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THE SYSTEM COPPER: CUPRIC OXIDE: OXYGEN.

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Previous Work.

In a recent paper¹ the authors published the results of measurements of the dissociation (oxygen) pressures of solid cupric oxide throughout the temperature range 900° to 1240°. In the present paper, these measurements have been extended to include: (1) the dissociation pressures of the liquid mixture of the two oxides throughout the range where this solution is in equilibrium with cuprous oxide; (2) the composition of the liquid in equilibrium with solid cupric oxide from the eutectic temperature to 1230° and with solid cuprous oxide from the eutectic temperature to the minimum melting point of cuprous oxide; (3) measurements, at 1120° and 1150°, of the dissociation pressures for different compositions of the liquid when no solid phase is present; (4) measurements of the dissociation pressures of cuprous oxide within the temperature range where a liquid rich in copper is a dissociation product.

In the authors' paper already referred to, it is shown that, within the temperature range investigated, solid solution of small amounts of cuprous oxide in cupric oxide does not occur and that solid solution of cupric in cuprous oxide is improbable. There is a eutectic at 1080.2° between the two oxides; at temperatures lower than 1080.2°, cupric oxide dissociates with the formation of oxygen and solid cuprous oxide; at higher temperatures, with the formation of oxygen and a liquid intermediate in composition between cupric and cuprous oxides. Because of the high pressures encountered, the investigation was not carried to the melting point of cupric oxide.

Heyn² has published the results of his investigations of the *T-X* (melting point) diagram of the system from pure copper to the composition 81.0% copper, 9.0% cuprous oxide by weight. He finds a eutectic at 3.4% cuprous oxide and 96.6% copper. Slade and Farrow³ have extended these measurements to the melting point of cuprous oxide, showing that, above 1195°, two immiscible liquids occur in the system. They have included, in addition, measurements for one of the several *P-T* curves.

The only oxides encountered in any of these investigations were cupric oxide (CuO) and cuprous oxide (Cu₂O), and there is no evidence that solid solution occurs in the system.

¹ Smyth and Roberts, *This Journal*, **42**, 2582 (1920).

² Heyn, *Z. anorg. Chem.*, **39**, 11 (1904).

³ Slade and Farrow, *Proc. Roy. Soc.*, **87**, 524 (1912).

Apparatus and Materials.

The identical apparatus described in our previous paper¹ was used for most of the work, except that the Toepler pump, which had been found unnecessary, was removed.

The platinum-platinrhodium thermocouples were calibrated frequently at the α - β inversion temperature of a sample of quartz whose inversion temperature had previously been determined by C. N. Fenner;² and at the melting point of pure gold, 1062.6°. In order to prevent the contaminating copper dissolved in the thermocouple leads from becoming oxidized during calibration and changing their indications, the calibration was carried out *in vacuo*. The volatility of lithia under these conditions would have rendered the melting point of lithium metasilicate (1201° =) much more uncertain than it already is, so that it was thought better to extrapolate the calibration curve from the gold point to the higher temperatures than to attempt a very uncertain determination of the lithium metasilicate point.

Cupric oxide was made, as described by us elsewhere,³ by the oxidation of heated metallic copper in a current of air, using material from the lot that had been used by Day, Clement and Sosman in determining the melting point of copper on the gas thermometer scale. An analysis of this copper, made for Day and Clement by E. T. Allen,⁴ shows 0.0083% of nonvolatile impurity.

Cuprous oxide was made from the cupric oxide described above by pumping off the oxygen at about 1000°. The cupric oxide, ground to pass through a screen having 200 meshes per linear inch, was placed in an alundum boat and heated in a porcelain tube connected to a vacuum pump. Owing to the permeability of the hot porcelain tube and to accidental leaks it was not possible to reduce the pressure in the tube below about 0.5 mm. of mercury. There was thus no danger of reducing the cuprous oxide, whose dissociation pressure at 1000° must be very much less than this. Heating and pumping were continued until no further gas was given off (for about 12 hours). The charge came from the furnace in the form of a compact bar, purplish on the surface, but forming a light red powder when ground to 200-mesh.

Oxygen was obtained from a cylinder of compressed electrolytic oxygen. After passing a sample of this gas over hot cupric oxide and then over phosphorus pentoxide it was found to contain about 0.1% of gas that was not absorbed by copper in ammonia solution. For the moderate pressure apparatus the gas was taken from the same cylinder that was used in our previous work; for the high pressure apparatus it was taken from another cylinder furnished by the same manufacturer.

Theoretical Discussion.

Since this is a system of two components, the phase rule, $F = C + 2 - P$, shows that four phases must be in equilibrium at an invariant point; three on a univariant curve, and two on a divariant surface, in the $P - T - X$ model. These relations are most conveniently represented on paper by considering the projections of the various univariant lines on the $P - T$ plane in conjunction with their projections on the $T - X$ plane.

We shall express the concentration, x , of a phase as the number of atoms of oxygen associated with each atom of copper. For compositions be-

¹ *Op. cit.*, pp. 2588-2591.

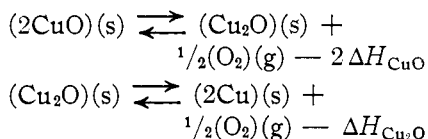
² Fenner, *Am. J. Sci.*, **36**, 377 (1913), Table III, No. 1.

³ Smyth and Roberts, *op. cit.*, p. 2592.

⁴ E. T. Allen, in paper by Day and Clement, *Am. J. Sci.*, **26**, 456 (1908).

tween Cu and CuO inclusive, this is exactly equivalent to the customary convention of stating that one mol of any phase contains x mols of cupric oxide and $(1 - x)$ mols of copper. Thus for copper, $x = 0$; for cuprous oxide, $x = 0.5$; for cupric oxide, $x = 1$. If we define one mol of oxygen gas as 32 g., it follows that one mol of any solid or liquid whose composition lies between Cu and CuO must contain 127.14 g. copper. This convention has the advantage that, provided we can ignore the copper content of the vapor phase, the dissociation of 1 mol of a solid or liquid phase yields 1 mol of another solid or liquid phase and a known quantity, γ mols, of oxygen, where γ is equal to the difference between the concentrations of the original and final solid or liquid phases.

There is no evidence that solid solution is a factor in this system; at relatively low temperatures solid cupric oxide dissociates with the formation of solid cuprous oxide and oxygen gas, and solid cuprous oxide with the formation of solid copper and oxygen gas. We shall therefore take, for our fundamental reactions,



where $2\Delta H_{\text{CuO}}$ and $\Delta H_{\text{Cu}_2\text{O}}$ represent the heat which must be supplied to the system, per mol of solid reacting, when the respective reactions proceed from left to right. That is, for dissociation, ΔH is a positive number.

The upper, $T - X$, diagram of Fig. 1 is a schematic representation of the solubility relations in the system, according to the plan we have just outlined. It will be seen that there are three quadruple points, (A), (B), and (C), at each of which four phases may coexist in equilibrium. These points are projected into the lower, $P - T$, diagram with their corresponding letters. Since any quadruple point is the intersection of the curves representing four univariant equilibria, one for each of the possible combinations of three of the four coexisting phases, we must have four $P - T$ curves radiating from each quadruple point in the $P - T$ diagram.

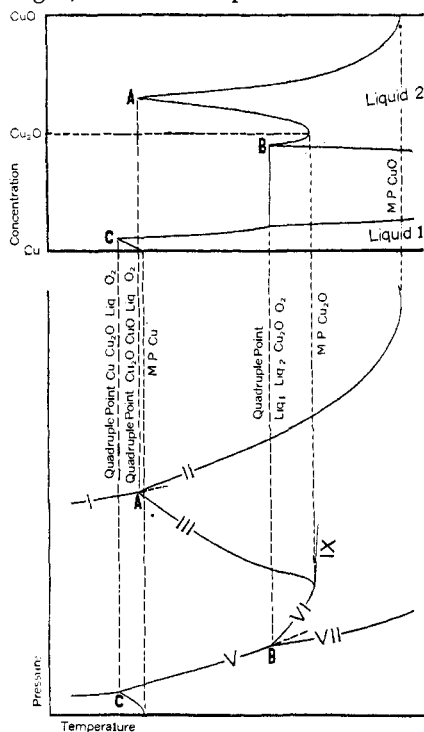


Fig. 1.—Hypothetical pressure—temperature—concentration relations in the system. Not drawn to scale.

Along a $P - T$ curve, "the actual value of dp/dt for any univariant equilibrium is given by (Gibbs') Equation 129, which . . . is equivalent to

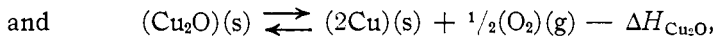
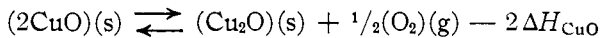
$$\frac{dp}{dt} = \frac{\Delta\eta}{\Delta V} \quad (1)$$

in which $\Delta\eta$ is the entropy change, ΔV the volume change of the reaction in question."¹ When the reaction proceeds at constant temperature and pressure, we may replace $\Delta\eta$ by Q/T , and ΔV is equal to the volume of the gas formed plus the increase, $\Delta V'$, in the volume occupied by the solid and liquid phases. Equation 1 may now be transformed to

$$\frac{dp}{dt} = \frac{1}{T} \cdot \frac{Q}{yV_g + \Delta V'} \quad (2)$$

where Q is the heat absorbed reversibly; T , the absolute temperature, y the number of mols of gas formed per mol of solid or liquid reacting, and V_g the volume of one mol of gas at the pressure and temperature under consideration.

In the case of the two fundamental reactions,



Q is equal to $2\Delta H_{\text{CuO}}$ and $\Delta H_{\text{Cu}_2\text{O}}$, respectively; y is $1/2$; and, since the pressures are low, $\Delta V'$ is negligible in comparison with V_g . The dp/dt equation for these reactions then becomes

$$\frac{dp}{dt} = \frac{1}{T} \cdot \frac{2\Delta H_{\text{CuO}}}{\frac{1}{2}V_g} = \frac{1}{T} \cdot \frac{4\Delta H_{\text{CuO}}}{V_g} \quad \text{and} \quad \frac{dp}{dt} = \frac{1}{T} \cdot \frac{2\Delta H_{\text{Cu}_2\text{O}}}{V_g} \quad (3)$$

If we assume ΔH constant, replace V_g by RT/p , and integrate, we obtain, respectively,

$$\ln p = -\frac{4\Delta H_{\text{CuO}}}{RT} + \text{a constant}, \quad \text{and} \quad \ln p = -\frac{2\Delta H_{\text{Cu}_2\text{O}}}{RT} + \text{a constant}. \quad (3a)$$

Thus, if the assumption of constancy for ΔH is justified, we should obtain a straight line by plotting $\ln p$ (or $\log_{10} p$) against $1/T$ for either reaction. We have shown elsewhere² that this is actually the case for the dissociation of solid cupric oxide over the temperature range from 900° to 1080° , and shall assume that it is also the case for the corresponding dissociation of cuprous oxide.

If a liquid phase enters into the reaction, Q is no longer equal to the heat of dissociation of a solid phase; and y , in general, is not equal to $1/2$. We may, however, assume that the reaction takes place in several reversible steps, one of which is one or the other fundamental reaction, and the others processes of expansion, and solution, or their opposites. The net

¹ Morey and Williamson, "Pressure-Temperature Curves in Univariant Systems," THIS JOURNAL, 40, 70 (1918).

² *Op. cit.*, p. 2600.

increase in the entropy of the system is then the algebraic sum of the increases for the several steps.

P-T Curves in the System Cuprous Oxide: Cupric Oxide: Oxygen.—At the quadruple point (A), in Fig. 1, CuO(s) , $\text{Cu}_2\text{O(s)}$, liquid, gas, we have the intersection of the $P - T$ curves for the following equilibria.

- | | | |
|-------|--------------------------------------|----------------|
| (I) | CuO(s), Cu ₂ O(s), Gas | (Dissociation) |
| (II) | CuO(s), Liquid, Gas | (Dissociation) |
| (III) | Liquid, Cu ₂ O(s), Gas | (Dissociation) |
| (IV) | CuO(s), Cu ₂ O(s), Liquid | (Fusion) |

We have already shown that Reaction I is $(2\text{CuO})\text{(s)} \rightleftharpoons (\text{Cu}_2\text{O})\text{(s)} + \frac{1}{2}(\text{O}_2)\text{(g)} - 2\Delta H_{\text{CuO}}$ and that the first equations of 3 and 3a apply to it.

Reaction II may be written $(2\text{CuO})\text{(s)} \rightleftharpoons \text{liquid} + \gamma_{\text{II}}(\text{O}_2)\text{(g)} + \Delta H_{\text{II}}$, and we shall assume that the reaction takes place in the following reversible steps:

(1) Dissociation of $2\gamma_{\text{II}}$ mols of (2CuO) with the formation of γ_{II} mols of oxygen at the temperature T and the pressure p_{I} corresponding to the temperature T on the $P - T$ curve for Reaction I; the reaction may be written $2\gamma_{\text{II}}(2\text{CuO}) = 2\gamma_{\text{II}}(\text{Cu}_2\text{O}) + \gamma_{\text{II}}(\text{O}_2) - 4\gamma_{\text{II}}\Delta H_{\text{CuO}}$. The entropy increase is $4\gamma_{\text{II}}\Delta H_{\text{CuO}}/T$.

(2) Isothermal compression of the gas from p_{I} to p_{II} , the pressure corresponding to T on the $P - T$ curve for Reaction II. The entropy increase is $\gamma_{\text{II}}R \ln p_{\text{I}}/p_{\text{II}}$.

(3) Fusion and mutual solution of the $2\gamma_{\text{II}}(\text{Cu}_2\text{O})$ formed by the reaction, together with the remaining $(1 - 2\gamma_{\text{II}})(2\text{CuO})$, resulting in the formation of 1 mol of the saturated liquid solution. The entropy increase is $+L_{\text{II}}/T$ where L_{II} is the heat of formation of the saturated solution at the temperature T and the pressure p_{II} . The sum of these entropy changes is

$$\Delta\eta = 4\gamma_{\text{II}} \frac{\Delta H_{\text{CuO}}}{T} + \gamma_{\text{II}}R \ln \frac{p_{\text{I}}}{p_{\text{II}}} + \frac{L_{\text{II}}}{T};$$

$$\Delta V = \gamma_{\text{II}}V_{\text{g}} + (V_1 - V_{\text{CuO}}).$$

Equation 1 becomes

$$\frac{dp}{dt} = \frac{\Delta\eta}{\Delta V} = \frac{4\gamma_{\text{II}} \frac{\Delta H_{\text{CuO}}}{T} + \gamma_{\text{II}}R \ln \frac{p_{\text{I}}}{p_{\text{II}}} + \frac{L_{\text{II}}}{T}}{\gamma_{\text{II}}V_{\text{g}} + (V_1 - V_{\text{CuO}})},$$

From a consideration of the $T - X$ diagram we know that γ_{II} is equal to the difference in oxygen content of (2CuO) and liquid, that is

$$\gamma_{\text{II}} = x_{2\text{CuO}} - x_1 = 1 - x_1.$$

Thus we may write

$$\frac{dp}{dt} = \frac{1}{T} \cdot \frac{(1 - x_1) \left(4\Delta H_{\text{CuO}} + RT \ln \frac{p_{\text{I}}}{p_{\text{II}}} \right) + L_{\text{II}}}{(1 - x_1)V_{\text{g}} + (V_1 - V_{2\text{CuO}})}. \quad (4)$$

By a similar process, we may obtain for Reaction III the equation

$$\frac{dp}{dt} = \frac{4y_{\text{III}} \frac{\Delta H_{\text{CuO}}}{T} + y_{\text{III}} R \ln \frac{p_{\text{I}}}{p_{\text{III}}} - \frac{L_{\text{III}}}{T}}{y_{\text{III}} V_{\text{g}} - (V_1 - V_{\text{Cu}_2\text{O}})}$$

In this case, $y_{\text{III}} = x_1 - x_{\text{Cu}_2\text{O}} = x_1 - 1/2$ and we obtain

$$\frac{dp}{dt} = \frac{1}{T} \cdot \frac{\left(x_1 - \frac{1}{2}\right) \left(4\Delta H_{\text{CuO}} + RT \ln \frac{p_{\text{I}}}{p_{\text{III}}}\right) - L_{\text{III}}}{(x_1 - 1/2)V_{\text{g}} - (V_1 - V_{\text{Cu}_2\text{O}})} \quad (5)$$

In general, neither Equation 4 nor 5 can be integrated because of the present impossibility of expressing x and L as functions of T .

For Reaction IV we obtain, by substitution in Equation 1,

$$\frac{dp}{dt} = \frac{1}{T} \cdot \frac{L}{\Delta V} \quad (6)$$

ΔV , the increase in volume, is very small in comparison with L , and for most substances has the same sign. We may therefore expect that Curve IV has a very great positive slope.

We have, then, the following equations for the four $P - T$ curves intersecting at the quadruple point (A).

$$(I) \quad \frac{dp}{dt} = \frac{1}{T} \cdot \frac{4\Delta H_{\text{CuO}}}{V_{\text{g}}} \quad (3)$$

$$(II) \quad \frac{dp}{dt} = \frac{1}{T} \cdot \frac{(1 - x_1) \left(4\Delta H_{\text{CuO}} + RT \ln \frac{p_{\text{I}}}{p_{\text{II}}}\right) + L_{\text{II}}}{(1 - x_1)V_{\text{g}} + (V_1 - V_{\text{CuO}})} \quad (4)$$

$$(III) \quad \frac{dp}{dt} = \frac{1}{T} \cdot \frac{\left(x_1 - \frac{1}{2}\right) \left(4\Delta H_{\text{CuO}} + RT \ln \frac{p_{\text{I}}}{p_{\text{III}}}\right) - L_{\text{III}}}{(x_1 - 1/2)V_{\text{g}} - (V_1 - V_{\text{Cu}_2\text{O}})} \quad (5)$$

$$(IV) \quad \frac{dp}{dt} = \frac{1}{T} \cdot \frac{L}{\Delta V} \quad (6)$$

We have shown elsewhere¹ that Curve II passes from the quadruple point to the minimum melting point of cupric oxide with increasing pressure and temperature. The slope at the quadruple point is greater than that of Curve I, and increases with rising temperature more rapidly than does that of the extrapolation of Curve I. Curve III extends from the quadruple point, with rising temperature, to the minimum melting point of cuprous oxide where it becomes tangent to the $P - T$ Curve IX for the condensed system, $\text{Cu}_2\text{O}(s) : \text{Cu}_2\text{O}(l)$. Just before this point is reached, the amount of gas liberated by the reaction has become so small that its volume is equal to the contraction of the liquid on solidification,

¹ *Op. cit.*, p. 2586.

the net change in volume is zero and dp/dt , in Equation 5, becomes negatively infinite. This results in a point of maximum temperature, beyond which the temperature falls to the melting point of cuprous oxide.

When the paper we have just referred to was written, we believed that the slope of Curve III might decrease continuously with rising temperature throughout its length. Actually, however, it increases over most of its length and does not pass through a point of inflection and begin to decrease until very close to the point of maximum temperature. The actual value of the slope is given by Equation 5. In the absence of more definite knowledge, it was necessary to assume ΔH_{CuO} and L_{III} constant, and $RT \ln p_{\text{I}}/p_{\text{III}}$ and $(V_1 - V_{\text{Cu}_2\text{O}})$ negligible. The variables T , x_1 , and V_g remain to be considered. After passing a possible point of maximum pressure, dp/dt is negative. Consequently V_g increases with rising temperature (since p decreases). We know that the liquid becomes richer in cuprous oxide as the temperature rises and as a consequence that x_1 decreases. Thus if the product TV_g increases more rapidly than $(x_1 - 1/2)$ decreases, the slope of the curve will increase. This is found to be the case.

The course of Curves I, II, and III, then, is similar to that shown schematically in Fig. 1.

In the case of the dissociation of the liquid solution of cupric oxide in cuprous oxide, where no solid phase is present, the equilibrium is divariant; but, for any fixed composition of the liquid, dp/dt can be determined from Equation 1, $dp/dt = \Delta\eta/\Delta V$.

In order that the composition of the liquid may remain constant, we shall assume that only an infinitesimal amount of oxygen is removed from it, and shall consider the reaction at any temperature, T , as taking place in several steps as follows.

(1) Separation from the liquid and solidification of dm mols of (2CuO) with an increase in entropy of $-dm q_1/T$.

(2) Dissociation of dm mols of solid (2CuO) at the pressure p_{I} corresponding to T on Curve I. The entropy increase is $dm 2\Delta H_{\text{CuO}}/T$.

(3) Isothermal compression or expansion of the $dm/2$ mols of (O_2) formed in step (2) from p_{I} to p_1 , the pressure corresponding to T for the liquid. The increase in entropy is $1/2 dm R \ln p_{\text{I}}/p_1$.

(4) Solution of dm mols of $(2\text{Cu}_2\text{O})$ in the liquid. The increase in entropy is $+ dm q_2/T$. The volume change ΔV for the whole process, neglecting the change in volume of the liquid, is $dm V_g/2$. Equation 1 now becomes,

$$\left(\frac{\partial p}{\partial t}\right)_x = \frac{dm \left(\frac{q_2 - q_1}{T} + \frac{1}{2} R \ln \frac{p_{\text{I}}}{p_1} + \frac{2\Delta H_{\text{CuO}}}{T} \right)}{dm V_g/2}$$

$$= \frac{1}{T} \cdot \frac{(q_2 - q_1) + \frac{1}{2} RT \ln \frac{p_I}{p_1} + 2\Delta H_{\text{CuO}}}{\frac{1}{2} V_g}$$

where q_2 and q_1 are the differential heats of solution per mol of solid (Cu_2O) and solid (2CuO), respectively. The difference $(q_2 - q_1)$, is equal to $-(\partial L/\partial x)_t$, the rate of change at constant temperature, of the heat of formation of the liquid, when the composition of the liquid is varied.¹ We may therefore write

$$\left(\frac{\partial p}{\partial t}\right)_x = \frac{1}{T} \cdot \frac{2\Delta H_{\text{CuO}} + \frac{1}{2} RT \ln \frac{p_I}{p_1} - \left(\frac{\partial L}{\partial x}\right)_t}{\frac{1}{2} V_g} \quad (7)$$

P — T Curves in the System Cuprous Oxide:Copper:Oxygen.—

The sequence of the $P - T$ curves around the quadruple point (C) where the phases in equilibrium with each other are Solid Cu, Solid Cu_2O , Liquid (1), Gas, is entirely analogous to that at point (A). However, as Slade and Farrow have shown,² the composition of the liquid in equilibrium with solid cuprous oxide does not change continuously with temperature but is discontinuous at 1195° . The $P - T$ curve V for the reaction, solid $\text{Cu}_2\text{O} \rightleftharpoons$ Liquid (1) + Gas therefore does not extend to the melting point of cuprous oxide, but only as far as a second quadruple point, (B), at 1195° .

At the quadruple point (B) (Fig. 1) we have the four phases, Liquid (1), Liquid (2), $\text{Cu}_2\text{O}(s)$, Gas, in equilibrium with one another at 1195° .³ At this point, therefore, we have the intersection of the four $P - T$ curves for the four possible combinations of three phases each, namely,

(V)	$\text{Cu}_2\text{O}(s)$, Liquid (1), Gas	(Dissociation)
(VI)	$\text{Cu}_2\text{O}(s)$, Liquid (2), Gas	(Dissociation)
(VII)	Liquid (2), Liquid (1), Gas	(Dissociation)
(VIII)	Liquid (2), Liquid (1), $\text{Cu}_2\text{O}(s)$	(Fusion)

As in the case of the quadruple point (A), we have the $P - T$ curve for the equilibrium in which no vapor phase plays a part, extending nearly vertically from the quadruple point to regions of higher pressure.

Curve V, $\text{Cu}_2\text{O} \rightleftharpoons$ Liquid (1) + gas, passes, with decreasing pressure and temperature to the quadruple point (C).

The course of Curve VI for the reaction $\text{Cu}_2\text{O}(s) \rightleftharpoons$ Liquid (2) + Gas, is entirely analogous to that of Curve II for the reaction $\text{CuO}(s) \rightleftharpoons$ Liquid + Gas, that is, its slope at the quadruple point must be greater than that of Curve V and must increase continuously until the melting

¹ Cf. Roozeboom, "Heterogene Gleichgewichte," 2, 1, 288, *et seq.*, 1904; G. N. Lewis and M. Randall, *THIS JOURNAL*, 43, 237 (1921).

² Slade and Farrow, *Op. cit.*, p. 527.

³ *Op. cit.*, p. 528.

point of cuprous oxide is reached. Here Curve VI becomes tangent to the $P - T$ Curve IX of the condensed system $\text{Cu}_2\text{O}(s)$, $\text{Cu}_2\text{O}(l)$. As we have already shown, Curve III for the reaction $\text{Liquid} \rightleftharpoons \text{Cu}_2\text{O}(s) + \text{Gas}$ is also tangent to Curve IX at this point; Curves III and VI are therefore continuous.

The slope of Curve VII for the reaction $\text{Liquid (2)} \rightleftharpoons \text{Liquid (1)} + \text{Gas}$ is less at the quadruple point than that of Curve V. The heat of reaction, Q , for Curve V includes the heat of formation of 1 mol of Liquid (1), while for Curve VII it includes the difference between the heats of formation of 1 mol of Liquid (1) and of Liquid (2). As the compositions of the two liquids do not change rapidly with temperature, we should then expect that the slope of Curve VII would remain increasingly less than that of Curve V and that the pressures along it would be very much less than those along Curve VI.

Experimental Results.

The results of our measurements of pressure and temperature for Reactions I, II and III are tabulated in Table I, and plotted in Fig. 2, where a logarithmic scale is used for the pressures. Values of pressure read from

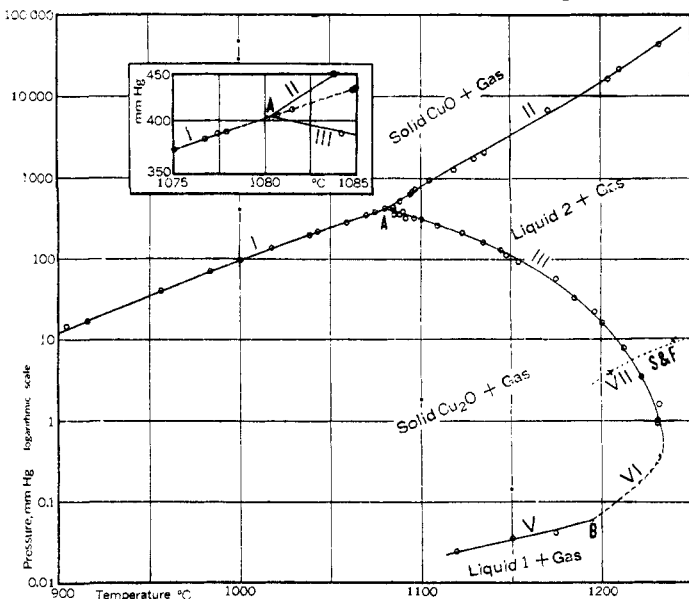


Fig. 2.—Pressure-temperature curves determined by the data. The ordinates are proportional to the logarithm of the pressure. The phases in equilibrium along each curve are: (I) CuO , Cu_2O , Gas; (II) CuO , Liquid (2), Gas; (III) Liquid (2), Cu_2O , Gas; (V) Cu_2O , Liquid (1), Gas; (VI) Cu_2O , Liquid (2), Gas. Curve (VII) is taken from the data of Slade and Farrow (op. cit. Fig. 5) for the phases Liquid (2), Liquid (1), Gas. The inset shows the region around the quadruple point (A), CuO , Cu_2O , Liquid (2), Gas, to a larger scale.

the plot at intervals of 20° are tabulated in Table II, and the lower pressures plotted to ordinary coördinates in Fig. 3.

TABLE I.
OBSERVED DISSOCIATION PRESSURES.
System $\text{CuO}:\text{Cu}_2\text{O}:\text{O}_2$.

I. $\text{CuO} \rightarrow \text{Cu}_2\text{O} + \text{O}_2$.		II. $\text{CuO} \rightarrow \text{liquid} + \text{O}_2$.		III. $\text{Liquid} \rightarrow \text{Cu}_2\text{O} + \text{O}_2$.	
$^\circ\text{C}$.	Mm. Hg.	$^\circ\text{C}$.	Mm. Hg.	$^\circ\text{C}$.	Mm. Hg.
838.8 ^a	4.62	1083.8 ^a	450	1084.2	373.7
05.0 ^a	14.92	1088.7 ^a	512	1085.3	360.8
915.6 ^a	17.20	1092.6 ^a	601	1085.5	393.0
956.2 ^a	41.06	1096.4 ^a	671	1088.5	353.5
956.1 ^a	40.82	1097.2 ^a	722	1090.1	387.4
983.5 ^a	68.50	1105.7 ^a	939	1091.9	314.6
983.3 ^a	70.50	1119.0 ^a	1258	1096.5	314.5
983.5 ^a	70.60	1130.0 ^a	1716	1100.3	302.0
1000.6 ^a	96.77	1135.8 ^a	2020	1109.2	257.0
1017.7 ^a	135.31	1171.0 ^a	6700	1123.0	205.5
1038.8 ^a	195.00	1204.4 ^a	16090	1131.3	219.7
1043.1 ^a	214.85	1210.6 ^a	24150	1134.8	157.1
1059.1 ^a	279.00	1232.5 ^a	44700	1139.9	167.7
1072.3	353.5			1144.7	127.0
1075.0	373.0			1150.0	115.5
1076.7	382.0			1153.3	89.0
1077.4	387.4			1154.6	92.0
1077.9	389.2			1175.1	57.4
1080.1	403.0			1185.4	33.0
1080.7 ^b	406.5			1196.9	22.2
1081.5 ^b	412.0			1200.8	16.5
1085.0 ^b	435.0			1211.7	9.8
				1221.8	3.5
				1233.8	1.54
				1230.1	1.03
				1231.3	0.95

^a Quoted from Tables IX and X of previous paper (Smyth and Roberts, *op. cit.*, pp. 2601, 2602.)

^b Metastable.

The methods used in determining the pressures along Curves (I) and (II) have been fully discussed elsewhere,¹ and need not be repeated. Except for a few points on Curve I close to the eutectic, no further determinations were made for these two curves. Three of these new points are at temperatures higher than the eutectic, that is, on the metastable part of Curve I, and, as may be seen in the large scale insert in Fig. 2, are in satisfactory agreement with the points determined in the stable region.

All of the determinations for Curve III, $\text{Liquid} \rightleftharpoons \text{Cu}_2\text{O}(s) + \text{Gas}$, are new. It was found that false equilibria at pressures lower or higher

¹ *Op. cit.*, pp. 2593 to 2602.

TABLE II.
DISSOCIATION PRESSURES AT ROUND TEMPERATURES.
System $\text{CuO}:\text{Cu}_2\text{O}:\text{O}_2$.

I. $\text{CuO} \rightarrow \text{Cu}_2\text{O} + \text{O}_2$		II. $\text{CuO} \rightarrow \text{liquid} + \text{O}_2$	III. $\text{Liquid} \rightarrow \text{Cu}_2\text{O} + \text{O}_2$
° C.	Mm. Hg.	Mm. Hg.	Mm. Hg.
900	12.6
920	19.4
940	29.6
960	44.6
980	66.2
1000	97.2
1020 ^b	140.7
1040 ^b	201.6
1060	285.9
1080	401.0
1080.2	402.3	402.3	402.3
(Eutectic)			
1100	557.1 ^a	740	305.0
1120	1325	220.0
1140	2410	140.0
1160	4390	79.5
1180	8210	40.5
1200	15200	17.0
1220	29100	4.75
1235	0.6
(m. p. Cu_2O)			
1240	57500

^a Metastable.

^b Cupric oxide heated in air (partial pressure $\text{O}_2 = 153$ mm.) would start to dissociate at 1026°.

than the true dissociation pressures were very common. The former were attributed to a sudden increase in the power of solid cuprous oxide to adsorb oxygen at the pressure existing in the system as the temperature approached that at which chemical combination was possible. The latter were invariably accompanied by the formation of a film of liquid over the whole surface and in the pores of the charge, so that on cooling, the surface of the charge was found to be glazed and the interior almost vitreous, although the charge as a whole had not melted. Therefore, in order to be

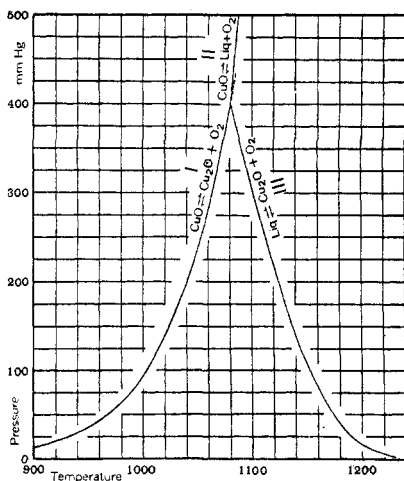


Fig. 3.—Pressure-temperature curves intersecting at the quadruple point (A): CuO , Cu_2O , liquid (2), Gas. The ordinates are proportional to the pressure.

sure what the condition of the charge was at any moment, that is, whether or not it was close to the equilibrium conditions for Curve III, the pressure and temperature readings at 5-minute intervals for several experiments were plotted on the same sheet of coordinate paper, as is done in Fig. 4.

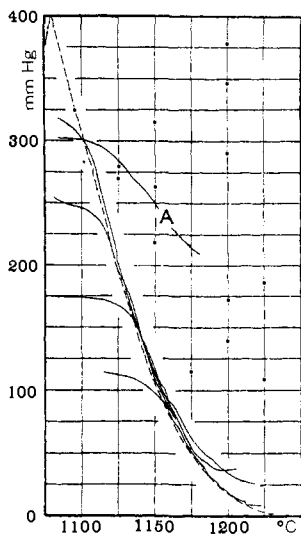


Fig. 4.—Actual change of pressure with temperature for several experiments in which cuprous oxide was heated in oxygen, the initial pressure being different in each case. The dotted line represents the univariant equilibrium Liquid (2), Cu_2O , Gas.

We were thus able to reject the more flagrant cases of false equilibria without the necessity of cooling the charge for examination. The points A and B in Fig. 8 of our previous paper¹ afford an excellent example of this effect of adsorption; while the curve marked A in Fig. 4 of the present paper shows the change of pressure with temperature after a film of liquid had formed over the surface of the charge.

At temperatures close to the melting point of cuprous oxide, measurement of the equilibrium pressure was complicated by the evolution of oxygen resulting from the reduction of the charge and of cuprous oxide vapor by the platinum crucible and thermocouple leads.

As the evolved oxygen is taken up by solid cuprous oxide, this effect was not serious when considerable solid was present. The measurement of temperature in this region is rendered uncertain by the continuous contamination of the thermocouple leads with copper derived from the vapor of cuprous oxide.

Composition of the Melt.—In every case the composition of the melt was determined by analysis of a charge that had been wholly melted and shown to be in a state of equilibrium with oxygen at a temperature and pressure falling on Curve II or Curve III. The (2CuO) content was determined from the gain in weight of the finely powdered charges when heated for 45 hours in a current of air at about 700° . The results of these determinations, expressed as the per cent. by weight of cupric oxide associated with the remaining copper in the charge, are tabulated in Table III and plotted in Fig. 5, together with the data for the system Cu : Cu_2O obtained by Heyn and by Slade and Farrow.

Melting Point of Cuprous Oxide.—Because of the evolution of oxygen already referred to, the melting point of pure cuprous oxide could not be determined directly. It was therefore, necessary to approximate it by

¹ *Op. cit.*, p. 2604.

extrapolating the $P - T$ and $T - X$ curves of Figs. 2 and 5. This extrapolation gives a temperature of 1235° and a pressure of 0.6 mm.

TABLE III.
OBSERVED COMPOSITIONS OF LIQUID (2) IN EQUILIBRIUM WITH Cu_2O OR CuO .
System $\text{CuO}:\text{Cu}_2\text{O}:\text{O}_2$.

Temperature, $^\circ\text{C}$.	In equilibrium with solid.	Per cent. by weight.	
		Cu_2O .	Cu .
1231.3	Cu_2O	57.2	42.8
1231.3	Cu_2O	58.1	41.9
1206.0	Cu_2O	60.9	39.1
1201.8	Cu_2O	61.6	38.1
1183.0	Cu_2O	62.8	37.2
1109.0	Cu_2O	67.8	32.2
1081.2	Cu_2O	68.7	31.3
1089.5	CuO	69.2	30.8
1107.8	CuO	71.9	28.1
1120.5	CuO	72.5	27.5
1160.0	CuO	76.7	23.3
1193.0	CuO	77.6	22.4
1216.5	CuO	79.7	20.3
1225.0	CuO	80.8	19.2

Melting Point and Equilibrium Pressure of the Cupric: Cuprous Oxide Eutectic.—After several attempts, two satisfactory cooling curves were obtained for mixtures of solid cupric oxide and liquid. On these curves the

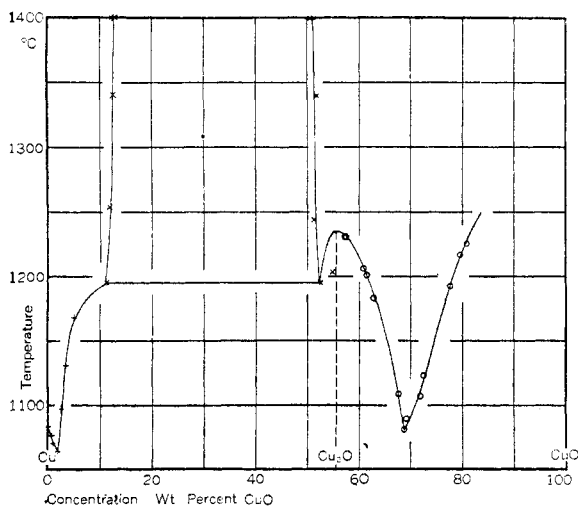


Fig. 5.—Temperature-concentration (melting point or solubility) diagram. The concentration is expressed as the percentage by weight of cupric oxide, associated with copper.

+ data of Heyn.

× data of Slade and Farrow.

○ data of Smyth and Roberts.

lowest temperatures reached during solidification were 1079.7° and 1080.6°, respectively, the mean being 1080.2°. The equilibrium pressure at the eutectic, 402.3 mm. of mercury, was calculated from the data with the aid of Equation 8 below. When cupric oxide is allowed to dissociate on heating, the pressure tends to follow the metastable portion of Curve I for a considerable distance beyond the eutectic until, very suddenly, melting begins, oxygen is evolved and usually a portion of the charge is ejected from the crucible. This material on coming in contact with the silica glass wall of the reaction chamber rapidly eats its way through it and causes a leak.

Absence of Solid Solution of Cupric Oxide in Cuprous Oxide.—In order to show whether or not solid solution of cupric oxide in cuprous oxide occurs to an appreciable extent, two charges of cuprous oxide were held in the furnace for 2 hours at 1050°; one under an oxygen pressure of 225.5 mm. of mercury (about 22 mm. below the corresponding dissociation pressure), and the other under an oxygen pressure of about 0.03 mm. of mercury. The latter pressure was maintained by continuous pumping throughout the experiment. The charges were subsequently analyzed for cupric oxide and their refractive indices determined. The results, which are tabulated in Table IV, show that the two charges were practically identical,

TABLE IV.
INVESTIGATION OF SOLID SOLUTION OF CuO IN Cu₂O.

Temperature. C.	Pressure. Mm. Hg.	Wt. per cent. CuO.	Refractive index. ^a
1048	225.5	0.5	2.86 ± 0.015
1048	0.03	0.6	2.86 ± 0.015

^a Owing to a slow chemical reaction between the cuprous oxide and the liquid in which it was immersed, a greater accuracy in the absolute value of the refractive index could not be attained. However, it is improbable that a difference of 0.01 between the two samples would not have been detected if present. The authors' thanks are due to Dr. H. E. Merwin for making this determination.

and, consequently, that solid solution at 1050° is insignificant. We have shown elsewhere¹ that solid solution of small amounts of cuprous oxide in cupric oxide at 984° does not occur; no evidence of solid solution was found at any temperature, so that we may confidently assume that solid solution between the two oxides is negligible at any temperature within the range studied.

Evaluation of $\ln p$, ΔH , and ΔF for Reaction I.—We now have several new pressure-temperature determinations for Reaction I, $(2\text{CuO})(s) \rightleftharpoons (\text{Cu}_2\text{O})(s) + \frac{1}{2}(\text{O}_2)(g) - 2\Delta H_{\text{CuO}}$, which are available for a recalculation of the equation connecting p and T . Again assuming that this equation is of the form $\log p = a \cdot (1/T) + b$, and applying a least square solution to the data of Cols. 1 and 2 in Table I, we obtain

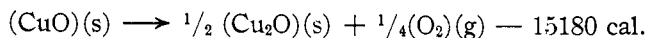
¹ *Op. cit.*, p. 2593.

$$\log p = \frac{-13261}{T} + 12.4043 \quad (8)$$

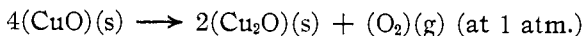
This is the equation with which the pressures in Col. 2 of Table II were calculated. Equation 8 may also be written

$$\ln p = \frac{-60719}{RT} + 28.560 \quad (8a)$$

where the value 1.9885 cal¹ has been chosen for R . This is the equation of the straight line I in Fig. 2. Referring to the first equation of 3a we see that the value 60719 in Equation 8a is equal to $4\Delta H_{\text{CuO}}$; ΔH_{CuO} is therefore equal to 15180; and, for temperatures in the vicinity of 1000°, we may write



For the reaction



the corresponding decrease in the free energy² is

$$-\Delta F = -60719 + 43.604 T.$$

Our earlier values³ were $\Delta H_{\text{CuO}} = 15142$ cal. and $-\Delta F = -60568 + 43.38 T$.

Dissociation Pressures of the Unsaturated Solution.—Three determinations were made at 1150° and one at 1120° of the dissociation pressure of the unsaturated liquid. In each case the fused charge was held at a temperature about 10° below the temperature in question, and at a pressure close to that chosen for the experiment, until

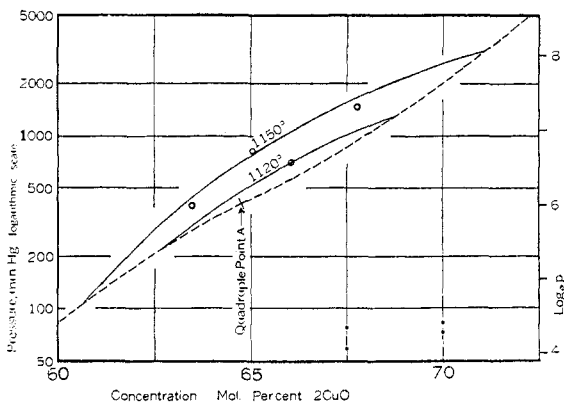


Fig. 6.—Pressure-concentration isotherms for Liquid (2) in the system $\text{Cu}_2\text{O} : \text{O}_2$. The dotted curve represents the equilibrium pressure for the saturated liquid in contact with solid cupric or cuprous oxide as the case may be. It is not an isotherm.

¹ *Smithsonian Phys. Tab.*, p. 408, 1920.

² J. Johnston, *THIS JOURNAL*, 30, 1359 (1908), Eq. VIa.

³ *Op. cit.*, p. 2606.

absorption of oxygen had practically ceased. The temperature was then raised, with an evolution of oxygen from the charge, and the equilibrium pressure determined at 1120° or 1150°.

The results of these measurements, together with the equilibrium pressures at 1120° and 1150° for Reactions II and III are tabulated in Table V and plotted as isotherms in Fig. 6. The compositions in both cases are expressed as the mol fraction of (2CuO) in a mixture of (2CuO) and (2Cu).

TABLE V.
DISSOCIATION PRESSURES OF LIQUID (2) AT 1120° AND 1150°.
System CuO:Cu₂O:O₂.

Temperature. °C.	Wt. per cent.		Mol. per cent.		Pressure. Mm. Hg.
	CuO.	Cu.	CuO.	Cu.	
	A. Unsaturated.				
1120	69.9	30.1	64.9	35.1	482.0
1150	68.6	31.4	63.5	37.5	389.2
1150	69.6	30.4	65.1	34.9	831.8
1150	72.5	27.5	67.8	32.2	1497.0
	B. Saturated with Cu ₂ O.				
1120	66.8	33.2	61.7	38.3	220.0
1150	65.1	34.9	59.9	40.1	107.0
	C. Saturated with CuO.				
1120	72.3	27.7	67.5	32.5	1320
1150	74.4	25.6	69.9	30.1	3280

The dotted line in Fig. 6 represents the change of equilibrium pressure with the concentration of the saturated solution.

Calculation of the Heat of Formation of the Liquid.—With the aid of Equations 4 and 5, it is possible to calculate the latent heat of formation of the saturated solution; and with the aid of Equation 6 to form some idea concerning that of the unsaturated solution.

In Equations 4 and 5 all of the quantities are known, or can be calculated directly from the data, with the exception of L , which is to be sought, and the second term of the denominator, which represents the small change of volume on melting. Then, for Reaction II, neglecting the volume change on melting,

$$L_{II} = (1 - x_1) \left(TV_g \frac{dp}{dt} - RT \ln \frac{p_I}{p_{II}} - 4\Delta H_{CuO} \right), \quad (9)$$

and for Reaction III

$$L_{III} = (x_1 - 1/2) \left(4\Delta H_{CuO} + RT \ln \frac{p_I}{p_{III}} - TV_g \frac{dp}{dt} \right). \quad (10)$$

In Fig. 7 the values of L_{II} and L_{III} calculated at temperatures 10° apart for Reactions II and III are plotted as gram calories per mol of solution against the mol composition of the liquid. A rather uncertain

extrapolation to $x = 50\%$ gives 12,500 gram calories for the heat of fusion of 1 mol of cuprous oxide, that is, about 87 calories per gram.

A consideration of the $P - T$ curves for the liquid will throw some light on the shape of the heat of formation curves for the liquid. These $P - T$ curves are plotted in Fig. 8, taking the data from the isotherms of Fig. 5, and plotting pressures to a logarithmic scale. The slope of the $P - T$ curves is given by Equation 7,

$$\left(\frac{\partial p_1}{\partial t}\right)_x = \frac{1}{T} \cdot \frac{2\Delta H_{\text{Cu}_2\text{O}} + \frac{1}{2} RT \ln \frac{p_1}{p_1} - \left(\frac{\partial L}{\partial x}\right)_t}{\frac{1}{2} V_g} \quad (7)$$

If we replace $2\Delta H_{\text{Cu}_2\text{O}}$ by its value in Equation 3 and remember that, for a perfect gas, $V_g = RT/P$, and that $1/P^1 \cdot dp/dt = d \ln p/dt$, we may write

$$\left(\frac{\partial L}{\partial x}\right)_t = \frac{RT^2}{2} \left[\frac{d \ln p_1}{dt} + \frac{1}{P^1} \ln \frac{p_1}{p_1} - \left(\frac{\partial \ln p_1}{\partial t}\right)_x \right], \quad (11)$$

where $d \ln p_1/dt$ and $(\partial \ln p_1/\partial t)_x$ are the slopes of curves in Fig. 7. As will be seen in Fig. 7, the $P - T$ curve for a liquid containing 67 mol per cent. of (2CuO) nearly coincides with Curve I, the $P - T$ curve for the metastable dissociation of solid cupric oxide into solid cuprous oxide. At this concentration on the 1150° isotherm, we should therefore expect a maximum or minimum value for the heat of formation of the liquid.

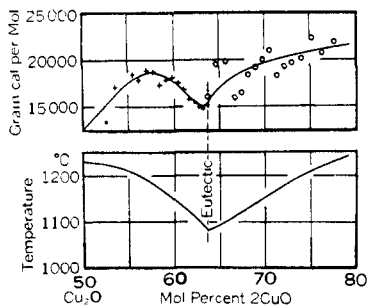


Fig. 7.—Upper diagram: heat of formation per mol of Liquid (2), from solid cupric and solid cuprous oxides; lower diagram: saturation temperatures; both plotted against the mol. percentage of (2CuO) in the liquid, the other component being (2Cu) .

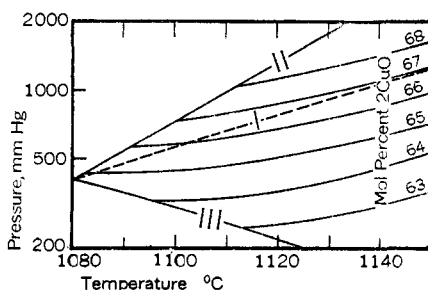


Fig. 8.—Pressure-temperature curves at constant composition for several compositions of Liquid (2) lying in the system $\text{Cu}_2\text{O}:\text{O}_2$. Curves (II) and (III), and the extrapolated (metastable) portion of Curve (I) are reproduced from Fig. 2. The pressure scale is logarithmic.

A calculation of Equation 11 shows that the slope $(\partial L/\partial x)_t$ has a small positive value at 63% which decreases with increasing (2CuO) content. Consequently, the heat of formation of the liquid at 1150° passes through a maximum at about 67% (2CuO) . At 1120° , the slopes of the curves are all very much less than that of Curve I, and increase with increase of

(2CuO) content. As before, the value of $(\partial L/\partial x)_t$ is positive at 63% (2CuO) and decreases as the (2CuO) content increases. As it has still a positive value at 67%, the maximum value of L must lie at a higher concentration than 67%.

In Fig. 6 it will be seen that the value of L increases as x increases from about 20% at 1150° to 27% at 1080°. In the preceding paragraph it was shown that, at constant temperature, L increases as x increases through, presumably, the whole of the composition range. We must therefore conclude that L is greater at the higher temperatures.

Dissociation Pressures in the System Cuprous Oxide: Copper: Oxygen.

—As we have pointed out, the measurement of dissociation pressures near the melting point of cuprous oxide is complicated by the evolution of oxygen as the vapor of cuprous oxide is reduced on coming in contact with platinum. We therefore placed the charge in a reaction chamber of silica glass connected to a McLeod gage. As cuprous oxide does not dissociate rapidly it was necessary to reduce the volume of the system as much as was practicable, to about 25 cc. in this case, part of this volume being occupied by the charge. Temperatures were measured by a thermocouple whose junction was tied to the outside of the reaction chamber near the center, thus eliminating platinum from the system.

With this apparatus we succeeded in determining three points on Curve V, $\text{Cu}_2\text{O}(s) \rightleftharpoons \text{Liquid (1)} + \text{Gas}$. These are tabulated in Table VI, and

TABLE VI.
OBSERVED EQUILIBRIUM PRESSURES FOR THE DISSOCIATION OF Cu_2O INTO LIQUID (1) AND VAPOR.

Temperature. C.	Pressure. Mm. Hg.
1119.2	0.028
1150.4	0.035
1184.6	0.041

plotted in Fig. 2. There is evidently a eutectic between cuprous oxide and silica near 1175°, for this temperature could not be exceeded without causing the silica tube to dissolve in the liquid to such an extent that air leaked through it. Curve V ends at 1195°, at the quadruple point (B), Solid Cu_2O , Liquid (1), Liquid (2), Gas. From this point we have drawn a dotted line (VI) to represent the $P - T$ curve for $\text{Cu}_2\text{O}(s) \rightleftharpoons \text{Liquid (2)} + \text{Gas}$, although no determinations of the equilibrium pressures are available.

The curve given by Slade and Farrow¹ for the equilibrium pressures for the reaction $\text{Liquid (2)} \rightleftharpoons \text{Liquid (1)} + \text{Gas}$ is reproduced as a dotted line in Fig. 2, and marked "VII (S + F)." This is the Reaction VII referred to under our heading "Theoretical Discussion," and as we have shown, the curve should pass through the quadruple point (B), and the

¹ *Op. cit.*, Fig. 5.

pressures along it should everywhere be less than the pressures at the corresponding temperatures on Curve VI or Curve III. As a matter of fact, the pressures along this curve were found by Slade and Farrow to be everywhere greater than those along Curve VI and, above 1218°, greater than those along Curve III.

This discrepancy might be considered as indicating that the upper portion of Curve III is metastable. In Slade and Farrow's experiments, however, the charge was heated in a magnesia boat placed in a platinum tube.¹ That the system also contained considerable cuprous oxide vapor, whether this was dissociated or not, is evident from the deposit of cuprous oxide that formed on the cooler parts of the tube. As already stated we found that cuprous oxide vapor is slowly reduced by platinum, copper dissolving in the platinum and oxygen being liberated. Thus it seems more probable that the data of Slade and Farrow's Table IV represent a reaction between this solution of copper in platinum, a mixture of cuprous oxide vapor, and oxygen, the liquid mixture in the boat absorbing oxygen so slowly that it did not reach its equilibrium composition, and that the pressures observed were in every case greater than the equilibrium pressure for Liquid (1), Liquid (2), Gas alone.

Summary.

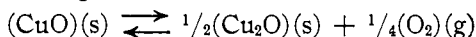
1. Solid solution between cupric oxide, cuprous oxide and copper has been shown to be non-existent or negligible, as judged by the dissociation pressures in the system.

2. In conjunction with the determinations of Heyn and of Slade and Farrow, we have established the $T - X$ (melting-point) relations from pure copper to the composition 81% cupric oxide + 19% copper by weight.

3. From a consideration of the $T - X$ diagram we have shown the general course of the $P - T$ curves in the system.

4. Data are presented for the three dissociation-pressure curves in the system $\text{Cu}_2\text{O} : \text{CuO} : \text{O}_2$; the melting point of the $\text{Cu}_2\text{O} : \text{CuO}$ eutectic is shown to be 1080.2° at 402.3 mm. mercury; and the melting point of cuprous oxide to be 1235° at 0.6 mm. mercury.

5. The energy changes for the reaction



and the heat of fusion of cuprous oxide have been calculated from the data.

6. Equilibrium pressures for the dissociation of cuprous oxide within the temperature range 1119° to 1184° are presented, and are shown to be in accord with our determinations in the system $\text{Cu}_2\text{O} : \text{CuO} : \text{O}_2$.

WASHINGTON, D. C.

¹ *Op. cit.*, p. 529.