136. *An Ion-sieve Reagent for Cæsium–Alkali-metal Separations.*

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The use of silver analcite as an ion-sieve reagent for separations of sodium, potassium, and rubidium from cæsium has been investigated. The removal of sodium and potassium from mixtures with cæsium (all as chlorides) occurred quantitatively, and readily at about 100°, according to the equation

$$MCl + xAgA(s) \longrightarrow AgCl(s) + MAg_{(x-1)}A_x(s)$$

where A denotes the anionic framework of analcite and M is Na or K. In the removal of sodium, no cæsium entered the silver analcite and the method is suitable for quantitative analysis. In the potassium–cæsium separation a phase change occurs involving a minor rearrangement of the silver analcite to the potassium analcite (leucite) structure, and a little cæsium may be incorporated during this process : a correction is thus needed in quantitative analysis, but the method is available for the removal of K$^+$ from Cs$^+$. The rubidium–cæsium separation is more difficult and requires the use of methanol (or ethanol) as solvent ; again a little cæsium may be incorporated during the phase change owing to modification of the silver analcite framework to the rubidium analcite one : the method may be useful, in certain circumstances, for purifications.

Hydrogen-ion exchange was observed when solutions of cæsium chloride, tetramethylammonium bromide, or tetraethylammonium iodide were treated with silver analcite :

$$H_2O + MX + xAgA(s) \longrightarrow AgX(s) + HAg_{(x-1)}A_x(s) + MOH.$$
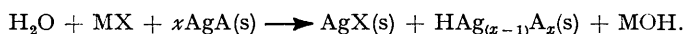
By using the iodide this exchange was followed up to 60% completion. It can only proceed when the crystal acts as a sieve or semipermeable membrane towards the cations in solution and when the ion displaced is precipitated as an insoluble compound.

THE separation of the alkali metals in mixtures of their salts has remained an analytical problem of importance and is at its most difficult for separation of rubidium from cæsium. The cæsium may be precipitated [1] as complexes such as Cs_2PbCl_6, $Cs_3Sb_2Cl_9$, and Cs_2SnCl_6 ; the rubidium complexes are more soluble but the separation is not quantitative. The separation can be effected [2] by precipitating the cæsium with antimony and ferric chloride, to give a complex of approximate composition $4CsCl,4SbCl_3,FeCl_3$. The use of silicotungstic acid as a reagent for the complete separation of these elements has also been developed.[2]

Chromatographic methods have been investigated and quantities less than 1 mg. have

[1] Browning, " Introduction to the Rarer Elements," Wiley, London, 1917; Treadwell and Hall " Analytical Chemistry," Vol. I, Chapman and Hall, London, 1946.
[2] Scott, " Standard Methods of Chemical Analysis," Vol. I, Van Nostrand, New York, 1947.

been separated, by paper chromatography, by Miller and Magee [3] and by Steel.[4] Ion-exchange chromatography was used by Cohn and Kuhn [5] for separation of sodium and potassium and for partial separations of potassium, rubidium, and cæsium, on the H-form of Dowex 50; and Kayas [6] completely separated sodium, potassium, rubidium, and cæsium on Amberlite IR-100.

As no specific reagent has been found for quantitative separation of rubidium from cæsium there is good reason to develop further methods, especially any based on a new principle. Barrer [7] obtained no ion exchange on treating synthetic analcite (Na-form), leucite (K-analcite), or NH_4-analcite with solutions of cæsium chloride at temperatures above 200°. On the other hand exchange occurred with rubidium or potassium salts even at lower temperatures. In the present work, therefore, we have investigated the potentiality of analcite as a quantitative ion-sieve reagent for the separation of cæsium from the other alkali-metal ions. Radioactive ^{137}Cs is an important by-product of uranium fission,[8] so that its purification may be of growing interest. Analcite is only one of a number of materials which it is hoped to investigate for ion-sieve properties of use in cation separations. These materials have now been synthesised rather easily in these laboratories and include the zeolites analcite, phillipsite, harmotome, mordenite, chabazite, and faujasite, together with several new zeolites of barium, lithium, sodium, and rubidium; and also the ion-exchanging felspathoids leucite, nosean, sodalite, and cancrinite.*

EXPERIMENTAL

The analcite ($NaAlSi_2O_6,H_2O$) used in these experiments was part of a sample prepared [10] hydrothermally from a gel of analcite composition under alkaline conditions at 200°. This hydrothermal growth of analcite has been described elsewhere. Silver analcite ($AgAlSi_2O_6,H_2O$) was made by grinding the exchanger together with about ten times its weight of silver nitrate and heating the mixture at 220—230° in an open beaker in an electrically heated furnace. Two such fusions, each lasting about 4 hr., were performed. After each treatment the mixture was cooled and immersed in water to dissolve the salts. The exchanger was then filtered off, washed, and air-dried. The changes in weight of the exchanger between the first and the second fusions were very small compared with those due to the first, so that the two treatments give virtually 100% exchange.

Pure salts of the alkali metals and commercial (B.D.H.) tetra-alkylammonium halides were used. Chloride and iodide ion were estimated by the standard method with silver nitrate solution. Except in experiments reported in Tables 1 and 5, the degree of removal of salt by ion exchange was found by evaporating to dryness the filtrate from the reaction system, and weighing the residue. In all the experiments silver analcite was treated with a solution of one or more salts. Sealed glass tubes were used to contain the reactants in all the experiments except those described in Tables 1 and 5 and in parts of Tables 6, 7, and 10. Since these tubes were revolved in electric ovens the contents were kept thoroughly mixed. For some of the experiments described in Table 10 the reactants were heated under reflux and in the others (Tables 1, 5, 6, and 7) they were in covered beakers on the water-bath. In the last-mentioned method mixing was not so efficient but was probably adequate considering the duration of the treatments.

Optical examination of the exchange products was made with a Leitz research microscope, and X-ray powder photography by means of a Hilger HRX X-ray unit with 9 cm. cameras and Cu-$K\alpha$ radiation.

RESULTS

In a first series of experiments (Table 1) silver analcite was treated on the water bath with solutions of alkali-metal chlorides :

$$MCl_{aq.} + xAgA(s) \rightleftharpoons AgCl(s) + MAg_{(x-1)}A_x(s) \quad . \quad . \quad . \quad . \quad (1)$$
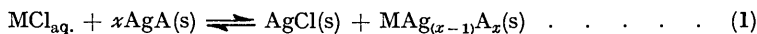
* Some of these results have been summarised by Barrer.[9] Others are as yet unpublished.
[3] Miller and Magee, *J.*, 1951, 3183.
[4] Steel, *Nature*, 1954, **173**, 315.
[5] Cohn and Kuhn, *J. Amer. Chem. Soc.*, 1948, **70**, 1886.
[6] Kayas, *J. Chim. phys.*, 1950, **47**, 1002.
[7] Barrer, *J.*, 1950, 2342.
[8] Cockcroft, *Roy. Inst. Chem. Monograph* No. 1, 1954.
[9] Barrer, Proc. Internat. Symp., " Reactivity of Solids," Gothenburg, 1952, p. 373.
[10] (a) Barrer, *Discuss. Faraday Soc.*, 1949, **5**, 326; (b) Barrer and White, *J.*, 1952, 1561.

where A represents the analcite framework. Because of the low solubility of silver chloride the reaction will proceed from left to right, unless an ion sieve effect supervenes so that the ion M^+ cannot diffuse into the analcite crystals; or unless, as is true of Li^+, the equilibrium very greatly favours the silver-rich form of the zeolite. The extent of reaction reported in Table 1 was

TABLE 1.

	LiCl		NaCl	KCl	RbCl	CsCl	
Salt (mg.)	20·9	20·9	23·4	21·3	20·8	23·0	23·0
Molar ratios AgA/MA	2·3	7·3	1·9	2·1	1·2	2·8	15·6
Time (hr.)	18	16	18	18	18	18	48
Cl removed (%)	74·1	87·2	99·2	99·1	26·2	7·0	36·0
Exchange of analcite (%)	32·2	11·9	52·2	47·2	21·8	—	—

estimated by the change in chloride content in the solution, the aqueous concentrations of alkali chloride being too low for formation of complexes such as $M[AgCl_2]$. For reasons discussed under hydrogen-ion exchange below, although with Cs^+ some Cl^- disappeared from solution this was accompanied, not by removal of Cs^+, but only by hydrolysis of cæsium chloride.

From Table 1 it is seen that extensive but not complete removal of Li^+ occurred under the experimental conditions used, that reaction with sodium and potassium was nearly complete, and that reaction with rubidium was incomplete. As will be seen later, there was no removal of cæsium ion

In a further series of experiments at 110° the blank correction to be applied to the weight of the evaporated filtrate from the reaction system was estimated as follows. A saline solution, or pure water, or water plus silver analcite was heated in glass tubes for various periods, and

TABLE 2. *Blank corrections.*

	Salt (mg.) (x)	Ag analcite (mg.)	Time (hr.)	Residue (mg.)	Residue — x (mg.)
RbCl	35·6	0	19	37·0	1·4
CsCl	46·0	0	16	47·6	1·6
—	0	0	0	1·4	1·4
—	0	0	24	0·8	0·8
—	0	0	24	1·8	1·8
—	0	166·3	24	1·4	1·4

the filtrate then evaporated to dryness to give the residue. The blank correction is this residue less the weight (x) of the original salt in the volume of water (5 ml.) taken. It is seen that this correction for a variety of conditions lies between 1 and 2 mg. In washing out reaction tubes, transference, and filtration, approximately 200 ml. of water were used in each experiment (cf. Tables 1—12).

A series of experiments was next conducted in which aqueous cæsium chloride was treated with silver analcite but the removal of the former was followed, not by estimation of chloride, but by weighing the total evaporated filtrate. The effect of a 5% conversion of cæsium chloride into cæsium hydroxide (cf. Table 5) would mean that this evaporation residue would be only 0·5% (or <0·25 mg.) less in weight than if no such exchange occurred. With the amounts of salt used (Table 3) this would be negligible. The weight of the residue less the weight (x) of cæsium chloride is to be compared with the blank corrections given in Table 2. Clearly

TABLE 3. *Treatment of cæsium chloride with silver analcite.*

CsCl (mg.) (x)	Ag analcite (mg.)	H_2O (ml.)	Time (hr.)	Temp.	Residue (mg.)	Residue — x (mg.)
51·2	149·8	10	24	95°	52·5	1·3
46·1	418·2	2	24	110	47·7	1·6
44·7	259·7	5	16	110	46·2	1·5
33·9	124·6	5	26	110	35·1	1·2

the removal of cæsium from the solution, by incorporation through ion-exchange into the silver analcite, is negligible. In considering Table 3 and the succeeding Tables it should be noted that the following weights of substances are approximately equivalent to each other and to silver analcite, if reaction as in equation (1) is complete : NaCl, 2·4 mg.; KCl, 3 mg.; RbCl, 5 mg.; CsCl, 7 mg.; AgA, 12 mg.

Since complete removal of rubidium chloride by ion exchange was not established in the experiment in Table 1, this was investigated more fully in experiments recorded in Table 4.

TABLE 4.   *Incorporation of rubidium into silver analcite by ion exchange.*

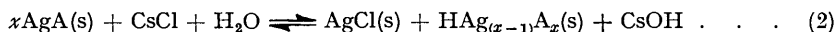| Expt.	RbCl (mg.)	Ag analcite (mg.)	H₂O (ml.)	Time (hr.)	Temp.	Residue (mg.)
a	40·1	165·6	5	24	95°	9·7
b	40·7	251·5	5	24	95	2·6
c	40·6	331·2	5	24	95	1·4
d	40·4	280·5	5	16	95	2·5
e	40·4	277·4	5	41	95	1·6
f	40·4	258·2	5	18	85	4·7
g	39·6	268·8	5	24	110	2·2
h	40·3	252·8	5	27	110	1·6
h	40·3	354·8	2	24	110	2·6
—	35·2	248·8	5	23	110	2·3
—	154·9	1083·1	5	24	110	2·5

After each run, the filtrate was evaporated to dryness and weighed, to give the residue (column 7). Experiments a, b, and c show the effect of increasing the amount of exchanger; d and e the influence of duration of experiment; and b, f, and g the effect of temperature. In the most favourable cases (c, e, and h) the residue is no more than the blank correction, and the removal is therefore quantitative. It is thus evident that complete removal of sodium, potassium, and rubidium from their solutions can be effected, whereas no cæsium ions are removed.

Hydrogen-ion Exchange.—Before consideration of the separation of mixed solutions the important associated phenomenon of hydrogen-ion exchange must be discussed. This is connected with the removal of chloride ion from solutions of cæsium chloride in contact with silver analcite. This removal was studied by heating the silver analcite with cæsium chloride solutions on the water-bath for 18 hr. Successive treatments of four portions of the same analcite sample were given. The results are in Table 5. The formation of silver chloride could be observed visually, and silver chloride was removed between treatments with cold

TABLE 5.   *Removal of Cl⁻ from cæsium chloride solutions.*

CsCl (mg.)	Molar ratio AgA/CsCl	Water (ml.)	Cl⁻ removed (%)	Cumulative H exchange (%) of Ag analcite
107·9	2·8	20	4·7	1·7
107·9	2·8	20	3·9	3·1
27·0	2·8	20	3·1	1·1
27·0	2·8	20	0·62	1·32
47·5	3·2	10	6·4	2·0
47·5	3·2	10	3·0	2·9
47·5	3·2	10	2·3	3·6
47·5	0·76	10	2·2	2·9
47·5	0·76	10	1·4	4·7
47·5	0·76	10	1·1	6·1

concentrated ammonia.* Since the cæsium was not removed (Table 3) but a proportion of the chlorine was, the reaction can be interpreted only as a hydrogen-ion exchange :

$$x\text{AgA(s)} + \text{CsCl} + \text{H}_2\text{O} \rightleftharpoons \text{AgCl(s)} + \text{HAg}_{(x-1)}\text{A}_x\text{(s)} + \text{CsOH} \quad . \quad . \quad . \quad (2)$$

The cæsium ions cannot enter the crystals, and removal of silver ions from the lattice by precipitation as silver chloride is accompanied by an equivalent influx of hydrogen ions from the solution, provided by dissociation of water. The extent of hydrogen-ion exchange of the analcite is given in column 5 of the Table.

The hydrogen-ion exchange recorded in Table 5 is not extensive. However, further experiments were conducted, with aqueous tetramethylammonium bromide and tetraethyl-ammonium iodide and silver analcite. Silver bromide and silver iodide were freely formed, the extent of reaction being promoted by the smaller solubility products of silver bromide and iodide as compared with that of the chloride. It was then shown in the following way that the removal of iodine as silver iodide was not accompanied by entry of NEt₄⁺ into the analcite. The exchange product and silver iodide were filtered off, and the iodine in the filtrate was precipitated, by silver nitrate, as silver iodide, and weighed. Excess of silver was removed as silver chloride, and repeated evaporations to dryness with hydrogen chloride converted all the

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* This treatment never exceeded 15 min. in duration. Treatment for an hour or more with the ammonia gave a loss in weight of the exchanger of 1—2%, after allowance for the silver chloride dissolved. If attributed only to exchange Ag⁺ ⇌ NH₄⁺ this would be <5% exchange. Such a marginal exchange should not affect the reaction between AgA and CsCl according to eqn. 2.

tetraethylammonium salt into the chloride. The tetraethylammonium chloride was finally dried at 120° to remove all or nearly all the excess of hydrochloric acid. The chloride-ion content was then determined as silver chloride : this was equivalent to a little more than the starting weight of tetraethylammonium iodide, but the small difference can be attributed to incomplete removal of hydrochloric acid from the salt. It was inferred that no NEt_4^+ was removed under conditions when more than 50% of the I^- was replaced from the solution, owing to H^+ replacing Ag^+ in the exchanger.

In these treatments of silver analcite with solutions of tetraethylammonium iodide, the exchanging solution developed a pH >10, in accordance with the reaction :

$$x\text{AgA(s)} + NEt_4I + H_2O \longrightarrow AgI(s) + HAg_{(x-1)}A_x(s) + NEt_4 \cdot OH \quad . \quad . \quad (3)$$

The total alkalinity due to two treatments of a sample of silver analcite with aqueous tetra-ethylammonium iodide was measured by titration with $N/100$-hydrochloric acid. Eqn. 3 being assumed valid, the titre corresponded to replacement of 60% of the Ag^+ by H^+ in the analcite. Finally, when silver iodide was extracted from the $HAg_{(x-1)}A_x$ by cold potassium iodide solution, the presumed $HAg_{(x-1)}A_x$ was, as required, demonstrably much lighter than the original silver analcite. Heating tetraethylammonium iodide solutions alone produced a pH of 9·7, but alkalinity so developed was much smaller than that observed after reaction with silver analcite.

Processes of hydrogen-ion exchange due to ion-sieve activity have now been found in these laboratories with analcite, chabazite,[11] faujasite,[12] ultramarine,[13] cancrinite, and sodalite,[10b] and must be regarded as a general phenomenon associated with ion-sieve action. The H-ion exchange forms are the fully crystalline, zeolitic or felspathoid solid " acids." Where two cations are present in solution, of which one but not the other can enter the exchanger crystals, hydrogen-ion exchange will not occur, for at pH $\sim$7 the hydrogen ions cannot compete for intracrystalline sites with the much greater concentration of that dissolved cation which can freely diffuse into the crystals. This point in most important for understanding of the ion-sieve separations of cationic species now to be described.

Separation of Sodium–Cæsium Chloride Mixtures.—Various mixtures of sodium and cæsium chloride and added solvent were treated with silver analcite under the conditions indicated in Table 6. The amount of sodium chloride removed was found by evaporation of the filtrate to dryness and weighing. The solvent was water except in the experiment marked * where methanol was used. The experiments were carried out in sealed tubes, except for that marked †

TABLE 6. *Separation of sodium–cæsium chloride mixtures.*

Ag analcite (mg.)	NaCl (mg.)	CsCl (mg.) (x)	Time (hr.)	Temp.	Solution (ml.)	Residue (mg.)	Residue − x (mg.)
136·6	13·5	103·9	24	110°	5	104·6	0·7
136·9	12·3	34·7	24	110	5	35·7	1·0
334·2	35·7	51·7	28	85	2	52·8	1·1
361·1	50·5	54·9	18	95	10 *	55·7	0·8
388·0	34·2	54·7	25	85	2 †	55·7	1·0

for which a covered beaker was the reaction vessel. The weights in column 8 are no more than the blank corrections in Table 2, and it may be concluded that every set of conditions recorded in Table 6 has led to quantitative removal of sodium from cæsium.

Separations of Potassium–Cæsium Chloride Mixtures.—Experiments designed to separate these mixtures were carried out in the same way as for the sodium–cæsium separation. The results are recorded in Table 7, where * and † have the same significance as previously. In the experiments marked ‡ the chloride contents of the residues were determined and were found to be slightly less than those of the original cæsium chloride. Either some hydrogen-ion exchange occurred with silver (cf. eqn. 2) after all the potassium had entered the crystals, or else a little cæsium was also incorporated. The negative values of the quantity (Residue − x) recorded in column 8 indicate that there is normally a slight removal of cæsium [since the blank deter-minations recorded in Table 2 lead us to expect a small positive value for (Residue − x)]. This phenomenon, encountered also with rubidium–cæsium chloride mixtures (Table 12), but not with sodium–cæsium chloride mixtures (Table 6), is discussed below.

The results recorded in Table 7 thus indicate quantitative removal of potassium from its mixtures with cæsium together with a very small incorporation of Cs^+ into the exchanger.

[11] Barrer and Sammon, unpublished work.
[12] Barrer and Buser, unpublished work.
[13] Barrer and Raitt, *J.*, 1954, 4641.

TABLE 7. *Separation of potassium–cæsium chloride mixtures.*

Ag analcite (mg.)	NaCl (mg.)	CsCl (mg.) (x)	Time (hr.)	Temp.	Solution (ml.)	Residue (mg.)	Residue − x (mg.)
126·5	14·1	35·4	24	110°	5	35·3	−0·1
126·7	14·0	37·0	24	110	5	36·2 ‡	−0·8
142·7	16·6	—	24	110	5	1·8	+1·8
144·5	12·5	—	4	110	5	1·4	+1·4
146·1	15·2	34·5	24	110	5	34·0 ‡	−0·5
274·0	51·3	68·1	18	95	10 *	67·1 ‡	−1·0
420·2	15·6	36·2	24	110	5	36·2	0·0
442·2	34·9	43·6	24	85	2	43·4	−0·2
499·9	38·6	54·8	24	85	2 †	54·0 ‡	−0·8

Separation of Rubidium–Cæsium Chloride Mixtures.—Mixtures of rubidium and potassium chloride with water (5 ml.) were first treated at 110° for 24 hr. in sealed tubes with varying proportions of silver analcite. The chlorides in the filtrate were determined as before, by evaporation to dryness and weighing (Table 8, column 5). An experiment without silver analcite gave a blank correction of 1·6 mg. (cf. Table 2), which was then subtracted from each residue (Table 8, column 6). Assuming negligible removal of cæsium chloride permits computation of the amount of rubidium chloride removed (column 7). The degree of separation increases as the amount of silver analcite increases up to a limiting figure of about 490 mg. However, quantitative separation was not achieved under the conditions reported in Table 8.

In a further study of this separation the rubidium and cæsium in the filtrate after reaction in sealed tubes at 110° were determined spectrochemically (we are indebted to Dr. R. L. Mitchell, of the Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen, for the spectrochemical determinations). Results are shown in Table 9. Experiments marked *a* (column 6) show the effect of varying the volume of water; and those marked *b* the effect of changing the proportions of the two salts. Fluctuations in sign in column 5 indicate only that the spectrochemical method is not very accurate, but the results support the view that only rubidium is removed from solution. Smaller volumes of solvent give better separations, and these are also improved if rubidium chloride is present in equivalent or in greater quantity than cæsium chloride.

TABLE 8. *Partial separations of rubidium–cæsium chloride : varying Ag analcite proportions.*

Ag analcite (mg.)	RbCl (mg.)	CsCl (mg.)	Total salt (mg.)	Residue (mg.)	Residue − corrn.	RbCl removed (%)
139·0	23·0	37·4	60·4	54·6	53·0	32
257·3	24·3	33·6	57·9	48·5	46·9	45
362·8	23·9	36·8	60·7	44·7	43·1	73
490·0	24·6	40·1	64·7	44·8	43·2	87
498·9	24·3	34·3	58·6	39·2	37·6	86
622·4	24·8	34·7	59·5	40·0	38·4	85

TABLE 9. *Partial separations of rubidium–cæsium chloride : varying proportions of solvent and of Rb : Cs ratio.*

Ag analcite (mg.)	RbCl (mg.)		CsCl (mg.)		H₂O (ml.)	Time (hr.)
	Initial	Removed	Initial	Removed		
0	23·3	0·0	0	−2·5	5	44
0	0	0·0	34·6	+0·4	5	14
544·8	24·6	11·2	39·3	−1·2	10 *ᵃ*	24
484·0	23·8	13·2	36·8	+0·7	5 *ᵃ*	24
531·6	23·4	19·2	33·8 *ᵇ*	+1·5	2 *ᵃ*	24
494·0	24·2	21·7	16·3 *ᵇ*	+0·5	5	24
471·9	13·3	7·6	32·8 *ᵇ*	−0·1	5	24
471·5	23·7	18·8	33·2	−1·0	5	12
503·0	23·8	17·4	39·7	+0·4	5	48

Since the removal of rubidium chloride from cæsium chloride was still not quantitative, experiments were conducted with solvents other than water. These were carried out in sealed tubes, with the exception of those in Table 10 marked * in which the solvent was boiled under reflux sufficiently vigorously to keep the exchanger in suspension.

The blank correction was taken as 1·5 mg., and the results in the bottom two rows of Table 10 indicate that quantitative separations of Rb⁺ and Cs⁺ can be obtained in closed systems by using organic solvents, but not under reflux conditions. Evidently organic solvents are better than water in effecting this separation by the ion-sieve method. In order to compare the effectiveness of water and methanol a series of experiments was conducted at 110°, each for 24 hr.

TABLE 10. *Separations of rubidium–cæsium chloride : non-aqueous solvents.*

Ag analcite (mg.)	491·5	544·3	503·5	536·4	534·8	285·5	453·9
RbCl (mg.)	24·1	23·2	23·9	24·5	23·7	24·7	23·4
CsCl (mg.)	32·7	37·5	34·5	37·7	33·1	36·4	33·8
Solvent	MeOH	MeOH	EtOH	EtOH	EtOH *	Pr^{n}OH *	Pr^{n}OH *
(ml.)	5	5	2	2	5	5	5
Time (hr.)	120	24	24	24	24	21	24
Temp.	85°	110°	110°	110°	78°	97°	97°
Residue (mg.)	34·2	39·0	36·7	39·5	50·0	59·7	48·4
Residue − corrn. (mg.)	32·7	37·5	35·2	38·0	48·5	58·2	46·9
RbCl removed (%) ...	100	100	97	99	35	12	44

TABLE 11. *Rubidium–cæsium chloride separation : comparison of water and methanol as solvent.*

Ag analcite (mg.)	RbCl (mg.)	CsCl (mg.)	Solvent (ml.)	Residue (mg.)	Residue − corrn. (mg.)	RbCl removed (%)
Water						
552·3	23·3	38·5	1	43·5	42·0	85
547·8	24·1	34·1	2	40·4	38·9	80
550·9	22·9	32·8	5	40·5	39·0	73
Methanol						
517·4	24·5	40·1	1	42·4	41·9	93
535·8	23·7	35·3	2	38·8	38·3	87
494·8	24·0	34·5	5	38·4	37·9	86

under comparable conditions. The results presented in Table 11 show that more complete separation still occurs when methanol is solvent. In these experiments with water as solvent the ordinary distilled water was used for washing out and the blank correction was taken, as before, to be 1·5 mg., but when methanol was the solvent, de-ionised water was used, with the lower blank correction of 0·5 mg. The effectiveness of the separation with methanol is not the same in the experiments recorded in Tables 10 and 11. Since different batches of silver analcite had been employed it was thought possible that the method of preparation of the silver analcite could influence the results. Three different, but similarly prepared, batches of this ion-sieve reagent were then used, and it was demonstrated (Table 12) that differences in completeness of the separation did arise, when methanol was the solvent. The recorded removal of >100% of rubidium chloride at the bottom of column 5 means that some cæsium chloride had also been removed in this case. This behaviour is discussed below.

TABLE 12. *Rubidium–cæsium chloride separation : effect of different preparations of Ag analcite.*

Ag analcite (mg.)	Batch	RbCl (mg.)	CsCl (mg.)	RbCl removed (%)
494·8	A	24·0	34·5	86
491·5	B	24·1	32·7	100
507·0	C	24·1	35·6	106

One may conclude that conditions can be realised for complete removal of Rb$^+$ from Cs$^+$ by using silver analcite as an ion sieve, but that these conditions are more stringent than are those required for the separations of Na$^+$ and K$^+$ from Cs$^+$.

X-Ray Examination of the Exchanger.—In order to obtain information regarding the limited removal of cæsium chloride [Table 12 (Ag analcite C) and Table 7] in presence of rubidium or potassium chloride, but not in presence of sodium chloride, or in absence of other electrolyte, various cationic forms of the exchanger were subjected to X-ray powder photography. Sodium analcite of refractive index ∼1·486, regenerated from silver analcite, gave an X-ray pattern with the same spacings and intensities as natural analcite; and a pattern with practically identical spacings but different intensities was also observed for silver analcite. For a product Na$_{0·4}$Ag$_{0·6}$AlSi$_2$O$_6$,H$_2$O the pattern was in spacings the same as, and in intensity midway between, the patterns of the pure sodium and the pure sodium form respectively. Moreover, all these mixed crystals had a single refractive index of ∼1·52. It is thus considered that no appreciable lattice change occurs during the Na ⇌ Ag exchange in analcite, and that the end members form a continuous series of solid solutions.

The X-ray diffraction pattern of potassium analcite (leucite) showed definite changes as compared with that of silver (or sodium) analcite. In an analcite of cationic composition K : Ag = 25 : 75 the diffraction pattern was very similar to that of silver analcite, but some of the

stronger lines of the leucite pattern were also superposed. Optical examination showed that crystals of two refractive indices were present, those of higher index being predominant. In an analcite of cationic composition $K : Ag = 50 : 50$, the X-ray pattern was similar to that obtained by superposing the separate patterns of leucite and of silver analcite. One may conclude from the optical and X-ray evidence that there is limited solid solubility of the pure end members potassium and silver analcite.

Finally, pure rubidium analcite gave a pattern with differences from those of the other pure cationic forms of the exchanger (Na, Ag, or K). The refractive index was $\sim$1·526. An analcite of cationic composition $Rb : Ag = 45 : 55$ was then investigated. The sample was made up of a fine powder in admixture with unfractured crystallites of normal size. The diffraction pattern of the fine powder was similar to that of rubidium analcite, and the refractive index was $<$1·53. The pattern of the coarse fraction containing some fine powder was similar to that of silver analcite, with superposition of some rubidium analcite lines. The majority of the crystals had refractive index $>$1·54. As with sodium and silver analcite, it is thus evident that rubidium and silver analcites show limited mutual solid solubility. These results are comparable with those of Barrer and his co-workers.[7, 14, 15]

DISCUSSION

Where limited solid solubility of the end members of an exchanging pair occurs, it has already been shown that hysteresis and nucleation phenomena occur.[15] Phase changes involving even minor rearrangements of the structural network often result in a high degree of ionic or molecular mobility during the process;[16] this enhanced mobility is, for example, the basis of the Hahn emanation method of following solid-state reactions. It therefore seems likely that a little cæsium can sometimes become incorporated in the new analcite phase during the phase transitions Ag-rich $\longrightarrow$ K-rich, or Rb-rich, analcites. On the other hand, in the Na^+–Ag^+ exchange where there is continuous solid solubility without any phase change, no incorporation of cæsium can occur. We consider this to be the explanation of the limited uptake of cæsium into silver analcite when exchanging with aqueous rubidium or potassium chloride, but not when exchanging with aqueous sodium chloride, or when dissolved alone.

The presence of even a small amount of cæsium in the analcitic lattices may, moreover, increase the difficulty of the final stages of exchange (*e.g.*, that of Rb^+ diffusing into the new Rb-rich phase) by blocking some of the diffusion paths along which the Rb^+ and residual Ag^+ must migrate. Such an effect will be more apparent the larger the migrating ion, and may then have a bearing upon the greater ease of effecting sodium–cæsium and potassium–cæsium separations compared with that of rubidium–cæsium.

The excellent sodium–cæsium separation, and the equally quantitative potassium–cæsium separation, leave only cæsium in the solution, and are readily accomplished. Methanol should be used for the rubidium–cæsium separation, and with different preparations of silver analcite three types of behaviour were observed : incomplete removal of rubidium chloride; complete removal of rubidium chloride; and complete removal of rubidium chloride with removal also of a little cæsium chloride. If a negligible amount of cæsium is removed in the first two cases, then rubidium may be freed from cæsium, since the rubidium which enters the silver analcite may be displaced again by ion exchange. In the third case, cæsium may be freed from rubidium, just as it may be freed from sodium and potassium. Thus if silver analcite could be made under such closely defined conditions that the extent of its reaction with rubidium chloride in admixture with cæsium chloride did not vary from sample to sample, then there would be the possibility of one of these two applications.

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[14] Barrer and Hinds, *J.*, 1953, 1879.
[15] Barrer and McCallum, *J.*, 1953, 4305.
[16] Cf. Buerger, *Amer. Miner.*, 1948, **33**, 101.