

source of error was eliminated. Full details of this work, and of complementary studies of the extraction of the iodides of gallium and thallium, will be published elsewhere.

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<sup>1</sup> Mathers, F. C., and Prichard, C. E., *Proc. Indiana Acad. Sci.*, **43**, 125 (1934).

<sup>2</sup> May, I., and Hofmann, J. I., *J. Wash. Acad. Sci.*, **38**, 329 (1948).

<sup>3</sup> Bassett, G., and Tomkins, F. S., *Analytical Chemistry of the Manhattan Project*, National Nuclear Energy Series, VIII, 1, 382 (McGraw-Hill, 1950).

<sup>4</sup> Wilkinson, G., and Grummit, W. E., *Nucleonics*, **9**, 52 (1951).

<sup>5</sup> Milner, G. W. C., *Analyst*, **76**, 488 (1951).

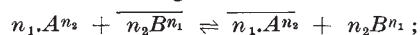
<sup>6</sup> Irving, H. M., *Quart. Rev. Chem. Soc.*, **5**, 200 (1951).

<sup>7</sup> Knox, K. L., and Spinks, J. W. T., *Canadian Chem.*, **30**, 88 (1946).

### Use of Ion Exchange Resins to determine the Charge of an Ion in Aqueous Solution

THE use of mono-functional ion-exchange resins with strongly acidic or basic groups provides an extremely simple and rapid technique for the determination of the ionic charge of an anion or cation in aqueous solution. The method has the further advantage of being applicable to solutions containing only very small concentrations of the unknown ion.

For any exchange reaction between two ions  $A$  and  $B$  of the same sign:



application of the law of mass action to the equilibrium leads to the expression:

$$K_c = \frac{[A^{n_2}]_{n_1} \times [B^{n_1}]_{n_2}}{[A^{n_2}]_{n_1} \times [B^{n_1}]_{n_2}}, \quad (1)$$

where  $A$  is the anion or cation of unknown charge ( $n_2$ ) and unknown concentration, and  $B$  is an ion of both known charge ( $n_1$ ) and known concentration. The square brackets signify concentrations in some suitable units, and the bar above an ion indicates that it is in the resin phase.

As first noted by Kressman and Kitchener<sup>1</sup>, an approximately constant value for  $K_c$  results if the 'concentrations' of the ions in the resin phase are represented by equivalent fractions and if no activity coefficient corrections are attempted with the ions in the aqueous phase. Concentrations in the aqueous phase may, for convenience, be expressed as equivalent concentrations. If  $X$  and  $\bar{X}$  represent equivalent fractions of the ion  $A$  in the solution and resin phases, respectively, equation (1) may be written:

$$K_c = \frac{\bar{X}^{n_1} \cdot (1 - X)^{n_2}}{(1 - \bar{X})^{n_2} \cdot X^{n_1}} \cdot C_s^{n_2 - n_1}, \quad (2)$$

where  $C_s$  is the total concentration of exchanging ions in the aqueous phase, expressed as equivalents per litre.

Provided that the initial concentration of  $B$  in the solution is at least a hundred times greater than that of  $A$ ,  $(1 - \bar{X})^{n_2}$  and  $(1 - X)^{n_2}$  each approximate to unity, and for  $C_s$  may be written  $C_B$ , the known concentration of ion  $B$  in solution, expressed in equivalents per litre. Let  $w$  be the weight of resin (initially all in the  $B^{n_1}$  ionic form) and  $\bar{C}$  its capacity in equivalents per gram. If  $V$  is the volume of the

solution in equilibrium with the resin and  $k_2$  and  $k_1$  are the values of some physically measurable property of  $A$  proportional to the number of molecules of  $A$  present in  $V$  litres of a solution before and after equilibration with the resin, then (2) may be expressed in the form:

$$\log \frac{k_1}{k_2 - k_1} = (n_2 - n_1 + 1) \log C_B + \log \left( \frac{V}{K_c \cdot w \cdot \bar{C}} \right). \quad (3)$$

To determine  $n_2$ , a series of solutions is prepared, each solution containing approximately the same concentration of  $A$  but a different, known, concentration of  $B$ . After measuring values of  $k_2$ , the solutions are then equilibrated with the resin, filtered, and the corresponding values of  $k_1$  found for the filtrates. (The exact concentrations of  $A$  corresponding to  $k_2$  and  $k_1$  need not be known.) Provided that  $V$  and  $w$  are kept constant in all experiments, the slope of the plot of  $\log k_1/(k_2 - k_1)$  against  $\log C_B$  enables  $n_2$  to be evaluated, as both the equivalent concentrations and the charge of  $B$  are known.

$k_2$  and  $k_1$  may be optical densities of the solution, polarographic step-heights, counts per minute of a radioactive element suitably incorporated into  $A$ , etc. Absorptiometric or polarographic techniques may be used with concentrations of  $A$  between about  $10^{-6}$  and  $10^{-3} M$ , and the use of a radioactive 'tracer' extends the range down to  $10^{-10} M$  or less.

$C_B$  may generally be varied within the range 0.01–0.5  $N$ ; but the choice of  $B$ , its concentrations, and the ratio  $V/w$  are best determined empirically so as to give the most suitable values of  $k_1$ . The ratio  $V/w$ , however, must not be less than about 5–10, or errors due to variable water absorption by the resin used may become significant. Mechanical agitation for one to two hours at a controlled temperature generally ensures a sufficient approach to equilibrium between solution and resin phases.

Using both absorptiometric and radioactive tracer methods, the procedure outlined above has been successfully applied to the determination of the ionic charge of both anions and cations resulting from the co-ordination of 'transitional' elements with organic and other groups. Details of the work will be published later.

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<sup>1</sup> Kressman, T. R. E., and Kitchener, J. A., *J. Chem. Soc.*, 1201 (1949).

### Monomeric Ferric Laurate in Toluene

METAL soaps occur as two distinct types of aggregate in non-polar solvents. The majority of mono- and di-valent soaps form large complexes held together by dipole association<sup>1</sup>. The trivalent aluminium compounds which are obtained as the basic mono- or di-soaps appear, on the other hand, to have a polymeric structure joined by metal-oxygen co-ordinate links<sup>2</sup> or by hydrogen bonds<sup>3</sup>. Solutions of the aluminium soaps exhibit characteristic visco-elastic phenomena and are believed to contain large fibrous aggregates.