fraction of decomposing aldehyde molecules which produce hydrogen gas increases linearly from 10% at λ 3130 to 31% at λ 2537.

Evidence is given which indicates that $RHCO + h\nu \longrightarrow RH + CO$ cannot represent the primary process in the dissociation of the aliphatic aldehydes, but that $RHCO + h\nu \longrightarrow R + HCO$ is in accord with experimental results.

LOS ANGELES, CALIFORNIA
RECEIVED NOVEMBER 20, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Activity of Water in Solutions of Barium Chloride[1]

BY ROY F. NEWTON AND EMERSON A. TIPPETTS[2]

Introduction

Hepburn[3] measured the vapor pressure of barium chloride solutions by a dew point method, and taking as a base the activity coefficient of a 0.5 M solution as calculated from the electromotive force determinations of Lucasse[4] he obtained from his measurements the activity coefficients of barium chloride in the more concentrated solutions. His results differed widely from those of Lucasse, and he emphasized a point of inflection in his curve in the neighborhood of the saturated solution, and deplored the fact that Lucasse's results did not extend to saturation. Since the results of our electromotive force measurements[5] at 25° are in close agreement with those of Lucasse, and show no indication of a point of inflection near saturation, it was considered desirable to reinvestigate the vapor pressure of barium chloride solutions.

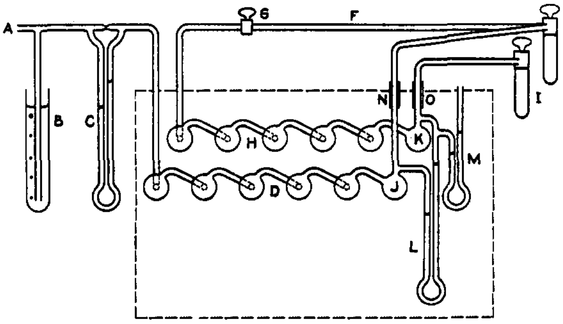

Fig. 1.—Apparatus for determination of vapor pressure.

Apparatus and Methods

The solutions used were prepared and analyzed as previously described by Tippetts and Newton.[5] The method of determination of vapor pressure was that of Washburn and Heuse[6] modified by Gibson and Adams[7] with slight further modifications.

Figure 1 shows an end view of the apparatus. The parts of the apparatus enclosed by the broken lines of the figure are surrounded by the water-bath, kept at 25.00 ± 0.01°. Cleaned air enters at A, at a pressure which is maintained constant by the head of water in B. The air passes through the flowmeter C and into a series of saturators D and J, containing water. The saturated air then passes through absorber E, returns through F and throttling stopcock G, into the saturators H and K containing solution, and thence through absorber I into the atmosphere. Saturators D and H are of the type described by Bichowsky and Storch[8] and are essentially the same as those used by Pearce and Snow.[9] Saturators J and K, which are simply large tubes half filled with liquid, are used to ensure final saturation with no measurable pressure drop in the saturator. Water manometers L and M, together with the barometer, serve to measure the pressure in J and in K. To prevent condensation in the tubes leading from the saturators to the absorbers, the air space surrounding these tubes is maintained two or three degrees warmer than the thermostat, and, in addition, rubber covered electric heating units N and O offset the cooling due to evaporation of water which splashes upon them. The absorbers E and I are U-tubes filled with anhydrous magnesium perchlorate. Each absorber is followed by a similar one to obviate the possibility of absorbing moisture from the solution following it or from the atmosphere.

The various parts of the apparatus were connected to one another in most places by means of ground glass joints; in a few places the connections were made by tightly fitting rubber sleeves within which the glass tubes were butted together so that scarcely any of the rubber was exposed to the saturated air. These were found satisfactory, although slight leakage resulted when the air passed through greater lengths of rubber tubing.

Check runs with varying rates of air flow showed that saturation was attained for rates as high as four liters per hour. The runs usually required about sixteen hours, in which time the gain in weight of the absorbers was approximately 1 g. each. During the runs, the barometer

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[1] Presented at the New York meeting of the American Chemical Society. April, 1935.

[2] Present address, du Pont Rayon Co., Buffalo, New York.

[3] Hepburn, *J. Chem. Soc.*, 550 and 1284 (1932).

[4] Lucasse. THIS JOURNAL. **47**, 743 (1925).

[5] Tippetts and Newton. *ibid.*, **56**, 1675 (1934).

[6] Washburn and Heuse, *ibid.*, **37**, 309 (1915).

[7] Gibson and Adams, *ibid.*, **55**, 2679 (1933).

[8] Bichowsky and Storch, *ibid.*, **37**, 2695 (1915).

[9] Pearce and Snow, *J. Phys. Chem.*, **31**, 231 (1927).

and the manometers were read hourly. Since the flow of air was nearly constant during a run, the arithmetic means of the pressure readings were used in the calculations.

Discussion of Results

The volumes of air passed through the saturators were not measured, but the vapor pressures were calculated from the known vapor pressure of pure water,[9] the total pressure at each of the two sets of saturators, and the weights of water absorbed, by means of the equation

$$\frac{p_0 - p_1}{p_1} = \frac{m_0(B_0 - p_0) - m_1(B_1 - p_0)}{m_1 B_1} \qquad (1)$$

in which p_0 and p_1 are the vapor pressures of pure water and of solution, respectively, m_0 and m_1 are the masses of water absorbed, and B_0 and B_1 are the total pressures at the saturators. Equation (1) may be derived from Dalton's law of partial pressures, but if water vapor deviates too much from the perfect gas law to apply Dalton's law, we can easily show that the terms of the left side of the equation may be replaced by the corresponding activities, if B_0 and B_1 are not very different, and if we accept the assumption of Lewis and Randall[10] that all gaseous solutions are very nearly perfect solutions.

An examination of equation (1) shows that the accuracy of the calculated activity is most dependent upon the accuracy of $m_0 - m_1$. Under the conditions of weighing, $m_0 - m_1$ is known with higher absolute precision than either m_0 or m_1, since nearly all of the most likely systematic errors in m_0 and m_1 cancel out in taking the difference; the error is believed to be less than 0.3 mg. This produces an error of about 0.04% or less in the activity; all other errors of measurement were of such order as to affect the result by less than 0.03%, and the values of a_1 from vapor pressures shown in Table I are believed to be in error by certainly less than 0.1%, and probably not over 0.07%.

Comparison with Results from Electromotive Forces

The activity of water in aqueous barium chloride was also obtained from the electromotive force measurements of Tippetts and Newton[5] by means of the equation

$$\mathrm{d} \log a_1 = -N_2/N_1 \, \mathrm{d} \log a_2 \qquad (2)$$

in which a_1 and a_2 are the activities of water and of barium chloride, respectively, and N_1 and N_2 are the corresponding mole fractions. For concentrations up to about 1 M the activity of barium chloride as determined by electromotive forces is well represented by the Hückel equation in the form

$$\text{og}\ a_2 = -\frac{3M\sqrt{c}}{1 + N\sqrt{c}} + 3Pc + 3 \log c + \log 4 \qquad (3)$$

in which c is the concentration in moles/liter, using at 25°, $M = 1.7529$, $N = 2.3306$ and $P = 0.1318$. Jones and Dole[11] found that the density of solutions of barium chloride may be represented at 25° by the purely empirical equation

$$d = 0.99707 + 0.1821\,c - 0.00407\,c^2 \qquad (4)$$

Expressing mole fractions in terms of concentrations by means of equation (4) and combining (2) and (3) and integrating, we obtain

$$\log a_1 = 0.006787\,x - 0.000118\,x^3 + 0.000004\,x^5 + 0.0075431\,x/(x + 0.42907) - 0.034916 \log (1 + 2.3306\,x) + 0.055813 \log (1 + 0.2799\,x) - 0.34444 \log (1 - 0.2799\,x) + 2.01214 \log (1 + 0.05209\,c) + 2.0247 \log (1 - 0.07836\,c) \qquad (5)$$

in which x is the square root of c.

For concentrations above 1 M, the activity coefficients of barium chloride can be represented within experimental error by the empirical equation

$$\log \gamma = -0.42665 - 0.1349\,m + 0.03003\,m^2 \qquad (6)$$

which was obtained from the data of Tippetts and Newton[5] above 1 M by the method of least squares. Combining with equation (2) and integrating, using $m = 1$ as a lower limit, we obtain

$$\log a_1 = 0.00231 - 0.02347\,m + 0.00036\,m^2 - 0.00108\,m^3 \qquad (7)$$

TABLE I

ACTIVITY OF WATER IN SOLUTIONS OF BARIUM CHLORIDE

Molality	a_1 from vapor pressure	a_1 from e. m. f.	Difference
0.3060	0.9868	0.9861	0.0007
.6848	.9681	.9677	.0004
.6848	.9680	.9677	.0003
.9143	.9555	.9555	.0000
1.1768	.9406	.9407	− .0001
1.1768	.9409	.9407	.0002
1.5890	.9155	.9154	.0001
1.5890	.9162	.9154	.0008
1.7880	.9021	.9022	− .0001

In Table I, values of the activity of water as determined from the vapor pressures of the authors are compared with those obtained from the electromotive force measurements by means of equations (5) and (7). In Fig. 2 the above values are graphically compared with those of Hepburn.[3]

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[10] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 225.

[11] Jones and Dole, THIS JOURNAL, 51, 1085 (1929).

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.

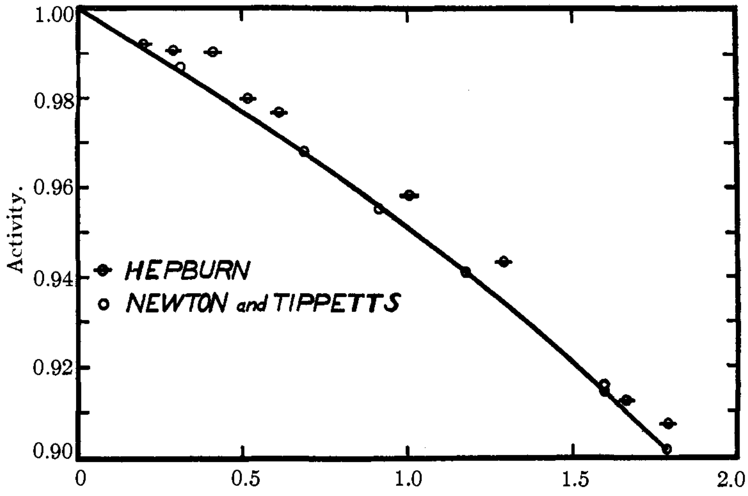

Fig. 2.—Activity of water in barium chloride solutions.

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).