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Calculation of Equilibrium Constants and Activation Energies for Some Reactions Involving Various Isotopic Species of Hydrogen, Water, and Hydrogen Sulfide*

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In part I, by means of statistical-mechanical theory, equilibrium constants are calculated for exchange reactions of the various isotopic forms of hydrogen, water and hydrogen sulfide. The calculations are made over a range of temperature and show the temperature dependence of the reactions. Part II concerns itself with the calculation of activation energies for these various reactions. The computations show that the reactions fall into three main classes. Hydrogen or deuterium, and water or hydrogen sulfide, can be expected to react by a chain mechanism at about 500°C. Water and hydrogen sulfide can be expected to react by either a chain or bimolecular mechanism around 400°C, and the isotopic forms of water or hydrogen sulfide with themselves at 200 to 300°C by a bimolecular mechanism.

INTRODUCTION

ONE of the earliest and most interesting applications of deuterium in chemical research was the preparation of various isotopic molecules and a study of the reactions between them. Knowledge of the equilibria and rates of such reactions is of importance as a preliminary step towards an understanding of more general reactions. Previously many authors[1] have calculated equilibrium constants alone, but these computations are obviously incomplete in the absence of any information concerning the rate of attainment of the equilibrium. In part I of this paper we calculate equilibrium constants from statistical-mechanical theory, and in part II, activation energies have been calculated for many of these same reactions, and conclusions are drawn concerning probable mechanisms.

PART I. EQUILIBRIUM CONSTANTS

Procedure

Two methods for the theoretical calculation of equilibrium constants from a knowledge of molecular constant data have previously been used. One method is indirect and involves calculating ΔE° from spectroscopic data and combining it with a calculated ΔS° to obtain ΔF°, and finally finding K by means of the relation $\Delta F^\circ = -RT \log_e K$.[2]

The statistical-mechanical calculation is much more direct and elegant, and simply depends

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* Contribution from the department of chemistry, University of Wisconsin, Madison, Wisconsin.

[1] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933); J. Am. Chem. Soc. **56**, 1885 (1934); Crist and Dalin, J. Chem. Phys. **2**, 735 (1934); Farkas and Farkas, Proc. Roy. Soc. (London) **A144**, 467 (1934); T. Förster, Zeits. f. physik. Chemie **B27**, 1 (1934); Farkas and Farkas, Trans. Faraday Soc. **30**, 1071 (1934); Urey and Greiff, J. Am. Chem. Soc. **57**, 321 (1935).

[2] See for example, Giauque, J. Am. Chem. Soc. **52**, 4808 (1930); ibid. **52**, 4816 (1930); **54**, 1731 (1932); Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933); Johnston and Long, ibid. **2**, 389 (1934).

upon the fact that an equilibrium constant is expressible as a ratio of the product of the partition functions for the product and reactant molecules.[3] It has been used, for example, by Crist and Dalin and Urey and Greiff[1] and is the method we shall use in this article.

All of the reactions we consider are stoichiometrically bimolecular, with the same number of reactant and product molecules. We may write

$$A+B\rightleftharpoons C+D. \tag{1}$$

A, B, C, and D denote di- or triatomic molecules, and in every case C and D are merely different isotopic species of A and B. We have

$$K=F_{(C)}F_{(D)}/F_{(A)}F_{(B)}. \tag{2}$$

Here F denotes the complete partition function for the molecule in question. In practice it is easier to calculate a product of F ratios rather than a ratio of products. Urey and Greiff[1] have given equations for calculating the F ratios for di- and triatomic molecules, but their equations are quite special and only apply to isotopic molecules of the same symmetry number. It is perhaps of interest and importance to arrive at their equations by starting with perfectly general expressions, applicable to all kinds of molecules.

It is assumed that it is a good approximation to express the partition function of a molecule as a product of translational, rotational, and vibrational parts, i.e.,

$$\begin{aligned}&F(\text{diatomic molecule})\\&=F(\text{trans.})F(\text{rot.})F(\text{vibr.})g_m i_m\\&=\frac{(2\pi mkT)^{\frac{3}{2}}V}{h^3}\cdot\frac{8\pi^2 IkT}{\sigma h^2}\\&\qquad\cdot\frac{e^{(E_0-\frac{1}{2}hc\omega_0)/kT}}{(1-\exp -hc\omega_0/kT)}g_m\cdot i_m.\end{aligned} \tag{3}$$

The term $((2\pi mkT)^{\frac{3}{2}}V)/h^3$ is the partition function for three degrees of translational motion. V is the volume in which the molecule moves, and the other symbols have their usual meaning.

The expression $(8\pi^2 IkT)/\sigma h^2$ represents the partition function for two degrees of rotational freedom. I is the moment of inertia of the molecule and σ the symmetry number, or number of orientations of the molecule which are physically indistinguishable. σ is 2 for molecules of the type X_2 and 1 for molecules like XY.

The vibrational partition function is $(1-e^{-hc\omega_0/kT})^{-1}$, where ω_0 is the fundamental vibrational frequency of the molecule.

The term $\exp\,(E_0-\frac{1}{2}hc\omega_0)/kT$ occurs because the zero of energy is taken to be that of the atoms at 0°K rather than that of the molecule. The expression $\frac{1}{2}hc\omega_0$ is the zero-point energy of the system, and E_0 the total energy. $E_0-\frac{1}{2}hc\omega_0$ is the heat of formation of the molecule from its atoms at 0°K.

g_m is a weight factor arising from electron states, and i_m a factor arising from nuclear spins. All the molecules we shall consider are in singlet electronic states, so that $g=1$ and need not be in the expressions explicitly.

From Eq. (3) we have, for diatomic molecules,

$$\begin{aligned}\frac{F_{(C)}}{F_{(A)}}&=\frac{(2\pi m_C kT)^{\frac{3}{2}}V}{h^3}\cdot\frac{8\pi^2 I_C kT}{\sigma_C h^2}\,\frac{e^{(E_{0C}-\frac{1}{2}kc\omega_{0C})/kT}}{(1-e^{-hc\omega_{0C}/kT})}i_C\bigg/\frac{(2\pi m_A kT)^{\frac{3}{2}}V}{h^3}\cdot\frac{8\pi^2 I_A kT}{\sigma_A h^2}\,\frac{e^{(E_0-\frac{1}{2}hc\omega_{0A})/kT}}{(1-e^{-hc\omega_{0A}/kT})}i_A\\&=\left(\frac{m_C}{m_A}\right)^{\frac{3}{2}}\frac{\sigma_A}{\sigma_C}\,\frac{i_C}{i_A}\,\frac{I_C}{I_A}\,\frac{(1-e^{-(hc\omega_{0A}/kT)})}{(1-e^{-(hc\omega_{0C})/kT})}e^{-\Delta E/kT},\end{aligned} \tag{4}$$

where $\Delta E=(E_{0A}-\frac{1}{2}hc\omega_{0A})-(E_{0C}-\frac{1}{2}hc\omega_{0C})$.

For the case of isotopic molecules where $E_{0A}=E_{0C}$, ΔE simply becomes $\frac{1}{2}hc(\omega_{0C}-\omega_{0A})$. If we consider the special case where $\sigma_A=\sigma_C$ and $i_C=i_A$ Eq. (4) reduces to the equation given by Urey and Greiff. (Their paper, Eq. No. (12).) In the case of H_2, HD and D_2 we must use

$$\Delta E'=\left(E_{0A}-\tfrac{1}{2}ch\omega_{0A}+\frac{B_{0A}ch}{4}\right)-\left(E_{0C}-\tfrac{1}{2}hc\omega_{0C}+\frac{B_{0C}hc}{4}\right),$$

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[3] See for example, R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, 1929).

TABLE I. *Molecular constants for diatomic molecules.*

MOLECULE	M (g)	σ	i	I_1/I_2	ω_0	B_e
H_2	2.0162[5]	2	4	$(D_2/H_2) = 1.9987$[7]	4371[6]	60.564[6]
HD	3.0228[5]	1	6	$(D_2/HD) = 1.499$[7]	3786[6]	45.439[6]
D_2	4.0294[5]	2	9		3092.3[6]	30.312[6]

TABLE III. *F ratios for various isotopic molecules.*

RATIO \ T°K	273.1	298.1	373.1	473.1	573.1	1000
D_2/HD	10.4493	8.9538	6.4893	4.8860	4.0764	2.8487
HD/H_2	33.375	29.397	22.352	17.603	15.114	11.137
D_2/H_2	348.74	263.21	145.05	86.008	61.611	31.726
D_2O/HDO	35.387	26.740	14.555	8.7650	6.3324	3.4323
HDO/H_2O	87.837	69.772	41.868	27.749	20.795	11.798
D_2O/H_2O	3108.2	1865.7	609.39	243.21	131.66	40.497
D_2S/HDS	11.223	9.3075	6.1830	4.4295	3.5867	2.4402
HDS/H_2S	57.150	47.190	31.010	22.050	17.460	11.850
D_2S/H_2S	641.39	439.22	191.73	97.670	62.624	28.916

since the moments of inertia of the molecules are so small. The B_e terms arise from the interaction between rotation and vibration.[4] Eq. (4) then becomes

$$\frac{F_{(C)}}{F_{(A)}} = \left(\frac{m_C}{m_A}\right)^{\frac{3}{2}} \frac{\sigma_A}{\sigma_C} \frac{i_C}{i_A} \frac{I_C}{I_A} \frac{(1-e^{-(hc\omega_{0A})/kT})}{(1-e^{-(hc\omega_{0C})/kT})} e^{-\Delta E'/kT}. \tag{5}$$

The translational partition function for polyatomic molecules is the same as for diatomic molecules. There are, however, now three degrees of rotational freedom, and the rotational partition function becomes $[8\pi^2(8\pi^3ABC)^{\frac{1}{2}}(kT)^{\frac{3}{2}}]/\sigma h^3$, where A, B and C are the three moments of inertia for the molecule in question.

For a polyatomic molecule we therefore have in general,

$$F(\text{polyatomic molecule}) = \frac{(2\pi mkT)^{\frac{3}{2}}V}{h^3} \frac{8\pi^2(8\pi^3ABC)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{\sigma h^3} \frac{e^{(E_0-\frac{1}{2}\Sigma hc\omega_i)/kT}}{\pi_i(1-e^{-hc\omega_i/kT})} i. \tag{6}$$

TABLE II. *Molecular constants for triatomic molecules.*

MOLECULE	M (g)	σ	i	A_1/A_2[11]	B_1/B_2[11]	C_1/C_2[11]	ω_1	ω_2	ω_3
H_2O	18.0162	2	4	$\frac{(D_2O)}{(H_2O)} = 1.798$	1.998	1.929	1595.4[8]	3600[8]	3756.35[8]
HDO	19.0228	1	6	$\frac{(D_2O)}{(HDO)} = 1.357$	1.267	1.339	1380[9]	2810[9]	3720[9]
D_2O	20.0294	2	9				1179[9]	2666[9]	2784[9]
H_2S	34.0162	2	4	$\frac{(D_2S)}{(H_2S)} = 1.887$	1.998	1.965	1236[10]	2615[10]	2632[10]
HDS	35.0228	1	6	$\frac{(D_2S)}{(HDS)} = 1.296$	1.346	1.328	1078[10]	1910[10]	2619[10]
D_2S	36.0294	2	9				898[10]	1906[10]	1940[10]

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[4] Mulholland, Proc. Camb. Phil. Soc. **24**, 280 (1928); Sutherland, ibid. **26**, 402 (1930); Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

[5] F. W. Aston, Nature **137**, 357 (1936).

[6] Jeppeson, Phys. Rev. **44**, 165 (1933).

[7] Calculated.

[8] H. Sponer, *Molekulspektren* (I. Julius Springer, 1935), p. 78.

[9] H. Sponer, ibid., p. 144.

[10] Bailey, Thompson, and Hale, J. Chem. Phys. **4**, 625 (1936).

[11] These ratios have been calculated from formulas derived from definition. For H_2O and D_2O we have, if α is the angle between the $O-H$ or $O-D$ bonds,

$$\frac{B_{(D_2O)}}{B_{(H_2O)}} = \frac{m_{(D)}}{m_{(H)}}; \qquad \frac{A_{(D_2O)}}{A_{(H_2O)}} = \frac{m_{(O)}+2m_{(H)}}{m_{(O)}+2m_{(D)}} \frac{B_{(D_2O)}}{B_{(H_2O)}}; \qquad \frac{C_{(D_2O)}}{C_{(H_2O)}} = \frac{m_O+2m_D \sin^2\alpha/2}{m_O 2m_H \sin^2\alpha/2} \frac{A_{(D_2O)}}{A_{(H_2O)}};$$

m_H, m_D, and m_O are the masses of the hydrogen, deuterium and oxygen atoms, respectively. For H_2O, $\alpha = 104°40'$. For H_2S, $\alpha = 111°30'$.

TABLE IV. *Equilibrium constants for isotopic exchange reactions.*

REACTION	CONSTANT	$\Delta\Sigma\omega_i$(cm^{-1})	273.1°K	298.1°K	373.1°K	473.1°K	573.1°K	1000.0°K
(1) $H_2 + D_2 \rightleftharpoons 2HD$	$K_1=\frac{F(HD)}{F(H_2)}\frac{F(HD)}{F(D_2)}$	109	3.19_4	3.28_3	3.44_4	3.60_3	3.70_8	3.91_0
(2) $H_2 + D_2O \rightleftharpoons HD + HDO$	$K_2=\frac{F(HD)}{F(H_2)}\frac{F(HDO)}{F(D_2O)}$	696	0.943_0	1.09_9	1.53_6	2.00_8	2.38_7	3.24_5
(3) $HD + H_2O \rightleftharpoons H_2 + HDO$	$K_3=\frac{F(H_2)}{F(HD)}\frac{F(HDO)}{F(H_2O)}$	−456	2.63_2	2.37_3	1.87_3	1.57_6	1.37_6	1.05_9
(4) $H_2 + D_2S \rightleftharpoons HD + HDS$	$K_4=\frac{F(HD)}{F(H_2)}\frac{F(HDS)}{F(D_2S)}$	278	2.97_4	3.15_8	3.61_5	3.97_4	4.21_4	4.56_4
(5) $HD + H_2S \rightleftharpoons H_2 + HDS$	$K_5=\frac{F(H_2)}{F(HD)}\frac{F(HDS)}{F(H_2S)}$	−291	1.71_2	1.60_5	1.38_7	1.25_3	1.15_5	1.06_4
(6) $D_2 + HDO \rightleftharpoons HD + D_2O$	$K_6=\frac{F(HD)}{F(D_2)}\frac{F(D_2O)}{F(HDO)}=\frac{K_1}{K_2}$	−587	3.38_7	2.98_6	2.24_3	1.79_4	1.55_3	1.20_5
(7) $D_2 + H_2O \rightleftharpoons HD + HDO$	$K_7=\frac{F(HD)}{F(D_2)}\frac{F(HDO)}{F(H_2O)}=K_1K_3$	−347	8.40_6	7.79_2	6.45_2	5.67_9	5.10_1	4.14_2
(8) $HD + D_2S \rightleftharpoons D_2 + HDS$	$K_8=\frac{F(D_2)}{F(HD)}\frac{F(HDS)}{F(D_2S)}=\frac{K_4}{K_1}$	169	0.931_0	0.962_0	1.05_0	1.10_3	1.13_7	1.16_7
(9) $D_2 + H_2S \rightleftharpoons HD + HDS$	$K_9=\frac{F(HD)}{F(D_2)}\frac{F(HDS)}{F(H_2S)}=K_1K_5$	−182	5.46_9	5.27_0	4.77_9	4.51_3	4.28_3	4.16_0
(10) $D_2 + H_2O \rightleftharpoons H_2 + D_2O$	$K_{10}=\frac{F(H_2)}{F(D_2)}\frac{F(D_2O)}{F(H_2O)}=\frac{K_1K_3}{K_2}$	−1043	8.91_3	7.08_8	4.20_1	2.82_8	2.13_7	1.27_6
(11) $D_2 + H_2S \rightleftharpoons H_2 + D_2S$	$K_{11}=\frac{F(H_2)}{F(D_2)}\frac{F(D_2S)}{F(H_2S)}=\frac{K_1K_5}{K_4}$	−460	1.83_9	1.66_9	1.32_2	1.13_6	1.01_6	0.911_4
(12) $H_2O + D_2S \rightleftharpoons D_2O + H_2S$	$K_{12}=\frac{F(D_2O)}{F(H_2O)}\frac{F(H_2S)}{F(D_2S)}=\frac{K_3K_4}{K_2K_5}$	−583	4.84_6	4.24_8	3.17_8	2.49_0	2.10_2	1.40_1
(13) $D_2O + H_2O \rightleftharpoons 2HDO$	$K_{13}=\frac{F(HDO)}{F(D_2O)}\frac{F(HDO)}{F(H_2O)}=K_2K_3$	240	2.48_2	2.60_9	2.87_7	3.16_6	3.28_4	3.43_8
(14) $HDO + D_2S \rightleftharpoons D_2O + HDS$	$K_{14}=\frac{F(D_2O)}{F(HDO)}\frac{F(HDS)}{F(D_2S)}=\frac{K_4}{K_2}$	−418	3.15_3	2.87_3	2.35_4	1.97_3	1.76_5	1.40_7
(15) $D_2O + H_2S \rightleftharpoons HDO + HDS$	$K_{15}=\frac{F(HDO)}{F(D_2O)}\frac{F(HDS)}{F(H_2S)}=K_2K_5$	405	1.61_5	1.76_5	2.13_1	2.51_6	2.75_8	3.45_3
(16) $H_2O + D_2S \rightleftharpoons HDO + HDS$	$K_{16}=\frac{F(HDO)}{F(H_2O)}\frac{F(HDS)}{F(D_2S)}=K_3K_4$	−178	7.82_6	7.49_6	6.77_1	6.26_4	5.79_8	4.83_5
(17) $H_2O + HDS \rightleftharpoons HDO + H_2S$	$K_{17}=\frac{F(HDO)}{F(H_2O)}\frac{F(H_2S)}{F(HDS)}=\frac{K_3}{K_5}$	−165	1.53_7	1.47_9	1.35_0	1.25_8	1.19_1	0.995_7
(18) $D_2S + H_2S \rightleftharpoons 2HDS$	$K_{18}=\frac{F(HDS)}{F(D_2S)}\frac{F(HDS)}{F(H_2S)}=K_4K_5$	−13	5.09_2	5.07_0	5.01_5	4.97_8	4.86_8	4.85_6

Hence, for polyatomic molecules,

$$\frac{F_{(D)}}{F_{(B)}}=\frac{\dfrac{(2\pi m_DkT)^{\frac{3}{2}}V}{h^3}\,\dfrac{8\pi^2(8\pi^3A_DB_DC_D)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{\sigma_Dh^3}\,\dfrac{e^{(E_0-\frac{1}{2}hc\Sigma\omega0_{iD}/kT}i_D}{\pi_i(1-e^{-hc\omega0_{iD}/kT})}}{\dfrac{(2\pi m_BkT)^{\frac{3}{2}}V}{h^3}\,\dfrac{8\pi^2(8\pi^3A_BB_BC_B)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{\sigma_Bh^3}\,\dfrac{e^{(E_0-\frac{1}{2}hc\Sigma\omega0_{iB})/kT}i_B}{\pi_i(1-e^{-hc\omega0_{iB}/kT})}}$$

$$=\left(\frac{m_D}{m_B}\right)^{\frac{3}{2}}\frac{\sigma_B}{\sigma_D}\frac{i_D}{i_B}\left(\frac{A_DB_DC_D}{A_BB_BC_B}\right)^{\frac{1}{2}}\Pi_i\frac{(1-e^{-hc\omega0_{iB}/kT})}{(1-e^{-hc\omega0_{iD}/kT})}e^{-\Delta E/RT}, \tag{7}$$

where $\Delta E=(E_{0B}-\frac{1}{2}hc\Sigma\omega0_{iB})-(E_{0D}-\frac{1}{2}hc\Sigma\omega0_{iD})$.

For isotopic molecules $E_{0B}=E_{0A}$, and therefore $\Delta E=\frac{1}{2}hc(\Sigma\omega_{iD}-\Sigma\omega0_{iB})$. For the cases when $\sigma_B=\sigma_D$ and $i_D=i_B$ Eq. (6) reduces to the zone given by Urey and Greiff. (See their paper Eq. (13).) We now apply Eqs. (5) and (7) to various isotopic molecules. The molecular constants used in the calculations are given in Tables I and II, and the F ratios in Table III.

The values in Table III may be used to calculate equilibrium constants for various reactions, as shown in Table IV.

The equilibrium constants given in Table IV have all been calculated directly from the F ratios shown in Table III. Obviously they are not all independent. The first five, however, may be taken as independent, while the last thirteen may be shown to be expressible in terms of the independent set. Other authors have previously calculated some of the constants of reactions involving isotopic hydrogen and water molecules, but we have repeated these calculations for the sake of the consistency and completeness of Tables III and IV.

The temperature variation of all the equilibrium constants is very largely determined by the exponential term in Eqs. (5) and (7). The value of this exponential term depends upon the differences in zero point energies of the products and reactants. The column in Table IV headed $\Delta\Sigma\omega_i$ gives this difference in cm^{-1}. A study of the table shows clearly that when the zero point energy of the products is greater than that of the reactants (ΔE_0 is positive) the reaction is endothermic and the constant increases with increase in temperature as is to be expected. When the difference in zero point energy is negative, the reaction is exothermic and the constant is found to decrease with increase in temperature. Reaction (18) is interesting in that its change in zero-point energy is practically zero and it is found to be practically independent of temperature.

Crist and Dalin[12] have calculated $1/K_3$ at various temperatures. They used slightly different values for the molecular constants, but their equilibrium constants are in rough agreement with ours. Thus by interpolation we find $1/K_3 = 0.43$, 0.56, 0.66, 0.74, 0.82, 0.88, and 0.90 at $T = 300$, 400, 500, 600, 700, 800, and 900°K, respectively. Crist and Dalin calculated for the corresponding temperatures the values 0.35, 0.51, 0.60, 0.68, 0.74, 0.79, and 0.83. They find experimentally $1/K_3 = 0.71$ at 799°K.

TABLE V. *Constants used in constructing Morse potential energy curves.*

BOND	$r_0(A°)$	$\omega_0(\text{cm}^{-1})$	D(kcal.)
H−H	0.74[16]	4375[16]	102.4[16]
O−H	0.97[16]	3660[16]	113.1[16]
S−H	1.35[8]	2600[8]	87.0[17]
O−O	1.32[18]	1304[19]	34.3[20]
S−S	2.08[18]	510[21]	64.0[20]
S−O	1.7[18]	612[19]	71.0[20]

Farkas and Farkas[13] calculated our $K_1 = 3.27$ at 293.1°K in perfect agreement with our value. They found experimentally our $K_3 = 2.67$ at 293.1°K and $K_3 = 1.15$ at 723°K, while Topley and Eyring[14] calculate $K_{13} = 3.26$ at 298.1 and 3.40 at 373.1°K. These values are decidedly higher than ours, and the discrepancy must be sought in a different choice of constants.

The large values for the equilibrium constants at room temperature for reactions (7), (10), (16), and (18) are of interest as well as the large temperature coefficient of reaction (10). Classically the equilibrium constants should approach 1 or 4 as the temperature is increased. It is to be noted that there is considerable departure from the classical values at ordinary temperatures, particularly in the case of reactions (2), (6), (7), (10), (12) and (16).

PART II. ACTIVATION ENERGIES

A knowledge of these constants given in part I is alone incomplete in the absence of any information concerning the rate of the reactions, and we now proceed to calculate the activation

TABLE VI. *Activation energies for reactions between hydrogen, water and hydrogen sulfide.*

REACTION	ACTIVATION ENERGY
(1) $D_2 + H_2O \rightleftharpoons HDO + HD$	65.1 kcal.
(2) $D_2 + H_2S \rightleftharpoons HDS + HD$	66.4
(3) $D_2O + H_2S \rightleftharpoons HDO + HDS$	49.3
(4) $H_2O + D_2O \rightleftharpoons HDO + HDO$	29.3
(5) $H_2S + D_2S \rightleftharpoons HDS + HDS$	39.4
(6) $D + H_2O \rightleftharpoons HDO + H$	4.9
(7) $D + H_2S \rightleftharpoons HDS + H$	3.5
(8) $D_2 + OH \rightleftharpoons HDO + D$	8.7
(9) $D + HDS \rightleftharpoons SH + D_2$	9.7

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[12] Crist and Dalin, J. Chem. Phys. **2**, 548 (1934).

[13] Farkas and Farkas, Trans. Faraday Soc. **30**, 1071 (1934).

[14] Topley and Eyring, J. Chem. Phys. **2**, 217 (1934).

[15] For references see Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 167 (1935).

[16] R. S. Mulliken, Rev. Mod. Phys. **4**, 1 (1932).

[17] Calculated from data in Bichowski and Rossini's *Thermochemistry*.

[18] Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).

[19] Calculated.

[20] Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

[21] D. Clark, Chem. Rev. **11**, 231 (1932).

energies in order to draw some conclusions about the rates.

Calculations

The method of calculating activation energies is the so-called semiempirical system of Eyring which has been described elsewhere.[15] We simply give in Table V the constants used for constructing the various Morse curves.

Results

The reactions, with their calculated activation energies are given in Table VI.

All of the reactions given in Table IV, except number 1[22] are merely isotopic variations of reactions (1) to (5) in Table VI, and their activation energies will differ only slightly from the values given for the above reactions due to small differences in zero point energies.

For each of the above reactions (1) to (5) we must now consider, in addition to a bimolecular mechanism, a chain mechanism.

Reaction (1): $D_2+H_2O\rightleftharpoons HDO+HD$

If the mechanism of this reaction is bimolecular the activation energy is as given in Table VI. However, the following chain mechanism appears plausible:

$$D_2\rightleftharpoons 2D, \qquad (1)$$

$$D+H_2O\rightleftharpoons HDO+H, \qquad (2)$$

$$H+D_2\rightleftharpoons HD+D. \qquad (3)$$

By the usual methods[23] it may be shown that for this mechanism the over-all activation energy for reaction (1) is equal to the activation energy of reaction (2), plus one-half the heat of dissociation of D_2, or $A=52.3+4.9=57.2$ kcal. Reaction (1) is the thermal dissociation of deuterium.

Reaction (2): $D_2+H_2S\rightleftharpoons HDS+HD$

If this reaction is kinetically bimolecular the activation energy is as given in Table VI. The following chain mechanism is also possible:

$$H_2S\rightleftharpoons H+HS, \qquad (1)$$

$$H+D_2\rightleftharpoons HD+D, \qquad (2)$$

$$D+H_2S\rightleftharpoons HDS+H. \qquad (3)$$

For this mechanism $A=\frac{1}{2}D_{S-H}+A_2=43.5+9.1=52.6$ kcal. D_{S-H} signifies the heat of dissociation of the $S-H$ bond. The thermal dissociation of H_2S rather than D_2 is considered because the $S-H$ bond is weaker than the $D-D$ bond.

Reaction (3): $D_2O+H_2S\rightleftharpoons HDO+HDS$

The activation energy for the bimolecular mechanism of this reaction is given in Table VI. The following chain mechanism must also be considered.

$$H_2S\rightleftharpoons H+HS, \qquad (1)$$

$$H+D_2O\rightleftharpoons HDO+D, \qquad (2)$$

$$D+H_2S\rightleftharpoons HDS+H. \qquad (3)$$

Here $A=\frac{1}{2}D_{S-H}+A_2=43.5+6.3=49.8$ kcal.

Reaction (4): $H_2O+D_2O\rightleftharpoons HDO+HDO$

The activation energy for this reaction, if it is kinetically bimolecular, is given in Table VI. The following chain mechanism, however, also suggests itself.

$$H_2O\rightleftharpoons H+OH, \qquad (1)$$

$$H+D_2O\rightleftharpoons HDO+D, \qquad (2)$$

$$D+H_2O\rightleftharpoons HDO+H. \qquad (3)$$

Here $A=\frac{1}{2}D_{O-H}+A_2=56.6+6.3=62.9$ kcal.

Reaction (5): $H_2S+D_2S\rightleftharpoons HDS+HDS$

The activation energy for this reaction, if it has a bimolecular mechanism, is given in Table VI. However, the following chain mechanism is also possible.

$$H_2S\rightleftharpoons H+HS, \qquad (1)$$

$$H+D_2S\rightleftharpoons HDS+D, \qquad (2)$$

$$D+H_2S\rightleftharpoons HDS+H. \qquad (3)$$

$A=\frac{1}{2}D_{S-H}+A_2=43.5+4.4=47.9$ kcal.

The preceding results are summarized in Table VII.

Discussion

The energies given in Table VII lead to some interesting conclusions. Thus, we see that the reactions between D_2 and H_2O, or D_2 and H_2S, both involve high activation energies, and both would be expected to go via a chain mechanism in the vicinity of 500°C because in forming the activated complex in the bimolecular mechanism

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[22] Reaction (1) of Table IV is not included in Table VI because it has been thoroughly studied previously. See Hirschfelder, Eyring, and Topley, J. Chem. Phys. **4**, 170 (1936), and L. Farkas and E. Wigner, Trans. Faraday Soc. **32**, 708 (1936).

[23] Cf. Sherman, Quimby and Sutherland, J. Chem. Phys. **4**, 732 (1936).

TABLE VII. *Activation energies for molecular and chain mechanisms.*

Reaction	Activation Energy (kcal.)	
	Bimolecular Mechanism	Chain Mechanism
(1) $D_2 + H_2O \rightleftharpoons HDO + HD$	65.1	57.2
(2) $D_2 + H_2S \rightleftharpoons HDS + HD$	66.4	52.6
(3) $D_2O + H_2S \rightleftharpoons HDO + HDS$	49.3	49.8
(4) $H_2O + D_2O \rightleftharpoons HDO + HDO$	29.3	62.9
(5) $H_2S + D_2S \rightleftharpoons HDS + HDS$	39.4	47.9

the hydrogen atoms are very close together, hence the repulsions are very large, necessitating a high energy requirement for its formation.

The reaction between D_2O and H_2S would be expected to proceed at a somewhat lower temperature, around 450°C, and as far as the calculations can show, both the bimolecular mechanism and the chain mechanism are about equally probable.

The exchange reactions between light and heavy water or light and heavy hydrogen sulfide should occur around 200 to 300°C and the bimolecular mechanism leads to a much lower activation energy than the chain mechanism proposed.

In view of the comparative scarcity of kinetically bimolecular reactions now known, reactions (4) and (5) are especially interesting. It is of interest to point out qualitatively the factors which lead to low activation energy for a bimolecular reaction. In both reactions (4) and (5) the H and D atoms are small compared to the O and S atoms. This means that in the activated complex, the H and D atoms are comparatively far apart, and hence the repulsion between them is small. Also, the O—O and S—S bonds are rather weak, so that the repulsions between these atoms are also rather small. These small repulsions lead to a comparatively stable activated complex, and hence a low activation energy.

It must be remembered that the above conclusions are really valid only under rather special conditions. The calculations apply to the reactions when they are carried out in the gas phase in the absence of catalysts such as walls, oxygen, moisture, light, impurities, etc. Also, the conclusions concerning mechanisms apply only when the reaction is far removed from equilibrium—i.e., at the beginning of the reaction. Moreover, the particular radical mechanisms suggested, although the most plausible, are not necessarily unique. For example, in reaction (5), it might be possible to postulate a free radical mechanism which leads to an activation energy lower than 39.4 kcal., although no such mechanism yet suggests itself.

There are several experimental studies of exchange reactions between deuterium and water, and between light and heavy water, but these have all been carried out catalytically.[24]

Conclusions

Equilibrium constants for various isotopic exchange reactions between hydrogen, water and hydrogen sulfide have been calculated. In the gas phase and in the absence of catalysts the various types of reactions considered fall into three classes:

1. The exchange reactions between isotopic species of hydrogen and water, and hydrogen and hydrogen sulfide will occur at high temperatures (500°C) and via chain mechanisms.
2. The exchange reactions between isotopic species of water and hydrogen sulfide will occur around 400°C and via a bimolecular and chain mechanism.
3. The exchange reactions between various isotopic species of water, and of hydrogen sulfide will occur around 200 to 300°C and via a bimolecular mechanism.

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[24] Bonhoeffer and Rummel, Naturwiss. **22**, 45 (1934); L. Farkas and A. Farkas, Trans. Faraday Soc. **30**, 107 (1934); A. Farkas and L. Farkas, J. Chem. Phys. **2**, 468 (1934); A. Farkas, Trans. Faraday Soc. **32**, 922 (1936).