

WE were interested to read of the success of Ekedahl, Högfeldt and Sillén in determining the separation factors of the silver-hydrogen exchange reaction from the elution boundaries obtained when a solution containing hydrogen ions is allowed to percolate through a column of a silver-saturated exchanger¹. It was DeVault² who first pointed out (in different symbols) that equation (5) of the paper by Ekedahl, Högfeldt and Sillén permitted the calculation of adsorption equilibrium data from elution boundaries. His equation has been further developed³ to give accurate equilibrium values even if the column is operated under non-equilibrium conditions. The improved method has been used⁴ for determining the separation factor for the sodium-hydrogen exchange on 'Dowex-50', and the accuracy obtained compared favourably with that of other methods. This was also the conclusion of Ekedahl *et al.*

Although this method is applicable in theory to the determination of any exchange equilibrium, it is not experimentally as straightforward in all cases as the recommendation of Ekedahl *et al.* suggests. When a multivalent ion (for example, Ba²⁺, La³⁺ or Th⁴⁺) is eluted with a monovalent ion (for example, H⁺ or Na⁺), the concentration of the multivalent ion in the eluate falls very sharply from its initial value. Thus, even in the case of elution of the relatively weakly absorbed Cu²⁺ with $N/5$ H⁺ from a column of 'Dowex-50', the ionic concentration of Cu²⁺ falls to about 10⁻³ molar, while the exchanger is still only about two-thirds converted to the hydrogen form⁵. In such cases we prefer to use the batch technique for accuracy.

Ekedahl *et al.* have also confirmed that the separation factor for an ion exchange reaction depends on the fraction of the two ions in the exchanger. This has often been reported since about 1918 for inorganic exchangers⁶, and since 1948 for exchangers of the synthetic resin type⁷. We ourselves have observed it on 'Dowex-50' with the following pairs of exchanging ions^{4,5,8}: Na⁺/H⁺; Ba²⁺/H⁺; La³⁺/NH₄⁺; Zn²⁺/UO₂²⁺; Ag⁺/H⁺; and Cu²⁺/H⁺. The phenomenon is now so general that any theory of ion exchange must adequately account for it.

An attempt has been made⁹ to explain such ion exchange behaviour on a thermodynamic model which takes into account the volume changes occurring when the ionic content of the exchanger is changed. However, this treatment does not allow adequately for the changes in the activities of the ions inside the exchanger. By treating an exchanger as if it were a concentrated aqueous electrolyte, we have been able to show that the activities of the ions inside the exchanger are in many instances more important in determining ion-exchange behaviour than the mere change in the exchanger volume. We have calculated, for example, the activity of the water inside a sodium-saturated exchanger from the observed amount of neutral salt which is taken up by the exchanger in solutions of sodium iodide and bromide, the observed water-contents of the exchanger, and the osmotic coefficients of sodium iodide and bromide in the aqueous solution obtained from tables. The osmotic coefficient of the pure sodium 'resinate' in different total molalities could thus be calculated, and the same values were obtained whether the sodium iodide or sodium bromide data were used.

By the reverse process, we have also calculated what the osmotic coefficient of aqueous sodium chloride solutions would be in 8-12 molar concen-

tration (if such solutions existed), and again the calculated data seem to agree with what would be expected from an extrapolation of the data given in tables for lower concentrations. We have also recently investigated how far this treatment can be applied quantitatively to the more difficult case of a pair of exchanging ions, and we conclude that, in this case, ionic interaction differing from that observed in purely aqueous solutions must play an important part in determining the shape of the adsorption isotherm. We suspect that this difference arises from the slightly ordered arrangement of negative charges in a cation-exchanger, so that the energy-level of a cation depends on the nature of its nearest neighbours. There will also be an effect from the competition of different types of cations for the limited amounts of hydration water. Either case could cause the observed increased deviation from ideality with increased cross-linking and decreased swelling ability. This work will shortly be reported in detail.

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¹ Ekedahl, E., Högfeldt, E., and Sillén, L. G., *Nature*, **166**, 723 (1950).

² DeVault, D., *J. Amer. Chem. Soc.*, **65**, 532 (1950).

³ Glueckauf, E., *J. Chem. Soc.*, 3280 (1949).

⁴ Duncan, J. F., and Lister, B. A. J., *J. Chem. Soc.*, 3285 (1949).

⁵ Duncan, J. F., Brown, P., and Dinham, M. (forthcoming publication).

⁶ Rothmund, V., and Kornfeld, G., *Z. anorg. allgem. Chem.*, **103**, 129 (1918).

⁷ Davidson, A. W., Argersinger, W. J., Stoenner, R. W., and Lowen, W. K., Tech. Report, Office of Naval Research, N.R. 057158 (1949); Pepper, K. W., Reichenberg, D., and McCauley, D. J., *J. Chem. Soc.*, 493 (1951); Strickland, J. D. H., *Farad. Soc. Discuss.*, No. 7, 157 (1949); Marinsky, J. A., and Coryell, C. D., Office of Naval Research, N.R. 026001 (1949); Duncan, J. F., and Lister, B. A. J., *Chem. and Indust.*, 26 (1949); *Farad. Soc. Discuss.*, No. 7, 156 (1949).

⁸ Duncan, J. F., and Lister, B. A. J., *Farad. Soc. Discuss.*, No. 7, 104 (1949).

⁹ Gregor, J., *J. Amer. Chem. Soc.*, **70**, 1293 (1948), and **73**, 642 (1951).

WHAT we have tried to find is rather "neater mathematics" and "useful approximations", to quote Dr. Glueckauf. Since our communications appeared¹, we have published some papers²⁻⁷ which we hope will explain our points more fully than was possible in two short communications or in this brief comment. In these papers, incidentally, we have tried to pay due regard to previous work, and refer to most of the papers quoted by Drs. Glueckauf and Duncan.

The 'ψ condition' is, of course, contained in the earlier work quoted by Dr. Glueckauf. Our point is, however, that by sticking to it consistently and using a graphical representation with $V-x$ diagrams, equilibrium processes in sorption columns can be described very simply and clearly. This approach has been applied to a number of cases²; the diagrams really seem to afford considerable help in finding out where the boundaries begin and end.

Another point is that the best approach to non-equilibrium processes in sorption columns seems to be first by considering the corresponding equilibrium process³. Where a sharp front would have been formed at equilibrium, it can be shown^{3,3} that a 'final form front' is obtained under non-equilibrium conditions. Unfortunately, most current kinetic approaches to sorption columns, except those of Johansson *et al.*¹¹, ourselves^{8,9}, and Glueckauf¹², either