

Using  $k_0$  for ethylxanthic acid as 16.0 at 0° (Fig. 1) and 270 at 25°, we obtain an average coefficient per 10° rise of 6.75.

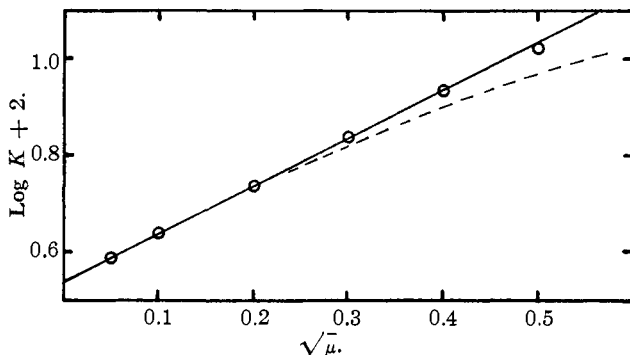


Fig. 4.—Variation in dissociation constant of methylxanthic acid with ionic strength (see Table XII): theoretical slope, +0.97.

### Summary

Measurements of the rate of decomposition of ethylxanthic acid have been made at 25° in acetic acid–acetate and aniline–anilinium ion buffers and the primary and secondary salt effects analyzed.

Previous measurements of the rates for ethyl and methylxanthic acids have been analyzed and shown to be complicated by salt effects. The influence of salts on the dissociation constants of these acids has been shown.

The temperature coefficient of the rate has been calculated and shown to be unusually high.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 91]

## THE DISSOCIATION PRESSURE OF SILVER OXIDE BELOW 200°

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### Introduction

Le Chatelier<sup>1</sup> first showed that the reaction  $\text{Ag}_2\text{O} = 2\text{Ag} + \frac{1}{2}\text{O}_2$  is reversible. Careful measurements of the equilibrium pressure were subsequently made by Lewis<sup>2</sup> over the temperature range 302–445°, and by Keyes and Hara<sup>3</sup> from 374 to 500°. Close agreement was shown between the results of these two investigations.

Aside from the considerable interest which attaches to this system

<sup>1</sup> Le Chatelier, *Z. physik. Chem.*, **1**, 516 (1887).

<sup>2</sup> Lewis, *THIS JOURNAL*, **28**, 139 (1906).

<sup>3</sup> Keyes and Hara, *ibid.*, **44**, 479 (1922).

*per se*, it represents an essential step in one of the available methods<sup>4</sup> of calculating the thermodynamically important value of the free energy of formation of water at 25°. For this purpose, however, it is necessary to extrapolate the observations over a range of temperature of about 300°, without adequate specific heat data to serve as a guide. In addition a correction must be made because of the fact that at the high pressures obtaining in the measurements of Lewis and of Keyes and Hara (20 to 390 atm.), the fugacity of oxygen differs markedly from its pressure, and the thermodynamic activity of the solid phases is also affected. For these reasons a determination of the silver oxide equilibrium at lower temperatures has appeared desirable.

In the present work it has been found that even at temperatures as low as 160–170°, finely divided silver slowly takes up oxygen in indefinitely large quantities, and the pressure finally reached after each addition of gas is *independent of the amount already taken up*. Similarly, when gas is withdrawn from the system the pressure gradually builds up and finally approaches the same value as before. From an extensive series of such measurements the dissociation pressure of the oxide has been determined at five temperatures over the range 173–191°. From these results new values have been calculated for the free energy of formation of silver oxide, and for the free energy of formation of water at 25°.

### Apparatus and Procedure

The apparatus was of the type recently used in this Laboratory for studies on gaseous sorption, and has been described by Benton and White.<sup>5</sup> Its essential parts are a bulb containing the solid under investigation, a mercury manometer to indicate the pressure in the bulb, a mercury-filled buret to measure the quantities of gas admitted or withdrawn, and a Töpler pump. The only difference between this new apparatus and the one previously described was the presence of a stopcock between the bulb and the remainder of the apparatus. This stopcock, the key of which was mercury-sealed at both ends, was the only one in the parts of the line communicating with the bulb, mercury seals being used elsewhere. The volume of the "free space" in the bulb and connecting capillary amounted to about 32 cc.

The bulb was maintained at the desired temperatures by means of an electrically heated vapor-bath, lagged with asbestos paper, in which ethylene glycol was boiled under reduced pressure. The pressure in this bath was accurately controlled by means of a regulator similar to that described by Smith.<sup>6</sup> Fluctuations in temperature did not exceed 0.05°, even over the long periods of observation which were found necessary. The temperatures were measured with a mercury thermometer graduated to 0.2°, which was carefully standardized by reference to a similar thermometer newly calibrated by the U. S. Bureau of Standards. The necessary corrections for the exposed thread of mercury were applied.

**Materials.**—Metallic silver was prepared as follows. A solution of the calculated amount of barium hydroxide was added to an 8% solution of twice recrystallized silver

<sup>4</sup> Lewis and Randall, "Thermodynamics," 1923, p. 479.

<sup>5</sup> Benton and White, *THIS JOURNAL*, 52, 2325 (1930).

<sup>6</sup> Smith, *Ind. Eng. Chem.*, 16, 22 (1924).

nitrate at 80°. The precipitate was washed with conductivity water until no trace of barium could be detected, and then with ten liters of conductivity water in one-liter portions. It was then dried in air for twelve hours at 50°, and in oxygen for twenty-four hours at 100°. The oxide was reduced with purified electrolytic hydrogen, first for thirty hours at 30° and then for one hundred and fifty-three hours at temperatures gradually increasing to 100°. To avoid subsequent changes in the activity of the sample, it was finally heated for four hours at 150° and for ten hours at 300°. The mass employed was 39.4 grams.

Oxygen was generated by electrolysis of c. p. sodium hydroxide solution between nickel electrodes. It was purified by successive passage over heated platinized asbestos, calcium chloride, soda lime and phosphorus pentoxide.

**Procedure.**—After the bulb containing the sample was sealed to the apparatus, the silver was again reduced for an hour or two at 250°, and then subjected to thorough evacuation at this temperature. The bulb was then brought to 173.0° and oxygen was admitted in successive small portions. After each addition, to a pressure of approximately one atmosphere, the pressure dropped rapidly at first and then more slowly, finally tending toward a constant value after many hours. This procedure was repeated until a total of about 190 cc. of oxygen had been taken up, equivalent to the conversion of 9.3% of the silver to silver oxide. In these measurements the times of observation were not long enough to give more than an upper limit to the true equilibrium pressure. For the final measurements of dissociation pressures, the system which had been partially oxidized to the extent just described, was treated with a further portion of oxygen at about atmospheric pressure, and the decrease in pressure as a function of time was followed until equilibrium had apparently been reached. A constant value was usually obtained in five or six days. Similar measurements were then carried out at successively higher temperatures, equilibrium being approached in each case from the side of higher pressures. The bulb was then thoroughly evacuated at room temperature, and heated to 173°. The approach to equilibrium could now be followed from the opposite side, by observing the pressure built up by decomposition of the oxide. Measurements of the latter kind were repeated at successively higher temperatures. All pressures recorded below are given in mm. of mercury at 0°.

### Experimental Results

The results of the final measurements on the dissociation pressure of silver oxide are collected in Table I. The direction in which equilibrium was approached is indicated by the plus or minus sign following the pressures given in Column 2, the plus sign denoting approach from the side of lower pressure, and the minus sign the reverse. In all cases the change of pressure in the last twenty-four hours of observation was less than 0.5 mm. The numerous experiments in which equilibrium was less closely approached will not be detailed here. The values of the average pressure

TABLE I  
DISSOCIATION PRESSURE OF SILVER OXIDE

$t, ^\circ\text{C.}$	$P, \text{mm.}$		$P, \text{av.}$	$1/T \times 10^4$	$\text{Log } P$
173.0	420.9+	422.9-	422	22.42	2.625
178.0	(514.2-)	511.6±	509	22.17	2.707
183.1	607.0-	603.3+	605	21.92	2.782
188.2	713.4+	721.5-	717	21.68	2.856
191.2	790.0±	786.0+	790	21.54	2.898

shown in Column 3 were obtained by weighting all the measurements in accordance with the times of observation.

A plot of the logarithm of the average pressure against the reciprocal of the absolute temperature is shown in Fig. 1. The extreme values of  $\log P$  indicated at each point show the limits within which the dissociation pressure has been determined with certainty. It will be seen that the observed points lie rather closely on a straight line. A curve very slightly concave toward the axes would fit the observations even better, indicating a very small decrease in the heat of formation with increasing temperature. However, the range of the observations is too small to permit a definite conclusion on this point. From the straight line drawn in Fig. 1 we find for the formation of one mole of silver oxide,  $\Delta H_{465} = -7020$  cal. Again because of the short range this value may be in error by as much as 200 cal.

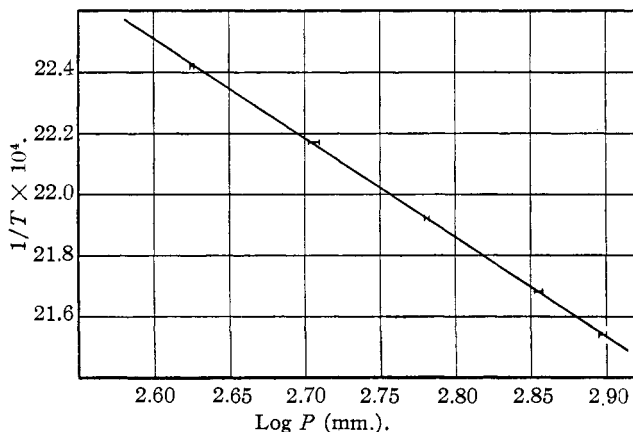


Fig. 1.—The dissociation pressures of silver oxide at 173–191°.

**Rate of Attainment of Equilibrium.**—The rates of formation and decomposition of silver oxide here observed are very much greater than those found by previous workers. This fact will be evident from Table II, which compares the rate of decomposition obtained by Lewis<sup>2</sup> at 325° with that found by us in an experiment at 173.0° (in this experiment the temperature was 174° for the first forty-nine hours).

TABLE II  
RATE OF DECOMPOSITION OF SILVER OXIDE

		A. Data of Lewis. Temperature 325°							
Time, hrs.		0	12	24	48	72	96	120	144
Pressure, atm.		0	18.5	26.5	29.8	30.1	31.5	31.8	31.8
		B. Data of Benton and Drake. Temperature 173.0°							
Time, hrs.		0	59	71	99	144	154	168	
Pressure, mm.		0	395	402	415	420	421	421	421

Thus the time necessary to reach apparent equilibrium was approximately the same in spite of the difference in temperature of more than 150°. The much greater reactivity of our sample is doubtless attributable to three main causes: (1) our oxide was prepared synthetically at 170–180° and had never been sintered by heating above 191°, (2) in our sample the original formation of the 9% of oxide presumably occurred in such a manner as to furnish a very large interface between the oxide phase and the unchanged silver—a situation which is known<sup>7</sup> to lead to relatively high rates in reactions of this type, (3) the extended preliminary measurements with our sample, involving repeated formation and decomposition of oxide at low temperatures, would be expected greatly to enhance the reactivity.

We have repeatedly observed that the rate of the reaction in either direction is affected to only a slight extent by the proportion of the silver which is oxidized. Typical data illustrating this point are shown in Table III, which gives the average rate of pressure drop, which is proportional to the rate of formation of oxide, as observed over the range 550–500 mm., with different amounts of oxide already present.

TABLE III  
RATE OF FORMATION OF OXIDE AT 173.0°

Oxide present, %	0.7	1.0	5.3
Av. pressure drop, mm. per hr.	2.8	3.3	3.0

It is probable, however, that with substantially larger proportions of oxide there would be less available interface between the solid phases, and slower rates would obtain.

A more detailed discussion of rates and their bearing on the catalytic action of silver in oxidation reactions will be given in a subsequent report.

### Discussion

While the results obtained show that a perfectly definite equilibrium is reached in the temperature range 173 to 191°, it is necessary to consider further the nature of the phases present at equilibrium. Since the system is found to be univariant, there must be three phases present—metallic silver, gaseous oxygen and a third phase which is an oxide of silver. It has been found that this oxide is formed from its elements with an evolution of heat which in the above range of temperature is close to 7000 cal. per mole. The averaged value<sup>8</sup> for the heat of formation of ordinary  $\text{Ag}_2\text{O}$  is 6960 cal. at 18° and slightly less at higher temperatures. The agreement of these two heats within the limits of error of our value appears to be conclusive evidence that we are dealing with the ordinary oxide  $\text{Ag}_2\text{O}$ , and not with a possible lower or higher oxide, nor with an allotropic form of  $\text{Ag}_2\text{O}$ . It is of

<sup>7</sup> Lewis, *Z. physik. Chem.*, **52**, 310 (1905). See also Langmuir, *THIS JOURNAL*, **38**, 2221 (1916).

<sup>8</sup> "International Critical Tables," **5**, 188 (1929).

course possible that both the silver and the oxide might exist in allotropic forms, whose differences in heat content as compared with the ordinary modifications might approximately cancel, but there is no definite evidence of any such allotropes in either case between room temperature and at least  $500^{\circ}$ . It is probable that the metallic silver phase is in reality a saturated solution of oxygen, or  $\text{Ag}_2\text{O}$ , in silver. However, estimates of the solubility based on the measurements of Steacie and Johnson<sup>9</sup> put the mole fraction of oxygen at these temperatures at not over  $2 \times 10^{-4}$ , so that the heat content and free energy of the silver would not be appreciably affected.

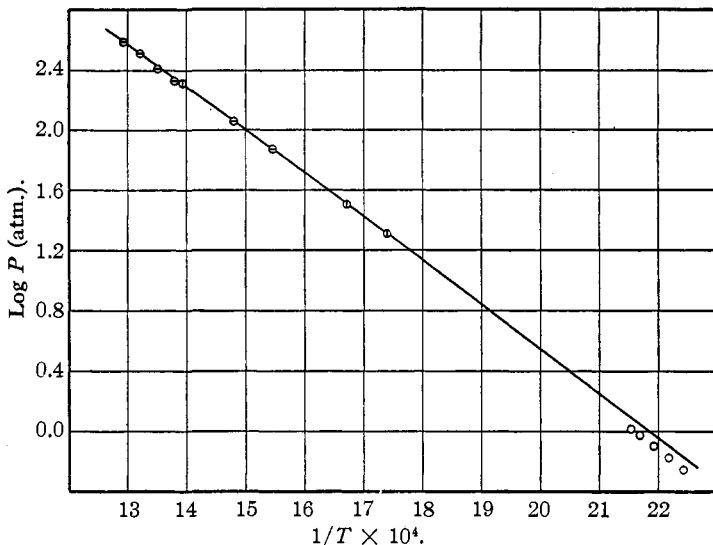


Fig. 2.—Comparison between the pressures observed at  $173$ – $191^{\circ}$  and those obtained at higher temperatures by Lewis and by Keyes and Hara:  $\ominus$ , Lewis;  $\omin�$ , K. and H.;  $\circ$ , B. and D.

The relationship of the data obtained in the range  $173$ – $191^{\circ}$  to those observed by Lewis<sup>2</sup> and by Keyes and Hara<sup>3</sup> is shown in Fig. 2. The curve there drawn is a plot of the equation employed by Lewis and Randall,<sup>10</sup>

$$\frac{\Delta F^{\circ}}{T} = -R \ln K = -\frac{7240}{T} - 1.0 \ln T + 21.95$$

It will be seen that our equilibrium pressures are considerably lower than those given by the above equation. At  $183.1^{\circ}$ , for example, we find a pressure of 605 mm., as compared with 728 mm. from the equation. The temperatures at which the pressure reaches one atmosphere are  $190.0$  and  $184.5^{\circ}$ , respectively.

<sup>9</sup> Steacie and Johnson, *Proc. Roy. Soc. (London)*, A112, 542 (1926).

<sup>10</sup> Ref. 4, p. 481.

**Activities at the Higher Pressures.**—Comparison of the present data with those obtained in the higher temperature range requires that the latter be corrected for the effect of the high pressures on the activity of each of the three phases. Lewis and Randall<sup>11</sup> have calculated these corrections for two experimental points which lie on the best representative curve. Thus at 598.1°K. they find a corrected pressure of 32.2 atm., compared with 32.0 observed; at 773.3°K. the corresponding values are 392.1 and 388.3. The details of the calculations are not given.

We have repeated these calculations as follows. In the absence of experimental data on the molecular volume of oxygen at temperatures above 200°, we have employed the equation of state for this gas developed by Keyes.<sup>3</sup> For the two points above mentioned, the molecular volumes of oxygen are thus found to be 1547.5 and 186.9 cc., respectively; the corresponding activities  $a$ , obtained from the equation  $a/P = Pv/RT$ , which is a sufficiently close approximation at these temperatures and pressures, are 32.3 and 444 atm. The activities of the silver and silver oxide have been calculated from the equation  $RT \ln a = \int_1^P V dP$ . The molecular volumes  $V$  have been taken as 10.27 for silver and 31.9 for the oxide<sup>12</sup> (the latter being the value derived from x-ray measurements), and both values have been assumed to be independent of temperature and pressure. The activities thus obtained are as follows: for silver, 1.006 at 598.1 and 1.065 at 773.3°K.; for silver oxide, 1.020 and 1.215 at the same two temperatures. A more exact calculation leading to slightly higher values can be carried out in the case of silver by introducing the change of volume with temperature and pressure. However, since the corresponding data are lacking for silver oxide, it seems best to perform the calculation in the same way for both solid phases.

For the reaction  $2Ag + \frac{1}{2}O_2 = Ag_2O$ , the true equilibrium constant  $K$  is given by the expression  $1/K^2 = a_{Ag}^4 \cdot a_{O_2} / a_{Ag_2O}^2$ . When the activities given above are introduced,  $1/K_{598.1}^2 = 31.8$  and  $1/K_{773.3}^2 = 386.9$ . These values do not differ greatly from 32.2 and 392.1 calculated by Lewis and Randall. It is difficult to estimate the reliability of these true equilibrium constants, in view of the approximations necessary in calculating the corrections. It appears that the uncertainty at 598.1° is probably very small. At 773.3°, however, the corrections amount to 29% for  $a_{Ag}^4$ , 14% for  $a_{O_2}$ , and 48% for  $a_{Ag_2O}^2$ . In these circumstances an uncertainty of 5 to 10% in  $1/K_{773.3}^2$  appears possible. No corrections are necessary in the case of the data reported in the present paper.

**Thermal Data.**—The heat of formation ( $-\Delta H$ ) at room temperature of one mole of silver oxide was found to be 5900 cal. by Thomsen, 7000

<sup>11</sup> Ref. 4, p. 480.

<sup>12</sup> "International Critical Tables," 1, 103, 342 (1926).

by Berthelot, and 6800, 7200 and 6300 in calculations by Lewis.<sup>2</sup> The value 5400 obtained by Mixer<sup>13</sup> is certainly too low. The conclusion may be drawn that the true value probably lies between 6300 and 7000. There are no data of any kind for the heat capacity of silver oxide. Application of Kopp's rule suggests that  $\Delta C_p$  for the formation of one mole of silver oxide at room temperature probably lies between 0 and 2. In the closely analogous case of cuprous oxide the existing data are consistent with the equation,  $\Delta C_p = -1.0 + 0.006 T$ .

**Comparison of Equilibria in the Two Temperature Ranges.**—If  $\Delta C_p$  is assumed to be independent of temperature, the equilibrium constant  $K$  is given by the expression

$$-R \ln K = \frac{\Delta H_0}{T} - \Delta C_p \ln T + I \quad (1)$$

It is evident from Fig. 2 that the corrected  $K$  values at high temperatures are inconsistent with the new results unless  $\Delta C_p$  exceeds the value 1.0 employed by Lewis and Randall. To bring all the data into agreement on the basis of Equation 1, a value of  $\Delta C_p = 3.2$  is necessary, and  $-\Delta H_{291}$  would then be 7800 cal. Both these values appear to be too large. The discrepancy is perhaps best appreciated by noting that if the values of  $1/K^2$  at 598.1 and 456.2°K. are taken as correct, the average heat of reaction in this range,  $\Delta H_{527} = -7050$ ; thus if  $\Delta C_p$  is positive,  $\Delta H_{291}$  must have a larger negative value, and thus lie outside the probable limits of uncertainty.

It does not appear unreasonable to assume that, in analogy with the case of cuprous oxide,  $\Delta C_p$  increases rapidly with temperature. We find that all the equilibrium measurements can be brought into agreement if  $\Delta C_p = -0.494 + 0.006 T$ , so that

$$-R \ln K = -\frac{7610}{T} + 0.494 \ln T - 0.003T + 14.80$$

Nevertheless,  $-\Delta H_{291}$  on this basis becomes 7500, which appears too large.

In view of the uncertainty in the heat capacity and heat of formation of silver oxide, and in the calculations of fugacities at the higher temperatures, we conclude that the measurements recorded in the present paper are not necessarily in disagreement with the earlier work. Direct thermal measurements on silver oxide are obviously badly needed.

Because the activity corrections are negligible and the extrapolation to room temperature covers a much shorter interval, the new results are better adapted to a calculation of  $\Delta F_{298}^\circ$ . If for lack of better values we adopt  $\Delta H_0 = -7240$  and  $\Delta C_p = 1.0$ , as given by Lewis and Randall, our data give the equation

$$\frac{\Delta F^\circ}{T} = -R \ln K = -\frac{7240}{T} - 1.0 \ln T + 21.76$$

<sup>13</sup> Mixer, *Am. J. Sci.*, **32**, 202 (1911).



Thus  $\Delta F_{298}^{\circ}$  becomes  $-2450$ , which is 2.3% less than the value derived by the above authors,  $-2395$ . It must be emphasized however, that a change in  $\Delta C_p$  can seriously affect the value of  $\Delta F_{298}^{\circ}$ .

By combination of  $\Delta F_{298}^{\circ}$  for silver oxide with certain other equilibria two methods are available for the calculation of the free energy of formation of water.<sup>4</sup> With the new value for silver oxide the two methods give for the formation of one mole of liquid water  $\Delta F_{298}^{\circ} = -56,520$  and  $-56,580$ , respectively. The average,  $-56,550$ , is within 30 cal. of the mean value obtained by three other independent methods, namely,  $-56,580$ .

### Summary

1. Metallic silver obtained by low-temperature reduction of the oxide reacts with oxygen at temperatures of 170-200°, forming a definite phase of silver oxide.

2. The equilibrium pressures have been determined in this range of temperature. Values obtained by formation and by decomposition of the oxide agree to within two to four mm., or about 0.5%.

3. The calculated heat of formation is the same within experimental error as that for ordinary silver oxide,  $\text{Ag}_2\text{O}$ .

4. The equilibrium pressures are about 17% lower than those which have been obtained by extrapolation of the results of other workers at 300-500°. This apparent discrepancy is probably to be attributed to uncertainties in the thermal and other data necessary for the extrapolation rather than in the equilibrium measurements themselves.

5. A value of  $-2450$  cal. is calculated for the free energy of formation of one mole of silver oxide at 25°. In spite of the fact that the new data diminish the extrapolation here necessary to a range of 150°, the above figure may be materially affected by the value chosen for the undetermined heat capacity of the oxide.

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