Ion Exchange in Ultramarine.

By R. M. Barrer and J. S. Raitt.

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A study has been made of the exchange behaviour of the felspathoid ultramarine. Ions which exchange fairly readily include Na^+, K^+, Li^+, Ag^+, Tl^+, Pb^{++}, Zn^{++}, and Cd^{++}. Ions which do not exchange readily include Ca^{++}, Sr^{++}, Ba^{++}, Mg^{++}, NH_4^+, Rb^+, and Cs^+. Factors such as ion size, valency, basigenic character, polarisability, and tendency to form covalent links and insoluble sulphides all appear to be involved in determining the relative affinity of ions for the crystal.

The instability of ultramarine under hydrothermal conditions reduced its value as a medium for the quantitative study of ion exchange. However, some equilibrium data were obtained, and a considerable number of kinetic studies were made. From the latter, ion-exchange diffusion coefficients, energies, free energies, and entropies of activation were determined for $Na^+ \longrightarrow Ag^+$, $Ag^+ \longrightarrow Na^+$, $Ag^+ \longrightarrow Li^+$, $Ag^+ \longrightarrow K^+$, and $Na^+ \longrightarrow Tl^+$. Mass-action equilibrium quotients expressed in terms of ion concentrations for the $Na^+ \rightleftharpoons Li^+$ exchange isotherm were reasonably constant. It was also found that ion exchange can proceed smoothly when various dry organic solvents are used in place of water.

X-Ray powder photographs of the ion-exchange products indicated that the ultramarine structure showed slight adjustments in lattice dimensions when different cations were introduced. Evidence of limited mutual solid solubility of end-members of an exchange pair was found only with silver- and zinc-ultramarines and with silver- and potassium-ultramarines.

The felspathoids, cancrinite, sodalite, nosean, hauynite, and ultramarine, are all capable of showing ion exchange. The first three can be readily synthesised by the hydrothermal method (Imhoff and Burkhardt, *Ind. Eng. Chem.*, 1943, **35**, 873; Alcock, Clark, and Thurston, *J. Soc. Chem. Ind.*, 1944, **63**, 292), and ultramarine prepared pyrolytically is available on a large scale. The last four of the above felspathoids are cubic and the structures are known (Pauling, *Proc. Nat. Acad. Sci.*, 1930, **16**, 453; *Z. Krist.*, 1930, **74**, 213; Barth, *ibid.*, 1932, **83**, 405; Jaeger, *Trans. Faraday Soc.*, 1929, **25**, 320). They are based on a basket-like aluminosilicate framework of linked rings of four and six SiO_4^{4-} (or AlO_4^{5-}) tetrahedra, each oxygen atom shared by two tetrahedra, so that the net anionic charge is equal to the number of Al atoms in the framework. This charge is neutralised by interstitial Na or Ca ions, and there are also intercalated salt " molecules " such as NaCl, Na_2SO_4, Na_2CO_3, $CaSO_4$, Na_2S_5. The frameworks appear to be robust enough to stand considerable heat treatment, and this stability combined with the known crystal structures makes the felspathoids a potentially important group of minerals for fundamental studies of ion exchange as a solid-state reaction. Another favourable aspect of the felspathoids for such work is that the crystals normally do not contain water. In the crystalline zeolites water is present, and changes in the amount of this water and in its bonding energy are factors which complicate the quantitative interpretation of exchange equilibrium (Barrer, " Colloque Internat. sur les Réactions dans L'Etat Solide," Paris, 1948, CNRS). Heats and entropies of hydration of ions in aqueous solutions are known in many instances, but the corresponding quantities for intracrystalline ions and water are not.

We now report the results of an investigation of the ion-exchange properties of ultramarine, the first of several studies designed to see how nearly the felspathoids come to being ideal exchangers. From the viewpoint of interpretation by statistical mechanical methods this ideal would correspond to an inert, wholly non-swelling, anionic framework, into the identical interstitial sites of which suitable cations A are introduced with displacement from these sites of an electrochemical equivalent of cations B. It will be seen in this paper that, although ultramarine is a useful medium for ion-exchange studies, it still falls short in various directions of the above ideal. All ultramarines are based upon a single anionic framework $(Al_6Si_6O_{24})_n^{6-}$, as demonstrated by *X*-ray photography (Jaeger, *loc. cit.*), but there are in different preparations different degrees of isomorphous replacement $Al \rightleftharpoons Si$, so that the framework can be more generally given as $[Al_{6+x}Si_{6-x}O_{24}]_n^{(6+x)-}$ where x may have positive or negative values. The anionic charge is neutralised by Na^+ ions, and in addition Na_2S_5 or other forms of sodium polysulphide are found in the cavities which exist in the framework. The composition has a connection with the depth and quality of colour in ultramarine, which may be further changed by replacement of S by Se or Te (*idem, ibid.*). Jaeger examined cation exchange in ultramarine, but there remain many gaps in our qualitative knowledge of this exchange, and quantitative data are almost non-existent.

EXPERIMENTAL

The ultramarine, a synthetic product, quality No. H4195, supplied by Messrs. Reckitt & Colman Ltd., was purified as follows. It was boiled in a large amount of water, unchanged kaolin being removed as a scum collecting on the surface of the water. The suspension was then well stirred and decanted into another vessel, leaving coarse impure material behind. The ultramarine was then filtered off, dried, and heated to 200° to sublime off free sulphur which was found to be present. The product then consisted of small particles of 1—10 μ diameter. Analysis of this purified ultramarine gave results which correspond closely to the formula $Na_5[Al_5Si_7O_{24}],Na_2S_5$.

Three methods for effecting ion exchange were employed: hydrothermal treatment with solutions of exchanging salts, heating with fused salts ($AgNO_3$, $TlNO_3$, $LiNO_3$, KCNS, $PbBr_2$), and heating with vapour of the exchanging salt (NH_4Cl). In the hydrothermal method the mixture was sealed in glass tubes and heated, while being rotated, in an air-thermostat. In fusion and vapour-phase methods the reactions occurred in furnaces or air-ovens thermostatically controlled. At temperatures below 60° a water-thermostat was used.

Ultramarine proved fairly stable in exchanges using melts or vapours of the inorganic salts, but treatment with aqueous solutions always caused some decomposition. This side reaction was minimised by use of low temperatures, by the use of non-aqueous media, by appropriate choice of salt, and by control of its concentration and pH. Thus, two drops of dilute sodium hydroxide solution added to the initial solution reduced decomposition in kinetic studies of the $Na^+ \longrightarrow Tl^+$ exchange, while addition of moist silver oxide acted similarly in the $Ag^+ \longrightarrow Na^+$ experiments. Nevertheless, it was necessary to allow for side reactions when estimating the extent of exchange. The side reaction was associated with liberation of sulphide from the ultramarine. In exchanges involving silver the sulphide appeared as silver salt in the final product. The amount of silver sulphide formed could be determined by loss of weight on extraction with potassium cyanide solution at room temperature. The extraction required not more than 7 min., and it was previously established that under these conditions exchange introducing K^+ was negligible.

Various methods were used to assess the percentage of exchange which had occurred. The difference of mass between the initial and final products was satisfactory where the exchange occurred between ions of considerably different atomic weight, *e.g.*, $Na^+ \rightleftharpoons Tl^+$ and $Na^+ \rightleftharpoons Ag^+$. Difficulty in the quantitative recovery of ultramarine for weighing was overcome by using a No. 4 sintered-glass crucible with a layer of Gooch asbestos deposited on the filter. This prevented choking of the septum by particles of ultramarine. The weighing method was not used where the difference in mass was slight, *e.g.*, $Na^+ \rightleftharpoons NH_4^+$. In other cases, and especially as a control method, the crystals were analysed chemically. Decomposition was effected by repeated evaporation with concentrated nitric or hydrochloric acid. The silica and alumina were then separated, and the metal cations determined by standard analytical techniques. The sodium content of the original ultramarine, for example, was determined as sodium sulphate, and as sodium zinc uranyl acetate, giving respectively 15·3% and 14·9% : 15·1% was taken as the correct value.

In some cases the reaction was followed from the amount of one cation lost or gained by the solution. For example, the result obtained by the weighing method in the $Na^+ \rightleftharpoons Tl^+$ exchange was checked by estimating thallium in the solution as chromate. Similarly, exchanges in which silver-ultramarine was the starting material were often followed by estimating the silver in the final solution, either as chloride, or by titration with standard thiocyanate solution.

In measurements of exchange isotherms of $Na^+ \rightleftharpoons Ag^+$ and $Li^+ \rightleftharpoons Ag^+$ the superior affinity of silver for ultramarine was such that in relatively dilute solutions of sodium nitrate or lithium nitrate the equilibrium concentration of silver nitrate was too small for estimation by chemical analysis. Accordingly, the e.m.f.s were determined of concentration cells such as

$$\mathrm{Ag}\ \left|\ \begin{array}{l} \mathrm{AgNO_3}\ (m_1) \\ \mathrm{NaNO_3}\ (m_2) \end{array}\ \right\|\ \left.\begin{array}{l} \mathrm{AgNO_3}\ (m_3) \\ \mathrm{NaNO_3}\ (m_1 + m_2 - m_3) \end{array}\ \right|\ \mathrm{Ag}$$

The solution in the left-hand compartment of known total molality $(m_1 + m_2)$ was the equilibrium solution after exchange in which it was desired to determine m_1. The solution in the right-hand compartment also had total molality $(m_1 + m_2)$, but the molality m_3 of the silver nitrate was known. According to the principle of ionic strength (Lewis and Randall, *J. Amer. Chem. Soc.*, 1921, **43**, 1112), the activity coefficients of Ag^+ ions in both compartments are about the same. Thus the e.m.f. gives a measure of the Ag^+ ion concentrations m_1, when m_3 is known. A calibration curve giving the e.m.f. as a function of m_1 at constant m_3 was first constructed. E.m.f.s were measured by using a valve voltmeter and Tinsley precision potentiometer. Accurately reproducible results were obtained down to 0·0001 molal. The liquid–liquid junction potential was minimised by a saturated potassium nitrate salt bridge.

In the studies of ion-exchange kinetics, sufficient of each of the exchanging salts was added to the reaction tube to ensure that the volume of solvent employed would be saturated with respect to both salts during the exchange. Thus the concentration of each exchanging ion is fixed during reaction. Where silver-ultramarine was treated with a saturated metal halide it was found unnecessary to add silver halide. Owing to the low solubility of silver halides, and to their tendency to form complexes with alkali-metal halide, the free silver-ion concentration was extremely low, a circumstance favouring extensive exchange. In a process controlled by diffusion in the crystals of ultramarine (and in absence of limited mutual solid solubility of the end members of the exchanged ultramarine, see p. 4649) the diffusion coefficient D can be obtained from the equation :

$$Q_t = (2A/V)Q_\infty\sqrt{Dt/\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here Q_t is the amount of exchange at time t, Q_∞ the equilibrium amount exchanged in crystals of total volume V and total surface A, and D is the diffusion coefficient. In the case of some kinetic experiments involving very short time intervals, the reaction tubes were initially quickly heated in an oil-bath to the required temperature.

The surface area, A, of the mineral was determined by the Kozeny liquid flow method (Carman, *J. Soc. Chem. Ind.*, 1939, **58**, 1; 1938, **57**, 225), water being used as flowing liquid. The purified sodium-ultramarine was found to have a surface area of 5730 cm.^{2} per g., while the heavier silver form gave A = 3380 cm.^{2} per g.

Results

Cation-exchange Forms.—A number of experiments were carried out to determine the behaviour of ultramarine in exchanges with different cations. The results of these experiments are shown in Tables 1 and 2. Only silver-ultramarine was readily formed in the pure state. The difficulty in obtaining 100% exchange experienced with other ions was complicated by the tendency of ultramarine to decompose under hydrothermal conditions (see p. 4642). Silver-ultramarine proved very useful in preparative work, for although silver was not easily replaced under ordinary conditions using solutions of nitrates or sulphates, yet it could be displaced by solutions of halides of the desired cations, because of the precipitation of insoluble silver salts.

TABLE 1. *Exchange reactions with univalent cations.*

Reactants *	Temp.	Time (hr.)	Method of estimating % exchange	Exchange
Na-U + $AgNO_3$ (melt)	225°	24	Weighing and analysis	100%
Na-U + $AgNO_3$ (aq.)	95	8	Weighing and analysis	95%, but extensive decomp.
Ag-U + NaCl (aq.)	95	30	AgCl formed	80%
Ag-U + $NaNO_3$ (aq.)	95	24	$AgNO_3$ formed	Negligible
Ag-U + LiCl (aq.)	75	2	Weighing and by AgCl formed	75%; some decomp.
Ag-U + LiCl (aq.)	110	1½	Analysis on solid extracted by KCN	84%; considerable decomp.
Ag-U + LiI (sat. aq.)	45	138	Weighing	78%
Ag-U + $LiNO_3$ (melt)	265	76	Weighing and by KCNS titration of $AgNO_3$ from melt	Negligible
Na-U + $LiNO_3$ (melt)	265	19	Weighing	84%
Ag-U + KCl (aq.)	75	50	Weighing and by AgCl formed	8%
Ag-U + KCl (aq.)	110	116	Weighing and by AgCl formed	50%
Ag-U + KI (sat. aq.)	110	136	Weighing and by AgI formed	81%
Na-U + KCNS (melt)	190	17	Weighing	28%
Na-U + KCNS (melt)	190	71	Weighing	34%
Na-U + RbCl (5·7M)	95	71	Weighing	4%
Ag-U + RbCl (4M)	118	178	AgCl formed (42% reaction) but greater than 100% exchange from change in wt. of mineral	H^+-ion,† but probably no Rb^+-ion, exchange
Na-U + CsCl (4·7M)	95	73	Weighing	No detectable reaction
Ag-U + CsCl (6·7M)	95	71	AgCl formed, 22% reaction; but *decrease* in wt. of mineral	Hydrogen-ion exchange †
Ag-U + CsCl (3M)	118	178	AgCl formed, but *decrease* in wt. of mineral	Hydrogen-ion exchange †
Na-U + NH_4Cl (vapour and solid)	250	96	Analysis	9%
Na-U + NH_4Cl (vapour and solid)	350	72	Analysis	23%
Ag-U + NH_4Cl (1·5M)	110	66	Weighing and by AgCl formed	17%
Na-U + $TlNO_3$ (melt)	235	216	Weighing and by Tl analysis in melt	29%
Na-U + excess $TlNO_3$ (melt)	240	140	Analysis of solid	32%
Ag-U + TlCl (sat. aq.)	110	140	Weighing and by AgCl formed	34%
Ag-U + TlCl (sat. aq.) + $TlNO_3$ (aq.)	110	136	AgCl formed	31%
Na-U + Tl_2SO_4 (aq.) + 2 drops 2% NaOH	180	120	—	Extensive decomp. to give Tl_2S

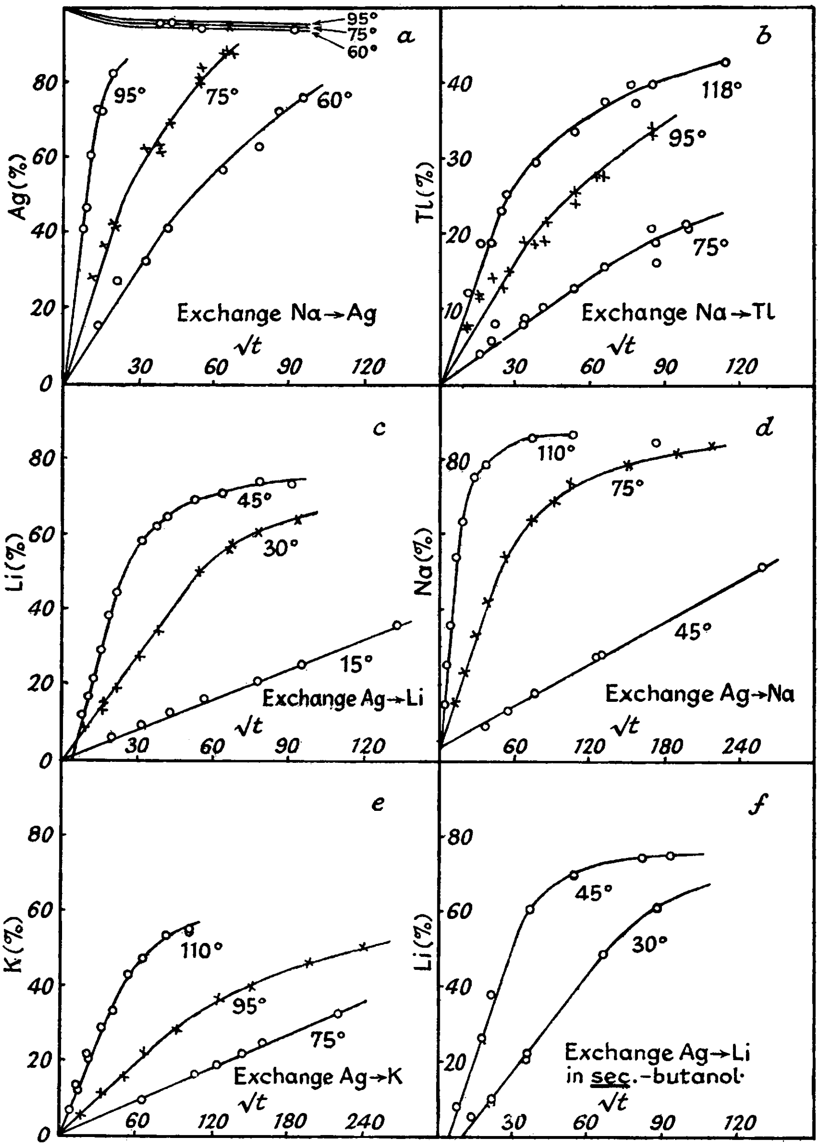
* The symbol U is used to denote ultramarine. † See Discussion.

TABLE 2. *Exchange reactions involving bivalent cations.*

Reactants	Temp.	Time (hr.)	Method of estimating % exchange	Exchange
Ag-U + $MgCl_2$ (aq.)	110°	140	—	Extensive decomp.
Ag-U + $MgCl_2$ (aq.)	110	17	Weighing and by AgCl formed	~16%, but considerable decomp.
Ag-U + $MgCl_2$ (aq.)	110	5	Weighing and by AgCl formed	20%; much less decomp.
Ag-U + $CaCl_2$ (7M)	95	95	Weighing and by AgCl formed	7%
Ag-U + $SrCl_2$ (aq.)	110	162	Weighing 1% and by AgCl formed 8% exchange	Slight exchange
Ag-U + $BaCl_2$ (aq.)	110	140	AgCl formed	3%
Na-U + $BaCl_2$ (aq.)	110	140	Weighing	2%
Ag-U + $ZnCl_2$ (aq.)	110	17	Weighing and by AgCl formed	68%
Ag-U + CdI_2 (2·5M)	110	194	Weighing and by AgI formed	42%
Ag-U + $PbCl_2$ (sat. aq.)	110	140	AgCl formed and by analysis of solid	50%
Na-U + $PbCl_2$ (sat. aq.)	110	166	Weighing	75%
Na-U + $PbBr_2$ (melt) ...	385	16	Weighing	43%

Although various attempts were made to prepare thallium-ultramarine of high thallium content, it was not possible to obtain appreciably more than 30% exchange. From sodium-ultramarine, heating with a large excess of fused thallous nitrate gave 32% exchange, while treatment of silver-ultramarine with hot thallous chloride solution resulted in 34% exchange.

FIG. 1. *Kinetics of exchange in ultramarine.*



A mixture of thallous chloride and nitrate was then used, to give a higher Tl^+-ion concentration, but this did not improve the % exchange (Table 1).

Colour changes often accompanied ion exchange in ultramarine. The intense blue of sodium-ultramarine changed to green in the silver form, and to brown in the lead-rich form. Potassium-rich ultramarine was coloured like the sodium form, but partial exchange towards lithium- or thallium-ultramarine gave a darker, richer shade of blue. Microscopical examination of the product of the $Ag^+ \longrightarrow Zn^{++}$ exchange showed that the crystals rich in zinc were pale brown.

The results of exchanges carried out in a variety of pure organic solvents are shown in Table 3. In some cases $\sqrt{t}$ is given to permit a comparison of the rate of reaction in the organic solvent with that in water. Before use these solvents were dried over freshly ignited quicklime and redistilled. Even with solvents which have minimum solvent power for electrolytes (*e.g.*, benzene), the extent to which reaction proceeds is noteworthy.

Cation-exchange Kinetics.—Kinetic studies were made for various cation pairs. In general the % exchange was a linear function of $\sqrt{t}$ over the earlier stages of the process, as shown in Fig. 1, and as required by equation (1).

In the $Ag^+ \longrightarrow Li^+$ exchange at 45° in aqueous solutions, and at 30° and 45° in *sec.*-butyl alcohol as solvent, the graphs of Fig. 1 cut the $\sqrt{t}$ axis instead of passing through the origin. This behaviour was associated with incomplete reaction in the preparation of the silver-ultramarine from the original sodium form. Thus over the earliest part of the subsequent $Ag^+ \longrightarrow Li^+$ exchange some replacement of Na^+ by Li^+, as well as the replacement of Ag^+ by Li^+, was occurring. Therefore the exchange measured by the silver chloride formed or by the change in weight of the ultramarine crystals was at the beginning slightly less than the total exchange which had actually taken place. When the work was repeated with lithium chloride, and silver-ultramarine specially treated to ensure complete exchange, the graphs obtained (Fig. 1*c*, curves at 30° and 15°) passed through the origin. They were then quite parallel to graphs originally found at 30° and 15° when using the impure silver-ultramarine which had not passed through the origin. In calculations of exchange diffusion coefficients only the initial slope and final extent of reaction are involved so that any displacement of the graph in the way described above is of little consequence.

TABLE 3. *Ion-exchange in non-aqueous solvents.*

Reactants	Solvent	Temp.	Reaction time	$\sqrt{t}$ (t in min.)	Exchange, %
Na-U + LiCl	Am^iOH	75°	17 hr. 20 min.	—	52
Ag-U + LiCl	,,	75	18 hr. 45 min.	—	78
Na-U + LiCl	Bu^sOH	75	24 hr. 20 min.	—	63
Ag-U + LiCl	,,	75	18 hr.	—	78
Ag-U + NaCl	,,	75	11 days 16 hr.	130	66
Na-U + LiCl	$COMe_2$	45	5 days	—	36
Ag-U + LiCl	,,	45	99 hr. 35 min.	77·3	74
Ag-U + LiCl	C_6H_6	45	11 days	126	27
Ag-U + NaCl	,,	75	23 days	182	36

A second effect was noted in the $Ag^+ \longrightarrow Na^+$ exchanges. Here the graphs of % exchange against $\sqrt{t}$ made a positive intercept on the axis of % exchange, at $t = 0$, instead of passing through the origin (Fig. 1*d*). This behaviour was associated with the presence of a little silver oxide initially in the silver-ultramarine which was extracted with the silver chloride in the separation (with ammonia) carried out after reaction. Thus the estimated silver was a little greater than it should have been, and the graph was displaced upwards parallel to the true graph. The sample of silver-ultramarine in this series had been stored for some time, and the presence of silver oxide can be attributed to hydrogen-ion exchange due to sorption of moisture [H_2O (adsorbed) $+ Ag^+ \longrightarrow AgOH\downarrow + H^+$].

Difficulty was experienced in measuring the exchange equilibrium position, since the very prolonged hydrothermal treatments often needed favour decomposition of the ultramarine. Nevertheless, the equilibrium exchange was measured at one temperature for the $Ag^+ \longrightarrow Li^+$, $Ag^+ \longrightarrow Na^+$, and $Ag^+ \longrightarrow K^+$ interchanges. In the $Na^+ \longrightarrow Tl^+$ exchange much thallous sulphide appeared when reaction proceeded for times in excess of those in Fig. 1*b*. In exchanges involving Ag^+ the correction (see p. 4642) for formation of silver sulphide became inaccurate when large amounts of the sulphide were formed by decomposition of the ultramarine. This effect is shown in the $Ag^+ \longrightarrow Na^+$ graph at 110°, where the final point appears lower than the preceding one.

The determination of equilibrium by approaching it from both directions was possible only with the exchange $Na\text{-}U + Ag_2SO_4 \rightleftharpoons Ag\text{-}U + Na_2SO_4$. The Ag and the Na form were the only two which were obtained with 100% exchange, and the use of incompletely exchanged material was considered desirable only if it could be prepared without recourse to long hydrothermal treatments which gave some decomposition. Ion-exchange forms obtained by using fused salts were generally rather free from any decomposition, but unfortunately only for silver-ultramarine were the end-products sufficiently highly exchanged to be useful in fixing equilibrium points from both directions.

With the $Ag^+ \longrightarrow Li^+$ exchange at 30° another method of measuring the end-point was used. A product with 66% Li exchange was prepared by a preliminary short hydrothermal treatment of silver-ultramarine, the product being reasonably free from decomposition. It was dried and annealed for 2 hr. at 120°. Kinetic measurements were then made upon both this partly exchanged form and pure silver-ultramarine. The kinetics of the partly exchanged material follow initially the equation :

$$Q'_t - Q_0 = (2A/V)(Q_\infty - Q_0)\sqrt{Dt/\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where Q_0 is the amount of exchange (66%) at $t = 0$, and other symbols are as in equation (1). The exchange kinetics of the pure silver-ultramarine follow equation (1). The initially linear graphs of Q'_t and Q_t against $\sqrt{t}$ are then extrapolated to intersect. The value of Q_t at this intersection point is equal to Q_∞. This can be seen from Fig. 2*a*, where we have to show that $Q_\infty = DB$. At the crossing point *C*, the value of $\sqrt{t}$ is the same for equations (1) and (2) and $Q'_t = Q_t$. Hence from these equations we find at this point that :

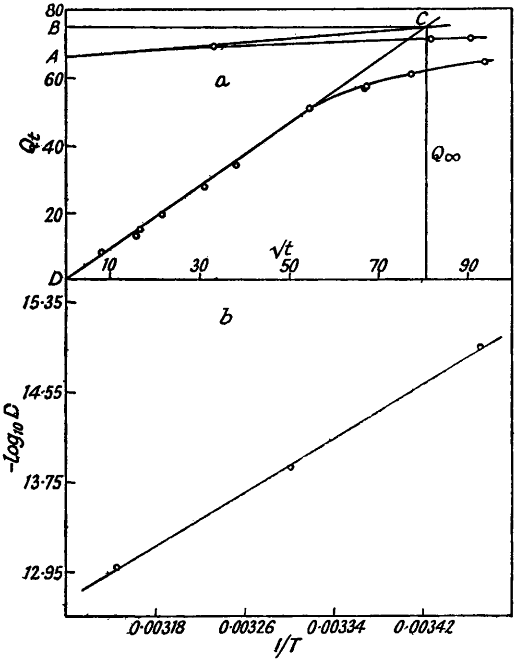


FIG. 2.

(*a*) *The* Ag$^+$ ⟶ Li$^+$ *exchange at* 30° *from crystals initially of different cationic composition.*

(*b*) *The influence of temperature upon ion-exchange diffusion coefficients of* Ag$^+$ ⟶ Li$^+$ *ultramarine.*

$$(Q'_t - Q_0)/(Q_\infty - Q_0) = Q_t/Q_\infty$$

and so

$$Q_\infty = \frac{Q_0 Q_t}{Q_t - (Q'_t - Q_0)} = \frac{AD \,.\, DB}{AD} = DB$$

The same method was less successful with the Na$^+$ ⟶ Tl$^+$ exchange because of the marked decomposition yielding thallous sulphide, and the end-point could only be estimated from the shape of the graph at 118°. Although absolute values of *D* may then be in error, the values of the energy of activation should be correct provided temperature has no great effect on the equilibrium point (*i.e.*, the heat of exchange, ΔH, is small).

The assumption that the end-points are little affected by temperature is in accordance with the experience of various workers. It has been observed in the zeolite chabazite (Barrer and Sammon, unpublished work), and in a variety of other exchangers (Rothmund and Kornfeld, *Z. anorg. Chem.*, 1918, **103**, 129; 1919, **108**, 215; Patton and Ferguson, *Canad. J. Res.*, 1937, **15**, *B*, 103; Boyd, Schubert, and Adamson, *J. Amer. Chem. Soc.*, 1947, **69**, 2818). Even where the valencies of the exchanging ions differ (*e.g.*, $Ca^{++} \rightleftharpoons 2Na^+$) the exchange equilibria remain comparatively insensitive to temperature (Vanselow, *Soil Sci.*, 1932, **33**, 95; Magistad, Fireman, and Mabry, *ibid.*, 1944, **57**, 371). Evidence that exchange equilibria in ultramarine were not much altered by temperature follows from inspection of Fig. 1*a* for the Ag$^+$–Na$^+$ interchange. There is no significant shift over the temperatures 60°, 75°, and 95°. This appears true also in the Ag$^+$–Li$^+$ exchange at 30° and 45° (Fig. 1*c*).

Exchange Diffusion Coefficients.—For all exchanging pairs studied kinetically, except

$Na^+ \rightarrow Tl^+$, it was possible to fix the equilibrium position for at least one temperature with moderate accuracy. At any temperatures for which direct measurement was not possible, it was assumed that these end-points varied little with temperature. It was then possible to determine exchange diffusion coefficients, D, from equations (1) and (2) (Table 4).

The values of D normally depended exponentially upon the temperature, according to the Arrhenius equation [$D = D_0 \exp(-E/\boldsymbol{R}T)$]. This is shown in Fig. 2*b* for the $Ag^+ \rightarrow Li^+$ exchange. From the data it was thus possible to find E and D_0. One now sets (Glasstone, Laidler, and Eyring, " The Theory of Rate Processes," McGraw-Hill, New York, 1941) :

$$D = d^2(\boldsymbol{k}T/\boldsymbol{h})\exp(-\Delta G^+/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where d is the distance moved in a unit diffusion, $\boldsymbol{h}$ is Planck's constant, and ΔG^+ the free energy of activation. The other symbols have their usual significance. d may be taken as 7·9 Å, the distance between successive equilibrium positions according to Jaeger's model for ultramarine (*loc. cit.*). Accordingly, ΔG^+ may be found, and finally ΔH^+ and ΔS^+, the heat and entropy of activation, from the relations

$$\left.\begin{aligned}\Delta H^+ &= E - \boldsymbol{R}T \\ \Delta S^+ &= (E - \boldsymbol{R}T - \Delta G^+)/T\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Uncertainties in the values of D and especially of E affect the magnitudes of heats, entropies, and free energies of activation. For example, in the $Ag^+ \rightarrow K^+$ exchange E varies according to temperature and the complicating factor of limited solid solubility arises (see p. 4649), so ΔS^+ is of little significance. The various quantities calculated from the kinetic studies are given in Table 4. Values of D_0 are larger than those usually found in ion migration (Boyd, Adamson, and Myers, *J. Amer. Chem. Soc.*, 1947, **67**, 2836; Kressman and Kitchener, *Discuss. Faraday Soc.*, 1949, **7**, 90). D for the exchange of $Na^+ \rightarrow Tl^+$ in ultramarine is numerically considerably smaller than is D for the same exchange in analcite (Barrer and Hinds, *J.*, 1953, 1879). The presence of polysulphide ions intercalated in the channels permeating the ultramarine structure may decrease the intracrystalline mobility of cations in this crystal as compared with analcite. Within the ultramarine system itself the results in Table 4 demonstrate clearly the influence of ion size on exchange. The value of ΔG^+, which is the rate-controlling factor, increases in the order Li < Na < K for those exchanges in which silver-ultramarine was the starting material. ΔG^+ is almost the same for the $Na^+ \rightarrow Tl^+$ and the $Ag^+ \rightarrow K^+$ exchanges, where the sums of the radii of the respective ion pairs are almost identical. However, the results of the $Na^+ \rightleftharpoons Ag^+$ exchanges at 75° show that ΔG^+ is lower in the sodium-rich than in the silver-rich form. This may be associated with a small contraction of the lattice of silver-ultramarine relative to that of sodium-ultramarine (see Fig. 5).

TABLE 4. *Exchange diffusion coefficients and related data.*

Exchange	Temp.	$D \times 10^{14}$ (cm.^{2} sec.$^{-1}$)	D_0 (cm.^{2} sec.$^{-1}$)	E (kcal./g.-ion)	Mean E	ΔG^+ (kcal./g.-ion)	ΔS^+ (cal./g.-ion/deg.)
$Na^+ \rightarrow Ag^+$	60°	0·89	5·0	23·6 (60—75°)	22·4	19·4	10
	75	4·1	5·4	22·3 (60—95°)		19·2	7
	95	22·2	5·1	21·3 (75—95°)		19·1	4
$Ag^+ \rightarrow Na^+$	45	0·047	0·59	23·9 (45—75°)	21·9	20·3	9
	75	1·25	0·79	21·9 (45—110°)		20·0	3
	110	17·1	0·60	19·8 (75—110°)		20·1	−3
$Ag^+ \rightarrow Li^+$	15	0·114	$4·2 \times 10^5$	28·1 (15—30°)	27·0	17·8	34
	30	1·31	$4·6 \times 10^5$	27·1 (15—45°)		17·3	30
	45	10·0	$4·2 \times 10^5$	25·9 (30—45°)		16·9	26
	75	455 *	—	—		15·9	—
$Ag^+ \rightarrow Li^+$ (in Bu^sOH)	30	1·10	$1·8 \times 10^3$	23·9	23·9	17·4	19
	45	7·22	$1·8 \times 10^3$			17·1	19
$Ag^+ \rightarrow K^+$	75	0·057	—	19·7 (75—95°)	—	22·2	—
	95	0·269	—	28·9 (75—110°)		22·3	—
	110	2·64	—	42·4 (95—110°)		21·6	—
$Na^+ \rightarrow Tl^+$	75	0·21	—	19·6 (75—95°)	16·1	21·3	—
	95	0·98	—	16·1 (75—118°)		21·4	—
	118	2·71	—	12·6 (95—118°)		22·0	—

* Obtained by extrapolation from Fig. 2*b*.

Exchange Isotherms.—Optical and *X*-ray data, and the form of exchange isotherms, have demonstrated that in analcite the end-members of an ion-exchange pair do not always give a continuous range of solid solutions (Barrer and Hinds, *loc. cit.*; Barrer, Baynham, and McCallum, *J.*, 1953, 4035). Diffusion coefficients will in general have different values in each phase, and moreover in case of limited solid solubility the interpretation of kinetic data requires modification and gives values of D different from those obtained by using equations (1) and (2). The corrections require a knowledge of limits of mutual solid solubility of the end-members, and so of the form of the exchange isotherm (Barrer and Hinds, *loc. cit.*). It was thus desirable to obtain isotherms and X-ray data in ultramarine to see whether limited solid solubility arises there also.

Exchange isotherms in ultramarine were not readily determined. Long equilibration times favoured some decomposition of the ultramarine. Moreover, the very great affinity of the ultramarine for silver made for such small equilibrium concentrations of aqueous Ag^+ that analytical methods of estimation were unsuitable. However, by the electrometric method (see p. 4643) parts of the exchange isotherms of the Ag^+–Li^+ and the Ag^+–Na^+ pairs were measured successfully (Figs. 3*a* and *b*). The isotherms demonstrate the remarkable affinity of ultramarine for silver.

Fig. 4 shows a more complete exchange isotherm obtained for the Li^+–Na^+ exchange. This exchange had not been studied kinetically, but the system was comparatively free from decomposition of ultramarine. The isotherm (obtained by the weighing method and also by analysis of the equilibrium mother-liquor) is continuous and thus indicates continuous solid solubility of the lithium and the sodium form of ultramarine. Values of the mass-action quotient $K = (Na/Li)_{cryst.}/(Li/Na)_{soln.}$ are given in Table 5, and are fairly constant.

FIG. 3. (*a*) *and* (*b*) *Portions of the exchange isotherms in ultramarine of* Ag–Na *and* Ag–Li *pairs.*

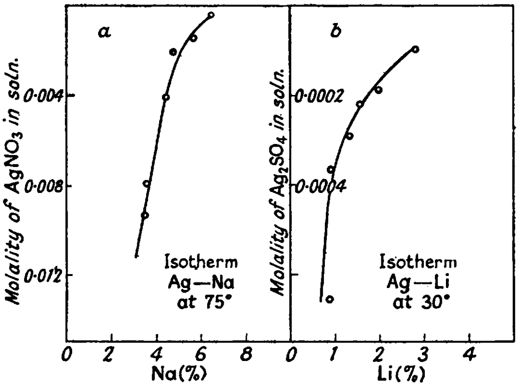


FIG. 4. *The* Na–Li *exchange isotherm in ultramarine.*

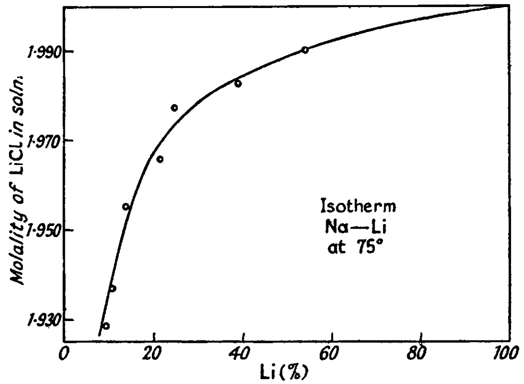


TABLE 5. *Mass-action quotients for the* Li^+–Na^+ *exchange in ultramarine.*

Exchange, % : $Na^+ \longrightarrow Li^+$	9·3	10·5	13·7	21·4	24·6	38·8	54·0
10^3K	3·80	3·81	3·64	4·72	3·71	4·34	5·72

X-*Ray Examination of Ion-exchanged Forms*.—In order to investigate further the possibility of limited mutual solid solubility of end-members, and also to demonstrate lattice changes associated with exchanges in crystals of ultramarine, X-ray powder photographs were taken of exchange forms enriched in various cations. In all cases the characteristic ultramarine pattern was preserved, but some adjustment of lattice dimensions occurred when ions of different radii were introduced. This effect is seen in Fig. 5 for ultramarine crystals having in order the cationic compositions 80% K + 20% Ag; 75% Pb + 25% Na; 71% Na + 29% Tl; 100% Na; 37% Ag + 63% Zn; 100% Ag; and 75% Li + 25% Ag.

The most expanded crystals are those rich in potassium and the most collapsed are those rich in lithium. Unit-cell determinations gave the following results for the cubic unit cell edge in Table 6. There is a general tendency for unit-cell dimension and ionic radii to increase together, but unit cells enriched in Ag^+, Tl^+, and Pb^{++}, which form insoluble sulphides and tend to show some covalency, are smaller than the ion-size sequence of Table 6 suggests.

The X-ray powder photographs of ultramarines of cationic content 60% K + 40% Ag and 80% K + 20% Ag give evidence of limited mutual solid solubility. Inspection of Fig. 6 shows displacement of lines, as noted above, between potassium-rich and silver-rich phases. If a continuous range of solid solutions is present any line in the spectrogram of an exchange product of intermediate cationic composition should be spaced between the corresponding lines of

TABLE 6. *Unit-cell dimensions of cation exchanged ultramarines.*

Cations present	Ionic radii (Å) *	Unit-cell edge (Å)
75% Li + 25% Ag	Li^+, 0·78 (0·60)	$8{\cdot}7_7$
100% Ag	Ag^+, 1·13 (1·26)	$8{\cdot}9_7$
37% Ag + 63% Zn	Zn^{++}, 0·83	$8{\cdot}9_8$
100% Na	Na^+, 0·95 (0·98)	$9{\cdot}0_5$
71% Na + 29% Tl	Tl^+, 1·49	$9{\cdot}0_7$
75% Pb + 25% Na	Pb^{++}, 1·32	$9{\cdot}1_0$
80% K + 20% Ag	K^+, 1·33 (1·33)	$9{\cdot}2_5$

* Values quoted are those of Goldschmidt (cf. Evans, " Crystal Chemistry," C.U.P., 1939, p. 171). Figures in parentheses are due to Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 1940, p. 346.

products respectively richer in potassium and in silver. In Fig. 6, however, the marked silver-ultramarine lines appear at the same spacing in all photographs but become weaker as the silver content decreases. Simultaneously certain lines associated with potassium-ultramarine (also marked) become stronger but again show no shifts in position. It may be inferred that the material is not homogeneous but that it consists of two solid phases, one rich in silver, the other in potassium.

FIG. 5. *Adjustments in* d-*spacings accompanying ion exchanges in ultramarine.*

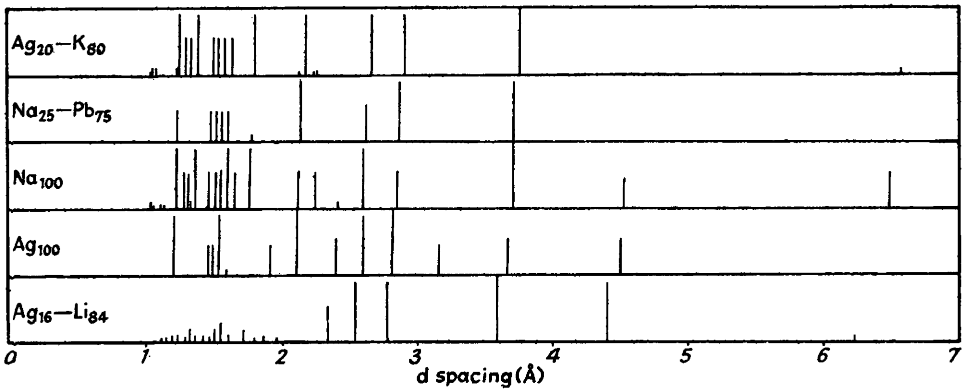
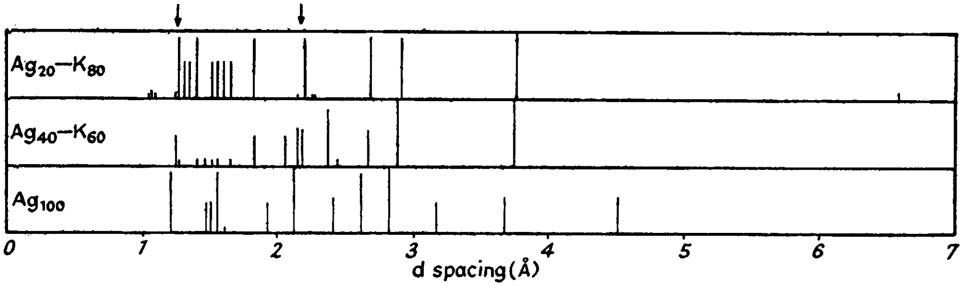


FIG. 6. X-*Ray evidence of limited mutual solid soluility of* K- *and* Ag-*ultramarines.*



The X-ray powder photographs of intermediate cationic compositions among other exchanging pairs were examined but the Ag–K-ultramarine system was the only one in which evidence of limited solid solubility was obtained. However, there was also optical evidence of the phenomenon in the product of the Ag^+–Zn^{++} exchange, where both green (Ag-rich) crystals and pale brown ones were found. The green crystals had $n > 1{\cdot}64$; the brown ones had $n < 1{\cdot}64$, and were thought to be the zinc-rich phase.

DISCUSSION

In Table 1 several instances of hydrogen-ion exchange are recorded. For example, in presence of aqueous cæsium chloride, silver chloride is formed from silver-ultramarine, and the weight of the ultramarine instead of increasing, as would be the case in the exchange

$Ag^+ \longrightarrow Cs^+$, decreases. In the analogous process with rubidium chloride solution, the decrease in weight of the silver-ultramarine was more than corresponded to 100% exchange of silver by rubidium, while the silver chloride actually displaced corresponded to only 42% exchange. These results are explained quite simply as the reaction :

$$MCl + H_2O + Ag\text{-}U = AgCl\downarrow + MOH + H\text{-}U$$

where M denotes Rb or Cs. Such hydrogen ion-exchange will only occur where (1) the Ag^+-ion concentration is very small in the solution, (2) the ion M^+ is too large to enter the crystals, for otherwise the hydrogen ion, which is at an extremely small concentration in the exchanging solution, will not be able to compete for the exchange sites in presence of the much higher concentrations of M^+ and of Ag^+. It is interesting that *crystalline* hydrogen aluminosilicates may be obtained by the above method, since treatment of aluminosilicates with acids normally decomposes them.

An ion-sieve effect as between Li^+, Na^+, and K^+ on the one hand, and Rb^+ and Cs^+ on the other, is now apparent from our data. The smaller alkali-metal ions will readily enter the crystals, but Rb^+ and Cs^+ do not. With analcite the corresponding sieve effect appeared between Li^+, Na^+, K^+, and Rb^+ on the one hand and Cs^+ on the other (Barrer, *J.*, 1950, 2342), so that in ion-exchange diffusion analcite is a somewhat more open structure than ultramarine. Chabazite is a still more open structure than analcite in ion exchange, since it will accept freely Li^+, Na^+, K^+, Rb^+, and Cs^+ (*idem, ibid.*).

Ionic radius is, however, only one factor which controls entry into the crystals. This is well illustrated by the failure of Rb^+ to exchange whereas Tl^+ is able to enter to the extent of about 30% exchange (Table 1). These ions are believed to have virtually identical radii. It will be seen from Tables 1 and 2 that, in fact, ions of those elements which form insoluble sulphides (Ag^+, Pb^{++}, Tl^+, Zn^{++}, Cd^{++}) display an affinity for the crystals of ultramarine often superior to that shown by much more electropositive and basigenic elements which form soluble sulphides or hydrogen sulphides (Rb^+, Ca^{++}, Sr^{++}, Ba^{++}). Since a polysulphide ion exists interstitially throughout ultramarine, this observation may be of considerable significance. It is not, however, the only other factor of importance, for in the silver and the thallium forms of analcite and of chabazite, in absence of any interstitial sulphide, the silver and thallium still show notable affinity for the crystals (Barrer and Hinds, *loc. cit.*; Barrer, *J.*, 1950, 2342) as compared even with ions like Na^+. The ability of an ion to exchange, and its affinity for the crystals, seems therefore to be increased by an increased polarisability and hence tendency to form covalent links.

Very little study has been made of the use of organic solvents in ion-exchange reactions. Wiegener and Muller (*Z. Pflanz. Dung.*, 1929, **14**, *A*, 332) measured exchanges between a synthetic calcium aluminosilicate gel and aqueous-alcoholic sodium, potassium, and cæsium chlorides, and more recently Kressman and Kitchener (*J.*, 1949, 1211) reported exchange experiments with a phenol–sulphonate resin where the solvents were aqueous alcohol and aqueous acetone. In the experiments recorded in Table 3 we have used pure, dry organic solvents. In the $Ag^+ \longrightarrow Li^+$ exchange the equilibrium position is little changed when water, acetone, *sec.*-butyl and *iso*pentyl alcohol are the solvents. The solvents were all mutually saturated with respect to each exchanging salt, so that the reaction may be of the type

$$\underset{\substack{\text{solid}\\\text{salt}}}{AX} + \underset{\substack{\text{in solid solution}\\\text{in A-U}}}{B\text{-}U} \rightleftharpoons \underset{\substack{\text{solid}\\\text{salt}}}{BX} + \underset{\substack{\text{in solid solution}\\\text{in B-U}}}{A\text{-}U}$$

which, as indicated by a statistical thermodynamic treatment (Barrer, " Colloque Internat. sur les Réactions dans L'Etat Solide," Paris, 1948, CNRS), should give a single end-point, the solvent merely being the vehicle for carrying ions A and B between the solid salts AX and BX and the ultramarine crystals. However, solvation of the solids AX and BX to give crystalline complexes (hydrates, alcoholates) is still possible, and also the formation of solid complexes such as $AgCl + NaCl \longrightarrow Na(AgCl_2)$ must be considered.

The University, Aberdeen. [*Received, June* 11*th*, 1954.]