386. *Ion-exchange in Crystals of Analcite and Leucite.*

By R. M. BARRER and L. HINDS.

The exchange reactions of analcite and leucite have been investigated quantitatively at low temperatures for the ion pairs Na–K, Na–Tl, Na–Rb, K–Tl, Tl–Rb, and Na–Ag. In most of these systems it was found that when several partly exchanged analcites or leucites were treated with identical exchanging solutions the end-points depended upon the initial compositions and previous histories of the analcites. The exchange isotherms for Na–K, Na–Tl, and K–Tl showed evidence of limited mutual solid solubility of the end-members in the exchange, and this was further established by optical, analytical, and *X*-ray methods. Exchange isotherms for Na–K show hysteresis. The dependence of both hysteresis and end-points on the initial composition of exchanger finds a natural explanation in terms of nucleation phenomena associated with mutual limited solubility of the end members.

The rates of exchange follow the $\sqrt{t}$ diffusion law. The kinetics for Tl–Na have been analysed in terms of two $\sqrt{t}$ diffusion equations, and values of the ion-exchange diffusion coefficient obtained. The Arrhenius energy of activation is 14,900 cal./g.-ion. The $\sqrt{t}$ law has been correlated with the nucleation and limited solid solubility phenomena.

Lithium analcite and analcites containing bivalent cations have previously proved very difficult to prepare. However, a lithium-rich and a lead-rich analcite have now been obtained. The lead appears to enter the crystals as a univalent complex $PbOH^+$.

MOST contemporary effort in the study of ion-exchange is concerned with gels and resins. Gels, whether inorganic or organic, are in some ways less satisfactory for the quantitative study of ion-exchange than crystals, which provide a definite exchanger framework, and may be chosen according to a number of crystal chemical properties. Crystalline exchangers include such layer-lattice minerals as clays and micaceous products (montmorillonite, illite, vermiculite) and also aluminosilicates with robust three-dimensional anionic networks (analcite, leucite, cancrinite, nosean, sodalite, chabazite, mordenite, and harmotome). From the latter group of crystals one may seek an exchanger with a charged, sieve-like three-dimensional anion, Z, wholly inert and rigid, into which cations may be inserted on identical sites, thereby displacing their electrochemical equivalent of other cations. The end-members for a pair of cations A and B would be AZ and BZ, and could then form a continuous range of ideal solid solutions.

A statistical thermodynamic approach to this model has been outlined (Barrer, " Colloque Internat. sur les Réactions dans l'État Solide," Paris, 1948, CNRS). For a reaction between the exchanger and two immiscible solid salts, AX and BX, each in equilibrium with its saturated solution :

$$AX_{\text{solid}} \rightleftharpoons AX_{\text{sat. aq.}}; \quad BX_{\text{solid}} \rightleftharpoons BX_{\text{sat. aq.}}$$

$$AX_{\text{sat. aq.}} + BZ \text{ (in solid solution with AZ)} \rightleftharpoons BX_{\text{sat. aq.}} + AZ \text{ (in solid solution with BZ)}$$

and for an anhydrous exchange medium (sodalite, ultramarine, nosean) the mol.-fractions N_A and N_B in the exchanger at equilibrium will be given by :

$$\frac{N_A}{N_B} = \frac{(j_{BX})^2 j_A}{(j_{AX})^2 j_B} \exp\left[-(E_{AX} - E_{BX} + \Delta E_{B,A})/RT\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Where the exchange medium is hydrated, but the number of water molecules is not altered by exchange (chabazite, mordenite)

$$\frac{N_A}{N_B} = \frac{(j_{BX})^2 j_A j_{H_2O,A}}{(j_{AX})^2 j_B j_{H_2O,B}} \exp\left[-(E_{AX} - E_{BX} + \Delta E_{B,A} + \Delta E_{H_2O})/RT\right] \quad . \quad . \quad . \quad . \quad (2)$$

Finally, where the water of hydration of the exchange medium is displaced into the solution (analcite)

$$\frac{N_A}{N_B} = \frac{(j_{BX})^2 j_A j_{H_2O,A}}{(j_{AX})^2 j_B j_{H_2O}} \exp\left[-(E_{AX} - E_{BX} + \Delta E_{B,A} + \Delta E'_{H_2O})/RT\right] \quad . \quad . \quad . \quad . \quad (3)$$

In these expressions j_{BX}, j_{AX} are the partition functions of the salts BX and AX; j_B, j_A are the partition functions for the cations B and A in their environment within the zeolite; $j_{H_2O,B}$ and $j_{H_2O,A}$ are these functions for intracrystalline water in association with A and B cations; and j_{H_2O} is the partition function of a water molecule in the saturated solution, respectively. E_{AX} and E_{BX} are the lattice energies of AX and BX; $\Delta E_{B,A}$ is the energy of replacement of A by B cations in the zeolite; ΔE_{H_2O} is the change in binding energy when A is replaced by B in the crystal; and $\Delta E'_{H_2O}$ is the energy of displacement of water from the crystal into the solution. It may be a reasonable approximation to replace any partition function $j(T)$ by $(\boldsymbol{k}T/\boldsymbol{h}\nu)$ where ν denotes the Debye frequency.

Equations (1)—(3) show several factors which determine the equilibrium points. Since lattice energies are known for many salts, in such a crystalline exchanger the energies of replacement of one cation by another might be found. Binding energies of water molecules can be determined from the change with temperature of the equilibrium water vapour pressure over crystals of the exchanger. It is, however, quite unknown whether even the robust framework aluminosilicates approach the conditions required for the validity of equations (1)—(3).

In any study of solid-state reactions, equilibrium and kinetic measurements will both be of significance. For ion-exchange the appropriate rate constant is the intracrystalline ion-exchange diffusion coefficient. No such diffusion coefficients have yet been determined for exchanges involving crystalline aluminosilicates, although any rational theory of ion-exchange must await the collection and analysis of such data. A study of ion-exchange in crystals has therefore been initiated in these laboratories with sodalite–nosean minerals and zeolites to study quantitatively exchange equilibria and kinetics as a simple type of solid-state reaction. The present work concerns exchange reactions of analcite and leucite. Considerable attention has recently been paid to some aspects of ion-exchange in analcite, mordenite, and chabazite (Barrer, *J.*, 1948, 2158; 1950, 2342) and in other species (Barrer and White, *J.*, 1951, 1167). Analytical and *X*-ray data have been obtained, and some quantitative conclusions reached. However, in these studies equilibrium and kinetic measurements were not the immediate objectives.

EXPERIMENTAL

Most exchanges were carried out in sealed glass tubes, which had first been boiled for 2—3 hr. in distilled water. The tubes with their charge of solid reactants and some water were clipped on to a slowly rotating plate in an air-thermostat. For experiments at high temperatures, stainless-steel autoclaves were used (Barrer, *J.*, 1948, 127). These had an internal capacity of ~20 ml., and were sometimes employed with thin silver tubes as inserts, to prevent contact of reactants with the steel walls. In other measurements the reactants were sealed in the glass tube, and the latter was placed inside the steel autoclave. A little water was then added to the autoclave, before sealing it, to act as pressure equaliser. It was then possible to carry out reactions in glass up to 150°, but above this temperature attack of the glass occurred. In other experiments exchange reactions were carried out with fused salts, such as potassium thiocyanate and thallous nitrate. Reactions were examined in the range 200—300° in the air thermostat.

The degree of exchange was measured in three ways: (*a*) by an ignition method, (*b*) by a weighing method, and (*c*) by chemical analysis. In a previous study (Barrer and G. Styan, unpublished) it was found in the reaction

$$\text{Na-analcite} + K^+, \text{aq.} = \text{K-analcite (leucite)} + Na^+, \text{aq.} + H_2O$$

that the extent of the exchange of sodium by potassium could be measured by the amount of water lost from the original analcite during exchange (Fig. 1*b*). The water content of the synthetic analcites was 8·46%, and that in leucite made from analcite by repeated treatments with potassium chloride was 0·75%. These two points were joined by a straight line (Fig. 1*b*) and this line gave the relation between loss in weight on ignition and the sodium and potassium contents. The circles give Barrer and Styan's analytical results.

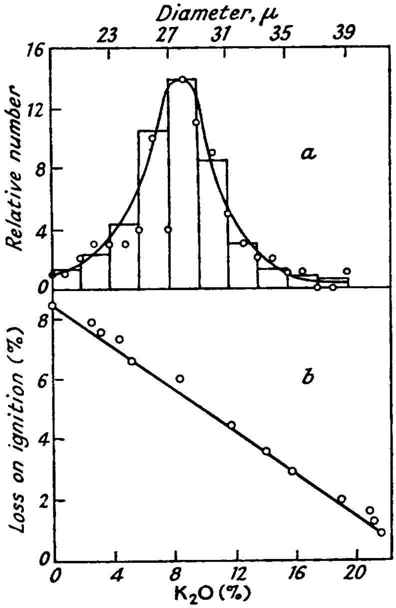

FIG. 1*a*. *A typical size-distribution curve of crystals of synthetic analcite.*

FIG. 1*b*. *Relation between water content and potassium oxide content of crystals intermediate in composition between analcite and leucite.*

Other ion-exchanged analcites besides leucite are anhydrous (*e.g.*, the Tl, Rb, Cs, and NH_4 forms as shown by Barrer, *J.*, 1950, 2342). The differences in weights of such cation pairs as Na–Tl, K–Tl, or Na–Rb are sufficient to allow the extent of exchange to be measured by weighing the exchanger before and after reaction (with due allowance for changing water content). In the third method of following the exchange (*c*, above) the procedures employed were standard ones, the silica and alumina being determined after decomposition of the mineral with fusion mixture, and the sodium and other alkali metals by the Lawrence Smith method (*e.g.*, Vogel, "Quantitative Analysis," Longmans Green and Co., 1939, p. 664). Thallium was estimated by an adaptation of the Andrews potassium iodate titration (*idem*, *ibid.*, p. 438): $KIO_3 + 2TlCl + 6HCl = KCl + 2TlCl_3 + ICl + 3H_2O$. Lead in lead analcite was estimated after removal of silica by treatment with hydrofluoric acid solution. The residue was extracted with acetic acid, and the extract diluted and filtered. After dilution to 200 ml. the solution was heated to boiling, and the lead determined as chromate.

Ion-exchange and recrystallisation products were examined optically, a Leitz polarising microscope and a Vickers projection microscope being used. Reactions were also followed by *X*-ray powder photography, a Hilger HRX unit with Cu-*K*α radiation being used. This method served not only to compare the exchange products but also to detect and characterise metamorphic minerals * which sometimes crystallised in place of the expected simple ion-exchanged analcites. Unit-cell determinations were effected with the aid of Bjurstrom charts.

In order to measure ion-exchange diffusion coefficients it was necessary to determine the external surface area of the crystallites. For this purpose, Kozeny's method was employed, degassed distilled water being used as flowing liquid (*e.g.*, Carman, *Discuss. Faraday Soc.*, 1948, **3**, 72). The area S of the bed of crystallites is then given by $S = \sqrt{\varepsilon^3 \Delta p / k \eta v L}$, for a liquid of viscosity η flowing under a pressure head Δp at velocity v through the bed of depth L; ε is the void volume in c.c. per c.c. of the bed, and $k = 5$ is Kozeny's constant.

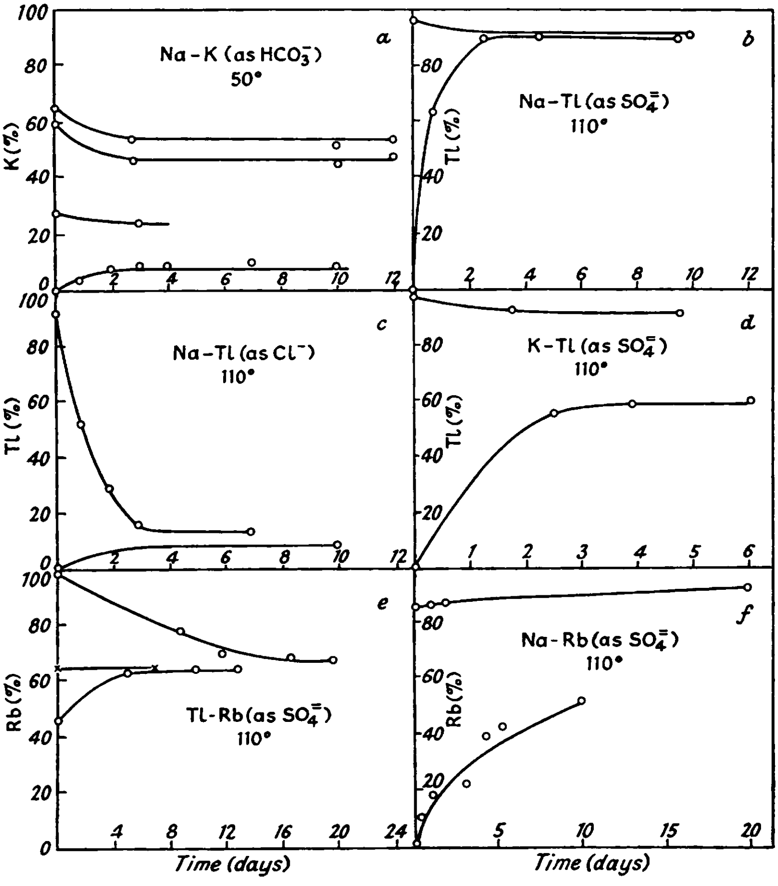

FIG. 2. *Variation of end-point with initial composition of crystals for exchanges involving solutions mutually saturated with each of a pair of salts.*

The analcite used in this work was synthesised hydrothermally from gels of composition $Na_2O,Al_2O_3,4SiO_2,xH_2O$ made by mixing sodium aluminate suspensions with silicic acid gel suspensions. Experimental conditions were varied in order to try to control the crystal sizes by (*a*) different rates of heating, (*b*) addition of sodium carbonate solution to raise the pH, (*c*) dilution, (*d*) seeding with analcite crystals, (*e*) alteration of reaction temperature between 200° and 300°, and (*f*) variation of the time of reaction. Although the extent of crystallisation could be affected especially by conditions (*b*), (*e*), and (*f*), no certain method of controlling the size of the crystals emerged. The size distribution among the crystallites in a typical preparation is shown in Fig. 1*a*. Occasionally, relatively uniform crystal sizes appeared. Since,

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* These and other recrystallisation reactions will be described later (Barrer, Hinds, and White, *J.*, in preparation).

however, no certain uniformity could be achieved the following results were obtained with sieved crystals, which were nevertheless heterogeneous in diameter.

Preparation of Lithium and Lead Analcite.—Barrer (*J.*, 1950, 2342) found that although analcite gives K, Rb, Tl, NH_4, and Ag forms by direct exchange with the sodium form, yet it was not possible to introduce significant amounts of Li, or of bivalent cations such as Ca or Ba. We have now been able to prepare analcites enriched in both lithium and lead by the following methods.

The silver form of analcite was obtained by heating analcite in fused silver nitrate. This was then treated at 110° with a concentrated brine of lithium chloride. Any silver displaced formed an anionic complex such as $Li[AgCl_2]$, and the concentration of free silver ion fell so low that reaction proceeded in the direction

$$Ag_2O,Al_2O_3,4SiO_2,2H_2O + 4LiCl, aq. = Li_2O,Al_2O_3,4SiO_2,2H_2O + 2Li[AgCl_2]$$

until extensive exchange was effected. Lithium analcite proved to be hydrated and possessed a cubit unit cell of $13{\cdot}5_0$ Å edge (to compare with $13{\cdot}6_7$ Å for the more expanded sodium form). The lithium analcite like sodium analcite was a sorbent towards small polar molecules such as ammonia.

Lead analcite was obtained by heating sodium analcite at 110° with saturated lead chloride, three treatments being given. The product gave an *X*-ray powder photograph with spacings characteristic of sodium analcite, indicating a cubic unit cell similar to that of sodium analcite. A certain amount of recrystallisation was also detected by optical examination.

The mineral freed of all lead chloride showed an increase in weight which, according to the reaction

$$xPbCl_2 + Na_2O,Al_2O_3,4SiO_2,2H_2O = [xPb,2(1-x)Na]O,Al_2O_3,4SiO_2,2(1-x)H_2O + 2xNaCl + 2xH_2O \quad . \quad (a)$$

would correspond to 94% exchange and to 34·4% of lead in the final product. However, two chemical analyses agreed in giving only 22·8% by weight of lead, so one must postulate a different mechanism of exchange :

$$2xPbCl_2 + Na_2O,Al_2O_3,4SiO_2,2H_2O = [xPbOH,(1-x)Na]_2O,Al_2O_3,4SiO_2,2(1-x)H_2O + 2xHCl + 2xNaCl \quad . \quad (b)$$

For this mechanism the increase in weight requires 32% exchange. This corresponds to 22·6% by weight of lead in the final product as compared with 22·8% actually found. It therefore seems probable that lead enters the crystals as a univalent complex $(PbOH)^+$. Such a unit * might be expected to fill interstices in the aluminosilicate framework more than K^+ and about the same as (Na^+,H_2O) or (Ag^+,H_2O). This, taken in conjunction with only 32% exchange, may account for the observation that a sodium analcite series of lattice spacings, and not the potassium analcite (leucite) series to be expected for mechanism (*a*), was actually observed (silver and sodium analcites give very similar *X*-ray spacings; Barrer, *J.*, 1950, 2342).

Reversibility of Exchange Reactions.—If analcites are treated with a solution which is kept saturated with respect to both a sodium and a potassium salt, one might expect to find the same end-point whatever the value of x between 0 and 1 in the starting material of composition $[xK,(1-x)Na]_2O,Al_2O_3,4SiO_2,2(1-x)H_2O$. Several experiments were carried to test this not only for Na–K exchange but for a variety of other ion-pairs. The results of some of these in Fig. 2, *a*—*f*, show that the end-point may often vary with the value of x in the initial exchange medium. The figure also shows the rate of approach to the end-point of the reaction.

A summary of initial and final compositions of the exchanger is given in Table 1. Different Tl–Rb mixed analcites gave a single end-point from a solution kept saturated with respect to both thallium and rubidium sulphates; and the same was true of two Na–Tl mixed analcites at 110° when saturated sulphate solutions of these two cations were used. However, at 75° the end-point was not the same for the two mixed analcites, nor was it the same when the saturated chloride solution was used to effect further exchange (Table 1). Indeed, it was usual to find end-points which varied with the initial composition, often by a wide margin (Na–K; Na–Rb; K–Tl; Na–Ag). In the Na–Ag exchanges a side reaction consisting in deposition of silver makes the result uncertain, but no such uncertainty arises in the other systems. This notable variability of end-point is discussed later (p. 1888) and is seen to be a simple consequence of

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* Radii of Pb^{++} and K^+ are 1·32 and 1·33 Å, respectively. The radius of Na^+ is 0·98 and of Ag^+ is 1·13 Å. Sodium and silver analcites are hydrated, but the potassium form is anhydrous (Barrer, *J.*, 1950, 2342).

nucleation phenomena arising in turn from limited solid solubility of end-members (*e.g.*, of $Na_2O,Al_2O_3,4SiO_2,2H_2O$ and $K_2O,Al_2O_3,4SiO_2$).

Exchange Isotherms.—Exchange isotherms were obtained on using solutions of constant total ionic strength and containing two electrolytes in various proportions. These are shown in Figs. 3, 4, and 5 for the Na–Tl, K–Tl, and Na–K pairs. For the first two exchanges the total molarity was 0·3 and the solution in each case was a mixture of the appropriate pair of salts. The end-points greatly favour the thallium-rich phase (Figs. 3 and 4). Both systems show substantial immiscibility between the extreme ion-exchanged forms, of a kind which will now be considered in more detail for the Na–K exchanges. The latter were carried out by using a mixture of sodium and potassium chlorides in solutions of total molarity 3·5, and here the end-points favour the sodium-rich phase (Fig. 5). The isotherm has one and possibly two regions where large changes occur in the potassium content of the crystals for negligible or small changes in potassium content of the solution. According to the phase rule, an invariant region requires the co-existence of two solid phases and solution in equilibrium. The situation is, however, here complicated because one of these phases may develop on or in, and consume, crystallites of the other (see p. 1887). One of these phases is necessarily richer in sodium, the other in potassium. The isotherm for exchange going from sodium analcite to potassium analcite (leucite) does not coincide with that for the converse change from leucite to analcite, and a considerable hysteresis is observed. The behaviour is compatible with limited solid solubility of one ion-exchanged form of the crystal in the other. Limited solid solubility had previously been established for analcites at higher temperatures under hydrothermal conditions (Barrer and McCallum, *J.*, in preparation). It now seems that limited solid solubility extends to very low temperatures.

TABLE 1. *End-points obtained when beginning with different compositions of exchanger.*

Initial cationic composition of analcite	Salts in satd. soltn.	Temp.	Final cationic composition of analcite
Na : K = 100 : 0	$NaHCO_3$ and $KHCO_3$	50°	Na : K = 92·1 : 7·9
Na : K = 72·2 : 27·8	$NaHCO_3$ and $KHCO_3$	50	Na : K = 75·9 : 24·1
Na : K = 41·1 : 58·9	$NaHCO_3$ and $KHCO_3$	50	Na : K = 52·8 : 47·2
Na : K = 36·1 : 63·9	$NaHCO_3$ and $KHCO_3$	50	Na : K = 46·3 : 53·7
Na : K = 100 : 0	$NaHCO_3$ and $KHCO_3$	110	Na : K = 33·8 : 66·2
Na : K = 17·1 : 82·9	$NaHCO_3$ and $KHCO_3$	110	Na : K = 41·2 : 58·8
Na : K = 4·1 : 95·9	$NaHCO_3$ and $KHCO_3$	110	Na : K = 5·5 : 94·5
Na : K = 1·4 : 98·6	$NaHCO_3$ and $KHCO_3$	110	Na : K = 4·2 : 95·8
Na : Tl = 100 : 0	Na_2SO_4 and Tl_2SO_4	110	Na : Tl = 9·0 : 91·0
Na : Tl = 4·2 : 95·8	Na_2SO_4 and Tl_2SO_4	110	Na : Tl = 8·7 : 91·3
Na : Tl = 100 : 0	Na_2SO_4 and Tl_2SO_4	75	Na : Tl = 13·4 : 86·6
Na : Tl = 9·6 : 90·4	Na_2SO_4 and Tl_2SO_4	75	Na : Tl = 9·8 : 90·2
Na : Tl = 100 : 0	NaCl and TlCl	110	Na : Tl = 91·9 : 8·1
Na : Tl = 8·7 : 91·3	NaCl and TlCl	110	Na : Tl = 86·8 : 13·2
Na : Rb = 100 : 0	Na_2SO_4 and Rb_2SO_4	110	Na : Rb = 48·1 : 51·9
Na : Rb = 15·3 : 84·7	Na_2SO_4 and Rb_2SO_4	110	Na : Rb = 6·5 : 93·5
K : Na : Tl = 98·6 : 1·4 : 0	K_2SO_4 and Tl_2SO_4	110	K : Tl = 39·6 : 60·4
K : Na : Tl = 0 : 3·1 : 96·9	K_2SO_4 and Tl_2SO_4	110	K : Tl = 7·6 : 92·4
Tl : Rb : Na = 96·9 : 0 : 3·1	Tl_2SO_4 and Rb_2SO_4	110	Tl : Rb = 64·5 : 35·5
Tl : Rb = 64·1 : 35·9	Tl_2SO_4 and Rb_2SO_4	110	Tl : Rb = 64·6 : 35·4
Tl : Rb = 46·2 : 53·8	Tl_2SO_4 and Rb_2SO_4	110	Tl : Rb = 63·8 : 36·2
Na : Ag = 100 : 0	Na_2SO_4 and Ag_2SO_4	75	Na : Ag = 45·8 : 54·2
Na : Ag = 8·4 : 91·6	Na_2SO_4 and Ag_2SO_4	75	Na : Ag = 62·4 : 37·6

Direct evidence of two coexistent solid phases among partly ion-exchanged analcites was obtained in three different ways. First, this was made quite clear by optical examination. At the end-points of the reaction, crystals of two distinct refractive indices were observed side by side for the exchanges Na–K, Na–Tl, and K–Tl when the final composition of the solid lay within certain limits. A composition Na : K = 57·4 : 42·6 of the solid in the first immiscibility region for the Na–K exchange was next studied. It proved possible partly to separate crystals of the two kinds from this composition by sedimentation. One fraction gave on analysis Na : K = 64 : 36, and the other Na : K = 41 : 59. Finally, *X*-ray evidence of the two phases was obtained for Na–K and Na–Tl exchanges. If *continuous* solid solubility were encountered, *X*-ray powder photographs would show a continuous change from the pattern characteristic of

FIG. **6(*a*).** ***Stages in the conversion of* Na*-analcite into* Tl*-analcite.*** *The intermediate* X*-ray powder photograph* (39% Tl) *shows simultaneous occurrence of* Na- *and* Tl*-analcite lines, and indicates two solid phases. The diffuseness of some of the lines for the intermediate composition* (39% Tl) *suggests small crystallites and nuclei, or some disorder.*

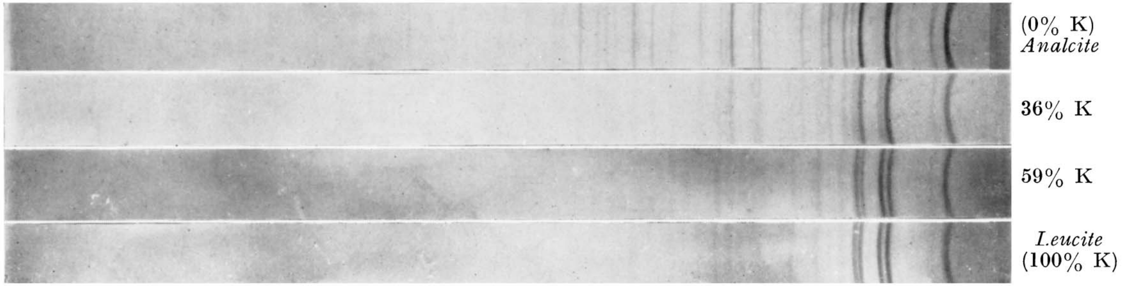

FIG. **6(*b*).** ***Stages in the conversion of* Na*-analcite into* K*-analcite* (*leucite*).** *The* X*-ray powder photographs for intermediate compositions* (36% *and* 59% *exchange*) *show analcite and leucite lines side by side, and so indicate two co-existing solid phases, one rich in* Na *and the other in* K.

one extreme form to that characteristic of the other. On the other hand, if two crystalline phases co-exist, the X-ray patterns of each phase will be present together, and a change in composition of the solid will result merely in weakening of the pattern of one form and the strengthening of that of the second form. X-Ray powder photographs show in fact this latter type of behaviour (Fig. 6).

FIG. 3.

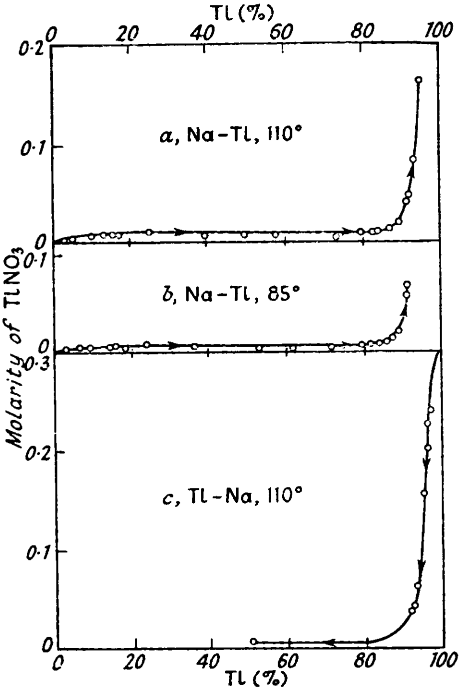

FIG. 4.

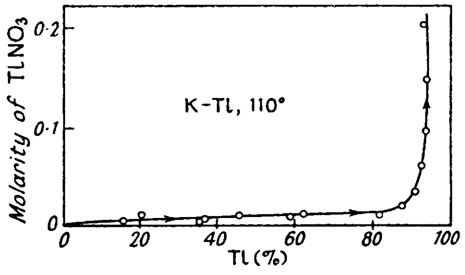

FIG. 5.

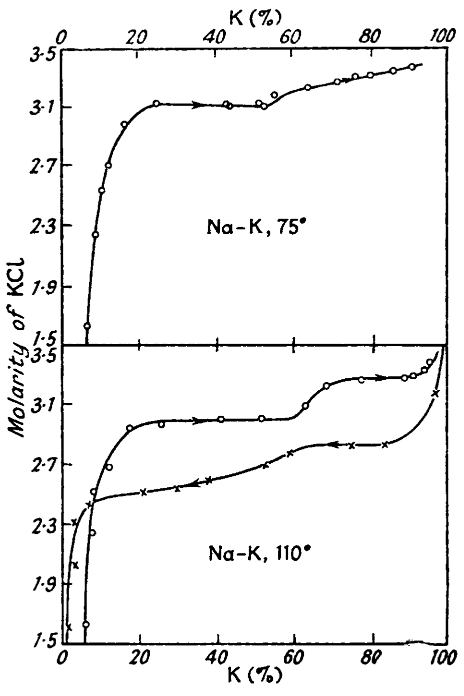

FIG. 3. *Typical exchange isotherms for* Na–Tl-*analcites. The total molarity of* $NaNO_3$ + $RbNO_3$ *is* 0·3M. *The isotherms give the molarity of* $TlNO_3$ *at the end-points as a function of* % *exchange of* Na *by* Tl *at* 110° *for the exchange approached from forward and reverse directions* (*Figs.* 3*a and c*); *and at* 85° *for the forward reaction* (*Fig.* 3*b*).

FIG. 4. *Exchange isotherm of* K- *and* Tl-*analcites in a solution of total molarity* 0·3M. *End-points are approached by the forward reaction* (*displacement of* K *by* Tl).

FIG. 5. *Exchange isotherms for* K–Na *in leucite–analcite system. The total molarity of the* NaCl + KCl *solution used is* 3·5M. *The isotherms at* 110° *and at* 75° *show the relatively invariant central section, and the isotherm at* 110° *shows also a substantial hysteresis.*

Exchange Kinetics.—The Na–Tl exchange kinetics were investigated at 75°, 85°, 95°, and 110°, samples of sodium analcite of surface area 2100 cm.²/g. being used in all runs. The exchanging pair of salts was Na_2SO_4 and Tl_2SO_4, and at all times sufficient of each salt was present to provide a saturated solution and an excess of the solid salts. Fig. 7 shows that over a considerable range of times and compositions of the solid a $\sqrt{t}$ diffusion equation is valid.

The application was first made of the simple diffusion law

$$Q_t/Q_\infty = (2A/V)\sqrt{Dt/\pi} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

for diffusion in a medium of area A and volume V, where Q_t and Q_∞ are the amounts of exchange at time t and at infinite time respectively. This equation then gave for the diffusion coefficient $D = D_0 \exp(-E/\mathbf{R}T)$ the values in Table 2. The Arrhenius energy of activation E over the interval 75—110° was 14·9 kcal./g.-ion, as compared with $E \sim 13$ kcal./g.-ion calculated on the basis of equation (4) from earlier measurements on the Na–K exchange (Barrer and Styan, *loc. cit.*). The values of D in Table 2 require a correction on account of the limited mutual solid solubility of the sodium and thallium analcites. Concentration gradients inwards from the surface $x = 0$ of any crystal must have a concentration discontinuity as shown in Fig. 8*b*. The immiscibility gap of Fig. 3 is wide, and one may, to simplify the treatment of the system at 110°, therefore neglect the sections *CD* or *FG* of Fig. 8*b*, corresponding to solubility of Tl-analcite in Na-analcite. The drop in thallium concentration along the lines *AB* and *AE* was

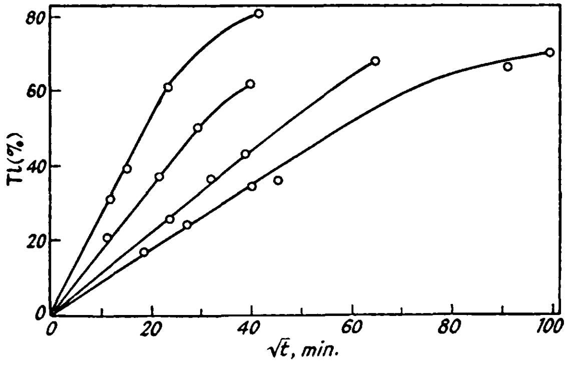

FIG. 7. *Some typical kinetic data for the* Na–Tl *exchange in leucite, showing the validity of the* $\sqrt{t}$ *diffusion law.*

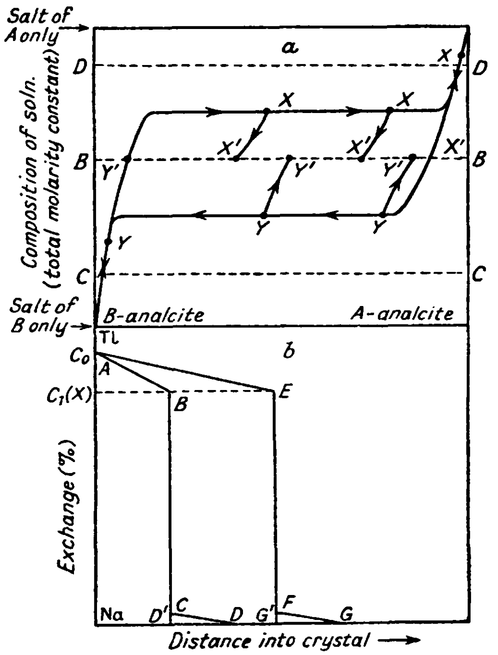

FIG. 8*a*. *Diagrammatic representation of hysteresis behaviour in ion exchange when there is limited mutual solid solubility of the end-members of the exchange reaction.*

FIG. 8*b*. *Concentration gradients in the crystals for two different times, when there is limited mutual solid solubility of the end-members of the exchange reaction.*

TABLE 2. *Exchange diffusion* Na–Tl.

Temp.	$10^{13}D$ (cm.^{2} sec.$^{-1}$)	10^4D_0 (cm.^{2} sec.$^{-1}$)	Temp.	$10^{13}D$ (cm.^{2} sec.$^{-1}$)	10^4D_0 (cm.^{2} sec.$^{-1}$)
110°	$4{\cdot}5_2$	1·43	85°	0·89	1·12
95	$2{\cdot}3_7$	1·68	75	0·63	1·44

approximately from 91% Tl to 87% Tl (% of the total exchangeable ions). If the concentration at A is C_0 and at B or E is C_1, and ABD' and AEG' are taken to represent the concentration–distance curves, then it can be shown (Hermans, *J. Colloid Sci.*, 1947, **2**, 387; Danckwerts, *Trans. Faraday Soc.*, 1950, **46**, 701) that

$$[C_0 - C_1(X)]/C_1(X) = \alpha\sqrt{\pi}\exp\alpha^2\operatorname{erf}\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $\alpha = X_1/2\sqrt{D't_1} = X_2/2\sqrt{D't_2}$, X_1 and X_2 denoting the positions of the concentration discontinuities BD' and EG' at times t_1 and t_2, respectively. One then finds

$$Q_t = \frac{2A[C_0 - C_1(X)]}{\operatorname{erf}\alpha}\sqrt{\frac{D't}{\pi}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where D' denotes the exchange diffusion coefficient in the regions AB or AE. Since $Q_\infty/V = C_0$, one may now compare equations (4)—(6) to obtain

$$D/D' = \{[C_0 - C_1(X)]/C_0\operatorname{erf}\alpha\}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Equation (5) was solved graphically for α, and C_0 and C_1 (X) being known (91% and 87%, respectively), the value of $D' = 6{\cdot}60 \times 10^{-12}$ cm.^{2} sec.$^{-1}$ at 110° was obtained. The magnitude of the correction for various values of $C_0 - C_1(X)$ (in % of total exchangeable ion) is given below for $C_0 = 91\%$:

$C_0 - C_1(X)$ (%)	$C_1(X)$ (%)	D'/D	$C_0 - C_1(X)$ (%)	$C_1(X)$ (%)	D'/D	$C_0 - C_1(X)$ (%)	$C_1(X)$ (%)	D'/D
0·25	90·75	104	6·0	85	9·3	10·0	81	$5{\cdot}8_2$
1·0	90	37·2	8·0	83	7·2	15·0	76	$3{\cdot}9_6$
4·0	87	14·6						

DISCUSSION

Hysteresis in the exchange isotherms (*e.g.*, Fig. 5) is the result of the growth of one solid phase by nucleation in or on the other. Thus in the exchange of sodium by potassium, as the potassium concentration in the crystal grows, a stage is reached when the potassium ions begin to cluster and nuclei of a potassium-rich phase form and grow into crystallites on or in the sodium-rich matrix. In a system involving immiscible solid phases P_1 and P_2, one developing within or on the other, additional free-energy terms due to strain and interfacial surface tension must be added to the free-energy difference ΔG_1 which would arise between those amounts of separated phases of P_1 and P_2 containing an Avogadro number N_0 of cationic charges. For a nucleus containing i cationic charges, the free energy of formation is then

$$\Delta g = i\Delta G_1/N_0 + \Delta g_\sigma + \Delta g_s$$

where Δg_σ and Δg_s are the interfacial and strain free-energy terms associated with the formation of the nucleus of P_2 in or on a matrix of P_1.

For a fixed concentration of solution, where the bulk phase of P_2 would be more stable than that of P_1, $i\Delta G_1/N_0$ would be negative. However, the term $(\Delta g_\sigma + \Delta g_s)$ is positive. As i increases, Δg is at first positive and increases until it reaches a maximum (*e.g.*, Thomas and Staveley, *J.*, 1951, 2572), after which the negative term $i\Delta G_1/N_0$ becomes dominant and Δg decreases without limit as i increases. After this maximum, therefore, the nucleus would grow spontaneously. There will, owing to statistical size fluctuations, be a certain flux of nuclei past the critical size, followed by their spontaneous growth into crystallites. Hysteresis in such a system arises if the flux density of nuclei past the critical size has a very sensitive dependence upon the composition of the exchanging solution. This leads effectively to a concentration threshold below which the flux density of nuclei is negligible and above which it has a measurable value. For the growth of P_2 in a matrix of P_1 this threshold lies above that for thermodynamic equilibrium between solution and P_1 and P_2 in bulk, because of the free-energy term $(\Delta g_\sigma + \Delta g_s)$. For the growth of P_1 in a matrix of P_2 the threshold concentration lies for the same reason below that for the thermodynamic equilibrium between solution and bulk phases P_1 and P_2.

The exchange isotherm, according to the preceding model, will have the shape of Fig. 8*a*, with two horizontal sections. If the properties of nuclei vary with their shape or with their position in or on the matrix, then finite flux densities of nuclei through the critical sizes will occur at different threshold concentrations for different groups of nuclei, and the horizontal sections of Fig. 8*a* will therefore become sloping to some extent. Such a state may be represented by Fig. 3.

On p. 1883 it was shown that the end-points in ion-exchanges of analcite often depend upon the initial cationic composition of the exchanger. This behaviour may be also traced to limited solubility and nucleation phenomena. One may consider an exchange isotherm as in Fig. 8*a*, obtained by using an exchanging solution of fixed total molarity (as in Figs. 3, 4, and 5). Conversion of B- into A-analcite follows the upper path, and the converse change follows the lower path in Fig. 8*a*. If the composition of the exchanging solution is kept constant during the exchange, as in Fig. 2, and so is represented by the line *BB*, and if the initial composition of the analcite corresponds to one of the three different points *X*, then the end-point must correspond to the appropriate one of the points *X'*. Similarly, with solids of compositions corresponding to the points *Y* on the lower curve the end-points are *Y'*. If the composition of the exchanging solution is represented by either line *CC* or *DD*, then, whatever the initial cationic composition of the analcite, the same end-point will be reached, independently of the past history of the specimen. The results of Table 1 and Fig. 2 can thus be readily interpreted.

The kinetics of exchange might at first be supposed, from the nucleation mechanism discussed, to give a sigmoid curve of Q_t/Q_∞ against t, as with barium azide and similar solids (*e.g.*, Garner and Southon, *J.*, 1935, 1705). However, the $\sqrt{t}$ diffusion law was observed instead. Nucleation can be expected to occur initially on or very near the surface of contact of each crystallite with the exchanging solution, which provides the necessary excess of the ion required for nucleation. However, lateral growth of nuclei over the surface must be much faster than the development in thickness, because the supply of ions by diffusion will be more rapid to surface layers than to deeper layers. Accordingly, nuclei form and develop quickly into a thin film of the new phase covering the old. Thereafter the boundary migrates into the crystal as in Fig. 8*b*, and the kinetics are governed by the $\sqrt{t}$ law.

It is now seen that the analcite framework does not give ideal solid solutions of one cationic form in the other, capable of leading to exchange equilibria as described in equations (1)—(3). One reason for this is that the aluminosilicate framework undergoes small but definite readjustments according to the size of the interstitial cations and according as they are hydrated or not (Barrer, *J.*, 1950, 2342). The radii of Tl^+ and Rb^+ are, however, virtually identical at 1·49—1·48 Å; neither ion-exchanged form is hydrated, and *X*-ray powder photographs give practically indistinguishable spacings (there are, of course, some differences in intensity of diffraction). It was therefore interesting that the end-points for three different initial cationic compositions of mixed $(Tl_2,Rb_2)O,Al_2O_3,4SiO_2$ are the same. Nevertheless, it was noted that at the end-points the crystals had become very finely divided. In other systems where crystal fracturing occurred this was definitely associated with nucleation and crystal growth of one phase on or in the other. Therefore the single end-point for Tl–Rb analcites in solutions saturated by both rubidium and thallium sulphates may arise merely because such solutions correspond in composition to lines such as *CC* or *DD* in Fig. 8*a*, and not because an immiscibility gap in the solid is absent. If this is so, limited mutual solid solubility of rubidium and thallium analcites must be attributed, not to structural differences in the anionic framework, but to another property such as a difference in the electro-positive character of the cations.

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