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The Reaction Velocity of Ion Exchange. II

BY F. C. NACHOD[1] AND W. WOOD

In an earlier paper[1a] the authors have shown that ion exchange reactions are bimolecular, second order reactions and that the rate can be measured using a simple technique which consisted in agitating small samples of solid exchanger with portions of the solution which was studied. The various commercial exchangers under observation exhibited extremely fast reaction velocities. This is in marked contrast to Cernescu's[2] studies who observed that only in the case of clays exchange equilibrium was established in five minutes, a velocity which closely agrees with our findings, whereas with a siliceous cation exchanger and with a chabazite, reaction periods of ten and ninety-two days, respectively, were required.

In this paper a few new phases of ionic exchange velocity are discussed. The three problems which were studied consisted of: (a) the influence of anions on the rate of cation exchange; (b) the influence of valence and position in the periodic system on the cation exchange velocity; (c) the correlation of equilibrium exchange and ionic properties.

The Influence of Anions on the Rate of Cation Exchange.—It has been observed that the nature of the anions has a very pronounced effect on the capacity of an ion exchange material operating on the "hydrogen cycle."[3] If, in an exchange reaction where H^+ ions are given up into the solution, the acids formed on the right-hand side of the equation are weak acids, the equilibrium is shifted in this direction and a much higher equilibrium exchange can be realized than if a strong acid had been formed. This may be illustrated in the following equations, where H_2Z denotes the cation exchanger with H^+ in the exchange positions

$$H_2Z + 2Na^+ + 2HCO_3^- \longrightarrow Na_2Z + H_2CO_3$$
$$H_2CO_3 \longrightarrow H_2O + CO_2$$

This anion effect was noticed by Jenny[4] in his studies with acid-treated clays who wrote the reaction for a sodium acetate exchange

$$\text{H-clay} + CH_3COO^- + Na^+ \rightleftarrows \text{Na-clay} + CH_3COOH$$

Freundlich,[5] referring to adsorption phenomena, observed with moss and peat, stated that the quantity of adsorbed cations depended on the anion and increased in the series

$$Cl, Br, NO_3 < SO_4 < \text{acetate}$$

but left open the question whether this effect should be ascribed to the strength of the acid or to the lyotropic series. Our experiments seem to indicate that both factors must play a role because three weak acids, having different ionization constants gave a capacity increase of the same magnitude, but a substantially higher value than for the case of the strong acids.

A number of exchange reactions were studied with a sulfonated coal type exchanger[6] (Zeo-Karb) at room temperature, employing the technique described before.[7] The results are shown graphically in Fig. 1. In the exchanges, the cation was Na^+, while the anions consisted of Cl^-, $SO_4^=$, NO_3^- on one hand and HCO_3^-, formate, and acetate on the other. The exchanges with weak acid salts yield values which all fall on a curve, just as the values with strong acid salts fall on the lower curve.[8] The equilibrium exchange is 75% higher for the weak acid salts but the reac-

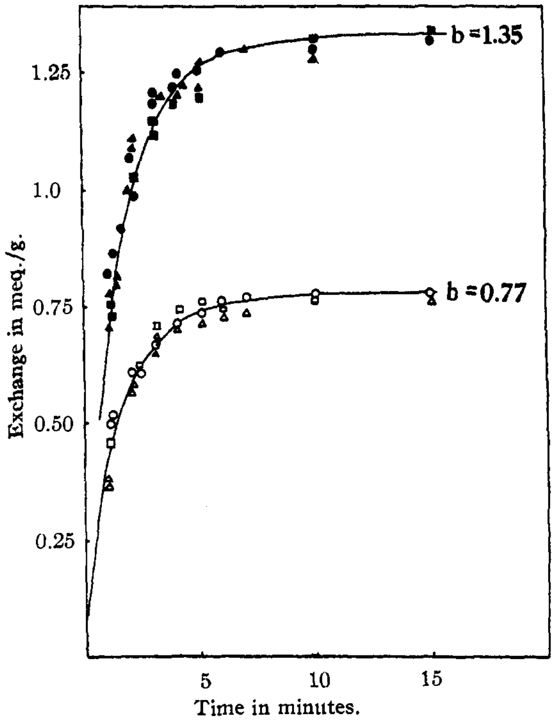

Fig. 1.—NaCl, ○; Na_2SO_4, □; $NaNO_3$, △; CH_3COONa, ●; HCOONa, ▲; $NaHCO_3$, ■.

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[1] Present address: The Atlantic Refining Company, Philadelphia, Penna.

[1a] Nachod and Wood, THIS JOURNAL, **66**, 1380 (1944).

[2] N. C. Cernescu, *Anuarul Institutului Geologic al Romaniei*, *XVI*, 853 (1931).

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

[4] H. Jenny, *J. Phys. Chem.*, **40**, 514 (1936).

[5] H. Freundlich, "Colloid and Capillary Chemistry," transl. by H. Stafford Hatfield, Methuen & Co., London, 1926, p. 217.

[6] The mechanism of ionic exchange in siliceous materials and soils has been studied extensively. *cf.* H. Jenny, *J. phys. Chem.*, **36**, 2217 (1932); G. Wiegner, *J. Landw.*, **60**, 111, 197 (1912); G. Wiegner, *Kolloid-Z.*, **51**, 49 (1930), while relatively little is known as yet about the behavior of organic ion exchangers.

[7] Ref. 1a, p. 1381

[8] The measurements were carried out by Eleanor Fabritiis and Mary Lajkowicz.

tion velocities calculated from both curves yielded identically the same value, *i. e.*, 9.6 × 10^{-1}. Thus, the approach to the two different equilibrium values takes place at identically the same rate (Fig. 1). The observed differences in equilibrium exchange values display essentially he same behavior referred to as hydrolytic activity by soil chemists.[9] It may be expected, in the case of soils just as observed with the studied cation exchangers, that the exchange velocities are unaffected by the positions of the respective exchange equilibria.

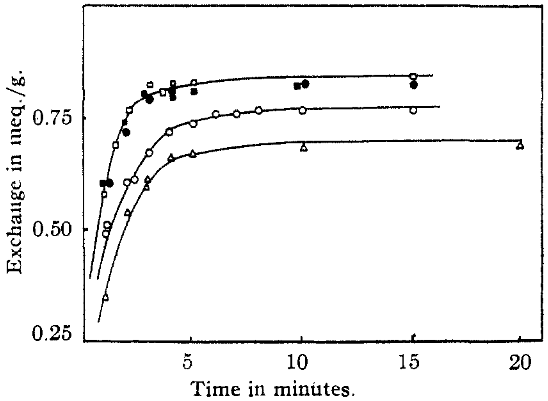

Fig. 2.—△, LiCl; ○, NaCl; □, KCl; ■, RbCl; ●, CsCl.

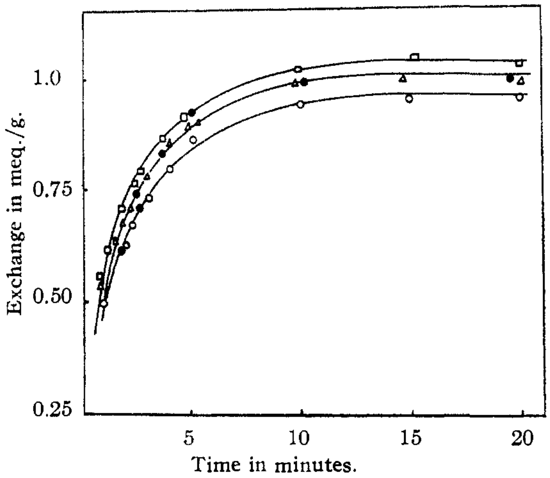

Fig. 3.—○, $MgCl_2$; △, $CaCl_2$; ●, $SrCl_2$; □, $BaCl_2$.

It must be kept in mind that the H^+ ions furnished by the exchange materials are given up by the functional groups of different degrees of ionization, *i. e.*, —SO_3H, —COOH, and —OH. The exchange equilibrium will depend upon the relationship between the ionization constant of the acid formed in the exchange reaction on the one hand and the "average" ionization constant of the solid acid, *i. e.*, the hydrogen ion exchange material.[10]

The Influence of Valence and Position in the Period System of Cations on the Fraction Velocity.—The position in the periodic system as well as the net charge have a definite effect on the reaction velocity as well as on the final equilibrium. The experiments reported in this section refer to chlorides of the alkali metal and alkaline earth series. The first group comprises LiCl, NaCl, KCl, RbCl and CsCl; the second, $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$. The exchange velocity curves are shown graphically in Figs. 2 and 3, and the rate constants calculated from these values are summarized in Table I.

Table I

Exchange reaction	Rate constant k in $\text{meq.}^{-1} \times \text{l.} \times \text{min.}^{-1}$
$H_2Z + Li^+$	8.7×10^{-1}
$H_2Z + Na^+$	9.6×10^{-1}
$H_2Z + K^+, Rb^+, Cs^+$	1.3
$H_2Z + Mg^{++}$	6.1×10^{-1}
$H_2Z + Ca^{++}$	6.6×10^{-1}
$H_2Z + Sr^{++}$	6.6×10^{-1}
$H_2Z + Ba^{++}$	7.0×10^{-1}

While the differences in rates are not so pronounced, it can be seen that the monovalent ions possess faster exchange rates than the divalent ions, and that within one group the ion of a lower position in the periodic system has the faster rate. However, the differences with respect to rate and equilibrium exchange value disappear or become less pronounced as one progresses downward in a group. The equilibrium exchange is 20 to 25% greater in the case of divalent ions, which may be due to the greater attraction of the charged particle to weakly ionized groups.

Equilibrium Exchange and Ionic Properties.—The equilibrium exchange, aside from being a function of the anions involved, if we deal with an exchange involving H^+ ions, is as we have seen

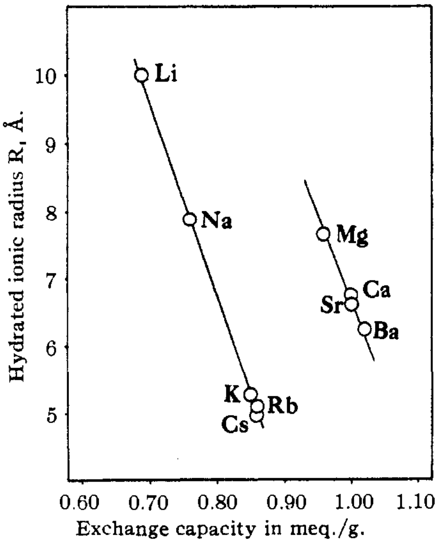

Fig. 4.

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(9) H. Kappen, "Die Bodenazidität," J. Springer, Berlin, 1929, pp. 107 f.

(10) H. F. Walton, *J. Phys. Chem.*, **47**, 382 (1943).

in Figs. 2 and 3 above, a function of the ionic charge and of the position in the periodic system. The writers have tried to establish a more complete picture by taking into consideration the size of the ions. Very little information is available on actual ionic radii determination. However, qualitatively we know that ions at the top of the group are most strongly hydrated, and little hydration is noted as the shielding effect of the electronic orbits increases. The series of hydrated ionic radii is just the reverse of the crystalline or gaseous ion radii. Remy[11] arrived at ionic radii values from mobility determinations. We have plotted the so-obtained hydrated ionic radii values against the equilibrium exchange and have found a very simple relationship between the two quantities as shown in Fig. 4.

All values of ions of the first group fall on a straight line and the same holds for the ions of the second group. The slope is the same for both groups indicating that ionic size really determines the relative accessibility of an exchange group. The shift of the two lines indicates the "charge effect."

The two curves may be interpreted by a universal equation, to correlate exchange capacity, hydrated ionic radius and valence. We have written the equation common to both curves

$$R = \alpha \times 28.3 \times \text{E.E.} + \beta(23.5 + 5.5V)$$

where R represents the hydrated ionic radius from Remy's data, E.E. the equilibrium exchange in meq./g., V the valence of the entering ion, and α and β are proportionality constants for each exchanger type, and are unity for the case of a sulfonated coal type cation exchange under the experimental conditions employed. Similar efforts to correlate valence and exchange were made by Gapon,[12] however not from the viewpoint or introducing the ion size in the exchange equation.

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

Summary and Conclusions

1. Additional rate determinations have been carried out, showing the effects of both anions and cations on the rates of cation exchange reactions.
2. If the cation is kept constant, but the anion is varied in a series of H^+ ion exchange experiments, the rate of approach of equilibrium exchange is the same but the values obtained with salts of weak acids are very much larger as contrasted with strong acid salts.
3. The cation exchange capacity increases as function of the charge of the cation; however, the monovalent ions exchange with faster rate than the divalent ions. Within a group, the ion in the lower part of the group exchanges faster and has a higher equilibrium exchange; at the end of the group the differences are less pronounced.
4. The variation of rate constants among the cations is generally what one would expect from their respective diffusion rates. However, the correlation is not ideal. So, *e. g.*, the ratio of ionic mobilities for K:Li, which ought to be the same as the ratio of their diffusion rates, is 1.9:1 while the ratio of the respective exchange rate was found to be 1.5:1. Thus, diffusion alone is not the rate determining factor but other effects, such as ionic size, charge, and steric availability of the exchange position in the exchanger play a decided role.
5. The equilibrium exchange for a series of ions in one group is a function of their size, *i. e.*, the hydrated ionic radius or volume, and a simple graphical relationship is pointed out which can be brought into a linear equation.

BIRMINGHAM, N. J. RECEIVED OCTOBER 2, 1944

[11] H. Remy, *Z. physik. Chem.*, **89**, 467, 483 (1915); *cf.* also H. Jenny, *Kolloid Beihefte*, **23**, 428 (1927); *J. Phys. Chem.*, **36**, 2217 (1932); G. Wiegner and H. Jenny, *Kolloid-Z.*, **42**, 268 (1927).

[12] E. N. Gapon, *J. Gen. Chem.* (U. S. S. R.), **13**, 382 (1943).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Determination of Equilibrium Constants for Butanes and Pentanes

BY HERMAN PINES, BRUNO KVETINSKAS, LOUIS S. KASSEL AND V. N. IPATIEFF

In recent years, several papers on the isomerization equilibrium constants of butanes[1,2] and pentanes[3] have appeared. Most of the work is open to criticism, however, because of the fact that the isomerization was accompanied by excessive decomposition which even became the predominant reaction in extreme cases. In the present investigation, the equilibrium constants were established by studying the isomerization from both the normal and the isoparaffin side, within wide temperature ranges and under experimental conditions designed to reduce to a minimum the amount of secondary reactions. Depending upon the temperature level investigated, the experiments were carried out in sealed tubes, a stirring autoclave, or a continuous flow type apparatus.

Experimental Methods

The catalysts used consisted of aluminum bromide or aluminum chloride, the latter usually deposited on a car-

[1] B. Moldavskii and T. Nizovkina, *J. Gen. Chem.* (U. S. S. R.), **9**, 1652 (1939).

[2] G. C. A. Schuit, H. Hoog, and J. Verheus, *Rec. trav. chim.*, **59**, Nos. 7-8, 793-810 (1940).

[3] B. Moldavskii, T. Nizovkina and R. A. Shterner, *J. Gen. Chem.* (U. S. S. R.), **10**, 1183 (1940).