A GENERAL THERMODYNAMIC THEORY OF ION EXCHANGE PROCESSES

Sir:

The specific volume of a strong (sulfonic) acid resin measured in water with the following cations in the exchange position is: H^+, 1.283; Na^+, 1.655; K^+, 1.434; Cs^+, 1.388; Mg^{++}, 1.665; Ca^{++}, 1.585; Ba^{++}, 1.453; Ag^+, 1.283. When an alkali metal resin is equilibrated with solutions of the same alkali ion, the specific volume decreases with increasing concentration, and usually becomes less than the pure water-equilibrated volume of the next heavier member of this group.[1]

These and other data, in conjunction with a simple mechanical model and classical physicochemical methods, provide a basis upon which exchange phenomena may be interpreted. The resin is an osmotic system in which the fixed, nondiffusible (anionic) groups act as though restricted by a semipermeable membrane separating the inner pore volume (V_i) from the external solution. V_i varies with the swelling pressures and the elasticity of the resin structure. V_i and total resin volume (V) can be determined by pycnometric[1] and other methods.[2]

Dry resins swell in water chiefly because of hydration of the fixed and counter ions and the osmotic pressure due to the latter. If a salt of the counter ion is added to the external water, Donnan effects virtually exclude it from the internal volume; a counter osmotic pressure is established with consequent reduction in swelling. The dependence of swelling upon the (calculable) counter osmotic pressure provides access to the $p-V$ relation; other methods may also be applicable.[3]

Consider the exchange process

$$\mathrm{A_i^+ + B_0^+ = A_0^+ + B_i^+}$$

where neither A^+ nor B^+ forms a weakly-dissociated compound with the fixed anion. The virtual osmotic work for $A_i^+ \rightarrow A_0^+$ is $\delta n\ RT \ln a_{A_i^+}/a_{A_0^+}$, and the virtual pV work is $\delta n p \bar{V}_{A_i^+}$. $\bar{V}_{A_i^+}$ may be determined experimentally.

The expressions for $B_0^+ \rightarrow B_i^+$ are similar, and, as $\delta w = 0$

$$RT \ln \left(\frac{a_{A^+}}{a_{B^+}}\right)_i \left(\frac{a_{B^+}}{a_{A^+}}\right)_0 = p(\bar{V}_{B^+} - \bar{V}_{A^+})_i$$

where p is of course the swelling pressure. The separation factor $K_D = a_{A_i^+}a_{B_0^+}/a_{B_i^+}a_{A_0^+}$ is then unity for $\bar{V}_{B_i^+} = \bar{V}_{A_i^+}$. This is the case for K^+ and NH_4^+. K_D is not a constant because p and the $\bar{V}$'s are not constants; the latter depend strongly upon $a_{A_i^+}/a_{B_i^+}$ in a manner determined by the ionic diameters.

If the fixed group is weakly acidic (—COOH) or a weakly dissociated ion-pair is formed (—SO_3Ag), the corresponding dissociation constants must be introduced into the expression above; volume change terms of the form $(\bar{V}_{A^+} + \bar{V}_{R^-} - \bar{V}_{AR})_i$ occur and the expression becomes too complex for development within the limits of this communication. The dissociation constant becomes a function of swelling pressure. This complication appears in the alkaline earths; the swelling of Mg^{++}, Ca^{++} and Ba^{++} resins is directly proportional to the solubility of the benzene sulfonates.

These concepts form the basis of a general theory of exchange processes, applicable also to cationic resins and non-aqueous systems,[4] which permits predictions of K_D from measurable physical quantities.

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(1) H. Chaya, Thesis, Polytechnic Institute of Brooklyn, June, 1947.

(2) R. A. Gortner, "Outlines of Biochemistry," J. Wiley and Sons, Inc., New York, N. Y., 1938.

(3) E. Posnjak, *Kolloidchem. Beih.*, **3**, 417 (1912).

(4) G. Wiegner, *J. Soc. Chem. Ind.*, **50**, 55 (1931).

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ON THE DYNAMIC STATE OF ANTIBODIES

Sir:

Experiments with N^{15} labeled amino acids carried out by Heidelberger, *et al.*,[1] have led these authors to the conclusion that normal serum proteins, as well as immune globulins, incorporate dietary amino acids during immunization. However, no exchanges were stated to occur with injected antibody though the authors found an excess of N^{15} in these substances which was about two to four times as high as their experimental error, and about one-fourth to one-eighth of their value for the active antibodies.

We have repeated these experiments using C^{14} leucine in the following manner:

A rabbit was actively immunized against *p*-azophenylarsonic acid-ovalbumin until the serum had a high titer of the corresponding antibodies. Ten days after the last injection (day 1) an injection of 10 cc. of concentrated rabbit pneumococcus antiserum (Type I) was given intravenously, followed by a similar injection on day 2. On the same day, an injection of 30 cc. of a 1% leucine solution was given intraperitoneally. The leucine contained C^{14} in the carboxyl group and had an activity of about 0.06 microcurie per milligram.[2] Similar injections of leucine were given on the three following days, 1.15 g. of leucine being injected in all.

Samples of serum were taken on days 5, 9 and 16. The antibodies were precipitated with the corresponding antigens, washed with saline (3x), distilled water (1x), alcohol and ether (2x), dried and analyzed for C^{14}. The results are given in the

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(1) M. Heidelberger, H. P. Treffers, R. Schoenheimer, J. Ratner and D. Rittenberg, *J. Biol. Chem.*, **144**, 555 (1942).

(2) The C^{14} used in this investigation was supplied by the Monsanto Chemical Co. and obtained on allocation from the U.S. Atomic Energy Commission. This work was supported by a grant from the Rockefeller Foundation.