Figure 5 illustrates a section of Fig. 2 through 5% lead.

Effect of Bismuth on the Partial Miscibility of Lead and Zinc (Median through Bismuth).—Figure 6 illustrates the effect of adding increasing quantities of bismuth to a mixture of equal proportions of lead and zinc by weight. This is a section through the middle point of the lead–zinc base and Bi (Fig. 2). Up to 70% bismuth, zinc freezes out from these alloys at almost constant temperature. With higher percentages of bismuth, the freezing point rapidly falls to that of pure bismuth. Binary arrests show a minimum at 40% bismuth, 30% lead, 30% zinc. This composition lies at the Zn–TE line (Fig. 2).

Sections of the diagram (Fig. 2) at 5% bismuth and 10% bismuth are given in Figs. 7 and 8, respectively. The sharp fall in the binary arrests at high percentages of zinc or near the zinc corner of Fig. 2 is clearly noticeable.

Effect of Zinc on the Miscibility of Lead and Bismuth (Median through Zinc).—Figure 9 illustrates the effect of adding increasing quantities of zinc to a mixture of equal proportions of bismuth and lead by weight. There are three separate lines. The upper line represents the freezing points of the alloys. The middle one shows the binary arrests and the lowest line the freezing points of the ternary eutectic.

A section of the diagram (Fig. 2) at 5% zinc is illustrated in Fig. 10. The binary arrests show a minimum at 55% bismuth, 40% lead and 5% zinc. As this composition lies on the Zn–TE line the primary arrest is also low and is hardly distinguishable from the binary arrest.

Microscopic Investigation.—The conclusions drawn from the phase rule considerations (discussed above) are supported by microphotographs of some of the alloys as given in Fig. 11.

Summary

In this system a tertiary eutectic is formed with 55% bismuth, 43% lead and 2% zinc. Its freezing point is 124°.

By addition of 10–15% or more of zinc to the miscible binary alloys of bismuth and lead, the ternary alloys (thus formed) become immiscible.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, PERMUTIT COMPANY]

The Reaction Velocity of Ion Exchange

BY F. C. NACHOD AND W. WOOD

Many investigators have studied ion exchange phenomena and approached the subject from various directions. A great number of papers come from the soil chemist and, consequently, deal largely with ionic distribution in soils. Other investigators have described industrial uses and applications. Data on ionic equilibria between exchanger and solution have been collected.

However, surprisingly little information can be gathered if one wants to learn something about the rates of reaction taking place between the ions in solution and in the ion exchange material. One encounters qualitative statements that the reaction proceeds rapidly at first[1,2] and then slows down as the equilibrium is approached.

DuDomaine, Swain and Hougen[3] focussed their attention on cation exchange softening rates. Their technique consisted in passing hard water through thin layers of exchange material. The small dimension of the bed permitted disregarding concentration gradients and the authors arrived at differential rate equations. Certain limitations of the procedure are stated by the authors (p. 553 of ref. 3) and no rate constants were given, nor was the order of the reaction determined by these experiments. The data obtained by these authors are of value only for a particular cation exchange and a particular water composition. No net reaction rate could be obtained by their procedure.

Beaton and Furnas[4] obtained transfer coefficients by considering base exchange to be analogous to heat transfer. Their data on the hydrogen–copper exchange show again that the reaction is very rapid and about 90%[5] of it is completed in thirty minutes.

The difference between a good and a bad exchanger was shown graphically by Austerweil.[6] His experiments show that the exchange reaction is extremely rapid and completed after approximately fifteen minutes.

The writers have endeavored to measure the rate of reaction of ion exchange and their results are given below.

The ion exchange materials which were studied comprise two classes. In the first class are siliceous materials of natural origin, *e. g.*, the glauconite or greensand type exchanger as well as synthetic siliceous gel type exchangers which all are cation exchangers. The organic materials which form the second class embrace cation exchangers, characterized by the functional groups —SO_3H,

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(1) J. R. Patton and J. B. Ferguson, *Can. J. Research*, **B15**, 103 (1937).

(2) H. F. Walton, *J. Franklin Inst.*, **232**, 318 (1941).

(3) J. duDomaine, R. L. Swain and O. A. Hougen, *Ind. Eng. Chem.*, **35**, 546 (1943).

(4) R. H. Beaton and C. C. Furnas, *ibid.*, **33**, 1500 (1941).

(5) Ref. 4, Fig. 1, p. 1503.

(6) G. Austerweil, *Bull. soc. chim.*, [5] **6**, 57 (1939).

—COOH, and —OH, may be either of the sulfonated coal[7] or of the synthetic resin,[8,9] category. The symbol H represents the exchangeable ion, which in this case is H. The anion exchange materials are all resins which contain functional amino groups, *i. e.*, RNH_2, R_2NH, and R_3N. The reaction mechanisms for the various exchange reactions will be discussed later on.

The reaction rate could be determined by following the rate with which ions from solution are removed by the solid ion exchanger or conversely the rate with which exchangeable ions are released from the exchange material into the solution. Both procedures were used and gave satisfactory results. The solid ion exchange material containing exchangeable ion was brought into contact with the solution containing the other type of exchangeable ion in considerable (4–5 fold) excess, and the system was vigorously agitated. In the experiments involving short periods from one-quarter minute to two minutes, the agitation was carried out manually; and in experiments involving longer periods, agitation was provided by a shaking wheel, rotating at 20 r. p. m. Due to the rotation of the reaction vessel in either case, the solid granules fall at random through the solution and concentration gradients in the liquid phase are minimized.

Experimental Part

The experimental technique was rather simple and somewhat crude. The ion exchanger was first "conditioned." By this is meant that its capacity was first exhausted with the ion which was to be taken up later on, then regenerated with a considerable excess of regenerant, rinsed free of excess regenerant, and air-dried. The "conditioned" air-dried material was placed in a bottle, the moisture content of the material was determined and suitable samples, mostly 1 g. of 20–30 mesh fraction (on a dry basis), were weighed out on a torsion balance with an accuracy of 0.2%. The samples (20–30 mesh size) were placed in 250-ml. Erlenmeyer flasks and generally 200 ml. of solution, containing the ion which was to undergo the exchange, was added. The contact periods were varied and the temperature was held constant within less than one degree for each series of experiments. In experiments at 0, 27, and 60° the thermostating was accurate to 0.5°. This rather crude temperature control is justified because the ion exchange equilibria in the low concentration range observed shift but little with temperature.[10]

The final justification of this crude temperature control was ascertained in the experiments dealing with the temperature coefficient of the reaction rate, where it was found that the reaction velocity was insensitive to a moderate temperature change.

After the time intervals had elapsed the supernatant solution was withdrawn rapidly and aliquots were analyzed.[11] In exchanges involving the hydrogen ion, the samples were titrated for acidity against methyl orange as indicator. For the exchanges involving the calcium ion, the residual calcium-content was titrated with potassium palmitate solution, following the method by Blacher, *et al.*[12,13]

Calculations.—In most experiments, 200 ml. of solution was employed; x denotes the amount of ions exchanged, a refers to the ions originally in the solution, and b refers to the ions from the exchanger in the maximum amount, released when equilibrium is reached. All these concentrations were expressed as milliequivalents per 200 ml. or total meq. A more rigid treatment would include the rate of the reverse reaction and would lead to a highly complex rate equation like the one derived by Bodenstein.[14] However, the reproducibility of the presented data does not warrant such a refined treatment. The k^1 values in the following tables are calculated on the basis of decadic logarithms and meq./200 ml. As all rate constants were given in meq.$^{-1}$ × l. × min.$^{-1}$, and based on natural logarithms, these k^1 values had to be multiplied by 5 and 2.303 and were listed under the k column.

In calculating the results we found that all our experimental values could be fitted into the simplest second order bimolecular reaction equation

$$dx/dt = k(a - x)(b - x)$$

Upon integration, considering $x = 0$ for $t = 0$ and $x = x$ for $t = t$ follows

$$k = \frac{1}{t} \times \frac{1}{a - b} \ln \frac{b(a - x)}{a(b - x)}$$ [15]

This finding is somewhat surprising because it implies the validity of two assumptions, *i. e.*, first, in spite of the fact that we deal with a heterogeneous reaction we can treat the solid phase which contains the exchangeable ion as if it were a dissolved reactant; and second, no attempt was made to use activities because the activity coefficient of the solid phase is not known but is probably unity, and in the concentration range of the experiments, *i. e.*, 0.01 to 0.001 N, the activity coefficients for the electrolytes also are relatively close to unity. On the other hand, we may deal with a compensation effect resulting in a net-charge of zero as was shown for a different system by Nachod.[16] It is of interest to note that in a complicated heterogeneous system, *i. e.*, the hydrolysis of ethyl acetate distributed between an aqueous and a benzene phase, Goldschmidt and Messerschmitt[17] arrived at a similar rate constant equation, only modified by a distribution coefficient term $C + 1/C$.

Cation Exchange Reactions.—The rates of exchange for the hydrogen exchange reaction for

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(7) S. B. Applebaum and R. Riley, *Ind. Eng. Chem.*, **35**, 186 (1943).

(8) R. Griessbach, *Z. Ver. deut. Chem.*, p. 13–16, Verlag Chemie Berlin (1939); *Angew. Chem.*, **52**, 215 (1939).

(9) B. A. Adams and E. L. Holmes, *J. Soc. Chem. Ind.*, **54**, 1T (1935).

(10) Ref. 1; also Walton, Ref. 2, p. 321.

(11) The exchange measurements were carried out by Eleanor Fabritiis, Elizabeth Goldy and Mary Lucas.

(12) C. Blacher, P. Grunberg and M. Kissa, *Chem.-Ztg.*, **37**, 56 (1913).

(13) M. Suter, *J. Am. Water Works Assoc.*, **29**, 1001 (1931).

(14) M. Bodenstein, *Z. physik. Chem.*, **29**, 307 (1899).

(15) *Cf.* also S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, N. Y., 1940, p. 1035, and other texts.

(16) F. C. Nachod, *Z. physik. Chem.*, **A182**, 209 (1938).

(17) A. Goldschmidt, *ibid.*, **31**, 235 (1899).

three commercial cation exchange materials were determined for the reaction

$$H_2Z + Ca^{++} \rightleftharpoons CaZ + 2H^+$$

The index two in the hydrogen ion exchanger, H_2Z, does not imply that the radical is divalent but is written solely for the sake of convenience. Figure 1 shows that different organic hydrogen ion exchangers, identically treated, may show considerable difference in exchange velocity.

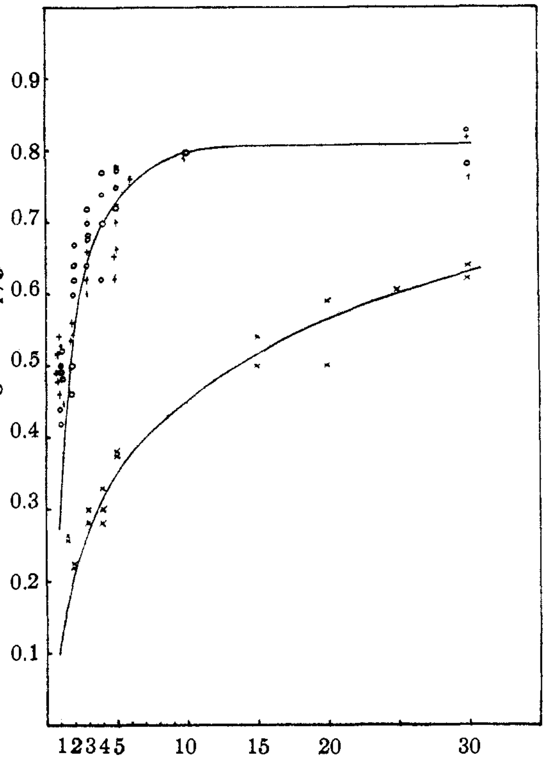

Fig. 1.—O, sulfonated coal; +, resin A; ×, resin B.

The open circles show the results at 27° of a sulfonated coal type exchanger; the + signs denote a resinous exchanger, Resin A; and the × signs, a much slower reacting material, Resin B. As an example, Table I shows the rate calculations for the sulfonated coal type and Resin A exchange materials. Experiments with other cation exchange resins (B and C) gave slower rate constants.

Temperature Effects.—The same reaction was studied also for different temperatures using the sulfonated coal-type of cation exchange material. The rate of 60° was the same within the limits of the experimental error, while for 0° a lower rate constant was found. This result might indicate that the exchange reaction is more or less independent of temperature and that the temperature coefficient of 0.91 per degree in the range from 0–27° and the absence of a temperature coefficient in the range from 27–60° is rather due to changes in diffusion rate than changes in exchange rate. The experimental data for the lower temperature are shown in Fig. 2.

TABLE I

RATE OF HYDROGEN ION EXCHANGE OF SULFONATED COAL AND RESIN A

(a = 4.02, b = 0.81)

t, min.	x, meq.	$a - x$, meq.	$b - x$, meq.	k^1	k^a
1	0.30	3.72	0.51	0.051	0.59
2	.50	3.52	.31	.059	.68
3	.64	3.38	.17	.063	.72
4	.70	3.32	.11	.062	.71
5	.73	3.29	.08	.059	.68
6	.75	3.27	.06	.055	.63
7	.77	3.25	.04	.054	.62
8	.78	3.24	.03	.051	.59
			Av.	.057	.66
					(k = 6.6 × 10^{-1})

[a] The true rate constant k for a second order reaction is obtained by multiplying k, the individual experimental rate constant, by 5 to bring the concentration on the basis of meq./l and by 2.303 to change from decadic to natural logarithms.

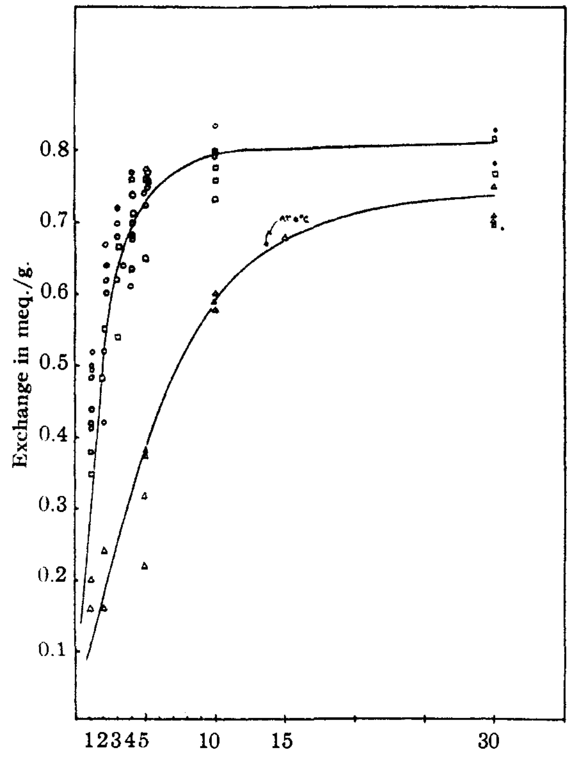

Fig. 2.—△, expts. at 0°; O, at 27°; □, at 60°.

The Hydrogen Re-exchange.—It is a well-established practice in water conditioning to regenerate the exchange material after it has become exhausted. The exhausted ion exchanger, CaZ, is restored to the original hydrogen condition by treating it with acid

$$CaZ + 2H^+ \rightleftharpoons H_2Z + Ca^{++}$$

We studied the rate of this reaction and found it to be somewhat faster than the hydrogen–calcium exchange. In all cation exchange reactions which were studied, the anion was the same for all experiments, namely, Cl^-. It was shown by Tiger and Sussman[18] that the nature of the anion has a pronounced effect upon the exchange capacity, *i. e.*, as an equilibrium quantity, and a similar effect may be expected for the reaction velocity. The influence of anions other than Cl^- on the cation exchange reaction rate is being studied and will be discussed in a later paper.

The Sodium Exchange Reaction.—To obtain a clearer understanding of the reaction velocity of cation exchange, the writers measured the rate of exchange of cation exchangers with Na^+ ion in the exchange position for Ca^{++} ion in solution. These exchange studies were carried out for the sulfonated coal type exchanger, for Resin A, for a processed natural zeolite of the greensand type, and for a synthetic siliceous, gel-type exchanger. The rate constants were found to be 6.0×10^{-1}, 2.9×10^{-1}, 1.6 and 2.6×10^{-1}, respectively, for the above exchange materials.

It is interesting to observe that the rate constant for the Na–Ca exchange is only 10% lower than the one for the H–Ca exchange for the same exchanger (sulfonated coal) at the same temperature. In consideration of the experimental accuracy the rates may be considered about the same.

In comparing the rates for sodium and hydrogen exchange for the sulfonated coal and Resin A, we note that there is no clear correlation. While in the hydrogen exchange the sulfonated coal and Resin A have the same rate constant at room temperature, the sodium exchange rate for Resin A is only about one-half of this value, whereas the sodium exchange rate of the sulfonated coal is only slightly lower than its hydrogen exchange rate.

The fastest rate of exchange is observed for the natural zeolite of the greensand type. However, we have here a material of somewhat finer mesh (mostly 30–50) size and also we believe that surface effects play a more pronounced role. The synthetic gel alumino silicate which may be written $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$ shows a slower rate of reaction than the greensand and is about twice as slow as the sulfonated coal type cation exchange.

The Anion Exchange or Acid Absorption Reaction.—In these experiments, a slightly different technique was employed. The exchange capacities for resin D and resin E were investigated in shaking tests,[19] using the Freundlich isotherm method in a manner described by Myers and collaborators.[20] The capacity data thus obtained

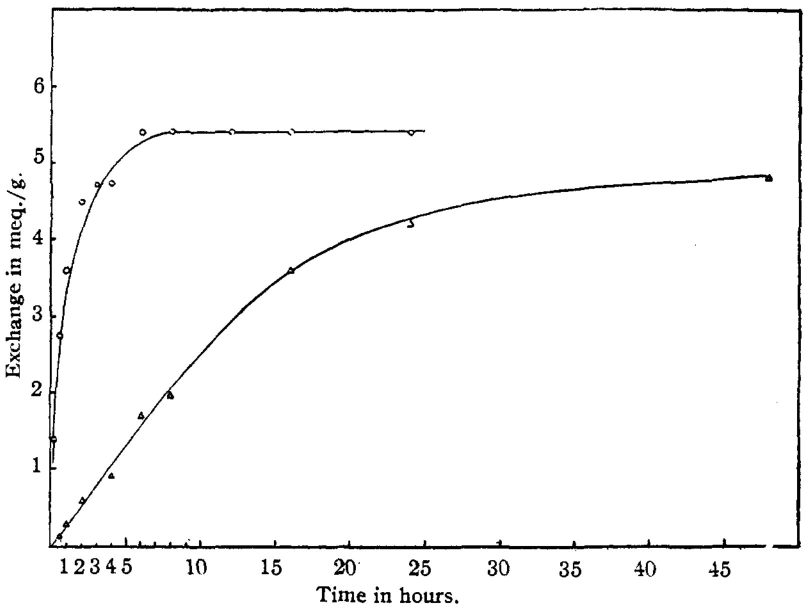

Fig. 3.—○, resin D; △, resin E.

TABLE II

RATE OF REMOVAL OF HCl AT 27° OF RESIN D

(a = 10, b = 5.4)

t, min.	x, meq.	$a - x$, meq.	$b - x$, meq.	$k^{11} \times 10^3$	$k \times 10$ (meq.$^{-1}$ × l × min.$^{-1}$)
60	3.2	6.8	2 2	0.67	1.55
120	4.1	5.9	1.3	.69	1.60
180	4.6	5.4	0.8	.65	1.50
240	4.9	5.1	.5	.67	1.55
300	5.1	4.9	.3	.68	1.57
360	5.2	4.8	.2	.67	1.55
420	5.3	4.7	.1	.72	1.66
			Av.	.68	1.57

($k = 1.57 \times 10^{-3}$)

TABLE III

RATE OF REMOVAL OF HCl AT 27° OF RESIN E

(a = 10, b = 5.4)

t, min.	x, meq.	$a - x$, meq.	$b - x$, meq.	$k^{11} \times 10^3$	$k \times 10^3$ (meq.$^{-1}$ × l. × min.$^{-1}$)
30	0.25	9.75	5.15	0.065	0.150
60	0.40	9.60	5.00	.061	.141
120	0.90	9.10	4.50	.067	.155
240	1.40	8.60	4.00	.059	.136
480	2.60	7.40	2.80	.068	.157
			Av.	.064	.148

($k = 1.48 \times 10^{-4}$)

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[18] H. L. Tiger and S. Sussman, *Ind. Eng. Chem.*, **35**, 188 (1943).

[19] The values for the calculation of the rate constants of anion exchangers were taken from isotherm measurements made by Dr. S. Sussman.

[20] R. J. Myers, J. W. Eastes and D. Urquhart, *Ind. Eng. Chem.*, **33**, 1270 (1941).

TABLE IV

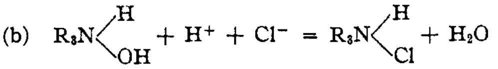
	Exchange material	Commercial name	Source	Exchange reaction	Temp., °C.	Rate constant (k in meq.$^{-1}$ × l. × min.$^{-1}$)
1	Sulfonated coal	Zeo-Karb	The Permutit Company	$H_2Z + Ca^{++}$	27 & 60	6.6×10^{-1}
2	Resin A	Amberlite 1R-100	Resinous Products and Chemical Co.	$H_2Z + Ca^{++}$	27	6.6×10^{-1}
3	Resin B	Ionac C	American Cyanamid Company	$H_2Z + Ca^{++}$	27	1.5×10^{-1}
4	Resin C	Duolite	Chemical Process Company (Calif.)	$H_2Z + Ca^{++}$	27	5.8×10^{-1}
5	Sulfonated coal	Zeo-Karb	The Permutit Company	$H_2Z + Ca^{++}$	0	1.7×10^{-1}
6	Sulfonated coal	Zeo-Karb	The Permutit Company	$CaZ + 2H^+$	27	8.4×10^{-1}
7	Sulfonated coal	Zeo-Karb	The Permutit Company	$Na_2Z + Ca^{++}$	27	6.0×10^{-1}
8	Resin A	Amberlite 1R-100	Resinous Products and Chemical Co.	$Na_2Z + Ca^{++}$	27	2.9×10^{-1}
9	Greensand type	Zeo-Dur	The Permutit Company	$Na_2Z + Ca$	27	1.6
10	Synthetic siliceous gel	Decalso	The Permutit Company	$Na_2Z + Ca^{++}$	27	2.6×10^{-1}
11	Resin D	De-Acidite	The Permutit Company	$R_3N + HCl$	27	1.6×10^{-3}
12	Resin E	Amberlite IR-4	Resinous Products and Chemical Co.	$R_3N + HCl$	27	1.5×10^{-4}

refer to a given reference point for the residual concentration. The individual constants k^{11} in the following Tables II and III are already in meq.$^{-1}$ × l. × min.$^{-1}$ but must be multiplied by 2.303 to obtain comparable rate constants on the basis of natural logarithms; Fig. 3 illustrates the acid absorption reaction.

It is interesting to note that the reaction velocities for this type of exchange material and for this type of reaction are approximately 400 to 4000 times slower. The removal of acids from solution may be either an absorption of the total acid considered as a molecule

$$\text{(a)} \quad R_3N + H^+ + Cl^- = R_3N{\cdot}HCl$$

or an anion exchange, written here for a hydroxide-regenerated anion exchanger in the form of a quaternary ammonium base



$$\text{(b)} \quad R_3N\langle{}^{H}_{OH} + H^+ + Cl^- = R_3N\langle{}^{H}_{Cl} + H_2O$$

Walton[21] postulated the acid absorption for the older type dyestuff anion exchange material and Tiger and Sussman used the same concept for the reaction mechanism[22] for anion exchange resins, but recent information[23] seems to indicate that both reactions probably take place simultaneously in the resinous materials.

We have summarized the reaction rates in the summary Table IV, which permits the reader to compare the rates studied at a glance.

Discussion[24]

The reaction rate depends on (a) concentration, (b) order of the collisions needed for reaction, (c) rate of bringing dissolved ions up to and away from the surface of the exchanger granules, (d) rate of diffusion of ions in and out of the granules, and (e) the activation energy of the exchange process. As regards (a) and (b), the fact that the reaction is kinetically bimolecular excludes collision, such as (covalent CaZ) + $2H^+ \rightleftarrows$ (covalent H_2Z) + Ca^{++}, since this would involve one of the concentrations to the second power.

This fits rather well into the picture of an exchanger as an anionic sponge filled with cations and exchange of ions takes place in a mechanism similar to the game "musical chairs."

For the sulfonated coal, where the temperature effect was studied and was found to be small, the activation energy is small, which agrees with the idea of ions from the solution hitting and penetrating the granule with other ions inside the granule simultaneously moving out.

The small temperature effect also implies that diffusion is not a rate determining step, which is further borne out by the similarity in rates of the reactions $Na_2Z + Ca^{++}$ and $H_2Z + Ca^{++}$. The difference of $CaZ + 2H^+$ is not too great to influence the situation.

One arrives at the conclusion that factor (c) is rate determining in the case of sulfonated coal between 27 and 60°. However, since other resins under identical agitation conditions show widely differing rates, other rate determining factors play a pronounced role. Other exchange reactions and temperature coefficient studies are planned for resins B, D and E, which probably will throw light on this problem.

Acknowledgment.—The authors wish to express thanks to Calvin Calmon, Paul C. Goetz, Sidney Sussman, Howard L. Tiger and Harold F. Walton for helpful criticisms and suggestions.

Conclusions

1. The reaction rates of various cation and anion exchangers were measured at various temperatures. It was found that the reactions were second order, bimolecular reactions and that the values could be calculated by using concentrations instead of activities.
2. The rate of anion exchange or acid absorption is very much slower than the rate of the cation exchange reactions, suggesting a different reaction mechanism for this class of exchangers.
3. Various commercial ion exchangers display differing reaction rates under the same experimental conditions.
4. These rate data permit prediction of operating characteristics and required contact periods for different temperatures and exchange unit designs.

BIRMINGHAM, N. J. RECEIVED JANUARY 7, 1944

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(21) Ref. 2, p. 315.

(22) Ref. 18, p. 187.

(23) S. Sussman, unpublished results, private communication.

(24) The writers are especially indebted to Professor Harold F. Walton of Northwestern University for his comments and views in the discussion.