Then $x = x_1 + x_2$,
but $x_1 = k_1 m$, where $k_1 = \text{constant}$,

so that the quantity of dye remaining in solution after the exchange adsorption is given by $(vc_0 - x_1)$. This will set up a reversible equilibrium which may be described, for example, by a Freundlich isotherm with constants k_2 and n . If c is the final concentration of dye in the solution,

$$x_2 = m \cdot k_2 \cdot c^n.$$

$$\text{Therefore } x = m(k_1 + k_2 c^n),$$

$$\text{or since } c = c_0 - x/v$$

$$x/m = k_1 + k_2(c_0 - x/v)^n.$$

This equation was found empirically by Gurwitsch¹⁰ but was misinterpreted and its significance overlooked. It defines a surface in the $(x - m - c_0)$ diagram which will be characteristic for each system. At constant c_0 and v we have:

$$\frac{dx}{dm} = \frac{k_1 + k_2 c^n}{1 + \frac{mn}{v} k_2 c^n - 1}.$$

As $m \rightarrow 0$ and thus $c \rightarrow c_0$, $dx/dm \rightarrow k_1 + k_2 c_0^n$. As $c \rightarrow 0$ with increasing m , $dx/dm \rightarrow k_1$. The shape of this (x, m) curve is represented by the full line in the diagram. Experiments by one of us (P. H. P.) with various clays, in which x was measured for methylene blue as a function of m at constant c_0 and v , gave results such as those for floridin shown in the graph. The agreement with the shape of the theoretical curve is reasonable, except where $x \rightarrow vc_0$. This discrepancy is probably due to the approximations used in the theory. It is smaller for Wyoming bentonite, for example, for which k_1 is greater than k_2 . For all values of m greater than a certain critical value m_0 , $x = \text{const.} = vc_0$; m_0 is the weight of clay which is exactly 'exchange-saturated' by vc_0 m.equiv. of dye, that is, the exchange adsorptive capacity of the clay is given by vc_0/m_0 . Although for some clays m_0 is rather

ADSORPTION OF METHYLENE BLUE ON FLORIDIN CLAY. $v = 50$ ml.
 $c_0 = 0.357$ PER CENT

indefinite, the value of $vc_0/m_0 = k_1$ agrees well with the base exchange capacity of the clays, as is to be expected. k_1 can be found from measurements such as those represented in the graph. Knowing k_1 , then k_2 and n can be found from the plot of $\log(x/m - k_1)$ against $\log c$. Alternatively, k_1 is given by the intercept of the $(x/m, c)$ plot on the axis of x . (We are indebted to Dr. M. Szwarc for pointing this out.)

Since the derivation of the theory outlined above is very general, it should be applicable wherever adsorption takes place by a combination of reversible and irreversible mechanisms; for example, dyeing, staining, adsorption on humus, peat, polymeric acids, ion-exchange resins, etc.

The subject will be treated more fully in a forthcoming publication.

P. H. PLESCH

Chemistry Department,
University, Manchester.

R. H. S. ROBERTSON

I Botanic Crescent,
Glasgow, N.W.
March 4.

¹ Michaelis and Ehrenreich, *Biochem. Z.*, **10**, 283 (1908).

² Freundlich and Poser, *Kolloid Chem. Beihefte*, **6**, 297 (1914).

³ (a) Michaelis, L., and Rona, P., *Biochem. Z.*, **97**, 57 (1919); (b) **102**, 268 (1920).

⁴ Swan and Urquhart, *J. Phys. Chem.*, **31**, 251 (1927).

⁵ Stadnikoff, *Kolloid Z.*, **31**, 19 (1922).

⁶ Fogle and Olin, *Indust. Eng. Chem.*, **25**, 1069 (1933).

⁷ Hendricks, S. B., *J. Phys. Chem.*, **45**, 65 (1941).

⁸ Grim, R. E., Allaway, W. H., and Cuthbert, F. L., *J. Amer. Ceramic Soc.*, **30**, 137 (1947).

⁹ For example, Seidell, A., *J. Amer. Chem. Soc.*, **40**, 312 (1918).

¹⁰ Gurwitsch, *Z. physik. Chem.*, **87**, 323 (1914).

A Simple Moving-Boundary Apparatus

Baxter and Gold¹ in their letter under the above title appear to be unaware of a paper by Drew and Hartley² describing the similar use of a single three-way tap arrangement for bringing together the leading and indicator solutions in the moving-boundary method of transport number measurement. As the apparatus described by Drew and Hartley was employed in the development of a new method for the measurement of transport numbers and might be overlooked, Baxter and Gold may be justified in directing attention to this simple experimental arrangement. I do not, however, share their views regarding the superiority of the tap arrangement over certain other conventional apparatus. I have had some experience of various types of moving-boundary apparatus, including one similar to that described by Baxter and Gold. I found that the air-lock device described by Hartley and Donaldson³ not only possessed the qualities claimed by Baxter and Gold for their tap arrangement but also was superior in other respects. Thus the air-lock device allows of greater ease of manipulation when the apparatus is supported in a thermostat, and its avoidance of a lubricant is a desirable feature in studies with non-aqueous media. Moreover, its inexpensiveness relative to a good-grade tap, its simplicity together with its ease of construction, render the device very appropriate for use in undergraduate practical courses.

R. H. DAVIES

Department of Chemistry,
University College,
Swansea.

¹ Baxter and Gold, *Nature*, **161**, 403 (1948).

² Drew and Hartley, *Trans. Farad. Soc.*, **30**, 655 (1934).

³ Hartley and Donaldson, *Trans. Farad. Soc.*, **33**, 458 (1937).