ENTHALPIES AND ENTROPIES OF ION–EXCHANGE REACTIONS

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Summary

By use of exchange isotherms determined at different temperatures, the chemical potentials and partial molar heats and entropies of the sodium-hydrogen ion-exchange reaction on a sulphonated polystyrene exchanger are evaluated. These show that both species are almost completely ionized in the exchanger, and very similar to their states in aqueous solution. In the high concentrations obtainable in the exchanger, however, there is some cation-cation interaction, which is practically linear with composition. A similar treatment of the barium-hydrogen system indicates that there is some interaction between the barium ion and the resinate structure.

I. INTRODUCTION

It has previously been shown (Duncan 1952; Glueckauf 1952) that a large number of experimental facts can be unified if one regards an ion exchanger of the sulphonated polystyrene type unreservedly as an aqueous electrolyte (e.g. sodium " resinate ") dissolved in the swelling water which the exchanger contains. Osmotic and activity coefficients can then be unambiguously evaluated from experiments with single-ion systems and used to predict distribution coefficients. In spite of this success, there still remains a number of phenomena which cannot be adequately explained. Some of them are discussed in the present paper, in which some earlier experimental data are reassessed.

II. DEVIATION FROM THEORY OF SIMPLE ION-EXCHANGE SYSTEMS

Treatment of an ion exchanger as if it were an aqueous solution of the exchanging ions leads to agreement of the calculated distribution constants with experiment only for exchangers of low cross-linking (Glueckauf 1952). At higher cross-linking the experimental mass-product is found to pass through a maximum and even to decrease, whereas the theoretical values always increase with increasing degree of saturation by the more strongly adsorbed ion. This may be seen by inspection of Figure 1, in which the theoretical values have been calculated as described earlier (Glueckauf 1952), assuming osmotic coefficients for the pure hydrogen and sodium resinates at the appropriate molality and the corresponding value of the swelling pressure. The experimental data are from the work of Reichenberg, Pepper, and McCauley (1949). The difference between the theoretical and experimental curves is a measure of the excess Gibbs free energy of the ions in the exchanger. A plot of this term for different degrees of cross-linking is shown in Figure 2. The theoretical and practical results are

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in as close agreement as can be expected at the hydrogen-saturated end of the
isotherm especially with extremely highly cross-linked exchangers. (Such
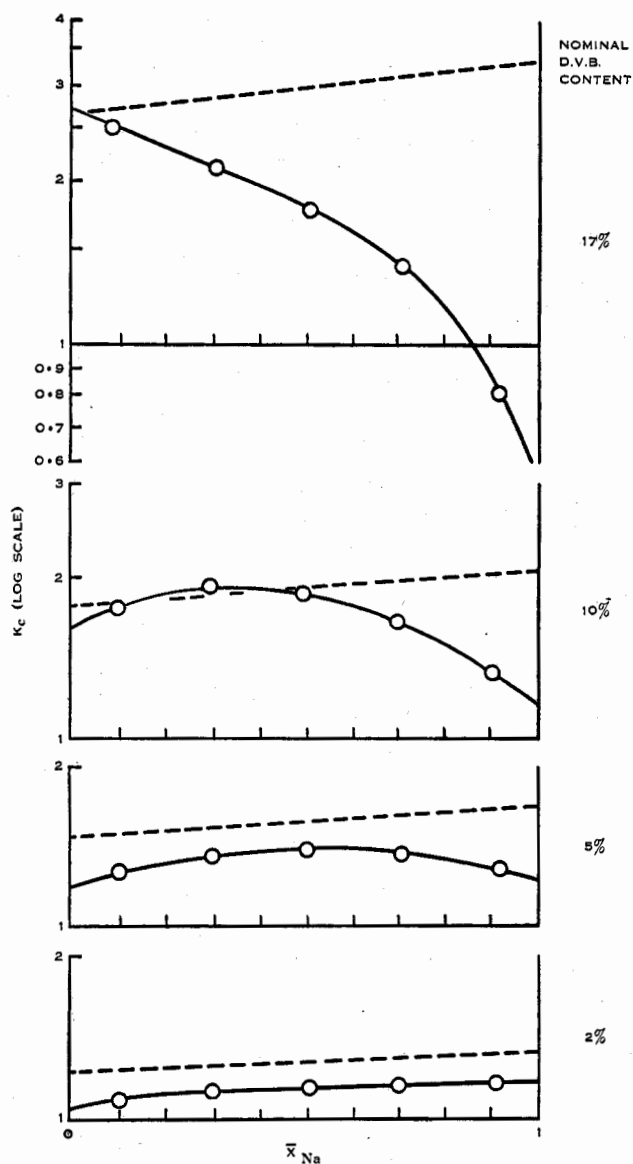deviations as there are could be accommodated by errors in the swollen resin

Fig. 1.—Predicted and experimental mass-product plots for
sodium-hydrogen systems.
          ——— Experimental values (Reichenberg, Pepper, and
                McCauley 1951).
          ···· Theoretically predicted values.
The percentage nominal D.V.B. content of the exchanger is
                        indicated.

volume and concentration, and more refined work would be necessary to ascertain whether they are real.) Nevertheless, the closeness of the experimental and theoretical curves means that the sodium " resinate " activity coefficient is almost the same in trace concentrations ($\overline{X}_{Na} = 0$) as in a sodium-saturated exchanger at constant ionic strength even in concentrations of 10–15 molal. It will be seen later that this agreement is fortuitous, and must be ascribed to the cancellation of two trends tending to alter the activity coefficient of the sodium ion in opposite directions, probably the following. Interaction which occurs between the sodium ion and the hydrogen ion (either directly or indirectly) will tend to depress the activity of the former (see below). But, as the concentration of sodium ions is decreased, the activity coefficient would normally be expected to rise (as it does with ordinary electrolytes of analogous type in
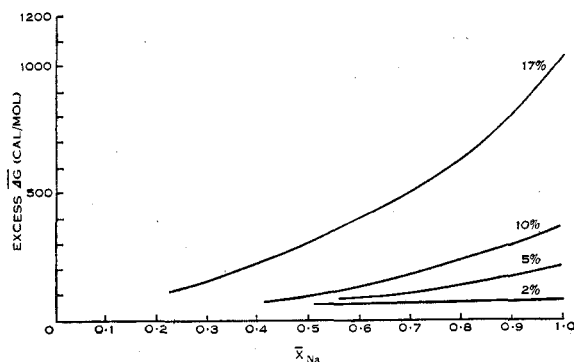

Fig. 2.—Excess Gibbs function for sodium-hydrogen exchange. (The nominal percentage D.V.B. content of the exchanger is indicated.)

aqueous solution when replaced at constant ionic strength with electrolytes of high activity coefficient). Specific interaction between the sodium and hydrogen ions must thus be sufficiently strong to cancel out the expected increase in free energy of the sodium ion at the hydrogen-saturated end of the isotherm.

Consider, now, the sodium-saturated end of the isotherm of Figure 1. The fact that the observed and theoretically-calculated values of the distribution coefficient may differ by as much as 80 per cent. implies that some assumption in the theoretical treatment is in error. One possible explanation is that, as $\overline{X}_{Na}$ increases, the sodium ion becomes partly ion-paired, or covalently-bound with the resinate structure. This is a very likely occurrence for silver and barium ions (see later), but is intrinsically unlikely with either sodium or hydrogen ions. Further, for this to be the explanation, the calculated value of the mass product would have to be less than the experimentally obtained value, whereas in fact it is greater. Also, consider how $\overline{\gamma}_{HX}$ and $\overline{\gamma}_{NaX}$ would vary in the equation

$$K_c = \frac{[\overline{Na}^+]}{[\overline{H}^+]} \times \frac{\{H\}}{\{Na\}} = \left[\frac{\overline{\gamma}_{HX}}{\overline{\gamma}_{NaX}}\right]_{I = [\overline{Na}^+] + [\overline{H}^+]}, \quad \ldots\ldots\ldots \quad (1)$$

where X is the common anion and I is the ionic strength. If there were no change in the water content of the exchanger, then by analogy with aqueous

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electrolytes both $\bar{\gamma}_{HX}$ and $\bar{\gamma}_{NaX}$ would be expected to decrease with increasing sodium ion fraction $\bar{X}_{Na}$. It follows, therefore, that $\bar{\gamma}_{HX}$ decreases more quickly with $\bar{X}_{Na}$ than does $\bar{\gamma}_{NaX}$. In other words, either sodium tends to become more ionic (as the exchanger becomes sodium-saturated), or the hydrogen becomes less ionic than would be expected from aqueous solutions of comparable concentrations. This conclusion is not affected by variations in the water content of the exchanger, although its validity is a little more difficult to verify.

These conclusions show that some further development of theory is necessary. By evaluating the partial thermodynamic functions of the ion-exchange system, supplementary information about the state of the ions in the exchanger can be obtained without any specific assumptions about the osmotic and activity coefficients of the exchanger itself.

III. EVALUATION OF PARTIAL THERMODYNAMIC QUANTITIES

In deriving thermodynamic functions from experimental data for an ion-exchange equilibrium, it has been customary to evaluate a Gibbs free energy,

$$\overline{\Delta G}_c = RT \ln K_c, \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

and the corresponding enthalpies and entropies. Some arbitrary assumption for the activities of the ions in the exchanger phase must be made to do this, although in the case of exchange between ions of the same valency type the value of $\overline{\Delta G}_c$ is the same for any assumption which is reasonable. Nevertheless, the quantities obtained are not independent of the nature of the resin phase and, further, they refer to the overall exchange reaction.

But, suppose we have an ion exchanger in equilibrium with a solution of two uni-univalent electrolytes MX and NX with a common anion. Then the work required to transfer 1 mole of the electrolyte MX from a solution at infinite dilution into the exchanger is

$$\overline{\Delta G} = RT \ln \{MX\}, \quad \ldots\ldots\ldots\ldots\ldots (3)$$

where $\{MX\}$ is the activity of MX in the aqueous mixture external to the ion exchanger. Knowing the value of $\overline{\Delta G}$ at two temperatures, we can then calculate the partial molal entropy and heat content terms, namely,

$$[\overline{\Delta S}]_{\overline{MX}} = -\left[\frac{\partial(\overline{\Delta G})}{\partial T}\right]_{\overline{MX}} = -R \ln \{MX\} - RT\left[\frac{\partial \ln \{MX\}}{\partial T}\right]_{\overline{MX}}, \quad \ldots (4)$$

and

$$[\overline{\Delta H}]_{\overline{MX}} = [T\overline{\Delta S}]_{\overline{MX}} + [\overline{\Delta G}]_{\overline{MX}}. \quad \ldots\ldots\ldots\ldots\ldots (5)$$

Note that the differentiations are made at constant $\overline{MX}$. This is analogous to the usual procedure in gaseous sorption, where the differential heats and entropies are determined by the appropriate differentiation, at constant surface coverage, of

$$\overline{\Delta G} = RT \ln p, \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

where p is the pressure of gas. The concentration of anion in the exchanger is normally very small when the solutions are dilute, and therefore for practicable

purposes we may assume the above differentiations to be performed at constant M, that is, at a given degree of saturation of the exchanger with the ion M. The evaluated quantities then give direct information about the thermodynamic properties of the resin phase without any restricting assumptions. Here, we do not make any postulates about the degree of ionization of the " resinate ", the degree of cation-cation or cation-anion interaction. But it will be seen later that information of this type can be adduced from the magnitude of the thermodynamic quantities.

IV. Evaluation of Partial Thermodynamic Quantities for the Sodium-Hydrogen System

To evaluate the free energy term

$$\overline{\Delta G} = 2RT \ln [\text{NaCl}] (\gamma^{\pm})_{\text{NaCl}}, \quad \ldots\ldots\ldots\ldots (7)$$

and the corresponding heats and entropies for the sodium-hydrogen exchange system in chloride solutions it is necessary to know the mean molal ionic activity coefficients $\gamma^{\pm}_{\text{NaCl}}$, $\gamma = _{\text{HCl}}$ in the external mixed solution at the two temperatures at which the exchange isotherm was determined. These are not available in the literature. One therefore assumes (i) that the activity coefficients are independent of temperature and (ii) that $\gamma^{\pm}_{\text{NaCl}}$ and $\gamma^{\pm}_{\text{HCl}}$ in binary mixtures of the two electrolytes may be evaluated by application of the Harned rule (Harned and Owen 1950). Both these assumptions are unobjectionable over a restricted temperature and concentration range. Hence, $\overline{\Delta G}$, $\overline{\Delta H}$, and $T\overline{\Delta S}$ were evaluated for both the sodium chloride and hydrochloric acid using experimental results reported earlier (Duncan and Lister 1949a). The latter two functions plotted against $\overline{X}_{\text{Na}}$, the proportion of sodium ions in the exchanger, are shown in Figures 3 and 4. Table 1 gives the experimental values from which the thermodynamic functions were calculated.

(a) The Partial Molal Enthalpies (Fig. 3)

First consider the sodium ion. It will be noticed that $\overline{\Delta H}_{\text{Na}}$ is negative and becomes less negative as the proportion of sodium in the exchanger increases. In other words, the sodium ions are more coordinated (either with water molecules or with anions) when they are present in trace amounts, and less when in macro-amounts. On the other hand, the reverse seems to be the case for the hydrogen ion, for which $\overline{\Delta H}_{\text{H}}$ becomes less positive (more negative) as the amount of hydrogen in the exchanger increases, that is, hydrogen ions are more ion-paired in low hydrogen concentrations. This is in accordance with Section II. The energies involved are small and the variation from one end of the isotherm to the other is clearly not great enough to modify the conclusion in Section I that the ionic species are effectively completely ionized over the whole range. In the case of the hydrogen ion, the trend seems a little surprising, as one would hardly expect $\overline{\Delta H}_{\text{H}}$ to decrease in this way merely by interaction with sodium ions. But interaction between the hydrated hydrogen ion and the resinate structure

TABLE 1

EVALUATION OF THERMODYNAMIC FUNCTIONS FROM EXPERIMENTAL DATA FOR Na/H EXCHANGE

The absolute accuracy is indicated by the number of significant figures, except for $\overline{\Delta H}_H$, for which the figures indicate only relative values and the absolute accuracy is only ± 2 per cent.

$\bar{X}_{Na}$	$(X_{Na})_{20}$	$(X_{Na})_{87}$	$\{NaCl\}_{20}$	$\overline{\Delta G}_{Na} = 2RT$ $\times \ln[\{NaCl\}(\gamma^{\pm}\}_{NaCl}]$	$\overline{\Delta H}_{Na}$	$(T\overline{\Delta S})_{Na}$	$\{HCl\}_{20}$	$\overline{\Delta G}_H = 2RT$ $\times \ln[\{HCl\}(\gamma^{\pm}\}_{HCl}]$	$\overline{\Delta H}_H$	$(T\overline{\Delta S})_H$
0·05	0·034	0·037	0·00446	-6380	-1270	5110	0·151	-2220	292	2510
0·10	0·058	0·074	0·00858	-5640	-1520	4120	0·143	-2300	234	2530
0·20	0·129	0·154	0·0191	-4680	-1110	3570	0·135	-2360	175	2540
0·30	0·215	0·246	0·0321	-4060	-848	3210	0·129	-2420	248	2660
0·40	0·301	0·342	0·0450	-3680	-804	2670	0·107	-2610	380	3090
0·60	0·504	0·552	0·0810	-2740	-572	2170	0·0705	-3140	596	3740
0·80	0·734	0·772	0·111	-2600	-322	2280	0·0404	-3780	920	4700

would be most likely to occur when the ionic strength is relatively high, and the water available for hydration is relatively low (i.e. at the sodium-saturated end of the isotherm). This would lead to a $\overline{\Delta H}_{\mathrm{H}}$ variation in the sense observed.
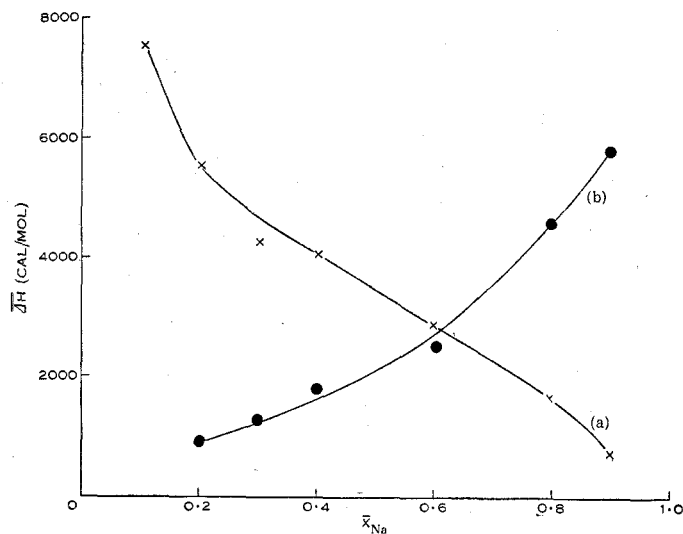

Fig. 3.—Partial molal heats for sodium chloride and hydrochloric acid in the sodium-hydrogen exchange reaction on " Dowex 50 ".

(a) Sodium (negative). (b) Hydrogen (positive).

Such an effect would also predominate in exchangers of high concentration (cross-linking) which would account for the more steeply falling values of K_c with increase of $\overline{X}_{\mathrm{Na}}$ (Reichenberg, Pepper, and McCauley 1951).
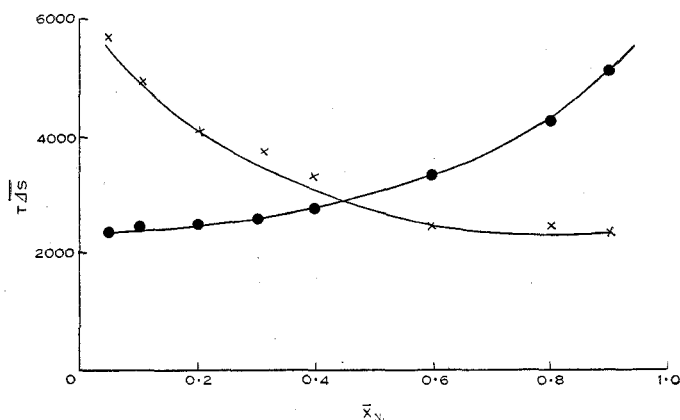

Fig. 4.—Partial molal entropies of sodium chloride and hydrochloric acid in the sodium-hydrogen exchange reaction on " Dowex 50 ".

$\times$ Sodium. ● Hydrogen.

(b) The Partial Molal Entropies (Fig. 4)

If there were no special interaction between the different ions, that is, if the partial molal heats were independent of the proportions of sodium and hydrogen ions present, the total configurational entropy would be given by

$$\bar{S}^c = R \ln \left[\frac{(N_H + N_{Na})!}{N_H! N_{Na}!} \right], \quad \ldots\ldots\ldots\ldots\ldots \quad (8)$$
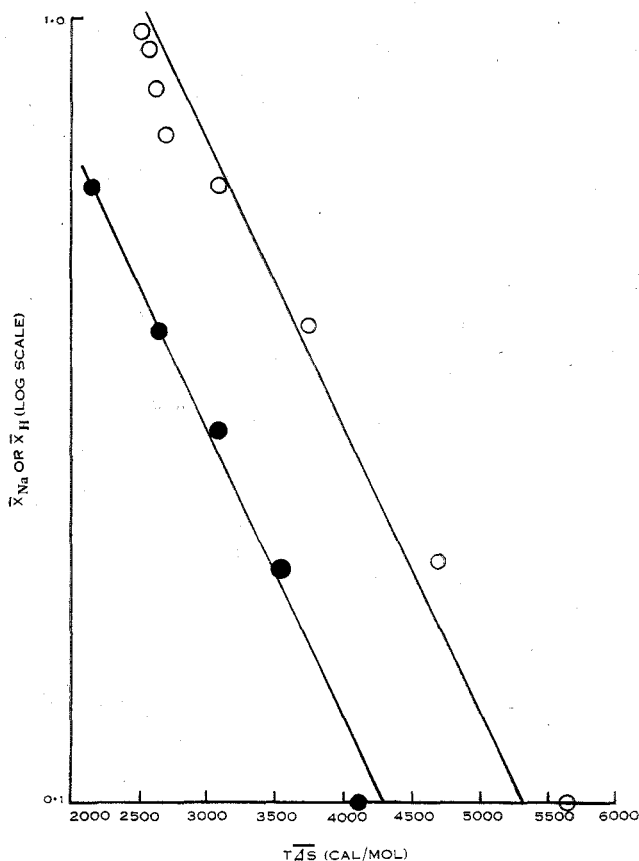
Fig. 5.—Variation of partial molal entropies of sodium-hydrogen exchange reaction with resin composition.

○ Sodium.   ● Hydrogen.   The lines are drawn with the theoretical slope.

where N_H and N_{Na} are the numbers of hydrogen and sodium ions respectively present in the mixture. Applying Stirling's approximation to this expression and differentiating, we obtain the equations

$$\overline{\Delta S^c_H} = -R \ln \bar{X}_H, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

$$\overline{\Delta S^c_{Na}} = -R \ln \bar{X}_{Na}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

for the configurational contributions to the partial molal entropies. These would be the only variable parts of the entropies, so that we might expect the

curves of $\overline{\Delta S}_{\mathrm{H}}$ against $\ln \overline{X}_{\mathrm{H}}$ and of $\overline{\Delta S}_{\mathrm{Na}}$ against $\ln \overline{X}_{\mathrm{Na}}$ to be linear. This is in fact so, as Figure 5 shows. The slopes of the curves there are actually $-2RT$, since the quantities calculated include contributions from the chloride ions.

We have, however, seen that there certainly is some specific interaction between the ions, that is, that the interaction energy between two hydrogen ions in the resin is not the same as that between two sodium ions, or between a sodium and a hydrogen ion. One effect of this would be that in a mixture of ions there would be a preferential grouping of ions in order to obtain the configuration of lowest energy. Equation (8), which is based on the assumption of a random distribution of ions, would then not hold. This is not a serious objection, however, since in ordinary liquid mixtures the correction necessary is usually small compared with others that must be made. The most important additional correction expected is that due to the changing influence of the surroundings on the vibrational properties of each ion. In liquid mixtures this is important, because the molecules are closely packed, but in ionic solutions and ion-exchange resins it will probably not be so, since the ions will be considerably further apart and the non-Coulomb interactions will be small. Thus it is not surprising to find that the ideal configurational entropy describes all the variation in the partial molal entropies. It is therefore reasonable to conclude that the entropy contributions to the Gibbs free energy do not account for the deviations from ideal behaviour already mentioned. Any deviations observed must be ascribed to the variation of the partial molal heats, which can only be the result of some specific interaction between the ions.

(c) The Heats and Entropies of Exchange

Consider, now, the relation between the partial thermodynamic quantities defined above, and the heats and entropies of exchange evaluated from a measure of the free energy $\overline{\Delta G}_c$, defined in terms of the mass-product as in equation (2). From equations (9) and (10), the overall entropy of exchanging 1 mole of sodium chloride for 1 mole of hydrochloric acid at infinite dilution is

$$\overline{\Delta S}_T = -R \ln \left[\frac{\overline{X}_{\mathrm{Na}}}{1 - \overline{X}_{\mathrm{Na}}} \right] = \overline{\Delta S}_{\mathrm{Na}} - \overline{\Delta S}_{\mathrm{H}}. \qquad \ldots \ldots \ldots (11)$$

Now in equation (11) one merely assumes that the two species are in a similar state without specifying whether they are ionic or covalently bound to the resin. If we evaluate the apparent heats and entropies of the reaction from equation (2), we have

$$[\overline{\Delta S}_c]_{\overline{X}_{\mathrm{Na}}} = -\left[\frac{\partial(\overline{\Delta G}_c)}{\partial T} \right]_{\overline{X}_{\mathrm{Na}}} = -\frac{\partial}{\partial T} \left[RT \ln \left\{ \frac{\overline{X}_{\mathrm{Na}}}{1 - \overline{X}_{\mathrm{Na}}} \times \frac{\{\mathrm{HCl}\}}{\{\mathrm{NaCl}\}} \right\} \right]_{\overline{X}_{\mathrm{Na}}}$$

$$= -R \ln \left\{ \frac{\overline{X}_{\mathrm{Na}}}{1 - \overline{X}_{\mathrm{Na}}} \right\} - \left[\frac{\partial(RT \ln \{\mathrm{HCl}\})}{\partial T} \right]_{\overline{X}_{\mathrm{Na}}} + \left[\frac{\partial(RT \ln \{\mathrm{NaCl}\})}{\partial T} \right]_{\overline{X}_{\mathrm{Na}}}$$

$$= \overline{\Delta S}_T + \overline{\Delta S}_{\mathrm{H}} - \overline{\Delta S}_{\mathrm{Na}}. \qquad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (12)$$

Hence it follows that for a simple ion-exchange reaction for which the interaction forces between the different types of cation and the fixed ionic structure are substantially the same the configurational contribution to the apparent free energy of exchange should be zero. In the case of the sodium-hydrogen exchange, it is remarkably small, not more than 2 cal/mol/°C (see Fig. 6). We must therefore conclude that the changes in the interaction between the ions are not sufficiently great to affect the partial entropy of the exchange reaction, which is much less sensitive to such changes than the partial heat. Further, it follows that to a first approximation such interaction as there is must be due to Coulomb forces only, and must be independent of the ionic type. This is clearly only approximately true since the partial enthalpy changes show that there is a small interaction dependent on composition, but it is sufficiently
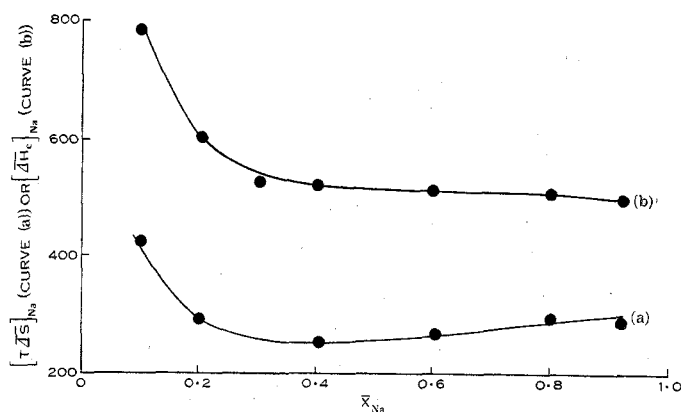

Fig. 6.—Curve (a) $T[\triangle \bar{S_c}]_{Na}$ and curve (b) $[\triangle \bar{H_c}]_{Na}$ plotted as functions of $\bar{X}_{Na}$.

small for the entropy changes to be practically ideal. We might expect therefore that the partial heats $\overline{\Delta H}_{Na}$ and $\overline{\Delta H}_H$ (which would be constant if there were no ionic interaction) would be to a first approximation linear with $\bar{X}_{Na}$. It will be seen from Figure 3 that this is so, except when $\bar{X}_{Na}$ is low (see Table 1).

Now, in gaseous sorption, Everett (1950) has shown that, if the excess entropy of a system forming a localized monolayer in the adsorber phase is plotted against the enthalpy, a straight line is obtained for a large number of adsorbates on gas charcoal, and this he suggests might very well be a general phenomenon, similar to the Barclay-Butler relation in liquids. In gaseous sorption the excess entropy is obtained by subtracting the term $-R \ln [\theta/(1-\theta)]$, where θ is the coverage, from the total entropy; in ion exchange the corresponding quantity is $-R \ln \bar{X}_{Na}/(1-\bar{X}_{Na})$. In other words, the entropy plotted in Figure 7 is in fact the excess entropy. A priori, one would expect a straight line to be obtained only for ion-exchange pairs in which the interaction forces are similar in type and different only in magnitude. Although with different exchangers, the three sets of results plotted in Figure 7 are of this type and give

quite a reasonable straight line.   The barium-hydrogen system (in which the interactions must be of quite a different type) falls well off the line (see Section V).
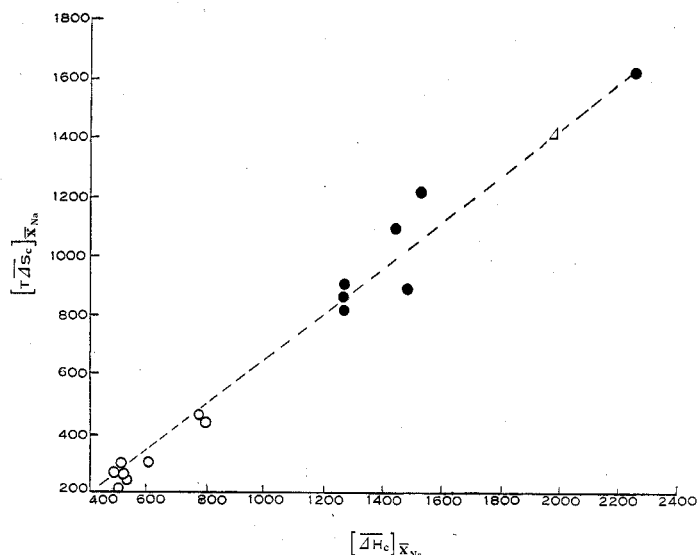

Fig. 7.—$[\overline{\triangle S_c}]_{\overline{X}_{Na}}$ plotted as a function of $[\triangle H_c]_{\overline{X}_{Na}}$.

   ○ Sodium-hydrogen exchange (Duncan and Lister 1949a).

   ● Potassium-hydrogen exchange (Cosgrove and Strickland 1950).

   △ Potassium-hydrogen exchange (Kressman and Kitchener 1949).

V. EVALUATION OF PARTIAL THERMODYNAMIC QUANTITIES FOR THE BARIUM-HYDROGEN SYSTEM

(a) Calculated and Experimental Mass Products

In replacing the hydrogen of an exchanger by barium ions there is consider-able contraction of the resin.   Assuming that the effective charge of the resin structure is unity (Glueckauf 1952), the ionic strength increases from $6 \cdot 13$ to $13 \cdot 18$.   Over this range $\overline{\gamma}_H^0$ increases from $1 \cdot 25$ to 390 (Duncan 1952) and $\overline{\gamma}_{Ba}^0$ from $0 \cdot 009$ to $0 \cdot 23$ (calculated from osmotic data (Glueckauf and Kitt, personal communication)), the absolute value of $\overline{\gamma}_{Ba}^0$ being fixed at $0 \cdot 227$ for $I = 13 \cdot 7$ by application of the Gibbs-Duhem equation to the exchange isotherm (Duncan and Lister 1949b ; Duncan, forthcoming publication).   We should therefore expect the mass-product to increase steeply with increasing $\overline{X}_{Ba}$. In fact, however, it was found to decrease somewhat as $\overline{X}_{Ba}$ tended to unity after passing through a maximum (Duncan and Lister 1949b).   Thus, theory is quite inadequate in explaining the shape of the isotherm in this case.   This is because of ionic interaction, the nature of which can be ascertained by con-sidering the partial thermodynamic quantities calculated from equilibrium data (Table 2).

(b) The Partial Molal Enthalpies (Fig. 8)

It will be noticed that $\overline{\overline{\triangle H}}_{Ba}$ is highly negative, but unlike $\overline{\overline{\triangle H}}_{Na}$ (Fig. 2) it becomes more negative as the exchanger becomes denuded of hydrogen ions.

TABLE 2

EVALUATION OF THERMODYNAMIC FUNCTIONS FROM EXPERIMENTAL DATA FOR Ba/H EXCHANGE

The absolute accuracy is indicated by the number of significant figures, except for $\Delta \bar{G}_H$ and $\Delta \bar{H}_H$, for which the figures indicate only relative values and the absolute accuracy is only ± 1 and ± 10 per cent. respectively

$\bar{X}_{Ba}$	$(X_{Ba})_{20}$	$(X_{Ba})_{37}$	$\{BaCl_2\}$	$\Delta \bar{G}_{Ba} = 3RT$ $\times \ln[[BaCl_2]/(\gamma^{\pm})BaCl_2]$	$\Delta \bar{H}_{Ba}$	$(T\Delta S)_{Ba}$	$\{HCl\}$	$\Delta \bar{G}_H = 2RT$ $\times \ln[[HCl]/(\gamma^{\pm})HCl]$	$\Delta \bar{H}_H$	$(T\Delta S)_H$
0·1	0·000314	0·000408	0·0000157	$-20{,}000$	2530	17500	0·154	-2260	1·2	2260
0·2	0·000626	0·000860	0·0000313	$-18{,}730$	3030	15700	0·154	-2260	1·4	2260
0·3	0·00106	0·00150	0·000053	$-17{,}800$	3310	14500	0·154	-2260	1·8	2260
0·4	0·00192	0·00273	0·000096	$-16{,}750$	3370	13400	0·153	-2262	3·3	2265
0·5	0·00363	0·00528	0·000181	$-15{,}680$	3550	12100	0·153	-2262	10·4	2270
0·6	0·00686	0·0118	0·000343	$-14{,}420$	5160	9260	0·153	-2262	32·3	2295
0·7	0·0123	0·0300	0·000615	$-13{,}330$	8510	4820	0·151	-2228	111·6	2340
0·8	0·0400	0·0830	0·00200	$-11{,}220$	6960	4260	0·147	-2310	344·4	2655

This implies that the barium ions become more ion-paired, as might be expected when it is remembered that on account of (i) the decrease in volume of the exchanger and (ii) the replacement of a singly charged by a doubly charged cation, the ionic strength practically doubles.

The behaviour of $\overline{\Delta H}_H$ in the sodium-hydrogen and the barium-hydrogen system is similar, but the absolute values are considerably lower in the latter case. This means that the hydrogen ion is in much the same ionic state as in the external solution, presumably because the barium ion requires practically no hydration water and, as will be seen in Section V(c), interacts more with the sulphonic acid groups than with the hydrogen ions.
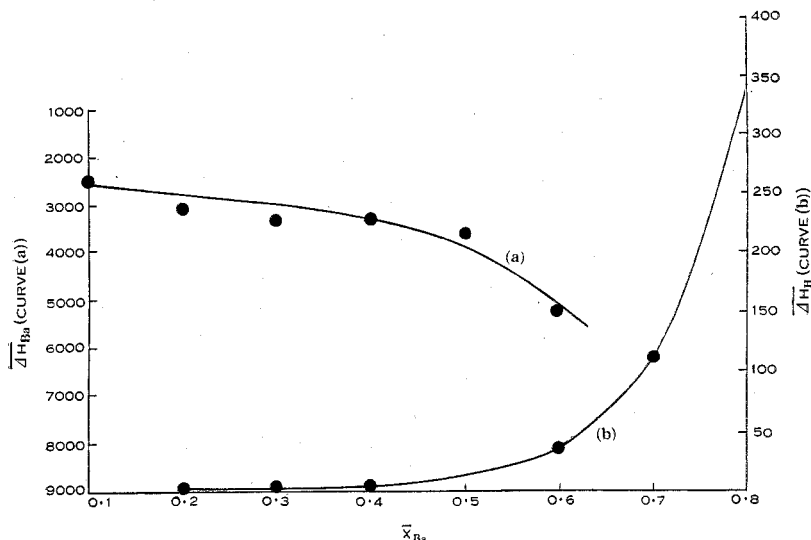

Fig. 8.—Partial molal heats of barium chloride and hydrochloric acid in the barium-hydrogen exchange reaction on " Dowex 50 ".

(a) Barium (negative). (b) Hydrogen (positive).

The value of $\overline{\Delta H}_H$ in a nearly completely hydrogen-saturated exchanger should be the same no matter what the nature of the other cation since the differences of ionic interaction becomes negligible. By extrapolating the plots of $\overline{\Delta H}_H$ for these two systems* to $\overline{X}_H = 1$ we obtain $\overline{\Delta H}_H$ practically equal to zero in both cases. This confirms the similarity of ionic state of the hydrogen ion in near-hydrogen-saturated exchangers and in the external solution. It

* The experimental results in the Na/H exchange reaction were determined with an early sample of exchanger which gave sharply decreasing values of K_c below $\overline{X}_{Na} = 0 \cdot 1$. Above $\overline{X}_{Na} = 0 \cdot 2$, the trend was normal (Duncan and Lister 1949a). Later samples did not show this defect (see Fig. 1), which feature we ascribed to inhomogeneities in the cross-linking of the resin. The values of $\overline{\Delta H}_{Na}$ below $\overline{X}_{Na} = 0 \cdot 2$ in Figure 3 are therefore omitted, as they are believed to be associated with this feature. The corresponding values of ΔH_H and ΔS_H would not of course be expected to show any deviations as the resin is nearly hydrogen saturated ; nor does ΔS_{Na} seem to be anomalous either.

also affords confirmation of our earlier conclusion (Duncan 1952) from salt
uptake and osmotic data that the hydrogen ion in an ion exchanger is practically
completely ionized.

Finally, since $\overline{\Delta H}_H$ does not vary widely over the greater part of the Ba/H
isotherm, we may conclude that any interaction in which the hydrogen takes
part must be practically constant. On the other hand, since the values of
$\overline{\Delta H}_{Ba}$ are quite high, there must be quite substantial interaction between the
barium ion and the resinate structure. This is confirmed by (i) the fact that
the barium resinate has a rather lower conductivity than would be expected
from solutions of barium salts at comparable concentrations (Heymann and
O'Donnell 1949) and (ii) the partial entropy values for the barium ion (see next
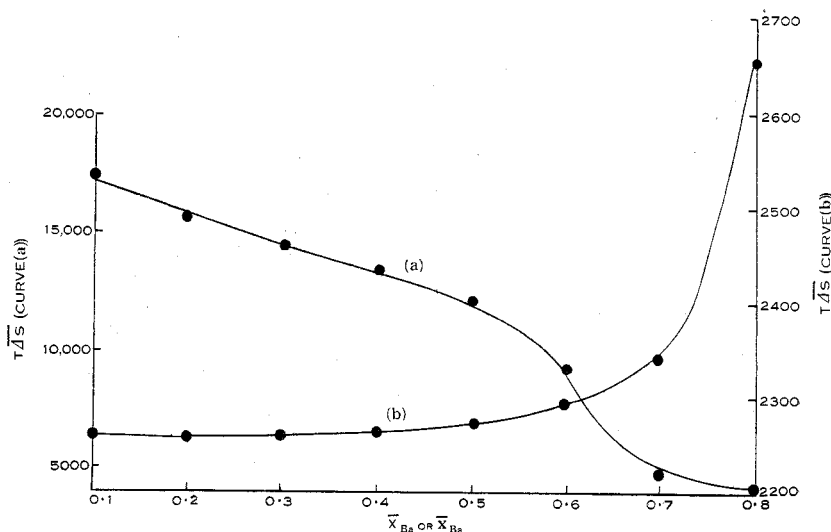section).

Fig. 9.—Partial molal entropies of barium chloride and hydrochloric acid in the
barium-hydrogen exchange reaction on " Dowex 50 ".

(a) Barium.   (b) Hydrogen.

(c) The Partial Entropies

These (shown in Fig. 9) are by no means straight lines. The theoretical
slope may be calculated by differentiation of the equation analogous to equation
(8), namely,

$$\bar{S}^c = R \ln \left\{ \frac{[\frac{1}{2}(2N_{Ba} + N_H)]!}{N_{Ba}! \, (\frac{1}{2}N_H)!} \right\}, \qquad \dots\dots\dots (13)$$

where N_{Ba} and N_H are the number of moles of the two ions. Hence it can be
shown that

$$\overline{\Delta S}_H^c = -\frac{R}{2} \ln \left(\frac{N_H}{2N_{Ba}} \right) = -\frac{R}{2} \ln \left[\frac{\bar{X}_H}{1 - \bar{X}_H} \right], \qquad \dots\dots (14)$$

and

$$\overline{\Delta S}_{\mathrm{Ba}}^{c} = -R \ln \left(\frac{2 N_{\mathrm{Ba}}}{N_{\mathrm{H}}} \right) = -R \ln \left\{ \frac{\overline{X}_{\mathrm{Ba}}}{1 - \overline{X}_{\mathrm{Ba}}} \right\}. \quad \ldots \ldots \quad (15)$$

The lines corresponding to these slopes are shown in Figure 10. They have respectively slopes of RT and $3RT$ for the hydrogen and barium resinates, the factors of 2 and 3 respectively arising because contributions from the mono-valent anions were included in the calculated free energies.

It will be seen from Figure 10 that in both cases the entropy plots only approximate to the theoretical slope when the ions are present in small amounts. This could arise at high barium-ion concentrations merely from the approximate
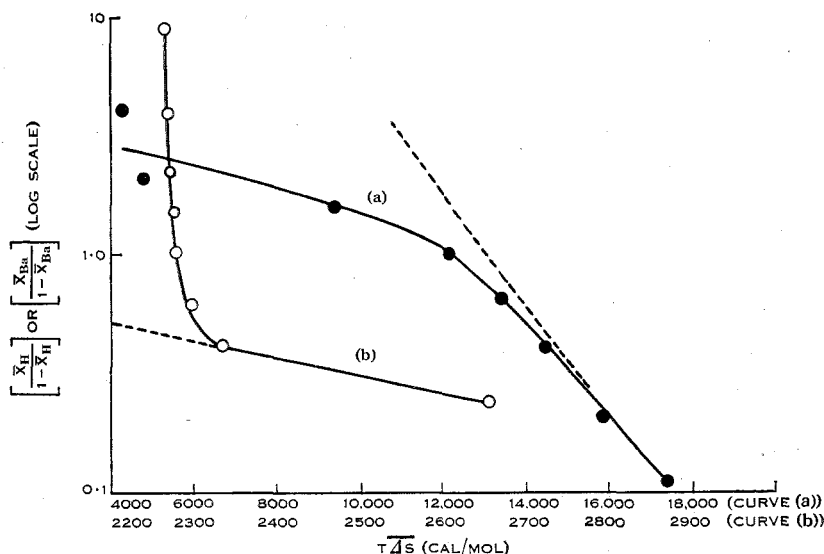

Fig. 10.—Variation of partial molal entropies of barium-hydrogen exchange reaction with resin composition.

(a) Barium. (b) Hydrogen. The lines are drawn with the theoretical slope.

nature of equation (13), which does not take into account the impossibility of a barium ion being fixed on two separated sites. But it cannot explain the hydrogen curve, which is most nearly of the theoretical slope just in the region where such an objection would obtain. Further, deviations at small values of $\overline{X}_{\mathrm{Ba}}$ are most unlikely to be due to such a cause, as it is in this region that equation (15) would be valid. On the other hand, such deviations would be expected even if equation (15) were exact, since the heat data for the barium ion show that there are considerable interaction forces. A fall in entropy with increasing $\overline{X}_{\mathrm{Ba}}$ would also be in agreement with the earlier conclusion that this interaction is predominantly anion-cation in type since the energies of the adsorption sites would be modified as the barium ions are introduced into the

exchanger. From the shape of the entropy plot for the hydrogen ion it is clear that this occurs.

If we now calculate the mean molar entropies and heats, namely,

$$T\overline{\Delta S}_M = T\bar{x}_{Ba}\overline{\Delta S}_{Ba} + T(\overline{X}_H)\overline{\Delta S}_H,$$

and

$$\overline{\Delta H}_M = \bar{x}_{Ba}\overline{\Delta H}_{Ba} + \overline{X}_H\overline{\Delta H}_H,$$

where $\bar{x}_{Ba}$ is the number of moles barium ion/equivalent of exchanger and $\overline{X}_H$ is the number of moles or equivalents of hydrogen ion/equivalent of exchanger, curves such as shown in Figure 11 are obtained. In this figure the abscissa
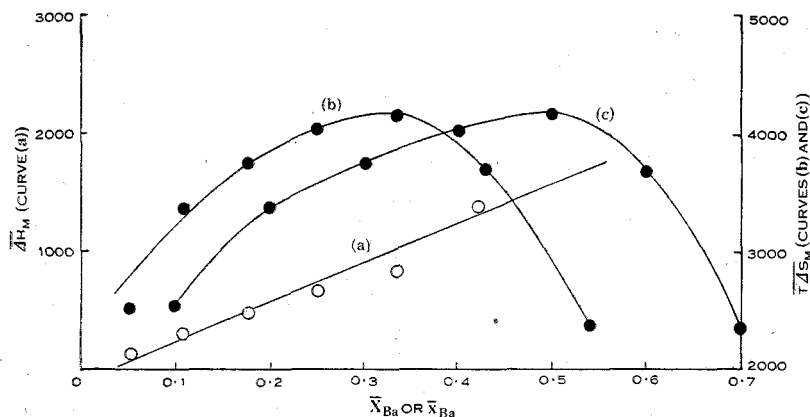

Fig. 11.—Mean molal entropy and heat for barium-hydrogen exchange.

(a) $\overline{\Delta H}_M$ as a function of $\overline{X}_{Ba}$.

(b) $T\overline{\Delta S}_M$ as a function of $\overline{X}_{Ba}$.

(c) $T\overline{\Delta S}_M$ as a function of $\bar{x}_{Ba}$.

is the molar fraction of the barium ion, $N_{Ba}/(N_{Ba}+N_H)$, where N is the number of moles of the appropriate species. It will be seen that the mean molal heat is almost linear with molar fraction, as would be expected if there were relatively little interaction between the two cations. On the other hand, the mean molal entropies are by no means symmetrical about the equimolar point, although it will be seen from Figure 11 that it is reasonably symmetrical with respect to the point where the number of equivalents of the two ions is the same. It would appear therefore that the fundamental quantity determining the statistical effects of ion exchange is the number of fixed anion groups per mole. This conclusion might have been expected, but it is worth emphasizing since some authors regard the number of ions as the significant quantity. On the other hand, it is evident that it is the number of ions which determines the enthalpy terms involved (whether these arise from anion-cation, or cation-cation inter-action) and that these are remarkably little affected by the number of fixed anion groups.

(d) Experimentally Evaluated Free Energies, Heats, and Entropies

The experimentally determined mass-product for the barium-hydrogen system

$$K_c = \frac{[\overline{Ba}]}{[\overline{H}]^2} \times \frac{\{H\}^2}{\{Ba\}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

may be written (Duncan and Lister 1949a, 1949b) in the form

$$K_c = \frac{\overline{X}_{Ba}}{(1-\overline{X}_{Ba})^2} \times \frac{w}{\overline{C}} \times \frac{\{HCl\}^2}{\{BaCl_2\}}, \qquad \ldots\ldots\ldots\ldots (17)$$

where w is the water content of the exchanger in ml/g hydrogen resin, and $\overline{C}$ is the capacity in m-equiv/g hydrogen exchanger.
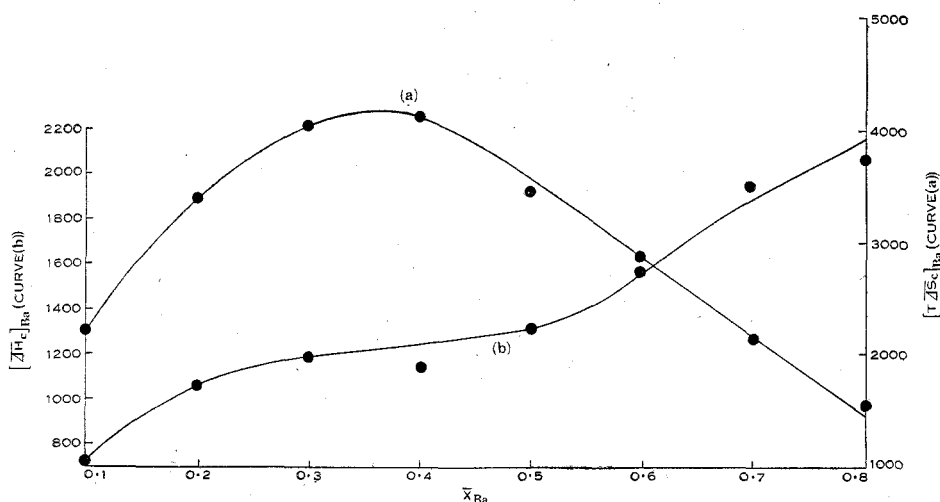

Fig. 12.—$T[\overline{\Delta S}_c]_{Ba}$ (curve (a)) and $[\overline{\Delta H}_c]_{Ba}$ (curve (b)) plotted as functions of $\overline{X}_{Ba}$.

Following Section IV it can then be shown that

$$[\overline{\Delta S}_c]_{\overline{X}_{Ba}} = -\left[\frac{\partial(\overline{\Delta G}_c)}{\partial T}\right]_{\overline{X}_{Ba}} = -\left[\frac{\partial w}{\partial T}\right]_{\overline{X}_{Ba}}. \qquad \ldots\ldots (18)$$

Thus, provided there is no change in the water content with temperature, for a given value of $\overline{X}_{Ba}$, the configurational entropy should be zero. The water content of an exchanger is undoubtedly temperature dependent. With a hydrogen-saturated sulphonated polystyrene (10 per cent. D.V.B.) in equilibrium with water the concentration was observed to fall from 6·8 at 25 °C to 5·9 at 0 °C (Glueckauf and Kitt, personal communication). But in the present case the variable water-content contributes not more than 0·03 cal/mol deg⁻¹ to the values of the entropies of exchange, which is insignificant. When the entropies of Figure 12 are compared with those of Figure 6, for uni-univalent systems it will be seen that the configurational entropy is very high for quite

moderate heat terms. Hence the Ba/H system must be fundamentally different in type from the Na/H and K/H exchange reactions, as had been concluded earlier.

VI. EFFECT OF VOLUME CHANGES ON THERMODYNAMIC QUANTITIES

Since volume changes are known to be large in some cases and the above equations are valid only when there is no volume change, it must now be shown that the above conclusions will not be significantly affected by neglect of these factors.

The partial thermodynamic quantities have been evaluated in order to assess the behaviour of the individual ions in the exchanger. We are not so much interested in the activity a_j of the species j in the external solution as in the activity $\bar{a}_j$ of that species in an unstrained exchanger of the same composition. These two quantities are related by the equation

$$\overline{\Delta G}_j = RT \ln a_j = RT \ln \bar{a}_j + Pv_j, \qquad \dots\dots\dots\dots (19)$$

where P is the " swelling pressure ", v_j is the molar volume of the species j, and $\overline{\Delta G}_j$ is the free energy excess over that of the species j in the standard state (infinite dilution in pure water). If P were constant, changes in $\overline{\Delta G}_j$ would then accurately reflect the changes in activity occurring in the exchanger. If P is not constant, then we must add a correction factor

$$\overline{\Delta G}_A = Pv_j, \qquad \dots\dots\dots\dots\dots\dots\dots (20)$$

together with the corresponding heats and entropies

$$\overline{\Delta H}_A = -v_j T \left[\frac{\partial P}{\partial T}\right]_x + Pv_j, \qquad \dots\dots\dots\dots\dots (21)$$

and

$$\overline{\Delta S}_A = -\frac{\partial(\overline{\Delta G}_A)}{\partial T} = -v_j \left[\frac{\partial P}{\partial T}\right]_x, \qquad \dots\dots\dots\dots (22)$$

where v_j is assumed to be temperature independent. In the case of the sodium-hydrogen system, the effect of the term $\overline{\Delta G}_A$ in the calculations is quite negligible. Even for the barium-hydrogen system, the error is not large. Thus Table 3 shows the error in the assessment of the partial thermodynamic functions for

TABLE 3

	Hydrogen Saturated Exchanger
P (for resinate) ..	280 atm
v_j (chloride)*	20 ml/mol
$\left[\dfrac{\partial P}{\partial T}\right]$ (for resinate) ..	1·52 atm/°C
$\overline{\Delta G}_A$	181 cal/mol
$\overline{\Delta H}_A$	169 cal/mol
$\overline{\Delta S}_A$	12 cal/mol

* Harned and Owen (1950).

the hydrogen ion, calculated from results of Glueckauf and Kitt (personal communication). The corresponding values for the barium ion would be of comparable magnitude. The shapes of the curves of Section V (Figs. 8–12) would not therefore be seriously affected.

VII. Conclusions

It will be seen that an examination of the temperature variation of the exchange reaction leads to information about the behaviour of cations in an ion exchanger quite distinct from the behaviour of the associated anions. The treatment shows that the sodium and hydrogen ions at concentrations of 6–10 molar are completely mobile and similar in ionic state to those existing in solution. The interaction between the two cations and between cations and anion is small, to a first approximation linear, and does not greatly alter the behaviour of either. On the other hand, interaction between barium ions and the resinate structure seems to be so strong that the barium cannot be regarded as a normal ion, such as might exist in dilute aqueous solutions. The hydrogen ion, however, is still completely ionized and freely mobile.

VIII. Symbols

In this paper the following symbols have been used :

$\overline{C}$, capacity of exchanger (m-equiv/g),

G, Gibbs free energy,

H, enthalpy,

K_c, mass law product allowing for the activity coefficients of the electrolytes in the aqueous solution,

I, ionic strength,

N, number of adsorption sites in an ion exchanger,

p, pressure of a gas,

P, energy change per unit volume (has the dimensions of pressure),

S, entropy,

v, molar volume,

w, weight of water taken up by an exchanger,

x, ionic molar fraction,

X, ionic equivalent fraction,

γ, mean molal ionic activity coefficient,

$\{\ \}$, thermodynamic activity,

$[\ ]$, molal concentration (mol/1000 g water).

A bar as in $\overline{H}$ or $\overline{\gamma}$ denotes that the quantity refers to the exchanger phase.

A heavy bar as in $\overline{\Delta S}$ denotes that the quantity is the partial thermodynamic function of the species in the appropriate phase.

No difference mark as in $[H]$ or γ_H denotes that the quantity refers to the external solution.

Suffix T as in $\overline{\Delta S}_T$ refers to both ions in the exchanger phase only.

Suffix 20, as in $NaCl_{20}$, refers to the temperature (20 °C).

Suffix c, as in $\overline{\Delta H}_c$, indicates that the quantity is derived from the mass-product K_c.

Suffix j, as in $\bar{a}_j$, refers to the component j.

Suffix A, as in $\overline{\Delta G}_A$, indicates that the quantity is a correction factor added to take account of resin swelling.

Superscript c, as in $\overline{\Delta S^c}$, refers to the configurational entropy calculated from statistical mechanics.

IX. ACKNOWLEDGMENTS

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