The curve represents the values from equations (5) and (7) while the points represent the individual determinations of Hepburn and those of the authors. Inspection of Table I shows an average deviation of about 0.03% and a maximum deviation of 0.08% between the electromotive force values and the vapor pressure values of the authors; the corresponding deviations of Hepburn's values are 0.5 and 0.8%. The very satisfactory agreement between our values by vapor pressure and by electromotive force measurements leads us to believe that they are essentially correct, and that Hepburn's measurements must be subject to some sources of error which he has overlooked. The point of inflection which Hepburn obtained in his curve for the activity coefficient of barium chloride appears likewise to be due to the errors in his measurements of vapor pressure.

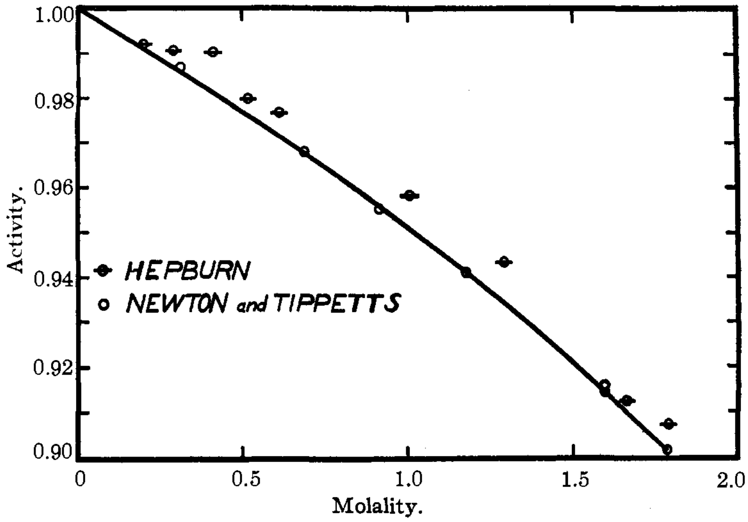

Fig. 2.—Activity of water in barium chloride solutions.

Summary

The vapor pressures of barium chloride solutions have been measured at 25° by an air saturation method similar to that used by Washburn and Heuse, and by Gibson and Adams.

The activity of water in barium chloride solutions has been calculated from the Hückel equation, using the constants obtained from the electromotive force measurements of Tippetts and Newton.

The results of the two methods are in very good agreement with each other, but not in agreement with those of Hepburn, which are internally somewhat inconsistent.

LAFAYETTE, INDIANA RECEIVED NOVEMBER 29, 1935

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Equilibria of the Reactions between Acetylene and Heavy Water at 25°[1]

BY L. H. REYERSON AND BRUCE GILLESPIE

In a previous communication[2] equilibrium values were reported for the exchange reaction $C_2H_2 + HDO \rightleftharpoons C_2HD + H_2O$. These values were obtained by using dilute solutions of deuterium oxide. Because of the low concentrations of deuterium the equilibrium values were calculated on the assumption that the other equilibria were involved to a negligible extent. Further work using concentrations varying from 28 to 97% of heavy water showed that the above assumption was not entirely allowable in this range and that the concentrations of all possible molecular species must be taken into account in making the calculations. The results of the additional work are here presented together with the calculated equilibrium constants for the equilibria involved.

The experimental method previously reported was refined somewhat in order to improve its accuracy. For example the bulbs were mounted on a rotor and continuously rotated during the run. This tended to keep the solution distributed over the walls of the vessel, thus leading to a more rapid establishment of equilibrium. The amount of heavy water solution introduced into each bulb was increased from about 1.0 to 2.0 cc. Density determinations made on this larger sample of water gave more accurate results. Readings on the manometer, which measured the pressure of acetylene in the bulbs, were made with a

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[1] This investigation was made possible by a grant from the Graduate School of the University of Minnesota.

[2] L. H. Reyerson and Bruce Gillespie, THIS JOURNAL, 57, 2250 (1935).

TABLE I

Initial percentage of D in water	Pressure C_2H_2, mm.	Moles of reactants at equilibrium H_2O	HDO	D_2O	C_2H_2	C_2HD	C_2D_2
97	570.75	0.00893	0.04135	0.05875	0.00402	0.01085	0.02048
97	357.84	.00525	.03372	.06642	.00151	.00580	.01564
55	618.24	.04091	.04981	.01860	.01806	.01324	.00680
55	373.76	.03606	.05108	.02220	.00970	.00835	.00503
50	732.51	.03947	.03634	.01027	.02559	.01413	.00547
50	355.44	.03594	.04756	.01931	.00963	.00779	.00442
50	351.73	.04022	.04986	.01896	.01061	.00786	.00408
28	353.64	.06498	.03712	.00650	.01535	.00518	.00123
28	353.38	.06519	.03706	.00646	.01552	.00530	.00127

cathetometer and the readings were corrected to 0° for the mercury manometer as well as the cathetometer. Van der Waals equation was used to calculate the amount of acetylene in the bulb. The constants used in making these various corrections were taken from "International Critical Tables." Making use of proper correction factors, the moles of acetylene introduced into the bulb were accurately determined. The change in the density of the water as a result of the exchange made it possible to calculate the number of moles of D which had been taken from the water by the acetylene.

The mechanism by which the deuterium exchange occurred at this temperature must have been due to the ionization of the acetylene molecule. One of the possible exchanges is $C_2H_2 \rightleftharpoons C_2H^- + H^+$ then $C_2H^- + D^+ \rightleftharpoons C_2HD$. As a result of the exchange however six different molecules exist at equilibrium in addition to the various ions. These six molecules are involved in seven possible equilibria. They are

$$
\begin{aligned}
&C_2H_2 + HDO \rightleftharpoons C_2HD + H_2O && (1)\\
&C_2HD + HDO \rightleftharpoons C_2D_2 + H_2O && (2)\\
&C_2H_2 + D_2O \rightleftharpoons C_2HD + HDO && (3)\\
&C_2HD + D_2O \rightleftharpoons C_2D_2 + HDO && (4)\\
&C_2H_2 + D_2O \rightleftharpoons C_2D_2 + H_2O && (5)\\
&D_2O + H_2O \rightleftharpoons 2HDO && (6)\\
&C_2D_2 + C_2H_2 \rightleftharpoons 2C_2HD && (7)
\end{aligned}
$$

In order to determine the molar concentrations of the six molecular species from the measured deuterium exchange it was necessary to know the equilibrium constants for reactions (6) and (7). K_6 has been determined by Topley and Eyring[3] and was found to be 3.26 at 25°. K_7 has been calculated by Glockler and Morrell[4] from Raman spectra and found to be 1.43 at 25°.

TABLE II

Initial percentage of D in water	Pressure C_2H_2, mm.	Time, hours	Equilibrium constants K_1	K_2	K_3	K_4	K_5
97	570.75	135	0.582	0.408	1.897	1.329	0.773
97	357.84	160	.599	.420	1.953	1.369	.820
55	618.24	114	.602	.422	1.963	1.375	.828
55	373.76	114	.607	.425	1.979	1.387	.842
50	732.51	160	.600	.420	1.955	1.370	.821
50	355.44	114	.611	.428	1.993	1.396	.853
50	351.73	227	.598	.419	1.949	1.365	.816
28	353.64	256	.591	.414	1.927	1.350	.798
28	353.38	116	.600	.420	1.956	1.371	.823
		Average	0.599	0.419	1.952	1.368	0.819

The measurement of the density of the water at equilibrium gives the amount of deuterium remaining after exchange. This value used together with K_6 makes it possible to calculate the amounts of H_2O, HDO and D_2O. The known amount of deuterium in the acetylene as determined by difference in the initial and final concentration of deuterium in the water used together with K_7 makes it possible to calculate the amounts of C_2H_2, C_2HD and C_2D_2. Following the above method the number of moles of each of the six molecular species involved in the various equilibria was calculated. The results are given in Table I. From these results the equilibrium constants for reactions (1), (2), (3), (4) and (5) at 25° were determined. These values are presented in Table II. The subscripts of K designate the constants for the reactions of the same number. Thus K_1 is the constant for reaction (1). It should be noted that pairs of duplicate experiments were run in which the time of reaction of one experiment was at least double that of the other. The constants in these cases showed little variation. In fact the constants for the longer timed experiments were slightly lower than those for the shorter time. Had equilibrium not been reached it should be expected that the K values in general would be larger when the experiments had run longer. It is believed that variations in the values of the constant for a given reaction are due to experimental errors.

In addition to the above experiments 97% heavy water was used to generate acetylene by allowing it to act on very pure calcium carbide.

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[3] Topley and Eyring, *J. Chem. Phys.*, **2**, 217–230 (1934).

[4] Glockler and Morrell, *ibid.*, **4**, 15 (1936).

This acetylene containing deuterium was used in two runs using water of normal deuterium concentration. An accident prevented an accurate determination of the exchange in the case of one of these experiments but in the other run the deuterium concentration in the water rose to over 30%. Assuming that the deuterium content of the acetylene was the same as the deuterium content of the water from which it was formed, the equilibrium constants were calculated as before. The results were as follows: $K_1 = 0.629$, $K_2 = 0.441$, $K_3 = 2.05$, $K_4 = 1.44$ and $K_5 = 0.904$. The assumption made is probably not the correct one and a change to 96 from 97% deuterium in the acetylene gives values for the constants which check the average values given in Table II very well. It seems very likely from other considerations as well as from experimental work that the deuterium concentration of the acetylene might well be less than the deuterium concentration in the water from which it was made. The results however are in sufficiently good agreement to establish the fact that equilibrium had been reached.

Discussion

The system under consideration is invariant at equilibrium and the amounts of the six molecular species will determine the equilibrium constants. Experimentally the amounts of H, D and C_2X_2 are determined, X of C_2X_2 being either H or D. Using this information together with the constants for equilibria (6) and (7) the above values were calculated. However an examination of the system shows that

$$(1) = {}^1/_2\,[(5) - (6) + (7)]$$
$$(2) = {}^1/_2\,[(5) - (6) - (7)]$$
$$(3) = {}^1/_2[(5) + (6) + (7)]$$
$$(4) = {}^1/_2\,[(5) + (6) - (7)]$$

If therefore the equilibrium constant of (5) were known in addition to the constants of (6) and (7) it would be possible to calculate the other four constants. From the above linear combinations we find that

$$K_1 = \sqrt{\frac{K_5 \times K_7}{K_6}} \qquad K_2 = \sqrt{\frac{K_5}{K_6 \times K_7}}$$
$$K_3 = \sqrt{K_5 \times K_6 \times K_7} \qquad K_4 = \sqrt{\frac{K_5 \times K_6}{K_7}}$$

It is of course possible to develop similar expressions using combinations of other constants.

The equilibrium constants are given to three places just as they came out in the calculations. We are not justified from the experimental technique in using constants to more than two decimal places. Taking the average value to two decimal places we have for the constants $K_1 = 0.60$, $K_2 = 0.42$, $K_3 = 1.95$, $K_4 = 1.37$ and $K_5 = 0.82$.

Summary

The equilibrium constants for the reactions between H_2O, HDO, D_2O, C_2H_2, C_2HD and C_2D_2 have been determined experimentally at 25°.

MINNEAPOLIS, MINNESOTA
RECEIVED DECEMBER 12, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Composition of Fatty Acid Films on Water Containing Calcium or Barium Salts

BY IRVING LANGMUIR AND VINCENT J. SCHAEFER

Dr. Katharine Blodgett[1] has shown that successive layers of fatty acids and fatty acid soaps can be transferred to glass or metal surfaces by raising and lowering these surfaces through the surface of water on which monomolecular fatty acid films have been spread. The ease in which such multimolecular films may be built up and the properties of the resulting films depend greatly on the *p*H of the water, the temperature, and particularly upon the presence of salts of divalent metals.

Very low concentrations of calcium and barium salts in alkaline water are sufficient to make the stearic acid films on the water solid. Dr. Blodgett has shown that the films skimmed off alkaline water containing calcium and barium leave a white solid residue when heated above 100°, whereas the stearic acid films skimmed off water containing no metallic salts melt at about 70°.

It is thus evident that the monomolecular films of fatty acids on water containing salts of alkaline earth metals contain these metals as constituents and that the multimolecular films transferred to solids are, under these conditions, essentially metallic soaps.

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[1] Blodgett, THIS JOURNAL, **57**, 1007 (1935).