Table I summarizes some of the pertinent results of this calculation. All values are for the hydrogen equilibrium separation of 1.40 atomic units. Two values are shown for z corresponding to the hydrogen molecule-ion calculation ($z = 1.38$) and to the simpler molecular orbital calculation of hydrogen ($z = 1.20$). Two values are also shown for p corresponding to the simpler molecular orbital calculation ($p = 0$) and for correlated molecular orbitals using the same p as found best by Hylleraas for helium ($p = 0.364$).

TABLE I

REPULSIVE POTENTIAL ENERGY, V_{12}, IN ATOMIC UNITS

	$z = 1.38$	$z = 1.20$
$p = 0$	0.733	0.658
$p = 0.364$	0.597	0.525

The contribution of V_{12} to the correlation energy would be given by the decrease in V_{12} as p is increased from zero to the best value for the correlated molecular orbital. As p is increased, however, the appropriate z would be expected to change from the value of 1.20, already known for the simple molecular orbital approximation, to a value such as 1.38 as found in the hydrogen molecule-ion calculation since the inclusion of a correlation factor in the wave function spreads out the probability distribution in somewhat the same way as does a decrease in z. Therefore from the information tabulated the contribution of V_{12} to the correlation energy would be calculated as 0.658 minus 0.597 or 0.061 atomic unit, or 1.66 e. v.

Changes in T_1, T_2, V_1 and V_2 in going from ordinary molecular orbitals to correlated molecular orbitals may also contribute to the correlation energy. The calculation of the various integrals in this case is unusually tedious and difficult and has not been carried out. However, study of the Hylleraas calculation of helium reveals that the principal effect is an increase in T_1 and T_2 with a slight decrease (increase negatively) of V_1 and V_2. The net result is an increase positively in these energy terms equal to about one-third of the decrease in V_{12}. If such a relationship holds also for hydrogen the total correlation energy should be roughly two-thirds of 1.66 e. v. or 1.1 e. v. That this is so close to the experimental value of 1.12 e. v. is probably a coincidence. Nevertheless it illustrates that correlated molecular orbitals give the right order of magnitude for the correlation energy and that more detailed calculations on such a basis should be successful.

This investigation was supported by a grant from the Abbott Fund of Northwestern University.

Summary

The ordinary expression of the electronic wave function of a molecule as a product of one-electron molecular orbital wave functions is modified by including factors for each pair of electrons such as $(1 + pr_{ij})$ where p is a constant and r_{ij} is the distance between electrons i and j. It is shown that this form has improved accuracy for the extreme cases of the separated and united atoms and also for normal internuclear distances in molecules.

EVANSTON, ILLINOIS RECEIVED JUNE 12, 1948

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Equilibrium and Velocity of the Sodium–Hydrogen Exchange on Carbonaceous Exchangers in Contact with Chloride Solutions

BY WALTER JUDA* AND MORRIS CARRON†

Introduction

The base exchange equilibrium on inorganic exchangers (clays, zeolites, etc.) has been the subject of many investigations. Some authors attempted unsuccessfully to apply simple mass action equations to the experimental data, and were therefore led to believe that the exchange equilibria could be more correctly represented by adsorption isotherms.(1) Other investigators, however, affirmed that mass action could account for the equilibria provided that the appropriate activities of the ions were used.(2) With the comparatively recent development of the carbonaceous exchangers the question of the exchange equilibrium was extended to materials of very different chemical constitution, namely, to sulfonated coals or synthetic resinous products containing, in the so-called hydrogen form, sulfonic acid groups, carboxylic acid groups or phenolic groups, or combinations of these groups, available for cation exchange. As in the case of the inorganic materials, the published data and interpretations leave it unsettled whether an appropriate mass action law or an adsorption isotherm can account more satisfactorily for the equilibria on the organic ex-

---

* Present address: Chemical Engineering Department, Massachusetts Institute of Technology, Cambridge, Mass.

† Present address: L. Farber Company, Worcester, Mass.

(1) G. Wiegner, *J. Soc. Chem. Ind.*, **50**, 65T (1931); H. Jenny, *J. Phys. Chem.*, **36**, 2217 (1932). (These papers include bibliographies of previous work on base exchange with inorganic exchangers.) H. Jenny, *ibid.*, **40**, 501 (1936); C. E. Marshal and R. S. Gupta, *J. Soc. Chem. Ind.*, **52**, 434T (1933).

(2) (a) A. P. Vanselow, *Soil Sci.*, **33**, 95 (1932). (b) J. Kielland, *Tids. Kjemi*, **15**, 74 (1935); *J. Soc. Chem. Ind.*, **54**, 233T (1935). (c) J. Møller, *Kolloid-Beihefte*, **46**, 1 (1937). (d) L. E. Davis, *Soil Sci.*, **59**, 379 (1945).

changers.[3] After this paper had been submitted for publication and while it was being revised, Boyd and collaborators[3e,f] published their work in which they derived a Langmuir adsorption isotherm and a mass action equation claiming formal equivalence of the two concepts.

In spite of the obvious similarities of the over-all exchange characteristics on the inorganic and organic materials, the exchange equilibrium and rates are not necessarily subject to identical treatments. Indeed the carbonaceous materials differ markedly from the inorganic ones, not only in chemical nature, but also in performance, and in particular the capacities of organic exchangers are essentially independent of their particle size, in contrast with the capacities of many inorganic materials.[4] This observation tends to support the view, adopted in this paper, that the cation exchange on sulfonic, carboxylic and phenolic groups is more apt to be analogous to a reaction than may be expected of the exchange on clay.

Following duDomaine, Swain and Hougen's[5] use of reaction rate equations for water softening by cation-exchange, Thomas[6] based his treatment of the heterogeneous ion-exchange in a system involving a solution percolating through a stationary bed on the possibility that some exchanges may be interpreted as second order reactions from the kinetic point of view. Nachod and Wood,[7] measuring the cation exchange velocities on carbonaceous exchangers, concluded from their data that these processes fit a second order rate equation. They used an excess of exchangeable ion in solution which was apparently of the order of 4 milliequivalents per gram of air-dried exchanger[7a] so that the reverse reaction could presumably be neglected. However, as will be shown below, this excess was far from sufficient for their sodium–hydrogen exchange measurements on ZEOKARB in the hydrogen form in contact with chloride solutions. Furthermore, all their determinations were apparently made with a single set of concentrations only, and this was considered insufficient to support the general conclusion of a second order reaction whether or not ions of different valences were exchanged. The kinetic analysis and investigations by Boyd and co-workers[3f] indicate that among the factors influencing the exchange velocity diffusion of the ions in and through the adsorbent particle or through a liquid film adhering to the particle is the rate-determining step.

It appeared worth while to examine in some detail one particularly simple exchange case on the carbonaceous materials for which only relatively few assumptions were necessary to write a mass action equation in a form in which it was subject to experimental test, and for which it was plausible and experimentally feasible to compare a so-called "concentration" equilibrium constant with the ratio of the apparent velocity constants of the opposing reactions of the same exchange. For this purpose the sodium–hydrogen exchange in the presence of chloride ions was chosen, and in this paper there are reported attempts at measuring and interpreting a so-called concentration equilibrium constant and apparent velocity constants of this exchange on the four carbonaceous exchangers: AMBERLITE IR-100AG (The Resinous Products and Chemical Company), IONAC C-200 (American Cyanamid Company), DOWEX 30 (now called Nalcite MX and marketed by the National Aluminate Company), and ZEOKARB (The Permutit Company). The equilibrium determinations were made with chloride solutions varying in concentration from 0.001 to 1 molar; the rate determinations were limited to concentrations below 0.2 molar for reasons which will be given below.

The Calculation of "Concentration" Equilibrium Constants.—If the sodium–hydrogen exchange process on carbonaceous exchangers in contact with chloride solutions is formally written as a chemical reaction according to

$$\text{(I)}\quad \mathrm{H_r^+ + Na_w^+ \rightleftarrows Na_r^+ + H_w^+}$$

the subscripts r and w denoting the exchanger phase and the water phase, then it is possible to examine experimental equilibrium data in terms of a simple relation of the mass action type. The assumptions underlying (I) will be discussed below.

In practice, the concentration of the hydrogen ions at equilibrium is determined experimentally. Assuming that the ionic strength of the water phase remains constant throughout the exchange, the ratio of the sodium ions to the hydrogen ions in the exchanger phase can be deduced from these determinations provided that one knows the initial number of hydrogen ions and sodium ions available for this exchange in the exchanger phase. By treating the acid exchanger (hydrogen form of the exchanger) with a large excess of sodium ions in the external chloride solution, practically all available hydrogen ions are forced out, permitting the measurement of what will be called the "sodium chloride" capacity M (which will be expressed in milliequivalents per gram of bone-dry exchanger). Thus, equilibrium experiments carried out either with initially purely acid exchangers and sodium chloride solutions or with "sodium chloride prepared" exchangers in the sodium form and hydrochloric acid solutions give experimental determinations of a "concentration equilibrium constant"

$$(\mathrm{H^+})_w(\mathrm{Na^+})_r/(\mathrm{H^+})_r(\mathrm{Na^+})_w = K_{\mathrm{H/Na}} \qquad (1)$$

---

(3) (a) R. J. Myers, J. W. Eastes and D. Urquhart, *Ind. Eng. Chem.*, **33**, 1270 (1941); (b) R. H. Beaton and C. C. Furnas, *ibid.*, **33**, 1500 (1941); (c) H. F. Walton, *J. Phys. Chem.*, **47**, 371 (1943); (d) R. K. Cannan, *Ann. N. Y. Acad. Sci.*, **47**, 135 (1946); (e) G. E. Boyd, J. Schubert and A. W. Adamson, THIS JOURNAL, **69**, 2818 (1947); (f) G. E. Boyd, L. S. Myers and A. W. Adamson, *ibid.*, **69**, 2836 (1947); (g) W. C. Bauman and J. Eichorn, *ibid.*, **69**, 2830 (1947).

(4) See, for example, R. J. Myers, J. W. Eastes and F. J. Myers, *Ind. Eng. Chem.*, **33**, 697 (1941).

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

(6) H. C. Thomas, THIS JOURNAL, **66**, 1664 (1944).

(7) (a) F. C. Nachod and W. Wood, *ibid.*, **66**, 1380 (1944); (b) *ibid.*, **67**, 630 (1945).

the parentheses denoting concentrations. The relation of $K_{H/Na}$ to the equilibrium constant expressed in terms of activities will be discussed below.

Let w_H be the initial weight (in grams) of the hydrogen form of the exchanger in contact with an initial volume, v_{Na}, (in cc.) of a sodium chloride solution of concentration, a, and let x_e be the hydrogen ion concentration at equilibrium. If, as is almost attainable in practice, the initial hydrogen ion concentration in the water phase is zero, and if initially the exchanger phase is entirely in the hydrogen form, Equation (1) may be written

$$x_e^2/(a - x_e)(b - x_e) = K_{H/Na} \qquad (2)$$

where, with a and x_e expressed in milliequivalents per liter, b is given by

$$b = 1000(w_H)(M)/v_{Na} \qquad (3)$$

since $w_H M$ milliequivalents of exchangeable hydrogen ions in the exchanger phase are in contact with v_{Na} cc. of aqueous solution.[8]

Similarly, contacting initially w_{Na} grams of the sodium chloride prepared sodium form of the resin with v_H cc. of hydrochloric acid of concentration, c, and having initially no sodium ions in solution and no exchangeable hydrogen ion present in the exchanger phase, Equation (1) may be written

$$x_e'^2/(c - x_e')(d - x_e') = 1/K_{H/Na} \qquad (2')$$

where x_e' is the sodium ion concentration in the aqueous phase at equilibrium and, where, with d and x_e' expressed in milliequivalents per liter, d is given by

$$d = 1000(w_{Na})(M)/v_H \qquad (3')$$

The Calculation of Exchange Velocity Constants.—It is not the purpose of this paper to discuss at any length the theoretical foundation of Thomas'[6] and Nachod and Wood's[7] idea that the velocity of ion exchange processes can be accounted for by a relation identical in form with a second order reaction rate equation. It is merely intended to test this concept in one particularly simple case; that is, the exchange process (I) is considered a case of opposing simultaneous reactions. In other words, the assumption is made that, ignoring interionic effects as a first approximation, the rate of process (I) may be written formally in terms of concentrations

$$d(H^+)_w/dt = k_{r/w}(H^+)_r(Na^+)_w - k'_{r/w}(H^+)_w(Na^+)_r \quad (4)$$

The subscript r/w indicates that the velocity constants defined by this relation are those corresponding to the cationic concentrations in two distinct phases (exchanger and water), it being assumed that the cationic charges are balanced entirely by chloride ions in the water phase and by fixed negative charges in the exchanger phase. This assumption is further discussed below.

Let $k_{r/w} = \beta k$ and $k'_{r/w} = \beta k'$ where β is a measure of the relative amounts of the exchanger phase and the water phase. (For example, β may be defined as grams of exchanger phase per liter of solution in contact with the exchanger phase.) If $(H_i^+)_r$ is the initial (unknown) hydrogen ion concentration in meq./gram in the exchanger phase, $\beta(H_i^+)_r$ is equal to b which has the value given in Equation (3). Then, expressing $(H^+)_r$ and $(Na^+)_r$ in milliequivalents per gram of exchanger phase, $(H^+)_w$ and $(Na^+)_w$ in milliequivalents per liter and t in minutes, the net rate of the forward process (I) starting with v_{Na} cc. of a sodium chloride solution of concentration, a, in contact with w_H grams of exchanger in the hydrogen form of capacity, M, is

$$dx/dt = k(a - x)(b - x) - k'x^2 \qquad (5)$$

where x is the hydrogen ion concentration at time t and b is equal to $1000(w_H)(M)/v_{Na}$. (By introducing β, relation (4) containing the concentrations in the exchanger phase which are not readily accessible to experimentation, has been transformed into (5) which can be subjected to experimental test.) In relation (5) it has been assumed that there are initially no hydrogen ions in the aqueous solution and the exchanger is entirely in the hydrogen form.

At equilibrium the net reaction rate, dx/dt, is zero, the hydrogen ion concentration having reached the value x_e and therefore

$$k(a - x_e)(b - x_e) = k'x_e^2 \qquad (6)$$

with

$$k/k' = K_{H/Na}$$

Substituting in Equation (5) k' with its value in terms of k, a, b and x_e from Equation (6) and integrating Equation (5) with the limit of $t = 0$ and $x = 0$, gives

$$\frac{x_e}{2ab - (a + b)x_e} \ln \frac{ab(x_e + x) - x_e(a + b)x}{ab(x_e - x)} = kt \qquad (7)$$

Experimentally, the hydrogen ion concentrations were measured at different times t; x was plotted *vs.* t, and the limiting constant value of x was used for x_e; a was the known initial sodium ion concentration in solution and b was known from Equation (4) after M had been determined for each particular exchanger.

Similarly, starting with hydrochloric acid of concentration, c, in contact with "the sodium chloride prepared" sodium form of the exchanger, the net rate of the reverse reaction is

$$dx'/dt = k'(c - x')(d - x') - kx'^2 \qquad (5')$$

Using

$$k'(c - x_e')(d - x_e') = kx_e'^2 \qquad (6')$$

Equation (5′) integrates to

$$\frac{x_e'}{2cd - (c + d)x_e'} \ln \frac{cd(x_e' + x') - x_e'(c + d)x'}{cd(x_e' - x')} = k't \qquad (7')$$

---

[8] Strictly, $1/M$ should be defined as the weight of the residual exchanger, that is the exchanger minus the exchangeable ions, capable of holding one milliequivalent of exchangeable cation so that for the hydrogen form the weight of total exchanger holding one milliequivalent of exchangeable ion would be $(1/M) + 0.001$, and that for the sodium form $(1/M) + 0.023$. However, M was determined by the same technique as the equilibrium determinations except that a large excess of sodium chloride was used, and with this technique the values of $1/M$ for the four exchangers studied were of the order of 0.4–1.1 and were reproducible within only about 10%. Hence this diistinction was neglected.

where x' is the sodium ion concentration in solution at the time t, x_e' the equilibrium sodium ion concentration, and where the integration constant has been eliminated by using the limiting condition $t = 0, x' = 0$.

Experimental

Capacities, equilibrium constants and velocity constants were determined at room temperature for the four carbonaceous exchangers marketed under the names AMBERLITE IR-100AG, IONAC C-200, DOWEX 30 (also called Nalcite MX), and ZEOKARB. The exchangers as received were moist, the water content varying in different shipments of the same exchanger and for the different exchangers. To obtain reproducible data it was found desirable to treat the exchanger as received either with a very large excess of sulfuric acid or with a very large excess of sodium chloride to convert it into the hydrogen form or the sodium form, respectively. In this preparation the following observations were made.

Preparation of the Hydrogen Form.—Samples of approximately 300 g. of AMBERLITE IR-100AG and ZEOKARB, moist as received, were contacted with about 2.5 liters of 4% sulfuric acid with occasional agitation, transferred to a Buchner, filtered and washed until the wash water was neutral to methyl orange and free from sulfate ions (barium chloride test). In an alternate procedure 100-g. samples of ZEOKARB, DOWEX 30, and AMBERLITE IR-100AG were washed in 200-300 cc. of distilled water and then contacted with one liter of 3-4% sulfuric acid for one hour with occasional stirring, transferred to a Buchner, filtered and washed until the wash water was neutral to methyl orange and free from sulfate ions.

Samples of the exchanger were dried to constant weight at 80-85°. Upon contacting approximately 1-g. samples of any of the three dry exchangers with about 5 cc. of distilled water, filtering and testing the water, it was found to be acid to methyl orange and to contain sulfate ions. A 25.0-g. sample of ZEOKARB in the hydrogen form, after preparation and drying at 80-85°, was then washed with 680 cc. of distilled water (in portions of approximately 100 cc.). The last portion was neutral to methyl orange and contained no sulfate ions. The combined wash waters were titrated with 0.536 N sodium hydroxide to a pH of 7; the volume require was 2.0 cc. The drying to constant weight at 80-85° was repeated, the sample was again washed, this time with 585 cc. of distilled water, and the wash waters were again titrated requiring 2.35 cc. of 0.0536 N sodium hydroxide, indicating about a tenfold decrease in water-removable acid. The sample was then allowed to dry for thirty-six hours at 80-85°; this time 550 cc. of distilled wash water was used to obtain methyl orange neutrality and a negative sulfate test, but as much as 35.3 cc. of 0.0536 N sodium hydroxide was again required to neutralize the combined wash waters, indicating that in this procedure the presumably sulfonated exchanger was probably somewhat decomposed by heat. Repeated washing and drying of the other two exchangers gave similar results.

Repeating the same procedure with a drying temperature of 50° also yielded acid wash waters containing the sulfate ion. Finally, to avoid as much as possible hydrogen ions in distilled waters contacted with the hydrogen form of the exchangers 100-g. samples of AMBERLITE IR-100AG, already partly in the hydrogen form as received, were soaked in 1000 cc. of (4%) sulfuric acid for one hour, filtered and washed once, dried to constant weight at room temperature in a 500-cc. gas bubbler through which a current of air was drawn, and finally screened to 20/40 mesh. This procedure was adopted to prepare the air-dried hydrogen form of all cation-exchangers tested by us.

To estimate the possible error introduced into the determinations of rate and equilibrium constants by hydrogen ions removable from the hydrogen form on contact with distilled water, weighed samples of this form were contacted with 100 cc. of distilled water for five minutes, using the technique described below, and 50-cc. aliquots of the water were titrated to a pH of 7 with standard sodium hydroxide solutions after separation of the wash water from the exchanger. Table I gives typical values of the correction h for two groups of exchangers prepared at different times and at different temperatures; h is the concentration of the hydrogen ions, in milliequivalents per liter, from $[w_H]^{8a}$ grams of exchanger in the hydrogen form contacted with 100 cc. of distilled water. For AMBERLITE IR-100AG and IONAC C-200 h is usually within the experimental error and was therefore neglected in the calculations of the rate and equilibrium constants. However, for DOWEX 30 and for ZEOKARB, h was greater than the experimental error. Therefore, for these two exchangers the equilibrium relation (Equation 2) becomes

$$\frac{(x_e^* - h)(x_e^*)}{[a - (x_e^* - h)]\,[b - (x_e^* - h)]} = \frac{x_e(x_e + h)}{(a - x_e)\,(b - x_e)} = K_{H/Na}$$

where $x_e^* = x_e + h$ is the experimental hydrogen ion concentration at equilibrium.

The rate Equation (5) should also be modified when h is to be taken into consideration. Strictly $dx/dt = k(a - x)(b - x) - k'(h + x)x$ rather than Equation (5) should be integrated. But since experimentally h is smaller than $0.05\,x$ in most cases (and $0.05\,x < h < 0.15\,x$ holds in all cases), k may be calculated from Equation (7) without introducing a significant error provided that in (7) $x = x^* - h$ is used.

Preparation of the "Sodium Chloride Prepared" Sodium Form.—Two procedures were used: in one method 100-g. samples of the hydro-

---

[8a] The brackets indicate that the material was air-dried (see below).

TABLE I

HYDROGEN ION CONCENTRATION IN WATER CONTACTED WITH CATION EXCHANGERS IN HYDROGEN FORM

	Air-dried at 23–28°		Air-dried at 30–35°	
Exchanger	$[w_H]$	h	$[w_H]$	h
Amberlite IR-100AG	1.00	0.17	1.00	0.23
	0.75	.13	0.75	.16
	0.32	.04	.48	.06
Ionac C-200	1.00	.06	.70	.20
	0.32	.04	.32	.11
Dowex 30 (Nalcite MX)	1.00	.33	.82	.51
	0.32	.09	.38	.24
ZeoKarb	1.00	.32	1.30	.94
	0.32	.11	.63	.47
			.15	.12

gen forms of the exchangers as prepared above were contacted with 4 l. of a sodium chloride solution containing a total of about 320 g. of sodium chloride for one hour at room temperature with occasional stirring, transferred to a Buchner, washed until the wash water was free of chloride ion and had reached a *p*H above 4, dried at room temperature to constant weight and screened to 20/40 mesh; in the other method 150-g. samples of exchanger as received (in either hydrogen or sodium form) were treated with 4 l. of a sodium chloride solution containing about 480 g. of sodium chloride and were then filtered, dried and screened as above. No correction was necessary for the removal of sodium ion from this sodium form by distilled water since we could not find evidence of any such removal by *p*H measurements, or chloride tests, on distilled waters contacted with the sodium forms. The effect of this drastic sodium chloride treatment on the exchangers is discussed below.

The Measurement of M.—In this paper, the so-called sodium chloride capacity, M, as defined above, is expressed in milliequivalents of exchangeable cation per gram of bone-dry exchanger. This basis is preferable to an air-dry basis as the air-dried materials are apt to contain appreciable and variable amounts of water. However, it is evident from the above-described heat treatments that the carbonaceous exchangers in the hydrogen form tend to decompose on prolonged exposure to even relatively low temperatures (85° and less). Hence the bone-dry basis is also somewhat indefinite unless the drying conditions are specified, including time of drying, temperature, and particle size of sample.

In the capacity determinations samples of the exchangers in the hydrogen form were air-dried as described above; significant errors in capacities due to too many successive drying–wetting cycles were avoided by using an air-dried sample and by determining its moisture content on a separate fraction which was then discarded. This moisture was determined by drying air-dried samples of 0.5–1.2 g., weighed to the next 0.001 g., 20/40 mesh, for twenty-four hours at 85°. Table II gives the moisture contents of the two separately prepared groups of air-dried exchangers referred to in Table I and used in the subsequent capacity, equilibrium and velocity determinations.

TABLE II

MOISTURE CONTENTS OF AIR-DRIED EXCHANGERS (IN PER CENT. OF AIR-DRIED EXCHANGER)

Exchanger	Air-dried at 23–28°	Air-dried at 30–35°
AMBERLITE IR-100AG—		
Hydrogen Form	10.5–11.0	8.5– 9.0
"NaCl Prepared" Sodium Form	7.5– 8.0	5.5– 6.0
IONAC C-200—Hydrogen Form	13.0–14.0	11.5–12.0
"NaCl Prepared" Sodium Form	9.3– 9.8	7.0– 7.5
ZEOKARB—Hydrogen Form	10.0–10.5	7.5– 8.0
"NaCl Prepared" Sodium Form	8.5– 9.0	5.5– 6.0
DOWEX 30—Hydrogen Form	12.0–12.5	10.6–11.1
"NaCl Prepared" Sodium Form	10.0–10.5	7.0– 7.5

In the following, the quantities in brackets refer to air-dried materials, the same quantities without brackets to "bone-dry" materials as defined above. In the capacity determinations, the air-dried exchanger in the hydrogen form ($[w_H]$ grams) was contacted, in a stoppered Erlenmeyer (or other suitable closed vessel) with a sodium chloride solution (v_{Na} cc.) of concentration, a, in meq./liter. The relative amounts of solution and exchanger were so chosen that the sodium chloride was present in large excess; the excess was varied from 6 to 100 milliequivalents of sodium chloride per gram of air-dried exchanger in a series of determinations on the same material. Each mixture was allowed to stand for at least one hour during which time it was occasionally agitated by hand. Then it was shaken vigorously and after allowing the exchanger to settle again aliquots of the supernatant solution were titrated with standard sodium hydroxide solution to a *p*H of 7.

In calculating values of [M], that is, of milliequivalents of exchangeable cation per gram of air-dried exchanger, from these determinations, that part of the hydrogen ion concentration which was due to decomposition of the exchanger during air-drying (measured by h) was subtracted from the titrated concentration, that is the values of [M] were given by $(H^+)_w v_{Na}/1000[w_H]$, where $(H^+)_w$ was the corrected hydrogen ion concentration. Table IIIA gives series of determinations for each of the four exchangers tested, including the values of $a, [w_H]$, the ratio $0.001v_{Na}/[w_H]$ (meq. of sodium chloride per gram of air-dried exchanger) and the corresponding value of [M]. As the excess of sodium chloride is increased, [M] reaches a maximum approximately constant limiting value which is converted to the bone-dry capacity, M, knowing the moisture content of the air-dried sample which was tested. The experimental range of M showing that M is reproducible to better than 10% and the average value are given at the bottom of each [M] column. In the case of the low capacity exchangers, AMBERLITE IR-

TABLE III

CAPACITY DETERMINATIONS

Excess NaCl in meq./g. air-dried exchanger	v_{Na}	A Hydrogen form $[w_H]$	a	[M]	[M]	c	B Sodium form $[w_{Na}]$	v_H	Excess H_2SO_4 in meq./g. air-dried exchanger
		(8.8% Moisture)		AMBERLITE IR-100AG		(5.7% Moisture)			
6.75	104.8	0.320	20.4	1.18	1.20	331	1.500	150	33.1
25.0	100	.100	25.0	1.37	1.14	426	1.500	175	49.7
45.0	50	.110	100	1.36	1.33	497	1.500	200	66.2
85.0	50	.200	340	1.30					
85.0	50	.200	340	1.40					
100.0	50	.100	200	1.38					
			M = 1.43–1.54		$M_{max.}$ = 1.41				
			$M_{av.}$ = 1.49		(1.48)				
			(1.58–1.60)						
		(11.7% Moisture)		IONAC C-200		(7.2% Moisture)			
6.75	104.5	0.320	20.6	1.69	1.53	331	1.000	150	49.7
25.0	100	.100	25.0	1.98	1.71	426	1.000	175	74.5
42.9	50	.102	87.5	2.15	2.00	497	1.000	200	99.3
53.8	50	.251	340	2.11					
67.2	50	.201	340	2.12					
80.0	100	.250	200	2.27					
100.0	50	.050	100	2.06					
			M = 2.33–2.57		$M_{max.}$ = 2.16				
			$M_{av.}$ = 2.42		(2.31)				
			(2.51–2.54)						
		(10.9% Moisture)		DOWEX 30		(7.3% Moisture)			
1.72	104.8	0.320	20.5	1.39	1.56	331	1.500	150	33.1
25.0	100	.100	25	1.89	1.95	426	1.500	175	49.7
43.3	50	.101	87.5	1.97	1.99	497	1.500	200	66.2
54.0	50	.250	340	2.04					
66.5	50	.203	340	2.05					
80.0	100	.250	200	2.06					
93.8	75	.120	150	2.05					
			M = 2.21–2.31		$M_{max.}$ = 2.15				
			$M_{av.}$ = 2.27		(2.32)				
			(2.49–2.57)						
		(7.8% Moisture)		ZEOKARB		(5.8% Moisture)			
6.75	104.8	0.320	20.7	0.90	0.75	331	1.500	150	33.1
20.6	50	1.000	413	1.22	0.83	426	1.500	175	49.7
40.0	100	0.500	200	1.22	0.85	497	1.500	200	66.2
43.3	50	.101	87.5	1.20					
66.9	50	.202	340	1.25					
75.0	100	.200	150	1.29					
79.5	50	.170	340	1.25					
			M = 1.30–1.40		$M_{max.}$ = 0.91				
			$M_{av.}$ = 1.34		(0.98)				
			(1.48–1.52)						

100AG and ZEOKARB, an excess of 20–25 meq. of sodium chloride per gram of air-dried exchanger was sufficient to reach the limiting value of [M], while the high capacity exchangers, IONAC C-200 and DOWEX 30, required 30–40 meq. per gram.

As equilibrium and rate data were also obtained by contacting the sodium chloride prepared sodium forms of the exchangers with hydrochloric acid solutions, it appeared desirable to check experimentally the capacities of the sodium forms; using the same technique as above, air-dried samples of these sodium forms were treated with increasingly large amounts of sulfuric acid in excess, the moisture contents of these air-dried samples having been determined on separate fractions, as described above. The results are given in Table III(B), including the maximum (bone-dry) M-value at the bottom of the [M] column.

The capacities shown in Table III appear to be somewhat lower than capacities measured in systems in which the solutions percolate through stationary exchanger columns. In reasonable agreement with our values, Walton[3c] gives a capacity for ZEOKARB of 1.43 meq./g. and Bauman[9] *a sulfuric acid capacity* for DOWEX 30 between 1.9–2.5 meq./g. (15–20 kilograins as $CaCO_3$ per cu. ft.). We did not find any published information on IONAC C200, but for AMBERLITE IR 1 (not IR 100) G. E. Boyd, J. Schubert and A. W. Adamson[3e] give a capacity of 1.7–1.8 meq./g. for low *p*H values.

The order of magnitude of $K_{H/Na}$ (see Table IV) was such that the single acid treatment, though drastic, was incomplete. Hence, to determine the residual sodium content of the exchanger in the hydrogen form, prepared as described above, 2-g. samples, weighed to the nearest milligram, were washed free of acid (h-correction) and were then allowed to stand in contact with 25 cc. of 0.954 N sulfuric acid for more than two hours with occasional agitation. After separation the solution was titrated and the same sample of exchanger was again contacted with 25 cc. of 0.954 N acid. This treatment was repeated until two successive leaches showed no further neutralization of acid. The total residual sodium contents, F_{Na}, estimated in this manner and expressed in meq./g. of bone-dry exchanger were: AMBERLITE IR 100, 0.04–0.07 (3 leaches); IONAC C200, 0.03–0.06 (3 leaches); DOWEX 30, 0.15–0.21 (3 leaches); ZEOKARB, 0.07–0.11, (3 leaches).

Furthermore, the capacity determinations themselves were subject to the same error of incomplete conversion. An estimate of this error was obtained from equation (1) using the values of $K_{H/Na}$ of Table IV (below) and the experimental values $(h + x_e)/(a - x_e) = (H^+)_w/(Na^+)_w$; the residual hydrogen contents due to this incomplete conversion were obtained in meq./g. of bone-dry exchanger, F_H, by multiplying this ratio by $1/K_{H/Na}[F_{Na} + x_e v_{Na}/1000 w_H]$. Combining the two errors gives an estimated order of corrected "forward" capacities $(M + F_{Na} + F_H)$ given in Table IIIA in parentheses below the $M_{av.}$ values.

The maximum residual hydrogen content, R_H, in meq./g. bone-dry exchanger, of the sodium forms prepared by treating the hydrogen forms with sodium chloride, as described, can now be estimated from equation (1) multiplying the values of $M/K_{H/Na}$ by the ratio

$$\frac{1000(M + F_H)w_H/v_{Na} + h}{a - 1000(M + F_H)w_H/v_{Na}} = \frac{(H^+)_w}{(Na^+)_w}$$

This estimate neglects the residual sodium content, R_{Na}, left in the exchangers in the capacity determinations of the sodium forms (by sulfuric acid) which can be estimated in a manner similar to F_H

$$R_{Na} = \frac{K_{H/Na}(x_e')}{(c - x_e')}\left[R_H + x_e' \frac{v_H}{1000 w_{Na}}\right]$$

Adding R_H and R_{Na} to the reverse capacities gives the estimated order of corrected reverse capacities given in Table IIIB in parentheses below the $M_{av.}$ values. For AMBERLITE IR-100 and for IONAC C200 the error was less than 10% and hence was neglected in the calculation of $K_{H/Na}$. However, for DOWEX 30 and for ZEOKARB the error was sufficiently important to calculate the corrected values of $K_{H/Na}$ given in parentheses below the $K_{av.}$ values in Table IV.

It should be noted that the capacity determinations were carried out in a "static" system in which a given weight of exchanger was in contact with a known volume of solution containing a large excess of electrolyte until equilibrium was reached. This method of measuring capacities differs fundamentally from capacity determinations in a flowing system in which concentrated electrolyte solutions are percolated through a stationary exchanger bed until exhaustion; this latter method gives higher apparent capacities as it involves the removal of hydrogen ions which are not available for exchange in dilute chloride solutions. The following experiments were carried out to illustrate the difference: 20.0-g. samples of air-dry incompletely converted DOWEX 30 exchanger in the hydrogen form (batch 2, residual $Na^+ = 0.15 - 0.21$ meq./g.) were placed in a glass column (1.5 cm. i. d., 10 cm. long) and 36.7 liters of a 1.00 N sodium chloride solution were passed through the column at a rate of 70–90 cc./min. At the start the *p*H of the first 10 cc. of effluent was 1.5, at the end the *p*H was 5.8. Upon titration of the combined effluent it was found that 2.50 meq. of hydrogen ion had been removed per gram of bone-dry exchanger. (Further addition of 1.00 N sodium chloride solution would probably have removed more hydrogen ion from the exchanger.) After this treatment 38.6 liters of distilled water of *p*H 6.5 were percolated through the exchanger bed; the *p*H of the effluent rose to a maximum of 9.4 after one liter had passed through and then decreased gradually to a value of 7.65 of the last liter. Clearly, part of the sodium introduced in the exchanger in the flowing system reappeared in the washwater as sodium hydroxide.

Upon titration it was found that the *alkalinity* removed by simple washing amounted to 0.22 meq. per gram of bone-dry exchanger. Subtracting this amount from the total of 2.50 gave a sodium chloride capacity of 2.28 meq./g. of bone-dry exchanger in good agreement with the uncorrected capacity measured in a static system.

This rise in *p*H during washing can thus be attributed to a hydrolysis of part of the sodium ions introduced into the exchanger by the continued exposure to the fresh, strong sodium chloride solution in the flowing system. Obviously, that part of the sodium ion which is removable by simple hydrolysis does not take part in the sodium–hydrogen exchange in dilute chloride solutions, but should and does count as part of the much larger total capacity measured by a reac-

---

(9) W. C. Bauman, *Ind. Eng. Chem.*, **38**, 46 (1946).

TABLE IV

CONCENTRATION EQUILIBRIUM CONSTANTS

A					B				
c	w_H	v_{Na}	x_a	$K_{H/Na}$	$K_{H/Na}$	x_a'	v_H	w_{Na}	c
AMBERLITE IR-100AG (M = 1.49)									
1.15	0.073	104.9	0.58	1.28					
3.03	.137	104.9	1.23	1.17					
4.77	.670	104.8	3.35	1.28	1.31	2.92	104.8	0.692	4.54
6.95	.438	104.9	3.43	1.20	1.31	3.85	104.9	.905	6.01
9.10	.893	104.8	5.65	1.31	1.19	5.22	104.8	.922	9.34
48.7	3.65	102.9	27.3	1.36					
99.8	7.30	100.0	55.1	1.27	1.38	210.6	91.65	24.05	549.0
814.0	26.45	61.7	366	1.10	1.19	415.2	87.49	40.83	1150
				$K_{av.}$ = 1.25	$K_{av.}$ = 1.28				
IONAC C-200 (M = 2.42)									
1.15	0.066	104.8	0.68	1.17	1.28	1.15	104.9	0.139	1.97
4.04	.283	104.8	2.55	1.10	1.61	2.50	104.8	0.232	6.01
9.22	.770	104.9	6.60	1.25	1.23	4.70	104.9	0.453	9.42
15.77	.618	104.9	7.71	1.13					
48.6	1.77	103.1	23.92	1.32					
102.5	3.53	97.75	48.1	1.08					
1194	16.78	33.6	636.8	1.27	1.41	230.1	89.92	16.98	559.4
1240	16.78	32.4	634.1	1.07	1.38	300.1	89.38	18.75	900.4
				$K_{av.}$ = 1.20	$K_{av.}$ = 1.38				
DOWEX-30 (M = 2.27)									
1.16	0.080	104.9	0.70	1.03	1.07	1.25	104.9	0.167	1.97
4.08	.339	104.9	2.61	0.98	1.28	2.83	104.9	.278	6.04
9.19	.879	104.8	6.35	1.12	1.09	6.18	104.8	.896	9.34
15.84	.731	105.0	7.93	1.01					
49.0	2.50	102.1	26.24	1.03					
103.3	4.01	96.85	48.6	0.95	1.50	229.1	90.76	18.82	554.2
1188	16.93	33.8	570.6	0.93	0.87	345.5	89.24	20.95	901.8
				$K_{av.}$ = 1.01 (1.13)	$K_{av.}$ = 1.16 (1.27)				
(M = 1.34) ZEOKARB (M = 0.91)									
1.16	0.138	104.9	0.62	0.62	1.17	1.04	104.8	0.279	1.95
4.07	0.581	104.9	2.35	.59	1.12	2.29	104.9	.446	6.01
9.25	0.897	104.9	4.55	.64	0.46	3.20	104.9	.457	9.40
15.80	1.199	104.9	6.77	.59					
50.5	4.61	99.03	26.09	.77					
102.3	9.22	97.85	52.5	.75	0.55	185.2	92.53	24.18	543.6
804.0	32.27	62.43	337.0	.68	0.58	325.0	91.24	40.46	1103
				$K_{av.}$ = 0.66 (0.72)	$K_{av.}$ = 0.78 (0.80)				

tion with sodium hydroxide or other alkaline solutions. The significance of the difference between the sodium chloride capacity and the total capacity will be discussed below.

Inspection of Table III shows a check of the hydrogen form capacities and the sodium form capacities of the synthetic resinous exchangers AMBERLITE IR 100AG, IONAC C200 and DOWEX 30. For the sulfonated coal exchanger ZEOKARB, however, the value of the sodium form capacity is much smaller than that of the hydrogen form. It is believed that this decrease is due to the lesser resistance to attrition of the modified natural material; that is, during the drastic sodium chloride treatment to prepare the sodium form (see above), the sulfonated coal was probably attacked and lost a substantial fraction of its initial capacity, presumably through splitting off of sulfonic acid groups. The fact that the sodium forms of the three other (resinous) exchangers also have slightly lower capacities than their corresponding hydrogen forms would indicate a similar attack to a much lesser degree. In the following the hydrogen form capacities of AMBERLITE IR 100AG, IONAC C200 and DOWEX 30 will be used for both forms of the exchangers, but in the case of ZEOKARB it is necessary to use the value of 1.34 for the hydrogen form and the value 0.91 for the sodium form.

It is interesting to compare the above figures for

ZEOKARB to the data of Nachod and Wood,[7b] who found (presumably on an air-dried basis) a capacity of 0.77 in chloride solutions, and a capacity of 1.35 in solutions of anions of weak acids (formate, acetate, bicarbonate). From a reading of their papers[7] it would seem that an excess of only about 4 meq. of sodium chloride per gram of air-dried exchanger was used and this was obviously very far from sufficient to replace substantially the available hydrogen on the exchanger by sodium, as shown in Table III(A).

The Measurement of $K_{H/Na}$.—In one series of runs equilibrium data were obtained using the technique of the capacity determinations, except that the ratio $0.001\, v_{Na}\, a/[w_H]$ was so chosen that the equilibrium concentrations fell within the limits $0.25 < (Na^+)_w/(H^+)_w < 2$.[10] It is evident from inspection of Equations (1), (2) and (2′) that the more the ratio $(Na^+)_w/(H^+)_w$ differs from unity, the larger the probable error in $K_{H/Na}$, due to small differences of relatively large numbers. In the case of determinations in which a or c was larger than 100 meq./l. the above limitation of the equilibrium concentration range was also indicated for reasons other than that of experimental accuracy, as will be discussed below.

Similarly, in another series of runs equilibrium determinations were made with the same technique, using the "sodium chloride prepared" sodium form of the air-dried exchanger ($[w_{Na}]$ grams) and hydrochloric acid solutions (v_H cc.) of concentration, c, and limiting the calculations of $K_{H/Na}$ to those runs in which the ratio $(Na^+)_w/(H^+)_w$, at equilibrium, was between 0.25 and 2.

In all experiments with dilute solutions ($a <$ 20 meq./l.) the ratio of the volume of solution to weight of dry exchanger was large enough to neglect any change in ionic strength of the water phase due to the wetting and swelling of the air-dried exchanger. This effect, however, was not negligible in more concentrated solutions in which the volume of the water phase was noticeably smaller than that of the chloride solution initially added. The corrected volume of the water phase (in cc.) was obtained in this case by dividing the number of milliequivalents of sodium chloride initially added by the chloride concentration, expressed in milliequivalents per cc. and determined by a Volhard titration[11] of an aliquot of the water phase after the exchanger phase had been thoroughly wetted by the solution. Here the assumption is made that the volume of the wet exchanger phase is independent of the relative amount of sodium and hydrogen ions present therein; this assumption appears to hold in the sodium–hydrogen exchange case in chloride solutions, but it is not necessarily correct in exchanges of other ions.

Finally, the limiting values of the concentration-time plots representing the rate data (Figs. 2–5) were also used to calculate values of $K_{H/Na}$ provided that they were such that the above limiting condition was fulfilled.

All equilibrium determinations were made at 28 ± 3° as the technique used for this work was not accurate enough to give significantly different values of $K_{H/Na}$ in duplicate runs at temperatures within this range.

Table IV(A) gives a, w_H, v_{Na}, x_e and $K_{H/Na}$ (calculated from Equations (2) and (3)); similarly, Table IV(B) gives c, w_{Na}, v_H, x'_e and $K_{H/Na}$ (calculated from Equations (2′) and (3′)).

Inspection of Table IV(A) shows that the "forward" $K_{H/Na}$, that is the concentration equilibrium constants measured by contacting the hydrogen forms of the exchangers with the sodium chloride solutions, are constant within about 20% over a concentration range of the water phase varying from about 0.001 N to about 0.8 N for AMBERLITE IR 100AG and ZEOKARB, and to about 1.2 N for IONAC C 200 and DOWEX 30. In view of this wide concentration range this variation does not appear excessive. For the three resinous exchangers, AMBERLITE, IONAC and DOWEX 30, the forward $K_{H/Na}$ has the relatively low value of 0.66 on the sulfonated coal exchanger ZEOKARB. The values of the equilibrium constants for ZEOKARB and AMBERLITE IR100 are in good agreement with previously published values.[3c,d]

Comparison of the "reverse" $K_{H/Na}$ given in Table IV(B) (obtained with the sodium forms and hydrochloric acid solutions) with the corresponding forward $K_{H/Na}$ of Table IV(A) shows a fair check. However, the reproducibility of the reverse $K_{H/Na}$ is poorer than that of the forward runs probably because of the variable extent of attack of the exchangers by the drastic sodium chloride treatment in the preparation of the sodium forms. This is also indicated by the fact that the values of the reverse $K_{H/Na}$ are consistently, but not significantly, larger than the corresponding forward values (higher capacities correspond to higher apparent values of the reverse $K_{H/Na}$). In the case of ZEOKARB the reverse capacity of 0.91 was used (the forward capacity of 1.34 would give an average reverse $K_{H/Na}$ of nearly 2); in spite of the two different capacities of the two forms of ZEOKARB the average reverse $K_{H/Na}$, though determined less accurately, is of the same order as the forward $K_{H/Na}$. This fact suggests the view that the solid coal constituents merely serve as a support for the active sulfonic acid groups which possess an average acid strength largely independent of their concentration in the exchanger phase.

The Measurement of the Velocity Constants.—Figure 1 shows a diagram of the apparatus

---

[10] In the case of the sodium–hydrogen exchanges from chloride solutions on the four specified materials the ratio of the numbers of hydrogen ions to sodium ions in the exchanger phase at equilibrium happens to be of the same order of magnitude as $(Na^+)_w/(H^+)_w$ so that this condition may equally be written for the ratio $(H^+)_r/(Na^+)_r$.

[11] Scott, "Standard Methods of Chemical Analysis," 5th ed., Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1939, p. 271–272.

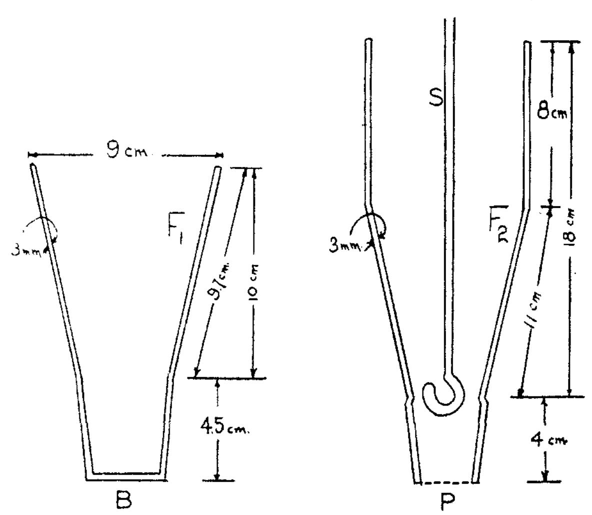


Fig. 1.—Rate measurement apparatus.

which was particularly satisfactory for rate determinations, since it permitted a rapid separation of the solid exchanger from the solution. The outer shell, A, was made from a female Ŧ 40/50 Pyrex joint, the bottom of which, B, was sealed off. The inner member, C, consisted of a male Ŧ 40/50 joint; to the narrower end of this joint was fused a 52-mesh, B&S No. 38, platinum wire screen, P. A funnel, F_2, having a conical section and a cylindrical section, as shown in the diagram, had the narrow end of the conical section fused to the wide end of the male joint. An electrically driven high-speed (2500 r. p. m.) glass stirrer, S, reached down into the space of the joint of the inner shell. In Fig. 1 the dimensions of the various parts of the apparatus are shown. For a measurement, the apparatus was assembled by clamping the cylindrical part of the inner container in a permanent position, fitting the female joint over the male joint (joint lubricated with Dow-Corning silicone stopcock grease for a tight fit) and supporting the outer container by a ringstand or other easily removable means.

To obtain a point of the concentration *vs.* time plot in rate determinations, a weight, $[w]$, of the exchanger under test (always 20/40 mesh) was placed on the platinum screen of the inner container; 100 cc. of distilled water, measured by pipet, was added to the inner container and the stirrer was started so that the solution and the exchanger were vigorously stirred throughout the run. After five minutes of stirring, allowing the exchanger to swell and become thoroughly wet with water, a known weight of a solution of sodium chloride, or hydrochloric acid, as the case may call for, of known concentration was added all at once, at $t = 0$, from a weighing bottle. A few seconds before the time t at which the change in concentration was determined, the support of A was removed and the outer container held in place by hand. At t, the outer container was suddenly pulled downward and the solution in the inner container flowed through the platinum screen into the outer container within less than two seconds, leaving the solid exchanger on the platinum screen. The hydrogen ion concentration at t in the solution was determined by titration with standard alkali to a *p*H of 7 (with a Beckman *p*H meter, No. 2000, Model G).

In the measurement of the velocity of process I going from left to right, to $[w_H]$ grams of the exchanger were added successively 100 cc. of distilled water and g grams of a solution of sodium chloride of density σ (in grams per cc.) and of concentration n (in equivalents per liter). Hence the initial sodium ion concentration a in meq./l. was $10\ n\ g/(\sigma + 0.01\ g)$. In all runs g was measured into a weighing bottle by means of a 5-cc. pipet delivering actually 4.95 cc., the bottle was weighed, the solution in it was poured into the rate measuring apparatus at $t = 0$, and the weighing bottle was weighed back to obtain g for each run. On the average g was 4.8 ± 0.1 g. Since g (and therefore a) was known for each individual run within better than 0.2%, a change of about 4% in g (and therefore in a), as did occur in duplicate runs, did not result in consistent differences which were greater than the margin of error in x. Therefore, for any series of runs with a given weight of exchanger we have $a = 48n/(\sigma + 0.048)$ which is correct within ± 2%. x (in meq./l.) is determined either by direct titration of the solution separated from the two exchangers, AMBERLITE IR-100AG and IONAC C-200, at the end of t minutes, or it is obtained for DOWEX 30 and for ZEOKARB by subtracting the corresponding correction h from the titrated value x^*.

Similarly, measuring the rate of process I going from right to left, to $[w_{Na}]$ grams of the "sodium chloride prepared" sodium form were added successively 100 cc. of distilled water and g grams of a solution of hydrochloric acid of concentration n (in equivalents per liter) and of density σ in grams per cc. The initial hydrogen ion concentration was then $c = 48n/(\sigma + 0.048) \pm 2\%$. In these runs x' (in meq./l.) was the sodium ion concentration in solution (meq./l.) at the time t, and it was obtained by subtracting the hydrogen ion concentration at t, $c - x'$, from the initial concentration c.

In Figures 2–5 the experimental values of x or x' are plotted *vs.* t, and each curve is numbered to correspond to the run number on the particular exchange tested.

These determinations were made at room temperature and it was found unnecessary to control the temperature more closely than to 28 ± 3°, as temperature differences within this range caused neither significant nor consistent changes in x or x' in duplicate runs. This observation confirms Nachod and Wood's statement regarding the temperature dependence[7a] of the exchange velocities (which suggests that diffusion is a rate determining step).

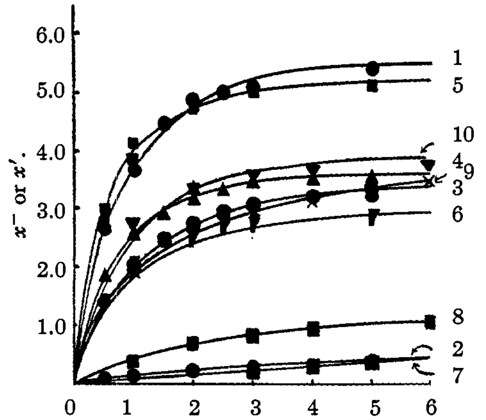


Fig. 2.—Amberlite IR-100.

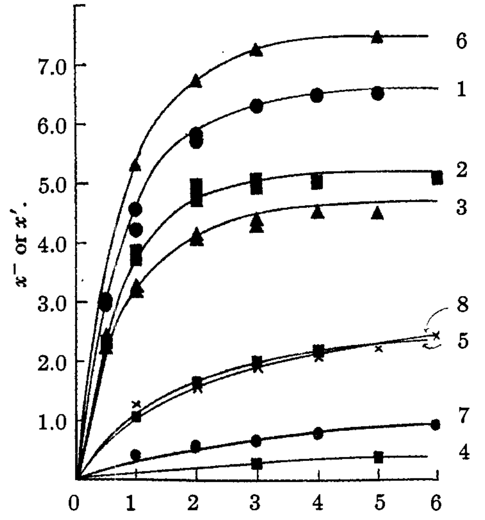


Fig. 3.—Ionac C-200.

It is apparent from inspection of Figs. 2–5 that the exchange rates in solutions of concentrations larger than 0.02 *N* and smaller than 0.001 *N* would be, respectively, too fast and too slow to give satisfactory data when measured with the technique described above. For this reason the rate measurements were limited to the concentration range of 0.001 to 0.02 *N*.

The curves fit Equation (7) or Equation (7′), respectively. Table V illustrates a typical calculation[11a] of *k*. Table VI gives the results of velocity determinations of the sodium–hydrogen exchange on the four exchangers at different sets of concentrations. The ranges under the *k* and *k*′ columns in Table IV show that in the individual runs *k* and *k*′ were constant often to better than

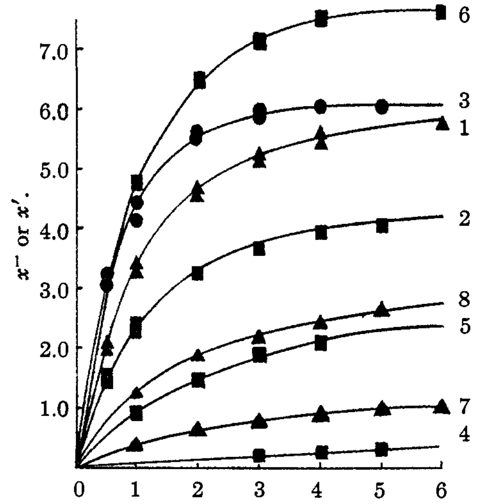


Fig. 4.—Dowex 30.

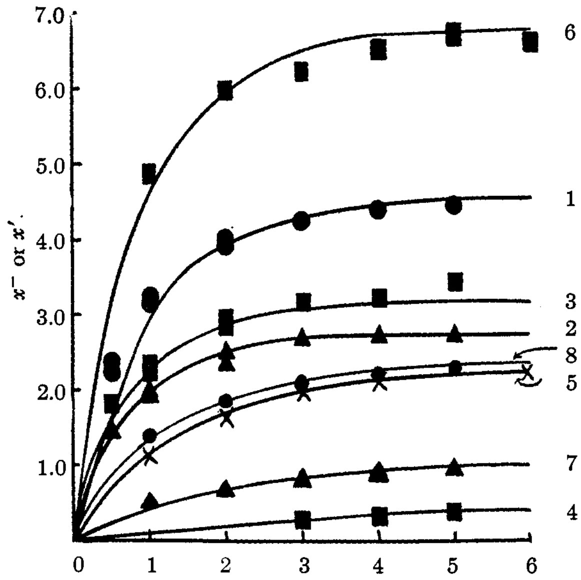


Fig. 5.—Zeokarb.

10% and usually better than 20%. These values are actually slightly in error because the small amounts of the residual sodium and hydrogen initially present in w_H and w_{Na} were neglected.

The value of *k* for ZEOKARB of 0.03–0.06 l. × meq.$^{-1}$ × min.$^{-1}$ differs from that given by Nachod and Wood[7b] by a factor of about 20. As demonstrated experimentally above, the excess of about 4 meq. of salt per gram of exchanger used by Nachod and Wood was far from sufficient to drive the exchange to completion. Therefore, Nachod and Wood's[7] simplified bimolecular rate equation in which the reverse reaction was assumed negligible was probably in error, the discrepancy in *k* being due to that erroneous assumption.

[11a] Run 3 on AMBERLITE IR 100AG was chosen as the example because more experimental points were obtained for this particular set of concentrations on AMBERLITE than for any other run (see Fig. 2, Curve 3). The reason for this was that in Run 3 on AMBERLITE our experimental technique was checked on two instruments and on two separate shipments of AMBERLITE prepared according to our standard procedure.

TABLE V

CALCULATION OF k FROM RUN 3 ON AMBERLITE IR-100AG

a = 4.77 meq./l., w_H = 0.670, M = 1.49 meq./g., v_{Na} = 104.8 cc., $b = 1000w_HM/v_{Na}$ = 9.53 meq./l., x_e = 3.35 meq./l.

t, min.	x, meq./l.	$ab(x_e + x)$	$x_e(a + b)x$	$ab(x_e - x)$	$\frac{ab(x_e + x) - x_e(a + b)x}{ab(x_e - x)} = Z$	ln Z	$k = \frac{x_e}{[2ab - (a + b)x_e]t} \ln Z$ l. × meq.$^{-1}$ × min.$^{-1}$
1.0	1.92	239.6	92.0	65.0	2.270	0.820	0.061
1.5	2.35	259.1	112.6	45.5	3.22	1.17	.058
2.0	2.71	275.5	129.8	29.1	5.01	1.61	.060
2.5	2.93	285.5	140.4	19.1	7.60	2.03	.060
3.0	3.06	291.4	146.6	13.2	10.99	2.40	.059
4.0	3.25	300.0	155.7	4.55	31.7	3.45	.064
5.0	3.29	301.9	157.6	2.73	52.9	3.85	.057

k = 0.057–0.064

$k_{av.}$ = 0.061

TABLE VI

VELOCITY CONSTANTS OF THE DIRECT AND REVERSE SODIUM–HYDROGEN EXCHANGE REACTIONS

Forward reaction						Reverse reaction					
Run	a, meq./l.	b, meq./l.	x_e, meq./l.	k l. × meq.$^{-}$ × min.$^{-1}$	$k_{av.}$ l. x meq.$^{-1}$ × min.$^{-1}$	Run	c, meq./l.	d, meq./l.	x_e', meq./l.	k' l. × meq.$^{-1}$ × min.$^{-1}$	$k'_{av.}$, l. × meq.$^{-1}$ × min.$^{-1}$
					AMBERLITE IR-100 AG (M = 1.49)						
2	0.91	1.95	0.66	0.075–0.082	0.079						
7	1.15	1.04	0.58	.079– .087	.083						
8	3.03	1.94	1.23	.075– .082	.079						
3	4.77	9.53	3.35	.057– .064	.061	6	4.54	9.84	2.92	0.067–0.081	0.073
9	6.95	6.22	3.43	.054– .062	.059	10	6.01	12.85	3.85	.048– .052	.050
1	9.10	12.70	5.65	.047– .052	.049	5	9.34	13.11	5.22	.045– .052	.049
4	20.4	4.07	3.52	.052– .057	.054						
					IONAC C-200 (M = 2.42)						
4	1.15	1.53	0.68	.062– .072	0.068	7	1.97	3.21	1.15	.051– .055	.053
5	4.04	6.53	2.55	.048– .052	.050	8	6.01	5.30	2.50	.036– .039	.038
1	9.22	19.95	6.60	.038– .042	.040	3	9.42	10.45	4.70	.044– .048	.045
6	15.77	14.26	7.71	.034– .041	.038						
2	20.60	6.39	5.15	.050– .055	.052						
					DOWEX-30 (M = 2.27)						
4	1.16	1.73	0.70	.040– .044	0.042	7	1.97	3.61	1.25	.056– .064	.060
5	4.08	7.34	2.61	.036– .039	.037	8	6.04	6.02	2.83	.042– .044	.043
1	9.19	19.04	6.35	.020– .027	.024	3	9.34	19.41	6.10	.041– .042	.042
6	15.84	15.80	7.93	.024– .027	.025						
2	20.53	6.08	4.35	.020– .024	.021						
				(M = 1.34)	ZEOKARB		(M = 0.91)				
4	1.16	1.76	0.62	.061– .066	0.062	7	1.95	2.39	1.04	.10 – .13	.110
5	4.07	7.42	2.35	.044– .045	.045	8	6.01	3.82	2.29	.064– .083	.071
1	9.25	11.46	4.55	.039– .043	.041	3	9.40	3.92	3.20	.110– .127	.118
6	15.80	15.32	6.77	.028– .030	.029						
2	20.68	3.67	2.80	.038– .044	.042						

The velocity constants are of the same order of magnitude for all four exchangers, DOWEX 30 being the slowest, and the reverse reaction being fastest on ZEOKARB (which shows up in the exceptionally low value of $K_{H/Na}$ of ZEOKARB). The values of k and k' calculated from runs with concentrations ranging from 0.001 to 0.02 N on the same exchanger are of the same order, but show a less than twofold variation which appears to be significant in that k and k' increase as the concentration decreases. Since the exchange involves ions in aqueous solution, a dependence of k and k' upon the ionic strength has to be expected.[12] In this respect it is noteworthy that the ratios k/k' (which are equal to $k_{r/w}/k'_{r/w}$) for values of the concentrations a and c of the same order are less dependent on the ionic strength than the individual values of k and k' (which should also vary with B). In Table VII the roughly averaged values of these ratios are compared with the values of the forward $K_{H/Na}$ of Table IV(A), and considering the uncertainty of the individual values of k and k' and that of $K_{H/Na}$ the agreement is quite satisfactory.

---

[12] See, for example, S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1st ed., 1941, pp. 423–430.

TABLE VII

COMPARISON OF FORWARD $K_{H/Na}$ WITH k/k'

Exchanger	$K_{H/Na}$ from forward equilibrium data	Range of a or c in meq./l.	Average k/k' from rate data
Amberlite IR-100 AG	1.10–1.36	1–3	1.1
		9–20	1.1
Ionac C-200	1.07–1.32	1–5	1.1
		9–20	1.1
Dowex-30 (Nalcite MX)	0.93–1.12	1–5	0.7
		9–20	.5
Zeokarb	0.59–0.75	1–2	.6
		4–20	.4

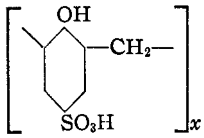
Discussion

Various assumptions have been made regarding the structure of the colloidal clays and of the non-carbonaceous zeolites in order to write equilibrium relations of the mass action law type in terms of activities.[13] For example, Vanselow[2a] described the mixture of a sodium clay and a potassium clay as a mixed crystal and assumed that the ratio of their activities is equal to the ratio of their mole fractions. Kielland[2b] called the exchanger phase, containing two species of cations, a solid solution and defined activity coefficients of the so-called metal zeolites. Recently, however, Davis[2d] pointed out that an ionic dissociation equilibrium exists involving the ions of the exchanger phase and that its role needs to be considered in the discussion of exchange equilibria. Previously, Moller,[2c] considering the exchanger phase as a completely dissociated electrolyte applied to the exchange equilibrium a broadened version of Brönsted's theory of individual ionic activity coefficients in mixtures of electrolytes and arrived at the assumption that the ratio of the activity coefficients of the cations in the exchanger phase is constant. His base exchange experiments with a potassium clay and an ammonium clay of different particle size in redistilled water provide strong evidence for a dissociation equilibrium in the exchanger phase although these experiments do not prove that the dissociation is complete.

Evidently, an experimental investigation of one particularly simple exchange of univalent ions is an inadequate basis for a general theoretical discussion. The present investigation merely illustrates that (1) the experimental equilibrium data of the sodium–hydrogen exchange on AMBERLITE IR-100AG, IONAC C-200, DOWEX 30 and ZEOKARB in contact with chloride solutions can be expressed as a good approximation by an equilibrium relation which is of the form of a simple mass action equation; the concentration equilibrium constants varying by less than 20% over a concentration range of 0.001 to 1 N; (2) the experimental kinetic data fit reasonably well a second order rate equation of opposing simultaneous reactions (although the velocity constants are slightly dependent upon concentration); (3) the ratios of the apparent velocity constants of the forward and reverse exchanges are of the same order of magnitude as the so-called concentration equilibrium constants.[14] This illustration is significant in itself and may be helpful in the later development of a general equilibrium relationship which must be derivable from kinetic considerations.

In the absence of specific information on the organic exchangers, it has been assumed that dissociation equilibria exist in the exchanger phase and that the sodium–hydrogen equilibrium between the exchanger phase and the chloride solution is governed by a mass action equilibrium relation involving the dissociated cations in the exchanger phase and in the chloride solution. A brief discussion of these assumptions follows.

To illustrate a typical carbonaceous exchanger it is convenient to choose the resinous product known as DOWEX 30 for which the structural formula (I) (in the hydrogen form) has been proposed.[9] It is plausible to consider the two functional groups (sulfonic acid and phenol) as corresponding to two very different acid strengths and, except when in contact with alkaline solutions, to neglect the dissociation of the phenolic group as its ionization constant is undoubtedly very small compared to that of the sulfonic acid group.[15] When air (or oven) dried granules of this (or a similar) exchanger in the hydrogen form are contacted with water, they swell to a jelly-like mass taking up almost their own weight of water. The



(I)

---

[13] Recently, Davis[2d] and Bauman and Eichorn[3g] proposed the assumption that the equilibrium between a colloidal clay or a carbonaceous exchanger in contact with an electrolyte solution is a Donnan equilibrium rather than a base exchange equilibrium. It is generally admitted that the exchange of cations from chloride solutions on wet organic exchangers leaves the total electrolyte concentration of the aqueous phase constant. This assumption implies that no chloride ions diffuse into the exchanger phase although a small number is presumably present in the film of solution adhering to the exchanger granules after their separation from the bulk of the solution by filtration. It is proposed that this film be considered part of the external phase and it is assumed that the ionic concentration in the film, though different from that of the solution, has a negligible effect on the average concentration of the external phase which can therefore be determined by analysis of the filtrate. In other words the base exchange concept, rather than the Donnan concept, is assumed to apply to the sodium-hydrogen exchange under discussion. However, in this particular case Davis' Donnan equilibrium concept leads to an equilibrium relation of the same form as the base exchange concept so that the experimental evidence presented in this paper cannot be used to prove or disprove the possibility of extending Davis' theory to carbonaceous exchangers.

[14] It does not follow that this conclusion may be extended to exchanges involving cations of different valences or other anions, particularly anions of weak acids. Experimental evidence (H. L. Tiger and S. Sussman, *Ind. Eng. Chem.*, **35**, 186 (1943); also Nachod and Wood[7b]) has been published showing that the capacities depend upon the anion and that they are larger in alkaline solutions than in neutral salt solutions.

[15] For other exchangers which may contain carboxylic groups besides sulfonic acid groups the same assumption for the carboxylic group is probably less justifiable, but is retained for the sake of convenience.

assumption is proposed that this jelly be considered as a special kind of a solution of an incompletely dissociated acid

$$\text{(II)}\quad —SO_3H \rightleftarrows —SO^-{}_3 + H_r^+$$

in which any particular sulfonic acid group maintains a definite position in the jelly regardless of whether it is at the moment a $—SO_3H$ group or a $—SO_3^-$ ion. On the other hand, the hydrogen constituent of this functional group is fixed in position only while a part of the $—SO_3H$ group but becomes mobile when it exists as a hydrogen ion. The mobile hydrogen ions are subject to thermal movement, which is influenced by the coulombic interaction between the fixed negative ions and the hydrogen ions in a manner similar to the interionic attraction in ordinary electrolyte solutions. Only the mobile hydrogen ions which are presumably dissolved in the jelly water are assumed capable of taking part in the exchange with the sodium ions of the external chloride solution.

Similarly, the sodium form jelly is assumed to be a special kind of a salt solution

$$\text{(III)}\quad —SO_3Na \rightleftarrows —SO_3^- + Na_r^+$$

The removal of sodium ion by means of water from an exchanger treated previously by an excess of neutral sodium chloride solution flowing through the exchanger bed (see above) would indicate that the sodium salt form is, if not completely, at least considerably more dissociated than the acid form. Hence, (the sodium forms having been made from the acid exchanger in static systems) it seems reasonable to neglect that portion of the hydrogen presumably present originally as undissociated $—SO_3H$ which is replaced by the entering Na_r^+ to form $—SO_3Na$, that is, to define the constant sodium chloride capacity available for process I as the dissociated cationic portion of the acid exchanger jelly. Equations II and III do not correspond to Boyd's[3e] "half-reactions" on AMBERLITE IR-1 since according to the above assumption the exchange proper represented by (I) is influenced by (II) and (III), while the sum of Boyd's two "half-reactions" corresponds to (I).

When the acid jelly is immersed in excess water the hydrogen ions are presumably capable of diffusing across the phase boundary into the water phase leaving an excess negative charge in the jelly which tends to prevent the hydrogen ions from moving far out into the external phase and which may be assumed to cause the formation of a diffuse ionic layer around the exchanger granules in which the excess positive charge decreases rapidly (exponentially) in the direction perpendicular to the phase boundary. This situation is analogous to the case of a silica wall bearing a fixed negative charge and holding a film of electrolyte solution which may be several hundred ångströms thick and in which the excess positive charge balances the fixed negative wall charge. The interfacial potential due to this charge separation is commonly called the ζ potential.[16] The existence of a ζ-potential at the boundary between colloids and an electrolyte solution is generally admitted.[17] Therefore, the extension of this concept to the jellied carbonaceous exchanger grains appears logical as this phase may be considered analogous to but intermediate between the silica wall and the colloidal particle.[18]

When sodium chloride is added to the external phase, both sodium ions and chloride ions diffuse into the wetting films, but only the sodium ions can cross the film and entering the exchanger phase, the chloride ions being presumably prevented from entering the internal phase by the excess negative charge therein. For each sodium ion crossing the film from the water phase into the jelly, the condition of electroneutrality of the water phase requires that one hydrogen ion must move out of the jelly into the water phase. As soon as some sodium ions in the water have been replaced by hydrogen ions from the jelly, the further exchange in this direction is opposed by the reverse process. In this sense this cation exchange may be called a reversible second order reaction. Since the experimental evidence indicates that the exchange velocity constants are not very sensitive to temperature changes, the velocities are probably dependent, to a large extent, upon the rates of diffusion of the hydrogen ions and sodium ions from the film into the two phases.[3] The reaction rate concept may be applied to processes in which diffusion is one of the rate determining factors.[19]

For ionic reactions in aqueous solutions the dependence of k upon the ionic strength is reasonably well accounted for by the relation $\ln k = \ln k_0^s + 1.02 z_A z_B \sqrt{\mu}$, where μ is the ionic strength, k_0^s the rate constant for an infinitely dilute solution and z_A and z_B the charges of the ions involved in the reaction.[12] In the present heterogeneous ion-exchange case in which k and k' increased with decreasing ionic strength, this simple relation did not, and should not be expected to, hold. It is not intended to discuss the observed variation in detail, but it seems probable that the higher values of the k and k' at lower ionic strengths are closer to the limiting rate constants for infinitely dilute solutions, particularly since k/k' is more nearly equal to $K_{H/Na}$ for the values of k and k' obtained in determinations with the more dilute solutions (see Table VII).

The cation exchange represented by equation (I) assumes also that the electrolyte in the water phase is completely dissociated and that the ionic strength of the water phase remains constant

---

(16) See, for example, Grinnell Jones and L. D. Frizzell, *J. Chem. Phys.*, **8**, 986 (1940).

(17) See, for example, I. Langmuir, *ibid.*, **6**, 873 (1938).

(18) Measurements of ζ-potentials of a cation exchange resin are now under way in this Laboratory. The streaming potential method is being used.

(19) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," 1st ed., 1941, Chapters IX and X, McGraw-Hill Book Co., Inc., New York, N. Y.

throughout the exchange. It does not apply to the cation exchange with external solutions containing the sodium salt of a weak acid (or containing sodium hydroxide) because in this case upon entering the water phase from the exchanger phase the hydrogen ions react with the hydroxyl ions thereby shifting the cation exchange equilibrium to the right. This reaction causes the non-dissociated fraction in the exchanger phase, that is the —SO$_3$H and —OH groups, to dissociate in the exchanger so that more hydrogen ions move out and react with hydroxyl ions in the water phase; consequently the corresponding amount of the sodium ions must move into the internal phase giving a total capacity in excess of the capacity corresponding to (1); this process is opposed by the hydrolysis of the sulfonate and phenolate groups formed.

The concentration equilibrium constant $K_{H/Na}$ is related to the equilibrium constant K_e of process (I) by the relation

$$\frac{(H^+)_w}{(Na^+)_w}\frac{(Na^+)_r}{(H^+)_r}\left(\frac{\gamma_{H^+}}{\gamma_{Na^+}}\right)_w\left(\frac{\gamma_{Na^+}}{\gamma_{H^+}}\right)_r = K_{H/Na}\left(\frac{\gamma_{H^+}}{\gamma_{Na^+}}\right)_w\left(\frac{\gamma_{Na^+}}{\gamma_{H^+}}\right)_r = K_e$$

where $(\gamma_{H^+}/\gamma_{Na^+})_w$ and $(\gamma_{Na^+}/\gamma_{H^+})_r$ denote the ratio of the cationic activity coefficients in the water and exchanger phases. $(\gamma_{H^+}/\gamma_{Na^+})_w$ in hydrochloric acid–sodium chloride solutions is equal to the square root of the ratio of the mean activity coefficients of the sodium chloride and the hydrochloric acid, $\gamma_{HCl}/\gamma_{NaCl}$, in their mixture, and this ratio can be estimated up to high total ionic strengths. For example, if the experimental conditions are so chosen that the ratio of the molal concentrations of the two cations, at equilibrium, is between 0.25 and 2, then $(\gamma_{H^+}/\gamma_{Na^+})_w$ has the values of 1.01–1.02, 1.02–1.035, 1.04–1.07 and 1.06–1.09 in 0.3, 0.5, 1.0 and 1.5 N solutions, respectively. This is shown in Table VIII which is based on Harned and Owen's discussion[20] of sodium chloride, hydrochloric acid mixtures and in which Harned's notation is used. The sources of the activity coefficients of sodium chloride and hydrochloric acid in pure water are indicated in the table. All data refer to solutions at 25°.

TABLE VIII

$$\log\,(\gamma_{H^+}/\gamma_{Na^+})_w = \log\,(\gamma_1/\gamma_2)^{(a)} = \log\left(\frac{\gamma_{1(0)}}{\gamma_{2(0)}}\right)^{(b)} - (\alpha_{12}m_2 - \alpha_{21}m_1)$$

m_1	m_2	$\alpha_{12}m_2 - \alpha_{21}m_1$	γ_1/γ_2	$(\gamma_{H^+}/\gamma_{Na^+})_w$
$m = m_1 + m_2 = 0.3$; $\alpha_{12} = 0.038$; $\alpha_{21} = -0.057$; $\gamma_{1(0)}/\gamma_{2(0)} = 1.054–1.068$				
0.05	0.25	0.0124	1.024–1.038	1.012–1.019
.10	.20	.0133	1.022–1.036	1.011–1.018
.20	.10	.0152	1.018–1.031	1.009–1.016
.25	.05	.0162	1.015–1.029	1.008–1.015
$m = m_1 + m_2 = 0.5$; $\alpha_{12} = 0.034$; $\alpha_{21} = -0.059$; $\gamma_{1(0)}/\gamma_{2(0)} = 1.089–1.121$				
0.1	0.4	0.0195	1.041–1.072	1.020–1.035
.2	.3	.0220	1.035–1.066	1.017–1.032
.3	.2	.0245	1.029–1.060	1.014–1.030
.4	.1	.0270	1.023–1.054	1.012–1.026
$m = m_1 + m_2 = 1$; $\alpha_{12} = 0.032$; $\alpha_{21} = -0.058$; $\gamma_{1(0)}/\gamma_{2(0)} = 1.208–1.241$				
0.2	0.8	0.0372	1.109–1.139	1.053–1.067
.3	.7	.0398	1.102–1.133	1.050–1.064
.5	.5	.0450	1.089–1.119	1.044–1.058
.7	.3	.0502	1.076–1.106	1.037–1.052
.8	.2	.0528	1.070–1.099	1.035–1.048
$m = m_1 + m_2 = 1.5$; $\alpha_{12} = 0.0315$; $\alpha_{21} = -0.058$ $\gamma_{1(0)}/\gamma_{2(0)} = 1.351–1.376$				
0.3	1.2	0.0622	1.171–1.192	. 1.082–1.092
.5	1.0	.0605	1.176–1.197	1.084–1.094
.8	0.7	.0685	1.154–1.175	1.075–1.084
1.0	.5	.0738	1.140–1.161	1.068–1.077
1.2	.3	.0791	1.126–1.147	1.061–1.070

[a] The subscripts 1 and 2 refer to hydrochloric acid and sodium chloride, respectively. [b] $\gamma_1(_0)$ and $\gamma_2(_0)$ are the activity coefficients of hydrochloric acid and sodium chloride, respectively, in pure water solutions. The values $\gamma_1(_0)$ and $\gamma_2(_0)$ at 25° were taken from "Phys. Chem. Tabellen," 3rd Ergänzungsband (1936), p. 2144 and p. 2153, respectively, with the exception of the value of $\gamma_1(_0)$ for m = 0.3 which was taken from the "International Critical Tables," Vol. VII, p. 233 (1930). [c] The values of α_{12} and α_{21} were taken from Harned, "The Physical Chemistry of Electrolyte Solutions," 1940, p. 468, Table 14–6–2.

Therefore, the error caused by assuming that $(\gamma_{H^+}/\gamma_{Na^+})_w$ is unity over the wide range of concentrations equal to, or below, 1.5 N is smaller than the experimental error on $K_{H/Na}$ provided that one chooses for the calculation equilibrium determinations in which the ratio of $(H^+)_w/(Na^+)_w$, at equilibrium, is between 0.25 and 2. If desirable, the correction may be made using the proper value of $(\gamma_{H^+}/\gamma_{Na^+})_w$.

$K_{H/Na}$ thus becomes a measure of the product $(\gamma_{H^+}/\gamma_{Na^+})_rK_e$ and it is proportional to K_e if $(\gamma_{H^+}/\gamma_{Na^+})_r$ is a constant. The experimental evidence presented in this paper confirms this, the measured values of $K_{H/Na}$ being substantially constant over a wide concentration range of the external chloride solution, and therefore it justifies the view that this exchange may be accounted for by an equilibrium relation of the mass action type. Furthermore, the usefulness of this concept is confirmed by the exchange velocity measurements which give apparent or "concentration" velocity constants, whose ratio is of the same order as $K_{H/Na}$.

We wish to thank the late Grinnell Jones for his valuable criticisms and suggestions.

Summary

The equilibrium and the velocity of the sodium–hydrogen exchange on the carbonaceous exchangers AMBERLITE IR-100AG, IONAC C-200, DOWEX 30 and ZEOKARB in contact with chloride solutions were accounted for by relations identical in form, respectively, with a mass action

---

[20] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1943, pp. 454–472.

equation and with a second order rate equation of simultaneous opposing reactions.

The "concentration" equilibrium constants, $K_{H/Na}$, were found to be constant to better than 20% over a concentration range of the water phase varying from 0.001 to about 1 *N*, the average values of $K_{H/Na}$ being 1.25 on AMBERLITE IR-100AG, 1.20 on IONAC C-200, 1.01 on DOWEX 30, and 0.66 on ZEOKARB. The assumptions underlying the mass action equation were discussed and $K_{H/Na}$ was shown to be proportional to an equilibrium constant expressed in terms of activities, the proportionality factor being the constant ratio of the activity coefficients of the hydrogen and sodium ions in the exchanger phase.

Confirming previously published views, the exchange velocities were shown to be reasonably well represented by a second order rate equation. The velocity constants *k* and *k'* of the forward and reverse reactions were found to depend somewhat upon the ionic strength of the water phase, a less than twofold increase of *k* and *k'* being observed as the concentration decreased from 0.02 to 0.001 *N*. This variation was probably due to interionic effects since the ratios, *k/k'*, of the velocity constants, determined independently using solutions of approximately the same ionic strengths, were of the same order as the equilibrium constants, $K_{H/Na}$.

CAMBRIDGE, MASSACHUSETTS RECEIVED[20] MAY 13, 1948

---

[20] Original manuscript received September 18, 1946.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF COLORADO]

Unsaturated Amino Acids. II. Allylglycine, β-Methallylglycine and Crotylglycine[1,2]

BY HARLAN L. GOERING,[3] STANLEY J. CRISTOL AND KARL DITTMER

Existing knowledge of the relationship between chemical structure and biological antagonism indicates that an interchange of a vinylene radical and a sulfur atom in biologically important compounds may form metabolite antagonists.[4] From this it seemed possible that a metabolite–antagonist relationship may exist between the two simple sulfur-containing, naturally occurring amino acids, cysteine and methionine, and their vinylene analogs. Allylglycine (2-amino-4-pentenoic acid, IVa) is so related to cysteine; it and two of its methyl homologs are the subject of this paper. These homologs, β-methallylglycine (2-amino-4-methyl-4-pentenoic acid, IVb) and crotylglycine (2-amino-4-hexenoic acid, VIII), were studied because of the interesting biological properties of allylglycine. These amino acids have also been found to be active biologically and have been studied in considerable detail.[5,6] Of these amino acids, allylglycine has been synthesized by Sörenson,[7] and it and β-methallylglycine have recently been synthesized by Albertson[8] by the alkylation of ethyl acetamidomalonate or ethyl acetamidocyanoacetate with allyl and β-methallyl chloride and subsequent hydrolysis of the alkylation products to the amino acids. We have used Albertson's method for these compounds and a similar method for crotylglycine.

The unsaturated alkylated intermediates give poor yields of amino acids when subjected to acid hydrolysis. In agreement with Fillman and Albertson,[9] we have found that these low yields are due to partial or complete lactonization across the γ,δ-double bond[10] with the formation of α-amino-γ-lactones. Our results are summarized in the flow sheet.

In contrast to Albertson's report, we have found that the hydrolysis of the allyl intermediate Ia with concentrated hydrochloric acid results in partial lactonization to IIIa,[11] as well as partial formation of allylglycine hydrochloride IIa. The difference between his results and ours may be explained by the fact that only in concentrated hydrochloric acid will lactonization of allylglycine occur rapidly. We have found that treatment of allylglycine with concentrated hydrochloric acid at reflux results in the lactonization of about 30% of the amino acid in six hours, whereas refluxing with 6 *N* acid for twenty hours results in lactonization of only 11%. Treatment of lactone hydrochloride IIIa with concentrated hydrochloric acid does not yield any of the unsaturated amino acid hydrochloride IIa, indicating that an equilibrium between the unsaturated amino acid and the lactone was not obtained in our hydrolysis.

Treatment of allylglycine hydrochloride IIa

---

[1] This work was supported in part by the Office of Naval Research.

[2] This paper was presented before the Division of Organic Chemistry at the Chicago meeting of the American Chemical Society, April 19-23, 1948.

[3] American Cyanamid Company Fellow.

[4] Complete references to this literature have been given in another paper.[5]

[5] Dittmer, Goering, Goodman and Cristol, THIS JOURNAL, **70**, 2499 (1948).

[6] Our synthesis of the third methyl homolog, α-methallylglycine (2-amino-3-methyl-4-pentenoic acid), led to a mixture of diastereoisomers, which has not yet been separated. The analog of methionine has also been prepared and will be reported in a separate communication.

[7] Sörenson, *Ber.*, **41**, 3389 (1908).

[8] (a) Albertson and Archer, THIS JOURNAL, **67**, 308 (1945); (b) Albertson, *ibid.*, **68**, 450 (1946).

[9] Fillman and Albertson, *ibid.*, **70**, 171 (1948).

[10] Linstead and Ryden, *J. Chem. Soc.*, 580 (1933).

[11] Fischer and Leuchs, *Ber.*, **35**, 3787 (1902).