``Isotopic Equilibria'' in the HydrogenHydrogen Oxide System

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Experiments are described in which the distribution of deuterium between hydrogen and water vapor at equilibrium at 800°K is investigated. The equilibrium constants of the reactions necessary to describe the system H_2, HD, D_2, H_2O, HDO and D_2O are calculated and the amount of each constituent calculated for various concentrations of deuterium. The distribution of deuterium between the hydrogen and the water is calculated and found to agree with the experimental data.

THE isotopic effect upon equilibrium constants of reactions involving diatomic molecules can be evaluated with precision. The necessary data are the energy levels of the molecules. H. C. Urey and D. Rittenberg[1] investigated the hydrogen iodide equilibrium and were able to predict the experimental results very satisfactorily.

In this research we have investigated a similar exchange reaction in which polyatomic molecules are involved. The energy levels of polyatomic molecules have not been established with nearly the same precision. Mecke and his collaborators[2] have secured the vibration frequencies and moments of inertia of the H_2O molecule and Topley and Eyring[3] have calculated the fundamental vibration frequencies and moments of inertia of the HDO and D_2O molecules, using the theory of Cross and Van Vleck.[4] The degree of precision is high enough so that the free energies can be calculated.

That an isotopic exchange takes place between water and hydrogen was first demonstrated by us[5] and some experimental values of the equilibrium constant for the reaction

$$HDO + H_2 \rightleftharpoons HD + H_2O$$
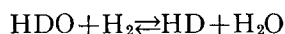
at high temperature were presented in a preliminary notice.[6] Other workers[7] have examined the isotope equilibrium at low temperatures in

the presence of catalysts. We have studied the equilibrium system involving the six constituents, H_2, HD, D_2, H_2O, HDO and D_2O.
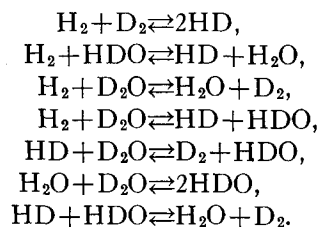
THEORETICAL

As we will show later, if the total concentration of deuterium is less than about 4 percent we can neglect the constituents D_2 and D_2O while if it is above about 96 percent we can neglect the concentrations of H_2 and H_2O. Consequently below 4 percent the only reaction involved is

$$H_2 + HDO \rightleftharpoons HD + H_2O$$
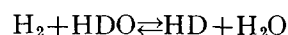
while above 96 percent we need concern ourselves only with the reaction

$$D_2 + HDO \rightleftharpoons HD + D_2O.$$
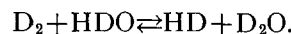
In these ranges of concentration, experiment will give satisfactory values for the equilibrium constants. At intermediate concentrations, however, all constituents must be considered giving the following equilibria:

$$H_2 + D_2 \rightleftharpoons 2HD,$$
$$H_2 + HDO \rightleftharpoons HD + H_2O,$$
$$H_2 + D_2O \rightleftharpoons H_2O + D_2,$$
$$H_2 + D_2O \rightleftharpoons HD + HDO,$$
$$HD + D_2O \rightleftharpoons D_2 + HDO,$$
$$H_2O + D_2O \rightleftharpoons 2HDO,$$
$$HD + HDO \rightleftharpoons H_2O + D_2.$$

By appropriate operations these can be reduced to three equations which involve all the components, namely:

$$(1) \qquad H_2 + D_2 \rightleftharpoons 2HD,$$
$$(2) \qquad D_2O + H_2 \rightleftharpoons H_2O + D_2,$$
$$(3) \qquad H_2 + HDO \rightleftharpoons HD + H_2O.$$

[1] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933). Rittenberg and Urey J. Am. Chem. Soc. **56**, 1885 (1934).
[2] Mecke, Baumann and Freudenberg, Zeits. f. Physik **81**, 313, 445, 465 (1933).
[3] Topley and Eyring, J. Chem. Phys. **2**, 217 (1934).
[4] Cross and Van Vleck, J. Chem. Phys. **1**, 357 (1933).
[5] Crist and Dalin, J. Chem. Phys. **1**, 677 (1933).
[6] Crist and Dalin, J. Chem. Phys. **2**, 442, 548 (1934).
[7] K. F. Bonhoeffer, Zeits. f. Elektrochemie **40**, 469 (1934). A. Farkas and L. Farkas, J. Chem. Phys. **2**, 468 (1934).

By appropriate combinations of these equations all the others can be obtained. This particular set was selected because the equilibrium constant of the first has been well established by theory and experiment,[8] and the third can be obtained directly by experiment at low concentrations of deuterium. The second equation is then required to complete the set.

It is possible to write three supplementary equations which contain the six components. These equations are

$$[H_2]+[HD]+[D_2]=100,$$
$$[H_2O]+[HDO]+[D_2O]=100,$$
$$[HD]+2[D_2]+[HDO]+2[D_2O]=2n.$$

The first two result from the experimental condition of equimolecular proportions for the hydrogens and the oxides, the setting of each equal to 100 being arbitrary. In the third equation (n) is taken as twice the total deuterium percentage. We have then the equations

$$\frac{b^2}{ac}=K_1 \quad (3.83), \quad (1) \qquad a+b+c=100, \quad (4)$$

$$\frac{dc}{af}=K_2 \quad (0.61), \quad (2) \qquad d+e+f=100, \quad (5)$$

$$\frac{bd}{ae}=K_3 \quad (0.79), \quad (3) \qquad b+2c+e+2f=2n. \quad (6)$$

where $[H_2]=a$; $[HD]=b$; $[D_2]=c$; $[H_2O]=d$; $[HDO]=e$; $[D_2O]=f$.

In order to calculate the equilibrium constant[9] of (2) we use

$$K_2=(f_{H_2O}\cdot f_{D_2})/(f_{D_2O}\cdot f_{H_2}),$$

where the distribution functions for H_2O and D_2 are

$$f_{H_2O}=\left[\exp-\frac{E_d}{kT}\right]\frac{[2\pi m_d kT]^{\frac{3}{2}}}{h^3}\frac{8\pi^2[8\pi^3(ABC)_d]^{\frac{1}{2}}}{2h^3}$$

$$\times (kT)^{\frac{3}{2}} \prod_{i=j,\,k,\,l} \frac{1}{1-\exp\,(-h\nu_i/kT)}\times 4,$$

[8] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933). Rittenberg, Bleakney and Urey, J. Chem. Phys. **2**, 48 (1934). A. Farkas and L. Farkas, Nature **132**, 894 (1933); Proc. Roy. Soc. **A144**, 467 (1934).
[9] See Topley and Eyring, J. Chem. Phys. **2**, 217 (1934).

$$f_{D_2}=\left[\exp-\frac{E_c}{kT}\right]\frac{[2\pi m_c kT]^{\frac{3}{2}}}{h^3}\sum_{v,\,j}p\exp\left(\frac{-E_{v,\,j}}{kT}\right).$$

ABC are the three moments of inertia, E is the zero point energy, h and k have their usual significance. The functions for D_2O and H_2 are similar except that the statistical factor for D_2O is 9. The equilibrium constant is given by

$$K_2=\exp\left[\frac{E_a+E_f-E_c-E_d}{kT}\right]\left[\frac{m_d m_c}{m_f m_a}\right]^{\frac{3}{2}}$$

$$\times\left[\frac{(ABC)_d}{(ABC)_f}\right]^{\frac{1}{2}}\frac{\Pi_d}{\Pi_f}\frac{Q_c}{Q_a}\times\frac{4}{9}.$$

The data for the Q's were obtained from the work of Urey and Rittenberg,[10] and of Johnston and Long.[11] The other necessary data were obtained from Topley and Eyring's work. The values of K_2 for 373°K and 800°K are 0.2 and 0.606, respectively, while those for K_3 are 0.48 and 0.79. Additional values are given in the preliminary note referred to above. The low temperature values compare favorably with the results of Bonhoeffer and of Farkas.[12]

By appropriate substitutions in Eqs. (1)–(6) we find the equations:

$$e^2=(K_1K_2/K_3{}^2)d(100-e-d), \quad (7)$$

TABLE I.

%D in total H₂ system	H₂(a)	HD(b)	D₂(c)	H₂O(d)	HDO(e)	D₂O(f)	$\frac{\alpha}{\beta}$
Temperature =800°K							
0	100	0	0	100	0	0	—
10	82.00	16.12	0.8265	79.13	19.57	1.30	0.81
30	52.91	39.42	7.68	45.77	43.23	11.00	.84
50	28.46	49.32	22.22	22.38	48.99	28.62	.88
70	10.94	43.58	45.48	7.723	39.09	53.18	.93
90	1.28	19.81	78.91	0.8253	15.97	83.20	.97
100	0	0	100	0	0	100	—
Temperature =373°K							
0	100	0	0	100	0	0	—
30	61.84	33.05	5.11	39.61	44.05	16.34	0.56
50	37.41	46.08	16.50	17.30	44.49	38.21	.65
70	16.11	45.57	38.23	5.25	31.50	63.24	.77
100	0	0	100	0	0	100	—

$\alpha=\dfrac{b+2c}{2(a+b+c)}$, the deuterium percentage in the hydrogen.

$\beta=\dfrac{e+2f}{2(d+e+f)}$, the deuterium percentage in the water.

[10] Reference 8.
[11] H. L. Johnston, and E. A. Long, J. Chem. Phys. **2**, 389 (1934).
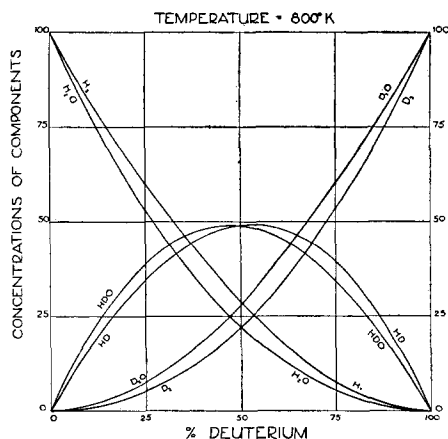[12] Reference 7.

FIG. 1. Equilibrium concentrations of hydrogen-hydrogen oxide systems. Temperature = 800°K. The ordinate represents the concentration of the components on the basis of 200 (see Eqs. (4) and (5)).
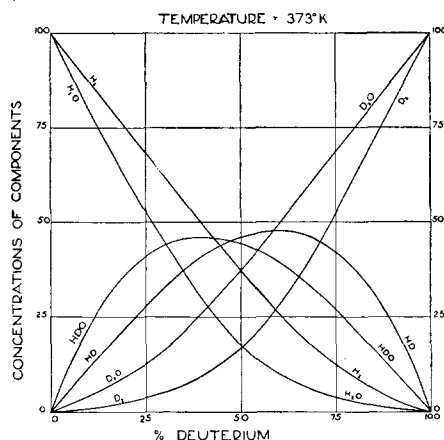

FIG. 2. Equilibrium concentrations for temperature of 373°K.

$$[K_1 d + 2K_3 e]100 \cdot K_3 e + [200 - e - 2d - 2n]$$

$$\times [K_1 d^2 + K_1 K_3 de + K_3{}^2 e^2] = 0, \quad (8)$$

$$c = \frac{100 K_3{}^2 e^2}{K_1 d^2 + K_1 K_3 de + K_3{}^2 e^2}. \quad (9)$$

The values of the constants given in (1), (2) and (3) in parenthesis are for 800°K and are used in the calculations that follow. Eqs. (7) and (8) were solved for different values of n. The concentrations of all the components can then be obtained from Eqs. (9), (4), (5) and (6). The results of the calculations are given in Table I and Figs. 1 and 2. In Fig. 2 are the results of the calculation for 373°C.

EXPERIMENTAL

The experiments were carried out in a Pyrex tube of 1565 cc capacity. This was sealed inside a larger tube containing boiling sulfur. The boiling point of the sulfur was controlled by maintaining a constant pressure of nitrogen over the sulfur. This was accomplished by means of a regulated heater in an auxiliary flask, the necessary contacts being made on a manometer.[15] A thermocouple calibrated with a type K potentiometer against boiling sulfur at atmospheric pressure, and against the freezing point of antimony gave the temperature of the reaction vessel within 0.5°C. The variation in temperature over the inner tube of the reaction vessel was less than 0.5°C and no variation with time was discernible. Platinum foil was put in the reaction vessel to catalyze the reaction. The water was first distilled into the vessel which was then filled with hydrogen to a pressure of 657 mm at 25°C. Deuterium rich hydrogen was prepared by passing water vapor over sodium, with continuous operation of a Toepler pump to remove the hydrogen produced. The
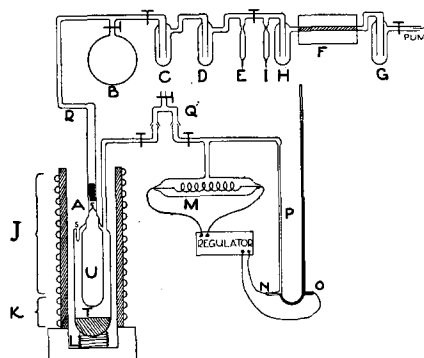

FIG. 3. When the breakseal A is broken by the plunger above it, the gas expands into the five liter flask B. The water is trapped out in C and D and later distilled into E which is sealed off and removed for measurement. The hydrogen is slowly passed over the copper oxide in the furnace F and the water formed trapped in G. Trap H prevents any back distillation of the water formed in F. This water is later distilled into I and removed. Coils J, K and L, wound on asbestos, are separately regulated to avoid superheating of the sulphur vapor T surrounding the reaction vessel U. Bulb M contains the heater which keeps the pressure constant. N and O are the metal contacts on the manometer P. Removing the cap Q and breaking the tube R makes it possible to shift the reaction vessel so that it can be immersed in dry ice and water distilled into it. S is a well for a thermocouple.

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[13] C. C. Coffin, J. Am. Chem. Soc. **55**, 3646 (1933).

reaction vessel was then heated in a furnace, $1\frac{1}{2}$ hours being required to come up to temperature. Trial showed that the reaction was about two-thirds complete in two hours and all runs thereafter were over eighteen hours in length. The exception is Experiment 4 where the original mixture was almost in the equilibrium proportions and the time was ten hours. At the end of the run the gases were withdrawn through a break seal while the reaction vessel was kept at the original temperature. The water was removed and the hydrogens were passed over hot copper oxide. The recovery of hydrogen and water was complete as was shown by weighing the separate fractions. The samples of water were analyzed with the interferometer as described previously.[14] The final analyses were taken to represent the equilibrium concentrations. The results are given in Table II. (See Fig. 3 for a description of the apparatus.)

TABLE II. *Experimental equilibrium data.*

No.	Time in hours	α	β	$\frac{\alpha}{\beta}$ exp.	$\frac{\alpha}{\beta}$ calc.
1*	42	2.36	3.02	0.784	0.79
2*	18	3.124	3.928	.794	.79
3*	38	2.93	3.82	.767	.79
4	10	30.19	36.74	.823	.85
5*	24	37.77	44.12	.856	.86
6*	48	38.662	44.757	.863	.86
7	27	83.40	88.32	.944	.96

* Ordinary hydrogen at start.
Temperature =800°K. Catalyst =platinum except (1) where copper was used. In (4) and (7) α and β at the start were about the same. The hydrogen molalities were 66 and 81 percent, respectively, of the water. A simple proof shows (as does actual calculation) that α/β exp. for (4) and (7) is directly comparable with α/β calc. which has been derived for the case where $a+b+c=d+e+f$.

During the course of the work the reaction vessel became considerably darker in color and eventually became almost completely opaque. Measurement of α and β and of the water before it was placed in the reaction vessel showed that a small amount of deuterium disappeared during the course of each run. Table III contains data on the loss of deuterium.

Δ $(\alpha + \beta)$ is roughly proportional to the length of the experiment. It certainly depends

[14] Crist, Murphy and Urey, J. Chem. Phys. 2, 112 (1934).

TABLE III.

No.	t	$(\alpha+\beta)_1$	$(\alpha+\beta)_2$	$\frac{\Delta(\alpha+\beta)}{(\alpha+\beta)_1}$	$\frac{\Delta(\alpha+\beta)}{t(\alpha+\beta)_1} \times 10^3$
(1)	42	6.25	5.38	0.139	3.31
(2)	18	7.33	7.05	.0382	2.12
(3)	38	7.33	6.75	.0792	2.08
(5)	24	85.213	81.89	.0389	1.62
(8)	43	85.213	84.325	.0104	0.243

t =time in hours. $(\alpha+\beta)_1$ =conc. of deuterium before being placed in furnace. $(\alpha+\beta)_2$ =conc. of deuterium after being placed in furnace. Expt. 8 = Blank run with water alone.

on the temperature and we should expect it to depend on the previous history of the vessel. However, the small size of the average deviation of α/β from runs (1), (2) and (3) and from runs (5) and (6) in Table II offers good evidence that α/β is affected but slightly by the loss of deuterium. The average deviation for experiments (1), (2) and (3) is 0.013 and for (5) and (6) is 0.004. The darkening of the vessel was first noticed during some experiments on the kinetics of the reaction $HDO+H_2 \rightleftharpoons H_2O+HD$. This indicates a reaction, probably, between hydrogen and the glass. There is also the possibility of an exchange between the deuterium oxides and the water in the glass. The experiments were run with proper care in the rapid heating of the vessel and rapid cooling so as to avoid large uncertainties in the time of the experiment, but the size of the deuterium loss makes the measurements in Pyrex unreliable for rate studies.

The experiments yield the ratio of the deuterium in the hydrogen components to that in the oxide components. With low concentrations of deuterium the four components concerned can be calculated readily and the equilibrium constant obtained. However, at high concentrations it is necessary to compare the ratio to that calculated from the equilibrium concentrations in Table I. The calculated values are given in the last column of Table II. The correspondence with the experimental ratios is satisfactory.