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TABLES OF OXYGEN PRESSURES CALCULATED
FROM THE HYDROGEN-WATER SYSTEM AND
FROM THE DISSOCIATION OF CUPRIC OXIDE

by

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TABLES OF OXYGEN PRESSURES CALCULATED FROM THE HYDROGEN-WATER SYSTEM AND FROM THE DISSOCIATION OF CUPRIC OXIDE

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ABSTRACT

The dissociation of various mixtures of hydrogen and water vapor and of cupric oxide has been calculated over a wide range of temperatures (from 600 to 1700°C for the H₂-H₂O system, and from 200 to 1000°C for CuO). The resulting partial pressures of oxygen are presented in tabular form.

INTRODUCTION

Investigations of oxidation-reduction equilibria and kinetics of oxide systems require a knowledge of the partial pressure of oxygen in the gas phase. It is a common practice for oxygen pressures to be established with the aid of the known standard free energies (ΔF°) for such reactions as

Unfortunately, few, if any, investigators distribute the results of their calculations of oxygen pressure $P(\text{O}_2)$; consequently, this labor undoubtedly has been repeated many times. The present tabulation started out to be just such a private list; therefore, no attempt has been made to make it all inclusive. However, for the hydrogen-water system these tables do present a variation of $P(\text{O}_2)$ over several decades at any chosen reaction temperature; in addition, for the dissociation of cupric oxide they give oxygen pressures ranging from about 10^{-20} to 0.1 atm. The hydrogen-water reaction has the advantage of acting in the manner of a buffered system, that is, adsorption or evolution of a small amount of oxygen by the walls of the reaction vessel will not grossly affect $P(\text{O}_2)$ because of the comparative excess of H₂O and H₂ in the atmosphere. The copper oxide reaction does not give this buffering action and, therefore, has doubtful utility at low oxygen

pressures. At higher pressures, however, above perhaps 10^{-8} or 10^{-7} atm, the cupric-cuprous oxide system has the advantage of allowing $P(O_2)$ to be very simply regulated by controlling a furnace whose temperature is independent of that of the reaction being studied. Moreover, use of the copper oxide dissociation eliminates the possibility of unwanted side reactions, such as the formation of hydrides or hydroxides.

Whenever oxygen-containing atmospheres derived from either the H_2 - H_2O or the Cu_2O - CuO systems are used to study an oxidation or reduction reaction, care should be taken that the reaction does not inadvertently change the partial pressure of oxygen of the gas phase. In general, the volume of gas should be large enough to act as an infinite reservoir as compared to the quantity of oxygen involved in the reaction.

HYDROGEN-WATER SYSTEM

Oxygen pressures for the hydrogen-water system were calculated from the relations

$$\Delta F^\circ = -RT \ln K$$

and

$$K = P(H_2O)/P(H_2)P(O_2)^{1/2} \quad .$$

Upon combining these equations and substituting $\log_{10}N$ (written as $\log N$) for natural logarithms, the following is obtained:

$$\log P(O_2) = \frac{2\Delta F^\circ}{2.303 RT} + 2 \log \left[\frac{P(H_2O)}{P(H_2)} \right] \quad , \quad (5)$$

where R , the gas constant, is taken as $1.987 \text{ cal/}^\circ\text{C-mole}$, and T is in $^\circ\text{K}$. The standard free energy for the formation of water is given by Kubaschewski and Evans⁽¹⁾ over the range from 298 to 2500 $^\circ\text{K}$ by the equation

$$\Delta F^\circ(\pm 1 \text{ kcal}) = -58,900 + 13.1T \quad . \quad (6)$$

Values for ΔF° are also given by Coughlin⁽²⁾ at selected temperature points in the interval from 298.16 to 2000 $^\circ\text{K}$. The oxygen pressures listed in Table I are based on Kubaschewski and Evans' equation, but they agree satisfactorily with values calculated from Coughlin's free energies. The water vapor pressures given in Table I correspond to three convenient temperature points: (a) 0.00053 Torr is the pressure above ice at -78.5°C [Dushman⁽³⁾], the sublimation point of solid CO_2 ; (b) 4.6 Torr is the pressure above water at 0°C , and (c) 12.8 Torr is the aqueous pressure at 15°C .

Table I
PARTIAL PRESSURE OF OXYGEN IN EQUILIBRIUM WITH HYDROGEN AND WATER VAPOR*

P(H ₂) Torr	P(H ₂ O) Torr	P(O ₂)* (atm) at the Listed Temperatures (°C)								
		600	625	650	675	700	725	750	775	800
800	4.6	6.1 (-29)	4.0 (-28)	2.4 (-27)	1.3 (-26)	6.5 (-26)	3.0 (-25)	1.3 (-24)	5.1 (-24)	1.9 (-23)
	12.8	4.8 (-28)	3.2 (-27)	1.9 (-26)	1.0 (-25)	5.1 (-25)	2.3 (-24)	1.0 (-23)	4.0 (-23)	1.5 (-22)
400	4.6	2.4 (-28)	1.6 (-27)	9.6 (-27)	5.2 (-26)	2.6 (-25)	1.2 (-24)	5.1 (-24)	2.0 (-23)	7.6 (-23)
	12.8	1.9 (-27)	1.3 (-26)	7.5 (-26)	4.1 (-25)	2.0 (-24)	9.4 (-24)	4.0 (-23)	1.6 (-22)	6.0 (-22)
200	4.6	9.8 (-28)	6.5 (-27)	3.9 (-26)	2.1 (-25)	1.0 (-24)	4.8 (-24)	2.0 (-23)	8.1 (-23)	3.0 (-22)
	12.8	7.6 (-27)	5.0 (-26)	3.0 (-25)	1.6 (-24)	8.2 (-24)	3.7 (-23)	1.6 (-22)	6.4 (-22)	2.4 (-21)
80	4.6	6.1 (-27)	4.0 (-26)	2.4 (-25)	1.3 (-24)	6.5 (-24)	3.0 (-23)	1.3 (-22)	5.1 (-22)	1.9 (-21)
	12.8	4.8 (-26)	3.2 (-25)	1.9 (-24)	1.0 (-23)	5.1 (-23)	2.3 (-22)	1.0 (-21)	4.0 (-21)	1.5 (-20)
40	4.6	2.4 (-26)	1.6 (-25)	9.6 (-25)	5.2 (-24)	2.6 (-23)	1.2 (-22)	5.1 (-22)	2.0 (-21)	7.6 (-21)
	12.8	1.9 (-25)	1.3 (-24)	7.5 (-24)	4.1 (-23)	2.0 (-22)	9.4 (-22)	4.0 (-21)	1.6 (-20)	5.9 (-20)
20	4.6	9.8 (-26)	6.5 (-25)	3.9 (-24)	2.1 (-23)	1.0 (-22)	4.8 (-22)	2.0 (-21)	8.1 (-21)	3.0 (-20)
	12.8	7.6 (-25)	5.0 (-24)	3.0 (-23)	1.6 (-22)	8.2 (-22)	3.7 (-21)	1.6 (-20)	6.4 (-20)	2.4 (-19)
8	4.6	6.1 (-25)	4.0 (-24)	2.4 (-23)	1.3 (-22)	6.5 (-22)	3.0 (-21)	1.3 (-20)	5.1 (-20)	1.9 (-19)
	12.8	4.8 (-24)	3.2 (-23)	1.9 (-22)	1.0 (-21)	5.1 (-21)	2.3 (-20)	1.1 (-19)	4.0 (-19)	1.5 (-18)
4	4.6	2.4 (-24)	1.6 (-23)	9.6 (-23)	5.2 (-22)	2.6 (-21)	1.2 (-20)	5.1 (-20)	2.0 (-19)	7.6 (-19)
	12.8	1.9 (-23)	1.3 (-22)	7.5 (-22)	4.1 (-21)	2.0 (-20)	9.4 (-20)	4.0 (-19)	1.6 (-18)	5.9 (-18)

		825	850	875	900	925	950	975	1000	1025
800	0.00053	9.0 (-31)	2.9 (-30)	9.4 (-30)	2.8 (-29)	8.0 (-29)	2.1 (-28)	5.9 (-28)	1.5 (-27)	3.6 (-27)
	4.6	6.7 (-23)	2.2 (-22)	7.0 (-22)	2.1 (-21)	6.0 (-21)	1.6 (-20)	4.4 (-20)	1.1 (-19)	2.7 (-19)
400	0.00053	3.6 (-30)	1.2 (-29)	3.8 (-29)	1.1 (-28)	3.2 (-28)	8.9 (-28)	2.3 (-27)	5.9 (-27)	1.5 (-26)
	4.6	2.7 (-22)	8.9 (-22)	2.8 (-21)	8.4 (-21)	2.4 (-20)	6.6 (-20)	1.7 (-19)	4.4 (-19)	1.1 (-18)
200	0.00053	1.5 (-29)	4.7 (-29)	1.5 (-28)	4.6 (-28)	1.3 (-27)	3.5 (-27)	9.4 (-27)	2.4 (-26)	5.8 (-26)
	4.6	1.1 (-21)	3.5 (-21)	1.1 (-20)	3.4 (-20)	9.6 (-20)	2.6 (-19)	7.0 (-19)	1.8 (-18)	4.3 (-18)
80	0.00053	9.0 (-29)	2.9 (-28)	9.4 (-28)	2.8 (-27)	8.0 (-27)	2.1 (-26)	5.9 (-26)	1.5 (-25)	3.6 (-25)
	4.6	6.7 (-21)	2.2 (-20)	7.0 (-20)	2.1 (-19)	6.0 (-19)	1.6 (-18)	4.4 (-18)	1.1 (-17)	2.7 (-17)
40	0.00053	3.6 (-28)	1.2 (-27)	3.8 (-27)	1.1 (-26)	3.2 (-26)	8.9 (-26)	2.3 (-25)	5.9 (-25)	1.5 (-24)
	4.6	2.7 (-20)	8.9 (-20)	2.8 (-19)	8.4 (-19)	2.4 (-18)	6.6 (-18)	1.7 (-17)	4.4 (-17)	1.1 (-16)
20	0.00053	1.5 (-27)	4.7 (-27)	1.5 (-26)	4.6 (-26)	1.3 (-25)	3.5 (-25)	9.4 (-25)	2.4 (-24)	5.8 (-24)
	4.6	1.1 (-19)	3.5 (-19)	1.1 (-18)	3.4 (-18)	9.6 (-18)	2.6 (-17)	7.0 (-17)	1.8 (-16)	4.3 (-16)
8	0.00053	9.0 (-27)	2.9 (-26)	9.4 (-26)	2.8 (-25)	8.0 (-25)	2.1 (-24)	5.9 (-24)	1.5 (-23)	3.6 (-23)
	4.6	6.7 (-19)	2.2 (-18)	7.0 (-18)	2.1 (-17)	6.0 (-17)	1.6 (-16)	4.4 (-16)	1.1 (-15)	2.7 (-15)
4	0.00053	3.6 (-26)	1.2 (-25)	3.8 (-25)	1.1 (-24)	3.2 (-24)	8.9 (-24)	2.3 (-23)	5.9 (-23)	1.5 (-22)
	4.6	2.7 (-18)	8.9 (-18)	2.8 (-17)	8.4 (-17)	2.4 (-16)	6.6 (-16)	1.7 (-15)	4.4 (-15)	1.1 (-14)

		1050	1075	1100	1125	1150	1175	1200	1225	1250
800	0.00053	8.5 (-27)	1.5 (-26)	4.4 (-26)	9.4 (-26)	2.0 (-25)	4.1 (-25)	8.1 (-25)	1.6 (-24)	3.1 (-24)
	4.6	6.4 (-19)	1.1 (-18)	3.3 (-18)	7.1 (-18)	1.5 (-17)	3.1 (-17)	6.1 (-17)	1.2 (-16)	2.3 (-16)
400	0.00053	3.5 (-26)	6.0 (-26)	1.7 (-25)	3.7 (-25)	8.0 (-25)	1.6 (-24)	3.2 (-24)	6.4 (-24)	1.2 (-23)
	4.6	2.6 (-18)	4.5 (-18)	1.3 (-17)	2.8 (-17)	6.0 (-17)	1.2 (-16)	2.4 (-16)	4.8 (-16)	9.2 (-16)
200	0.00053	1.3 (-25)	2.4 (-25)	6.9 (-25)	1.5 (-24)	3.2 (-24)	6.5 (-24)	1.3 (-23)	2.5 (-23)	4.9 (-23)
	4.6	1.0 (-17)	1.8 (-17)	5.2 (-17)	1.1 (-16)	2.4 (-16)	4.9 (-16)	9.8 (-16)	1.9 (-15)	3.7 (-15)
80	0.00053	8.5 (-25)	1.5 (-24)	4.4 (-24)	9.4 (-24)	2.0 (-23)	4.1 (-23)	8.1 (-23)	1.6 (-22)	3.1 (-22)
	4.6	6.4 (-17)	1.1 (-16)	3.3 (-16)	7.1 (-16)	1.5 (-15)	3.1 (-15)	6.1 (-15)	1.2 (-14)	2.3 (-14)
40	0.00053	3.5 (-24)	6.0 (-24)	1.7 (-23)	3.7 (-23)	8.0 (-23)	1.6 (-22)	3.2 (-22)	6.4 (-22)	1.2 (-21)
	4.6	2.6 (-16)	4.5 (-16)	1.3 (-15)	2.8 (-15)	5.8 (-15)	1.2 (-14)	2.4 (-14)	4.8 (-14)	9.2 (-14)
20	0.00053	1.3 (-23)	2.4 (-23)	6.9 (-23)	1.5 (-22)	3.2 (-22)	6.5 (-22)	1.3 (-21)	2.5 (-21)	4.9 (-21)
	4.6	1.0 (-15)	1.8 (-15)	5.2 (-15)	1.1 (-14)	2.4 (-14)	4.9 (-14)	9.8 (-14)	1.9 (-13)	3.7 (-13)
8	0.00053	8.5 (-23)	1.5 (-22)	4.4 (-22)	9.4 (-22)	2.0 (-21)	4.1 (-21)	8.1 (-21)	1.6 (-20)	3.1 (-20)
	4.6	6.4 (-15)	1.1 (-14)	3.3 (-14)	7.1 (-14)	1.5 (-13)	3.1 (-13)	6.1 (-13)	1.2 (-12)	2.3 (-12)
4	0.00053	3.5 (-22)	6.0 (-22)	1.7 (-21)	3.7 (-21)	8.0 (-21)	1.6 (-20)	3.2 (-20)	6.4 (-20)	1.2 (-19)
	4.6	2.6 (-14)	4.5 (-14)	1.3 (-13)	2.8 (-13)	5.8 (-13)	1.2 (-12)	2.4 (-12)	4.8 (-12)	9.2 (-12)

*P(O₂) may be calculated for interpolated or extrapolated values of P(H₂O) or P(H₂) at constant temperature with the relations

$$P_1(O_2) = P_2(O_2) \left[\frac{P_1(H_2O)}{P_2(H_2O)} \right]^2 \quad P_1(O_2) = P_2(O_2) \left[\frac{P_2(H_2)}{P_1(H_2)} \right]^2$$

**The term 6.1 (-29) should be read as 6.1 x 10⁻²⁹ atm etc

Table I Cont'd

P(H ₂) Torr	P(H ₂ O) Torr	P(O ₂) (atm) at the Listed Temperatures (°C)								
		1275	1300	1325	1350	1375	1400	1425	1450	1475
800	0.00053	5.7 (-24)	1.0 (-23)	1.9 (-23)	3.3 (-23)	5.8 (-23)	1.0 (-22)	1.7 (-22)	2.8 (-22)	4.5 (-22)
	4.6	4.3 (-16)	7.9 (-16)	1.4 (-15)	2.5 (-15)	4.4 (-15)	7.5 (-15)	1.3 (-14)	2.1 (-14)	3.4 (-14)
	12.8	3.4 (-15)	6.2 (-15)	1.1 (-14)	2.0 (-14)	3.4 (-14)	5.9 (-14)	9.9 (-14)	1.6 (-13)	2.7 (-13)
400	0.00053	2.3 (-23)	4.3 (-23)	7.6 (-23)	1.3 (-22)	2.3 (-22)	4.0 (-22)	6.6 (-22)	1.1 (-21)	1.9 (-21)
	4.6	1.7 (-15)	3.2 (-15)	5.7 (-15)	1.0 (-14)	1.7 (-14)	3.0 (-14)	5.0 (-14)	8.4 (-14)	1.4 (-13)
	12.8	1.3 (-14)	2.5 (-14)	4.4 (-14)	7.9 (-14)	1.4 (-13)	2.3 (-13)	3.9 (-13)	6.5 (-13)	1.1 (-12)
200	0.00053	9.2 (-23)	1.7 (-22)	3.1 (-22)	5.3 (-22)	9.3 (-22)	1.6 (-21)	2.7 (-21)	4.4 (-21)	7.3 (-21)
	4.6	6.9 (-15)	1.3 (-14)	2.3 (-14)	4.0 (-14)	7.0 (-14)	1.2 (-13)	2.0 (-13)	3.3 (-13)	5.5 (-13)
	12.8	5.4 (-14)	9.9 (-14)	1.8 (-13)	3.1 (-13)	5.5 (-13)	9.4 (-13)	1.6 (-12)	2.6 (-12)	4.3 (-12)
80	0.00053	5.7 (-22)	1.0 (-21)	1.9 (-21)	3.3 (-21)	5.8 (-21)	1.0 (-20)	1.7 (-20)	2.8 (-20)	4.5 (-20)
	4.6	4.3 (-14)	7.9 (-14)	1.4 (-13)	2.5 (-13)	4.4 (-13)	7.5 (-13)	1.3 (-12)	2.1 (-12)	3.4 (-12)
	12.8	3.4 (-13)	6.2 (-13)	1.1 (-12)	2.0 (-12)	3.4 (-12)	5.9 (-12)	9.9 (-12)	1.6 (-11)	2.7 (-11)
40	0.00053	2.3 (-21)	4.3 (-21)	7.6 (-21)	1.3 (-20)	2.3 (-20)	4.0 (-20)	6.6 (-20)	1.1 (-19)	1.9 (-19)
	4.6	1.7 (-13)	3.2 (-13)	5.7 (-13)	1.0 (-12)	1.7 (-12)	3.0 (-12)	5.0 (-12)	8.4 (-12)	1.4 (-11)
	12.8	1.3 (-12)	2.5 (-12)	4.4 (-12)	7.9 (-12)	1.4 (-11)	2.3 (-11)	3.9 (-11)	6.5 (-11)	1.1 (-10)
20	0.00053	9.2 (-21)	1.7 (-20)	3.1 (-20)	5.3 (-20)	9.3 (-20)	1.6 (-19)	2.7 (-19)	4.4 (-19)	7.3 (-19)
	4.6	6.9 (-13)	1.3 (-12)	2.3 (-12)	4.0 (-12)	7.0 (-12)	1.2 (-11)	2.0 (-11)	3.3 (-11)	5.5 (-11)
	12.8	5.4 (-12)	9.9 (-12)	1.8 (-11)	3.1 (-11)	5.5 (-11)	9.4 (-11)	1.6 (-10)	2.6 (-10)	4.3 (-10)
8	0.00053	5.7 (-20)	1.0 (-19)	1.9 (-19)	3.3 (-19)	5.8 (-19)	1.0 (-18)	1.7 (-18)	2.8 (-18)	4.5 (-18)
	4.6	4.3 (-12)	7.9 (-12)	1.4 (-11)	2.5 (-11)	4.4 (-11)	7.5 (-11)	1.3 (-10)	2.1 (-10)	3.4 (-10)
	12.8	3.4 (-11)	6.2 (-11)	1.1 (-10)	2.0 (-10)	3.4 (-10)	5.9 (-10)	9.9 (-10)	1.6 (-9)	2.7 (-9)
4	0.00053	2.3 (-19)	4.3 (-19)	7.6 (-19)	1.3 (-18)	2.3 (-18)	4.0 (-18)	6.6 (-18)	1.1 (-17)	1.9 (-17)
	4.6	1.7 (-11)	3.2 (-11)	5.7 (-11)	1.0 (-10)	1.7 (-10)	3.0 (-10)	5.0 (-10)	8.4 (-10)	1.4 (-9)
	12.8	1.3 (-10)	2.5 (-10)	4.4 (-10)	7.9 (-10)	1.4 (-9)	2.3 (-9)	3.9 (-9)	6.5 (-9)	1.1 (-8)

		1500	1525	1550	1575	1600	1625	1650	1675	1700
800	0.00053	7.3 (-22)	1.2 (-21)	1.9 (-21)	2.8 (-21)	4.4 (-21)	6.6 (-21)	1.0 (-20)	1.5 (-20)	2.1 (-20)
	4.6	5.5 (-14)	8.8 (-14)	1.4 (-13)	2.1 (-13)	3.3 (-13)	5.0 (-13)	7.5 (-13)	1.1 (-12)	1.6 (-12)
	12.8	4.3 (-13)	6.8 (-13)	1.1 (-12)	1.7 (-12)	2.6 (-12)	3.9 (-12)	5.8 (-12)	8.7 (-12)	1.3 (-11)
400	0.00053	2.9 (-21)	4.7 (-21)	7.3 (-21)	1.1 (-20)	1.7 (-20)	2.7 (-20)	4.0 (-20)	6.0 (-20)	8.6 (-20)
	4.6	2.2 (-13)	3.5 (-13)	5.5 (-13)	8.6 (-13)	1.3 (-12)	2.0 (-12)	3.0 (-12)	4.5 (-12)	6.5 (-12)
	12.8	1.7 (-12)	2.7 (-12)	4.3 (-12)	6.6 (-12)	1.0 (-11)	1.6 (-11)	2.3 (-11)	3.5 (-11)	5.1 (-11)
200	0.00053	1.2 (-20)	1.9 (-20)	2.9 (-20)	4.5 (-20)	7.0 (-20)	1.1 (-19)	1.6 (-19)	2.4 (-19)	3.5 (-19)
	4.6	8.8 (-13)	1.4 (-12)	2.2 (-12)	3.4 (-12)	5.3 (-12)	8.0 (-12)	1.2 (-11)	1.8 (-11)	2.6 (-11)
	12.8	6.9 (-12)	1.1 (-11)	1.7 (-11)	2.7 (-11)	4.1 (-11)	6.2 (-11)	9.3 (-11)	1.4 (-10)	2.0 (-10)
80	0.00053	7.3 (-20)	1.2 (-19)	1.9 (-19)	2.8 (-19)	4.4 (-19)	6.6 (-19)	1.0 (-18)	1.5 (-18)	2.1 (-18)
	4.6	5.5 (-12)	8.8 (-12)	1.4 (-11)	2.1 (-11)	3.3 (-11)	5.0 (-11)	7.5 (-11)	1.1 (-10)	1.6 (-10)
	12.8	4.3 (-11)	6.8 (-11)	1.1 (-10)	1.7 (-10)	2.6 (-10)	3.9 (-10)	5.8 (-10)	8.7 (-10)	1.3 (-9)
40	0.00053	2.9 (-19)	4.7 (-19)	7.3 (-19)	1.1 (-18)	1.7 (-18)	2.7 (-18)	4.0 (-18)	6.0 (-18)	8.6 (-18)
	4.6	2.2 (-11)	3.5 (-11)	5.5 (-11)	8.6 (-11)	1.3 (-10)	2.0 (-10)	3.0 (-10)	4.5 (-10)	6.5 (-10)
	12.8	1.7 (-10)	2.7 (-10)	4.3 (-10)	6.6 (-10)	1.0 (-9)	1.6 (-9)	2.3 (-9)	3.5 (-9)	5.1 (-9)
20	0.00053	1.2 (-18)	1.9 (-18)	2.9 (-18)	4.5 (-18)	7.0 (-18)	1.1 (-17)	1.6 (-17)	2.4 (-17)	3.5 (-17)
	4.6	8.8 (-11)	1.4 (-10)	2.2 (-10)	3.4 (-10)	5.3 (-10)	8.0 (-10)	1.2 (-9)	1.8 (-9)	2.6 (-9)
	12.8	6.9 (-10)	1.1 (-9)	1.7 (-9)	2.7 (-9)	4.1 (-9)	6.2 (-9)	9.3 (-9)	1.4 (-8)	2.0 (-8)
8	0.00053	7.3 (-18)	1.2 (-17)	1.9 (-17)	2.8 (-17)	4.4 (-17)	6.6 (-17)	1.0 (-16)	1.5 (-16)	2.1 (-16)
	4.6	5.5 (-10)	8.8 (-10)	1.4 (-9)	2.1 (-9)	3.3 (-9)	5.0 (-9)	7.5 (-9)	1.1 (-8)	1.6 (-8)
	12.8	4.3 (-9)	6.8 (-9)	1.1 (-8)	1.7 (-8)	2.6 (-8)	3.9 (-8)	5.8 (-8)	8.7 (-8)	1.3 (-7)
4	0.00053	2.9 (-17)	4.7 (-17)	7.3 (-17)	1.1 (-16)	1.7 (-16)	2.7 (-16)	4.0 (-16)	6.0 (-16)	8.6 (-16)
	4.6	2.2 (-9)	3.5 (-9)	5.5 (-9)	8.6 (-9)	1.3 (-8)	2.0 (-8)	3.0 (-8)	4.5 (-8)	6.5 (-8)
	12.8	1.7 (-8)	2.7 (-8)	4.3 (-8)	6.7 (-8)	1.0 (-7)	1.6 (-7)	2.3 (-7)	3.5 (-7)	5.1 (-7)

DISSOCIATION OF CUPRIC OXIDE

Oxygen pressures were determined from the dissociation of CuO by the relation

$$\Delta F^\circ = -RT \ln P(O_2)^{1/2},$$

which may be rearranged into the form

$$\log P(O_2) = -2\Delta F^\circ / 2.303 RT \quad (7)$$

Kubaschewski and Evans give ΔF° for this reaction between 298 and 1300°K as

$$\Delta F^\circ (\pm 0.5 \text{ kcal}) = 34,950 + 6.1T \log T - 44.3T \quad . \quad (8)$$

Coughlin lists values of ΔF° for the formation of Cu_2O and CuO at several points between 298.16 and 2000°K. Combination of these free energies in the term

$$\Delta F^\circ (2\text{Cu} + 1/2 \text{O}_2 \rightarrow \text{Cu}_2\text{O}) - 2 \Delta F^\circ (\text{Cu} + 1/2 \text{O}_2 \rightarrow \text{CuO})$$

gives values for $\Delta F^\circ (2\text{CuO} \rightarrow \text{Cu}_2\text{O} + 1/2 \text{O}_2)$ which agree satisfactorily with those given by equation (8). It should be emphasized that these expressions for ΔF° apply only when an equilibrated mixture of CuO , Cu_2O , and O_2 is present in the system. When this condition is fulfilled, neither nonstoichiometric compositions nor the further dissociation of Cu_2O can introduce an error.

The oxygen pressures calculated from equations (7) and (8) and listed in Table II have been confirmed by Berkowitz,⁽⁴⁾ who analyzed the oxygen content of a helium stream which had been passed over heated $\text{CuO}/\text{Cu}_2\text{O}$.

Table II

DISSOCIATION PRESSURE OF OXYGEN FROM CUPRIC OXIDE

Temp (°C)	P(O ₂) (atm)	Temp (°C)	P(O ₂) (atm)
200	8.6 (-21)	625	3.0 (-6)
225	3.1 (-19)	650	8.0 (-6)
250	8.0 (-18)	675	2.0 (-5)
275	1.5 (-16)	700	5.0 (-5)
300	2.2 (-15)	725	1.2 (-4)
325	2.6 (-14)	750	2.5 (-4)
350	2.5 (-13)	775	5.4 (-4)
375	2.0 (-12)	800	1.1 (-3)
400	1.3 (-11)	825	2.2 (-3)
425	7.8 (-11)	850	4.2 (-3)
450	4.1 (-10)	875	7.9 (-3)
475	1.9 (-9)	900	1.4 (-2)
500	7.9 (-9)	925	2.5 (-2)
525	3.0 (-8)	950	4.4 (-2)
550	1.1 (-7)	975	7.4 (-2)
575	3.5 (-7)	1000	1.2 (-1)
600	1.0 (-6)		

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