

## Heavy Water Inert, Due to Low Association

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Citation: *The Journal of Chemical Physics* **2**, 107 (1934); doi: 10.1063/1.1749419

View online: <http://dx.doi.org/10.1063/1.1749419>

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was filled to about 60 cm pressure and sealed off. The reaction vessel was kept at the chosen temperature for a period about 15 times longer than would be necessary for ordinary hydrogen iodide to attain equilibrium. The reaction vessel was then pumped out through a break seal and the iodine and hydrogen iodide frozen out in traps with liquid air. The iodine and hydrogen iodide were dissolved in water and the solution analyzed for  $I_2$  and  $H^+$ . At no time were the gases in contact with anything but glass. The fraction decomposed,  $h$ , was calculated from the equation

$$h = 2[I_2]/(2[I_2] + [HI]),$$

where  $[I_2]$  is the moles of  $I_2$  at equilibrium, and  $[HI]$  the moles of  $HI$  at equilibrium. The results are given in Table I.  $h_B$  is the value Bodenstein<sup>2</sup> gives for ordinary hydrogen iodide.  $\Delta h$  is the difference in the fraction decomposed of the sample rich in deuterium iodide and pure protium iodide.

The concentrations of the 13.5 and 40.0 percent samples were determined by W. Bleakney on his mass-spectrograph.<sup>3</sup>

TABLE I.

Conc. $H^2$	$h$ exp.	$h$ calc.	$\Delta h$ exp.	$\Delta h$ calc.
$T = 398^\circ C$				
0.0%	0.20719	—	$h_B = 0.20703$	
13.5	0.20838	0.20878	0.00119	0.00175
$T = 468^\circ C$				
0.0	0.22724	—	$h_B = 0.22772$	
40.0	0.23287	0.23326	0.00563	0.00602
72.1	0.23877	0.23904	0.01153	0.01180

The concentration of the 72.1 percent sample was determined by burning 500 cc of hydrogen iodide and determining the concentration of deuterium in the resultant water by the interferometric method which will be published shortly by Crist, Murphy and Urey. They assume that the molecular volume of deuterium oxide is the same as protium oxide. However, if the mol volume is that claimed by G. N. Lewis, the concentration of the sample will be about 76.5 percent. A change of 1 percent in the concentration of the deuterium will change  $\Delta h$  by 0.00013. This uncertainty will, however, not apply to the 13.5 and 40.0 percent samples since the concentrations were determined by the mass-spectrograph. It is to be noted that all our  $\Delta h$ 's are lower than those calculated. It is doubtful, however, if this is significant since we estimate that our experimental error is about 0.00040 in  $\Delta h$ . If we assume that our concentration of deuterium in the last sample is 76.5 percent then the difference between the  $\Delta h$  exp. and  $\Delta h$  calc. will be about 0.00084. This seems to be definitely larger than our experimental error.

While this experiment was conducted in the gaseous phase there is no reason to doubt that similar deviations from the classical value of the equilibrium constant will be found for reactions in condensed systems.

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January 15, 1934.

<sup>2</sup> M. Bodenstein, Zeits. f. physik. Chemie **29**, 295 (1899).

<sup>3</sup> Bleakney, Phys. Rev. **34**, 157 (1929); **39**, 536 (1932).

### Heavy Water Inert, Due to Low Association

Lewis and MacDonald<sup>1</sup> have reported the viscosities of heavy water over a considerable range of temperature. The very important question arises as to the effect of the extra proton in the nucleus of hydrogen upon the associ-

ation of water. Bingham and Spooner<sup>2</sup> have given the temperature constants for ordinary hydrogen and for oxygen at 50, 100 and 200 rhes, as reproduced in Table I. As fluidities have been found to be additive, the temperature required to give ordinary water a fluidity of 200 rhes would be 131.6°K, provided that the water remained unassociated. As shown in Table I, the observed value (328.9°K) is very much higher, leading to an association of 2.50.

The fluidity of heavy water is quite different from the fluidity of ordinary water, so that it is necessary to conclude that the additional proton affects the fluidity of water and presumably therefore the temperature constant of fluidity. (See Fig. 1.) If this is so, the simplest assumption is that the effect is additive, so that if the constant of hydrogen is 59.3 at 200 rhes the constant for deuterium is 118.6°, for the same fluidity. This would lead to a higher calculated temperature of 250.2° required to give deuterium oxide a fluidity of 200 rhes, again on the *proviso* that the water in question is non-associated. This is in accordance with the observed fact that heavy water is more viscous than

TABLE I.

	50 rhes	100 rhes	200 rhes
Hydrogen temperature constant (Bingham and Spooner)	45.9	50.4	59.3
Oxygen temperature constant	13.9	13.6	13.0
Observed temperature K for ordinary water	269.7	293.3	328.9
Calculated temperature K for ordinary water	105.7	114.4	131.6
Association of ordinary water	2.55	2.56	2.50
Deuterium temperature con- stant	91.8	100.8	118.6
Observed temperature K for deuterium oxide	277.8	301.7	(336.7)
Calculated temperature K for deuterium oxide	197.5	215.2	250.2
Association of deuterium oxide	1.41	1.40	(1.34)

<sup>1</sup> Lewis and MacDonald, J. A. C. S. **55**, 4730 (1933).

<sup>2</sup> Bingham and Spooner, J. Rheology **3**, 221 (1932).

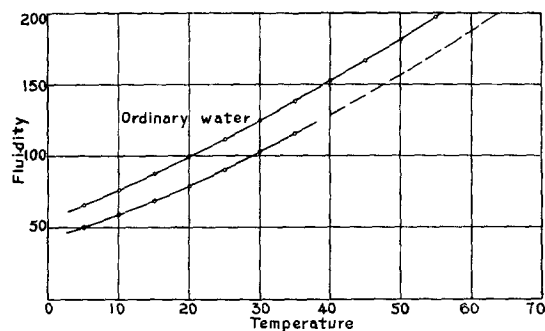


FIG. 1. Temperature-fluidity curve for deuterium oxide.

ordinary water. But even though heavy water is more viscous, the same method of calculation indicates that deuterium oxide is very much less associated than is ordinary water, 1.34 as compared with 2.50. If the oxygen of ordinary water possesses "residual valencies" as claimed by organic chemists, the additional protons in the deuterium would be expected to lower the free energy of the oxide. Deuterium oxide is not only less associated than ordinary water but the temperature coefficient of association of deuterium oxide is less, as proved by the association at 50 and 100 rhes. It has about the same association as such

mildly associated substances as methyl formate or propionaldehyde. Deuterium oxide may therefore be regarded as rather inert chemically. The increased molecular weight would be expected to raise the freezing-point and boiling-point but the increase in the boiling-point given as  $1.4^{\circ}$  might be considerably greater were it not for the lower association. The decrease in surface tension, dielectric constant and refractive index are unanimous in indicating a lower association. The inert character of deuterium oxide is demonstrated by the fact that in it starch fails to react with enzyme, that seeds fail to germinate, that spirogyra fails to develop and that animal life perishes. It is assumed that deuterium oxide is not poisonous, since it is present in ordinary water, but it is quite clear that the life processes noted above may involve chemical reactions. Almost all aqueous solutions involve hydration. It is therefore not surprising that sodium chloride and barium chloride are relatively insoluble in heavy water, and it might be expected that the difference will prove to be less marked in the case of potassium chloride, silver nitrate and mercuric chloride, which dissolve with less evidence of hydration.

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