potassium ferrocyanide. From the calculated electrode potentials the activities of the ferrocyanide ion were computed using equation (1). The activity coefficients of the ferrocyanide ion for the several molalities were determined by dividing the activities by the corresponding molalities.

In addition the activities of the silver ion can be calculated from the relation

$$E_{298} = 0.7978 + 0.05915 \log a_{Ag^+}$$

where 0.7978 v. is the standard electrode potential for the silver electrode.[3] The activities of the ferrocyanide and silver ions being known, the activity product constant for silver ferrocyanide

$$K_a = (a_{Ag^+})^4 \times (a_{Fe(CN)_6^{----}})$$

can be evaluated. In Table IV calculations are brought together under headings which are self-explanatory.

If s is the molal solubility of silver ferrocyanide, $4s$ and s are the molal solubilities of the silver and ferrocyanide ions, respectively. Taking the solubilities equal to the activities, the equation

$$(4s)^4 \times s = 256s^5 = 1.546 \times 10^{-41}$$

is obtained. Solving for s, the value 2.27×10^{-9}, the molal solubility of silver ferrocyanide in water, is obtained.

TABLE IV

m	$a_{Fe(CN)_6^{----}} \times 10^2$	$\gamma_{Fe(CN)_6^{----}}$	$a_{Ag^+} \times 10^{10}$	$K_a \times 10^{41}$
0.01	0.8143	0.81	2.089	1.552
.02	1.518	.76	1.786	1.546
.04	2.742	.69	1.542	1.549
.06	3.686	.61	1.429	1.537
.08	4.585	.57	1.355	1.546
.10	5.357	.54	1.303	1.546
				1.546 Av.

Summary

From a series of measurements at 25°, the potential of the electrode $Ag,Ag_4Fe(CN)_6,Fe(CN)_6^{----}$ ($a = 1$) is found to be 0.1943 v.

The activity product constant and the molal solubility in water of silver ferrocyanide, 1.546×10^{-41} and 2.27×10^{-9}, respectively, have been calculated.

IOWA CITY, IOWA RECEIVED NOVEMBER 2, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Interaction of Ozone and Hydrogen Peroxide in Aqueous Solution

BY WILLIAM C. BRAY

In 1917 Rothmund and Burgstaller[1] concluded that hydrogen peroxide at low concentration is an efficient catalyst for the decomposition of ozone

$$2O_3 = 3O_2 \quad (1)$$

and that

$$H_2O_2 + O_3 = H_2O + 2O_2 \quad (2)$$

is the net reaction when the peroxide is present in large excess. The latter result is well supported by their four quantitative experiments[1] (p. 297), and by the work of others. Proof of the catalytic action of hydrogen peroxide depends on the results of their three rate experiments in the presence of dilute sulfuric acid; they determined the concentrations of both ozone and peroxide, and calculated the ratios of decomposed ozone to decomposed peroxide. These ratios decreased rapidly during each experiment. In spite of evident inaccuracies in the experimental data, it will be shown in this paper that the results are in fair agreement with the relation

$$\frac{v_1 + v_2}{v_2} = \frac{-d(O_3)/dt}{-d(H_2O_2)/dt} = 1 + 5.2\,\frac{(O_3)}{(H_2O_2)} \quad (3)$$

where v_1 and v_2 are the rates of reactions (1) and (2), respectively. The two rates and the two corresponding concentrations are the values at a given instant during an experiment. At high and low values of the concentration ratio, the limiting stoichiometric results are reactions (1) and (2), respectively. It is evident, therefore, that ozone at low concentration is not a catalyst for the decomposition of hydrogen peroxide in dilute acid solution.

Weiss[2] recently has plotted the Rothmund and Burgstaller ratios of the "mean consumption values," $\Delta O_3/\Delta H_2O_2$, against the ratios of the "corresponding mean values of the concentrations." Equation (3) was not revealed by this non-differential method; but the results did indicate that relative rates and relative concentrations might be related, and led me to estimate actual instead of average rates.

Table I contains the results of calculations made with the assistance of Mr. E. L. Derr. In expt. I $-d(H_2O_2)/dt$ could not be determined

(1) Rothmund and Burgstaller, *Monatsh.*, **38**, 295–303 (1917).

(2) Joseph Weiss, *Trans. Faraday Soc.*, **31**, 668–681 (1935).

TABLE I

RATES AT 0° IN 0.01 N SULFURIC ACID

	Time, min.	Concn. (10^3) Moles per liter (O_3)	(H_2O_2)	Rates (10^6) $(v_1 + v_2) = \frac{-d(O_3)}{dt}$	$v_2 = \frac{-d(H_2O_2)}{dt}$	Specific Rates $(\alpha + \beta) = \frac{(v_1 + v_2)}{(H_2O_2)(O_3)}$	$\beta = \frac{v_2}{(H_2O_2)(O_3)}$	Ratios Concn. $\frac{(O_3)}{(H_2O_2)}$	Rates $\frac{(v_1 + v_2)}{v_2}$
I	0	1.77	0.40	40.2	1.65	56.8	2.33	4.43	24.3
	5	1.58	.384	36.8	1.64	60.7	2.70	4.12	22.4
	14	1.32	.372	32.1	1.63	72.8	3.70	3.55	19.7
	24	1.00	.363	25.4	1.62	70.0	4.46	2.76	15.7
	39	0.630	.330	17.2	1.61	79.7	7.46	1.91	10.7
	56	.407	.302	12.1	1.60	98.4	13.0	1.35	7.6
II	0	1.50	0.785	115	11.5	97.7	9.77	1.91	10.0
	6	1.00	.720	66	8.6	91.7	11.9	1.39	7.68
	14	0.51	.660	34.5	6.0	102	17.8	0.772	5.75
	22	.35	.625	19.1	4.3	87.3	19.6	.560	4.45
	30	.205	.595	10.3	3.3	84.5	27.0	.345	3.12
	45	.108	.545	4.5	2.4	76.3	37.6	.198	2.04
III	0	1.08	1.69	153	35	84	19.2	0.640	4.37
	6	0.46	1.53	54	19.5	76.8	27.7	.301	2.78
	13	.25	1.44	23	10.3	62.2	27.6	.174	2.25
	20	.135	1.39	10	5.9	53.2	31.4	.097	1.90
	39	.045	1.32	2.5	2.4	42	40.5	.034	1.04

accurately, and was assumed to be nearly constant. In the remaining cases logarithms of the concentrations of ozone and of hydrogen peroxide were plotted against time, smooth curves were drawn, and values of first order specific rates were determined by measuring the slopes of many tangents. Calculations were continued until each set of specific rates gave a smooth curve in a time diagram. The rates in Table I were determined by multiplying Rothmund and Burgstaller's concentrations by the corresponding specific rate, and were found to be consistent with values obtained by drawing tangents to concentration–time curves.

Values of the concentration ratio, $(O_3)/(H_2O_2)$, and the corresponding values of the rate ratio $(v_1 + v_2)/v_2 = -d(O_3)/dt \div -d(H_2O_2)/dt$, are listed in the last two columns of Table I, and are plotted in Fig. 1. The line corresponds to equation (3). The ordinate intercept, 1, is exact; but, on account of uncertainties in the rates (especially v_2 in expt. I), the factor 5.2 is not accurate and may not be exactly constant. The conclusion

$$\frac{v_1}{v_2} = \frac{\text{Rate of Reaction 1}}{\text{Rate of Reaction 2}} = 5.2\ (O_3)(H_2O_2) \qquad (4)$$

is therefore presented only as a first approximation.

This relation signifies that the rate of each reaction depends on the concentration of a single intermediate substance, X; and that the principal (or only) processes involving the consumption of X are its reactions with O_3 and H_2O_2. It is therefore highly probable that the absolute rates of reactions (1) and (2) are determined by the rate of formation of X and its distribution between these two competing reactions.

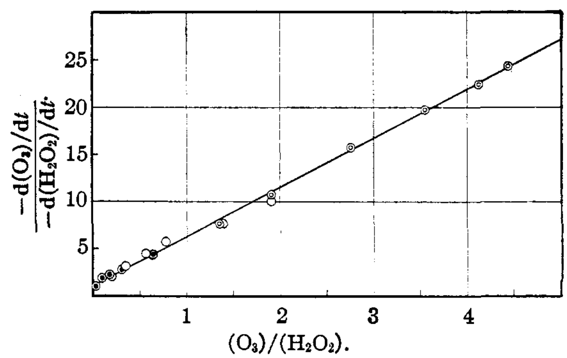

Fig. 1.—Rate ratio *vs.* concentration ratio: ◉, ○ and ● correspond to Expts. I, II and III, Table I.

A study of the absolute rates in Table I led to the adoption of the following simple theory, again as a first approximation.

$$\text{First step } H_2O_2 + O_3 \xrightarrow{k_1} X + \ldots. \qquad (5a)$$

$$\text{Second steps } X + O_3 \xrightarrow{k_3} \ldots. \qquad (5b)$$

$$\text{and } X + H_2O_2 \xrightarrow{k_5} \ldots. \qquad (5b')$$

$$\text{Net results } 2O_3 = 3O_2\ (1)$$
$$\text{and } H_2O_2 + O_3 = H_2O + 2O_2\ (2)$$

Arrows are used to designate the rate-determining steps. The concentration of X is small, and rapidly reaches a steady state

$$(X) = k_1(H_2O_2)(O_3)/[k_3(O_3) + k_5(H_2O_2)] \qquad (6)$$

Therefore the rate equations for reactions (1) and (2) are

$$v_1 = 2k_3(O_3)(X) = \frac{2k_1(H_2O_2)(O_3)}{1 + k_5(H_2O_2)/k_3(O_3)} = \alpha(H_2O_2)(O_3) \quad (7)$$

$$v_2 = k_5(H_2O_2)(X) = \frac{k_1(H_2O_2)(O_3)}{1 + k_3(O_3)/k_5(H_2O_2)} = \beta(H_2O_2)(O_3) \quad (8)$$

By comparing the ratio of equations (7) and (8) with equation (4) we find that

$$k_3/k_5 = 2.6 \text{ and } \alpha/\beta = 5.2(O_3)/(H_2O_2) \quad (9)$$

Reactions (1) and (2) may therefore be regarded as second order reactions. α and β are their specific rates and the sum, $\alpha + \beta$, is the specific rate for the total consumption of ozone. The values of the specific rates listed in Table I were calculated from the experimental results by means of the equations

$$\alpha + \beta = (v_1 + v_2)/(H_2O_2)(O_3) \text{ and } \beta = v_2/(H_2O_2)(O)_3$$

In Fig. 2 these values of $\alpha + \beta$ and of β are plotted against the concentration ratio, $(O_3)/(H_2O_2)$. As this ratio decreases toward zero, $\alpha +$

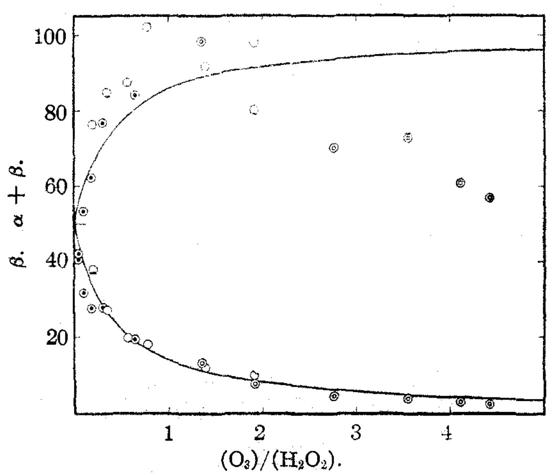

Fig. 2.—Specific rates *vs.* concentration ratio: ◉, ○ and ● correspond to Expts. I, II and III, Table I.

β and β approach the same limiting value, approximately 50, which, therefore, is the value of the specific rate, k_1, equation (5a). The smooth curves in Fig. 2 represent the theoretical values of $\alpha + \beta$ and β, calculated by means of the equations, *cf.* (6) to (9)

$$\beta = 50/[1 + 2.6(O_3)(H_2O_2)]$$

and

$$(\alpha + \beta)/\beta = 1 + 5.2(O_3)/(H_2O_2)$$

When the concentration ratio is less than 2 the agreement with the experimental results is as good as could be expected. The only measurements beyond this range are the first four of Expt. I. In these cases, as the proportion of peroxide becomes smaller, $\alpha + \beta$ decreases from the maximum value attained at equal concentrations of ozone and peroxide, instead of rising to the expected limit, $2k_1 = 100$. The corresponding values of β are also too low by about the same percentage amounts. These discrepancies may be due to errors in the measured concentrations or estimated rates. On the other hand, it may be necessary to modify the theory to explain the maximum in the values of $\alpha + \beta$, *e. g.*, by assuming an additional path for the decomposition of ozone, and lowering the specific rate, k_1, to about 35. It should also be noted that there is no experimental evidence that the rates would be unaltered by changes in the concentration of hydrogen ion. In spite of these uncertainties, however, it seems safe to conclude that a large part of the interaction of ozone and hydrogen peroxide may be explained without assuming the chain mechanism advocated by Weiss.[2]

Intermediate Compounds

For the intermediate substance, X, the choice lies between H_2O_3 and HO. Another possibility, H_2O_5, may be regarded as a short-lived transition state in reaction (10a), which corresponds to (5a).

$$H_2O_2 + O_3 \xrightarrow{k_1} H_2O_3 + O_2 \quad (10a)$$

$$H_2O_3 + O_3 \xrightarrow{k_3} H_2O_2 + 2O_2 \quad (10b)$$

$$\text{and } H_2O_3 + H_2O_2 \xrightarrow{k_5} H_2O_2 + H_2O + O_2 \quad (10b')$$

$$2O_3 = 3O_2 \ (1) \text{ and } H_2O_2 + O_3 = H_2O + 2O_2 \ (2)$$

In the two competing reactions, (10b) and (10b′), one molecule of H_2O_3 gives up one atom of oxygen to either ozone or peroxide, and one molecule of H_2O_2 is left as product. The present experimental results require the additional assumption that the direct decomposition of H_2O_3 into H_2O and O_2 is negligible in comparison with reactions (10b) and (10b′).

Oxides of the composition X_2O_3 have been prepared for cesium,[3] rubidium[3] (p. 416) and potassium.[4] The best evidence that these are pure substances is furnished by the results of experiments[4c] with potassium superoxide.[5] The reaction $2KO_2 = K_2O_3 + {}^1/_2O_2$ is reversible, and

(3) E. Rengade, *Ann. chim. phys.*, [8]. **11**, 375 and 391 (1907).

(4) (a) Ref. 3, p. 419; (b) de Forcrand, *Compt. rend.*, **158**, 991 (1914); (c) Kraus and Whyte, THIS JOURNAL, **48**, 1789 (1926).

(5) For proof that the formula is KO_2, not K_2O_4, see Neuman (and Pauling), *J. Chem. Phys.*, **2**, 231–233 (1935), and Kassatochkin and Kotow, *ibid.*, **4**, 458 (1936).

may be driven to completion by heating KO_2 in a metal container in a vacuum at a temperature in the neighborhood of its melting point; little if any K_2O_3 is decomposed under these conditions. If potassium trioxide is $4K^+ \cdot O_2^{=} \cdot 2O_2^-$, it is to be expected (see below) that treatment with acid will yield $2H_2O_2 + O_2$, as de Forcrand[4b] has claimed. If, on the other hand, the negative ion in the solid is $O_3^{=}$, we may obtain evidence for reactions (10b) and (10b′) by treating K_2O_3 with water in the presence and absence of hydrogen peroxide and of ozone. However, negative results in these experiments would not disprove the theory, since H_2O_3 could be formed as an unstable intermediate in the reaction between hydrogen peroxide and ozone in aqueous solutions even though the ion, O_3^{--}, is not the negative constituent of solid K_2O_3.

In the alternative mechanism, the much discussed free radicals, HO and HO_2, are formed as intermediates

$$H_2O_2 + O_3 \xrightarrow{k_1} HO + HO_2 + O_2 \quad (11a)$$

$$HO + O_3 \xrightarrow{k_3} HO_2 + O_2 \quad (11b)$$

$$\text{and } HO + H_2O_2 \xrightarrow{k_5} HO_2 + H_2O \quad (11b')$$

$$2HO_2 \xrightarrow{k_6} H_2O_2 + O_2 \quad (12)$$

$$2O_3 = 3O_2 \ (1) \qquad \text{and } H_2O_2 + O_3 = H_2O + 2O_2 \ (2)$$

In the competing reactions, (11b) and (11b′), an HO molecule receives an atom of oxygen from either ozone or hydrogen peroxide. The steady state concentration of HO_2 is determined by the equation, $(HO_2) = k_1(H_2O_2)(O_3)/k_6^{1/2}$; and that of HO by equation (6). The direct reaction

$$HO + HO_2 = H_2O + O_2 \quad (13)$$

is negligible in comparison with (11b) and (11b′). Rate laws (7) and (8) are also in agreement with a system of reactions in which O_3 and H_2O_2 react only with HO_2 and H_2O_2 is formed from HO

$$HO_2 + O_3 \longrightarrow HO + 2O_2 \quad (14b)$$

$$\text{and } HO_2 + H_2O_2 \longrightarrow HO + H_2O + O_2 \quad (14b')$$

$$2HO \longrightarrow H_2O_2 \quad (15)$$

This system was rejected in favor of (11) and (12) on account of the experimental results for the photochemical, mercury-sensitized reaction between hydrogen and oxygen gases. Bates[6] has concluded that the high yields of H_2O_2 can be accounted for by (12), but not by (15). Bonhoeffer and Harteck[7] also reject (15).

(6) Bates, THIS JOURNAL, **55**, 426–427 (1933); *J. Chem. Phys.*, **1**, 457–465 (1933).

(7) Bonhoeffer and Harteck, "Grundlagen der Photochemie," Steinkopff Verlag, Dresden, 1933, p. 260.

Decomposition of HO_2

Evidence that reaction (12) is rapid in aqueous solutions is furnished by the quantitative results published by Harcourt[8] in 1862. When pure potassium superoxide[5] is treated with water vapor, or dissolved in water acidified with sulfuric acid, oxygen gas and peroxide are formed in equimolal quantities. The reaction with an acid solution

$$2K^+O_2^-(\text{solid}) + 2H^+ = H_2O_2 + O_2 + 2K^+ \quad (16)$$

is rapid and practically free from side reactions. If we make the reasonable assumption that some of the superoxide ion, O_2^-, is converted into the weak acid, HO_2, during this reaction, we may conclude that HO_2 is not a catalyst for the decomposition of H_2O_2, and that reaction (14b′) is negligible in comparison with (12). Moreover the reaction assumed by Weiss[2]

$$2HO_2 = H_2O + O_3 \quad (17)$$

must also be negligible in comparison with (12).

Harcourt,[8] Holt and Sims,[9] and Kraus and Whyte[4c] prepared pure sodium peroxide, Na_2O_2, and could find no evidence of the existence of a compound with higher oxygen content. Harcourt was able to obtain a 96 to 99% yield of H_2O_2 in the reaction with a dilute acid

$$Na_2O_2(\text{solid}) + 2H^+ = H_2O_2 + 2Na^+ \quad (18)$$

The quantity of oxygen liberated during this reaction "is least when the peroxide is in the state of fine powder, and is projected little by little into a large excess of acidulated water."

On account of the evidence presented in the two preceding paragraphs, it seemed impossible to accept the experimental results of Weiss[2] that ozone is formed in considerable amount when "potassium and sodium superoxides" are decomposed with sulfuric acid. Examination of his analytical methods showed that he had made an incorrect assumption, *viz.*, that one mole of ozone reduces two equivalents of permanganate and liberates two moles of oxygen. The actual facts are: a dilute solution of ozone containing sulfuric acid does not reduce permanganate at low concentration, but does slowly oxidize manganese dioxide to permanganate without significant catalytic decomposition of the ozone. These conclusions are based on a twenty-two hour experiment of Rothmund and Burgstaller,[10] and are in agreement with qualitative results recently obtained in this Laboratory by Mr. H. F. Myers and Mr. G. Purvis.

(8) A. Vernon Harcourt, *J. Chem. Soc.*, **14**, 267–290 (1862).

(9) Holt and Sims, *ibid.*, **65**, 438 (1894).

(10) Rothmund and Burgstaller, *Monatsh.*, **34**, 683 (1913).

Decomposition of Ozone

The decomposition of ozone is rather slow in acid solutions at 0°, and the rate increases rapidly as the concentration of hydroxide ion is increased. Rothmund and Burgstaller[10] (pp. 665–692), in their careful and extensive rate measurements in dilute acid and alkaline solutions, obtained evidence that two reactions were taking place simultaneously, even though the results were not reproducible. Four years later[1] they attributed the lack of reproducibility to the presence of extremely small but variable amounts of hydrogen peroxide, and showed that the catalytic action of this impurity would account for a large part of the observed decomposition of ozone in 0.01 normal acid solution. Weiss[2] did not discuss this possibility when he used the kinetic data in dilute acid solutions to support his chain reaction theory for the decomposition of ozone. This omission, however, does not weaken his conclusion that there is a bimolecular reaction between ozone and hydroxide ion, $O_3 + OH^- = O_2^- + HO_2$. This part of his theory is supported by the results of his spectroscopic investigation, in which he demonstrated the presence of superoxide ion, O_2^-, in a solution of ozone in 7 M potassium hydroxide at −40°.

If we accept this result, and assume that the ionization constant of HOO is nearly the same as that of HOCl,[11] *ca.* $5(10^{-8})$, we may calculate approximately the equilibrium constant and free energy of reaction (17). I have chosen a value, $\Delta F^\circ_{298.1} = -23$ kcal., which is midway between the widely divergent values −13 and −33 that correspond, respectively, to the energy data of Haber and Weiss,[12] and of Weiss.[2] Weiss listed heats evolved and gave 34 kcal. for reaction (17).

Energy Relations

For the substances considered in this paper, I have collected values of the heat content at 0°K., and of the free energy of formation from gaseous atoms at 298.1°K. The data in Table II are believed to be accurate within 1 kcal., except in the cases HO and HO_2.

TABLE II

ENERGIES IN KILOCALORIES

	H_2 (g)	O_2 (g)	O_3 (g)	H_2O (g)	H_2O (l)	H_2O_2 (g)	H_2O_2 (aq)	HO (g)	HO_2 (g)
$-\Delta H^0_0$	102	117	141	219	...	253	...	116	169
$-\Delta F^\circ_{298.1}$	95	110	126	205	207	230	237	109	155

The value of $-\Delta H^0_0 = 116$ kcal. for HO is that calculated by Bates,[13] and $-\Delta F^\circ_{298.1}$ is assumed to be 7 units less; *cf.* the same difference for H_2 and for O_2. The values of $-\Delta H^0_0$ adopted by Haber and Weiss[12] and by Weiss[2] were probably 118 and 102 kcal.

The value of $-\Delta F^\circ_{298.1} = 155$ kcal. for HO_2 is based on the free energy estimated for reaction (17), and $-\Delta H^0_0$ is assumed to be 14 units greater; *cf.* the same difference for H_2O gas. The electromotive forces given by Haber and Weiss correspond to $-\Delta F^\circ_{298.1} = 160$ kcal. The estimate of Heitler[2] (p. 672) of the heat evolved in the reaction $H + O_2 = HO_2$ corresponds to $-\Delta H^0_0 = 177$, and that of Weiss to 162 kcal.

In the preceding paragraph no distinction was made between $HO_2(g)$ and $HO_2(aq)$, which is equivalent to assuming that $\Delta F^\circ_{298.1} = 0$ in the reaction $HO_2(g) = HO_2(aq)$. The additional uncertainty in the energy values for $HO_2(g)$, introduced by this assumption, is probably not greater than 1 or 2 kcal., since the values of $\Delta F^\circ_{298.1}$ for the reacting $H_2O_2(g) = H_2O_2(aq)$ and $O_2(g) = O_2(aq)$ are −6.7 and +4.0 kcal., respectively.

Standard free energies calculated by means of the data in Table II are listed in Table III. Except when otherwise stated, the substances are in the gaseous state.

TABLE III

STANDARD FREE ENERGIES AT 25°

Reaction no.	Equation	$-\Delta F^\circ_{298.1}$
1	$2O_3 = 3O_2$	78
2	$H_2O_2(aq) + O_3 = H_2O(l) + 2O_2$	64
11a	$H_2O_2(aq) + O_3 = HO + HO_2 + O_2$	11
11b	$HO + O_3 = HO_2 + O_2$	30
11b′	$HO + H_2O_2(aq) = HO_2 + H_2O$	16
12	$2HO_2 = H_2O_2(aq) + O_2$	37
13	$HO + HO_2 = H_2O(l) + O_2$	53
14b	$HO_2 + O_3 = HO + 2O_2$	48
14b′	$HO_2 + H_2O_2(aq) = HO + H_2O + O_2$	34
15	$2HO = H_2O_2(aq)$	19
17	$2HO_2 = H_2O(l) + O_3$	23

The great decreases in free energy shown in Table III signify that for each reaction in acid or neutral solutions the equilibrium lies far to the right. These energy data are consistent with the assumption that reactions (11a), (11b and 11b′) and (12), which constitute the alternative mechanism, are one-directional. This would not have been so if we had accepted the values of Weiss for HO and HO_2; for in the case of (11a) $\Delta F^\circ_{298.1}$ would then have been +9 instead of −11 kcal. There is

(11) Skrabal, *Monatsh.*, **70**, 168–192 (1937).

(12) Haber and Weiss, *Proc. Roy. Soc.* (London), **147A**, 349 (1934).

(13) Bates, *Z. physik. Chem.*, Bodenstein-Band, **329** (1931).

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

(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.