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THE EQUILIBRIUM $H_2O + HD = HDO + H_2$.

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The equilibria of chemical reactions involving light and heavy hydrogen (H and D) of the type

$$AH + BD \rightleftharpoons AD + BH$$

were first discussed by Urey and Rittenberg 1 who showed that in general the equilibrium constant of such reactions

$$K = \frac{[\mathrm{AD}] \; [\mathrm{BH}]}{[\mathrm{AH}] \; [\mathrm{BD}]}$$

will differ from unity on account of the different zero point energies, masses and moments of inertia of the corresponding "light" and "heavy" compounds.

The present paper deals with the equilibrium

$$H_2O + HD \rightleftharpoons HDO + H_2.$$

Bonhoeffer and Rummel^{2,3} found the equilibrium constant of this reaction to be 3.8 at room temperatures and we obtained 4 in some

- ¹ Urey and Rittenberg, J. Chem. Physics, 1, 137, 1933.

- ² Bonhoeffer and Rummel, Naturwiss., 22, 45, 1933.
 ³ Bonhoeffer, Z. Elektrochem., 40, 469, 1934.
 ⁴ Farkas and Farkas, Proc. Roy. Soc., A., 146, 623, 1934.

preliminary experiments * nearly the same value at this temperature and The importance of this equilibrium which was about 2 at 100° C. pointed out in a preceding paper,⁵ however, suggested a more accurate study. We have carried out this investigation in the following way, making use of the fact that the exchange reaction between water and hydrogen takes place in the presence of certain catalysts⁶:---

(I) Heavy water of known D-content was brought into contact with hydrogen in presence of a catalyst and the change in the D-content of the hydrogen was followed until equilibrium was reached. Since in these series of experiments the heavy water was present in large excess, its D-content is relatively unaffected, thus permitting a high degree of accuracy in the determination of the equilibrium constant.

(2) Heavy steam of known D-content and light hydrogen were mixed in certain proportions in the presence of a catalyst, and again the equilibrium concentration of D in the hydrogen was determined. This method was less accurate than the former, because small errors in the determination of the D-content of the hydrogen evidently affect the equilibrium constant considerably.

For both methods the experimental arrangement was very simple. After having filled the reaction vessel of volume 8 c.c. with 0.5 g. heavy



water † and with several mgm. of palladium or platinum black and theair exhausted, hydrogen was added to 10-20 mm. pressure. Then from time to time samples hydrogen. of about 0.004 c.c. at N.T.P. were

withdrawn from the reaction vessel by means of a capillary lock (volume o·2 c.c.) and their D-content determined (after having frozen out the water vapour) by the microthermo-conductivity method.⁷ The time required for the attainment of the equilibrium varied with temperature, activity and amount of the catalyst used, but was usually less than one or two hours. Fig. 1 shows the change of the D-content of the hydrogen with time when in contact with 66.8 per cent. heavy water at 20° C. Practically the same concentration, namely, 38.2 per cent. D was reached, starting with 90 per cent. D_2 instead of H_2 and 66.8 per cent. heavy water.

Table I. shows the equilibrium D-content in the hydrogen in per cent. $(= G_{\rm D}, \text{ column 2})$, and the D-content of the water $(= W_{\rm D}, \text{ column 1})$ in equilibrium at 20° C. In column 3 the ratio

$$\frac{G_{\mathbf{H}} \cdot W_{\mathbf{D}}}{G_{\mathbf{D}} \cdot W_{\mathbf{H}}}, \quad G_{\mathbf{H}} = 100 - G_{\mathbf{D}}, \quad W_{\mathbf{H}} = 100 - W_{\mathbf{D}}$$

* In fact, the present investigation will show that the equilibrium constants reported in previous papers were somewhat too high. The equilibrium constants given in our joint paper with Yudkin (Proc. Roy. Soc., 115B, 373, 1934) were obviously not very accurate, as indicated by their variation in different experiments

† The D-content of the water was determined by density measurements, and checked by the micro-thermoconductivity method, the water being decomposed on a hot tungsten filament to hydrogen and tungstic oxide.

⁵ Farkas and Farkas, J. Chem. Physics, 2, 468, 1934.
 ⁶ Horiuti and Polanyi, Nature, 132, 819, 1933.
 ⁷ Farkas and Farkas, Proc. Roy. Soc., 144A, 467, 1934.

is given. This ratio is related to the equilibrium constant of the reaction $H_2O + HD \rightleftharpoons HDO + H_2$, as will be seen below, and is practically independent of the D-content of the water.

The temperature dependence of the equilibrium was investigated at 3° , 40° , 65° and 100° C. At 65° and 100° , however, the hydrogen samples

were not extracted during the establishment of the equilibrium, but the vessel was sealed up after having been filled, heated for one or two hours, and then the whole hydrogen was taken out by breaking a suitable glass peak by means of an electromagnet. (The results obtained are given in Table IV.)

D-Content of the Water in Per Cent. $W_{\rm D}$.	D-Content of the Hydrogen in Per Cent. $G_{\rm D}$.	$\begin{array}{c} \text{Ratio} \\ G_{\text{H}} \cdot W_{\text{D}} \\ G_{\text{D}} \cdot W_{\text{H}} \end{array}$
20·5	7·4	3·22
25·9	9·8	3·21
41·0	17·9	3·19
66·8	38·5	3·22
73·6	46·8	3·17

TABLE I.—TEMPERATURE 20° C.

The second series of experiments were carried out at 450° C. in a quartz vessel in which the hydrogen was mixed with heavy steam. In order to accelerate the exchange reaction again a catalyst was used. In this case a thin platinum wire o 1 mm. diameter and 10 cm. long was substituted for the platinum black since the use of the latter implies the danger of hydrogen absorption, and thus the alteration of the original ratio of water : hydrogen.* The data for these experiments are given in Table II.

TABLE	II.—TEMPERATURE	4500	С.
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	Original Mixture.			Equilibrium Mixture.		
Hydrogen mm. Hg.	Steam mm. Hg .	Per Cent. D. in the Steam.	Hydrogen Per Cent. D. (G _D .)	Steam Per Cent. D. (V _D .)	$\frac{G_{\mathbf{H}} \cdot V_{\mathbf{D}}}{G_{\mathbf{D}} \cdot V_{\mathbf{H}}}.$	
8·1 10·0 7·0	18.0 17.8 18.5	19·4 19·4 70·8	12·7 11·8 46·9	13.7 12.8 53.1	1·09 1·10 1·29	

The Calculation of the Equilibrium Constants.

The equilibrium between the six molecular species H_2 HD, D_2 , H_2O , HDO and D_2O in the gaseous state is given by the equilibria

$$H_2 + D_2 \rightleftharpoons 2HD \quad K_1 = \frac{[HD]^2}{[H_2][D_2]} \quad . \quad . \quad (I)$$

$$H_2O + D_2O \rightleftharpoons 2HDO \quad K_2 = \frac{[HDO]^2}{[H_2O] [D_2O]} \quad . \quad . (2)$$

$$H_2O + HD \rightleftharpoons HDO + H_2$$
 $K_3 = \frac{[HDO] [H_2]}{[H_2O] [HD]}$. (3)

These three equilibria define completely all other equilibria involving these molecular species, and the constants of all other equilibria can be expressed in terms of these three constants, *e.g.*

* Such an absorption of gas did not matter in the first series of experiments when water was used.

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$$H_2O + D_2 \rightleftharpoons D_2O + H_2, \quad K_4 = \frac{[D_2O] [H_2]}{[H_2O] [D_2]} = \frac{K_3^2 K_1}{K_2}.$$
 (4)

$$H_2O + D_2 \rightleftharpoons HDO + HD, \quad K_5 = \frac{[HDO] [HD]}{[H_2O] [D_2]} = K_3K_1 \quad .$$
 (5)

$$HDO + HD \Rightarrow D_2O + H_2, \quad K_6 = \frac{[D_2O] [H_2]}{[HDO] [HD]} = \frac{K_3}{K_2} \quad . \quad (6)$$

$$D_2O + HD \rightleftharpoons HDO + D_2, \quad K_7 = \frac{[HDO] [D_2]}{[D_2O] [HD]} = \frac{K_2}{K_3K_1}$$
 (7)

It is possible to derive the constant K_3 from the experimental results, provided K_1 and K_2 are known, in the following manner.

In a temperature region in which the rotational motion of the molecules is fully excited and the vibrational motion is not yet excited the equilibrium constants K_1 and K_2 are given by

$$-\ln K_{1} = \frac{2\epsilon_{\rm HD} - \epsilon_{\rm H_{s}} - \epsilon_{\rm D_{2}}}{RT} - \frac{3}{2} \ln \frac{M_{\rm HD}^{2}}{M_{\rm H_{s}} \cdot M_{\rm D_{s}}} - \ln \frac{I_{\rm HD}^{2}}{I_{\rm H_{s}} \cdot I_{\rm D_{s}}} - \ln 4 \quad (8)$$

$$-\ln K_{2} = \frac{2\epsilon_{\rm HDO} - \epsilon_{\rm H_{2}O} - \epsilon_{\rm D_{2}O}}{RT} - \frac{3}{2} \ln \frac{M_{\rm HDO}^{2}}{M_{\rm H_{2}O} \cdot M_{\rm D_{2}O}} - \ln \frac{\tilde{I}_{\rm HDO}^{2}}{\tilde{I}_{\rm H_{2}O} \cdot \tilde{I}_{\rm D_{2}O}} - \ln 4 \quad (9)$$

M and I designating the masses and moments of inertia of the corresponding molecules in the case of water \overline{I} represents $\sqrt{I_{A} \cdot I_{B} \cdot I_{C}}$, where I_{A} , I_{B} and I_{C} are the three moments of inertia of the water molecule and ϵ the zero point energy given by

$$\epsilon = hc \left(\frac{1}{2}\omega - \frac{1}{4}\omega\chi\right) \qquad . \qquad . \qquad . \qquad (10)$$

 $h = Planck's constant, c = velocity of light, \omega = vibrational frequency$ and ωx = the anharmonicity constant; in the case of water we have to consider the three vibration frequencies ω_{σ} , ω_{π} , ω_{δ} and put for the zero point energy:

$$\epsilon = hc \left[\left(\frac{1}{2} \omega_{\sigma} - \frac{1}{4} \omega_{\sigma} x_{\sigma} \right) + \left(\frac{1}{2} \omega_{\pi} - \frac{1}{4} \omega_{\pi} x_{\pi} \right) + \left(\frac{1}{2} \omega_{\delta} - \frac{1}{4} \omega_{\delta} x_{\delta} \right) \\ - \frac{1}{4} \omega_{\sigma \pi} x_{\sigma \pi} - \frac{1}{4} \omega_{\sigma \delta} x_{\sigma \delta} - \frac{1}{4} \omega_{\pi \delta} x_{\pi \delta} \right] \quad (IOa)$$

The term ln 4 is introduced since symmetrical molecules are transformed into unsymmetrical ones.

 K_1 was derived by Urey and Rittenberg¹ using the known mass, zero point energy and moment of inertia of H₂ and the values for the molecules HD and D₂ calculated from the mass of D according to the general formulæ for the isotopic effect in molecular spectra. The formula obtained

$$\log K_1 = -\frac{34}{T} + 0.6276 \qquad . \qquad . \qquad (11)$$

$$2\epsilon_{\rm HD} - \epsilon_{\rm H_2} - \epsilon_{\rm D_2} = \Delta E_1 = -155 \text{ cal.},$$

using the numerical values, was proved experimentally by Rittenberg, Bleakney and Urey.⁸

The constant K_2 was calculated by Topley and Eyring ⁹ using a set

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⁸ Rittenberg, Bleakney and Urey, J. Chem. Physics, 2, 48, 1934.
⁹ Topley and Eyring, J. Chem. Physics, 2, 217, 1934.

of frequencies and moments of inertia for the molecules HDO and D₂O derived half-empirically, and is given by

$$\log K_2 = -\frac{34 \cdot I}{T} + 0.6231 \qquad . \qquad . \qquad (12)$$

$$2\epsilon_{\text{HD0}} - \epsilon_{\text{H}_20} - \epsilon_{\text{D}_20} = \Delta E_2 = -156 \text{ cal.}$$

Whereas there is very little doubt that the constant K_1 is correct within a few per cent. the uncertainty in the constant K_2 is somewhat greater, since both the vibrational frequencies and the anharmonicity constants for the molecules HDO and D₂O are not well known. Nevertheless we will see that the values for K_2 employed must be nearly the correct ones.

In order to obtain the equilibrium constant K_3 for the gaseous phase we have to calculate the D-content of the water vapour $V_{\rm D}$ from the Dcontent of the water $W_{\mathbf{D}}$ which is different from the former owing to the different vapour pressures of H_2O and D_2O . To calculate V_D from W_D we can assume as first approximation that the vapour pressure of HDO* will be the algebraic mean between that of H_2O and D_2O *i.e.*, the vapour pressure of mixtures of H₂O and D₂O varies linearly with the concentration of the components. Then

$$V_{\rm D} = \frac{W_{\rm D}}{W_{\rm H} \frac{p_{\rm H_2O}}{p_{\rm D_2O}} + W_{\rm D}} \qquad . \qquad . \qquad (13)$$

 p_{H_2O} and p_{D_2O} designating the vapour pressures of pure H₂O and pure $D_2O.\dagger$ According to Lewis and Macdonald ¹⁰ the ratio $p_{H_{10}}/p_{D_{20}}$ has the values opposite.

The actual calculation of the equilibrium constant K_3 is shown in Table III. Column 2, the D-content of the vapour $V_{\rm D}$, has been obtained by equation (13). The percentage of the molecules H₂, HD, D₂, H₂O, HDO and D₂O in the gaseous phase has been calculated using the relations

Temperature °C.	$P_{\rm H_2O}/P_{\rm D_2O}$
3	1·18 ‡
20	1·15
40	1·125
65	1·09
100	1·057

$$[HD] = -\frac{K_1}{4-K_1} + \sqrt{\left(\frac{K_1}{4-K_1}\right)^2 + \frac{4K_1}{4-K_1}G_D \cdot G_H} \quad . \quad (I4)$$

$$[D_2] = G_D - \frac{1}{2}[HD]$$
 (15)

$$[H_2] = G_H - \frac{1}{2}[HD]$$
 (16)

* This compound does not exist alone in the liquid phase, since the equilibrium

H₂O + D₂O \rightleftharpoons 2HDO is immediately established by ionisation. [↑] Practically the same result is obtained if one assumes, *cf*. Topley and Eyring,⁹ that the vapour pressure of HDO is the geometric mean of those of H₂O and D₂O and the vapour pressure of a mixture of H₂D and D₂O is given by

$$p = \frac{1}{100} [(H_2O)p_{H_2O} + (HDO)p_{HDO} + (D_2O)p_{D_2O}],$$

the distribution of the molecules H_2O , HDO and D_2O in the liquid being governed by the same equilibrium as in the gaseous phase, namely, by the equilibrium 2.

Extrapolated.

¹⁰ Lewis and Macdonald, J. Amer. Chem. Soc., 55, 3057, 1934.

Per C	Cent, D	in the								-			
Water	. Vapo	ur. Gas.		Water.			Vapou	г.		Gas.			
W _D .	V _D .	G _D .	(HDO).	(H ₂ O).	(D ₂ O).	[HDO]. [H ₂ O]. [D ₂ O].	[HD].	[H ₂].	[D ₂].	K ₃ '.	K3.
20·5 25·9 41·0 66·8 73·6	18·4 23·2 37·5 63·6 70·8	7:4 9:8 17:9 38:5 46:8	31·4 36·8 45·9 42·2 37·2	63·8 55·7 36·1 12·1 7·8	4·8 7·5 18·0 45·7 55·0	29·I 34·3 44·6 44·0 39·5	67·0 59·65 40·2 14·4 9·4	3·9 6·05 15·2 41·6 51·1	13.5 17.36 28.5 45.2 47.2	85.85 81.52 67.85 38.9 29.6	0.65 1.12 3.65 15.9 23.2	3·12 3·10 3·02 3·01 2·99	2·76 2·70 2·64 2·63 2·64
											Mean	3.05	2.67

TABLE III.—TEMPERATURE 20° C.

with $K_1 = 3.27$ at 20° C., and the analogous relations for HDO, D₂O and H₂O with $K_2 = 3.22$ at 20° C.* In a similar way the equilibrium concentrations of HDO, D₂O and H₂O in the liquid have been calculated, assuming the same equilibrium constant K_2 for the liquid as for the gaseous phase. The equilibrium constants for the gaseous reaction

$$H_2O + HD \rightleftharpoons HDO + H_2 \\ K_3 = \frac{[HDO] [H_2]}{[H_2O] [HD]}$$

are listed in column 5.

together with the equilibrium constant

$$K'_{3} = \frac{(\text{HDO}) [\text{H}_{2}]}{(\text{H}_{2}\text{O}) [\text{HD}]}$$
 (17)

of the reaction

$$(H_2O)_{lig.} + [HD]_{gas} \rightleftharpoons (HDO)_{lig.} + [H_2]_{gas} \quad . \quad . \quad (17a)$$



samples of water of different D-content

As it will be observed the equilibrium constants calculated in this way are very nearly independent of the concentration, and give the mean value of 2.67 for the gaseous system and 3.05 for the water-hydrogen system at 20° C. In Fig. 2 the D-content of water vapour and of hydrogen in equilibrium with water of different D-content is shown graphically.

The experiments at other temperatures up to 100° C. have been evaluated in a similar way. The constants listed in Table IV. represent means of the values obtained in different series and with

* As an elementary calculation shows, K_s is identical with the ratio $\frac{G_{\rm H} \cdot V_{\rm D}}{G_{\rm D} \cdot V_{\rm H}}$ if $K_1 = K_s = 4$. That the values for this ratio listed in Table I. are nearly independent of the concentration is explained by the fact that K_1 and K_2 do not differ much from 4.

Table V. contains the results obtained at 450° C. when the vapour of heavy water was mixed with hydrogen.

The theoretical formula for the equilibrium constant K_3 is given by

$$-\log K_{3} = \frac{\epsilon_{\text{HDO}} + \epsilon_{\text{H}_{2}} - \epsilon_{\text{H}_{2}} - \epsilon_{\text{HD}}}{2 \cdot 3 RT} - \frac{3}{2} \log \frac{M_{\text{HDO}} \cdot M_{\text{H}_{2}}}{M_{\text{H}_{2}} \cdot M_{\text{HD}}} - \log \frac{I_{\text{HDO}} \cdot I_{\text{H}_{2}}}{I_{\text{H}_{2}} \cdot I_{\text{HD}}}$$
(18)

For the sum of the second and third term in this expression we obtain -0.1335 (using decimal logarithms) if we assume that the geometric configuration of

the water molecule is not changed when the H-atom is replaced by a D-atom. The value of ΔE_3 = $\epsilon_{H2O} - \epsilon_{H2}$ can be derived by comparison of the theoretical

TABLE IV.

not				
when ⁻ om is by a The <u>-</u>	Temperature °C.	$\frac{G_{\mathbf{H}} \cdot W_{\mathbf{D}}}{G_{\mathbf{D}} \cdot W_{\mathbf{H}}}.$	K ₃ '.	K ₃ .
$\begin{array}{c} \mathbf{\Lambda} E_{3} \\ \mathbf{\epsilon}_{\mathbf{H}_{3}} \\ \mathbf{c}_{\mathbf{n}} \\ \mathbf{c}_{\mathbf{n}} \\ \mathbf{c}_{\mathbf{n}} \\ \mathbf{c}_{\mathbf{n}} \\ \mathbf{b}_{\mathbf{y}} \\ \mathbf{c}_{\mathbf{n}} \\ $	3 40 65 100	3.6 2.8 2.6 2.2	3·46 2·64 2·57 2·13	2·97 2·46 2·37 2·00
otion1				

formula (18) with the experimental values for K_3 listed in Tables III., IV., and V. The ΔE_3 values calculated in this way vary somewhat about 750 cals. Fig. 3 shows that the equilibrium constants calculated on the basis of the formula

$$\log K_3 = \frac{750}{2 \cdot 3 RT} - 0 \cdot 1335$$
 . . . (18a)

are in very good agreement with the experimental values. Thus the heat of reaction of (3) is + 750 cals. at absolute zero and the free energy change ΔF° at 298.1° abs. 568 cals.

TABLE V.-TEMPERATURE 450° C.

Water Vapour.	Hydrogen.	
Per Per Per Per Cent. Cent. Cent. Cent. D. HDO. H ₂ O. D ₂ O.	Per Cent. Per Cent. Per Cent. D. HD. Hg	Per Cent. D ₂
13.7 23.4 74.6 2.0 12.8 22.2 76.1 1.7 53.1 49.0 22.4 28.6	12.7 22.0 76.3 11.8 20.7 77.85 46.9 49.2 28.5	I·7 I·09 I·45 I·10 22·3 I·26 Mean I·15

From $\Delta E_3 = 750$ cals. we obtain for $\epsilon_{H_{2}0} - \epsilon_{HD0} = 750 + 817 = 1567$ cals. as the difference in the zero point energies of the two water species H₂O and HDO. This difference in the zero point energies can also be calculated from spectroscopic data according to the formula 10*a*. Bartolomé and Clusius ¹¹ have recently investigated the infra-red spectrum of the molecules D₂O and HDO. The harmonic frequencies (in cm.⁻¹) deduced from the observed frequencies are listed in Table VI.

¹¹ Bartholomé and Clusius, Naturwiss., 22, 420, 1934; Z. Elektrochem., 40, 529, 1934.

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together with some frequencies calculated according to theoretical formulæ of Teller * 12 (in brackets).

The six anharmonicity constants ωx for the H₂O molecule are known from Mecke's 13 analysis of the infra-red spectrum to be 40, 72, 20, 100, 20 and 20 cm.⁻¹, respectively. Assuming that ωx varies with the square of the frequency in the isotopic molecule, as it is the case in diatomic



molecules, the anharmonicity constants can be calculated for the HDO and D₂O molecules. With these figures we obtain

 $\epsilon_{D_2O} = 9527$ cals. $\epsilon_{\rm H_2O} = 13097$ cals., $\epsilon_{\rm HDO} = 11393$ cals.,

and thus for the difference $\epsilon_{H_s0} - \epsilon_{HD0} = 1704$ cals.

This value does not differ very much from the experimental value of 1567 cals. The discrepancy of 127 cals. which is, however, certainly larger than the experimental error may be due to several causes : to

	ω _σ .	ω _π .	ωგ.
H ₂ O	3895	3803	1635
HDO	3844	(2848)	1424
D ₂ O	2850	(2707)	1218

TA	BL	Æ	VI.
	_		

the somewhat uncertain calculation of the zero point energy from the first vibrational frequencies, to small errors both in the determination of the vibrational frequencies of HDO and in the experimental measurements of $K_{\mathbf{3}}$ and to the incorrectness of the assumption that the binding energy in a molecule does not

change replacing a H-atom by a D-atom which has been made in the calculation of the equilibria. That the binding energy in the isotopic molecule may actually change was pointed out by Topley and Eyring⁹ for the water molecules and is made probable by the large isotopic shift observed in the electronic levels of OD by Johnston ¹⁴ and in those of HD observed by Jeppesen.¹⁵

* We are indebted to Dr. Teller for the calculation of these frequencies.

¹² E. Teller, Det. kgl. Danske Videnskabernes Selskab, 1934.

18 Mecke, Z. Physik, 81, 313, 1933.

¹⁴ Johnston, *Physic. Rev.*, **45**, 79, 1934.
¹⁵ Jeppesen, *Physic. Rev.*, **45**, 480, 1934.

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On the other hand we have no explanation for the discrepancy between the equilibrium constant $K'_3 = 3.8$ found by Bonhoeffer and Rummel³ and the value $K'_3 = 3.05$ (at 20° C.) found in this investigation although the former is the value in agreement with the zero point energies given above.

In addition it may be mentioned that the evaluation of K_3 is based upon the values of K_2 obtained from formula 12 which are to a certain degree unreliable. The value of K_3 is however not very sensitive to an alteration of K_2 and the actual calculation shows that smaller values for K_2 (e.g., 2.6, $\Delta E_2 = -280$ cals.) would lead to a smaller K_3 (higher values for K_2 are very improbable) but that in this case the calculated K_3 constants would show a marked shift with concentration. For this reason it is very likely that the values of K_2 actually used were nearly correct the more since the data of Table VI. give $\Delta E_2 = -162$ cals. The limit of error for ΔE_3 cannot exceed \pm 50 cals. even if we allow for the uncertainty in the value of K_2 .

We are very much indebted to Professor E. K. Rideal, F.R.S., for his interest in our work and to the Central British Fund for German Jewry and to Imperial Chemical Industries for a financial grant.

Summary.

The equilibrium constant of the reaction $H_2O + HD \rightleftharpoons HDO + H_2$

$$K_3 = \frac{[\text{HDO}] \cdot [\text{H}_2]}{[\text{H}_2\text{O}] \cdot [\text{HD}]}.$$

has been determined over the temperature range 3 to 450° C. The equilibrium constant in the gaseous state is 2.61 at 25° C. and varies with temperature according to the formula

$$\log K_{3} = \frac{750}{2 \cdot 3 RT} - 0.1335.$$

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