STUDIES IN SOLID - LIQUID EXTRACTION

A thesis presented by

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SUMMARY - DIFFUSION OF LIQUIDS IN POROUS MEDIA.

The object of the work was to investigate the effects of temperature and solute concentration on the process of diffusion in porous solids. This was done by immersing previously impregnated earthenware slabs in a moving stream of liquid and allowing absorption or desorption of the solute to proceed for measured intervals of time.

The experimental results indicated that the mass transfer was in accordance with Fick's law and that values of D, the diffusion coefficient, could be estimated from semi-log plots of the fraction of solute absorbed or desorbed against t, time in seconds.

The derived values of D were correlated with temperature T in the customary relationship,

$$D = A \exp(-E/RT)$$

where A = a constant

E = an activation energy.

It was found that the activation energy E was not independent of the solute concentration. With KCl as solute, it was apparent that for desorption experiments, the calculated values of E were very nearly identical for N and 3N solutions.

Absorption experiments, however, give results which differed markedly from those for desorption. The general tendency was for the values of D to be smaller at lower temperatures but to increase more rapidly with increasing temperature than the corresponding values for desorption. Consequently, the derived values of E were much higher for absorption than desorption. The results for sucrose were similar but, in this case, desorption proceeded more rapidly than absorption though again solute concentration appeared to be the dominating factor in determining the relative rates of absorption for 0.3M and M solutions.

Experiments were carried out with slabs of different physical characteristics and in one series of experiments, (slabs whose mean pore diameter was one micron and solute M sucrose) there appeared to be an interaction between the slab structure and the diffusing molecules. Comparison of the apparent lengths of the paths followed by the diffusing molecules seemed to indicate that the diameter of the smaller pores and the length of a sucrose molecule may well be of comparable dimensions.

From consideration of the experimental results, there would appear to be certain fundamental differences between the rates of absorption and desorption. The explanation for these differences is not obvious though it is felt that the pore distribution, particularly the number and diameters of the smaller pores making up the voidage, play an important part in determining rates of mass transfer to or from the slabs.

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NOTE:

For convenience, of the figures illustrating the experimental results, only Figs. 13, 18, 23, 28 and 33 have been placed in the text. The others, (Figs. 9-12, 14-17, 19-22, 24-27 and 29-32, inclusive) are to be found in Appendix C.

1. INTRODUCTION.

1.1 The object of the research.

The primary object of the research was to study the phenomena of the diffusion of liquids in porous solids. A review of the work previously carried out in this subject led to the preparation of a programme of experimental work to determine whether or not the rate of absorption or desorption of a solute could be predicted from a knowledge of the physical properties of the diffusing solute and the porous medium to or from which mass transfer is taking place.

One of the most important physical properties of the solute is the rate at which it will diffuse in free solution. A brief summary of the various theoretical treatments of diffusion in free solution has therefore been included in the survey of the work and results of other investigators.

1.2.1. An outline of the study of diffusion in liquids.

The study of diffusion in liquids was begun in the latter half of the nineteenth century but the absence of an adequate kinetic theory of liquids precluded a completely successful correlation of the experimental results with the physical properties of the diffusing substances.

Early attempts at achieving this correlation took two principal forms,

(a) the adaptation of the existing kinetic theory of gases to take account of the difference in state between gases and liquids, and,

(b) the examination of the relationship between diffusivity and viscosity as suggested by the Stokes-Einstein equation.

From the kinetic theory of gases it was known that the translational velocity of a molecule is inversely proportional to the square root of its molecular weight; thus if the rate of diffusion varies directly as the translational velocity then the diffusivity varies inversely as the square root of the molecular weight. Early investigators extended the application of this rule from the diffusion of gases to the diffusion of dissolved gases and other solutes in liquids. An extensive attempt of this nature was made, in 1930, by Arnold (1) who also summarized the results of earlier workers.

The relationship between viscosity and diffusivity was suggested independently by Sutherland (2) and Einstein (3) from Stokes' law,

$$D = akT \qquad (1.1)$$

where D = diffusion coefficient
a = mobility of the diffusing particle
k = Boltzmann constant
T = absolute temperature

The mobility a of a spherical particle moving in a continuous liquid medium is given by Stokes' law as

$$a = \frac{1}{6\pi\eta r} \qquad (1.2)$$

where η = viscosity of the liquid medium.

r = radius of the spherical particle.

Investigation revealed that this equation gave good agreement with the experimental data only where the diffusion of large solute molecules in a medium of much smaller solvent molecules was being considered.

The modern concept of the liquid state has made possible the evaluation of more satisfactory kinetic theories of liquids. This has been accomplished by the adoption of a simplified model of the liquid state upon which the statistical mechanical and thermodynamical treatments may be based. These theories and the models from which they were derived are discussed in detail by Frenkel (4), Born (5), Kirkwood (6), Fürth (7), Onsager and Fuoss (8) and others, but their complexity is such as to make their application to chemical engineering problems difficult.

The kindred phenomena of viscosity and diffusion have been studied extensively by Eyring and his co-workers (9-13). By the application of the theory of reaction rates they succeeded in deriving relationships from which the diffusion coefficient D and the viscosity η may be calculated.

In the case of diffusion the solute molecules are considered as replacing some of the solvent molecules in the adopted model of the liquid state. Periodically these solute molecules leave their existing positions and take up new positions within the structure. Eyring suggested that the rate at which this occurs is:-

$$K = \frac{kT}{h}\frac{f^*}{f}\exp(-E/kT) \qquad (1.3)$$

where K = a specific reaction rate constant for the number of times per second that solute molecules assume new positions.

f^* = a partition function for the activated state.

f = a partition function for the normal state.

E = an activation energy.

k = Boltzmann constant.

h = Planck constant.

T = absolute temperature.

To enable the partition functions f^* and f to be evaluated, Eyring assumed that each molecule is constrained to move within a small volume by its neighbours but that within this volume its movement is unrestricted. Thus if the partition function of the liquid as a whole may be calculated from that of an average molecule moving within the fields of its neighbours, then:-

$$f = (2\pi mkT/h^2)^{3/2} \iiint \exp(-V/RT)\, dx.dy.dz.$$

$$= (2\pi mkT/h^2)^{3/2}\, V_f \qquad (1.4)$$

where V_f = the potential due to the presence
of neighbouring molecules,
and V_f = $\iiint \exp(-V/RT)\, dx.dy.dz.$ (1.5)

This evaluation of f depends upon V being constant. A detailed study of the effect of the neighbouring molecules by Lennard-Jones and Devonshire (14) indicated that this was nearly true until the centre molecule was almost in contact with one of its neighbours.

Equation (1.4) takes account only of the translational degrees of freedom since the contributions of the rotational and vibrational degrees will be the same for both the initial and activated states. For the activated state the partition function need only be calculated for two degrees of freedom:-

$$f^* = (2\pi mkT/h^2)\, V_f^{2/3} \qquad (1.6)$$

$$\text{hence } f^*/f = (h^2/2\pi mkT)^{1/2}\, V_f^{-1/3} \qquad (1.7)$$

Eyring defined the diffusion coefficient D as:-

$$D = \delta^2 K$$

where δ = the distance between successive
equilibrium positions of the
solute molecule.

K = a specific reaction rate constant for the number of times per second that solute molecules assume new positions.

$$\text{hence } D = \delta^2 \frac{kT}{h} \frac{f^*}{f} \exp(-E/RT) \qquad (1.9)$$

and substituting for f^*/f,

$$D = \delta^2 V_f^{-1/3} \left[\frac{kT}{2\pi m} \right]^{\frac{1}{2}} \exp(-E/RT) \qquad (1.10)$$

where E = the activation energy per mole of diffusing substance.

From a similar treatment of viscosity, Eyring also derived an equation of the same form as the Stokes-Einstein equation:-

$$\frac{D\eta}{kT} = \frac{\delta_1}{\delta_2 \delta_3} \qquad (1.11)$$

where δ_1 = the perpendicular distance between two neighbouring layers of molecules sliding past one another.

δ_2 = the distance between two neighbouring molecules in the direction of motion.

δ_3 = the distance between neighbouring molecules in the plane normal to the direction of motion.

This equation is exact only for self-diffusion in liquids as it assumes similar rate constants for the processes of diffusion in liquids as,

$$\frac{D\eta}{kT} = \frac{\delta_1}{\delta_2\delta_3}\ \frac{\delta_d^2}{\delta_v^2}\ \frac{K_d}{K_v} \qquad (1.12)$$

where K_d and K_v are the respective rate constants for the processes of diffusion and viscosity and δ_d and δ_v are the respective distances between equilibrium positions for diffusion and viscosity. Even in its simpler form this relationship gives better agreement than the Stokes-Einstein equation when the solute and solvent molecules are of comparable dimensions.

Equation (1.10) suggests an exponential relationship between D the diffusion coefficient, and T the absolute temperature but as the free volume V_f and the distance between successive equilibrium positions δ are themselves dependent upon temperature further simplification is virtually impossible. Taylor (15), however, re-examined the data of Cohen and Bruins (16) for the diffusion of tetrabromoethane in tetrachloroethane solutions using equation (1.13) to correlate the results.

$$D = A \exp(-Q/RT) \qquad (1.13)$$

where Q = an activation energy, kcal/mole

A = an experimental constant.

Taylor found that a plot of log D vs. T gave a satisfactory linear correlation with an activation energy of 3490 calories (3.49 kcal).

A similar treatment of the data of Scheffer and Scheffer (17) for the diffusion of mannitol in water gave a plot which curved slightly towards the 1/T axis. Calculation of the activation energy over intervals of 10°C. revealed that the activation energy decreased with increasing temperature. A similar trend in the activation energy for the viscous flow of water was noted by Eyring and Ewell (18) who suggested that it was caused by the hydrogen bond structure of the liquid.

An alternative relationship between D and T was proposed by Christensen (19),

$$D \quad = \quad BT^{1/2}\exp(-E/RT) \qquad (1.14)$$

where E is an activation energy and B an experimental constant.

A more general attempt to correlate liquid diffusion coefficients with the physical properties of the solute and solvent was made by Wilke (20) who suggested a diffusion factor F defined by the equation,

$$F \quad = \quad T/D\eta \qquad (1.15)$$

From the experimental data Wilke showed that, as predicted by Eyring's theory of reaction rates and the Stokes-Einstein equation, F was substantially independent of temperature. To take account of the properties of the solvent Wilke proposed a solvent factor φ which he defined as the average ratio of F for the diffusion of a solute in a given solvent to F for the diffusion of the same molal volume in water. Using these constants Wilke was able to prepare a chart from which the diffusion factor F for a solute of known molal volume diffusing in a given solvent could be estimated. It was found that for solute-solvent systems whose diffusion coefficients had been determined experimentally the average deviation between the calculated and experimental values was about 10%.

Scheibel (21) derived an empirical equation to take the place of the family of curves suggested by Wilke. The only restriction on the application of this equation is the necessity of the molal volume of the solute to be at least twice that of the solvent.

An alternative correlation was proposed by Othmer and Thakar (22) who derived an equation relating D and η by considering diffusion and viscosity as rate processes varying as exponential functions of the temperature.

$$\log D = -\frac{E_d}{E_v} \log \eta + C \qquad (1.16)$$

where E_d and E_v are activation energies for the processes of diffusion and viscosity and C a constant. It has been suggested that for dilute solutions E_d and E_v should be nearly equal. Thus a plot of log D vs. log η for water should give a straight line of slope -1.0 In fact, Othmer and Thakar found that the mean slope of a number of plots of log D of various solutes in water against log η was -1.10 The constant C represents the logarithm of diffusion coefficients at the temperature at which the viscosity of water is one centipoise, i.e., 20.06°C. The value of log D at this temperature will depend upon the size of the solute molecule, i.e., the molal volume. Othmer and Thakar plotted log D against the logarithm of the molal volume and obtained the relation,

$$10^5\, D_w^o \;=\; 14.0/V_m^{0.6} \tag{1.17}$$

where D_w^o = the value of the diffusion coefficient in water at 20°C.

V_m = the molal volume.

Equation (1.17) when substituted in equation (1.16) gives the more general result,

$$10^5\, D_w^o \;=\; 14.0/V_m^{0.6}\;\eta_w^{1.1} \tag{1.18}$$

Othmer and Thakar extended equation (1.18) to diffusion in liquids other than water:-

$$10^5\, D_s \;=\; 14.0/1.1(L_s/L_w)\;V_m^{0.6}\,\eta_w\,\eta_s^o \tag{1.19}$$

where L_s = latent heat of vaporization of the solvent.

L_w = latent heat of vaporization of water.

η_s^o = solvent viscosity at 20°C.

It is interesting to note that Lewis (23), in attempting to correlate measured integral diffusion coefficients of various organic compounds in water and a number of organic solvents, found that the correlation proposed by Arnold (1) gave reasonably good agreement where applicable but that the correlations proposed by Wilke (20), Scheibel (21), and Othmer and Thakar (22) were generally unsatisfactory for organic solvents.

1.2.2 A summary of previous work in the diffusion of liquids in porous media.

Although earlier workers had carried out some investigations into the effect of the solid structure on the diffusion process, the first extensive experiments were carried out by Friedman and Kraemer (24) in the course of their study of the structure of gels. They devised a new experimental technique and utilised the equation derived by March and Weaver (25) for the fraction of solute which has diffused into a porous solid of given thickness from a layer of solution of equal thickness whose concentration has been maintained uniform throughout by constant stirring. The experimental results indicated that diffusion coefficients for systems of this nature were considerably smaller than those measured in free solution and also, that as the concentration of gelatin in the gels was increased the observed diffusion coefficients decreased. It was suggested that the differences between the observed values and those for diffusion in free solution were caused by,

(a) the mechanical blocking effect of the solid,

(b) the drag on the diffusing molecules caused by their proximity to the walls of the capillaries through which diffusion is taking place, and,

(c) the difference in viscosity between the liquid in the gel and water at the same temperature.

To take account of these factors the following relationship was proposed,

$$D_s = D_g(1 + 2.4r/R)(1 + \alpha)(1 + \beta) \qquad (1.20)$$

where D_s = diffusion coefficient in free solution.

D_g = diffusion coefficient in the gel.

r = radius of the diffusing molecule.

R = radius of the pores in the gel.

α = a correction factor for the difference in viscosity between the liquid in the gel and water at the same temperature.

β = a correction for the mechanical blocking effect.

This work was continued by Friedman (26) and (27) who studied the effect of the solute molecular weight on the diffusion process and the structure of agar gels. The structure of cellulose acetate gels was investigated by Klemm and Friedman (28).

Cady and Williams (29) extended the experimental methods of Friedman and Kraemer to the diffusion of various non-electrolytes into wood. It was found that the ratio r/R was of primary importance in determining the type of mass transfer taking place. From the experimental results three types of diffusion were postulated,

(a) "hindered diffusion", in which the ratio r/R was comparatively large and could not be neglected,

(b) "free diffusion", in which the effective pores were small enough to prevent mixing of the water in the wooden block with the external solution but were large enough to allow practically unrestricted diffusion of the solute molecules, and,

(c) "stirred diffusion", in which the pores were so large that mechanical mixing with the liquid in the pores of the wooden block took place as the solution was stirred.

The contribution of Newman (30) and (31) to the theory of drying and diffusion from slabs enabled alternative experimental techniques to be evolved. Newman suggested theoretical solutions of the equation,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (1.21)$$

for rectangular parallelepipeds (with and without sealed edges), cylinders, and spheres. While primarily intending the use of these equations to solve drying problems, Newman also suggested their application to the extraction of material from porous solids. The solutions derived by Newman were restricted to systems of a finite type but numerous other investigators have derived solutions for the infinite and semi-infinite systems and in limited cases for systems where the diffusion coefficient is a function of the solute concentration.

The first major attempt to apply these solutions to the extraction of a solute from an inert carrier material was made by Boucher, Brier, and Osburn (32) who extracted soybean oil from porous clay slabs. The slabs, whose edges had been sealed to ensure that diffusion would occur through only the principal faces, were impregnated under vacuum with phosphatide-free oil, placed in an extraction chamber and subsequently extracted with either tetrachloroethylene or a mixture of carbon tetrachloride and ethylene dichloride as the solvent.

It was found, that for Reynolds' numbers between 14.7 and 20,400 the rate of extraction was independent of the solvent flow rate. This suggested that compared with the resistance of the carrier material itself, the resistance of the boundary layer at the slab surface was of negligible importance. It was also observed that the diffusion coefficients calculated for this system were independent of the initial concentration of soybean oil. An attempt was also made to correlate the calculated diffusion coefficients for the three temperatures at which experiments had been carried out (80°, 120° and 160°F.). It was found that the diffusion coefficient was related to the product of the viscosities of the oil and solvent. The form of the relationship was,

$$D = a(\eta_o \eta_s)^{-b} \tag{1.22}$$

where a and b are constants, η_o and η_s are the viscosities of the oil and solvent respectively.

King, Katz, and Brier (33) extended this work to the extraction of batches of flaked soybeans of various thicknesses with mixtures of soybean oil and trichloroethylene. They found that the latter part of the extraction curves did not tend to a linear form as predicted by the theoretical equation and that duplicate experiments for flakes of one thickness could not be represented by a theoretical extraction curve with one constant diffusion coefficient. Microscopic examination of the flaked soybeans suggested that the irregular nature of the solid structure was responsible for the differences between the observed results and those predicted by theory. This explanation was confirmed by Osburn and Katz (34) who examined the effect of the pore structure on the mathematical solutions of Fick's law. They also postulated the existence of solids such that the simple solution of Fick's law must be modified to take account of,

(a) a solid of uniform thickness, but of irregular composition, which may require more than one diffusion coefficient to give an exact equation from which extraction rates may be calculated, and,

(b) a mixture of solids of two different thicknesses in various proportions.

The effect upon the mathematical solution of the differential equation is similar for both postulates and one or other is suggested as the explanation of the unsatisfactory correlation, with existing theory, of the results obtained by King, Katz, and Brier.

The investigation of the solvent extraction of oil bearing seeds was continued by Fan, Morris, and Wakeham (35) who extracted sliced peanut kernels with industrial solvents. The essential difference between this work and that carried out by King *et al.* lay in the improved method of preparing the vegetable material for extraction. While King *et al.* relied upon flaking the soybeans with an industrial internal roll flaker, thus distorting and rupturing a large number of the oil bearing cells, Fan *et al.* mounted the peanut kernel in paraffin wax and sliced the resulting blocks of wax and kernels with a microtome. This ensured the production of more uniform slices and a reduction in the number of damaged cells. A plot of the experimental results revealed that while the initial curvature indicated that a fraction of the oil was being extracted more rapidly than predicted by theory, the latter part of the curve did tend to a linear form. This confirmed that the latter part of the extraction process was taking place in accordance with Fick's law. The high initial rate of extraction was considered to be caused by the presence of readily extractable oil released by those cells ruptured in the preparation of the slices. The results agreed with the suggestion, of Boucher, Brier, and Osburn (32), that the measured diffusion coefficients would decrease with increasing solvent viscosity since of the two solvents used, the less viscous gave the more rapid extraction rates. It was also found that the rates of extraction were dependent on the initial moisture content of the kernels and that the extraction rate and consequently the measured diffusion coefficients decreased with increasing moisture content.

The most recent investigation of the applicability of Fick's law to the extraction of soybean oil from soybeans is that of Othmer and Agarwal (36) who extracted soybeans with commercial hexane containing varied amounts of soybean oil. It was found that the quantity of oil extracted, the residual oil content and the rate of extraction were independent of the concentration of oil in the solvent. It was therefore concluded that the controlling factor was not molecular diffusion. Othmer and Agarwal obtained correlations of the residual oil content and rate of extraction with the extraction time and the specific surface of the flakes and observed that the rate of extraction decreased very rapidly with decreasing oil concentration and increasing flake thickness,

$$- dC/dt = 0.173\ S^{3.97}\ C^{3.5} \tag{1.23}$$

where $- dC/dt$ = rate of extraction.

S = specific surface of the flakes.

C = residual oil concentration.

From the experimental evidence Othmer and Agarwal concluded that the rate of extraction was controlled by the rate of permeation of the soybean cells by the solvent and that consequently the laws controlling viscous or capillary flow should be considered. On this basis a theoretical equation was derived which was similar in form to that evolved from the experimental results,

$$- dC/dt = A\ f(C) \tag{1.24}$$

A detailed investigation of the rates of extraction from inert porous media has been carried out by Piret, Ebel, Kiang and Armstrong (37) who measured rates of extraction from,

(a) precision bore capillary tubes,
(b) glass tubes packed with glass spheres, and,
(c) porous alumina spheres.

It was found that the diffusion coefficients derived from the experiments with capillary tubes were in close agreement with the corresponding values for the integral diffusion coefficients of the respective solutes as measured in free solution. In the experiments with tubes packed with glass spheres, lower values of diffusion coefficients were obtained and it was suggested that this was caused by the blocking effect of the glass spheres and that this effect could be accounted for in the theoretical equation by adopting a pore shape factor K^2. K was defined as the ratio of the actual distance travelled by the diffusing molecules to the theoretical minimum distance indicated by the dimensions of the carrier solid. A preliminary series of experiments was carried out with the alumina spheres in which, after grading for porosity and diameter, the spheres were impregnated under vacuum with a solution whose integral diffusion coefficient was known. From an experimental plot of percentage solute unextracted against time, the pore shape factors of various sets of spheres were determined and used to calculate diffusion coefficients of other solutes in subsequent experiments.

The effects of initial solute concentration and extraction temperature were also investigated and from the experimental results it was concluded that the initial solute concentration had no effect on the extraction rate. The results were limited to experiments at only three temperatures and consequently no extensive conclusions could be drawn from them.

Wall, Grieger and Childers (38) proposed a method for measuring integral diffusion coefficients using porous earthenware "frits". These frits or discs were filled by allowing them to stand for 48 hours in the solution whose diffusing coefficient was to be measured. The frit was then suspended, in a bath of pure solvent, from the arm of a balance. The rates of mass transfer to or from the frit could be measured by the apparent changes in weight of the frit and diffusing coefficients calculated from the experimental results and the appropriate theoretical equation. Wall et al. reported identical rates of absorption and desorption.

2. EXPERIMENTAL PROGRAMME.

Examination of the work previously carried out in the study of diffusion of liquids in porous media led to the preparation of a programme of research to consider the following aspects of the problem.

2.1 Comparison of the processes of absorption and desorption.

Previously attention has been mainly directed towards the measurement of the rates at which substances were desorbed from porous solids. However, although the mathematical solution of Fick's law is identical for both processes, there is no extensive experimental evidence to suggest that a substance may not be desorbed more quickly than absorbed or vice versa. In fact the theoretical treatment of this problem by Crank and Henry (39) indicates that where the diffusion coefficient increases with increasing solute concentration the process of absorption should take place more rapidly than that of desorption and that conversely when the diffusion coefficient decreases with the increasing solute concentration the process of desorption should take place more rapidly than that of absorption.

It was decided, therefore, to carry out both desorption and absorption experiments in an attempt to determine whether the effect of the porous solid was identical for both cases.

2.2 The effect of initial solute concentration.

In recent years the precise measurement of differential diffusivities (40), (41), and (42) has revealed that in many cases the solute concentration has a considerable influence on the differential diffusion coefficient. It would be expected, therefore, that the initial solute concentration would be of primary importance in determining the rate at which a substance is either absorbed or desorbed. Piret et al. investigated the effect of initial concentration on the desorption of potassium chloride from porous alumina spheres and concluded that variation of initial concentration had no effect on the data. It was felt, however, that potassium chloride was an unfortunate choice of solute in that the differential diffusivity decreases with increasing solute concentration until it reaches a minimum after which it begins to increase. Thus the total variation is possibly not sufficiently great to be observed in non-steady state experiments with porous solids which are much less accurate than the experimental techniques used in the measurement of differential diffusivities. Alternatively the experimental procedure adopted by Piret *et al.* may not have been sufficiently sensitive to detect differences in the rates of desorption caused by variation of the initial solute concentration.

It was decided, therefore, to use two solutes, potassium chloride and sucrose, and to carry out experiments at two concentrations, namely, N and 3N for potassium chloride and 0.3M and M for sucrose. The differential diffusivity of sucrose decreases with increasing concentration so that these two solutes provide not only a contrast in the magnitude of the diffusing particles but in the effect of solute concentration on the differential diffusivity.

2.3 The effect of temperature on the diffusion process.

A limited amount of data on the effect of temperature on the diffusion process was found in the literature. Tolliday, Woods and Hartung (43) studied the diffusion of electrolytes through copper ferrocyanide membranes and concluded that the activation energy for this process was greater than the corresponding activation energy for diffusion in free solution. This was confirmed by Christensen (19) in the course of his study of the diffusion of sodium chloride through wooden laminae. Christensen found that large variations existed in the activation energies for different species of wood, but that all the observed values were greater than the activation energy for the diffusion of sodium chloride in water.

It was proposed, therefore, to carry out both absorption and desorption experiments over the temperature range 20 - 80°C. to determine,

(a) if the exponential relationship between the diffusion coefficient and temperature suggested by Taylor (15) for diffusion in free solution would also give a satisfactory correlation for diffusion in porous media.

(b) whether the activation energies for the processes of absorption and desorption were identical, and,

(c) if the activation energy for the diffusion of a non-electrolyte in a porous medium was greater than that for diffusion in free solution.

2.4 The effect of the physical properties of the carrier solid.

It is reasonable to assume that the porosity, the number of pores per unit area and the mean pore diameter would be of importance in determining the rates at which substances were absorbed or desorbed. It was therefore proposed to carry out experiments with at least two different carrier materials. In fact, three grades were used as after some preliminary experiments had been carried out with slabs 0.1 inches thick it was decided to continue the work with slabs of 0.2 inches thickness. Unfortunately, however, one of the grades (the CF.6) was no longer in production and a substitute had to be used. Table 2.1 gives the physical characteristics of the porous materials employed. These various grades of materials have been referred to by the manufacturer's catalogue numbers throughout the text.

Table 2.1 Characteristics of the porous media.

Material (grade no.)	Mean Pore Diameter (microns)	Porosity (% free space)
H.125	1	48
CF.6	6	37
B.5	4	40

The convention has been adopted of denoting slabs of 0.1 inches thickness by the prefix (1), i.e. (1) H.125 slabs, and similarly those of 0.2 inches thickness by the prefix (2).

3. THE MATHEMATICAL TREATMENT OF DIFFUSION.

3.1 Introduction.

The fundamental laws governing diffusion in a homogeneous medium were expressed by Fick (44) and may be written as,

$$\frac{dm}{dt} = -D \frac{\partial C}{\partial x} \qquad (3.1)$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (3.2)$$

Equation (3.1) gives the rate of permeation or transfer of a solute in a direction perpendicular to a reference plane, through unit area during unit time in terms of the concentration gradient $\partial C/\partial x$ and the diffusion coefficient D. Equation (3.2) gives the rate of accumulation of matter at a given point in the medium as a function of the time. This equation may be derived from the first by considering a material balance for the transfer of a solute to and from an element of thickness dx located between two reference planes x and x + dx. Diffusion is assumed to take place only through unit cross-sectional area in the positive direction of the x-axis.

The rate of transfer of matter to the element is given by,

$$(dm/dt)_x = -D \frac{\partial}{\partial x} (C) \qquad (3.3)$$

and from the element by,

$$(dm/dt)_{x + dx} = -D \frac{\partial}{\partial x} (C + \frac{\partial C}{\partial x} dx) \qquad (3.4)$$

Therefore, since the rate of accumulation of matter is the difference of the rates of transfer to and from the element, it is thus given by the difference of equations (3.3) and (3.4),

$$(dm/dt)_x - (dm/dt)_{x + dx} = -D \frac{\partial}{\partial x} (C) + D \frac{\partial}{\partial x} (C + \frac{\partial C}{\partial x} dx)$$

$$= D \frac{\partial}{\partial x} [\frac{\partial}{\partial x} dx] \qquad (3.5)$$

and by definition,

$$(dm/dt)_x - (dm/dt)_{x + dx} = \frac{\partial C}{\partial t} dx \qquad (3.6)$$

therefore,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (3.7)$$

This equation may be extended to diffusion in any direction by the inclusion of terms in the right hand side of the equation to take account of diffusion in the directions of the y- and z-axes,

$$\frac{\partial C}{\partial t} = D [\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}] \qquad (3.8)$$

Equation (3.7) may also be transformed to polar co-ordinates by the use of the customary transformations,

$$x = r \sin a \cos b$$
$$y = r \sin a \sin b$$
$$z = r \cos a$$

and consequently equation (3.7) becomes,

becomes,

$$\frac{\partial C}{\partial t} = \frac{D}{r}\left\{\left[\frac{\partial}{\partial r}\left(r^2\,\frac{\partial C}{\partial r}\right)\right] + \frac{1}{\sin a}\,\frac{\partial}{\partial a}\left[\sin a\frac{\partial C}{\partial a}\right] + \frac{1}{\sin^2 a}\,\frac{\partial^2 C}{\partial b^2}\right\} \qquad (3.9)$$

which for a sphere may be reduced to,

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\,\frac{\partial C}{\partial r}\right] \qquad (3.10)$$

with $\partial C/\partial a$ and $\partial^2 C/\partial b^2$ both equal to zero.

As the basic theory of diffusion is analogous to that of the conduction of heat in solids, an extensive treatment of the possible transformations of the fundamental equation will be found in text-books relevant to this subject, e.g., Carslaw (45) or Carslaw and Jaeger (46).

Equations (3.7) and (3.8) may be solved for specified conditions under which diffusion is taking place. In general these solutions may be classified as those for,

(a) infinite solids,
(b) semi-infinite solids, and,
(c) finite solids.

with varying boundary conditions. A very full treatment of all three cases, together with the possible boundary conditions, will be found in Barrer (47), Crank (48), and to a lesser degree in Jost (49). Only the solutions necessary for the experimental work will be given in the text.

3.2.1 Desorption from a finite slab.

The boundary conditions selected for desorption from a finite slab were,

(a) that the solute concentration should be maintained at zero at the slab surfaces, and,

(b) that the solute concentration in the slab at zero time should be a function of the dimensions of the slab.

These conditions imply that the following mathematical conditions must be satisfied by the solution of the partial differential equation,

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right] \qquad (3.11)$$

$$C = 0 \text{ at } x = 0,\ x = a\ ;\ y = 0,\ y = b; \text{ and } z = 0,\ z = c. \qquad (3.12)$$

$$C = f(x,y,z) \text{ when } t = 0 \qquad (3.13)$$

The solution is based upon that given by Carslaw (45), p.108, for the conduction of heat in a rectangular parallelepiped of dimensions a, b, and c.

The expression,

$$\sin\frac{l\pi}{a}x\ \sin\frac{m\pi}{b}y\ \sin\frac{n\pi}{c}z\ \ \exp\left[-D\pi^2 t\left(\frac{l^2}{a^2} + \frac{m^2}{b^2} + \frac{n^2}{c^2}\right)\right]$$

satisfies conditions (3.11) and (3.12)

Extending Fourier's sine series to the case of f(x,y,z) we would have,

$$f(x',y',z') = \frac{8}{abc}\sum_{l=1}^{\infty}\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\Big[\sin\frac{l\pi}{a}x\,\sin\frac{m\pi}{b}y\,\sin\frac{n\pi}{c}z$$

$$\int_0\!\!\int_0\!\!\int_0 f(x',y',z')\,\sin\frac{l\pi}{a}x'\,\sin\frac{m\pi}{b}y'\,\sin\frac{n\pi}{c}z'\;dx'.dy'.dz'\Big]$$

hence the required solution will be given by,

$$C = \sum_{l=1}^{\infty}\sum_{m=1}^{\infty}\sum_{n=1}^{\infty} A_{l,m,n}\,\sin\frac{l\pi}{a}x\,\sin\frac{m\pi}{b}y\,\sin\frac{n\pi}{c}z\,\exp\Big[-D\pi^2t\Big(\frac{l^2}{a^2}+\frac{m^2}{b^2}+\frac{n^2}{c^2}\Big)\Big]$$

where,

$$A_{l,m,n} = \frac{8}{abc}\int_0^a\!\!\int_0^b\!\!\int_0^c f(x',y',z')\,\sin\frac{l\pi}{a}x'\,\sin\frac{m\pi}{b}y'\,\sin\frac{n\pi}{c}z'\;dx'.dy'.dz'$$

Now where $f(x',y',z')$ is constant and equal to C_o,

$$A_{l,m,n} = \frac{8C_o}{lmn\pi^3}\int_0^a\!\!\int_0^b\!\!\int_0^c \sin\frac{l\pi}{a}x'\,\sin\frac{m\pi}{b}y'\,\sin\frac{n\pi}{c}z'\;dx'.dy'.dz'$$

$$= \frac{8C_o}{lmn\pi^3}\,(1-\cos l\pi)(1-\cos m\pi)(1-\cos n\pi)$$

thus, where l,m or n is even, the function $A_{l,m,n}$ is zero but where l,m, and n are odd the function becomes,

$$A_{l,m,n} = (4/\pi)^3\,\frac{C_o}{lmn}$$

Hence,

$$C = (4/\pi)^3\,C_o\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty}\frac{\sin(2p+1)\frac{\pi x}{a}\,\sin(2q+1)\frac{\pi y}{b}\,\sin(2r+1)\frac{\pi z}{c}}{(2p+1)(2q+1)(2r+1)}$$

$$\exp\Big[-D\pi^2t\Big[\frac{(2p+1)^2}{a^2}+\frac{(2q+1)^2}{b^2}+\frac{(2r+1)^2}{c^2}\Big]\Big]$$

(3.14)

If Q_d is defined as the quantity of solute remaining in the slab after time t, then,

$$Q_d = \iiint C \, dx.dy.dz.$$

therefore,

$$Q_d = (4/\pi)^3 C_o \int_0^a\!\int_0^b\!\int_0^c \sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty} \frac{\sin(2p+1)\frac{\pi x}{a}\ \sin(2q+1)\frac{\pi y}{b}\ \sin(2r+1)\frac{\pi z}{c}}{(2p+1)(2q+1)(2r+1)} \exp\left[-D\pi^2 t\left[\frac{(2p+1)^2}{a^2} + \frac{(2q+1)^2}{b^2} + \frac{(2r+1)^2}{c^2}\right]\right] dx.dy.dz.$$

now,

$$\int_0^a \sin(2p+1)\frac{\pi x}{a} = -\frac{a}{\pi(2p+1)} \left[\cos(2p+1)\frac{\pi x}{a}\right]_0^a$$

$$= \frac{2}{\pi(2p+1)}$$

Therefore,

$$Q_d = (8/\pi^2)^3 \, abc \, C_o \sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty} \frac{\exp\left[-D\pi^2 t\left[\frac{(2p+1)^2}{a^2} + \frac{(2q+1)^2}{b^2} + \frac{(2r+1)^2}{c^2}\right]\right]}{(2p+1)^2(2q+1)^2(2r+1)^2} \qquad (3.15)$$

The quantity of solute present in the slab at time t = 0 is the volume of the slab multiplied by the initial concentration, i.e.,

$$Q_o = abc \, C_o \qquad (3.16)$$

therefore E_d, defined as the ratio of the amount of solute retained after time t to that present at time t = 0, is given by the ratio of equations (3.15) and (3.16),

$$E_d = (8/\pi^2)^3 \sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty} \frac{\exp\left[-D\pi^2 t\left[\frac{(2p+1)^2}{a^2} + \frac{(2q+1)^2}{b^2} + \frac{(2r+1)^2}{c^2}\right]\right]}{(2p+1)^2(2q+1)^2(2r+1)^2} \tag{3.17}$$

3.2.2. The absorption of a solute from a solution to a porous slab.

If,

$$C = (4/\pi^2)^3\ c \sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty} \frac{\sin(2p+1)\frac{\pi x}{a}\ \sin(2q+1)\frac{\pi y}{b}\ \sin(2r+1)\frac{\pi z}{c}}{(2p+1)(2q+1)(2r+1)}$$

$$\exp\left[-D\pi^2 t\left[\frac{(2p+1)^2}{a^2} + \frac{(2q+1)^2}{b^2} + \frac{(2r+1)^2}{c^2}\right]\right]$$

is a solution of equation (3.8) then its negative must also be a solution, i.e., with C as given above $C_o - C$ 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 C_o

Thus the solution of equation (3.8) for the absorption of a solute is,

$$C = C_o\left[1 - (4/\pi^2)^3 \sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty} \frac{\sin(2p+1)\frac{\pi x}{a}\ \sin(2q+1)\frac{\pi y}{b}\ \sin(2r+1)\frac{\pi z}{c}}{(2p+1)(2q+1)(2r+1)}\right.$$

$$\left.\exp\left[-D\pi^2 t\left[\frac{(2p+1)^2}{2} + \frac{(2q+1)^2}{2} + \frac{(2r+1)^2}{2}\right]\right]\right]$$

Now if Q_a is defined as the quantity of solute absorbed by the slab after time t,

$$Q_a = abc\, C_0 \left[1 - (8/\pi^2)^3 \sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty} \frac{\exp\left[-D\pi^2 t\left[\frac{(2p+1)^2}{a^2} + \frac{(2q+1)^2}{b^2} + \frac{(2r+1)^2}{c^2}\right]\right]}{(2p+1)^2(2q+1)^2(2r+1)^2} \right] \tag{3.18}$$

The maximum amount of solute absorbed by the slab would be such as to make the concentration of solute the same within the slab as without, i.e. C This would be accomplished after infinite time, therefore let

$$Q_\infty = abc\, C_0 \tag{3.19}$$

Hence the ratio of the quantity of solute absorbed after time t to that absorbed after infinite time may be obtained from equations (3.18) and (3.19).

$$E_a = 1 - (8/\pi^2)^3 \sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty} \frac{\exp\left[-D\pi^2 t\left[\frac{(2p+1)^2}{a^2} + \frac{(2q+1)^2}{b^2} + \frac{(2r+1)^2}{c^2}\right]\right]}{(2p+1)^2(2q+1)^2(2r+1)^2} \tag{3.20}$$

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

3.3.1. The applicability of Fick's law to diffusion in porous media.

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

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \cdot \frac{\partial C}{\partial x}\right) \qquad (3.21)$$

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. Similarly although the alternative relationships between the differential diffusivity and other physical properties such as chemical potential or mobility have yielded successful correlations of measured diffusion coefficients with theory, they are hardly suitable for direct application to diffusion in porous media.

As it was found that the experimental results tended, in the main, to a linear form it was concluded that the use of Fick's law to calculate mean or integral diffusion coefficients was reasonably satisfactory.

3.3.2. The assumption that diffusion occurs throughout the total volume of the slab.

Obviously diffusion only occurs in the porous volume of the solid which is normally only between 30-50% of the total volume. The effect of this is to reduce substantially the area of the slab surfaces at which diffusion is taking place. However, while equation (3.1) must be modified to take account of this,

$$dm/dt = - p\,D\,(dC/dx) \qquad (3.22)$$

where p is the porosity of the slab. The derived equation, (3.2) does not depend upon the porosity as p appears in both sides of the equation and thus may be eliminated.

The porosity must also be considered when the expression for the concentration in the slab, at any time t, is being integrated,

$$\text{i.e., } Q_d = p \int_0^a\!\int_0^b\!\int_0^c C\,dx.dy.dz.$$

and similarly,

$$Q_o = p\,C_o\,abc$$

Therefore as p is present in both the numerator and denominator of the fraction Q_d/Q_o the porosity of the solid may be neglected in this solution of Fick's law.

3.3.3. The assumption that the distance travelled by the diffusing particles is that minimum distance suggested by the dimensions of the solid.

The effect of the solid structure in causing the diffusing particles to follow paths more tortuous, and consequently more elongated, than they would in free solution cannot, however, be neglected. Two similar corrections have been proposed to take account of this:-

(a) Babbit (50) 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.,

$$\frac{\partial C}{\partial t} = rD \frac{\partial^2 C}{\partial x^2} \qquad (3.23)$$

where r is always less than one.

(b) Piret, Ebel, Kiang and Armstrong (37) suggested a pore shape 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 ratio of the actual distance travelled by a diffusing particle to the theoretical distance suggested by the dimensions of the solid.

It would appear that the pore shape factor proposed by Piret *et al.* is the better of the two since it is more consistent with the fact that it is the square of the dimensions of the solid which appear in the exponential terms of the mathematical solution of Fick's law. It is very unlikely, however, that it would be possible to calculate either K^2 or r and they must be derived as experimental constants.

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

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

4. EXPERIMENTAL TECHNIQUE.

4.1. The general form of the experiments.

Before describing either the apparatus or the experimental technique in detail it will be convenient to give a brief outline of the nature of the experiments and to illustrate the function of each piece of the apparatus.

The experiments may be divided into two groups, absorption experiments and desorption experiments. The desorption experiments were carried out by impregnating the porous earthenware slabs with distilled water and then immersing them in a moving stream of solution thus allowing mass transfer to occur from the solution to the slabs. This technique was reversed for desorption experiments where the slabs were impregnated with a solution of known concentration and then immersed in a moving stream of distilled water thus allowing mass transfer to take place from the slab to the distilled water.

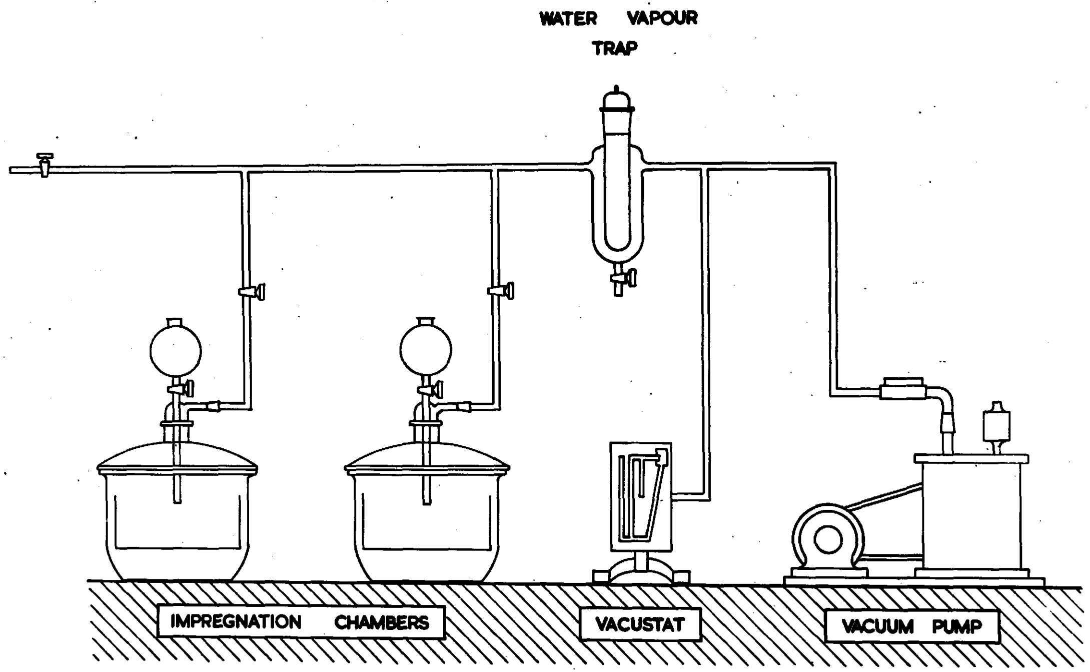
Each experiment may be considered to take place in three stages, i.e.,

(a) the preparation of the earthenware slabs by impregnating them with either distilled water or some solution of known concentration.

(b) the introduction of the slabs to the diffusion cell where a stream of liquid flows past the slabs and diffusion takes place from either the slabs to the liquid or vice versa.

(c) if the slabs are to be used more than once, it is necessary to remove any solute from the slabs which had been retained from the previous experiment before they may be used for a subsequent experiment.

A detailed description of the apparatus used in these three stages is given in the following section.



APPARATUS USED IN THE IMPREGNATION OF THE POROUS EARTHENWARE SLABS

FIG. I

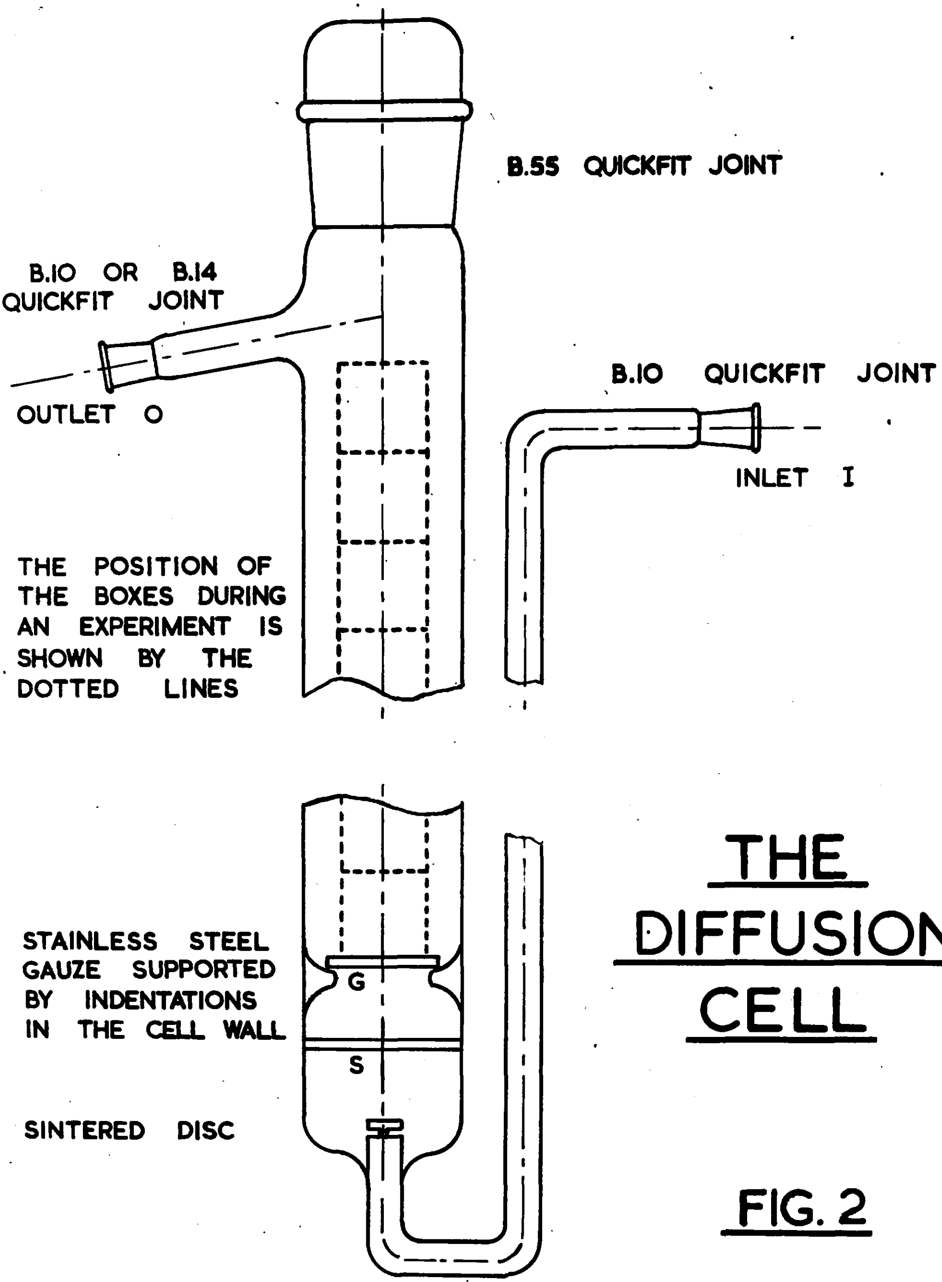
4.2. A detailed description of the apparatus.

4.2.1. The impregnation system.

The impregnation of the slabs was carried out in the apparatus shown in Fig. 1. It consisted essentially of Pyrex desiccators which served as impregnation chambers. The slabs were placed in a glass crystallising dish which fitted into the desiccator bodies as shown. When the system had been evacuated by the vacuum pump, liquids could be introduced into the dishes via the dropping funnels. The absolute pressure in the system was measured by an Edwards' "Vacustat" and both the "Vacustat" and the pump were protected by a Drikold - acetone water vapour trap.

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 sintered glass disc (porosity 1) was used to even out minor fluctuations in flow when distilled water or solutions of low viscosity were being circulated. The resistance of the disc to more viscous solutions (e.g. M sucrose) was so great that it had to be omitted from cells employed in experiments with such solutions.



THE DIFFUSION CELL

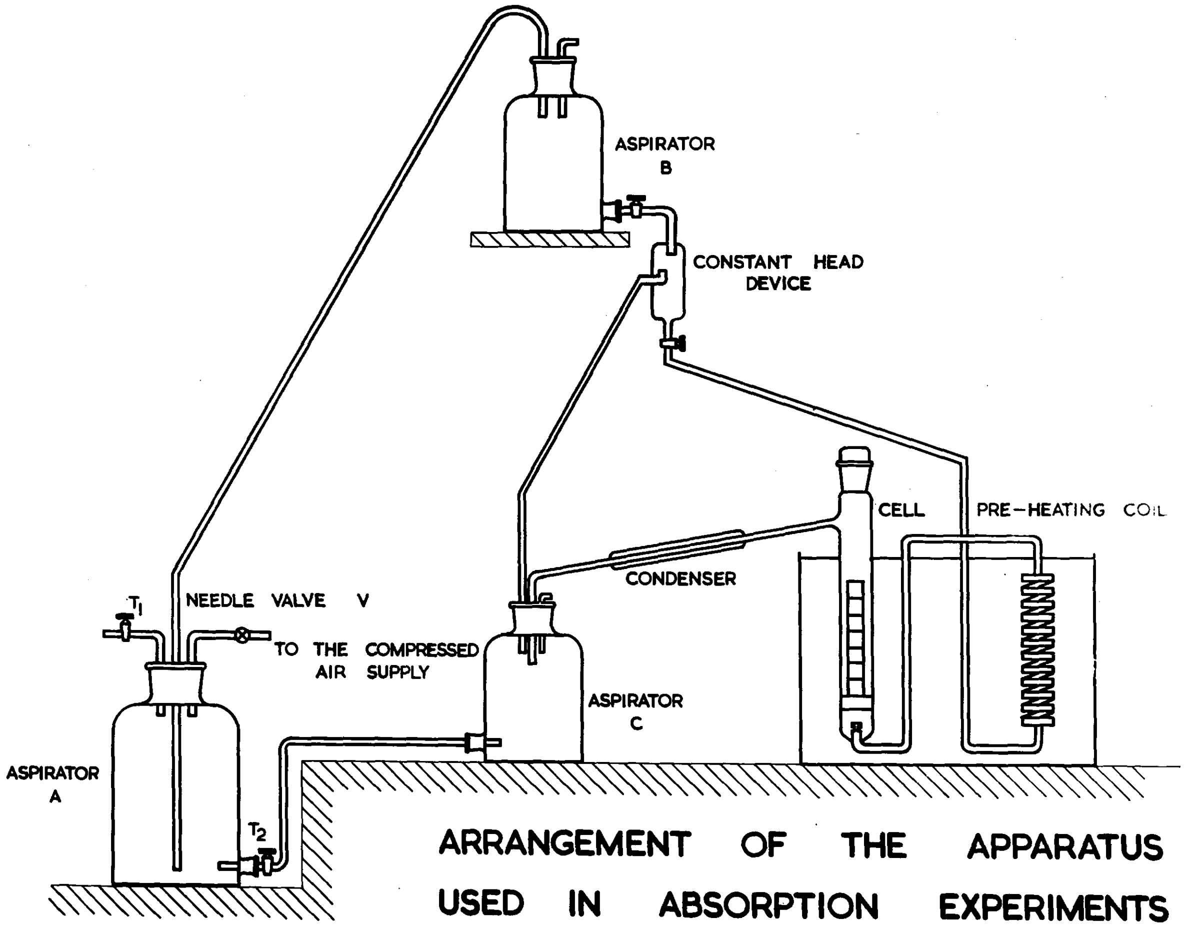
FIG. 2

The stainless steel 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, as shown.

The diffusion cell and a glass coil for preheating the liquid were immersed in a thermostatically controlled water bath which maintained the temperature at ±0.05°C. to the desired value.

4.2.3. The supply of liquid to the diffusion cell.

In absorption experiments it was necessary to recirculate the solution through the diffusion cell. A diagram of the apparatus used to accomplish this is shown in Fig. 3. The solution was 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. Compressed air was found to have a great advantage over the more conventional pumping methods in eliminating contamination of the solution, particularly when KCl solutions were being used. From the aspirator B the solution travelled



ARRANGEMENT OF THE APPARATUS USED IN ABSORPTION EXPERIMENTS

FIG. 3

to the preheating coil via the constant head device and a flowmeter (not shown in Fig. 3). 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.

In desorption experiments it was possible to let the distilled water leaving the diffusion cell to flow to waste. The apparatus was thus simpler and aspirators A and C were dispensed with. 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. The overflow from the constant head was returned to the reservoir.

4.2.4. The total extraction of the slabs.

The total extraction of the slabs took place in the apparatus shown in Fig. 4. This method of extraction enabled the quantity of solute retained by each group of slabs to be estimated as a check on the gravimetric method of analyses usually employed.

FIG. 4

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 the specified thickness. Some preliminary experiments were carried out with the object of finding a suitable method of sealing the edges of the slabs. No completely satisfactory way was found to do this however and it was therefore decided to carry out the experiments using the slabs as rectangular parallelepipeds, that is diffusion taking place simultaneously to or from all the surfaces instead of as finite solids with mass transfer occurring at only the principal faces. This method complicates the calculation of the theoretical equation but it prevents errors arising due to imperfect sealing of the slab edges.

The freshly prepared slabs were continuously extracted for a minimum of fifteen hours to remove any dust or loose material from the newly cut surfaces. After extraction the slabs were dried overnight at 110°C. before measuring the overall dimensions 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. The most uniform 42 slabs were selected and graded into 14 groups of three such that each group had the same mean thickness.

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 increased 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 the length and breadth of the slabs as these dimensions are of considerably less importance than the thickness.

The mean dimensions of the slabs were subsequently used to calculate the theoretical equation for that particular grade of material. A specimen calculation of this equation will be given in a following section.

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 and the water vapour trap filled with the Drikold-acetone mixture before the vacuum pump was started.

It was found that the amount of liquid retained by the slabs depended to some extent on the vacuum employed in the impregnation system and to a lesser degree upon the length of time the slabs were allowed to stand in the impregnation liquid before the vacuum was broken. By standardising the initial conditions, however, it was found possible to reproduce the weight of liquid absorbed by the slabs to within 1%. The conditions adopted 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 *et al.* 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 where the actual diffusion process takes place.

4.3.3. The diffusion process.

Before the impregnated slabs were placed in the diffusion cell and the experiment begun 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. or 300 at 80°C. These values were within the limits for which Boucher, Brier and Osburn (32) 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, before being replaced in their respective aluminium tins and replaced in the oven.

The slabs were dried overnight at a suitable temperature, normally 110°C. for experiments with KCl and 75°C. for experiments with sucrose. After their removal from the oven the slabs were placed in a desiccator for 30 minutes before weighing. Thus 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 slabs were then extracted continuously for 8 - 16 hours, depending on whether KCl or sucrose was the solute, before being used again.

4.3.4. The analytical technique.

4.3.4.1. Solute - KCl.

The concentration of KCl solutions were estimated initially by titration with silver nitrate by the method suggested by Kolthoff and Stenger (51) but it was found that the comparatively large fluctuations in laboratory temperature experienced when the total extractors (there were two sets) were in use caused this method to become somewhat unreliable and to produce inconsistent results. It was decided, therefore, to measure the concentration of KCl solutions by conductivity measurements.

The apparatus described by Thomas and Nook (52) was constructed but the accuracy of measurement obtained was

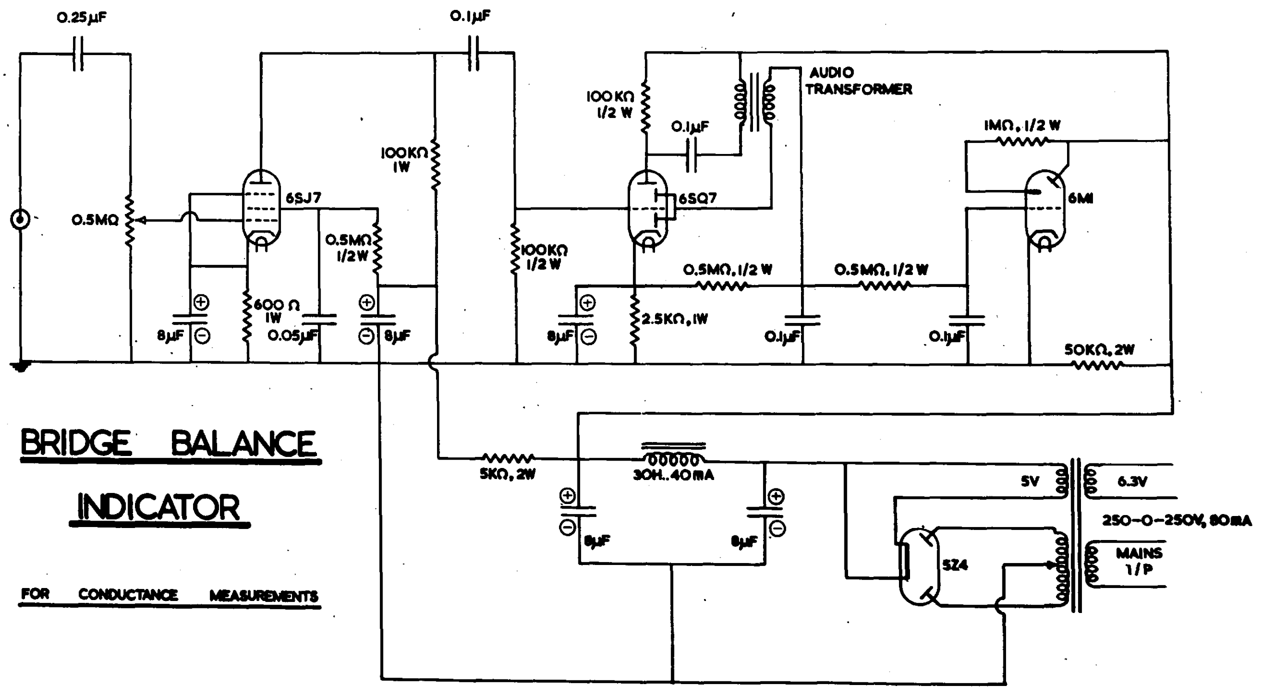
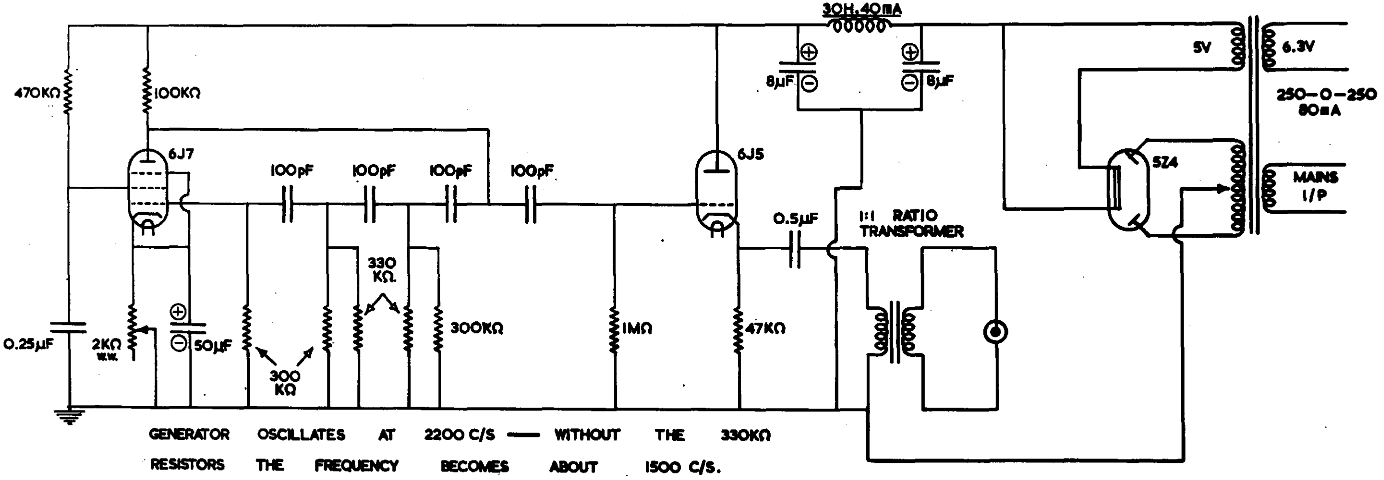

BRIDGE BALANCE INDICATOR
FOR CONDUCTANCE MEASUREMENTS
0.25µF
0.5MΩ
8µF
6SJ7
600 Ω 1W
0.05µF
0.5MΩ 1/2W
8µF
100KΩ 1W
0.1µF
100KΩ 1/2 W
8µF
100 KΩ 1/2 W
0.1µF
6SQ7
2.5KΩ, 1W
AUDIO TRANSFORMER
0.5MΩ, 1/2 W
0.1µF
0.5MΩ, 1/2 W
0.1µF
1MΩ, 1/2 W
6M1
50KΩ, 2W
5KΩ, 2W
30H., 40mA
8µF
8µF
5Z4
5V
6.3V
250-0-250V, 80mA
MAINS I/P

FIG. 5

unsatisfactory owing, in part, to the phase shift introduced by the capacitance of the conductivity cell. It is significant, however, that when tests were carried out on fixed resistors the greatest accuracy obtainable was ± one ohm when a resistance of 450 ohms was being measured. The accuracy diminished further when the fixed resistor was replaced by the conductivity cell.

It was thus apparent that the accuracy of measurement reported by Thomas and Nook could not be reproduced with the apparatus as constructed and that some modification would be necessary. The balance position is indicated by the maximum shadow angle on the magic eye indicator and the presence of stray parasitic currents obscures small changes in this angle as the balance position is approached. A detailed discussion of the effects of stray currents is given by Bender, Biermann and Winger (53), together with the measures which may be taken to eliminate them. The Wagner earth suggested by Bender et al. was incorporated into the apparatus and an immediate improvement was noted in the accuracy with which measurements could be carried out.

Fig. 5 shows the circuit used in the construction of the bridge-balance indicator. It is almost identical with that of Thomas and Nook, except that the 6E5 cathode tuning indicator is replaced by a 6MI and the 6X4 rectifier by a 5Z4. Fig. 6 is the



GENERATOR OSCILLATES AT 2200 C/S — WITHOUT THE 330KΩ RESISTORS THE FREQUENCY BECOMES ABOUT 1500 C/S.

SIGNAL GENERATOR

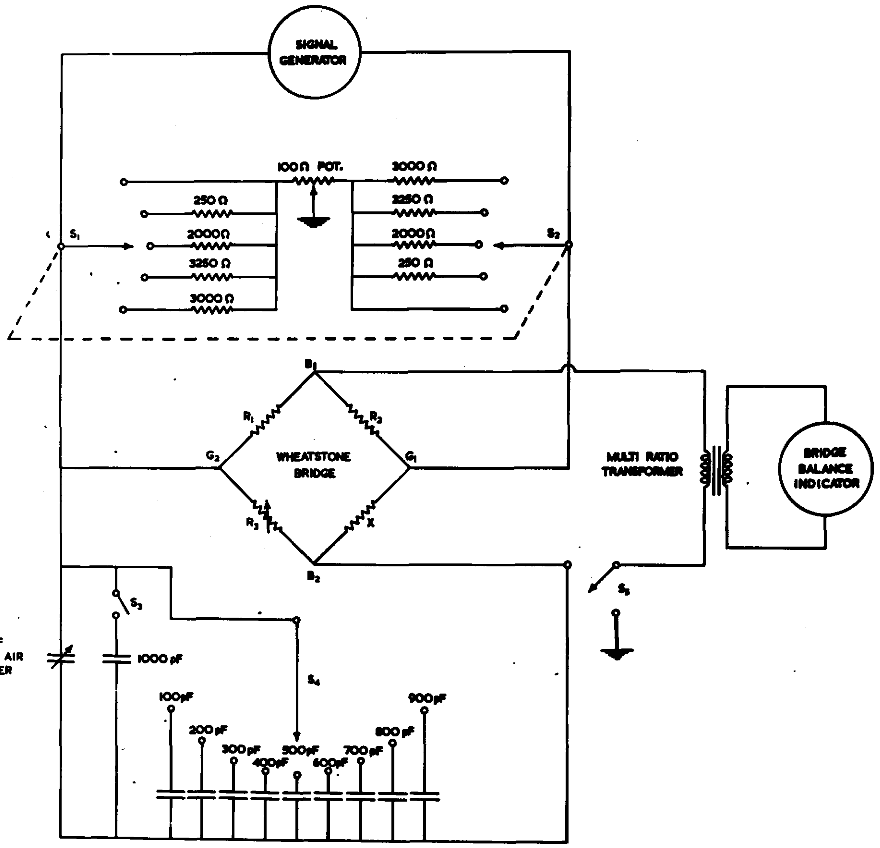
FOR CONDUCTANCE MEASUREMENTS

FIG. 6

circuit proposed by Findlay (54) for a suitable signal generator, the only modification being the increase of the signal frequency from 1500 c/s to 2200 c/s. This was carried out during the initial experiments with the Thomas - Neok circuit and, after the successful inclusion of the Wagner ground, was not altered though it has no advantage over the original value.

Fig. 7 gives the general arrangement of the completed circuit including the Wagner earth and the variable capacitance used to balance the capacitance of the conductivity cell. The leads used in the apparatus were fully screened and the signal generator in addition to being screened was kept at least 15 feet from the bridge-balance indicator. The Wagner earth may be used with bridge arms of any ratio, a suitable earth ratio being selected by the ganged switches S_1 and S_2. The capacitance of the cell was balanced by the selection value of capacitor by S_4 and by the final adjustment of the 100pf. variable air condenser to give exact balance. Should it be necessary, the switch S_3 may be closed to introduce an additional capacitance of 1000pf.

After the cell has been balanced as nearly as possible the switch S_5 was moved to the earth position and the 100 ohm potentiometer adjusted to give maximum shadow angle of the



APPARATUS FOR CONDUCTANCE MEASUREMENTS

FIG. 7

cathode tuning indicator. The switch S_5 was then restored to its original position and the cell rebalanced as before. This procedure was repeated until rebalancing of the cell did not necessitate further adjustment of the Wagner earth.

The apparatus was found to be capable of measuring cell resistances of the order of 180 ohms to 0.1 ohms quite readily, i.e. an accuracy of 1 in 1,800. As the conductivity of the solution varies directly with temperature the measurements were carried out in a water bath regulated to 25.00 ± 0.01 °C.

Solutions of N and 3N KCl are rather too concentrated to make direct measurement of their conductivities practicable with a commercial conductivity cell. It was therefore decided to dilute both solutions to approximately 0.03N which gave a cell resistance of about 180 ohms. In the case of N KCl this was accomplished by taking 30ml. in a class A pipette and adding it to a litre standard flask which was then made up to the graduation mark in a water bath maintained at 20°C. The procedure was the same for 3N solutions except that a 20 ml. pipette and a two litre flask were used.

The apparatus was standardised directly against a series of solutions whose normalities ranged from 0.02970N to 0.03030N. In the case of N solutions this corresponded to a concentration range of 0.990N to 1.010N and the concentration of an unknown solution was estimated from a plot of concentration vs. resistance. The limiting factor in the analyses of the KCl solutions was the accuracy with which the standard flasks were calibrated. As no balance was available which would weigh a two litre flask of distilled water to an accuracy sufficient to recalibrate the flasks, it was necessary to accept the tolerances on these flasks as the limits of accuracy of the estimations.

4.3.4.2. Solute - sucrose.

The estimation of concentration of sucrose solutions presented no difficulties, the measurements being carried out in a polarimeter and the necessary accuracy readily obtained.

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

These calculations may be conveniently considered in four sections:-

5.1. the calculation of the theoretical equation for the particular set of slabs being considered,

5.2. the calculation of the values of Q_0, previously defined as the quantity of solute present at zero time in desorption experiments, and Q_∞ defined as the quantity of solute present after infinite time in absorption experiments, 5.3. the calculation of integral diffusion experiments from the experimental and theoretical plots, and,

5.4. the calculation of activation energies for the diffusion process from the correlation suggested by Taylor (15),

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

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 c.

The theoretical equation for desorption has been shown to be,

$$E_d = (8/\pi^2)^3 \sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty} \frac{\exp\left[-D\pi^2 t\left[\frac{(2p+1)^2}{a^2} + \frac{(2q+1)^2}{b^2} + \frac{(2r+1)^2}{c^2}\right]\right]}{(2p+1)^2(2q+1)^2(2r+1)^2} \qquad (3.17)$$

the complex form of this equation necessitates the consideration of a large number of terms. Generally the values of the first twenty terms were calculated though many of these were only important in the early stages of the extraction (i.e. for high values of E_d) and need not be considered in the calculation of E_d to three significant figures. It was felt, however, that it was necessary to ensure that the calculation was sufficiently accurate to prove whether or not the relationship between E_d and $D\pi^2t$ gave a reasonably linear plot on semi-log. paper.

A portion of the complete calculation for the (2)H.125 slabs will illustrate the method employed. The mean dimensions of these slabs were,

thickness, a = 0.198 inches
breadth, b = 0.754 inches
length, c = 1.372 inches

The terms considered in the calculation are shown in Table 5.1.

Table 5.1. The functions of the slab dimensions used in the calculation of the theoretical equation.

$(2p+1)^2$	$(2q+1)^2$	$(2r+1)^2$	Q	N
1	1	1	27.80	1
1	1	9	32.05	9
1	9	1	41.87	9
9	1	1	231.9	9
1	1	25	40.55	25
1	25	1	95.53	25
25	1	1	640	25
1	1	49	53.30	49
1	49	1	112.32	49
1	9	9	46.12	81
9	1	9	236.1	81
9	9	1	246.0	81
1	9	25	54.62	225
1	25	9	74.27	225
1	9	49	67.37	441
1	49	9	116.48	441
1	25	25	82.77	625
1	25	49	95.52	1225
1	49	25	124.98	1225
1	49	49	137.73	2401

where $Q = \frac{(2p+1)^2}{a^2} + \frac{(2q+1)^2}{b^2} + \frac{(2r+1)^2}{c^2}$

and $N = (2p+1)^2 \, (2q+1)^2 \, (2r+1)^2$

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 exponential terms in equation (3.17). It was found that a range of values of $D\pi^2t$ from 0.001 to 0.050 gave values of E_d from 0.775 to 0.137. The calculated values of E_d for some of the chosen values of $D\pi^2t$ are given in Tables 5.2.1 and 5.2.2.

It can be seen that the importance of the smaller terms decreases steadily until, for $D\pi^2t$ taken as 0.050, more than half of the terms could be omitted without a significant change in the final value of E_d.

Table 5.3 gives the calculated values of E_d used in deriving the theoretical plot of E_d vs. $D\pi^2t$. Fig. 8 illustrates this and the corresponding theoretical plot for the (1)H.125 slabs. The tabulated values of E_d for the other slabs appear in Appendix A.

Inspection of the equation for the absorption of a solute by a slab shows that the calculated values for E_d are in fact also the calculated values for $(1-E_a)$,

i.e.,

$$E_a = 1 - (8/\pi^2)^3 \sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty} \frac{\exp\left\{-D\pi^2 t\left[\frac{(2p+1)^2}{a^2} + \frac{(2q+1)^2}{b^2} + \frac{(2r+1)^2}{c^2}\right]\right\}}{(2p+1)^2\,(2q+1)^2\,(2r+1)^2} \qquad (3.20)$$

$$= 1 - E_d$$

or $\quad E_d = 1 - E_a$

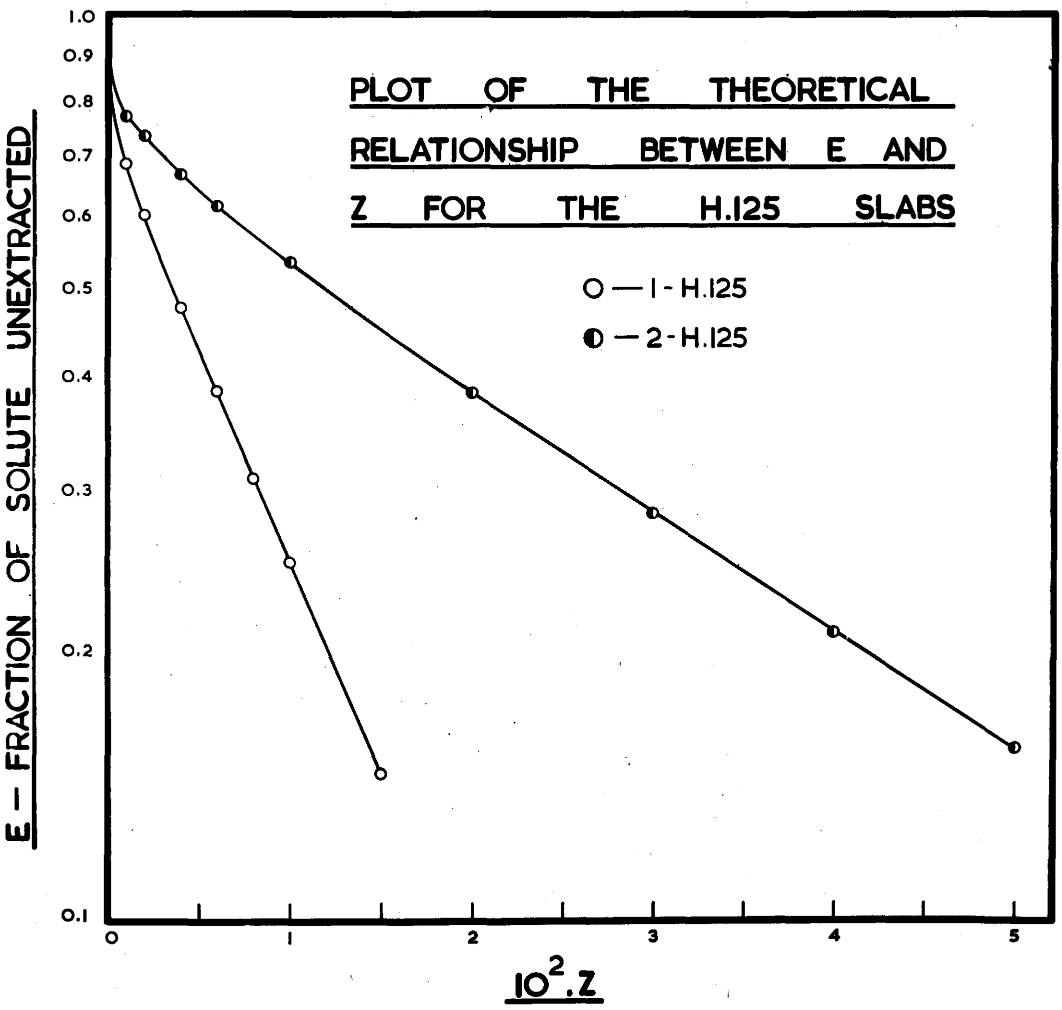

PLOT OF THE THEORETICAL RELATIONSHIP BETWEEN E AND Z FOR THE H.125 SLABS
○ — 1 - H.125
◐ — 2 - H.125
E — FRACTION OF SOLUTE UNEXTRACTED
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
2
3
4
5
$10^2.Z$

FIG. 8

Therefore one plot of the theoretical equation is sufficient for both absorption and desorption experiments.

Table 5.2.1. The estimated values of E_d for Z = 0.001 and 0.006.

	Z = 0.001			Z = 0.006		
N	ZQ	exp (-ZQ)	α	ZQ	exp (-ZQ)	α
1	0.02780	0.97258	0.97258	0.16680	0.84637	0.84637
9	0.03205	0.96846	0.10761	0.19230	0.82506	0.09167
9	0.04187	0.95902	0.10656	0.25123	0.77862	0.08651
9	0.23188	0.79284	0.08809	1.3913	0.24876	0.02764
25	0.04055	0.96026	0.03841	0.24330	0.78404	0.02992
25	0.09553	0.90890	0.03636	0.57316	0.56374	0.02255
25	0.64004	0.52727	0.02109	3.84	0.02149	0.00086
49	0.05330	0.94855	0.01936	0.31979	0.72630	0.01482
49	0.11223	0.89384	0.01824	0.67339	0.50998	0.01041
81	0.04612	0.95493	0.01168	0.27673	0.75826	0.00936
81	0.23613	0.78968	0.00975	1.4168	0.24242	0.00299
81	0.24595	0.78196	0.00965	1.4757	0.22862	0.00282
225	0.05462	0.94684	0.00421	0.32773	0.72056	0.00320
225	0.07427	0.92843	0.00413	0.44560	0.64044	0.00284
441	0.06737	0.93485	0.00212	0.40423	0.66749	0.00151
441	0.11648	0.89005	0.00202	0.69889	0.49714	0.00113
625	0.08277	0.92057	0.00147	0.49660	0.68060	0.00109
1225	0.09552	0.90891	0.00074	0.57309	0.56376	0.00046
1225	0.12498	0.88251	0.00072	0.74989	0.47242	0.00039
2401	0.13773	0.87133	0.00036	0.82639	0.43763	0.00018
			$\Sigma 1.45515$			$\Sigma 1.15673$
	$E_d = (8/\pi^2)^3 . \Sigma\alpha$ $= (8/\pi^2)^3 . 1.45515$ $= \underline{0.775}$			$E_d = (8/\pi^2)^3 . \Sigma\alpha$ $= (8/\pi^2)^3 . 1.15673$ $= \underline{0.616}$		

Table 5.2.2. The estimated values of E_d for $Z = 0.020$ and 0.050.

	$Z = 0.020$			$Z = 0.050$		
N	ZQ	exp (-ZQ)	a	ZQ	exp (-ZQ)	a
1	0.55600	0.57350	0.57350	1.3900	0.24908	0.24908
9	0.64100	0.52677	0.05853	1.6025	0.20139	0.02238
9	0.83744	0.43282	0.04809	2.0936	0.12327	0.01371
9	4.64	0.00973	0.00108	-	-	-
25	0.81100	0.44441	0.01778	2.0275	0.13166	0.00527
25	1.9105	0.14800	0.00592	4.78	0.00840	0.00034
25	-	-	-	-	-	-
49	1.0660	0.34439	0.00703	2.6650	0.00960	0.00142
49	2.2446	0.10597	0.00216	5.61	0.00366	0.00007
81	0.92244	0.39755	0.00491	2.3061	0.09965	0.00123
81	4.72	0.00889	0.00011	-	-	-
81	4.92	0.00730	0.00009	-	-	-
225	1.0924	0.33540	0.00149	2.7311	0.06515	0.00029
225	1.4853	0.22640	0.00101	3.713	0.02391	0.00011
441	1.3474	0.25991	0.00059	3.369	0.03441	0.00008
441	2.3296	0.09733	0.00022	5.82	0.00297	0.00001
625	1.6553	0.19103	0.00031	4.14	0.01592	0.00003
1225	1.9103	0.14803	0.00012	4.78	0.00840	0.00001
1225	2.4996	0.08211	0.00007	-	-	-
2401	2.7546	0.06363	0.00003	-	-	-
			$\Sigma 0.72304$			$\Sigma 0.29403$
	$E_d = (8/\pi^2)^3.0.72304$ $= \underline{0.386}$			$E_d = (8/\pi^2)^3.0.29403$ $= \underline{0.157}$		

Table 5.3. Calculated values of E_d for selected values of $D\pi^2 t$.

$D\pi^2 t$	E_d
0.001	0.775
0.002	0.734
0.004	0.669
0.006	0.616
0.010	0.533
0.020	0.385
0.030	0.284
0.040	0.210
0.050	0.157

5.2. The calculation of Q_0 and Q_∞ .

Before proceeding with the method of calculating the values of Q_0 and Q_∞ it is necessary to consider the time taken by a slab to reach the temperature of the liquid in the diffusion cell. There are two reasons for doing so,

(a) if the slabs do not reach this temperature rapidly it cannot be said that diffusion to or from the slabs is taking place at this liquid temperature, and,

(b) if the slabs do reach the liquid temperature quickly then some expansion of the impregnated liquid must take place which, in the case of desorption, implies that since the coefficients of expansion are not equal solute is being removed from the slabs by a mode of mass transfer other than diffusion.

In making an estimate of the time taken to reach the liquid temperature it is reasonable to assume, as an approximation, that the conduction of heat is occurring through only the principal faces of the slabs. In fact, as heat is also being conducted through the edges of the slabs, this assumption will give a calculated time greater than the actual time.

5.2.1. Solution of the differential equation for the conductance of heat in a solid bounded by two parallel planes.

This solution is readily available in the literature concerning the conduction of heat in solids and may be expressed as,

$$T = T_a + (T_b - T_a)\frac{x}{l} + \frac{2}{\pi}\sum_{1}^{\infty}\frac{T_b\cos(n\pi) - T_a}{n}\sin(n\pi/l)\exp(-kn^2\pi^2t/l^2)$$

$$+ \frac{2}{l}\sum_{1}^{\infty}\sin(n\pi/l)\exp(-kn^2\pi^2t/l^2)\int_{0}^{l} f(x')\sin(n\pi/l)x'\,dx' \qquad (5.1)$$

where T = the slab temperature at any point x

T_a = the temperature at the first face.

T_b = the temperature at the second face.

$f(x')$ = the temperature at any point x at time $t = 0$

t = time in seconds

k = the thermal diffusivity of the slab.

This equation may be simplified as,

$T_a = T_b$ = the temperature of the liquid in the diffusion cell, T_d

and

$f(x') =$ a constant, i.e. the impregnation temperature T_i.

Equation (5.1) becomes

$$T = T_d - (4T_d/\pi) \sum_{0}^{\infty} \frac{\sin(2m+1)\frac{\pi x}{l}}{(2m+1)} \exp\left[-(2m+1)^2\pi^2kt/l^2\right]$$

$$+ (4T_i/\pi) \sum_{0}^{\infty} \frac{\sin(2m+1)\frac{\pi x}{l}}{(2m+1)} \exp\left[-(2m+1)^2\pi^2kt/l^2\right] \qquad (5.2)$$

We are interested in that part of the slab which will take longest to reach the liquid temperature, which, in this case, will be at the centre of the slab, where x will equal $l/2$. Substituting in equation (5.2) we have,

$$(T)_{x=l/2} = T_d - \frac{4}{\pi}(T_d - T_i) \sum_{0}^{\infty} \frac{1}{2m+1} \exp\left[-(2m+1)^2\pi^2kt/l^2\right] \qquad (5.3)$$

If T_d and T_i are known and a value assumed for k this equation may be solved for various values of t. It is apparent that the time lag between the slabs being introduced into the diffusion cell and their reaching the operating temperature will be greatest at the maximum operating temperature, i.e. 80°C.

Thus assuming,

T_d = 80°C.

T_i = 15°C.

C_p = 0.316 cal./g.°C.

= 3.3 g./cc.

K = 0.0015 cal./sec.cm^2 °C/cm.

Therefore,

k = 0.0015/0.316 X 3.3 cm^2/sec.

= 0.00145

This value of k is calculated assuming the slabs to be virtually all silica (in fact they are 90% silica).

$$(T)_{x = l/2} = 80 - \frac{260}{\pi} \sum_{0}^{\infty} e^{-z} + \frac{1}{3} e^{-9z} + \frac{1}{5} e^{-25z} \quad \ldots\ldots\ldots\ldots \quad (5.4)$$

where $z = k\pi^2 t/l^2$

Examination of this equation suggests that for values of t greater than 10 seconds, the second and third terms may be neglected. Table 5.4 gives values of T calculated for a range of two minutes after the introduction of the slabs into the diffusion cell.

Table 5.4. Calculated values of T when x = 1/2.

t	z	e^{-z}	T
10*	0.555	0.5741	32.4
30	1.665	0.1892	64.4
60	3.33	0.0358	77.0
90	5.00	0.0064	79.5
12[redacted]	[redacted]	[redacted]	[redacted]

*The second term, $\frac{1}{3}e^{-9z}$ has been included in this calculation of t.

It can be seen that the slabs have almost reached the operating temperature after one minute. It is reasonable to assume therefore, that in experiments of some thirty minutes duration, the time taken by the slabs to reach the experimental temperature will not be of critical importance. It is almost certain, however, that the sudden rise in temperature will cause the liquid within the slabs to expand and that consequently some of this liquid will be expelled from the slabs.

If it is assumed that, as the coefficient of expansion of the porous material is very small compared with that of water, the expansion of the slabs themselves may be neglected then the volume of the liquid expanding from the slabs may be calculated.

This would, however, represent the extreme case for in desorption solute would be transferred simultaneously by the diffusion and expansion processes. In the early stages of the extraction process it is clearly impossible to separate the two modes of mass transfer, but it is felt that consideration of the expansion process gives a better approximation to the experimental conditions, certainly in absorption, if not in desorption experiments.

5.2.2.1. The calculation of Q_∞

Q_∞ has been defined as the quantity of solute absorbed by the slabs after infinite time. If the expansion of the impregnated distilled water is neglected then Q_∞ may be found from,

$$Q_\infty = \frac{W_i}{D_i^W} \, G \, \frac{D_i^s}{D_{20}^s} \qquad (5.5)$$

where 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.

D_{20}^s density, at 20°C., of the solution from which the solute is being absorbed.

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

Considering now the expansion of distilled water from the slabs let,

V = the porous volume of the slabs.

W_a = weight of liquid in the slabs at the temperature at which absorption is taking place.

If the coefficient of expansion of the slabs is small compared with that of distilled water then the porous volume V may be regarded as constant. As a first approximation this assumption would appear reasonable.

Then,

$$V = \frac{W_i}{D_i^W}$$

and $$W_a = V D_a^W$$

where D_a^W = density of water at the temperature at which absorption is taking place.

therefore $$W_a = W_i \frac{D_a^W}{D_i^W}$$

Knowing the value of W_a we may then calculate the volume of water remaining in the slabs after expansion relative to the impregnation temperature,

$$\frac{W_a}{D_i^W} = W_i \frac{D_a}{(D_i^W)^2}$$

therefore,

$$Q_\infty = W_i G \frac{D_a^W D_i^s}{D_{20}^s (D_i^W)^2} \qquad (5.6)$$

the ratio of the values of Q_∞ is given by the ratio of equations (5.5) and (5.6),

$$\frac{\text{Eq.}(5.5)}{\text{Eq.}(5.6)} = \frac{(D_i^W)^2}{D_i^W \; D_a^W}$$

$$= \frac{D_i^W}{D_a^W}$$

In the extreme case, i.e. at an operating temperature of 80°C. and an impregnation temperature of 15°C.

$$D^W/D^W = 0.99912/0.97186$$

$$= 1.028$$

Thus the corrected value of Q_∞ is about 3% less than the value calculated neglecting expansion effects.

This treatment does not consider the very small reduction in concentration caused by the addition of the volume of the water retained by the slabs (about 30ml.) to the volume of the solution being circulated (about 15 litres).

5.2.2.2. The calculation of Q_0.

Q_0 has been previously defined as the quantity of solute present in the slabs at time t equal to 0 and as before, neglecting expansion effects, Q_0 may be calculated from,

from,

$$Q_o = W_i \, G/D_{20}^s \qquad (5.7)$$

where W_i = weight of solution retained by the slabs at the impregnation temperature.

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

D_{20}^s = density of the impregnation solution at 20°C

Comparison of this expression with equation (5.5) shows that they are virtually identical except that the term D_i^w in equation (5.5) is replaced by D_i^s which then cancels out with the similar term in the numerator leaving equation (5.7).

Considering now the expansion of solution from the slabs,

let V = the porous volume of the slabs.

W_d = weight of liquid in the slabs at the desorption temperature.

D_d^s = density of the solution at the desorption temperature.

As before,

$$V = W_i/D_i^s$$

and $$W_d = V\,D_d^s$$

therefore $$W_d = W_i D_d^s/D_i^s$$

The volume of solution remaining in the slabs after expansion will be,

$$\frac{W_d}{D_i^s} = W_i \frac{D_d^s}{(D_i^s)^2}$$

therefore,

$$Q_o = W_i G \frac{D_i^s D_d^s}{(D_i^s)^2 D_{20}^s} \qquad (5.8)$$

The ratio of the two expressions for Q_o may be found from the ratio of equations (5.7) and (5.8),

$$\frac{\text{Eq.(5.7)}}{\text{Eq.(5.8)}} = \frac{D_i^s D_{20}^s}{D_d^s D_{20}^s}$$

$$= D_i^s / D_d^s$$

In the case of the desorption of 3N KCl at 80°C. and impregnation at 15°C.

$$D_i^s / D_d^s = 1.1406/1.1089$$

$$= 1.036$$

thus the correction is about 4% of the figure calculated by the simpler method.

5.3. The calculation of integral diffusion coefficients.

It is apparent from the plot E_d vs. Z (fig. 8) that for values of E_d less than 0.4 the theoretical equation may be written as,

$$\log E_d = m'Z + C' \qquad (5.9)$$

and inspection of the experimental results suggests that for E_d less than 0.4 they too may be expressed as,

$$\log E_d = m''t + C'' \qquad (5.10)$$

Combining equations (5.9) and (5.10) we have,

$$\log \frac{E_{d2}}{E_{d1}} = m'(Z_2 - Z_1)$$

$$= m''(t_2 - t_1)$$

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

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

i.e.,

$$D = \frac{1}{\pi^2} \frac{m''}{m'} \qquad (5.11)$$

By expressing m' and m'' in terms of $\log E_d$, t and Z and substituting in equation (5.11) we have,

have,

$$D = \frac{1}{\pi^2} \frac{Z_2 - Z_1}{t_2 - t_1} \qquad (5.12)$$

As we could have equally well started with log $(1-E_a)$ it follows that equation (5.12) holds for both absorption and desorption.

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

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

In the summary of the study of diffusion in liquids given earlier it has been shown that Eyring's work leads to the assumption of an exponential relationship between D, the diffusion coefficient, and T the absolute temperature,

$$D = \frac{\delta^2}{V_f^{1/3}} \left[\frac{kT}{2\pi m} \right]^{\frac{1}{2}} \exp(-E/RT) \qquad (1.10)$$

Unfortunately, both δ and V_f are functions of T which prevents further simplification of equation (1.10). The normally accepted equation for the correlation of experimental data is that suggested by Taylor (15),

$$D = A \exp(-Q/RT) \qquad (1.13)$$

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

from

$$\log \frac{D_2}{D_1} = -\frac{Q}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \qquad (5.13)$$

The plot was examined for signs of regular curvature indicative of hydrogen bonding affecting the slope of the line but as none was visible it was concluded that the value of Q could also be calculated by the method of least squares, in order that some idea of the limits of accuracy of the correlation could be obtained. It is probable that the variation in the individual values of the diffusion coefficients is of a greater order than the curvature of the plot of D vs. 1/T and consequently no definite conclusions about curvature are possible.

It is reasonable to assume that the measurements of the temperature at which the experiments were carried out were free from error and also that errors arising in the measured diffusion coefficients were independent of the temperature at which the experiments were carried out. For these experimental conditions Paradine and Rivett (55) suggest that for expressions of the form,

$$y = A \exp (Bx)$$

the constants A and B should be calculated from,

$$\Sigma y^2 \log y = \log A \, \Sigma y^2 + B \, \Sigma x y^2 \qquad (5.14)$$

$$\Sigma x y^2 \log y = \log A \, \Sigma x y^2 + B \, \Sigma x^2 y^2 \qquad (5.15)$$

Unfortunately, these equations for the calculation of the constants are not easily applicable to the calculation of the variance of Q. This was done by the more conventional method to gain an approximate figure for the limits of accuracy.

A specimen calculation for the desorption of N KCl from the (2)H.125 slabs completes this section.

5.5. Specimen calculation.

From the theoretical plot of E_d vs. Z it was found that for E_2 equal to 0.4 and E_1 equal to 0.15, that

$$D = \frac{0.03291}{9.870} \times \frac{6.452}{60} \times \frac{1}{t_2 - t_1} \qquad (5.16)$$

where the term 6.452/60 is a conversion factor relating the units in.²/min. to cm.²/sec. The calculated values of D are given in Table 5.5.

Table 5.5. Integral diffusion coefficients for the desorption of N KCl from the (2)H.125 slabs.

$T^\circ C$	$t_2 - t_1$	10^5 D	
20.0	43.10	0.832	0.83
30.0	39.20	0.961	0.96
40.0	30.85	1.162	1.16
50.0	26.75	1.340	1.34
59.9	22.75	1.576	1.58
69.6	19.85	1.806	1.81
80.2	16.80	2.134	2.13

The values of D shown in the third column of Table 5.5 were used to calculate the activation energy Q but for comparison with other results "rounded-off" figures such as are shown in the fourth column were used.

To simplify the statistical calculation y was taken as 10^6 D and x as $10^3/T$; thus it was necessary to multiply the derived value of A by 10^{-6} but those terms containing x were multiplied by 10^{-3} before the completion of the calculation.

Table 5.6 indicates the necessary functions of x and y employed in the derivation of A and Q.

Table 5.6. Statistical calculation of the constants A and Q.

Table 5.6 is shown in two parts, the first containing x, y and log y while the second part gives the derived values of y^2, xy^2, x^2y^2, $y^2\log y$ and $xy^2\log y$.

x	y	log y
3.413	8.32	2.1187
3.300	9.61	2.2628
3.195	11.62	2.4527
3.096	13.40	2.5953
3.004	15.76	2.7575
2.915	18.06	2.8937
2.826	21.34	3.0606

y^2	xy^2	x^2y^2	$y^2\log y$	$xy^2\log y$
69.2224	236.2561	806.3419	146.6615	500.5557
92.3521	304.7619	1005.7144	208.9743	689.6153
135.0244	431.4030	1378.3325	331.1743	1058.1020
179.5600	555.9178	1721.1214	466.0121	1442.7734
248.3776	746.1263	2241.3634	684.9012	2057.4433
326.1636	950.7669	2771.4855	943.8196	2751.2342
455.3956	1286.9480	3636.9149	1393.7838	3938.8329
1506.0957	4512.1800	13561.2740	4175.3285	12438.5568

Therefore

$$10^{-3}\Sigma xy^2 = 4.5121800$$

$$10^{-6}\Sigma x^2y^2 = 0.013561274$$

$$10^{-3}\Sigma xy^2\log y = 12.4385568$$

$$\log A' = \frac{\Sigma y^2\log y\ \Sigma x^2y^2 - \Sigma xy^2\log y\ \Sigma xy^2}{\Sigma y^2\ \Sigma x^2y^2 - (\Sigma xy^2)^2}$$

$$\log A' = \frac{56.6227508 - 56.1250072}{20.4245765 - 20.3597684}$$

$$= 7.6803$$

therefore,

$$A' = 2.165 \times 10^3$$

$$\text{then}\quad \underline{A = 2.165 \times 10^{-3}}$$

Similarly,

$$-Q/R = \frac{\Sigma y^2\ \Sigma xy^2\log y - \Sigma xy^2\ \Sigma y^2\log y}{\Sigma y^2\ \Sigma x^2y^2 - (\Sigma xy^2)^2}$$

$$= -106.1692/0.0648081$$

$$Q = 3255 \text{ cals.}$$

the values of activation energies are generally expressed in kcal, i.e.,

$$\underline{Q = 3.26 \text{ kcal}}$$

These calculations have been carried out to a greater number of significant figures than is justified by the accuracy of the experimental results but it was found that a lesser number of figures introduced errors due to rounding off such products as xy^2 to the appropriate number of places.

6. EXPERIMENTAL RESULTS.

6.1 Introduction.

It is convenient to consider the experimental results in two sections,

(a) the results for the preliminary series of experiments with slabs whose thickness was 0.1 inches (0.25 cm.), and,

(b) the results for the more detailed study of the processes of absorption and desorption with slabs of double this thickness i.e. 0.2 ins. (0.5 cm.).

The preliminary tests of the experimental technique consisted of desorption experiments with the (1)H.125 and (1)CF.6 grades of material using N and 3N KCl as solutes. These experiments revealed that values of E_d toward the end of the extraction process, i.e., $E_d < 0.2$, showed much more variations than those in the range $0.4 > E_d > 0.2$. This was particularly true of the desorption of N KCl.

This lack of accuracy was undoubtedly a result of the comparatively small weight of solute retained by these slabs after impregnation, e.g. impregnation of the (1)CF.6 slabs with N KCl gave 150 milligrams of solute before extraction. Consequently it was not unusual to find that for values of

$E_d < 0.2$, the weight of unextracted solute was about 20 mg. This value is derived from four separate weighings and thus if the accuracy of the balance is ± 0.2 mg. and it is assumed that there are no other errors in the experimental technique resulting in losses in weight of the slabs, e.g. minor abrasions of the slabs etc., then the greatest accuracy which may be expected is ± 0.8 mg. or about ± 4%.

The obvious way by which the accuracy of the experiments may be improved is to increase the weight of solute retained by the slabs after impregnation. When the preliminary series of experiments had been completed it was decided, therefore, to continue the experiments with slabs of a greater thickness. There are, however, two factors which limit the extent to which the thickness may be increased,

(a) as the thickness is increased the range of values of E_d for which the theoretical equation may be regarded as linear decreases, and,

(b) the time taken for a solute to be absorbed or desorbed is a function of the square of the thickness and consequently if the thickness is too great the duration of the experiments becomes inconveniently long. In fact, some of the experiments with sucrose took 10 hours to complete, necessitating a large quantity of distilled water if the flow rate is to be maintained at 10-12 litres per hour.

It was decided to increase the thickness of the slabs to about 0.2 ins. (0.5 cm.). This extended the duration of the experiments by a factor of 4 and gave a theoretical equation which could still be regarded as linear for values of $E_d < 0.4$.

Plots of the experimental results are given but only the derived integral diffusion coefficients are given in sections 6.2 and 6.3. The detailed experimental results from which the plots of E_d and $1-E_a$ vs. t were prepared are given in Appendix B.

6.2. Results for the desorption of KCl from (1)H.125 and (1)CF.6 slabs.

The experimental plots of E_d vs. t are given in Figs. 9 - 12 and the corresponding plots of D vs. 1/T in Fig. 13. The derived integral values of D are given in Table 6.1.

Table 6.1. Integral values of D for the (1)H.125 and (1)CF.6 slabs.

T°C.	10^5D-(1)H.125		10^5D-(1)CF.6	
	N KCl	3N KCl	N KCl	3N KCl
20	0.86	0.85	0.55	0.52
30	0.99	1.02	0.67	0.64
40	1.25	1.25	0.77	0.73
50	1.45	1.49	0.89	0.90
60	1.68	1.74	1.04	1.05
70	1.91	2.00	1.23	1.22
80	2.20	2.23	1.41	1.40

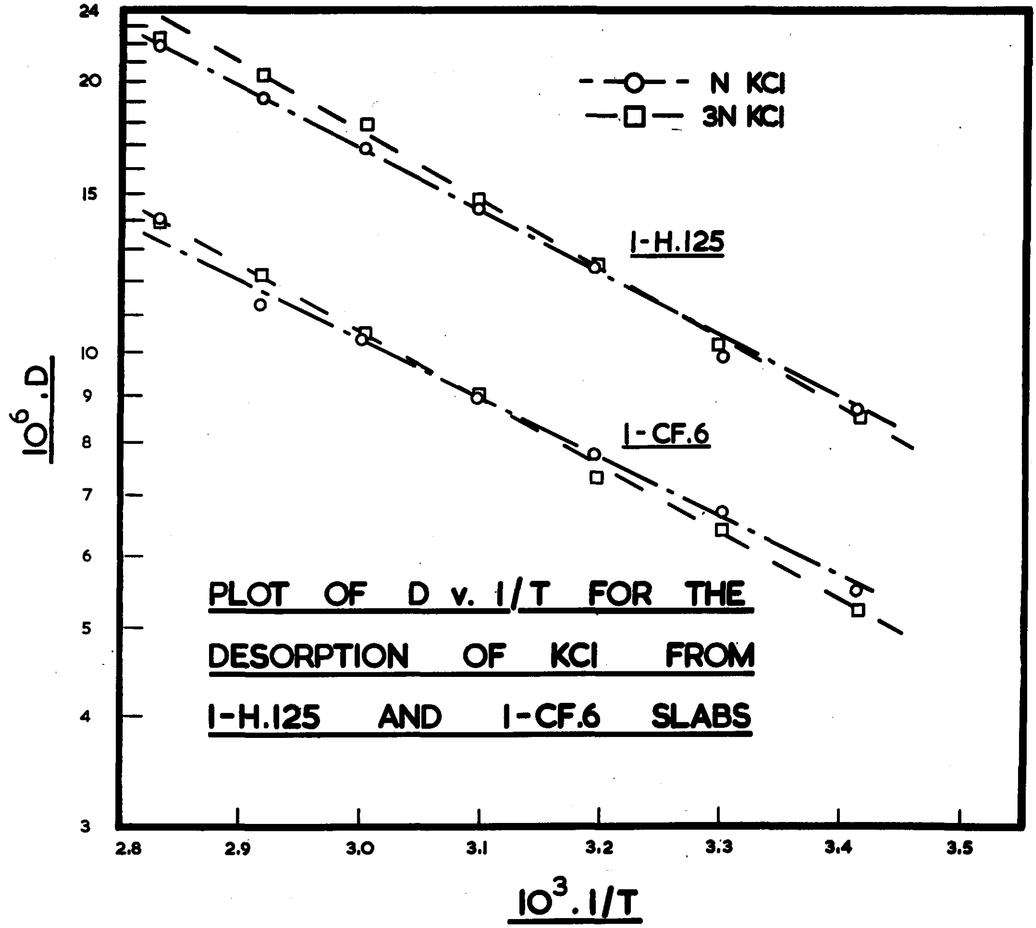

N KCl
3N KCl
1-H.125
1-CF.6
PLOT OF D v. 1/T FOR THE DESORPTION OF KCl FROM 1-H.125 AND 1-CF.6 SLABS
24
20
15
10
9
8
7
6
5
4
3
2.8
2.9
3.0
3.1
3.2
3.3
3.4
3.5
$10^6 . D$
$10^3 . 1/T$

FIG. 13

Table 6.2 gives the calculated constants A and Q in the equation

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

Table 6.2. Calculated values of A and Q.

Solute	10^3 A		Q kcal/mol.	
	(1)H.125	(1)CF.6	(1)H.125	(1)CF.6
N KCl	2.22	1.51	3.23	3.28
3N KCl	2.54	1.81	3.33	3.41

6.3. Results for the absorption and desorption of KCl and sucrose for the (2)H.125 and (2)B.5 slabs.

As has been stated earlier the B.5 grade of material was used as a substitute for the CF.6 grade, the production of which had been discontinued in the interval between the preparation of the slabs of 0.1 ins. thickness and the decision to use slabs of 0.2 ins. thickness.

Figs. 14 - 17 give the experimental results for the absorption and desorption of N and 3N KCl for the (2)H.125 slabs. Fig. 18 is the semi-log. plot of the derived values of D vs. 1/T. Figs. 19 - 23 give the corresponding results for the (2)B.5 slabs. Tables 6.3 and 6.5 show the derived values of D and Tables 6.4 and 6.6 the calculated values of A and Q.

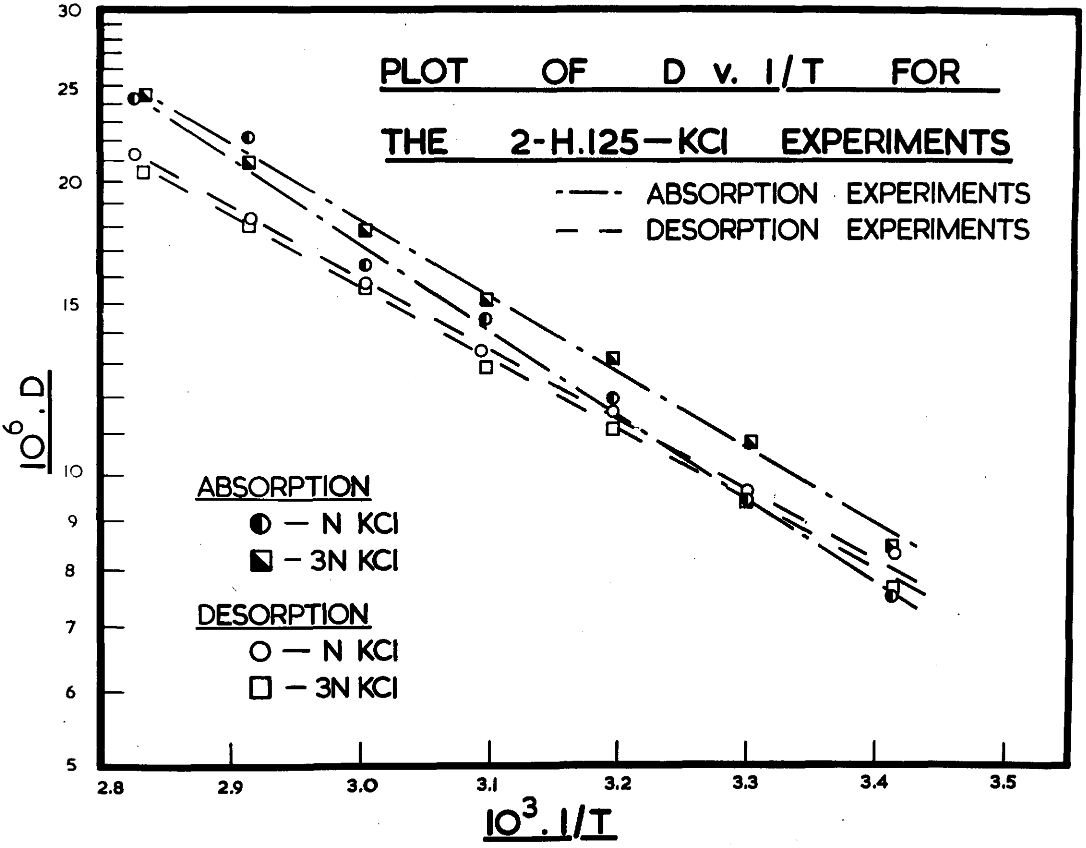

PLOT OF D v. 1/T FOR THE 2-H.125—KCl EXPERIMENTS
-·-·- ABSORPTION EXPERIMENTS
— — DESORPTION EXPERIMENTS
ABSORPTION
◐ — N KCl
◩ — 3N KCl
DESORPTION
○ — N KCl
□ — 3N KCl
$10^6 . D$
30
25
20
15
10
9
8
7
6
5
2.8
2.9
3.0
3.1
3.2
3.3
3.4
3.5
$10^3 . 1/T$

FIG. 18

Table 6.3. Integral values of D for the (2)H.125 slabs.

T°C.	10^5D - absorption		10^5D - desorption	
	N KCl	3N KCl	N KCl	3N KCl
20	0.75	0.85	0.83	0.77
30	0.94	1.08	0.96	0.94
40	1.19	1.31	1.16	1.12
50	1.45	1.51	1.34	1.29
60	1.69	1.79	1.58	1.56
70	2.22	2.09	1.81	1.83
80	2.42	2.44	2.13	2.04

Table 6.4. Calculated values of A and Q for the (2)H.125 slabs.

Solute	Absorption		Desorption	
	10^3 A	Q kcal/m	10^3 A	Q kcal/m
N KCl	7.56	4.02	2.17	3.26
3N KCl	3.63	3.51	2.55	3.38

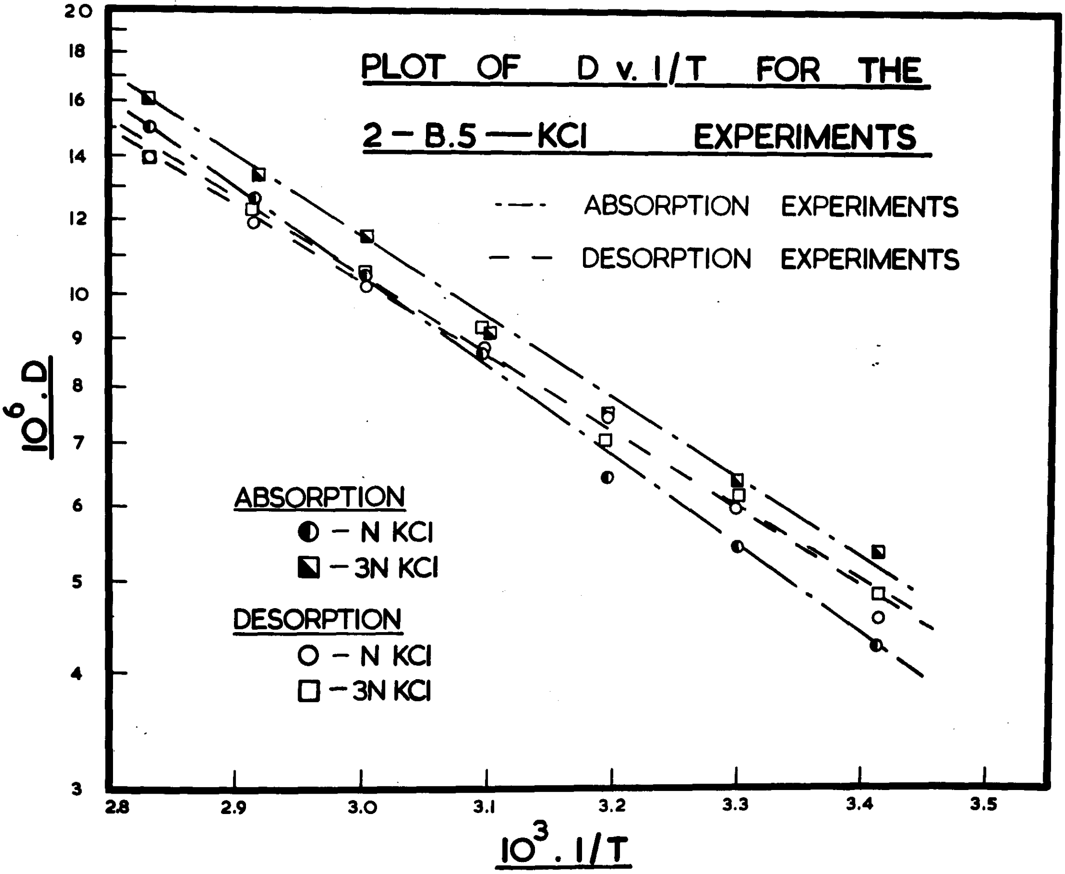

PLOT OF D v. 1/T FOR THE
2 – B.5 —KCl EXPERIMENTS
-·-·- ABSORPTION EXPERIMENTS
– – DESORPTION EXPERIMENTS
ABSORPTION
◐ – N KCl
◪ – 3N KCl
DESORPTION
○ – N KCl
□ – 3N KCl
10^6. D
20
18
16
14
12
10
9
8
7
6
5
4
3
2.8
2.9
3.0
3.1
3.2
3.3
3.4
3.5
10^3. 1/T

FIG. 23

Table 6.5. Integral values of D for the (2)B.5 slabs.

$T^{o}C.$	$10^{5}D$ - absorption		$10^{5}D$ - desorption	
	N KCl	3N KCl	N KCl	3N KCl
20	0.43	0.54	0.46	0.49
30	0.54	0.64	0.60	0.61
40	0.74	0.75	0.74	0.75
50	0.87	0.92	0.88	0.93
60	1.05	1.17	1.02	1.06
70	1.27	1.34	1.19	1.23
80	1.51	1.61	1.39	1.39

Table 6.6. Calculated values of A and Q for the (2)B.5 slabs.

Solute	Absorption		Desorption	
	10^{3} A	Q kcal/m	10^{3} A	Q kcal/m
N KCl	5.98	4.20	2.41	3.61
3N KCl	4.36	3.93	2.05	3.49

Figs. 24 - 27 give the experimental results for the absorption and desorption of 0.3M and M sucrose for the (2)H.125 slabs. Fig. 28 is the semi-log. plot of the derived values of D <u>vs.</u> 1/T. Figs. 29 - 33 give the corresponding results for the (2)B.5 slabs.

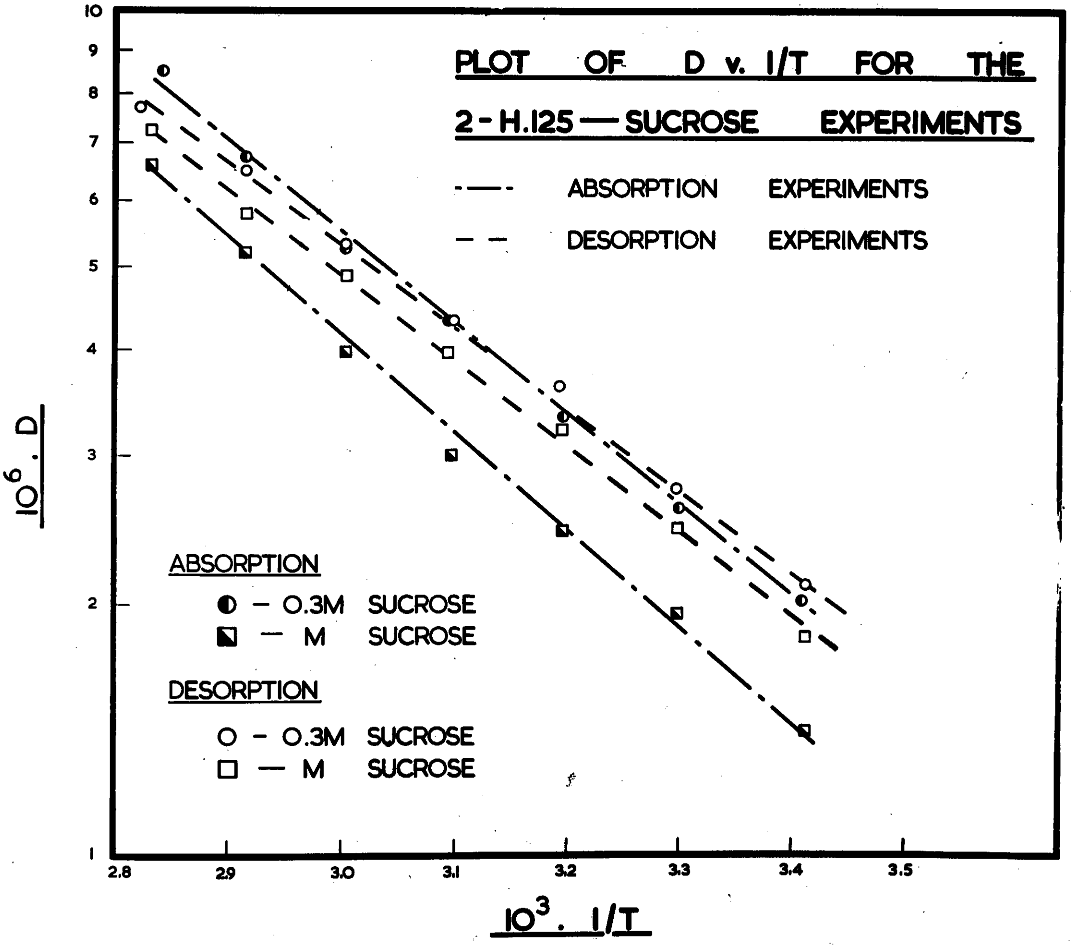

PLOT OF D v. 1/T FOR THE
2-H.125 — SUCROSE EXPERIMENTS
-·-·- ABSORPTION EXPERIMENTS
- - DESORPTION EXPERIMENTS
ABSORPTION
◐ – 0.3M SUCROSE
◪ — M SUCROSE
DESORPTION
○ – 0.3M SUCROSE
□ — M SUCROSE
$10^6 . D$
10
9
8
7
6
5
4
3
2
1
2.8
2.9
3.0
3.1
3.2
3.3
3.4
3.5
$10^3 . 1/T$

FIG. 28

Tables 6.7 and 6.9 illustrate the derived integral values for the diffusion coefficient and Tables 6.8 and 6.10 the calculated values of A and Q.

Table 6.7. Integral values of D for the (2)H.125 slabs.

T°C.	10^5D - absorption		10^5D - desorption	
	0.3M Suc.	M Suc.	0.3M Suc.	M Suc.
20	0.201	0.141	0.210	0.183
30	0.259	0.194	0.273	0.246
40	0.332	0.244	0.361	0.322
50	0.431	0.300	0.433	0.397
60	0.529	0.396	0.530	0.486
70	0.671	0.517	0.647	0.576
80	0.818	0.658	0.766	0.720

Table 6.8. Calculated values of A and Q for the (2)H.125 slabs.

Solute	Absorption		Desorption	
	10^3 A	Q kcal/m	10^3 A	Q kcal/m
0.3M Suc.	11.8	5.09	3.64	4.32
M Suc.	14.3	5.40	4.17	4.48

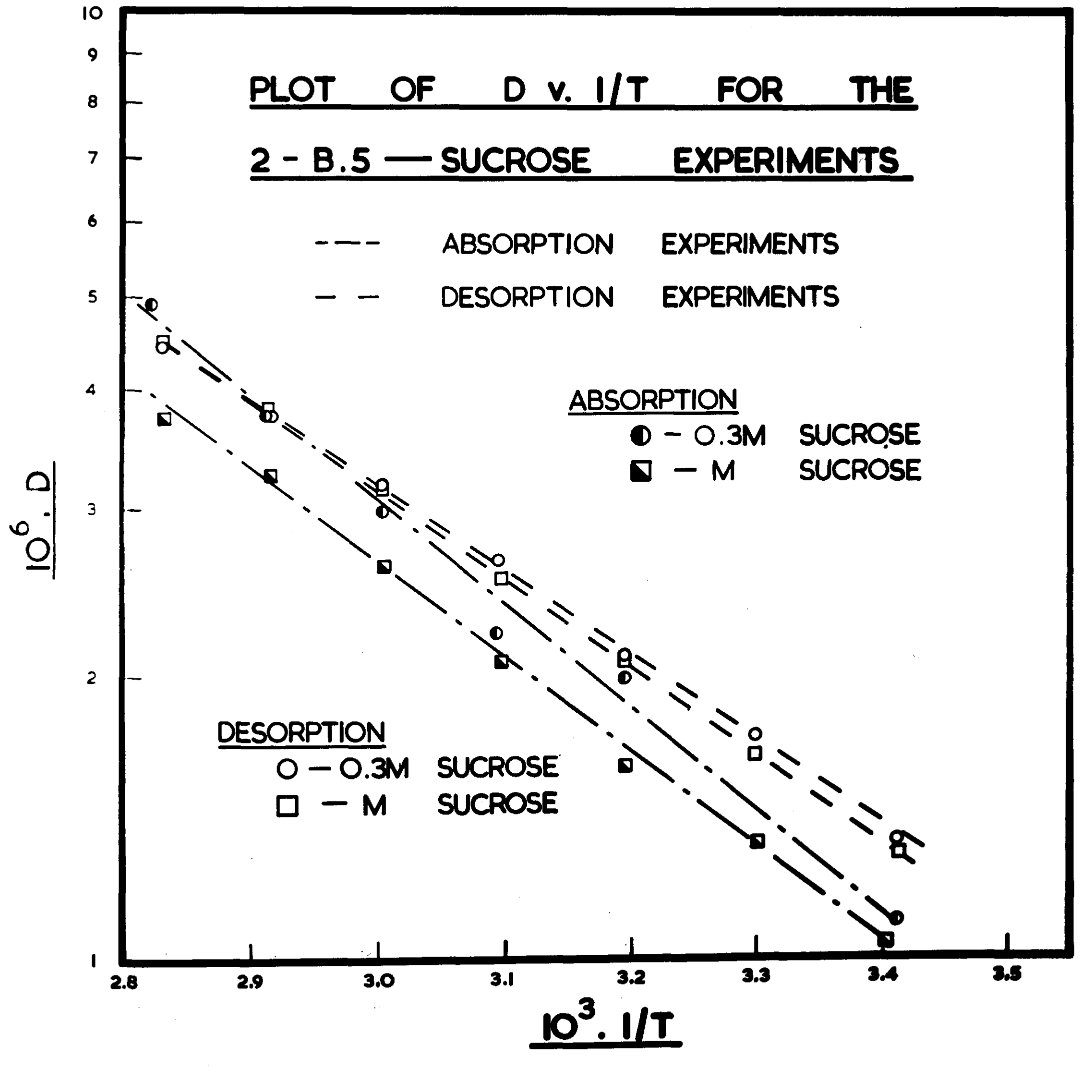

PLOT OF D v. I/T FOR THE
2 - B.5 — SUCROSE EXPERIMENTS
---- ABSORPTION EXPERIMENTS
— — DESORPTION EXPERIMENTS
ABSORPTION
◐ – 0.3M SUCROSE
◩ – M SUCROSE
DESORPTION
○ – 0.3M SUCROSE
□ – M SUCROSE
10
9
8
7
6
5
4
3
2
1
$10^6 . D$
2.8
2.9
3.0
3.1
3.2
3.3
3.4
3.5
$10^3 . 1/T$

FIG. 33

Table 6.9. Integral values of D for the (2)B.5 slabs.

T °C.	10^5D - absorption		10^5D - desorption	
	0.3M Suc.	M Suc.	0.3M Suc	M Suc.
20	0.119	0.104	0.133	0.130
30	0.172	0.133	0.172	0.165
40	0.198	0.161	0.210	0.209
50	0.253	0.207	0.265	0.253
60	0.299	0.261	0.317	0.316
70	0.377	0.326	0.377	0.350
80	0.491	0.373	0.443	0.450

Table 6.10. Calculated values of A and Q for the (2)B.5 slabs.

Solute	Absorption		Desorption	
	10^3 A	Q kcal/m	10^3 A	Q kcal/m
0.3M Suc.	3.73	4.69	1.41	4.04
M Suc.	2.44	4.53	1.99	4.27

7. DISCUSSION OF THE EXPERIMENTAL RESULTS.

Before attempting to interpret the significance of the experimental results, there are one or two general aspects which may be considered.

7.1. The Consistency of the Results.

In the course of the experimental programme two principal types were observed:-

TYPE 1: Absorption or desorption curves which, although themselves quite regular, gave lines whose slopes were inconsistent with those of the others of that group.

e.g. in fig. 29, the results for the desorption of the 0.3M sucrose, the extraction curve for 40°C. suggests that the desorption of sucrose has taken place more slowly than would have been expected. This is confirmed by examination of the corresponding plot of D vs. 1/T in fig. 33.

TYPE 2: Experimental results whose spread was such as to prevent any reliable estimate being made of the slope of the absorption or desorption curve.

A series of duplicate experiments revealed, as would be expected, some variation in the points towards the end of the desorption (or absorption) process. It is thought that experimental errors of this type were responsible for anomalous results of type (1) and it was decided, therefore, not to repeat experiments exhibiting this type of error since the results as reported give an indication of the consistency of the results to be expected from this experimental technique. In the case of errors of type (2) examination of the weights of the slabs before and after impregnation suggested that either the slabs had not been fully impregnated or more frequently that the residual solute had not been completely extracted after the previous experiment. Duplicate experiments were carried out for results indicating this type of error but when the probable causes were recognized and precautions taken to avoid them, the need for duplicate experiments was considerably reduced.

7.2. The Comparative Accuracy of Absorption and Desorption Experiments.

Examination of the experimental results indicates that the spread of the results for absorption experiments is invariably greater than for the corresponding desorption experiments. It is thought that this is almost certainly due to the experimental technique itself. In each experiment, whether absorption or desorption, the surfaces of the slabs must be wiped

1) after removal from the impregnation chamber and,
2) after removal from the diffusion cell,

with a cloth saturated in the appropriate liquid. The importance of these operations is not, however, the same in the two processes. Consideration of the desorption experiments shows that the second wiping, i.e. that after leaving the diffusion cell, is of negligible importance as the concentration of solute in the liquid at the slab surfaces is extremely small and the solute is practically distilled water and consequently as the slabs are to be oven dried it does not matter whether what is to all intents and purposes solute free liquid, is removed from or deposited on the surfaces of the slabs. The wiping of the slabs after impregnation is more important but even this may probably be neglected as the solute at the slab surface is removed practically instantaneously and consequently the removal or addition of a thin film of solution will have little effect on the overall extraction time.

Considering now absorption experiments, it is at once apparent that by similar reasoning the effect of wiping after impregnation is also probably of little importance; but that the most important operation is the wiping after the removal of the slabs from the diffusion cell. Here it is obvious that any liquid film will consist of solution at the experimental solute concentration and that even a film of the order of one ten-thousandth of an inch thickness (0.0025 mm.) will introduce an appreciable error.

e.g. in the absorption of molar sucrose the amount of solute absorbed after infinite time would be about 1000 mg. The surface area of a group of slabs is 8.75 ins.^{2} (56.3 cm.^{2}) and thus the presence of a film of 0.0001 inches thickness will result in the addition of 1.43×10^{-2}cc. of solution to the surfaces of the slabs. This is equivalent to about 5 mg. of solute and although this is small compared with the amount of solute absorbed (between 600 - 900mg.) it must be remembered that it is $1 - E_a$ which is being plotted. Consequently, if $E_a = 0.850$, an additional 5 mg. of solute reduces $1 - E_a$ from 0.150 to 0.145 - a significant error on one cycle semi-log paper. Thus the results for absorption will always tend to be less accurate than the corresponding desorption experiments.

7.3. The Significance of the Experimental Results.

In attempting to establish the relative importance of the factors contributing to the rate at which a solute was absorbed or desorbed, it was found that solute concentration and temperature could not be considered independently and it was decided therefore to divide the discussion into three main sections:-

1) the effect of the physical properties of the solute on the diffusion process,

2) the effect of the physical properties of porous medium from which or into which mass transfer was taking place, and
3) consideration of possible explanations for the disagreement between the results for absorption and desorption.

7.3.1. The Effect of the Physical Properties of the Solute.

(a) Desorption Experiments:

The experimental results for the desorption runs suggest that the rate of desorption is substantially independent of the initial solute concentration. Examination of the results for KCl (figs. 18 and 23) shows that the plot of D *vs.* 1/T for N and 3N solutions lie very close together. For sucrose, however, the results for the two different types of slab do not agree. Those for the (2)B.5 slabs (fig. 33) are similar to the results for KCl, but there is a marked difference in the rates at which 0.3M and M solutions are desorbed from the (2)H.125 slabs. It is thought, therefore, that this may be attributable to the effect of the solid structure rather than to the properties of the solute.

Thus the results for desorption are in agreement with the experimental results reported by Piret, Ebel, Kiang and Armstrong (37).

Concentration appears to have little effect on the activation energies for desorption. Unfortunately, the method suggested by Paradine and Rivett (55) for the statistical determination of the constants in the equation of the form,

$$y = A \exp (Bx)$$

cannot be readily extended to the calculation of the limits of accuracy of the constants. In order to gain some knowledge of this, limits were calculated from the conventional "least squares" method. The values obtained by this method were of the order of ± 0.05 to ± 0.1 kcal. and it is reasonable to assume that this gives some indication of the accuracy of the constants derived by the more complex method.

Thus the differences between the activation energies for the two concentrations is of the order of the expected experimental error. Consequently there is no evidence that solute concentration has any influence on the activation energy though in the case of KCl the fact that in five out of six series of experiments (including the results of the preliminary tests) the activation energies for 3N solutions are greater than those for N solutions seems to suggest that a small difference does exist. It follows, of course, that if the rate of desorption is independent of solute concentration then the activation energy must also be independent of concentration.

It is difficult to obtain activation energies for diffusion in free solution with which to compare those calculated from the experimental results, but the following values were estimated from the available integral diffusion coefficients,

KCl Q = 3.6 kcal/mole
Sucrose Q = 4.6 kcal/mole

It must be emphasized that these values were calculated over a smaller temperature range (10 - 40°C.) than those of the experimental results (20 - 80°C.) If these values of Q are correct, then it follows that the activation energies for the desorption process are smaller than those for diffusion in free solution.

(b) Absorption Experiments:

The experimental results indicate that the solute concentration is of importance in determining the rate at which a solute will be absorbed. It is of interest that for more concentrated solutions its effect is as predicted by Crank and Henry (39). In the case of KCl where the differential diffusivity after passing through a minimum, increases with increasing concentration, the absorption of 3N solutions takes place more quickly than the corresponding desorption process. N KCl solutions are not always absorbed more readily than desorbed; in this case temperature appears to be the controlling factor. The results for sucrose where the differential diffusivity decreases with increasing concentration indicate that M solutions are desorbed more readily than absorbed, but once again temperature appears to control the relative rates of absorption and desorption for the more dilute solutions.

The concentration also appears to influence the magnitude of the activation energy. In most cases the activation energies for the more dilute solutions are greater than those for the more concentrated, the differences being such as to preclude their being attributed to experimental error. The exception is the absorption of M sucrose by the (2)H.125 slabs, but as the results for this series of experiments differ in so many aspects from the results for the others and it is thought that the porous solid must exert an important influence on this series of experiments.

It is also apparent that the activation energies for absorption are greater than those for diffusion in free solution but not so much greater as those reported by Christensen (19).

7.3.2. The Effect of the Physical Properties of the Porous Solid.

It has been previously suggested (50)(37) that one of the effects of the solid structure on the diffusion process would be to increase the distance which must be travelled by a diffusing particle. Consequently the ratio of the diffusion coefficient in free solution to that for diffusion in a slab should be constant. This ratio has been defined as K^2 where K is the ratio of the distance travelled by a diffusing particle to the apparent distance as suggested by the dimensions of the solid structure.

Estimating the integral diffusion coefficients for free solution as 1.60 and 1.73 x 10^{-5} for N and 3N KCl and 0.46 x 10^{-5} for 0.3M and M sucrose, the values of K^2 have been calculated for the desorption and absorption of KCl and sucrose at 20°C. These values are given in Tables 7.1 and 7.2 respectively.

Table 7.1. - Values of K^2 for Desorption at 20°C.

Solute	K^2 - (2)H.125		K^2 - (2)B.5	
	Obs.	Calc.	Obs.	Calc.
N KCl	1.93	2.00	3.48	3.26
3N KCl	2.24	2.24	3.53	3.49
0.3M Sucrose	2.19	2.11	3.46	3.36
M Sucrose	2.51	2.42	3.54	3.54

Table 7.2. - Values of K^2 for Absorption at 20°C.

Solute	K^2 - (2)H.125		K^2 - (2)B.5	
	Obs.	Calc.	Obs.	Calc.
N KCl	2.13	2.10	3.72	3.64
3N KCl	1.99	2.03	3.20	3.39
0.3M Sucrose	2.29	2.42	3.86	3.86
M Sucrose	3.40	3.26	4.48	4.42

The values in the "observed" columns are based on the experimental diffusion coefficients and those in the "calculated" columns, on the smoothed values recalculated from the derived equations relating D and T. It is impossible to interpret the values of K^2 for absorption as the solute concentration appears to be the controlling factor, and any differences existing in K^2 are completely obscured by the variation of D with concentration. For desorption, however, where solute concentration appears to have little influence, comparison of the values of K^2 for N KCl and M sucrose indicates that K^2 for sucrose is greater than that for KCl. This is true for both types of slab but its difference is more marked for the (2)H.125 slabs,

i.e. for (2)H.125 $K^2_{\text{sucrose}}/K^2_{\text{KCl}} = 1.21$

(2)B.5 $K^2_{\text{sucrose}}/K^2_{\text{KCl}} = 1.09$

These ratios have been calculated using smoothed values of D. If the experimental results are used, the ratios become 1.30 and 1.02 respectively. This suggests that the relative dimensions of the slab pores and solute molecules may be of considerable importance in determining the rate at which the solute diffuses through the slab. It is true that the mean pore size of the (2)H.125 slabs is one micron (as determined by B.S.S. 1969), which is many times larger than even the sucrose molecules, but an appreciable number of the pores must be very much smaller than this. It is of interest to note that in the only other comparative experiments of absorption and desorption in porous media, no differences were observed in the rate at which the two processes took place. The significant difference between these experiments carried out by Wall, Grieger and Childers (38) and those described here lies in the method of introducing the solute to the slabs. Wall et al. prepared their frits by allowing them to stand in the appropriate solution, initially for a week and thereafter for one day, as it was found that the frits reached constant weight after one week during the initial "filling" period and that after this one day was sufficient to bring them into equilibrium with the solution.

When an attempt was made to impregnate the (2)H.125 slabs by this method, it was found, that as reported by Wall et al., little increase in weight was observed after two or three days but that even after a week the amount of solution absorbed was only 75% of that absorbed during impregnation under vacuum.

In view of this and the difference in the values of K^2 for sucrose and KCl, it must be concluded that a substantial number of the pores are of such dimensions as to restrict diffusion by frictional resistances or by the reflection of solute molecules from the solid walls.

7.3.3. Possible Explanations for the Dissimilarities in Absorption and Desorption Experiments.

Consideration of the experimental results for absorption and desorption indicates that the two processes are affected differently by solute concentration and temperature. Essentially the difference is that the rate of desorption and the corresponding activation energy are substantially independent of solute concentration and temperature, whereas both the rate of absorption and the activation energy seem to vary markedly with concentration and temperature.

For desorption, on which rather more experimental work has been done, Boucher, Brier and Osburn (32) have shown that the resistance to diffusion of the liquid film at the slab surface is of small importance compared with the resistance of the carrier material itself. Various authors have suggested that besides increasing the length of path followed by diffusing molecules, the solid structure may also be responsible for other resistances to diffusion such as anomalous solvent viscosity effects and collisions between the diffusing particles and the pore walls. In these circumstances, it is perhaps reasonable to assume that the effect of solute concentration may be small. Also, as the number of diffusing particles affected by their proximity to the pore walls will increase with increasing temperature, the plots of D vs. 1/T for diffusion in free solution and desorption should always diverge as T increases. Consequently, the slope of the plot and hence the activation energy will always be less for desorption than for diffusion in free solution.

If the effects of temperature and concentration on the desorption process are a consequence of the diffusion process being controlled by the slab resistance, then consideration of the effects of concentration and temperature on the absorption process suggests that the resistances to mass transfer in the two processes are not identical. Christensen (19) has suggested that a possible explanation of activation energies greater than those for diffusion in free solution, is the existence of energy barriers within the porous structure of the solid, which oppose diffusion. The activation energies obtained for the desorption experiments do not altogether support this theory, as it implies that there are resistances to diffusion in one direction but not in the other.

One alternative explanation is that in the absorption of a solute the liquid film resistance at the slab surface may be of more importance. In desorption experiments, the diffusing particles are constrained to travel in the direction of the concentration gradient. In absorption experiments, however, the solute molecules may also travel in the direction of the bulk flow of the solution thus reducing the driving force causing mass transfer. If the liquid film resistance is the controlling factor, then solute concentration would assume at least the same importance as for diffusion in free solution while temperature would be also important as the thickness of the interface film would decrease with decreasing viscosity.

If these explanations are correct, it would be reasonable to expect that:

a) for desorption, activation energies would decrease with decreasing pore size, i.e. for any given solute the activation energy for the (2)H.125 slabs would be less than that for the (2)B.5 slabs,

b) for absorption, the film resistance would be dependent, to some extent, on the roughness of the slab surface. As the (2)B.5 material was considerably rougher than the (2)H.125, greater activation energies would be expected for slabs of the former material, and,

c) if, at higher temperatures, the film resistance becomes negligible, then the difference between the rates of absorption and desorption will decrease with increasing temperature, but diffusion coefficients for absorption should never exceed those for desorption.

It is apparent that (a) and (b) suggest that activation energies for diffusion into or from the (2)B.5 slabs should always be greater than the corresponding values for the (2)H.125 slabs. The experimental results for KCl are in agreement with this, but the activation energies for the experiments with sucrose invariably show a converse trend. Examination of the results also indicates that they are in complete disagreement with the hypothesis expressed in (c). Thus the experimental evidence only partially supports the premise of the film resistance being the controlling factor in absorption experiments.

An alternative explanation for the dissimilar results for the two processes may be found in the essential difference between the experimental techniques employed in preparing the slabs for immersion in the diffusion cell. In desorption experiments, the slabs are impregnated under vacuum and thus the solute is forced into the pores of the solid, while in absorption experiments, the slabs are only impregnated with distilled water, the solute having to diffuse into the pores from the circulating solution. The results reported by Wall, Grieger and Childers (38) have already been discussed (P.20), and as Wall *et al.* report identical rates of absorption and desorption, for what are probably only partially impregnated porous solids, it may be concluded that the differences in the ratio of absorption and desorption observed in the present work are caused by the effect of the smaller pores on the diffusion process, i.e. diffusion into small pores may not take place as readily as diffusion from pores into which a solute has been forced.

Another factor which may influence the relative rate of absorption and desorption, is the rate at which the slabs reach the operating temperature. The attempt made to calculate this depends upon the assumption that the slab is a rectangular parallelepiped and, consequently, the time taken will be a simple function of the dimensions of the slab. In fact, however, in a similar manner to diffusion, the conduction of heat also will follow a tortuous path and furthermore, should heat transfer take place from the solid structure to the impregnated liquid, then liquid film resistances between the pore walls and the liquid may assume considerable importance. Thus absorption at higher temperatures, where the solute is already at the operating temperature, may take place more rapidly than desorption where the solute is initially at approximately 20°C. It is doubtful, however, whether this would account wholly for the differences in the ratio of absorption and desorption shown by the experimental results.

8. CONCLUSIONS.

It may be concluded that the rates of desorption from and absorption into porous materials will depend upon the physical properties of the solute and the size and distribution of the pores within the solid.

Generally, it may be expected that the rate of desorption will be almost independent of solute concentration but that the rate of absorption will not. Similarly the effects of temperature will also be dissimilar. In absorption, it will largely depend upon solute concentration but it will, in any case, result in activation energies larger than that for diffusion in free solution, whereas in desorption the effect of temperature will probably be substantially independent of concentration but will result in activation energies less than that for diffusion in free solution.

The reasons for these dissimilarities would appear to be so complex as to render very difficult the prediction of the relative rates of absorption and desorption.

APPENDIX A.

The solutions of the theoretical equation for diffusion necessary for the calculation of integral diffusion coefficient from the experimental results.

A.1. Preliminary experiments with (1) H.125 and (1) CF.6 slabs.

The mean values of the thickness a, width b, and length c in inches, are given in Table A.1.

Table A.1. Dimensions of the (1) H.125 and (1) CF.6 slabs used in the preliminary experiments.

Material	a	b	c
(1) H.125	0.0996	0.792	1.354
(1) CF.6	0.0990	0.760	1.374

Table A.2.

Z	$E_{H.125}$	$E_{CF.6}$
0.001	0.687	0.686
0.002	0.601	0.600
0.004	0.477	0.476
0.006	0.386	0.384
0.008	0.309	0.307
0.010	0.250	0.247
0.015	0.146	0.144

A.2. Experiments with the (2) H.125 and (2) B.5 Slabs.

The mean values of a, b, and c are given in Table A.3.

Table A.3. Dimenions of the (2) E.125 and (2) B.5 Slabs.

Material	a	b	c
(2)H.125	0.1979	0.756	1.373
(2) B.5	0.1980	0.754	1.490

Table A.4.

Z	E	
	(2)H.125	(2) B.5
0.001	0.775	0.775
0.002	0.734	0.736
0.004	0.669	0.671
0.006	0.616	0.618
0.010	0.533	0.536
0.020	0.385	0.389
0.030	0.284	0.287
0.040	0.210	0.213
0.050	0.157	0.159

APPENDIX B.

Appendix B illustrates a specimen calculation sheet, shown in Table B.1, (on the following page) and explains the various steps in the calculation of the values of E_d and $1 - E_a$.

The results for the individual groups of slabs are indicated by the reference letters A to G.

Column (1).

This gives the weights of the aluminium containers plus slabs, then the weight of the containers alone, and consequently by subtraction the weights of the slabs prior to impregnation.

Column (2).

This gives the combined weights of the containers together with their associated slabs following impregnation with distilled water. Hence the weights of the impregnated slabs.

Column (3).

This gives the weights of the containers plus the slabs after oven drying for 12 - 16 hours, then the individual weights of the containers. Hence the weights of the slabs plus absorbed sucrose.

Table B.1. A specimen calculation sheet.

Date:- 4/4/55. Test Series: Absorption 0.3M Sucrose by (2)H.125 slabs.

Impregnation pressure: 0.15mm. Hg. Impregnation temperature: 17°C.

Operating temperature: 50.2°C.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
A	25.0516 9.0656 15.9860	29.3618 9.0678 20.2940	25.4308 9.0657 16.3651	4.3080	454.8	379.1	0.834	0.166	140
B	25.2622 9.0653 16.1969	29.5297 9.0664 20.4633	25.6118 9.0655 16.5463	4.1950	442.9	349.4	0.789	0.211	110
C	25.3374 9.0691 16.2683	29.6917 9.0699 20.6218	25.5758 9.0683 16.5075	4.3535	459.6	239.2	0.520	0.480	40
D	25.2329 9.0640 16.1689	29.5810 9.0678 20.5132	25.5084 9.0636 16.4458	4.3443	458.6	276.9	0.604	0.396	55
E	25.0498 9.0696 15.9802	29.3595 9.0712 20.2883	25.3480 9.0705 16.2775	4.3081	454.8	297.3	0.654	0.346	70
F	25.4232 9.0580 16.3652	29.7764 9.0612 20.7152	25.7961 9.0577 16.7384	4.3500	459.2	373.2	0.813	0.187	125
G	25.2750 9.0674 16.2076	29.6376 9.0676 20.5700	25.6145 9.0676 16.5469	4.3624	460.5	339.3	0.737	0.263	95

(a) KCl Estimations.

Cell resistance.

(1) = ohms.
(2) = ohms.
(3) = ohms.
mean = ohms.

concentration =

(b) Sucrose Estimations.

Polarimeter readings.

(1) = 13.80°
(2) = 13.79°
(3) = 13.80°
(4) = 13.82°
(5) = 13.80°
mean = 13.80°

concentration = 103.759 gm.

Column (4).

Column (4) is derived from the subtraction of the results in numbers (1) and (2) and is a measure of the weight of water retained by the slabs after impregnation.

In Columns (1) - (4) the weights are measured in grams.

Column (5).

This represents the calculated values of Q_{∞} in milligrams, the calculation being carried out as outlined in Section 5.2.2.1.

Column (6).

Column (3) less Column (1) gives the weights of sucrose absorbed by the slabs, i.e. Q_a in milligrams.

Column (7).

This gives the value of the ratio of Q_a/Q_{∞} previously defined as E_a and is, of course, Column (6) divided by Column (5).

Column (8).

The actual figure required for the experimental plot is $1 - E_a$ and these values are given in Column (8).

Column (9).

This gives the period of time, in minutes, for which the various slabs were immersed in the solution being circulated.

The calculation sheets for desorption experiments were basically similar to these for absorption experiments, the only difference being in the different methods used for calculating the various values of Q_d.

APPENDIX C. EXPERIMENTAL VALUES OF E_d AND $1 - E_a$.

C.1. Preliminary Experiments with (1)H.125 and (1)CF.6 Slabs.

C.1.1. Desorption of N KCl from (1)H.125 Slabs.

T = 20.2°C.	t	2.5	5.0	7.5	10.0	12.5	17.5	22.5
	E_d	0.664	0.534	0.420	0.354	0.281	0.185	0.125
T = 30.0°C.	t	2.5	5.0	7.5	10.0	12.5	15.0	20.0
	E_d	0.629	0.481	0.375	0.303	0.231	0.184	0.115
T = 40.2°C.	t	2.5	5.0	7.5	10.25	12.5	15.0	-
	E_d	0.593	0.432	0.309	0.231	0.167	0.124	-
T = 50.0°C.	t	2.5	4.0	5.5	7.5	9.5	11.5	13.5
	E_d	0.548	0.431	0.347	0.269	0.196	0.146	0.116
T = 60.0°C.	t	1.5	3.0	4.5	6.0	7.5	9.0	10.5
	E_d	0.621	0.474	0.367	0.294	0.219	0.173	0.144
T = 69.8°C.	t	1.5	3.0	4.5	6.0	7.5	9.0	-
	E_d	0.594	0.439	0.329	0.236	0.156	0.142	-
T = 80.1°C.	t	1.5	2.5	3.5	4.5	5.5	6.5	7.5
	E_d	0.569	0.461	0.365	0.311	0.234	0.190	0.164

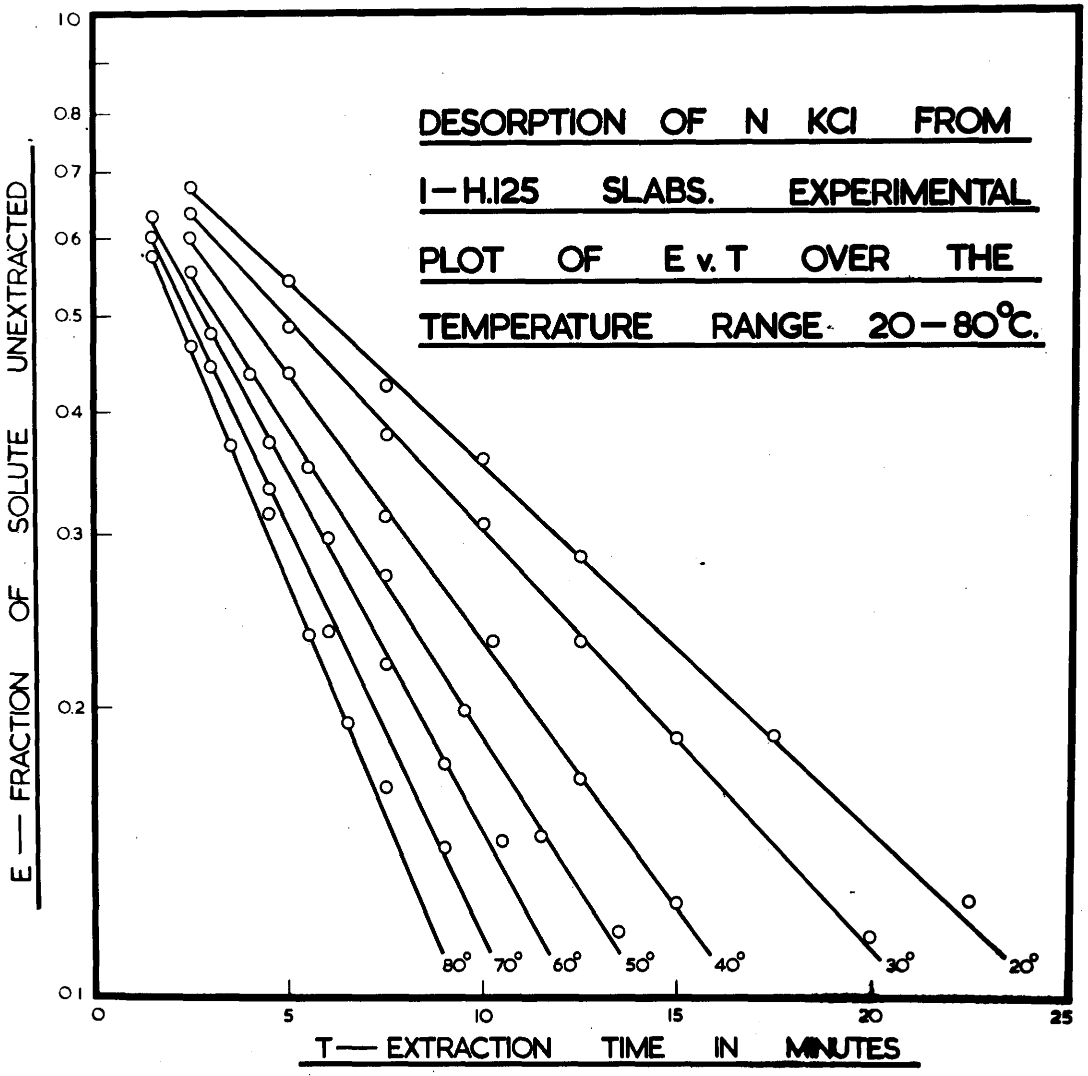

DESORPTION OF N KCl FROM
I—H.125 SLABS. EXPERIMENTAL
PLOT OF E v. T OVER THE
TEMPERATURE RANGE 20—80°C.
E — FRACTION OF SOLUTE UNEXTRACTED
T — EXTRACTION TIME IN MINUTES
1.0
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
5
10
15
20
25
80°
70°
60°
50°
40°
30°
20°

FIG. 9

C.1.2. Desorption of 3N KCl from (1)H.125 Slabs.

$T = 20.0^\circ C.$	t	2.5	5.0	7.5	10.0	12.5	17.5	22.5
	E_d	0.643	0.515	0.413	0.340	0.277	0.181	0.131
$T = 30.5^\circ C.$	t	2.5	5.0	7.5	10.0	12.5	15.0	20.0
	E_d	0.618	0.470	0.364	0.283	0.219	0.172	0.117
$T = 40.0^\circ C.$	t	2.5	5.0	7.5	10.0	12.5	15.0	17.5
	E_d	0.582	0.418	0.307	0.233	0.170	0.123	0.0975
$T = 50.0^\circ C.$	t	2.5	4.0	5.5	7.5	12.5	15.0	-
	E_d	0.536	0.417	0.338	0.259	0.119	0.0921	-
$T = 60.1^\circ C.$	t	1.5	3.0	4.5	6.0	7.5	9.0	10.5
	E_d	0.594	0.450	0.329	0.273	0.207	0.157	0.129
$T = 70.0^\circ C.$	t	1.5	2.5	3.5	5.0	6.5	8.0	9.5
	E_d	0.582	0.475	0.391	0.290	0.213	0.157	0.125
$T = 80.0^\circ C.$	t	1.5	2.5	3.5	4.75	5.5	6.5	7.5
	E_d	0.545	0.416	0.348	0.264	0.221	0.184	0.149

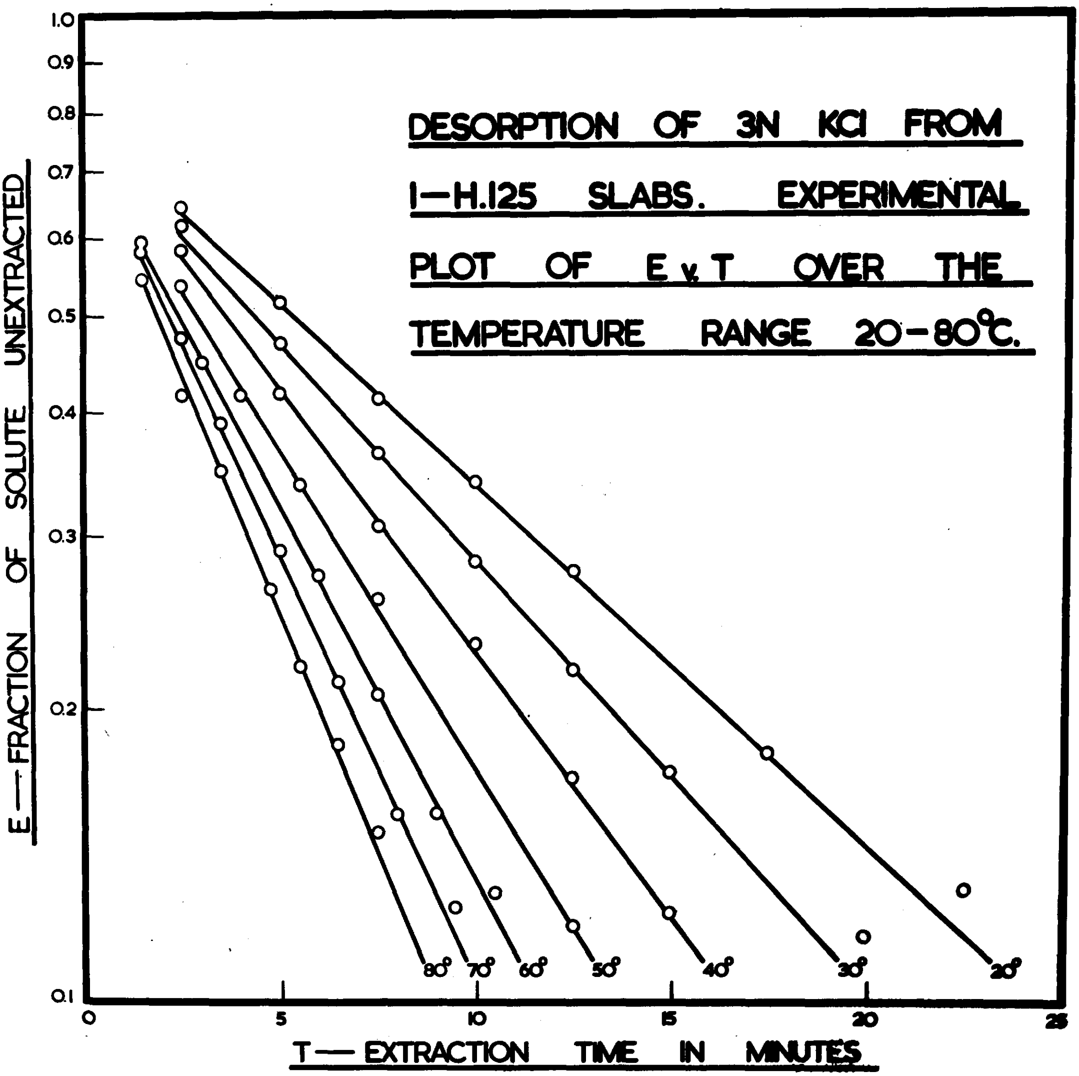

DESORPTION OF 3N KCl FROM
I—H.125 SLABS. EXPERIMENTAL
PLOT OF E v. T OVER THE
TEMPERATURE RANGE 20–80°C.
E — FRACTION OF SOLUTE UNEXTRACTED
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
T — EXTRACTION TIME IN MINUTES
0
5
10
15
20
25
80°
70°
60°
50°
40°
30°
20°

FIG. 10

C.1.3. Desorption of N KCl from (1)CF.6 Slabs.

T = 20.0°C.	t	2.5	5.0	7.5	10.0	12.5	17.5	22.5
	E_d	0.730	0.664	0.542	0.489	0.428	0.322	0.272
T = 29.9°C.	t	2.5	5.0	7.5	10.0	15.0	20.0	-
	E_d	0.708	0.580	0.484	0.413	0.298	0.224	-
T = 40.2°C.	t	2.5	5.5	7.5	10.0	12.5	17.5	22.5
	E_d	0.672	0.522	0.454	0.383	0.302	0.209	0.150
T = 50.0°C.	t	3.0	5.0	8.0	11.0	14.0	18.0	21.0
	E_d	0.625	0.532	0.396	0.315	0.240	0.165	0.127
T = 60.0°C.	t	2.5	5.0	7.5	10.0	12.5	15.0	17.5
	E_d	0.610	0.467	0.345	0.272	0.213	0.166	0.133
T = 70.0°C.	t	2.0	3.5	5.0	6.5	8.0	10.5	12.5
	E_d	0.623	0.511	0.413	0.357	0.276	0.217	0.182
T = 79.8°C.	t	1.5	3.5	5.0	6.5	8.0	9.5	12.0
	E_d	0.645	0.459	0.392	0.307	00.257	0.202	0.148

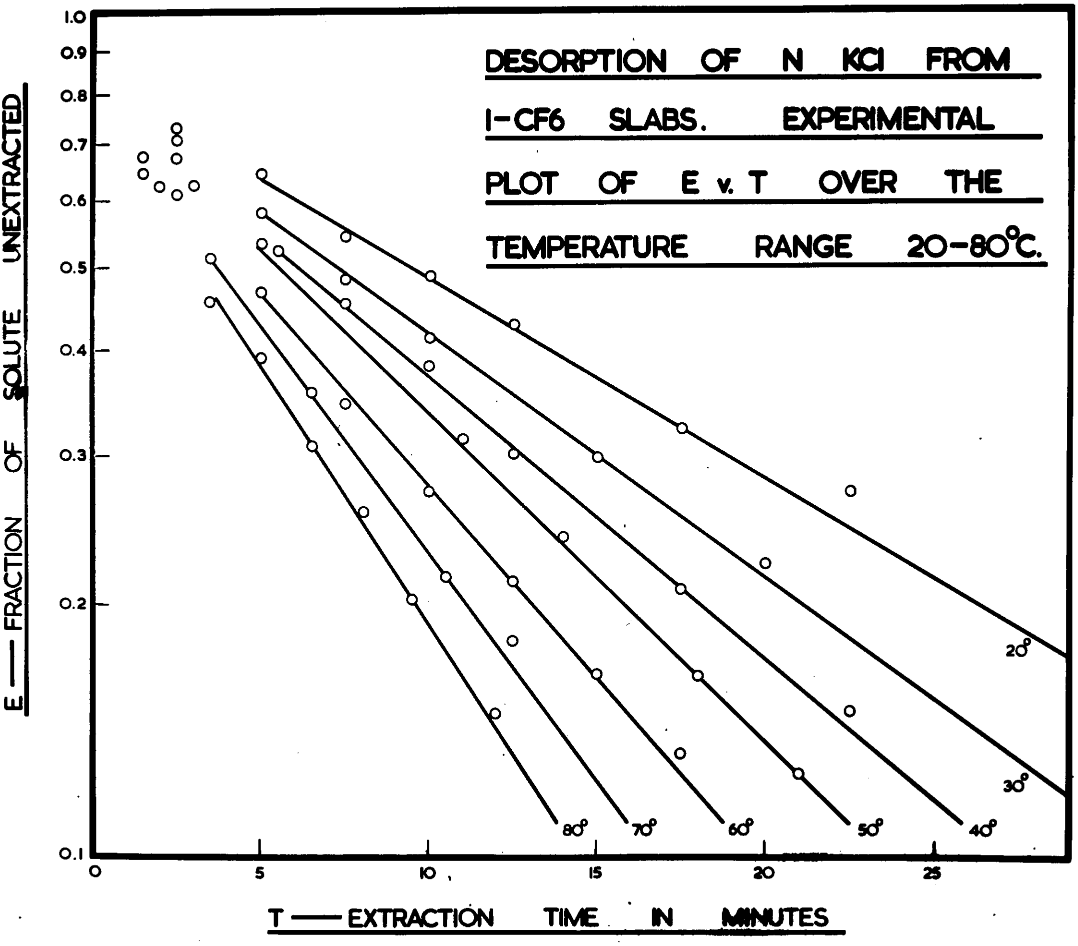

DESORPTION OF N KCl FROM 1-CF6 SLABS. EXPERIMENTAL PLOT OF E v. T OVER THE TEMPERATURE RANGE 20-80°C.
E —— FRACTION OF SOLUTE UNEXTRACTED
T —— EXTRACTION TIME IN MINUTES
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
5
10
15
20
25
20°
30°
40°
50°
60°
70°
80°

FIG. 11

C.1.4. Desorption of 3N KCl from (1)CF.6 Slabs.

T = 20.0°C.	t	5.0	10.0	12.5	15.0	20.0	25.0	30.0
	E_d	0.587	0.451	0.393	0.349	0.269	0.218	0.174
T = 30.0°C.	t	2.5	5.0	7.5	10.0	15.0	20.0	25.0
	E_d	0.641	0.520	0.491	0.413	0.296	0.223	0.169
T = 39.8°C.	t	2.5	5.0	7.5	10.0	12.5	17.5	22.5
	E_d	0.665	0.537	0.433	0.362	0.293	0.212	0.148
T = 50.0°C.	t	3.0	5.0	8.0	11.0	14.0	17.0	20.0
	E_d	0.603	0.497	0.382	0.291	0.218	0.163	0.129
T = 60.1°C.	t	2.5	5.0	7.5	10.0	12.5	15.0	17.5
	E_d	0.616	0.445	0.337	0.260	0.204	0.159	0.122
T = 70.0°C.	t	2.0	3.5	5.0	6.5	10.5	12.5	–
	E_d	0.627	0.516	0.420	0.349	0.211	0.169	–
T = 80.0°C.	t	1.5	3.5	4.5	6.0	7.5	9.0	10.5
	E_d	0.637	0.465	0.399	0.324	0.260	0.203	0.171

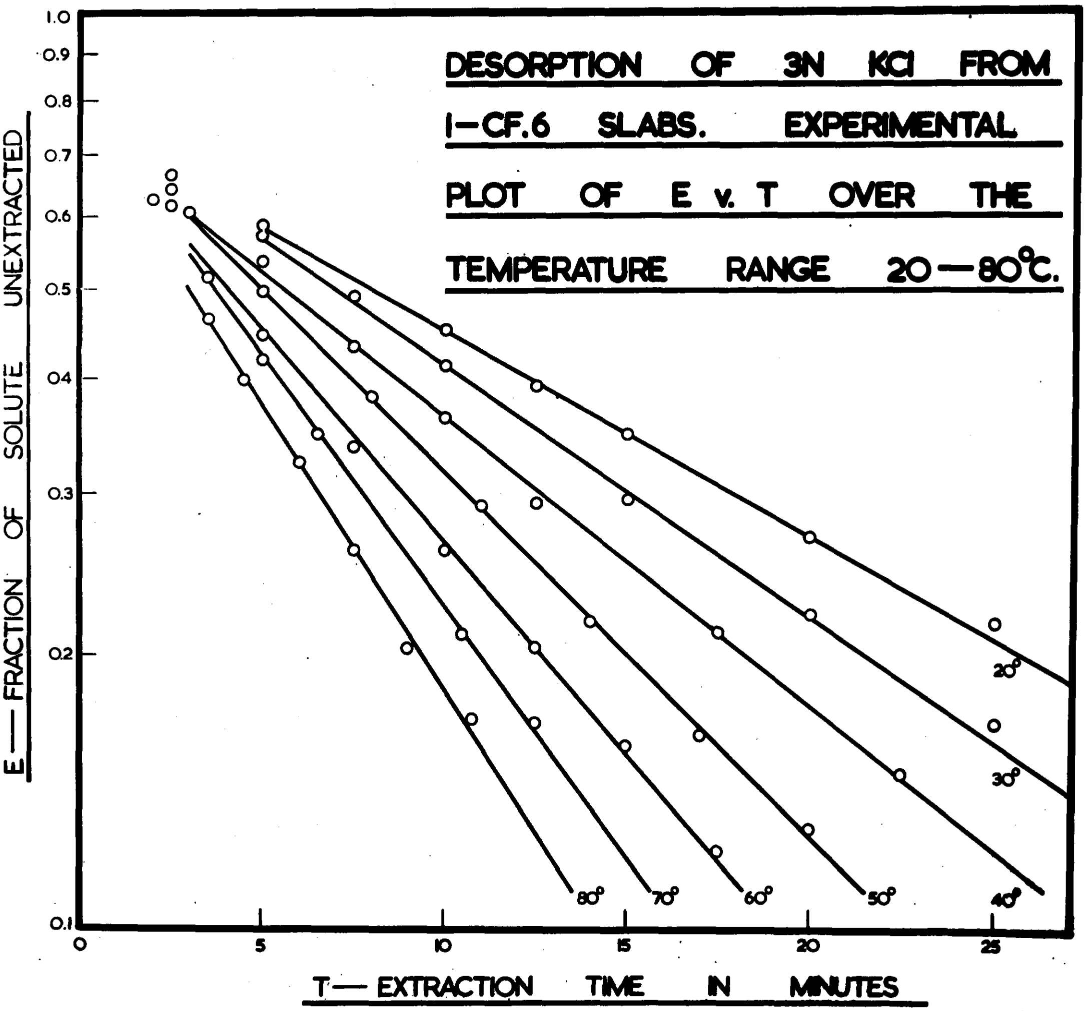

DESORPTION OF 3N KCl FROM I-CF.6 SLABS. EXPERIMENTAL PLOT OF E v. T OVER THE TEMPERATURE RANGE 20—80°C.
E — FRACTION OF SOLUTE UNEXTRACTED
T — EXTRACTION TIME IN MINUTES
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
5
10
15
20
25
20°
30°
40°
50°
60°
70°
80°

FIG. 12

C.2. ABSORPTION AND DESORPTION OF KCl WITH (2)H.125 AND (2)B.5 SLABS.

C.2.1. Desorption of N KCl from (2)H.125 Slabs.

T = 20.0°C.	t	10.0	20.0	30.0	40.0	50.0	60.0	70.0
	E_d	0.610	0.478	0.391	0.304	0.252	0.200	0.155
T = 30.0°C.	t	10.0	20.0	30.0	40.0	50.0	60.0	70.0
	E_d	0.591	0.442	0.343	0.263	0.198	0.162	0.121
T = 40.0°C.	t	10.0	15.0	20.0	25.0	30.0	40.0	50.0
	E_d	0.555	0.471	0.401	0.336	0.298	0.216	0.156
T = 50.0°C.	t	10.0	15.0	20.0	30.0	40.0	50.0	-
	E_d	0.520	0.421	0.350	0.239	0.178	0.117	-
T = 59.9°C.	t	10.0	15.0	20.0	25.0	30.0	35.0	45.0
	E_d	0.489	0.403	0.311	0.249	0.200	0.167	0.112
T = 69.6°C.	t	10.0	15.0	20.0	25.0	30.0	35.0	40.0
	E_d	0.442	0.343	0.265	0.208	0.163	0.129	0.0974
T = 80.2°C.	t	7.5	10.0	12.5	15.0	20.0	25.0	30.0
	E_d	0.479	0.409	0.369	0.297	0.232	0.172	0.123

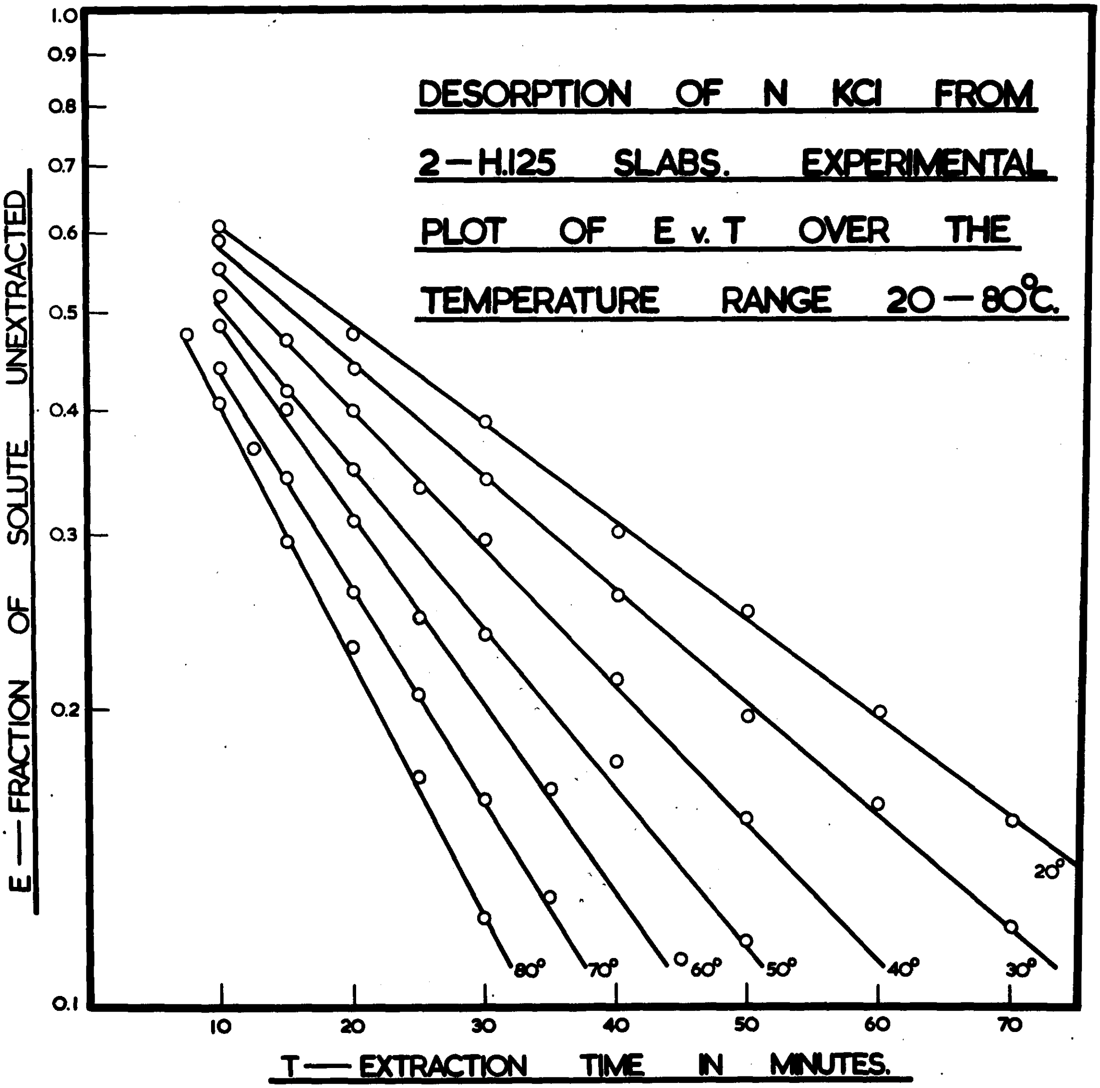

DESORPTION OF N KCl FROM
2-H.125 SLABS. EXPERIMENTAL
PLOT OF E v. T OVER THE
TEMPERATURE RANGE 20-80°C.
E — FRACTION OF SOLUTE UNEXTRACTED
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
10
20
30
40
50
60
70
T — EXTRACTION TIME IN MINUTES.
80°
70°
60°
50°
40°
30°
20°

FIG. 14

C.2.2 Desorption of 3N KCl from (2)H.125 Slabs.

T = 20.2°C.	t	10.0	20.0	30.0	40.0	50.0	60.0	-
	E_d	0.615	0.478	0.387	0.305	0.256	0.207	-
T = 30.0°C.	t	10.0	20.0	30.0	40.0	50.0	60.0	70.0
	E_d	0.580	0.427	0.324	0.255	0.194	0.153	0.120
T = 40.1°C.	t	10.0	15.0	20.0	25.0	30.0	40.0	50.0
	E_d	0.554	0.457	0.384	0.331	0.284	0.214	0.157
T = 50.0°C.	t	10.0	15.0	20.0	30.0	40.0	45.0	50.0
	E_d	0.530	0.417	0.347	0.240	0.168	0.146	0.121
T = 60.0°C.	t	10.0	15.0	20.0	25.0	30.0	35.0	45.0
	E_d	0.478	0.380	0.305	0.242	0.202	0.151	0.106
T = 70.1°C.	t	10.0	15.0	20.0	25.0	30.0	35.0	40.0
	E_d	0.450	0.343	0.267	0.215	0.167	0.125	0.109
T = 80.0°C.	t	7.5	10.0	12.5	15.0	20.0	25.0	30.0
	E_d	0.488	0.421	0.368	0.313	0.242	0.184	0.145

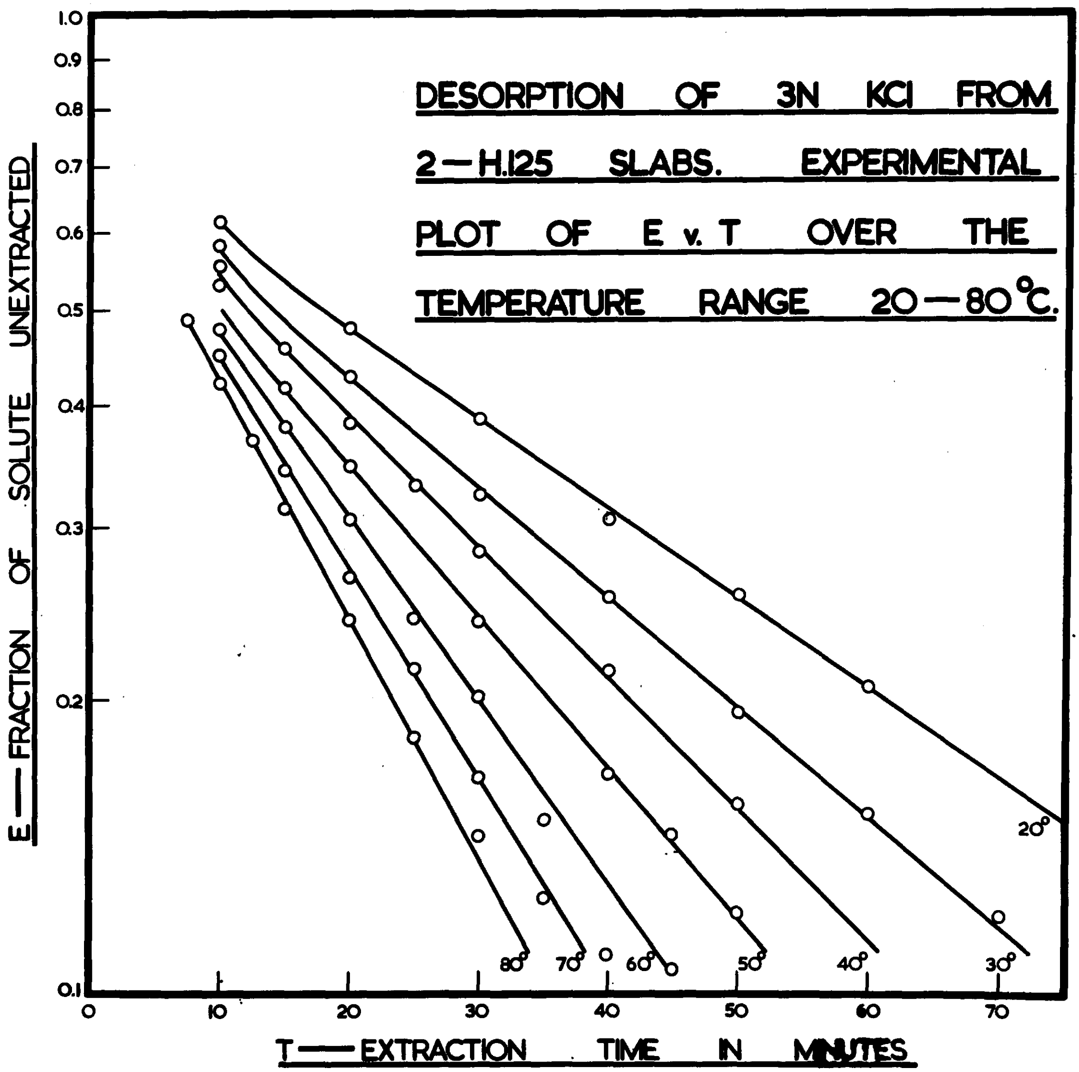

DESORPTION OF 3N KCl FROM
2 — H.125 SLABS. EXPERIMENTAL
PLOT OF E v. T OVER THE
TEMPERATURE RANGE 20 — 80 °C.
E — FRACTION OF SOLUTE UNEXTRACTED
T — EXTRACTION TIME IN MINUTES
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
20°
30°
40°
50°
60°
70°
80°

FIG. 15

C.2.3. Absorption of N KCl by (2)H.125 Slabs.

T = 20.1°C.	t	15.0	27.5	35.0	45.0	55.0	65.0	75.0
	$1-E_a$	0.555	0.415	0.360	0.291	0.232	0.192	0.158
T = 29.9°C.	t	10.0	20.0	30.0	40.0	50.0	60.0	70.0
	$1-E_a$	0.590	0.440	0.336	0.260	0.201	0.164	0.123
T = 40.0°C.	t	15.0	20.0	26.0	30.0	35.0	40.0	50.0
	$1-E_a$	0.462	0.389	0.316	0.277	0.238	0.211	0.148
T = 50.0°C.	t	10.0	15.0	20.0	25.0	30.0	37.5	45.0
	$1-E_a$	0.509	0.424	0.349	0.283	0.236	0.178	0.128
T = 60.1°C.	t	10.0	15.0	20.0	25.0	30.0	35.0	40.0
	$1-E_a$	0.461	0.369	0.293	0.232	0.186	0.144	0.115
T = 70.0°C.	t	10.0	12.5	15.0	17.5	20.0	25.0	30.0
	$1-E_a$	0.429	0.374	0.302	0.277	0.233	0.175	0.123
T = 80.0°C.	t	10.0	12.5	15.0	17.5	20.0	25.0	30.0
	$1-E_a$	0.381	0.319	0.269	0.229	0.202	0.144	0.100

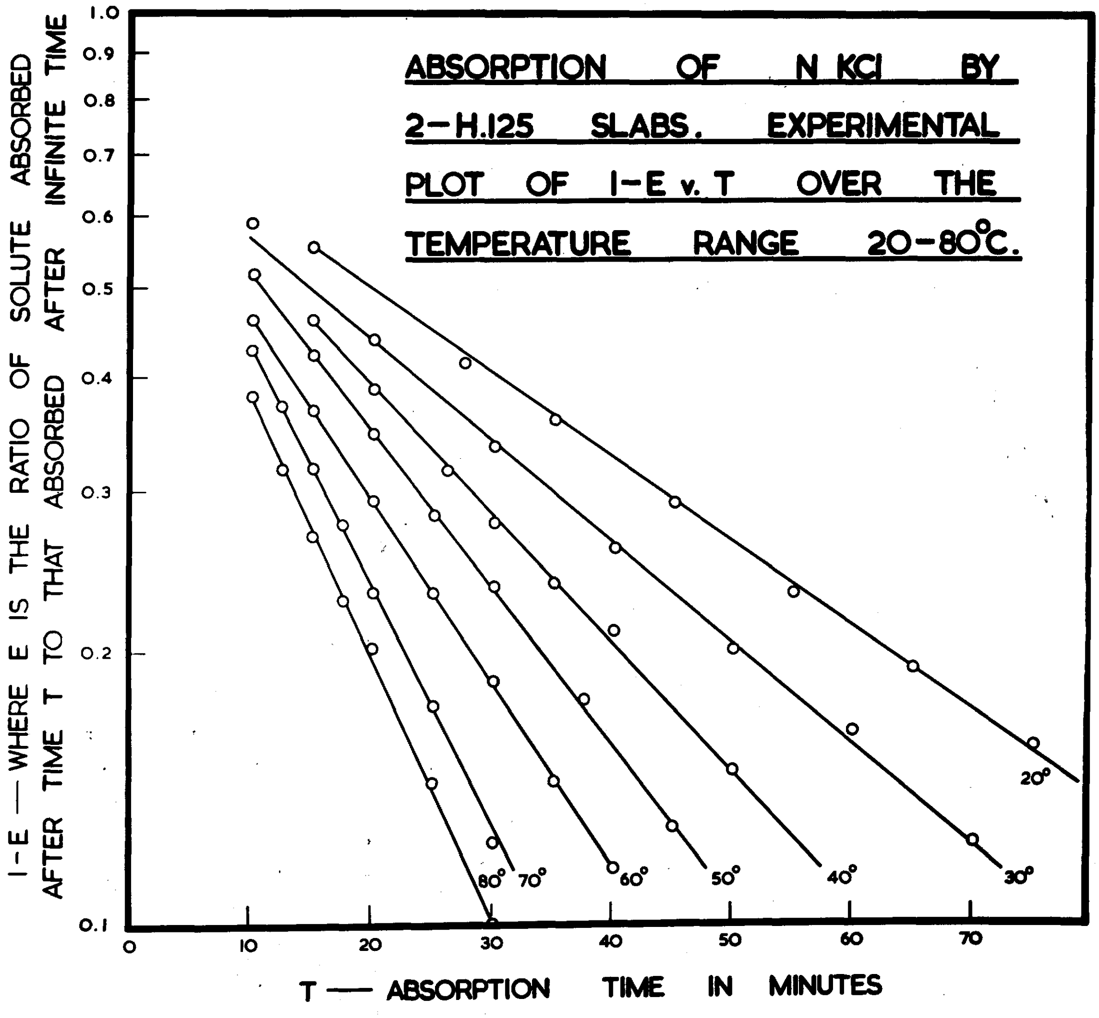

ABSORPTION OF N KCl BY 2-H.125 SLABS. EXPERIMENTAL PLOT OF 1-E v. T OVER THE TEMPERATURE RANGE 20-80°C.
1-E — WHERE E IS THE RATIO OF SOLUTE ABSORBED AFTER TIME T TO THAT ABSORBED AFTER INFINITE TIME
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
T — ABSORPTION TIME IN MINUTES
80°
70°
60°
50°
40°
30°
20°

FIG. 16

C.2.4. Absorption of 3N KCl by (2)H.125 Slabs.

T = 20.0°C.	t	10.0	20.0	30.0	40.0	50.0	60.0	70.0
	$1-E_a$	0.608	0.473	0.371	0.296	0.237	0.195	0.137
T = 29.9°C.	t	10.0	15.0	20.0	30.0	40.0	50.0	60.0
	$1-E_a$	0.571	0.485	0.415	0.306	0.237	0.178	0.127
T = 40.0°C.	t	10.0	15.0	20.0	25.0	30.0	40.0	50.0
	$1-E_a$	0.527	0.445	0.370	0.313	0.256	0.180	0.134
T = 50.0°C.	t	10.0	15.0	20.0	25.0	30.0	40.0	45.0
	$1-E_a$	0.479	0.387	0.312	0.255	0.208	0.160	0.114
T = 60.2°C.	t	5.0	10.0	15.0	20.0	25.0	30.0	35.0
	$1-E_a$	0.605	0.454	0.348	0.268	0.219	0.166	0.105
T = 70.2°C.	t	5.0	10.0	15.0	20.0	25.0	30.0	40.0
	$1-E_a$	0.577	0.426	0.317	0.239	0.184	0.141	0.0928
T = 79.8°C.	t	5.0	10.0	15.0	20.0	25.0	30.0	40.0
	$1-E_a$	0.540	0.385	0.274	0.195	0.145	0.101	0.0490

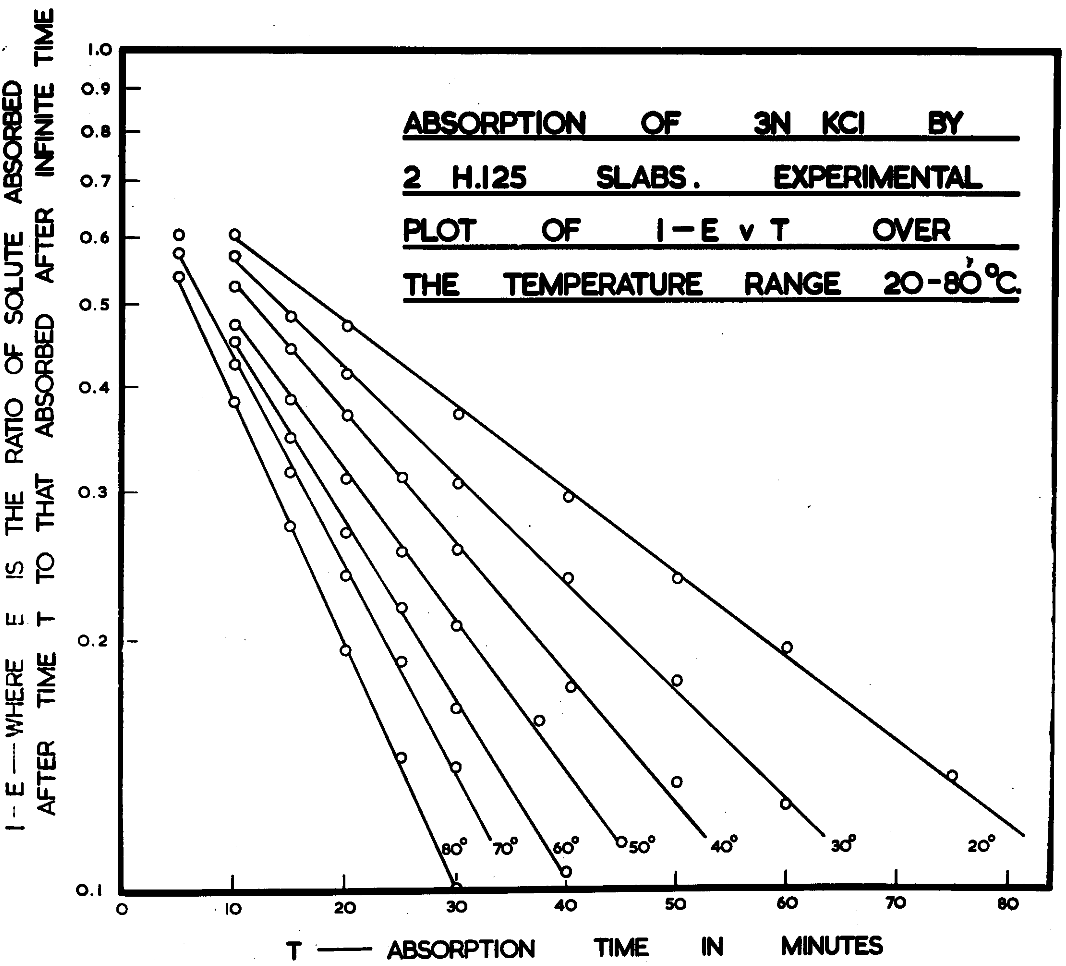

ABSORPTION OF 3N KCl BY 2 H.125 SLABS. EXPERIMENTAL PLOT OF 1-E v T OVER THE TEMPERATURE RANGE 20-80°C.
1-E — WHERE E IS THE RATIO OF SOLUTE ABSORBED AFTER TIME T TO THAT ABSORBED AFTER INFINITE TIME
T — ABSORPTION TIME IN MINUTES
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
80
80°
70°
60°
50°
40°
30°
20°

FIG. 17

C.2.5. Desorption of N KCl from (2)B.5 Slabs.

T = 20.0°C.	t	30.0	45.0	60.0	75.0	90.0	110.0	130.0
	E_d	0.509	0.418	0.346	0.282	0.241	0.182	0.144
T = 30.1°C.	t	21.0	35.0	50.0	65.0	80.0	95.0	110.0
	E_d	0.536	0.422	0.323	0.259	0.203	0.154	0.120
T = 40.0°C.	t	15.0	25.0	35.0	45.0	55.0	70.0	85.0
	E_d	0.568	0.455	0.370	0.309	0.256	0.186	0.137
T = 50.0°C.	t	15.0	25.0	35.0	45.0	55.0	65.0	75.0
	E_d	0.532	0.409	0.317	0.250	0.202	0.160	0.122
T = 60.0°C.	t	15.0	21.0	30.0	37.5	45.0	52.5	60.0
	E_d	0.497	0.419	0.340	0.261	0.208	0.175	0.142
T = 70.0°C.	t	10.0	15.0	20.0	27.5	35.0	42.5	50.0
	E_d	0.547	0.459	0.374	0.305	0.234	0.185	0.150
T = 80.0°C.	t	10.0	15.0	20.0	25.0	30.0	35.0	40.0
	E_d	0.517	0.432	0.357	0.288	0.239	0.199	0.164

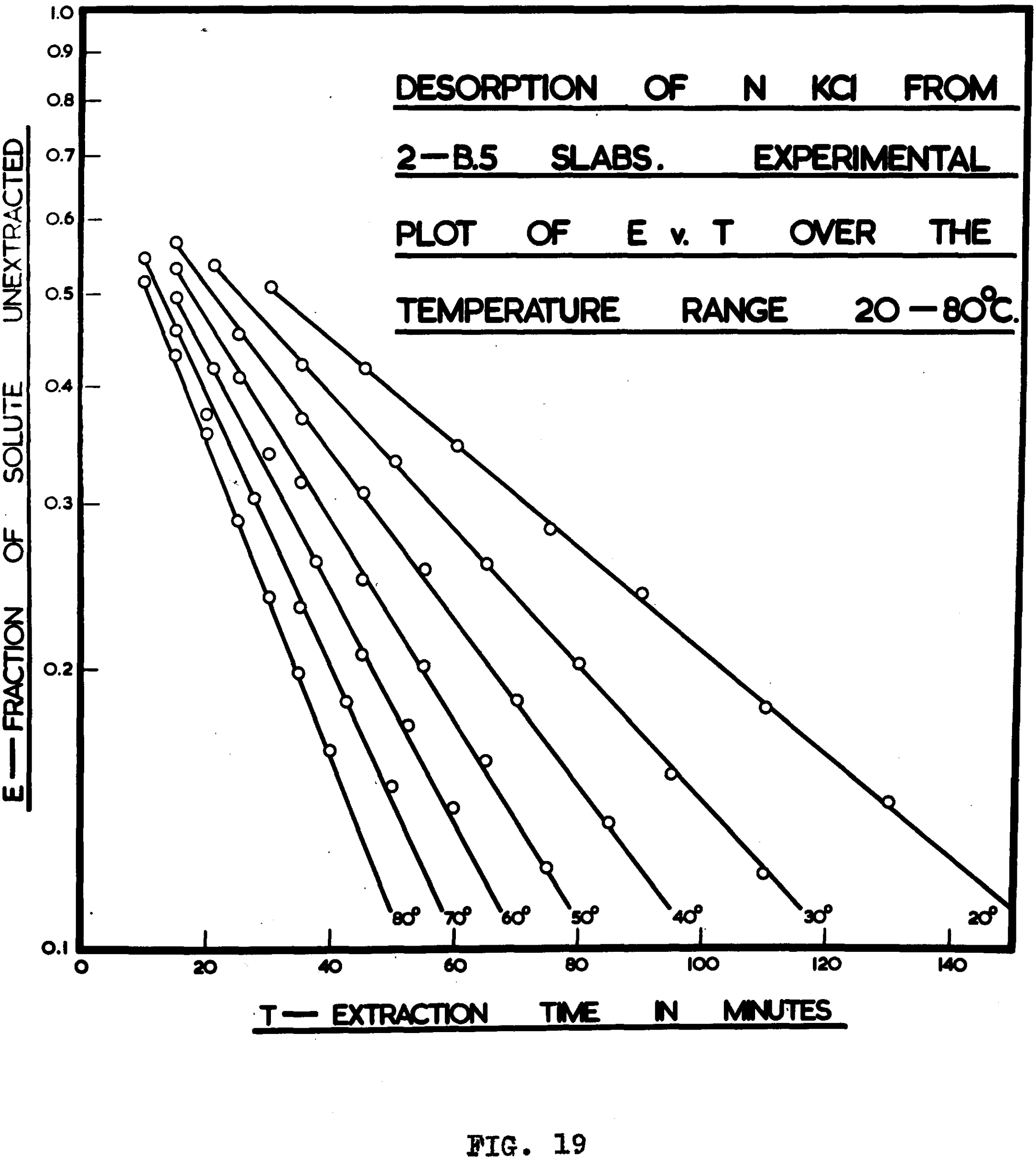

DESORPTION OF N KCl FROM 2—B.5 SLABS. EXPERIMENTAL PLOT OF E v. T OVER THE TEMPERATURE RANGE 20—80°C.
E — FRACTION OF SOLUTE UNEXTRACTED
T — EXTRACTION TIME IN MINUTES
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
20
40
60
80
100
120
140
80°
70°
60°
50°
40°
30°
20°

FIG. 19

C.2.6. Desorption of 3N KCl by (2)B.5 Slabs.

T = 20.1°C.	t	30.0	45.0	60.0	75.0	90.0	110.0	130.0
	E_d	0.492	0.402	0.327	0.272	0.220	0.170	0.131
T = 30.0°C.	t	20.0	35.0	45.0	55.0	70.0	85.0	100.0
	E_d	0.532	0.414	0.345	0.288	0.228	0.174	0.143
T = 40.1°C.	t	15.0	25.0	35.0	45.0	55.0	70.0	85.0
	E_d	0.556	0.443	0.356	0.288	0.235	0.173	0.132
T = 50.0°C.	t	15.0	22.5	30.0	40.0	50.0	60.0	70.0
	E_d	0.522	0.426	0.347	0.272	0.211	0.167	0.136
T = 60.0°C.	t	15.0	20.0	30.0	37.5	45.0	52.5	60.0
	E_d	0.478	0.408	0.298	0.241	0.199	0.160	0.133
T = 69.8°C.	t	10.5	15.0	20.0	26.0	35.0	42.5	50.0
	E_d	0.523	0.448	0.370	0.306	0.218	0.175	0.142
T = 80.0°C.	t	10.0	15.0	20.0	25.0	30.0	35.0	40.0
	E_d	0.504	0.412	0.338	0.275	0.232	0.194	0.163

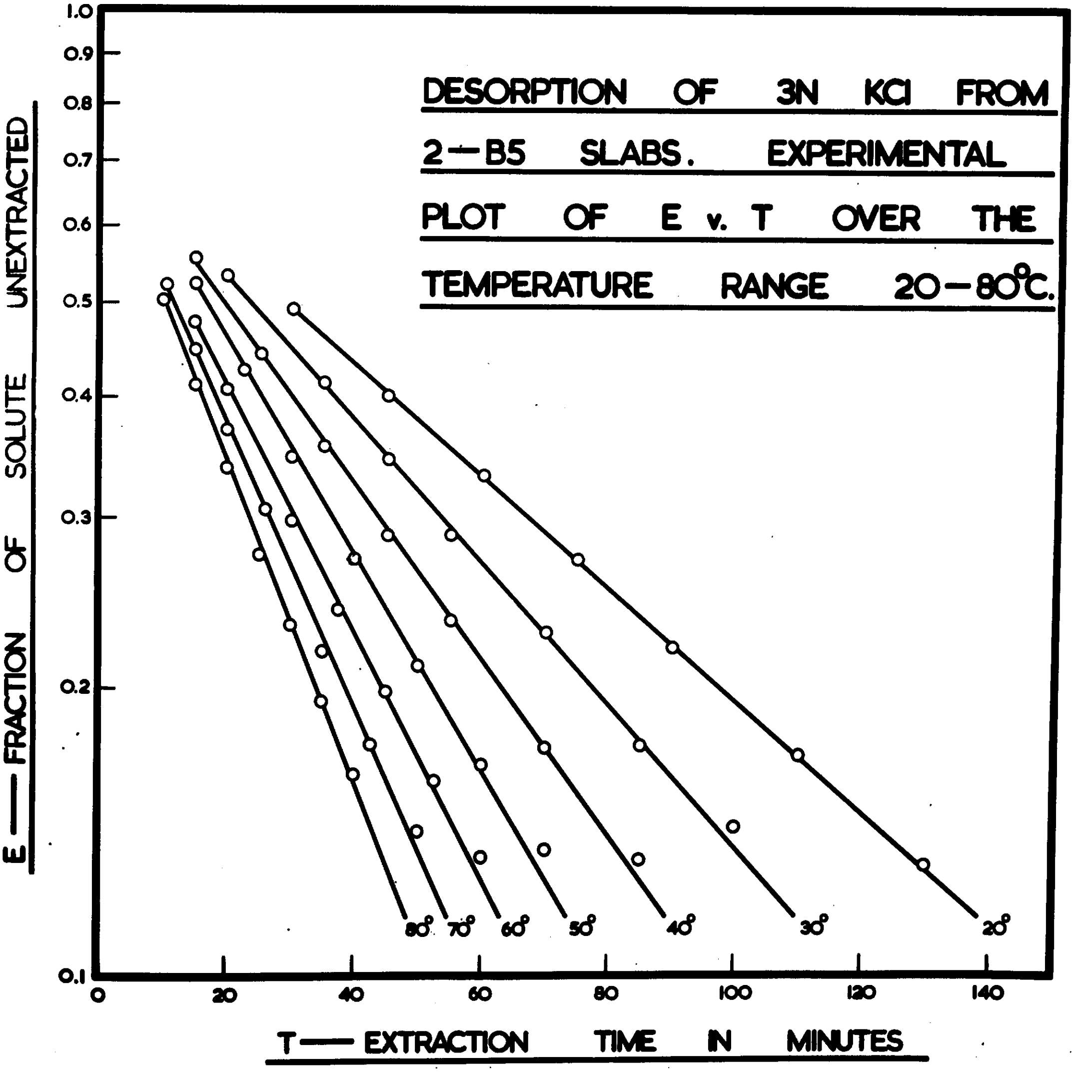

DESORPTION OF 3N KCl FROM 2—B5 SLABS. EXPERIMENTAL PLOT OF E v. T OVER THE TEMPERATURE RANGE 20—80°C.
E —— FRACTION OF SOLUTE UNEXTRACTED
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
T —— EXTRACTION TIME IN MINUTES
0
20
40
60
80
100
120
140
80°
70°
60°
50°
40°
30°
20°

FIG. 20

C.2.7. Absorption of N KCl by (2)B.5 Slabs.

T = 20.1°C.	t	30.0	50.0	70.0	90.0	110.0	130.0	150.0
	$1-E_a$	0.514	0.395	0.307	0.249	0.197	0.152	0.129
T = 30.0°C.	t	20.0	35.5	50.0	65.0	80.0	100.0	120.0
	$1-E_a$	0.537	0.415	0.332	0.255	0.217	0.154	0.121
T = 40.0°C.	t	20.0	30.0	40.0	50.0	60.0	75.0	90.0
	$1-E_a$	0.509	0.411	0.338	0.270	0.225	0.162	0.133
T = 50.0°C.	t	15.0	25.0	35.0	45.0	55.0	67.5	80.0
	$1-E_a$	0.517	0.404	0.314	0.244	0.199	0.156	0.109
T = 60.0°C.	t	10.0	20.0	30.0	40.0	50.0	60.0	72.0
	$1-E_a$	0.569	0.420	0.319	0.244	0.189	0.132	0.094
T = 70.0°C.	t	10.0	15.0	20.0	30.0	40.0	50.0	60.0
	$1-E_a$	0.538	0.448	0.382	0.271	0.184	0.131	0.095
T = 79.8°C.	t	10.0	15.5	20.0	25.5	30.0	40.0	50.0
	$1-E_a$	0.514	0.396	0.339	0.283	0.223	0.150	0.092

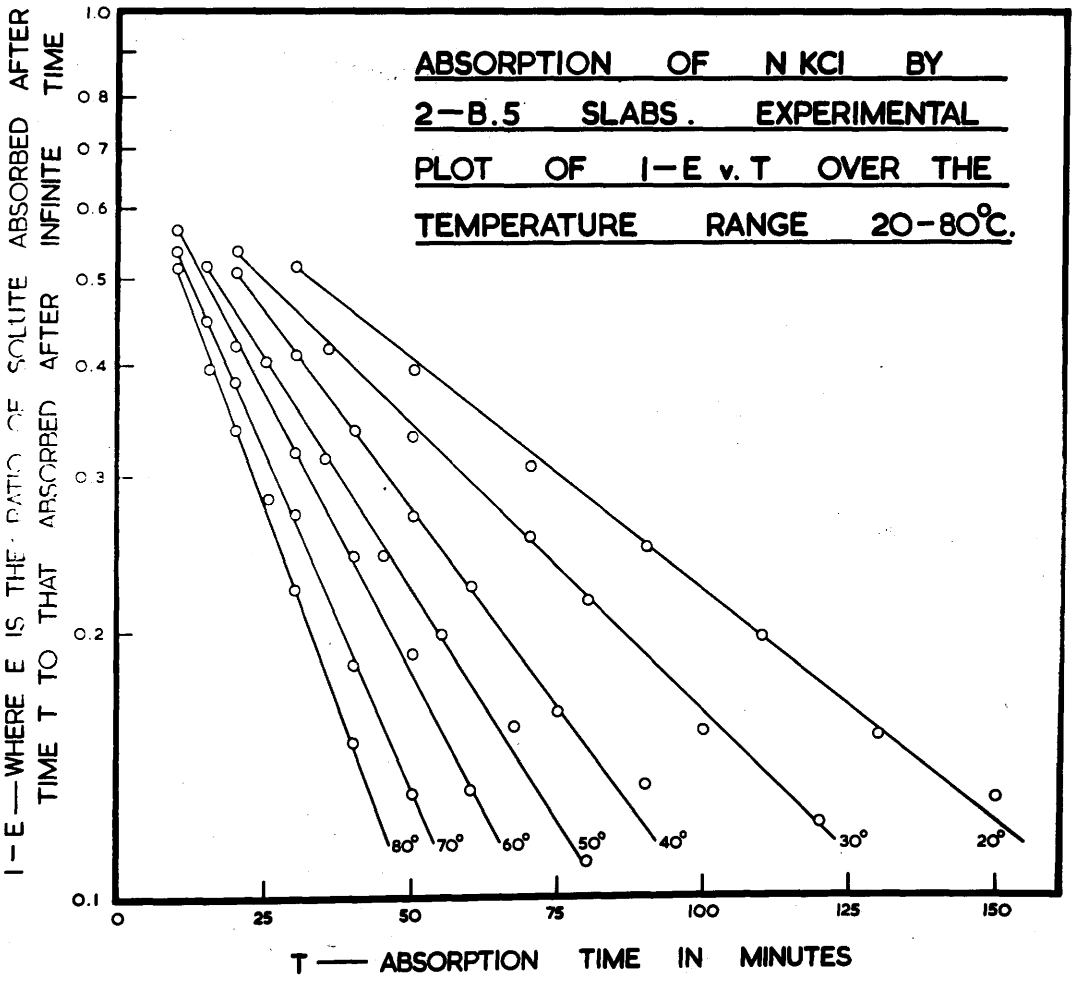

ABSORPTION OF N KCl BY 2–B.5 SLABS. EXPERIMENTAL PLOT OF 1–E v. T OVER THE TEMPERATURE RANGE 20–80°C.
1–E —— WHERE E IS THE RATIO OF SOLUTE ABSORBED AFTER TIME T TO THAT ABSORBED AFTER INFINITE TIME
1.0
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
25
50
75
100
125
150
T —— ABSORPTION TIME IN MINUTES
80°
70°
60°
50°
40°
30°
20°

FIG. 21

C.2.8. Absorption of 3N KCl by (2)B.5 Slabs.

T = 20.0°C.	t	18.0	35.0	55.0	65.5	80.0	95.5	110.0
	$1-E_a$	0.586	0.448	0.335	0.294	0.238	0.185	0.147
T = 30.1°C.	t	15.0	20.0	30.0	45.0	60.0	75.0	91.0
	$1-E_a$	0.572	0.524	0.429	0.322	0.259	0.200	0.153
T = 40.0°C.	t	10.0	20.0	30.0	40.0	50.0	65.0	80.0
	$1-E_a$	0.605	0.478	0.382	0.312	0.248	0.194	0.135
T = 50.2°C.	t	10.0	15.0	25.0	35.0	45.5	55.0	65.0
	$1-E_a$	0.584	0.515	0.389	0.305	0.235	0.198	0.146
T = 59.9°C.	t	5.0	10.0	20.0	30.0	41.0	50.0	60.0
	$1-E_a$	0.672	0.561	0.401	0.299	0.213	0.158	0.125
T = 69.8°C.	t	10.0	15.0	20.0	25.0	30.0	40.0	50.0
	$1-E_a$	0.535	0.452	0.368	0.311	0.255	0.177	0.121
T = 80.0°C.	t	10.0	15.0	20.0	30.0	40.0	50.0	60.0
	$1-E_a$	0.517	0.394	0.317	0.205	0.132	0.0832	-

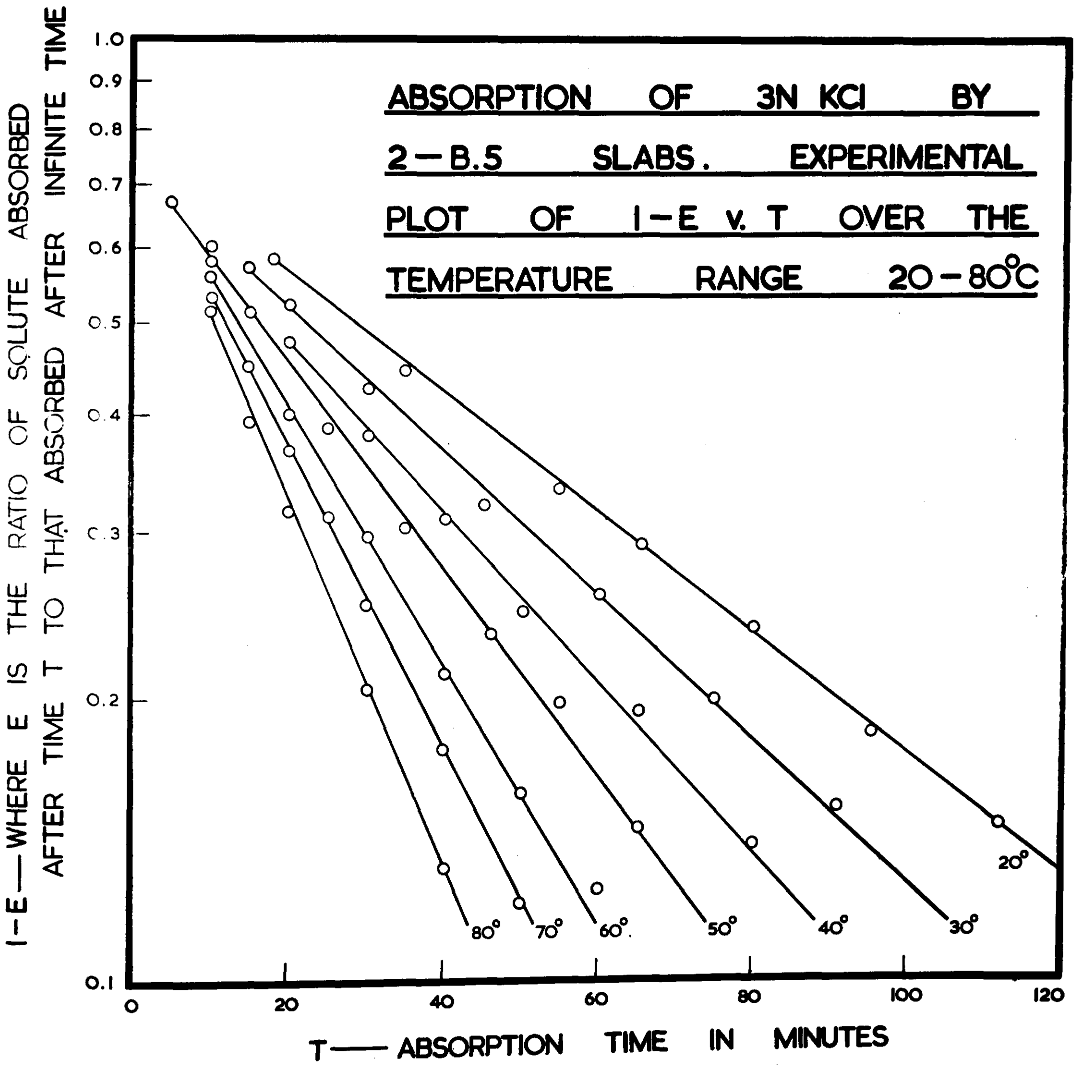
ABSORPTION OF 3N KCl BY 2—B.5 SLABS. EXPERIMENTAL PLOT OF 1—E v. T OVER THE TEMPERATURE RANGE 20—80°C
1-E —— WHERE E IS THE RATIO OF SOLUTE ABSORBED AFTER TIME T TO THAT ABSORBED AFTER INFINITE TIME
T —— ABSORPTION TIME IN MINUTES
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
20
40
60
80
100
120
80°
70°
60°.
50°
40°
30°
20°

FIG. 22

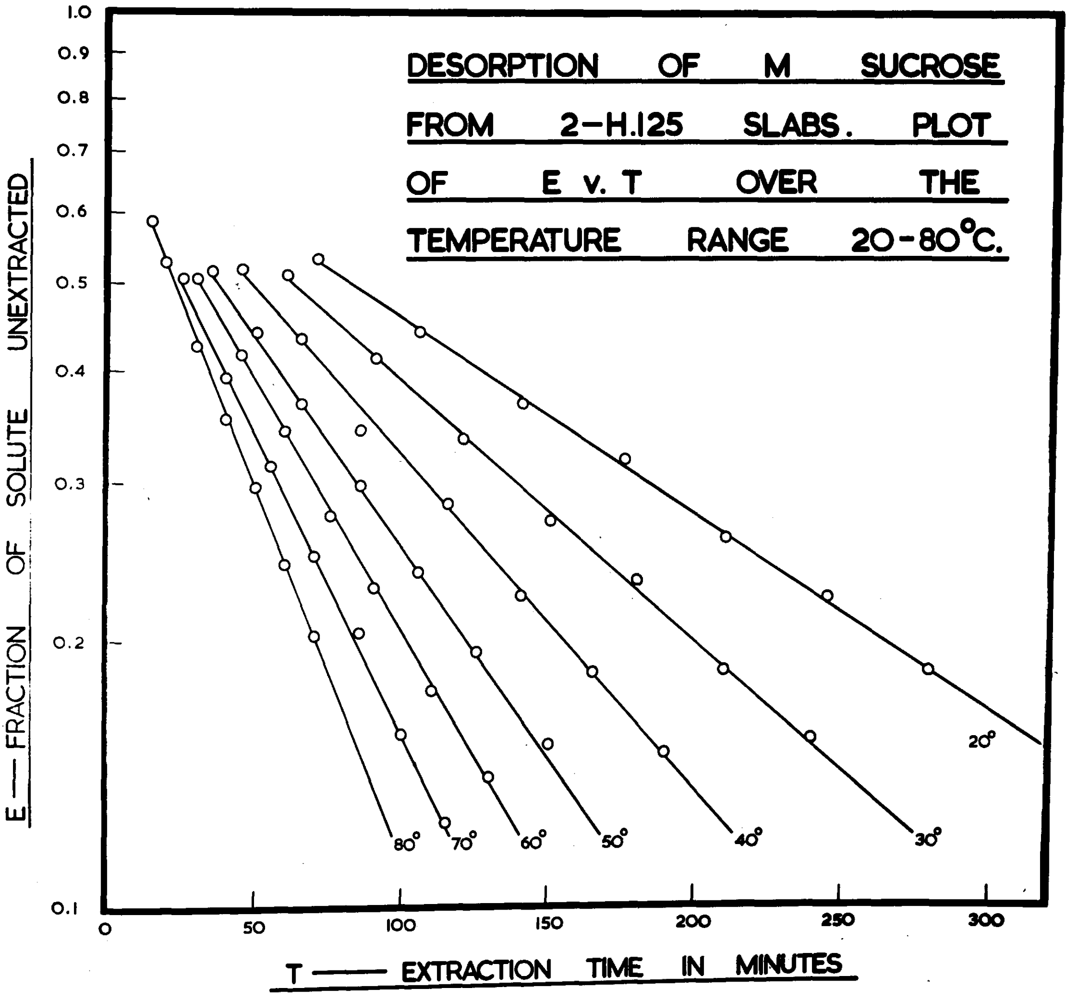
C.3. ABSORPTION AND DESORPTION OF SUCROSE WITH (2)H.125 AND (2)B.5 SLABS.

C.3.1. Desorption of 0.3M Sucrose from (2)H.125 Slabs.

T = 20.0°C.	t	60	80	100	130	160	190	240
	E_d	0.600	0.520	0.483	0.405	0.336	0.285	0.214
T = 30.2°C.	t	40	65	90	120	150	180	210
	E_d	0.579	0.479	0.392	0.320	0.254	0.197	0.164
T = 40.0°C.	t	40	60	80	100	120	150	180
	E_d	0.520	0.430	0.355	0.289	0.236	0.187	0.132
T = 50.0°C.	t	30	50	70	90	110	130	150
	E_d	0.538	0.421	0.331	0.258	0.211	0.165	0.128
T = 60.0°C.	t	20	35	50	65	80	100	120
	E_d	0.583	0.460	0.372	0.303	0.241	0.180	0.128
T = 70.0°C.	t	15	30	45	60	75	90	105
	E_d	0.640	0.476	0.360	0.279	0.212	0.167	0.125
T = 80.0°C.	t	15	20	30	40	50	60	70
	E_d	0.578	0.513	0.418	0.339	0.273	0.223	0.182

C.3.2. Desorption of M Sucrose from (2)H.125 Slabs.

T = 20.0°C.	t	70.0	105	140	175	210	245	280
	E_d	0.531	0.442	0.366	0.316	0.260	0.222	0.184
T = 30.2°C.	t	60	90	120	150	180	210	240
	E_d	0.510	0.414	0.335	0.271	0.232	0.184	0.154
T = 40.0°C.	t	45	65	90	115	140	165	190
	E_d	0.519	0.435	0.343	0.284	0.229	0.183	0.148
T = 50.2°C.	t	35	50	65	85	105	125	150
	E_d	0.516	0.441	0.368	0.298	0.238	0.194	0.152
T = 60.0°C.	t	30	45	60	75	90	110	130
	E_d	0.507	0.417	0.341	0.275	0.229	0.174	0.140
T = 70.0°C.	t	25	40	55	70	85	100	115
	E_d	0.507	0.393	0.313	0.248	0.204	0.156	0.124
T = 80.2°C.	t	15	20	30	40	50	60	70
	E_d	0.584	0.528	0.425	0.354	0.297	0.243	0.202



DESORPTION OF M SUCROSE FROM 2-H.125 SLABS. PLOT OF E v. T OVER THE TEMPERATURE RANGE 20-80°C.
E — FRACTION OF SOLUTE UNEXTRACTED
T — EXTRACTION TIME IN MINUTES
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
50
100
150
200
250
300
80°
70°
60°
50°
40°
30°
20°

FIG. 25

C.3.3. Absorption of 0.3M Sucrose by (2)H.125 Slabs.

T = 20.2°C.	t	60	90	120	150	200	250	300
	$1-E_a$	0.547	0.460	0.385	0.320	0.250	0.194	0.144
T = 30.0°C.	t	60	90	120	150	180	210	250
	$1-E_a$	0.481	0.386	0.314	0.263	0.207	0.167	0.125
T = 39.8°C.	t	40.0	65	90	115	140	165	190
	$1-E_a$	0.520	0.411	0.327	0.262	0.209	0.171	0.130
T = 50.2°C.	t	40	55	70	95	110	125	140
	$1-E_a$	0.466	0.380	0.329	0.244	0.190	0.166	0.145
T = 60.0°C.	t	30	40	50	65.0	80.0	95	110
	$1-E_a$	0.481	0.415	0.351	0.293	0.231	0.192	0.150
T = 70.0°C.	t	20	30	40	50	60	75	90
	$1-E_a$	0.520	0.428	0.359	0.319	0.248	0.197	0.143
T = 79.0°C.	t	15	20	30	40	50	60	70
	$1-E_a$	0.516	0.427	0.373	0.294	0.227	0.192	0.149

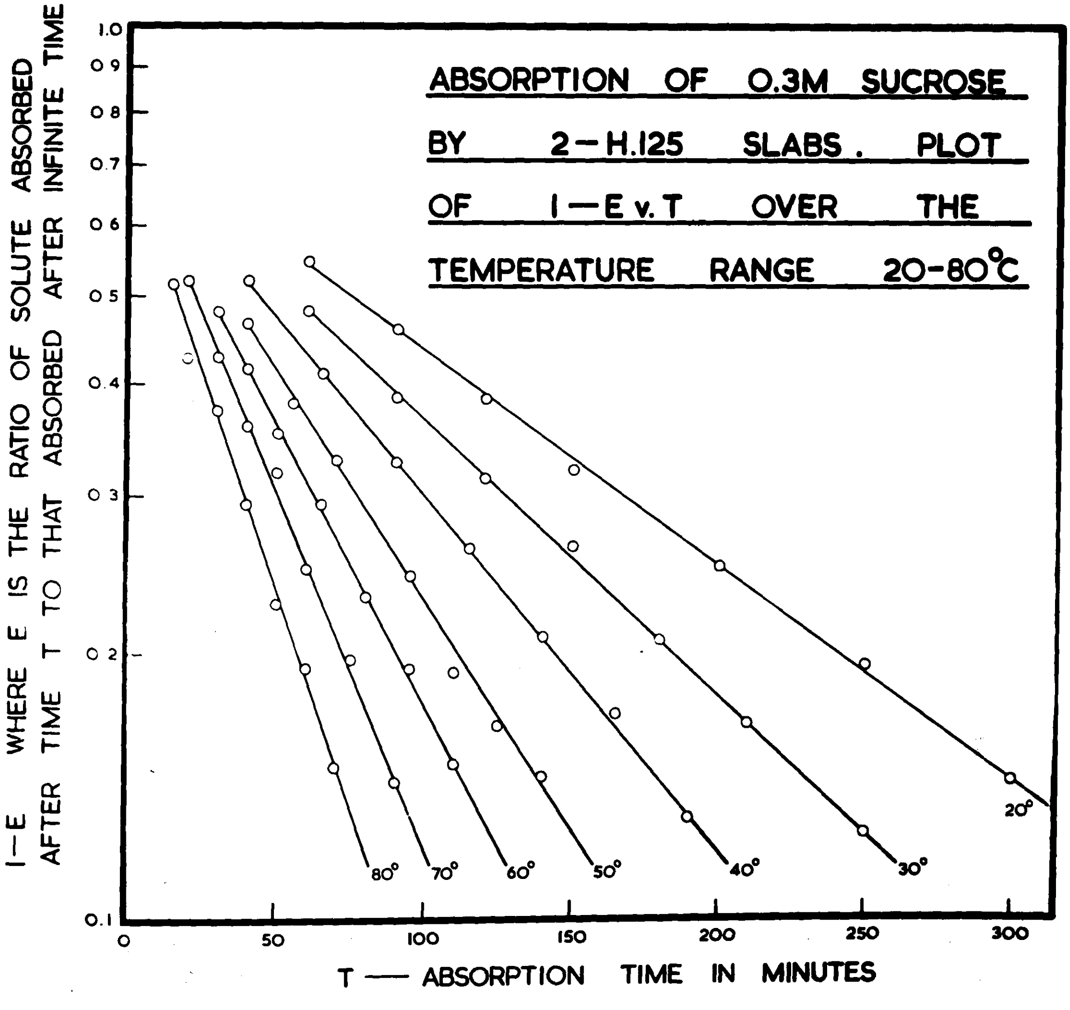

ABSORPTION OF 0.3M SUCROSE BY 2-H.125 SLABS. PLOT OF 1-E v. T OVER THE TEMPERATURE RANGE 20-80°C
1-E WHERE E IS THE RATIO OF SOLUTE ABSORBED AFTER TIME T TO THAT ABSORBED AFTER INFINITE TIME
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
50
100
150
200
250
300
T — ABSORPTION TIME IN MINUTES
80°
70°
60°
50°
40°
30°
20°

FIG. 26

C.3.4. Absorption of M Sucrose by (2)H.125 Slabs.

T = 20.0°C.	t	110	160	210	270	330	390	450
	$1-E_a$	0.468	0.377	0.307	0.254	0.196	0.160	0.126
T = 30.1°C.	t	75	125	175	225	275	325	375
	$1-E_a$	0.476	0.356	0.278	0.213	0.171	0.124	0.0973
T = 39.9°C.	t	60	100	140	180	220	260	300
	$1-E_a$	0.465	0.355	0.273	0.201	0.157	0.127	0.0965
T = 50.0°C.	t	50	85	120	155	190	225	260
	$1-E_a$	0.441	0.340	0.250	0.188	0.145	0.107	0.0842
T = 59.9°C.	t	40	70	100	130	160	190	220
	$1-E_a$	0.471	0.350	0.240	0.172	0.131	0.0971	0.0648
T = 70.0°C.	t	30	55	80	105	130	155	180
	$1-E_a$	0.479	0.334	0.235	0.161	0.117	0.0810	0.0560
T = 80.1°C.	t	25	35	45	55	65	80	95
	$1-E_a$	0.465	0.396	0.332	0.274	0.212	0.172	0.138

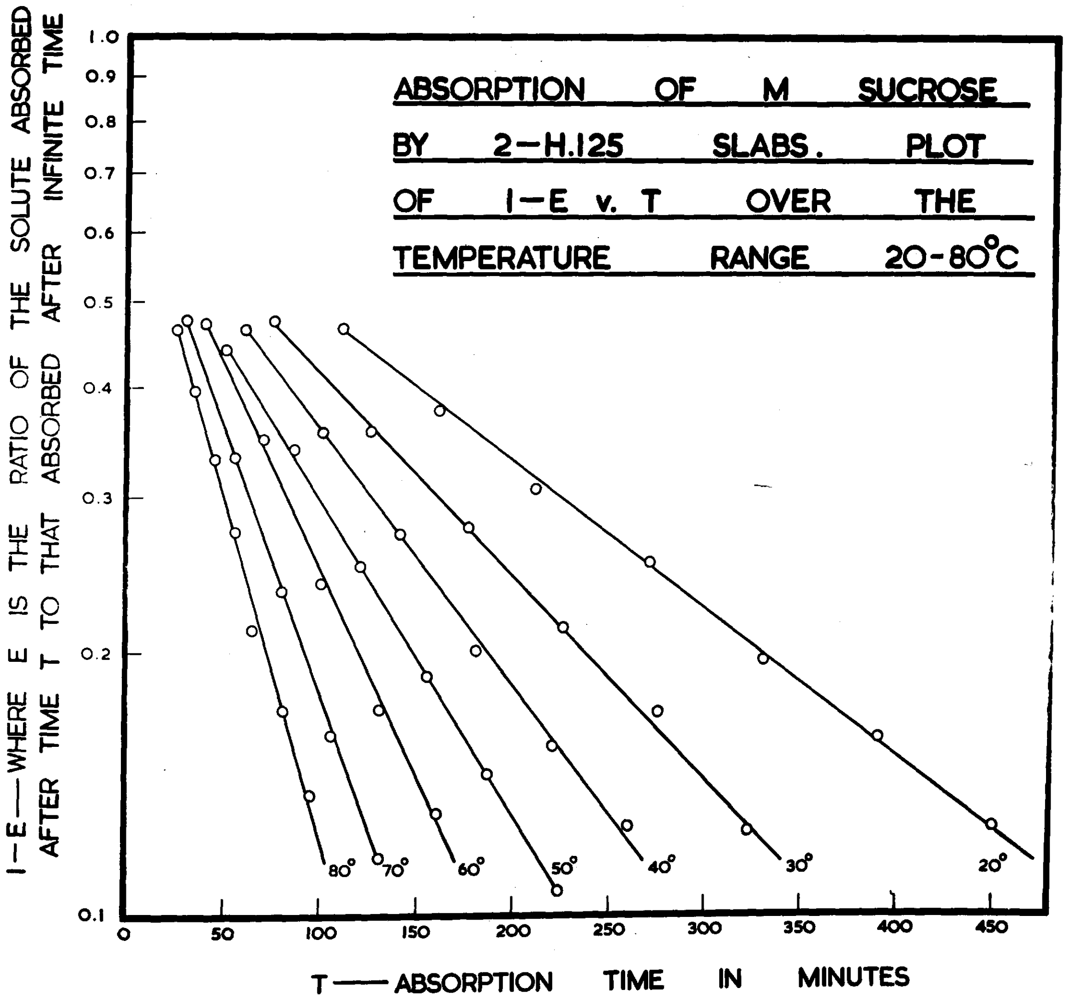

ABSORPTION OF M SUCROSE BY 2-H.125 SLABS. PLOT OF 1-E v. T OVER THE TEMPERATURE RANGE 20-80°C
1-E —— WHERE E IS THE RATIO OF THE SOLUTE ABSORBED AFTER TIME T TO THAT ABSORBED AFTER INFINITE TIME
T —— ABSORPTION TIME IN MINUTES
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
50
100
150
200
250
300
350
400
450
80°
70°
60°
50°
40°
30°
20°

FIG. 27

C.3.5. Desorption of 0.3M Sucrose from (2)B.5 Slabs.

T = 20.2°C.	t	75	125	175	225	275	325	375
	E_d	0.595	0.483	0.399	0.334	0.285	0.235	0.192
T = 30.0°C.	t	60	100	150	200	250	300	350
	E_d	0.580	0.474	0.366	0.282	0.236	0.185	0.144
T = 40.0°C.	t	75	110	145	180	220	270	300
	E_d	0.479	0.390	0.329	0.259	0.205	0.156	0.134
T = 50.1°C.	t	60	80	100	130	160	190	220
	E_d	0.483	0.431	0.358	0.290	0.230	0.187	0.150
T = 60.0°C.	t	40	65	90	115	145	170	200
	E_d	0.534	0.415	0.339	0.273	0.216	0.168	0.132
T = 70.0°C.	t	20	40	60	85	110	135	160
	E_d	0.633	0.492	0.392	0.300	0.228	0.178	0.141
T = 80.2°C.	t	20	30	40	55	70	85	100
	E_d	0.597	0.515	0.452	0.362	0.304	0.254	0.212

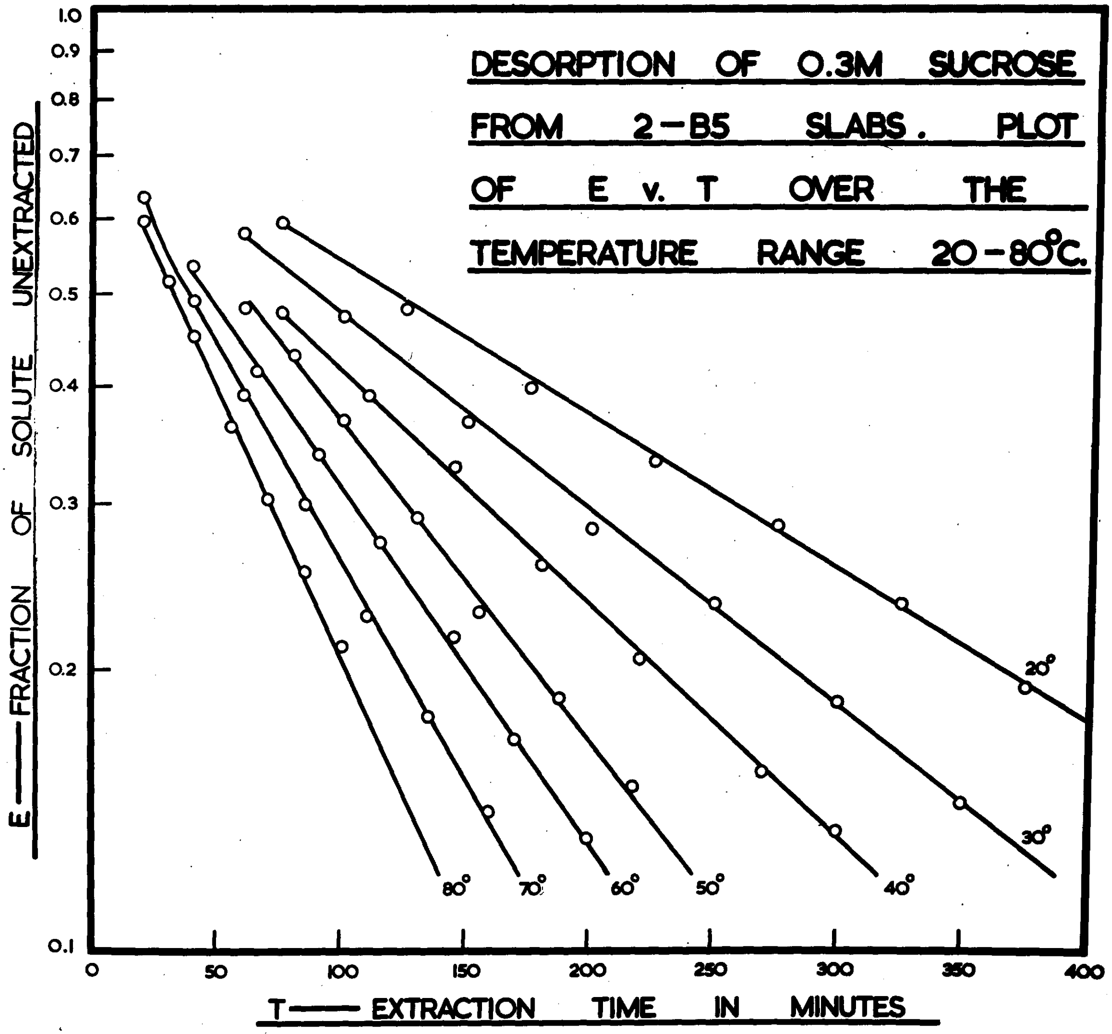

DESORPTION OF 0.3M SUCROSE FROM 2-B5 SLABS. PLOT OF E v. T OVER THE TEMPERATURE RANGE 20-80°C.
E — FRACTION OF SOLUTE UNEXTRACTED
T — EXTRACTION TIME IN MINUTES
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
50
100
150
200
250
300
350
400
20°
30°
40°
50°
60°
70°
80°

FIG. 29

C.3.6. Desorption of M Sucrose from (2)B.5 Slabs.

T = 20.0°C.	t	100	150	200	250	300	350	400
	E_d	0.535	0.457	0.382	0.314	0.262	0.219	0.189
T = 30.1°C.	t	100	140	180	220	260	300	350
	E_d	0.477	0.412	0.333	0.286	0.236	0.190	0.155
T = 40.1°C.	t	60	90	120	150	180	215	250
	E_d	0.542	0.459	0.376	0.319	0.269	0.219	0.182
T = 50.0°C.	t	60	80	100	130	160	190	220
	E_d	0.503	0.424	0.372	0.299	0.236	0.192	0.159
T = 60.0°C.	t	40	65	90	115	140	170	200
	E_d	0.534	0.425	0.336	0.278	0.216	0.181	0.132
T = 70.1°C.	t	45	60	75	90	110	130	160
	E_d	0.474	0.400	0.344	0.289	0.237	0.197	0.140
T = 80.0°C.	t	30	45	60	75	90	110	130
	E_d	0.533	0.447	0.363	0.305	0.250	0.193	0.157

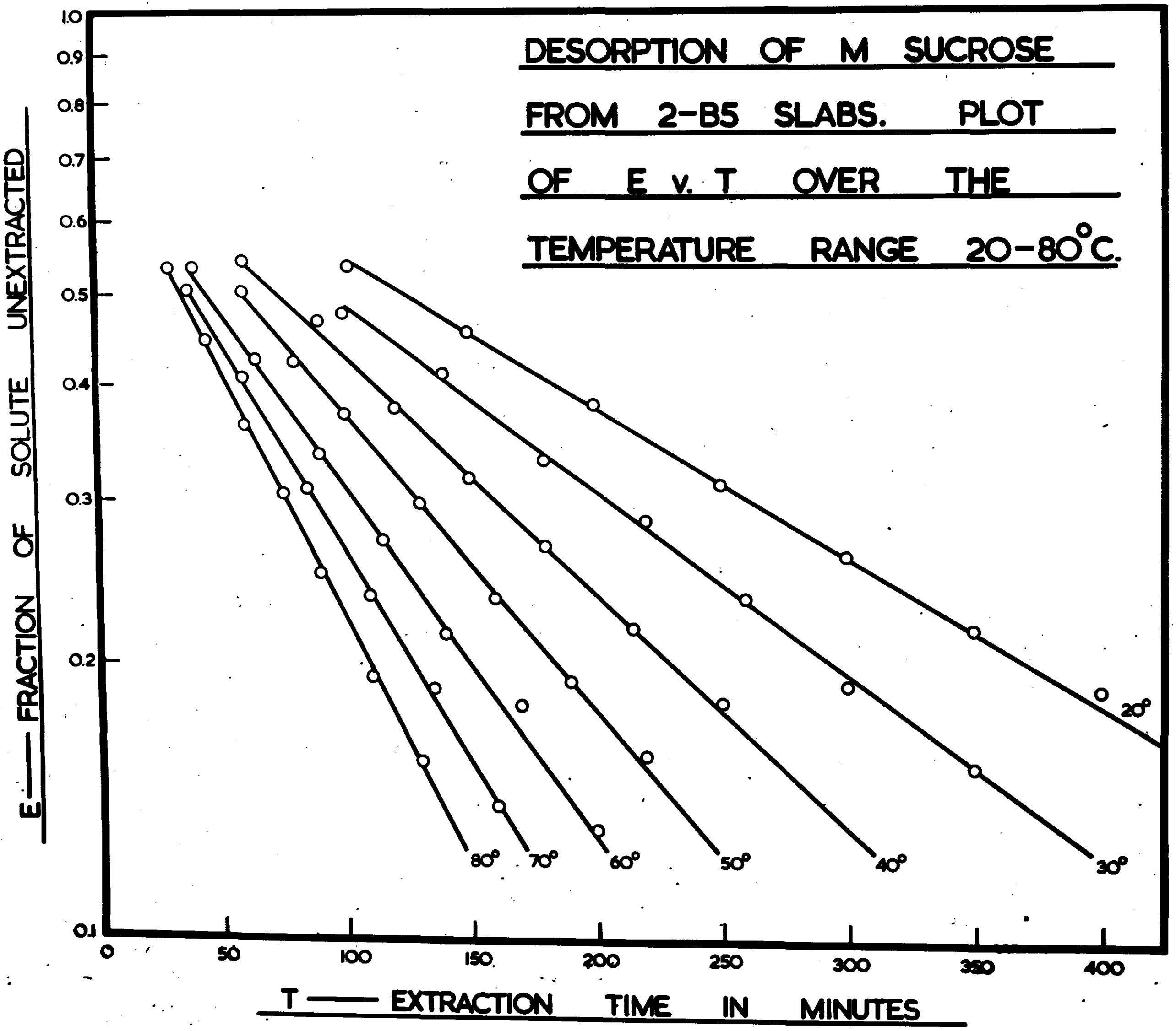

DESORPTION OF M SUCROSE FROM 2-B5 SLABS. PLOT OF E v. T OVER THE TEMPERATURE RANGE 20-80°C.
E —— FRACTION OF SOLUTE UNEXTRACTED
T —— EXTRACTION TIME IN MINUTES
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
50
100
150
200
250
300
350
400
20°
30°
40°
50°
60°
70°
80°

FIG. 30

C.3.7. Absorption of 0.3M Sucrose by (2)B.5 Slabs.

T = 20.2°C.	t	120	180	240	300	360	420	480
	$1-E_a$	0.478	0.394	0.328	0.265	0.222	0.175	0.144
T = 30.1°C.	t	100	150	200	250	300	350	400
	$1-E_a$	0.472	0.368	0.291	0.229	0.185	0.142	0.117
T = 40.1°C.	t	75	105	140	180	220	260	300
	$1-E_a$	0.512	0.411	0.326	0.272	0.218	0.175	0.143
T = 50.2°C.	t	70	100	130	160	190	220	250
	$1-E_a$	0.432	0.351	0.281	0.229	0.189	0.151	0.123
T = 60.0°C.	t	40	60	90	115	140	165	190
	$1-E_a$	0.508	0.427	0.328	0.252	0.203	0.162	0.125
T = 70.4°C.	t	40	60	80	100	120	140	160
	$1-E_a$	0.461	0.373	0.303	0.248	0.195	0.168	0.133
T = 80.2°C.	t	20	35	50	65	80	100	120
	$1-E_a$	0.567	0.454	0.381	0.307	0.248	0.165	0.145

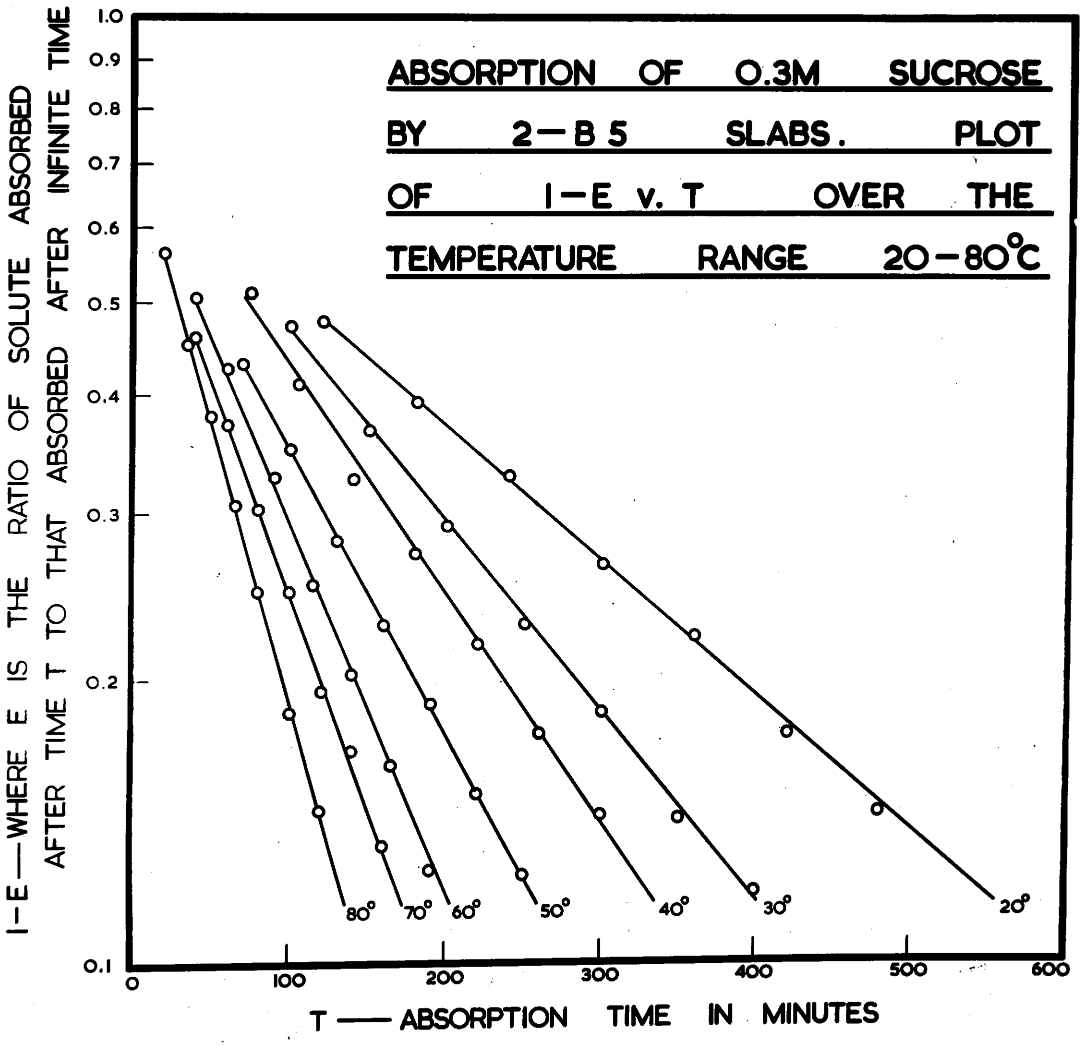

ABSORPTION OF 0.3M SUCROSE BY 2—B 5 SLABS. PLOT OF I—E v. T OVER THE TEMPERATURE RANGE 20—80°C
I-E —WHERE E IS THE RATIO OF SOLUTE ABSORBED AFTER TIME T TO THAT ABSORBED AFTER INFINITE TIME
T — ABSORPTION TIME IN MINUTES
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
100
200
300
400
500
600
80°
70°
60°
50°
40°
30°
20°

FIG. 31

C.3.8. Absorption of M Sucrose by (2)B.5 Slabs.

T = 21.0°C.	t	150	225	300	375	450	530	600
	$1-E_a$	0.440	0.354	0.274	0.226	0.183	0.157	0.132
T = 30.0°C.	t	120	190	260	330	400	470	540
	$1-E_a$	0.434	0.328	0.269	0.202	0.153	0.120	0.080
T = 40.0°C.	t	120	180	240	300	360	420	480
	$1-E_a$	0.384	0.282	0.223	0.171	0.131	0.0934	0.0851
T = 49.9°C.	t	80	130	180	235	280	330	380
	$1-E_a$	0.445	0.311	0.253	0.184	0.138	0.108	0.0753
T = 59.9°C.	t	60	100	140	180	220	260	300
	$1-E_a$	0.431	0.326	0.244	0.180	0.134	0.104	0.0757
T = 70.0°C.	t	60	90	120	150	180	210	240
	$1-E_a$	0.370	0.275	0.207	0.161	0.125	0.0974	0.0733
T = 79.8°C.	t	30	60	80	100	120	140	170
	$1-E_a$	0.456	0.340	0.277	0.223	0.179	0.140	0.106

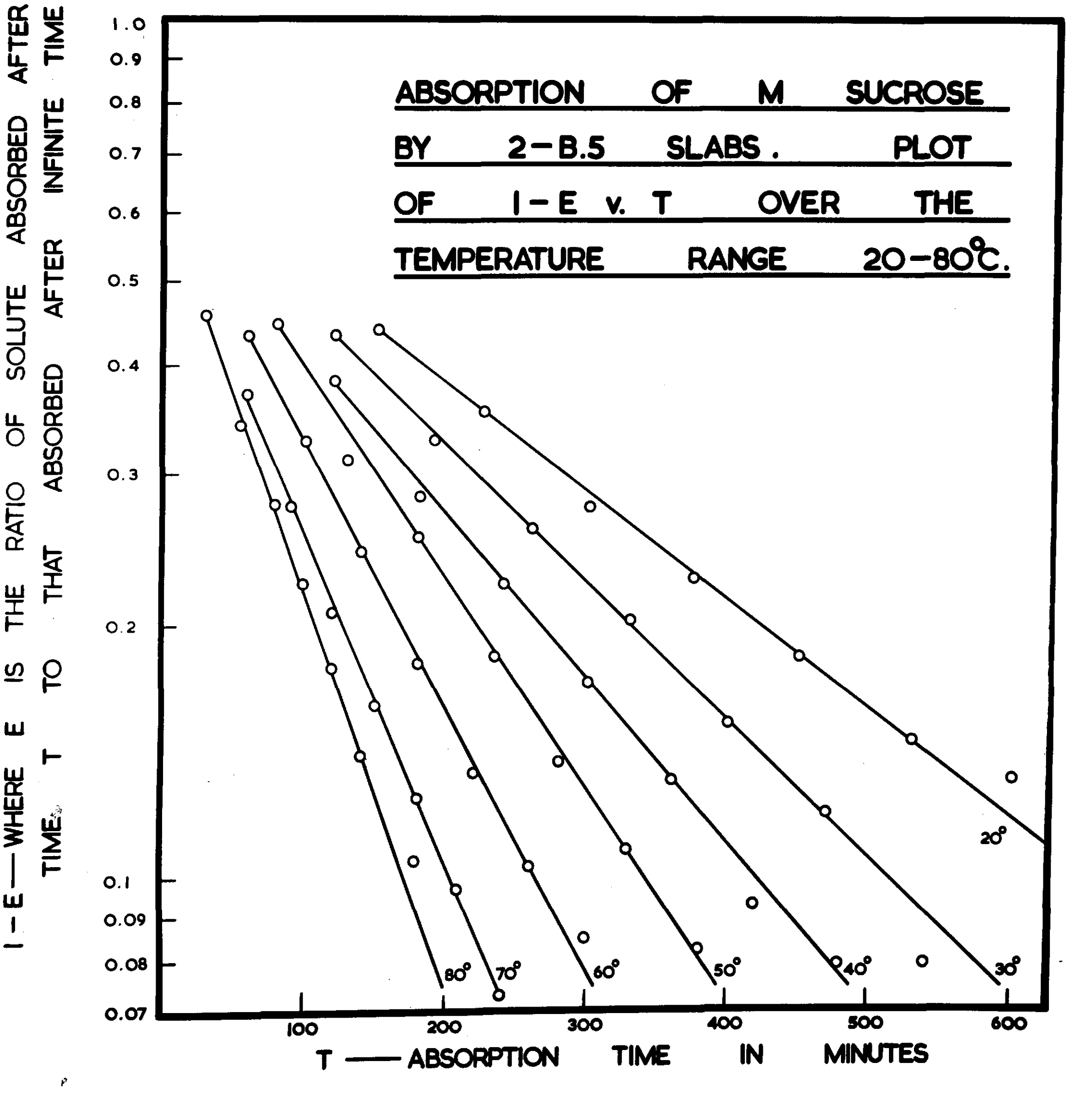

ABSORPTION OF M SUCROSE BY 2-B.5 SLABS. PLOT OF I-E v. T OVER THE TEMPERATURE RANGE 20-80°C.
I-E — WHERE E IS THE RATIO OF SOLUTE ABSORBED AFTER TIME T TO THAT ABSORBED AFTER INFINITE TIME
T — ABSORPTION TIME IN MINUTES
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.09
0.08
0.07
100
200
300
400
500
600
80°
70°
60°
50°
40°
30°
20°

FIG. 32

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