THE EQUILIBRIUM BETWEEN HYDROGEN SULPHIDE AND HEAVY WATER.

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Received 19*th April*, 1937.

The purpose of this work was to measure the equilibrium constant for the reaction $H_2S + HDO = HDS + H_2O$ and compare the value obtained with that calculated from spectroscopic data. Since the method used for estimating deuterium concentrations of heavy water was only useful for the range 0·5 per cent., it was not feasible to measure other constants of the system hydrogen sulphide plus heavy water.

Experimental.

A weighed amount of water of known deuterium constant was brought into reaction with hydrogen sulphide in a vessel of known volume at a measured pressure, and the change in deuterium content was determined.

The reaction vessel was a pyrex flask of 1½-2½ litres capacity, provided with a side tube for the entry of gas, and an appendix some 12 cm. long by 12 mm. diameter was fused onto the drawn out neck, in which the water was frozen out during the admission and withdrawal of the gas. It was connected when required to a vacuum system with manometer, and a trap in which the hydrogen sulphide was stored as a solid. (Fig. 1.)

The hydrogen sulphide used in this reaction was prepared by dropping hydrochloric acid onto crystals of sodium sulphide, and was washed with water to remove hydrogen chloride, dried with phosphorus pentoxide, and stored by freezing with liquid air.

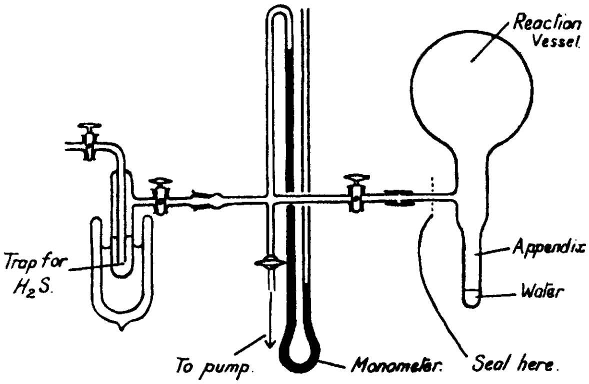

FIG. 1.

The method of procedure was briefly as follows: The heavy water of deuterium content 4-5 per cent. was weighed into the cleaned and dried reaction vessel from a specially designed weight pipette, in such a manner that it dropped into the appendix, and not on to the walls of the vessel. The water was frozen out, and the vessel was connected to the vacuum system and pumped out, the loss of water being negligible. Hydrogen sulphide was then allowed to evaporate into the vessel, which was then warmed up to room temperature, the freezing mixture being removed from the appendix. When the whole vessel had attained room temperature, the pressure of gas was measured and the side tube sealed off. The vessel was inverted so that the water drained down into the bulb, presenting a large surface for the heterogeneous interchange. It was found in preliminary experiments that very slight traces of grease markedly hindered the reaction, by covering the surface.

When the reaction was complete, the vessel was again inverted and a freezing mixture applied to the appendix, so that the water drained and distilled back, and was frozen out. The vessel was again connected to the vacuum system, and the hydrogen sulphide pumped off, or distilled back into the trap. The appendix was cut off with the frozen water in it. To remove traces of hydrogen sulphide dissolved in the water it was distilled *in vacuo*, in an apparatus figured in a previous paper.[1] It was then treated with a small amount ($\frac{1}{2}$ g.) of dried mercuric oxide to remove final traces of hydrogen sulphide, and redistilled. It was shown in blank experiments using ordinary water that this procedure was efficient in removing hydrogen sulphide, leaving the density of ordinary water unchanged.

The deuterium content of the water was estimated by determining its density, using a float and varying the temperature according to the method already described. As a check on the purity of the water each specimen was redistilled and the density redetermined.

To test whether a true equilibrium was reached, a back exchange was done, approaching the equilibrium from the other side. A specimen of hydrogen sulphide from a previous run was used, with an enhanced and known deuterium content, and ordinary distilled water was used in place of heavy water. In collecting the gas in the trap, a phosphorus pentoxide tube was inserted between the reaction vessel and the vacuum system. The value found in this run agreed well with the others.

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[1] Small and Wolfenden, *J.C.S.*, 1936, 1811.

Results and Discussion.

The concentration of deuterium in the gas is found from the drop in deuterium content of the water. To calculate the equilibrium constant it is necessary to know the separate concentrations of all the molecular species present; for this purpose the constant $K_1 = (HDO)^2/(H_2O)(D_2O)$ and the corresponding one for the different isotopic forms of hydrogen sulphide must be known. Topley and Eyring [2] calculated the former to be 3·24 at 15° C. A value of four was taken for the latter; the concentrations found for the species HDS and HDO are not sensitive to the precise values assigned to these constants in the range of deuterium concentrations being considered.

TABLE I.—Experimental Results.

Run Number.	1.	2.	3.	4.	5. (Back Reaction.)
Mols. of Gas	0·1015	0·0990	0·100	0·0592	0·0890
Mols. of Water	0·185	0·273	0·1175	0·1415	0·146
Initial D content of gas (per cent.)	—	—	—	—	2·00
Initial D content of water (per cent.)	5·364	5·364	4·099	4·099	0·02
Final D content of water (per cent.)	4·385	4·637	2·993	3·494	0·930
Constant for heterogeneous reaction	0·397	0·428	0·405	0·430	0·450
Time in days	2	2	20	20	2

The mean value found for the constant for the heterogeneous reaction, $H_2S_{gas} + HDO_{liq.} = HDS_{gas} + H_2O_{liq.}$ was 0·422 ± 0·019.

To obtain from this result the value of the constant for the reaction occurring entirely in the gas phase it is necessary to multiply by the factor $\frac{(HDO)_{liq.}(H_2O)_{gas}}{(H_2O)_{liq.}(HDO)_{gas}}$. Assuming Henry's law, this is the ratio of the vapour pressures of H_2O and HDO. The vapour pressure of HDO is taken, following Topley and Eyring,[2] as the geometric mean of those of H_2O and D_2O, and using the data of Wahl and Urey [3] this factor has the value 1·075 at 15° C.

The value of the constant for the reaction in the gas phase becomes 0·453 ± 0·020 at 15° C.

The general expression [4] for the equilibrium constant for a reaction of this type is :—

$$\log_e K = -\Delta E/RT + 3/2\Sigma \log_e M + \tfrac{1}{2}\Sigma \log_e (I_A I_B I_C),$$

where ΔE is the change in zero-point energy for the reaction, the M's are the molecular weights, and the I's are the moments of inertia for the molecules, the summation being taken counting the reactants negative and the resultants positive. The moments of inertia for the isotopic molecules were calculated treating them as rigid planar structures and using the configurations and dimensions given by Sponer; [5] these were assumed to be unaltered by substitution of deuterium for protium.

[2] Topley and Eyring, *J. Chem. Physics*, 1934, **2**, 217.
[3] Wahl and Urey, *ibid.*, 1935, **3**, 411.
[4] Giauque, *J.A.C.S.*, 1930, **52**, 4808.
[5] Sponer, *Molekülspektren*, 1935, Berlin.

When the experimental part of this work was done, no analysis had been made of the spectra of the isotopic hydrogen sulphides, and it was therefore necessary to calculate their vibration frequencies, which was done using the equations given by Ellis and Sorge [6] for a simple central force system. Though the absorption spectra of the hydrogen sulphides have now been investigated,[7] and values may be obtained for the zero-point energies from the data published, the calculated values are retained, as it is of interest that in the case of simple molecules like those under consideration, such good results can be obtained by a relatively simple method of calculation, from a knowledge solely of the properties of the molecules containing protium. In Table II. below, the first set of values for H_2S and HDS are derived from the vibration frequencies calculated as indicated above, and the second set are derived from the published results of the actual analysis of the spectra, making allowance for the effect of anharmonicity. The corresponding values for the zero-point energy difference and constant for the reaction in the gas phase are placed alongside. The values used for the water molecules are derived from the values calculated by Topley and Eyring for the vibration frequencies, allowing a half-quantum per vibrational mode.

TABLE II.—MOLECULAR DATA.*

Molecule.	I_A.	I_B.	I_C.	Zero-point Energy.	ΔE.	K Calc.
H_2O	1·03	1·97	3·00	13104		
HDO	1·22	3·14	4·36	11330		
H_2S	2·75	3·15	5·90	9296 † 9515 ‡	479 §	0·436
HDS	3·17	5·49	8·66	8001 † 8204 ‡	463 ‖	0·448

* I's in gm. cm.^{2} × 10^{-40} and zero-point energies in Cals./Mol.
† Calculated.
‡ From spectra.
§ From calculated zero-point energies.
‖ From zero-point energies derived from spectra.

In an exchange reaction where the molecules taking part are fairly large, the terms arising from the differences in molecular weight and moment of inertia are small. The values found for the second and third terms are + 0·0356 and — 0·0353 respectively, so that they cancel out almost exactly, and the free energy of the reaction becomes identical with the difference in zero-point energy :

$$\Delta F = -RT \log_e K = \Delta E$$

Summary.

The heterogeneous exchange equilibrium between heavy water and hydrogen sulphide is measured at 15° C., and the homogeneous equilibrium constant in the gas phase calculated from the result. The value obtained is compared with the values derived from calculations of zero-point energy and from spectroscopic data.

[6] Ellis and Sorge, *J. Chem. Physics*, 1934, **2**, 556.
[7] Bailey, Thompson, and Hale, *ibid.*, 1936, **4**, 625.

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