INTERCHANGE EQUILIBRIUM BETWEEN ACETYLENE AND HEAVY WATER.

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The interchange equilibrium of the reaction,

$$C_2H_2 + HDO_{liq} = C_2HD + H_2O_{liq} \qquad (1),$$

has recently been studied experimentally by Gillespie and Reyerson⁽¹⁾⁽²⁾. We calculated the equilibrium constant K_l from existing spectroscopic data and found an excellent agreement with the experimental value.

K_g of the gas reaction, $C_2H_2 + HDO_{gas} = C_2HD + H_2O_{gas}$, can be expressed in term of molecular constants. Assuming that the rotational degree of freedom is fully excited and, according to Urey⁽³⁾, that the interatomic potential energy is not affected by isotopic replacement, we have

$$\log K_g = -\frac{\Sigma\varepsilon_0}{kT} + \frac{3}{2}\log\frac{M_{C_2HD}M_{H_2O}}{M_{C_2H_2}M_{HDO}} + \log\frac{I_{C_2HD}}{I_{C_2H_2}}\left(\frac{I_{H_2O}}{I_{HDO}}\right)^{\frac{3}{2}} + \log\frac{Q_{C_2HD}\cdot Q_{H_2O}}{Q_{C_2H_2}\cdot Q_{HDO}} \qquad (2),$$

where $$\Sigma\varepsilon_0 = \sum_{C_2HD}^{3n-5}\frac{h\nu_0}{2} + \sum_{H_2O}^{3n-6}\frac{h\nu_0}{2} - \sum_{C_2H_2}^{3n-5}\frac{h\nu_0}{2} - \sum_{HDO}^{3n-6}\frac{h\nu_0}{2},$$

$$\frac{1}{2}\sum^{3n-5(6)}\nu_0 = \frac{1}{2}\sum^{3n-5(6)}\nu_e + \frac{1}{4}\sum_i^{3n-5(6)}\sum_j^{3n-5(6)} x_{ij},$$

ν_e is harmonic frequency, x_{ij} anharmonicity constant, $I = \sqrt[3]{I_A I_B I_C}$ mean moment of inertia, $Q = \prod^{3n-5}(1-e^{-\frac{h\nu_0}{kT}})^{-1}$ for acetylene, and $Q = \prod^{3n-6}(1-e^{-\frac{h\nu_0}{kT}})^{-1}$ for water molecule. The present calculation was based on the following spectroscopic data:

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(1) Reyerson and Gillespie, *J. Am. Chem. Soc.*, **57** (1935), 2250.

(2) Reyerson and Gillespie, *Ibid.*, **58** (1936), 282.

(3) Urey and Rittenberg, *J. Chem. Physics*, **1** (1933), 137. Urey and Greiff, *J. Am. Chem. Soc.*, **57** (1935), 321.

	C_2H_2	C_2HD	H_2O	HDO
Moment of inertia	23.50×10^{-40}(4)	27.90×10^{-40}(8)	I_A 1.03×10^{-40}(7) I_B 2.07 I_C 3.10	1.18×10^{-40}(7) 3.74 4.92
Fundamental frequency ($cm.^{-1}$)	ν_{s_2} 3372(4) ν_{s_1} 1974 ν_a 3288 δ_a 729* δ_s 618*	3350(5) 1860 2550 541(6)* 679*	ν_1 3654(7) ν_2 3756 ν_δ 1596	2720(7) 3750 1403

* Twofold degenerated.

Anharmonicity constants x_{ij} were taken from Mecke's analysis(9) for H_2O and from Herzberg's for C_2H_2(4)(10); x_{ij} for HDO and C_2HD were computed by assuming the proportionality, $x_{ij} \infty \nu_i\nu_j$; $\frac{1}{2}\Sigma\nu_e$, $\frac{1}{4}\Sigma x_{ij}$, and $\frac{1}{2}\Sigma\nu_0$ calculated from the original data are given below:

	C_2H_2	C_2HD	H_2O	HDO
$\frac{1}{2}\sum\nu_e$	5773 $cm.^{-1}$	5195 $cm.^{-1}$	4603 $cm.^{-1}$	4008 $cm.^{-1}$
$\frac{1}{4}\sum_{ij}x_{ij}$	52	45	35	26
$\frac{1}{2}\sum\nu_0$	5825	5240	4638	4034

We obtain therefore from expression (1)

$$\log K_g = -\frac{54}{0.434RT} - 0.524 + \frac{1}{0.434}\log\frac{Q_{C_2HD}\cdot Q_{H_2O}}{Q_{C_2H_2}\cdot Q_{HDO}} \qquad (3)$$

with $K_g = 0.62$ at 25°C.

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(4) Herzberg and Spinks, *Z. Physik*, **91** (1934), 386.
(5) Sutherland, *Nature*, **134** (1934), 775.
(6) Randall and Sleator, *Phys. Rev.*, **45** (1934), 124.
(7) Barker and Sleator, *J. Chem. Physics*, **3** (1935), 660.
(8) Herzberg, Patat and Spinks, *Nature*, **133** (1934), 951.
(9) Macke, *Z. Phys.*, **81** (1933), 445, 465.
(10) Herzberg and Funke, *Phys. Rev.*, **49** (1936), 100.

The last term of the expression gives a small correction arising from the small deformation frequencies of acetylene molecule.

K_l for the equilibrium (1) can readily be calculated by combining (3) and the constant K_w of the equilibrium,

$$H_2O_{gas} + HDO_{liq} = H_2O_{liq} + HDO_{gas} ,$$

determined by one of the authors(11). We have finally,

$$K_l = K_g K_w = 0.59 \text{ at } 25°C., \text{ where } K_w = 0.96 \text{ at } 25°C.$$

The agreement with the recent experimental data $K_l = 0.599$(2) at 25°C. is satisfactory.

One could also use other sets of frequencies due to different authors as given below:

Fundamental freq.		Harmonic freq.(13)		
C_2H_2(12)		H_2O		HDO
ν_{s_2}	3370	ν_1	3895	3844
ν_{s_1}	1975	ν_2	3803	2848
ν_a	3277	ν_δ	1635	1424
δ_a	729 *			
δ_s	600 *			

* Twofold degenerated.

The result is nearly unaltered by replacing ν_0's of water with those due to Clusius and Bartholomé ($K_{l\cdot 25°C.} = 0.62$) whereas one obtains $K_{l\cdot 25°C.} = 0.66$, if Mecke's value for acetylene were used instead of Herzberg's. Assignment of δ_s has been frequently under discussion(14), the discrepancy of the frequency between these authors being the chief cause of the above difference in theoretical values. Our result is in favour of the assignment $\delta_s = 618$ cm.$^{-1}$ rather than $\delta_s = 600$ cm.$^{-1}$ in agreement with Morino's theoretical results.

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(11) Horiuti and Okamoto, this Bulletin, **10** (1935), 282.

(12) Mecke, *Z. physik. Chem.*, B, **17** (1932), 1.

(13) Farkas and Farkas, *Trans. Faraday Soc.*, **30** (1934), 1071. Clusius and Bartholomé, *Z. Elektrochem.*, **40** (1934), 529. Teller, *Det Kg. Danske Vidensk. Selskab*, (1934).

(14) Morino, *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **26** (1934), 1; see also Morino and Mizushima, *Physik. Z.*, **18** (1935), 600.