

Gibbs energy of formation of CuCrO_4 and phase relations in the system Cu–Cr–O below 735 K

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Abstract

A solid state galvanic cell incorporating yttria-stabilized zirconia electrolyte and ruthenium(IV) oxide electrodes has been used to measure the equilibrium chemical potential of oxygen corresponding to the decomposition of CuCrO_4 in the range 590–760 K. For the reaction $\text{CuO}(\text{tenorite}) + \text{CuCr}_2\text{O}_4(\text{spinel}) + 1.5\text{O}_2(\text{g}) \rightarrow 2\text{CuCrO}_4(\text{orth})$, $\Delta G^\ominus = -183\,540 + 249.6T(\pm 900) \text{ J mol}^{-1}$. The decomposition temperature of CuCrO_4 in pure oxygen at a pressure of $1.01 \times 10^5 \text{ Pa}$ is $735(\pm 1) \text{ K}$. By combining the results obtained in this study with data on the Gibbs energy of formation of CuCr_2O_4 and CuCrO_2 reported earlier, the standard Gibbs energy of formation of CuCrO_4 and the phase relations in the system Cu–Cr–O at temperatures below 735 K have been deduced. Electron microscopic studies have indicated that the decomposition of CuCrO_4 to CuCr_2O_4 is topotactic.

INTRODUCTION

Some of the oxide phases in the system Cu–Cr–O are active catalysts for several oxidation, hydrogenation, dehydrogenation and alkylation reactions. The Adkins catalyst [1, 2] usually contains CuO and CuCr_2O_4 and is frequently prepared by the thermal decomposition of CuCrO_4 . Copper chromate (CuCrO_4) may be either the starting material or an intermediate product in the preparation of the catalyst. Since the literature does not contain any information on the thermodynamic properties of CuCrO_4 , its Gibbs energy of formation has been determined in this study as a function of temperature using a solid oxide galvanic cell.

Cells incorporating solid electrolytes and platinum electrodes have been extensively used [3] in thermodynamic studies on oxides at temperatures

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higher than 800 K, which is above the decomposition temperature of CuCrO_4 . Recently new catalytic electrodes have been developed which permit the measurement of oxygen potential at lower temperatures. An electrode made of ruthenium(IV) oxide has been shown to respond to oxygen pressure above 498 K [4]. An electrode made from scandia-doped urania mixed with platinum has been found to respond to oxygen pressure above 623 K [5]. The low temperature response characteristics of the ruthenium oxide electrode are used for measuring the equilibrium oxygen potential corresponding to the decomposition of CuCrO_4 from 590–760 K.

The thermodynamic properties of CuCr_2O_4 and CuCrO_2 and phase equilibria in the system Cu–Cr–O at higher temperatures have been studied by Jacob et al. [6]. By combining information on the Gibbs energy change accompanying the decomposition of CuCrO_4 with known data for CuCr_2O_4 , the standard Gibbs energy of formation of CuCrO_4 has been obtained. The phase relations in the system Cu–Cr–O at low temperatures were deduced from the thermodynamic data.

EXPERIMENTAL

Materials

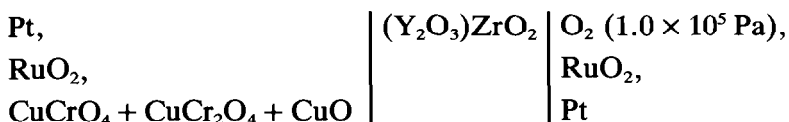
Copper chromate was prepared by mixing aqueous solutions of high purity (>99.99%) $\text{Cu}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and evaporating the resulting solution to dryness. The precursor thus obtained was heated at 510 K in air for 15 ks to eliminate volatile components and to decompose the nitrate. The formation of the chromate can be represented as



The phase purity of CuCrO_4 was confirmed by X-ray diffraction. An equilibrium mixture of CuO with tenorite (ten) and CuCr_2O_4 with spinel (sp) structure was obtained by decomposing CuCrO_4 in air at 823 K. The oxygen gas used in this study was 99.99% pure. It was passed through NaOH to remove CO_2 and then dried by silica gel and anhydrous P_2O_5 .

EMF measurement

The reversible emf of the solid state cell



was measured as a function of temperature. The cell is written such that the right hand electrode is positive. An yttria-stabilized zirconia tube was used as the solid electrolyte. The tube was leak tested and found to be impervious. A coating of RuO_2 was applied on the inside of the tube near

the closed end and along a circular band 5 mm wide on the outside of the tube, approximately 3 mm from the closed end. A 10% aqueous solution of RuCl_3 was applied on the tube by a brush. After drying, the tube was heated in air at 1073 K for 18 ks. A highly adherent black film of RuO_2 was obtained by this treatment. A platinum wire wound tightly around the RuO_2 electrode was used as an electrical lead. The wire was insulated to prevent contact with the zirconia tube except at the electrode. Contact with the RuO_2 electrode inside the tube was made by pressing a platinum mesh, spot welded to a platinum wire, against the oxide with an alumina tube.

The apparatus was assembled as shown in Fig. 1. The working electrode was prepared by compacting an intimate mixture of CuCrO_4 , CuCr_2O_4 and CuO in the molar ratio 2:1:1 inside the silica bulb. A fine platinum mesh was placed over the three-phase mixture and the solid electrolyte tube was pressed into the oxide to make a firm contact. The contact between the RuO_2 electrode on the side of the zirconia tube and the oxide mixture was restricted to a small area around the tube

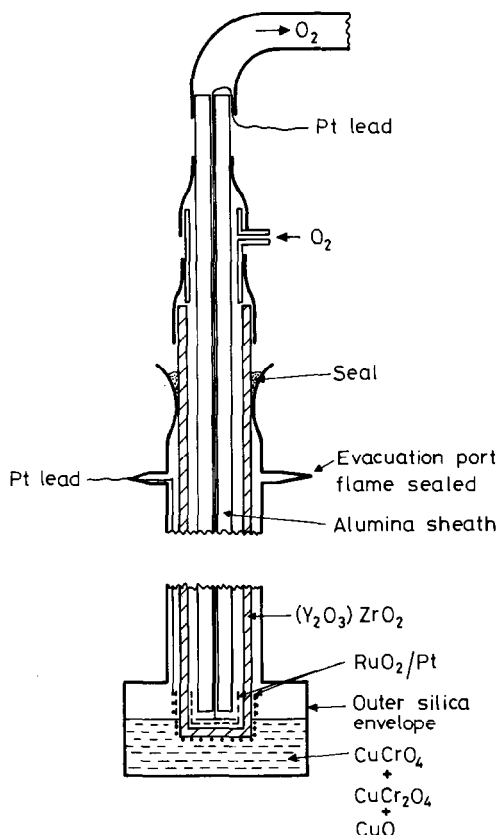


Fig. 1. Schematic diagram of the apparatus used for emf measurement.

approximately 1 mm in depth. The gap between the neck of the outer silica tube and the solid electrolyte tube was closed with Araldite. The outer silica tube was evacuated through a side arm to a pressure of 0.1 Pa and then flame sealed. During the experiment, the equilibrium oxygen partial pressure was established inside the silica tube by the decomposition of CuCrO_4 .

The apparatus was lowered into a vertical resistance furnace with the electrodes located in the constant temperature zone. The temperature was controlled to ± 0.5 K and measured with a Pt/Pt–13%Rh thermocouple placed adjacent to the silica bulb containing the oxide mixture. A cylindrical sleeve made of stainless steel was placed between the furnace tube and the outer silica enclosure of the apparatus. The sleeve was earthed to minimize induced emf on the platinum leads of the cell.

Pure, dry oxygen gas at a pressure of 1.01×10^5 Pa was passed through the inside of the zirconia tube. The pressure of oxygen was controlled by adjusting the level of mercury in a cascade of bubblers placed at the gas exit. The cell was first heated to 700 K and emf measurement was started. Subsequently the cell was taken through several cycles of increasing and decreasing temperature. The time required to attain a steady emf varied from 3 to 70 ks depending on temperature. The response was sluggish but reproducible at low temperatures. At each temperature, after the emf attained a steady value, its reversibility was checked by microcoulometric titration in both directions. A small quantity of electricity ($\approx 50 \mu\text{A}$ for 300 s) was passed through the cell, transporting oxygen ions to the positive electrode. This caused an infinitesimal displacement from equilibrium at both electrodes. The emf was monitored as a function of time after the titration. The current was then passed in the opposite direction. The emf was found to return to the same value after each titration. The emf was found to be reproducible on temperature cycling. The emf was also unaffected by a change in the flow rate of oxygen between 1 and 3 ml s^{-1} .

At the end of the experiment the electrodes were examined by X-ray diffraction and optical and electron microscopy. The phase composition of the three-phase electrode was found to be unaltered during the emf measurement. For electron microscopy, the electrode was initially ground to a fine powder. The results indicated certain orientation relationships between the CuCrO_4 and CuCr_2O_4 phases. To ensure the absence of artifacts arising from grinding, CuCrO_4 particles in the size range 0.3–1 μm were prepared and then partially decomposed. The powders were then examined by selected area electron diffraction.

RESULTS AND DISCUSSION

The variation of the reversible emf of the solid state cell with temperature is shown in Fig. 2. It was difficult to obtain a reproducible

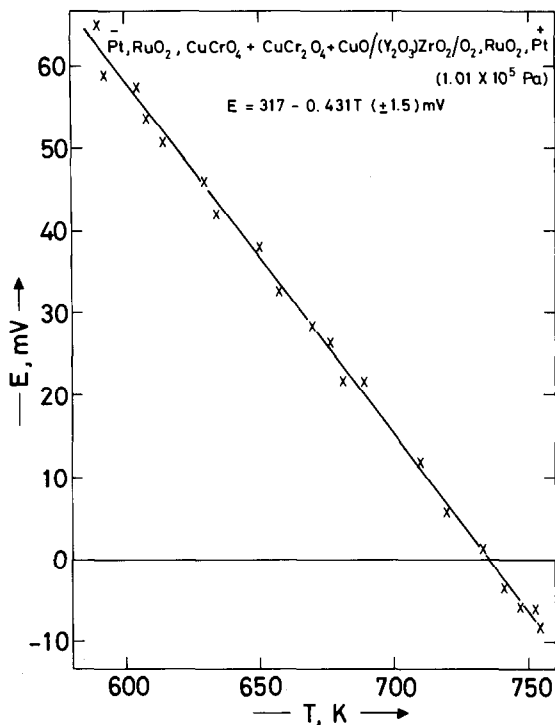
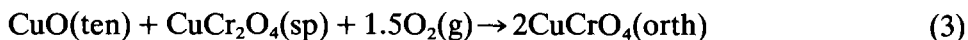


Fig. 2. Temperature dependence of the emf of the solid state cell.

emf below 590 K. At temperatures above 760 K, the oxygen pressure in the apparatus becomes significantly greater than atmospheric and the seals give way. Within experimental error, the emf was found to be a linear function of temperature. The least mean-square regression analysis gave the expression

$$E = 317 - 0.43T (\pm 1.5) \text{ mV} \quad (2)$$

Since $(\text{Y}_2\text{O}_3)\text{ZrO}_2$ is a predominantly ionic conductor in the range of temperature and partial pressure of oxygen covered in this study, the emf is directly related to the chemical potential of oxygen over the working electrode, defined by



$$\Delta\mu_{\text{O}_2} = -\eta FE = -122\,360 + 166.4T (\pm 600) \text{ J mol}^{-1} \quad (4)$$

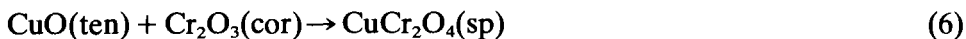
where $\eta = 4$ is the number of electrons involved in the reaction, F is the Faraday constant and E is the emf in V. The standard Gibbs energy change for reaction (3) is

$$\Delta G_3^\ominus = -183\,540 + 249.6T (\pm 900) \text{ J mol}^{-1} \quad (5)$$

The equilibrium decomposition temperature of CuCrO_4 in pure oxygen is

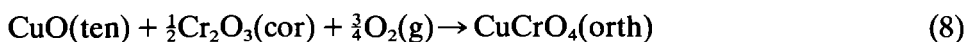
735(±1) K. In air, CuCrO₄ would decompose at 682(±1) K under equilibrium conditions. The decomposition temperature is expected to be significantly higher under dynamic conditions because of the slow rate of reaction.

In an earlier study, Jacob et al. [6] measured the Gibbs energy of formation of CuCr₂O₄ in the temperature range 900–1350 K. For the reaction



$$\Delta G_6^\ominus = 3667 - 15.85T(\pm 425) \text{ J mol}^{-1} \quad (7)$$

Because accurate information is not available on the heat capacity of all the phases, enthalpy and entropy changes for the solid state reaction are assumed to be independent of temperature. Then, for the formation of CuCrO₄ according to the scheme



$$\Delta G_8^\ominus = -89\,940 + 116.9T(\pm 1000) \text{ J mol}^{-1} \quad (9)$$

The Gibbs energy of formation of CuCrO₄ from solid CuO and CrO₃ or from the elements can be readily calculated. However, since the thermodynamic properties for solid CrO₃ are not well established, it is not desirable to use solid CrO₃ as a reference state in a thermodynamic evaluation. For the formation of CuCrO₄ from the elements, the present results in conjunction with evaluated data for CuO and Cr₂O₃ from Pankratz [7] give $\Delta H_{298.15}^\ominus = -815.9(\pm 12) \text{ kJ mol}^{-1}$. Similarly, the standard entropy of CuCrO₄ is $S_{298.15}^\ominus = 120.1(\pm 14) \text{ J mol}^{-1} \text{ K}^{-1}$. It would be useful to have independent measurement of these values by calorimetric techniques.

Selected area electron diffraction of partially decomposed CuCrO₄ revealed the presence of well crystallized and oriented CuCr₂O₄, but there was no evidence for the presence of CuO. Probably the fine particle size of CuO or reflections that overlap those of the other phase (CuCrO₄, CuCr₂O₄) was responsible for this negative observation. Electron diffraction indicated that the orientations of CuCr₂O₄ and CuCrO₄ are related

$$a_{\text{CuCr}_2\text{O}_4} \parallel a_{\text{CuCrO}_4}, b_{\text{CuCr}_2\text{O}_4} \parallel c_{\text{CuCrO}_4} \quad \text{and} \quad c_{\text{CuCr}_2\text{O}_4} \parallel -b_{\text{CuCrO}_4}$$

The presence of a topotactic relationship between CuCr₂O₄ and CuCrO₄ despite the change in symmetry is interesting. The structure of CuCrO₄ is orthorhombic, space group *Cmcm*, with $a = 0.5433 \text{ nm}$, $b = 0.8968 \text{ nm}$ and $c = 0.5890 \text{ nm}$. The CuCr₂O₄ phase has a tetragonally distorted spinel structure, space group $1\bar{4}2d$, with $a = 0.604 \text{ nm}$ and $c = 0.778 \text{ nm}$. The symmetry change is probably accommodated by the introduction of twins in CuCr₂O₄. Although not detected by electron

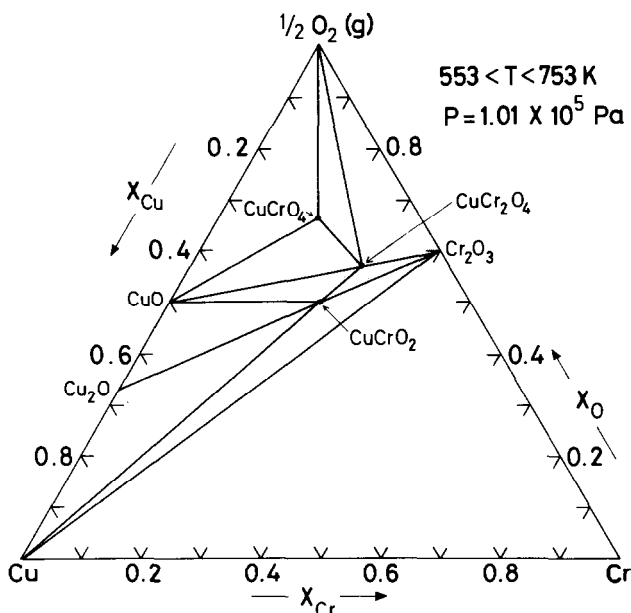


Fig. 3. Equilibrium phase diagram for the system Cu–Cr–O; $553 < T < 753$ K.

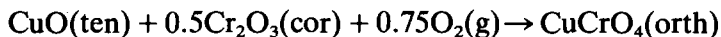
microscopy, very broad peaks of CuO were seen in the X-ray powder diffractogram of partially decomposed CuCrO_4 , suggesting poor atomic periodicity.

The equilibrium phase diagram for the Cu–Cr–O system below 753 K computed from the thermodynamic data is shown in Fig. 3. The data for CuCr_2O_4 , CuCrO_2 , CuO and Cu_2O are taken from ref. 6. Below 753 K, CuCrO_4 becomes a stable phase. It is interesting to see that CuCrO_2 does not coexist with CuCrO_4 . The oxidation of Cu^+ ions to Cu^{2+} occurs before the oxidation of Cr^{3+} to Cr^{6+} in ternary oxides. The phase relationships remain invariant with temperature below 753 K down to ≈ 553 K. At lower temperature, phases such as CrO_3 and CrO_2 may become stable along the Cr–O binary. No definite information on phase stability or thermodynamic properties of solid CrO_3 and CrO_2 is available in the literature. From a thermodynamic point of view, CuCr_2O_4 is an entropy stabilized compound and should decompose to CuO and Cr_2O_3 below 231 K. However, it would be very difficult to observe this decomposition because of the expected slow rate of reaction.

SUMMARY

A galvanic cell with an oxide solid electrolyte has been used for the first time for the measurement of thermodynamic properties of ternary oxides at temperatures as low as 590 K. This has been facilitated by the catalytic properties and low temperature response of the RuO_2 electrode. The

Gibbs energy of formation of the compound CuCrO_4 has been measured in the range 590–760 K. For the reaction



$$\Delta G^\ominus = -89\,940 + 116.9T (\pm 1000) \text{ J mol}^{-1}$$

The equilibrium decomposition temperature of the compound is $735(\pm 1)$ K in pure oxygen and $682(\pm 1)$ K in air at a pressure of 1.01×10^5 Pa. The decomposition products are CuO and CuCr_2O_4 .

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