

SELF- AND EXCHANGE-DIFFUSION
IN MORDENITE

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ABSTRACT

Self-diffusion coefficients of seven cations were measured in their fully exchanged forms of mordenite at various temperatures. For the univalent cations, i.e. Na^+ , K^+ , Rb^+ and Cs^+ , self-diffusion coefficients at room temperature were between $5 \times 10^{-15} \text{ cm}^2 \text{ sec}^{-1}$ for Cs^+ and $2.5 \times 10^{-13} \text{ cm}^2 \text{ sec}^{-1}$ for Na^+ . Energies of activation were: approx. 8 kcal per g ion for sodium and potassium, 20.2 kcal per g ion for rubidium, and 4.3 kcal per g ion for caesium. An attempt was made to explain the anomalous value for caesium on the basis of a difference in sites, and hence in diffusion paths.

The bi-valent ions studied were Ca^{++} , Sr^{++} and Ba^{++} . Exchange forms contained approx. 75% Ca^{++} , 50% Sr^{++} and 75% Ba^{++} respectively, the remaining ions being sodium in all cases. In the strontium exchange form only one-quarter of the strontium ions were readily accessible to the radiotracer at temperatures below 100°C . Self-diffusion coefficients were of the order of $10^{-17} \text{ cm}^2 \text{ sec}^{-1}$ for Ca^{++} and Ba^{++} , and $10^{-15} \text{ cm}^2 \text{ sec}^{-1}$ for Sr^{++} . The behaviour of the strontium ion was explained in terms of a difference in equilibrium sites.

Self-diffusion coefficients were also determined in bi-ionic samples containing known amounts of Na^+ and K^+ . These D^* values showed a definite non-linear variation with the cationic composition of the zeolite.

Ion-exchange rates were determined for several pairs of cations. For the Na^+/K^+ system, exchange rates were also measured starting with heteroionic samples. Better agreement with theory was obtained by considering

self-diffusion coefficients as constant and equal to those in the homoionic forms than by using D_{Na}^* and D_K^* values measured in the heteroionic forms. This approach gave fairly good agreement for the sorption-desorption analogue. Helfferich and Plesset's theory was found to predict the same order of rates as obtained experimentally in the Na^+/K^+ system but it failed completely for the Na^+/Rb^+ system.

A C K N O W L E D G E M E N T S

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INTRODUCTION

A zeolite is essentially a defect form of silica in which some of the SiO_4^{4-} tetrahedra have been replaced by those of AlO_4^{5-} . These tetrahedra are almost exactly equal in size so no strain is introduced into the structure but for every AlO_4^{5-} present one cation of unit valency is required to preserve electroneutrality.

As in the case of regular tecto-silicates a variety of stacking patterns of tetrahedra are to be found. The number of aluminium atoms present differs from zeolite to zeolite and the Al/Si ratio is controlled by only one limiting factor: the impossibility, for stability reasons, of Al-O-Al bridges (ref. 1).

The cations which balance the negative charge caused by the aluminium ions are distributed along with water molecules in the vacant interstices of the zeolite. They have a remarkable mobility and can diffuse freely along the channels and in the cavities of the anionic framework. It is this ease of diffusion which makes such materials excellent cation exchangers.

CLASSIFICATION OF ZEOLITES

A three-dimensional structure with the $(\text{Si}, \text{AlO}_4)$ tetrahedron as the basic building unit can be realized in several different ways. Each particular zeolite consists of one such spatial arrangement of tetrahedra, so classification in terms of geometric structure is obviously not feasible.

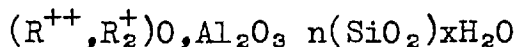
A more convenient classification has been suggested by Hey (1929)⁽²⁾ and is based on the strength of linkages between tetrahedra. According to this classification there are three main types of zeolites:

- (1) Fibrous zeolites: these have strong linkages in one direction only, e.g. natrolite.
- (2) Lamellar zeolites: linking is much stronger in two directions than in the third, e.g. heulandite.
- (3) Framework zeolites, which possess a rigid three-dimensional structure with strong bonding in all directions.

Zeolites of the last group are of particular interest. They provide almost ideal media for the study of ion exchange because:

- (a) they do not swell or shrink on ion exchange;
- (b) exchange is isotropic and rapid;
- (c) they are perfectly crystalline and thus the positions of most of the atoms in their structure can be determined by X-ray methods.

Mordenite, analcite and chabazite all belong to this class, and like all other zeolites can be defined by the formula



where R is a cation.

POSITIONS OF CATIONS IN ZEOLITES

The anionic framework structure of zeolites is fairly easily determined by X-ray methods. However, location of cations and water molecules is far more difficult. Certain sites in the structure are more favourable for cation occupation than others. However, X-ray data show that over a long period all the sites are filled for a part of the time. This indicates that the cations are in constant motion from site to

site and suggests a random-walk model. High self-diffusion coefficients for analcite⁽³⁾ and chabazite⁽⁴⁾ confirm this picture.

The positions of some cations in certain zeolites have been established. Taylor⁽⁵⁾ and Beattie⁽⁶⁾ have studied ion-exchanged analcites and sodium chabazite respectively. Broussard and Shoemaker⁽⁷⁾ have discussed the positions of cations in NaX, and Barrer and Meier⁽⁸⁾ have shown that Na-A contains at least two kinds of cation sites. However, other cations, known to be present in the structure, must be more loosely bound and are not detected by X-ray diffraction techniques.

As regards the forces which control diffusion of zeolitic cations, it is not yet possible to predict or define them exactly. It can only be stated here that they consist of dispersion and repulsion forces and direct coulombic interactions with the anionic framework. In such a situation the energy of activation for self-diffusion is of the utmost importance since it is one of the few sources of information about these internal interactions.

POSITION OF WATER MOLECULES IN ZEOLITES

The position of water molecules in zeolites is somewhat uncertain. They are physically adsorbed in the zeolite, filling the interstitial voids in the structure and not bound like true water of crystallization. Their mobility (most zeolites show at least partial reversible dehydration) indicates that like cations the water molecules are in continuous motion. However, they are subject to very powerful interactions with their environment, the heat of sorption being quite large for physical sorption⁽⁹⁾.

The influence of water molecules on self-diffusion coefficients is not yet clearly understood. Obviously they must hinder diffusion and thus possibly increase the energy of activation. However, they also have a screening effect reducing coulombic interactions between the cations and negatively charged framework, and this will lower the energy of activation for diffusion. There is also the possibility that a part of the water content of a zeolite is tied up as a solvated cation. This is the case in ion-exchange resins, and if it is true for zeolites one may expect self-diffusion coefficients to decrease with increasing hydration.

Self-diffusion of water molecules themselves in zeolites has been studied by comparatively few workers. Tiselius⁽¹⁰⁾ has evaluated these diffusion coefficients in heulandite from rates of water sorption, while Pemsler⁽¹¹⁾ has measured diffusion coefficients associated with exchange of certain ions.

Barrer and Fender⁽¹²⁾ also have used sorption methods to study the diffusion of water in zeolites, and their work is of some interest here since they have determined activation energies. These are given in the table below, and have values in the same range as ionic energies of activation for self diffusion.

TABLE 1

<u>Crystal</u>	$D^{\ddagger}(\text{at } 45^{\circ}\text{C})$ $\text{cm}^2\text{sec}^{-1}$	$D_{\bullet}^{\ddagger}$ $\text{cm}^2\text{sec}^{-1}$	$E^{\ddagger}$ kcal/mole
Chabazite	1.26×10^{-7}	1.2×10^{-1}	8.7
Gmelinite	5.4×10^{-8}	2.0×10^{-2}	8.1
Heulandite	2.07×10^{-8}	7.6×10^{-1}	11.0

SELF DIFFUSION IN ZEOLITES

Though quite a lot of work has been done on ion-exchange equilibria in zeolites very little attention has been paid to the kinetics of the self- and exchange-diffusion processes. In fact, only two zeolites, analcite and chabazite, have been studied in any detail from this point of view. The results obtained and their significance will now be briefly described.

SELF DIFFUSION IN ANALCITE

Analcite, which has a general formula $R_2O, Al_2O_3, 4SiO_2$ (where R is a univalent cation) consists of a system of interconnected channels, diffusion through which is controlled by two kinds of periodic "windows":

- (1) 6-membered oxygen rings of $2.3 \text{ \AA}$ free diameter
- (2) 8-membered oxygen rings of $2.4 \text{ \AA}$ free diameter.

Barrer and Rees⁽⁴⁾ have studied the self diffusion of the following ions: Na^+ (diameter $1.9 \text{ \AA}$), K^+ (diameter $2.66 \text{ \AA}$), Rb^+ (diameter $2.96 \text{ \AA}$), and Cs^+ (diameter $3.38 \text{ \AA}$). In each case self diffusion was studied in the fully exchanged form of the cation examined. The sodium form of the zeolite contained one water molecule per sodium ion present, but the other cationic forms were anhydrous.

Self diffusion was followed using radio-tracers, and D^* values were determined at various temperatures. Values of D_0 and the activation energy E were then calculated from the equation

$$D^* = D_0 \exp(-E/RT) \quad . \quad (1)$$

The data obtained by them are tabulated in Table 2.

TABLE 2. Self diffusion in analcite

Cation	$D^{\ddagger}$ at 25°C cm ² /sec	D_0 cm ² /sec	E kcal/g.ion
Na ⁺	1.14×10^{-13}	2.35×10^{-8}	11.5
K ⁺	1.96×10^{-17}	2.57×10^{-5}	16.4
Rb ⁺	8.27×10^{-22}	4.04×10^{-7}	20.1
Cs ⁺	9.51×10^{-24}	2.09×10^{-5}	26.1

The values of E show that the larger the cation the more difficult it is for it to overcome the barrier presented by the windows. It is of interest to examine the significance of this function E. Since it represents the energy required by a cation to be able to diffuse through the zeolite it obviously consists of various energy terms. The most important of these are: a coulombic energy term ΔE_C , a polarization energy term ΔE_{ϕ} , and a dispersion-repulsion term $\Delta E_{D.R.}$,

$$\text{i.e. } E = \Delta E_C + \Delta E_{\phi} + \Delta E_{D.R.} \quad (2)$$

Barrer and Rees⁽¹³⁾ have shown that if α is the polarizability of the diffusing cation,

$$\Delta E_{\phi} + \Delta E_{D.R.} \approx (B + C)\alpha \quad (3)$$

where B and C are constants

$$\therefore E = \Delta E_C + (B + C)\alpha \quad (4)$$

Barrer and Rees plotted polarizability of cations against activation energies for self-diffusion in analcite and obtained the approximately linear relationship in Fig. 1. This shows that ΔE_C is almost constant throughout the range of cations examined, and that changes in E are due to differences in polarizability.

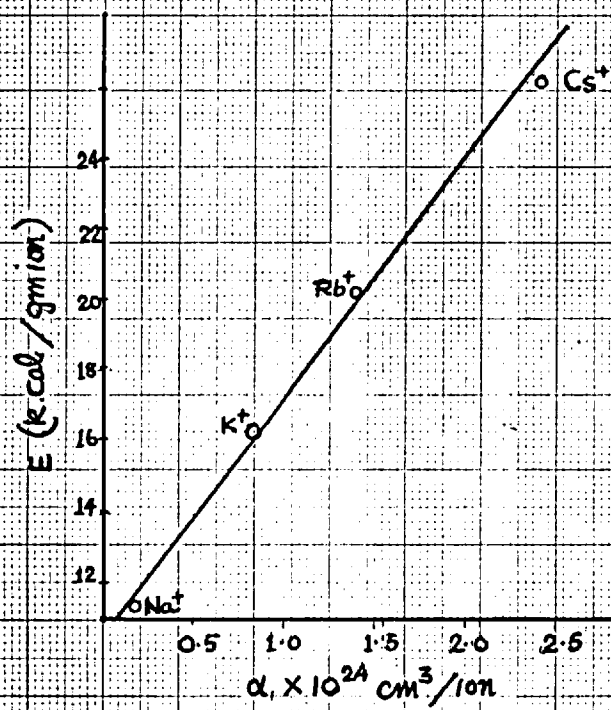


FIG. 1

Assuming the transition state theory to hold for this diffusion process:

$$D_0 = 2.72 \frac{kTd^2}{h} \exp\left(\frac{\Delta S^*}{R}\right) \quad (5)$$

where ΔS^* is the entropy of activation, d is the distance moved in each unit self-diffusion jump, and k and h have their usual meaning. If $d=4.75\text{\AA}$ (as shown by X-ray data for analcite) then

$$\begin{aligned} \Delta S &= -15 \text{ cal.mole}^{-1}\text{deg}^{-1} \text{ for Na}^+, \text{K}^+ \text{ and Cs}^+ \\ \Delta S &= -23 \text{ cal.mole}^{-1}\text{deg}^{-1} \text{ for Rb}^+. \end{aligned}$$

These high values of ΔS show that the saddle point represents a more ordered state, which Barrer and Rees interpreted as a simultaneous movement of the oxygen atoms making up the window away from the centre of the window.

SELF DIFFUSION IN CHABAZITE

This zeolite has been studied in greater detail. Barrer, Rees and Bartholomew⁽⁴⁾ have studied self-diffusion of three divalent ions Ca^{++} , Sr^{++} and Ba^{++} in addition to Na^+ , K^+ , Rb^+ and Cs^+ , and also measured the two individual self-diffusion coefficients in some samples of chabazite containing two species of cation. A few exchange-diffusion coefficients have also been determined.

The chabazite framework differs from that of analcite in that the free diameter of the window is now $3.9\text{\AA}$ - considerably greater than the diameter of any of the cations examined. The main feature of the structure is the characteristic chabazite cage. Each cage (and there is one per unit cell) has six octagonal, two hexagonal and twelve quadrilateral ring faces, and is

connected to the neighbouring six cages by the eight-membered rings; these rings are the controlling factor in the self-diffusion process. The values obtained by Barrer, Bartholomew and Rees are tabulated below.

TABLE 3. Self diffusion in chabazite

Cation	D^* cm ² sec ⁻¹ (at 25°C)	D_0 cm ² sec ⁻¹	E kcal/g.ion
Na ⁺	6.03x10 ⁻¹²	3.95x10 ⁻⁷	6.55
K ⁺	6.82x10 ⁻¹²	9.42x10 ⁻⁷	7.01
Rb ⁺	17.81x10 ⁻¹²	17.3 x10 ⁻⁷	6.75
Cs ⁺	0.55x10 ⁻¹²	1.66x10 ⁻⁷	7.55
Ca ⁺⁺	4.04x10 ⁻¹⁴	55.1 x10 ⁻⁷	13.81
Sr ⁺⁺	2.56x10 ⁻¹⁴	101.0x10 ⁻⁷	14.59
Ba ⁺⁺	0.11x10 ⁻¹⁴	3.90x10 ⁻⁷	8.85

As shown above the monovalent ions have an activation energy of approx. 7 kcal/g.ion while the bivalent ions Ca⁺⁺ and Sr⁺⁺ have an activation energy of about twice this value. Ba⁺⁺, however, has an extraordinary low value of 8.8 kcal/g.ion. These figures show that the main contribution to E must in this case be ΔE_C , the coulombic interaction term, since E is doubled when the charge of the cation is doubled. However, values obtained for Ba⁺⁺ are apparently anomalous though attempts have been made to explain them on the basis of a difference in sites.

D^* values in chabazite are larger than those obtained in analcite as one would expect since the window is so much larger.

From D_0 values, ΔS has once again been calculated as for analcite and values of approx. -20 cal.mole⁻¹deg⁻¹

are obtained. These negative entropies of activation suggest the coupling in motion of more than one species. In chabazite one plausible explanation is that activation and the unit diffusion step requires a certain ordering of water molecules within the zeolite.

Barrer, Bartholomew and Rees have tried to determine self-diffusion coefficients of Ca^{++} and Sr^{++} in samples of chabazite containing a mixture of these ions. Seven such samples, each containing a different ratio of ionic concentrations have been studied, and roughly linear relationships between D_s^* and the square of the mole fractions of the respective ions were obtained. It must be mentioned, however, that these results cannot be considered very reliable since the Si/Al ratio was not constant for all samples. This being so the linear plot of D^* against concentration may in fact be a very poor approximation. However, the experiments at least establish that D^* is not constant in zeolites but does vary with ionic concentration.

EXCHANGE DIFFUSION IN ZEOLITES

Most theories of ion-exchange kinetics have been developed with a view to explaining diffusion in resins and hence they all assume that D_A^* and D_B^* are constants. This assumption is not justifiable in zeolites. However, in spite of this it is interesting to consider how far these theoretical approaches fit zeolite data. The most sophisticated theory of ion exchange, and one most suitable for application to zeolites, is the one developed by Helfferich and Plesset⁽¹⁴⁾. This theory has been described in some detail in a later section, and here it will only be pointed out that it differs from previous treatments in

recognizing:

- (a) that $n_A^* \neq D_B^*$
- (b) that this difference sets up an electrical potential gradient which accelerates the slower ion and retards the faster one in order to maintain electrical neutrality.

(4) Helfferich and Plesset's theory has been applied to data on the $\text{Ca}^{++}/\text{Sr}^{++}$ system in chabazite but with little success. However, one system only was examined and obviously further data is required before anything definite can be said about the applicability of the theory.

SOME GENERAL STATEMENTS ON DIFFUSION IN ZEOLITES

From this brief description of work on analcite and chabazite we can draw the following conclusions:

- (a) the values of D^* vary ~~inversely~~ ^{directly} with free diameter of the diffusion channels;
- (b) activation energy is a resultant of various kinds of interaction whose relative importance depends on the type of zeolite. Thus dispersion-repulsion forces predominate in narrow channelled structures like analcite while coulombic forces are more important in open frameworks like chabazite;
- (c) entropies of activation have negative values, i.e. the cation at the top of the energy barriers represents a more ordered state;
- (d) D^* values of a particular ion in a zeolite are dependent on its ionic concentration within the zeolite.

REASONS FOR PRESENT STUDY

Chabazite and analcite obviously represent two extremes as far as framework-cation interaction is concerned. Physically they provide very open, and fairly confined, diffusion channels respectively. It is now necessary to consider what happens in the intermediate case, i.e. where the maximum free diameter is only slightly greater than required for the passage of a cation. Mordenite appears to be ideal for this purpose. It has two main kinds of channels:

- (1) large channel with free diameter of $6.6 \text{ \AA}$;
- (2) smaller channel interconnecting the large channels with a free diameter of $4 \text{ \AA}$ but containing a constriction of $2.8 \text{ \AA}$ free diameter half-way along the channel.

These would give free passage to Na^+ , K^+ , Rb^+ , Ca^{++} , Sr^{++} and Ba^{++} . Cs^{++} would pass easily through the larger channels but would be hindered by the $2.8 \text{ \AA}$ window.

A determination of self-diffusion coefficients of these ions in mordenite would therefore add to our understanding of activation energies and at the same time help us in attempts at predicting values for other zeolite systems.

Another aspect of the present project is a study of D_A^* and D_B^* in a bi-ionic zeolite containing varying proportions of A^+ and B^+ . This has been attempted before⁽⁴⁾ but the results were not very satisfactory. In ion-exchange resins (Boyd et al.⁽¹⁵⁾) self-diffusion coefficients do not vary greatly with concentration because of the random nature of the sites. However,

in zeolites there are usually two or three groups of sites of heterogeneous potential. The variation of self-diffusion coefficients with concentration may help us to elucidate these differences.

Finally a few pairs of ion-exchange coefficients have been determined and an attempt has been made to interpret these in terms of Helfferich and Plesset's theory. Obviously this theory cannot be applied to zeolitic diffusion in its present form but it is important to know where its limitations and failures lie. For this reason the Na^+/K^+ system has been considered in some detail, and exchange diffusion coefficients measured starting with exchangers containing various Na^+/K^+ ratios from the pure Na^+ to the pure K^+ form. Attempts have been made to interpret these results in terms of self-diffusion coefficients determined in the 'pure' forms and in the bi-ionic Na^+/K^+ mordenite.

2. THEORETICAL

2.1 ION EXCHANGE AS A KINETIC PROCESS

2.1.1 The rate determining step. In this project we are not primarily concerned with ion-exchange equilibrium. For our purposes ion exchange must be considered as a time-dependent phenomenon, and the questions we have to answer are the same as in any kinetic process.

Let us consider the exchange reaction $A^+ + BZ \rightarrow AZ + B^+$ (where A and B are ions involved in the exchange, and Z represents the zeolite framework). The exchange process is made up of two steps:

- (1) The diffusion of A^+ ions through the solution interface, and simultaneously (to maintain electrical neutrality) the diffusion of B^+ ions across the interface and away from the surface.
- (2) The diffusion of A^+ ions through the zeolite towards the exchange site, and the simultaneous diffusion of B^+ ions through the zeolite towards the solution.

Apart from these two interdiffusion steps there is the actual chemical exchange reaction. But in cases studied so far this process is comparatively fast and never rate-determining.

The conditions for electro-neutrality also have an effect on the mechanism. They make ion exchange a stoichiometric process and fluxes (in equivalents) of the two exchanging ions always remain equal even if mobilities are different.

To decide which of the two steps mentioned before is rate controlling it is necessary to know the conditions under which the experiment was carried out.

Boyd et al (1947) studied the case of an ideal particle in a well-stirred solution. He then suggested a model based on the Nernst liquid layer concept. According to this each ion-exchanger particle placed in a well-stirred solution is surrounded by a thin film - a zone of defined thickness with no convection, separated from the completely agitated solution by a sharp boundary. This is, of course, a drastic simplification since in actual fact the convection of the solution by turbulent or laminar flow recedes continuously from the bulk solution to the solid surface. However, it has been found to describe diffusion phenomena at interfaces very accurately, and is still accepted as a suitable model.

Applying this model, one can distinguish between two possible rate-determining steps:

- (a) Interdiffusion of counter ions within the exchanger itself (particle-controlled diffusion).
- (b) Interdiffusion of counter ions in the adherent films (film-controlled diffusion).

In particle-controlled diffusion, concentration gradients occur in the particles only whereas in film-controlled diffusion they occur only in the film. In actual fact, however, there is no sharp dividing line between the two. Every ion exchange is film-controlled during an initial, if extremely short, period and if the rates of particle and film-controlled diffusion are similar, both mechanisms effect the total rate. In all ion exchangers, high concentration of fixed ionic groups, low degree of crosslinking, small particle size, dilute solutions and inefficient agitation favour film-controlled diffusion. There is also the effect of the relative values of diffusion coefficients in the solution and zeolite respectively.

Boyd, Adamson and Myers (15) have shown that with a given system the conditions under which particle or film diffusion was rate controlling were determined by the ratio

$$\frac{\pi^2 D_z \delta k}{3 D_s r}$$

where D_s and D_z are the diffusion coefficients in solution and zeolite respectively, r is the radius of the particles, δ is the thickness of the Nernst layer, and k is the ratio B_z^+/B_s^+ where B_z^+ and B_s^+ are the final equilibrium concentrations in zeolite and solution respectively. If this ratio is greater than one, particle diffusion is rate controlling if less, film-diffusion control occurs.

2.1.2 Rate laws and diffusion coefficients. Since the rate of ion exchange is determined by diffusion processes, rate laws can only be formulated by application of the diffusion equation in one or other of its various forms.

In any diffusion process, considering one dimension only, the diffusion coefficient is defined as the rate of transfer of the diffusing substance across unit area of a section divided by the space gradient of concentration at the section. Thus, if the rate of transfer is F , the concentration of the diffusing substance is C , and the space coordinate normal to the section is x .

$$F = -D \frac{\delta C}{\delta x} \quad (6)$$

This is Fick's law and represents the most general form of the diffusion equation applicable to all diffusion processes. To interpret it in terms of physical forces it is necessary to define the various parameters more rigidly using definite frames of reference. These have been discussed by Barrer(16)

and Hartley and Crank (17).

Self-diffusion coefficients

Self-diffusion coefficients are designated D^* and conditions under which they can be determined are uniform chemical composition and a gradient of labelled molecules or ions. It is assumed, of course, that labelled and unlabelled entities are identical so far as diffusion is concerned.

Let n_A be the number of unlabelled molecules of A; n_A^* the number of labelled molecules of A; and n_B the number of molecules of B. Then according to the conditions mentioned above

$$\frac{\delta(n_A + n_A^*)}{\delta x} = 0 \quad \text{and} \quad \frac{\delta n_B}{\delta x} = 0$$

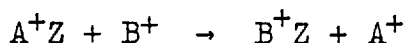
$J_A^* = -D_A^* \frac{\delta C_A^*}{\delta x}$ per unit crosssection normal to x.

Since there is no mass flow and labelled and unlabelled molecules are otherwise identical, D^* is a measure of the true mobility of the labelled species with respect to the stationary environment. However, the interpretation of this mobility and hence of diffusion coefficients in zeolites is an extremely complex task. As in all ion exchangers, conditions under which diffusion occurs are specific and environmental effects become far more important than in homogeneous media. The matrix takes up a considerable proportion of the volume of the medium and obstructs diffusion, causing, particularly in zeolites and other rigid-framework networks, a channelling effect within the structure. The theory of ion-exchange in its present form by-passes these difficulties by considering

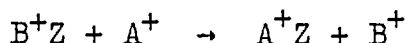
the ion exchanger as a single quasi-homogeneous phase regardless of differences in molecular dimensions or geometric structure. The nature of an 'effective' self-diffusion coefficient calculated on the basis of such assumptions is still largely unknown, though factors effecting its value can be stated qualitatively.

Even less is at present known about the significance of exchange diffusion coefficient. The conditions of the experiment in this case require a chemical concentration gradient and the ions involved in the exchange belong to different species. The relationship between self- and exchange-diffusion coefficients has been studied (18) and this has been described in a later section.

The same authors have drawn an analogy between gas sorption (Crank and Park (19)) and ion exchange in order to explain values of exchange diffusion coefficients. According to the analogy, the value of the diffusion coefficient D_{AB} determined for any exchange reaction



is, in fact, an integral value over the concentration range present in the particle during the experiment. D_{BA} , i.e. the diffusion coefficient for the reaction



is another such integral. If the analogy holds, then

$$\frac{1}{2}(D_{AB} + D_{BA}) = \frac{1}{C_0} \int_0^{C_0} D \delta c \quad (7)$$

where C_0 is the final concentration of the incoming ion in the particle which was initially free from this ion.

However, ion-exchange data shows that this relationship does not hold, possibly the concentration range C_0 to 0 is too large and also unlike their analogues in a sorption system D_{AB} and D_{BA} differ greatly in magnitude.

2.2 SOLUTIONS OF THE DIFFUSION EQUATION

Isotopic exchange due to particle diffusion assuming D^* to be constant

Let us consider a system with isotopic counter ions A and A^* . Initially all the ions A are in the particle.

Flux of A in the particle is:

$$J_A = -\bar{D} \text{grad } \bar{C}_A \text{ (bars refer to interior of particle)} \quad (8)$$

By Fick's second law:

$$\frac{\delta \bar{C}_A}{\delta t} = -\text{div } J_A \quad (9)$$

Combining (1) and (2) (Crank (20)) for diffusion in spheres:

$$\frac{\delta \bar{C}_A}{\delta t} = \bar{D} \left(\frac{\delta^2 \bar{C}_A}{\delta r^2} + \frac{2}{r} \frac{\delta \bar{C}_A}{\delta r} \right) \quad (10)$$

r = radial space coordinate or distance from the centre of the particle.

This equation must be solved under appropriate initial and boundary conditions.

Initial conditions are: all ions A are in the ion-exchanger at a uniform concentration $\bar{C}_A^0$ and no A is in the solution, i.e.

$$\left. \begin{array}{l} r > r_0, t = 0, \bar{C}_A(r) = 0 \\ 0 < r < r_0, t = 0, \bar{C}_A(r) = \bar{C}_A^0 = \text{constant} \end{array} \right\} \quad (11)$$

where r_0 = particle radius.

There are two possible types of boundary conditions, the infinite volume conditions where concentration of A in the solution remains negligible throughout, e.g. shallow bed methods, and the finite volume conditions which are applicable to batch methods. The second type will be considered here since they are more important in this project.

The conditions in the finite volume method can be explained in terms of material balance:

loss of A from ion exchanger = gain of A by solution,
equilibrium at the interface being assumed.

Boundary conditions can then be formulated as follows:

$$r = r_0, t > 0, \bar{C}_A(t) = \frac{3\bar{V}\bar{C}}{r_0\bar{V}\bar{C}} \int_0^t J_A(t)dt \quad (12)$$

A solution for equation (10) under conditions (11) and (12) have been worked out by Patterson (21) for the corresponding heat transfer problem, but unfortunately this is not very useful for our purposes since it gives a convergent value only when $\bar{D}t/r_0^2 \gg 0.1$ and this range extends far beyond the half-time for exchange.

Barrer (22) has derived an equation for gas sorption which can be conveniently applied to the self-diffusion of ions. He has first considered a single sphere of sorbent of radius a , and then deduced the more general form for a powder of small spheres. Henry's law was assumed to operate and the diffusion equation was solved for these boundary conditions.

If V_g is the volume of the gas phase, V_s is the volume of the sorbent, u_0 is the initial gas phase concentration of the sorbate, then at $t=0$, $Q_0=u_0V_g$ =gas released into the volume V_g in contact with the sorbent. The general isotherm relating the gas-phase concentration of sorbate (u) and sorbate concentration (v) in sorbent is

$$\frac{k_1 u}{1+k_2 u} = v \quad (13)$$

but Henry's law is a limiting case of this isotherm in which

$$k_1 u = v \quad (14)$$

The diffusion equation has been used in the form

$$\frac{\delta(rV)}{\delta t} = D \frac{\delta^2(rV)}{\delta r^2} \text{ for } a > r > 0, t > 0 \quad (15)$$

with boundary conditions

$$\begin{aligned} v &= v_0 \text{ for } a > r > 0 & t &= 0 \\ v &= k_1 u \text{ for } r = a & t &> 0 \\ u &= u_0 \text{ for } r > a & t &= 0 \end{aligned} \quad (16)$$

and the equation

$$V_g \frac{\delta u}{\delta t} + 4\pi a^2 D \frac{\delta V}{\delta r} = 0 \text{ at } r = a, t > 0 \quad (17)$$

A quantity K_1 is then defined:

$$K_1 = V_g / (k_1 V_s) \quad (18)$$

By standard methods (Carslaw and Jaeger, 'Conduction of Heat', O.U.P., 1947, p. 205) Barrer then derives:

$$v_1 = v(r) = \frac{1}{K_1 + 1} \left[\frac{Q_0}{V_s} + v_0 \right] + \frac{6a}{r} \left(\frac{Q_0}{V_s} - K_1 v_0 \right) \sum_{a_1^2 S} \frac{\sin a_{1n} \tau}{\sin a_{1n} a} \times \frac{\exp(-a_{1n}^2 \tau)}{9(K_1 + 1) + a_{1n}^2 K_1^2} \quad (19)$$

where $\tau = \frac{D_1 t_1}{a^2}$ and a_{1n} is the n^{th} positive root of the

equation

$$\tan a_1 a = \frac{3a a_1}{3 + K_1 a^2 a_1^2}.$$

In the gas phase the concentration u follows from equation (19), where $\tau = a$, since $u_1 = v_1/k_1$

$$u_1 = \frac{1}{(K_1 + 1)k_1} \left[\frac{Q_0}{V_s} + v_0 \right] + \frac{6}{k_1} \left(\frac{Q_0}{V_s} - K_1 v_0 \right) \sum_{a_1^2 S} \frac{\exp(-a_{1n}^2 \tau)}{9(K_1 + 1) + a_{1n}^2 K_1^2} \quad (20)$$

Q_1 , the quantity of gas remaining unsorbed after time t_1 is simply $V_g x u$, while the quantity sorbed Q_t is

$$Q_0 + v_0 V_S - Q_1 .$$

The solutions obtained can be generalized from the single sphere to a powder of N spherical particles all equal in size. In this case if v_s is the volume of a small single sphere $V_S = N v_s$. For example, equation (17) becomes

$$\frac{V_g}{N} \frac{\delta u}{\delta t} + 4\pi a_1^2 D_1 \frac{\delta V}{\delta r} = 0 .$$

When $v_0=0$ Barrer solves equation (19) using methods described by him elsewhere (Barrer 1938 (23)) and obtains

$$\frac{Q_t}{Q_\infty} = (K+1) \left\{ 1 - \frac{1}{\alpha + \beta} \left[\alpha e^{-\alpha^2 \tau} (1 + \operatorname{erf} \alpha \sqrt{\tau}) - \beta e^{-\beta^2 \tau} (1 + \operatorname{erf} \beta \sqrt{\tau}) \right] \right\} \quad (21)$$

where α and β are the roots of the equation

$$\chi^2 - 3\chi/K - 3/K = 0 .$$

Both exponentials and error functions can be expanded as series and for very small values of $\sqrt{\tau}/K$ only the first term in the expansion need be considered; this gives various equivalent forms of a ' $\sqrt{t}$ law':

$$\left. \begin{aligned} \frac{Q_t}{Q_\infty} &= \frac{6(K+1)}{K} \sqrt{\frac{\tau}{\pi}} \\ &= \frac{6}{a} \frac{K+1}{K} \sqrt{\frac{Dt}{\pi}} \\ &= \frac{6}{a} \left(\frac{Q_0}{Q_0 - Q_\infty} \right) \sqrt{\frac{Dt}{\pi}} \end{aligned} \right\} \quad (22)$$

The last form is the one most conveniently applicable to the ion-exchange analogue. Considering the particular case of self-diffusion assuming that D^* is constant, and remembering that the radioactive isotope is initially in

the solution phase, the terms can be redefined as follows:

u = concentration of radioactive cation in solution

v = concentration of radioactive cation in solid

v_g = volume of solution

Q_0 = initial count of solution

Q_t = loss in activity of solution at time t

Q_∞ = loss in activity of solution at equilibrium.

$(\frac{6}{a})$ can be substituted by $(\frac{2A}{V})$ where A =the total surface area of the exchanger, and V is the reciprocal of the density.

2.3. ZEOLITIC EXCHANGE AS AN ACTIVATED PROCESS

2.3.1 Interpretation in terms of transition state theory

Barrer (24) has given a fairly thorough description of diffusion in lattices. He has considered Frenkel, Schottky and zeolitic mechanisms, and explained the significance of the activated state in terms of the transition state theory. In his treatment, the activated state is represented by a raised energy level lying between the lower initial and final state of the diffusing species. The activation energy corresponds to the difference between the activated and initial states: in other words, it is the energy barrier which has to be overcome in passing from the initial to the final state. Using this approach and by considering the speed with which the diffusing species travels over the energy barrier, Barrer has derived the general expression for D in any diffusion process:

$$D = d^2 \frac{kT}{h} \frac{F^*}{F_n} e^{-E/RT} \quad (23)$$

where d = the distance travelled in a single jump;

F^* = the partition function for the motion treated as a simple translation over the top of the energy barrier;

F_n = the partition function of the normal state;

E = the energy of activation;

k and h have their usual meanings.

In the case of zeolitic diffusion, however, this expression must be multiplied by a probability term which denotes the chance that an activated interstitial ion will find a vacant site to migrate into. This term is $(N^1 - n)/N^1$ where N^1 = the total number of sites, and n = the number of occupied sites.

Therefore we obtain:

$$D = d^2 \frac{kT}{h} \frac{F^\ddagger}{F} e^{-E/RT} \left(\frac{N^1 - n}{N^1} \right) \quad (24)$$

$$\text{or } D = d^2 \frac{kT}{h} e^{-\Delta A^\ddagger/RT} \left(\frac{N^1 - n}{N^1} \right) \quad (25)$$

$$\text{or } D = d^2 \frac{kT}{h} e^{\Delta S^\ddagger/R} e^{-\Delta E^\ddagger/RT} \left(\frac{N^1 - n}{N^1} \right) \quad (26)$$

where the thermodynamic symbols have their usual meanings and terms with ‡ s refer to the activated state.

Comparing equation (26) to Arrhenius equation

$D^\ddagger = D_0 \exp -E/RT$, we get

$$D_0 = e^{\Delta S^\ddagger/R} \left(\frac{kT}{h} \right) d^2 \frac{1}{(2.72)^{N^1}} \left(\frac{N^1 - n}{N^1} \right) \quad (27)$$

where $n \ll N^1$, $\left(\frac{N^1 - n}{N^1} \right) \approx 1$. This is a convenient expression for calculating entropies of activation, and has been used in this project.

2.3.2 Calculation of activation energy

Activation energies for self-diffusion of various cations in mordenite have been calculated using the simple Arrhenius equation $D^\ddagger = D_0 \exp (-E/RT)$. $D^\ddagger$ has been determined at various temperatures, and E has been calculated from a plot of $\log_{10} D^\ddagger$ vs $\frac{1}{T^\circ} \text{ K}^{-1}$.

2.4 THEORIES OF ION EXCHANGE

So far we have discussed only self-diffusion, and we have made the assumption that $D^\ddagger$ is constant and independent of time and concentration. This is justifiable for isotopic exchange, but is certainly not a

general rule. For ion exchange involving different ions it is quite incorrect. Here the situation is extremely complex. Factors like selectivity, specific interactions, electrolyte sorption and desorption, and electronic coupling of ionic forces, are no longer negligible. A quantitative treatment has so far not been attempted, and it is likely that a rigorous theory based on conventional mathematical methods is impossible. However, solutions have been obtained for the most important limiting cases, though even these had to be worked out on computers.

Before examining some of these solutions the factors mentioned above will be considered qualitatively. The most important of them is the coupling of ionic forces. This is inherent in the ion-exchange process, being a consequence of the electroneutrality condition for the exchange reaction. Considering the exchange of two kinds of ions of different mobility, the faster one of course tends to diffuse at a higher rate, but any charge transfer caused by this builds up a diffusion potential which slows down the faster ion and accelerates the slower one. Thus the net counterionic fluxes remain equivalent.

Selectivity of the zeolite, conveniently expressed in terms of the separation factor $\alpha_B^A = \frac{\bar{C}_A^A \bar{C}_B^B}{\bar{C}_B^A \bar{C}_A^B}$ (where bars refer to the interior of the particle) can affect the rate of both particle and film controlled diffusion. One way of avoiding deviations due to selectivity in a theoretical approach is to assume the boundary conditions necessary for infinite solution volume

$$r=r_0, t>0 \quad \bar{C}_A(t)=0,$$

i.e. the concentration of A at the interface remains effectively zero irrespective of selectivity.

The effects of specific interactions, swelling, electrolyte sorption and desorption, and the presence of co-ions, will not be discussed here since they are not important in zeolites, the first two being practically non-existent and the others being negligible because of Donnan exclusion. The effect of gradients of activity coefficients, however, must be considered in a detailed analysis. In a system with a concentration gradient the overall flux J is made up of the diffusion flux $(J)_{\text{diff}}$ and the electrical transference flux $(J)_{\text{el}}$.

The electrical transference flux $(J)_{\text{el}} = u_i z_i C_i \text{grad } \varphi$:

u_i = electrochemical mobility of species i

z_i = valence of i

φ = electrical potential.

The diffusion flux is

$J(\text{diff}) = \mu_i C_i \text{grad } \mu_i$, where

$\mu_i = D_i (\text{grad } C_i + C_i \text{grad } \ln f_i)$ = chemical potential species (f_i = activity coefficient).

Another factor which cannot be neglected is the variation of the individual self-diffusion coefficients of ions. The assumption that these are constant through all ranges of concentration has been found experimentally to be incorrect for zeolites.

In principle all the above factors can be accounted for by using more refined equations for all the mobile species and integrating these under accurate boundary conditions, but this is not feasible. It is certainly impossible to obtain rigorous analytical solutions and the numerical solutions available have the usual limitations of such methods - applicability only to specific values, numerous measurements of parameters, and

the necessity to establish the dependence of various parameters on variables.

Early attempts at theories of ion exchange did not account for any of the effects discussed above. They all (Glueckauf (25), Holm (26), Kressman and Kitchener (27), Reichenberg (28), Rosen (29)) assume Fick's first law with a constant diffusion coefficient, and thus ignore the effect of the electric field. In place of the self-diffusion coefficient they describe an empirical interdiffusion coefficient so that equal rates and identical concentration profiles are predicted for the forward and backward reactions. This, of course, is not found experimentally and the approximation gets rapidly worse as the difference between self-diffusion coefficients increases.

Of these early theories, work on film-diffusion control by Adamson(30), extended by Dickel(31) is of interest. It includes the effect of selectivity and uses individual diffusion coefficients, however the electric field is neglected. Recent theories of ion exchange have been more refined, and of these, the one put forward by Helfferich and Plesset is definitely the most significant.

2.4.1 Helfferich and Plesset's theory

Helfferich and Plesset (14) considered a resin with constant cross-linking and treated it as a quasi-homogeneous phase. They assumed: (1)

(1) Self-diffusion coefficients for a mobile ion are constant for a given resin, i.e. independent of ionic concentration (Helfferich and Ocker(32), Boyd and Soldano(33), Tottenbaum and Gregor(34));

- (2) Any coupling of ionic forces other than electrical is negligible;
- (3) Concentration of fixed ionic groups throughout the resin is constant;
- (4) Concentration change and flux of co-ions are negligibly small compared to those of the counterions provided the concentration of the solution is not too high and that of the ionic groups is not too low;
- (5) There is no swelling of the resin during exchange.

They then applied the following rate laws:

- (1) The transference equation which states that in an electric field the transference $(J_i)_{el}$ of an arbitrary species i in the direction of the current is proportional to the gradient of the electric potential ϕ , to the concentration C_i and the electrochemical valence z_i of the species.

$$(J_i)_{el} = -u_i z_i C_i \text{grad} \phi \quad (28)$$

(u , the proportionality factor, is defined as the electrochemical mobility of species i).

- (2) The Nernst-Einstein relation

$$u_i = \frac{D_i F}{RT} \quad (29)$$

D_i = self-diffusion coefficient of the species (this relation is derived for ideal solutions but can be used as a good approximation in an ion-exchange crystal possibly because the smallness of the pores prevents the formation of ionic clouds, most deviations from the equation being caused by deformation of ionic clouds by electric field (Helfferich (35))).

(3) Fick's law: This represents purely statistical diffusion.

$$(J_i)_{\text{diff}} = -D_i \text{grad } C_i \quad (8)$$

Combining equations (28). (29) and (8), the total resulting flux is

$$J_i = (J_i)_{\text{diff}} + (J_i)_{\text{el}} = -D_i (\text{grad } C_i + z_i C_i \frac{F}{RT} \text{grad } \phi) \quad (30)$$

This is called the Nernst Planck equation, and holds in ideal systems for all the mobile species present. It must be solved under appropriate conditions. Inherent in the equation are assumptions that effects of convection, pressure gradients, and activity coefficients are negligible.

Helfferich and Plesset discussed both film and particle diffusion control; here we shall consider only the latter treatment in detail. In this case the system is subject to the following restrictions:

$$(a) \quad Z_A \bar{C}_A + Z_B \bar{C}_B = \text{constant} \quad (31)$$

(condition of electroneutrality)

$$(b) \quad Z_A J_A + Z_B J_B = 0 \quad (32)$$

(since there is no electric current)

Combining these two equations with the Nernst-Planck equation we get

$$J_A = - \left[\frac{\bar{D}_A^* \bar{D}_B^* (Z_A^2 \bar{C}_A + Z_B^2 \bar{C}_B)}{Z_A^2 \bar{C}_A \bar{D}_A^* + Z_B^2 \bar{C}_B \bar{D}_B^*} \right] \text{grad } \bar{C}_A \quad (33)$$

The quantity inside the square brackets is called the interdiffusion coefficient D_{AB} . It is not a constant, its value being dependent not only on $\bar{D}_A^*$ and $\bar{D}_B^*$ but on the relative concentrations of A and B, i.e. on the ionic composition of the crystal which changes in course of the exchange process.

Helfferich and Plesset have then introduced the equation of continuity in the form

$$\delta C_A / \delta t = -\text{div}(J) \quad (34)$$

On substituting (33) into (34) an expression is obtained which can be written conveniently in the dimensionless form in terms of the following dimensionless parameters:

$$\gamma = Z_A C_A / C \quad \tau = D_A t / r_0^2 \quad \rho = r / r_0$$

$$a = (Z_A D_A / Z_B D_B) - 1 \quad b = Z_A / Z_B - 1$$

where t is time, r is the radial coordinate, and r_0 is the radius of the bead. The detailed derivation of resulting equation will not be considered here, but the final form is as follows:

$$\frac{\delta r}{\delta \tau} - \frac{1}{1+a\gamma} \left[(1+b\gamma) \frac{\delta^2 \gamma}{\delta \rho^2} + \frac{b-a}{1+a\gamma} \left(\frac{\delta \gamma}{\delta \rho} \right)^2 + \frac{2(1-b\gamma)}{\rho} \frac{\delta \gamma}{\delta \rho} \right] = 0 \quad (35)$$

The fraction q_A of the species A still present in the sphere at dimensionless time τ has been expressed in terms of the solution $\gamma(\rho, \tau)$ of equation (35) as follows:

$$q_A(\tau) = 3 \int_0^1 \gamma(\rho, \tau) \rho^2 \delta \rho.$$

The ion-exchange rate defined as the decrease with time of the amount Q_A of the species A (in moles) present in the spheres may be written as

$$- \frac{dQ_A}{dt} = -VC \frac{\delta q_A}{\delta t} = - \frac{VCD_A}{r_0^2} \frac{dq_A}{d\tau} \quad (36)$$

where V is the total volume of ion exchanger used. For counter ions of equal valence $Z_A = Z_B$ so that $b=0$, the general equation (35) may then be simplified by introducing the variable

$$u = \ln(1+a\gamma).$$

This gives

$$\frac{\delta u}{\delta \tau} - \frac{1}{\rho^2} \frac{\delta}{\delta \rho} \left(\rho^2 \frac{\delta u}{\delta \rho} \right) = 0 \quad (37)$$

and Helfferich and Plesset have used this convenient form of the equation for numerical integration.

The simplest possible initial and boundary conditions have been used, i.e.

$$\left. \begin{array}{l} 0 \leq \rho < 1, \quad \tau = 0, \quad \gamma(\rho) = 1 \\ \rho \geq 1, \quad \gamma(\rho, \tau) = 0 \end{array} \right\} \quad (38)a \text{ and } b$$

The second condition corresponds to infinite solution volume, while the first represents more general limiting laws which can be approached by experimental methods. However, it is also possible to obtain a solution for the case in which the distribution is

$$\left. \begin{array}{l} 0 \leq \rho < 1, \quad \tau = 0, \quad \gamma(\rho) = \gamma_0 \\ \rho \geq 1, \quad \gamma(\rho, \tau) = 0 \end{array} \right\}$$

where γ_0 may have any value in the range $0 < \gamma_0 \leq 1$. This of course represents a problem where γ_0 is the uniform initial value of γ in the sphere. Under the simple conditions (38a) and (38b) Helfferich and Plesset have evaluated (37) numerically for six values of the ratio D_A/D_B .

An explicit expression for $F(\tau)$, the fractional attainment of equilibrium, has been obtained by them, and this approximates the numerically computed results to ± 0.01 . According to this

$$F(\tau) = (1 - \exp\{\pi^2[f_1(a_1)\tau + f_2(a)\tau^2 + f_3(a)\tau^3]\})^{\frac{1}{2}}$$

for $Z_A = Z_B$

$$\left. \begin{array}{l} f_1(a) = - \frac{1}{.570 + 0.430a(.775)} \\ f_2(a) = + \frac{1}{.260 + 0.782a} \\ f_3(a) = - \frac{1}{.165 + 0.117a} \end{array} \right\} \begin{array}{l} \text{range of validity} \\ 10 > D_A^*/D_B^* > 0.1 \end{array}$$

for $Z_A/Z_B = \frac{1}{2}$

$$\left. \begin{aligned} f_1(\alpha) &= -\frac{1}{0.64 + 0.36\alpha^{(0.368)}} \\ f_2(\alpha) &= -\frac{1}{0.96 + 2.0\alpha^{(0.4635)}} \\ f_3(\alpha) &= -\frac{1}{.27 + 0.09\alpha^{(1.14)}} \end{aligned} \right\} \begin{array}{l} \text{range of validity} \\ 1 \leq D_A^*/D_B^* \leq 20 \\ \text{to within an error of} \\ 0.012 \text{ in } Q_t/Q_\infty \end{array}$$

for $Z_A/Z_B = 2$, two different sets of coefficients have been used:

$$\left. \begin{aligned} f_1(\alpha) &= -\frac{1}{0.35 + 0.650\alpha^{(0.86)}} \\ f_2(\alpha) &= \frac{1}{0.03 + 1.012\alpha^{2.06}} \\ f_3(\alpha) &= \frac{1}{.00265 + .354\alpha^{2.671}} \end{aligned} \right\} \text{for } 0 \leq \tau \leq 0.04$$

$$\left. \begin{aligned} f_1(\alpha) &= \frac{1}{0.438 + 0.562\alpha^{(0.777)}} \\ f_2(\alpha) &= \frac{1}{0.127 + 0.915\alpha^{1.057}} \\ f_3(\alpha) &= \frac{1}{.008 + 0.365\alpha^{(0.453)}} \end{aligned} \right\} \text{for } \tau \geq 0.04$$

the range of validity in both cases being 0.05.

If equation (33) is examined it can be seen that if $\bar{C}_A \rightarrow 0$, $D_{AB} \rightarrow D_A^*$, i.e. the ion present in the smaller concentration has the stronger effect on the rate of interdiffusion. This general rule can also be derived directly from the Nernst-Planck equation (Helfferich, 1956). The physical explanation is simply that the electric field acts on each individual ion thus causing a large transference of the major component while leaving the minor one almost unaffected. Helfferich and Plesset

have used this as a basic argument; according to their theory when ion A is initially in the exchanger if a solution containing ion B is brought into contact with it, there is immediate surface exchange of A and B. The B-rich layer then advances towards the centre of the exchanger so that the rate of exchange is determined by the diffusion of A through this layer; A being present in the smaller quantity D_{AB} depends mainly on D_A . If A is much faster than B a comparatively sharp boundary moves radially inwards, the concentration of A being smaller near the surface than at the centre of the sphere. If B is the faster ion, the boundary is diffuse and reaches the centre rapidly. The interdiffusion coefficient increases from the surface to the centre of the particle and exhaustion is more uniform. Thus a faster rate of exchange can be expected when the faster ion is initially in the exchanger. Here the Helfferich and Plesset theory differs from earlier ones which predicted equal rates for the forward and backward reactions.

Helfferich (36) has carried out experiments using a sulphonic acid resin and ions Na^+ and H^+ , and obtained a quite satisfactory quantitative test for his theory except when he used D_A^* and D_B^* values determined for .1M solutions to predict rates for more concentrated equilibrium solutions. However, its applicability to zeolites is not so straightforward as in the case of synthetic resins. The assumption that D_A^* and D_B^* are constants is not justified here.

2.4.2 The relationship between self- and exchange-diffusion coefficients

Experimental results show that Helfferich and Plesset's equation does not adequately describe the situation

in zeolites. In view of this Barrer, Bartholomew and Rees (18) have re-examined the relationship between D_{AB} , the differential interdiffusion coefficient, and D_A^* and D_B^* . They have used an irreversible thermodynamic approach and also introduced the effect of the flux of water molecules. Considering that ions 1 and 2 and water molecules 3 are flowing in accordance with Fick's law:

$$\left. \begin{aligned} J_1 &= -D_{AB} \frac{\delta C_1}{\delta x} \\ J_2 &= -D_{AB} \frac{\delta C_2}{\delta x} \\ J_3 &= -D_{H_2O} \frac{\delta C_3}{\delta x} \end{aligned} \right\} \quad (39)$$

While by the Nernst-Planck equation

$$J_1 = -D_1 \left\{ \frac{\delta C_1}{\delta x} + \frac{C_1 F Z_1}{RT} \frac{\delta V}{\delta x} \right\} \quad (40)$$

and similarly for J_2 ,

$$\frac{\delta V}{\delta x} = \text{the potential gradient}$$

$$D_1 = \text{the intrinsic diffusion coefficients.}$$

For electrical neutrality per unit volume of the crystal

$$Z_1 C_1 + Z_2 C_2 = \text{constant} \quad (31)$$

For electrical neutrality through any plane

$$Z_1 J_1 + Z_2 J_2 = 0 \quad (32)$$

Combining the above equations, they obtained

$$D_{AB} = \frac{D_1 D_2 (C_1 Z_1^2 + C_2 Z_2^2)}{D_1 C_1 Z_1^2 + D_2 C_2 Z_2^2} \quad (41)$$

They then considered the irreversible thermodynamic

formulation for J , and obtained the equation

$$J_1 = C_1 \left[L_{11} \frac{\delta \mu_1}{\delta x} + L_{12} \frac{\delta \mu_2}{\delta x} + L_{13} \frac{\delta \mu_3}{\delta x} + L_{14} Z_1 \frac{\delta V}{\delta x} \right] \quad (42)$$

where $L_{14} = (L_{11} + L_{12} \frac{Z_2}{Z_1})F$.

The L 's are phenomenological coefficients and μ_1, μ_2, μ_3 are those parts of the chemical potentials of ions 1, 2, and 3 which at constant temperature and pressure depend on concentration only. Comparison of equation (40) and (42) gives

$$D_1 = C_1 \sum_{n=1,2,3} L_{1n} \frac{\delta \mu_n}{\delta C_1} \quad (43)$$

and

$$D_2 = C_2 \sum_{n=1,2,3} L_{2n} \frac{\delta \mu_n}{\delta C_2} \quad (44)$$

When L_{12}, L_{21}, L_{13} and L_{23} are negligible, this gives

$$D_{AB} = \frac{D_A^* D_B^* (C_1 Z_1^2 + C_2 Z_2^2) \frac{\delta \ln a_1}{\delta \ln C_1} \frac{\delta \ln a_2}{\delta \ln C_2}}{D_A^* C_1 Z_1^2 \frac{\delta \ln a_1}{\delta \ln C_1} + D_B^* C_2 Z_2^2 \frac{\delta \ln a_2}{\delta \ln C_2}} \quad (45)$$

where the self-diffusion coefficient D_A^* and D_B^* are given by $RT L_{11}$ and $RT L_{22}$ respectively. The above expression has been shown to be incorrect by Barrer and Rees (37) because while the Nernst-Planck equations in the form used are valid only for ideal solutions, the irreversible thermodynamic formulations for J_1 and J_2 and hence the expression for D_1 and D_2 are valid for all solutions.

Barrer and Rees have derived the general relationship between D_{AB} and D_A^* and D_B^* without using the Nernst-Planck equation. From equation (39) and (42) they obtained

$$D_{AB} = C_1 \left[\sum_{n=1,2,3} L_{1n} \frac{\delta \mu_n}{\delta C_1} + (Z_1 L_{11} + Z_2 L_{12}) F \frac{\delta V}{\delta C_1} \right] \quad (46)$$

$$D_{AB} = C_2 \left[\sum_{n=1,2,3} L_{2n} \frac{\delta \mu_n}{\delta C_2} + (Z_2 L_{22} + Z_1 L_{21}) F \frac{\delta V}{\delta C_2} \right] \quad (47)$$

Combining the electrical neutrality condition,

$$Z_1 C_1 + Z_2 C_2 = \text{constant}$$

or

$$Z_1 \frac{\delta C_1}{\delta x} + Z_2 \frac{\delta C_2}{\delta x} = 0 \quad (48)$$

and equation (11) they got

$$D_{AB} = C_2 \frac{Z_2}{Z_1} \left[\sum_{n=1,2,3} L_{2n} \frac{\delta \mu_n}{\delta C_1} + (Z_2 L_{22} + Z_1 L_{21}) F \frac{\delta V}{\delta C_1} \right] \quad (49)$$

Equations (46) and (49) give

$$D_{AB} = \sum_{n=1,2,3} (Z_1 C_1 L_{1n} R - Z_2 C_2 L_{2n}) \frac{\delta \mu_n}{\delta C_1} \bigg/ Z_1 (1+R) \quad (50)$$

$$\text{where } R = \frac{Z_2 C_2 (Z_2 L_{22} + Z_1 L_{21})}{Z_1 C_1 (Z_1 L_{11} + Z_2 L_{12})}.$$

This equation is perfectly general and makes no assumptions, but it cannot be used as such because of the difficulty of determining phenomenological coefficients. However, it can be expressed in various limiting forms which can be more easily evaluated. Neglecting all cross-coefficients and assuming $\delta \mu_3 / \delta C_1 = 0$ we get

$$R = \frac{C_2 Z_2^2 L_{22}}{C_1 Z_1^2 L_{11}} = \frac{D_B^* C_2 Z_2^2}{D_A^* C_1 Z_1^2}$$

the equation then becomes

$$D_{AB} = \frac{D_A^* D_B^* (C_1 Z_1^2 \frac{\delta \ln a_2}{\delta \ln C_2} + C_2 Z_2^2 \frac{\delta \ln a_1}{\delta \ln C_1})}{D_A^* C_1 Z_1^2 + D_B^* C_2 Z_2^2} \quad (51)$$

If the ions A and B in the zeolite constitute an ideal solution

$$D_{AB} = \frac{D_A^* D_B^* (C_2 Z_2^2 + C_1 Z_1^2)}{D_A^* C_1 Z_1^2 + D_B^* C_2 Z_2^2}$$

which is the Helfferich and Plesset's equation shown to be inadequate for zeolites (Barrer, Bartholomew and Rees (18)).

Barrer, Bartholomew and Rees applied the equation (45) to data on calcium and strontium chabazite, but no agreement was obtained. Later, equation (51), the correct form of equation (45), was applied to this data, but the same values of D_{AB} were obtained because $\frac{\delta \ln a_1}{\delta \ln C_1} \approx \frac{\delta \ln a_2}{\delta \ln C_2}$. This equality which requires also that

$$\frac{\delta \ln f_1}{\delta \ln C_1} = \frac{\delta \ln f_2}{\delta \ln C_2} \quad (\text{where } f_1 \text{ and } f_2 \text{ are ionic activity coefficients in the zeolite})$$

is not fortuitous but a consequence of the Gibbs-Duhem equation.

The reason for the failure of equation (51) may be that correct values of D_A^* and D_B^* were not used. As experiments on mordenite have confirmed, D_A^* and D_B^* vary considerably with concentration of the cation. However, it is also possible that the inapplicability of equation (51) is due to the assumption that cross-coefficients have been neglected, this being correct only for true interstitial diffusion in salts and not for a replacement mechanism. In this project equation (51) has been applied to data obtained from the Na/K system in mordenite.

2.5 STRUCTURE OF MORDENITE

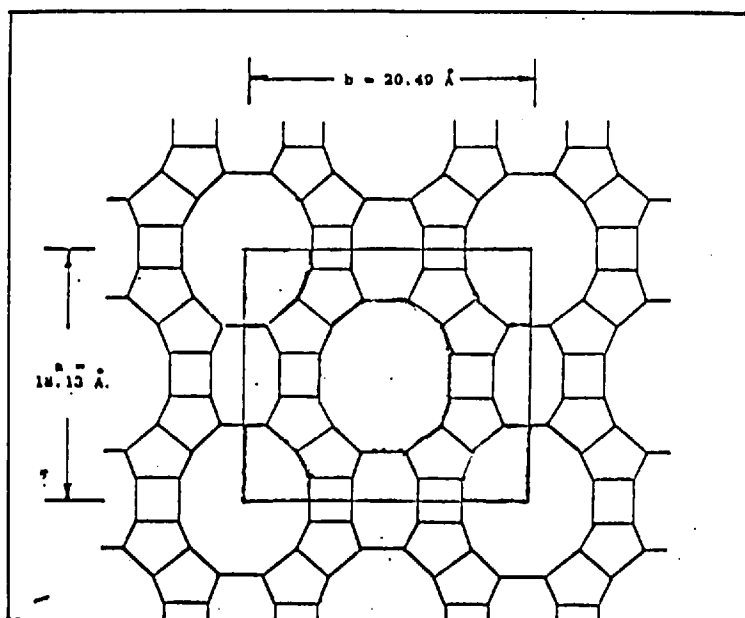
The sample of mordenite used in this work was the natural mineral obtained from Harbourville, N.S., supplied by Ward's Natural Science Establishment, N.Y. On analysis it was found to have the following composition:

	SiO ₂	Al ₂ O ₃	Na ₂ O	CaO	K ₂ O	H ₂ O
moles	10.98	1.00	0.77	0.03	0.19	6.25

The sodium form prepared hydrothermally was found to have a composition corresponding to the formula Na₈Al₈Si₄₀O₉₆27H₂O.

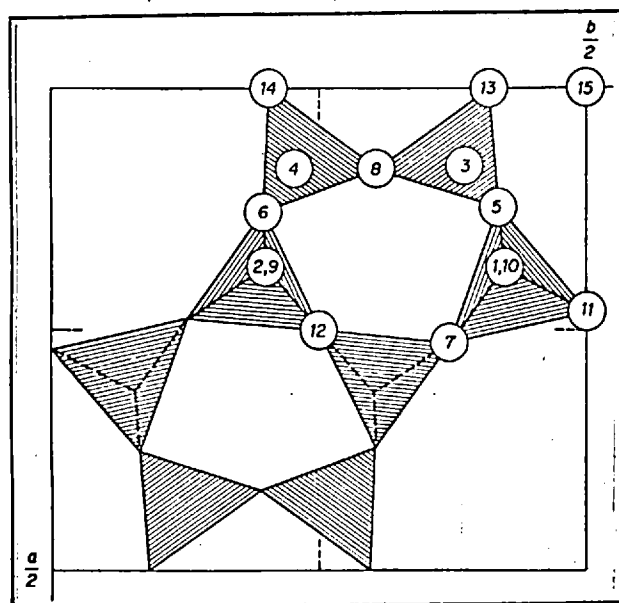
Meier (38) has carried out a detailed X-ray analysis on natural sodium mordenite. According to this the crystals are orthorhombic, and the unit cell of the Na⁺ form has the dimensions a=18.13Å, b=20.49Å, c=7.52Å.

The aluminosilicate structure of mordenite is composed of a characteristic type of chain in which five-membered rings of tetrahedra prevail. Each (Al,Si)O₄ tetrahedron is a part of one or more of such loops, and this is probably the cause of the extraordinary stability of this zeolite. The largest channels in the structure have a free diameter of 6.6Å, which are formed by rings of twelve tetrahedra and are parallel to the (001) direction. They are interconnected by smaller channels of free diameter approx. 4.0 parallel to the (010) direction. The smaller channels have periodic windows of approx. 2.8Å which must be the controlling factor in the diffusion process. This is shown in figs. 3a and c. Fig. 3a shows the window parallel to b, the minimum free diameter is 4.0Å as shown. However, in passing from one large channel to the next an ion encounters two such windows, displaced from each other by $\frac{1}{2}c$. This constricts the passage as shown in fig. 3b. Assuming that the



INTRA CRYSTALLINE CHANNELS IN MORDENITE

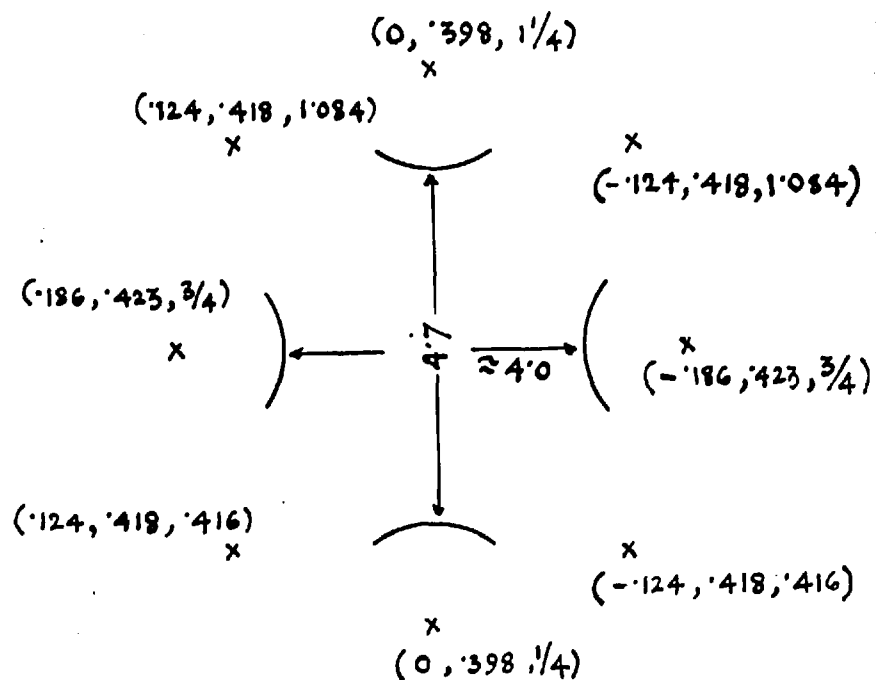
FIG. 2 a

PROJECTION OF THE FRAMEWORK
ALONG $[001]$

No	Atom	x	y	z
1	Si ₁	0.196	0.427	0.536
2	Si ₂	0.196	0.191	0.540
3	Si ₃	0.089	0.384	1/4
4	Si ₄	0.087	0.225	1/4
5	O ₁	0.124	0.418	0.416
6	O ₂	0.128	0.197	0.416
7	O ₃	0.263	0.373	0.504
8	O ₄	0.083	0.305	1/4
9	O ₅	0.184	0.199	3/4
10	O ₆	0.186	0.423	3/4
11	O ₇	0.231	1/2	1/2
12	O ₈	1/4	1/4	1/2
13	O ₉	0	0.398	1/4
14	O ₁₀	0	0.210	1/4
15	Na ₁	0	1/2	0
	Na ₂		not located	

ATOMIC COORDINATES FOR
SODIUM MORDENITE

FIG. 2 b



8-MEMBERED RING WINDOW INSIDE OF MAIN CHANNEL

FIG. 3a

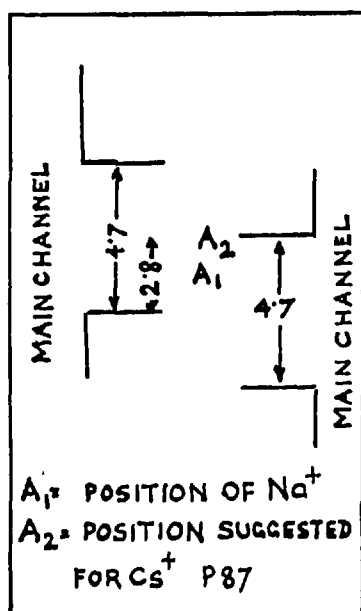
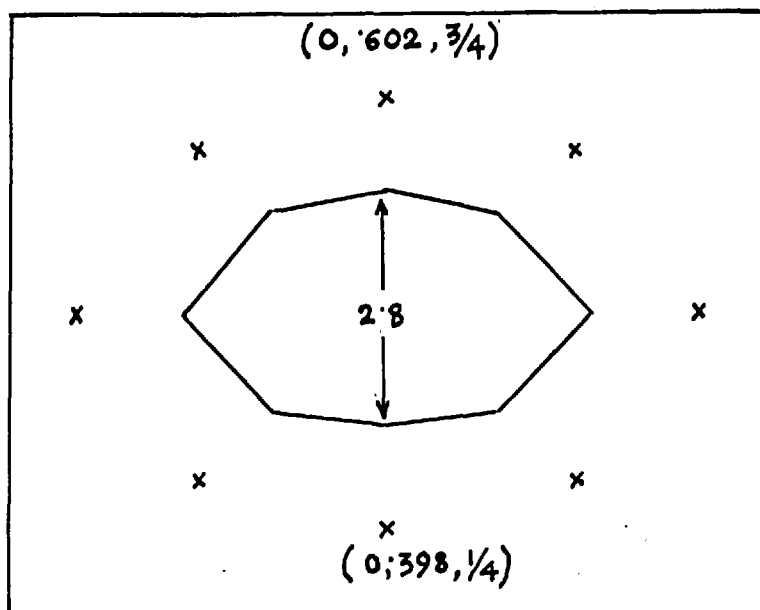
SCHEMATIC DIAGRAM
SHOWING PASSAGE
FROM ONE MAIN
CHANNEL TO ANOTHER

FIG. 3b



OBLIQUE SECTION

FIG. 3c

diffusing ion can move slightly to one side of the pair of O_9 oxygen atoms, the free diameter is $\sim 3.0 \text{ \AA}$ (the oxygen atoms being numbered as in fig. 2b, which shows the projection of the framework along (001)).

Sorption data on natural mordenite shows that molecules whose critical diameter is greater than $4.4 \text{ \AA}$ are excluded from the framework. This suggests that crystal imperfections exist, e.g. stacking faults, of which comparatively few would be required to inhibit diffusion. In synthetic mordenite, however, the same effect is not observed and molecules like C_6H_6 (diameter $> 4.4 \text{ \AA}$) are sorbed quite easily (Eberly (39)), so it is unlikely that stacking faults exist in this material.

Fig. 2b shows the position of a sodium ion. Only four of the eight sodium ions per unit cell have been located by Meier. These are in the positions shown i.e. $(0\frac{1}{2}0)$: the remaining four are distributed at random in the large channels. From self-diffusion data obtained in this project it seems probable that the sites occupied by the caesium ion in caesium mordenite are different from those occupied by Na^+ in the sodium form. In view of this, possible sites for the caesium ions have been briefly investigated. Assuming that in caesium mordenite, as in the sodium form, four Cs^+ are randomly placed, four possible arrangements have been considered for the remaining four caesium ions:

- (1) 4 Cs^+ placed at $(0 \ .210 \ \frac{3}{4})$ positions
- (2) 4 Cs^+ placed at $(0 \ .305 \ \frac{3}{4})$ positions
- (3) 4 Cs^+ placed at $(0 \ .380 \ \frac{3}{4})$ positions
- (4) 4 Cs^+ placed at $(0 \ .455 \ \frac{3}{4})$ positions.

The intensity of scattering in each case has been calculated and compared to the experimentally determined intensity.

This has been done as follows: using the formula for a centro-symmetric structure

$$F(h \ k \ l) = \sum_n f_n e^{\frac{B \sin^2 \theta}{\lambda^2}} \cos 2\pi(hx_n + ky_n + lz_n)$$

B = temperature factor

f_n = form factor for the n^{th} atom,

the structure factor for each Cs^+ position was calculated. These factors were algebraically added to the structure factors for the mordenite framework. The resultants were then compared to the visually estimated values obtained from powder photographs of caesium mordenite. This comparison is shown in fig. 28. Plots of intensities of diffraction are shown as they occur in the diffraction pattern. Distribution (4) comes closest to representing the observed values. This places the caesium ion at $(0 \ .455 \ \frac{3}{4})$, a site quite deep inside an opening in the side of the large channel and in fact not far from the sodium ion site located by Meier. There is one important difference, however: the caesium ion is placed centrally and right inside the $4.0 \text{ \AA}$ opening and is almost resting on the oxygen atom opposite while the Na^+ occupies a slightly staggered position to one side of the $4.7 \text{ \AA}$ opening. Thus to come out into the large channel the sodium ion has to negotiate a $2.8 \text{ \AA}$ ring, while the free diameter for Cs^+ coming out is $4.7 \text{ \AA}$. This is shown schematically in fig. 3b.

3. APPARATUS AND EXPERIMENTAL TECHNIQUES

3.1 Introduction and choice of method

So far work done on ion-exchange self-diffusion kinetics has been concerned mainly with ion-exchange resins and not zeolites. These studies are based on two types of experiments, the shallow-bed and batch methods.

In the shallow-bed method a thin layer of ion-exchange particles in 'A' form is placed on a fine platinum screen or glass-sintered disc and solution BY is forced through the layer at a high flow rate. The change in effluent concentration with time is then measured. This can be done quite conveniently if the ion-exchanger is laced with the radioactive isotope of A, the effluent solution being passed through a counter and its activity continuously recorded. This gives exchange flux as a function of time and fractional attainment of equilibrium as a function of time can be obtained by graphical integration. The boundary conditions closely approach infinite solution volume, and this makes calculation convenient.

Batch techniques have been tried in various forms by different workers and a few of these methods are briefly described below, (Boyd and Soldano's method (53)). The ion-exchanger AZ is spiked with radioactive A and the exchange with solution BY is carried out in a reaction vessel the total volume of solution being 200 cc. Fractional attainment of equilibrium with time is determined by removing aliquots (1 microlitre) at particular values of time and counting their radioactivity. This method has been used to determine self-diffusion coefficients but can, of course, also be applied to ion-exchange studies.

Kressman (43) has used a slightly different technique. The ion exchanger is placed in a platinum wire cage which forms the centre of a centrifugal stirrer. When the stirrer, which is immersed in the electrolyte solution, is started, the centrifugal forces press the beads against the sides of the cage. Solution from below is sucked in through the central part of the cage and forced out radially through the layers of beads and openings in the casing. This provides a rapid circulating flow of the solution over the beads. The rate of exchange is once again determined by withdrawing and analysing aliquots at known values of time.

Dickel (36) has described another method. This does not use radiotracers but depends on conductivity measurements and has only a limited scope.

Barrer and Rees (3) have used a very simple batch technique in their self-diffusion studies on analcite. Their method which was also used by Bartholomew (4) has been adopted in this project, and is described in detail in section 3.8.

It has the advantages of being quite straightforward and quick, and having easily reproducible conditions, though it suffers from some of the usual disadvantages of batch methods, e.g. it has finite volume boundary conditions which make calculation of diffusion coefficients more tedious than infinite volume conditions of the shallow-bed methods, and convenient continuous recording techniques cannot be used. However, counting of individual samples is always more accurate and can be done with a minimum of statistical error and, also, variables like temperature and volume of solution, etc., are fairly easily controlled making results more reliable than by shallow-bed methods where it is difficult to keep the flow rate at a constant value.

3.2 Materials used

The zeolite used as the starting material in all experiments was natural mordenite from Harbourville, N.S., supplied by Wards Natural Science Establishment, Rochester, N.Y. A typical sample of this gave, on chemical analysis:

	SiO ₂	Al ₂ O ₃	Na ₂ O	CaO	K ₂ O	H ₂ O
Moles	10.98	1	.768	.0318	.188	6.25

Standard lines of natural mordenite were obtained from X-ray powder photographs of the sample.

All chemical reagents used were of the highest obtainable purity. Radioactive isotopes used were as follows: Na²² (half-life 2.6 years); K⁴² (half-life 12.5 hours); Rb⁸⁶ (half-life 18.6 days); Cs¹³⁴ (half-life 2.3 years); Ca⁴⁵ (half-life 164 days); Sr⁸⁵⁺⁸⁹ (half-life 50 days); Ba¹³³ (half-life 7.5 years). They were all supplied by the Radiochemical Centre, Amersham, and were 100% pure.

3.3 Preparation of various cation forms of mordenite

The hand-picked mineral was broken down in a porcelain mortar until it could be sieved between 18 and 32-mesh sieves for preparation of the univalent forms, and through 200-mesh sieves for the divalent forms.

In all cases the 'pure form' was prepared by exchanging the ions originally present by those of the required cation from a concentrated solution of its salt; chlorides were used in all cases except for sodium which was used in acetate form and calcium for which Ca(NO₃)₂ was used.

For the sodium form the exchange was carried out at 60° using a saturated sodium acetate solution in rotating tubes. The complete exchange took approximately five weeks, the solution being changed at the end of the first two days and then every fifth day. The potassium, caesium and rubidium forms were prepared from the sodium form under the same conditions except that chlorides were used and the exchange was followed by lacing the sodium form with Na²². The following degrees of conversion were achieved: K⁺ = 96%, Rb⁺ = 94%, Cs⁺ = 98%.

The bivalent forms took longer to prepare. Natural mordenite was used as starting material and was treated at 60°C with saturated solutions of BaCl₂, Ca(NO₃)₂, and SrCl₂ respectively. However, only 40% exchange for the Sr form and 50% for the Ca⁺⁺ and Ba⁺⁺ forms was observed after four weeks at 60°C and three weeks at 90°C. Fresh starting material was then taken and treated with saturated solutions of the salts at 215°C. in steel autoclaves, the solutions being changed every fifth day. After three weeks, no further replacement was found to be occurring and exchange was assumed to be complete. The final samples contained 72.51% calcium, 73.0% barium and 49.27% strontium respectively.

Sodium mordenite was again used as starting material in the preparation of the bi-ionic Na, K form; a part of the material used in self-diffusion runs was used to ensure that the Si/Al ratio was always constant. It was laced with Na²² and treated with a solution of KCl till equilibrium was reached (approx. one week at 60°C). The solution and solid phase were then separated, and the solid washed in distilled water while the solution was analysed by counting its radioactivity. From this, the ratio Na⁺/K⁺ in solid was known, and so were the amounts

of Na^+ and K^+ in the equilibrium solution. Various samples differing in Na^+/K^+ ratio were prepared from the laced ^{sodium} ~~strentium~~ mordenite using different concentrations of KCl solution.

3.4 Analysis of the cationic forms of mordenite

Gravimetric analysis was carried out using the standard method for a soluble silicate (Vogel (1957) (40)).

Determination of silica: About 0.4 g of the finely powdered sample of mordenite was accurately weighed out in a platinum dish, 10-15 ml of water were added, and the mixture was stirred till thoroughly wet; about 25 ml of 1:1 HCl were then added with continuous stirring. The liquid was then evaporated to dryness on a water bath and the platinum dish placed in an air oven at 110-120°C for one hour to dehydrate the silica. 5 ml of concentrated HCl were then added, the mixture thoroughly stirred, and then made up to about 75 cc with distilled water. The basin was then again placed on the water bath for 10-20 minutes before filtering through a Whatman No.41 filter paper. The precipitate was washed first with warm 1:20 HCl, and then with hot water till free from chlorides. The filtrate and washings were poured into the original dish, evaporated to dryness on the water bath, and then heated again at 110-120°C for one hour. The process of extraction with HCl and filtration was then repeated, and the filtrate kept aside for further analysis. The precipitates in the two filter papers were heated under a Meker burner for determination as SiO_2 . The residue of SiO_2 was heated to a constant weight and finally treated with about 1 ml of water, 2 or 3 drops of concentrated H_2SO_4 , and about 5 ml of A.R. hydrofluoric acid, and

evaporated first under a small flame in a fume cupboard and ^{then} with a Meker burner. The loss in weight gave the exact amount of SiO_2 , the rest of the precipitate, if any, being Al_2O_3 .

Alumina: The filtrate was made up to about 150 cc, methyl red indicator added, and also excess of solid NH_4Cl . The solution was heated to boiling and then 1:1 ammonia added drop by drop, stirring continuously till just alkaline. The solution was then boiled for one minute and filtered on a No. 41 filter paper. The precipitate was washed with hot 1.7% ammonium chloride solution until free from acid and then ignited to a constant weight in a platinum crucible. The residue from the silica determination was added to this weight to give the total per centage of alumina. When alkaline earth metals were present the alumina from the first precipitation was dissolved in warm conc. HCl and reprecipitated using 1:1 ammonia. The filtrate being combined with the one from the first precipitation.

Alkaline earth metals: These were determined by the standard procedures, calcium being determined as oxalate monohydrate, and barium and strontium as sulphates (Vogel, 1957).

Alkali metals: Sodium and potassium were determined in two ways, flame photometrically and radiochemically, the radiochemical method being far more accurate. Radio tracer methods were also used in the determination of rubidium, caesium, strontium and barium. The method was as follows. A known weight of the finely ground sample was equilibrated with a solution of the salt of the metal being determined. The solution was of a known

strength, and contained the radiotracer. When equilibration could be assumed complete, i.e. after at least two days for the univalent forms and five days for the divalent forms, the solid and solution were separated. The tracer being now homogeneously distributed between zeolite and solution phases, the concentration of cations in the zeolite could be found from the loss in counts from the solution.

Water content: Loss of weight on heating to a dull red heat gave the water content of the sample being analysed.

3.5 Density measurements

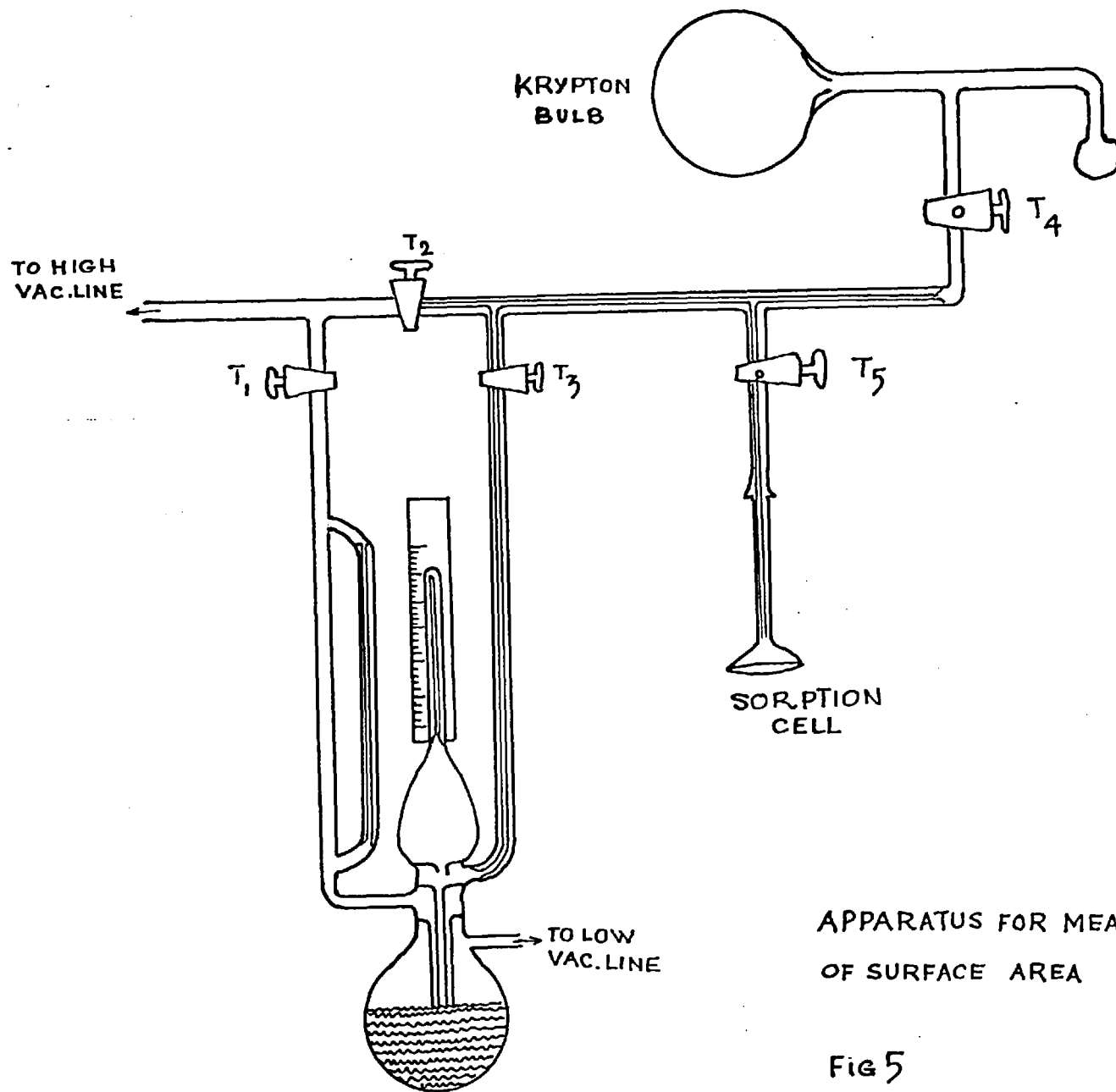
The density of samples was measured using a relative density bottle. The volume of the bottle was determined by weighing empty and full of distilled water, thermostatted at 25°C for about 20 minutes. The following quantities were then measured:

W_1 g = wt. of density bottle
 W_2 g = wt. of density bottle + distilled water
 W_3 g = wt. of density bottle + crystals
 W_4 g = wt. of density bottle + distilled water + crystals;

the ρ = density of crystals is given by

$$\rho = \frac{(W_3 - W_1)d}{(W_2 + W_3) - (W_4 + W_1)} \text{ g/cc}$$

d = density of water at 25°C.



APPARATUS FOR MEASUREMENT
OF SURFACE AREA

Fig 5

3.6 Surface area measurements

Surface area was by far the most ambiguous of the parameters determined. The methods used, a krypton adsorption method and a photographic projected-area method, gave widely differing values of surface area.

3.6.1 Krypton adsorption method

This method consisted of the measurement of adsorption of krypton on the external surface of the zeolite sample at liquid nitrogen temperature at various pressures. The results were interpreted in terms of the B.E.T. theory to give the surface area of the sample.

The apparatus used is shown in the figure and is similar to the one used by Bartholomew (4). The McLeod gauge is of a special kind, the pressure of the gas enclosed in the bulb being measured against high vacuum instead of against the pressure in the doser volume.

The McLeod gauge and sorption cell were calibrated using mercury and the rest of the apparatus, i.e. volume between taps T_2 , T_3 , T_4 , T_5 , using krypton. A known volume of gas (krypton supplied by British Oxygen Co. Ltd. stated to be 99-100% Kr balance Xe by makers) at a known pressure was cut off in the McLeod gauge bulb and then expanded into the part of the system to be calibrated. From the final pressure of the gas, the volume was determined using Boyle's law.

Surface areas were then determined as follows: taps T_4 and T_5 were closed and the system thoroughly outgassed. When a high vacuum had been established a known weight of the mordenite sample was introduced into the sorption cell, which was then attached to the apparatus and surrounded by a saturated solution of Cardice in

acetone. This solution which has a temperature of -78°C froze the water mols present in the channel of the mordenite ensuring that they remained in their original positions, preventing krypton adsorption within the channels. After about an hour the tap T_5 was opened and the sorption cell outgassed for about 45 minutes, then the Cardice in acetone solution was removed and liquid nitrogen immediately placed around the cell up to mark A. The system was then given at least an hour to reach thermal equilibrium, liquid nitrogen from the same source also being placed around the side arm of the krypton bulb.

When equilibrium had been attained, taps T_2 and T_5 were closed and a dose of krypton introduced into the system. The pressure was measured, T_5 opened, and system given about 45 minutes for complete adsorption and equilibrium. When pressure was found to be constant over a period of time, the equilibrium pressure reading was taken as final. T_5 was then again closed and a fresh dose of krypton introduced, its pressure noted and adsorption allowed to continue by opening T_5 . The time required for adsorption of the second dose being about half an hour, and third and successive doses requiring only about fifteen minutes.

The adsorption data was then used to calculate the volume of krypton required to cover a monolayer:

$$\frac{P}{v(P_0 - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \frac{P}{P_0}$$

P_0 = saturated vapour pressure of supercooled liquid krypton at liquid nitrogen temperature (Meihuizen and Crommedin, 1937) (41).

P = true equilibrium pressure over crystals at this temperature (experimental values have to be corrected for thermal transpiration) (Rosenberg)(42).

v = volume of gas adsorbed in ml reduced to N.T.P.

V_m = volume of krypton to cover a monolayer.

C = constant.

Plotting $\frac{P}{v(P_0-P)}$ against $\frac{P}{P_0}$ gives V_m = slope + intercept.

The exact temperature of the liquid nitrogen was required to calculate P_0 and also V . This was found from the vapour pressure of the krypton in the storage bulb. Liquid nitrogen from the same source as used in the experiment was placed round the side arm of the krypton bulb for about fifteen minutes, T_4 was then opened and the vapour pressure of solid krypton measured on the McLeod gauge. The temperature of liquid nitrogen was then determined from vapour pressure-temperature data for krypton (44).

Surface area could then be evaluated

$$A = \frac{V_m N_{pKr}}{22.414 \times 10^3 \times W}$$

N = Avogadro's number

ρ_{Kr} = Cross-sectional area of a krypton molecule taken as $19.5 \text{ \AA}^2$ (45)

W = weight in g of sample.

3.6.2 Surface area by photographic method

This method was used for the univalent cation forms of mordenite. Since it was a visual method and used a projection technique, the values obtained must be considered purely as external areas, which neglected minute cracks, irregularities and all internal surfaces.

To determine the surface area of a particular sample a known weight of it was placed on a microscope in the negative carrier of an enlarger. The particles were carefully spread out so that they were not in contact with

each other. Their enlarged image was then projected on the baseboard and photographed. The magnification was measured by placing a square 1 cm in length on the slide along with the sample particles.

The projected area of the enlarged particles could be determined quite easily by tracing out the photograph on a uniform transparent graph paper, cutting out the area of each particle, and comparing the total weight of these cut out areas with the weight of 10 cm square of the same paper. This projected area divided by the magnification was $\frac{1}{4}$ the total surface area (46).

3.7 Counting equipment and techniques

A liquid Geiger-Müller counter, type B6H, was used to count all radioactive isotopes except those using Ca^{45} . The counter was halogen quenched, and had a working voltage of 410 volts. Counts were recorded on an Ekco scalar 530E in conjunction with a probe unit 1014A of dead time 270μ secs. The counter tube held about 10 cc of the sample, and was 10% efficient towards β particles.

K^{42} and Rb^{86} were the only two isotopes whose short half-life had to be taken into consideration. K^{42} was counted against time to obtain the correct standard at the required time. The log of number of counts was plotted against minutes for this purpose. The slope of this straight line also gave the half-life of the isotope, thus acting as a check on the equipment. The standard for Rb^{86} (half-life 18 days) was counted every two hours.

Ca^{45} which is a weak β emitter, was counted as a solid using an end-window Geiger-Müller counter with a window thickness 2.3 mg.cm^{-2} in conjunction with the same circuit as described for the liquid counter. The counting

sample was prepared as follows. Discs of glass fibre filter paper, Whatman GF/B, were cut out and fixed to aluminium planchets of 1 in. diameter by means of discs of polythene of equal size. .5 ml of the solution to be counted was then pipetted on to the discs with a micro-syringe pipette; .5 cc of oxalic acid solution, containing an equivalent amount of oxalate ion, were then added. The sample was then evaporated to dryness under an infra-red lamp. In all the runs the counting of Ca^{45} was done by using the same volume of solution over the same area every time so that any self-adsorption effects were constant and hence could be ignored.

In every case the total number of counts in each observation was at least 10,000 so that the error in counting was less than 1%.

3.8 Determination of self-diffusion coefficients

The method applied by Barrer and Rees to determine D^* values for cations in analcite, and by Bartholomew to chabazite, was employed throughout this work.

The experiments were carried out in diffusion tubes of the shape shown in the diagram. For the self-diffusion runs 0.2 g of zeolite particles was first weighed into the side arm of the tube, and 20 cc of solution were then introduced into the main bulb of the tube by means of a pipette with a length of flexible polythene tubing attached to its end. The end of the tube was placed in the bulb of the diffusion cell. The B_{10} Quickfit joint was then greased with silicon grease, and the steel spring put into position to hold the joint firmly in place. This arrangement could be used for temperatures up to 80°C, but above this the cone and

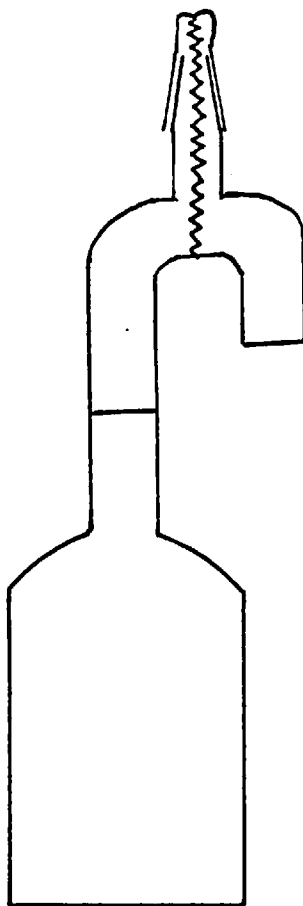


FIG 4

socket arrangement was replaced by a glass tube which could be sealed off in an oxy-coal gas flame. At least five tubes with identical amounts of solid and solution were prepared, carefully fixed to a rotatable plate in an air thermostat and left for at least four hours to reach thermal equilibrium. The temperature of the thermostat used was controllable to $\pm 0.2^{\circ}\text{C}$.

The run was started by rotating the plate and thus bringing the solid and liquid phases into contact. At known times from the start of mixing, tubes were removed from the thermostat and the liquid and solid phases separated as quickly as possible. For the univalent forms this could be done quite easily by decantation, and took only about 30 seconds. However, for smaller particle sizes of the bivalent forms, centrifuging was necessary and in this case the whole process, i.e. sedimentation and separation, took approximately 50 seconds.

The separated solution was then allowed to reach room temperature before being counted. In all cases except two of the sodium runs, the tracer was initially in solution, and the equation used was

$$Q_{\infty} = \frac{(\text{No. of equivs. of cation in solid phase})}{(\text{No. of equivs. of cation in solid + solution})} \times Q_0$$

The value of the term inside the brackets was in all cases adjusted to exactly $\frac{1}{2}$, i.e. the number of equivalents of cation in solution was made equal to the number of equivalents in the solid phase. Q_0 was proportional to the initial count of the solution.

When the tracer was in the solid, the same equation in a slightly modified form could be used. The factor $Q_0 / Q_0 - Q_{\alpha}$ was, as in the previous case, represented

by

$$\frac{\text{No. of equivs. of cation in solid + solution}}{\text{No. of equivs. of cation in solution}}; \frac{Q_t}{Q_\infty}$$

which always represents the fractional attainment of equilibrium, was evaluated as follows:

Q_t = no. of counts in solution at time t

Q_∞ = no. of counts in solution at equilibrium.

If Q_0^1 is the number of counts in the solid at $t=0$,

$$Q_\infty = Q_0^1 \times \frac{\text{No. of equivs. of cation in solution}}{\text{No. of equivs. of cation in solid + solution}}.$$

3.9 Determination of self-diffusion coefficients in heteroionic mordenite

Preparation of the heteroionic samples has been described in detail in a previous section. As mentioned there, every sample contained a known percentage of potassium which was inactive, and a known percentage of sodium which was laced with Na^{22} . The apparatus and technique used for determination of self-diffusion coefficients in the heteroionic forms were similar to those in the fully-exchanged mordenite. In this case the exchange solution was prepared containing exactly the same ratio of NaCl/KCl as present in the equilibrium solution in the preparation of each sample. Thus it could be assumed that since the solution and solid contained ratios of Na/K , obtainable at equilibrium, no further ion exchange would occur and self diffusion would be the only process taking place. The KCl in solution was laced with K^{42} while the NaCl was kept inactive. As before, the solid and solution were brought into contact and rotated for known times, and then separated as quickly as possible. The solution was allowed to reach room temperature and then counted for

300 sec. Five such counts were taken, being spaced over a time of about 5 hours. The solution was then carefully preserved, the log. of the number of counts was plotted against time for each solution, and from the straight lines obtained the activity of all the solutions could be found out at one particular time. The activity of the solution before exchange was also determined at this value of time in the same way.

After about 8 days, when it could be assumed that any activity due to K^{42} had decayed to a negligible value, the solutions were again counted in the normal way to determine the amount of Na^{22} present in them. Since the activity of Na^{22} originally in the solid was known from the amount coming out into the solution at time t , the fractional attainment of equilibrium with time could be obtained and the value of D_{Na}^* could be calculated at 60° (all experiments being performed at this temperature). For the potassium ion the activity due to K^{42} alone at a particular value of time t , on the day of the experiment, could be obtained by subtracting the number of counts due to Na^{22} from the total activity at t , this being known from the graph as described before. The activity due to K^{42} alone in the solution before exchange being also known from the graph, Q_t/Q_∞ could be easily calculated and plotted against time, and hence D_K^* found out for each sample. The entire range of concentration between pure Na and pure K was thus studied at $60^\circ C$. One particular sample (57.2% Na) was examined at four different temperatures to determine the value of the activation energy.

3.10 Determination of ion-exchange rates

The technique used here was not very different from what has been described for self diffusion. The

solution in this case contained a twenty-fold excess of the ion which was to be introduced into the zeolite so that the value of $Q_0 / (Q_0 - Q_\infty)$ could be taken as 1. In all cases the tracer was initially in the zeolite, and the amount of exchange at time t was proportional to Q_t , the number of counts in solution at time t . Q_∞ was calculated on the assumption that at equilibrium all the ions would be exchanged, and hence was represented by the activity initially in the zeolite.

The samples used in ion-exchange runs were the same as those used for self diffusion so that the Si/Al ratio was identical.

4. RESULTS

4.1 Self diffusion

Self-diffusion coefficients of the following cations: Na^+ , K^+ , Cs^+ , Rb^+ , Ca^{++} , Ba^{++} , Sr^{++} , in their respective exchange forms of natural mordenite were determined. Cation exchange samples used contained in every case the maximum percentage of the particular cation obtainable. They were prepared by repeated exchange with concentrated solution of salt of the cation as described in the experimental section. The samples prepared were thoroughly analysed using standard chemical procedure, and the results of these analyses are given on pp. 107-8.. They have been tabulated as percentage composition by weight and in moles ($\text{Al}_2\text{O}_3=1$). The univalent forms all contain the same $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio since they were all prepared using sodium mordenite as the starting material. In no case was complete exchange possible, and after the concentration cited had been reached, any further attempts at exchange caused breaking of the crystals and other surface effects. For the bivalent cation forms, the maximum attainable percentage of the required cation was comparatively low in all cases, being only 49.27% for strontium, 73.0% for barium, and 72.51% for calcium, the value for barium being similar to that observed in zeolon by C. J. Williams (47).

Surface areas of all samples were measured using krypton adsorption methods. The univalent sample surface areas being also determined by the visual method described in Section 3.6.2.

The absolute values of D^* are dependent on the value of surface area. Unfortunately, however, it is not yet possible to say whether the B.E.T. areas are the

TABLE 4. Surface areas of samples used.

Exchange form	B.E.T. areas in $\text{cm}^2 \text{ p. g}$	Visual area in $\text{cm}^2 \text{ g}^{-1}$
Sodium	2.52×10^3	70.8
Potassium	6.37×10^3	78.6
Rubidium	4.981×10^3	64.3
Caesium	4.981×10^3	64.0
Calcium	9.086×10^3	
Strontium	10.604×10^3	
Barium	10.102×10^3	

ones effective for ion exchange. As the figures show, B.E.T. areas differ drastically from those obtained by the photographic method, and it is likely that they are larger than the true values since they include the areas of cracks and other surface irregularities to which ions in solution may not have access. However, the visual areas are definitely even less accurate since here surface irregularities are neglected completely. Comparison of results by the two methods show that in both cases caesium and rubidium have about the same surface area, while potassium is larger than either of these. However, the values for sodium are somewhat anomalous, the B.E.T. area being much smaller than indicated by the photographic method. The B.E.T. area of a sample of natural mordenite (which contains a large proportion of sodium) sieved to the same size has been determined and found to be $2.8 \times 10^3 \text{ cm}^2 \text{ g}^{-1}$. This is almost the same as the area of the sodium form obtained from a sample which had been sieved after exchanging. This probably indicates that there is

some hydrolysis and a slight increase of surface area during exchange. D^* values have been calculated for the univalent forms using both B.E.T. and photographic surface areas, and these are shown in Table 6.

The fractional attainment of equilibrium, i.e. Q_t/Q_∞ for self diffusion has been plotted against $\sqrt{t}$, and the graphs are shown on pp. 60 and 61. The curves are similar to those obtained from experiments on chabazite and analcite. However, in this case the univalent forms give an average intercept on the y axis of about .05, while the corresponding value for chabazite is .02. In general, as temperature increases it is observed that the intercept becomes smaller, e.g. in potassium and rubidium. This effect has also been obtained in analcite, particularly for ions with high activation energies. Of the univalent ions, the caesium curves have the smallest intercepts, and these increase with temperature instead of decreasing. This effect has been observed for barium in chabazite, which again is similar in having an abnormally low activation energy. Barrer and Rees⁽¹³⁾ suggested that intercepts are due to a very rapid surface exchange. It is likely that this occurs in the time lag before the actual ion-exchange reaction starts, the magnitude of this time lag being dependent on the activation energy.

Self diffusion in the divalent forms of mordenite has also been plotted (Fig. 7). The strontium form which could only be obtained in 49.27% strontium concentration even at 225°C appears to contain only 25% of exchangeable strontium ions at room temperature, and the curves produce an intercept of only .025. However, the intercept does not have any effect on the initial slope

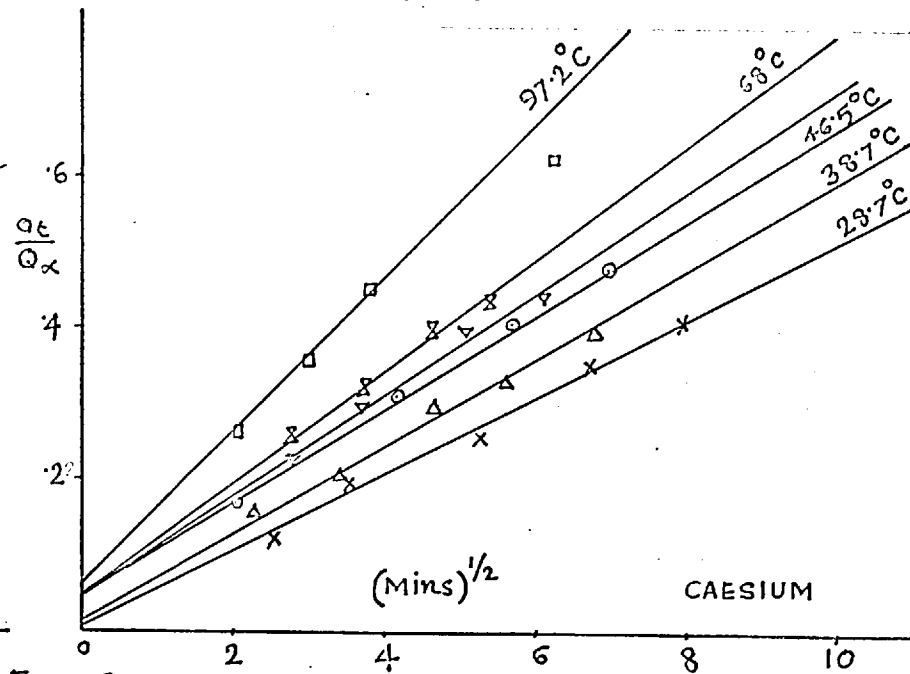
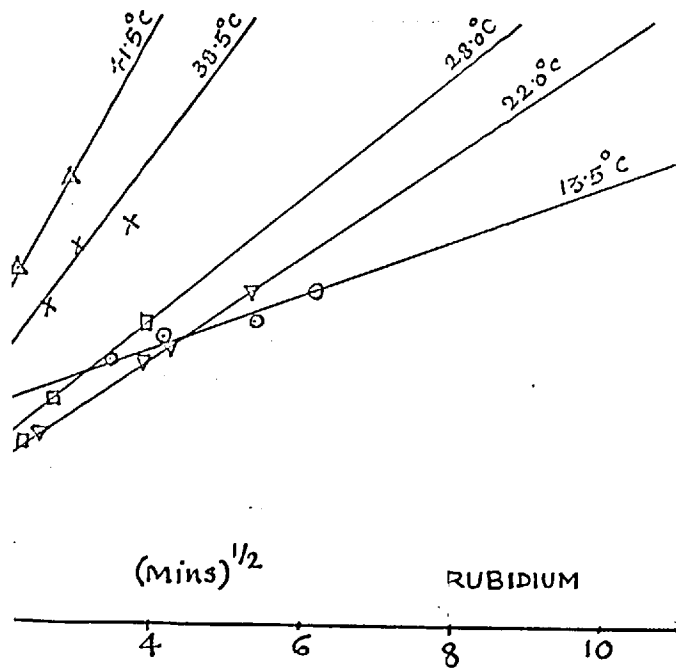
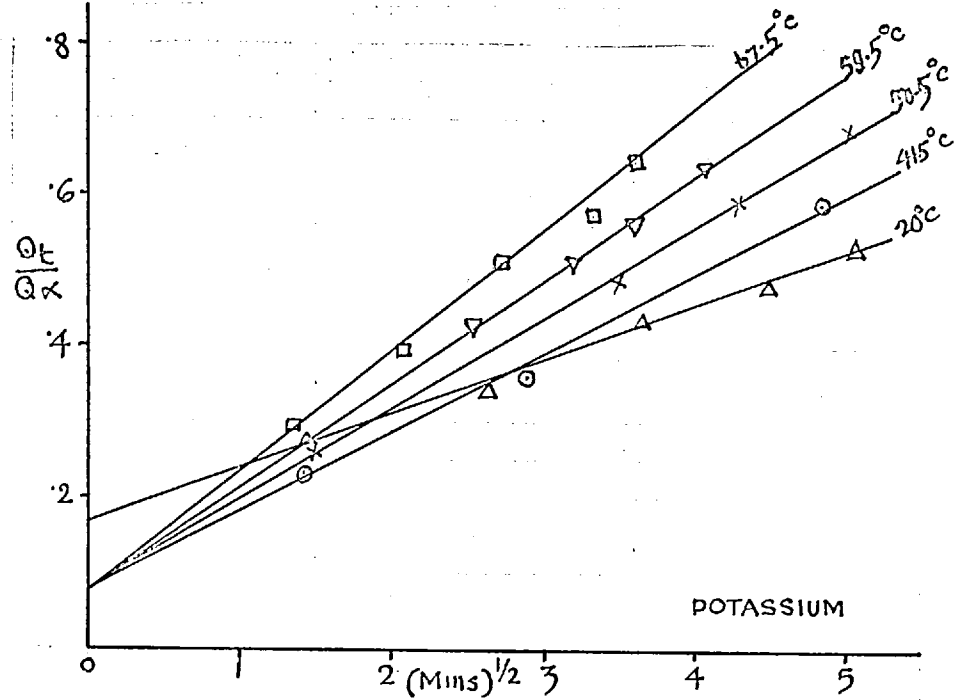
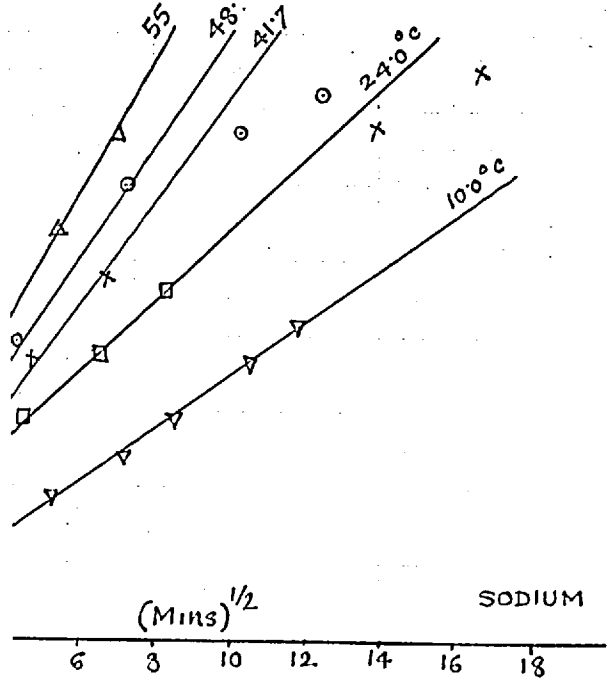
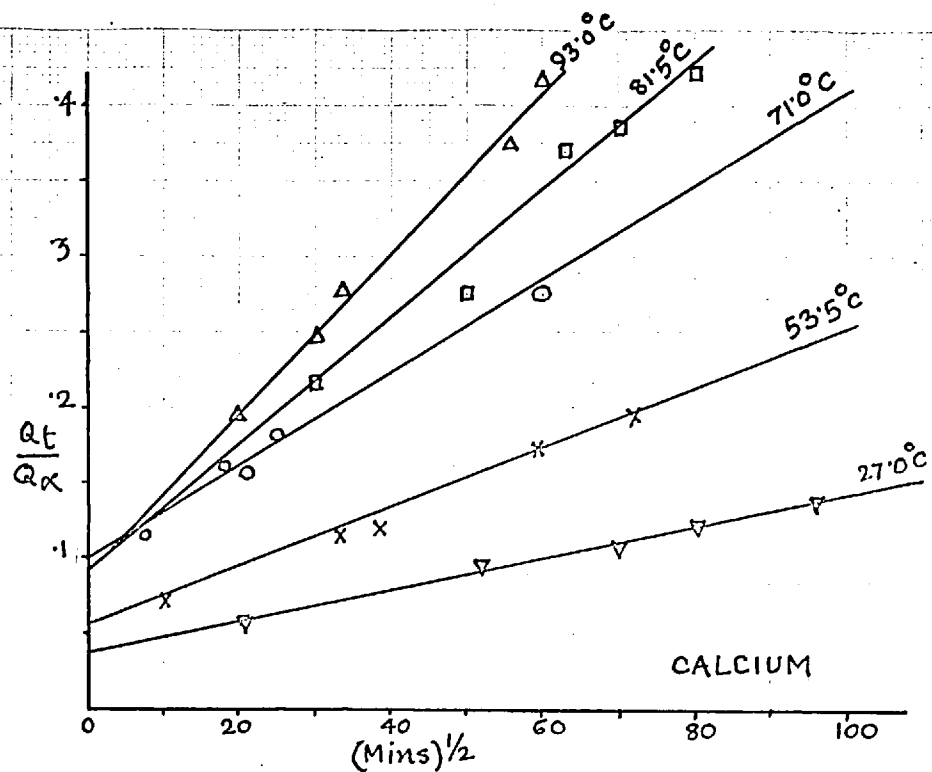
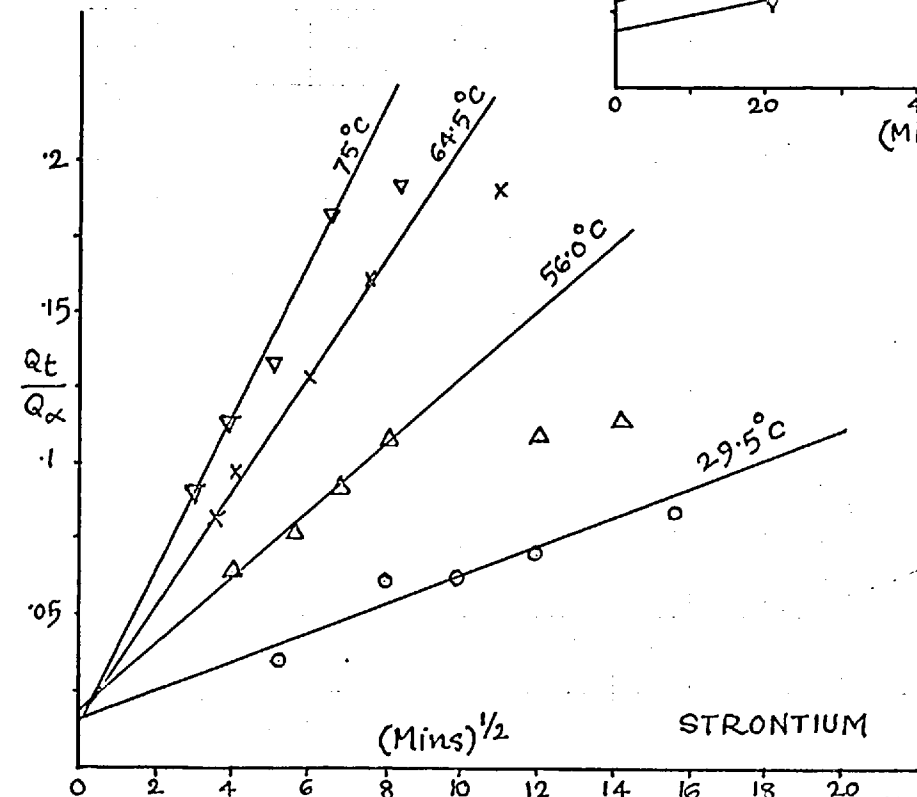


FIG. 6



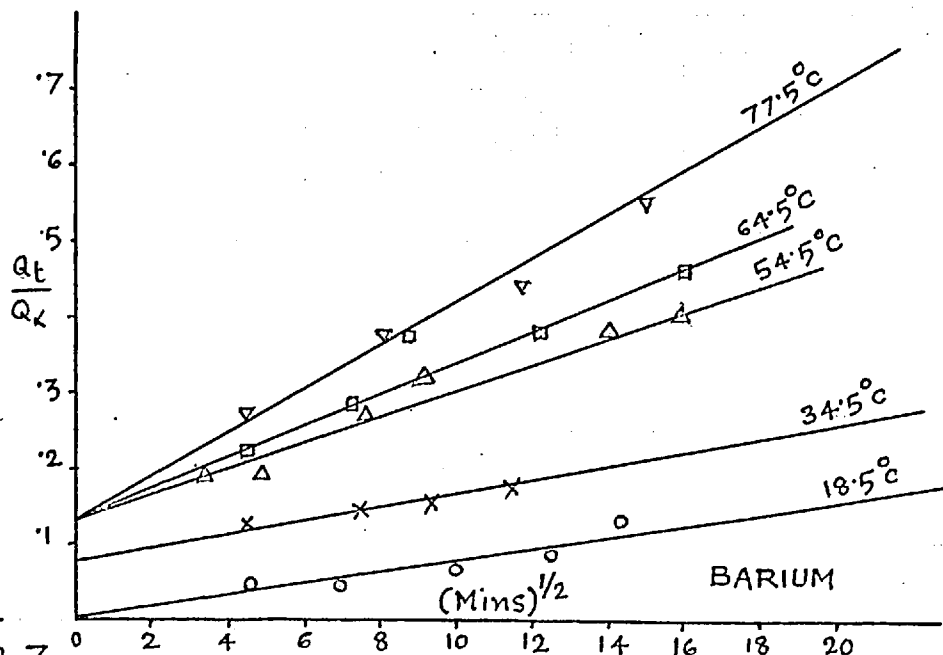
CALCIUM

$(\text{Mins})^{1/2}$



STRONTIUM

$(\text{Mins})^{1/2}$



BARIUM

$(\text{Mins})^{1/2}$

FIG. 7

of the curves, and hence does not interfere with determination of the rate. Q_t/Q_∞ is found to be linear with $\sqrt{t}$ up to at least .5 in all cases (except strontium), and this also is in agreement with data on chabazite and analcite. In drawing the linear slopes, the method of least mean squares was used. However, scatter, which was due to heterogeneity of particle size, was not much in most cases. A point of basic importance which was confirmed before beginning these experiments was that the diffusion was particle controlled. This was done by performing a self-diffusion run using, as usual, 0.2 g of sodium mordenite, but exchanging it with a solution of NaCl 1/10th of the strength used in the rest of the runs. However, the rate at that particular temperature did not change with the concentration of the solution, indicating that the diffusion is particle controlled.

Determination of activation energies

$\log_{10} D^*$ was plotted against $1/T^\circ K$ and satisfactory straight lines were obtained showing that Arrhenius equation $D^* = D_0 \exp (-E/RT)$ is valid. From the slopes the energies of activation, and hence values of D_0 , were calculated.

TABLE 5.

Exchange form	Ion radius in Å	E in kcal/ g ion	D_0 $\text{cm}^2\text{sec}^{-1}$
Sodium	0.95	8.73	4.89×10^{-7}
Potassium	1.33	7.14	2.11×10^{-8}
Rubidium	1.48	20.26	85.1
Caesium	1.69	4.31	9.72×10^{-12}
Calcium	0.99	10.45	3.65×10^{-10}
Strontium	1.13	15.97	3.86×10^{-5}
Barium	1.35	10.14	9.72×10^{-9}

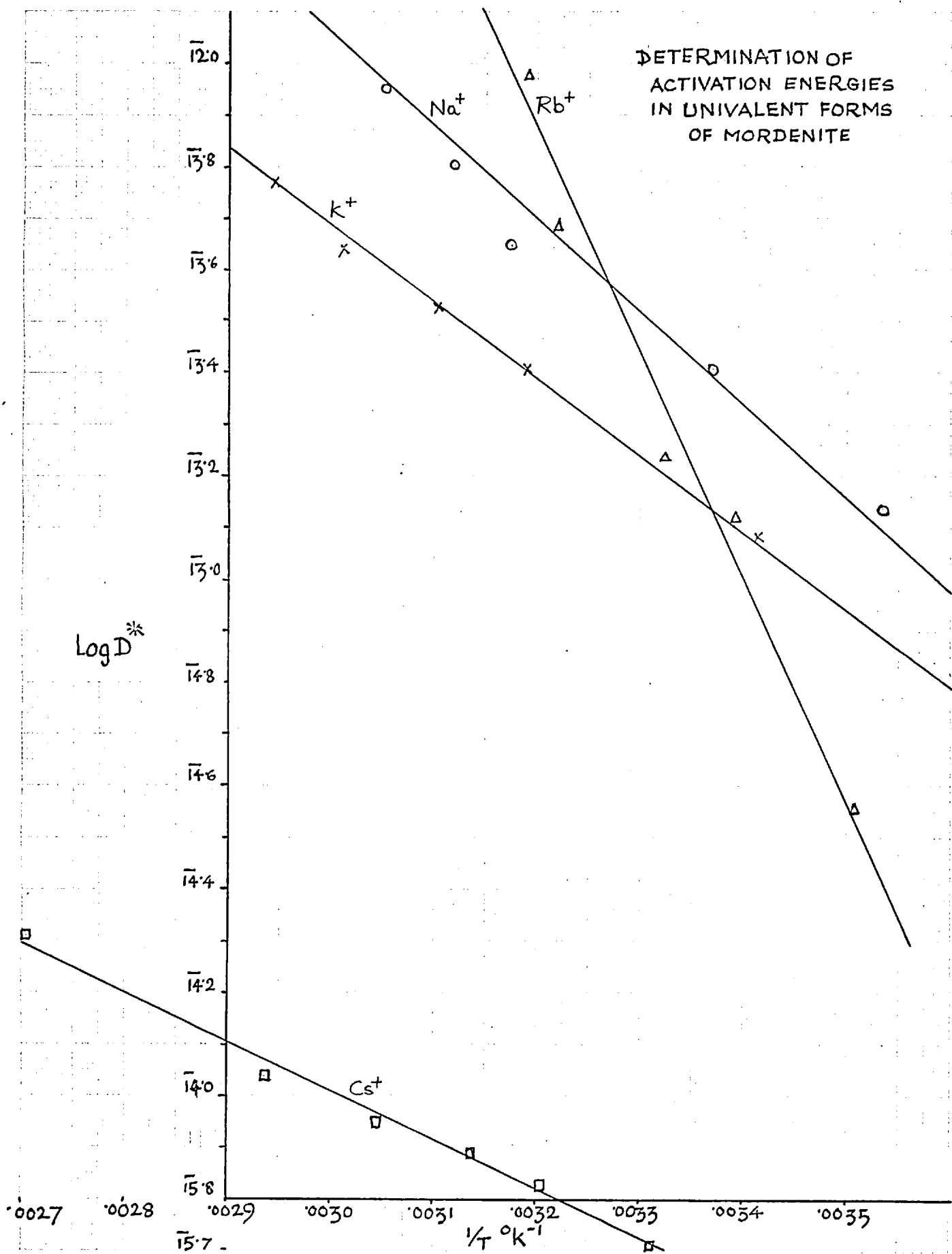


FIG. 8

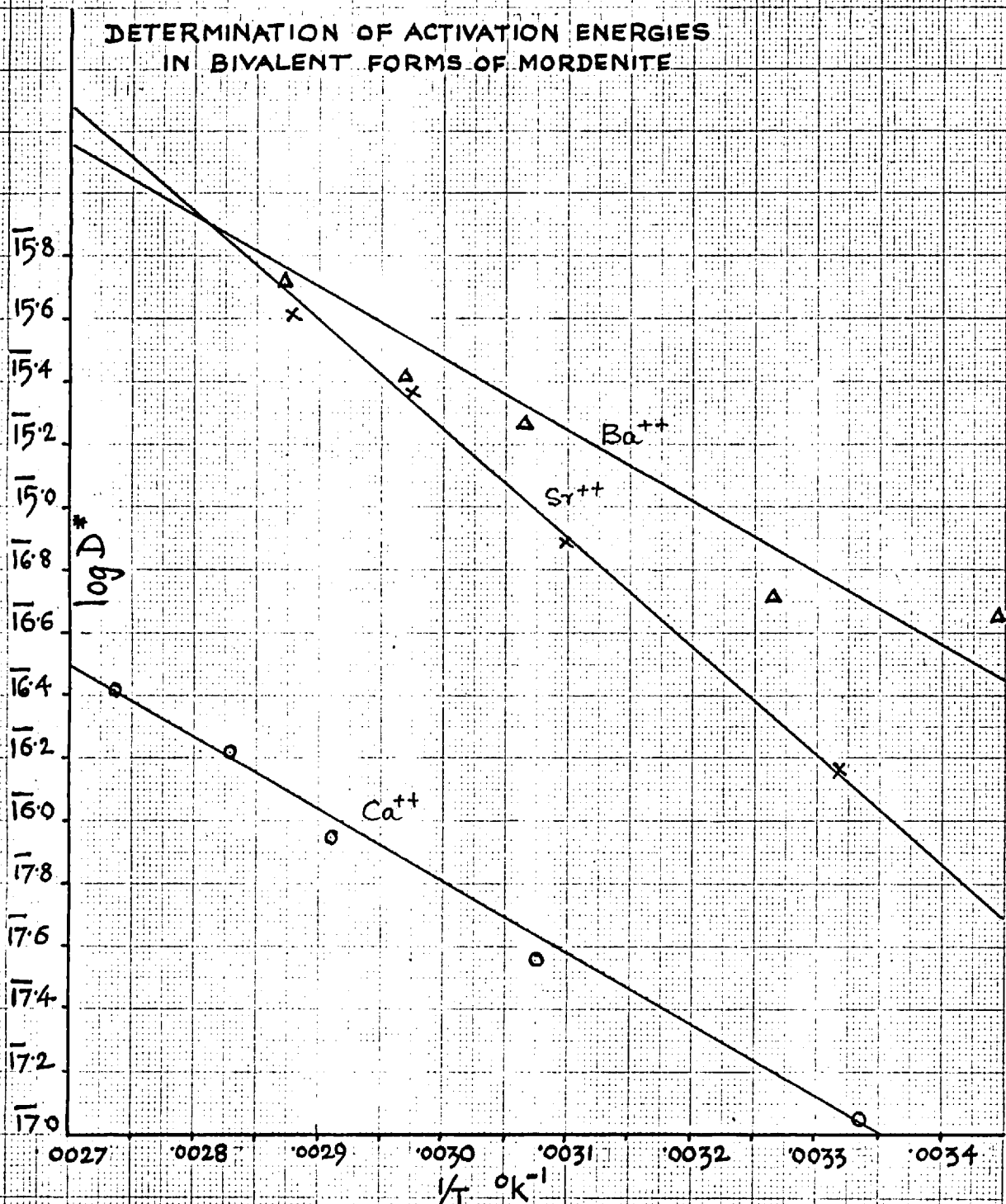


FIG. 9

Self-diffusion in heteroionic mordenite

Self-diffusion coefficients of sodium and potassium ions have been determined for samples of bi-ionic mordenite along the entire concentration range, i.e. from nearly 100% sodium to nearly 100% potassium. This particular pair of ions was chosen because of the similarity in self-diffusion coefficients, activation energies, and water content of the fully exchanged forms. Al/Si ratios were identical. Simultaneous experimental determination of self-diffusion coefficients was fairly easy since the difference in the half-lives of the isotopes used (K^{42} and Na^{22}) is considerable. Experimental techniques have been described in Section 3.9.

While preparing the heteroionic samples, the Na/K isotherm was studied and is shown in fig. 15. The samples were prepared in all cases from sodium mordenite. This was laced with a known amount of Na^{22} so that the amount exchanged was known, and also the ratio of Na/K both in the solid and solution. The self-diffusion coefficients were then determined as described in the experimental section. The main sources of error were in the values of surface area and in the factor $Q_0/Q_0 - Q_\infty$ which, in this case, could not be adjusted to 2. Another difficulty was that in some cases the exchange was very quick and small values of time had to be taken and this reduced accuracy.

The variation of fractional attainment of equilibrium with time is shown in figures 10-12. The temperature in all these experiments was 60°C. As can be seen, the scatter in these graphs is not greater than in those of the fully-exchanged forms, and Q_t/Q_∞ appears to be linear with $\sqrt{t}$ up till at least .6 in all cases. However,

the intercept takes various values. For Na^+ it begins with a very low value for the fully-exchanged form, and for 89.5% Na. However, at 81.55% Na a value of .2 is obtained, the intercept being maintained at about this value until about 55% Na, when it again drops and becomes almost negligible.

Values of D_{Na}^* and D_{K}^* at various concentrations along with surface area values are given in Table 9, page 90. Fig. 14 shows curves obtained at various temperatures from experiments on a sample containing .57 Na^+ . The activation energy for self diffusion in this sample determined from these rates was 7.514 kcal/g.ion.

Bartholomew has obtained a steady decrease in D^* as the mole-fraction of the ion in chabazite decreases. However, he used samples varying in surface area and Si/Al ratio, and the graphs obtained by him show a considerable scatter of points and cannot be regarded as very reliable. Other similar data on zeolites are not available. Some work has been done on ion exchangers (Boyd and Soldano (1953)), and in these diffusion coefficients have found to be constant. This is not very significant since the diffusion mechanism is probably different in our rigid framework structures.

Ion-exchange results

Ion exchange has been studied in the following pairs of ions: Na/K, Na/Rb, Na/Cs. The first system was examined quite closely, rates of ion exchange in three bi-ionic samples being determined apart from rates in the fully-exchanged forms. The samples for the Na/K system were all prepared from the sodium mordenite used in the self-diffusion runs and had the same Si/Al ratio.

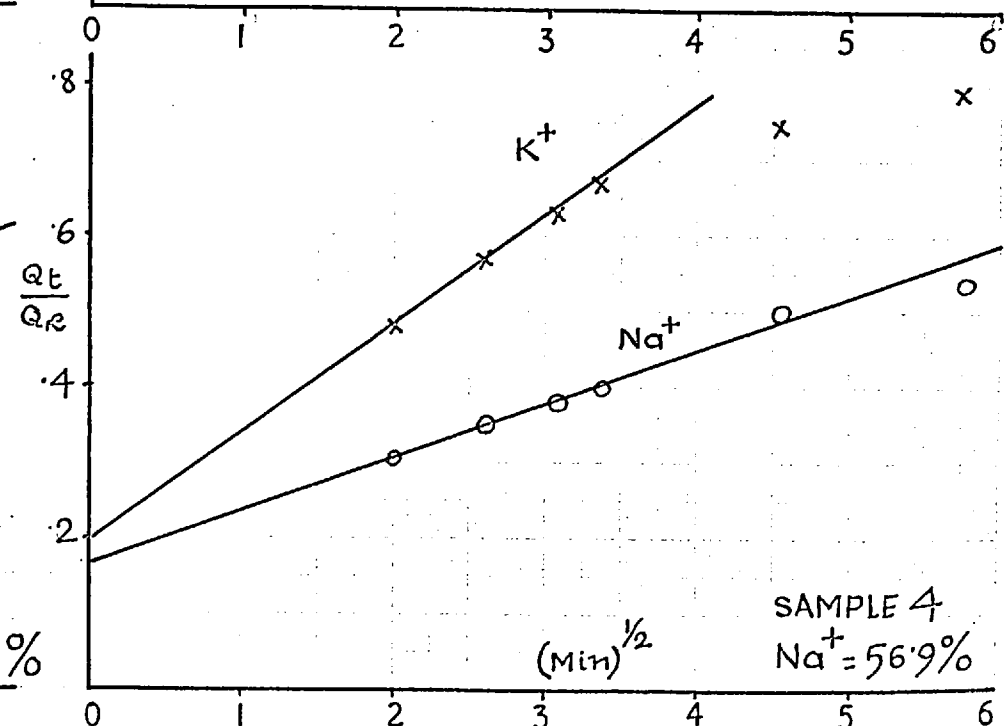
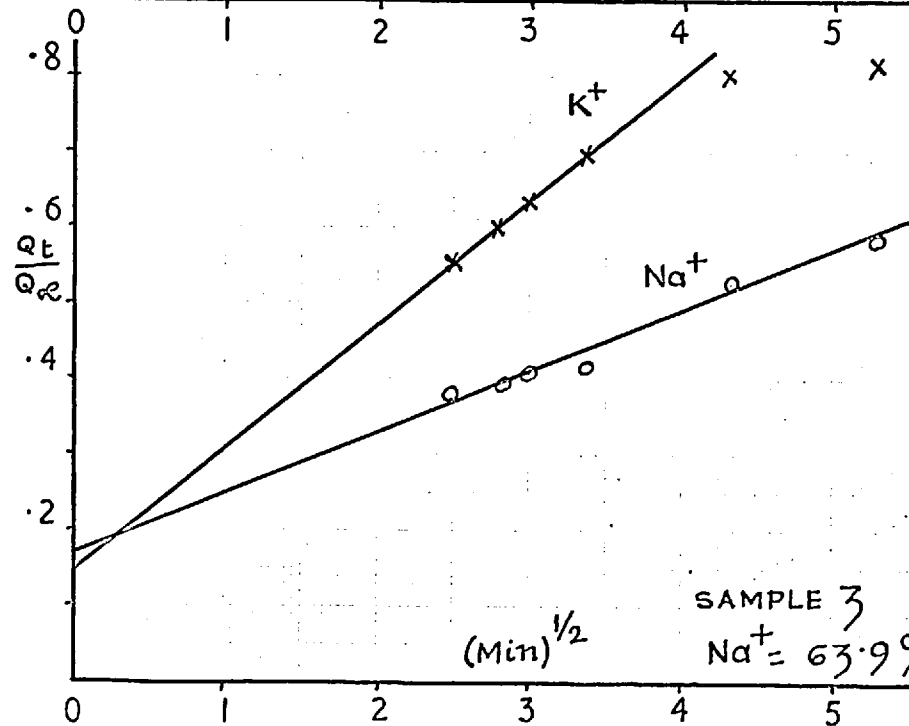
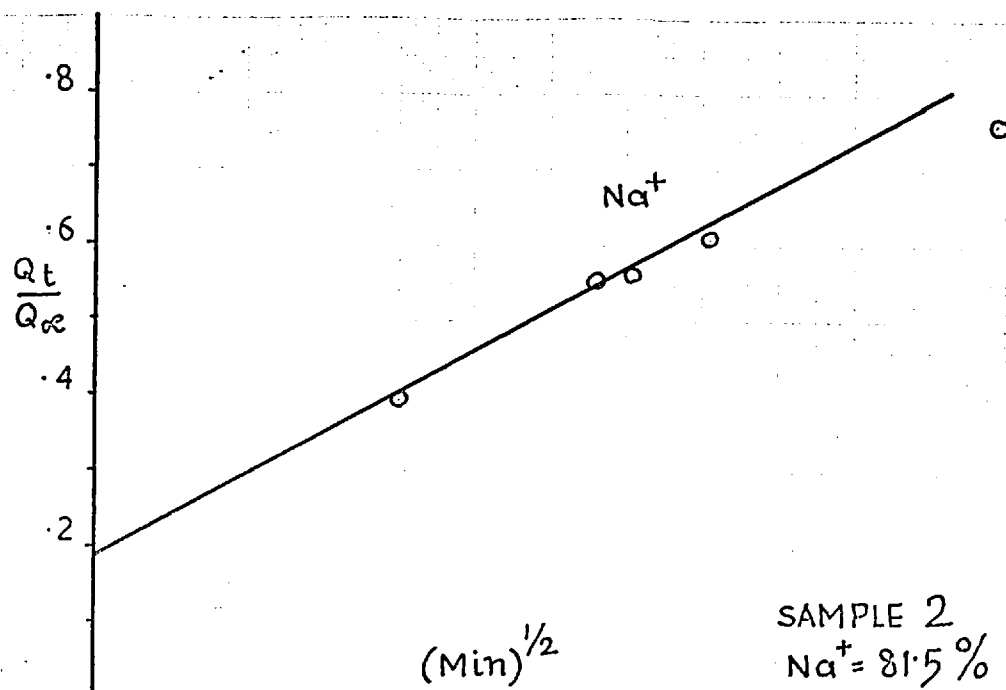
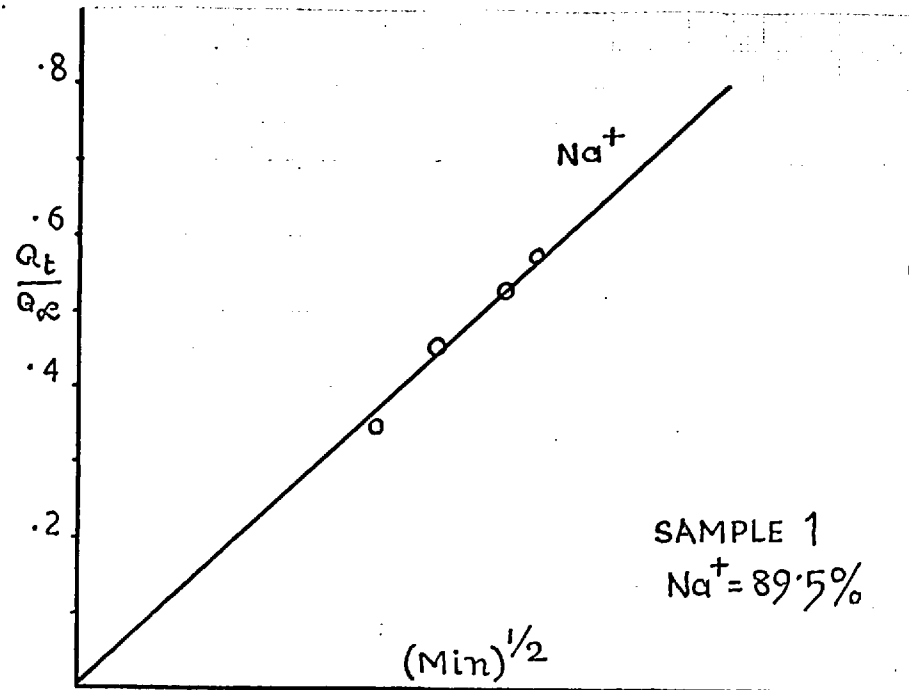


FIG. 10

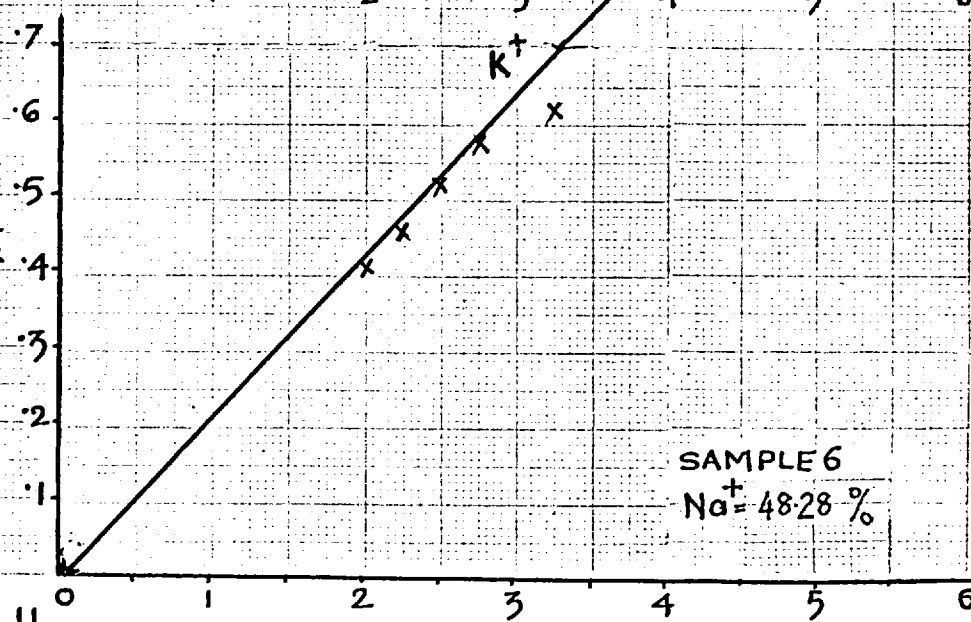
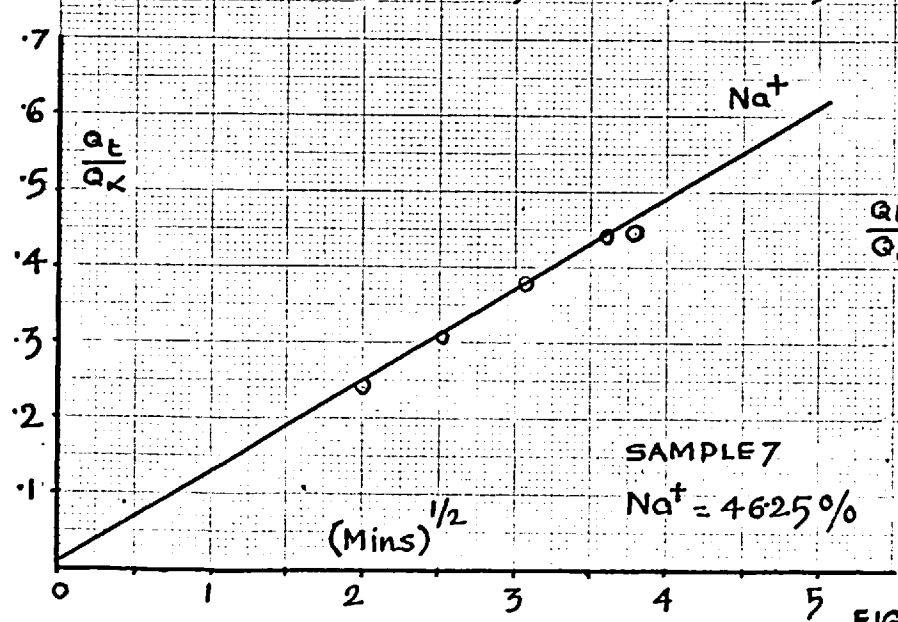
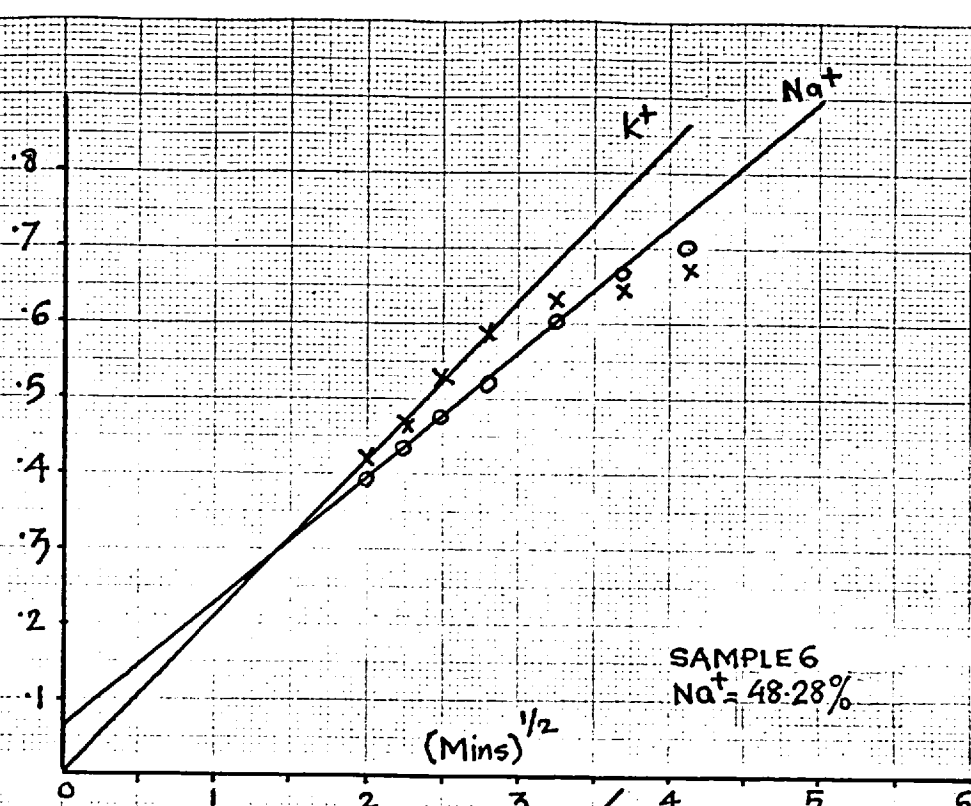
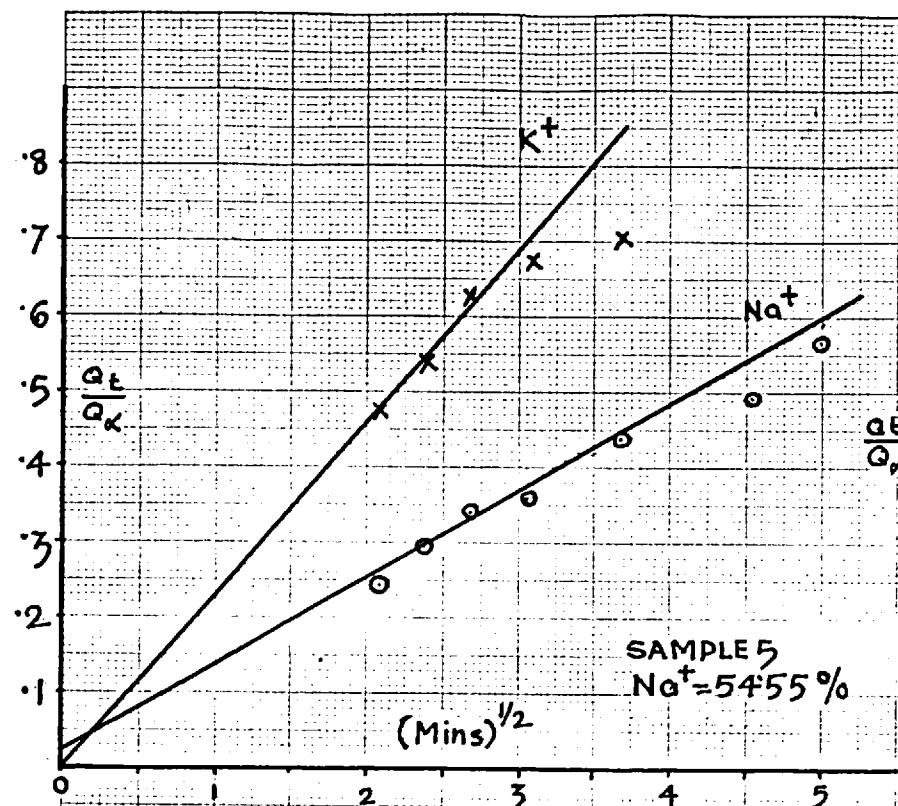


FIG. 11

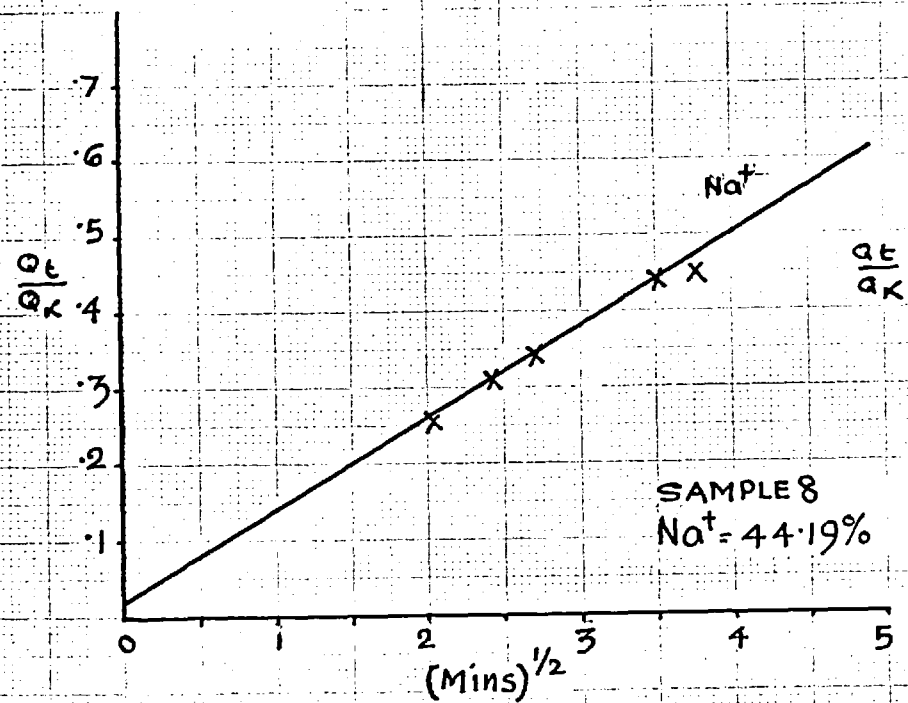
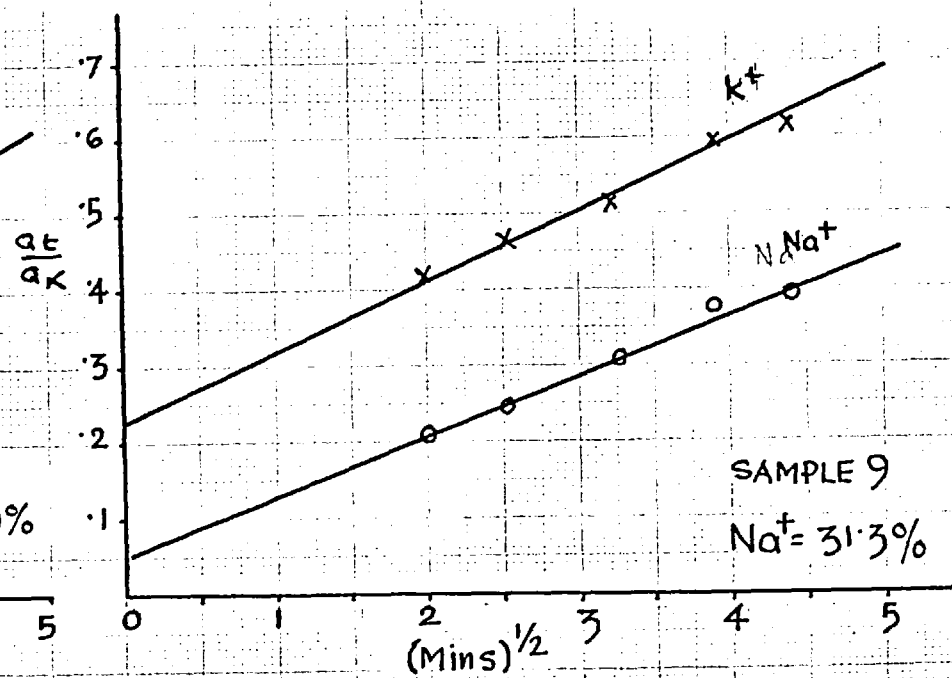


FIG. 12



SELF-DIFFUSION COEFFICIENTS OF K^+ AND Na^+ AS A FUNCTION OF CONCENTRATION OF Na^+ IN THE BII IONIC ZEOLITE

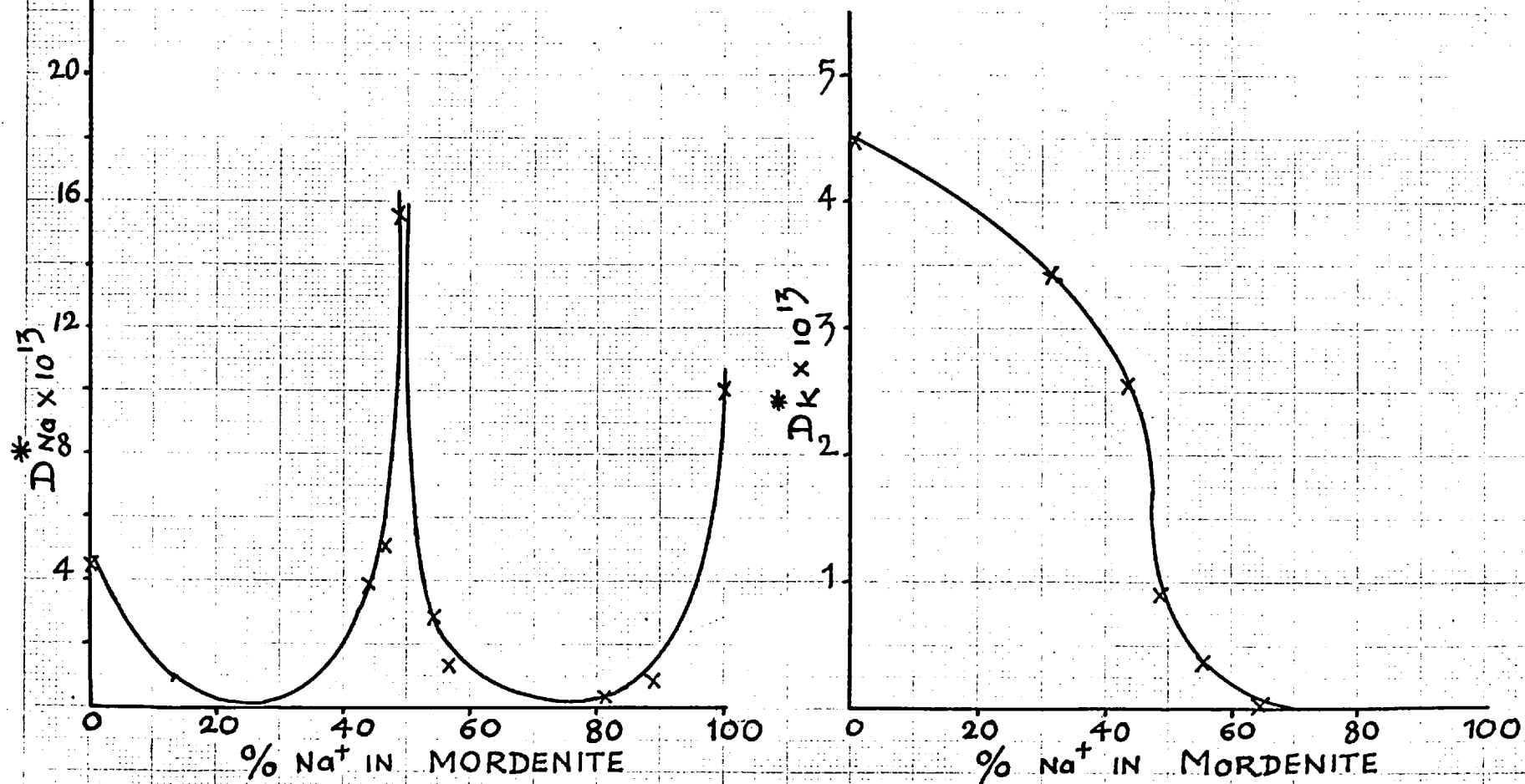


FIG.13

DETERMINATION OF ACTIVATION ENERGY IN BIIONIC SAMPLE CONTAINING 57.2% Na⁺

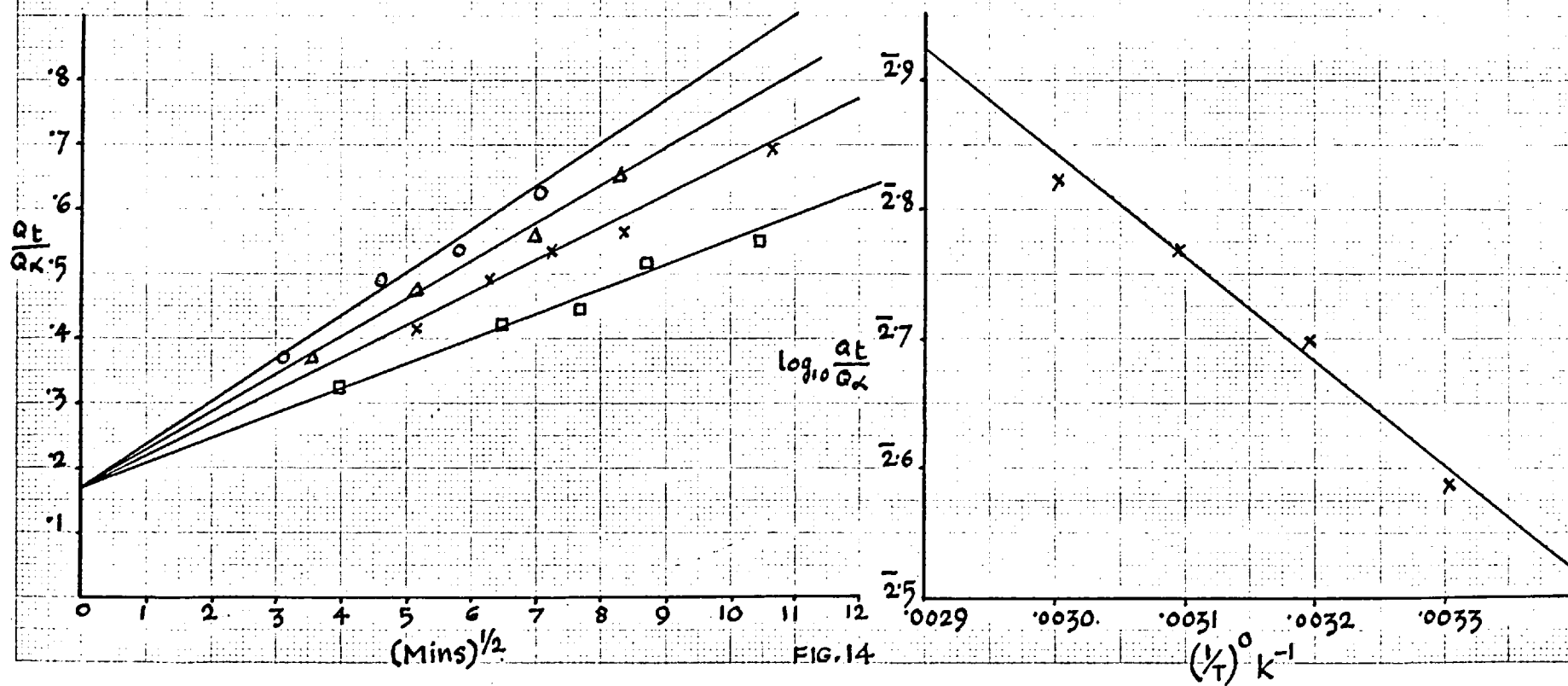


FIG. 14

Results have been compared with those calculated from Helfferich and Plesset's theory and those predicted by application of Crank and Park's sorption data methods. Exchange rates are shown in Figs. 18-20. The data for the Na^+/K^+ system and Rb^+/Na^+ system has been adjusted for constancy of area at the ingoing surface per cm^2 of sample. Deviation from the $\sqrt{t}$ law is observed but not as early as in corresponding curves for bivalent ions in chabazite. Also unlike these chabazite curves definite intercepts on the Q_t/Q_∞ axis are obtained.

In all cases the tracer was initially in the solid, and the exchange solution contained twenty times the amount of incoming ion required for complete exchange.

The factor $\frac{Q_0}{Q_0 - Q_\infty}$ was thus only slightly less than one.

The bi-ionic samples of $\text{Na}^+\text{K}^+\text{M}$ were exchanged in a similar manner, and results obtained are shown in Figs. 26 and 27.

TABLE 6. Self-diffusion coefficients in univalent forms of mordenite

Cation	Temp. °C	$D^*A^2 \times 10^{-7}$ $\text{cm}^6\text{g}^{-2}\text{sec}^{-1}$	A cm^2g^{-1}	$D^*(\text{B.E.T.})$ $\text{cm}^2\text{sec}^{-1} \times 10^{-13}$	$D^*(\text{visual})$ $\text{cm}^2\text{sec}^{-1} \times 10^{-10}$	Activation energy k.cal.g.ion
Sodium (Water content = $29\text{H}_2\text{O}/\text{unit}$ cell)	10.0	8.715	$\{\text{B.E.T.}\} = 2.52 \times 10^3$ $\{\text{visual}\} = 70.8$	1.37	1.74	8.74
	24.0	16.166		2.54	3.21	
	41.7	28.132		4.43	5.62	
	48.2	40.076		6.31	7.99	
	55.0	56.674		8.92	11.31	
	60.0			10		
	(from graph)					
Potassium (Water content = $27\text{H}_2\text{O}/\text{unit}$ cell)	20	49.429	$\{\text{B.E.T.}\} = 6.37 \times 10^3$ $\{\text{visual}\} = 78.6$	1.22	8.0	7.14
	41.5	103.19		2.54	16.7	
	50.5	135.94		3.35	22.0	
	59.5	176.26		4.34	28.53	
	67.5	237.94		5.86	38.51	
	60.0			4.66		
	(from graph)					
Rubidium (Water content = $27.3\text{H}_2\text{O}/\text{unit}$ cell)	13.5	8.60	$\{\text{B.E.T.}\} = 4.98 \times 10^3$ $\{\text{visual}\} = 64.3$	0.34	2.08	20.26
	22.0	32.54		1.31	7.87	
	28.0	42.48		1.71	10.27	
	38.5	119.27		4.81	28.6	
	41.5	231.7		9.34	56.03	
	60.0			53.76		
	(from graph)					
Caesium (Water content = $14.2\text{H}_2\text{O}/\text{unit}$ cell)	28.75	1.24	$\{\text{B.E.T.}\} = 4.98 \times 10^3$ $\{\text{visual}\} = 64.0$	0.05	0.30	4.31
	38.75	1.67		0.07	0.41	
	46.5	1.91		0.08	0.46	
	56.5	2.20		0.09	0.54	
	68.0	2.72		0.10	0.67	
	97.2	4.97		0.20	1.21	
	60.0			0.10		
	(from graph)					

TABLE 7. Self-diffusion coefficients in bivalent forms of mordenite

Calcium ($32.4\text{H}_2\text{O}/\text{unit cell}$)

Temp. °C	$D^*(\text{cm}^2\text{sec}^{-1})$	Area cm^2g^{-1}	Ionic radius Å	Activation energy in kcal/g ion
27	1.13×10^{-17}	9.086×10^3	0.99	10.45
53.5	3.626×10^{-17}			
71	8.923×10^{-17}			
81.5	16.485×10^{-17}			
93.0	26.252×10^{-17}			
Strontium ($33.2\text{H}_2\text{O}/\text{unit cell}$)			1.13	15.97
75	4.130×10^{-15}	10.064×10^3		
64.5	2.351×10^{-15}			
56.0	$.783 \times 10^{-15}$			
29.5	$.149 \times 10^{-15}$			
Barium ($32.0\text{H}_2\text{O}/\text{unit cell}$)			1.35	10.14
77.5	5.103×10^{-15}	10.102×10^3		
64.5	2.576×10^{-15}			
54.5	1.836×10^{-15}			
34.5	0.509×10^{-15}			
18.5	0.453×10^{-15}			

EXCHANGE EQUILIBRIA ISOTHERM

FOR K^+ / Na^+ + MORDENITE

(UNCORRECTED FOR ACTIVITY COEFFICIENTS)

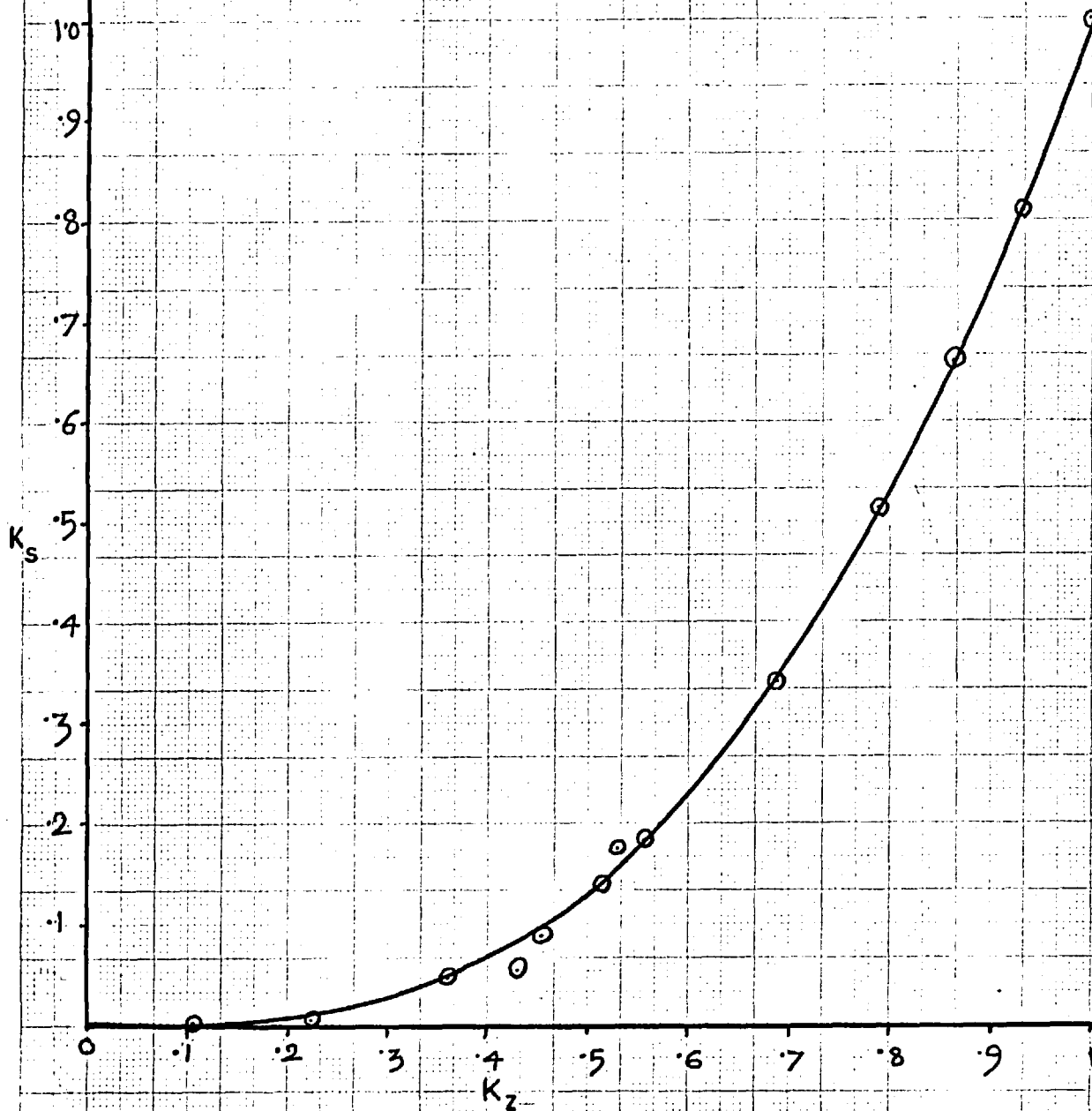


FIG. 15

EXCHANGE EQUILIBRIA ISOTHERMS AT 60°C

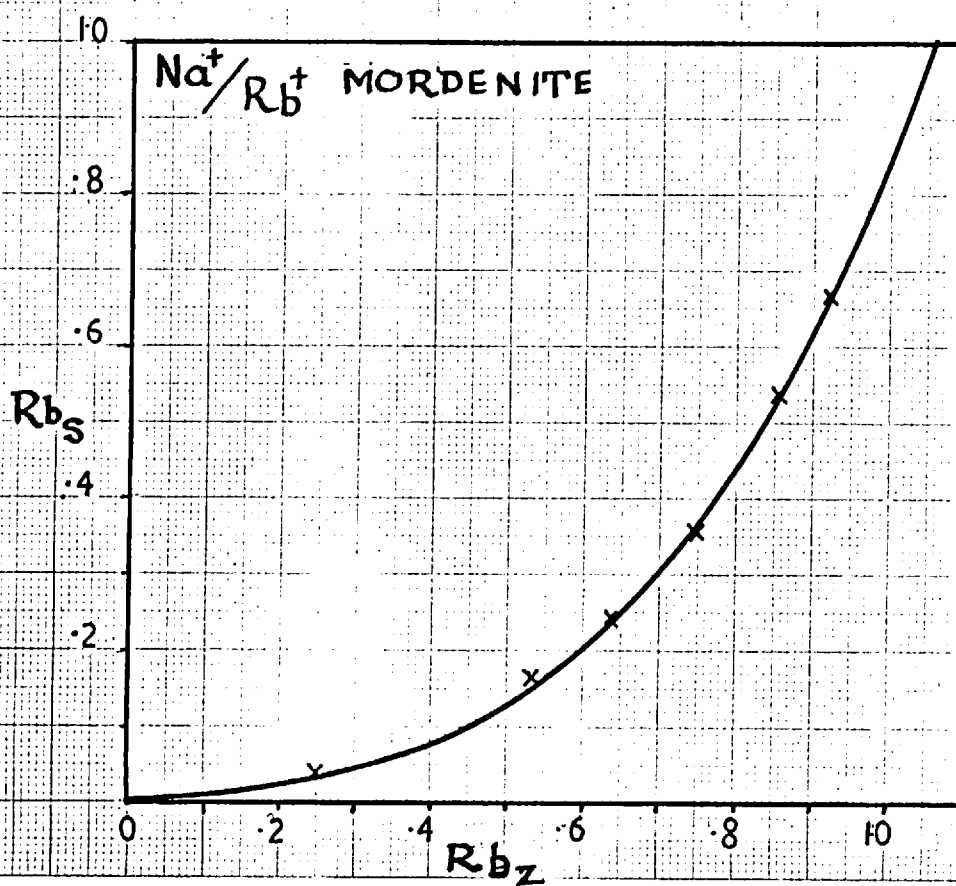
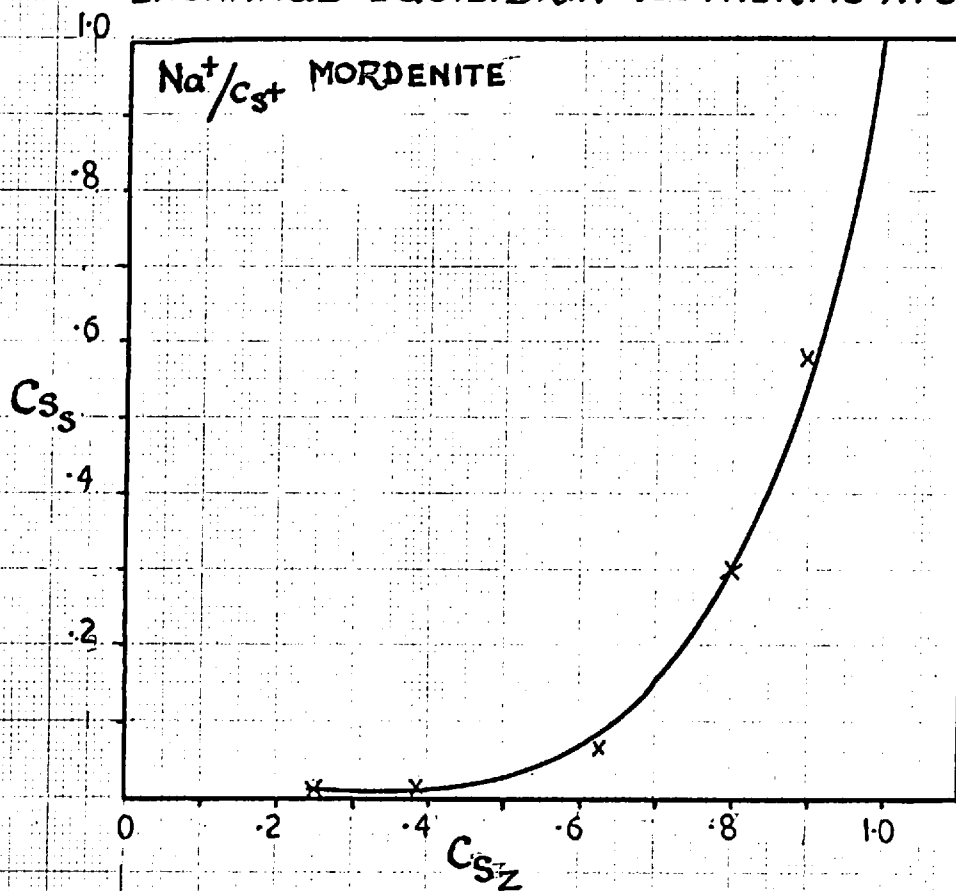


FIG. 16

EXCHANGE EQUILIBRIA ISOTHERM AT 60°
FOR Na^+/Sr^+ MORDENITE

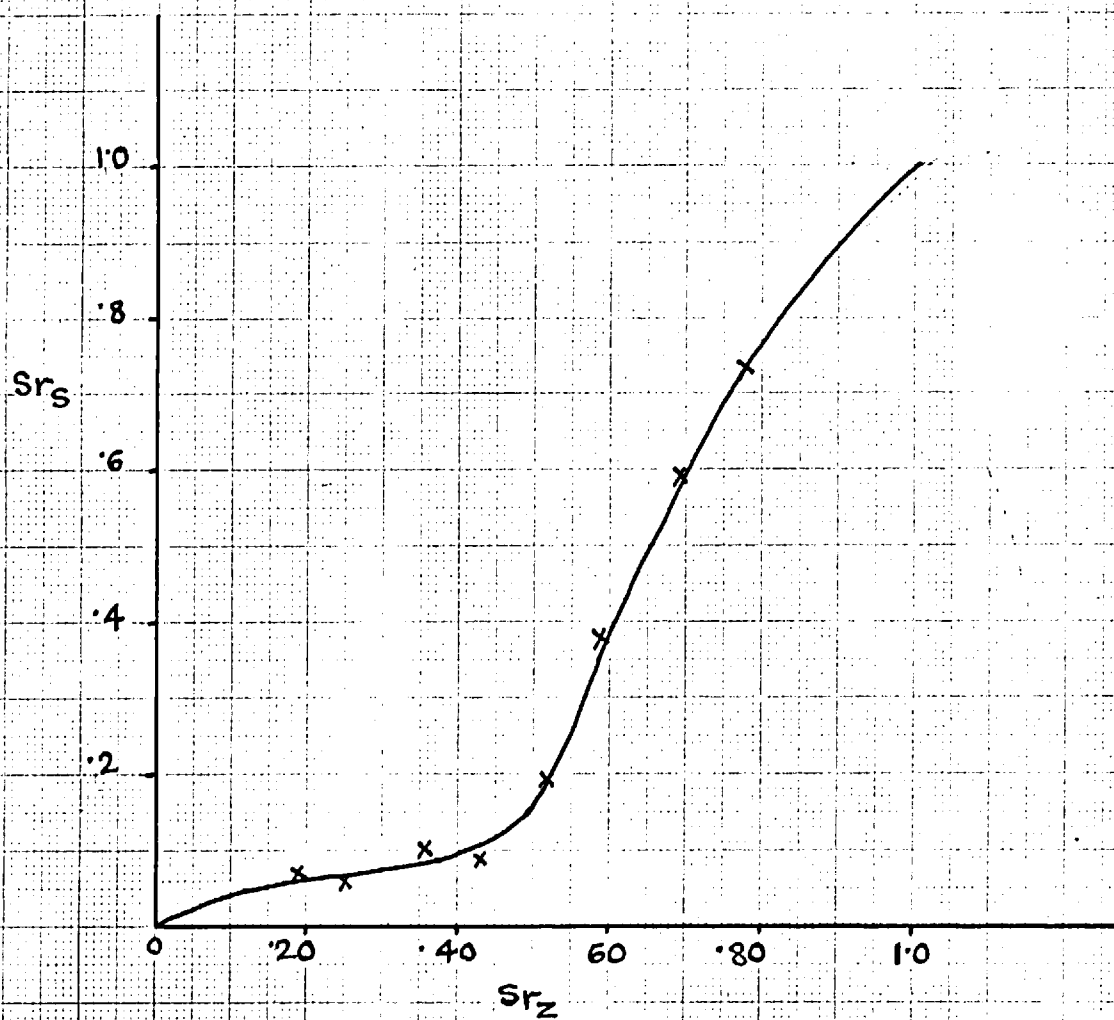


FIG. 17

FRACTIONAL ATTAINMENT OF COMPLETE EXCHANGE

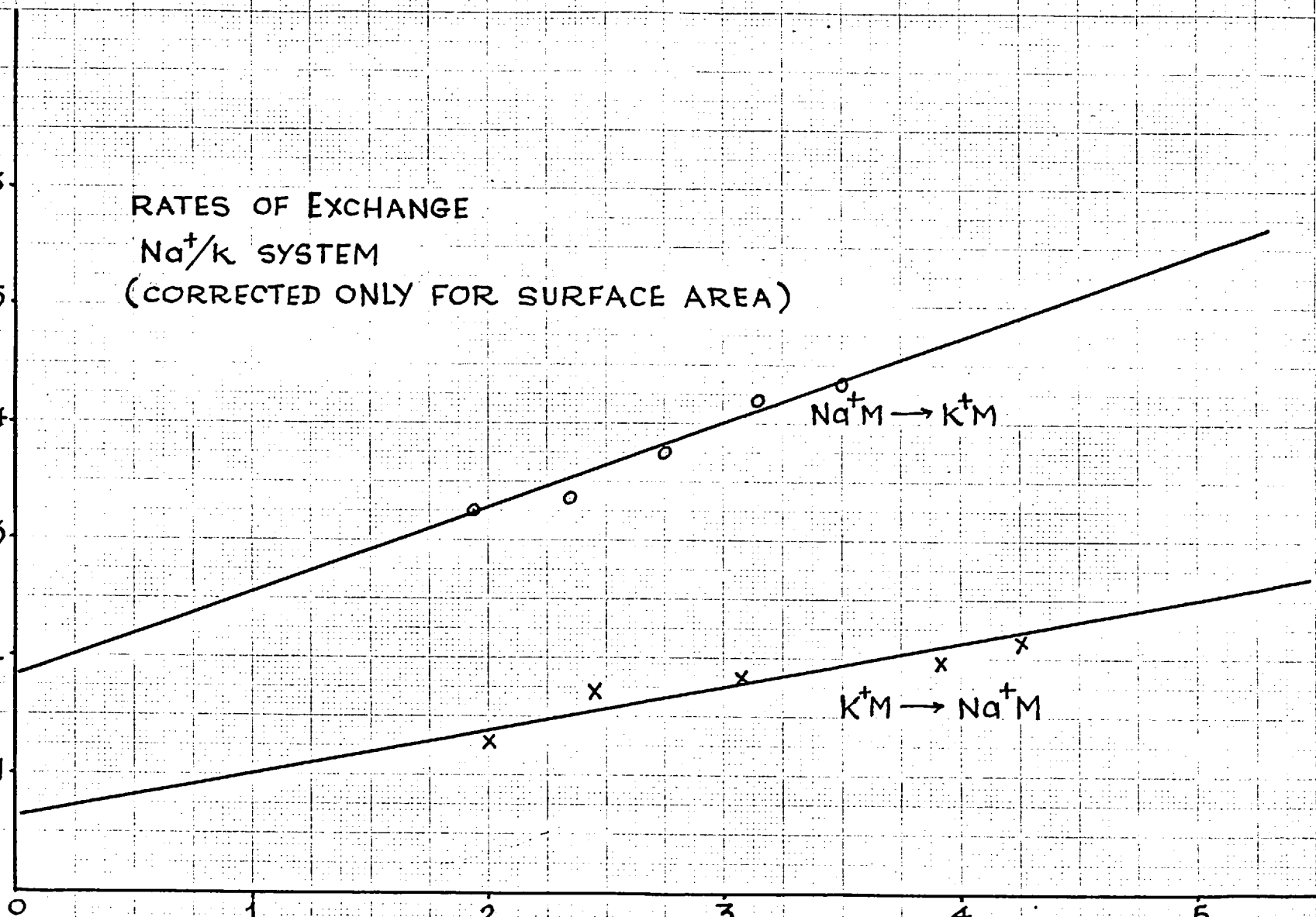
RATES OF EXCHANGE
 Na^+/K SYSTEM
(CORRECTED ONLY FOR SURFACE AREA)

$\text{Na}^+\text{M} \rightarrow \text{K}^+\text{M}$

$\text{K}^+\text{M} \rightarrow \text{Na}^+\text{M}$

(Mins)^{1/2}

FIG. 18



ION EXCHANGE RATES

Na⁺/Rb SYSTEM [CORRECTED ONLY FOR SURFACE AREAS]

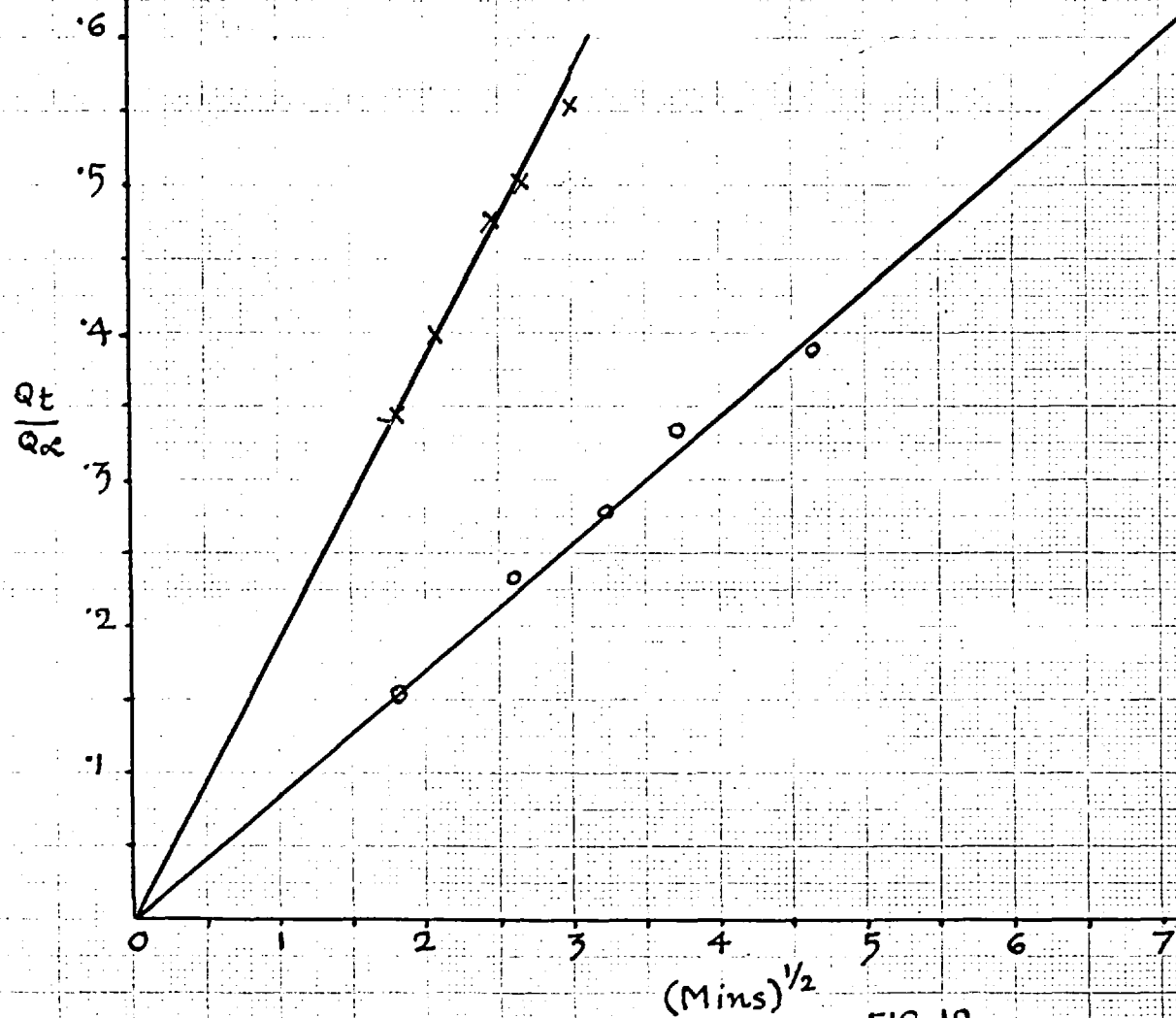


FIG. 19

ION-EXCHANGE RATES
 Na^+/Cs^+ SYSTEM

[CORRECTED ONLY FOR SURFACE AREA]

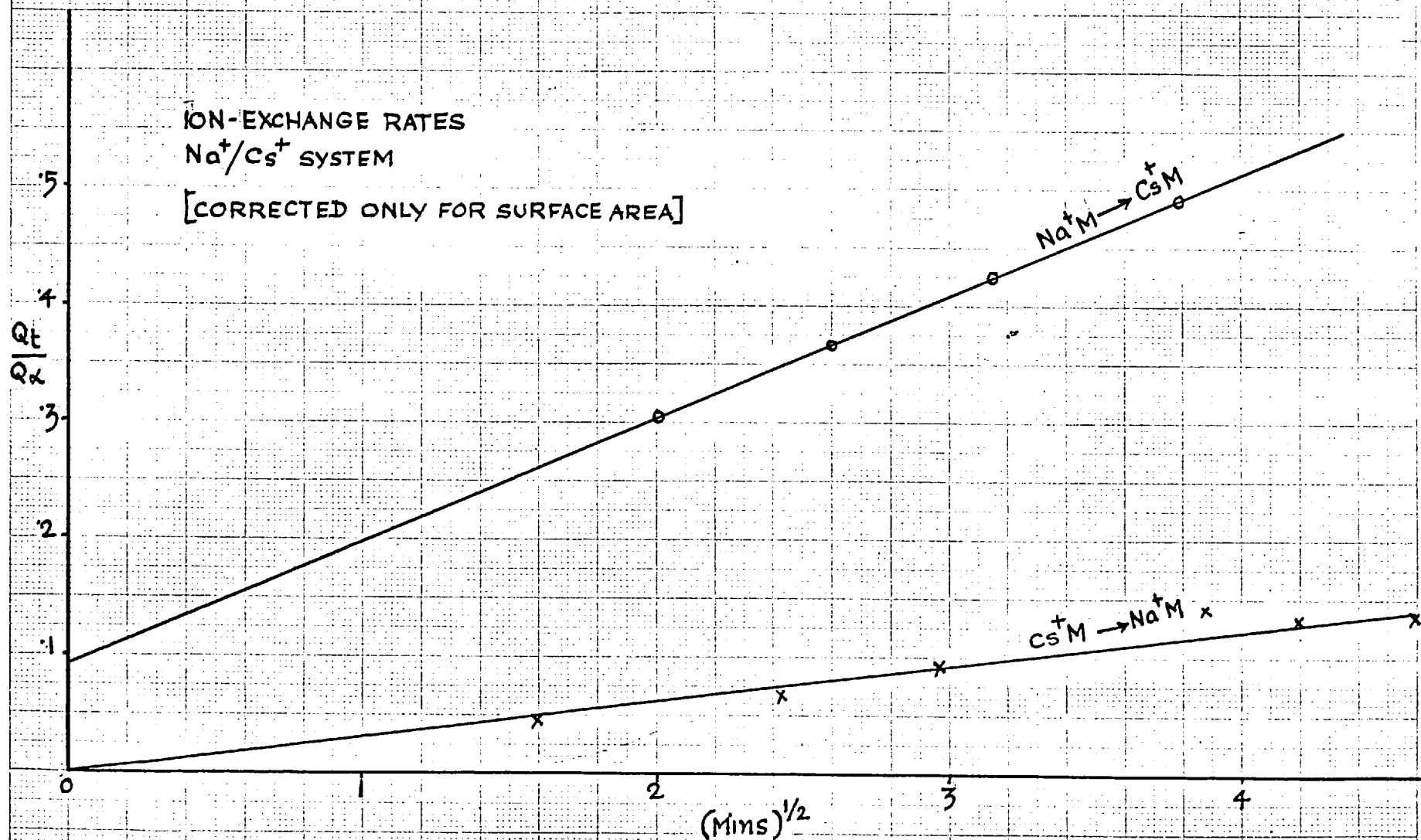


FIG.20

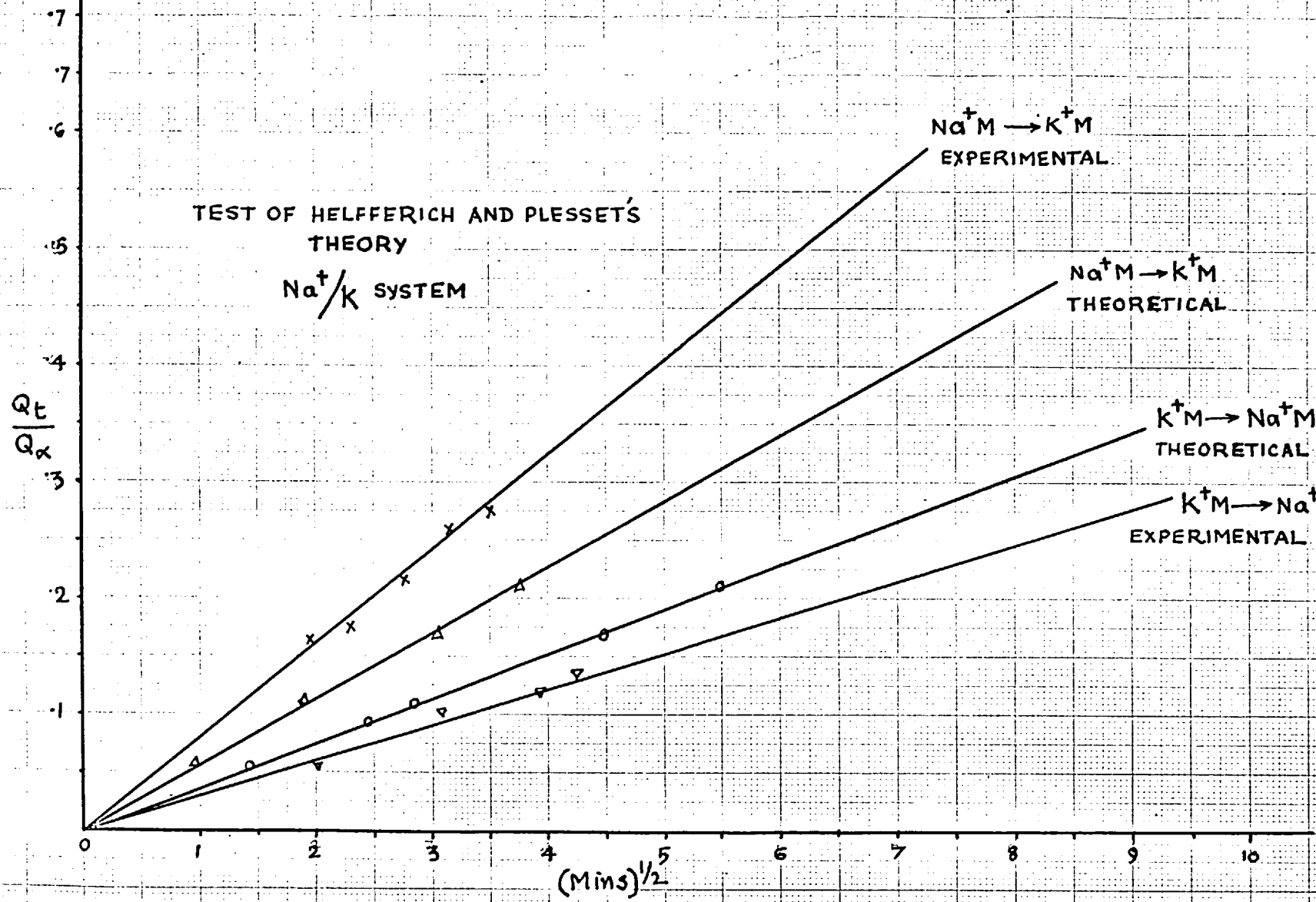
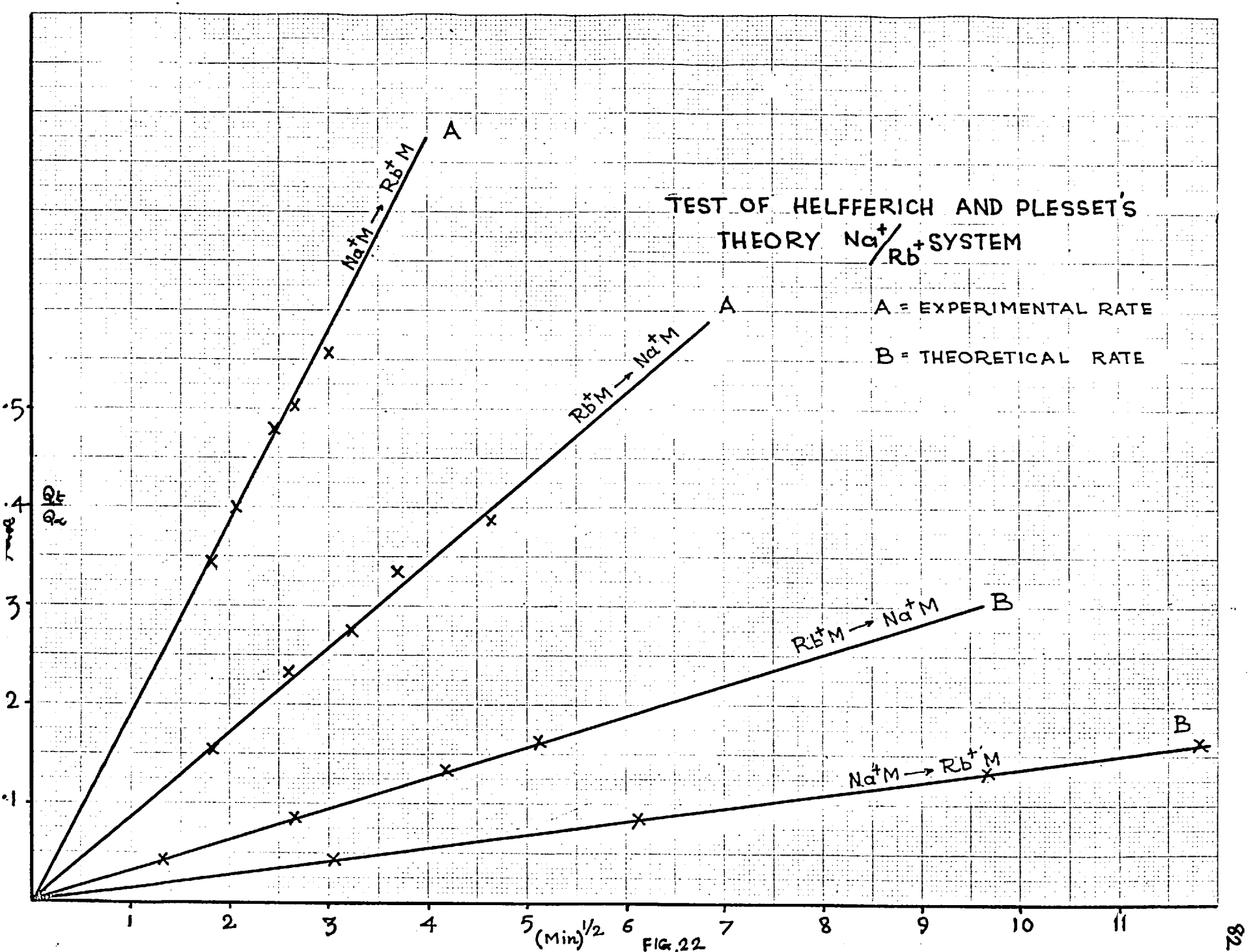


FIG.21



5. DISCUSSION

5.1 Self-diffusion coefficients and activation energies of fully exchanged univalent forms

Values of self-diffusion coefficients in mordenite are given in Tables 6 and 7. For the univalent forms both B.E.T. and visual areas have been used to calculate D^* . It is not definite which of these two areas is the better figure for the area controlling diffusion into the sample. Both are incorrect, the B.E.T. area being too large since it includes cracks and irregularities which are rapidly smoothed out, and the visual one being too small because it ignores all surface defects. However, it is thought that B.E.T. areas are more reproducible from sample to sample, and D^* s calculated from them have greater significance. In the univalent forms $D_{B.E.T.}^*$ lies between $2.5 \times 10^{-13} \text{ cm}^2\text{sec}^{-1}$ for Na^+ and $.05 \times 10^{-13} \text{ cm}^2\text{sec}^{-1}$ for Cs^+ at room temperature. Considering similar data for other zeolites (Barrer and Rees (3) found a range of 1.15×10^{-13} for Na^+ to 1.86×10^{-24} for Cs^+ in analcite which has diffusion channel diameters of $2.3 \overset{\circ}{\text{\AA}}$ and $2.4 \overset{\circ}{\text{\AA}}$; Barrer, Bartholomew and Rees (4) studying chabazite, free diameter $3.9 \overset{\circ}{\text{\AA}}$, got between $1.95 \times 10^{-11} \text{ cm}^2\text{sec}^{-1}$ for Rb and 4.9×10^{-13} for Cs^+). The values for mordenite are as can be expected for free diameter values of $4.4 \overset{\circ}{\text{\AA}}$ to $2.8 \overset{\circ}{\text{\AA}}$.

The values of D^* decrease with increasing ionic radius from Na^+ to Cs^+ , this once again is in agreement with previous work and can be explained as before on the basis that as the cations increase in size they are squeezed more and more during their passage through the windows and hence diffusion through the channels becomes slower. However, the activation energies do not follow a regular pattern. After a value of 20.26 kcal p. g ion for Rb^+

the unusually low value of 4.30 kcal p. g ion is observed for Cs^+ . Obviously this can be caused either by a difference in cation sites in caesium mordenite or by the mechanism of diffusion being different in this form of the zeolite. The possibility that the sites occupied by the Cs^+ in the caesium form are different from those occupied by Na^+ in sodium-mordenite has been investigated to a certain extent. According to Meier's work on the crystal structure of sodium mordenite, of the eight sodium ions per unit cell only four have definite locations at $(0, \frac{1}{2}, 0)$: these lie in the 2.8 Å windows. The other four are randomly distributed, probably in the 8-fold and 12-fold positions in the large channels.

Assuming that in caesium-mordenite also, four Cs^+ are randomly placed, four possible arrangements have been considered for the remaining four caesium ions per unit cell:

- (1) 4 Cs^+ placed at $(0, .210, \frac{3}{4})$ positions
- (2) 4 Cs^+ placed at $(0, .305, \frac{3}{4})$ positions
- (3) 4 Cs^+ placed at $(0, .380, \frac{3}{4})$ positions
- (4) 4 Cs^+ placed at $(0, .455, \frac{3}{4})$ positions.

The theoretical analysis described in section 2.5 shows that distribution (4) gives the best agreement with experiment. This represents a site for the Cs^+ ion quite deep inside an opening in the side of the large channel, and in fact quite close to the site of the Na^+ ion obtained by Meier, the only difference being that the Cs^+ ion is placed centrally right inside the 4.0 Å opening and is almost resting on the oxygen atom opposite while the Na^+ occupies a slightly staggered position to one side of the 4.7 Å opening. Thus to come out into the large channel the Na^+ ion has to negotiate a 2.8 Å ring while the free diameter for a Cs ion coming out is 4.7 Å.

This is shown schematically in fig. 3b. This explains the low activation energy for the Cs ion and is probably also the reason for the low diffusion rate since the Cs^+ unlike the Na^+ can come out into the large channel in one direction only. In any case, the possibility that the mechanism of diffusion is different cannot be ignored. Even if 50% of the Cs^+ are in the small channels in the positions mentioned it is unlikely that they diffuse down these in an unrestricted manner. The diameter of these channels is $4.0 \text{ \AA}$, and Cs^+ ionic diameter is $3.4 \text{ \AA}$, so it is impossible for two Cs^+ ions to pass each other, and it is doubtful whether diffusion occurs at all here.

All these points indicate that the self-diffusion coefficients and activation energy for the Cs^+ form obtained here refer to diffusion in the large channels only. The activation energy is low because the potential barrier of the $2.8 \text{ \AA}$ ring is replaced by the much lower barrier offered by a $4.0 \text{ \AA}$ window, and the D^* values are small, first because the Cs^+ ions in the openings of the larger channels can come out in one direction only, and secondly because the smaller channels **are not used as** diffusion paths and so do not contribute to the self-diffusion rate.

5.2 Self-diffusion coefficients and activation energies in the bivalent forms

D^* values for bivalent mordenite are shown in table 7. The calcium and barium results will be considered first, the maximum exchanges attainable for these forms being 72.5% and 73% respectively, the rest being Na^+ . This was in agreement with observations on zeolon (synthetic mordenite) - C.J.Williams (47) - where only 72%

conversion could be obtained for Ba^{++} . Since Zeolon contains no stacking faults this must be due to some other structural effect common to both zeolites. During preparation of the samples it was observed that 50% exchange was quite easily obtained at only 60°C . After this, however, the exchange rate became extremely slow and was appreciable only at the high temperature (215°C) used. It is probable that the first 50% of the Na^+ ions which were comparatively easily replaced were the ones in the larger channels. In replacing the next 25%, the Ba^{++} ions which being bivalent may take up positions different from those of the sodium ions, may block the entrance to the small channel and prevent the exchange of the last two Na^+ ions per unit cell. If this is so, then in the sample containing 75% Ba, 25% Na or 3Ba^{++} and 2Na^+ per unit cell, all three 3Ba^{++} will be in the larger channels. The comparatively low activation energies of approx. 10 kcal.p g. ion are in agreement with this picture since the potential energy barrier of the 2.8 Å ring does not exist. Apart from this, the values for Ca^{++} and Ba^{++} are approximately twice the Cs^+ value, so it is likely that all three refer to diffusion in the main channels only, where due to the large diameter, coulombic interactions between the framework and cations can be expected to predominate.

In strontium mordenite the situation is different. Results obtained for this ion are the most anomalous. At 60°C only about 40% exchange could be obtained, the next 10% being pushed in very slowly even at 215°C . When self-diffusion was studied in the sample containing 50% Sr^{++} and 50% Na^+ , only $\frac{1}{4}$ th of the strontium ions were found to be accessible to the tracer ion in solution. It seems likely that these exchangeable Sr^{++} ions were

the ones pushed in at 215° which have taken up sites which block the passage of the remaining strontium ions.

These exchangeable ions, i.e. $\frac{1}{4}$ of the strontium content of the zeolite or $(\frac{1}{4} \times 50)\%$ of the total cation content definitely occupy sites different from those occupied by the previous $\frac{3}{4}$ of the Sr^{++} ions. It may be that at 215°C the first $\frac{3}{4}$ of the Sr^{++} ions were forced into the small channels; while the last $\frac{1}{4}$ occupied sites in the larger channels. Thus self diffusion of all the Sr^{++} ions present in the sample used may consist of two kinetic steps, the first due to the Sr^{++} ions in the larger channels and the second involving the Sr^{++} in the smaller channels. However, the second step probably has a very high activation energy and hence it is not observable at the temperature at which the self-diffusion runs were performed. This explanation, which places the Sr^{++} in the small channels, appears likely from a consideration of the behaviour of Sr^{++} in other zeolites, e.g. in NaX, ref. (48) where it can occupy positions inside the hexagonal prisms.

Another possible explanation may be that the last $\frac{1}{4}$ of Sr^{++} ions have taken up positions in the larger channels which due to the presence of stacking faults in the crystal stop access to the rest of the channel. This is supported by the fact that $\frac{1}{4}$ of the strontium content, i.e. 12.5% of the total cation content, represents less than one Sr^{++} ion per unit cell, and hence these Sr^{++} ions are unique not because of their position in the unit cell but because of their location in the crystal and their position with respect to the stacking faults.

However, the above discussion concerns only the sample of 50% Sr^{++} 50% Na^{+} prepared at 215°C . At 60° the sites occupied may be quite different. The Sr/Na isotherm

has been obtained at this temperature and is shown in fig. 17. The isotherm is irregular and shows selectivity reversal at 50% concentration. Complete conversion was possible in this case, while at 215°C it stopped at 50%. However Sr^{++}M prepared in this way was not used in the self-diffusion runs because it took too long to prepare a suitable sample, points on the isotherm requiring a minimum of 10 weeks to reach equilibrium with the solution phase.

5.3 Entropies of activation in mordenite

Values of entropies of activation of various cationic forms of mordenite are shown in table 8. They have been calculated using the equation

$$D_0 = \frac{kT}{h} 2.72 d^2 \exp \left(\frac{\Delta S}{R} \right) \quad (5)$$

d has been taken as $4\overset{\circ}{\text{A}}$ for the univalent forms. In the divalent forms, each divalent cation replaces two univalent ones, so d can be expected to be approx. $8\overset{\circ}{\text{A}}$ in a '100% divalent' sample. However, the Sr^{++} form contained only 50% Sr^{++} and Ca^{++} and Ba^{++} forms each contained 75% divalent cation, the rest being Na^+ in all cases, so d was taken as $6\overset{\circ}{\text{A}}$ for Sr^{++} and $7\overset{\circ}{\text{A}}$ for Ca^{++} and Ba^{++} .

The values of ΔS obtained for Na^+ and K^+ are similar to those obtained in chabazite (4). A negative entropy of activation in the range -15 to -25 cal mole $^{-1}$ deg $^{-1}$ seems to be common in univalent zeolitic self-diffusion. The negative sign indicates that the actual diffusion step involves a more ordered state than the normal unactivated condition. In mordenite this may be due to an ordering of water molecules necessary before diffusion from one site to the next can occur.

Rb^+ has a very unusual ΔS value. This is the only case known so far of a positive entropy of activation. It seems to indicate that Rb^+ (diameter $2.96\overset{\circ}{\text{\AA}}$) finds it energetically preferable to sit in the $2.8\overset{\circ}{\text{\AA}}$ window even though this means decreasing the freedom of the eight oxygen atoms making up the window. A diffusion step from one site to the next will then involve a relaxation of the lattice at the saddle point and thus increase entropy.

Cs^+ also seems to be irregular. It has an unusually large negative entropy of activation. However this can be explained on the basis of the position of the Cs^+ site suggested in section 5.1. As described there, the Cs^+ ion has a reduced number of diffusion paths. For every two paths available to a Na^+ ion in the small channel, the corresponding Cs^+ ion has only one, the fact that entropy is doubled for Cs^+ seems to confirm this picture.

The values of ΔS for Ca^{++} and Ba^{++} are also very high and this supports the suggestion that self diffusion of these ions measured in this project refers to the main channels only, so that as in caesium-mordenite, the number of diffusion paths is reduced. However, ΔS for Sr^{++} is completely anomalous, and obviously more data on this ion is necessary before anything definite can be said about its diffusion process.

Table 8.
Entropies of activation in mordenite.

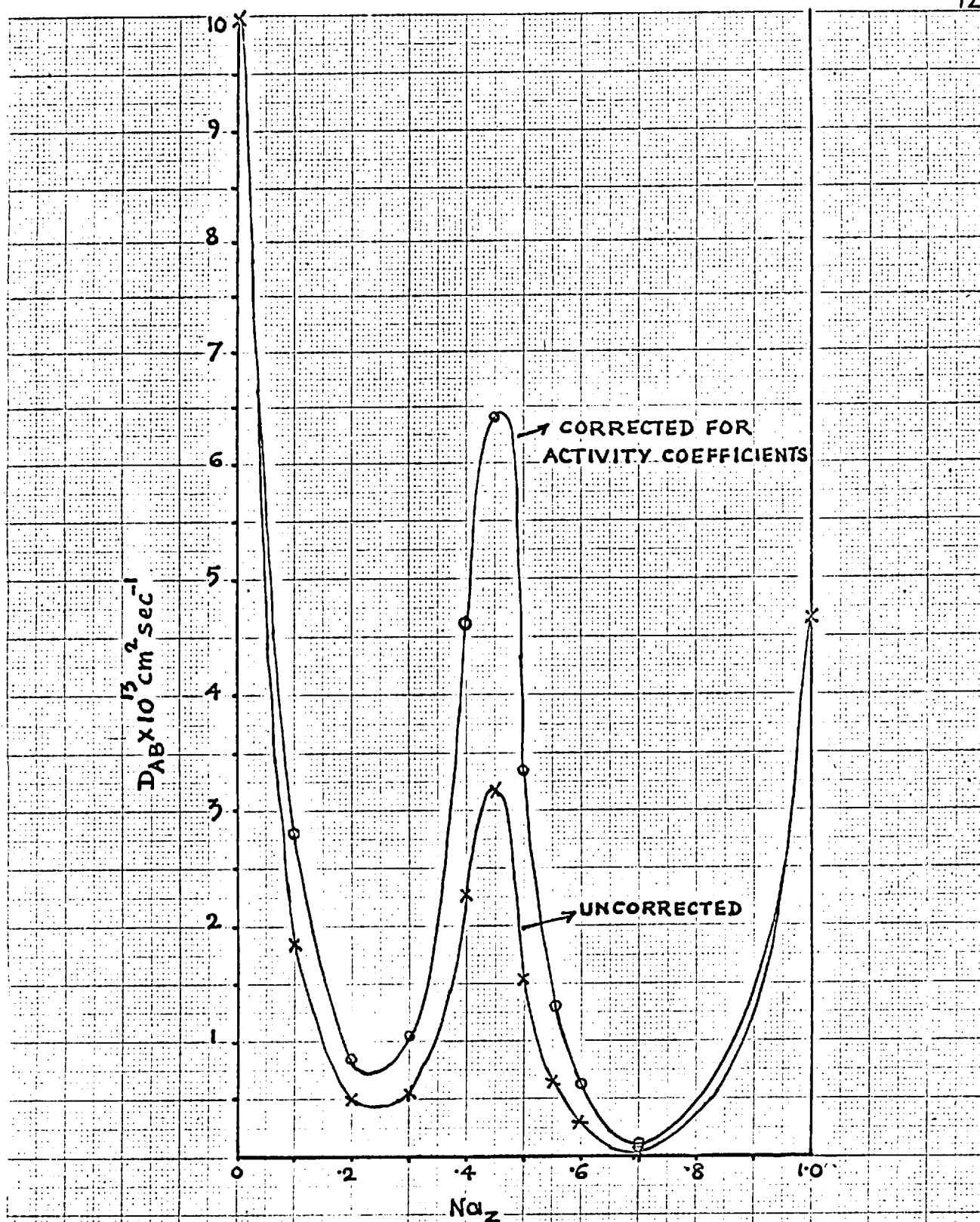
Cation	ΔS cal.mole ⁻¹ deg ⁻¹	d in $\overset{\circ}{\text{\AA}}$
Sodium	-21.85	4
Potassium	-28.1	4
Rubidium	+15.7	4
Caesium	-43.3	4
Calcium	+38.3	7
Strontium	-14.8	6
Barium	-31.8	7

TABLE 9. Self diffusion in bi-ionic mordenite.

Sample	Mol fraction of ions present	Surface area B.E.T. cm^2g^{-1}	D_{Na}^* $\text{cm}^2\text{sec}^{-1}$	D_{K}^* $\text{cm}^2\text{sec}^{-1}$
1	$\text{Na}^+ = .895$ $\text{K}^+ = .105$	3.86×10^3	$.77 \times 10^{-13}$	
2	$\text{Na}^+ = .815$ $\text{K}^+ = .185$	5.39×10^3	$.46 \times 10^{-13}$	
3	$\text{Na}^+ = .639$ $\text{K}^+ = .361$	5.01×10^3	$.96 \times 10^{-13}$	$.584 \times 10^{-14}$
4	$\text{Na}^+ = .569$ $\text{K}^+ = .431$	4.44×10^3	1.28×10^{-13}	1.05×10^{-14}
5	$\text{Na}^+ = .545$ $\text{K}^+ = .455$	5.01×10^3	2.89×10^{-13}	3.39×10^{-14}
6	$\text{Na}^+ = .483$ $\text{K}^+ = .517$	3.99×10^3	15.55×10^{-13}	9.1×10^{-14}
7	$\text{Na}^+ = .463$ $\text{K}^+ = .537$	4.96×10^3	5.05×10^{-13}	
8	$\text{Na}^+ = .442$ $\text{K}^+ = .558$	6.13×10^3	3.93×10^{-13}	2.56×10^{-13}
9	$\text{Na}^+ = .313$ $\text{K}^+ = .687$	3.64×10^3	6.43×10^{-13}	3.46×10^{-13}

5.4 Self diffusion in bi-ionic forms of mordenite

Fig. 13 shows the variation of D_{Na}^* and D_K^* with the mol fraction of Na^+ ions in the zeolite. Sodium-mordenite was the starting material in the preparation of all samples used in these experiments, varying amounts of Na^+ being replaced by K^+ in different samples. Since the Na^+ ions likely to be replaced first are the ones in the main channels, it is reasonable to assume that in samples containing less than 50% Na^+ , most of these sodium ions are in the window sites in the smaller channels while most of the K^+ ions are in the main channels. This may explain the rather low values of D_{Na}^* before about 45% Na^+ concentration since the diffusion rate obtained experimentally is probably to a large extent a measure of the diffusion rate in the small channels with only a small contribution from the rate of diffusion down the main channels. The value of D_K^* in this range decreases steadily as the number of sodium ions increases. This probably measures diffusion in the large channels and the gradual fall is to be expected since the probability of exchanging a potassium ion is proportional to the number of such ions all other conditions being approximately constant. At 50% concentration of Na^+ , however, a very sharp increase in D_{Na}^* is observed accompanied by a sharp fall in D_K^* . The value of D_{Na}^* obtained here is actually larger than obtained in the fully exchanged sodium form, this effect (also observed in the Na/Rb exchange system where the effective D_{Na}^* has been shown to have a value much greater than D_{Na}^* determined by self-diffusion experiments on the 'pure' form) is probably due to some kind of coupling effect between the fluxes of the sodium and potassium ions but no definite explanation can be attempted at this stage.



INTERDIFFUSION COEFFICIENT AS A FUNCTION OF MOLE FRACTION OF Na^+ IN ZEOLITE

FIG. 23

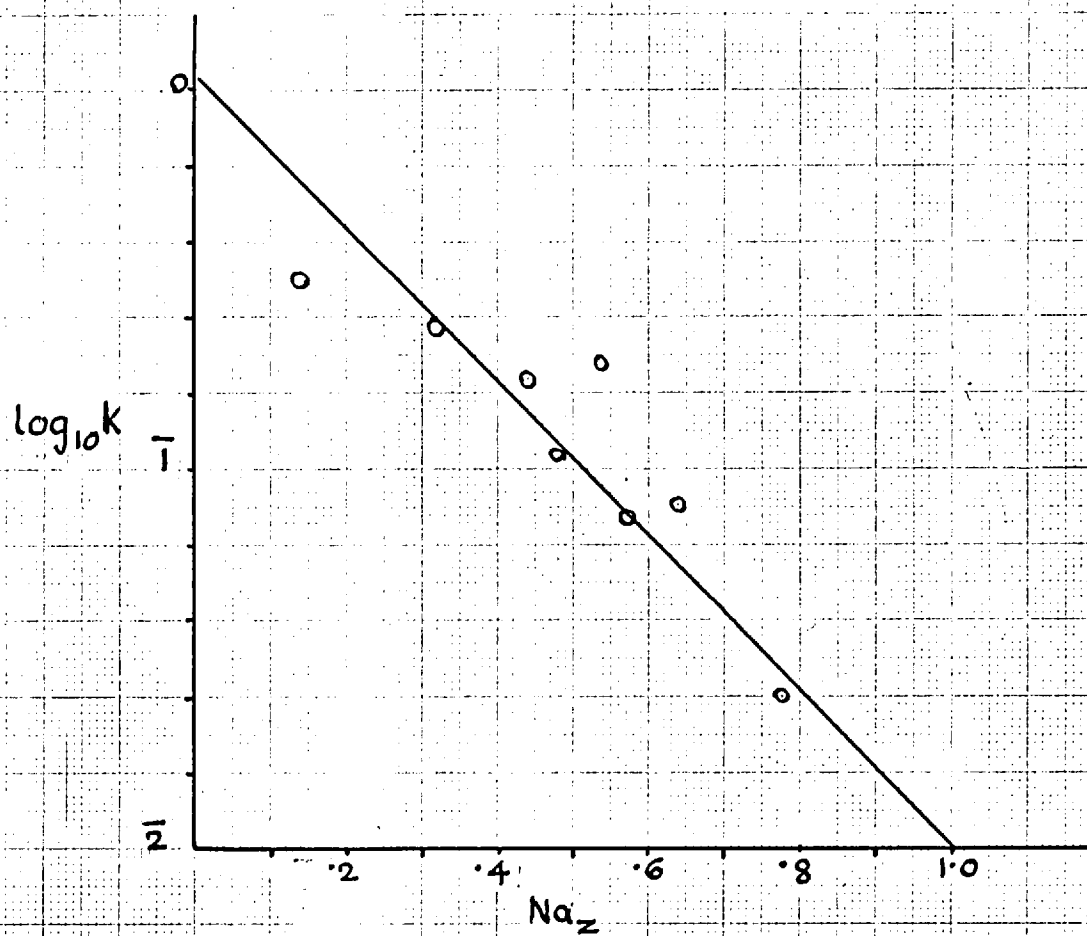
KIELLAND PLOT FOR Na^+/K^+ MORDENITE

FIG.24

VARIATION OF ACTIVITY COEFFICIENTS OF Na^+ AND K^+ WITH
WITH MOLE FRACTION OF THESE IONS IN MORDENITE

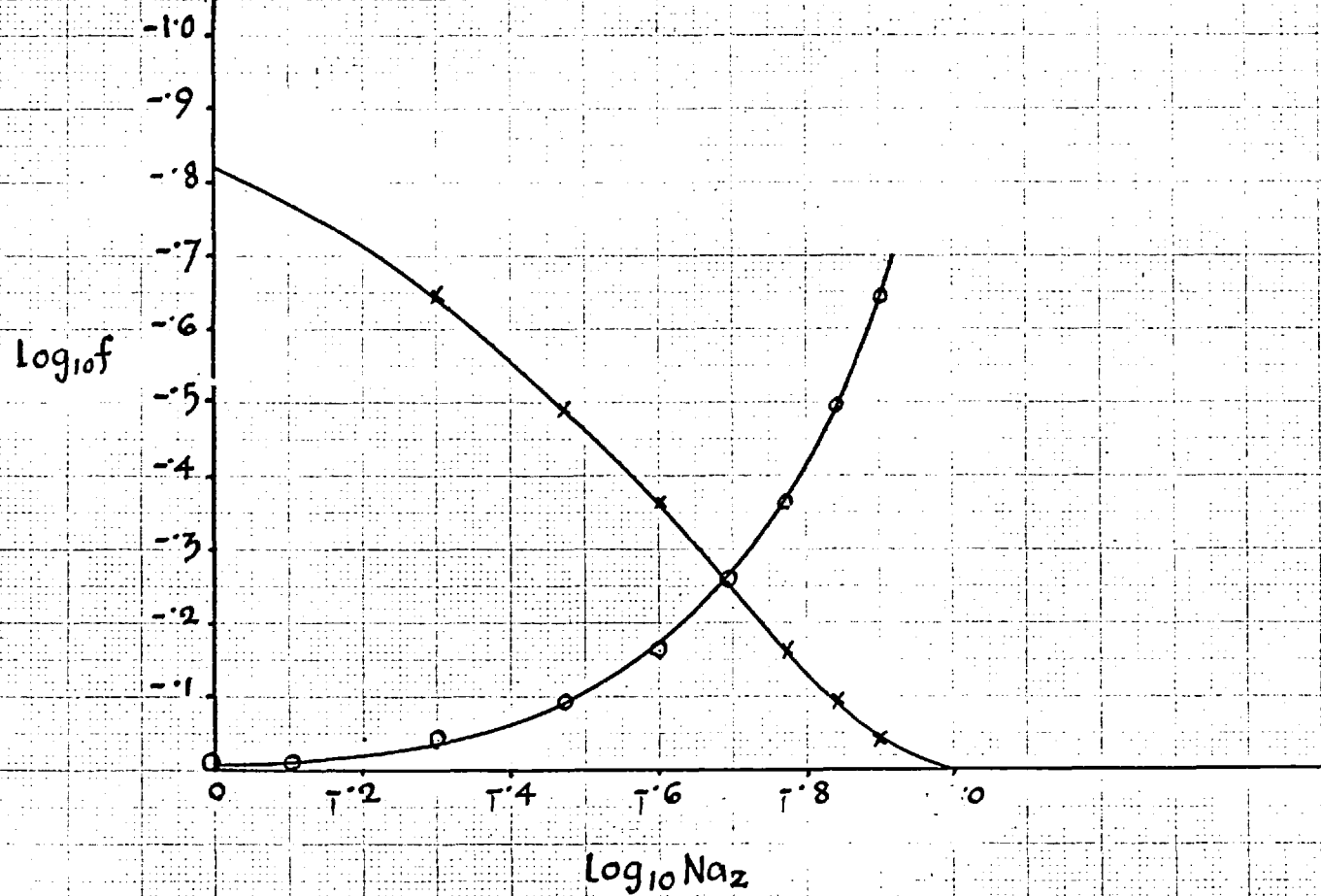


FIG. 25

ION-EXCHANGE IN $\text{Na}^+\text{K}^+\text{MORDENITE}$

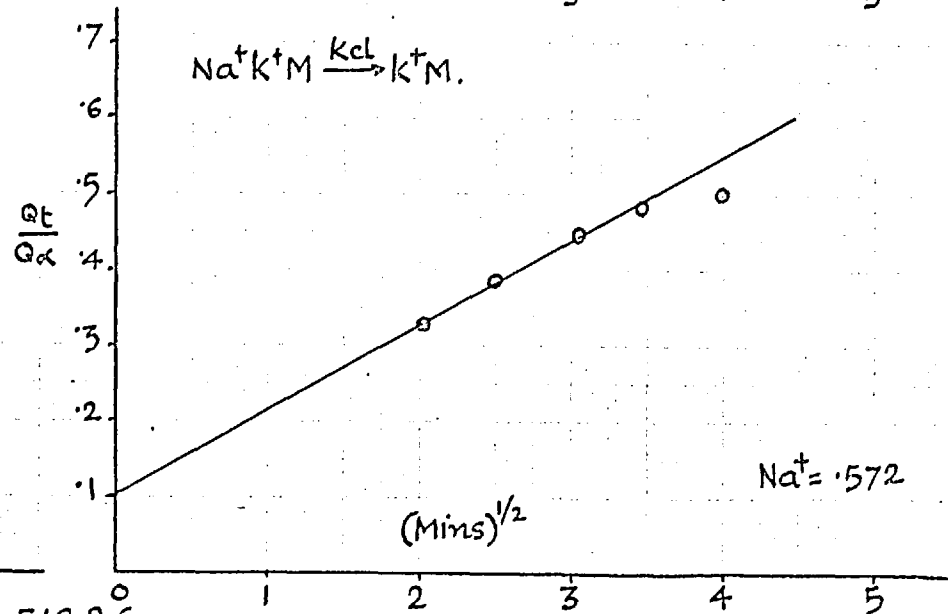
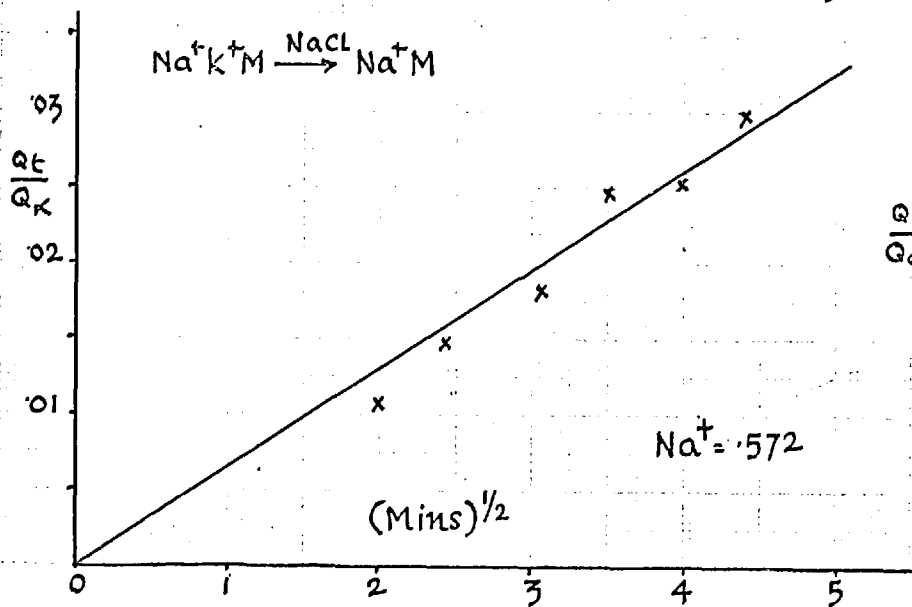
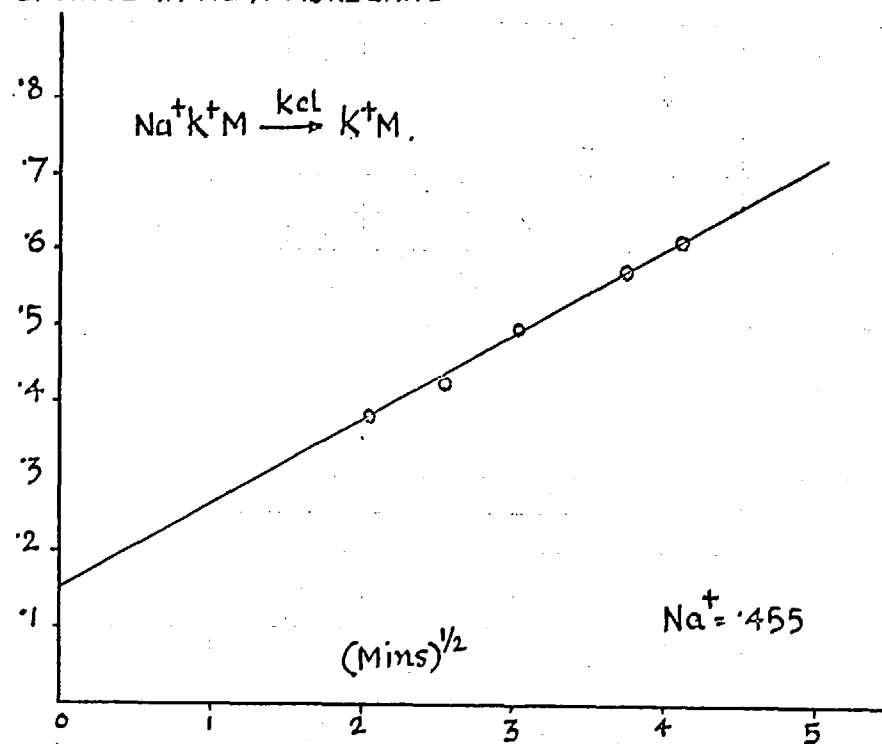
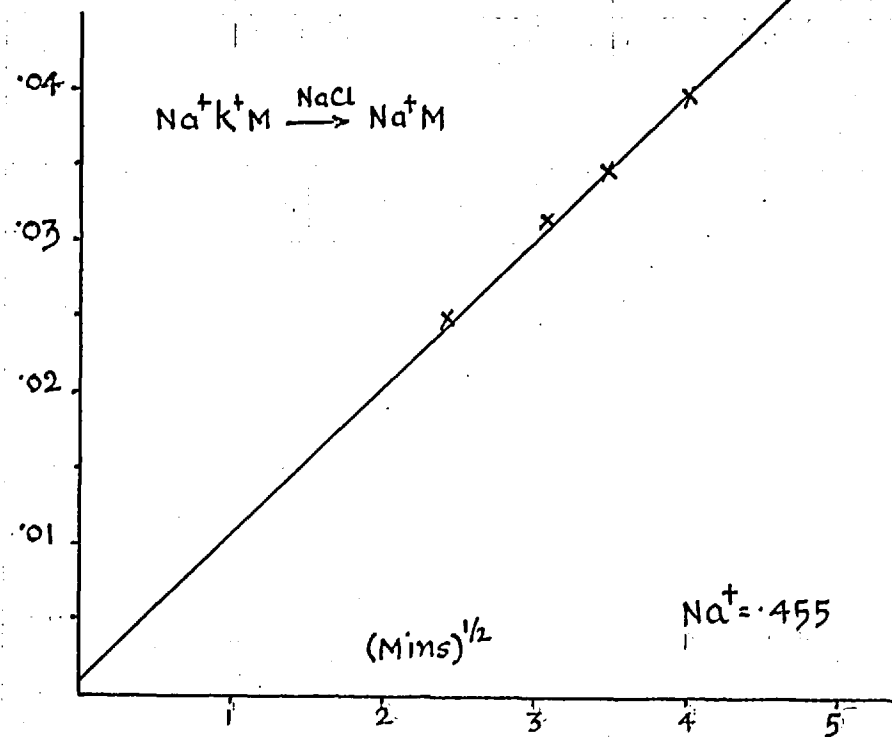


FIG.26

ION-EXCHANGE IN Na^+K^+ MORDENITE

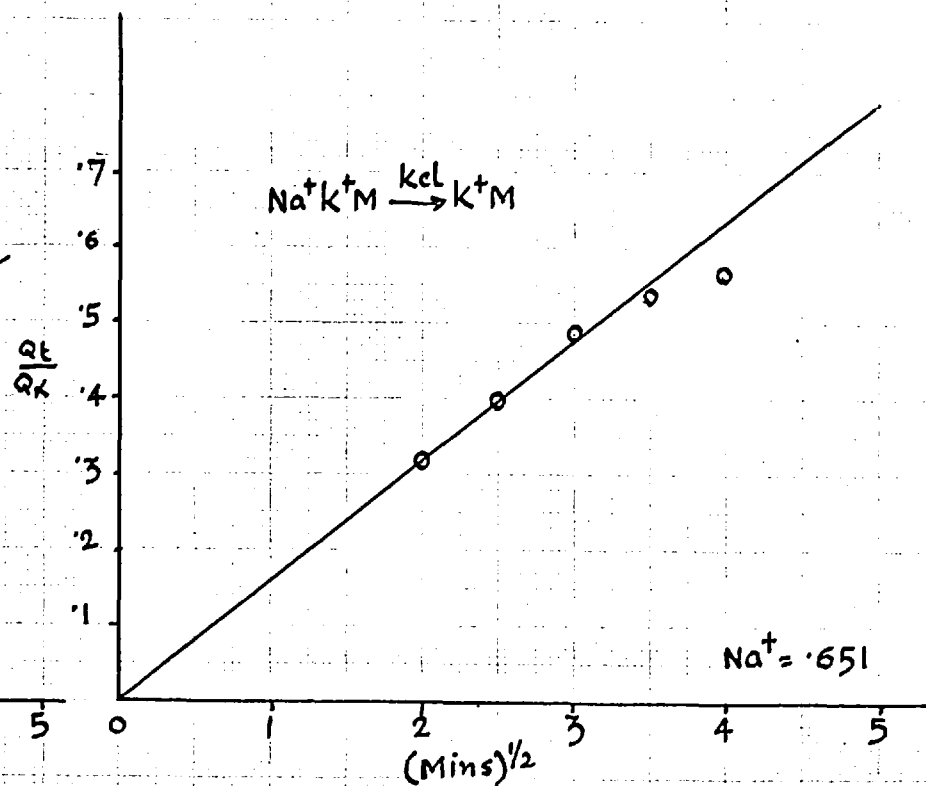
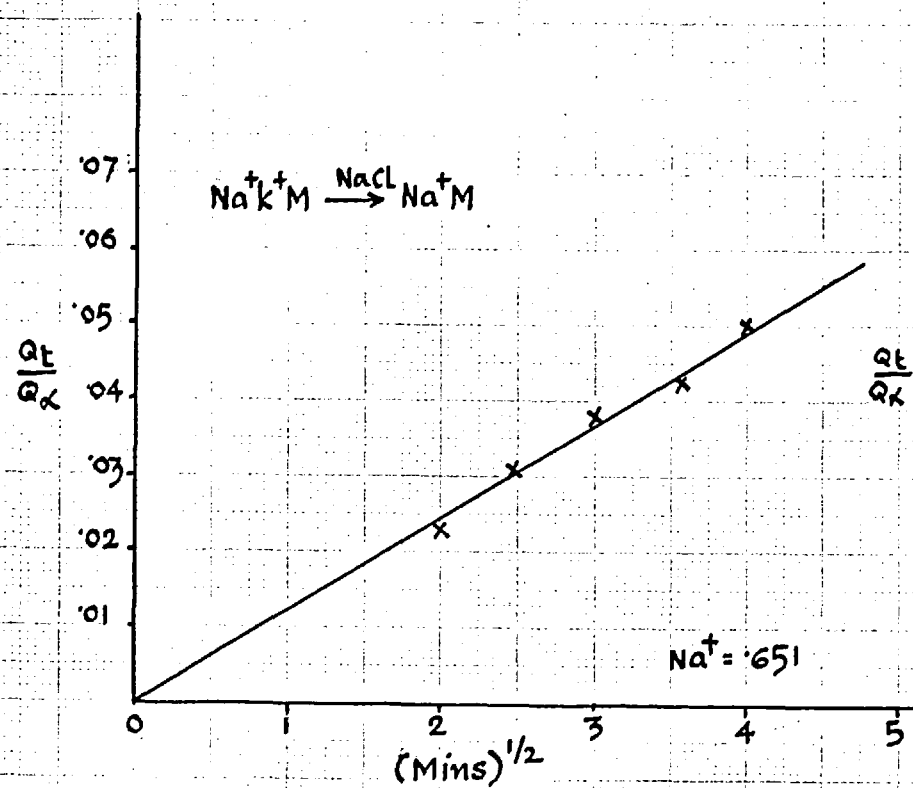


FIG.27

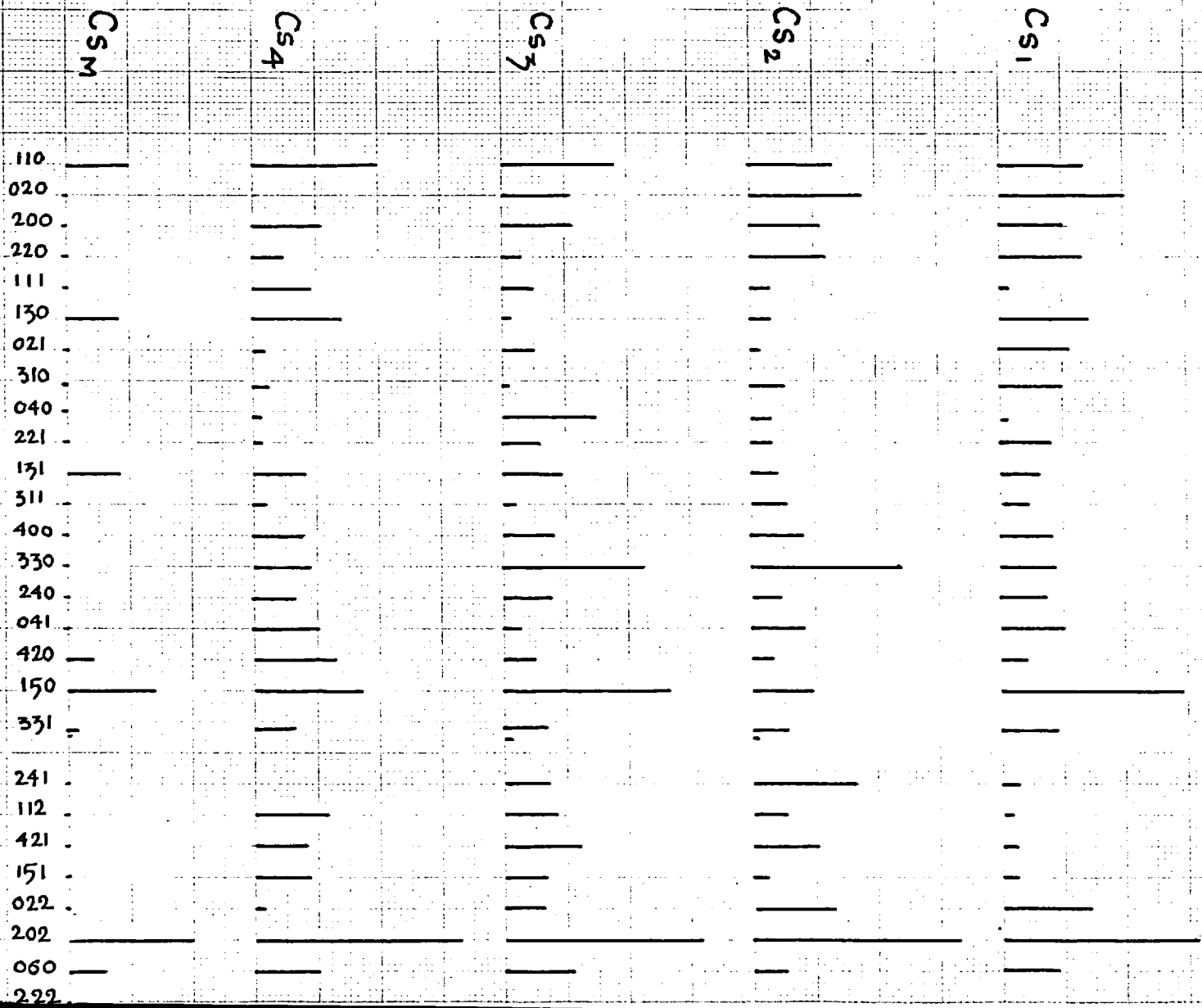


FIG 28

After 50% Na^+ concentration the graphs follow a similar pattern, D_{Na}^* and D_{K}^* both take quite low value probably with a minimum at about 75% Na^+ but the significance of this is not known. D_{AB} values calculated from

$$D_{\text{AB}} = \frac{D_{\text{K}}^* D_{\text{Na}}^*}{D_{\text{Na}}^* C_{\text{Na}^+} + D_{\text{K}}^* C_{\text{K}^+}} \quad \text{have been plotted against mol}$$

fraction of Na^+ in the zeolite and these also show a maximum at about 50%. The experiments thus show a definite non-linear variation of D_{Na}^* and D_{K}^* with mol-fraction of ions present in the zeolite. The activation energy has been determined at only one point (.57 Na) and was found to be the same here as in the fully-exchanged forms.

5.5 Discussion of ion-exchange rates

The primary object of the ion-exchange studies described in this project was to consider the applicability of Helfferich and Plesset's theory (14). Using the numerical solution of the diffusion equation obtained by these authors, rates have been calculated for the forward and backward exchanges in the Na/K and Na/Rb systems, and these are represented in figs. 21 and 22. Rates for the Na/Cs system have not been calculated since the equation used

$$Q_t/Q_\infty = \left(1 - \exp\left\{\pi^2[f_1(\alpha)\gamma + f_2(\alpha)\gamma^2 + f_3(\alpha)\gamma^3]\right\}\right)^{\frac{1}{2}}$$

is reasonably accurate only in the range $10 > D_A^*/D_B^* > 0.1$. D^* values are assumed constant by Helfferich and Plesset; here they have been assumed to have the values obtained for the fully exchanged forms at the temperature of the exchange (60°C):

$$D_{Na}^* = 10^{-12} \text{ cm}^2\text{sec}^{-1}$$

$$D_K^* = 4.7 \times 10^{-13} \text{ cm}^2\text{sec}^{-1}$$

$$D_{Rb}^* = 5.4 \times 10^{-12} \text{ cm}^2\text{sec}^{-1}$$

Q_t/Q_∞ was evaluated for various values of γ which is a dimensionless time factor = $\frac{D_A^* t}{r_0^2}$ where D_A^* is the self-diffusion coefficient of the ion initially in the zeolite, and r_0 = radius of the particles which are assumed to be spheres of equal radius. Thus each value of γ gave on substitution two values of t , one for the backward and one for the forward reaction. In this way theoretical rates for the Na/K and Na/Rb systems were obtained and they are shown in figs. 21 and 22 along with the experimental curves, all four rates being adjusted to the same value of r_0 or (A_p) to make them comparable.

The experimental rate for the Na^+ ion coming out of the zeolite is faster than the rate of the reverse exchange as predicted by the theoretical curves. As shown in fig. 21 the theoretical rates do not coincide with experimental rates but lie in between them. However the agreement between theory and experiment is at least of the right order of magnitude though in view of the variation of D^* values and other irregularities in the zeolite system, this may be entirely fortuitous.

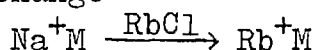
The Rb/Na system has also been treated in the same manner. Here D^* values in the fully exchanged forms are as follows:

$$D_{Na}^* = 10^{-12} \text{ cm}^2\text{sec}^{-1}$$

$$D_{Rb}^* = 5.4 \times 10^{-12} \text{ cm}^2\text{sec}^{-1}$$

Fig. 22 compares the experimental and theoretical curves. It is likely that the wide difference between predicted

and observed rates is due to the effective value of D_{Na}^* or D_{Rb}^* or both being different from the values in the fully-exchanged forms which have been used in the calculation. Assuming that only the effective value of D_{Rb}^* is different and effective D_{Na}^* is still equal to 10^{-12} then in the exchange



D_A^*/D_B^* is not .2 as theoretically expected but takes some value greater than one; D_A^* being constant this would give a lower rate than predicted (35). However, this is not observed, the experimental rate being much greater than the theoretical one, indicating that effective D_A^* or D_{Na}^* is actually much greater than the value used in the calculation of rates.

For the $Rb^+M \xrightarrow{NaCl} Na^+M$ exchange, theoretically D_A^*/D_B^* has been assumed equal to approx. 5. However, since D_A^* is obviously shown to be less than D_B^* , since the exchange process with Rb^+ initially in the zeolite is slower than when Na^+ is initially present, D_A^*/D_B^* must have a value less than one. If D_{Rb}^* had a value of 5.4×10^{-12} as assumed in the theoretical calculation, then the experimentally observed rate would be expected to be higher than predicted. This is shown to be true in the figure, indicating that D_{Rb}^* probably has an effective value of approx. 5.4×10^{-12} , while D_{Na}^* has an effective value greater than this. A rough comparison of expected $\sqrt{t}$ for certain values of Q_t/Q_∞ when D_A/D_B takes various values indicates that in the Rb^+/Na^+ system D_{Rb}^*/D_{Na}^* is probably less than .1 which makes application of Helfferich and Plesset's equation very inaccurate.

It is obvious from fig. 13 that D_{Na}^* will probably vary with composition in the Na/Rb system and without experimental proof we can only postulate that D_{Na}^* must be

very large at some intermediate composition to explain the exchange results.

For the Cs/Na system Helfferich and Plesset's equation is not applicable since this does not come in the range $10 > D_A/D_B > .1$. However, the rate of the reaction $\text{Cs}^+\text{M} \xrightarrow{\text{NaCl}} \text{Na}^+\text{M}$ is much slower than the reverse as may be expected from the Helfferich and Plesset's theory since D_{Cs}^* is much smaller than D_{Na}^* .

The sorption-desorption analogue

Referring to Crank and Park's work (19) on sorption and desorption data the equation

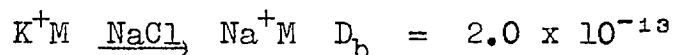
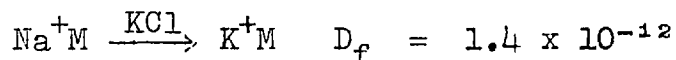
$$\bar{D} = \frac{1}{C_1 - C_2} \int_{C_2}^{C_1} D \cdot dc$$

has been used to interpret the ion-exchange results. $D(c)$ is taken as the differential interdiffusion coefficient described by Helfferich and Plesset in the case of the Na/K system equal to

$$\frac{D_K^* D_{\text{Na}}^*}{D_K^* C_{\text{K}^+} + D_{\text{Na}}^* C_{\text{Na}}},$$

C_{Na^+} and C_{K^+} being concentration in the zeolite expressed as mole fractions. This being true of course only if D_A and D_B used by Helfferich can be equated to the respective self-diffusion coefficients. Since D_K^* and D_{Na}^* are known over the entire range of concentration from $C_{\text{Na}^+} = 0$ to 1, the above differential interdiffusion coefficient can be evaluated at various concentrations and the integration can be performed graphically by determining the area under the curve obtained by plotting D_{AB} against C_{Na^+} . This procedure gave a value for integral $\bar{D}_{\text{AB}} = 1.5135 \times 10^{-13}$.

Now if D_f is the rate of the forward reaction



therefore $\frac{1}{2}(D_f + D_b) = 7.905 \times 10^{-13} \text{ cm}^2\text{sec}^{-1}$.

This is not in very good agreement with the value obtained by graphical integration. However, if the values of D_{Na}^* and D_{K}^* are taken as constant and equal to the values for the fully exchanged forms, the integral can be easily evaluated and $\bar{D}_{AB}$ becomes equal

$$\text{to } \frac{D_{\text{Na}}^* D_{\text{K}}^*}{(C_1 - C_2)(D_{\text{Na}}^* - D_{\text{K}}^*)} 2.303 \log_{10} \frac{(D_{\text{Na}}^* - D_{\text{K}}^*)C_2 + D_{\text{K}}^*}{(D_{\text{Na}}^* - D_{\text{K}}^*)C_1 + D_{\text{K}}^*}$$

when $C_1 \rightarrow 0$ and $C_2 \rightarrow 1$

$$\bar{D}_{AB} = \frac{D_{\text{Na}}^* D_{\text{K}}^*}{(D_{\text{K}}^* - D_{\text{Na}}^*)} 2.303 \log_{10} \frac{D_{\text{Na}}^*}{D_{\text{K}}^*}.$$

This gives $\bar{D}_{AB} = .67318 \times 10^{-12} \text{ cm}^2\text{sec}^{-1}$. Similar data for the Na/Rb and Na/Cs systems are shown in the table.

Ion exchange system	$\bar{D}_{AB}$ obtained graphically in $\text{cm}^2\text{sec}^{-1}$	$\bar{D}_{AB}$ obtained by assuming constant D^* in $\text{cm}^2\text{sec}^{-1}$	$\frac{1}{2}(D_f + D_b)$ in $\text{cm}^2\text{sec}^{-1}$
Na/K	1.5135×10^{-13}	6.7×10^{-13}	7.9×10^{-13}
Na/Rb		2.01×10^{-12}	4.7047×10^{-12}
Na/Cs		4.63×10^{-14}	146.6×10^{-14}

the agreement between the last two columns must be considered reasonable; however, $\bar{D}_{AB}$ obtained graphically has a quite different value. The assumption that the initial forward or backward rate represents a simple average of D_{AB} values over the entire range of concentration

is rather uncertain. Possibly a weighted average would represent these quantities better. This seems likely particularly when the slower ion is initially in the zeolite; the exchange rate in this case proceeds radially inwards toward the centre of the particle not with a sharp boundary of highly exchanged zeolite but in a diffuse manner. The experimental rate observed initially is then definitely not a simple average of D_{AB} rates at various concentrations, since at any particular time these rates are being shown by unequal numbers of ions and so contributing to the experimental value to different extents.

Apart from this there is the difference between D_f and D_b which is very small in sorption work but which in an ion-exchange process is bound to be appreciable unless $D_A^* = D_B^*$. Ideally $\bar{D}_{AB}$ values should be determined from D_f and D_b values over a very small range of concentrations, but time does not permit such a study.

The evaluation of differential D_{AB} must also be examined here. Barrer, Rees and Bartholomew (4) have considered the expression

$$D_{AB} = \frac{D_1 D_2 (C_1 Z_1^2 + C_2 Z_2^2)}{D_1 C_1 Z_1^2 + D_2 C_2 Z_2^2}$$

and using an irreversible thermodynamic approach determined the significance of the Nernst-Planck diffusion coefficients D_1 and D_2 in terms of D_A^* and D_B^* obtaining the expression

$$D_{AB} = \frac{D_A^* D_B^* (C_1 Z_1^2 + C_2 Z_2^2) \frac{\delta \ln a_1}{\delta \ln C_1} \frac{\delta \ln a_2}{\delta \ln C_2}}{D_A^* C_1 Z_1^2 \frac{\delta \ln a_1}{\delta \ln C_1} + D_B^* C_2 Z_2^2 \frac{\delta \ln a_2}{\delta \ln C_2}}$$

They applied this to data on $\text{Ca}^{++}/\text{Sr}^{++}$ chabazite, but did not get any agreement. Barrer and Rees (37) have shown this equation to be incorrect. They have derived a general relation, and data on the Na/K system has been considered on the basis of the new equation, which is

$$D_{AB} = \frac{D_A^* D_B^* (C_2 Z_2^2 \frac{\delta \ln a_1}{\delta \ln C_1} + C_1 Z_1^2 \frac{\delta \ln a_2}{\delta \ln C_2})}{D_A^* C_1 Z_1^2 + D_B^* C_2 Z_2^2} \quad .$$

This equation has been used here. First the Na/K isotherm was analysed and it was found that the Kielland equation was applicable. This being so, values of logarithms of activity of coefficients of the ions Na^+ and K^+ could be plotted as functions of the $\log C_{\text{Na}^+}$

(Fig. 25). $\frac{\delta \ln f_1}{\delta \ln C_1}$ and $\frac{\delta \ln f_2}{\delta \ln C_2}$ were evaluated at various

concentrations. $\frac{\delta \ln a_1}{\delta \ln C_1}$ and $\frac{\delta \ln a_2}{\delta \ln C_2}$ were derived from these

and substituted in the equation, when D_K^* and D_{Na}^* were assumed to have the values obtained for the fully exchanged forms $\bar{D}_{AB}$ was equal to $11.45 \times 10^{-13} \text{ cm}^2 \text{ sec}^{-1}$. Integration using values of $D_{\text{Na}}^* \times D_K^*$ determined at various mole fractions of Na^+ gave a value $2.25 \times 10^{-13} \text{ cm}^2 \text{ sec}^{-1}$, an improvement on the $\bar{D}_{AB}$ value of $1.5 \times 10^{-13} \text{ cm}^2 \text{ sec}^{-1}$ obtained without correction for activity coefficients (see Fig. 23) but still rather low compared to the experimental value of $7.9 \times 10^{-13} \text{ cm}^2 \text{ sec}^{-1}$.

In all cases the concentration of incoming ion in the solution was twenty times the amount required for complete exchange, so if we apply Crank and Park's methods (19) for interpretation, the exchange diffusion coefficients obtained represent the entire kinetic process from

Ion exchange in Na^+K^+ mordenite

Sample	Mol. fraction of ions present	D_f		D_b	
		$\text{Na}^+\text{K}^+\text{M}$	K^+M	$\text{Na}^+\text{K}^+\text{M}$	Na^+M
1	.455 Na^+ .545 K^+	2.15×10^{-14}		1.57×10^{-14}	
2	.57 Na^+ .43 K^+	1.36×10^{-12}		5.8×10^{-16}	
3	.65 Na^+ .35 K^+	2.7×10^{-12}		1.83×10^{-14}	
	'pure' Na^+	$\text{Na}^+\text{M} \text{ --- } \text{K}^+\text{M}$ 1.38×10^{-12}			
	'pure' K^+			$\text{K}^+\text{M} \text{ --- } \text{Na}^+\text{M}$ 1.83×10^{-13}	

the initial concentration of a particular ion in the sample to complete exchange into the pure form and integration must be carried out over these limits. This can be done graphically from Fig. 23 (showing variation of D_{AB} with C_{Na}). However, it is obvious that this gives no agreement at all. Interpretation by this method is probably unreliable anyway, except over very small concentration ranges.

The values of D_b where K^+ is the outgoing ion are very much lower than those for D_f , and this is not surprising since D_K^* is less than D_{Na}^* at all these values of concentration. D_f increases as the concentration of Na^+ increases in the zeolite. Coupling effects between ionic fluxes must be coming into play, and though the exact effect of these on D_{AB} cannot be stated, it is possible to say qualitatively that in order to maintain electrical neutrality, the faster ion (in this case sodium) accelerates the slower one so that there is an equality of electrical fluxes. This suggests that the

difference in D_{Na}^* and D_K^* has some effect on the rate of exchange.

From Figs. 13 and 26 we obtain values:

$D_{Na}^* - D_K^*$	D_f	Mol. fraction of Na^+
2.3×10^{-13}	2.14×10^{-14}	.455
1.81×10^{-13}	1.36×10^{-12}	.57
$.86 \times 10^{-13}$	2.68×10^{-12}	.65

Thus, D_f increases as the difference in self-diffusion coefficients decreases.

D_b , however, shows a very low value at 57.18% and is obviously more dependent on D_K^* which is the outgoing ion. The variation of D_b and D_f shows once again that in mordenite D_{Na}^* and D_K^* are by no means constant. However, further data on bi-ionic samples is necessary for a detailed explanation to be possible.

ANALYSIS OF UNIVALENT FORMS

Exchange form	Na ⁺ % moles		K ⁺ % moles		Rb ⁺ % moles		Cs ⁺ % moles	
SiO ₂	68.4	10.52	66.3	10.52	60.39	10.52	66.79	10.52
Al ₂ O ₃	11.03	1	10.69	1	9.738	1	10.77	1
Na ₂ O	6.452	0.973	0.265	0.041	0.3065	0.052	0.142	0.022
K ₂ O	0.102	0.01	9.506	0.962				
Rb ₂ O					17.8	0.944		
Cs ₂ C							15.4	0.979
H ₂ O	14.04	7.2	13.218	6.75	11.72	6.82	6.82	3.62

ANALYSIS OF BIVALENT FORMS

Exchange form	Ca ⁺⁺		Sr ⁺⁺		Ba ⁺⁺	
	%	moles	%	moles	%	moles
SiO ₂	67.7	10.71	65.50	10.59	63.28	10.79
Al ₂ O ₃	10.73	1	10.49	1	9.95	1
Na ₂ O	1.78	.27	3.15	.495	1.57	.26
K ₂ O	.99	.01	.21	.022	.11	.015
CaO	4.28	.725				
SrO			5.25	.49		
BaO					10.92	.73
H ₂ O	15.35	8.10	15.38	8.3	14.15	8.0

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A P P E N D I X

DATA FOR FIGURES IN THESIS

Fig 6

Sodium

temp °C	$t^{\frac{1}{2}}$ min $^{\frac{1}{2}}$	Qt/Q_{∞}
10°C	5.24	0.186
	7.196	0.234
	8.563	0.285
	10.612	0.366
	11.810	0.418
24°C	3.082	0.224
	4.538	0.290
	6.580	0.377
	8.354	0.463
41.7°C	3.100	0.249
	4.891	0.369
	6.746	0.478
	11.010	0.536
	14.071	0.678
48.2°C	2.195	0.227
	3.300	0.295
	4.360	0.394
	7.315	0.597
	10.350	0.669
	12.561	0.720
55°C	2.100	0.286
	3.414	0.357
	5.476	0.536
	7.060	0.662
	10.321	0.754

$$\frac{Q_0}{Q_0 - Q_{\infty}} = 2 \quad A = 2.52 \times 10^3 \text{ cm}^2$$

Fig 6

Potassium

temp °C	$t^{\frac{1}{2}}$ min $^{\frac{1}{2}}$	Qt/Q_{∞}
20°C	1.449	0.274
	2.646	0.342
	3.674	0.435
	4.500	0.481
	5.109	0.536
41.5°C	1.414	0.232
	2.898	0.363
	4.848	0.611
	5.666	0.670
50.5°C	1.500	0.259
	3.507	0.485
	4.313	0.590
	5.020	0.686
67.5°C	1.342	0.299
	2.074	0.398
	2.720	0.521
	3.331	0.575
	3.605	0.643
59.5°C	1.516	0.275
	2.550	0.424
	3.210	0.513
	3.621	0.563
	4.093	0.634

$$\frac{Q_0}{Q_0 - Q_{\infty}} = 2 \quad A = 6.37 \times 10^3 \text{ cm}^2$$

Caesium

temp I°C	$t^{\frac{1}{2}}$ min $^{\frac{1}{2}}$	Qt/Q_{∞}
28.5°C	2.551	0.126
	3.550	0.192
	5.244	0.254
	6.710	0.352
	7.900	0.410
38.7°C	2.300	0.153
	3.461	0.206
	4.644	0.300
	5.610	0.325
	6.783	0.399
56.5°C	2.811	0.225
	3.706	0.298
	5.054	0.389
	6.100	0.440
68°C	2.780	0.261
	3.741	0.322
	4.647	0.399
	5.410	0.436
46.5°C	2.073	0.172
	2.757	0.226
	4.154	0.312
	5.690	0.407
97.2°C	2.061	0.263
	3.000	0.357
	3.800	0.457

$$\frac{Q_0}{Q_0 - Q_{\infty}} = 2 \quad A = 4.981 \times 10^3 \text{ cm}^2$$

Rubidium

temp I°C	$t^{\frac{1}{2}}$ min $^{\frac{1}{2}}$	Qt/Q_{∞}
13.5°C	1.673	0.273
	3.500	0.349
	4.195	0.375
	5.477	0.399
	6.251	0.437
22°C	2.551	0.246
	3.980	0.348
	4.281	0.362
	5.400	0.439
28°C	1.370	0.187
	1.931	0.222
	2.323	0.239
	2.781	0.291
	4.000	0.395
38.5°C	1.387	0.251
	1.752	0.317
	2.646	0.418
	3.209	0.478
	3.768	0.522
41.5°C	1.292	0.281
	1.891	0.395
	2.293	0.465
	3.010	0.585

$$\frac{Q_0}{Q_0 - Q_{\infty}} = 2 \quad A = 4.98 \times 10^3 \text{ cm}^2$$

Fig. 7

Calcium

temp T°C	$t^{\frac{1}{2}}$ min $^{\frac{1}{2}}$	Qt/Q_{∞}
27°C	21.0	0.055
	52.2	0.095
	70.0	0.109
	80.0	0.121
	96.0	0.138
53.5	10.7	0.076
	33.3	0.114
	38.7	0.121
	50.9	0.174
	70.2	0.195
71	7.70	0.114
	18.4	0.160
	21.0	0.156
	25.1	0.183
	60.0	0.278
81.5	30.0	0.215
	49.9	0.278
	62.9	0.373
	70.0	0.387
	80.0	0.422
93.0	20.0	0.195
	30.0	0.247
	33.3	0.277
	55.8	0.375
	60.0	0.416

$$\frac{Q_0}{Q_0 - Q_{\infty}} = 2 \quad A = 9.086 \times 10^3 \text{ cm}^2$$

Barium

temp T°C	$t^{\frac{1}{2}}$ min $^{\frac{1}{2}}$	Qt/Q_{∞}
18.5°C	4.528	0.0470
	6.928	0.0389
	10.100	0.0690
	12.572	0.0871
	14.210	0.1250
34.5°C	4.583	0.1249
	7.450	0.1465
	9.354	0.1567
	11.490	0.1740
54.5°C	3.391	0.1972
	4.950	0.1790
	7.553	0.2690
	9.247	0.3156
	14.000	0.3825
64.5	16.000	0.3941
	4.528	0.2195
	7.211	0.2811
	8.689	0.3761
	10.050	0.3435
77.5	12.251	0.3754
	16.000	0.4611
	4.582	0.2691
	8.215	0.3712
	11.700	0.4400
	15.522	0.5551
	19.550	0.6170

$$\frac{Q_0}{Q_0 - Q_{\infty}} = 2 \quad A = 10.102 \times 10^3 \text{ cm}^2$$

Strontium

temp °C	time ^{$\frac{1}{2}$} min ^{$\frac{1}{2}$}	Q_t/Q_∞
29.5°C	5.292	0.0341
	8.000	0.0618
	9.849	0.0617
	12.000	0.0733
	15.621	0.0849
56°C	4.000	0.0649
	5.612	0.0755
	6.823	0.0920
	8.062	0.1076
	12.020	0.1086
	14.111	0.1150
64.5°C	3.555	0.0825
	4.062	0.0976
	5.916	0.1295
	7.681	0.1611
	11.000	0.1902
75°C	3.010	0.0891
	3.968	0.1147
	5.119	0.1330
	6.595	0.1822
	8.337	0.1912

$$\frac{Q_0}{Q_0 - Q_x} = 2 \quad A = 10.604 \times 10^3 \text{ cm}^2$$

Figure 10

Sample	Mol Fraction in Zeolite	Cation	time $\frac{1}{2}$ min $\frac{1}{2}$	Q_t/Q_∞	$Q_\infty / (Q_\infty - Q_t)$
1	.1049 K^+ .8951 Na^+	Na^+	1.974	0.350	9.62
			2.345	0.459	
			2.783	0.526	
			3.000	0.575	

Figure 10

Sample	.1845 K^+	Na^+	2.000	0.395	5.45
2	.8155 Na^+		3.279	0.556	
			3.520	0.500	
			4.031	0.611	
			5.925	0.765	
			9.290	0.860	

Figure 10

Sample	.361 K ⁺	Na ⁺	2.491	0.371	2.77
3	.639 Na ⁺		2.810	0.390	
			3.000	0.405	
			3.390	0.417	
			4.311	0.526	
			5.292	0.580	

Figure 10

Sample	Mol Fraction in Zeolite	Cation	time $\frac{1}{2}$ min $\frac{1}{2}$	Q_t/Q_∞	$Q_0/Q_\infty - Q_t$
3	.361 K^+ .639 Na^+	K^+	2.491	0.555	22.2
			2.810	0.601	
			3.000	0.631	
			3.390	0.696	
			4.311	0.802	
			5.292	0.818	

Figure 10

Samples	.4309 K ⁺	Na ⁺	2.000	0.310	2.33
4	.5091 Na ⁺		2.610	0.351	
			3.082	0.371	
			3.351	0.396	
			4.556	0.495	
			5.745	0.534	
			7.085	0.623	

Figure 10

Sample	.4309 K^+	K^+	2.000	.481	18.2
4	.5091 Na^+		2.610	.569	
			3.082	.633	
			3.351	.675	
			4.556	.743	
			5.745	.784	
			7.085	.837	

Figure

Sample	Mol Fraction of Cation in Zeolite	Cation	$\min \frac{1}{2}$	Q_t/Q_∞	$Q_t/Q_\infty - Q_\infty$
5	.5455 Na^+	Na^+	2.062	0.2466	2.19
	.4545 K^+		2.391	0.2921	
			2.665	0.3400	
			3.051	0.3591	
			4.983	0.565	

Figure

Sample

5	.5455 Na^+	K^+	2.062	0.474	11.1
	.4545 K^+		2.391	0.541	
			2.665	0.626	
			3.051	0.679	
			3.674	0.701	
			4.983	0.752	

Figure

Sample

6	.5172 K^+	Na^+	2.000	0.396	2.04
	.4828 Na^+		2.250	0.431	
			2.470	0.473	
			2.771	0.523	
			3.241	0.609	
			3.674	0.665	
			4.123	0.672	

Figure 11

Sample	Mol Fractions in Zeolite	Cation	min $\frac{1}{2}$	Qt/Q _∞	Q ₀ /Q _∞ - Q _∞
6	K = .5172	K ⁺	2.000	0.422	7.14
	Na ⁺ = .4828		2.250	0.463	
			2.470	0.528	
			2.771	0.587	
			3.241	0.626	
			3.674	0.644	
			4.123	0.701	

Figure 11

Sample					
7	.5375 K ⁺	Na ⁺	2.000	0.247	1.86
	.46 25 Na ⁺		2.549	0.308	
			3.082	0.376	
			3.601	0.435	
			3.807	0.445	

Figure 12

Sample					
8	.5581 K ⁺	Na ⁺	2.021	0.2596	1.79
	.4419 Na ⁺		2.410	0.305	
			2.700	0.3418	
			3.501	0.437	
			3.745	0.448	

Figure 12

Sample	Mol Fractions in Zeolite	Cation	min $\frac{1}{2}$	Q_t/Q_∞	$Q_s/Q_s \cdot Q_x$
9	.687 K^+	Na^+	2.000	0.211	1.46
	.313 Na^+		2.530	0.241	
			3.241	0.305	
			3.905	0.374	
			4.416	0.388	

Figure 12

Sample		Cation	min $\frac{1}{2}$	Q_t/Q_∞	$Q_s/Q_s \cdot Q_x$
9		K^+	2.000	0.422	2.74
			2.530	0.466	
			3.241	0.514	
			3.905	0.597	
			4.416	0.612	

Ion Exchange

Figure 18

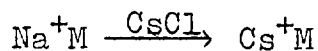
Na ⁺ Mordenite ——— K ⁺ Mordenite		K ⁺ Mordenite ——— Na ⁺ Mordenite		
$t^{\frac{1}{2}}$ min $^{\frac{1}{2}}$	$\frac{Qt}{Q_{\infty}}$	$t^{\frac{1}{2}}$ min $^{\frac{1}{2}}$	$\frac{Qt}{Q_{\infty}}$	$\frac{Qt}{Q}$ (Corrected to $A\rho = .7987 \times 10^4$)
1.93	.326	2.000	0.207	0.1224
2.34	.336	2.449	0.275	0.1626
2.74	.376	3.082	0.288	0.1703
3.16	.421	3.937	0.307	0.1818
3.50	.435	4.251	0.345	0.2039
$A = .03896 \times 10^4 \text{ cm}^2$		$A = .6371 \times 10^4 \text{ cm}^2$		
$\rho = 2.05 \text{ gm. cm}^{-3}$		$\rho = 2.12 \text{ gm. cm}^{-3}$		
intercept = 0.16		intercept using corrected value = .065		

Figure 19

Na ⁺ Mordenite ——— Rb ⁺ Mordenite		Rb ⁺ Mordenite ——— Na ⁺ Mordenite		
$t^{\frac{1}{2}}$ min $^{\frac{1}{2}}$	$\frac{Qt}{Q_{\infty}}$	$t^{\frac{1}{2}}$ min $^{\frac{1}{2}}$	$\frac{Qt}{Q_{\infty}}$	$\frac{Qt}{Q_{\infty}}$ (Corrected to $A\rho = .7987 \times 10^4$)
1.820	0.342	1.820	0.225	0.1555
2.062	0.400	2.601	0.338	0.2336
2.449	0.481	3.240	0.398	0.2751
2.646	0.501	3.713	0.485	0.3352
3.000	0.555	4.663	0.561	0.3879
$A = 0.3896 \times 10^4 \text{ cm}^2$		$A = .4981 \times 10^4 \text{ cm}^2$		
$\rho = 2.05 \text{ gm cm}^{-3}$		$\rho = 2.19 \text{ g cm}^{-3}$		

Figure 20.

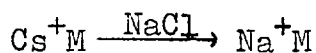
Ion-exchange rates.



Time ^{$\frac{1}{2}$} (mins) ^{$\frac{1}{2}$}	$\frac{Q_t}{Q_\infty}$
2.00	0.304
2.59	0.363
3.15	0.426
3.78	0.491

$$A = 0.3896 \times 10^4 \text{ cm}^2$$

$$\rho = 2.05 \text{ g cm}^{-3}$$



Time ^{$\frac{1}{2}$} (mins) ^{$\frac{1}{2}$}	$\frac{Q_t}{Q_\infty}$	$\frac{Q_t}{Q_\infty}$ (corrected for $A\rho=0.7987 \times 10^4$ cm^2)
1.58	0.096	.045
2.43	0.136	.067
2.98	0.185	.092
3.87	0.281	.142
4.21	0.262	.131
4.58	0.264	.135

$$A = 0.4981 \times 10^4$$

$$\rho = 2.17 \text{ g cm}^{-3}$$

Figures 26 and 27

Ion exchange in bi-ionic samples

Sample	Mol fraction of ions present	$\text{Na}^+ \text{K}^+ \text{M} \xrightarrow{\text{KCl}} \text{K}^+ \text{M}$		$\text{Na}^+ \text{K}^+ \text{M} \xrightarrow{\text{NaCl}} \text{Na}^+ \text{M}$	
		$(\text{mins})^{\frac{1}{2}}$	$\frac{Q_t}{Q_\infty}$	$(\text{mins})^{\frac{1}{2}}$	$\frac{Q_t}{Q_\infty}$
1	$\text{Na}^+ = .455$	2.01	0.381	2.0	0.017
	$\text{K}^+ = .545$	2.56	0.426	2.45	0.025
		3.02	0.493	3.04	0.032
	$A = 4.387 \times 10^3 \text{ cm}^2$	3.74	0.572	3.48	0.034
	$\rho = 2.09 \text{ g cm}^{-3}$	4.12	0.612	4.00	0.04
2	$\text{Na}^+ = 0.572$	2.03	0.326	2.00	0.011
	$\text{K}^+ = 0.428$	2.5	0.387	2.43	0.015
		3.04	0.443	3.08	0.018
		3.48	0.480	3.54	0.025
	$A = 4.911 \times 10^3 \text{ cm}^2$	4.00	0.509	4.00	0.025
	$\rho = 2.09 \text{ g cm}^{-3}$			4.40	0.030
3	$\text{Na}^+ = .651$	2.00	0.316	2.0	0.023
	$\text{K}^+ = .349$	2.45	0.393	2.47	0.031
		3.00	0.483	3.00	0.038
	$A = 5.223 \times 10^3 \text{ cm}^2$	3.48	0.533	3.57	0.042
	$\rho = 2.09 \text{ g cm}^{-3}$	3.97	0.568	4.00	0.051

Figure 14.

Activation energy of bi-ionic samples

Temp.	(mins) ^{$\frac{1}{2}$}	$\frac{Q_t}{Q_\infty}$
60°C	3.15	.371
	4.61	.490
	5.8	.531
	7.1	.630
49.5	3.6	.372
	5.15	.475
	7.0	.561
	8.32	.653
39.5	5.15	.414
	6.3	.495
	7.27	.535
	8.35	.566
	10.65	.699
29.5	4.0	.325
	6.51	.42
	7.73	.444
	8.69	.521
	10.45	.550