inside the crystal. Since the Q-value of the reaction is 4·785 MeV., it appears that the efficiency of this crystal is somewhat reduced for heavily ionizing particles.

JAMES SCHENCK

Oak Ridge National Laboratory,
Oak Ridge, Tennessee.
Aug. 28.

[1] Jordan, W. H., "Annual Review of Nuclear Science", 1, 220, Fig. 4 (1952).
[2] Siegbahn, K., *Phys. Rev.*, **70**, 127 (1946).
[3] Bell, P. R., and Jordan, W. H., *Phys. Rev.*, **79**, 392 (1950).

Measurement of Activated Diffusion of Adsorbed Molecules

IN continuation of a previous study[1] on the contribution of 'surface diffusion' to the transport of adsorbed molecules within porous adsorbents, rates of adsorption of n-butane have been measured.

For this purpose, a small metal beam balance was constructed which could be operated under high vacuum conditions. The weighing was performed with movable riders manipulated by means of external controls through ground joints in the enclosing glass tube. The beam was 5 cm. long and fitted with agate knife edges. A sensitivity of $\tan \alpha = 0·022$ per 1 mgm. was achieved. The pan carrying the adsorbent was hung on a thin glass rod 30 cm. below the balance and was surrounded by a glass tube inserted in a temperature bath. In the present investigation, an electronically controlled low-temperature thermostat[2] was used with 'dry ice' as refrigerant. Any given temperature in the range from room temperature to $- 80°$ C. could be maintained within $\pm 0·1°$ C. for any desired period.

In order to simplify the mathematical treatment of the diffusion problem, rates of adsorption were measured at constant pressures. These were maintained by adsorbing a certain quantity of butane at a convenient temperature, say, $0°$ C., on an amount of silica gel 100-500 times greater than that of the adsorbent under investigation on the balance.

After proper degassing, the adsorbent was cooled to the desired temperature and the balance system then connected to the constant-pressure device. The increase in weight of the adsorbent (4–125 mgm.) was followed with time, until equilibrium was reached. At $- 14°$ C. this occurred in about three hours, while at the lowest temperature $(- 79·5°$ C.) experimental periods were as long as 30 hr. From a plot of w_τ/w_∞ versus time (w_τ and w_∞ are weight increases at time τ and at equilibrium), overall diffusion coefficients could be evaluated using a solution of the general differential equation of diffusion for a system of finite length and for the particular boundary conditions. The range $w_\tau/w_\infty = 0·4$ to 0·6 was chosen to give representative values for the diffusion coefficient.

Rates of adsorption of n-butane in porous silica plugs were measured at various temperatures ($- 14°$ to $- 80°$ C.), porosities ($\varepsilon = 0·72$ to 0·53) and surface coverages ($y/y_m = 0·37$ to 6·9, where y_m is monolayer capacity in millimoles/gm.). The plugs (0·3 gm.) were formed by compressing Linde silica (300 m.²/gm.) into small steel cylinders, thus allowing adsorption to occur only through one plane.

In order to demonstrate the feasibility of the above method and to indicate the bearing of surface dif-

fusion on molecular transport in porous media, some of the results obtained may be quoted. For a plug of porosity 0·53 and a surface coverage of $y/y_m = 0·9$, the following overall diffusion coefficients were obtained : 7·20, 2·33 and 0·64 × 10⁻⁵ cm.²/sec. at $- 14·4°$, $- 44·2°$ and $- 79·5°$ respectively. Following Barrer's[3] calculations for the transient state of gas flow into a porous system, these coefficients are corrected for Knudsen streaming. In this way, the corresponding surface diffusion coefficients are obtained : 5·04, 1·87 and 0·60 × 10⁻⁵ cm.²/sec. This indicates that, under the above conditions, 70, 80 and 94 per cent of the total transport is due to the mobility of adsorbed molecules along the surface. From these diffusion coefficients an activation energy of 3,000 cal./mole results, corresponding to 47 per cent of the adsorption energy.

At the lower temperatures, diffusion coefficients vary only slightly with the porosity of the adsorbent, whereas at higher temperatures there is a considerable increase with porosity. In this range the activation energy is also somewhat greater. Diffusion coefficients depend markedly on the surface coverage. For example, at a coverage $y/y_m = 0·37$, $\varepsilon = 0·72$ and $t = - 44·5°$ C., an overall diffusion coefficient of $4·08 × 10⁻⁵$ cm.²/sec. was obtained. This increased steadily with greater coverage and reached a maximum value of $8·56 × 10⁻⁵$ cm.²/sec. in the multilayer region at $y/y_m = 3·0$, whereafter it decreased.

As a whole, these results are in agreement with those obtained in experiments based on a steady-state flow method, as recently reported by Carman[4].

I wish to thank Dr. P. C. Carman, who made the permeability data necessary for the calculation of the Knudsen streaming available to me. This communication is published with the permission of the South African Council for Scientific and Industrial Research, Pretoria.

R. A. W. HAUL

National Chemical Research Laboratory,
South African Council for
Scientific and Industrial Research,
Pretoria.
Oct. 3.

[1] Haul, R. A. W., *Z. Angew. Chem.*, **62**, 10 (1950).
[2] Haul, R. A. W., and Theron, J. J., *J. Sci. Instr.*, **28**, 236 (1951).
[3] Barrer, R. M., and Barrie, J. A., *Proc. Roy. Soc.*, A, **213**, 250 (1952).
[4] Carman, P. C., and Raal, F. A., *Proc. Roy. Soc.*, A, **209**, 38 (1951).

Activity Data and the Association of Hydrogen Chloride in Concentrated Solutions

IN some experiments in which concentrated solutions of hydrochloric acid were employed it was necessary to consider the part played by associated hydrogen chloride in determining its properties. Examination of data on the activity of hydrogen chloride[1] showed that the curve relating mean activity (a) to concentration (c) was continuous throughout, although its slope increased markedly at about 2 N.

Up to 4 N the activity coefficient γ is given with reasonable accuracy by the semi-empirical relationship :

$$\log \gamma = \frac{- Ac}{1 + Bc} + Dc + Ec^2 - \log (1 + 0·036m) \quad (1)$$