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

$$A_i^+ + B_0^+ = A_0^+ + B_i^+$$

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.

(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

(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.

table. The numbers indicate counts per 10 mg. of substance per minute, after subtraction of the back-ground rate of 10 counts. The error was less than 1 count per minute.

	R-Azo-ovalbumin	Pneumococcus I	Serum proteins
First bleeding (day 5)	11	12	59
Second bleeding (day 9)	18	8	53
Third bleeding (day 16)	26	no antibody isolated (amount too small)	39

As a control on the purity of the precipitates, two experiments were carried out in which a small amount of pneumococcus I antiserum was added to radioactive serum containing no pneumococcus antibodies. After thorough mixing and standing for one hour in the refrigerator, the corresponding polysaccharide was added to precipitate the antibodies. The precipitate was worked up in the same way as the others but contained no C^{14} (less than 0.1 count per minute per mg.).

The order of magnitude of the radioactivity found in the passive antiserum was essentially the same as that found by Heidelberger and Schoenheimer, *viz.*, about one-fifth to one-sixth of the serum proteins. Our results are in line with theirs, though we think it very probable that an exchange takes place with the injected or passive transfer antibody.

A detailed paper on this subject will be published later.

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NEW BOOKS

Elsevier's Encyclopaedia of Organic Chemistry. Volume 13, **Tricyclic Compounds.** Series III, **Carboisocyclic Condensed Compounds.** E. JOSEPHY AND F. RADT, EDITORS. Elsevier Publishing Company, Inc., 215 4th Avenue, New York 3, N. Y., 1946. xx + 1265 pages; 17.5 × 26 cm. Subscription Price, $78.00; Serial Price, $91.00; Single Volume Price, $104. Volume 14, **Tetracyclic and Higher-Cyclic Compounds.** Series III, **Carboisocyclic Condensed Compounds.** New York, 1940. xx + 711 pages; 17.5 × 26 cm. Subscription Price, $45.00; Serial Price, $52.50; Single Volume Price $60.00.

Elsevier is a monumental new encyclopedia of organic compounds comparable to Beilstein but written in English. The work was undertaken in Amsterdam in 1937 under the editorship of Drs. Edith Josephy and F. Radt, both formerly of the Beilstein staff. Volume 14, Tetracyclic and Higher-Cyclic Compounds, which includes sterols, sex hormones, triterpenes, and carcinogenic hydrocarbons, was selected as the first volume to be published because of the current interest in these fields. This volume was completed in 1940 but could not be published until 1946 because of the war. Volume 13, which includes anthracene, phenanthrene, the resin acids, dicyclopentadiene, trycyclene, also bears the publication date 1946 and has just become available. Further volumes are scheduled for publication at intervals of about six months. The whole range of organic compounds is to be covered in a total of twenty volumes in thirty-eight parts. The production plan provides for completion of the work by 1963.

Elsevier is no English-language version of Beilstein; it is a thoroughly excellent competitive compendium with a character all its own. The most substantial difference in the scope of the two works is that Beilstein covers the patent literature whereas Elsevier does not; the absence of references to patents in the new work is a shortcoming in some fields but of little consequence in others. Elsevier shares with Beilstein a high quality of accuracy, reliability and thoroughness. It contains more and better formulas and numerous summarizing reaction charts; it is printed on good paper in easily readable type; and the whole scheme of publication of the new compendium represents a certain advance over the classical German documentation of organic chemistry. It is my opinion, however, that the one work supplements, rather than supplants, the other. What the user of either work most urgently requires is data and references of the most recent possible date. Immeasurable research time can be saved by any combination of reference works that will expedite literature searches. Since Beilstein and Elsevier operate on different publication schedules such that new volumes of each will cover recent literature in alternate fields, the combination of the two is bound to afford a better general coverage than either alone. For this reason alone, if for no other, Elsevier can be recommended as a worthwhile investment for the library of any active center of research already equipped with Beilstein.

The avowed ultimate goal of the Elsevier publication is to include complete references to the literature until four years prior to publication. The recently published Volume 13 bears evidence that this high standard of attainment may eventually be realized. This volume, published as of 1946 under the difficult circumstances of the post-war period, covers the whole literature through 1936 and includes most or all key references concerning the structure of compounds through 1941 or 1942. This high speed of documentation is achieved in part by use of an ingenious scheme for the citation of references; each item of information in the text is followed by a parenthetical citation of the year of publication and the name of the first author. The full references are then listed by years at the end of short sections. One advantage of the scheme is that additional references of any date can be entered at the last minute without disturbance of any sequence of reference numbers. Another is the avoidance of the frequent repetition of reference citations (*cf.* Beilstein). Another is that the reader can see from a glance at the list of references for a given section the date to which the literature survey has been carried.

The data cited in Elsevier were almost all taken directly from the original papers. A total of 229 journals were consulted in the composition of Volume 14. In the case of a few papers from obscure journals both the *Chemisches Zentralblatt* and *Chemical Abstracts* were consulted.

The system of arrangement employed in Elsevier is a simple and rational one based upon structure; closely re-