259. *Cation Exchange with a Synthetic Phenolsulphonate Resin. Part I. Equilibria with Univalent Cations.*

By T. R. E. KRESSMAN and J. A. KITCHENER.

A study has been made of the factors determining the position of equilibrium reached when a cation-exchange resin is placed in aqueous solutions of univalent metal salts. The sulphonate groups in the resin (the structure of which is discussed) are the only exchange groups operating below pH 8.

The equilibria are independent of concentration and largely of the anion. Exceptions which occur with Tl^+ and H^+ can be explained by incomplete dissociation. The equilibria are approximately represented by the law of mass action, and the equilibrium constants for Li^+, H^+, Na^+, K^+, Rb^+, and Cs^+ are a function of the hydrated ionic size expressed as the $a°$ parameter of the Debye–Hückel theory.

The temperature coefficient of the K^+–H^+ system leads to the value of 1·95 kcals./g.-mol. for the heat of exchange; the free energy of exchange is 0·54 kcal./g.-mol. at 25°. The relatively large difference between these two values is interpreted as indicating that a change of hydration occurs when the cation passes from the solution to the solid phase.

Physical adsorption (as distinct from exchange) does not occur with highly dissociated neutral salts and acids, but becomes significant with chloroacetic acid.

SEVERAL approaches have been made to the physical chemistry of equilibrium cation exchange. Rothmund and Kornfeld (*Z. anorg. Chem.*, 1918, **103**, 129; 1919, **108**, 215) developed the empirical equation

$$(c_1/c_2)_{\text{solid}} = K(c_1/c_2)^p_{\text{soln.}} \qquad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where c_1 and c_2 are the concentrations at equilibrium of the cations 1 and 2, and K and p are constants. Although this represents much of the data, it has no theoretical basis and has proved of little value in the development of the subject.

Other workers (*e.g.*, Ungerer, *Kolloid Z.*, 1925, **36**, 228; Renold, *Kolloid-Beih.*, 1935, **43**, 1) have represented the uptake of a particular ion A^+ from its solutions by a form of Freundlich adsorption isotherm. This view is equally empirical and neglects the behaviour of the other ion B^+. The two ions must play an equally important and symmetrical rôle in determining the final position of equilibrium.

A more acceptable treatment of ion exchange regarded as an adsorption process has been given by Boyd, Schubert, and Adamson (*J. Amer. Chem. Soc.*, 1947, **69**, 2818). This regards the cations A and B as competing for fixed separate sites in the solid, which are sufficiently far apart for the affinity per ion at every site to be the same and independent of the surrounding sites. Consequently, the system is formally analogous to Langmuir adsorption of a binary gas mixture, for which the adsorption isotherm is

$$(x/m)_{A^+} = kb_1[A^+]/(1 + b_1[A^+] + b_2[B^+]) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $(x/m)_{A^+}$ is the amount of A^+ adsorbed per unit weight of adsorbent, $[A^+]$ and $[B^+]$ are the respective equilibrium concentrations of A^+ and B^+ in solution; and k, b_1, and b_2 are constants.

Yet another point of view regards ion exchange as a Donnan membrane equilibrium, since one set of ions—those of the solid—are prevented from diffusing by the nature of the material, while the other three ions in the system, A^+, B^+, and X^-, can diffuse freely. The equations of the Donnan equilibrium may, therefore, be applied immediately (Baumann and Eichhorn, *J. Amer. Chem. Soc.*, 1947, **69**, 2832).

The laws governing the equilibria in ion exchange can be treated equally well without recourse to any specific molecular theory by applying simple thermodynamics, *i.e.*, the exact form of the law of mass action, to the fundamental exchange equation :

$$R^-A^+ + B^+X^-, \text{aq.} \rightleftharpoons R^-B^+ + A^+X^-, \text{aq.} \quad . \quad . \quad . \quad . \quad (3)$$
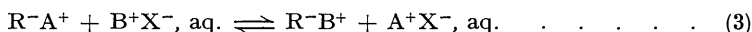
which yields the equation :

$$a_{RB}a_{AX}/a_{RA}a_{BX} = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It then remains to find expressions in practical terms for the various activities in the two phases. The relative activities of the two cations in the solid will be in the ratio of their concentrations provided the ionic sites in the solid are sufficiently far apart not to interact appreciably.

More generally, the activities could be replaced by products of concentration and activity coefficient. Because of the lack of data, however, most authors have used concentrations instead of activities in solution and have ignored entirely the possibility of non-ideality in the solid phase.

PRELIMINARY CONSIDERATIONS.

Reversibility of the Equilibrium.—Renold (*loc. cit.*), using an aluminosilicate exchanger, found that different equilibrium positions were reached when approached from both sides, the tendency being to retain in the exchanger the ion with which it was originally saturated. Walton (*Trans. Illinois State Acad. Sci.*, 1941, **34**, No. 2, 124) showed that the graphs for the distribution ratios of calcium and sodium ions between a solution and a sulphonated-coal exchanger did not coincide when the equilibrium was approached from different sides. When the same sample of exchanger was again completely converted into the one form and the distribution ratios again determined, the graph lay between the original graphs. He concluded from this that the characteristics of the exchanger are conditioned by the ion with which it was last saturated and that after a number of conversions of the exchanger from one ion into the other it approaches a truly reversible state.

Experiments described later indicate that the equilibria studied in the present work (at least with univalent cations) are completely reversible.

Influence of the Anion.—Ungerer (*Z. Pflanz. Dung.*, 1930, **18**, *A*, 342; 1932, **23**, *A*, 353) in his study of the exchange of calcium aluminosilicate with the alkali-metal salts of a large number of anions, observed that the equilibrium position was a function of the anion. This was explained as a dehydration of the dissolved cations by the anions, with a resulting increased affinity of the exchanger for the smaller cation so produced. This, however, ignores the presence of the calcium ion and, furthermore, there is no independent evidence that the hydration of a cation in solution is in any way affected by that of the anion.

Ungerer's results are not in accordance with those of other workers. Thus, Patton and Ferguson (*Canadian J. Res.*, 1937, B, **15**, 103) found the same equilibrium position was obtained with a gel-type aluminosilicate exchanger in the sodium form and solutions of calcium nitrate and acetate; a slightly different one occurred with chloride. Ramann and Spengel (*Z. anorg. Chem.*, 1916, **95**, 115) observed the same equilibrium with chlorides, nitrates, and sulphates in the NH_4^+–Na^+, NH_4^+–K^+, and Na^+–K^+ systems.

The results of the present study (see below) also are not in keeping with those of Ungerer, but confirm those of Patton and Ferguson and of Ramann and Spengel. In addition, it will be shown in Part II (following paper) that the effect of the anion depends largely upon the valency of the cation involved.

Choice of Ion-exchanger.—Many discrepancies appear in the literature of ion exchange, some of which have undoubtedly arisen because different workers have used different ion-exchange materials. The results obtained are greatly dependent upon the nature of the exchanger (Melsted and Bray, *Soil Sci.*, 1947, **63**, 209; Alexander, " Colloid Chemistry," VI, 1946, p. 201), a fact which has not been sufficiently recognised. It is accordingly important that the nature of the exchanger used should be defined as precisely as possible.

The modern synthetic resinous ion exchangers are, therefore, particularly suitable for fundamental studies, as a variety of structures can be built up and, in many, all the groups are freely accessible for exchange (in contrast to certain zeolites, cf. Patton and Ferguson, *loc. cit.*). In addition, an adequate knowledge of the molecular structure of the resin can generally be deduced.

The work described in this paper is concerned with the conditions prevailing when a synthetic resinous cation exchanger containing nuclear sulphonate groups is allowed to come to equilibrium with solutions of salts of univalent cations.

The resin is a cross-linked condensation product of formaldehyde with phenol and sodium phenolsulphonate (see Experimental), and the structure suggested by Houwink (*Trans. Faraday Soc.*, 1936, **32**, 125) can be accepted as its basic skeleton, although he has shown (" Physikalische Eigenschaften und Feinbau von Natur- und Kunstharzen," Leipzig, 1934) that no regular pattern exists in the molecule. However, if an attempt is made to prepare the sulphonate resin without the addition of the free phenol, no gel is obtained but merely a sticky semi-crystalline mass. It is therefore concluded that phenolsulphonic acid will not form cross links with formaldehyde in alkaline solution, only a low-molecular-weight lineate being formed. (This occurs only in alkaline solution : in acid solution an insoluble cross-linked product is obtained, a large number of $-CH_2-$ bridges being formed at the expense of the $-SO_3H$ groups, some of which are ejected as sulphuric acid.) Hence the three-dimensional cross links are evidently formed through the unsulphonated nuclei, the sulphonated nuclei being linked with two $-CH_2-$ bridges only. Houwink's diagrammatic structure must, therefore, be modified and the molecule will be of the form of Fig. 1.

Fig. 1.
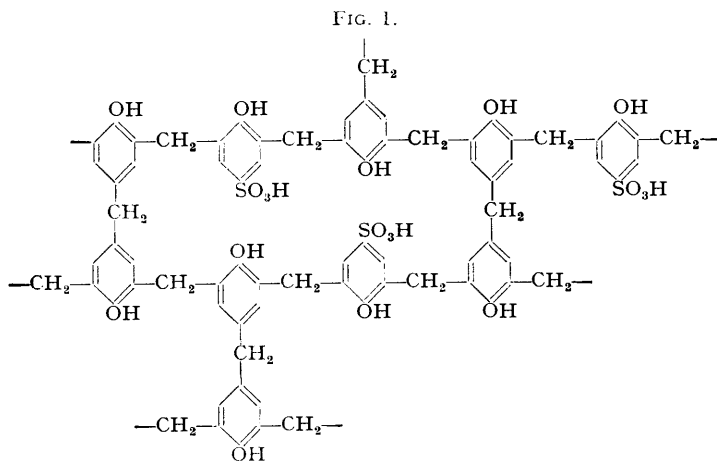
By measuring the degree of sulphonation of the phenol during the preparation of the resin, the relative number of sulphonated and unsulphonated nuclei was found to be 5 : 7. The

monomeric weight, calculated from this ratio, is 1714. This weight contains five sulphonate groups and hence the equivalent weight of the resin, considered as a sulphonic acid, is 343. A direct determination of the total number of exchangeable hydrogen ions gave the value of 350. This same figure was obtained whatever the concentration of the salt solution and whatever the particle size of the resin grains. It was also independent of the salt used, whatever the anion and whatever the valency of the cation (at least up to a valency of 4), so long as the pH of the salt solution was below about 8. It is, therefore, considered that the figure truly represents the total number of exchangeable hydrogen ions attached to sulphonate groups.

A comparison of the measured equivalent weight with that calculated from the probable structure indicates that 97·5% of the calculated sulphonate groups are free for ion exchange. An independent check of this figure, by determination of the sulphur content of the resin by a combustion method, gave the figure 95·6%. The sulphur not in the form of sulphonate groups is probably present as sulphone links, while a small amount may exist as ester links ($-SO_3 \cdot CH_2^-$).

The phenolic hydroxyl group, being weakly acidic, does not exchange ions except above about pH 10 and, since the whole of the present work is concerned with equilibria below pH 8, this group never comes into play, the SO_3^- group being the only active group operating.

<div align="center">EXPERIMENTAL.</div>

Materials used.—The ion exchanger was prepared as follows. 1600 G. of phenol and 1600 g. of 98% sulphuric acid were mixed together and heated on a water-bath at 95° for 30 minutes. Sodium hydroxide solution (20%) was then added to neutralise the mixture, about 3500 ml. being required; a further 800 ml. were added as catalyst. To the solution were added 1600 g. of phenol and 1760 g. of paraform, together with 100 g. of sodium chloride which, in an unknown manner, renders the final resin much more easily granulated. The reaction mixture was evaporated until a gel was obtained, which was dried at 100° for 12 hours and then heated to 150° for 15 hours.

The resin was crushed to −10 mesh and soaked in water for about 15 minutes. The wet resin was then introduced into a glass tube of suitable size, in such a manner that no air bubbles were trapped between the particles. Hydrochloric acid (*ca.* 2N) was allowed to flow downwards through the column of resin at about 100 ml. per minute until the acidity of the effluent was the same as that of the influent. The resin was then washed with distilled water to remove excess of acid and the remains of a small amount of low-molecular-weight side products. To minimise any possible changes in the physical nature of the resin, it was air-dried at room temperature to a residual moisture content of about 25% only. The moisture content was accurately determined by drying a small sample to constant weight at 120° and was allowed for when weighing out the resin for the equilibrium measurements. The air-dried product was graded by sieving and stored in tightly stoppered bottles.

The non-volatile impurities in the hydrogen resin so prepared were determined by burning a sample in air : an ash of only 0·07% was obtained.

Stability of the Resin.—In the form of its metal salts the resin is quite stable, but in the presence of moisture the hydrogen form undergoes slow hydrolysis, and any but a freshly prepared sample contains traces of sulphuric acid. This effect is negligible for ordinary practical purposes, but it was considered desirable to eliminate it altogether for accurate work and, for this reason, the stable salt forms were always used as the starting points for those equilibrium measurements involving the hydrogen ion. This hydrolysis has been observed also in other synthetic organic exchangers containing nuclear sulphonic acid groups, including sulphonated coal, and the fact must be borne in mind when interpreting the results of previous workers.

Preparation of the Metal Forms of the Resin from the Hydrogen Form.—This was carried out by a method similar to that used for converting the crude resin into the hydrogen form. A glass tube of sufficient size to hold the desired quantity of resin was used, and a solution of a convenient neutral salt of the appropriate cation was allowed to flow over it until no more acid appeared in the effluent. The excess salt was washed off with water, and the resin air-dried to a residual moisture content of about 25%. The moisture content was determined as above.

Measurement of the Equivalent Weight.—The equivalent weight of the hydrogen resin considered as a sulphonic acid was measured by titrating the hydrogen ion displaced from a sample of the resin by an excess of sodium chloride, afterwards drying and weighing the sample.

About 6—8 g. of the air-dried resin were soaked in water and introduced into a small tube to form a column about 14 cm. high, and free from entrapped air bubbles. Any traces of acid were washed away by passing water downwards through the column. An approximately 0·25N-sodium chloride solution was then passed through the resin at a rate of 4—6 drops per second, and the effluent collected in approximately 100-ml. lots, which were titrated with N-sodium hydroxide. When no more acidity came away, the total volume of sodium hydroxide was noted, which represents the total replaceable hydrogen ions in the quantity of resin taken. No further acid was liberated when the resin was kept in contact with the sodium chloride solution overnight.

The resulting sodium resin was washed with water until free from chloride and dried at 120° to constant weight.

The methods used for determining the equivalent weights of the metal forms of the resin differed according to the particular metal ion in the resin. That of the ammonium form was measured by boiling an accurately weighed sample with sodium hydroxide solution and distilling the ammonia into standard acid. Ignition in oxygen of a weighed quantity of any of the alkaline-earth forms yielded a residue consisting of the pure sulphate, which was weighed. The tendency always, on ignition, is to form the pure sulphate; if, however, this is unstable then the residue was treated accordingly. Thus,

4 K

the aluminium form yielded the pure oxide, but certain of the forms containing other cations yielded residues of indefinite composition, which were then dissolved in acid and the cation determined by a standard procedure.

Ignition of the alkali-metal forms yielded the sulphates which, however, readily fused round the remaining resin and prevented complete combustion. The method employed here, therefore, was to convert the resin into the hydrogen form with an excess of hydrochloric acid, using the apparatus just described, and wash off the excess acid with water. The equivalent weight of the hydrogen form was then measured as previously described.

Preliminary Measurements of Velocity of Attainment of Equilibrium.—In order to determine how long was needed for equilibrium to be reached between a salt solution and the resin, some preliminary experiments were carried out of the rate of exchange in closed bottles with shaking at $25° \pm 0.1°$.

The system H-resin–KCl was chosen, and 10 milliequivs. of resin and 100 ml. of 0.1N-potassium chloride were used. (The use of the slightly unstable hydrogen form was justified here, since high accuracy was not required.) The resin was weighed into a 200-ml. stoppered bottle, and the potassium chloride introduced quickly by means of a pipette with a wide jet. Both the bottle and the chloride solution had previously been kept in a thermostat at 25°. The bottle was stoppered and shaken in the thermostat for 1 minute; the solution was then quickly decanted from the resin, and the acid produced as a result of the exchange was titrated in an aliquot portion of the solution with 0.1N-sodium hydroxide. This was repeated for different times up to 30 minutes. The final equilibrium value was obtained by shaking for 30 minutes and then allowing the system to stand at 25° for 3 days.

It was found that 90% of the equilibrium amount of acid was formed within 2.5 minutes with $-10 + 20$-mesh resin particles, and within 0.2 minute with $-44 + 60$-mesh particles. In each case 99% was obtained within 30 minutes (cf. Nachod and Wood, *J. Amer. Chem. Soc.*, 1944, **66**, 1380; Bauman, *Ind. Eng. Chem.*, 1946, **38**, 46). In the subsequent equilibrium measurements, periods many times longer than this were allowed, to ensure complete equilibrium. Large organic cations exchanged much more slowly and, here, duplicate samples of resin plus solution were left for different periods of time until identical results indicated that equilibrium had been reached.

Equilibrium Measurements.—A similar technique was used for the equilibrium determinations proper. Salt forms of the resin were always used because of the instability of the hydrogen resin. Generally NH_4^+ was used as the reference ion, for convenience of accurate analysis. The resin and the appropriate salt solution were introduced into a stoppered bottle in a thermostat at 25° and shaken manually at intervals during several hours. It was then left in the thermostat for several (usually 3—7) days. The solution was decanted from the resin, and an aliquot portion analysed for one of the ions involved in the exchange. Together with the number of exchangeable ions in the resin, and the quantity and concentration of the salt solution, sufficient data are available to calculate the equilibrium concentrations of both ions in both phases.

The same equilibrium position exactly was reached with all particle sizes of resin between 10 and 60 mesh, indicating that all the sulphonate groups are equally accessible to the exchanging cations.

RESULTS.

Reversibility.—That the equilibria studied in the present work (at least with univalent cations) are completely reversible was demonstrated in an indirect manner by allowing various volumes of hydrochloric acid of known concentrations to come to equilibrium with known weights of potassium resin. The curve for the distribution of the ions between the resin and the solution was then plotted. Another series of equilibrium measurements was made by allowing samples of potassium resin to come to equilibrium with the acid and, when equilibrium had been attained, it was pushed back by the addition of known amounts of potassium chloride (*i.e.*, one of the products of the reaction) of the same concentration as the original hydrochloric acid, and the system again allowed to come to equilibrium. The distribution of the ions between the two phases was plotted on the same axes as before. Fig. 2 shows that the points lie exactly on the curve obtained without the addition of potassium chloride.

Effect of Concentration.—Fig. 2 shows also that the same equilibrium position is attained whatever the concentration of the ions in solution. This agrees with the findings of other workers for univalent cations on aluminosilicate exchangers (*e.g.*, Wiegner and Muller, *Z. Pflanz. Dung.*, 1929, **14**, *A*, 327; Ivanov and Gapon, *J. Physical Chem., Russia*, 1941, **15**, 659). This is observed only with cations of equal valency : dilution of a system containing ions of different valency causes the ion of higher valency to pass into the solid phase. This behaviour is an attribute of the two-phase system involved, as has been shown mathematically by Ivanov and Gapon (*loc. cit.*).

Influence of the Anion.—The NH_4^+–K^+ system gave identical positions of equilibrium with the anions : Cl', NO_3', SO_4'', ClO_3', H_2PO_4', $Fe(CN)_6'''$, $Fe(CN)_6''''$, $H \cdot CO_2'$, $C_6H_5 \cdot SO_3'$, I', $(COO)_2''$. The NH_4^+–Tl^+ system, on the other hand, gave a different position of equilibrium in nitrate solution from that in sulphate : the equilibrium constants are 12.7 and 9.2 respectively (see Fig. 4 and table). Thallous salts are well known to show incomplete dissociation (see, *e.g.*, Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," 1943, p. 396) and, in general, bivalent anions lead to a lower dissociation than univalent. This fact provides a satisfactory explanation of the results.

It is now recognised that many of the simple alkali-metal salts also are not entirely dissociated in solution (see, *e.g.*, Harned and Owen, *op. cit.*, pp. 145 *et seq.*); but the dissociation is sufficiently high and that of ammonium salts is sufficiently similar to that of the corresponding alkali-metal salts, that no significant difference is observed in the position of equilibrium as the anion is changed.
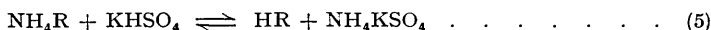
An extreme effect of low salt dissociation will be dealt with in detail in Part II, where it will be shown that scarcely any mercuric ion will pass into the solid phase from a solution of mercuric chloride.

FIG. 2.
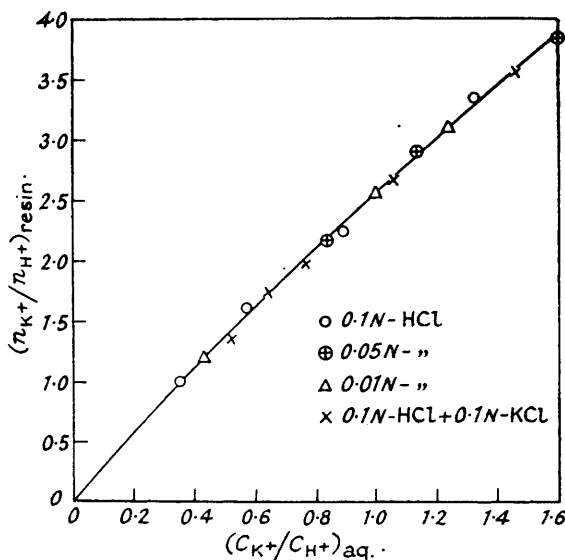
Certain apparent exceptions in the NH_4^+–K^+ system should be mentioned. The following anions resulted in slightly different positions of equilibrium: $C_6H_5 \cdot CO_2'$, $CH_3 \cdot CO_2'$, HSO_4', hydrogen phthalate. With the exception of the last two there is no obvious reason for the different behaviour of these anions. The similarity in structure of benzoate to benzenesulphonate ion (which latter leads to a normal equilibrium), and of acetate to formate (which also behaves normally), would seem to preclude differences in dissociation of the salts.

It is likely that an exchange of the hydrogen ion also occurs to a certain extent with hydrogen phthalate, thus confusing the issue. This is certainly so with the HSO_4' ion, where a considerable exchange of hydrogen ion occurs:

$$NH_4R + KHSO_4 \rightleftharpoons HR + NH_4KSO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in addition to:

$$NH_4R + KHSO_4 \rightleftharpoons KR + NH_4HSO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$
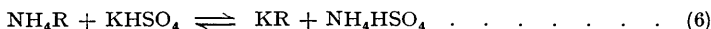
Equilibria among Univalent Cations.—To compare the affinity of the resin for univalent cations, equilibrium measurements were carried out with the ammonium form of the resin and solutions of the appropriate metal salt. (The hydrogen form was avoided for the reason already mentioned.) The chlorides of the alkali metals, the nitrate of silver, and the nitrate and sulphate of thallium were used.

In Fig. 3 the equivalent percentage of the univalent ion in the resin phase is plotted against that in the aqueous phase. The equivalent percentage is defined as follows:

$$\text{Equivalent \% } M^+ \text{ in resin phase} = \frac{100 \text{ (meq. MR)}}{\text{Total meq. resin}} = \frac{100 \text{ (meq. MR)}}{\text{meq. MR} + \text{meq. } NH_4R} \quad . \quad . \quad . \quad (7)$$

$$\text{Equivalent \% } M^+ \text{ in aqueous phase} = \frac{100 \text{ (meq. } M^+)}{\text{Total meq. salt}} = \frac{100 \text{ (meq. } M^+)}{\text{meq. } M^+ + \text{meq. } NH_4^+} \quad . \quad . \quad . \quad (8)$$

This method of plotting has the advantage that the equilibrium positions of all ions, whatever the valency, can be plotted on the same axes, thus giving a direct comparison of their affinities.
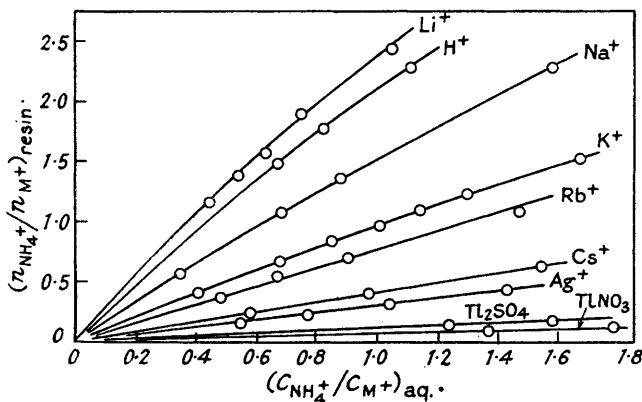
The method is less suitable, however, when it is desired to obtain a quantitative correlation between the equilibrium positions within a series of ions of the same valency. For this purpose
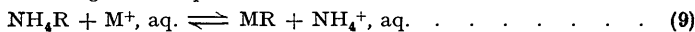
Fig. 3.
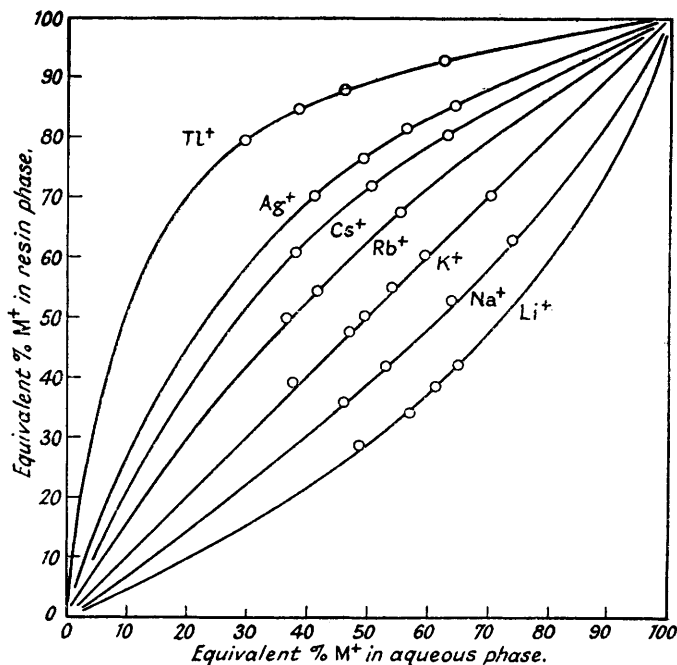
O *Experimental points.*
— *Theoretical curves calculated from the* K *values obtained from Fig. 4.*

Fig. 4.

it is better to use the mass-action functions, from which the equilibrium constant can be calculated. For the equilibria involving the NH_4^+ ion and univalent cations

$$NH_4R + M^+, aq. \rightleftharpoons MR + NH_4^+, aq. \quad . \quad . \quad . \quad . \quad . \quad . \quad \textbf{(9)}$$

the stoicheiometric equilibrium constant is given by

$$K = \frac{C_{M^+, res.} \cdot C_{NH_4^+, aq.}}{C_{NH_4^+, res.} \cdot C_{M^+, aq.}} = \left(\frac{C_{NH_4^+}}{C_{M^+}}\right)_{aq.} \bigg/ \left(\frac{C_{NH_4^+}}{C_{M^+}}\right)_{res.} \quad . \quad . \quad . \quad . \quad . \quad \textbf{(10)}$$

and will be obtained from the graph of

$$(C_{NH_4^+}/C_{M^+})_{aq.} \text{ against } (C_{NH_4^+}/C_{M^+})_{res.}$$

as plotted in Fig. 4. (The concentration of each cation in the solid phase is expressed as the number of equivs. of the cation to the total number of equivs. of cations in that phase. It is expressed in the aqueous phase as equivs. per l.)

Approximately straight lines are obtained, although a significant curvature does exist which appears to decrease with increasing affinity between the resin and the ion, *i.e.*, decreasing from

lithium to thallium. However, the curves cover a progressively smaller range of composition of the resin phase in this order, and, if they were all extended to cover the same range, the departure from linearity would probably be of the same relative magnitude in each case.

FIG. 5.
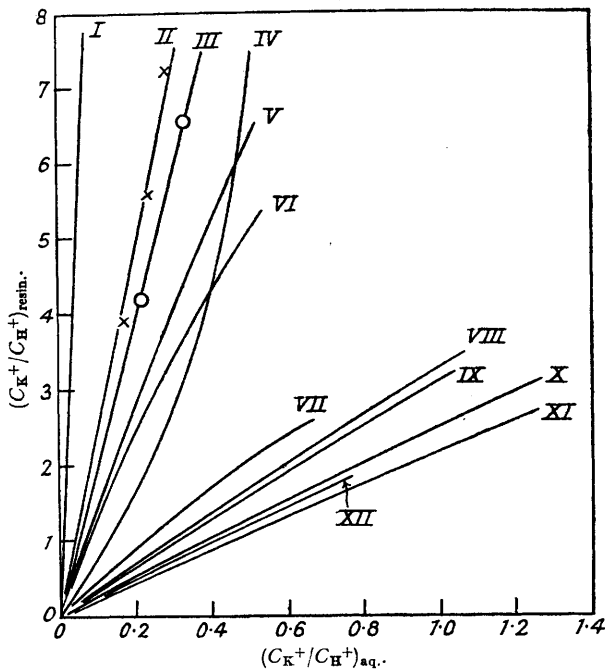
I, *Acetic acid.*
II, *Monochloroacetic acid,* 0·1N (*corr.*).
III,   ,,   ,, 0·05N (*corr.*).
IV, *Oxalic acid.*
V, *Monochloroacetic acid,* 0·05N (*uncorr.*).
VI,   ,,   ,, 0·1N (*uncorr.*).

VII, *Sulphuric acid.*
VIII, *Hydrochloric acid,* 1·5°.
IX, *Dichloroacetic acid.*
X, *Hydrochloric acid* 25°.
XI,   ,,   ,, 40°.
XII, *Trichloroacetic acid.*

All at 25° unless otherwise stated.

The curvature of the lines is not so great, however, as to preclude either a mean value or the limiting value of the slope being used to calculate the equilibrium constant. The departure from constancy is at the most only a few units %. The table shows the mean values of the stoicheiometric equilibrium constants at 25° for the equilibria against NH_4^+ obtained from Fig. 4.

A series of curves illustrating the equilibria between a potassium resin and solutions of acids having various dissociation constants is shown in Fig. 5.

Exchange equilibrium constants and ionic sizes.

Cation.	Equilm. const. against NH_4^+ at 25°.	Chlorides. Harned & Owen.	Chlorides. Stokes & Robinson.	Nitrates. Harned & Owen.	Crystal radius, A.*	Hydrated radius, A., from mobility.†
Li+	0·40	5·56	4·32	5·23	0·60	2·31
H+	0·47	5·60	4·47	—	—	—
Na+	0·67	4·49	3·97	3·15	0·95	1·78
K+	1·05	3·86	3·63	1·77	1·33	1·22
NH₄+	1·00	(1·81)	—	—	1·48	1·21
Rb+	1·70	3·50	3·49	1·63	1·48	1·18
Cs+	2·40	2·97	—	1·54	1·69	1·16
Ag+	3·20	—	—	2·0	1·26	1·45
Tl₂SO₄	9·2	—	—	—	1·44	1·20
TlNO₃	12·7					

* The crystal radii are from Pauling (" The Nature of the Chemical Bond," 1944, p. 346).
† The hydrated radii are calculated from the equation given by Walden (" Elektrochemie nicht-wässriger Losungen," 1924, p. 189), using the mobility figures quoted in Landolt–Börnstein's Tabellen, Ergänzungsband IIIc, 2059 (1936).

DISCUSSION.

Relative Ion–Resin Affinities.—From the equilibrium constants given in the table the approximate equilibrium constant for any pair of the ions can be calculated. Thus the equilibrium constant for the K^+–Rb^+ equilibrium will be approximately $(K_{NH_4^+/K^+})/(K_{NH_4^+/Rb^+})$. This is sufficiently accurate to allow an estimate to be made of the separation of univalent cations from admixture in solution, which might be effected by an exchanger of the phenolsulphonate type. The method is equally applicable to mixtures containing more than two cations. However, a precise value of the equilibrium constant in any particular case cannot be predicted without a consideration of the specific influence of individual ions on the activity coefficients of salt mixtures. Thus, in the example above, the activity coefficient of K^+ in the presence of Rb^+ is not exactly the same as in the presence of the same concentration of NH_4^+.

Various workers have attempted to correlate the position of equilibrium, which gives a measure of the relative affinity of the ions for the exchanger, with other known and measurable properties of the ions. Jenny (*J. Physical Chem.*, 1932, **36**, 2217), using an aluminosilicate exchanger, obtained a linear relationship between his " symmetry value " and the reciprocal of the crystal radius of the cation. However, he appreciated that the hydrated and not the crystal radius must be the determining factor. Since the hydrated and the crystal radii change in opposite directions, his results are qualitatively consistent with this concept.

Nachod and Wood (*J. Amer. Chem. Soc.*, 1945, **67**, 629), using a sulphonated-coal exchanger, found a linear relationship between the extent of the exchange occurring in an arbitrarily standardised series of experiments and the hydrated ionic radius obtained from mobility measurements.

In neither case is a straight line or even a smooth curve obtained when the results of the present work are plotted by the methods of Jenny and of Nachod and Wood (cf. table). By the method of Nachod and Wood the ions Li^+, Na^+, and K^+ are found to lie on a straight line, but Rb^+ and Cs^+ are more strongly attracted than their hydrated radii require, and they cause a sharp break in the curve. The ions Ag^+ and Tl^+ have mobilities between Na^+ and K^+ and K^+ and Rb^+, respectively, yet their equilibrium positions lie beyond that of Cs^+, so that these do not lie on a curve at all. It is clear, therefore, that the hydrated ionic radius as determined from mobility measurements is not the determining factor.

Recently Boyd, Schubert, and Adamson (*ibid.*, 1947, **69**, 2818) studied the equilibrium conditions in a phenol sulphonate resin exchanger, Amberlite IR-1. This apparently carries $-CH_2 \cdot SO_3^-$ exchange groups similar to, though not identical with, the nuclear $-SO_3^-$ groups in the exchanger used in the present work. These authors used the "distance of closest approach" $a°$ of the Debye–Hückel equation

$$-\log \gamma_\pm = A \sqrt{\mu} / (1 + Ba° \sqrt{\mu}) \quad . \quad . \quad . \quad . \quad . \quad (11)$$

as an index of ionic size, and they plotted the reciprocal $1/a°$ against the standard free energy of formation of the metal-resin salt obtained from the equilibrium constant K :

$$-\Delta G°_{MR} = \boldsymbol{R}T \log_e K \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

A straight line was drawn through the points, suggesting that $a°$ is the factor determining the affinity.

Unfortunately, several unsatisfactory features mar the validity of this work. First, lithium appears to have been plotted with the erroneous value for $-\Delta G°_{MR}$ of $+60$, whereas their Table VII gives it as -60 : the latter figure is obviously the correct one, since it is consistent with other data in the paper. Secondly, the $a°$ value used for sodium is quoted from Brown and MacInnes (*J. Amer. Chem. Soc.*, 1935, **57**, 1357) as 5·2, instead of 4·45. Thirdly, there appears to be an arithmetical error in the calculation of $a°$ for ammonium chloride from the data quoted by Latimer (" The Oxidation States of the Elements ") : a re-calculation gives a value of about 2 instead of 4·5. However, the activity data on ammonium chloride are too sparse to provide a satisfactory basis for calculation and it is probably advisable to omit NH_4^+ from the discussion altogether.

When these discrepancies are corrected, the points no longer lie on a straight line, but do lie roughly on a smooth curve. The equilibrium constants for H^+ and the alkali-metal ions in the present work, when similarly plotted with the same $a°$ values, give a curve of the same type. This conception of using the distance of closest approach to correlate affinities appears, therefore, to be an improvement on that of crystal or hydrated radii.

The utility of the method is restricted, however, by the incompleteness as well as by the uncertainty of much of the existing activity data, especially as the value of $a°$ is very sensitive to small differences in activity coefficients. In addition, $a°$ is not a fundamental constant, and the value obtained depends largely on the concentration at which equation (11) is applied.

In an attempt to test the idea further, $a°$ values have been calculated at $0·1$N and $25°$ from activity data collected by Harned and Owen (*op. cit.*, pp. 547, 562—564) (see table). The incompleteness of the available data renders it impossible to include in one series all the cations studied. The chlorides of Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ yield $a°$ values which give a straight line when the reciprocals are plotted against log K, as Fig. 6 shows. The hydrogen ion lies slightly, but significantly, off the line in the direction indicating too high an affinity for its $a°$ value. This is clearly the effect of incomplete ionisation of the hydrogen resin considered as an acid. It is understandable, as potentiometric titrations indicate that the parent phenol- and cresol-sulphonic acids have dissociation constants of the order of 10^{-2}.

The only salt of silver for which an $a°$ value is obtainable is the nitrate. The calculation of $a°$ values for the alkali-metal nitrates should then enable silver to be included in the series. The values obtained are shown in the table. With the possible exception of Li$^+$ and Na$^+$, these are seen to be so low as to have no real significance, as the higher terms of the Debye–Hückel theory begin to have an influence (see MacInnes, " The Principles of Electrochemistry," 1939, p. 164) and, in addition, silver nitrate and the alkali nitrates are known to show abnormal behaviour in solution (*idem*, *ibid.*, pp. 164, 334). It is, therefore, at present impossible to draw any conclusions whatever in regard to silver. Similar difficulties exist with Tl$^+$ (see Harned and Owen, *op. cit.*, pp. 396, 397).

Stokes and Robinson (*J. Amer. Chem. Soc.*, 1948, **70**, 1870) have recently put forward a semi-empirical modification of the Debye–Hückel equation. Their $a°$ values, although limited to H$^+$, Li$^+$, Na$^+$, K$^+$, and Rb$^+$, are also found to yield a straight line when the reciprocals are plotted against log K as before, the point for the hydrogen ion again lying in a position indicating incomplete ionisation of the hydrogen resin (see table, and Fig. 6).

Summarising, the use of the $a°$ parameter appears to be a sound means of correlating the affinities of the univalent cations, but the lack of sufficient activity data and the limitations of the Debye–Hückel equation raise such serious restrictions that no satisfactory proof of the validity of the concept can be obtained at present.


Fig. 6.

Equilibria Involving the Hydrogen Ion.—It has long been recognised (Jenny, *J. Physical Chem.*, 1932, **36**, 2253; *Kolloidchem. Beih.*, 1927, **23**, 428; Wiegner, *J. Soc. Chem. Ind.*, 1931, **50**, 103T) that the general laws governing the exchange of metal ions, *i.e.*, in more or less neutral solution, do not apply when the hydrogen ion is involved.

Detailed discussions have hitherto been confined to inorganic aluminosilicate exchangers, and only one brief mention of the subject has been made from the standpoint of the organic cation exchangers (Boyd, Schubert, and Adamson, *loc. cit.*, p. 2829).

It is obvious from the literature and the results of the present work that the two types of exchanger behave differently towards the hydrogen ion. Jenny (*loc. cit.*, 1927) showed that the hydrogen ion is more strongly held by a zeolite than any of the other univalent ions, the series for chlorides being H > Cs > Rb > NH$_4$ > K > Na > Li. The hydrogen ion, under the same conditions, shows a comparatively feeble affinity for organic exchangers containing sulphonic groups, the series being (see Fig. 4) Li < H < Na < (K, NH$_4$) < Rb < Cs. This is the same position as found by Boyd, Schubert, and Adamson (*loc. cit.*) for the methylenesulphonic acid exchanger used by them.

This low affinity indicates that it is the hydrated radius of the ion, like that of the metal
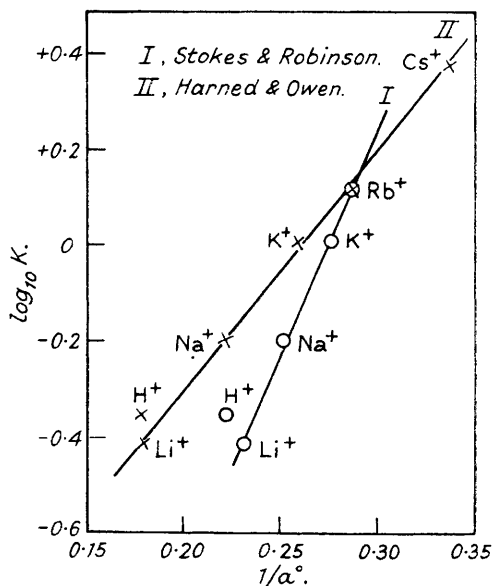
cations, which is the determining factor, and both forms of the resin can be regarded as largely ionised, though not dissociated.

The high affinity of the hydrogen ion for the zeolites, on the other hand, must be regarded as the result of the capacity of the >Al·O– group to form the covalently linked >Al·OH group. Accordingly, the zeolite behaves as a weak acid, while the resin sulphonic acid behaves as a strong acid.

From this point of view, the equilibrium

$$\text{K-exchanger} + \text{HA} \rightleftharpoons \text{H-exchanger} + \text{KA} \quad . \quad . \quad . \quad . \quad (13)$$
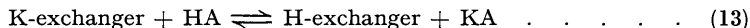
(where HA is the acid in the aqueous solution) is seen to be analogous with the competition of two acids for the same base : when H-exchanger is the weaker acid the equilibrium lies to the right, and *vice versa*. This is exemplified by the curves of Fig. 5.

The amount of exchange occurring with the stronger acids, *e.g.*, hydrochloric, sulphuric, dichloroacetic, is in each case the same at 0·1N and at 0·05N, but increased dilution of monochloroacetic acid appears to cause *less* hydrogen ion to pass into the resin phase (Fig. 5, curves V and VI). This behaviour is not in accord with the law of mass action, nor can it be explained by dissociation (which would have the opposite effect). It has been found to be due to physical adsorption of the undissociated molecules of the weak acid on the resin. This adsorption was measured by placing samples of hydrogen resin in contact with known volumes of 0·1N- and 0·05N-monochloroacetic acid solutions and titrating the acidity of the aqueous solution before and after. The adsorption was 0·113 and 0·0604 milliequiv. per g., respectively, after allowance for the trace of sulphuric acid coming from the hydrogen resin, already referred to.

When corrected for this adsorption, the equilibrium curves for monochloroacetic acid occupy the positions shown in Fig. 5 (curves II and III). It is seen that *more* hydrogen ion now passes into the resin phase from the more dilute solution than from the less dilute, in accordance with the increased dissociation which occurs on dilution. The true equilibrium position obtained by this correction is considerably different from the apparent one, and this must obviously be considered when interpreting equilibrium results involving weak acids. It is likely, for example, that the anomalous position occupied by dichloro- and trichloro-acetic acids ($K_a = 5 \times 10^{-2}$ and 2×10^{-1}), adjacent to the strong acids, is a result of this effect.

The property of physical adsorption possessed by synthetic resin gels has already been recognised and deliberately enhanced (Dutch Patent 59,449; Brit. Pat. Appl. 29,197/45). It is not surprising, therefore, that a resinous cation exchanger should possess the same property.

Much greater physical adsorption occurs when large unionised molecules are involved. Thus, the resin will adsorb the non-ionic molecules of the wetting agent " Lissapol N " (I.C.I.) to the extent of 5—10% of its own weight. No adsorption occurs with strong acids, where the number of undissociated molecules is small, or with the highly dissociated neutral salts, even when the cation is as large as phenylbenzyldimethylammonium (see Part III).

Energetics of Cation Exchange.—The fact that the affinity of different univalent cations appears to be in the same order as their a° parameters might be taken to mean that the ions are held at similar distances from the sulphonate ion by purely Coulombic attraction and, consequently, the smaller the cation the greater the affinity, since the energy will be given by e^2/Da° (D is the dielectric constant). There can be little doubt that this concept (previously arrived at in a cruder form by Jenny and others) is broadly correct, but further consideration of the energy changes involved shows that the problem is more complex than this simple picture implies.

It is, unfortunately, very difficult to estimate accurately the interaction energy of two ions at their distance of closest approach. In addition to the Coulombic attraction, allowance ought to be made for the attraction due to mutual polarisation and the van der Waals forces and, in the opposite sense, for repulsive forces. As these factors cannot be assessed with any reliability, it is usual to neglect all three on the grounds that their net result, at least, may be small compared with the Coulomb energy.

There remains the difficulty that the dielectric constant of the medium near an ion is not that of the pure medium. Webb (*J. Amer. Chem. Soc.*, 1926, **48**, 2589) gives values of the " effective dielectric constant " at different distances from an ion. Extrapolating Webb's figures, the dielectric constant to be used for H^+ and K^+, whose chlorides * have a° values of 5·6 and 3·9 A., are 45 and 40 respectively, giving energies of Coulomb attraction of 1·30 kcals./g.-mol. for H^+ and 2·10 kcals./g.-mol. for K^+. Hence, the change of Coulomb

* Strictly an a° value for the cation-sulphonate contact should be used. However, this is not known and cannot be calculated, but that for the corresponding chloride will not be very different.

energy on replacing a potassium ion in the resin by a hydrogen ion is an absorption of 0·80 kcal./g.-mol.

These figures may be compared with the thermal data obtained from a study of the equilibrium

$$KR + HCl \rightleftharpoons HR + KCl \qquad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The equilibrium constant, defined by

$$K = [KCl][HR]/[HCl][KR] \qquad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

is found to have the values 0·30, 0·40, and 0·466 at 1·5°, 25·0° and 40·0°, respectively (see Fig. 5). Applying the van't Hoff isochore, the standard heat of reaction $\Delta H°$ is $+1·95$ kcals./g.-mol. The standard free energy of exchange $\Delta G°$ is given by $-\Delta G° = \boldsymbol{R}T . \log_e K$, which yields a value of $+\Delta G° = +0·54$ kcal./g.-mol. at 25°. Hence, from the equation $\Delta G° = \Delta H° - T\Delta S°$, the value of $T\Delta S°$ is $+1·41$ kcals./g.-mol.

The entropy contribution is thus nearly as great as the heat of reaction, and of opposite sign, leading to a low value for the free energy of exchange. This indicates almost certainly that there is a change in the degree of hydration of the ions when they pass from the solution to the solid phase : a mere interchange of ions would not be accompanied by a change of entropy. Further, the calculated Coulomb energy of exchange (*viz.*, 0·80 kcal.) is only about half of the heat of exchange (1·95 kcals.). The rest of the latter probably comes from the heat of hydration. Judging by its position in the exchange series, H^+ is more hydrated than K^+; consequently, if some dehydration occurs when an ion is taken up during the reaction (14), there is likely to be a net *decrease* in the total amount of water bound by hydration. Hence, energy must be supplied, which will be a positive contribution to ΔH. This corresponds with the positive entropy change already found from the equilibrium data.

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