still sufficient uncertainty to warrant serious consideration of the simpler mechanism involving H_2O_3 formation in reaction (10a).

If the mechanism does involve H_2O_3, reactions (10a), (10b) and (10b′) should be one-directional to give the observed rate laws. Accordingly it is estimated that the free energy decrease in reaction (10a), $H_2O_2(aq) + O_3(g) = H_2O_3(aq) + O_2(g)$, lies between 17 and 47 kcal. Even with the lower estimate, $H_2O_3(aq)$ is stable with respect to $HO + HO_2$. By means of this lower value, $\Delta F^{\circ}_{298.1}$ for $H_2O_3(aq)$ is calculated to be -270, and ΔH^{0}_{0} for $H_2O_3(g)$ is estimated to be -295 kcal.

Summary

Analysis of the rate data of Rothmund and Burgstaller on the interaction of ozone and hydrogen peroxide at 0° in 0.01 *N* sulfuric acid shows agreement with the relation $-d(O_3)/dt \div -d(H_2O_2)/dt = 1 + 5.2(O_3)/(H_2O_2)$. Their conclusions are confirmed: hydrogen peroxide is a catalyst for the decomposition of ozone, while ozone is not a catalyst for the decomposition of hydrogen peroxide. The limiting result at relatively low concentration of ozone is a bimolecular reaction with a specific rate of 50. (The units are moles per liter and minutes.) It is concluded that ozone and hydrogen peroxide react competitively with an intermediate substance formed in this bimolecular reaction, and that the ratio of the specific rates is 2.6 to 1.

Two mechanisms are considered, each of which explains the results satisfactorily. They involve intermediate formation of H_2O_3 or of $HO + HO_2$.

Attention is called to the quantitative results of Harcourt, published in 1862, on the reaction of potassium superoxide, KO_2, with dilute sulfuric acid and with water vapor. It is concluded that hydrogen peroxide is not catalytically decomposed in the presence of HO_2 and O_2^-, and that the specific rate of the reaction $2HO_2 = H_2O_2(aq) + O_2$, is much greater than that of either $2HO_2 = O_3 + H_2O(l)$ or $HO_2 + H_2O_2(aq) = HO + H_2O(l) + O_2$.

The decreases of free energy in the various intermediate reactions are estimated.

The conclusions presented in this paper differ from those published by Weiss in 1935.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Dissociation Pressures of Deuterates of Cupric Sulfate and of Strontium Chloride[1]

BY FRANCIS T. MILES AND ALAN W. C. MENZIES

The current interest in this subject is evidenced by the fact that, since the present work was completed, dissociation pressure measurements upon one of these deuterates have been reported by investigators in three other laboratories.[2-5]

Materials and Method.—The materials were from the same samples as those described elsewhere.[6] An additional check upon the concentration of the deuterium water was made possible by a melting point determination on a portion distilled from the deuterates to another part of the sealed apparatus employed.

The method used was a comparative one in which the difference of dissociation pressures of deuterates and the corresponding hydrates was measured in a differential tensimeter. This procedure favors cancellation of systematic error. The salts named were chosen for study because dissociation pressures of their hydrates are well established.[7-14] The manometric liquid employed was outgassed butyl phthalate, the suitability of which was tested by experiments which showed that significant solution and diffusion of water vapor through the manometer, or significant deuterium-hydrogen interchange, were both absent. Known weights of the salts, rendered anhydrous as described elsewhere,[6] were completely rehydrated within the apparatus by application of water in the vapor phase, at pressures falling short of those necessary to yield saturated solutions. Salts thus hydrated were then effloresced to a composition intermediate between those of the hydrates (or deuterates) whose equilibrium pressure was desired,[15] the amount of water removed for this purpose being measured in calibrated capillary tubes, later sealed off the apparatus. In a check experiment to measure the

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(1) The material of this article forms a portion of a thesis submitted by F. T. Miles in partial fulfilment of the requirements for the Ph.D. degree at Princeton University.

(2) Perpérot and Schacherl, *J. phys. radium*, [7], **6**, 439 (1935).

(3) Partington and Stratton, *Nature*, **137**, 1075 (1936).

(4) Bell, *J. Chem. Soc.*, 459 (1937).

(5) Schacherl and Behounek, *Nature*, **138**, 406 (1936).

(6) Miles and Menzies, THIS JOURNAL, **59**, 2392 (1937).

(7) Bolte, *Z. physik. Chem.*, **36**, 517 (1901).

(8) Menzies, THIS JOURNAL, **42**, 1951 (1920).

(9) Baxter and Lansing, *ibid.*, **42**, 419 (1920).

(10) Carpenter and Jette, *ibid.*, **45**, 578 (1923).

(11) Schumb, *ibid.*, **45**, 342 (1923).

(12) Menzies and Hitchcock, *J. Phys. Chem.*, **35**, 1660 (1931).

(13) Logan, *ibid.*, **36**, 1035 (1932).

(14) Collins and Menzies, *ibid.*, **40**, 379 (1936).

(15) The question of the tetrahydrate of cupric sulfate postulated by T. I. Taylor and others will be discussed elsewhere.

absolute dissociation pressure over penta- and trihydrates of cupric sulfate at 25°, a constant reading was reached in three hours which was a trifle below, rather than above, the accepted value of 7.8 mm. Details of procedure and precautions to be observed have been discussed elsewhere.[8,12,14] Temperatures were maintained constant to ±0.03°, and were compared within 0.02° with the scale of the Reichsanstalt. Extrapolation of pressures observed using 98.1% D_2O to values for 100% D_2O was accomplished by the method of Lewis and Cornish.[16] Our pressure values may well be inaccurate even beyond ±0.1 mm., owing to contingencies other than mere error of observation.[14]

Results

In obtaining the dissociation pressures of the deuterates by difference, we took those of the hydrates from the work of Collins and Menzies.[14] Their value for the pressure from strontium chloride hexahydrate dissociating at 25° was, incidentally, confirmed by an absolute measurement of pressure after cooling the deuterate side of a tensimeter to −75° and sealing it off. Since the temperature pressure relation for dissociating salt hydrates can be expressed, over the range here studied, by a linear equation in log p and $1/T$ within the error of experiment, observations were made at only two temperatures, 25 and 50°. In Table I the pressures for intermediate temperatures are computed by the equations

$$CuSO_4\cdot(5 \rightleftarrows 3)D_2O;\ \log p = 10.7427 - 2946.82/T \quad (1)$$

$$SrCl_2\cdot(6 \rightleftarrows 2)D_2O;\ \log p = 10.4662 - 2850.31/T \quad (2)$$

In Table I, which shows also the results of others, and hereafter, we shall refer to the system $CuSO_4\cdot 5H_2O \rightleftarrows CuSO_4\cdot 3H_2O + 2H_2O$ as A, to the corresponding deuterate system as B, to the system $SrCl_2\cdot 6H_2O \rightleftarrows SrCl_2\cdot 2H_2O + 4H_2O$ as C and to the corresponding deuterate system as D.

TABLE I

DISSOCIATION PRESSURES IN THE SYSTEMS A, B, C AND D IN MM.

	A	B	B	C	D	D
T, °C.	C. and M.[14]	M. and M.	Others	C. and M.[14]	M. and M.	Bell[4]
20	5.3	4.9	4.4 [5]	5.8	5.5	
25	7.8	7.2	5. [2] 6.655[3] 6.5 [4] 6.6 [5]	8.3	8.0	6.9
30	11.3	10.5	9.285 [3] 9.3 [4] 9.9 [5]	11.9	11.5	10.7
35	16.1	15.1	13.7 [4]	16.9	16.4	14.9
39	21.3	20.0	19.4 [4]	22.1	21.6	
40	22.8	21.4	21.0 [5]	23.6	23.1	20.4
50	44.0	41.9	42.1 [5]	44.8	44.1	
60	81.6	78.7	80.9 [5]	81.8	81.2	

The Heats Concerned.—The heats of dissociation for the above reactions in systems B and D as evaluated from equations (1) and (2) above and from the equations of Collins and Menzies[14] for systems A and C are: A, 13.2_2; B, 13.4_8; C, 12.8_6 and D, 13.0_4 kcal. for one mole of water, as obtained by applying the factor 4.575 to the coefficient of $1/T$ in the equations. If we deduct from these values the latent heats of vaporization[17] at 37.5° of the appropriate varieties of water, 10.36 and 10.67 cal., respectively, we arrive at the heats of hydration of the lower hydrates by one mole of liquid water. These are A, 2.8_6; B, 2.8_1; C, 2.5_0 and D, 2.3_7, the heat of this reaction being smaller for both deuterates than for the analogous hydrates.

In agreement with this relative order of magnitude for the cases A and B, Partington and Stratton[3] report the heat of hydration per mole of water for A as 2.780 and for B, 2.218 cal. On the contrary, Bell[4] finds the heat of dissociation in system B 9% higher than that in A. He states no heat values for system A but, using our values for this, we arrive at a heat of hydration for B of 3.7_4 cal., to compare with 2.8_6 cal. for A, showing a higher heat value in the case of the deuterate. The p-t data of Schacherl and Behounek[5] lead to heat values similar to Bell's for system B.

Discussion.—Table I exhibits sufficiently well the experimental results of this work, and makes clear that there is serious discordance among the results of the various observers. At 25°, three independent investigations show excellent concordance, with a pressure for system B near 6.6 mm. while our value is 7.2.[18] This 8% difference is hardly negligible in the study of theoretical significance, and therefore merits discussion.

Besides making measurements on various deuterate systems, Bell worked also with two hydrate systems, one of which, dissociating strontium chloride hexahydrate, has fortunately been studied, especially at 25°, by some of the most reliable workers in this field, to whom Bell does not refer. This makes possible a comparison of the results of others at 25° with Bell's pressure of 7.3 mm. Bolte[7] obtained 8.4, Baxter and Lansing[9] 8.37, Schumb[11] 8.52, and Collins and Menzies[14] 8.3_5. Frowein[19] reported 7.5, but his results are now

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[16] Lewis and Cornish, THIS JOURNAL, **55**, 2617 (1933).

[17] Miles and Menzies, *ibid.*, **58**, 1067 (1936).

[18] First reported by Miles, Shearman and Menzies as being 8% below the pressure for system A [*Nature*, **138**, 121 (1936)].

[19] Frowein, *Z. physik. Chem.*, **1**, 5, 362 (1887).

known[8] to be unreliable. Hüttig and Slonim[20] reported 6.35, but we understand, from a very courteous conversation, that they prefer our value to their own in this case. It therefore seems possible that some systematic error has given Bell a value 8.14 − 7.3 = 1.1 mm. low, and that the same error may vitiate his other results. The authors[2] of the value 5 mm. at 25° for system B warn us that this was merely a preliminary measurement which was later rectified.

It has been pointed out elsewhere[12,14] that the measurements at higher temperatures on such systems are more likely to be accurate, and agreement to 0.5% with our value is found at 50° in system B in work from another laboratory.[5] We may, therefore, take the pressure for this system at 50° as established at 41.9 mm. We can avoid lower temperature measurements in securing *t*–*p* values for another point, namely, the transition point of $CuSO_4(5 \rightleftarrows 3)D_2O$ in contact with saturated solution which is reported upon elsewhere[6] as 96.2°. This point on the *t*–*p* graph for saturated solutions is also a point on the dissociation pressure curve of system B. An estimate, good to 1% in the range 25–90°, of the aqueous pressure of saturated solutions of cupric sulfate pentahydrate, which have been measured experimentally with good concordance by Speranski[21] and by Collins and Menzies,[14] is obtained by multiplying by the factor 1.022 the pressure computed from the pressure of pure water and the measured solubility, using Raoult's law and assuming two ions. For saturated solutions of cupric sulfate pentadeuterate, whose pressures we measured from 20 to 50°, we found a similar factor, 1.03. Thus one can compute as 552 mm. the pressure of the saturated pentadeuterate solution at 96.2°, knowing the solubility of the salt and the vapor pressure of deuterium water. Error in the transition temperature would be of small significance, because the *p*–*t* curves of saturated solution and of system B have similar slopes in the region at and below the transition temperature. In this way we secure, by an independent method, a new pair of values of *t* and *p* for system B.

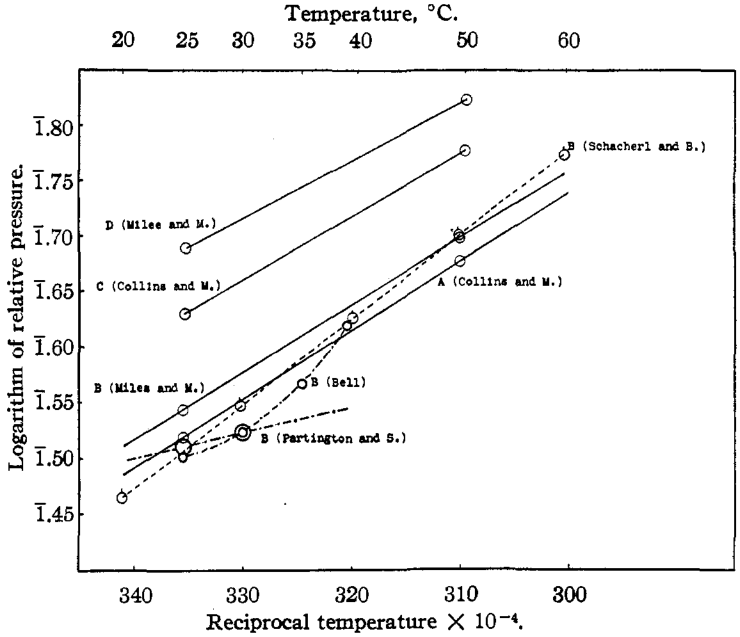

Fig. 1.—Logarithm of relative pressure against reciprocal temperature for the systems A, B, C, and D.

The measurements of Carpenter and Jette[10] and of Collins and Menzies[14] agree in showing that, for system A, the log *p* against $1/T$ line is sensibly straight over the temperature range 25 to 90°,—a particular case of a general truth. If we may assume that the same is true for system B, we may use the pressure data at 50 and 96.2° to establish a similar straight line for this system. This yields a pressure of 7.4 mm. at 25°, thus disfavoring the lower pressures reported by other workers.

Relative Pressures.—In comparing in graphical form the results of the various observers for system A, clarity is gained if one employs log *p* and $1/T$ as variables, since it is well known that, through moderate temperature ranges, the graphs so obtained for dissociating salt hydrates are very nearly rectilinear. A much more open scale will, however, be secured if one employs, instead of absolute dissociation pressures, rather the ratio of the dissociation pressure to the vapor pressure of pure water, of the appropriate variety, at the same temperature. Such ratios are fractional, and will here be called relative pressures. When plotted against reciprocal temperature, the logarithm of relative pressure should diverge from rectilinearity no more than does that of the vapor

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[20] Hüttig and Slonim, *Z. anorg. allgem. Chem.*, **18**, 65 (1929).

[21] Speranski, *Z. physik. Chem.*, **78**, 101 (1912).

pressure of water when plotted in like manner. Through the temperature range 20 to 60°, a straight line with log p and $1/T$ as variables reproduces the experimental pressure values for either variety of water with error not in excess of 0.5%.

In Table II are shown values for relative pressures in systems A and B, in computing which we employed the ordinary water pressures found in "International Critical Tables,"[22] the deuterium water pressures of Miles and Menzies,[16] the pressures for system A given by Collins and Menzies[14] and the various pressures for system B as reported in Table I.

TABLE II

RELATIVE PRESSURES IN PERCENTAGE FOR SYSTEMS A AND B COMPUTED FROM DATA OF VARIOUS OBSERVERS

	A	B	B	B	B
T, °C.	C. and M.	M. and M.	S. and B.	Bell	P. and S.
20	30.5	32.4	29.2		
25	32.9	35.0	32.1	31.6	32.3
30	35.5	37.7	35.6	33.4	33.4
35	38.3	40.6		39.9	
39	40.6	43.0		41.7	
40	41.2	43.6	42.7		
50	47.6	50.3	50.5		
60	54.6	57.7	59.3		

These values are graphed in the manner described in Fig. 1, where we have added also our lines for the relative pressures in systems C and D.

If the modest extrapolation, which we have shown in Fig. 1, from the values of Partington and Stratton be allowable by reason of their utilization of four significant figures in expressing pressure, we can state that the relative pressure lines for system B as derived from the experimental data of all the other observers intersect the relative pressure line for system A as graphed in every case, contrary to our finding in this regard. It will be seen that, although it is true that the relative pressure lines of the other workers pass close to the same point at 25°, this is by no means the case at other temperatures.

Summary

Dissociation pressures in the systems consisting of deuterium water vapor and cupric sulfate penta- and trideuterate and also strontium chloride hexa- and dideuterate are reported in the temperature range 25 to 50°, and compared with analogous hydrate pressures. The related heat values are deduced and compared with those of others, and attention is called to certain discrepancies of our values from those obtained in three investigations by other workers.

PRINCETON, N. J. RECEIVED NOVEMBER 15, 1937

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[22] "I. C. T.," Vol. III, 1926, p. 212.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORIES OF THE UNIVERSITY OF CHICAGO]

The Amine Catalysis of the Dealdolization of Diacetone Alcohol

BY F. H. WESTHEIMER AND HERZL COHEN

In their study of the dealdolization of diacetone alcohol catalyzed by amines, John Miller and Kilpatrick[1] observed that, at constant buffer ratio, the rate of the reaction increased with increasing buffer concentration. From this, they concluded that the aldol condensation is an example of general base catalysis, using these words in the sense defined by Brönsted.[2] Previously, however, French[3] had found that, in phenol–phenolate ion buffers, the rate is controlled by the hydroxyl ion concentration alone. The present work was undertaken to clear up this discrepancy.

For this purpose, the rate of the dealdolization of diacetone alcohol was measured in solutions buffered by methylamine and methylammonium chloride, by dimethylamine and dimethylammonium chloride, by trimethylamine and trimethylammonium chloride, and by triethylamine and triethylammonium chloride, all at 18° and at a constant ionic strength. The work of John Miller and Kilpatrick was verified and amplified with the first two amines. Molecular trimethylamine and molecular triethylamine, however, were found to be completely without effect on the rate of the reaction. The experimental results, together with the conclusions to be derived therefrom are presented in this paper.

Experimental

Apparatus and Method.—The rate of the reaction is easily and accurately measured dilatometrically.[4] The instrument employed was similar to that of Brönsted and

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[1] John Miller and Kilpatrick, THIS JOURNAL, **53**, 3217 (1931).

[2] Brönsted, *Chem. Rev.*, **5**, 231 (1927).

[3] French, THIS JOURNAL, **51**, 3215 (1929).

[4] Koelichen, *Z. physik. Chem.*, **33**, 129 (1900).