{2\sqrt{Dt}}\right)\right.\right.$$

$$\left.\left. + \operatorname{erfc}\left(\frac{z+2d\delta}{2\sqrt{Dt}}\right) - \operatorname{erfc}\left(\frac{d+2d\delta + z}{2\sqrt{Dt}}\right)\right)\right] \quad \ldots\ldots\ldots\ldots\ldots(62)$$

$$\text{Now}\quad Q_t = \int_0^a\int_0^b\int_0^c C \; dx\, dy\, dz \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(63)$$

$$\therefore\quad Q_t = \frac{64\ ab\ C_o}{\pi^4} \sum_{p=0}^{\infty}\sum_{q=0}^{\infty} \frac{\exp.-D\pi^2\left[\left(\frac{2p+1}{a}\right)^2 + \left(\frac{2q+1}{b}\right)^2\right]t}{(2p+1)^2(2q+1)^2}$$

$$\times \Bigg[d + 4\sqrt{\frac{Dt}{\pi}} - 2\sqrt{Dt}\sum_{r=0}^{\infty}\Bigg((-1)^{r+1}\left(\frac{4rd}{2\sqrt{Dt}}\right) \mathrm{erfc}\left(\frac{rd}{2\sqrt{Dt}}\right)$$

$$+ (-1)^{r}\frac{4}{\sqrt{\pi}} \ \exp.\left(-\frac{rd}{2\sqrt{Dt}}\right)^{2}\Bigg)\Bigg] \quad \ldots\ldots\ldots\ldots\ldots\ldots (64)$$

$$\text{and} \quad E_D = \frac{Qt}{Qo} = \frac{Qt}{abd\ C_o} \quad \ldots\ldots\ldots\ldots\ldots\ldots (65)$$

$$\therefore \quad E_D = \frac{64}{\pi^4}\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\frac{\exp.-D\pi^2\left[(\frac{2p+1}{a})^2 + (\frac{2q+1}{})^2\right]t}{(2p+1)^2\,(2q+1)^2}\Bigg[1 + 4\sqrt{\frac{Dt}{\pi d^2}}$$

$$-2\sqrt{\frac{Dt}{d^2}}\sum_{r=0}^{\infty}\Bigg((-1)^{r+1}\left(\frac{4rd}{2\sqrt{Dt}}\right)\mathrm{erfc}\left(\frac{rd}{2\sqrt{Dt}}\right) + (-1)^{r}\frac{4}{\sqrt{\pi}}\ \exp.\left(\frac{rd}{2\sqrt{Dt}}\right)^{2}\Bigg)\Bigg] \quad \ldots\ldots\ldots\ldots\ldots\ldots (66)$$

A detailed mathematical account of this solution is given in appendix B.

3.3.2. The solution of Fick's second law for the experimental conditions used for absorption.

Since equation (62) is a solution of Fick's second law its negative must also be a solution i.e. with C as given, Co - C is also a solution. The solute concentration within the boundaries of the slab at time t = 0 is given by C = 0 while the solute concentration at the slab surfaces is maintained constant and equal to Co.

Thus the solution of Fick's second law for absorption is

$$C = Co \left[1 - \frac{16}{\pi^2} \sum \sum \text{....etc} \right] \text{as in equation 62} \quad ....(67)$$

$$\therefore \; Q_a = a.\ b.\ d.\ Co \left[1 - \frac{16}{\pi^2} \sum \sum \text{...etc} \right] \quad ....(68)$$

The maximum amount of solute absorbed by the slab would be such as to make the concentration of the solute the same as outside the slab i.e. C_o This would be accomplished after infinite time, therefore let $Q_\infty = abd\ Co$ .....(69)

Hence the ratio of the quantity of solute absorbed after time, t, to that absorbed after infinite time may be obtained from equations (68) and (69)

$$E_a = 1 - \frac{16}{\pi^2} \sum \sum \text{.... etc.} \quad ....(70)$$

This treatment of diffusion in porous slabs depends upon the assumptions discussed below.

3.4.1. The application of Fick's law to diffusion in porous media.

The simple solution of Fick's law given here is based upon the diffusion coefficients being constant and independent of the solute concentration. While solutions have been proposed for the more general relationship

$$\frac{\partial c.}{\partial t} \qquad \frac{\partial}{\partial x} \left(D \; \frac{\partial c}{\partial x} \right) \quad ....(71)$$

it was felt that their application to the experimental data would be extremely difficult, if not impossible, and would scarcely be justified by the accuracy of experiments of this type.

By applying the linear dimensions of the slabs to the theoretical solution of Fick's law, it was found that the graph of E_D vs. $D\pi^2t$ tended, between the limits of $D \langle 0.4, \rangle 0.15$ to a straight line. As it was found that the experimental results also tended to a linear form, it was concluded that mass transfer was due to molecular diffusion, and the use of Fick's law to calculate mean or integral diffusion coefficients was reasonably satisfactory.

The solid is, however, not without effect on the diffusion process. These effects will now be discussed.

3.4.2. The reduction in volume through which diffusion can take place.

Obviously diffusion occurs only in the free space available in the pores of the solid.

Fick's second law is $\dfrac{\partial c}{\partial t} = D.\dfrac{\partial^2 c}{\partial x^2}$

which when corrected for porosity, P, becomes

$$P.\frac{\partial c}{\partial t} = P.D.\frac{\partial^2 c}{\partial x^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(72)$$

P, may therefore be eliminated.

The expression for the concentration of solute in the slabs at any time, t, is

$$Q_d = \int_0^a \int_0^b \int_0^d C \; dx \; dy \; dz$$

and the expression for the concentration of solute in the slabs at time, t = 0 is

$$Q_o = = C_o . a. b. d.$$

Correcting these expressions for porosity

$$Q_d = P \int_0^a \int_0^b \int_0^d C \; dx \; dy \; dz \quad \text{..........(73)}$$

$$Q_o = P. C_o . a. b. d. \quad \text{..................(74)}$$

But $E_D = \frac{Q_d}{Q_o}$ from which P is eliminated.

The effect of the solid in reducing the volume through which diffusion can take place can therefore be neglected in this application of Fick's law.

3.4.3. The tortuosity of the pores within the solid.

In a porous solid the paths which the diffusing bodies have to follow are more tortuous and therefore much longer than the dimensions of the solid suggest.

Several similar corrections have been proposed to account for this.

(A) Piret et al.[87] suggested a pore shaped factor K^2 where K^2 is the ratio of the actual time to the theoretical time necessary to reach a given percentage extraction or K is the ratio of the actual distance travelled by a diffusing particle to the theoretical distance suggested by the dimensions of the solid.

(B) A correction has been introduced by Fatt[93].

The transport equation for transient diffusion across an interface between two porous discs is

$$\frac{d\,R_t}{d\sqrt{t}} = \frac{V_L + V_U}{L_U\,V_L}\sqrt{\frac{D.}{\pi}} \quad \ldots\ldots\ldots\ldots\ldots(75)$$

where R_t = the transport ratio

t = time

$V_U + V_L$ = pore volumes of the upper and lower porous discs.

L_U = bulk length of the upper disc.

D = diffusion coefficient.

By assuming a constant value for D and substituting this along with actual measurements in equation (75) values of $\frac{d\,R_t}{d\sqrt{t}}$ can be obtained.

On comparing these values with actual results the ratio

$$\left(\frac{d\,R_t}{d\sqrt{t}}\right)_{calc.}\Bigg/\left(\frac{d\,R_t}{d\sqrt{t}}\right)_{actual.} \quad \ldots\ldots\ldots\ldots\ldots(76)$$

is obtained.

This then is the tortuosity, k, of the porous disc, where $k = \frac{l_u}{L_U} = \frac{\text{actual fluid path length}}{\text{bulk length of disc.}}$

(C) Babbitt[97] has suggested that the diffusion coefficient D should be reduced by a factor, r, where r is the ratio of the minimum theoretical distance to the actual length of the path through the solid i.e.

$$\frac{\partial c}{\partial t} = r.\,D.\frac{\partial^2 c}{\partial x^2} \qquad \ldots\ldots\ldots\ldots\ldots(77)$$

(D) Petersen[95], on the other hand, states that extremely large values of tortuosity factors are obtained from some experimentally measured effective diffusivities within pelleted, or extruded, solids and claims, that postulating pore constrictions within the solid, forms a more satisfactory explanation for the greatly reduced values of D_e, the effective diffusivity, than attempting to interpret them on the basis of tortuosity alone.

There is however no satisfactory technique to characterise independently the structure of pores within compacted materials. The validity of Petersen's ideas therefore cannot be proved.

It would appear, therefore, that the effect of increasing the path length through which the diffusing particles must pass can be accounted for in terms of relative coefficients or relative path lengths.

3.4.4. The effect of adsorption.

Since the slabs afford a large internal surface area, there is ample opportunity for adsorption of the solute molecules or ions.

McBain and Liu[88] have pointed out that if adsorption of the solute molecules occurs and even if it extends to a thickness of several molecules, it is probably largely obscured by the fact that the average pore diameter is approx. $10^{-3} - 10^{-4}$ molecular diameters.

Stokes, however,[41] found that at concentrations below 0.05 N. KCl., the integral diffusion coefficients determined by diffusion through a porous glass diaphragm became increasingly higher than the corresponding values determined by experimental techniques. This, he ascribed to a surface transport effect. Further evidence for this is provided by Mysels and McBain[99].

In the present work the effect of adsorption will be neglected in calculating the experimental integral diffusion coefficients.

3.4.5. The assumption that the material through which diffusion is taking place is homogeneous.

To avoid the possibility of a systematic error arising owing to one or more of the groups being different in composition from the others, the groups of slabs used in the experiments were never placed in the same order in the diffusion cell. The first series of experiments for each type of slab was examined and as the deviation from the mean lines drawn through the points appeared to be quite random, except for the M1 slabs, it was concluded that no group differed appreciably from the others and that the material could be regarded as homogeneous.

The scatter of the experimental results for M1 slabs is discussed fully in section 6.1.3.2.

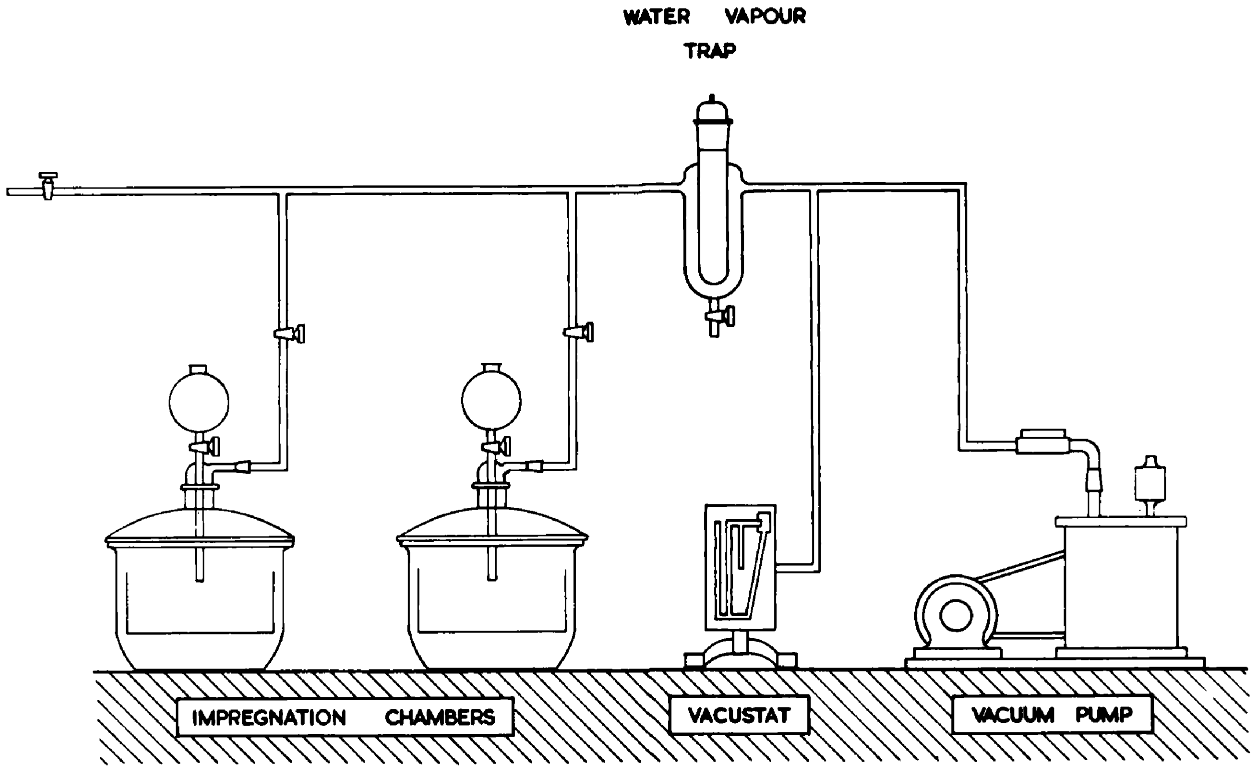
4. EXPERIMENTAL TECHNIQUE.

Before describing the experimental technique, in detail, a precis of the procedure will be given and will be followed by a description of the construction and function of each piece of apparatus.

4.1. Précis of experimental procedure.

The experiments carried out fall suitably into two categories, namely; the diffusion into a flowing stream of water of electrolytic solutions from porous media previously impregnated with solution, and the absorption under similar conditions of electrolytic solutions into the media which had been previously impregnated with air-free distilled water. Both types of experiment follow the same pattern. This can be conveniently divided into four stages:-

1. The impregnation of the slabs with either distilled water or some electrolytic solution of known concentration.
2. The introduction of the slabs into the diffusion cell where a stream of liquid flows past the slabs and diffusion takes place under specified conditions either from the slabs to the liquid or vice versa.
3. The total extraction of the electrolyte remaining in the slabs after the diffusion process so that they



APPARATUS USED IN THE IMPREGNATION OF THE POROUS EARTHENWARE SLABS

FIG. I

may be used for further experiment.

4. The analysis of the electrolytic solutions.

4.2. A detailed description of the apparatus.

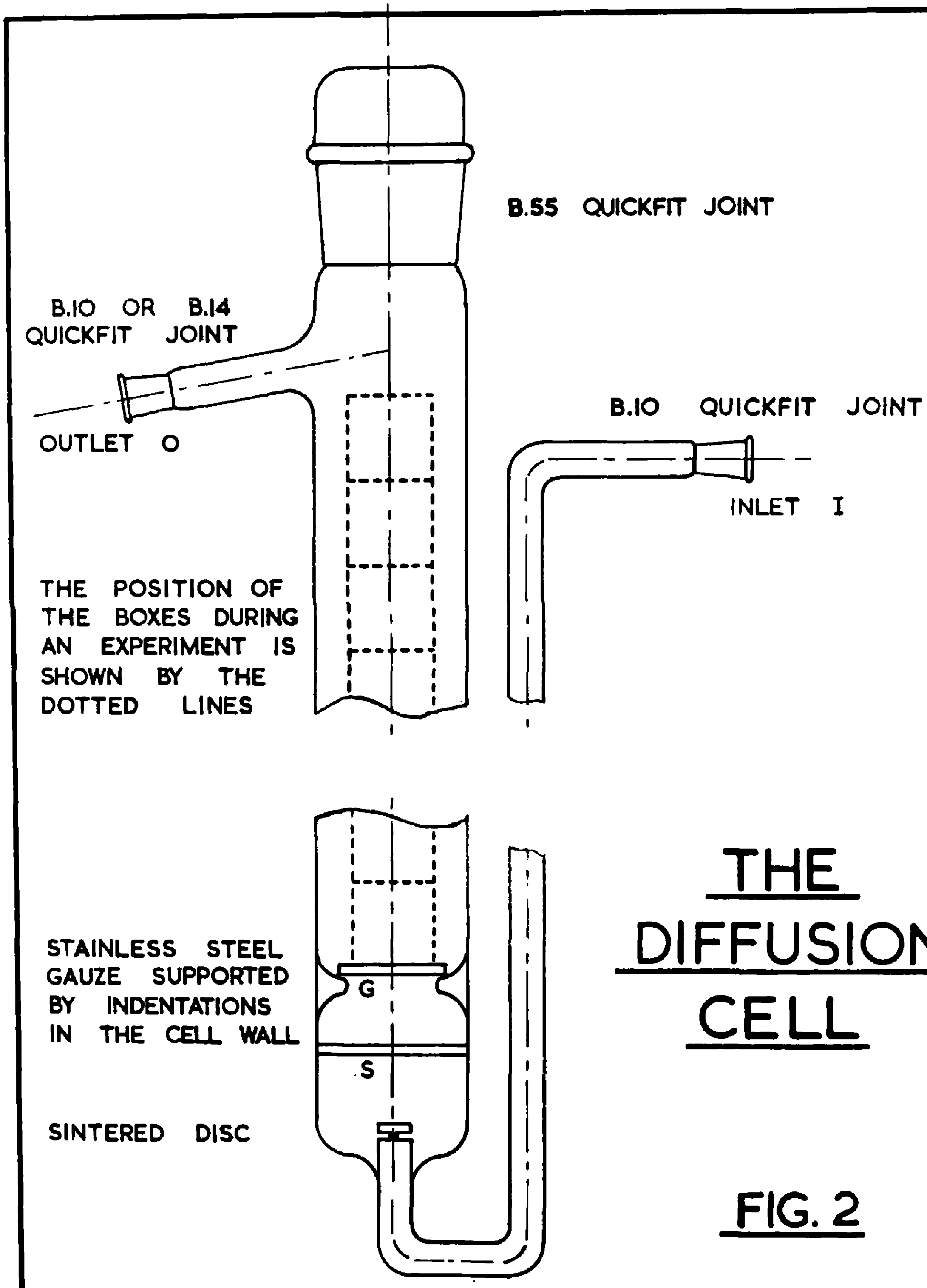
4.2.1. The impregnation unit.

The apparatus (Fig.1.) consisted of a vacuum pump connected in turn to an Edwards' "Vacustat" for measuring the absolute pressure in the system, a "Drikold" - acetone water vapour trap to protect both the pump and "Vacustat" and finally to two Pyrex desiccators fitted with dropping funnels. Into the body of each desiccator was fitted a metal grid upon which the crystallising dishes containing the slabs to be impregnated could sit.

Before each impregnation, the desiccators and dropping funnels were thoroughly dried, all glass - glass joints coated with silicone stop-cock grease and the water vapour trap filled with a mixture of "Drikold"-acetone. The large crystallising dishes containing the slabs were then placed in the desiccators and the apparatus set up as shown.

4.2.2. The diffusion cell.

The transfer of material to or from the slabs took place in the diffusion cell shown in Fig.2. The cell was primarily a specially lengthened B.55 socket into which liquid flowed at the inlet I and out at the outlet O. The



THE DIFFUSION CELL

FIG. 2

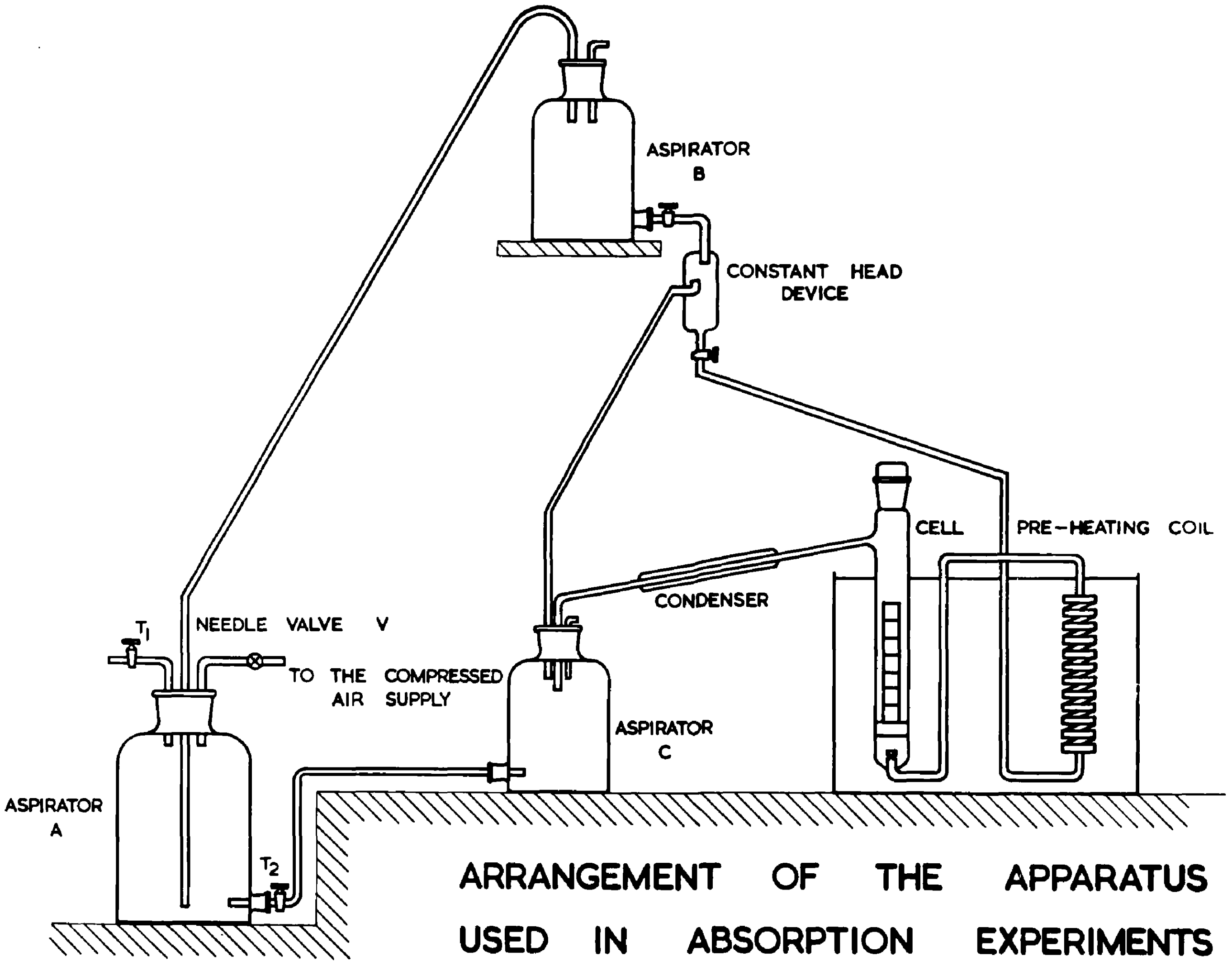
sintered glass dish (porosity 1) was used to even out minor fluctuations or channelling in the liquid being circulated. The stainless steel - or monel, depending on which electrolytic solution was in use - gauze G served both to protect the sintered disc and to support the containers for the earthenware slabs. These containers were made from formaldehyde resin boxes (in fact, children's building bricks) from which the bases had been removed and slots machined in two opposite faces. Each box carried one set of three slabs and the boxes were placed one on top of the other, but at different angles to one another.

The diffusion cell and a glass coil for preheating the liquid flowing through the cell were immersed in a thermostatically controlled water bath in which the temperature variation was ± 0.05°C. of the desired value.

4.2.3. The supply of liquid to the diffusion cell.

A. Absorption experiments

After some trials with metering pumps it was decided that in order to avoid contamination of the highly corrosive electrolytic solutions it would be better to transport these solutions using a compressed air system. A diagram of the apparatus used to recirculate the solution through the diffusion cell is shown (Fig.3.). The solution was



ARRANGEMENT OF THE APPARATUS USED IN ABSORPTION EXPERIMENTS

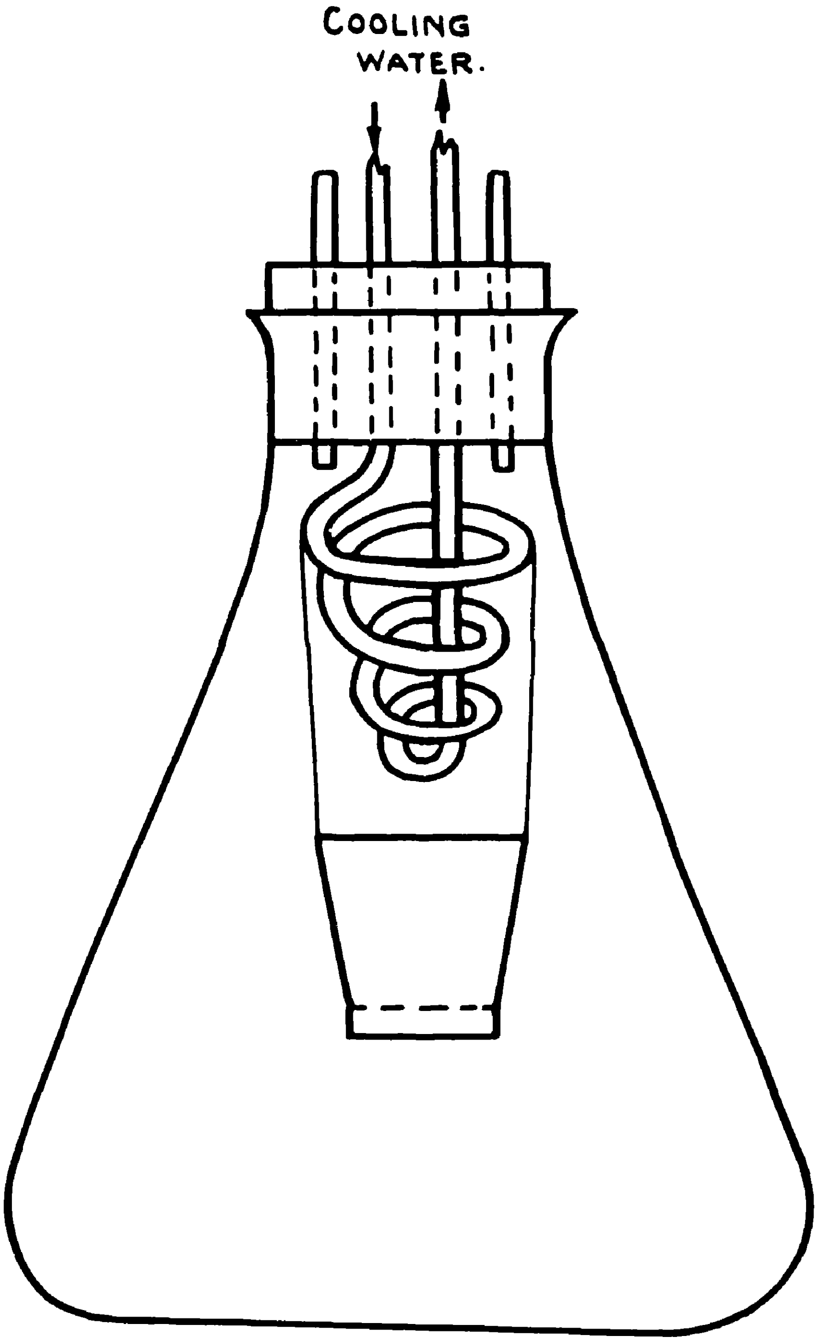
FIG. 3

prepared initially in aspirator A from where it was elevated to aspirator B by closing the taps T_1 and T_2 and opening the needle valve V which controlled the compressed air supply. From aspirator B the solution travelled to the preheating coil via the constant head device and a flowmeter. From the preheating coil the solution entered the cell and passed through it to the aspirator C where both the liquid leaving the cell and the overflow from the constant head device were collected. Aspirator C also served as a temporary reservoir when some of the solution was being elevated from A to B.

The very small reduction in concentration caused by the addition of the volume of the water retained by the slabs (about 30 ml.) to the volume of the solution being circulated (about 15 litres) is considered to be negligible.

B. Desorption experiments.

The distilled water, contaminated with electrolyte which had diffused from the slabs, was allowed to run to waste. The apparatus, therefore, did not require a recirculating system and aspirators A and C were removed. The distilled water was pumped from a reservoir of about 100 litres capacity to the aspirator B from where it flowed to the cell via the constant head device and flowmeter as before.



A TOTAL EXTRACTION UNIT.

FIGURE 4.

4.2.4. The "Total Extractors".

The total extraction of the slabs took place in the apparatus shown in Fig.4. Batteries of these units were arranged in parallel with a cooling water supply. Each unit consisted of a 1000ml. conical flask fitted with a four-holed rubber stopper which supported both a cooling coil and sintered glass filter and also provided vents to the atmosphere.

The slabs to be cleaned of residual electrolyte were placed in the filters and the water in the flasks heated to boiling. The boiling rate was adjusted so that the reflux was just sufficient to keep the glass filters continually full.

The nett effect was a Soxhlet type apparatus in which a stream of hot distilled water flowed past the slabs, removed any electrolyte and returned to the bulk solution.

4.3. A detailed description of the experimental technique.

4.3.1. The preliminary treatment of the slabs.

The porous earthenware slabs were obtained from Messrs. Aerox Ltd., Hillington Industrial Estate, Glasgow, S.W.2., who prepared the slabs to the required overall dimensions from sheets of material of specified thickness.

The materials used to manufacture these different grades of porous ceramic consist mainly of alumino-silicate aggregates specially graded for particle size. The aggregate makes up about 96% of the material, the remaining 4% consisting of clays used to keep the aggregate in suspension and to bond it during firing.

The slabs were used as rectangular parallelopipeds, that is diffusion taking place simultaneously to or from all surfaces instead of as finite solids with mass transfer occurring at only the principal faces. This method necessitates a more complicated method for the calculation of the theoretical equation but it prevents errors arising should one try unsuccessfully to seal the slab edges with some impermeable wax.

Before use the slabs were freed from dirt and loose material by impregnating them with a solution of mixed electrolytes and removing this from the slabs in the "total extractors". The process was repeated several times. They were then dried overnight at 110°C., and the overall dimensions measured by micrometer. Any slabs showing a marked irregularity in thickness were rejected as unsuitable. All the slabs, however, revealed some irregularity when the thickness was measured and a general variation of about ± 0.002" was observed.

For the H125 slabs, 21 of the most uniform were selected, and graded into 7 groups of 3 such that each group had the same mean thickness. For the other types of slabs V3, V5, V10, and M1, the most uniform 18 slabs of each type were selected and graded into 6 groups.

There are certain advantages in using groups of three slabs instead of individual slabs, e.g.,

(a) The resultant increase in the weight of solute retained by the slabs increases the accuracy of the gravimetric estimations.

(b) An attempt could be made to compensate for the variation of thickness of individual slabs by grading them into groups of the same mean thickness. This correction is not strictly accurate as the exponential terms in the theoretical equation depend upon the square of the thickness. The error resulting from this may probably be ignored as it is of the same order as the error due to the variation in thickness of the individual slabs. No attempt was made to correct for variations in length and breadth of the slabs as these dimensions are of considerably less importance than the thickness, unless the variation was excessive.

(c) The wiping of the slabs after removal from the impregnation chamber and from the diffusion cell are critical parts of the experimental technique; any error arising from these wipings is probably smaller than could be expected for single slabs.

The mean dimensions of the slabs were subsequently used to calculate the theoretical equation for that particular grade of material.

The slabs were finally prepared for use by extracting them once more for 6-8 hours to remove any dust or loose material resulting from the measuring and grading processes.

4.3.2. The impregnation of the slabs.

The slabs to be impregnated were removed from the oven in which they had been dried overnight and allowed to stand in a desiccator for 30 minutes. Each group of three slabs was placed in a tared airtight aluminium tin and weighed. After weighing the slabs were removed from the tins and placed in a crystallising dish which was in turn fitted into the impregnation chamber. The apparatus was then assembled as described in 4.2.1.

By standardising the conditions for impregnation it was found possible to reproduce the weight of liquid absorbed by the slabs to within 1%. The conditions were,

(a) The impregnation chamber was evacuated until a pressure 0.15-0.2 mm. of mercury was attained and this was maintained for 30 minutes after which the liquid with which the slabs were to be impregnated was introduced into the chamber via the dropping funnel without breaking the vacuum.

(b) The slabs were then allowed to stand for one hour before the vacuum was broken and the crystallising dish containing the slabs withdrawn from the impregnation chamber.

After the dish was removed the temperature of the impregnation liquid was measured. The slabs were then wiped with a cloth saturated with the impregnation liquid as suggested by Piret <u>et al</u>.[87] to remove the excess liquid before the impregnated slabs were replaced in the aluminium tins and reweighed.

When desorption experiments were being carried out, the remaining impregnation liquid was collected and analysed to determine the solute concentration. This was necessary as flash evaporation in the impregnation chamber resulted in an appreciable increase in the solute concentration.

After weighing, the slabs were placed in their carriers and introduced into the diffusion cell.

4.3.3. The diffusion process.

Before the impregnated slabs were placed in the diffusion cell the liquid flow rate and temperature were adjusted to the required values. The flow rate was maintained at between 10 and 12 litres per hour which was equivalent to a Reynolds' No. of about 100 at 20°C. This value is within the limits for which Boucher, Brier, and Osburn[82] concluded that the diffusion process was independent of liquid flow rate. The temperature was adjusted by varying the water bath temperature and observing the result on a thermometer immersed in the liquid flowing through the cell.

The liquid was allowed to pass through the cell until steady state conditions of temperature and flow were achieved after which the slabs were placed in the cell, in random order, at noted time intervals. The slabs were left in the cell for the desired time and then removed. After their removal the slabs were slipped out of their containers and wiped with a cloth saturated in the liquid leaving the cell, and either replaced in their respective aluminium Petri dishes or placed directly into the total extractors, depending upon whether a gravimetric or a volumetric method was to be used for the estimation of the residual quantity of electrolyte.

If a gravimetric method was to be used the Petri dishes containing the slabs were placed in the oven and dried overnight at 110°C. After removal from the oven they were allowed to cool in a desiccator for 30 minutes before weighing. The slabs were then placed in the "total extractors" and cleaned for 8 hours before being redried for further use.

If a volumetric method was to be used the slabs were continuously extracted for 8 hours and the resultant solution remaining in the flasks analysed as described later. The slabs when dried overnight were then ready for further use.

By both methods a measure of the weight of solute retained by each group of slabs was obtained. Knowing the impregnation liquid temperature and concentration, the values of Q_{∞} and Q_0 could be calculated from the weight of liquid absorbed by the slabs during impregnation. The ratio of the weight of solute retained by each set of slabs to either Q_{∞} or Q_0 - depending on whether absorption or desorption was taking place - gave values of E. These values were plotted against the appropriate time values to give a final experimental graph.

4.3.4 The analytical technique.

Grade "A" apparatus was used for all volumetric analysis. The specific gravities required for the calculation of Q_{∞} and Q_0 were measured using graduated 50 ml. density bottles. All weighings were done on an air-damped balance contained in a thermostatically controlled cupboard.

Gravimetric analysis was used wherever possible but could not be used for acids or for solutes having associated water of crystallisation. Particular methods of estimating the various solutes and mixtures of such are shown in table 4.1.

TABLE 4.1. Particular Methods of Estimating Various Solutes.

SOLUTE	METHOD OF ESTIMATION
KCl	Gravimetric or titration with $AgNO_3$.
HCl	Titration with NaOH.
LiCl	Titration with $AgNO_3$.
KNO_3	Gravimetric.
HNO_3	Titration with NaOH.
CH_3COOK	Gravimetric.
HCl/KCl	Titration with NaOH to give acid. Titration with $AgNO_3$ to give total chloride. KCl by difference.
HCl/LiCl	As for HCl/KCl.
KCl/CH_3COOK	Gravimetric to give total solids. Titration with $AgNO_3$ to give chloride. Acetate by difference.
KCl/KNO_3	Gravimetric for total solids. Titration with $AgNO_3$ for chloride. Nitrate by difference.

4.3.4.1. Estimation of the solute remaining in the slabs after diffusion process.

(a) Gravimetric analysis.

After removal from the diffusion cell the slabs were placed in their appropriate tared Petri dish and dried overnight in the oven at 110°C. They were allowed to cool in a desiccator for 30 minutes before weighing.

(b) Volumetric analysis.

After removal from the diffusion cell the slabs were continuously extracted for 8 hours. The resultant solutions were transferred to 500 ml. graduated flasks and made up to the mark at 20°C. The concentrations of these solutions were estimated by pipetting 50 ml. and titrating with the appropriate standard solution.

4.3.4.2. Estimation of the concentration of the original solutions.

(a) Gravimetric analysis.

5 ml. portions of the original solution diluted to $\frac{1}{5}$ strength were pipetted into tared evaporating basins and left overnight in the oven at 110°C. They were then cooled for 30 minutes in desiccators and reweighed.

(b) Volumetric analysis.

50 ml. of the original solution were pipetted into a 500 ml. flask and made up to the mark at 20°C. 20 ml.portions of the resultant solution were titrated with the appropriate standard solution.

5. CALCULATION OF INTEGRAL DIFFUSION COEFFICIENTS AND ACTIVATION ENERGIES FROM EXPERIMENTAL DATA.

These calculations may be conveniently divided into five sections:-

5.1. The derivation of the theoretical equations for diffusion under the specified boundary conditions, and the substitution into this of the dimensions of the particular set of slabs being used, to obtain a theoretical relationship between E_D and t (time) for predetermined values of $D\pi^2t$.

5.2. The derivation of equations for calculating values of Q_∞ previously defined as the quantity of solute present after infinite time in absorption experiments and Q_o defined as the quantity of solute present at zero time in desorption experiments and the substitution of experimental data into these equations to calculate Q_o and Q_∞.

5.3. The calculation of values of E_D from experimental data.

5.4. The calculation of integral diffusion experiments from the experimental and theoretical plots.

5.5. The calculation of activation energies for the diffusion process from the correlation suggested by Taylor[26].

$$\text{i.e.} \quad D = A \exp.(-Q/RT)$$

These sections will be discussed in detail in the following pages.

5.1. The calculation of the theoretical equation.

The first step in this calculation is to determine the dimensions of the slabs by means of micrometer measurements. Considering the relative importance of the individual dimensions the mean of six readings was taken for the thickness, a, of three for the breadth, b, and of two for the length, d.

The theoretical equation for desorption has been shown to be

$$E_D = \frac{64}{\pi^4} \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \frac{e^{-D\pi^2 \left[\left(\frac{2p+1}{a}\right)^2 + \left(\frac{2q+1}{\;}\right)^2\right]t}}{(2p+1)^2(2q+1)^2} \left[1 + 4\sqrt{\frac{Dt}{\pi d^2}}\right.$$

$$\left. -2\sqrt{\frac{Dt}{d^2}} \sum_{r=0}^{\infty} (-1)^{r+1} \left(\frac{4rd}{2\sqrt{Dt}}\right) \text{erfc.} \left(\frac{rd}{2\sqrt{Dt}}\right) + (-1)^r \frac{4}{\pi} e^{\left(\frac{-rd}{2\sqrt{Dt}}\right)^2} \right]$$

As the "error function" (erf) of a large number (i.e. $>$ 2) is almost unity, values of erf (1-erf) must be very small. Full advantage of the use of the above equation containing error functions can therefore be obtained by taking d as the largest slab dimension, i.e. the length.

As D, the diffusion coefficient, and t, the time, are both unknown it is necessary to assume some value of the product $D\pi^2t$ to evaluate the above equation. It was found that a range of values of $D\pi^2t$ from .001 to 0.050 gave values of E_D from 0.153 to 0.833.

Table 5.1 gives the average dimensions of the slabs and table 5.2 the calculated values of E_d for the chosen values of $D\pi^2t(z)$. These theoretical values are shown in graph form in Graph 1.

Inspection of the equation for the absorption of a solute by a slab shows that the calculated values of E_d are in fact also the calculated values of $(1-E_A)$. Therefore one plot of the theoretical equation is sufficient for both absorption and desorption experiments.

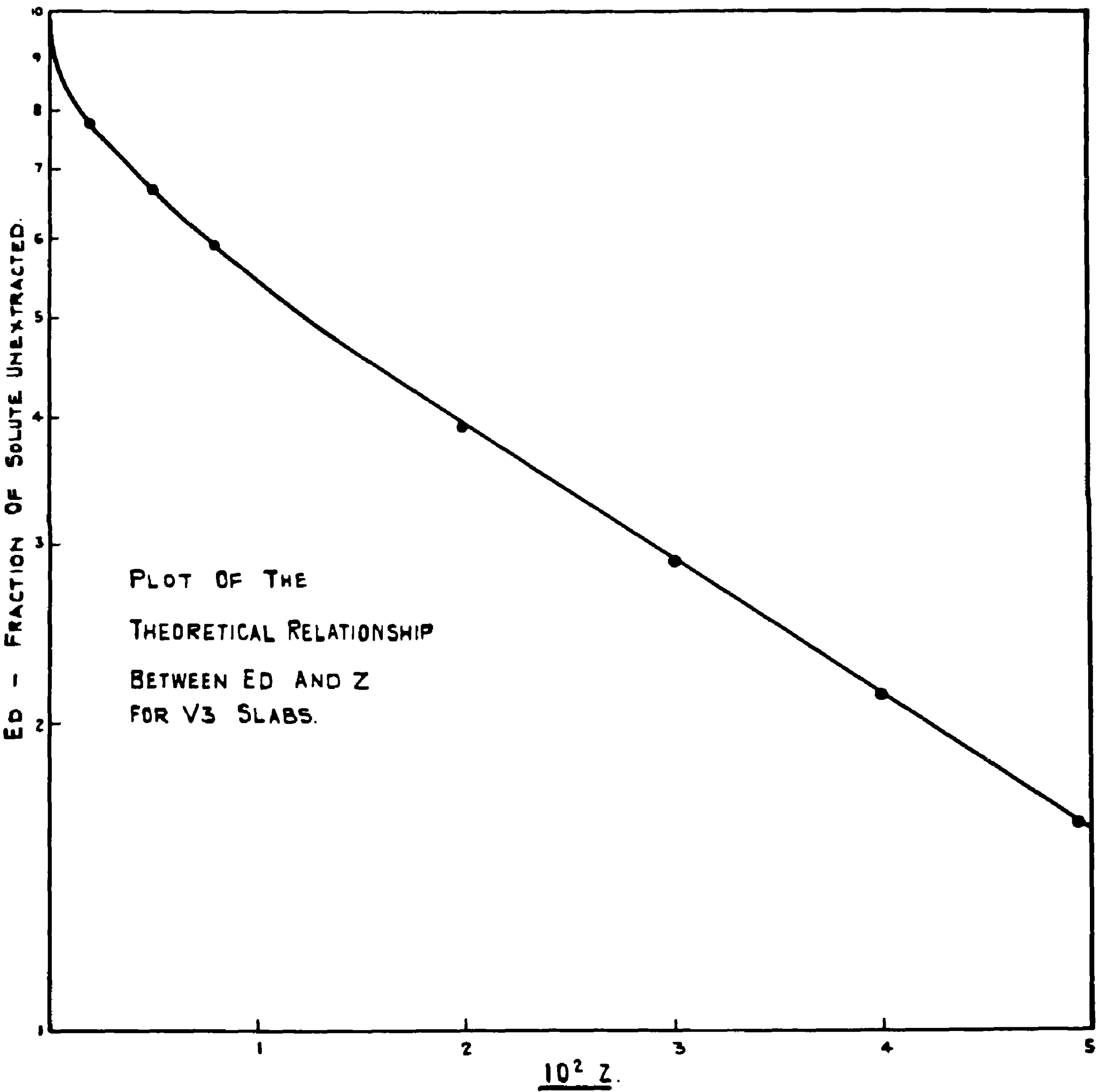
TABLE 5.1. AVERAGE DIMENSIONS OF SLABS

SLAB TYPE	AVERAGE LENGTH	AVERAGE BREADTH	AVERAGE WIDTH
H.125	1.4857	.7413	.1956
V 3	1.4991	.7616	.1975
V 5	1.5022	.7446	.1971
V 10	1.4862	.7432	.1975
M 1	1.4824	.7525	.1974

TABLE 5.2. CALCULATED VALUES OF E_D FOR SELECTED VALUES OF $D\pi^2 t$.

H125		V 3		V 5	
Z	E_D	Z	E_D	Z	E_D
.06	.113	.05	.158	.05	.157
.05	.153	.04	.213	.04	.211
.03	.282	.03	.288	.03	.286
.02	.389	.02	.392	.02	.391
.01	.543	.01	.548	.01	.546
.008	.586	.008	.590	.008	.589
.006	.636	.005	.668	.005	.667
.003	.733	.002	.779	.002	.778
.001	.833	—	—	—	—

V10		M1	
Z	E_D	Z	E_D
.05	.157	.05	.158
.04	.212	.04	.212
.03	.286	.03	.287
.02	.391	.02	.392
.01	.546	.01	.547
.008	.589	.008	.589
.005	.669	.005	.667
.002	.778	--	--


Ed - Fraction of Solute Unextracted.
10
9
8
7
6
5
4
3
2
1
Plot Of The
Theoretical Relationship
Between Ed And Z
For V3 Slabs.
1
2
3
4
5
10² Z.

Graph. I.

5.2.1. Introduction to the derivation of equations for calculating Q_0 and Q_∞.

The temperature of the slabs after impregnation was usually about 15°C. Therefore the immersion of the slabs into the diffusion cell at a temperature of, say, 50°C., which was the highest temperature used, should result in the introduction of two errors in the experimental technique:-

(1) A delay in time before the liquid in the slabs reaches the temperature of the liquid in the diffusion cell.

(2) An expansion of the liquid in the slabs, which, since the expansion of the slabs is very small compared with that of the liquid, will cause mass transfer of this liquid from the slabs into the bulk solution by means other than ordinary diffusion.

Considering (1):-

By assuming that heat transfer takes place primarily through the two principal faces of the slabs it can easily be shown by substitution in equation (78), which is readily available in literature, that the time taken for the centre of the slabs - the position farthest from the heat source - to reach the operating temperature is negligible in experiments lasting approximately 30 minutes.

Thus:-

$$T = T_a + (T_b - T_a)\frac{x}{L} + \frac{2}{\pi}\sum_{L}^{\infty}\frac{T_b\cos(n\pi) - T_a}{n}\exp. - \frac{k\,n^2\pi^2}{L^2}$$

$$+ \frac{2}{L}\sum_{L}^{\infty}\sin\left(\frac{n\pi}{L}\right)\exp.\left(-\frac{k\,n^2\pi^2 t}{L^2}\right)\int_0^L f(x')\sin\left(\frac{n\pi}{L}\right)dx \qquad \ldots\ldots\ldots(78)$$

where T = the temperature of the slab at any point x

T_a and T_b = the temperature at the faces a and b

t = time (seconds)

f(x) = the temperature at any point x at time t = 0

k = the thermal conductivity of the slab.

Now since $T_a = T_b = T_d$ the equation reduces to

$$T_x = \frac{1}{2} = T_d - \frac{4}{\pi}(T_D - T_i)\sum_{0}^{\infty}\frac{1}{2m+1}\exp.\left(-\frac{(2m+1)^2\pi^2 kt}{L^2}\right)\ldots(79)$$

By substituting the following values

T_d = 80°C: T_i = 15°C: k = 0.0014 (assuming the slabs to be almost pure silica) and expanding the terms within the summation,

$$T_x = \frac{1}{2} = 80 - \frac{4 \times 65}{\pi}\sum_{0}^{\infty} e^{-B} + \frac{1}{3}e^{-9B} \qquad \ldots\ldots(80)$$

where $B = \frac{k\,\pi^2\,t}{L^2}$,

Macdonald[1] found that the difference between the operating temperature and the temperature of the slabs one minute after immersion into the diffusion cell was of such a value that could be neglected.

Considering (2):-

It has been shown above that the slabs reach the experiment operating temperature within a few minutes of introduction into the diffusion cell. This quick rise in temperature will almost certainly cause an expansion of the liquid in the slabs. Assuming that the coefficient of expansion of the slabs is negligible compared with that of the water or electrolytic solution the volume of liquid expanding from the slabs may be calculated.

5.2.2. The derivation of an equation for Q_∞

If the expansion of the distilled water in the slabs is neglected an equation for calculating Q_∞ can be derived in the terms of the following nomenclature.

W_i = weight of distilled water within the impregnated slabs at the impregnation temperature.

D_i^W = density of water at the impregnation temperature.

D_i^S = density at the impregnation temperature, of the solution from which the solute is being absorbed.

G = the concentration in g./litre of this solution at 20°C.

Volume of water impregnated into the slabs

$$= \frac{\text{weight of water impregnated into the slabs}}{\text{density of the water impregnated into the slabs}}$$

$$= \frac{W_i}{D_i^W} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (81)$$

If this volume of water were replaced by solution at impregnation temperature then:-

The weight of solution) (volume of water at impregnation
which the slabs could) = (temperature x density of solu-
absorb after infinite) (tion at impregnation temperature
time

$$= \frac{W_i \times D_i^s}{D_i^w} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(82)$$

.°. Volume of solution which the slabs could absorb at 20°C.

$$= \frac{\text{weight of solution at impregnation temperature}}{\text{density of solution at } 20^\circ\text{C.}}$$

$$= \frac{W_i \; D_i^s}{D_i^w \; D_{20}^s} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(83)$$

.°. Weight of solute which the slabs could absorb

$$= \text{volume of solution at } 20^\circ\text{C.} \times \text{concentration at } 20^\circ\text{C.}$$

$$= \frac{W_i \; D_i^s \; G}{D_i^w \; D_{20}^s} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(84)$$

Considering now the expansion of the distilled water from the slabs:-

The free space available in the porous slabs (V), assumed to be constant $= \dfrac{W_i}{D_i^w}$

The weight of liquid in) (free space available x density
the slabs at the temp-) =(of water at the temperature of
erature of absorption(W_a) (absorption (D_a^w)

$$\therefore \quad W_a = \frac{W_i \; D_a^w}{D_i^w} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(85)$$

Dividing both sides of equation (85) by D_i^W

$$\frac{W_a}{D_i^W} = \frac{W_i \; D_a^W}{D^W \; D_i^W} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (86)$$

Now allowing for expansion replace $\frac{W_i}{D_i^W}$ by $\frac{W_a}{D_i^W}$ in equation(84).

$$\therefore \quad Q_\infty = \frac{W_i \; G \; D_a^W \; D_i^S}{(D_i^W)^2 \quad D_{20}^S} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots (87)$$

5.2.3. The derivation of an equation for Q_0

If the expansion of the distilled water in the slabs is neglected an equation for calculating Q_0 can be derived in the terms of the above nomenclature.

The weight of solution impregnated into the slabs = W_i

Volume of solution) = (weight of solution
in the slabs at 20°C.) = (density of solution at 20°C.

$$= \frac{W_i}{D^S_{20}} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (88)$$

Weight of solute) = (volume of solution x
in the slabs) = (concentration at 20°C.

$$= \frac{W_i . G.}{D^S_{20}} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (89)$$

$$\therefore \quad Q_0 = \frac{W_i \; G}{D^S_{20}} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (90)$$

Considering now the expansion of the solution from the slabs:-

The free space available in the pores (V) assumed to be constant

$$= \frac{\text{weight of solution at impregnation}}{\text{density of solution at impregnation}}$$

$$= \frac{W_i}{D^s_i} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(91)$$

$$\left.\begin{array}{l}\text{The weight of liquid in} \\ \text{the slabs at the temp-} \\ \text{erature of desorption} \\ (W_d)\end{array}\right) = \left(\begin{array}{l}\text{free space x density of solu-} \\ \text{tion at the temperature of} \\ \text{desorption}\end{array}\right.$$

$$= \frac{W_i \; D^s_d}{D^s_i} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(92)$$

Dividing both sides of equation (92) by D^s_i

$$\frac{W_d}{D^s_i} = \frac{W_i \; D^s_d}{(D^s_i)^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(93)$$

Now the volume of solution remaining in the slabs after expansion will be $\frac{W_d}{D^s_i}$

Equation (90) can be written $Q_o = \frac{W_i . G . D^s_i}{D^s_i \quad D^s_{20}} \qquad \ldots\ldots\ldots(94)$

Replacing $\frac{W_i}{D^s_i}$ by $\frac{W_d}{D^s_i}$

$$Q_o = \frac{W_i . G . D^s_d}{D^s_{20} \quad D^s_i} \qquad \ldots\ldots\ldots\ldots(95)$$

5.2.4. Comparative accuracy of the equations derived for Q_∞ and Q_0

The ratio of equations (84) and (87) $= \dfrac{D_i^w}{D_a^w}$

The ratio of equations (90) and (95) $= \dfrac{D_i^s}{D_d^s}$

For a temperature of impregnation of 18°C and a temperature of desorption or absorption of 50°C. these ratios are of the order of 1.02 - 1.03. The equations derived allowing for expansion therefore afford a 2-3% correction on the original equations.

5.3. The derivation of an equation for calculating integral diffusion coefficients.

It is apparent from the plot E_d vs Z (GRAPH I. ~~Fig.5~~) that for values of E_d less than 0.4 the theoretical plot tends to a straight line which can be represented by the equation

$$\log E_d = m'Z + C' \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (96)$$

Inspection of the experimental results suggest that for E_d less than 0.4 the plots of E_d vs time also tend to straight lines which may be expressed as

$$\log E = m''t + C'' \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (97)$$

Considering any two values of E_d, say E_{d_1} and E_{d_2} on both theoretical and experimental plots:-

From the theoretical plot

$$\log E_{d_1} = m'Z_1 + C' \quad \ldots\ldots\ldots\ldots\ldots\ldots(98)$$

$$\log E_{d_2} = m'Z_2 + C' \quad \ldots\ldots\ldots\ldots\ldots\ldots(99)$$

(98) - (99)

$$\log \frac{E_{d_2}}{E_{d_1}} = m'(Z_2 - Z_1) \quad \ldots\ldots\ldots\ldots\ldots\ldots(100)$$

and similarly from the experimental plots:-

$$\log \frac{E_{d_2}}{E_{d_1}} = m''(t_2 - t_1) \quad \ldots\ldots\ldots\ldots\ldots\ldots(101)$$

as $Z = D\pi^2 t$,

$$m'\pi^2 D(t_2 - t_1) = m''(t_2 - t_1) \quad \ldots\ldots\ldots\ldots\ldots\ldots(102)$$

i.e.,

$$D = \frac{1}{\pi^2} \cdot \frac{m''}{m'} \quad \ldots\ldots\ldots\ldots\ldots\ldots(103)$$

Now $$m'' = \frac{\log(E_{d_2} - E_{d_1})}{t_2 - t_1} \quad \ldots\ldots\ldots\ldots\ldots(104)$$

and $$m' = \frac{\log(E_{d_2} - E_{d_1})}{Z_2 - Z_1} \quad \ldots\ldots\ldots\ldots\ldots(105)$$

Therefore substituting in equation (103)

$$D = \frac{1}{\pi^2} \frac{(Z_2 - Z_1)}{(t_2 - t_1)} \quad \ldots\ldots\ldots\ldots\ldots(106)$$

As we could have equally well started with log $(1 - E_A)$ it follows that equation (106) holds for both absorption and desorption.

The values of D calculated using this equation are integral values over the range $0.15 < E_d < 0.4$ or $0.15 < 1-E_a < 0.4$.

From the theoretical plot of E_D vs. Z it was found that for E_D equal to 0.4 and E_D equal to 0.15, that

$$D = \frac{\quad}{9.870} \times \frac{6.452}{60} \times \frac{1}{t_2 - t_1} \qquad \ldots\ldots\ldots\ldots(107)$$

where the term 6.452/60 is a conversion factor relating the units in /min. to cm./sec.

The calculation of the activation energy for the diffusion process from the derived integral diffusion coefficients.

Eyring has suggested that diffusivity and temperature are related by the equation

$$D = \frac{\delta^2}{V_f^{1/3}} \left[\frac{kT}{2\pi m}\right]^{1/2} \exp.(-E/RT) \qquad \ldots\ldots\ldots\ldots\ldots(108)$$

This equation cannot however be further simplified as both are functions of T. The normally accepted equation for the correlation of experimental data is that suggested by Taylor[26]

$$D = A \exp.(-Q/RT) \qquad \ldots\ldots\ldots\ldots\ldots\ldots(109)$$

Q may be readily found from a plot of D vs. 1/T on semi-log. paper, i.e. from

$$\log \frac{D_2}{D_1} \quad - \frac{Q}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \ldots\ldots\ldots\ldots(110)$$

6. DISCUSSION OF RESULTS

6.1. Introduction.

6.1.1. Summary of experimental runs.

Table 6.1.1. shows the physical properties of the slab types used. The nomenclature is that of the suppliers, Aerox Ltd., Hillington Estate, Glasgow. The average dimensions of the slabs have been given previously in Table 5.1.

TABLE 6.1.1.

Slab Type	Max. Pore Size (Microns)	Porosity Per Cent	Permeability	Electrical Resistance Factor
H125	1.25	48.0	0.8	3.00
V3	3.05	41.7	1.6	5.70
V5	5.00	42.4	3.0	5.45
V10	10.00	40.1	6.4	5.86
M1	0.57	30.7	0.2	7.75

Definitions of the physical properties:-

Pore size - British Standard 1696 (1953)

Porosity = The ratio of the volume of water absorbed by a slab to the total volume of the slab.

Permeability = The volume of water in c.c.s at 20°C. passed in one hour through one sq.cm. of slab under a pressure of 10 cms. of water.

Electrical Resistance Factor = The ratio of the resistance of a slab impregnated with an electrolytic solution to the resistance of a body of the same electrolytic solution and the same gross dimensions.

The experimental runs carried out were:-

(1) Introductory runs to acquire experimental technique. The desorption of N. KCl from H125 slabs at 20, 30, 40, 50°C.

(2) The absorption and desorption of N. and 2N. solutions of HCl, KCl, LiCl, KNO_3, HNO_3 and KAc to and from H125 slabs at 20°C.

(3) The absorption and desorption to and from H125 slabs at 20°C. of the following mixtures.

N.KCl : N.HCl   N.KCl : N.KAc

N.KCl : N.KNO_3 N.HCl : N.LiCl.

(4) The absorption and desorption of N.HCl, N.KCl and N.LiCl to and from H125, V3, V5, V10 and M1 slabs at temperatures of 20, 30, 40 and 50°C.

6.1.2. A theoretical estimation of the percentage accuracy of the experimental results.

Throughout the discussion of the results much importance will be attached to the accuracy of the experimental results. It is necessary therefore that both a theoretical and an actual error should be estimated.

By assuming an experimental error for each measurement in the experimental procedure a maximum theoretical percentage error was calculated on the mathematical basis shown below. A detailed mathematical account is given in appendix C.

In general if $N = \frac{p.q}{a.b}$ and the possible errors in p, q, a and b are δp, δq, δa and δb then

$$N' = \frac{(p + \delta p)(q + \delta q)}{(a - \delta a)(b - \delta b)}$$

where N' is the largest possible value of N.

$$\therefore \quad N' = \frac{p(1 + \frac{\delta p}{p})\ q(1 + \frac{\delta q}{q})}{a(1 - \frac{\delta a}{a})\ b(1 - \frac{\delta b}{b})}$$

$$\approx \frac{pq}{ab} \cdot \frac{1 + \frac{\delta p}{p} + \frac{\delta q}{q}}{1 - \frac{\delta a}{a} - \frac{\delta b}{b}}$$

$$\therefore \quad \frac{N'}{N} \approx (1 + \frac{\delta p}{p} + \frac{\delta q}{q})(1 + \frac{\delta a}{a} + \frac{\delta b}{b})$$

Expanding and neglecting second order terms

$$\frac{N'}{N} = 1 + (\frac{\delta p}{p} + \frac{\delta q}{q} + \frac{\delta a}{a} + \frac{\delta b}{b})$$

Similarly for the smallest value of N (N'')

$$\frac{N''}{N} = 1 - (\frac{\delta p}{p} + \frac{\delta q}{q} + \frac{\delta a}{a} + \frac{\delta b}{b})$$

$$\therefore \text{ The error in } N = \pm \ (\frac{\delta p}{p} + \frac{\delta q}{q} + \frac{\delta a}{a} + \frac{\delta b}{b}$$

The estimated error in values of E , is approximately ± 3.0%. This error, however, does not take account of the manual wiping of the slabs. The effects of these wipings have been shown to be negligible (see section 6.1.3.4.).

The percentage error in the values of $\bar{D}$, the integral diffusion coefficient, has been calculated in the section on the statistical analysis of the experimental results (see section 6.7.). This was found to be ± 3½ %.

6.1.3. Preamble.

6.1.3.1. Introductory runs on H125 slabs.

Although Macdonald[1] has shown that the experimental procedure is of reasonable accuracy and gives straight line plots of log E_d vs. time, between E_d values of 0.40 and 0.15, a few introductory runs were made using N.KCl and H125 slabs before proceeding with the basic experimental programme.

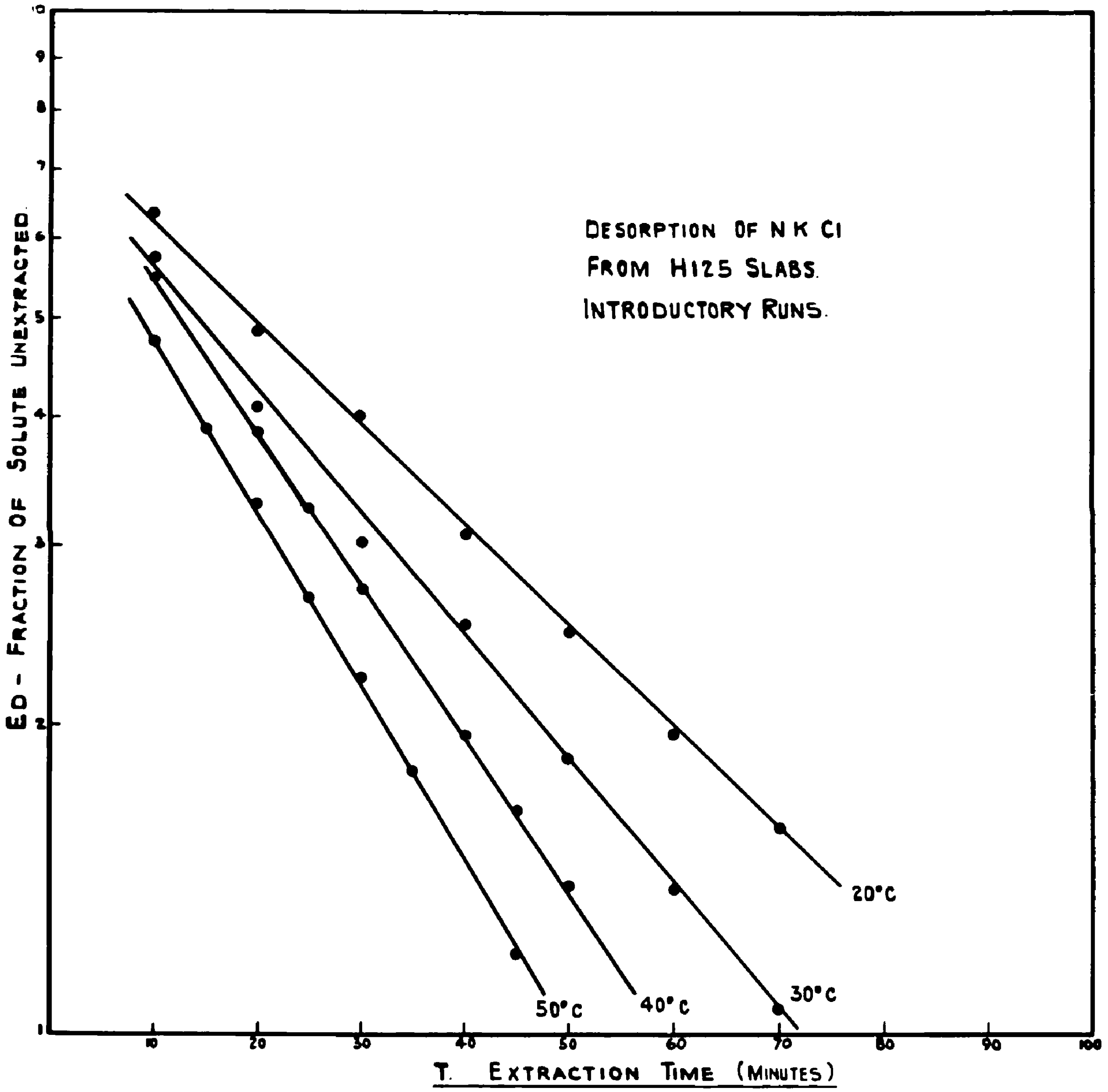
From these introductory runs it was found that:-

(1) a. Plots of log E_d vs. time gave straight lines between E_d values of 0.40 and 0.15 (Graph 2).

b. There was little scatter of the experimental values of E_d from the mean line through them, and, therefore, no one group of slabs was giving a consistently high or low value of E_d.

(2) Experimental runs were repeatable and gave values of E_d varying by ± 4%. This compares favourably with the theoretically estimated value of ± 3%.

(3) In the plot of log D vs. 1/T there was a slight scatter of points from the mean straight line through them.



DESORPTION OF N K Cl
FROM H125 SLABS.
INTRODUCTORY RUNS.

GRAPH 2.

Therefore, even although plots of log E_d *vs.* time gave straight lines, the diffusion coefficient derived from the slopes of these lines were not necessarily correct.

6.1.3.2. Initial runs on V3, V5, V10 and M1 slabs.

No introductory runs were carried out on V3, V5, V10 or M1 slabs but the initial runs on these slabs, namely; the desorption of N.KCl at 20-50°C., were examined to ascertain the scatter of the experimental values of E_d from the mean line through them. (See graphs 3-6).

From these graphs it was found that:-

(1) For V3 and V5 slabs the scatter was very small

(2) For V10 slabs the scatter was greater than for V3 and V5 slabs but appeared to be random in that no one group of slabs gave a consistently high or low value of E_d.

(3) For M1 slabs there was a large scatter with several groups giving consistently high or low values of E_d.

On visual examination of these slabs several were found, in contrast to others, to have parts of their surface area slightly glazed. Such slabs gave high values of E_d. The worst of these were discarded but even so later results on M1 slabs also showed a large scatter of E_d values.

In the further use of V10 and M1 slabs much care was taken in drawing the mean line through the experimental values of E_d. When the values of $\bar{D}$ obtained from the slopes of these lines were plotted on log $\bar{D}$ vs. 1/T there was little scatter from the mean line.

6.1.3.3. General observations on the continuous loss in weight of the slabs.

As the experimental programme proceeded it was noticed that each group of slabs was, for some reason other than that of minor abrasions, continually losing weight.

The average weight of a group of three slabs was approximately 15.5 gms. The average loss in weight over a period of nine months was 0.30 gms. The day to day loss in weight did not appear to have any effect on the experimental results. During section 4 of the experimental programme, however, when repeating the desorption of N.KCl from H125 slabs at 20-50°C. it was noticed that for each run the diffusion coefficient was larger than had been found during the introductory runs on H125 slabs. The percentage increases in diffusivity are shown in Table 6.1.3.3. These increases are within the estimated percentage error but are significant in that all the later values of the diffusion coefficient are larger than the corresponding earlier values.

Table 6.1.3.3. Values of $\bar{D}$ for the desorption of N.KCl from H125 slabs.

Temp °C.	Original Runs		Repeat Runs		Percentage Difference
	Experimental $\bar{D} \times 10^5$	Corrected $\bar{D}_c \times 10^5$	Experimental $\bar{D} \times 10^5$	Corrected $\bar{D}_c \times 10^5$	
20	0.645	0.645	0.652	0.652	1.09
30	0.818	0.810	0.820	0.828	2.22
40	0.980	1.00	1.050	1.020	2.00
50	1.240	1.240	1.220	1.270	2.45

Note. The values of $\bar{D}_c$ were estimated from the mean lines in the plots of log $\bar{D}$ vs. 1/T.

On remeasuring the slabs, the decrease in width was not sufficiently large to justify the extent of the increase in diffusivity. It was thought therefore, that the slabs were continually being eroded not only on the external surfaces but also on the pore walls. This may explain the increase in the diffusivity.

In view of this increase in diffusivity with use, it was decided, that, as the differences between rates of absorption and desorption, which it was hoped to detect, may be small, the corresponding desorption and absorption runs should be done immediately following one another, even although this meant some inconvenience in alternating the liquid flowing through the diffusion cell. In this way the effect of increase in diffusivity with use was cut to a minimum.

This difference in diffusivity was not detected until the beginning of section 4 of the experimental programme but fortunately in sections 2 and 3 no corresponding desorption and absorption runs were ever done with more than four intervening runs.

6.1.3.4. The effects of manual wiping of the slabs.

During any experimental run, either absorption or desorption, there are two occasions when the slabs are wiped with a cloth saturated with the appropriate liquid, namely; after removal from the impregnation solution and after removal from the diffusion cell. These manual wipings may account for some of the scatter of E_d values from the mean line in plots of E_d vs. time.

Considering the desorption of N.KCl:-

(1) In the first wiping any excess impregnation solution is removed from the slabs before weighing. The weight of KCl impregnated into the slabs varies with the porosity of the slab type, e.g., for H125 slabs it is, on average, 0.39 gms. and for V10 slabs it is, on average, 0.33 gms. The average weight impregnated is 0.34 gms.

By assuming that careful wiping is capable of leaving on, or removing in excess, a film of solution

1×10^{-4} inches thick over the total surface area, the average error in the weight of KCl impregnated is 2×10^{-4} gms. The average percentage error is approximately ± 0.05% .

(2) The solution being removed during the second wiping is so dilute that, assuming the same error in film thickness, the effect is negligible.

Considering the absorption of N.KCl:-

(1) Assuming the same error in film thickness the possible error in the weight of water impregnated is 2.4×10^{-3} gms. The weight of water impregnated is, on the average of all types of slab, approximately 4.5 gms. The percentage error caused by wiping is therefore approximately ± 0.05% .

In the calculation of the value of the denominator of E_A where $E_A = {}^{Q}t/Q_{\infty}$ it is assumed that the water originally impregnated will, after infinite time, become N.KCl. The percentage error is therefore also in terms of KCl.

(2) The solution being removed by wiping after removal from the diffusion cell is N.KCl. Assuming the same error in film thickness the error in the weight of KCl absorbed is $\pm 2 \times 10^{-4}$ gms. The average weight of KCl absorbed approximately half way through any experiment is 1.7×10^{-1} gms. The average percentage error is

therefore ± 0.1%.

Theoretically therefore the errors arising from manual wiping of the slabs are negligible compared with the estimated percentage error.

6.2. The effect of porous media on diffusivities.

It is normally accepted that although a substance diffusing to or from a porous medium appears to have a lower diffusion rate than when diffusing in free solution, the actual speed of each particle is reduced only slightly - the retarding forces being adsorption on the pore walls and, or, a drag at the proximity of the wall. The apparent reduction in diffusion is caused by the particles having to travel through a mean path far in excess of that suggested by the dimensions of the porous medium and by the fact that diffusion does not take place from the total surface area of the medium but only from the open pores.

The introduction of a factor to account for the apparent reduction in diffusivity was first made by Piret et al.[87]. They proposed a factor K^2 to characterise each of a selection of porous media, where K^2 is the ratio of the diffusion coefficient in free solution to that for diffusion in a porous medium. It follows therefore, that the greater the value of K^2 the greater is the effect of the porous medium on the diffusing particles.

Values of K^2 for the absorption and desorption at 20°C. of N solutions of several electrolytes to and from slabs H125, V3, V5, V10 and M1 are shown in Table 6.2.a. The experimental integral diffusion coefficients from which these values were calculated are listed in Table 6.2.b.

Table 6.2.c. shows the integral diffusion coefficients in free solution for N. concentrations.

In some instances the value obtained in the literature had to be corrected to a standard temperature of 20°C.: for this a correction of 2½ per cent per degree centigrade was allowed[87].

TABLE 6.2.a. Values of K^2 for desorption and absorption at 20°C

Slab	Desorption			Absorption		
Type	HCl	KCl	LiCl	HCl	KCl	LiCl
H125	2.58	2.46	2.47	2.22	2.46	2.21
V3	2.87	2.67	2.59	2.53	2.67	2.41
V5	3.49	3.40	3.31	3.49	3.40	3.03
V10	3.49	3.35	3.21	3.49	3.34	2.94
M1	4.38	4.00	3.31	3.64	4.00	3.21

TABLE 6.2.b. Diffusion coefficients for N. solutions at 20°C.

Slab Type	KCl Abs.	KCl Des.	HCl Abs.	HCl Des.	LiCl Abs.	LiCl Des.
	$\bar{D} \times 10^5$		$\bar{D} \times 10^5$		$\bar{D} \times 10^5$	
H125	0.65	0.65	1.25	1.07	0.48	0.45
V3	0.60	0.60	1.09	0.96	0.44	0.41
V5	0.47	0.47	0.79	0.79	0.35	0.32
V10	0.48	0.48	0.79	0.79	0.36	0.33
M1	0.40	0.40	0.76	0.63	0.33	0.32

TABLE 6.2.c. Estimated integral diffusion coefficients in free solution for N. solutions at 20°C.

Solute	$\bar{D} \times 10^5$
KCl	1.60
HCl	2.76
LiCl	1.06

Figures 5 and 6 which are in the main self-explanatory provide an easy method for comparison of K^2 values.

Figure 5 (Desorption) shows that:-

(1) The values of K^2 for any one slab type, with the exception of M1 slabs, are of the same numerical order for all three electrolytes.

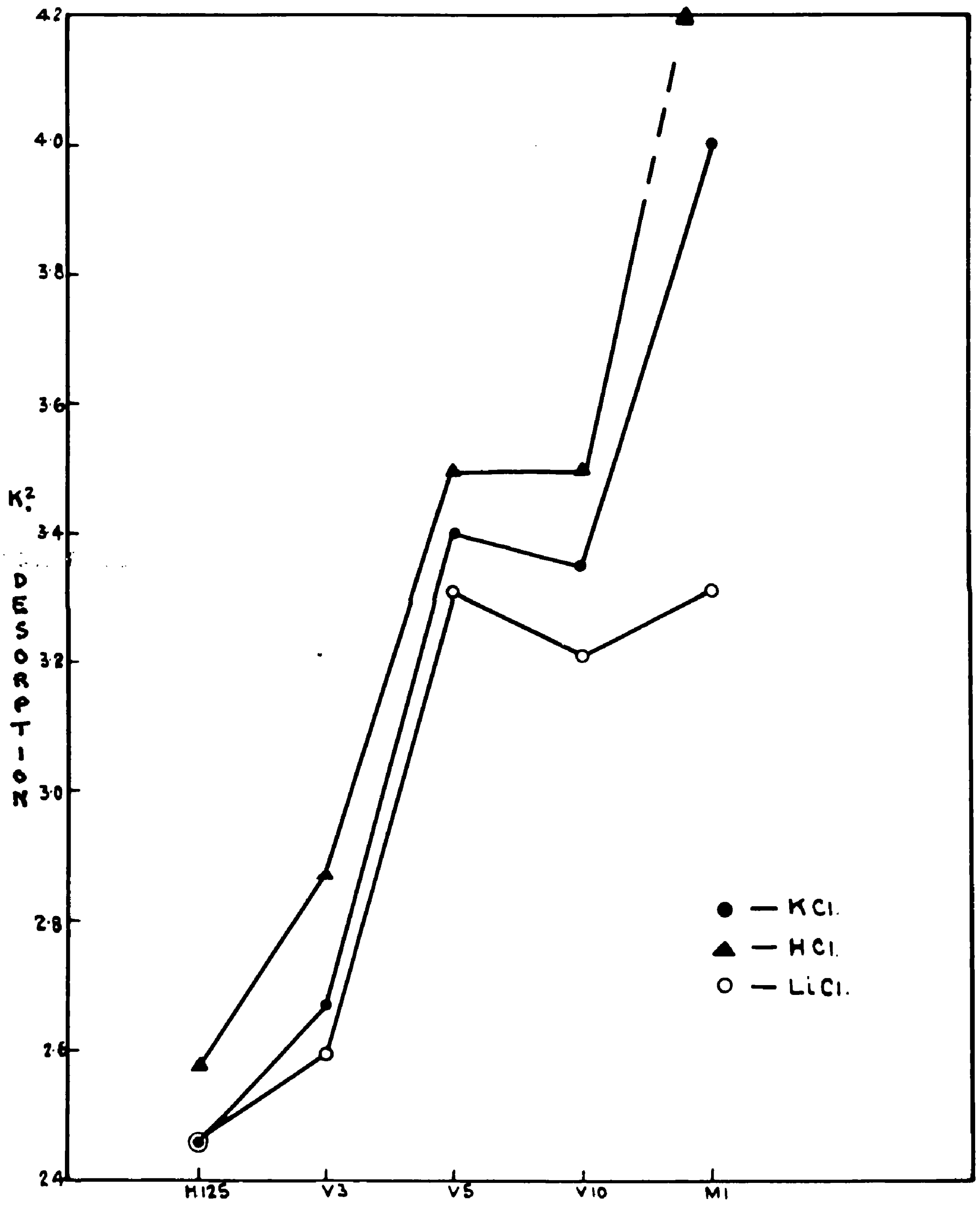

4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
K_s^2
DESORPTION
H125
V3
V5
V10
M1
SLAB TYPE.
● — KCl.
▲ — HCl.
○ — LiCl.

FIGURE 5.

(2) The values of K^2 for all slab types are greater for HCl than they are for KCl and are greater for KCl than they are for LiCl.

It had been hoped to obtain a relationship between some of the physical properties of the slabs, in particular the electrical resistance factor, and the values of K^2. There is a similarity between K^2 and the electrical resistance factor for H125, V5, V10 and M1 slabs but not for V3 slabs and in effect there is no complete relationship between slab properties and K^2 values.

Examination of Figure 6 (absorption) shows that in general the values of K^2 for absorption follow the same trends as those for desorption but that the values of K^2 for KCl are greater than the corresponding values for HCl with the exception of the values for V5 and V10 slabs.

It will be seen later (see section 6.3.) that for KCl absorption is equal to desorption for all slab types and for HCl absorption is quicker than desorption with the exception of V5 and V10 slabs. For these slabs it was found that absorption was equal to desorption but there was no apparent explanation for this: no explanation is offered, therefore, for the corresponding anomalous values of K^2. By neglecting these results which with everything considered (see section 6.7. on statistical analysis) seem to be experimentally incorrect it appears that during absorption - in contrast to desorption - each slab type has a greater effect on KCl than on HCl.

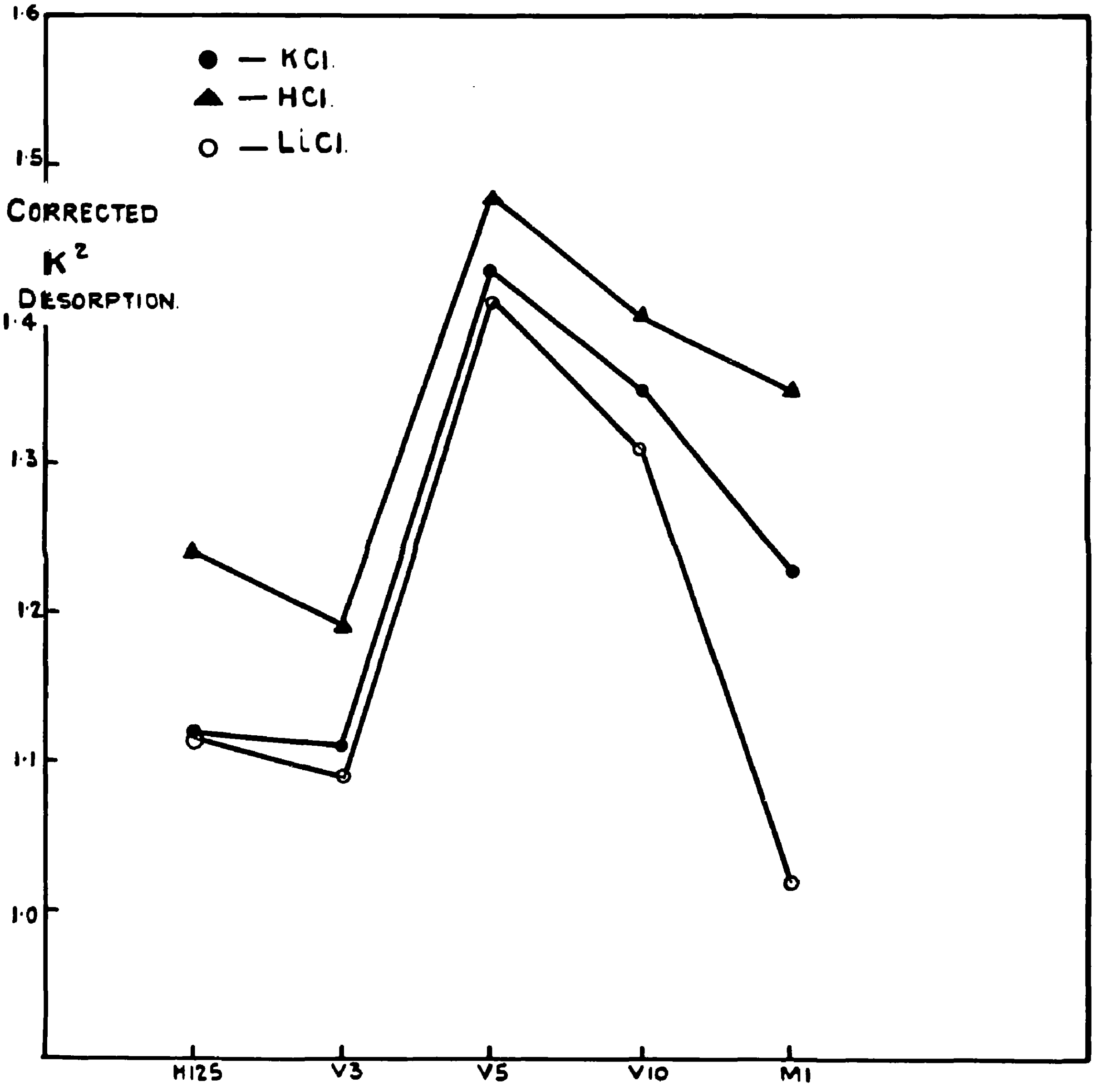
Piret's method of calculating K^2 characterises each slab type but does not take into account the effect of porosity. By correcting the experimental values of the integral diffusion coefficients to a standard porosity (in the present case to 100% porosity) and using the corrected values to recalculate K^2, the corrected K^2 values so obtained give a more realistic allowance for the tortuosity of the slabs.

The corrected values of K^2 are given in Table 6.2.d. and in Figures 7 and 8.

<u>TABLE 6.2.d.</u> <u>Values of K^2 corrected for porosity.</u>

Slab	Desorption			Absorption		
Type	HCl	KCl	LiCl	HCl	KCl	LiCl
H125	1.24	1.18	1.17	1.06	1.18	1.06
V3	1.19	1.11	1.09	1.05	1.11	1.01
V5	1.48	1.43	1.41	1.49	1.43	1.28
V10	1.40	1.35	1.31	1.40	1.35	1.19
M1	1.35	1.23	1.02	1.12	1.23	0.99

<u>NOTE</u>: The value of corrected K^2 for the absorption of N.LiCl into M1 slabs is theoretically impossible. The smallest value possible is unity. The difference between the smallest possible value and this value for



● — KCl.
▲ — HCl.
○ — LiCl.
CORRECTED K^2 DESORPTION.
1·6
1·5
1·4
1·3
1·2
1·1
1·0
H125
V3
V5
V10
M1
SLAB TYPE.

FIGURE. 7.

M1 slabs is probably within the limits of the experimental error.

Examination of these results shows that:-

(1) The corrected values of K^2, for both absorption and desorption are much nearer to unity than the uncorrected values.

(2) There has been considerable alteration in the apparent tortuosity of several types of slabs, e.g. originally V3 slabs had a greater tortuosity than H125 slabs whereas after correction for porosity the tortuosity of H125 slabs is larger than that of V3 slabs.

(3) The values of corrected K^2 for any one slab type, with the exception of M1 slabs, are of the same numerical order.

(4) The values of corrected K^2 for all the slab types follow the same pattern as the original K^2 values in that for desorption they decrease from HCl - KCl - LiCl and for absorption they decrease from KCl - HCl - LiCl.

It will be seen that the five slab types affect any one electrolyte e.g. HCl to varying degrees. The degree to which the diffusivity of HCl is apparently reduced must therefore depend upon one or more of the physical properties of the slabs and not upon the solute properties.

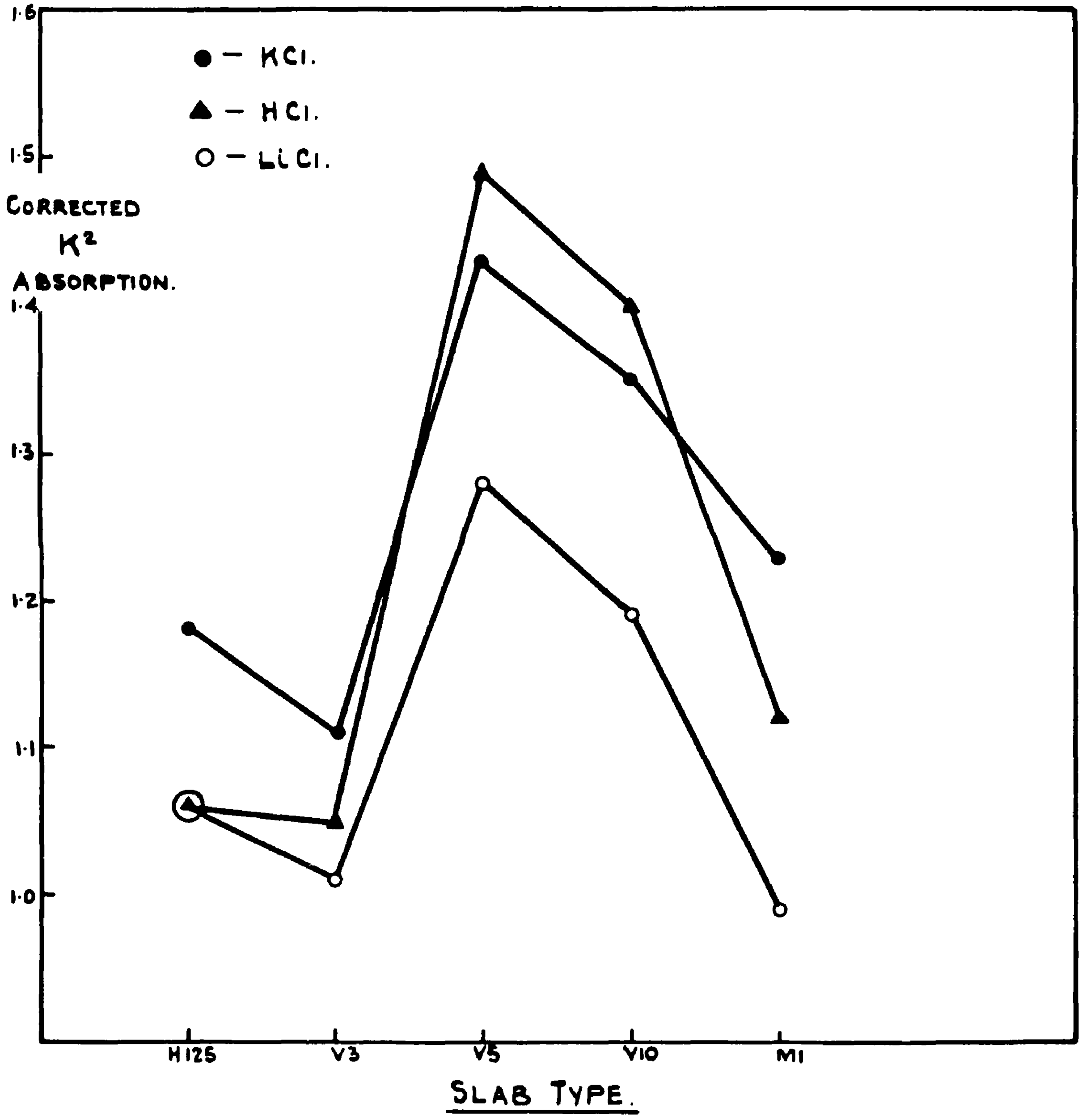

● – KCl.
▲ – HCl.
○ – LiCl.
Corrected
K^2
Absorption.
1·6
1·5
1·4
1·3
1·2
1·1
1·0
H125
V3
V5
V10
M1
Slab Type.

Figure 8.

It has been shown that porosity cannot be the only factor affecting the diffusivities otherwise all the corrected values of K^2, for any one electrolyte and five types of slab, would be equal. Since the corrected values of K^2 do not increase or decrease regularly with increasing pore size the controlling factor must be the internal structures of the slabs.

The corrected values of K^2 for HCl, KCl and LiCl diffusing from any one slab type e.g. H125 slabs, are of the same numerical order but are not equal. They decrease from HCl - KCl - LiCl. This suggests that there are possibly varying degrees of adsorption of the ions on the pore walls, and, or, varying degrees of drag on the ions at the proximity of the pore walls. As there is a common ion in the three electrolytes the retarding effects must be dependent upon the physical properties of the other ions, namely; K^+, H^+ and Li^+. The sizes of these ions when hydrated increase from H^+ - K^+ - Li^+. It appears therefore that the largest ion is retarded to the least extent.

In contrast to desorption, for the absorption of HCl, KCl and LiCl into H125 slabs, the K^+ ions are in general retarded more than the H^+ ions although both the H^+ and K^+ ions are retarded more than the Li^+ ions. This result has its origin in the variation of diffusivity with variation in concentration.

The ratios of corrected K^2 values are shown in Table 6.2.e.

TABLE 6.2.e. Ratios of corrected K^2 - Desorption.

	H125	V3	V5	V10	M1
HCl : KCl	1.05	1.06	1.04	1.04	1.10
HCl : LiCl	1.06	1.09	1.05	1.07	1.32
LiCl: KCl	1.01	1.02	1.01	1.03	1.20

It will be seen that any one ratio is almost constant for H125, V3, V5 and V10 slabs. It follows therefore that even although the slabs have a greater effect on H^+ ions than they have on K^+ ions for desorption, they affect these ions in the same ratio, with the exception of M1 slabs.

The question now arises, "Why should the smaller ions be retarded to a greater extent than the larger ions?"

If the surface area available within the slabs is insufficient to allow adsorption of all the ions in a normal solution then it is reasonable to assume that there will be comparatively more small ions adsorbed than large ions adsorbed. The smaller ions will therefore be retarded to a greater extent than the larger ions.

If this reasoning is correct it follows that for more concentrated solutions the differences in corrected K^2 values between, say, HCl and KCl for any one type of slab should diverge and for weaker solutions they should converge.

Conclusions

(1) The controlling factor in the apparent retardation of ions diffusing to or from porous media is the internal structure of media.

(2) There is a secondary effect dependent upon the size of the ions.

(3) Porous media do not affect diffusing electrolytes to the same extent. In general electrolytes containing smaller ions are retarded to a greater extent than those containing larger ions.

(4) The ratio of the effects of the slabs on the ions is in general approximately constant.

6.3. Comparison of rates of absorption and desorption.

In order to avoid unnecessary repetition, throughout the discussion the "rate of absorption" and "the rate of desorption" will be spoken of as absorption and desorption.

The experimental results for the absorption and desorption of N. solutions of HCl, KCl and LiCl from H125, V3, V5, V10 and M1 slabs at temperatures of 20, 30, 40 and 50°C. are given in appendix A.

Plots of E_d vs. time for the desorption of N.KCl from each type of slab are shown in Graphs 2a and 3-6. Similar graphs were obtained for HCl and LiCl - the scatter of points in these being dependent upon the slab type but not upon the solute.

The integral diffusion coefficients, denoted $\bar{D}$, derived from these experimental results are shown in Table 6.3.a. The column $\bar{D}_c$ shows the corrected values of $\bar{D}$ taken from the mean lines in Graphs 7-11.

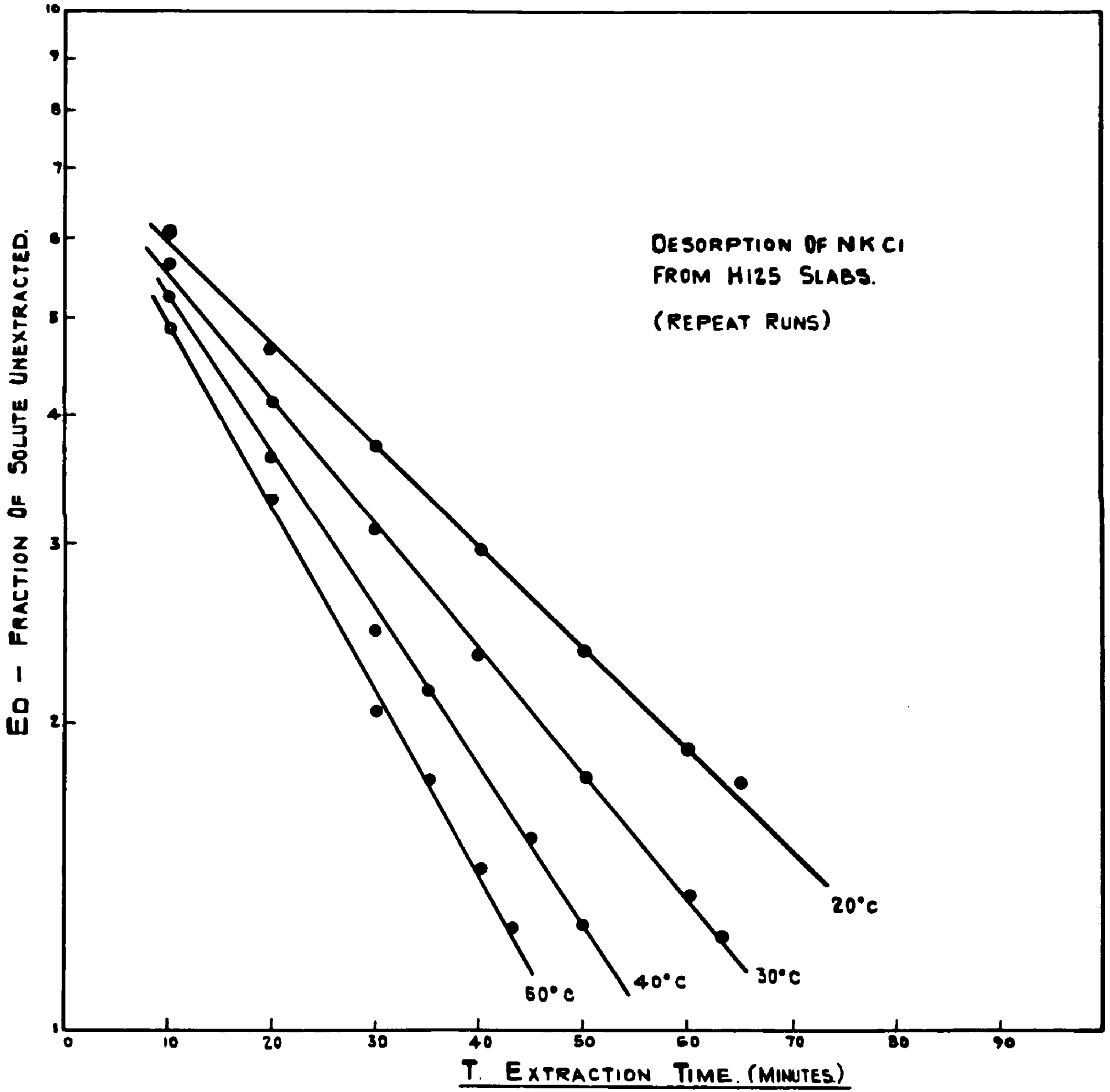
TABLE 6.3.a.

H125

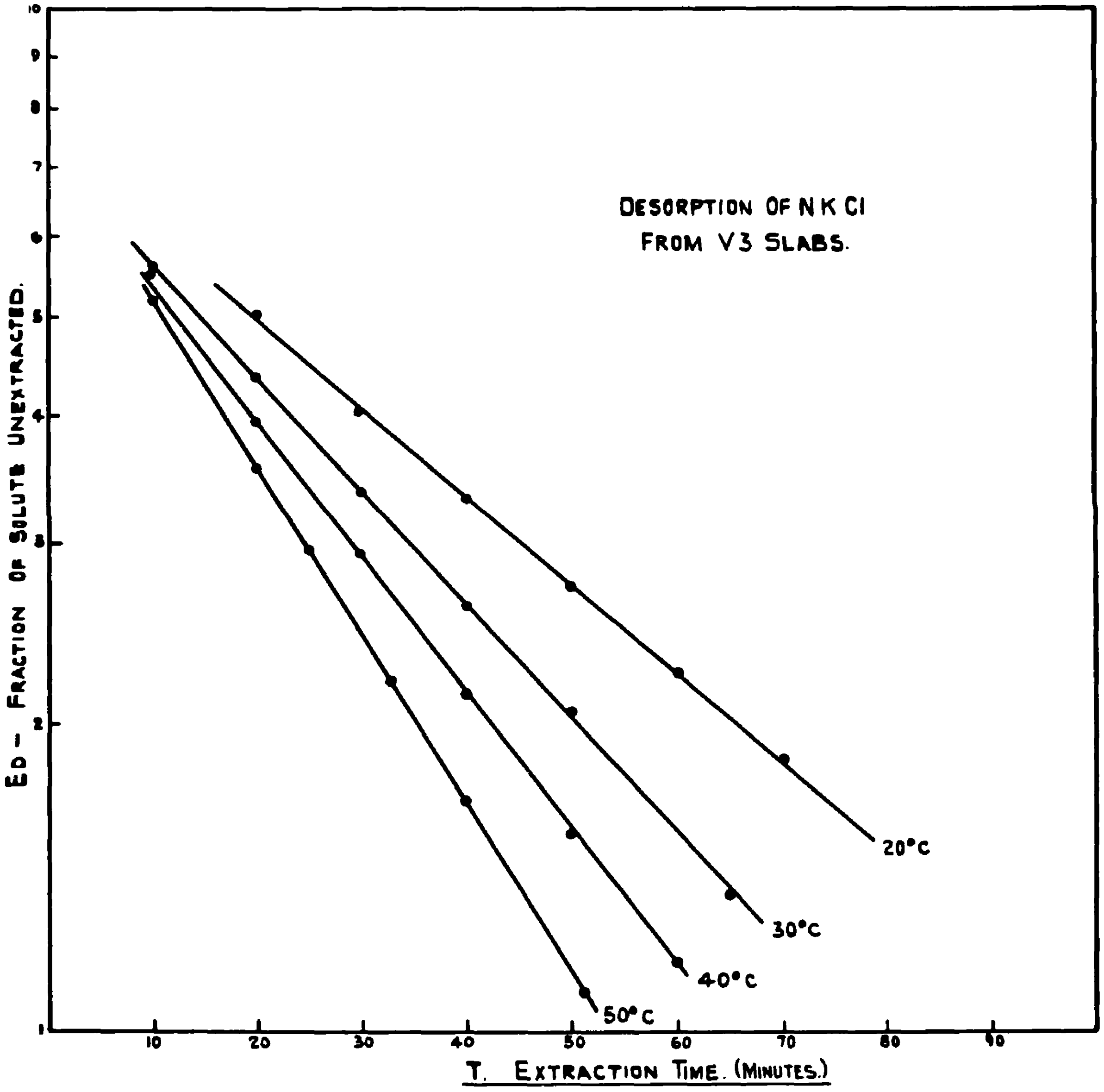
Run	N. HCl			N. KCl			N. LiCl		
	t_2-t_1 min.	$\bar{D}$ x 10^5	$\bar{D}_c$ x 10^5	t_2-t_1 min.	$\bar{D}$ x 10^5	$\bar{D}_c$ x 10^5	t_2-t_1 min.	$\bar{D}$ x 10^5	$\bar{D}_c$ x 10^5
D20	26.1	1.106	1.07	44.3	0.652	0.65	66.5	0.434	0.45
D30	21.8	1.325	1.33	35.2	0.820	0.830	52.9	0.546	0.56
D40	17.8	1.623	1.62	27.5	1.050	1.02	42.6	0.679	0.69
D50	15.0	1.925	1.94	23.7	1.220	1.27	34.1	0.847	0.85
A20	22.9	1.260	1.25	44.3	0.652	0.65	60.7	0.475	0.48
A30	17.1	1.688	1.62	35.2	0.820	0.83	45.8	0.629	0.64
A40	14.3	2.020	2.00	27.5	1.050	1.02	34.1	0.847	0.84
A50	11.9	2.424	2.44	23.2	1.245	1.27	26.3	1.100	1.07

V3

D20	32.2	0.900	0.96	48.2	0.600	0.60	73.2	0.395	0.41
D30	24.1	1.202	1.15	38.4	0.754	0.75	60.2	0.481	0.48
D40	20.4	1.420	1.42	31.5	0.919	0.92	52.5	0.552	0.55
D50	16.5	1.755	1.76	26.4	1.097	1.12	45.9	0.630	0.64
A20	27.4	1.060	1.09	47.8	0.606	0.60	65.9	0.439	0.44
A30	21.0	1.379	1.35	39.0	0.743	0.75	49.6	0.583	0.57
A40	17.3	1.675	1.68	31.5	0.919	0.92	41.5	0.699	0.70
A50	13.7	2.11	2.11	25.0	1.158	1.12	32.2	0.900	0.87


DESORPTION OF NKCl
FROM H125 SLABS.
(REPEAT RUNS)
ED - FRACTION OF SOLUTE UNEXTRACTED.
10
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
90
T. EXTRACTION TIME. (MINUTES.)
20°C
30°C
40°C
50°C

GRAPH 2.a.



DESORPTION OF N K Cl
FROM V3 SLABS.
ED – FRACTION OF SOLUTE UNEXTRACTED.
10
9
8
7
6
5
4
3
2
1
10
20
30
40
50
60
70
80
90
20°C
30°C
40°C
50°C
T. EXTRACTION TIME. (MINUTES.)

G'RAPH 3.

V5

Run	N. HCl t_2-t_1 min.	N. HCl $\bar{D}$ x 10^5	N. HCl $\bar{D}_c$ x 10^5	N. KCl t_2-t_1 min.	N. KCl $\bar{D}$ x 10^5	N. KCl $\bar{D}_c$ x 10^5	N. NaCl t_2-t_1 min.	N. NaCl $\bar{D}$ x 10^5	N. NaCl $\bar{D}_c$ x 10
D20	35.1	0.830	0.79	63.2	0.461	0.47	91.7	0.318	0.32
D30	30.3	0.962	0.96	50.9	0.573	0.58	74.3	0.392	0.39
D40	25.7	1.135	1.16	42.0	0.693	0.70	59.5	0.490	0.48
D50	20.8	1.400	1.38	35.7	0.817	0.82	51.2	0.569	0.57
A20	35.1	0.830	0.79	63.3	0.460	0.47	81.0	0.360	0.35
A30	30.3	0.962	0.96	50.0	0.583	0.58	68.6	0.424	0.44
A40	25.7	1.135	1.16	42.0	0.693	0.70	51.2	0.569	0.55
A50	20.8	1.400	1.38	34.8	0.838	0.82	43.8	0.665	0.67

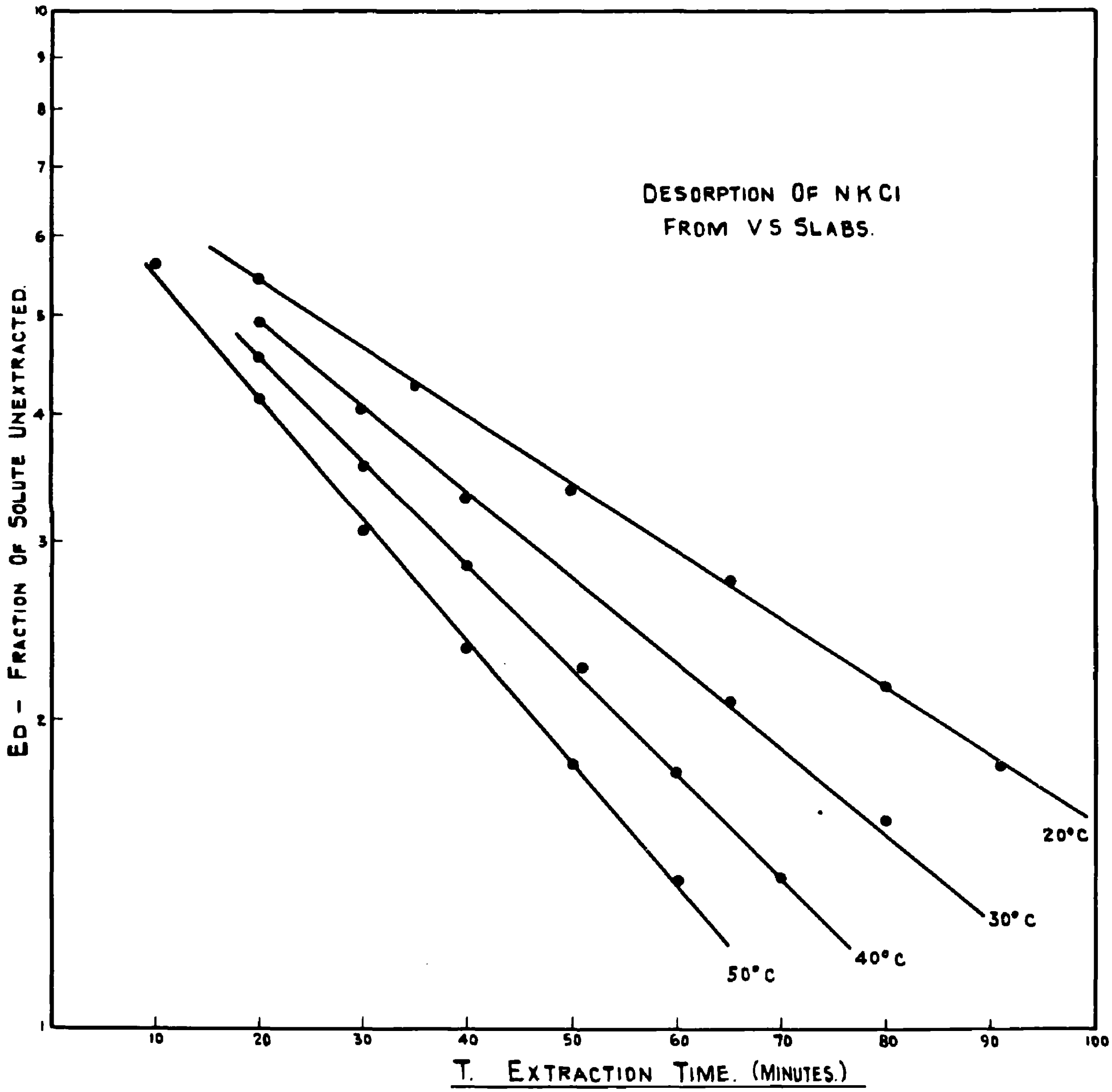
V10

Run	N. HCl t_2-t_1 min.	N. HCl $\bar{D}$ x 10^5	N. HCl $\bar{D}_c$ x 10^5	N. KCl t_2-t_1 min.	N. KCl $\bar{D}$ x 10^5	N. KCl $\bar{D}_c$ x 10^5	N. NaCl t_2-t_1 min.	N. NaCl $\bar{D}$ x 10^5	N. NaCl $\bar{D}_c$ x 10
D20	35.0	0.835	0.79	58.0	0.504	0.48	90.2	0.325	0.33
D30	32.1	0.912	0.98	52.6	0.556	0.58	76.0	0.385	0.37
D40	24.5	1.195	1.19	42.5	0.688	0.70	63.0	0.464	0.46
D50	19.9	1.470	1.43	35.1	0.833	0.83	53.2	0.550	0.55
A20	35.0	0.835	0.79	56.3	0.519	0.48	81.3	0.360	0.36
A30	32.1	0.912	0.98	54.7	0.535	0.58	64.3	0.455	0.44
A40	24.5	1.195	1.19	42.5	0.688	0.70	51.3	0.592	0.57
A50	19.9	1.470	1.43	35.1	0.833	0.83	40.6	0.720	0.72

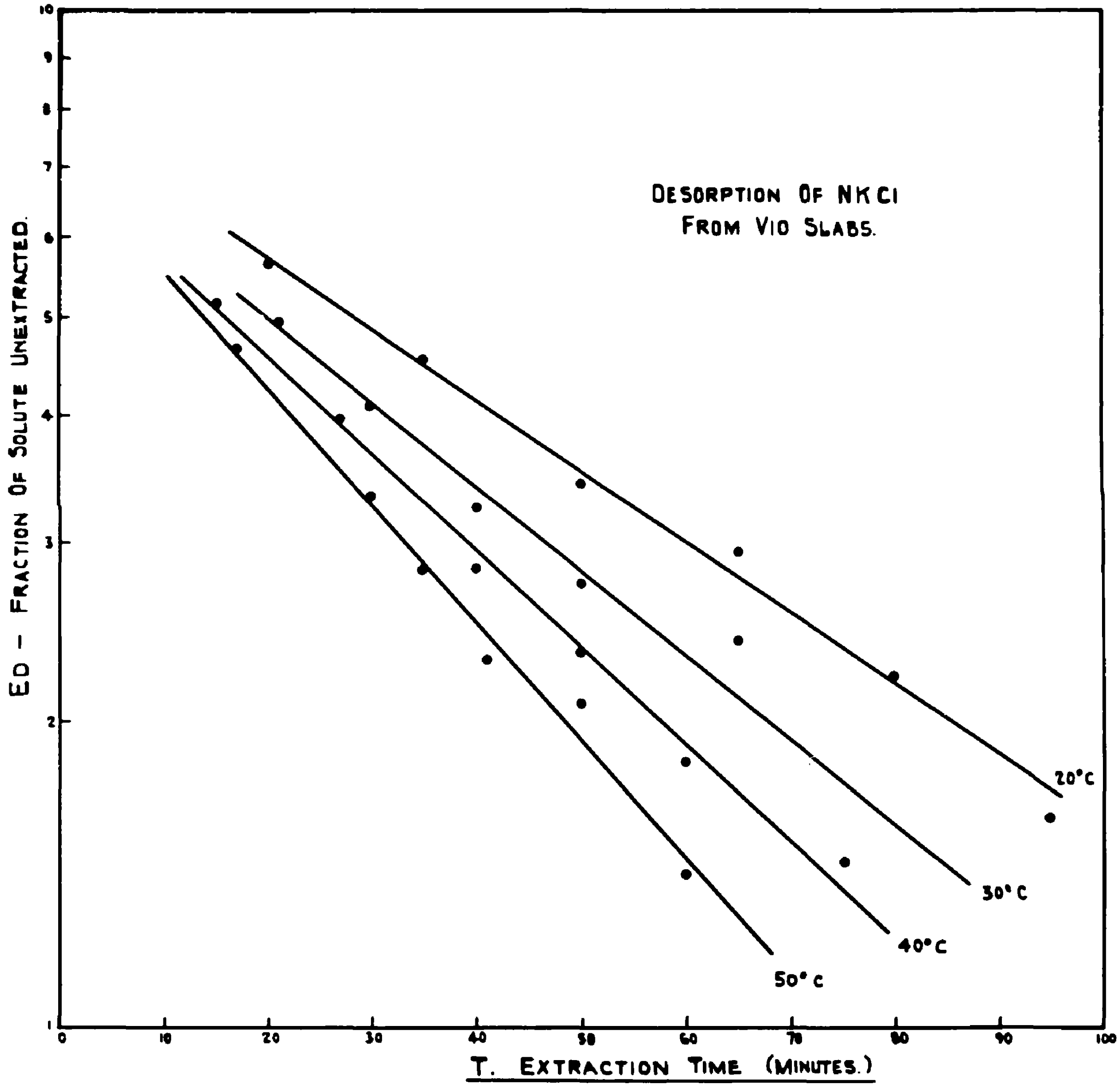
M1

Run	N. HCl t_2-t_1 min.	N. HCl $\bar{D}$ x 10^5	N. HCl $\bar{D}_c$ x 10^5	N. KCl t_2-t_1 min.	N. KCl $\bar{D}$ x 10^5	N. KCl $\bar{D}_c$ x 10^5	N. NaCl t_2-t_1 min.	N. NaCl $\bar{D}$ x 10^5	N. NaCl $\bar{D}_c$ x 10
D20	46.5	0.633	0.63	69.3	0.424	0.40	93.2	0.316	0.32
D30	36.1	0.815	0.82	49.1	0.598	0.51	80.5	0.365	0.36
D40	27.3	1.077	1.04	48.5	0.606	0.64	64.9	0.453	0.46
D50	23.3	1.262	1.29	39.2	0.750	0.78	56.3	0.522	0.54
A20	38.1	0.772	0.76	77.3	0.381	0.40	83.8	0.351	0.34
A30	29.6	0.990	0.96	55.1	0.533	0.51	68.8	0.427	0.44
A40	27.3	1.077	1.18	4488	0.656	0.64	51.7	0.569	0.55
A50	19.8	1.485	1.49	39.1	0.753	0.78	43.6	0.674	0.68

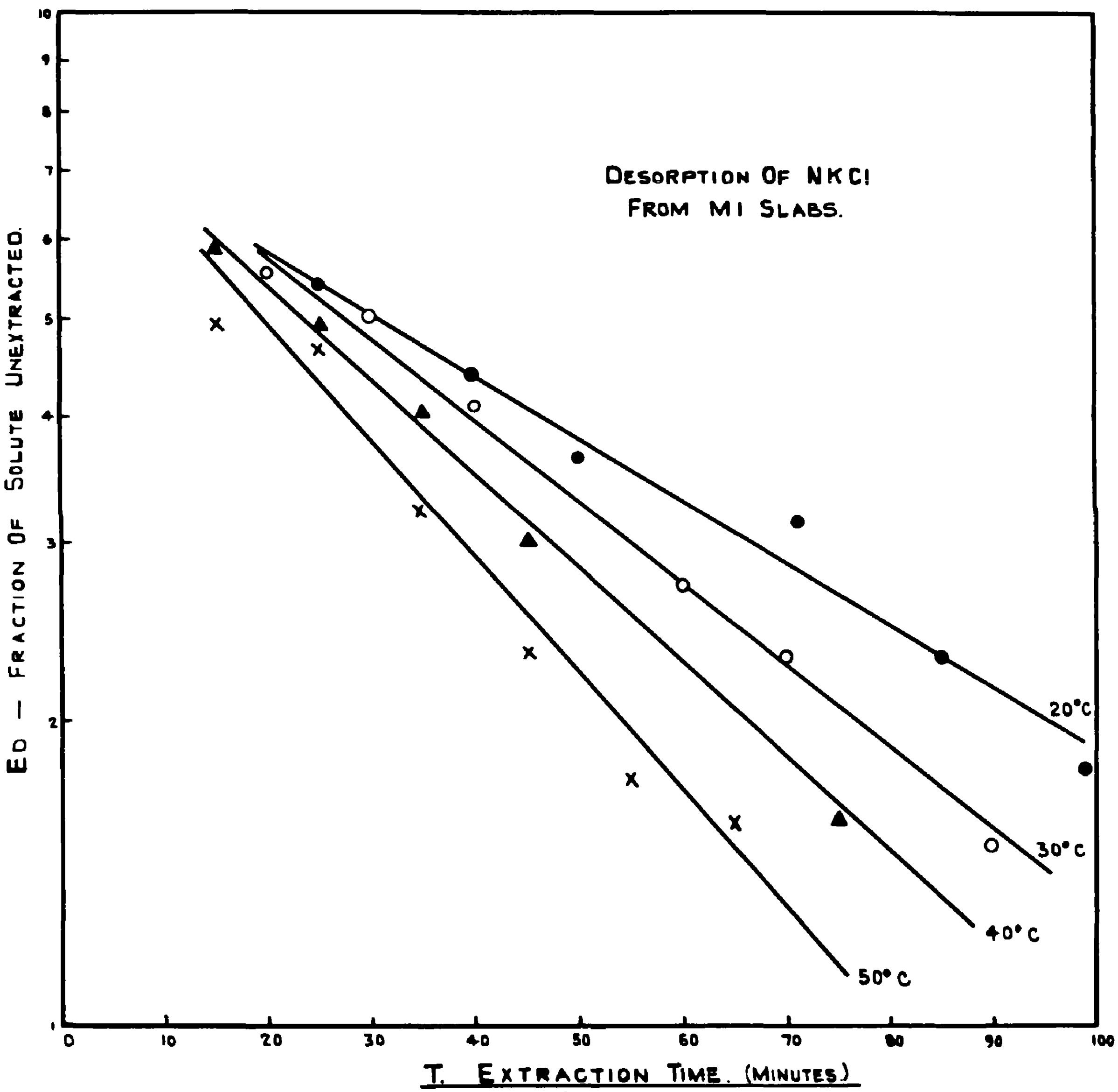
<u>NOTE</u> In the plots of E_d, or $1-E_a$, <u>vs.</u> time for corresponding desorption and absorption runs for N.HCl diffusing from V5


Desorption Of NKCl
From VS Slabs.
Ed - Fraction Of Solute Unextracted.
10
9
8
7
6
5
4
3
2
1
10
20
30
40
50
60
70
80
90
100
T. Extraction Time. (Minutes.)
20°C
30°C
40°C
50°C

Graph 4.


DESORPTION OF NKCl
FROM VIO SLABS.
ED - FRACTION OF SOLUTE UNEXTRACTED.
T. EXTRACTION TIME (MINUTES.)
20°C
30°C
40°C
50°C
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
80
90
100

GRAPH. 5


Desorption Of NKCl
From M1 Slabs.
Ed — Fraction Of Solute Unextracted.
T. Extraction Time. (Minutes.)
10
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
90
100
20°C
30°C
40°C
50°C

GRAPH 6

and V10 slabs, the values of E_d and $1-E_a$ were so mixed that it was thought justifiable to consider that absorption and desorption were equal and to draw one mean line through these values of E_d and $1-E_a$.

Graphs 7-11 show the plots of log $\bar{D}$ vs. $^1/_T$ for all the experimental runs mentioned above. From the plots of log $\bar{D}$ vs. $^1/_T$ it will be seen that:-

(1) KCl. Absorption is equal to desorption at all temperatures irrespective of the slab type used.

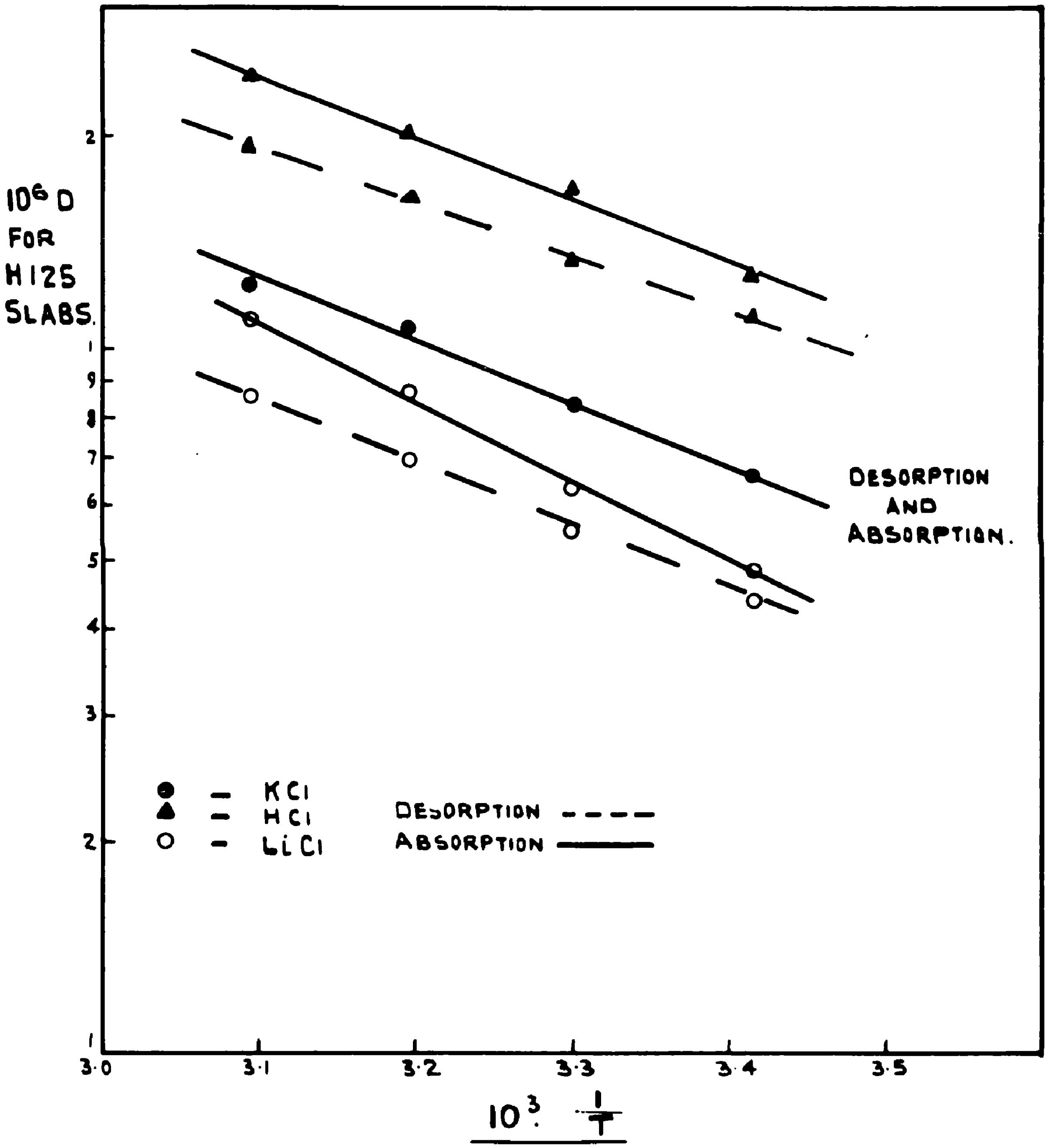
(2) HCl. Absorption is quicker than desorption at all temperatures for slabs H125, V3 and M1. Absorption is equal to desorption at all temperatures for slab types V5 and V10.

(3) LiCl. Absorption is quicker than desorption at all temperatures irrespective of the slab type used.

Crank and Henry[95] have shown mathematically that if the diffusivity of a substance increases uniformly with increasing concentration then absorption into a porous medium should be quicker than desorption from the same medium.

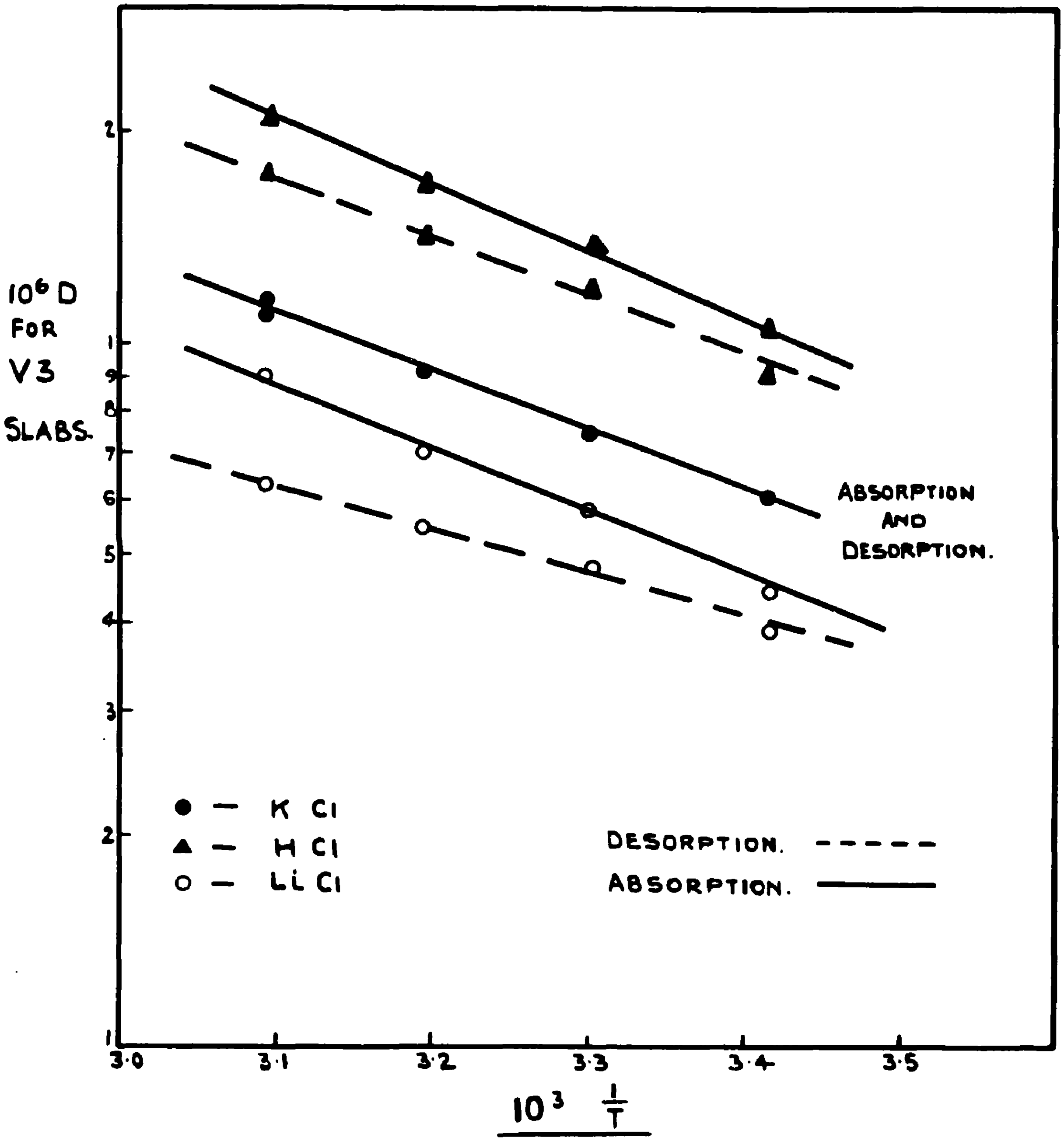
The variation of diffusivity in free solution with increase in concentration for KCl, HCl and LiCl[56] is shown in Graph 12.

With increase in concentration the diffusivities in free solution of each of these electrolytes pass through a minimum at approximately 0.1 N. After passing through this

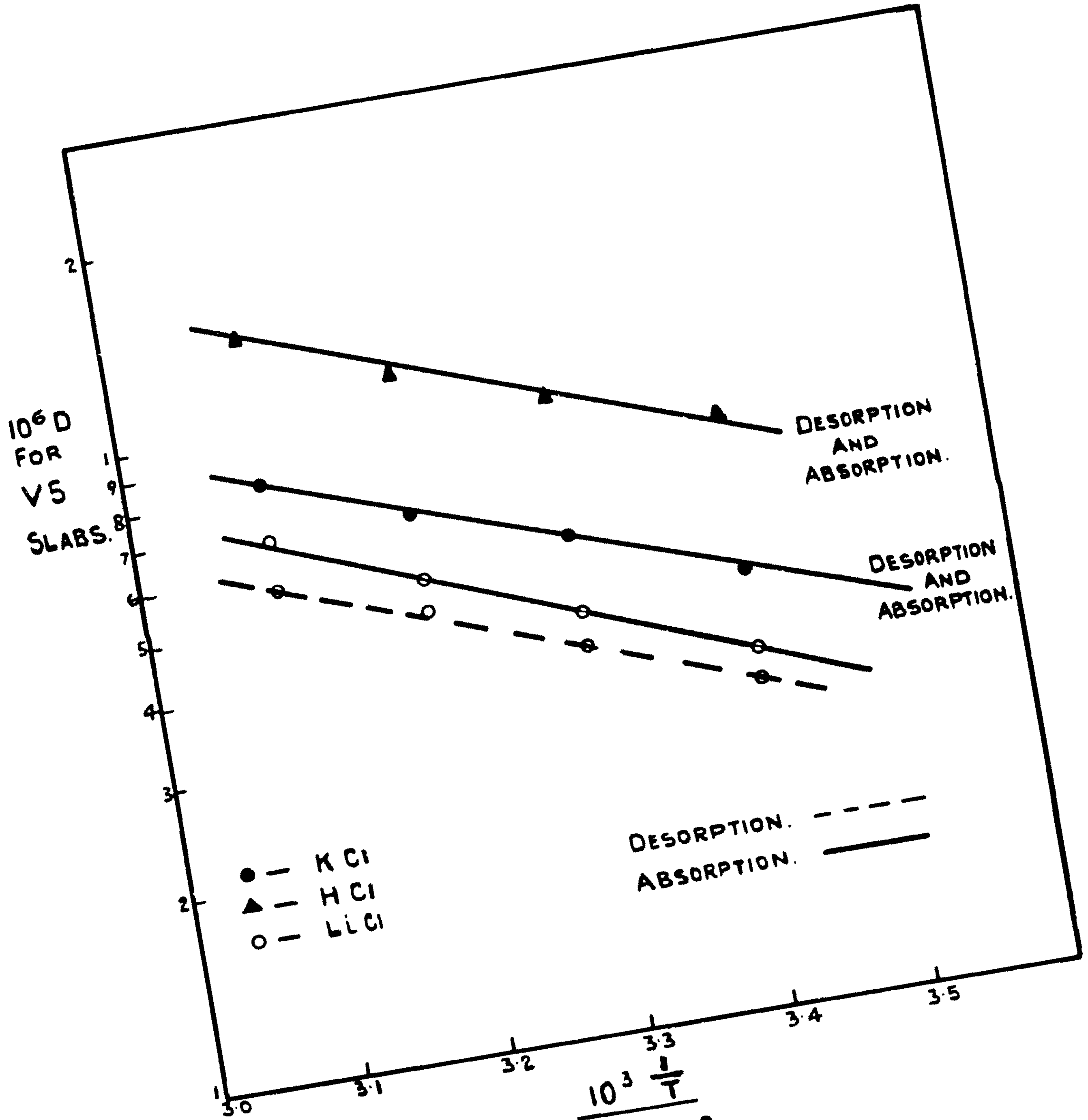


10⁶ D FOR H125 SLABS.
2
1
9
8
7
6
5
4
3
2
1
3·0
3·1
3·2
3·3
3·4
3·5
DESORPTION AND ABSORPTION.
● – KCl
▲ – HCl
○ – LiCl
DESORPTION ----
ABSORPTION ——
10³ · 1/T

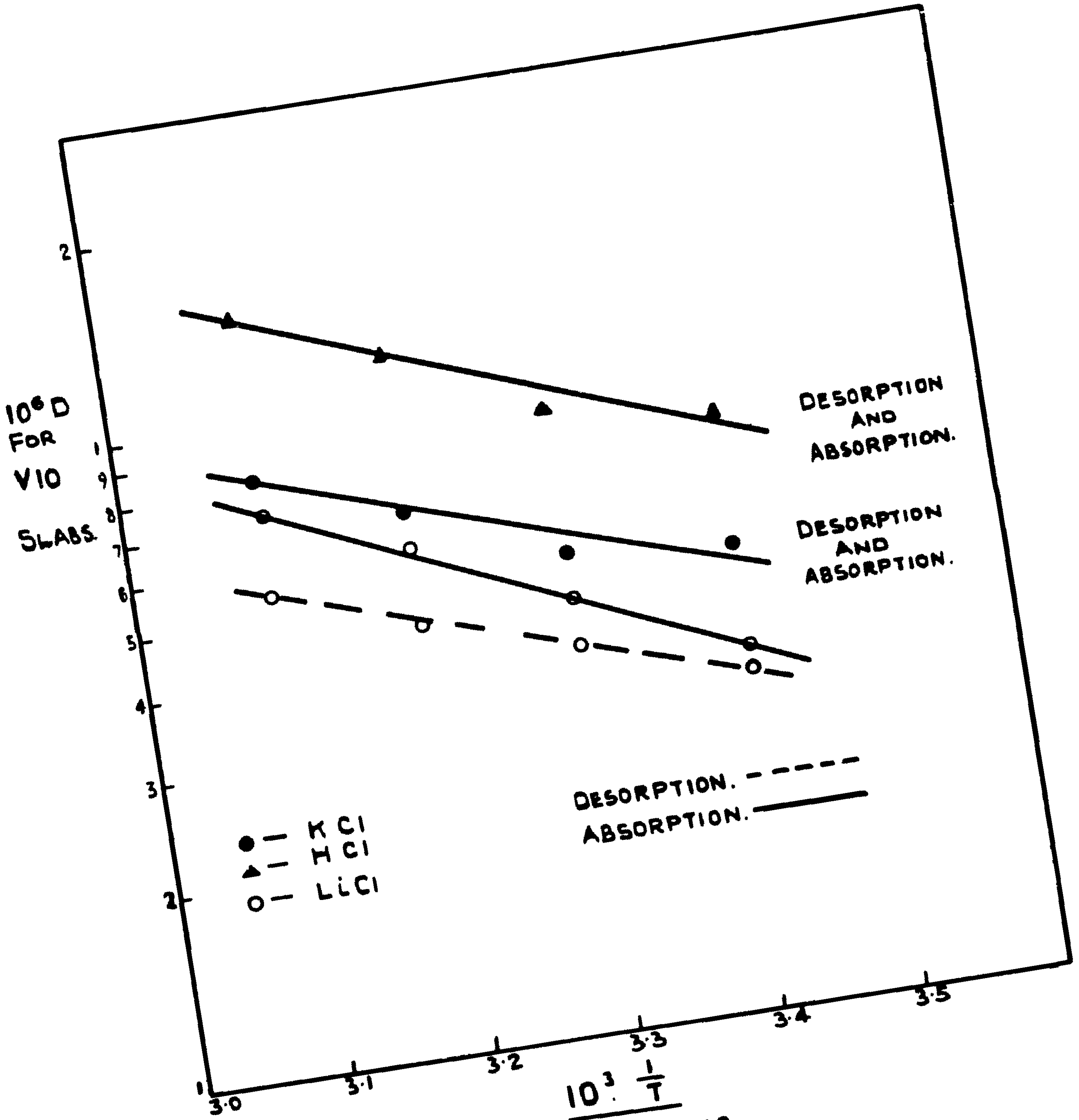
GRAPH. 7


10⁶ D FOR V3 SLABS.
2
1
9
8
7
6
5
4
3
2
1
3·0
3·1
3·2
3·3
3·4
3·5
ABSORPTION AND DESORPTION.
● — K Cl
▲ — H Cl
○ — Li Cl
DESORPTION. - - - - -
ABSORPTION. ———
10³ 1/T

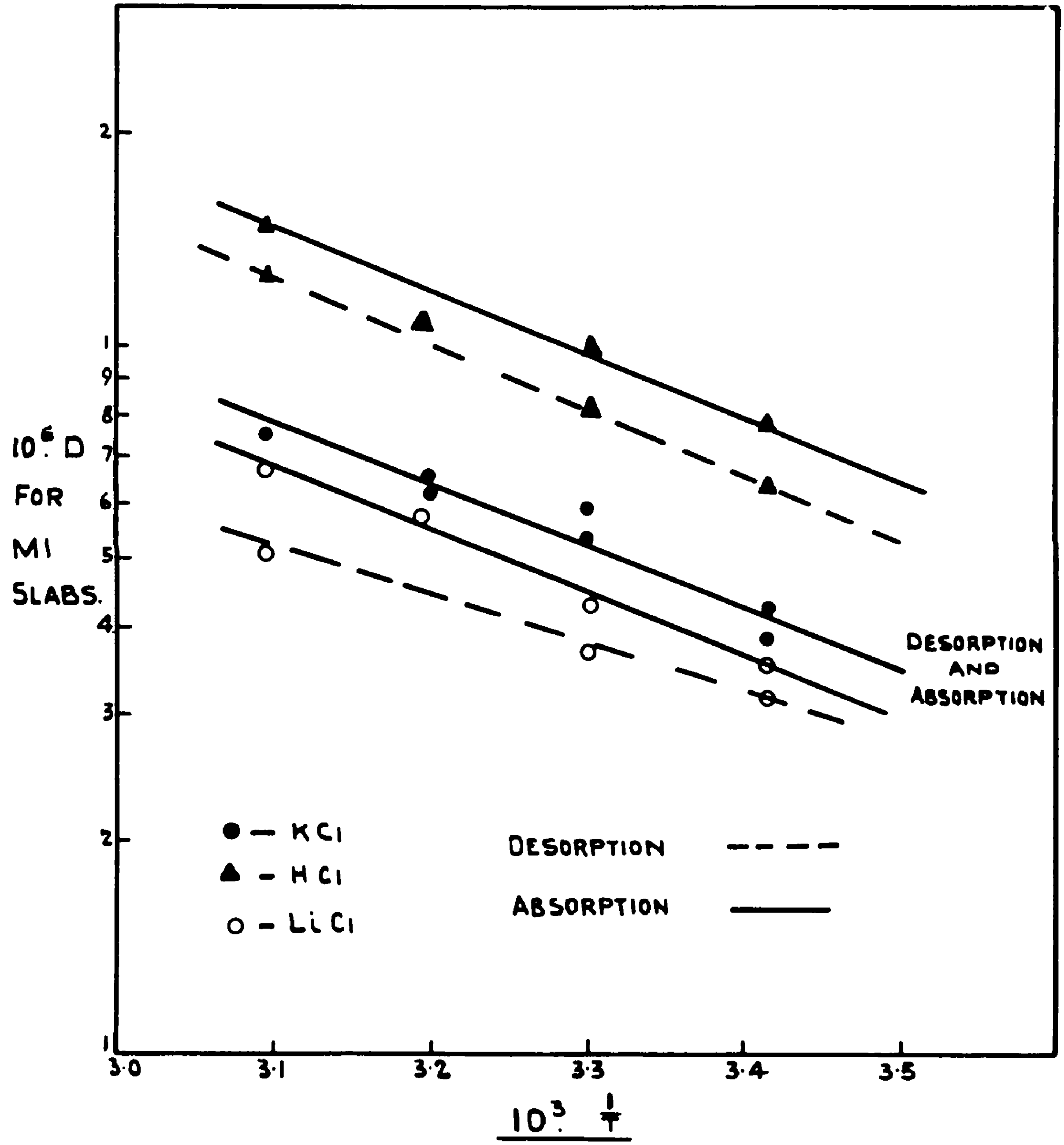
GRAPH. 8.


10⁶ D FOR V5 SLABS.
2
1
9
8
7
6
5
4
3
2
1
3·0
3·1
3·2
3·3
3·4
3·5
10³ 1/T
DESORPTION AND ABSORPTION.
DESORPTION AND ABSORPTION.
DESORPTION.
ABSORPTION.
● — K Cl
▲ — H Cl
○ — Li Cl

GRAPH. 9.


10⁶ D FOR V10 SLABS.
2
1
9
8
7
6
5
4
3
2
1
3·0
3·1
3·2
3·3
3·4
3·5
10³ 1/T
DESORPTION AND ABSORPTION.
DESORPTION AND ABSORPTION.
DESORPTION.
ABSORPTION.
● — K Cl
▲ — H Cl
○ — Li Cl

GRAPH. 10.



2
1
9
8
7
6
5
4
3
2
1
$10^6 D$
FOR
MI
SLABS.
3·0
3·1
3·2
3·3
3·4
3·5
$10^3 \cdot \frac{1}{T}$
DESORPTION AND ABSORPTION
● – KCl
▲ – HCl
○ – LiCl
DESORPTION
ABSORPTION

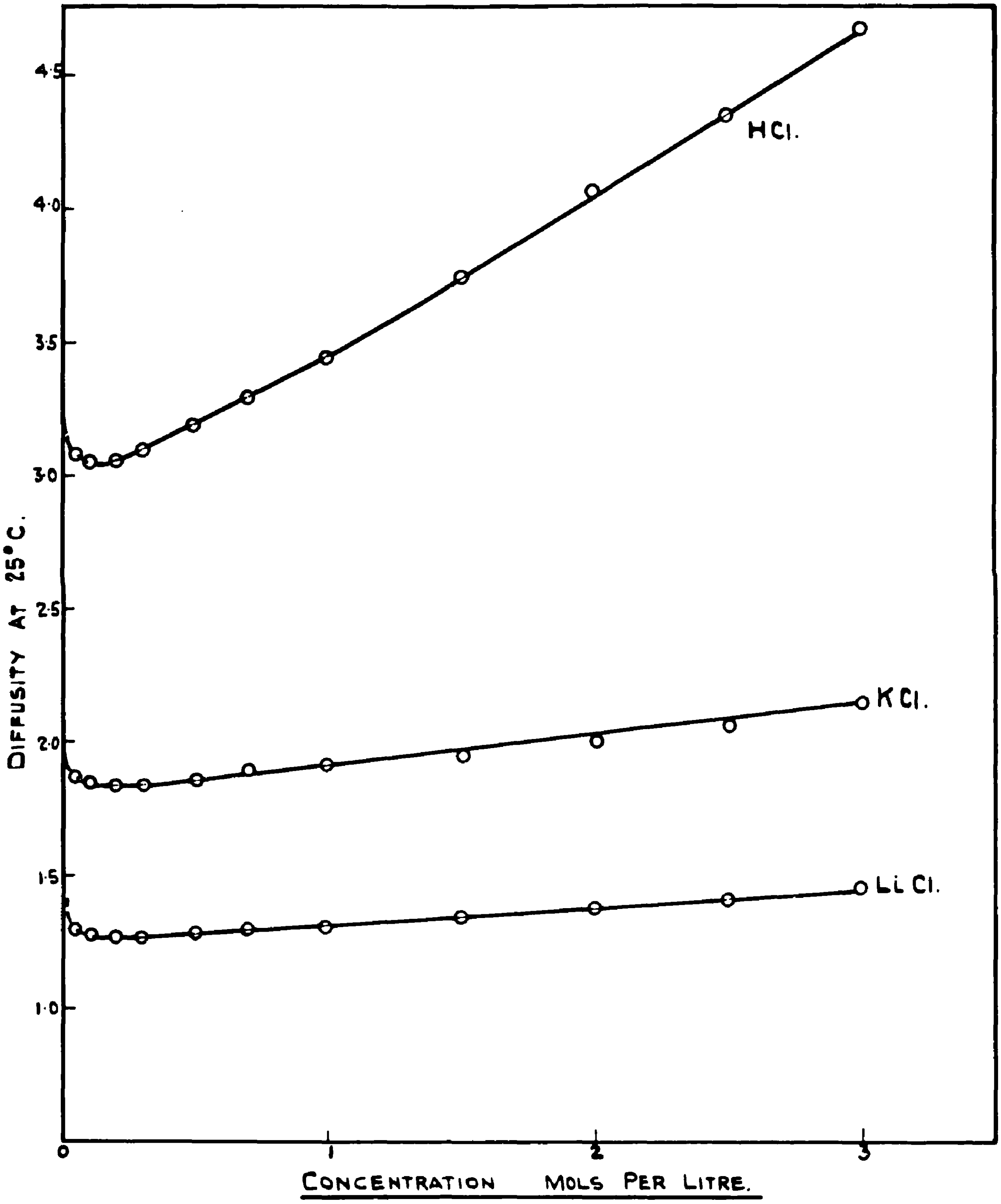
GRAPH. II

minimum, the diffusivities of the electrolyte do not increase at the same rate. The diffusivity of HCl increases at a greater rate than do the diffusivities of either KCl or LiCl. The diffusivity of KCl increases at a slightly greater rate than does that of LiCl. The rates of increase for KCl and LiCl are such that the values of diffusivity at a concentration of 1N. are only slightly greater than the values at 0.05 N. In fact with concentration increase from 0.05 N. to 1N. there is very little overall increase in diffusivity.

One would expect therefore that for N.HCl absorption should be quicker than desorption and for N.KCl and N.LiCl absorption should be only slightly quicker than desorption. The experimental technique is probably not sufficiently accurate to detect the small difference in absorption and desorption for KCl and LiCl. In the present work, therefore, absorption should be equal to desorption for KCl and LiCl.

From the experimental results it can be concluded that:-

(1) For N.HCl the rates of absorption and desorption to and from M1, H125 and V3 at temperatures of 20-50°C. are as would be expected from the above suggestions. The rates of absorption and desorption to and from slab types V5 and V10 are not as one would expect. The reason for absorption and desorption being equal for these slabs can possibly have its foundation in their larger pore size. It is more probable however that the results are experimentally incorrect. (See



4·5
4·0
3·5
3·0
2·5
2·0
1·5
1·0
DIFFUSITY AT 25° C.
HCl.
KCl.
LiCl.
0
1
2
3
CONCENTRATION MOLS PER LITRE.

GRAPH. 12.

section 6.7 on the statistical analysis of these results).

(2) For N.KCl all the results are in agreement with the above suggestions.

(3) For N.LiCl one would expect absorption and desorption to be equal. That the results are no so may possibly be because the porous slabs have a smaller influence on the Li^+ ions than on H^+ or K^+ ions.

Between concentrations of 0.05N. and 3N.KCl there is an appreciable increase in the diffusivity in free solution. If the previous reasoning is correct, this increase in diffusivity with concentration will result in absorption being quicker than desorption for 3N. solutions of KCl to such an extent as will be readily detected by the present experimental technique. Confirmation of this has already been given[1] for two types of slabs namely H125 and B5, for temperatures from 20-80°C.

In the same work[1] it was found that for N.KCl absorption was quicker than desorption at the lower temperatures and absorption was slower than desorption at the higher temperatures. This does not agree with either the present reasoning or the present results.

The percentage differences between absorption and desorption for Macdonald's results have now been calculated and are shown in Table 6.3.b.

TABLE 6.3.b. Values of $\bar{D} \times 10^5$ for H125 slabs

Temp. °C.	Absorption	Desorption	Difference Abs. - Des.	Percentage Difference
20	0.75	0.83	0.08	- 10.7
30	0.94	0.96	0.02	- 2.13
40	1.19	1.16	0.03	+ 2.59
50	1.45	1.34	0.11	+ 8.2
60	1.69	1.58	0.11	+ 6.95
70	2.22	1.81	0.41	+ 22.7
80	2.42	2.13	0.29	+ 13.6

Values of $D \times 10^5$ for B5 slabs

Temp. °C.	Absorption	Desorption	Difference Abs. - Des.	Percentage Difference
20	0.43	0.46	0.03	- 7.0
30	0.54	0.60	0.06	- 11.1
40	0.74	0.74	-	-
50	0.87	0.88	0.01	- 1.15
60	1.05	1.02	0.03	+ 2.94
70	1.27	1.19	0.08	+ 6.73
80	1.51	1.39	0.12	+ 8.65

Examination of this Table shows that the percentage differences are within the estimated experimental error for the intermediate temperatures and are outside the error at the higher and lower temperatures. The results **therefore cannot** be explained on the basis that the differences between absorption and desorption are within the calculated experimental error.

Assuming the present reasoning to be correct Macdonald's results for N.KCl suggest that absorption must be affected by the porous media to a greater or less extent than desorption, depending upon the temperature of the system. If this is not so then the results suggest the corollary that the rate of variation of diffusivity in free solution with increasing concentration depends upon temperature, and, in fact, that at 20°C. the overall effect of increasing concentration from 0.05N. to 1 N. is a reduction in diffusivity and at 60°C is an increase in diffusivity.

A further comparison of absorption and desorption can be drawn from the results for the absorption and desorption of 2N. solutions of HCl, KCl, LiCl, KNO_3 and HNO_3 to and from H125 slabs at 20°C. The results derived from these runs are given in Table 6.5.a.

Examination of this Table shows:-

(1) Absorption is quicker than desorption for 2N.KCl HCl and LiCl.

(2) Desorption is quicker than absorption for 2N.KNO_3

(3) Absorption is quicker than desorption for 2N.HNO_3

The results for 2N. KCl, HCl, LiCl and KNO_3 are in agreement with the present reasoning. The results for 2N. HNO_3 are the direct opposite of what should be expected provided the present reasoning is correct.

A comparison of rates of absorption and desorption to and from porous media has also been made by Wall et al.[91]. They found that absorption was equal to desorption.

Summing up all work on the comparison of absorption and desorption, we have a suggested theory with experimental evidence from runs on N.KCl, N.HCl, 2N.HCl, 2N.KCl, 2N.KNO_3 and 3N.KCl[1], and also from work by Wall et al., supporting this theory. There are also some results which do not agree with the suggested theory. These are for N.LiCl, 2N.HNO_3 and N.KCl[1].

Conclusions:-

In general the properties of the individual slab types have no bearing upon whether absorption is quicker than desorption or vice versa. The controlling factors are functions of the physical properties of the solutes and especially the variation of diffusivity with concentration.

6.4. Activation energies.

Macdonald[1] has shown previously that for absorption into and desorption from porous slabs, the diffusion coefficients vary with temperature in accordance with the equation suggested by Taylor[26], i.e.

$$\bar{D} = A \exp. \left(- \frac{Q}{RT} \right)$$

The diffusion coefficients for the absorption and desorption of N. solutions of HCl, KCl and LiCl to and from slab types H125, V3, V5, V10 and M1 have been given in Table 6.3.a. As expected plots of $\log \bar{D}$ vs $^1/_T$ gave straight lines. The activation energies calculated from these plots are shown in Table 6.4.a. Figure 9 provides an easy method for the comparison of these values.

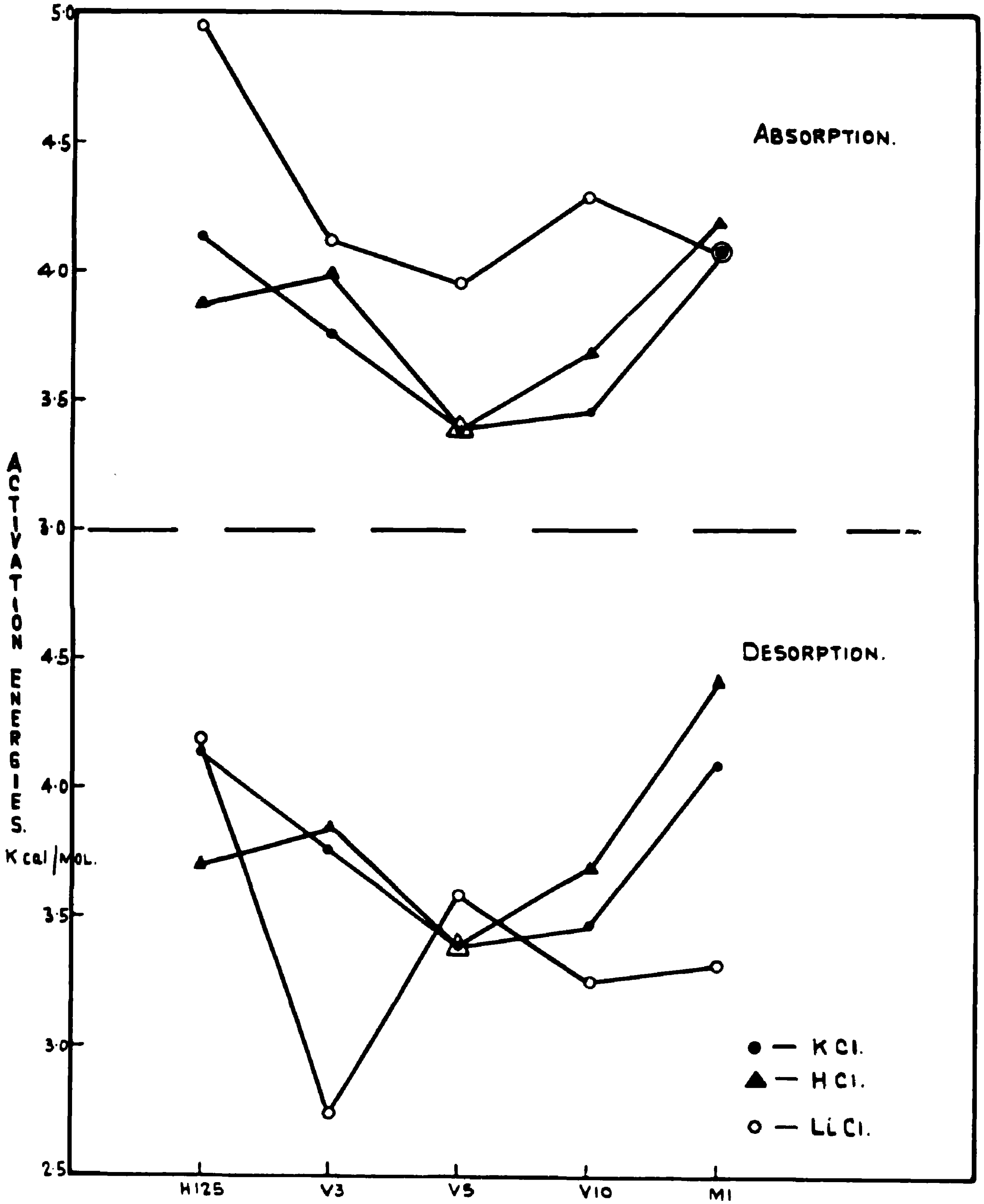
TABLE 6.4.a. Activation Energies in K.cal./mol.

Slab	KCl		HCl		LiCl	
Type	Abs.	Des.	Abs.	Des.	Abs.	Des.
H125	4.14	4.14	3.88	3.71	4.95	4.17
V3	3.76	3.76	3.98	3.84	4.12	2.74
V5	3.39	3.39	3.41	3.41	3.96	3.57
V10	3.47	3.47	3.68	3.68	4.29	3.25
M1	4.09	4.09	4.18	4.42	4.09	3.31

Examination of Table 6.4.a. and Figure 9 shows that:-

(1) The activation energies for the absorption and desorption of KCl are equal. The value obtained, 4.14 k.cal./mol. is of the same order as the activation energies found for the absorption of N.KCl to H125 slabs by Macdonald namely 4.02 k.cal./mol. It is however much higher than Macdonald's value of 3.26 k.cal./mol. for desorption.

(2) For HCl the activation energies for absorption and



ABSORPTION.
DESORPTION.
ACTIVATION ENERGIES. K cal/MOL.
5·0
4·5
4·0
3·5
3·0
4·5
4·0
3·5
3·0
2·5
H125
V3
V5
V10
M1
● — K Cl.
▲ — H Cl.
○ — Li Cl.
SLAB TYPE.

FIGURE 9.

desorption vary as follows.

(a) For H125 and V3 slabs the activation energies for absorption are greater than the corresponding activation energies for desorption.

(b) For M1 slabs the activation energy for desorption is greater than the activation energy for absorption.

(c) For V5 and V10 slabs the activation energies are equal.

(d) The activation energies for desorption follow the same trend as the activation energies for absorption and that, except for H125 slabs, the activation energies for the absorption and desorption of HCl follow a pattern similar to that for the activation energies for KCl.

(3) For LiCl all the activation energies for absorption are greater than the corresponding desorption values. The values for desorption and absorption do not ,however, follow similar trends. The values for absorption, with the exception of the values for M1 slabs, follow a pattern similar to that for the absorption of HCl and KCl. The values for desorption vary very widely and do not warrant further discussion.

With a few exceptions it can be generally concluded that:-

(1) Activation energies are functions of the slab type used.

(2) Irrespective of slab type, where absorption is quicker than desorption, the activation energy for absorption

is greater than the activation energy for desorption.

(3) The activation energies for the absorption of HCl, KCl and LiCl and for the desorption of HCl and KCl follow similar trends and decrease for individual slab types from LiCl - KCl - HCl.

(4) There is no apparent relationship between the normally accepted physical properties of the slabs and the activation energies. There is, however, a reciprocal similarity between the activation energies and the values for corrected K^2.

6.5. The effect of initial solute concentration on desorption and absorption

The experimental results for the absorption and desorption of N. and 2N. solutions of KCl, KNO_3, HCl, LiCl, HNO_3 and KAc to and from H125 slabs at 20°C. are given in appendix A.

The values of the integral diffusion coefficients derived from these results are shown in Table 6.5.a. The column "Percentage Difference" in this table gives the percentage increase or decrease in the integral diffusion coefficients for increase in concentration from N. to 2N.

TABLE 6.5.a.

Compound	Strength	Run	$t_2 - t_1$ minutes	$\overline{D}$ x 10^5	Percentage Difference
HNO_3	N	Des.	27.7	1.04	+ 0.7
	2N	Des.	27.5	1.05	
	N	Abs.	26.4	1.09	+ 3.0
	2N	Abs.	25.6	1.13	
LiCl	N	Des.	67.1	.430	+ 6.3
	2N	Des	63.2	.457	
	N	Abs.	61.4	.470	Nil.
	2N	Abs.	61.4	.470	
KCl	N	Des.	44.9	.643	+ 2.2
	2N	Des.	43.9	.657	
	N	Abs.	44.9	.643	+ 8.5
	2N	Abs.	41.4	.698	
KNO_3	N	Des.	47.5	.608	- 7.2
	2N	Des.	51.1	.564	
	N	Abs.	50.7	.569	- 5.5
	2N	Abs.	53.6	.538	
HCl	N	Des	27.7	1.04	+ 12.5
	2N	Des.	24.6	1.17	
	N	Abs.	23.6	1.22	+ 10.7
	2N	Abs.	21.4	1.35	
KAc	N	Des	61.7	.468	Nil
	2N	Des	61.7	.468	
	N	Abs.	60.2	.479	Nil
	2N	Abs.	60.2	.479	

The variation in diffusivity in free solution for variation in concentration for KCl, HCl and LiCl has already been given (see section 6.3.). The diffusivities of all three increase with increase in concentration from N to 2N. For KNO_3 and HNO_3 a similar increase in concentration results in a decrease in the diffusivity in free solution.

6.5.1. Desorption.

The values of $\bar{D}$ in Table 6.5.a. show that for KCl, HCl and LiCl variation in initial concentration from N to 2N results in appreciable increases in the rates of desorption. The percentage increase in each case is more than could be expected from experimental error.

For KNO_3 variation in initial concentration from N. to 2N. results in a decrease in the rate of desorption of 7.2%.

These experimental variations correspond to the variation of the diffusivities in free solution for a similar variation in concentration. For HNO_3 the percentage increase in the rate of desorption is within the experimental limits and therefore must be neglected.

For KAc there is no apparent difference between the rates of desorption for N and 2N concentrations.

The effect of variation in initial solute concentration on rates of desorption has been investigated previously. Piret et al.[87] used three types of porous medium of increasing complexity with several electrolytes and found that variation in initial concentration did not affect the rates of desorption. Macdonald used two types of slabs and increased the initial solute concentration from N. to 3N. He also suggested that desorption was independent of the initial solute concentration. His results are shown in Table 6.5.b.

TABLE 6.5.b.

Temp. °C.	H125			B5		
	$\bar{D}x10^5$		Percentage Difference	$\bar{D}x10^5$		Percentage Difference
	N.	3N.		N.	3N.	
20	0.83	0.77	-7.2	0.46	0.49	+6.5
30	0.96	0.94	-2.1	0.60	0.61	+1.7
40	1.16	1.12	-3.4	0.74	0.75	+1.3
50	1.34	1.29	-3.7	0.88	0.93	+5.7
60	1.58	1.56	-1.3	1.02	1.06	+3.9
70	1.81	1.83	-	1.19	1.23	+3.4
80	2.13	2.04	-4.2	1.39	1.39	-

Examination of Table 6.5.b. shows that generally

(1) For H125 slabs desorption of 3N.KCl is slower than desorption of N.KCl.

(2) For B5 slabs desorption of 3N.KCl is quicker than desorption of N.KCl.

Macdonald has assumed that these differences are negligible when compared with the increase in diffusivity in free solution between N. and 3N. concentrations. However they occur not for one temperature but for several and the percentage differences are for most cases outwith that expected from experimental error. It is possible therefore that initial solute concentration is not without some effect on the rates of desorption.

It might also be noted that for H125 slabs desorption of N. solutions is quicker than desorption of 3N. solutions whereas for B5 slabs desorption of N. solutions is slower than desorption of 3N. solutions. This latter variation is in agreement with the variation in diffusivity in free solution for increase in concentration whereas the former is not.

6.5.2. Absorption.

Examination of Table 6.5.a. shows that for KCl, HCl and KNO_3 the rates of absorption vary with increase in concentration from N. to 2N. as do their diffusivities in free solution. In LiCl and KAc no differences were detected in the absorption rates for N. and 2N. solutions. For HNO_3 an increase in the rate of absorption of 3.0% was detected. This variation is the opposite of the variation of diffusivity in free solution for a similar increase in concentration.

The effect of initial solute concentration on absorption rates has been investigated previously[1]. An increase in the rates of absorption for an increase in concentration from N. to 3N. was found for KCl diffusing into H125 and B5 slabs.

Conclusions.

The present work shows that, in general, for both absorption and desorption, variation in initial solute concentration affects the diffusion coefficients of electrolytes diffusing to and from a porous medium (H125 slabs) in the same manner as it affects diffusion in free solution.

In contrast to this previous workers[1,87] found that desorption rates were independent of initial solute concentration but that absorption rates[1] varied with increasing concentration in the same manner as the diffusivities of the electrolyte in free solution.

6.6. The absorption and desorption of mixtures of electrolytes to and from H125 slabs at 20°C.

The experimental results for these runs are given in appendix A. The integral diffusion coefficients derived from the results are shown in column 2 of Table 6.6.a. Column 3 of this Table gives the integral diffusion coefficients for HCl, KCl, LiCl, HNO_3, KNO_3 and KAc solutions of

N concentration diffusing to and from H125 slabs at 20°C. The differences and percentage differences between the diffusion coefficients of an electrolyte diffusing in a mixture and in a solution of N concentration are shown in columns 4 and 5.

TABLE 6.6.a

1. Mixture	2. $\bar{D}$ in mixture	3. $\bar{D}$ in normal solution of N. concentration	4. Difference	5. Percentage Difference
Des. (HCl	1.840	1.040	+ 0.800	+ 77.0
(KCl	0.576	0.643	- 0.067	- 10.4
Des. (HCl	2.090	1.040	+ 1.050	+101.0
(LiCl	0.464	0.430	+ 0.034	+ 7.9
Abs. (HCl	2.050	1.220	+ 0.830	+ 68.0
(KCl	0.623	0.643	- 0.020	- 3.1
Abs. (HCl	2.630	1.220	+ 1.410	+116.0
(LiCl	0.421	0.479	- 0.058	- 12.1
Des. (KCl	0.724	0.643	+ 0.081	+ 12.6
(KAc	0.477	0.468	+ 0.009	+ 1.9
Des. (KCl	0.656	0.643	+ 0.013	+ 2.0
(KNO_3	0.583	0.608	- 0.025	- 4.1
Abs. (KCl	0.863	0.643	+ 0.220	34.2
(KAc	0.379	0.479	- 0.100	- 20.8
Abs. (KCl	0.793	0.643	+ 0.150	23.3
(KNO_3	0.502	0.569	- 0.067	- 11.8

Considering mixtures HCl:KCl and HCl:LiCl :-

It will be seen from Table 6.6.a. that for both absorption and desorption HCl diffuses in these mixtures much more quickly than it does normally. This increase may be caused either, by the increase in ionic concentrations in the mixtures, which are in effect equivalent to 2N. concentration, or, by the accompanying diffusion of KCl and LiCl.

Table 6.6.b. is similar to Table 6.6.a. except that the diffusion coefficients of the components of the mixtures are compared with the diffusion coefficients of the electrolytes in solutions of 2N. concentration.

TABLE 6.6.b.

1. Mixture	2. $\bar{D}$ in mixture	3. $\bar{D}$ in normal solution of 2N. concentration	4. Difference	5. Percentage Difference
Des. (HCl	1.840	1.170	+ 0.670	+ 57.3
(KCl	0.576	0.657	- 0.081	- 12.3
Des. (HCl	2.090	1.170	+ 0.920	+ 78.6
(LiCl	0.464	0.457	+ 0.007	+ 1.5
Abs. (HCl	2.050	1.350	+ 0.700	+ 51.9
(KCl	0.623	0.698	- 0.075	- 10.7
Abs. (HCl	2.630	1.350	+ 1.280	+105.5
(LiCl	0.421	0.470	- 0.049	- 10.4
Des. (KCl	0.724	0.657	+ 0.067	+ 10.2
(KAc	0.477	0.468	+ 0.009	+ 1.9
Des. (KCl	0.656	0.657	- 0.001	- 0.2
(KNO_3	0.583	0.564	+ 0.019	+ 3.4
Abs. (KCl	0.863	0.698	+ 0.165	+ 23.7
(KAc	0.379	0.479	- 0.100	- 20.9
Abs. (KCl	0.793	0.698	+ 0.095	+ 13.6
(KAc	0.502	0.538	- 0.036	- 6.7

Examination of this Table shows that the increases in the diffusivity of HCl are only slightly lower than the corresponding increases in Table 6.6.a. The large increases in diffusivity, therefore, are not caused by the increase in ionic concentration.

Vinograd and McBain[60] have shown that the diffusivities of cations (present only in small concentration) are increased by the accompanying diffusion of an electrolyte in which the diffusivity of the cation is slower than its anion.

Since the chloride ions are common to each of the diffusing electrolytes in the mixtures, the increases in the diffusivity of HCl may be considered essentially as increases in the diffusivity of the hydrogen ions. The present results therefore agree with the findings of Vinograd and McBain[60] and show also that the increase in the diffusivity of the hydrogen ions increases with decrease in the diffusivity of the other cation present in the mixture.

Examination of Tables 6.6.a. and 6.6.b. also shows that in three out of four cases the diffusivity of the cations, other than hydrogen, in the mixtures, are lower than the values for diffusion in a normal solution. These results are in agreement with a secondary conclusion of Vinograd and McBain[60] namely, that the diffusion of cations (present only in small concentrations) is decreased by the accompanying diffusion of an electrolyte in which the cation diffuses faster than its anion.

Considering mixtures KCl:KAc and KCl:KNO_3 :-

In these mixtures, in which the potassium ions are common, it will be seen that the larger and slower acetate and nitrate ions increase the speed of the chloride ions - with the acetate ions increasing the speed of the chloride ions to a greater extent than do the nitrate ions, while the diffusivities of they themselves are reduced. These results are in agreement with the corollaries of the conclusions of Vinograd and McBain[60].

Examination of Tables 6.6.a. and 6.6.b. will show that the increases or decreases in the diffusivities of the components of the mixtures are of a diverse nature. Therefore, although general conclusions could be deduced from them no quantitative estimations were possible.

This was disappointing in that it had been hoped to expand this section to include the quantitative effects of variation of slab type, temperature, and process taking place, on the percentage increases, or decreases, in the diffusivities of the components of the mixtures.

No further work was attempted on this section, but provided a more accurate and reliable technique can be evolved it may be a line of research worthy of investigation.

6.7.1. A statistical analysis of the experimental diffusion coefficients for the absorption and desorption of N.HCl, N.KCl and N.LiCl to and from H125, V3, V5, V10 and M1 slabs at 20-50°C.

Throughout the discussion of the results, although a few general relationships between the variables M, S, T and L have been obtained, there have been exceptions to most of them.

To investigate these relationships and their exceptions it was decided to do a statistical analysis on the uncorrected diffusion coefficients.

An analysis of variance on the logarithms of the experimental diffusion coefficients gives the following Table (Table 6.7.a.) in which:-

M = the process taking place, i.e. absorption or desorption
S = the type of slab
L = the electrolytic solution
T = the temperature of the experiment.

TABLE 6.7.a.

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Squares	Component of Variance.
L	2	2.77501900	1.38750950	$-\sigma_0^2 + 2\sigma^2_{L.S.T.}$ $+5\sigma^2_{L.T.M.} + 4\sigma^2_{L.S.M.}$ $+10\sigma^2_{L.T.} + 8\sigma^2_{L.S.}$ $+20\sigma^2_{L.M.} + 40\sigma^2_{L^2}$
T	3	1.17556762	0.39185587	
S	4	0.67854770	0.16963692	
M	1	0.05050793	0.05050793	
L.T	6	0.00180233	0.00030039	
L.M	2	0.03231727	0.01615863	
L.S	8	0.00893606	0.00111701	etc.
T.S	12	0.00758841	0.00063237	
T.M	3	0.00360630	0.00120210	
S.M	4	0.00707028	0.00176757	
L.S.T.	24	0.01321512	0.00055063	
L.S.M.	8	0.00968670	0.00121084	
L.T.M.	6	0.00453717	0.00075620	
S.M.T.	12	0.00092158	0.00007680	$\sigma_0^2 + 3\,\sigma^2_{M.S.T.}$
Residual	24	0.00550396	0.00022933	σ_0^2
Total	119	4.77482743		

By comparing the residual (0.00022933) with the smallest second order interaction i.e. (S.M.T.) it will be seen that the residual is larger than the interaction. The interaction therefore is not significant.

$$\text{The new residual is } \frac{0.0092158 + 0.00550396}{36}$$

$$= 0.00017849 \text{ with 36 degrees of freedom.}$$

Comparing the new residual with the L.S.T. interaction gives

$$F = \frac{0.00055063}{0.00017849}$$

$$= 3.08 \text{ with } N_1 = 24 \text{ and } N_2 = 36$$

The value for F lies close to the .1 per cent level of significance. The interaction L.S.T. is therefore significant.

Comparing the new residual with the L.T.M. interaction gives

$$F = \frac{0.00075620}{0.00017849}$$

$$= 4.24 \text{ with } N_1 = 6 \text{ and } N_2 = 36$$

This value for F lies close to the 0.5 per cent level of significance. The interaction L.T.M. is therefore significant.

Comparing the new residual with the L.S.M. interaction gives

$$F = \frac{0.00121084}{0.00017849}$$

$$= 6.78 \text{ with } N_1 = 8 \text{ and } N_2 = 36$$

This value is more significant than the 0.1 per cent level of significance. The interaction L.S.M. is therefore significant.

Since the only second order interaction which is not significant is S.M.T., the factorial design can now be split up into three separate factorials for each of the solutions. An analysis of variance will now be carried out for each of the electrolytic solutions.

6.7.2. HCl

An analysis of variance for the absorption and desorption of N.HCl to and from the five slab types at temperatures of 20-50°C. gives the following Table (Table 6.7.b.)

TABLE 6.7.b.

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Squares	Component of Variance.
T	3	0.39008368	0.13002789	$-\sigma_0^2 + 2\sigma_{T.S.}^2 + 5\sigma_{T.M.}^2 + 10\sigma_T^2$
S	4	0.26630545	0.06657636	
M	1	0.02031756	0.02031756	
M.S	4	0.01436218	0.00359054	
M.T	3	0.00053987	0.00017996	
S.T	12	0.00622211	0.00051851	$\sigma_0^2 + 2\sigma_{S.T.}^2$
Residual	12	0.00293212	0.00024434	σ_0^2
Total	39	0.70076297		

By comparing the residual (0.00024434) with the smallest first order interaction i.e. (M.T.) it will be seen that the latter is smaller than the residual and therefore is not significant.

$$\text{The new residual} = \frac{0.00293212 + 0.00053987}{15}$$

$$= 0.00023147 \text{ with } 15 \text{ degrees of freedom.}$$

Comparing the new residual with the S.T. interaction gives

$$F = \frac{0.00051851}{0.00023147}$$

$$= 2.24 \text{ with } N_1 = 12 \text{ and } N_2 = 15.$$

This value lies close to the 5 per cent level of significance. Therefore, the interaction is significant. Similarly the interaction M.S. is highly significant.

It has been noted previously (section 6.2.) that the results for V5 and V10 are possibly experimentally incorrect. If this is so the interaction M.S might not be significant. A secondary analysis of the results for HCl will be carried out omitting the V5 and V10 results. (See section 6.7.5.)

6.7.3. KCl

An analysis of variance for the absorption and desorption of N.KCl to and from the five slab types at temperatures of 20-50°C. gives the following Table. (Table 6.7.c.)

TABLE 6.7.c.

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Squares	Component of Variance.
T	3	0.36707087	0.12235696	As in TABLE 6.7.b.
M	1	0.00001071	0.00001071	
S	4	0.24421030	0.06105258	
M.S.	4	0.00054582	0.00013646	
M.T.	3	0.00088913	0.00029638	
S.T.	12	0.00920699	0.00076725	
Residual	12	0.00214237	0.00017853	
Total	39	0.62407619		

By comparing the residual (0.00017853) with the smallest first order interaction i.e. (M.S) it will be seen that the latter is smaller than the residual and therefore is not significant.

$$\text{The new residual} = \frac{0.00054582 + 0.00214237}{16}$$

$$= 0.00016801 \text{ with 16 degrees of freedom.}$$

Comparing the new residual with the M.T. interaction gives

$$F = \frac{0.00029638}{0.00016801}$$

$$= 1.76 \text{ with } N_1 = 3 \text{ and } N_2 = 16.$$

At the 5 per cent level of significance the interaction M.T is possibly insignificant. [Further investigation is required to show whether this is true or not. It is suspected that the values for M1 slabs are the exceptions to the interaction. A secondary analysis will be carried out for KCl omitting these values (see section 6.7.6.].

$$\text{The new residual} = \frac{0.00054582 + 0.00214237 + 0.00088913}{19}$$

$$= 0.00018828 \text{ with 19 degrees of freedom.}$$

Comparing the new residual with the S.T. interaction gives

$$F = \frac{0.00076725}{0.00018828}$$

$$= 4.08 \text{ with } N_1 = 12 \text{ and } N_2 = 19.$$

This value lies between the 1 per cent and the .1 per cent levels of significance. The interaction S.T. therefore, is significant.

6.7.4. LiCl

An analysis of variance for the absorption and desorption of N.LiCl to and from the five slab types at temperatures of 20-50 C. gives the following Table (Table 6.7.d.)

TABLE 6.7.d.

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Squares	Component of Variance.
T	3	0.42021541	0.14007180	
M	1	0.06249693	0.06249693	
S	4	0.17696801	0.04424200	As in Table 6.7.b.
M.S	4	0.00184898	0.00046224	
M.T	3	0.00671446	0.00223815	
S.T	12	0.00537444	0.00044787	
Residual	12	0.00618804	0.00051567	
Total	39	0.67496927		

By comparing the residual (0.00051567) with the smallest first order interaction i.e. (S.T.) it will be seen that the latter is smaller than the residual and therefore is not significant.

Similarly the H.S. interaction is not significant.

$$\text{The new residual} = \frac{0.00618804 + 0.00537444 + 0.00184898}{28}$$

$$= 0.00047898 \text{ with 28 degrees of freedom.}$$

Comparing the new residual with the M.T. interaction gives

$$F = \frac{0.00223815}{0.00047898}$$

$$= 4.67 \text{ with } N_1 = 3 \text{ and } N_2 = 28.$$

This value lies close to the 1 per cent level of significance. The interaction M.T is significant.

Since the interactions S.T and M.S are insignificant the residual can also be compared with the S component of variance.

$$\text{This gives} \quad F = \frac{0.04424200}{0.00047898}$$

$$= 92.3$$

The effect of the slabs therefore is highly significant.

6.7.5. HCl

A statistical analysis for the absorption and desorption of N.HCl to and from slab types H125, V3 and M1 at 20-50°C. gives the following Table (Table 6.7.e.)

TABLE 6.7.e.

Source of Variance	Degrees or Freedom	Sum of Squares	Mean Squares	Component of Variance.
S	2	0.19714648	0.09857324	$-\sigma_0^2 + 4\sigma_{S.M}^2$
T	3	0.26725129	0.08908376	$+2\sigma_{ST}^2 + 8\sigma_S^2$
M	1	0.03386259	0.03386259	
S.T	6	0.00128628	0.00021438	
S.M	2	0.00081715	0.00040838	
M.T	3	0.00089979	0.00029993	$\sigma_0^2 + 3\sigma_{MT}^2$
Residual	6	0.00257220	0.00042870	σ_0^2
Total	23	0.50383578		

Since the "mean squares" for the interactions M.T, S.M and S.T. are less than the residual these interactions are insignificant.

The new residual

$$= \frac{0.00128628 + 0.00081715 + 0.00089799 + 0.00257220}{17}$$

$$= 0.00032786$$ with 17 degrees of freedom

The effects of S, T and M, therefore, are highly significant

6.7.6. KCl

A statistical analysis for the absorption and desorption of N.KCl to and from slab types H125, V3, V5 and V10 at 20-50°C. gives the following Table. (Table 6.7.f.)

TABLE 6.7.f.

Source of Variance	Degree of Freedom	Sum of Squares	Mean Squares	Component of Variance.
M	1	0.00004925	0.00004925	$\sigma_o^2 + 4\sigma^2_{M.S.} + 4\sigma^2_{M.T.} + 16\sigma^2_{M.}$
S	3	0.16559992	0.05519997	
T	3	0.29224815	0.09741605	
S.M	3	0.00005126	0.00001709	
S.T	9	0.00530861	0.00058985	
M.T	3	0.00026692	0.00008897	$\sigma_{o}^2 + 4\sigma^2_{M.T.}$
Residual	9	0.00029836	0.00003315	σ_o^2
Total	31	0.46382047		

By comparing the residual (0.00003315) with the smallest first order interaction S.M. it will be seen that the latter is smaller than the residual and, therefore, is not significant.

$$\text{The new residual} = \frac{0.00029836 + 0.00005126}{12}$$

$$= 0.00002914 \text{ with 12 degrees of freedom.}$$

Comparing the new residual with the M.T. interaction gives

$$F = \frac{0.00008897}{0.00002914}$$

$$= 3.05 \text{ with } N_1 = 3 \text{ and } N_2 = 12.$$

This value lies close to the 5 per cent level of significance and, therefore, is considered to be significant.

Comparing the new residual with the S.T. interaction gives

$$F = \frac{0.00058985}{0.00002914}$$

$= 20.2$ with $N_1 = 9$ and $N_2 = 12$.

This value is highly significant. Therefore the interaction S.T. is significant.

6.7.7. Percentage errors.

As the interaction S.M.T. in Table 6.7.a. was insignificant the residuals in the other tables can be taken as measures of the experimental error.

e.g. For HCl

$$\text{Residual} = \sigma_0^2 = 0.00024434$$

$$\therefore \sigma_0 = \pm 0.0156$$

and since the dependent variable is in logarithms to the base 10 form the percentage error is equal to

$$\left[(\text{anti-log} \pm 0.0156) - 1 \right] \times 100$$

i.e. the percentage error $\pm 3.5\%$

Similarly the percentage errors for KCl and LiCl are

KCl	± 3.5%
LiCl	± 5.1%

Also if it is assumed that the residual in Table 6.7.a. is due to only the error then the percentage error for the complete factorial experiment is ± 3.5%.

6.7.8. Summary of effects

For HCl

$$\log D = f_1(S,T) + f_2(M,S)$$

and $\log D = f_1(S) + f_2(M) + f_3(T)$ if the experiments for V5 and V10 are neglected.

For KCl

$$\log D = f(S,T)$$

and $\log D = f_1(M,T) + f_2(S,T)$ if the experiments for M1 are neglected.

For LiCl

$$\log D = f_1(M,T) + f_2(S).$$

CONCLUSIONS

1. The accuracy of the experimental procedure is ± 3-4% .

2. The values of the diffusion coefficients for substances diffusing to and from porous media at various temperatures are dependent upon the physical build-up of the media, the process taking place, and the temperature at which the process is taking place but are not necessarily dependent upon functions of the same combinations of these variables. e.g. It was found that for

   N.HCl

   $$\log D = f_1(S.T) + f_2(M.S)$$

   N.KCl

   $$\log D = f(S.T)$$

   N.LiCl

   $$\log D = f_1(M.T) + f_2(S).$$

3. Diffusion in a porous medium appears to be slower than in free solution. The apparent reduction in diffusivity is due mainly to the tortuosity of the pores within the medium. It is not affected by the pore diameters used but is dependent to a slight extent upon the size of the diffusing particles and in some instances to the process taking place.

4. Variation in initial solute concentration affects the rate of diffusion to and from a porous medium in the same manner as it affects diffusion in free solution.

5. The physical properties of a porous medium have no bearing upon whether absorption is quicker than desorption. The factor which determines which process is the quicker is the variation of the diffusivity of the solute in free solution with increase in concentration.

6. The values of the activation energies, for both absorption and desorption to and from porous media vary as follows:-

   For any one solute they are dependent upon the physical properties of the media.

   For any one medium they are dependent upon the physical properties of the solutes.

APPENDIX A. - EXPERIMENTAL VALUES OF E_D AND $1-E_A$

H125 - N.KCl - DESORPTION (INITIAL RUNS)

T - 20°C.	t.	10.	20.	30.	40.	50.	60.	70.
	E.	.632	.488	.402	.308	.247	.198	.159
		.640	.475	.400	.317	.253	.192	.155
T - 30°C.	t.	10.	20.	30.	40.	50.	60.	70.
	E.	.573	.412	.302	.250	.185	.137	.106
		.580	.409	.298	.252	.191	.145	.990
T - 40°C.	t.	10.	20.	25.	30.	40.	45.	50.
	E.	.550	.388	.325	.271	.196	.165	.139
T - 50°C.	t.	10.	15.	20.	25.	30.	35.	45.
	E.	.475	.390	.329	.267	.222	.181	.120

H125 - 20°C

DESORPTION

N.KCl	t.	10.	20.	30.	40.	50.	60.	70.
	E.	.620	.485	.384	.306	.248	.203	.164
2N.KCl	t.	10.	20.	30.	40.	50.	60.	70.
	E.	.627	.471	.365	.296	.236	.190	.152
N.HCl	t.	5.	10.	15.	20.	25.	30.	35.
	E.	.653	.527	.444	.365	.310	.251	.216
2N.HCl	t.	5.	11.	15.	20.	25.	30.	35.
	E.	.641	.479	.413	.337	.274	.225	.191

ABSORPTION

N.KCl	t.	10.	20.	30.	40.	50.	60.	70.
	1-E	.630	.484	.378	.311	.251	.199	.166
2N.KCl	t.	10.	20.	30.	40.	50.	60.	70.
	1-E.	.652	.480	.360	.300	.222	.181	.149
N.HCl	t.	5.	110.	15.	20.	25.	30.	35.
	1-E.	.650	.484	.394	.321	.258	.205	.169
2N.HCl	t.	5.	10.	15.	20.	25.	30.	35.
	1-E.	.520	.472	.366	.296	.234	.193	.141

H125 - 20°C.

DESORPTION

$N.KNO_3$	t.	10.	20.	30.	40.	50.	60.	71.
	E.	.652	.498	.404	.330	.270	.220	.172
$1.9N.KNO_3$	t.	10.	20.	30.	40.	50.	60.	70.
	E.	.655	.514	.410	.342	.283	.235	.195
$N.HNO_3$	t.	5.	10.	15.	20.	25.	30.	35.
	E.	.659	.525	.423	.353	.292	.245	.206
$2N.HNO_3$	t.	5.	10.	15.	20.	25.	30.	35.
	E.	.644	.506	.412	.335	.282	.234	.191

ABSORPTION

$N.KNO_3$	t.	10.	20.	30.	40.	50.	60.	70.
	1-E.	.633	.495	.408	.332	.279	.225	.190
$1.9N.KNO_3$	t.	10.	20.	30.	40.	50.	60.	70.
	1-E.	-	.621	.444	.362	.305	.255	.218
$N.HNO_3$	t.	10.	15.	20.	25.	30.	35.	41.
	1-E.	.544	.451	.373	.316	.267	.226	.186
$2N.HNO_3$	t.	5.	10.	15.	20.	25.	30.	35.
	1-E	.654	.522	.439	.359	.303	.254	.220

H125 - 20°C.

DESORPTION

N.LiCl	t.	13.	26.	39.	52.	65.	78.	91.
	E.	.665	.519	.414	.346	.288	.250	.197
2N.LiCl	t.	13.	26.	39.	52.	65.	78.	91.
	E.	.645	.505	.410	.333	.274	.225	.187
N.KAc	t.	15.	30.	45.	60.	75.	91.	105.
	E.	.600	.459	.353	.279	.219	.170	.136
2N.KAc	t.	15.	30.	45.	60	75.	90.	105.
	E.	.600	.455	.351	.276	.223	.171	.139

ABSORPTION

N.LiCl	t.	13.	26.	39.	52.	65.	78.	91.
	1-E.	.628	.462	.374	.307	.251	.198	.156
2N.LiCl	t.	13.	26.	39.	52.	67.	78.	88.
	1-E	.621	.481	.377	.302	.244	.194	.170
N.KAc	t.	15.	30.	45.	60.	75.	90.	100
	1-E	.609	.469	.362	.284	.218	.175	.149
2N.KAc	t.	15.	30.	45.	60.	75.	90.	105
	1-E	.604	.452	.352	.280	.217	.172	.135

THE ABSORPTION AND DESORPTION OF MIXTURES OF ELECTROLYTES TO AND FROM H125 SLABS AT 20°C.

The experimental results shown for the mixtures had on occasions to be augmented to include a smaller time range for the slower component. This was done by carrying out the run in the usual manner but analysing only for the slower component. The values obtained for such subsidiary runs are not shown here.

Desorption.

KCl : KNO_3

	t	10	20	30	40	50	60	70
KCl	E_d	0.623	0.480	0.367	0.293	0.233	0.200	0.143
KNO_3	E_d	0.640	0.521	0.413	0.339	0.279	0.220	0.188

KCl : HCl

	t	10	15	20	30	35	40	50
KCl	E_d	0.683	0.618	0.560	0.459	0.421	0.374	0.306
HCl	E	0.415	0.300	0.223	0.125	0.094	-	-

KCl : KAc

	t	15	25	35	45	60	80	95
KCl	E_d	0.543	0.406	0.317	0.252	0.171	0.109	-
KAc	E_d	0.593	0.491	0.426	0.358	0.276	0.205	0.104

HCl : LiCl

	t	5	10	15	20	25	30	35
HCl	E_d	0.556	0.392	0.273	0.194	0.139	-	-
LiCl	E_d	0.811	0.735	0.678	0.630	0.577	0.529	0.499

Absorption

$KCl : KNO_3$

	t	10	20	30	40	50	60	70
KCl	$1-E_A$	0.581	0.435	0.333	0.250	0.198	0.148	0.113
KNO_3	$1-E_A$	0.668	0.537	0.451	0.375	0.316	0.269	0.230

KCl : HCl

	t	10	15	25	30	35	45	60
KCl	$1-E_A$	0.636	0.571	0.457	0.409	0.365	0.299	0.217
HCl	$1-E_A$	0.383	0.278	0.135	-	-	-	-

KCl : KAc

	t	17	25	35	45	60	80	95
KCl	$1-E_A$	0.624	0.546	0.463	0.406	0.330	0.260	0.214
KAc	$1-E_A$	0.461	0.369	0.262	0.205	0.132	-	-

HCl : LiCl

	t	10	15	25	30	39	60	85
HCl	$1-E_A$	0.355	0.231	0.073	-	-	-	-
LiCl	$1-E_A$	0.693	0.634	0.542	0.506	0.443	0.324	0.240

H125. N.KCl

DESORPTION

T - 20°C.	t.	10.	20.	30.	40.	50.	60.	65.
	E.	.610	.468	.374	.296	.236	.189	.175
T - 30°C.	t.	10.	20.	30.	40.	51.	60.	63.
	E.	.566	.412	.310	.233	.177	.135	.123
T - 40°C.	t.	10.	20.	31.	35.	40.	45.	50.
	E	.526	.366	.247	.215	.181	.154	.127
T - 50°C.	t.	10.	19.	30.	30.	35.	40.	43.
	E.	.489	.331	.206	.209	.176	.143	.126

ABSORPTION

T - 20°C.	t.	10.	20.	30.	40.	50.	60.	70.
	1-E.	.622	.474	.379	.302	.243	.202	.156
T - 30°C.	t.	10.	20. =	28.	37.	45.	55.	65.
	1-E.	.565	.412	.330	.256	.209	.160	.119
T - 40°C.	t.	10.	20.	25.	30.	35.	41.	51.
	1-E.	.529	.358	.309	.258	.215	.174	.130
T - 50°C.	t.	9.	14.	20.	23.	30.	35.	46.
	1-E	.501	.403	.313	.274	.207	.162	.105

V3. N.KCl

DESORPTION

T - 20°C.	t.	20.	30.	40.	50.	61.	70.
	E.	.501	.405	.331	.270	.225	.184
T - 30°C.	t.	10.	20.	30.	40.	50.	65.
	E.	.588	.434	.337	.259	.206	.136
T - 40°C.	t.	10.	20.	30.	40.	50.	60.
	E.	.557	.394	.296	.213	.156	.117
T - 50°C.	t.	10.	20.	25.	33.	40.	51.
	E.	.522	.358	.297	.220	.168	.109

ABSORPTION

T - 20°C.	t.	15.	25.	40.	51.	65.	75.
	1-E.	.574	.455	.334	.273	.207	.167
T - 30°C.	t.	21.	30.	41.	50.	60.	70.
	1-E.	.444	.347	.268	.212	.167	.129
T - 40°C.	t.	10.	20.	30.	40.	50.	58.
	1-E	.552	.402	.287	.213	.152	.123
T - 50°C.	t.	5.	15.	24.	25.	35.	45.
	1-E.	.638	.424	.292	.284	.193	.123

V5. N.KCl

DESORPTION

T - 20°C.	t.	20.	35.	50.	65.	80.	91.
	E.	.547	.428	.337	.273	.217	.180
T = 30°C.	t.	20.	30.	40.	55.	65.	80.
	E.	.495	.404	.334	.250	.209	.160
T - 40°C.	t.	20.	30.	40.	51.	60.	70.
	E.	.459	.356	.287	.227	.178	.141
T - 50°C.	t.	10.	20.	30.	40.	50.	60.
	E.	.568	.413	.308	.236	.182	.139

ABSORPTION

T - 20°C.	t.	20.	35.	50.	65.	80.	95.
	1-E.	.553	.437	.338	.274	.226	.177
T = 30°C.	t.	20.	30.	40.	50.	65.	80.
	1-E.	.505	.405	.333	.243	.205	.162
T = 40°C.	t.	20.	30.	40.	50.	60.	70.
	1-E.	.455	.347	.283	.229	.183	.142
T - 50°C.	t.	10.	20.	30.	40.	50.	60.
	1-E.	.567	.408	.314	.232	.176	.130

V10. N.KCl.

DESORPTION

T - 20°C.	t.	20.	35.	50.	65.	80.	95.
	E.	.565	.454	.342	.296	.222	.162
T - 30°C.	t.	21.	30.	40.	50.	65.	80.
	E.	.495	.410	.324	.274	.240.	.159
T - 40°C	t.	15.	27.	40.	50.	60.	75.
	E.	.514	.396	.284	.233	.183	.146
T - 50°C.	t.	17.	30.	35.	41.	50.	60.
	E.	.457	.335	.282	.229	.209	.142

ABSORPTION

T - 20°C.	t.	20.	35.	50.	65.	80.	95.
	1-E.	.575	.441	.343	.258	.221	.201
T - 30°C.	t.	20.	30.	40.	55.	65.	80.
	1-E.	.506	.422	.351	.276	.200	.188
T - 40°C.	t.	20.	30.	40.	50.	60.	70.
	1-E.	.475	.385	.282	.259	.185	.131
T - 50°C.	t.	10.	20.	30.	40.	51.	60.
	1-E.	.577	.437	.307	.273	.202	.116

M1. N.KCl

DESORPTION

T - 20°C.	t.	25.	40.	50.	71.	85.	102.
	E	.546	.443	.367	.317	.231	.175
T - 30°C	t.	20.	30.	40.	60.	70.	90.
	E.	.556	.506	.410	.272	.231	.150
T - 40°C.	t.	15.	25.	35.	45.	55.	75.
	E.	.592	.498	.405	.301	.321	.160
T - 50°C.	t.	15.	25.	35.	45.	55.	65.
	E.	.497	.469	.325	.234	.176	.160

ABSORPTION

T - 20°C.	t.	25.	40.	55.	70.	85.	110
	1-E.	.580	.518	.417	.299	.300	.205
T - 30°C.	t.	26.	40.	50.	60.	70.	85.
	1-E.	.521	.456	.380	.287	.227	.185
T - 40°C.	t.	20.	30.	40.	50.	60	75.
	1-E.	.552	.481	.373	.284	.220	.190
T - 50°C.	t.	15.	25.	38.	50.	66.	73.
	1-E.	.587	.475	.339	.240	.211	.136

H125 - N.HCl.

DESORPTION

T - 20°C.	t.	5.	10.	15.	20.	25.	30.	35.
	E.	.669	.526	.451	.369	.303	.255	.203
T - 30°C.	t.	5.	10.	15.	18.	23.	25.	30.
	E.	.620	.480	.378	.327	.269	.250	.197
T - 40°C.	t.	5.	9.	12.	14.	17.	21.	27.
	E.	.592	.459	.393	.370	.305	.237	.183
T - 50°C.	t.	5.	9.	12.	14.	19.	22.	26.
	E.	.551	.430	.352	.258	.219	.185	.140

ABSORPTION

T - 20°C.	t.	6.	10.	15.	21.	25.	30.	35.
	1-E.	.590	.495	.391	.308	.258	.212	.167
T - 30°C.	t.	7.	11.	15.	16.	21.	22.	28.
	1-E.	.525	.418	.333	.311	.247	.213	.157
T - 40°C.	t.	5.	8.	11.	15.	18.	20.	25.
	1-E.	.549	.447	.371	.274	.222	.200	.143
T - 50°C.	t.	5.	10.	10.	15.	18.	20.	25.
	1-E.	.527	.346	.339	.228	.164	.172	.103

V3. N.HCl

DESORPTION

T - 20°C.	t.	10.	20.	30.	35.	40.	50.
	E.	.538	.399	.280	.255	.216	.160
T - 30°C.	t.	10.	15.	20.	25.	30.	35.
	E.	.499	.402	.327	.272	.217	.178
T - 40°C.	t.	5.	10.	15.	20.	25.	30.
	E.	.591	.460	.342	.278	.211	.175
T - 50°C.	t.	5.	10.	14.	18.	21.	25.
	E.	.556	.411	.325	.249	.214	.167

ABSORPTION

T - 20°C.	t.	11.	18.	24.	30.	35.	40.
	1-E.	.512	.397	.314	.260	.214	.179
T - 30°C.	t.	5.	10.	16.	20.	24.	30.
	1-E.	.601	.478	.361	.301	.248	.187
T - 40°C.	t.	5.	10.	15.	20.	25.	31.
	1-E.	.585	.427	.323	.244	.185	.132
T - 50°C.	t.	5.	10.	15.	20.	25.	30
	1-E.	.541	.376	.281	.186	.132	.100

V5. N.HCl.

DESORPTION

T - 20°C.	t.	10.	20.	30.	40.	45.	50.
	E.	.581	.441	.333	.265	.219	.199
T - 30°C.	t.	7.	15.	21.	28.	34.	40.
	E.	.578	.437	.356	.280	.240	.197
T - 40°C.	t.	5.	12.	18.	26.	30.	35.
	E.	.626	.441	.362	.263	.221	.190
T - 50°C.	t.	5.	10.	15.	20.	25.	30.
	E.	.584	.457	.356	.270	.226	.180

ABSORPTION

T - 20°C.	t.	10.	15.	20.	30.	35.	43.
	1-E.	.585	.505	.440	.332	.299	.252
T - 30°C.	t.	10.	15.	21.	30.	35.	40.
	1-E.	.536	.435	.363	.269	.226	.191
T - 40°C.	t.	5.	12.	18.	26.	30.	35.
	1-E.	.634	.459	.349	.241	.224	.177
T - 50°C.	t.	5.	10.	15.	20.	25.	30.
	1-E.	.599	.443	.362	.280	.202	.174

V10. N.HCl

DESORPTION

T - 20°C.	t.	10.	21.	30.	40.	45.	50.
	E.	.608	.434	.343	.257	.221	.197
T - 30°C.	t.	8.	14.	20.	28.	35.	40.
	E.	.545	.450	.347	.285	.248	.211
T - 40°C.	t.	7.	12.	18.	25.	30.	35.
	E.	.577	.456	.361	.263	.235	.194
T - 50°C.	t.	5.	10.	15.	20.	25.	30.
	E.	.610	.464	.359	.285	.227	.188

ABSORPTION

T - 20°C.	t.	10.	20.	30.	35.	40.	50.
	1-E.	.591	.450	.342	.299	.260	.196
T - 30°C.	t.	10.	20.	25.	31.	38.	45.
	1-E.	.558	.383	.315	.281	.217	.179
T - 40°C.	t.	7.	12.	18.	25.	30.	35.
	1-E.	.594	.445	.388	.288	.235	.185
T - 50°C.	t.	5.	10.	15.	20.	25.	30.
	1-E.	.608	.463	.362	.286	.215	.171

M1. N.HCl.

DESORPTION

T - 20°C.	t.	15.	25.	35.	45.	55.	65.
	E.	.591	.437	.375	.281	.201	.180
T - 30°C.	t.	10.	18.	26.	34.	40.	45.
	E.	.583	.468	.364	.306	.298	.205
T - 40°C.	t.	10.	15.	22.	28.	35.	40.
	E.	.589	.465	.343	.312	.256	.192
T - 50°C.	t.	10.	15.	20.	25.	30.	35.
	E.	.543	.410	.348	.305	.222	.216

ABSORPTION

T - 20°C.	t.	16.	25.	35.	40.	45.	55.
	1-E.	.531	.405	.350	.291	.258	.202
T - 30°C.	t.	10.	20.	30.	35.	40.	45.
	1-E.	.577	.406	.332	.252	.209	.198
T - 40°C.	t	10.	15.	20.	28.	40.	45.
	1-E.	.570	.440	.384	.289	.209	.160
T - 50°C.	t.	10.	15.	20.	25.	30.	35.
	1-E.	.485	.387	.284	.223	.221	.147

H125 - N.LiCl

DESORPTION

T - 20°C.	t.	30.	40.	50.	70.	80.	90.
	E.	.477	.401	.357	.256	.216	.194
T - 30°C.	t.	30.	40.	50.	60.	70.	80.
	E.	.425	.354	.290	.238	.197	.166
T - 40°C	t.	20.	30.	40.	50.	60.	70.
	E.	.485	.380	.294	.237	.191	.158
T - 50°C.	t.	10.	20.	30.	40.	50.	60.
	E.	-	.428	.320	.238	.182	.135

ABSORPTION

T - 20°C.	t.	30.	40.	50.	70.	80.	90.
	1-E.	.441	.384	.321	.246	.197	.171
T - 30°C.	t.	30.	40.	50.	60.	70.	80.
	1-E.	.388	.314	.256	.204	.166	.135
T - 40°C.	t.	20.	30.	40.	50.	60.	70.
	1-E.	.425	.315	.241	.190	.138	.101
T - 50°C.	t.	20.	30.	35.	40.	50.	60.
	1-E.	.415	.286	.244	.185	.136	--

V3. N.LiCl

DESORPTION

T - 20°C.	t.	30.	45.	60.	70.	85.	100
	E.	.529	.427	.349	.300	.250	.202
T - 30°C.	t.	30.	40.	50.	60.	75.	90.
	E.	.470	.381	.330	.284	.218	.170
T - 40°C.	t.	30.	40.	50.	60.	70.	80.
	E.	.394	.322	.274	.225	.188	.154
T - 50°C.	t.	20.	30.	40.	50.	60.	71.
	E.	.461	.355	.297	.232	.188	.156

ABSORPTION

T - 20°C.	t.	30.	45.	60.	70.	80.	90.
	1-E.	.482	.385	.306	.265	.229	.195
T - 30°C.	t.	20.	40.	51.	60.	70.	
	1-E.	.480	.314	.259	.209	.176	
T - 40°C.	t.	20.	30.	40.	50.	60.	70.
	1-E.	.465	.363	.279	.215	.175	.136
T - 50°C.	t.	20.	31.	40.	50.	60.	70.
	1-E.	.477	.325	.243	.185	.137	--

V5. N.LiCl

DESORPTION

T - 20°C.	t.	40.	60.	80.	100.	120.	140.
	E.	.510	.427	.319	.274	.213	.179
T - 30°C.	t.	20.	40.	60.	80.	100.	120
	E.	.598	.450	.346	.267	.205	.160
T - 40°C.	t.	20.	30.	40.	53.	65.	80.
	E.	.551	.464	.403	.311	.258	.199
T - 50°C.	t.	30.	40.	50.	60.	70.	80.
	E.	.430	.347	.295	.242	.204	.159

ABSORPTION

T - 20°C.	t	40.	60.	80.	100.	120.	140.
	1-E.	.491	.379	.300	.239	.184	-
T - 30°C.	t.	25.	40.	50.	65.	80.	100
	1-E.	.515	.414	.359	.286	.226	.114
T - 40°C.	t.	25.	40.	50.	60.	70.	80.
	1-E.	.475	.348	.295	.244	.200	.165
T - 50°C.	t.	20.	30.	40.	50.	60.	70.
	1-E.	.523	.401	.323	.257	.209	.163

V10. N.LiCl

DESORPTION

T - 20°C.	t.	31.	50.	70.	90.	110.	130.
	E.	.585	.468	.377	.299	.241	.189
T - 30°C.	t.	20.	40.	60.	75.	90.	105.
	E.	.583	.459	.342	.281	.235	.197
T - 40°C.	t.	25.	35.	50.	65.	80.	90.
	E.	.522	.439	.345	.266	.214	.282
T = 50°C.	t.	20.	30.	40.	60.	70.	80.
	E.	.525	.440	.369	.247	.212	.172

ABSORPTION

T - 20°C.	t.	20.	40.	60.	80.	100.	120.
	1-E.	.602	.469	.370	.290	.227	.183
T = 30°C.	t.	20.	40.	60.	75.	90.	100
	1-E.	.559	.420	.303	.244	.197	.164
T - 40°C.	t.	25.	40.	50.	60.	70.	80.
	1-E.	.471	.350	.293	.244	.196	.162
T - 50°C.	t.	10.	20.	30.	40.	50.	60.
	1-E.	.560	.435	.348	.263	.215	.166

M1. N.LiCl

DESORPTION

T - 20°C.	t.	40.	60.	80.	100.	120.	140.
	1-E.	.595	.464	.342	.297	.263	.195
T - 30°C.	t.	20.	40.	60.	80.	100.	120.
	1-E.	.666	.520	.408	.301	.252	.288
T - 40°C.	t.	30.	50.	70.	80.	90.	100.
	1-E.	.562	.398	.280	.256	.210	.294
T - 50°C.	t.	30.	40.	50.	65.	80.	90.
	1-E.	.515	.416	.381	.259	.233	.180

ABSORPTION

T - 20°C.	t.	20.	40.	60.	80.	100.	120.
	1-E.	.660	.575	.392	.348	.263	.229
T - 30°C.	t.	30.	40.	50.	65.	80.	100.
	1-E.	.553	.457	.400	.307	.281	.291
T - 40°C.	t.	25.	40.	50.	60.	70.	80.
	1-E.	.510	.417	.322	.291	.205	.183
T - 50°C.	t.	20.	30.	40.	50.	60.	70.
	1-E.	.547	.411	.349	.271	.236	.162

APPENDIX B. THE SOLUTION OF FICK'S LAW FOR SPECIFIED BOUNDARY CONDITIONS.

$$\frac{1}{D}\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{y^2} + \frac{\partial^2 c}{z^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots 1.$$

$c = 0$ at $x = 0, a$; $y = 0, b$; $z = 0, d$.

$c = c_o$ at $t = 0$; $0 < x < a$; $0 < y < b$; $0 < z < d$.

Apply a double Fourier Transform to equation 1. where

$$\phi = \int_o^a \int_o^b c \sin \frac{m \pi x}{a} \sin \frac{n \pi y}{b} \, dx.dy.$$

This satisfies the conditions on x and y boundaries.

Multiply both sides of equation 1. by $\sin \frac{m \pi x}{a} \sin \frac{n \pi y}{b}$ and integrate w.r.t. x and y from 0 to a, and 0 to b.

$$\therefore \quad \frac{1}{D}\frac{\partial \phi}{\partial t} = -\pi^2 \left(\frac{m^2}{a^2} + \frac{n^2}{b^2}\right)\phi + \frac{\partial^2 \phi}{\partial z^2} \qquad \ldots\ldots\ldots\ldots\ldots 2.$$

Now apply a Laplace transform in t to equation 2.

$$\psi = \int_o^\infty \phi \exp.(p\,t)\,dt$$

$$\therefore \quad \frac{d^2\psi}{d z^2} - \psi \left[\pi^2 \left(\frac{m^2}{a^2} + \frac{n^2}{b^2}\right) + \frac{p}{D}\right] = \frac{\phi_o}{D} = -K_{m.n.}$$

where ϕ_o = value of ϕ at $t = 0$

$$\frac{d^2\psi}{dz^2} - l^2 \psi = -k$$

$$\therefore \quad \psi = A \exp.(l\,z) + B \exp.(-\,l\,z) + \frac{k}{l^2}$$

on $z = 0$ $\psi = 0$

$$\therefore \quad A + B + \frac{k}{l^2} = 0$$

on $z = d \quad \psi = 0$

$$\therefore \quad A \exp.\,(l\,d) + b\,(-\,l\,d) + \frac{k}{l^2} = 0$$

$$\therefore \quad A = -\left[\frac{1 - \exp.(-ld)}{\exp.(ld) - \exp.(-ld)}\right]\frac{k}{l^2}$$

$$\text{and} \quad B = \left[\frac{\exp.(ld) - 1}{\exp.(ld) - \exp.(-ld)}\right]\frac{k}{l^2}$$

$$\therefore \quad \Psi = -\frac{k}{l^2}\left[\frac{1 - \exp.(-ld)}{\exp.(ld) - \exp.(-ld)}\right]\exp.(lz)$$

$$- \frac{k}{l^2}\left[\frac{\exp.(ld) - 1}{\exp.(ld) - \exp.(-ld)}\right]\exp.(-lz) + \frac{k}{l^2}$$

$$\Psi = -\frac{k}{l^2}\Big[\exp.-l(d-z) - \exp.-l(2d-z) + \exp.(-lz)$$

$$-\exp.-l(d+z)\Big]\sum_{s=0}^{\infty}\exp.-2lds + \frac{k}{l^2}$$

$$= \frac{k^2}{l^2} - \frac{k^2}{l^2}\Bigg[\sum_{s=0}^{\infty}\exp.-l(d-z+2ds) - \sum_{s=0}^{\infty}\exp.-l(2d-z+2ds)$$

$$+ \sum_{s=0}^{\infty}\exp.-l(z+2ds) - \sum_{s=0}^{\infty}\exp.-l(d+z+2ds)\Bigg]$$

The Laplace transform of this function gives

$$\therefore \phi = k\,D\,\exp.(-ft) - k\,D\,\exp.(-ft)\left[\sum_{s=0}^{\infty}\operatorname{erfc}\left(\frac{d + 2ds - z}{2\sqrt{Dt}}\right)\right.$$

$$- \sum_{s=0}^{\infty}\operatorname{erfc}\left(\frac{2d + 2ds - z}{2\sqrt{Dt}}\right) + \sum_{s=0}^{\infty}\operatorname{erfc}\left(\frac{z + 2ds}{2\sqrt{Dt}}\right)$$

$$\left. - \sum_{D=0}^{\infty}\operatorname{erfc}\left(\frac{d + 2ds + z}{2\sqrt{Dt}}\right)\right]$$

$$\therefore C = \frac{4}{ab}\sum_{m=1}^{\infty}\sum_{n=1}^{\infty} k\,D\,\exp.(-ft)\,\sin\frac{m\pi x}{a}\,\sin\frac{n\pi y}{b}$$

$$\left[1 - \sum_{s=0}^{\infty}\left\{\operatorname{erfc}\left(\frac{d + 2ds - z}{2\sqrt{Dt}}\right) - \operatorname{erfc}\left(\frac{2d + 2ds - z}{2\sqrt{Dt}}\right)\right.\right.$$

$$\left.\left. + \operatorname{erfc}\left(\frac{z + 2ds}{2\sqrt{Dt}}\right) - \operatorname{erfc}\left(\frac{d + 2ds + z}{2\sqrt{Dt}}\right)\right\}\right]$$

$$\text{Now } k = \frac{\phi_o}{D} = \frac{1}{D}\int_0^a\int_0^b C_o \sin\frac{m\pi x}{a}\,\sin\frac{n\pi y}{b}\,dx.\,dy.$$

$$= \frac{C_o}{D}\left[-\frac{a}{m\pi}\cos\frac{m\pi x}{a}\right]_0^a\left[-\frac{b}{n\pi}\cos\frac{n\pi y}{b}\right]_0^b$$

$$= \frac{C_o}{D}\left[-1 + (-1)^m\right]\left[-1 + (-1)^n\right]\frac{ab}{m\,n\,\pi^2}$$

$$= \frac{4\,a\,b\,C_o}{m\,n\,\pi^2\,D}$$ if m and n are both odd

or $= 0$ otherwise.

$$\therefore\; C = \frac{16\,C_o}{\pi^2} \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \frac{\exp.\ -D\pi^2\left[\left(\frac{2p+1}{a}\right)^2 + \left(\frac{2q+1}{b}\right)^2\right] t}{(2q+1)\,(2p+1)}\ X$$

$$\sin\frac{(2p+1)\,\pi\,x}{a}\ \sin\frac{(2q+1)\,\pi\,y}{b}\left[1 - \sum_{s=0}^{\infty}\left\{\text{etc.}\right\}\right]$$

Now $Q = \int_0^a \int_0^b \int_0^c C\ dx.\ dy.\ dz.$

$$\text{Now} \int_0^a \sin\frac{(2p+1)\,\pi\,x}{a}\,dx = \left[-\frac{a}{\pi(2p+1)}\cos\frac{(2p+1)\,\pi\,x}{a}\right]_0^a$$

$$= \frac{2a}{(2p+1)\pi}$$

$$\text{and similarly} \int_0^b \sin\frac{(2q+1)\,\pi\,y}{b}\,dy = \frac{2b}{(2q+1)\pi}$$

$$\text{Also} \int_0^d \operatorname{erfc}\,(d' + tz)dz = \frac{1}{t}\left\{(d' + tc)\operatorname{erfc}\,(d' + tc)\right.$$

$$\left. - d'\operatorname{erfc}(d') - \frac{1}{\pi}\exp.-(d' + tc)^2 + \frac{1}{\pi}\exp.-(d')^2\right\}$$

$$I = \int_0^d \left[1 - \sum \left\{ \text{etc.} \right\} \right] dz$$

$$= d - 2\sqrt{Dt} \left\{ \left[-\left(\frac{2ds}{2\sqrt{Dt}}\right) - \left(\frac{2ds}{2\sqrt{Dt}}\right) \right] \text{erfc} \left(\frac{2ds}{2\sqrt{Dt}}\right) \right.$$

$$+ \left[\left(\frac{2ds + d}{2\sqrt{Dt}}\right) + \left(\frac{2ds + d}{2\sqrt{Dt}}\right) + \left(\frac{2ds + d}{2\sqrt{Dt}}\right) + \left(\frac{2ds + d}{2\sqrt{Dt}}\right) \right] \text{erfc} \left(\frac{2ds + d}{2\sqrt{Dt}}\right)$$

$$+ \left[-\left(\frac{2ds + 2d}{2\sqrt{Dt}}\right) + \left(\frac{2ds + 2d}{2\sqrt{Dt}}\right) \right] \text{erfc} \left(\frac{2ds + 2d}{2\sqrt{Dt}}\right)$$

$$\left. + \frac{1}{\sqrt{\pi}} \left[2 \exp.-\left(\frac{2ds}{2\sqrt{Dt}}\right)^2 - 4 \exp.\left(\frac{2ds + d}{2\sqrt{Dt}}\right)^2 + 2 \exp.\left(\frac{2ds + 2d}{2\sqrt{Dt}}\right)^2 \right] \right\}$$

$$= d - 2\sqrt{Dt} \sum_{s=0}^{\infty} \left[-4\left(\frac{2ds}{2\sqrt{Dt}}\right) \text{erfc}\left(\frac{2ds}{2\sqrt{Dt}}\right) + 4\left(\frac{2ds + d}{2\sqrt{Dt}}\right) \right.$$

$$\left. \text{X erfc}\left(\frac{2ds + d}{2\sqrt{Dt}}\right) + \frac{1}{\sqrt{\pi}} \left[4 \exp.-\left(\frac{2ds}{2\sqrt{Dt}}\right)^2 - 4 \exp.-\left(\frac{2ds}{2\sqrt{Dt}}\right)^2 \right] \right]$$

$$+ 4\sqrt{\frac{Dt}{\pi}}$$

$$\therefore I = d + 4\sqrt{\frac{Dt}{\pi}} - 2\sqrt{Dt} \sum_{r=0}^{\infty} \left\{ (-1)^{r+1}\, 4\left(\frac{rd}{2\,Dt}\right) \text{ X } \text{erfc}\left(\frac{rd}{2\,Dt}\right) \right.$$

$$\left. + \frac{4}{\pi} (-1)^r \exp.-\left(\frac{rd}{2\,Dt}\right)^2 \right\}$$

$$\therefore\ Q = \frac{16\ C_o}{\pi^2} \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \left[\frac{\exp.D\pi^2 \left[(\frac{2p\ +\ 1}{a})^2 + (\frac{2q\ +\ 1}{b})^2 \right] t}{(2p + 1)\ (2q + 1)} \right. \quad X$$

$$\left[\frac{2a}{(2p + 1)\pi} \right] \left[\frac{2b}{(2q + 1)\pi} \right] \left[d + 4\sqrt{\frac{Dt}{\pi}} \right.$$

$$\left. \left. - 2\sqrt{Dt} \sum_{r=0}^{\infty} \left((-1)^{r+1}\ 4(\frac{rd}{2\ Dt})\ \text{erfc}(\frac{rd}{2\ Dt}) + \frac{4}{\ }\ (-1)^r\ \exp.-(\frac{rd}{2\ Dt})^2 \right) \right] \right]$$

$$= \frac{64\ ab\ C_o}{\pi^4} \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \left[\text{etc.........as above.} \right]$$

$$\therefore\ E_D = \frac{Q}{Q_o} = \frac{Q}{abd\ C_o} = \frac{64}{\pi^4} \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \left[\frac{\exp.D\pi^2 \left[(\frac{2p+1}{a})^2 + (\frac{2q+1}{b})^2 \right] t}{(2p + 1)^2\ (2q + 1)^2} \right.$$

$$X \left[1 + 4\sqrt{\frac{Dt}{\pi d^2}} - 2\sqrt{\frac{Dt}{d^2}} \sum_{r=0}^{\infty} \left((-1)^{r+1}\ (\frac{4rd}{2\sqrt{Dt}})\ \text{erfc}(\frac{rd}{2\sqrt{Dt}}) \right. \right.$$

$$\left. \left. \left. + (-1)^r\ \frac{4}{\sqrt{\pi}}\ \exp.-(\frac{rd}{2\sqrt{Dt}})^2 \right) \right] \right]$$

APPENDIX C. ESTIMATION OF A THEORETICAL PERCENTAGE ERROR FOR THE EXPERIMENTAL PROCEDURE.

It has been shown that the error in N where $N = \frac{pq}{ab}$, and the errors in p, q, a and b are δp δq δa and δb is

$$= \pm \left(\frac{\delta p}{p} + \frac{\delta q}{q} + \frac{\delta a}{a} + \frac{\delta b}{b}\right)$$

Desorption

1. Considering Q_o

$$Q_o = W_i \times G \times \frac{D_i^s \, D_d^s}{(D_i^s)^2 \, D_{20}^s} \text{ ......equation 95 see page 73}$$

$$= W_i \times G \times \text{Density Ratio}$$

1.1. Percentage error in W_i

Assuming the error in each weighing to be ± 0.0002 gms., and since W_i is calculated from 4 weighings, the possible error is 4 x ± 0.0002 gms. i.e. 0.0008 gms.

The approximate value of W_i is 5.0 gms.

$$\therefore \text{ The percentage error in } W_i = \pm \frac{0.0008}{5} \times 100$$

$$= \pm 0.016\%$$

1.2. Percentage error in the Density Ratio.

The error in this shall be considered negligible.

1.3. Percentage error in G.

The analysis of the impregnation solution is carried out by pipetting 50 ml. of solution into a standard 500 ml. flask and titrating 20 ml. portions of the resultant solution with a standard N/10 silver nitrate solution.

$$\therefore G \text{ (The original concentration)} = \frac{X \times N_1 \times F_1 \times 500}{20 \times 50} \quad \ldots\ldots(1)$$

where X = the volume of silver nitrate solution required for the titration.

N_1 = the normality of the silver nitrate solution.

F_1 = a factor for converting volume of silver nitrate to gms. of KCl.

1.3.1. Percentage error in "making up to the mark" in a 500 ml. flask.

Assuming the error to be ± 0.1 ml.

$$\text{Percentage error} = \pm \frac{0.1}{500} \times 100$$

$$= \pm 0.02\%$$

1.3.2. Percentage error in pipetting 20 ml. of solution

Assuming the efror to be ± 0.1 ml.

$$\text{Percentage error} = \pm \frac{0.1}{20} \times 100$$

$$= \pm 0.5\%$$

1.3.3. Percentage error in pipetting 50 ml. of solution.

Assuming the error to be ± 0.1 ml.

$$\text{Percentage error} = \pm \frac{0.1}{50} \times 100$$

$$= \pm 0.20\%$$

1.3.4. Percentage error in 'X'

Assuming the error to be ± 0.05 ml.

$$\text{Percentage error} = \pm \frac{0.05}{20} \times 100$$

$$= \pm 0.25\%$$

1.3.5. Percentage error in N_1

The silver nitrate solution was standardised against 20 ml. portions of a standard N/10 solution of KCl.

1.3.5.1. Percentage error in the normality of the standard N/10 solution of KCl.

The error in two weighings of KCl = 2 x $\pm$ 0.0002

The approximate weight of KCl required for 500 ml. of N/10 solution = 4.0 gms.

$$\therefore \text{ Percentage error in weighing KCl} = \pm \frac{0.0004}{4} \times 100$$

$$= \underline{\pm 0.01\%}$$

This weight of KCl has to be dissolved into a 500 ml. flask.

The error involved in this is $\underline{\pm 0.02\%}$

The total error in the normality of the standard KCl solution is therefore ($\pm$ 0.01%) + ($\pm$ 0.02%) = $\underline{\pm 0.03\%}$

1.3.5.2. Percentage error in titrating the silver nitrate solution against the standard KCl solution.

Pipetting error = $\pm$ 0.5%

Titration error = $\pm$ 0.25%

$$N_1 = \frac{V_2N_2}{V_1}$$

$$\therefore \text{ Percentage error in } N_1 = (\pm 0.5) + (\pm 0.03) + (\pm 0.25)$$

$$\approx \pm 0.78\%$$

Substituting the above values in equation (1) the percentage error in G is

$$= \frac{(\pm 0.25)(\pm 0.78)(\pm 0.02)}{(\pm 0.05)(\pm 0.2)}$$

$\approx (\pm 0.25) + (\pm 0.78) + (\pm 0.02) + (\pm 0.05) + (\pm 0.2)$

$\approx \underline{\pm 1.3\%}$

Substituting the errors for W_i and G in equation (95) the percentage error in Q_o is

$\approx (\pm 0.016) + (\pm 1.3)$

$\approx \underline{1.32\%}$

2. Considering Q_t

Q_t is estimated by one of two methods, gravimetric and volumetric, depending upon what solute is in use.

2.1. Gravimetric estimation.

Q_t is obtained from four weighings. The error is therefore ± 0.0008 gms.

Q_t varies with time; considering two values of 't', one for 't' small and the other for 't' large:-

The approximate weight of KCl remaining in the slab after diffusion is 0.18 gms. for 't' small, and 0.07 gms. for 't' large.

$$\therefore \text{The percentage errors} = \pm \frac{0.0008}{0.18} \times 100 \quad \text{or} \pm \frac{0.0008}{0.07} \times 100$$
$$= \pm 0.44\% \quad \text{or} \pm 1.14\%$$

2.2. Volumetric estimation.

Q_t is estimated by transferring the solutions left in the "total extractors" to 500 ml. graduated flasks and titrating 50 ml. portions of these solutions with silver nitrate solution.

$$\therefore \quad Q_t = \frac{X \times 500 \times N_1 \times F_1}{50}$$

where X = volume of $AgNO_3$ solution required for titration

N_1 = normality of the $AgNO_3$ solution

F_1 = factor for converting X ml. $AgNO_3$ solution to gms. of KCl.

The approximate volumes of silver nitrate solution required are; for small 't', 3.0 ml. and for large 't' 1.5 ml. Assuming the percentage error in a titration to be ± 0.02 ml., the percentage errors in the estimations of KCl are,

$$\text{for small 't'} = \frac{0.02}{3.0} \times 100 = \pm 0.67\%$$

$$\text{for large 't'} = \frac{0.02}{1.5} \times 100 = \pm 1.33\%$$

The corresponding percentage errors in Q_t are

$$\text{for small 't'} \approx (\pm 0.67) + (\pm 0.02) + (\pm 0.78) + (\pm 0.20)$$
$$\approx \pm 1.67\%$$

$$\text{for large 't'} \approx (\pm 1.33) + (\pm 0.02) + (\pm 0.78) + (\pm 0.20)$$
$$\approx \pm 2.33\%$$

3. Considering E_d

3.1. Gravimetric estimation of Q_t

$$E_d = \frac{Q_t}{Q_o}$$

The percentage error in E_d for small 't' $= \dfrac{(\pm 0.44)}{(\pm 0.02)(\pm 1.5)}$

$$\approx (\pm 0.44) - (\pm 1.3)$$

$$\approx \underline{\pm 1.74\%}$$

The percentage error in E_d for large 't' $= \dfrac{(\pm 1.14)}{(\pm 0.02)(\pm 1.5)}$

$$\approx (\pm 1.14) - (\pm 1.3)$$

$$\approx \pm 2.44\%$$

3.2. Volumetric estimation of Q_t

The percentage error in E_d for small 't' $\approx (\pm 1.67) - (\pm 1.3)$

$$\approx \pm 2.97\%$$

The percentage error in E_d for large 't' $\approx (\pm 2.33) - (\pm 1.3)$

$$\approx \pm 3.63\%$$

The percentage errors for values of E_d for absorption runs are probably of the same order as those for desorption.

The "average" maximum theoretical error in E_d values is therefore approximately ± 3%

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