Some Experiments on Heavy Hydrogen

THE micro method for the determination of concentrations of para-hydrogen recently described by one of us[1] has been used to determine the concentration of ordinary hydrogen and its heavy isotope in their mixtures.

Calibration experiments were carried out on samples of hydrogen prepared by decomposing water of known H : D ratio (where D, deuterium, is used to designate the heavy isotope H^2) by a hot tungsten wire[2]. The water samples, ranging from 3 per cent to very nearly 100 per cent D_2O content, were very kindly presented by Dr. P. Harteck (Cavendish Laboratory).

The determination of the concentration of the isotope in hydrogen by means of this thermal conductivity method can be performed with an accuracy of ± 0.2 per cent in a few minutes, requires only 0.002 c.c. of gas at N. T. P. and allows not merely the total ratio H : D to be determined, but actually the percentages of the three components, H_2, HD, and D_2 in the sample may readily be found. By these means the following experiments have been carried out :

(1) The formation of the mixed molecule HD when mixtures of ordinary H_2 and D_2 (of at least 95 per cent purity) are in contact with a hot nickel wire has been studied. From this change to the equilibrium mixture of the three molecules, the equilibrium constant K of the reaction $H_2 + D_2 \rightleftharpoons 2$ HD, where

$$K = \frac{(H_2).(D_2)}{(HD)^2}$$

may be determined. At temperatures higher than room temperatures we find K to be about $\frac{1}{3}$, and independent of temperature, in agreement with the theoretical value given by Urey and Rittenberg[3]. This means that the reaction proceeds with a negligible heat of reaction. The accompanying table shows the calculated values for the equilibrium concentrations of HD formed in samples of hydrogen of known D_2 content, compared with the experimental results.

D_2 (per cent)	HD formed (per cent)	
	calc.	observed
11	19	22
35	42	44
40	45	44
54	47	49
60	45	46
82	27	22

These experiments should be carried to lower temperatures, when the determination of the equilibrium constant should allow conclusions to be drawn as to the spin and the statistics of the D-nucleus.

(2) The diffusion of hydrogen through palladium has been studied and we find that, at lower temperatures, the gas diffusing from a thin palladium tube has a higher H : D ratio (at 150° C. by some 50 per cent) than that of the original gas, but at higher temperatures the gas becomes 'heavier'. The residual gas is naturally concentrated. The gases recovered contain the equilibrium mixture of the three molecules. The simplest conclusion is that the energy of activation for the D-diffusion is somewhat greater than that for the H-diffusion, but the problem is complicated by the different solubilities of H and D. It may also be mentioned that some separation of the two isotopes is always obtained when they diffuse through a small nozzle at low pressures, as for example when they are being pumped through a valve.

(3) The formation of the equilibrium mixture from H_2 and D_2 proceeds in the homogeneous gas phase above 600° C. ; it takes place not only by the mechanism involving the atoms :

$$H + D_2 \rightleftharpoons HD + D$$
$$D + H_2 \rightleftharpoons HD + H$$
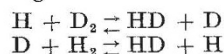
but perhaps also by the molecular exchange reaction :

$$H_2 + D_2 \rightarrow 2 \text{ HD}.$$

The activation energy of this reaction must be higher than 60 kcal. The reaction involving the atoms has an activation energy of the same order as that of the thermal ortho-para-hydrogen conversion[4]. The formation of HD does not occur at −195° C. on charcoal. With water vapour at higher temperatures, a similar molecular exchange reaction is found to occur with a collision efficiency of the same order of magnitude as that between H_2 and D_2.

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[1] A. Farkas, Z. phys. Chem., B, 22, 344 ; 1933.
[2] Cf. Urey, Murphy and Brickwedde, J. Chem. Phys., 1, 512 ; 1933.
[3] J. Chem. Phys., 1, 137 ; 1933.
[4] Z. phys. Chem., B, 10, 419 ; 1930.

The Unimolecular Film in Heterogeneous Reactions

THE formation of unimolecular films on solid surfaces has been demonstrated by Langmuir[1] for gases and by Carver[2] for toluene, but others employing different materials have obtained results interpreted as indicating an adsorbed layer of multimolecular character. At the moment the position is such that "definite agreement about the validity of direct experimental evidence is hardly reached"[3] and for this reason it may be of value to record the discovery of two unimolecular films made during our most recent work on the combination of hydrogen with sulphur in Pyrex glass. For the first time, so far as we are aware, this reaction has now been studied at low hydrogen pressures of the order of 3 mm. at the temperature employed, namely, 343° C. In the light of previous experience[5], the most rigid precautions were taken to ensure the absence of oxygen or moisture from the reactants.

It has already been established[4], in this laboratory, that sulphur vapour and hydrogen at pressures up to 760 mm. combine with a velocity which is proportional to the pressure of hydrogen and to the square root of the sulphur concentration, but independent of the area of glass surface. This rule is strictly followed down to pressures of hydrogen of the order of 40 mm. at 343° C., at which point there is still no evidence of anything except the pure homogeneous reaction. Below this pressure, however, the velocities become higher than would be expected from the gaseous reaction, and, furthermore, increase as the area of glass surface is extended.

An investigation of the reaction under these conditions, the experimental details of which would be out of place here, has shown that two reactions