ION EXCHANGE

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EXCHANGE between ions in solution and ions adsorbed or otherwise held in a solid phase is a subject in which great interest has been maintained during the last decade. Whilst previously the main application of ion exchange was in the use of zeolites as water softeners, the last few years have extended the interest of these materials to the analytical, physical, and inorganic chemist, as well as to the process chemist, the biologist, and the physician.

During the last twelve months a considerable volume of work in this field has been published by a group of American workers, largely as a result of the use of exchange materials in the Plutonium Project. The main applications and lines of research have now been established and a considerable step forward has been made in our understanding of the basic reactions involved. Several reviews of ion exchanges have been written,[1] the most comprehensive one in English being that of H. F. Walton [2] (1941). In the present Review, apart from the uses and applications of ion exchangers which are mentioned in the last section, a critical discussion of the more fundamental aspects of the subject is made. The different types of exchanger available are also discussed and an attempt is made to guide workers in the choice of an exchanger for a particular purpose.

Ion exchange may occur either by exchange of a cation, or by exchange of an anion. The original work of J. T. Way [3] was concerned with cationic exchange in soil. Potassium chloride was passed through a bed of soil and the potassium found to exchange with the calcium in the soil in equivalent amount. An exchange reaction of this type may be formally represented by the equilibrium

$$\mathrm{Ca_E} + 2\mathrm{K_S^+} \rightleftharpoons \mathrm{Ca_S^{2+}} + 2\mathrm{K_E}$$

where the subscripts E and S refer to the ions in the solid exchanger and in solution respectively. This reaction may be caused to proceed in either direction by washing the exchanger with a solution containing the appropriate ion.

Although exchange of anions may occur on inorganic and colloidal substrates, the main class of substance on which anionic exchange is

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[1] K. K. Gedroiz, *Kolloid Chem. Beih.*, 1929, **29**, 149; H. Jenny, *ibid.*, 1927, **23**, 428; R. J. Myers, " Advances in Colloid Science ", 1942, **1**, 317; M. Randall and J. Y. Cann, *Chem. Reviews*, 1930, **7**, 369; G. Wiegner, *J. Soc. Chem. Ind.*, 1931, **50**, 65T; L. Wiklander, *Kgl. Lantbruks Högskul Ann.*, 1946, **14**, 1.

[2] *J. Franklin Inst.*, 1941, **232**, 305.

[3] *J. Roy. Agric. Soc.*, 1850, **11**, 313.

exhibited is a resin type of material containing weakly basic nitrogen groups. Although these gel-like materials will exchange anions quantitatively according to a reaction of the type

$$(\mathrm{R{\cdot}NH_3})\mathrm{Cl} + \mathrm{NaBr} \rightleftharpoons (\mathrm{R{\cdot}NH_3})\mathrm{Br} + \mathrm{NaCl}$$

they are normally used to absorb acids from solution by a reaction which may be written

$$\mathrm{R{\cdot}NH_2} + \mathrm{HCl} = (\mathrm{R{\cdot}NH_3})\mathrm{Cl}.$$

Before one can effectively discuss the properties of the different exchangers available, it is necessary to describe how these substances are obtained, and their general structure.

Types of Exchangers

Cationic Exchangers.—Three main groups of cationic exchange materials are available and these will be dealt with in turn.

Natural and synthetic siliceous compounds. In minerals, ion exchange is most marked in the aluminosilicates containing cross-linked sheets of SiO_4 tetrahedra, *e.g.*, zeolites, montmorillonite, and other clay minerals, ultramarines, glauconites, and the chabazites. Felspars and kaolinite also show the phenomenon but to a lesser degree. A common feature of such minerals is an open structure permitting a free flow of ions in and out of the lattice, and there are indications that a large crystal volume per oxygen atom is associated with a large exchange capacity.

The synthesis of materials with zeolitic properties has been developed from the work of R. Gans [4] on precipitated and melted permutites. Mixtures of quartz, clay, and soda ash when fused together gave materials of the approximate composition $Na_2Al_2Si_3O_{10}$, in which all the sodium and any calcium present as impurity could be replaced by other cations. The diffusion of ions in aluminosilicates prepared by fusion [5] is faster than in the naturally occurring materials but it is still too slow for successful application. A second method of preparation, *i.e.*, addition of sodium silicate to sodium aluminate or aluminium sulphate (or both) in aqueous solution, gives either a gelatinous precipitate or a gel. The latter, which is of greater importance, may be pressed and dried and caused to disintegrate into small granules by the addition of water. The products have the composition $Na_2O,Al_2O_3,nSiO_2,xH_2O$, where n is usually 5 or 6 but may be as high as 12. The ratio of SiO_2 to Al_2O_3 seems to affect the capacity,[6, 7] there being a maximum value, variously reported as 3—4 : 1, 6 : 1, and 9 : 1, for which the interatomic spacing is most favourable. Further information on naturally occurring and synthetic siliceous compounds will be found in the review by Walton.[2]

Carbonaceous exchangers. Besides the mineral constituents, there is a

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[4] *Jahr. Kgl. Preuss. Geol. Landesanst. Bergakad. Berlin*, 1905, **26**, 179 ; 1906, **27**, 63 ; D.R.-P., 197,111 (1906) ; U.S.P., 1,131,503 (1911).

[5] G. Schulze, *Z. physikal. Chem.*, 1915, *A*, **89**, 168.

[6] S. Mattson, *Soil Sci.*, 1928, **25**, 289 ; S. Mattson and J. S. Csiky, *ibid.*, 1935, **39**, (2), 161

[7] G. Wiegner, *J. Soc. Chem. Ind.*, 1931, **50**, 103T.

second class of compound present in soil capable of ionic exchange. These are organic materials, the humic acids and the proteins. The former have cation-exchanging properties and the latter may exchange either cations or anions. All proteins on the negative side of the isoelectric point contain replaceable hydrogen ions; casein, for example, contains about 1 milliequivalent (meq.) of replaceable hydrogen per gram.[8] Owing to the presence of humic acids, lignite and brown coal possess considerable exchanging power, and this can be increased by mild oxidation with moderately concentrated nitric acid.[9, 10] The humification of substances such as wood, peat, brown coal, bituminous coal, anthracite, etc., can be made more complete by treating them with substances, *e.g.*, sulphuric or phosphoric acid, which bring about the removal of water.[11, 12] In manufacture, this is often accompanied by partial sulphonation with oleum, sulphur trioxide, chlorosulphonic acid, etc. The products form a class of exchanger of high commercial value.[13] A most important feature of these sulphonated coal exchangers is their high stability to acids, which enables them, in contrast to the siliceous materials, to be used in the hydrogen-exchange cycle in solutions of low pH, *i.e.*, they may be regenerated to the hydrogen form by washing with dilute acid. At very low pH values, however, they tend to peptise. The exchange capacity of these exchangers is quite high, of the order 1·5—2·5 meq./g. They behave as gels, swelling reversibly to about 30% above their original size when placed in water, and are hygroscopic, absorbing up to 25% by weight of water from moist air. A further advantage in commercial use is that they do not impart any silica to water in contact with them. Sulphonated coal exchangers contain up to 6% of sulphur present as sulphonic acid groups. The exchange is, however, not entirely due to these groups but also to some extent to carboxyl and phenolic groups. They resemble in their physicochemical properties the graphitic and sulphographitic acids which have pronounced permutoidal properties.[14, 15]

Resinous exchangers. The manufacture of synthetic resins showing exchange properties has developed from the work of B. A. Adams and E. L. Holmes.[16] Since this work, published in 1935, rapid progress has been made in the improvement and application of resinous exchangers. Fundamental studies and characterisation of naturally occurring exchange materials such as bentonite and greensand and of sulphonated coals are difficult on account of structural differences and the large variety of exchangeable groups present. With the advent of organic resin exchangers,

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[8] E. Graf, *Koll. Beih.*, 1937, **46**, 229.

[9] G. Austerweil, B.P. 497,708 (1937).

[10] W. Harz and F. Gerschner, D.R.-P. 672,489 (1936).

[11] G. Austerweil, *Bull. Soc. chim*, 1939, **6**, 55.

[12] Phillips and Pain, Fr.P. 788,692 (1936).

[13] S. B. Applebaum and R. Riley, *Ind. Eng. Chem.*, 1938, **30**, 80; N.V. Octooien Maatschaapij " Activit ", B.P. 509,710 (1938); Fr.PP. 778, 922 (1934), 784,348 (1935).

[14] U. Hofmann and W. Rüdorff, *Trans. Faraday Soc.*, 1938, **34**, 1017.

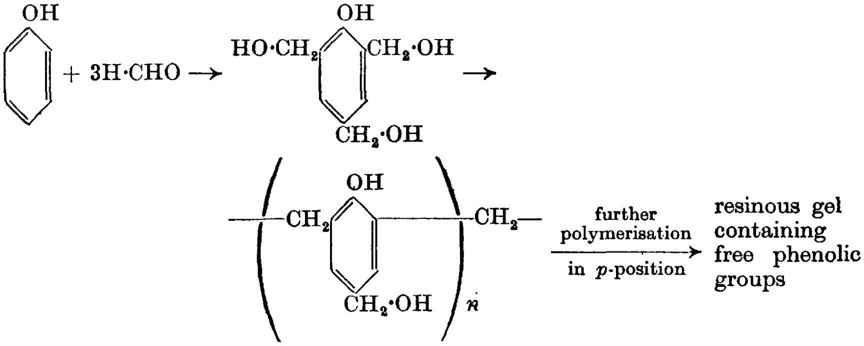
[15] H. Thiele, *Kolloid Z.*, 1937, **80**, 1.

[16] *J. Soc. Chem. Ind.*, 1935, **54**, 1T; B.P. 450,308–9 (1934).

for which the number of types of exchangeable groups may be predetermined, exchangers containing only one exchangeable group (*e.g.*, the —SO_3H group) may be made. This is leading to a much clearer understanding of the exchange process. Further, it is becoming possible to predict the behaviour of materials of various structures and to manufacture resins with the desired properties for a particular purpose.

For the successful manufacture of exchange resins, two conditions are necessary. First, the material must have a highly developed cross-linked structure to impart insolubility, and secondly, it must contain a multiplicity of centres at which exchange may occur. These centres may be any of three general types : carboxylic (—CO_2H), phenolic (—OH), and sulphonic acid (—SO_3H) groups. The development of resins with increased capacity depends on increasing the density of the active groups without seriously affecting the cross-linkages. The introduction of hydrophilic groups must also be kept in check in order that swelling shall not be too pronounced.

Adams and Holmes found that the condensation (followed by polymerisation) of phenols, especially polyhydric phenols, with formaldehyde could produce substances which exhibit ionic exchange. The reaction may be represented as follows :



Owing to the greater density of phenolic groups, polyhydric phenol–formaldehyde resins have a larger capacity than those derived from monohydric phenols.[17] Developments of the original Adams and Holmes patents suggested the use of tannins as starting materials,[18] but these are not well defined and tend to produce resins of varying properties and lower stability.

Later work [19] showed that very active exchangers could be prepared by introducing into the phenol–aldehyde structure, either before or after condensation, strongly acidic groups such as aliphatic or aromatic sulphonic acids. One of a series of resins manufactured by I.G. Farbenindustrie [20]

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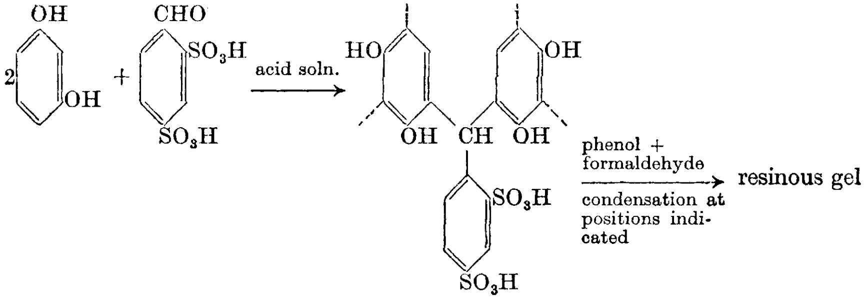
[17] E. I. Akeroyd and G. Broughton, *J. Physical Chem.*, 1938, **42**, 343.

[18] E. L. Holmes, B.P. 474,361 (1936) ; W. H. Kirkpatrick, U.S.PP. 2,094,359 (1936) ; 2,106,486 (1936).

[19] H. Wassenegger and W. Sutterlin, U.S.P. 2,228,159 (1937) ; H. Wassenegger, R. Griessbach, and W. Sutterlin, U.S.P. 2,228,160 (1939) ; H. Wassenegger and K. Jaeger, U.S.P. 2,204,539 (1938).

[20] N. E. Topp, B.I.O.S. 621, Item 22.

(Wofatit KS) is formed from benzaldehyde-2 : 4-disulphonic acid, phenol, resorcinol, and formaldehyde according to the scheme :



On the other hand, the sulphonic acid group may be attached to the phenolic compound (as in the condensation of *o*- and *p*-phenolsulphonic acids with formaldehyde to give Dowex 30 [21]).

Exchange resins have been produced containing all three main types of active groups. Perhaps the best known of these are the Amberlites (I.R.-1 and I.R.-100H), in one of which (I.R.-1) it has been concluded, from measurements of capacity and dissociation constants,[22] that the carboxylic groups are *ortho* to the phenolic groups. A disadvantage in the use of Amberlite I.R.-1 is its moderate reducing action ; [22] silver ions are reduced to metallic silver, and mercuric to mercurous salts. In addition, nitric acid in concentrations greater than 2N attacks the resin rapidly. These disadvantages, however, although not specifically reported, may apply in like measure with other resins.

A new class of exchange resin has recently been developed by the Dow Chemical Company of America. It consists of a cross-linked aromatic hydrocarbon skeleton containing nuclear sulphonic acid groups, and is formed by the polymerisation of polyvinyl aryl compounds, *e.g.*, divinyl-benzenes, -toluenes, -xylenes, -naphthalenes, -alkyl- or -halogeno-benzenes or -phenyl-ethers.[23] In Dowex 50, a resin of this type extensively used in recent American work [24] (see later section), most of the sulphur is present as free nuclear sulphonic acid groups but a small amount (0·5%) is accounted for by sulphone cross-linkages. It is available in spherical particles of various sizes, each particle appearing to be a homogeneous gel. In comparison with many types of synthetic exchanger, it has a high capacity (4·9 meq./g.) and, on account of the hydrocarbon skeleton, it is stable to strong acids, alkalis, and oxidising agents even at high temperatures (100°). The nuclear sulphonic acid groups are the only active centres present at any pH, and this, together with its stability, allows the exchange properties of the —SO_3H group to be studied over a wider range of conditions than hitherto possible.

One or two other exchangers are perhaps worthy of note, although they

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[21] W. C. Bauman, *Ind. Eng. Chem.*, 1946, **38**, 46.

[22] G. E. Boyd, J. Schubert, and A. W. Adamson, *J. Amer. Chem. Soc.*, 1947, **69**, 2818.

[23] G. F. D'Alelio, U.S.P. 2,366,007 (1942).

[24] W. C. Bauman and J. Eichhorn, *J. Amer. Chem. Soc.*, 1947, **69**, 2830.

have not been as widely used as those already considered. Resins with exchange properties have been obtained by the reaction of furfuraldehyde (95%) with sulphuryl chloride or phosphorus oxychloride.[25] The polymerisation of mixtures of (1) styrene, (2) maleic anhydride, and (3) a compound containing a $CH_2{=}C\langle$ group and one other polymerisable group, and the polymerisation of (3) above with an acyclic acid derivative $CH_2{:}CR{\cdot}CO_2H$, where R is hydrogen, a halogen, alkyl, aryl, or alkaryl groups, have also been suggested as methods of making cationic exchangers.[26]

Anionic Exchangers.—Although there are many examples of systems in which cationic exchange is known to take place, there are relatively few reports of true anionic exchange. These are almost all in the field of inorganic chemistry. The term "anionic exchanger" is often applied, however, to materials which absorb acid molecules from aqueous solution. Although such absorbents are particularly efficient in removing acids, many of them are known to absorb, to a greater or lesser degree, other substances such as neutral organic molecules, inorganic salts, etc. The physical chemistry of acid absorbents is therefore closely allied to that of surface adsorption from solution.

Exchange and adsorption on inorganic substrates. So-called exchange adsorption has been known in colloid chemistry for many years. For instance, precautions have to be taken in analytical procedure to reduce the exchange adsorption of chloride ions on a precipitate of barium sulphate. Other examples given by I. M. Kolthoff [27] are the replacement by iodate of the sulphate radicals of barium sulphate and the chloride radicals of silver chloride. In colloid chemistry, however, exchange adsorption is closely related to reactions of ionic micelles and the neutralisation of charges on small colloidal particles, and in practice it is often extremely difficult to distinguish between true exchange adsorption and simple adsorption of whole molecules.

Anions may be adsorbed on charcoal; usually this is a case of simple adsorption but exchange adsorption has also been observed, notably in the displacement of phosphate from blood charcoal by the following ions, given in order of ease of replacement: [28] pyrophosphate, fluoride, oxalate, tartrate, acetate, sulphate and nitrate (equal), and chloride.

Work on the simple adsorption of acids (in the absence of exchange) has been widespread, and numerous examples are known, as for instance the adsorption of oxalic acid on alumina,[29] of seven organic acids and sulphuric acid on chromium hydroxide, aluminium hydroxide, and ferric hydroxide,[30] and of several fatty acids on freshly precipitated zirconium hydroxide.[31] Clay will also take up anions [32] and has been recommended

[25] American Cyanamid Co., B.P. Applic. 874/45.

[26] British Thomson-Houston Co., B.P. Applic. 10,753–4/43.

[27] *Kolloid-Z.*, 1934, **68**, 190.

[28] F. Axmacher, *ibid.*, 1932, **59**, 298.

[29] P. H. Dewey, *J. Physical Chem.*, 1932, **36**, 3187.

[30] K. C. Sen, *ibid.*, 1927, **31**, 1840.

[31] S. N. Chakravarty and K. C. Sen, *Z. anorg. Chem.*, 1930, **186**, 357.

[32] S. Mattson, *Soil Sci.*, 1929, **28**, 179, 373.

as an adsorbent for removing fluorine from drinking water.[33] The use of acid adsorbents, such as dolomite, lime, and magnesia, has been the practice in many fields. A discussion of acid-removing substances of an inorganic nature which depend for their action on surface adsorption is outside the scope of this Review.

Exchange and adsorption on organic substrates. The use of organic substrates for the removal of anions from solution has been confined almost entirely to the class of materials formed by the condensation of organic nitrogen compounds with aldehydes. These compounds contain weakly basic radicals of the —NH_2 and =NH type which would be expected to form salts such as $(\text{—NH}_3)\text{Cl}$ and $(\text{=NH}_2)\text{Cl}$. It is these groups which are largely responsible for the acid-adsorbing properties of the materials, for, as with cationic exchangers, if these active groups are destroyed, the materials become inert.

The fundamental condensation reaction for the fabrication of anionic exchangers was given by Adams and Holmes [16] in 1935, namely, the condensation of aromatic amines with formaldehyde. In principle, the reaction is the same as that used for making cationic exchangers, and later work has been along the lines of attempting modifications of this reaction to give resins of larger capacity and greater efficiency rather than in adopting any new approach to the problem. Relatively little attention has yet been paid to such factors as the rate of removal of ions, the reduction of solubility and the ease of decomposition of the resins.

The most efficient anionic exchanger reported by Adams and Holmes in 1935 was that obtained from the condensation of *m*-phenylenediamine with formaldehyde. After activation with alkali, it had strongly acid-adsorptive properties. The basic chemistry of this reaction has been given, together with manufacturing details.[20] If some of the nitrogen atoms help to form bridges between neighbouring benzene nuclei, this might account for the report by G. Broughton and Y. N. Lee [34] that the observed capacities of some of the aromatic amines are considerably smaller than those calculated from the known nitrogen content.

Several attempts have been made to increase the capacity of exchangers based on *m*-phenylenediamine, for instance, by the introduction of cyano-groups, either before or after condensation.[35] Alternatively, a resin structure containing substituted amine groups may be obtained by alkylation.[36] The use of an alkylating agent containing a basic group is also suggested.[37] E. L. Holmes has proposed modifying the original reaction so as to reduce the number of chemically blocked amino-groups by using monosaccharides to replace in part the aldehyde employed in the condensation reaction.[38] An attempt has been made to increase the capacity of the resin by making

[33] W. G. Swope and R. H. Hess, *Ind. Eng. Chem.*, 1937, **29**, 424.
[34] *J. Physical Chem.*, 1939, **43**, 737.
[35] I. G. Farbenind., B.P. 495,401 (1937).
[36] *Idem, ibid.*, 495,032 (1937).
[37] *Idem, ibid.*, 495,402 (1937).
[38] E. L. Holmes, B.P. 472,404 (1936).

a greater surface available for exchange. This was done by depositing the resin on a fine coke, charcoal, or pumice surface.[39]

Condensation products of formaldehyde and aliphatic nitrogen-containing compounds (*e.g.*, polyamines, urea, etc.) have been used as exchangers.[40] Another method of preparation is by the reaction of polyhalogen derivatives of high-molecular-weight compounds with ammonia or acyclic polyamines under special conditions,[41] and of guanidino-substituted aromatic compounds with aldehydes.[42]

Other substances which have been suggested as anionic exchangers are the sparingly soluble ammonium, sulphonium, and phosphonium bases,[43] insoluble basic dyes,[44] and amides (including sulphonamides).[45] Aniline-black, the oxidation product of aniline, has been used to remove acids from water.[46, 47] The use of natural products has not been overlooked, protein substances, such as horsehair, wool, horn, etc., having been suggested; [48] the condensation of aldehydes with albuminoids and proteins [49] also gives anionic exchanging material.

Choice of Exchanger

The choice of an ion exchanger for a particular purpose is a matter in which advantages and disadvantages must be carefully considered. It is desirable at this stage to give an indication of the sort of considerations which might affect the choice of exchanger, and of the properties of some of the commercially available products.

Exchange Capacity and Chemical Structure.—Although ion exchange has been observed in many different systems, it is generally recognised that the most efficient exchangers are those which contain one or more of the following groups:

Cationic	*Anionic*
Alkali and alkaline-earth aluminosilicates	—NH_2 (aromatic amino-group)
—SO_3H (aromatic nuclear sulphonic acids)	=NH (aromatic imino-group)
—$CH_2{\cdot}SO_3H$	—NH_2 (aliphatic amino-group)
—CO_2H	=NH (aliphatic imino-group)
—OH (phenolic)	

The exchange ability of the naturally occurring aluminosilicates is sometimes very poor, as in the case of the mineral garnet, ($Mg_3Al_2Si_3O_{12}$), but it may be excellent, as in the case of glauconite, $K(FeAl)Si_2O_6$, which is the main constituent of greensand. Very little modification of the properties

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[39] E. L. Holmes, L. E. Holmes, and W. G. Prescott, B.P. 506,291 (1937).

[40] W. W. Groves, B.P. 489,173 (1937); American Cyanamid Co., B.PP. 566,789 (1942), 562,402–3 (1941).

[41] Dupont de Nemours & Co., B.PP. 548,107 (1940), 547,732 (1940).

[42] W. W. Triggs, B.P. 575,266 (1943).

[43] O. M. Urbain and W. R. Stemen, U.S.P. 2,102,203 (1935).

[44] G. Austerweil and A. Friedler, *Compt. rend.*, 1937, **205**, 1235.

[45] R. Griessbach, Beihefte Z. ver. deut. Chem. No. 31, *Angew. Chem.*, 1939, **52**, 215.

[46] Permutit Co. Ltd., B.P. 490,799 (1937).

[47] Phillips and Pain, Fr.P. 826,408 (1937).

[48] *Idem, ibid.*, 821,308 (1937).

[49] G. Austerweil, B.P. 497,928, (1937).

of the naturally occurring aluminosilicates can be made. The synthetic zeolites are not as efficient as the best naturally occurring aluminosilicates (*e.g.*, glauconite) or as rapid in action,[2] probably because of their more compact structure. By far the best synthetic zeolites are produced by precipitation. Those with a gel structure exhibit fairly high exchange capacities and are unaffected by heating to 200°; in this property they have a great advantage over the synthetic organic exchangers. All the synthetic aluminosilicates are attacked by carbonic acid but the gel type is less liable to chemical attack than that produced by fusion.[50] Synthetic aluminosilicates are most effective when adsorbing small ions; large ions, such as the quaternary ammonium salts, are not adsorbed.[51]

The organic resinous materials may contain in their structure a carboxylic, sulphonic, or phenolic group, either singly, or together. Since the degree of dissociation of each of these groups will depend on the pH, it is clear that each group will have a definite pH range over which it is active. From general considerations, it is to be expected that the phenolic group can act as a hydrogen-ion exchanger only in solutions of pH greater than about 7; on the other hand, since sulphonic acids are strong acids, dissociation will occur even at very low pH, and it is this group which largely accounts for the exchange ability of cationic resins at pH's below about 3. The carboxyl groups are normally effective over a pH range between about 3 and 7; for one cationic resin it has been estimated by G. E. Boyd, J. Schubert, and A. W. Adamson [22] that the dissociation constant of the carboxylic acid groups present is about $8{\cdot}5 \times 10^{-4}$, which compares with a value of $10{\cdot}6 \times 10^{-4}$ for salicylic acid.

It is clear, therefore, that the exchange capacity of a cationic resin will depend on the type of groups which are exchanging. If carboxylic and phenolic groups are present, the capacity will also depend on pH. A fair idea of the types of groups which are exchanging may therefore be obtained by titrating the cationic exchanger with alkali. Figs. 1 (*a*) and (*b*) give two of the possible types of curve obtained when the number of milliequivalents of cation adsorbed is plotted against pH.

Exchangers may also be obtained with phenolic groups or carboxylic groups only in their structure. Examples of the former are the phenol–formaldehyde resins normally used as anionic exchangers, which, by virtue of their phenolic groups, also exchange with cations at pH's above 8.

In general, the type of resin which is used is of little consequence when the pH range is less than about 5 as it is only for higher values of pH that a significant difference in the behaviour of the different types is noticed.

In the case of the organic anionic exchangers, there is very little systematic information available as to the effect of structure on capacity. The adsorption isotherm of an anionic exchanger is shown schematically in Fig. 1 (*c*), from which it will be seen that the capacity is critically dependent on pH. The efficiency of removal of acids from solution by a weakly basic

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[50] A. S. Behrman, *Ind. Eng. Chem.*, 1927, **19**, 445.

[51] W. Eitel, "Physik. Chemie der Silikate" (Voss, Leipzig, 1929), p. 421.

anionic exchanger is determined mainly by its basicity. For this reason, the amino- and imino-substituted resins usually have the greater capacity. Hitherto, however, very little work has been done to correlate the shape of the capacity–pH curve with the basicity of amino-containing synthetic resins. By determining the nitrogen content of the resin and assuming that all the nitrogen atoms are available for salt formation, an estimate may be made of the maximum capacity, but this only gives a rough indication of the relative efficiency of different resins.

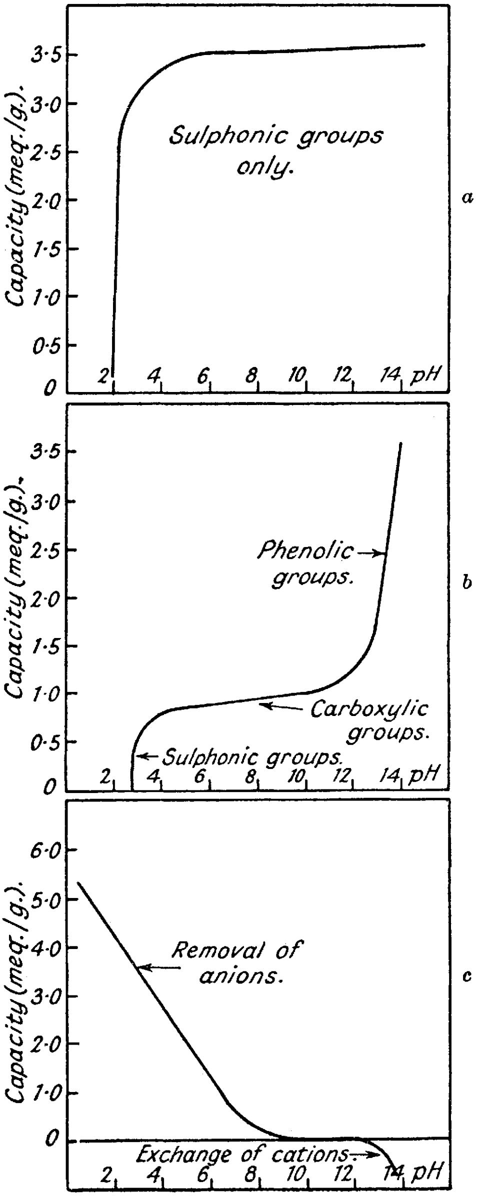

Fig. 1

Since most anionic resins are based on a phenol–formaldehyde structure, they contain active phenolic groups, the hydrogen atoms of which can undergo cationic exchange in alkaline solution. This is schematically represented by the lower portion of Fig. 1 (*c*).

Rate of exchange. Nearly all the commercially available exchangers are fairly fast in action, and there is not normally much to choose between them. Some of the aluminosilicates, however, are slow and may take two or three days to reach equilibrium.[52] Whilst it is desirable in general to use a fast exchanger, there may be circumstances in which a slow one would be of advantage, *e.g.*, in the use of exchangers as catalytic bodies.

Exchange isotherms. In describing the physicochemical properties of an exchanger, it is not sufficient to know the total capacity at a given pH. A cationic exchange process is a competition between two ions

[52] B. A. J. Lister, unpublished work.

for the adsorptive seats on the exchanger and subject to limitations mentioned later obeys the law of mass action. For an exchanger which has a more or less constant capacity over a wide pH range (*i.e.*, there are no complications due to the use of carboxylic or phenolic groups at high pH values) the exchange constant of the reaction

$$\mathrm{Na}_{\mathrm{S}}^{+} + \mathrm{H}_{\mathrm{R}} = \mathrm{Na}_{\mathrm{R}} + \mathrm{H}_{\mathrm{S}}^{+}$$

(where the subscripts S and R refer to the solution and the resin phase respectively) may be written

$$K_a = a_{\mathrm{Na_R}} . a_{\mathrm{H_S^+}} / a_{\mathrm{Na_S^+}} . a_{\mathrm{H_R}} \quad . \quad . \quad . \quad . \quad (1)$$

where the a values represent the activities of the ions in the resin phase and in solution. For a given exchanger, it is desirable to know the value of this and similar constants for other ions, before making a choice of the exchanger required for a particular purpose. If the mass-action equation is obeyed over the whole range of concentrations, these constants will give complete information about the behaviour of the resin, and enable its chromatographic properties to be predicted. Unfortunately, the law of mass action is not obeyed by most exchangers, and in such cases it is necessary to determine the exchange isotherm. Equation (1) may be rewritten

$$\frac{a_{\mathrm{Na_R}}}{a_{\mathrm{H_R}}} = \frac{a_{\mathrm{Na_S^+}}}{a_{\mathrm{H_S^+}}} \times K_a \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or, if X_{R} and X_{S} are the molar fractions of the sodium ion in the resin and in solution, and the activities of the ions in the aqueous phase and in the resin are assumed to be equal to their concentrations,

$$\frac{X_{\mathrm{R}}}{1 - X_{\mathrm{R}}} = \frac{X_{\mathrm{S}}}{1 - X_{\mathrm{S}}} \times K_a \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For the exchange of univalent ions, the shape of the curve of X_{S} against X_{R} has been given by Bauman and Eichhorn,[24] but in practice, isotherms may deviate from these ideal shapes very considerably, and if they do, complete exchange isotherms must be determined before the properties of the resin can be reliably predicted.

Physical properties. Even if the physicochemical properties of the exchanger are reliably known, the resin may be discarded on account of its physical properties. Some of these can be most disturbing.

Probably the most important physical property is that of swelling when the resin is placed in water or in salt solutions. Swelling, which may be of the order of 30%, can result in considerable changes in the bed dimensions in a chromatographic column, and hence to poor separations. The manufacturers have attempted in various ways to keep the swelling properties of their products to a minimum, but in general it may be said that if the resin does swell appreciably, very little modification can be made by the user, and if the effect is troublesome, the exchanger should be discarded.

The solubility of the resin in water may also be a difficulty. This is particularly unpleasant in experiments where micro or radio-tracer quantities of substances are being extracted or purified. The solubility may be reduced

TABLE I

Exchanger.	Made by :	Type.	Active groups.	Maximum capacity (meq./g. dry exchanger).	Refs. to fundamental data.
		Cationic exchangers [a]			
Dowex 50 . . .	Dowex Chem. Co.	" Aromatic hydrocarbon polymer "	—HSO_3 only [24]	4·92 [24]	24
„ 30 . . .	„ „ „	Synthetic resin [21]	—HSO_3, —OH		24
Amberlite I.R.-1 .	Resinous Prods.	„ „	Probably —HSO_3, —CO_2H and —OH [22]	2·3—2·5 [22]	22
„ I.R.-100	„ „	„ „		Between 1 and 2 [57]	53
Zeokarb 215 . .	Permutit Co.	„ „	" Largely due to —SO_3H groups "	2·3	54, 55
„ 216 . .	„ „	„ „	No —SO_3H groups, only —CO_2H groups [55]	2·3	54, 55
„ H . . .	„ „	Carbonaceous	—SO_3H and —CO_2H groups	1·6	55
Wofatit R resin .	I.G. Farben-industrie	Synthetic resin	—OH only		45
„ C „ .	„ „	„ „	—CO_2H(some —OH)	2·1 [b]	55, 45, 20
„ P or A resin	„ „	„ „	—$CH_2{\cdot}SO_3H$	1·1 [b]	55, 45, 20
„ K „	„ „	„ „	Aromatic —SO_3H and —OH	2·0 [b]	55, 45, 20
„ KS „	„ „	„ „	„ „ „ „	1·9 [b]	55, 20
Decalso	Permutit Co.	Sodium aluminosilicate [55]		0·8	55
Greensand . . .	Natural	„ „ „		Approx. 0·1—0·2 [c]	45
		Anionic exchangers [d]			
Amberlite I.R.-4B .	Resinous Prods.	Synthetic resin		About 6(pH 2)	56
Deacidite B . .	Permutit Co.	„ „		„ 3·5 in 1% HCl	55
„ E . .	„ „	„ „		„ 6 in 1% HCl	55
Wofatit M . . .	I.G. Farben-industrie	„ „	=NH	0·4—1·0 [e]	20

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[53] Resinous Products & Chemical Co. Laboratory Manual, " Amberlite Ion Exchange Resins ".

[54] Permutit Co. Ltd., " What is Ion Exchange ? ".

[55] Permutit Co. Ltd., private communication.

[56] R. Kunin and R. J. Myers, *J. Amer. Chem. Soc.*, 1947, **69**, 2874.

[57] Private observations by the authors.

Notes on Table I

(*a*) The maximum capacity of a cationic exchanger signifies that capacity obtaining when the exchanger is in contact with a solution containing, as the only cation, that ion with which the exchanger is saturated (*i.e.*, the molar fraction of the cation in solution is unity). This is not always the most convenient way of expressing capacity data. For instance, in water softening and similar commercial practice, it is customary to use the " break-through " capacity (*i.e.*, that capacity at which cations are first detectable in the effluent from an exchange column). The " break-through " capacity is usually expressed in kg. of CaO per 100 litres of resin. Although the densities of most exchangers are about 0·8—0·9 kg./l., some (*e.g.*, Zeokarb H) are considerably less.

(*b*) These values are estimated from experimental capacity data provided by the Permutit Co. Ltd.[65] Volume capacity data are given elsewhere.[23, 54]

(*c*) Estimated from an assumed density of 0·8—0·9 kg./l.

(*d*) It is difficult to compare anionic exchangers satisfactorily since capacities depend on pH, nature of the anion, etc. The figures given are rough values only.

(*e*) Estimated from densities given in the literature.[23]

Note : Since this table was compiled, four new exchangers have been produced by the Resinous Products and Chemical Co., viz., I.R.-120 and I.R.-105 containing active sulphonic acid groups, I.R.-C50, a carboxylic exchanger, and I.R.-A400, a strongly basic exchanger which will remove chloride ions even from solutions of sodium chloride over a pH range of 1 to 10.

by continuous washing and recycling with acid (presumably the lower polymers are washed out) but there is always a very slight solubility to which exception may be taken. Most of the resinous types of exchanger are subject to this difficulty ; the aluminosilicates may be better from this point of view in certain instances, but are liable to give colloidal silica in solution.

The decomposition of the exchangers at high temperatures may be objectionable in some work. Most of the synthetic resins are stable up to 60° or so, and some even to 100°, but the aluminosilicates do not lose their exchange properties even at higher temperatures.

The exchangers must also be stable towards acids. Most of the carbonaceous exchangers, phenol–formaldehyde condensed resins and aromatic hydrocarbon polymers, are unattacked by 2 or 3M-acid solutions ; the aluminosilicates, on the other hand, tend to disintegrate in acid solution.

The commercially available exchangers. Some of the different resins available commercially are enumerated in Table I. As far as possible, an indication of their properties is given but these data are by no means complete. Only those data are quoted for which reliable references are available. As most of the physicochemical and other work has been done when using these exchangers, reference will be made in the next two sections to the particular exchanger used in the work described.

Physical Chemistry

Stability of Exchanger.—It is known that both the aluminosilicate and the resinous types of cationic exchanger are soluble in water, but it is difficult to find in the literature reliable values for their solubility. From the silicate exchangers, alkali and silicic acid are probably dissolved, whilst the solubility of the resinous exchangers is probably due to the solution of low polymers.

Hydrolysis may be a contributing factor towards the solubility of some of the exchangers. For instance, if the hydrogen form of Amberlite I.R.-100H is shaken with water, an equilibrium pH value[57] of about 3—4 is found, independent over wide limits of the volume of solution and the weight of resin. This value is likely to fall to 2 on standing, presumably owing to further hydrolysis. Similar results[57] are obtained with Zeokarb 215. Hydrolysis of the anionic synthetic resins may be quite serious. The capacity of a substance such as Amberlite I.R.-4 is critically dependent on pH, and therefore as soon as the resin is washed with water, a considerable amount of adsorbed material is lost. This should be remembered when anionic exchangers are being used, and rinsing of columns of such material should be stopped as soon as the pH of the eluate has reached a value of 3—4.

The reproducibility of the resin in a reference state is important. It has become the custom to refer all capacity data to the weight of the resin obtained after heating to constant weight at 110° in air. This may be determined directly, or, if analytical data are available for the sorption of a given cation, the weight in the completely anhydrous state may be estimated from the percentage saturation by a method of successive approximations given by Boyd, Schubert, and Adamson.[22] Although the use of the anhydrous state of the resin is desirable in any data related to the absolute amount adsorbed, yet this is not necessary in determining many of the physicochemical properties. The mass-action constant K_a (for the exchange of univalent ions at least) and the shape of the exchange isotherm may be determined using only the total capacity of a given quantity of resin, irrespective of its weight in the dry state. Nor are such fundamental studies usually affected by the particle size of the exchanger; because of the gel-like structure of most of the synthetic exchangers, the equilibrium adsorption is quite independent of the state of subdivision.

Application of the Law of Mass Action.—As an initial approach to the physicochemical study of exchange, the law of mass action gives a fairly clear understanding. Consider the exchange reaction

$$\mathrm{Na}_{\mathrm{S}}^{+} + \mathrm{H}_{\mathrm{R}} = \mathrm{Na}_{\mathrm{R}} + \mathrm{H}_{\mathrm{S}}^{+}$$

By the law of mass action, which is obeyed to a greater or lesser degree by a large number of exchangers, we may obtain the mass-action constant as in equation (1) above. One way of testing the validity of equation (1) is as follows:

If each of the activity terms is replaced by the product of the activity coefficient (f) and the concentration (c), the equation

$$\log \frac{c_{\mathrm{Na_R}}}{c_{\mathrm{H_R}}} + \log \frac{f_{\mathrm{Na_R}}}{f_{\mathrm{H_R}}} = \log \frac{c_{\mathrm{Na_S^+}} f_{\mathrm{Na_S^+}}}{c_{\mathrm{H_S^+}} f_{\mathrm{H_S^+}}} + \log K_a . \quad . \quad . \quad (4)$$

is obtained. This equation was shown to be valid by Boyd, Schubert, and Adamson[22] using Amberlite I.R.-1. They obtained a straight line when $\log c_{\mathrm{Na_R}}/c_{\mathrm{H_R}}$ was plotted against $\log c_{\mathrm{Na_S^+}} f_{\mathrm{Na_S^+}}/c_{\mathrm{H_S^+}} f_{\mathrm{H_S^+}}$, the activity coefficients of the ions in the resin being assumed to be unity, and the concentrations in this phase proportional to the molar fractions.

If the law of mass action is true, and the total capacity of a given exchanger for cations is constant, then the weight of a univalent cation taken up on the resin should be quite independent of the absolute concentration of the cation in the solution—it should depend only on the ratio of the concentration of the cation and the hydrogen ion (see equation 3). This has also been confirmed experimentally.[22] The equilibrium constant K_c in experiments in which the cationic concentration was as low as 10^{-4}—10^{-5}M was nearly the same as the constant obtained using approximately 0·1N-solution. Bauman and Eichhorn [24] have also varied the normality for the NH_4^+/H^+ system from 0·01 to 4 and have shown that K_c for Dowex 50 remains constant below concentrations of 0·1M.

For the two cationic exchangers, Amberlite I.R.-1 and Dowex 50, the values of K_c obtained for several different univalent systems have been shown to hold to a first approximation over wide ranges of concentration. The initial assumption that the activity of the ions in the adsorbed phase is proportional to the molar fraction is therefore substantially true, *i.e.*, there is ideal solution of the ions in the resin. This is of great advantage in the physicochemical investigation of the properties of resins.

Although the above theory is apparently simple, it was not until quite recently that resins were obtained which obeyed the law of mass action. Compare, for instance, the results of E. Glueckauf [58] for the exchange of copper on the hydrogen form of Zeokarb HI (see Fig. 2). Here the adsorption isotherm shows clearly that the law of mass action is not obeyed and that the ion which is present in solution in the smallest amount is adsorbed preferentially, especially for very low and very high copper concentrations.

Several different equations have been suggested to accommodate the deviations from the law of mass action. One was that of V. Rothmund and G. Kornfeld,[59] namely :

$$c_{A_R}/c_{B_R} = K(c_{A_S}/c_{B_S})^p$$

where the subscripts R and S refer to the concentrations of ions A and B in the resin and in solution respectively. The constant p usually has values between about 0·5 and 1. This equation has achieved quite wide success ; Walton [60] gives values of p and K for systems where A = Na^+, Ba^{2+}, and H^+, and B = K^+, Ca^{2+}, and Na^+, using a Zeokarb as adsorbent.

H. Jenny [61] assumed that there is a definite number of attraction points per unit area and, using a statistical derivation, obtained an isotherm equation which is obeyed experimentally for colloidal clay systems over a considerable range of concentration. Jenny's equation is, however, not generally true for a wide range of different systems.

Much work on the theory of exchange has been done by E. N. Gapon,[62]

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[58] *J.*, 1947, 1302.

[59] *Z. anorg. Chem.*, 1918, **103**, 129.

[60] *J. Physical Chem.*, 1943, **47**, 371.

[61] *Ibid.*, 1936, **40**, 501.

[62] *J. Phys. Chem. Russia*, 1938, **11**, 782 ; *J. Gen. Chem. Russia*, 1937, **7**, 1447, 1453, 2801, 2806 ; *Chem. Zentr.*, 1941, **1**, 875 ; *Colloid J.* (*U.S.S.R.*), 1937, **3**, 859.

who derives different adsorption isotherm equations to describe the behaviour of the following systems: the exchange of barium and cadmium ions on bentonite, and sodium and ammonium ions on permutite; the exchange of silver and iodide ions on silver iodide and sodium on zeolites. He has also discussed the applicability to different isotherms of an empirical equation proposed by P. Vageler.[63]

The application of so many different equations to exchange systems shows how difficult it has been in the past to obtain ideal solution of the adsorbed ions in the solid phase (*i.e.*, proportionality of the activities of the ions in the solid phase to their molar fractions). A comparison of the behaviour of the two exchangers Amberlite I.R.-1 and Dowex 50 with those previously available brings out the advance which has been made in producing these two materials.

Exchange Isotherms.—The most convenient way of expressing the behaviour of a given exchanger is by means of an exchange isotherm. It being assumed that the law of mass action is obeyed by cationic exchangers, equation (3) gives the relation between the molar fraction of the univalent cation X_R in the exchanger, and the molar fractions of the same cation in solution. In the case of exchange between two ions which are univalent (or in general, of the same valency) the shape of the exchange isotherm is theoretically independent of the absolute concentration of the two ions in solution. This is not true for exchange between ions of different valency. Take, for instance, the reaction

$$\mathrm{Ca}_{\mathrm{S}}^{2+} + 2\mathrm{H}_{\mathrm{R}} = 2\mathrm{H}_{\mathrm{S}}^{+} + \mathrm{Ca}_{\mathrm{R}}$$

With the same assumption as in the previous case, *viz.*, that the activities of the ions in the solid phase are proportional to their molar fractions, the mass-action constant K_a is given by

$$\frac{X_{\mathrm{R}}}{(1 - 2X_{\mathrm{R}})^2} = K_a \times \frac{C_{\mathrm{R}}}{C_{\mathrm{S}}} \cdot \frac{X_{\mathrm{S}}}{(1 - 2X_{\mathrm{S}})^2} \quad . \quad . \quad . \quad (5)$$

where X_R (or X_S) is the number of moles of calcium ions in the exchanger (or in solution) divided by C_R (or C_S); C_R is the total equivalent capacity of the exchanger and C_S the total equivalent concentration in solution. In exchange reactions between ions of different valency, therefore, the shape of the exchange isotherm is not independent of the absolute concentration of the exchanging ions in the aqueous phase although the value of K_a still remains a parameter of the exchange equilibrium. Bauman and Eichhorn [24] have given the plot of $2X_R$ against $2X_S$ for different values of K_aC_R/C_S. From the shape of the exchange isotherm it is easy to see which of the two ions is adsorbed preferentially by the exchanger. This also provides a simple method of determining the extent to which the system being considered obeys the law of mass action.

Exchange isotherms are often determined experimentally by equilibrium methods in which the resin is stirred with a solution containing the exchanging ion. The concentrations of the replaced ion and the exchanging

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[63] " Der Kationen und Wasserhaushalt des Mineralbodens " (Springer, Berlin, 1932).

ion in solution are measured when equilibrium has been achieved. An isotherm thus determined, however, can be directly related to the behaviour of an exchanger when used as a packing in a " chromatographic " column. Also, by the reverse process, the exchange isotherm may be determined from a study of the behaviour of the exchanger under column operation. Chromatography has been treated theoretically by J. N. Wilson,[64] J. Weiss,[65] D. de Vault,[66] E. Glueckauf.[58, 67] and others. The use of chromatographic data to determine the adsorption isotherm and the mass-action constant has not yet been very extensive, but a good example of the treatment of experimental data by such methods is given by Glueckauf, who calculated the exchange isotherm of a copper–hydrogen system (reproduced in Fig. 2).

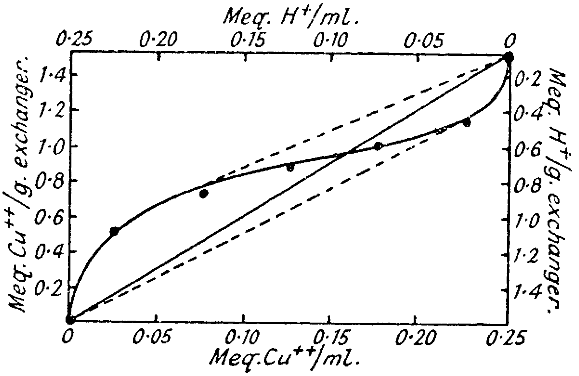

FIG. 2

The full line of Fig. 2 represents the isotherm calculated from chromatographic data, whilst the points are determined from equilibria obtained under batch conditions.

If the system obeys the mass-action law it is possible to determine the constant K_a by this method. By using the elution technique, the mass-action law has been shown to hold [68] for the exchanger I.R.-100H, and an exchange isotherm has been obtained from chromatographic data for the Na/H exchange which agrees with that obtained under batch conditions. The portion of the exchange isotherm near the origin, under conditions where the molar fraction of one of the ions in the resin phase is rather small, can be obtained very accurately by the chromatographic method. The method is also convenient, since only one experiment is required to determine the whole range of the isotherm; it should be of particular value in investigating exchange of radio-tracer amounts of material, where there may be significant deviations from the mass-action law.

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[64] *J. Amer. Chem. Soc.*, 1940, **62**, 1583.

[65] *J.*, 1943, 297.

[66] *J. Amer. Chem. Soc.*, 1943, **65**, 532.

[67] *Proc. Roy. Soc.*, 1946, *A*, **186**, 35; *Nature*, 1945, **156**, 748.

[68] J. F. Duncan, unpublished work.

If the mass-action data are known for a series of ions, the extent to which they may be separated by elution from an ion-exchange column operating under equilibrium conditions may be estimated. In practice, separation of ions by such a method is often attempted under conditions which are far from suitable for the attainment of equilibrium. Such non-equilibrium separations have been studied theoretically by G. E. Boyd, L. S. Myers, and A. W. Adamson,[69] who have shown that it is essential in separation work to employ small grain size, slow flow rates, and deep beds. A useful expression to find the minimum bed depth required to effect a separation of two ions is given by B. H. Ketelle and G. E. Boyd.[70] A theoretical analysis of column separation processes has also been given by S. W. Mayer and E. R. Tompkins.[71]

Titration Curves of Cationic Exchangers.—A second method used considerably in the past to characterise exchangers has been the determination of titration curves. The main difference between an exchange isotherm and a titration curve is that the former is normally determined under conditions where a definite small range of pH exists in solution, whilst the latter indicates the total exchange capacity over a wide range of pH. For exchangers which have sulphonic acid groups only as their exchanging species, the total capacity will be independent of pH over a wide range. For a mixed sulphonic–carboxylic–phenolic exchanger, however, this is not necessarily the case, although there is normally very little difference for pH values of less than 5.

A considerable number of titration curves have been measured by R. Griessbach [45] for resins containing $—SO_3H$, $—CH_2{\cdot}SO_3H$, $—CO_2H$, or $—OH$ as the active group,[1] and only some are of a shape which can be accounted for by means of the law of mass action. The titration method was employed in the past to estimate differences in exchange of cations of different size, valency, etc. The curves given by Griessbach, using an aromatic sulphonic acid type resin, clearly show that, of the alkali metals, lithium hydroxide is the least complete in its exchange whilst rubidium hydroxide is the most easily removed from solution. These findings are in accordance with the results of Jenny,[72] who showed that the exchange of ions on permutites was in reverse of the order predicted by Coulomb's law, *i.e.*, in exchange ability $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. This order is, however, the same as was found for the mobility of these ions in aqueous solution, which suggests either that the size of the ion in solution plays an important part in exchange or that the determining factor in exchange is one which also influences the size of the ion in solution. So far as multivalent ions are concerned, it has long been known that the greater the ionic charge, the more complete is the exchange adsorption, and preferential adsorption of multivalent ions has been observed by workers using both true exchangers and also columns of alumina, etc., on which exchange does not occur. A typical series is given by J. A. Swartout [73] in order of decreasing efficiency of exchange: $Th^{4+} > La^{3+} > Ba^{2+} > Na^+$.

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[69] *J. Amer. Chem. Soc.*, 1947, **69**, 2849.
[70] *Ibid.*, p. 2800.
[71] *Ibid.*, p. 2866.
[72] *J. Physical Chem.*, 1932, **36**, 2217.
[73] M.D.D.C. Report 442.

This series falls into line with the values obtained for the mass-action constant K_a for multivalent ions. In general, the K_a values are much higher than for univalent ions, sometimes being as high as 30 or 40. The real reason why multivalent ions should be more strongly adsorbed is not yet known ; this is an interesting field for future investigation. Boyd, Schubert, and Adamson,[22] however, have shown that for univalent ions, at least, the free energy of zeolite formation is a linear function of $1/a^0$, where a^0 is the distance of closest approach of the ions given by the Debye–Hückel equation. These authors also state that a ready qualitative evaluation of the relative magnitude of a^0 may be found directly from the activity coefficient–concentration plots, a^0 being larger the higher these curves lie in the plot. By using such methods it has been possible to show that one might expect the following sequences of adsorption to obtain :

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$$
$$Zn^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+}$$
$$La^{3+} > Ce^{3+} > Pr^{3+} > Nd^{3+} > Sm^{3+} > Eu^{3+} > Y^{3+} > Sc^{3+} > Al^{3+}$$

These series have largely been confirmed by experiment, but owing to the difficulty of comparing the activity curves of uni-, bi-, and multi-valent ions, it has not yet been possible to give a general comparison between these groups. However, the following series has been observed experimentally : [22]

$$La^{3+} > Y^{3+} \gg Ba^{2+} \gg Cs^{+} > Rb^{+} > K^{+} > H^{+} > Li^{+}$$

Titration Curves of Anionic Exchangers.—Hitherto, the discussion has centred almost exclusively on cationic exchangers. This has necessarily been so, for by far the greater part of the work has been with these exchangers which are more amenable to treatment by the mass-action law. It is now convenient to extend this discussion to the physical chemistry of anionic exchangers.

The removal of acids by anionic exchangers is due to salt formation of the basic groups contained in the resin, *e.g.*, $R{\cdot}NH_2 + HCl = (R{\cdot}NH_3)Cl$. This reaction, as it is written, is not an exchange reaction, and although the cationic exchangers have capacities independent of pH over a wide range, yet the amount of acid taken up by an anionic exchanger is critically dependent on pH. A typical capacity curve for an anionic exchanger is shown in Fig. 1 (*c*) ; the total capacity varies from zero at pH 7—10 to a high value at a pH of 2 or 3.

A large number of adsorption isotherms have been determined by Kunin and Myers [56] for several different acids adsorbed by the exchanger I.R.-4B. Their results show the following :

(1) The adsorption isotherms of hydrochloric acid and nitric acid were of the same order although the latter was definitely more strongly adsorbed than the former. Other univalent anions of highly ionised acids were adsorbed in the following sequence : hydroxide > nitrate > iodide = bromide > chloride (> fluoride).

(2) For the removal of weakly ionised acids, such as acetic, salicyclic, oxalic, etc., by Amberlite I.R.-4B, the amount adsorbed rose sharply from

1 meq./g. at pH 4 or 5 to 5 meq./g. or more at pH 3, in contrast to the strong acids for which there was a more gradual rise. These curves were not correlated with the known values of the dissociation constants of the acids. This would probably be difficult, since it is not clear at the moment whether it is necessary to assume that the resin–liquid interface is permeable to neutral acid molecules or not. Such a treatment will have to be made, however, before it can be said that anionic exchangers are properly understood.

The following sequence was given for the exchange affinities of the different ions they studied : sulphate > chromate > citrate > tartrate > nitrate > arsenate > phosphate > molybdate > acetate = iodide = bromide > chloride > fluoride.

(3) In general, the extent to which uni-, bi-, and ter-valent acids are held by the exchanger increases with basicity, and this is similar to the increase of cationic exchange of multivalent ions. The differences for hydrochloric, sulphuric, and phosphoric acids seemed to be most marked in solutions of low pH, but there was no general quantitative relation between the adsorption obtained at different pH's. In another paper, however, R. J. Myers, J. W. Eastes, and D. Urquhart [74] have found the acid-binding capacity of Amberlite I.R.-4 towards these three acids to be roughly : hydrochloric acid, 2·46 ; sulphuric acid, 4·1 ; phosphoric acid, 8·0 millimoles/g. Although these figures refer to a particular exchanger, many other exchangers give differences of this order. If all the replaceable hydrogen atoms of these acids were used, the maximum molar capacity towards dibasic and tribasic acids would be expected to be one-half and one-third respectively of that towards monobasic acids. It is clear that this is not the case. Nor are the figures quoted above in agreement with the suggestion that only the most easily dissociable hydrogen atom is used for binding the acid to the exchanger, thus : $R{\cdot}NH_2 + H_nX \rightarrow (R{\cdot}NH_3)H_{n-1}X$. If this were the only mechanism involved, one would expect the maximum molar capacity to be the same for the three acids. A complete explanation of the observed capacities remains to be given.

True Exchange in Anionic Systems.—The removal of acids from solution by means of synthetic nitrogen-containing systems may be regarded simply as adsorption of whole acid molecules on the resin. On the other hand, it has been suggested [56] that a more correct picture is one of exchange between the anion and a postulated hydroxyl group residing on the resin, *viz.*, $(R{\cdot}NH_3)OH + Cl^- \rightleftharpoons (R{\cdot}NH_3)Cl + OH^-$, the hydroxyl ion being removed by combination with a hydrogen ion.

There has been no evidence mentioned above which can give any indication of which of these mechanisms is likely to be true. It is known, however, that anions will exchange with one another irrespective of the behaviour of the hydrogen ion. Thus, in the original work by Adams and Holmes [16] it was shown that if a dilute solution of calcium sulphate were passed over a resin which had been previously saturated with hydrochloric

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[74] *Ind. Eng. Chem.*, 1941, **33**, 1270.

acid, the sulphate radical was removed by exchange adsorption with the chloride ion on the resin: schematically,

$$2(R{\cdot}NH_3)Cl + CaSO_4 \longrightarrow (R{\cdot}NH_3)_2SO_4 + CaCl_2$$

A very similar reaction has been observed[75] with a melamine–formaldehyde polymer which had been previously saturated with chloride ion. This was treated for lengths of time up to one minute with dilute calcium sulphate solution. The calcium sulphate was partly adsorbed at first, but after 30 seconds the calcium ions began to reappear in solution, accompanied by the chloride ion. This, it was suggested, shows that the exchange process consists of an initial adsorption followed by true exchange.

Kunin and Myers[56] have also made experiments in which an anionic exchanger was saturated with chloride ion before being allowed to exchange with another ion. The percentage adsorbed was plotted against the so-called "symmetry ratio" (proposed by Jenny[72]), *i.e.*, the ratio of the number of equivalents of anion added as soluble electrolyte to the equivalents added as exchangeable anion. In all except one of the reactions studied exchange took place. The exception was sodium borate, for which, although chloride was removed from the resin, no adsorption of borate occurred; hydrolysis was suggested as the cause. Many of the exchange curves were shown to obey a Freundlich isotherm equation, but the mass-action equation did not hold for any. It was thought that this "may merely be due to inability to obtain the true activities in the solid phase".

There is good evidence for regarding nitrogen-containing resins as true anionic exchangers therefore, and although direct evidence is still lacking, it is assumed that the active groups of the wet resin are the hydroxyl groups of $(R{\cdot}NH_3)OH$ rather than free $—NH_2$ groups. Since the basic strength of the resin is low, the hydroxyl-ion activity is very small also. It is for this reason that anions are adsorbed mainly in acid solution, although there is a small exchange of anions even in neutral solution. The pH of a solution in equilibrium with most of these anionic exchangers usually has a value of 7—8.

The regeneration of anionic resins with sodium hydroxide would be the obvious way to replace the adsorbed anions with hydroxyl groups, and this may be done. Most anionic exchangers, however, will absorb cations from the solution at high pH, by virtue of their phenolic or imino-groups, and the removal of such exchanged cations requires prolonged washing with water. It is more usual, therefore, to regenerate anionic exchangers with sodium carbonate solution; the carbonate radical is presumably hydrolysed to hydroxyl.

Kinetics of Exchange.—The rate at which the ionic exchange reaction occurs had not been studied in detail until quite recently. Silicate exchangers have been investigated by G. Wiegner and K. W. Müller,[76] who showed that the rate of exchange was dependent on the structure of the

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[75] G. Austerweil, *Bull. Soc. chim.*, 1941, **8**, 546.

[76] *Trans. 3rd Intern. Congr. Soil Sci.*, 1936, **3**, 5.

silicate, and by N. C. Cernescu,[77] who compared the rate of exchange of clay, permutite, and chabazite, showing that clay is the fastest. R. H. Beaton and C. C. Furnas [78] have considered base exchange as analogous to heat transfer, and have obtained transfer coefficients. They have been able to show that for the hydrogen–copper exchange on a carbonaceous zeolite, the exchange is 90% complete in 30 minutes. J. du Domaine, R. L. Swain, and O. A. Hougen [79] have also made experiments to investigate the rate of softening of hard water. F. C. Nachod and W. Wood [80] were among the first to make a serious attempt to investigate the kinetics of exchange. They studied the reaction of calcium ions with about ten different cationic exchangers previously converted into the hydrogen or sodium form. They also studied two anionic exchangers.

Cationic exchange. If ion exchange is to be regarded as a reaction between a liquid component and a simple solid component, for which the activity in solution is constant, then the reaction $n\mathrm{H}_\mathrm{R} + \mathrm{M}_\mathrm{S}^{n+} \rightarrow n\mathrm{H}_\mathrm{S}^{+} + \mathrm{M}_\mathrm{R}$ should obey a first-order reaction law, whatever the value of n. Such a law has never been observed. On the contrary, Nachod and Wood, for instance, showed that for a large number of exchangers, the $\mathrm{Ca}^{2+}/\mathrm{H}^{+}$ exchange obeyed a second-order law, of the form $\mathrm{d}x/\mathrm{d}t = k(a - x)(b - x)$, where a is the concentration of the calcium ion in solution, x is the amount exchanged in a time t, and b is the total capacity of the resin ; k had a value of $1\text{—}10 \times 10^{-1}$ meq.$^{-1}$ × l. × min.$^{-1}$. These findings are in agreement with results of B. A. J. Lister [52] for the exchange of tervalent cerium on Zeokarb HIP. W. Juda and M. Carron [82] have also concluded that the exchange velocities of several cation exchangers can be represented by a second-order rate equation.

It is clear, therefore, that the simple picture given above is not true. Unfortunately, the results of other workers are not sufficiently extensive to decide for how many reactions a second-order law holds. If it were generally true for all reactions involving uni-, bi-, or ter-valent ions, it would suggest that the rate-determining reaction is of the form

$$\mathrm{M}_\mathrm{S}^{n+} + \mathrm{H}_\mathrm{R} \rightarrow \mathrm{M}_\mathrm{R}^{(n-1)+} + \mathrm{H}_\mathrm{S}^{+},$$

in which the activity of the hydrogen in the resin is proportional to its molar fraction—as assumed in the mass-action treatment of ion exchange. The work of G. E. Boyd, A. W. Adamson, and L. S. Myers [83] on cationic exchangers, and of R. Kunin and R. J. Myers [84] on anionic exchangers, suggests that diffusion of the ions from the solution into the resin phase is the rate-determining process. More work is necessary before it is possible to say whether their postulates make a reaction mechanism of the above type unnecessary or not, but it should be mentioned that the curves obtained

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[77] *Anuar. inst. geol. Romaniei*, 1931, **16,** 777.

[78] *Ind. Eng. Chem.*, 1941, **33,** 1500.

[79] *Ibid.*, 1943, **35,** 546.

[80] *J. Amer. Chem. Soc.*, 1944, **66,** 1380.

[81] *J.*, 1948, 1272.

[82] Div. Phys. and Inorg. Chem., Amer. Chem. Soc., Sept. 1947.

[83] *J. Amer. Chem. Soc.*, 1947, **69,** 2836.

[84] *J. Physical Coll. Chem.*, 1947, **51,** 1111.

by the different authors are rather similar in shape, although interpreted in different ways.

Bauman and Eichhorn [24] have written the rate of exchange of the reaction :

$$\mathrm{Na}_{\mathrm{S}}^{+} + \mathrm{H}_{\mathrm{R}} \rightarrow \mathrm{Na}_{\mathrm{R}} + \mathrm{H}_{\mathrm{S}}^{+}$$

as

$$\mathrm{R}_n = k_1 a_{\mathrm{Na}_{\mathrm{S}}} a_{\mathrm{H}_{\mathrm{R}}} - k_2 a_{\mathrm{H}_{\mathrm{S}}} a_{\mathrm{Na}_{\mathrm{R}}}$$

By comparing this expression when R_n is zero (*i.e.*, at equilibrium) with that obtained by the application of Donnan equilibrium (see below) they conclude that $k_1 = k_2$, and since for dilute solutions the activity coefficients in the aqueous phase are unity, then

$$\mathrm{R}_n = k_1 f_{\mathrm{H}_{\mathrm{R}}} c_{\mathrm{Na}_{\mathrm{S}}} c_{\mathrm{H}_{\mathrm{R}}} - k_1 f_{\mathrm{Na}_{\mathrm{R}}} c_{\mathrm{H}_{\mathrm{S}}} c_{\mathrm{Na}_{\mathrm{R}}}$$

This equation has been confirmed by several different methods using Dowex 50 and the cations Li^+, Na^+, NH_4^+, K^+, and Ag^+. The mass-action constants obtained from rate data (equal to the rate of the back reaction divided by the rate of the forward reaction) did not agree exactly with that obtained from equilibrium data, although they were in the correct order. The deviations were assumed to be due to volume changes which occur when the resin is saturated with different cations.

The kinetics of exchange has been extensively treated from the point of view of diffusion by Boyd, Adamson, and Myers.[83] These authors obtain theoretical expressions for diffusion of ions (*a*) through a liquid film bounding a spherical particle (a logarithmic law), and (*b*) in and through an adsorbent particle itself (a parabolic law). The rate of the actual exchange reaction was also shown to obey a logarithmic law.

The three equations they obtained have been compared with experimental data for the exchange of alkali-metal ions on Amberlite I.R.-1. The experimental results showed that the parabolic law predicted for diffusion in the resin phase was obeyed only for solutions of concentration greater than 0·1M ; for solutions below 0·003M a logarithmic law was followed. If the latter were due to chemical reaction, one would expect (*a*) the rate to be independent of particle size, and (*b*) a large temperature dependence. Neither of these was found, and it was concluded that a diffusion mechanism was obtaining, the exchange rate being limited in this case by the ease with which the ions diffuse through a liquid film surrounding the solid resin particles.

Although this is the most recent work on the kinetics of cationic exchangers, the subject has still to be completed. It is not yet clear whether diffusion is the only important factor in determining rate of exchange.

Anionic exchange. The kinetics of anionic exchange were studied by Nachod and Wood [80] incidentally to their cationic studies. They investigated the rate of adsorption of hydrochloric acid on a Deacidite and on Amberlite I.R.-4B and found velocity constants of 10^{-3} to 10^{-4} meq.$^{-1}$ × l. × min.$^{-1}$. They considered that this suggested a mechanism different from that obtaining in the case of cationic exchange for which the velocity constants were about a thousand-fold bigger. The results were not such as to indicate which of the following equations represents the true mechanism

(a) $R{\cdot}NH_2 + HCl \longrightarrow (R{\cdot}NH_3)Cl$
(b) $(R{\cdot}NH_3)OH + HCl \longrightarrow (R{\cdot}NH_3)Cl + H_2O$

Almost the only other contribution to this field has been the work of Kunin and Myers,[84] who have investigated the kinetics of four different anionic exchangers using many different acids, and have studied the effect of pretreatment of the resin, concentration of solution, amount exchanged, mobility of exchangeable ions, salt concentration, temperature, and stirring conditions. They conclude that for most anionic exchange resins the rate-determining step is the diffusion of the ions through the gel structure. This conclusion is supported by abundant evidence.

Kunin and Myers have also studied the exchange of anionic species (*e.g.*, exchange of chloride with sulphate). Their results support the mechanism of anionic exchange rather than acid adsorption for the removal of acids from solution.

Effect of Temperature on Exchange.—The thermodynamics of exchange may be studied by examining the influence of temperature. It appears from the little work which has been done that temperature has a remarkably small effect on both the equilibrium constant and the rate of reaction. The following is a summary of the results so far obtained :

(*a*) Boyd, Schubert, and Adamson [22] found that the effect of temperature on the exchange of potassium with a sodium-saturated resin was so small that the enthalpy of exchange was very close to zero. This might have been expected with ions so closely similar.

(*b*) Nachod and Wood [80] found that the rate of exchange of a sulphonated-coal type of cationic exchanger was the same at 60° as at room temperature, although a slightly lower rate was found at 0°. It was concluded that the exchange reaction is more or less independent of temperature, and that the difference between room temperature and 0° " is rather due to changes in diffusion rate than changes in exchange rate ".

(*c*) Kunin and Myers [84] found a lower rate of exchange at 1° than at 30° for the adsorption of hydrochloric acid on Amberlite I.R.-4B.

In spite of the indications of the above experiments that temperature has a small influence on exchange, Ketelle and Boyd [70] found that, using the citrate complex method (see below), increasing the temperature of a column of Dowex 50 to nearly 100° considerably enhanced the separation of ytterbium and thulium, and they recommended that the separation of rare earths be performed at a higher rather than a lower temperature.

It is clear that the work so far described is only a beginning. The determination of the heat of exchange and of the influence of temperature on the subsidiary processes such as diffusion, hydration, etc., needs to be fully worked out. It would certainly be surprising if temperature were found to have little or no influence on exchange, since most of the rate-determining factors are known to be influenced by temperature.

Donnan Equilibrium.—It has been suggested by different authors that, because of the gel-like structure of most resinous ion exchangers, ions will penetrate and exist to a greater or lesser extent in solution inside the gel. The system may then be treated as a Donnan equilibrium in which the overall gel surface acts as a semipermeable membrane.

Now, if we regard the surface of a cationic exchanger as comprising such a membrane, and the solid resin anion R^- as being the ion which cannot pass through it, then we may write a Donnan equilibrium of the type

$$\begin{array}{c|c} \mathrm{Na}_{\mathrm{R}}^{+} & \mathrm{Na}_{\mathrm{S}}^{+} \\ \mathrm{H}_{\mathrm{R}}^{+} & \mathrm{H}_{\mathrm{S}}^{+} \\ \mathrm{Cl}_{\mathrm{R}}^{-} & \mathrm{Cl}_{\mathrm{S}}^{-} \\ \mathrm{R}^{-} & \end{array}$$

membrane

According to the Donnan theory, the free energy of substances on both sides of the membrane must be the same, from which it follows [85] that :

$$a_{\mathrm{Na}_{\mathrm{R}}} . a_{\mathrm{Cl}_{\mathrm{R}}} = a_{\mathrm{Na}_{\mathrm{S}}} . a_{\mathrm{Cl}_{\mathrm{S}}}$$

and

$$a_{\mathrm{H}_{\mathrm{R}}} . a_{\mathrm{Cl}_{\mathrm{R}}} = a_{\mathrm{H}_{\mathrm{S}}} . a_{\mathrm{Cl}_{\mathrm{S}}}$$

where the symbols are defined as in equation (1).

Bauman and Eichhorn [24] have shown that if these two equations are divided and one assumes that the aqueous solutions are dilute, one obtains a relation between the concentrations in the resin and solution such that

$$\frac{c_{\mathrm{Na}_{\mathrm{R}}}}{c_{\mathrm{Na}_{\mathrm{S}}}} \times \frac{c_{\mathrm{H}_{\mathrm{S}}}}{c_{\mathrm{H}_{\mathrm{R}}}} = \frac{f_{\mathrm{H}_{\mathrm{R}}}}{f_{\mathrm{Na}_{\mathrm{R}}}} = K_c \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where f values are activity coefficients and c values are molar concentrations.

It will be seen that the first part of this expression is the same as that obtained by application of the mass-action equation to the reaction

$$\mathrm{Na}_{\mathrm{S}}^{+} + \mathrm{H}_{\mathrm{R}} \rightleftharpoons \mathrm{Na}_{\mathrm{R}} + \mathrm{H}_{\mathrm{S}}^{+}$$

and therefore the constancy of the expression is no proof of the existence of a Donnan equilibrium. Further, the mass-action constant is equal to the ratio of the activity coefficients of the ions in the resin phase. As these activities have not been determined experimentally, a direct test of this prediction cannot be made. Bauman and Eichhorn,[24] however, have noticed that the mass-action constants (for Dowex 50 at least) increase in order of decreasing activity coefficients of corresponding salts for a large number of cations. They suggest " it is quite possible that ion-exchange equilibrium in Dowex 50 is determined simply by the difference in activity coefficients between the outside solution, and the very highly concentrated resin solution, without involving any specific affinity of the —SO_3 groups for one ion over another ". Such an assumption would be incompatible with the simple mass-action law, for it would necessarily require the activity coefficients in the resin phase to be other than unity as postulated in

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[85] See Glasstone, " Textbook of Physical Chemistry " (Macmillan, London, 1947).

equation (4). In this case one must replace f_{H_R}/f_{Na_R} by K_c and write equation (4) as

$$\log c_{Na_R}/c_{H_R} - \log K_c = \log K_a + \log c_{Na_S^+}/c_{H_S^+}$$

the aqueous solution being assumed to be dilute enough for $f_{Na_S^+}$ and $f_{H_S^+}$ to be unity. Then

$$K_c.K_a = \frac{c_{Na_R}}{c_{H_R}} \times \frac{c_{H_S^+}}{c_{Na_S^+}} = K_c$$

i.e., K_a is unity for all univalent ions. If this is so and $K_c = f_{H_R}/f_{Na_R}$ is the only factor determining the degree of exchange of a given ion (as postulated by Bauman and Eichhorn) the apparent constancy of K_c must be explained. Both f_{H_R} and f_{Na_R} must necessarily depend on the values of c_{H_R} and c_{Na_R} (even though the total capacity and ionic strength are constant) and therefore K_c would not be expected to be a constant over the whole of the isotherm.[86]

Another requirement of the Donnan conditions given above—equivalence of activity of the hydrochloric acid and sodium chloride in the resin phase and in solution—is that there must be a definite concentration of anions in the resin phase. This means that there is always some anion adsorbed as well as cation, and therefore exchange phenomena can never be exactly equivalent. Non-equivalent exchange has been observed for sodium aluminosilicates. Jenny [1] reports that chloride ion is adsorbed by sodium and magnesium aluminosilicates, in the latter case in quantities up to 0·65 meq./g. Strong anion adsorption of bivalent ions on casein from aqueous-alcoholic solutions has also been observed. On the other hand, it should be pointed out that equivalence of exchange has been reported by several different authors (*e.g.*, Way,[3] Jenny,[1] A. Renold,[87] Rothmund and Kornfeld [59]).

Another means of varying the position of the Donnan equilibrium would be to vary the nature of the anion, since this would be expected to alter the activity coefficient of the anion. Some experiments of Nachod and Wood [88] show that the nature of the anion does in fact alter the position of equilibrium. This has also been observed by E. Ungerer,[89] who investigated the exchange of calcium aluminosilicate with potassium salts. He found the following sequence of increasing adsorption

$$CNS^- < IO_3^- < I^- < ClO_3^- < NO_3^- < Cl^- < SO_4^{2-} < CrO_4^{2-} < CH_3 \cdot COO^- < Fe(CN)_6^{4-}$$

Other workers [90] have concluded that the anion had no effect on exchange.

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[86] By making reasonable assumptions for the activity coefficients of the ions in the resin phase the Reviewers have been able to show that K_c would be constant only over the centre portion of the adsorption isotherm. The treatment is based on an application of equations of the type: $\log f_{HCl} = \log f^{\circ}_{HCl} - \alpha_{12}c_{NaCl}$ familiar in solution theory (see H. S. Harned and B. B. Owen, " The Physical Chemistry of Electrolytic Solutions ", Reinhold, 1943).

[87] *Kolloid Beih.*, 1935, **43,** 1.

[88] *J. Amer. Chem. Soc.*, 1945, **67,** 629.

[89] *Z. Pflanz. Dung. Boden.*, 1930, **18** *A*, 342; 1932, **23,** *A*, 353.

[90] J. R. Patton and J. B. Ferguson, *Canadian J. Res.*, 1937, **15B,** 103; E. Raman and A. Spengel, *Z. anorg. Chem.*, 1918, **103** 129; 1919, **108,** 215.

There has been so much disagreement between investigators in this field that more work is necessary before the essential facts, let alone the theory of ion exchange, can be reliably established.

Applications of Ion Exchange

Removal of Simple Inorganic Ions.—The earliest, and still perhaps the most important, application of ion-exchange materials is the softening of water. Until quite recently the active materials in such softeners were natural and synthetic zeolites working in the sodium cycle. The replacement of materials by resinous exchangers was an improvement in that the high capacity, rapid action, and low resistance to flow of the latter permitted greater through-puts than was hitherto possible. Also, with resinous exchangers, no silicic acid is given up to the water.

The removal of cations of salts contained in water can be achieved by filtration through a hydrogen-saturated exchanger, the resultant solution containing free mineral acids and carbonic acid. By such a method almost complete removal of salts may be achieved from waters rich in carbonate, for the carbonic acid formed may be conveniently removed by degassing. If a substantial quantity of mineral acid is formed in solution, it may be removed by passage through an anionic exchanger. This two-stage process, given the name " demineralisation " or " deionisation ", can produce water of quality about the same as that of distilled water. In the second stage of the process the anions are only removed in acid solution.

The application of ion-exchange materials, particularly Ba/Ag zeolite, to render sea water potable has received attention [91] and patents have been obtained. The " demineralisation " process may find application in many industries where a cheap supply of high-purity water is essential. In addition to the supply of feed water for high- and low-pressure boilers, application has been considered in the food, textile,[92] dyeing,[93] dairying, pigment, and brewing industries. The literature dealing with water purification by ion exchange is very extensive and cannot be dealt with fully in this Review. We may mention, however, discussions by Myers,[1] Walton,[2] and Griessbach [45] on the general principles and by W. U. Gallaher and H. F. Weckwerth,[94] F. Bachmann,[95] and E. Nordell [96] on the economic aspects.

Apart from water purification, great interest has been shown in the purification of sugar, the ion exchangers being used to remove contaminating foreign ions. Among the advantages claimed are an increased yield, better

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[91] H. Ingleson, *J. Soc. Chem. Ind.*, 1945, **64**, 305 ; W. V. Conzolazio, N. Pace, and A. C. Ivy, *Smithsonian Reports*, Pub. 3820, 1935, 153 ; E. I. Akeroyd, E. L. Holmes, and A. Klein, *J. Soc. Chem. Ind.*, 1946, **65**, 28 ; H. D. Meincke, U.S.P. 2,391,258 (1944) ; R. T. Pemberton, A. J. R. Walter, and E. L. Holmes, B.P. 553,233 (1941).

[92] H. Miedendorp, *Rayon Textile Monthly*, 1947, **28**, 79 ; S. N. Miller, *ibid.*, p. 130 ; R. N. Nessler, *ibid.*, p. 82.

[93] A. Richter, *Melliand-Textilber.*, 1939, **20**, 279.

[94] *J. Amer. Water Works Assoc.*, 1947, **39**, 147.

[95] *Ibid.*, 1944, **36**, 876.

[96] *Chem. and Met. Eng.*, 1943, **50**, 112.

quality, and prevention of scale, leading to smoother and more efficient evaporation. In a test [97] in which 20,000 gallons of sugar juice were purified by ion exchange, 72·6% of total non-sugars, 92·5% of the ash-producing, and 90—98% of the nitrogenous substances were removed. Sugar recovery was increased by 10·5%, but the production of molasses, although of higher quality, decreased by 20·8% in consequence. An increased inversion of sucrose may cause trouble and the acidity has to be carefully controlled. In other food industries, the purification of gelatin [98] and fruit juices [99] has been studied. As examples of the many other reported uses of exchangers for removing ionic impurities from organic materials may be quoted the removal of traces of sodium and copper from oils,[100] of mineral acids from lactic acid solutions,[101] and the deacidification of formalin.[102]

Purification of a normally ionic substance from other ionic impurities may be effected if the substance can be converted into a non-ionic form in which it is not taken up by the exchanger. Such procedure has been carried out in the case of the purification of zirconium solutions from iron, titanium, beryllium, and lanthanum by converting the zirconium into colloidal form and then passing the solution through a column of Amberlite I.R.-100.[103] The ionic impurities were taken up and an uncontaminated zirconia sol was obtained in the effluent.

In addition to the removal of unwanted ions from solution, a similar method may be used for the concentration of valuable trace metals on the exchanger. Examples of this are the recovery, on cation-exchange materials, of copper from dilute solution [20, 104] (*e.g.*, from cuprammonium rayon plants), of silver from photographic film residues,[20] and of magnesium from sea water.[105] By anion exchange, Cr, Au, Fe, Mo, Pd, Pt, and V have been recovered from dilute solutions in the form of complex anions,[106] and tartrates have been recovered from grape wastes.[107]

Removal and Separation of Organic Substances.—A number of cases are known where the process is applied to the isolation and purification of complex organic materials. Various hexose phosphates have been purified by adsorption first of cations (present mostly as acetates) on Amberlite

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[97] E. A. Haagensen, *Sugar*, 1946, **41**, 36.

[98] E. L. Holmes, B.P. 548,205 (1941), D.R.-P. 741,401 (1940) ; A. Rousselot, *Compt. rend.*, 1943, **216**, 54.

[99] R. E. Buck and H. H. Mottern, *Ind. Eng. Chem.*, 1945, **37**, 635 ; H. Hadorn, *Mitt. Lebensm. Hyg.*, 1946, **37**, 114 ; S. W. Challinor, M. E. Kieser, and A. Pollard, *Nature*, 1948, **161**, 1023.

[100] H. G. Schulze, U.S.P. 2,375,694 (1941).

[101] J. C. Hesler and A. S. Behrman, U.S.P. 2,415,558 (1942).

[102] American Cyanamid Co., B.P. 573,051 (1942).

[103] J. A. Ayres, *J. Amer. Chem. Soc.*, 1947, **69**, 2879.

[104] H. L. Tiger and P. C. Goety, U.S.P., 2,397,575 (1938).

[105] J. J. Grebe and W. C. Bauman, U.S.P. 2,387,898 (1942) ; M. J. Hunter and W. C. Bauman, U.S.P. 2,409,861 (1942).

[106] S. Sussman, F. C. Nachod, and W. Wood, *Ind. Eng. Chem.*, 1945, **37**, 618.

[107] J. R. Matchett, R. R. Legault, C. C. Nimmo, and G. K. Notter, *ibid.*, 1945, **36**, 851.

I.R.-100 and then of the ester (a strong acid) on Amberlite I.R.-4.[108] Acetic acid and other weak organic acids, dextrins, proteins, etc., pass through unchanged and soluble impurities are washed out with water. Commercial pectinase has been freed from traces of pectin methyl esterase,[109] but, according to L. H. Lampitt,[110] the purification of pectin by ion exchange is not to be recommended as it results in the splitting off of certain combined inorganic material.

Many organic nitrogen-containing compounds form substituted ammonium salts in solution. Such substances, under certain pH conditions, behave as electrolytes and take part in ion-exchange reactions in a similar way to inorganic salts. Considerable effort has been made towards isolation and recovery of amino-acids. Fundamental investigations of the effect of a number of factors on the adsorption of amino-acids on Amberlites I.R.-100 and I.R.-4 have been made by C. S. Cleaver, R. A. Hardy, and H. G. Cassidy,[111] and on resinous and carbonaceous exchangers by D. T. Englis and H. A. Fiess.[112] Attempts during the last few years to separate various amino-acids from simple mixtures and from protein hydrolysates have been attended by considerable success.[113] Group separations can be accomplished by using exchangers containing different acid groupings; carboxyl exchangers (*e.g.*, Wofatit C) will adsorb only the basic amino-acids, whereas exchangers containing sulphonic acid groups will take up the weakly acidic as well as the basic amino-acids. E. Sperber [114] reports the use of an anionic exchanger in the middle chamber of the three-chamber electrodialysis apparatus as a buffer in the group separation of basic, neutral, and acidic amino-acids. Alkaloids behave in a similar way to amino-acids.[115]

Further interesting uses which are claimed for the exchange process are the recovery, on an anion exchanger, of a new antianæmia vitamin (probably belonging to the B complex) from liver and kidney tissue,[116] and the complete removal, on Amberlite I.R.-100, of thiamine in the presence of riboflavine.[117]

Simple Ionic Separations.—By percolating a solution through a column of cation exchanger, all cations may be replaced by hydrogen ions or sodium ions provided that the exchangeable ions of the resin are in excess over those in solution. A solution containing no free acid can similarly be

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[108] R. M. McCready and W. Z. Hassid, *J. Amer. Chem. Soc.*, 1944, **66**, 560.

[109] R. J. McColloch and Z. I. Kertesz, *J. Biol. Chem.*, 1945, **160**, 149.

[110] *J. Soc. Chem. Ind.*, 1927, **66**, 121.

[111] *J. Amer. Chem. Soc.*, 1945, **67**, 1343.

[112] *Ind. Eng. Chem.*, 1944, **36**, 604.

[113] T. Wieland, *Ber.*, 1944, **77**, 539; R. J. Brock, U.S.P. 2,386,926 (1942); *Arch. Biochem.*, 1946, **11**, 235; M. S. Bergdoll and D. M. Doty, *Ind. Eng. Chem.* (*Anal.*), 1946, **18**, 600; A. Tiselius, B. Drake, and L. Haddahl, *Experientia*, 1947, **3**, 21.

[114] *J. Biol. Chem.*, 1946, **166**, 75.

[115] S. Sussman, A. B. Mindler, and W. Wood, *Chem. Ind.*, 1944, **57**, 455, 549; N. Applezweig, *J. Amer. Chem. Soc.*, 1944, **66**, 1990; N. Applezweig and S. E. Ronzone, *Ind. Eng. Chem.*, 1946, **38**, 576.

[116] J. J. Pfiffner, A. Arbor, S. B. Binkley, E. S. Bloom, and A. D. Emmett, U.S.P. 2,407,096 (1948).

[117] D. S. Herr, *Ind. Eng. Chem.*, 1945, **37**, 631.

produced by use of an anion adsorbent. Such separations are discussed fully in the section on analytical uses and will not be dealt with further here.

The affinity of an exchanger for a cation, and conversely the ease of release on regeneration, are known to depend on several factors including valency, the size of the ion, and pH. Several series have been given above showing the order of preference of various cations for a given exchanger. If an exchanger is put into contact with a solution containing two species of ions, at equilibrium there will be a greater relative concentration on the exchanger of that ion having the greater adsorption affinity. Ionic competition in such a static system has been studied [118] for mixtures of Na^+, K^+, Mg^{2+}, Ca^{2+}, and H^+ ions in the presence of clays and bentonites, the relative ease of release being in the above order, with the hydrogen ions the most strongly adsorbed.

From a consideration of the law of mass action applied to a system containing two ionic species A^+ and B^+ in contact with a hydrogen-ion exchanger, an estimate may be made of the degree of separation expected. The greater the difference between the two equilibrium constants the easier will be the separation of the two ions.

Valency plays a large part in adsorption affinity, and, in general, ions of higher valency are more readily adsorbed and less easily removed than those of lower valency. The differences in affinity, however, particularly with ions of similar valency, are quite small, and to obtain any effective separation, a multi-stage process must be used. The chromatographic technique offers such a process and has been widely used in this connection, considerable degrees of separation having been obtained by the method in its simplest form. One of the most striking applications of simple chromatography with ion-exchange materials (apart from complexing action—see later) has been the partial separation of rare-earth metals by R. G. Russell and D. W. Pearce.[119] By percolating a mixed solution of rare-earth nitrates through a 50-ft. column of sodium zeolite they were able to obtain significant enrichments of some of the ions. They found that La^{3+}, Nd^{3+}, and Sm^{3+} ions were enriched in the filtrate fractions, while on regeneration of the siliceous exchanger with sodium chloride solution, Y^{3+}, Er^{3+}, and Yb^{3+} were concentrated in the regenerant fractions. Work by B. A. J. Lister and M. L. Smith [81] on the resolution of simple Ce^{3+}–Nd^{3+} mixtures using a similar column technique with a hydrogen-ion exchanger also showed significant separations, but in this case, contrary to the experience of Russell and Pearce, the ion of greater Goldschmidt radius (Ce^{3+}) was preferentially held by the exchanger. R. Kozak and H. F. Walton [120] have found that mixtures of Cu^{2+}–Ni^{2+}, Cd^{2+}–Zn^{2+}, and Ag^+–Cu^{2+} can be partially separated by the chromatographic technique, but, although the method could be improved by increasing the column length, they conclude that it is less satisfactory than conventional chemical

[118] R. H. Bray, *J. Amer. Chem. Soc.*, 1942, **64**, 954.

[119] *Ibid.*, 1943, **65**, 595.

[120] *J. Physical Chem.*, 1945, **49**, 471.

methods. Their results, however, are not very significant because of the large flow rate used. Fractionation of a radium–barium mixture using a multi-stage chromatographic method is described by A. F. Reid.[121] His experimental results correspond to a separation factor of 1·22 and the method looks quite promising.

In competition between ions of unequal valency, the total concentration of the solution may be important. L. Wiklander [122] has examined the equilibrium between a solution containing Ca^{2+} and NH_4^+ ions and an exchanger over a wide range of concentration, and has found a large variation in the Ca^{2+}/NH_4^+ ratio on the exchanger between 1N- and 0·0001N-solutions. With mixtures of ions of equal valency, it is generally considered that concentration has little or no effect.

The experiments quoted above were concerned with the separation of two (or more) species percolated through material containing a third exchangeable ion. Separation of two ionic species may also be obtained by the normal elution chromatography technique, the two ions being adsorbed as a thin band at the top of the column and eluted with a solution containing a third ion (already adsorbed on the major part of the column).

Theoretical treatment of such a system is complex and the more important aspects only will be discussed here. By the use of a series of equations given by Glueckauf [123, 124] it is possible to calculate the distribution of ions in binary chromatograms for solutes following either Langmuir or Freundlich isotherms. (An exchange system of two ions of the same valency following a mass-action law can be shown to lead to a Langmuir adsorption isotherm equation with respect to one of the exchanging ions.) In this type of system, separation is facilitated by working at high adsorption densities, but no advantage is gained from using high solute concentrations when the adsorbent is already nearly saturated.

In the case of mixtures of closely similar solutes for which only partial enrichment may be achieved, it is advantageous to develop with a solution containing a third, more strongly adsorbed solute of at least equal concentration. A system fully studied by Glueckauf is the partial separation of Mn^{2+} and Cu^{2+} ions on Zeokarb H.I. by development with N-sulphuric acid, for which the measured elution curves showed excellent agreement with those calculated on the basis of a Langmuir isotherm.

Factors of great importance in separation work on ion-exchange columns are flow rate and grain size of exchanger. If either of these is too large, equilibrium conditions will not be attained. The influence of incomplete local equilibrium is similar to diffusion effects and is very marked at the high concentration gradients existing at the boundaries of chromatograms. The disturbance of boundaries by non-equilibrium is considered by Glueckauf, and systematic experiments showed that the quality and sharpness of boundaries continuously improved with reduction of grain size and

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[121] *Ind. Eng. Chem.*, 1948, **40**, 76.

[122] *Svensk Kem. Tids.*, 1945, **47**, 54.

[123] *J.*, 1947, 1302, 1321.

[124] E. Glueckauf and J. I. Coates, *ibid.*, pp. 1308, 1315.

flow rate. There is an optimum flow rate, since the boundary when using a very small rate of flow will be disturbed by diffusion effects. Diffusion is relatively less important than non-equilibrium phenomena, and in the system studied by Glueckauf (Cu^{2+}–Mn^{2+} system) the optimum flow rate was below the lowest flow rate measured (0·001 cm./sec.). Under the most favourable conditions studied (flow rate 0·001 cm./sec., grain size 0·01 mm.) sharp boundaries were obtained extending over only 0·1—1% of the threshold volume. In a great deal of the published chromatographic work the importance of non-equilibrium phenomena has been overlooked and it would be as well in future work if the shapes of the boundaries obtained are carefully checked.

Separation by Elution with Complexing Solutions.—As a result of work in the Manhattan Project, a new chromatographic technique has been evolved based on elution from columns of ion-exchange material with solutions which form complexes with the adsorbed ions. The method has been shown to be remarkably efficient for the separation of fission products, including rare-earth metals, and the work represents a considerable advance both in the application of exchange methods to separation work and in the understanding of the exchange process.

Since the effective concentration of an ion in solution may be reduced by complex formation, any cation can be replaced from a resin containing it by a dilute solution of a second cation and a compound which will form a complex with the bound cation. For example, a resin in contact with a solution containing hydrogen and zirconium ions in equivalent molar concentration and at a sufficiently low pH, will be largely in the zirconium form. If oxalate ions are now added to the solution, a negatively charged zirconium oxalate complex is formed and the resin reverts almost completely to the hydrogen form. The method of separating ions by this method consists essentially of adsorbing the mixture of ions as a narrow band at the top of an exchange column and then eluting with a material which will enter into complex formation with the ions to be separated. The complexing agent used in almost all the American work on rare-earth separations was a citric acid solution buffered with ammonium citrate. When such an ammonium citrate buffer is passed through a column of exchanger predominantly in the hydrogen form, exchange occurs between ammonium and hydrogen ions resulting in a fall in pH. Thus the pH of the first effluent will be approximately that of citric acid and this value will gradually rise until, at equilibrium, the pH of the original buffer solution is reached. If a mixture of ions had been previously adsorbed at the top of the column, the release of hydrogen ions in solution would prevent the formation of any metal–citrate complex ; the metal ions would remain adsorbed on the exchanger until the hydrogen-ion concentration had decreased to the point where the complex is stable. As a result, no metal–complex ions can precede the pH which will permit their existence, and the rate of movement of the eluted ions is governed by the movement of the pH boundary.

Let us consider a cerous ion, Ce^{3+}, adsorbed on a column. When an ammonium citrate solution, at a pH which will just support the formation of a complex ion, is passed through the column, exchange will take place according to the scheme:

$$3(NH_4^+)_S + Ce_R \rightleftharpoons 3(NH_4)_R + Ce_S^{3+} \quad . \quad . \quad . \quad (7)$$

The cation will also enter into further equilibrium with the complexing ion H_2Cit^-:

$$Ce^{3+} + 3H_2Cit^- \rightleftharpoons Ce(H_2Cit)_3 \quad . \quad . \quad . \quad . \quad (8)$$

The fraction of the total cerium found in the complex is determined by the ratio of the equilibrium constants of reactions (7) and (8). When the resin is in the hydrogen form, there exist the equilibria

$$(NH_4^+)_S + H_R \rightleftharpoons (NH_4)_R + H_S^+ \quad . \quad . \quad . \quad (9)$$

and

$$H^+ + H_2Cit^- \rightleftharpoons H_3Cit \quad . \quad . \quad . \quad . \quad (10)$$

and increase in hydrogen-ion concentration brought about by reaction (9) causes the reversal of reaction (8) and the readsorption of the Ce^{3+} ions on the resin.

In the case of two ions A^{n+} and B^{n+}, a separation factor α can be calculated from the respective equilibrium distribution coefficients. Thus:

$$\alpha = K_d^A/K_d^B \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where the distribution coefficient (K_d) is defined as the ratio of the concentration of the ion (either free, or complexed) in the resin phase and in solution. Whilst some separation of closely similar ions is possible without complexing action, it is clear that the differences in adsorbabilities are enhanced by differences in the homogeneous equilibria in the aqueous phase.

The distribution ratio is strongly dependent on pH, since it is this which predominantly determines the degree of complexing. Experimental results by E. R. Tompkins and S. W. Mayer [125] have shown that with fall of pH, the value of K_d rises rapidly and the ratio of the distribution coefficients for any two cations increases. At higher pH values the separation factor decreases, approaching the value expected if complexing agent were not used. It appears that the univalent H_2Cit^- ion is the only citrate ion effective for the separation of rare earths, and as a result, the operation of separation columns at pH's above 3·5 will considerably decrease their efficiencies.

The effect of temperature on K_d will probably be determined by the temperature dependence of the first dissociation constant of citric acid. With solutions less than 6×10^{-3}M the distribution coefficient is independent of the rare-earth concentration.

From information on the dissociation constants of some of the complexes of the ions under consideration, it is possible to calculate the values of α that would be obtained when each of a number of complexing agents is used for elution. The relative merits of a number of conditions can thus quite readily be evaluated, and conditions chosen to give satisfactory separation. Practically all American work on rare-earth separations was carried out with citric acid as the complexing compound, and little informa-

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[125] *J. Amer. Chem. Soc.*, 1947, **69**, 2859.

tion is available on the merits of other complexing agents. It is fairly certain, however, that citric acid is not the only, and probably not the most effective, eluant, and this is borne out by figures given [125] for the distribution coefficients of europium and element 61 in the presence of several different complexing agents.

One of the first examples of the application of this technique was the demonstration that zirconium and columbium could be selectively eluted from a fission product mixture by dilute oxalic acid.[126] Although this method is a considerable advance on other known methods for separating elements of the rare-earth series, an examination of the American work shows that only quite small amounts of material can be handled at one time, and that the resolution of mixtures is still a very time-consuming operation necessitating careful control.

The study of simple binary and tertiary mixtures such as Ce^{3+}–Y^{3+} [127] and Nd^{3+}–Pr^{3+} [128] by Spedding and others has led to the establishment of conditions which may be used in the large-scale separation of complex mixtures. Radiochemical tracer technique was largely employed to follow the separation. It was shown that there is a critical bed length beyond which no improvement in separation can be achieved [130] and that for a given column size there is a certain sample weight for which the degree of separation is optimum.[128] Citric acid concentration is important and 0·5—5·0% solutions were used throughout the work, more rapid elution being obtained with the higher concentrations. The order of elution of the rare-earth metals is the reverse of the order of ionic (crystal) radii and of the atomic numbers ; [70, 129] it is also the reverse of the order of basicity (predicted by von Hevesy). The most difficult groups of elements to separate are the triads : Dy, Y, Ho ; Tm, Yb, Lu ; and Sm, Eu, Gd. As an example of a small-scale separation may be quoted that of a mixture of middle rare earths containing 0·1 mg. Ho_2O_3 and 1 mg. each of Dy_2O_3, Gd_2O_3, Eu_2O_3, and Sm_2O_3.[70] The bed of Dowex 50 (of 270—350 mesh) was 97 cm. long and of 0·26 sq. cm. cross-section, and the use of a working temperature of 100° permitted the employment of a high flow rate (1·0 ml./sq. cm./min.), thereby reducing the time of the experiment. The use of a higher temperature was shown to result in sharper separations, and the stability of Dowex 50 at 100° gives this exchanger an advantage over the Amberlites. The separation was complete in about 100 hours, during which time 1500 ml. of citrate solution had passed through the column.

From a knowledge of the order of elution, qualitative and quantitative analysis of unknown constituents of rare-earth mixtures is possible. Determinations of cationic trace impurities may be made, and a sample of erbium oxide which was considered by spectrographic analysis to be pure was shown to contain 10 p.p.m. of thulium.[70] Examination of samples containing neutron-bombarded praseodymium and neodymium salts have led to

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[126] E. R. Tompkins, J. X. Khym, and W. E. Cohn, *J. Amer. Chem. Soc.*, 1947, **69**, 2769.

[127] F. H. Spedding *et al.*, *ibid.*, p. 2777.

[128] *Ibid.*, p. 2786.

[129] J. A. Marinsky, L. E. Glendenin, and C. D. Coryell, *ibid.*, p. 2781.

the first positive identification of two isotopes of element 61 of 47-hour and 3·7-year half-lives.[129]

Separations on a pilot-plant scale have been carried out by Spedding and his group,[130] using columns of Amberlite I.R.-100 8 ft. long and 4 in. in diameter. The columns were found to work satisfactorily up to loads of 100 g. of rare-earth oxide. With a flow rate of 0·5 cm./min. (*i.e.*, 40 ml./min.) all the rare earths contained in 50 g. of commercial neodymium carbonate (Nd_2O_3 80·1, Sm_2O_3 10·4, Pr_6O_{11} 8·4, Gd_2O_3 1·0%) were eluted with about 1200 litres of 0·5% citrate solution, the run lasting some 20 days. From this starting product were obtained 21·5 g. of pure Nd_2O_3 ($>$ 99·9%) and 5·2 g. of a pure Sm_2O_3–Gd_2O_3 mixture. Similar work was carried out with the yttrium-group earths, and multigram quantities of highly pure gadolinium and yttrium salts were obtained.

Tracer-quantity Separation.—The adsorption isotherm of a tracer cation M^{a+} is linear over a very wide concentration range of the tracer, and the ratio of tracer cation in the resin to cation in solution is a constant. This may be seen by applying the law of mass action, assuming the distribution ratio of the hydrogen ion to be constant.

According to the law of mass action, changes in concentration should not affect the degree of separation of two ions of the same valency in simple systems without the use of complexing agents. From a consideration, however, of the number of exchanges taking place per unit length of the column, it has been suggested [125] that the separation between two solutes present in macro-quantities would be poorer than that of tracer quantities of two substances. In addition, if the concentration in solution of solute ions exceeds a certain value (3×10^{-4}M for Dowex 50 and 4×10^{-7}M for Amberlite I.R.-1) the equilibrium distribution coefficient is affected, this again causing a decrease in the degree of separation.

Only meagre quantitative data are available to compare the separations obtained using macro-quantities (order of 1 mg.) and tracer amounts (*ca.* 10^{-10} g.) but work with the Ce^{3+}–Y^{3+} system on Amberlite I.R.-1 [127] showed that with these elements the use of tracer quantities gave inferior separations compared with those obtained with macro-amounts. In both cases a decrease in pH resulted in improved separation. At present, therefore, it is difficult to predict what would happen at higher concentrations from experiments with tracer quantities, and caution should be exercised in assuming that values for the mass-action constant determined in one range of concentration are true for the other, unless this has been experimentally shown.

The Separation of Isotopes.—The classical work on the separation of isotopes by ion exchange was made by T. I. Taylor and H. C. Urey.[131] They investigated the enrichment of lithium isotopes brought about by passing lithium chloride down a column of natural zeolite of 30—100 ft. length. This work has been reviewed previously.[132]

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[130] *Ibid.*, p. 2812.

[131] *J. Chem. Physics*, 1937, **5**, 597; 1938, **6**, 429.

[132] *Ann. Reports*, 1938, **34**, 143.

A considerably greater enrichment of lithium isotopes has been obtained by Glueckauf[133] under conditions especially favourable to equilibrium (*i.e.*, very fine grain size and slow flow rate). From a column of Zeokarb H.I. of 1 metre length he obtained less than 1% of ^{6}Li in his head fraction.

Almost the only other work in this field was done by A. K. Brewer,[134] who investigated the separation of potassium isotopes in phosphate rocks and soils and on greensand. In the latter case, it was shown that ^{41}K is more firmly adsorbed than ^{39}K.

One would expect the separation of isotopes by this method to be determined primarily by an exchange reaction of the type $M^{H}_{S} + M^{L}_{R} \rightleftharpoons M^{H}_{R} + M^{L}_{S}$, where M^{H} and M^{L} are the cations of the heavy and light isotopes respectively. The equilibrium constant of such a reaction is given by

$$K_a = \frac{f(M^{H}_{R})}{f(M^{L}_{R})} \times \frac{f(M^{L}_{S})}{f(M^{H}_{S})} = \frac{a_{^{7}Li_{R}}}{a_{^{6}Li_{R}}} \times \frac{a_{^{6}Li_{S}}}{a_{^{7}Li_{S}}}$$

where the f values represent the overall partition functions for the various species.

H. C. Urey and L. J. Greiff[135] have shown that the equilibrium constants of chemical exchange reactions may be calculated from spectroscopic data, provided the vibration frequencies of the respective isotopic molecules be known. Whilst this calculation can be made for simple cases such as the exchange of chlorine isotopes between free chlorine and hydrogen chloride, in the case of ionic exchange between a liquid and solid phase there are two difficulties : first, the calculation of the partition function of an ion, and secondly, the estimation of the vibration frequencies (and partition function) of the species M^{H}_{R} and M^{L}_{R}. It is therefore not possible to calculate the mass-action constant from spectroscopic data. One would, however, expect that the greatest separation of isotopes would be obtained in those cases for which there is the greatest difference in vibration frequencies between the species M^{H}_{R} and M^{L}_{R} (assuming that there is very little difference between the partition functions of the ions) and this would occur for isotopes which have proportionately large differences in atomic weight, *i.e.*, for those of small atomic weight.

Analytical Uses.—Both cationic- and anionic-exchange materials have been employed for quantitative determination of ions in aqueous solution. The technique is somewhat similar to the chromatographic methods of inorganic analysis using columns of activated alumina, 8-hydroxyquinoline, etc. On these adsorbents, however, the separate zones are either visible or can be rendered visible on the white column material, whereas with dark exchange resins, the zone lengths cannot be seen. Chromatographic methods are now receiving much attention, and a survey of analytical work[136] published in 1946 shows that of all papers on separation methods in that year, 25% deal with chromatography and ion exchange. It is

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[133] Private communication.

[134] *J. Amer. Chem. Soc.*, 1939, **61**, 1597.

[135] *Ibid.*, 1935, **57**, 321.

[136] F. C. Strong, *Anal. Chem.*, 1947, **19**, 968.

recommended in that survey that advanced analytical courses should contain instruction on chromatography and ion-exchange methods.

The greatest advances in the use of ion-exchange material in analytical chemistry have been made by O. Samuelson and his co-workers,[137–149] and it is his work that forms the basis of applications in this field. The determination of cations may be carried out in one of two ways: (*a*) the cation is adsorbed by percolating the solution through an exchange column, the column is washed, and the cation then eluted and analysed, or (*b*) after adsorption, washing, and elution, the hydrogen-ion concentration of the eluate is determined by alkalimetric titration or other means, and is assumed equivalent to the cation which has displaced it from the resin. The greatest advantage from the use of the exchange technique is that the initial cations and anions may be completely separated from one another and determined separately, thus rendering simple the analysis of one ion in a solution containing a second ion (of opposite charge) which normally interferes with its determination. A table is given by Samuelson [137] showing the possibilities of separating anion and cation in simple salt solutions using a cationic exchanger.

The order of accuracy of determinations with simple salts is illustrated by the work of Samuelson,[144] who showed that nitrates, chlorates, and metaphosphates of a number of different metals could be determined to within 0·4%.

Most of the interferences in the determination of sulphate can be overcome [138] by first passing the solution through a bed of hydrogen-saturated exchanger, and this procedure may be used in the determination of sulphur in pyrites after conversion into sulphate. The removal of the cation when determining sulphate in a solution of the aluminium salt gives a true result under conditions where the value obtained by the normal procedure is often low owing to adsorption.[139] Determinations of the alkali metals in the presence of sulphate,[149] phosphate,[143] chromate, molybdate, tungstate, phosphomolybdate, and phosphotungstate [145] are simplified. Hydrogen-saturated exchangers cannot always be used because the formation of acid in solution may interfere, and in such cases a resin previously saturated with ammonium ions is convenient; elution and regeneration are effected by percolation through the bed of dilute solutions of ammonium salts. Vanadium (as vanadate) can be separated from alkali metals [139] by passage through an ammonium-ion exchanger, and the alkali metals determined after regeneration of the exchanger; the determination of iron and aluminium in the presence of phosphate [141] is simplified. The polarographic determination of selenite,[148] which has been considered impracticable in

[137] *Tek. Tidskr.*, 1946, **76**, 561.
[138] *Z. anal. Chem.*, 1939, **116**, 328.
[139] *Svensk Kem. Tids.*, 1939, **51**, 195.
[140] *Ibid.*, 1940, **52**, 115.
[141] *Ibid.*, p. 241.
[142] *Ibid.*, 1942, **54**, 170.
[143] *Ibid.*, 1945, **57**, 91.
[144] *Ibid.*, p. 158.
[145] *Ibid.*, p. 250.
[146] *Ibid.*, 1946, **58**, 247.
[147] *Ibid.*, 1947, **59**, 13.
[148] *Ingeniors Vetenskaps Akad., Stockholm*, 1946, 1.
[149] Runneberg, *Svensk Kem. Tids.*, 1945, **57**, 114.

solutions containing Fe^{3+}, Al^{3+}, Co^{2+}, Mn^{2+}, or Zn^{2+} ions, is satisfactory after removal of these cations on an exchange column. Exchange methods of analysis are not limited to simple compounds but are also applicable to solutions containing complexes. The removal and recovery of potassium from the complex cyanides [144] $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, $K_3Cr(CN)_6$, $K_3Co(CN)_6$, $K_4Mo(CN)_8,2H_2O$, and $K_4W(CN)_8,2H_2O$ is over 99·8%.

The use of anionic exchangers in analysis has not been studied at all fully, but we may mention the determination [150] of dicarboxylic amino-acids in protein hydrolysates on a column of Amberlite I.R.-4B.

A most important analytical application is the determination of traces. This field has been comparatively little studied but the work so far described makes it apparent that here the exchange technique is a very powerful tool. The determination of copper in milk (< 1 p.p.m.) using a Zeokarb [151] gave results which, although a little low compared with spectrophotometric dithizone methods, were in good agreement with the polarographic method. More extensive experiments,[152] however, with Amberlite I.R.-100 in the ammonium condition give a better idea of the usefulness of the technique. Solutions of 0·1N-ammonium phosphate were used to carry traces of Cu^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+}, and Mn^{2+} in concentration approximately 10^{-4}M, the trace metals were adsorbed on a column of exchanger and after being washed were eluted with hydrochloric acid. In the absence of excess cations in the solution containing the trace metals, there was good adsorption and the recovery was practically complete. The high recoveries of materials present in quantities not greater than 20 μg. suggested the possibility of analysing for trace metals samples of plant materials as small as 1 g. with an accuracy of about 10%. It was found that partial separation of cations could be achieved by using a series of acid eluants of different concentration.

A point which must be watched is the tendency of some solutions to form complexes. This, as well as the formation of colloids (as in solutions of ferric salts), may give low results for the cation adsorbed.

In analytical work, care must be taken both in the choice of exchanger and in details of technique. Such properties as stability, solubility, and constancy of composition are very important, particularly in trace analysis, and in these respects the analytical-grade materials now available (*e.g.*, in the Amberlite series) are preferable. The rate of percolation must be quite carefully controlled and it is best to work under equilibrium, or near equilibrium, conditions. The tendency in published work has been for the flow rate to be too great, and this may either lead to incomplete removal or necessitate the use of larger quantities of exchanger.

Catalytic and Buffering Actions.—The use of base-exchanging substances in the field of contact catalysis is not new. In the literature before 1930, references are made [153] to catalysts suitable for use in producing oxidation

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[150] R. K. Cannan, *J. Biol. Chem.*, 1944, **152,** 401.

[151] H. A. Cranston and J. B. Thompson, *Ind. Eng. Chem. Anal.*, 1946, **18,** 323.

[152] J. P. R. Riches, *Nature*, 1946, **158,** 96; *Chem. and Ind.*, 1947, 656.

[153] A. O. Jaeger, B.PP. 286,212 (1928), 304,640 (1928), 309,024 (1929); U.S.PP. 1,782,353 (1926), 1,694,620 (1927); *Ind. Eng. Chem.*, 1929, **21,** 627.

products of aromatic hydrocarbons. They contained base-exchange substances and catalytically active elements such as V, W, Mo, Cu, Ni, U, Cr, or Zn combined in non-exchangeable form. These and similar zeolitic materials [154] act as carriers for the heavy-metal ion.

More recently the carbonaceous and resinous exchangers have been employed as catalysts in a number of organic reactions. Cationic exchangers in the hydrogen-saturated form may be considered as strong acids of high equivalent weight and, as such, are able to replace mineral acids in many acid-catalysed reactions. One of the early examples of a sulphonated carbonaceous exchanger acting as a catalyst was in the hydrolysis of starch to glucose.[155] H. C. Cheetham [156] reports catalysis of condensation of resins by an acid-regenerated cationic exchanger and a salt, and H. M. Spurlin [157] used a methylated anionic exchanger and sodium chloride as a substitute for calcium oxide in the synthesis of pentaerythritol. It is possible, however, that in both cases there occurred reaction between the exchanger and the salt, giving in the first case mineral acid, and in the second case free sodium hydroxide which then acted as the catalytic material. Since the publication of reports [158] describing the large-scale use in Germany of Wofatit exchangers as catalysts for esterification, ester exchange, and hydrolysis reactions, American and British work has shown the possibilities of catalysis of a wide range of organic reactions by using hydrogen-saturated exchangers. In particular, S. Sussman [159] has examined, in this connection, esterification reactions, ester hydrolysis and alcoholysis, acetal synthesis and alcoholysis, alcohol dehydration, and sucrose inversion. In one example studied, the synthesis of *n*-butyl oleate, the yield was still over 96% after five runs. The preparations of triacetin (75% yield), glycol diacetate (48%), and ethyl chloroacetate (87·5%) are other examples of esterification given by Sussman. The esterification of furfuryl alcohol (an extremely acid-sensitive material) was successful and there was no resinification. The exchanger used in this work was generally Zeokarb-H but a sulphonated phenol–formaldehyde resin was also used with equal success. The nature of the exchanger is apparently not important as long as it contains strongly acidic groups. Ester hydrolysis has been studied by G. G. Thomas and C. W. Davies [160] as well as by Sussman. The former authors found that, on using Amberlite I.R.-100, methyl and ethyl acetates underwent hydrolysis according to a first-order law, whereas the hydrolysis of *n*-butyl and benzyl acetates followed a zero-order law so long as ester was present as a separate phase. C. L. Levesque and A. M. Craig [161]

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[154] Compagnie française des Procèdes Houdry, Fr.P., 845,009 (1938); Houdry Process Corpn., B.P. 519,808 (1938); J. H. Brant and R. L. Hasche, U.S.P. 2,245,567 (1939).

[155] N. V. Octooien Maatschappij "Activit", B.P. 509,710 (1938).

[156] U.S.P. 2,334,904 (1940).

[157] U.S.P. 2,364,925 (1942).

[158] R. J. Myers, F.I.A.T., P.B. 42,802 (1946); Diericks, Office of Technical Services, Dept. of Commerce, Wash., B.P. 866 (1945).

[159] *Ind. Eng. Chem.*, 1946, **38**, 1228.

[160] *Nature*, 1947, **159**, 372.

[161] *Ind. Eng. Chem.*, 1948, **40**, 96.

have examined the esterification of butanol and oleic acid in the presence of a hydrogen exchanger and have found that after an initial slow period the reaction is essentially of the second order. The velocity constant is directly proportional to the surface area of the catalyst per unit weight of reactants. Sussman found the hydrolysis of *n*-butyl oleate difficult, probably because of the presence of a three-phase system, but on the introduction of a mutual solvent, a 9% yield was obtained. Some evidence was obtained for the dehydration of castor oil with Zeokarb-H but conclusive results were not forthcoming owing to the decomposition of the catalyst at the necessarily high temperatures. A pronounced inversion of sucrose was noted [159] after 30 minutes at 90°, and Jenny [72] has found that the mutarotation of glucose is catalysed by the hydroxyl form of an anionic exchange resin.

There are considerable advantages in the use of exchangers as acid–base catalysts. For instance, (1) they can be used with acid-sensitive reactants and with high-boiling compounds, (2) separation of the catalyst after reaction is a simple matter of filtration and centrifuging, and (3) the catalyst may be re-used many times, fresh catalyst being required only to make up mechanical losses.

From a consideration of the law of mass action, it is apparent that exchange resins which are partially saturated with hydrogen ions should act as buffers for controlling the pH of solutions since an exchanger with a given molar fraction of H^+ ions in the resin phase will always be in equilibrium with a definite concentration of hydrogen ions in solution. This is particularly important in the fermentation industries, for example, for controlling the fermenting solution in lactic acid production.[162] The use of exchangers makes possible the buffering not only of hydrogen ions but of any cation. An example is the buffering of calcium and sodium ions in milk.[163] By passing cows' milk over an exchanger containing calcium and sodium in the right proportion, the ratio of these two ions in the milk can be reduced to that of human milk. Among the many possible inorganic applications, Griessbach [45] mentions the removal of hydrogen ions in nickel electrolysis.

Determination of Physicochemical Constants.—Improved understanding of the ion-exchange process has made possible the application of exchange materials to the determination of a number of physicochemical constants. Such a method has the advantage of requiring only tracer concentrations of the substance under examination, and the systems can be studied with the aid of radio-chemical counting technique. Work so far described in this field includes studies of complexes, determination of activity coefficients, the determination of the state, valency, and basicity of a radio-element, and investigations with radio-colloids.

The determination of the dissociation constant of a complex ion involves the measurement of the degree of adsorption of a cation in solution of known and constant ionic strength in the absence and in the presence of a

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[162] N. V. Octooien Maatschappij "Activit", Fr.P. 805,092 (1936).

[163] J. F. Lyman, E. H. Browne, and H. E. Otting, *Ind. Eng. Chem.*, 1933, **25**, 1297.

specific complexing agent. The two important equilibria may be represented as

$$\mathrm{M}_x\mathrm{A}_y^d \rightleftharpoons x\mathrm{M}^{a+} + y\mathrm{A}^{b-}, \text{ where the dissociation constant } K_c = \frac{c^x_{\mathrm{M}^{a+}} \cdot c^g_{\mathrm{A}^{b-}}}{c_{\mathrm{M}_x\mathrm{A}_y^d}} \quad . \quad (12)$$

$$\mathrm{M}_\mathrm{S}^{a+} + a\mathrm{H}_\mathrm{R} \rightleftharpoons \mathrm{M}_\mathrm{R} + a\mathrm{H}_\mathrm{S}^+, \text{ where } K_c = \frac{c_{\mathrm{M}_\mathrm{R}} \cdot c^a_{\mathrm{H}_\mathrm{S}^+}}{c_{\mathrm{M}_\mathrm{S}^{a+}} \cdot c^a_{\mathrm{H}_\mathrm{R}}} \quad . \quad . \quad (13)$$

For tracer concentrations it is found that $c_{\mathrm{M}_\mathrm{R}}/c_{\mathrm{M}_\mathrm{S}^{a+}}$ is constant, and this ratio (λ_0) represents the slope of the linear isotherm for low values of $c_{\mathrm{M}_\mathrm{R}}$. If the experimental conditions are such that these equations hold, then bv substitution of the value for λ_0 in equation (12) we have that

$$K_c = \frac{c^x_{\mathrm{M}_\mathrm{R}} \cdot c^y_{\mathrm{A}^{b-}}}{\lambda_0^x \cdot c_{\mathrm{M}_x\mathrm{A}_y^d}} = \frac{a^x \cdot c^y_{\mathrm{A}^{b-}}}{\lambda_0^x\left(S - \dfrac{a}{\lambda_0}\right)}$$

where a = amount of M^{+a} adsorbed, and S = total amount of M still in solution. Equating the values of K_c for the results at two different concentrations and solving for λ_0, one obtains the expression

$$\lambda_0 = \frac{(a_1)(a_2)^x(c_{\mathrm{A}_2^{b-}})^y - (a_2)(a_1)^x(c_{\mathrm{A}_1^{b-}})^y}{(S_1)(a_2)^x(c_{\mathrm{A}_2^{b-}})^y - (S_2)(a_1)^x(c_{\mathrm{A}_1^{b-}})^y}$$

From this the value of K_c can be determined. J. Schubert [164, 165] has applied this argument to the determination of the dissociation constants of strontium tartrate and strontium citrate ($^{89}\mathrm{Sr}$ concentration = *ca.* 10^{-11} mole/litre), and his results are in very good agreement with values obtained by other methods. Samuelson [166, 148] has measured the dissociation of the ferrimetaphosphate complex. The method is applicable over wide ranges of temperature and pH, is simple and rapid to carry out, and gives results of good accuracy and precision.

The usefulness of ion exchangers for determining activity coefficients was first examined by A. P. Vanselow [167] and has more recently been studied by Schubert.[164] Both workers base their arguments on the law of mass action, and arrive at the expression $f_{\mathrm{A}^+} = \frac{K_c}{K_a} \times f_{\mathrm{B}^+}$, for the activity coefficients f_{A^+} and f_{B^+} of the ions in solutions, where K_c and K_a are the mass-action and thermodynamic equilibrium constants for the reaction $\mathrm{A}_\mathrm{S}^+ + \mathrm{B}_\mathrm{R} \rightleftharpoons \mathrm{A}_\mathrm{R} + \mathrm{B}_\mathrm{S}^+$. The value of K_a is assumed to be the same as the value of K_c measured in dilute solutions of B^+. (Bauman and Eichhorn [24] found that, for $\mathrm{NH}_4^+/\mathrm{H}^+$ exchange on Dowex 50, the value of K_c became constant at concentrations below 0·1N). Also, if A^+ is present in only trace concentration then the activity coefficient of B^+ may be taken as the

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[164] *J. Physical Coll. Chem.*, 1948, **52,** 340.

[165] *Ibid.*, p. 350.

[166] *Svensk Kem. Tids.*, 1944, **56,** 277.

[167] *J. Amer. Chem. Soc.*, 1932, **54,** 1307 ; *Soil Sci.*, 1932, **33,** 95.

same as that of its pure solution. So by selecting a bulk electrolyte whose activity coefficients are known, we can measure directly the activity coefficient of an electrolyte present in concentrations of the order of 10^{-8}M in a solution of the same ionic strength as that of B^+. This is not the same as the activity coefficient of the ion A^+ in a solution of zero ionic strength and therefore the measurement is only of limited value. The method can be applied to multicomponent systems, and knowing the activity coefficient of any one ion in the system, then that of any other ion may be determined. Vanselow examined the Ca^{2+}/Ba^{2+} exchange on bentonite and his results were in fair agreement with those calculated from published data. Schubert [168] has measured the activity coefficients of radiotracers in uranyl nitrate solutions.

A qualitative determination of the state of an unknown radio-element in solution, whether anionic, cationic, or colloidal, can be made rapidly by studying its exchange reactions under a number of conditions, and by comparing its behaviour with ions of known valency and basicity. Ion exchange affords an excellent method, rapid and relatively simple to carry out, for determining the nature of a radio-element in solution and for classifying chemically an unknown radioisotope.

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[168] J. Schubert, unpublished work.