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Oxygen potentials, Gibbs' energies and phase relations in the Cu–Cr–O system

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Thermodynamic properties of ternary compounds, cuprous and cupric chromites ($CuCrO_2$, $CuCr_2O_4$), and oxygen potentials corresponding to three three-phase regions in the Cu–Cr–O system have been measured in the temperature range 900 to 1350 K using a solid state galvanic cell incorporating calcia-stabilized zirconia. Cuprous chromite was found to be nearly stoichiometric. The compositions of non-stoichiometric cupric chromite saturated with CuO and Cr_2O_3 have been determined using electron microprobe and energy dispersive X-ray analysis. The results of this study resolve discrepancies in Gibbs' energies of cuprous and cupric chromites reported in the literature. A ternary phase diagram for the Cu–Cr–O system at 1150 K and phase relations in air for the Cu_2O–CuO–Cr_2O_3 system as a function of temperature have been derived based on the new thermodynamic data. The phase diagram given in the literature is found to be inaccurate.

1. Introduction

A knowledge of the equilibrium relationships in the Cu–Cr–O system is useful for determining the conditons under which copper melts react with the basic refractories in melting furnaces, and for the preparation and use of copper–chromium oxide catalysts. Gadalla and White [1] deduced thermodynamic data for $CuCrO_2$ and $CuCr_2O_4$ using a thermogravimetric technique to detect the reduction temperatures of prefired CuO–Cr_2O_3 mixtures in air and oxygen. Schmahl and Minzl [2] measured the oxygen partial pressure corresponding to the reactions

$$4\,CuCr_2O_4(s) \rightarrow 4\,CuCrO_2(s) + 2\,Cr_2O_3(s) + O_2(g) \qquad (1)$$

and

$$2\,CuO(s) + 2\,CuCr_2O_4(s) \rightarrow 4\,CuCrO_2(s) + O_2(g) \qquad (2)$$

Zalazinskii *et al.* [3] measured the stability of $CuCrO_2$ from 973 to 1273 K using a H_2/H_2O gas equilibrium technique. The Gibbs' energy of formation of $CuCr_2O_4$ was determined by Tretjakow and Schmalzried [4] between 1000 and 1500 K employing an e.m.f. technique, with calcia-stabilized zirconia as the solid electrolyte. Róg *et al.* [5] employed ion exchanged β-alumina as a solid electrolyte to determine the Gibbs' energy of formation of $CuCrO_2$ and $CuCr_2O_4$ at 1070 K. Rosen [6] measured the oxygen partial pressure for the coexistence of Cu, Cr_2O_3 and $CuCrO_2$ using a stabilized zirconia cell between 1100 and 1300 K.

The free energies of formation of $CuCrO_2$ from component oxides reported in the literature [1–3, 5, 6] are compared in Fig. 1. Results of Schmahl and Minzl [2] and Rosen [6] are in reasonable agreement. The slopes of lines representing the results of Gadalla and White [1] and Zalazinskii *et al.* [3] have opposite sign. However, all four investigators agree within experimental error at 1200 K. The free energy data for $CuCr_2O_4$ presented in Fig. 2 show considerable disagreement. Table I gives the comparison of the enthalpy of formation of $CuCr_2O_4$ obtained from free energy data and calorimetric value of Müller and Kleppa [7], using oxide ($2PbO \cdot B_2O_3$) melt solution calorimetry at 1173 K. Despite numerous studies on this system [1–7] there is still considerable disagreement between values obtained by different techniques. The present study aims to resolve the discrepancies in the thermodynamic data on $CuCrO_2$ and $CuCr_2O_4$ and re-evaluating phase relations in the Cu–Cr–O system.

The oxygen potential corresponding to Cu_2O–CuO equilibrium has been firmly established by direct dissociation temperature measurements [8–12] and e.m.f. measurements [13–15]. These measurements agree well with the calorimetric heat of formation of Cu_2O, and CuO, and their standard entropies obtained from heat capcaity determination [16]. The oxygen potential for Cu–Cu_2O equilibrium has been measured by the e.m.f. technique [17] in the temperature range of 973 to 1353 K, in good agreement with the calorimetric data.

TABLE I Enthalpy of formation of $CuCr_2O_4$(sp) from CuO(ten) and Cr_2O_3(cor)

Reference	ΔH^0(kJ mol^{-1})
Müller and Kleppa [7] (calorimetry)	10.4 (± 1)
Schmahl and Minzl [2] (dissociation pressure)	3.8
Gadalla and White [1] (dissociation pressure)	76.0
Tretjakow and Schmalzried [4] (e.m.f.)	− 51.0 (± 1.5)
Present study (e.m.f.)	3.7 (± 2)

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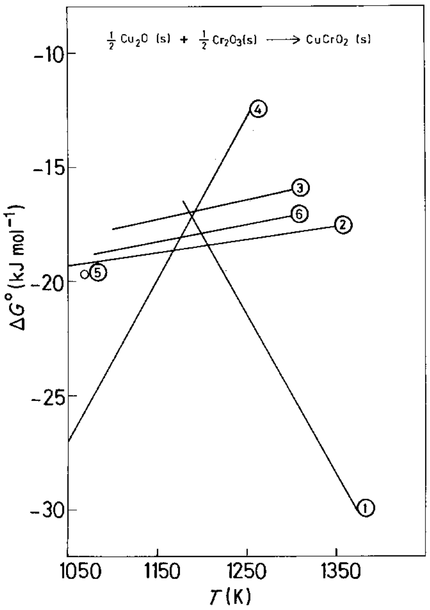

Figure 1 Comparison of the standard free energy of formation of $CuCrO_2$ from component oxides as a function of absolute temperature. 1 Gadalla and White [1], 2 Schmahl and Minzl [2], 3 Rosen [6], 4 Zalazinskii *et al.* [3], 5 Róg *et al.* [5], 6 present study.

2. Experimental procedure

2.1. Materials

Stabilized ZrO_2 tubes containing 7.5 wt % CaO and fine, 99.99% pure, powders of copper and copper oxides were used. Cuprous and cupric chromites were synthesized by heating pressed pellets of component oxides in appropriate molar ratios in Al_2O_3 crucibles kept inside evacuated SiO_2 capsules at 1373 K for 260 ksec. Cycles of grinding, pelletizing and heating were repeated on each sample to ensure complete reaction. The formation of interoxide compounds was confirmed by X-ray diffraction. Argon used for e.m.f. measurements was 99.98% pure. It was subsequently dried and then deoxidized by passing through a column of titanium granules maintained at 1173 K.

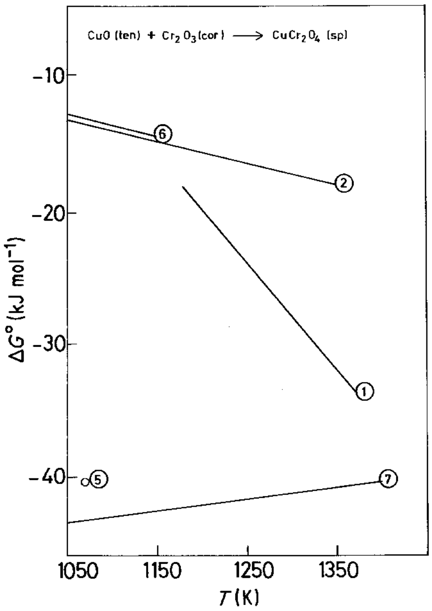

Figure 2 Comparison of the standard free energy of formation of $CuCr_2O_4$ from component oxides as a function of absolute temperature. 1 Gadalla and White [1], 2 Schmahl and Minzl [2], 5 Róg *et al.* [5], 6 present study, 7 Tretjakow and Schmalzried [4].

2.2. Apparatus and procedure

The preparation of electrodes was similar to that described in [18]. Fine powders of component metal and metal oxides were mixed in equimolar proportions, compacted into pellets, and sintered in vacuum at 1373 K. The apparatus and cell arrangements were similar to those used in [18]. The e.m.f. of the cells

$$\text{Pt, CuO} + CuCr_2O_4 + CuCrO_2/(CaO)ZrO_2/O_2\text{, Pt (900–1150 K)} \quad \text{(I)}$$

$$\text{Pt, } CuCr_2O_4 + CuCrO_2 + Cr_2O_3/(CaO)ZrO_2/O_2\text{, Pt (900–1350 K)} \quad \text{(II)}$$

and

$$\text{Pt, Cu} + CuCrO_2 + Cr_2O_3/(CaO)ZrO_2/Cu + Cu_2O\text{, Pt (950–1340 K)} \quad \text{(III)}$$

were measured as a function of temperature, with a high impedance ($> 10^{12}\,\Omega$) digital voltmeter. The electrodes consisting of CuO + $CuCr_2O_4$ + $CuCrO_2$ in Cell I and $CuCr_2O_4$ + $CuCrO_2$ + Cr_2O_3 in Cell II were kept inside long calcia-stabilized zirconia tubes. These tubes were evacuated before the experiments and sealed under vaccum. Separate streams of argon gas were passed over two halfs of Cell III. The reversibility of the cells were checked by pasing small currents in either directions through the cell. In each case, the e.m.f. returned to the original value. The time required to reach the equilibrium varied from 20 to 80 ksec for each cell. The cell temperature was measured with Pt/Pt–13% Rh thermocouple. The e.m.f. was independent of the flow rate of gases over the electrodes, and was reproducible when approached from lower and higher temperatures. The phases present in the electrode pellets and their compositions were established before and after the experiments by X-ray diffraction, electron microprobe and energy dispersive X-ray analysis. No significant changes occurred in phase composition of the electrodes during the experiments. Cupric chomite was found to be non-stoichiometric. Its composition for CuO and Cr_2O_3 saturation have been measured on samples quenched from 1150 K.

3. Results

The variation of the e.m.f. of the Cells I, II and III with temperature is shown in Fig. 3. The temperature dependence of the e.m.f.s can be represented by

$$E_{\mathrm{I}} = 412 - 0.353\,T\,(\pm 1.5)\ \mathrm{mV} \quad (3)$$

$$E_{\mathrm{II}} = 393 - 0.271\,T\,(\pm 1.5)\ \mathrm{mV} \quad (4)$$

$$E_{\mathrm{III}} = 245 - 0.052\,T\,(\pm 1.0)\ \mathrm{mV} \quad (5)$$

The oxygen potential corresponding to the Cu + Cu_2O reference electrodes is given by [17]

$$\Delta\mu_{O_2} = -335\,389 + 143.21\,T\,\mathrm{J\,mol^{-1}} \quad (6)$$

The standard free energy change for reaction,

$$2\,Cu_2O + O_2 \rightarrow 4\,CuO$$

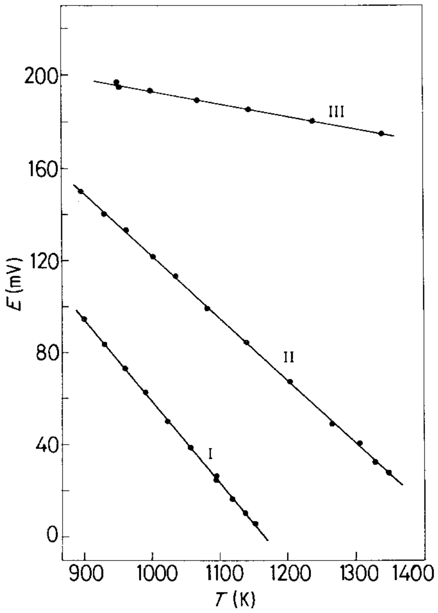

Figure 3 Variation of the e.m.f. of Cells I, II and III with absolute temperature.

is given by [15]

$$\Delta G^0 = -260\,889 + 187.82\,T\,(\pm 400)\,\mathrm{J\,mol^{-1}} \quad (7)$$

The e.m.f.s of Cells I, II, and III are related to the Gibbs' energy change for the following reactions by the Nernst equation

$$4\,\mathrm{CuCrO_2(s)} + \mathrm{O_2(g)} \rightarrow 2\,\mathrm{CuO(s)} + 2\,\mathrm{CuCr_2O_4(s)}$$

$$\Delta G^0 = -159\,025 + 136.3\,T\,(\pm 600)\,\mathrm{J\,mol^{-1}} \quad (8)$$

$$4\,\mathrm{CuCrO_2(s)} + 2\,\mathrm{Cr_2O_3(s)} + \mathrm{O_2(g)} \rightarrow 4\,\mathrm{CuCr_2O_4(s)}$$

$$\Delta G^0 = -151\,690 + 104.6\,T\,(\pm 600)\,\mathrm{J\,mol^{-1}} \quad (9)$$

$$\mathrm{Cu_2O(s)} + \mathrm{Cr_2O_3(s)} \rightarrow 2\,\mathrm{CuCrO_2(s)}$$

$$\Delta G^0 = -47\,280 + 10.0\,T\,(\pm 200)\,\mathrm{J\,mol^{-1}} \quad (10)$$

By combining Equations 8 and 9 the standard free energy of formation of cupric chromite from component oxides is obtained

$$\mathrm{CuO\ (ten)} + \mathrm{Cr_2O_3\ (cor)} \rightarrow \mathrm{CuCr_2O_4\ (sp)}$$

$$\Delta G^0 = 3667 - 15.85\,T\,(\pm 425)\,\mathrm{J\,mol^{-1}} \quad (11)$$

4. Discussion

The Gibbs' energy of formation of $\mathrm{CuCrO_2}$ obtained in this study is compared in Fig. 1 with data reported in the literature [1–3, 5, 6]. These results are in good agreement with the values reported by Schmahl and Minzl [2], Róg *et al.* [5] and Rosen [6]. The temperature dependence of Gibbs' energy reported by Gadalla and White [1] and Zalazinskii *et al.* [3] are clearly out of line with the rest of the measurements, and current understanding of the entropy changes for solid state reactions. The standard free energy of formation of $\mathrm{CuCr_2O_4}$ from the component oxides obtained in this study is compared with the literature data [1, 2, 4, 5] in Fig. 2. It is in excellent agreement with that of Schmahl and Minzl [2] but disagrees with other data [1, 4, 5]. The results of Tretjakow and Schmalzried [4] indicate negative enthalpy of formation of $\mathrm{CuCr_2O_4}$ from CuO and $\mathrm{Cr_2O_3}$, while the rest of the data in Table I show a positive enthalpy of formation, in qualitative agreement with calorimetric data [7]. The divergence of the data of Róg *e al.* [5] for $\mathrm{CuCr_2O_4}$ suggests that they were unable to substitute completely $\mathrm{Cu^{2+}}$ ions for $\mathrm{Na^+}$ ions in the conduction plane of β-alumina. Unspecified oxygen potential over their electrodes is another source of uncertainty in the data of Róg *et al.* [5].

Phase relations in the Cu–Cr–O system at 1150 K, based on the present electrochemical measurements, phase analysis and thermodynamic data are shown in Fig. 4. The partial pressure of oxygen corresponding to the various three-phase regions are also shown:

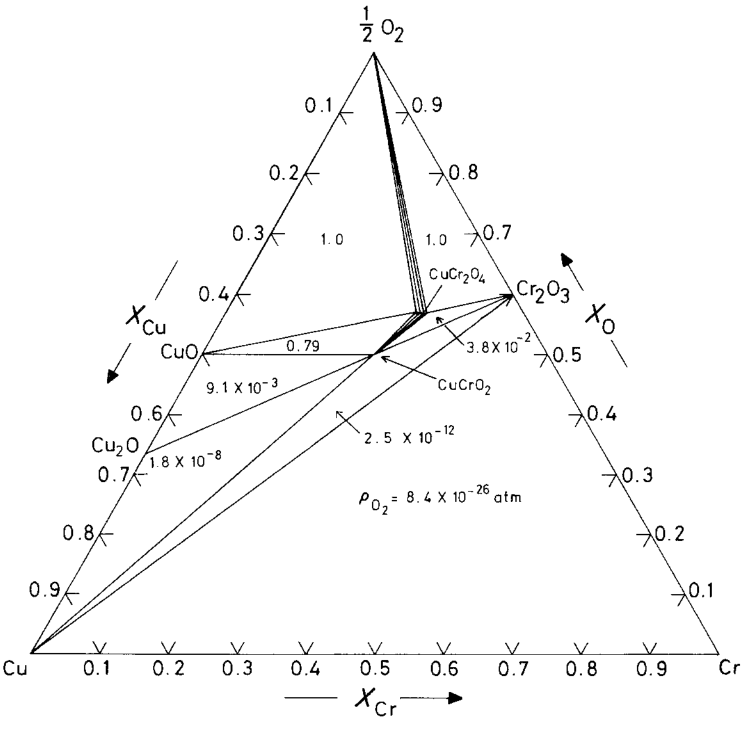

Figure 4 Ternary phase diagram of the Cu–Cr–O system at 1150 K.

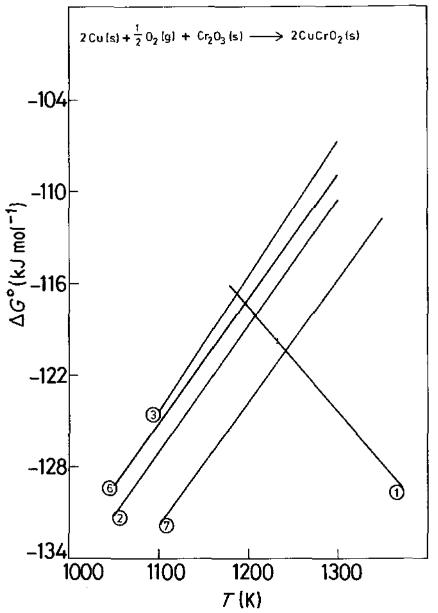

Figure 5 Comparison of standard free energy of formation of $CuCrO_2$ from Cu, Cr_2O_3 and O_2 as a function of absolute temperature. ① Gadalla and White [1], ② Schmahl and Minzl [2], Rosen [6], ⑥ present study, ⑦ Tretjakow and Schmalzried [4] (reinterpreted).

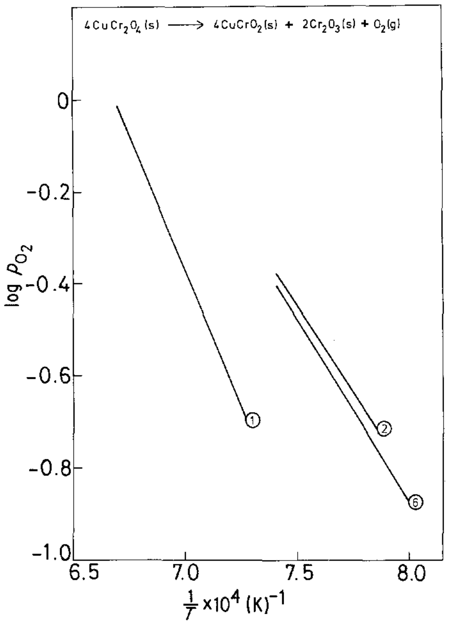

Figure 6 Variation of log P_{O_2} with the reciprocal of absolute temperature for the equilibrium involving $CuCr_2O_4$, $CuCrO_2$ and Cr_2O_3, ① Gadalla and White [1], ② Schmahl and Minzl [2], ⑥ present study.

three of these oxygen potentials are obtained from e.m.f. measurements and the remaining are derived from the data on corresponding binaries [15, 19]. Cuprous chromite ($CuCrO_2$) does not exhibit significant non-stoichiometry. The composition of cupric chromite ($CuCr_2O_4$) saturated with CuO, lies on the line joining $CuCr_2O_4$ and Cu_2CrO_4. The compound Cu_2CrO_4 with chromium ions in the tetravalent state, although unstable at oxygen pressures up to 1.01×10^5 Pa, is likely to be stable at high oxygen pressures. The non-stoichiometric $CuCr_2O_4$ with $Cu/Cr > 0.5$ at higher oxygen partial pressure may be conceived of as a solid solution of Cu_2CrO_4, possibly with (2–4) spinel structure, in $CuCr_2O_4$. The solubility of Cu_2CrO_4 in $CuCr_2O_4$ at 1150 K is $8(\pm 3)$ mol %. Cupric chromite ($CuCr_2O_4$) saturated with Cr_2O_3 contains approximately 3 mol % of dissolved Cr_2O_3.

Tretjakow and Schmalzried [4] used an electrode comprising of Cu, $CuCr_2O_4$ and Cr_2O_3 to measure the stability of $CuCr_2O_4$. The phase diagram of Cu–Cr–O system (Fig. 4) clearly shows that these phases cannot be in equilibrium. The interpretation of the e.m.f. results of Tretjakow and Schmalzried [4] must therefore be based on the relative amounts of the three phases present in the electrode. If excess of copper was present the high temperature equilibrium phases would have been Cu, $CuCrO_2$ and Cr_2O_3. Reinterpretation of the results of Tretjakow and Schmalzried [4] then yields the free energy change for the reaction

$$2\,Cu + 1/2O_2 + Cr_2O_3 \rightarrow 2\,CuCrO_2 \qquad (12)$$

$$\Delta G^0 = -nFE + RT\ln(0.21)^{1/2}$$

$$\Delta G^0 = -220\,200 + 80.358\,T\,\mathrm{J\,mol^{-1}} \qquad (13)$$

The standard free energy change for Reaction 12 recalculated from the e.m.f. measurements of Tretjakow and Schmalzried [4] is shown in Fig. 5 in comparison with the data obtained in this study and those reported in the literature [1, 2, 6]. Reasonable agreement (± 6 kJ) with the results of this study, Schmahl and Minzl [2] and Rosen [6] indicate that Tretjakow and Schmalzried [4] probably measured the stability of $CuCrO_2$ rather than $CuCr_2O_4$.

When three condensed phases and a gas phase are in equilibrium in a ternary system such as Cu_2O–CuO–Cr_2O_3, the system is monovariant; at a given P_{O_2} these phases coexist at a unique temperature. The variation of log P_{O_2} with the reciprocal of the absolute temperature obtained in the present study is compared with the literature data for Reactions 1 and 2 in Fig. 6 and Fig. 7, respectively. The temperature corresponding

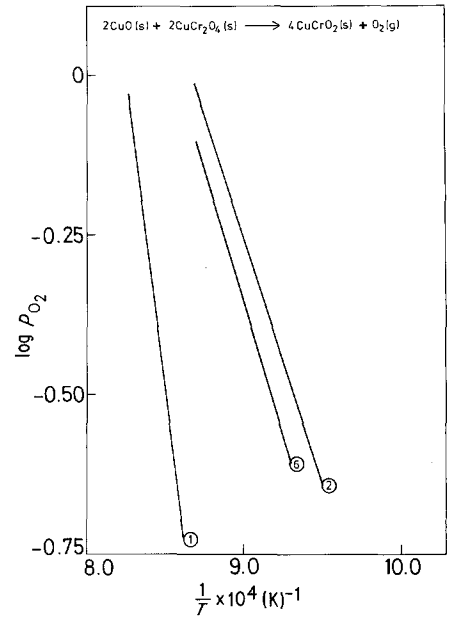

Figure 7 Variation of log P_{O_2} with the reciprocal of absolute temperature for the equilibrium between CuO, $CuCr_2O_4$ and $CuCrO_2$. ① Gadalla and White [1], ② Schmahl and Minzl [2], ⑥ present study.

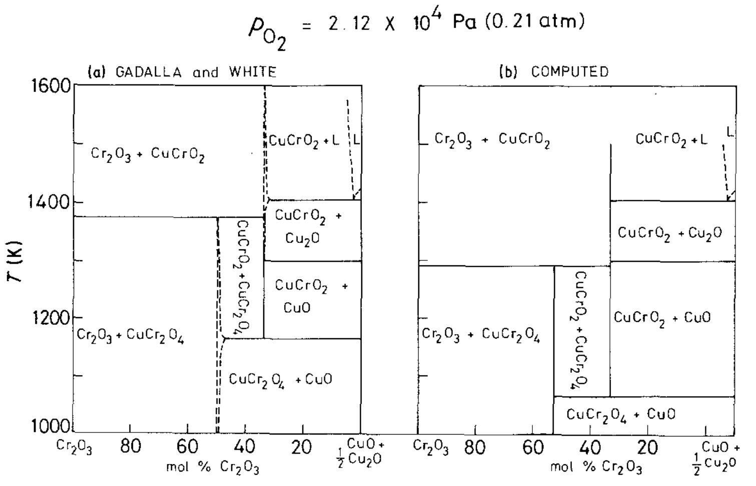

Figure 8 Isobaric section of the ternary system, Cu_2O–CuO–Cr_2O_3 at 2.12 × 10^4 Pa oxygen pressure (a) Gadalla and White [1], (b) present study.

to the coexistence of various condensed phases at an oxygen pressure of 2.12 × 10^4 Pa (0.21 atm) calculated from the present thermodynamic data is used to compose the isobaric section shown in Fig. 8. The corresponding diagram of Gadalla and White [1] is also shown for comparison. Since 1 mol CuO gives 0.5 mol Cu_2O on dissociation, the number of moles of Cu remains unchanged when 0.5 mol Cu_2O is one of the components; then the compositions can be expressed in terms of Cr_2O_3 and CuO + 1/2Cu_2O. The vertical lines represent interoxide compounds and horizontal lines represent invariant equilibria involving three condensed phases and oxygen gas at defined pressure. There are significant qualitative differences in the phase diagram derived from new thermodynamic data and that reported earlier [1]. The reaction temperatures differ by as much as 100 K. Gadalla and White [1] measured dissociation temperatures by a thermogravimetric method during heating. They did not confirm the reproducibility of their results on cooling. Since solid state reactions encountered in the decomposition studies of Gadalla and White [1] are associated with slow kinetics, it is understandable that their dissociation temperatures are well above the equilibrium temperatures computed in this study.

It had been shown earlier [15, 20] that the entropy of formation of 2–3 cubic spinels from component oxides with rocksalt and corundum structures can be represented by

$$\Delta S_f^0 = -7.32 + \Delta S^{CM} + \Delta S_{JT}^{Rand} \text{ J K}^{-1}\text{mol}^{-1} \quad (14)$$

where ΔS^{CM} is the configurational entropy of crystal due to cation mixing at two different lattice sites and $\Delta S_{JT}^{Rand} = nR \ln 3$ is the entropy arising from the randomization of Jahn–Teller distortions. The entropy of formation of cupric chromite ($CuCr_2O_4$) estimated for the reaction

$$CuO(r.s.) + Cr_2O_3(cor) \rightarrow CuCr_2O_4(sp) \quad (15)$$

is given by

$$\Delta S_f^0 = -7.32 + \Delta S^{CM} + R \ln 3$$

The values of ΔS^{CM} based on the cation distribution parameter (x) of 0.9908 for $(Cu_xCr_{1-x})_{tet}[Cu_{1-x}Cr_{1+x}]_{oct}$ calculated using octahedral site preference energies for Cr^{3+} and Cu^{2+} from Dunitz and Orgel [21] is 0.93 J K^{-1} mol^{-1}. Ohnishi [22] measured the cation distribution parameter in $CuCr_2O_4$ as 0.9. The corresponding value for ΔS^{CM} is 6 J K^{-1} mol^{-1}. For the rocksalt to tenorite structure transformation the entropy change is −4.2 J K^{-1} mol^{-1}. Therefore the entropy change for Reaction 11 can be estimated as 6.93 J K^{-1} mol^{-1} based on cation distribution calculated from octahedral site preference energies and 12.0 J K^{-1} mol^{-1} based on measured cation distribution. The second law entropy change for Reaction 11 obtained in this study is 15.85 (±2) J K^{-1} mol^{-1}. The higher measured entropy is probably due to the non-stoichiometry of $CuCr_2O_4$.

5. Summary

The standard free energies for the formation of cuprous chromite ($CuCrO_2$) and cupric chromite ($CuCr_2O_4$) from component oxides, measured by an e.m.f. technique, are given by

$$\Delta G^0 = -47\,280 + 10.0\,T\,(\pm 200)\text{ J mol}^{-1}$$

and

$$\Delta G^0 = 3667 - 15.85\,T\,(\pm 425)\text{ J mol}^{-1}$$

The results of the present study for cuprous chromite agree well with those reported by Schmahl and Minzl [2], Róg *et al.* [5] and Rosen [6], but do not agree with that of Gadalla and White [1] and Zalazinskii *et al.* [3]. The results obtained in this study for cupric chromite are in excellent agreement wth Schmahl and Minzl [2] but do not agree with that of Gadalla and White [1], Tretjakow and Schmalzried [4] and Róg *et al.* [5]. From the phase relations for the Cu–Cr–O system, it can be shown that the phase mixtures used by Tretjakow and Schmalzried [4] in their measurements cannot be in thermodynamic equilibrium. Based on the thermodynamic data obtained in this study an isobaric section of the Cu_2O–CuO–Cr_2O_3 system at P_{O_2} = 2.12 × 10^4 Pa (0.21 atm) is computed. The reaction temperatures differ from those of Gadalla and White [1] obtained during heating. The disagreement is probably due to slow kinetics of decomposition reactions.

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