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A THERMODYNAMIC STUDY OF THE Cu–Cr–O SYSTEM BY THE EMF METHOD

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ABSTRACT

The equilibrium oxygen pressures of the three-phase regions [Cu, Cr_2O_3, $Cu_2Cr_2O_4$], [Cu, Cu_2O, $Cu_2Cr_2O_4$] and [CuO, Cu_2O, $Cu_2Cr_2O_4$] were measured as a function of temperature by the solid oxide electrolyte electromotive force method. The measured Gibbs energy of the reaction $Cu_2O + Cr_2O_3 = Cu_2Cr_2O_4$ ($\Delta G°$) was found to be $-46608 + 7.8328\ T$ J mol^{-1} (1075–1275 K). The evaluated Gibbs energy of formation of $Cu_2Cr_2O_4$ ($\Delta G^{\circ}_{f,Cu_2Cr_2O_4}$) was found to be $-1332900 + 332.761\ T$ J mol^{-1} (900–1350 K).

INTRODUCTION

The copper–chromium oxides are important catalysts and are of interest because of the use of Cr_2O_3-refractories in copper refining. However, the thermodynamic stabilities in the Cu–Cr–O system are not well-known: the phase diagrams reported by Gadalla and White [1] are inconsistent with other thermodynamic results, and catalyst studies [2–4] rely on extensive analyses, such as XPS (X-ray photoelectron spectroscopy) to determine oxidation states and phases. A better understanding of the thermodynamic stabilities would aid catalyst preparation and use.

The high-temperature Cu–Cr–O system is shown schematically in Fig. 1, with pertinent three-phase regions and corresponding equilibria labelled I to VI. High oxygen pressure ($\gg 1$ atm) regions are not included in this study.

The so-called "copper chromite" catalysts are frequently used in highly reducing atmospheres, e.g., in the hydrogenation of vegetable oils and methanol synthesis. Hence, the stabilities of $Cu_2Cr_2O_4$ and of Cu_2O and CuO saturated with $Cu_2Cr_2O_4$ were examined in the present study by measuring the equilibrium oxygen pressures of regions II, III and IV, respectively.

An evaluation of the measured and literature results for ΔG°_{II} (including derived results from equilibria V and VI) was also carried out.

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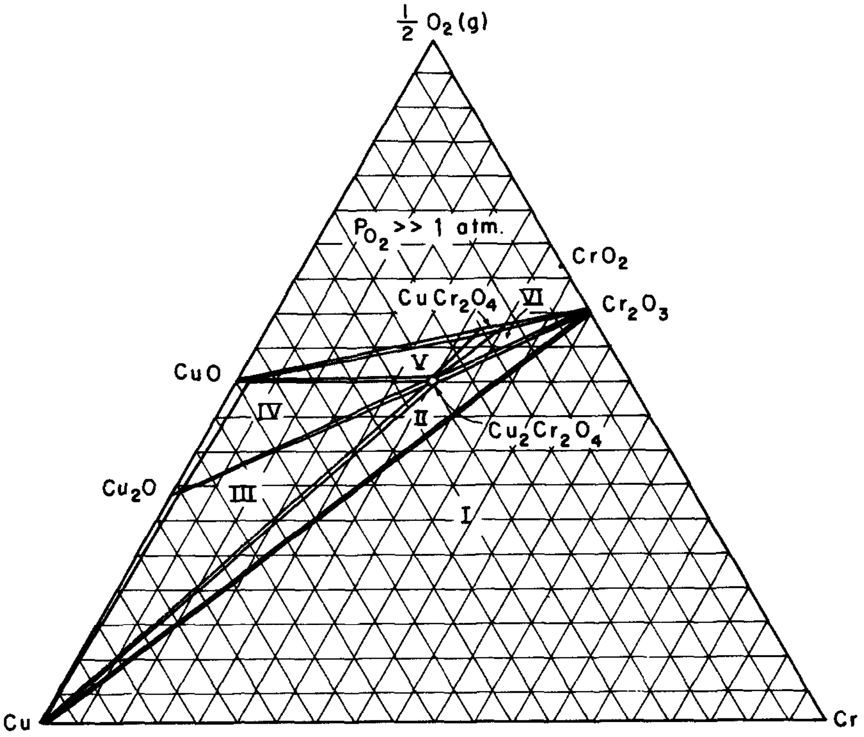

I $2Cr + \frac{3}{2}O_2(g) = Cr_2O_3$ (Cu saturated)

II $2Cu + Cr_2O_3 + \frac{1}{2}O_2(g) = Cu_2Cr_2O_4$

III $2Cu + \frac{1}{2}O_2(g) = Cu_2O$ ($Cu_2Cr_2O_4$ saturated)

IV $Cu_2O + \frac{1}{2}O_2(g) = 2CuO$ ($Cu_2Cr_2O_4$ saturated)

V $Cu_2Cr_2O_4 + \frac{1}{2}O_2(g) = CuO + CuCr_2O_4$.

VI $Cu_2Cr_2O_4 + Cr_2O_3 + \frac{1}{2}O_2(g) = 2CuCr_2O_4$

Fig. 1. Cu–Cr–O schematic diagram with three-phase equilibria; some regions are enlarged for clarity.

EXPERIMENTAL

In this study the equilibrium oxygen potentials of the three-phase regions [Cu, Cr_2O_3, $Cu_2Cr_2O_4$], [Cu, Cu_2O, $Cu_2Cr_2O_4$] and [CuO, Cu_2O, $Cu_2Cr_2O_4$] were determined using the EMF cells

$$\text{Cu, } Cr_2O_3\text{, } Cu_2Cr_2O_4 \,|\, ZrO_2(+CaO) \,|\, \text{Cu, } Cu_2O \quad (1)$$

$$\text{Cu, } Cu_2O\text{, } Cu_2Cr_2O_4 \,|\, ZrO_2(+CaO) \,|\, \text{Cu, } Cu_2O \quad (2)$$

$$\text{CuO, } Cu_2O\text{, } Cu_2Cr_2O_4 \,|\, ZrO_2(+CaO) \,|\, \text{CuO, } Cu_2O \quad (3)$$

Cell 1 gives $\Delta G°$ of the reaction $Cu_2O + Cr_2O_3 = Cu_2Cr_2O_4$, and cells 2 and 3 show the effect of saturation with $Cu_2Cr_2O_4$ on the equilibria $2Cu + 1/2O_2 = Cu_2O$ and $Cu_2O + 1/2O_2 + 2CuO$, respectively.

Materials

The materials used were Cu, 99.99%; Cu_2O, 99.9%; CuO, 99.4% and Cr_2O_3, 99.999%; $Cu_2Cr_2O_4$ was synthesized by grinding together equimolar portions of Cu_2O and Cr_2O_3 powders, making into pellets and sintering in air for 48 h at 960°C followed by air-cooling. The formation was verified by X-ray diffraction using Ni-filtered Cu K_α radiation, with Al foil used to reduce film fogging due to Cr fluorescence.

Apparatus and procedure

The EMF cell design has been previously reported [5]. The ZrO_2 (+11 wt.% CaO) electrolyte tubes from the Nippon Kagaku Togyo Co., Ltd. were 5 mm ID × 7 mm OD × 50 mm long with a flat closed end. Platinum wires with platinum foil at the cell junctions and spot-welded Kanthal extensions were used as leads. The sample mixture-containing electrolyte tube, reference mixture-containing alumina crucible and the alumina lead wire sheaths were bonded together with alumina cement which also served as a gaseous diffusion barrier above the sample and reference mixtures. After the cement had dried, the cell was placed into a mullite tube and loaded into a Kanthal-element furnace having a constant temperature zone. The cell was evacuated for 3 h at 250°C to remove moisture and then slowly heated to the desired temperature. The furnace temperature was maintained ±0.5°C by a Barber–Colman 560 controller. Temperatures were measured by Type K thermocouples checked against a standardized Type S thermocouple. Thermocouple and sample EMF values were measured by a Keithley 191 voltmeter. The sample was considered equilibrated when the EMF remained constant for 3 h. Reversibility was checked by polarization with an opposite potential of 1.5 V for 10 s. An EMF recovery within 15 min was considered satisfactory. Additionally, sample temperatures were chosen alternatingly higher and lower to ensure detection of any metastable results.

RESULTS

The EMF data of cells 1–3 are given in Table 1 and Figs. 2 and 3. The data have been corrected by subtraction of 0.16 ± 0.10 mV, which was the temperature-independent result (1023–1273 K) of three cells each having $Cu + Cu_2O$ in both sample and reference positions. The resulting EMF equations are

$$\epsilon_1 = 241.523 - 0.040590\,T\ (\pm 0.24)\ \text{mV}\ (1075\text{–}1275\ \text{K})$$

$$\epsilon_2 = 2.5438 - 0.001714\,T\ (\pm 0.17)\ \text{mV}\ (1123\text{–}1323\ \text{K})$$

$$\epsilon_3 = 6.581 - 0.004844\,T\ (\pm 0.13)\ \text{mV}\ (1122\text{–}1268\ \text{K})$$

TABLE 1

EMF data

Cell 1		Cell 2		Cell 3	
Cu, Cr_2O_3, $Cu_2Cr_2O_4$ | CSZ * | Cu, Cu_2O		Cu, Cu_2O, $Cu_2Cr_2O_4$ | CSZ * | Cu, Cu_2O		Cu_2O, CuO, $Cu_2Cr_2O_4$ | CSZ * | CuO, Cu_2O	
T°C	EMF (mV)	T°C	EMF (mV)	T°C	EMF (mV)
801.5	198.04	(Run 1)			
849.2	195.88	852.7	0.682	849.0	1.130
852.4	195.74	903.4	0.592	897.5	0.939
906.1	193.59	952.4	0.485	946.0	0.661
955.0	191.76	1001.3	0.374	994.6	0.439
957.2	191.65	1047.0	0.320		
1002.2	189.72	(Run 2)			
		849.6	0.539		
		903.7	0.501		
		953.8	0.379		
		999.5	0.310		
		1050.3	0.261		

* CSZ = $ZrO_2(CaO)$.

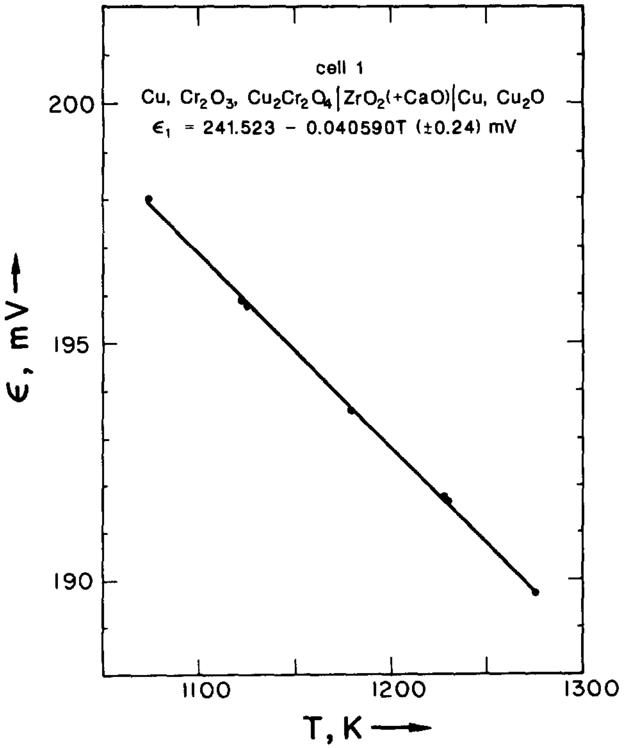

Fig. 2. Results of EMF Cell 1.

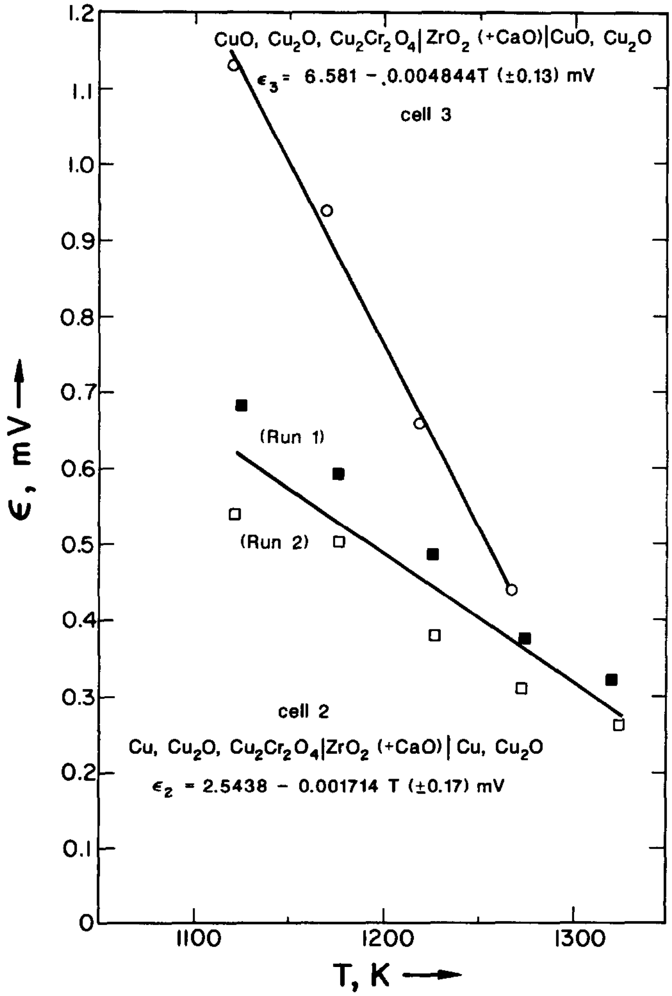

Fig. 3. Results of EMF Cells 2 and 3.

From the Nernst relationship $\Delta G^\circ = -nF\epsilon$, cell 1 gives

$$\Delta G^\circ = -46\,608 + 7.8328\,T\ (\pm 50)\ \mathrm{J\,mol^{-1}}$$

for the cell reaction $Cu_2O + Cr_2O_3 = Cu_2Cr_2O_4$. Addition of $\Delta G^\circ_{\mathrm{f,Cu_2O}}$ [6] gives

$$\Delta G^\circ_{\mathrm{II}} = -213\,135 + 78.7628\,T\ \mathrm{J\,mol^{-1}}\ (1075\text{–}1275\ \mathrm{K})$$

with $\log p_{O_2}(\mathrm{atm}) = -\dfrac{22\,264}{T} + 8.2276$

for the reaction $2Cu(s) + Cr_2O_3 + 1/2O_2(g) = Cu_2Cr_2O_4$. For cells 2 and 3, the relationship $\Delta G = -nF\epsilon = -RT \ln[p_{O_2}(\mathrm{RHS})/p_{O_2}(\mathrm{LHS})]^{1/2}$ gives

$$\log p_{O_2}(\mathrm{Cu, Cu_2O, Cu_2Cr_2O_4}) = \log p_{O_2}(\mathrm{Cu, Cu_2O}) - \frac{51.3(\pm 3.4)}{T} + 0.0346$$

$$\log p_{O_2}(\mathrm{Cu_2O, CuO, Cu_2Cr_2O_4}) = \log p_{O_2}(\mathrm{Cu_2O, CuO})$$
$$- \frac{132.7(\pm 2.6)}{T} + 0.0977$$

Addition of $\log p_{O_2}$ (Cu, Cu_2O) and $\log p_{O_2}$ (Cu_2O, CuO) expressions [6] gives the respective results

$$\log p_{O_2}(\mathrm{Cu, Cu_2O, Cu_2Cr_2O_4})\ (\mathrm{atm}) = -\frac{17\,448}{T} + 7.445\ (1123\text{–}1323\ \mathrm{K})$$

$$\log p_{O_2}(\mathrm{Cu_2O, CuO, Cu_2Cr_2O_4})\ (\mathrm{atm}) = -\frac{13\,433}{T} + 9.618\ (1122\text{–}1268\ \mathrm{K})$$

DISCUSSION

Reaction II: $2Cu(s) + Cr_2O_3 + 1/2O_2(g) = Cu_2Cr_2O_4$

The ΔG°_{II} expressions from this study and results reported in the literature are given in Table 2 and Fig. 4. The data of earlier studies [1,7–9] were re-evaluated using IPTS-68 temperatures. For derivations involving Cu_2O or CuO, the following expressions [6] were used

$$\Delta G^\circ_{f,Cu_2O} = -166\,527 + 70.930\ T\ \mathrm{J\ mol^{-1}}\ (1000\text{–}1339\ \mathrm{K})$$

$$\Delta G^\circ_{f,CuO} = -146\,919 + 81.029\ T\ \mathrm{J\ mol^{-1}}\ (1000\text{–}1339\ \mathrm{K})$$

The derivation of ΔG°_{II} from the p_{SO_2}–T data of Schenck and Keuth [7] for $3Cu(l) + Cr_2O_3 + 1/2SO_2(g) = Cu_2Cr_2O_4 + 1/2Cu_2S$ (s or l) will not be given in detail. Essentially, with Cr_2O_3 and $Cu_2Cr_2O_4$ considered as pure components, the activities of Cu(l) and Cu_2S(l) were calculated using Cu–S [15] and Cu–O–S [16,17] data to find ΔG° of the above reaction. Reference data for Cu_2S(s) [18], Cu_2S (l) [15], Cu (s, l) [19] and SO_2(g) [20] were then used to obtain ΔG°_{II}.

From studies [1,8,14] of the relatively high oxygen pressure regions V and VI of Fig. 1, ΔG°_{II} was derived as $\Delta G^\circ_{II} = -2\Delta G^\circ_{V} + \Delta G^\circ_{VI} + 2\Delta G^\circ_{f,CuO}$.

The results of Tretjakov and Schmalzried [9] for the EMF cells Cu, Cr_2O_3, $Cu_2Cr_2O_4$ * $|ZrO_2(+CaO)|O_2$(air) and Cu, $Cu_2O|ZrO_2(+CaO)|O_2$(air) give $\Delta G^\circ = -51\,329 + 7.7191\ T$ J mol^{-1} for the reaction $Cu_2O + Cr_2O = Cu_2Cr_2O_4$. The reference $\Delta G^\circ_{f,Cu_2O}$ [6] was then used to obtain ΔG°_{II}.

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* These authors were uncertain whether $CuCr_2O_4$ or $Cu_2Cr_2O_4$ was the equilibrium phase.

TABLE 2

ΔG° of Reaction II: $2Cu(s)+Cr_2O_3+1/2O_2(g) = Cu_2Cr_2O_4$

ΔG°_{II} (J mol^{-1})	T (K)	Method	Researcher (year)
-106700	1351.6	Derived [a]	Schenck and Keuth (1940) [7]
$-263300+114.3\ T$	1390–1429	Derived [b]	Schenck and Keuth (1940) [7]
$-39847 \quad -64.297\ T$	1164–1350	Derived [c]	Gadalla and White (1964) [1]
$-212229+77.944\ T$	1050–1350	Derived [c]	Schmahl and Minzl (1965) [8]
$-217856+78.649\ T$	1000–1350	EMF [d]	Tretjakov and Schmalzried (1965) [9]
$-363217+200.12\ T$	973–1273	H_2O/H_2 analysis	Zalazinskii et al. (1969) [10]
$-221806+88.581\ T$	1085–1305	EMF [d]	Rosen (1975) [11]
$-225781+91.533\ T$	970–1220	EMF [d]	Rog and Kozlowska-Rog (1980) [12]
-130060	1070	EMF [c]	Rog et al. (1981) [13]
$-213806+80.965\ T$	950–1340	EMF [d]	Jacob et al. (1985) [14]
$-210667+78.1136\ T$	900–1350	Derived EMF [c,d]	Jacob et al. (1985) [14]
$-213135+78.7628\ T$	1075–1275	EMF [d]	This study
$-212796+79.252\ T$	900–1350		Evaluated value

[a] From $3Cu(l)+Cr_2O_3+1/2SO_2(g) = Cu_2Cr_2O_4+1/2Cu_2S(s)$ result.

[b] As (a), with Cu_2S (l).

[c] From $Cu_2Cr_2O_4+1/2O_2(g) = CuO+CuCr_2O_4$ and $Cu_2Cr_2O_4+Cr_2O_3+1/2O_2(g) = 2CuCr_2O_4$ results.

[d] Using $ZrO_2(+CaO)$ electrolyte.

[e] Using Cu^+-substituted β-Al_2O_3 electrolyte.

Figure 4 shows that the temperature dependence of the derived result of Gadalla and White [1] is wrong. Samples containing $CuCr_2O_4$ were heated and the temperatures of reduction via reactions V and VI were noted by weight loss. Due to the slowness of the reaction kinetics, these temperatures are considerably higher than the equilibrium values. This was verified by DTA results of $CuO + CuCr_2O_4$ samples in this laboratory. At 1 atm O_2, the observed temperature of reaction V increased 10°C per 1°C min^{-1} increase in heating rate.

The results of Zalazinskii et al. [10] from the analysis of H_2O/H_2 are also inconsistent. A similar deviation is apparent when their $CuAlO_2$ and $CuFeO_2$ results are compared to those of Paulsson et al. [21] and Jacob and Alcock [22], respectively.

Other than the results of Gadalla and White [1] and Zalazinski et al. [10], Fig. 4 shows reasonable agreement. A "Third-Law" analysis using $S^\circ_{Cu_2Cr_2O_4,298\ K} = 170.4$ J K^{-1} mol^{-1} (calculated by the structural analog method of Helgeson et al. [23] using $S^\circ_{Cu_2Fe_2O_4,298\ K} = 177.4$ J K^{-1} mol^{-1} [24] and lattice parameter-calculated molar volumes) and an estimated $Cu_2Cr_2O_4$ heat capacity equation indicates that the data of Schmahl and Minzl [8], Tretjakov and Schmalzried [9], Jacob et al. [14] (both sets) and the present

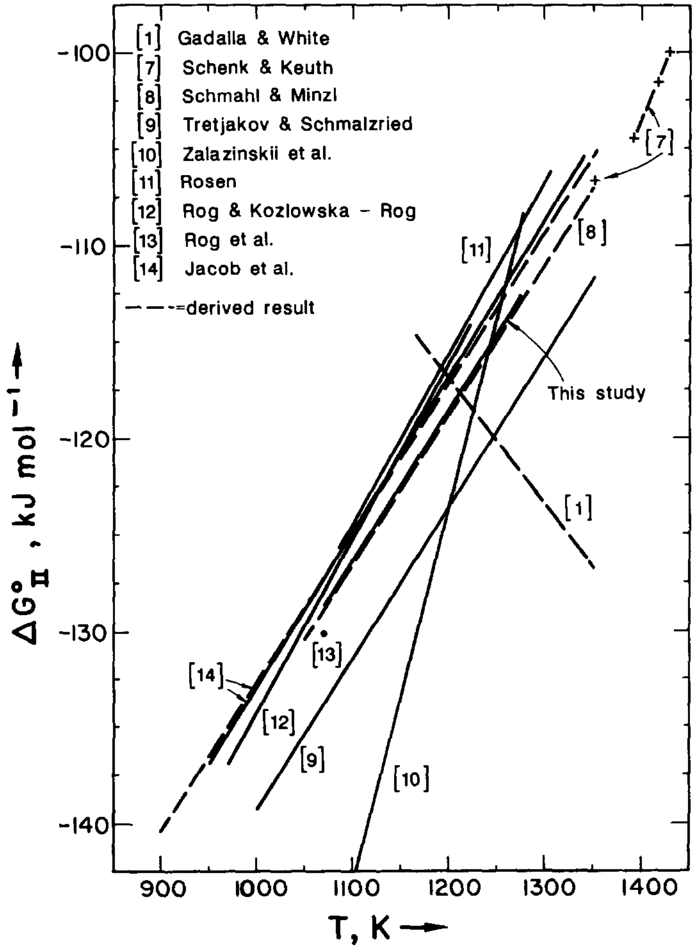

Fig. 4. ΔG° vs. T; results for reaction II: $2Cu(s)+Cr_2O_3+1/2O_2(g)=Cu_2Cr_2O_4$.

study exhibit the most reasonable temperature dependences. Omitting the over-negative result of Tretjakov and Schmalzried, these results * give

$\Delta G^\circ_{II} = -212796 + 79.252\ T$ J mol^{-1} (900–1350 K)

Addition of $\Delta G^\circ_{f,Cr_2O_3}$ [25] gives

$\Delta G^\circ_{f,Cu_2Cr_2O_4} = -1332900 + 332.761\ T$ J mol^{-1} (900–1350 K)

Reaction III: $2Cu + 1/2O_2 = Cu_2O$ ($Cu_2Cr_2O_4$ saturated)

The only available equilibrium data are from this study using the EMF cell Cu, Cu_2O, $Cu_2Cr_2O_4|ZrO_2(+CaO)|$Cu, Cu_2O for which the half-cell

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* A weighing factor of 0.5 was used for results derived from equilibria [V] and [VI] which are considered less exact due to a reported stoichiometry range for $CuCr_2O_4$ [1,14].

reactions are

$$\text{(LHS) } 2\mathrm{Cu(sat.)} + 1/2\mathrm{O_2} = \mathrm{Cu_2O(sat.)} \quad \Delta G^\circ = -RT \ln \frac{a_{\mathrm{Cu_2O}}}{a_{\mathrm{Cu}}^2 \cdot p_{\mathrm{O_2}}^{1/2}}$$

$$\text{(RHS) } \mathrm{Cu_2O} = 2\mathrm{Cu} + 1/2\mathrm{O_2} \quad \Delta G^\circ = -RT \ln p_{\mathrm{O_2}}^{1/2}$$

$$\text{Since } \Delta G^\circ(\mathrm{LHS}) = -\Delta G^\circ(\mathrm{RHS}),\ \ln\left(\frac{a_{\mathrm{Cu_2O}}}{a_{\mathrm{Cu}}^2}\right) = \ln\left[\frac{p_{\mathrm{O_2}}(\mathrm{LHS})}{p_{\mathrm{O_2}}(\mathrm{RHS})}\right]^{1/2}$$

From a Henry's law assumption for the behavior of Cr in Cu and the data point of Gachon et al. [26], for the measured oxygen pressure at 850°C the Cr concentration in Cu is only $x_{\mathrm{Cr}} = 3 \times 10^{-14}$, hence $a_{\mathrm{Cu}} = 1$. Substitution of results from cell 2 then gives $\log a_{\mathrm{Cu_2O}} = -(25.6(\pm 1.7))/T + 0.0173$ (1123–1323 K). This gives $a_{\mathrm{Cu_2O}} = 0.987$ at 850°C indicating that the solubility of $\mathrm{Cu_2Cr_2O_4}$ in $\mathrm{Cu_2O}$ is very small (≈ 1 mol % as $\mathrm{Cr_2O_3}$).

Reaction IV: $\mathit{Cu_2O + 1/2O_2 = 2CuO}$ *(*$\mathit{Cu_2Cr_2O_4}$ *saturated)*

The previous studies [1,8] reported values the same as for the binary $\mathrm{Cu_2O}$–CuO system reaction. In the present study, the EMF cell $\mathrm{Cu_2O}$, CuO, $\mathrm{Cu_2Cr_2O_4}\,|\,\mathrm{ZrO_2(+CaO)}\,|\,\mathrm{Cu_2O}$, CuO was used to directly measure the small difference between the oxygen pressures. From the half cell reactions

$$\ln\left(\frac{a_{\mathrm{CuO}}^2}{a_{\mathrm{Cu_2O}}}\right) = \ln\left[\frac{p_{\mathrm{O_2}}(\mathrm{LHS})}{p_{\mathrm{O_2}}(\mathrm{RHS})}\right]^{1/2}$$

assuming $a_{\mathrm{Cu_2O}}$ ($\mathrm{Cu_2Cr_2O_4}$ sat.) to be equal in regions III and IV leads to

$$\log a_{\mathrm{CuO}} = -\frac{46.0(\pm 1.5)}{T} + 0.0331$$

This gives $a_{\mathrm{CuO}} = 0.982$ at 850°C indicating that the solubility of $\mathrm{Cu_2Cr_2O_4}$ in CuO is somewhat larger than in $\mathrm{Cu_2O}$. This is reasonable since substitution of $\mathrm{Cr^{3+}}$ (+vacancies) for $\mathrm{Cu^{2+}}$ creates fewer lattice defects than does substitution for $\mathrm{Cu^{+}}$.

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