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Gibbs free energy of formation of the solid phases $Cu_2Y_2O_5$ and $CuYO_2$ determined by the E.M.F. method

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Abstract

Employing the following electrochemical cells with solid zirconia electrolyte:

$Cu_2Y_2O_5$, $CuYO_2$, Y_2O_3/O^{2-}/air

Cu, $CuYO_2$, Y_2O_3/O^{2-}/air

as well as with CaF_2 solid electrolyte

air, CuO, $Cu_2Y_2O_5$, YOF/F^{1-}/YOF, Y_2O_3, air

Gibbs free energies of formation of the solid $CuYO_2$ and $Cu_2Y_2O_5$ phases were determined in the temperature range 973–1323 K. The results obtained in this study were used to derive the Gibbs free energy change of the reaction of formation of these two compounds from the respective oxides:

$$\Delta G^{\ominus}_{f,ox} = 7265 \pm 8.31\,T \quad \mathrm{J\,mol^{-1}}$$

for the reaction:

$$1/2\,Cu_2O + 1/2\,Y_2O_3 = CuYO_2$$

and

$$\Delta G^{\ominus}_{f,ox} = 6670 - 7.05\,T \quad \mathrm{J\,mol^{-1}}$$

for the reaction:

$$2\,CuO + Y_2O_3 = Cu_2Y_2O_5$$

Keywords: $CuYO_2$; $Cu_2Y_2O_5$; EMF; Gibbs energy

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1. Introduction

Double oxides in the Cu–Y–O ternary system are relatively well known. The formation of orthorhombic $Cu_2Y_2O_5$ (known as 'blue phase') in air was described by Arjomand and Machin [1]. Its existence was then confirmed by Roth et al. [2], who also constructed a tentative diagram of the Cu_2O–Y_2O_3 system. Under reduced oxygen pressure, $Cu_2Y_2O_5$ decomposes into $CuYO_2$. This delafossite-type compound was first identified by Ishiguro et al. [3]. Zhang and Osamura [5] showed that the decomposition reaction from $Cu_2Y_2O_5$ to $CuYO_2$ does not occur in air. Under high oxygen pressure, the formation of $CuYO_3$ phase was also reported by Arjomand and Machin [1]. This compound, however, is unstable in air and does not exist under lower oxygen pressures. Recently, Gadalla and Kongkachuichay [4] suggested the formation of another compound in air, $Cu_2YO_{2.5}$, which is reported to exist between 1263 and 1378 K in the CuO-rich part of the CuO–Y_2O_3 pseudo-binary system. Since $Cu_2Y_2O_5$ decomposes under reduced oxygen pressure, it is not likely that $Cu_2YO_{2.5}$ would exist under similar conditions.

However, despite a large number of studies that have been concerned with the thermodynamic properties of $CuYO_2$ and $Cu_2Y_2O_5$, there is still noticeable discrepancy between the $\Delta H^{\ominus}_{f,ox}$ and $\Delta S^{\ominus}_{f,ox}$ values determined for the formation reaction for these compounds from single oxides. Recently, Lazarev et al. [6] presented a review of the thermodynamic properties of high-T_c superconductors in which they pointed out that the values obtained by the EMF method, in general, disagree with calorimetric data. Zhou and Navrotsky [7] showed that $\Delta H^{\ominus}_{f,ox}$ varies from -20 to $+20\,kJ\,mol^{-1}$ when one compares data obtained from different sources for the $Cu_2Y_2O_5$ phase. Taking into account the observed discrepancies, it was decided to reinvestigate the system with two different types of electrochemical cells. This procedure may help to analyse the possible reasons for the observed differences resulting from the applied e.m.f. technique.

2. Experimental

2.1. Materials

Copper oxide (99.99%) was obtained from Johnson and Matthey. Yttrium oxide, Y_2O_3, was 99.999% pure and was obtained from Aldrich Chemicals. $Cu_2Y_2O_5$ (blue phase) was synthesized by heating pressed pellets containing a mixture of CuO and Y_2O_3 (2:1 mole ratio) for 50 h in oxygen at 1273 K with one intermediate grinding. $CuYO_2$ (grayish-yellow phase) was prepared by heating $Cu_2Y_2O_5$ under a stream of argon for 24 h at about 1250 K. Yttrium fluoride, YF_3, obtained from Aldrich Chemicals (99.9%) was used to produce YOF. Powders of YF_3 and Y_2O_3 were mixed (1:1 mole ratio) and fired at 1000°C in argon and dry oxygen respectively, for 24 h with one intermediate grinding. Formation of the required compounds was confirmed by an X-ray analysis. The $CuYO_2$ sample showed traces of Cu_2O and Y_2O_3. The compounds were used in the preparation of the working electrodes for the respective electrochemical cells.

2.2. Procedure

At first, an EMF cell of the type

$$Cu_2O + Y_2O_3 + Cu_2Y_2O_5/ZrO_2 + CaO/air \qquad (I)$$

was used. A schematic diagram of the cell assembly is shown in Fig. 1. The composition of the investigated electrode was characterized by an excess of Y_2O_3. After some time the cell produced stable e.m.f. values, and worked reproducibly for about one week in the temperature range 920–1300 K. The e.m.f. vs. temperature dependence can be represented by the following least-squares fit

$$E_I = 0.5830 - 0.0004101\,T \qquad (1)$$

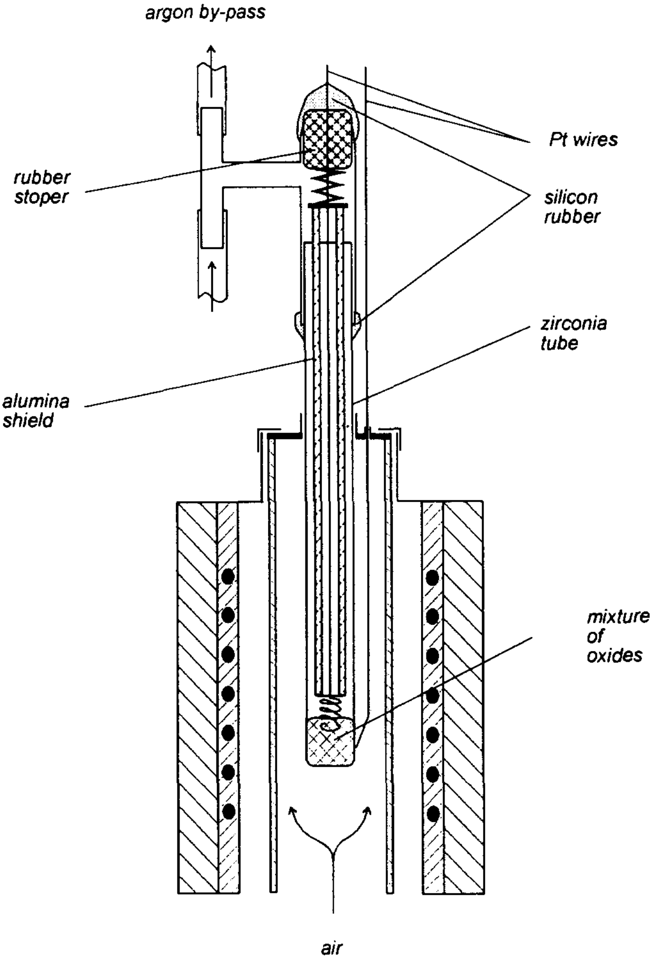

Fig. 1. Schematic cell assembly with zirconia electrolyte.

However, an X-ray analysis of the investigated working electrode recorded after the experiments showed that Cu_2O practically disappeared from the mixture and $CuYO_2$ was found to be present in the sample. Thus, the final equilibrium state of the working electrode apparently corresponded to the $Y_2O_3 + CuYO_2 + Cu_2Y_2O_5$ three-phase field.

Consequently, two EMF cells of the type

$$Y_2O_3 + CuYO_2 + Cu_2Y_2O_5/ZrO_2 + CaO/air \tag{II}$$

and

$$Cu + CuYO_2 + Y_2O_3/ZrO_2 + CaO/air \tag{III}$$

were used for oxygen potential measurements over the $Y_2O_3 + CuYO_2 + Cu_2Y_2O_5$ and $Cu + CuYO_2 + Y_2O_3$ three-phase fields. In our experiments, calcia-stabilized zirconia was used as the electrolyte and dry air was used as the reference electrode. A sample consisting of mixed oxide powders was kept at the bottom of the electrolyte tube. Electrical contact was made using a platinum lead wire; contact was assured by pressing an alumina shield with a flat base onto the sample. An inert atmosphere was maintained inside the cell by passing purified argon gas through the system.

Experiments were performed in a vertical, resistance furnace. The cell was kept in the furnace within the constant temperature zone, and the sample at the bottom of the electrolyte tube was always placed in this zone. After a constant temperature was reached, the cell was left overnight to attain an equilibrium state, and then the EMF was recorded with a Keithley 197A digital voltmeter. The temperature was cycled in the range 900–1300 K, and the full run was completed after about 10 days.

3. Results

3.1. Oxygen potential measurements

Electromotive force values obtained for cell II are shown in Fig. 2. Results were treated by the least-squares method, and are represented by the equations

$$E_{II} = 0.56935 - 0.0004013\,T \tag{2}$$

Also, in Fig. 2, values recorded for cell I are shown for comparison. The EMF vs. temperature dependence derived from the results obtained for cell III (which are shown in Fig. 3) takes the form

$$E_{III} = 0.9425 - 0.0004935\,T \tag{3}$$

Oxygen potential over the three-phase fields is related to the measured e.m.f. by the relationship

$$E = \frac{RT}{4F} \cdot \ln\left(\frac{P''_{O_2}}{P'_{O_2}}\right) \tag{4}$$

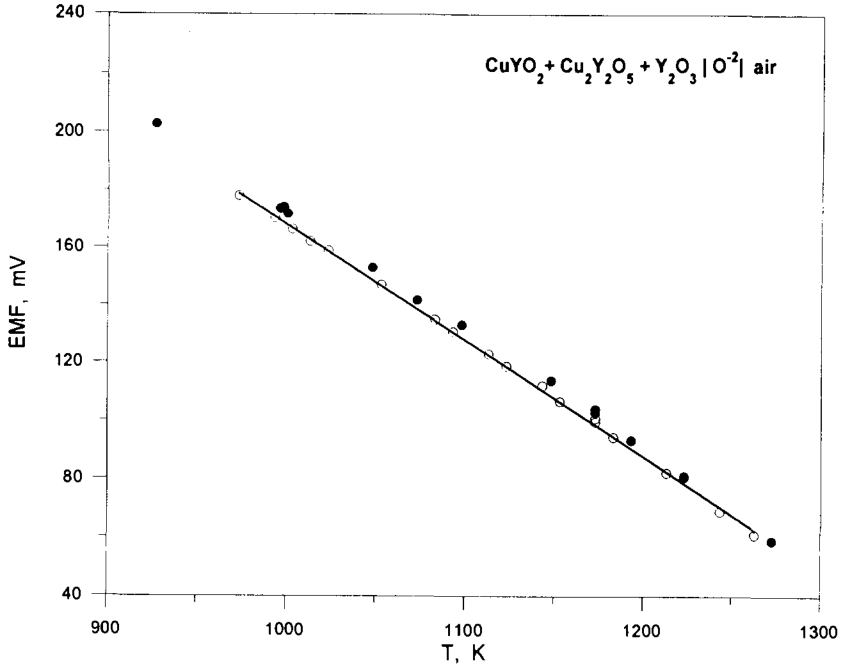

Fig. 2. Variation of e.m.f. with temperature: M, with cell I; N, with cell II.

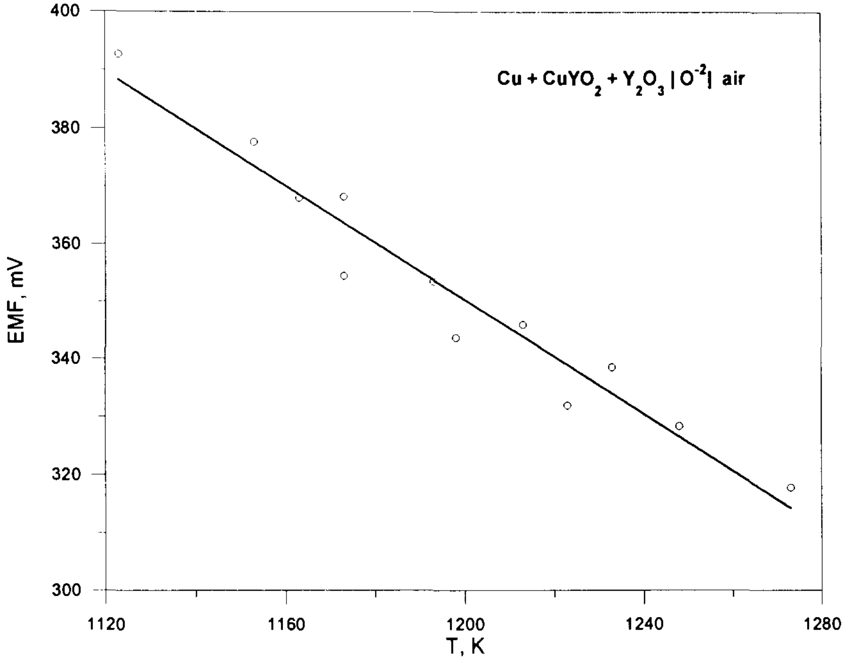

Fig. 3. Variation of e.m.f. with temperature for cell III.

where P''_{O_2} is the oxygen partial pressure of the reference electrode, P'_{O_2} the oxygen partial pressure exerted by the working electrode, $F = 96580$ J/V mol, E the EMF (V), R the gas constant and T the absolute temperature (K).

Since the equilibrium oxygen pressure for the three-phase fields represented by the working electrodes of cells II and III is determined by the following reactions

$$2\,CuYO_2 + 1/2\,O_2 = Cu_2Y_2O_5 \tag{5}$$

and

$$2\,Cu + Y_2O_3 + 1/2\,O_2 = 2\,CuYO_2 \tag{6}$$

the respective Gibbs free energy changes of these reactions can be calculated from their equilibrium constant and Eqs. (2)-(4). An X-ray study performed on the investigated electrodes of cells II and III after the experiments confirmed the existence of a three-phase equilibrium as described by reactions (5) and (6). Consequently, the Gibbs free energy changes of reactions (5) and (6) were calculated and are given in the forms

$$\Delta G^{\ominus}_{T}(5) = -109\,870 + 70.95\,T \quad (J) \tag{7}$$

and

$$\Delta G^{\ominus}_{T}(6) = -181880 + 88.75\,T \quad (J) \tag{8}$$

Combining the obtained results with the Gibbs free energy changes of the reactions

$$1/2\,Cu_2O = 2\,Cu + 1/2\,O_2 \tag{9}$$

and

$$2\,Cu_2O + 1/2\,O_2 = 2\,CuO \tag{10}$$

one can determine the Gibbs free energy of formation of $CuYO_2$ and $Cu_2Y_2O_5$ from the respective oxides according to the reactions

$$1/2\,Cu_2O + 1/2\,Y_2O_3 = CuYO_2 \tag{11}$$

$$2\,CuO + Y_2O_3 = Cu_2Y_2O_5 \tag{12}$$

in the following form

$$\Delta G^{\ominus}_{f,ox}(11) = -7265 + 8.31\,T \tag{13}$$

$$\Delta G^{\ominus}_{f,ox}(12) = 6670 - 7.05\,T \tag{14}$$

The thermochemical data for the $Cu + Cu_2O$ and $CuO + Cu_2O$ equilibria described by reactions (9) and (10) were taken from our earlier study [8] because they were obtained on the experimental setup used in the present experiment.

3.2. EMF measurements with single-crystal CaF_2 solid electrolyte

The application of a CaF_2-type electrolyte for the thermodynamic study of compounds based on oxides has been discussed by Levitskii [9]. The cell construction used in this study essentially followed that applied by Alcock and Baozhan Li [10] to the study of thermodynamic properties of the Cu–Sr–O system. The following electrochemical cell was assembled

$$\text{air, Pt/Y}_2\text{O}_3\text{, YOF//CaF}_2\text{//YOF, CuO, Cu}_2\text{Y}_2\text{O}_5\text{/Pt, air} \qquad \text{(IV)}$$

the construction of which is shown schematically in Fig. 4. The cell was placed in a horizontal resistance furnace whose temperature was controlled by an Omega CR9700 temperature controller. The experimental temperature was measured with a Pt–PtRh10 thermocouple. A current of dry, synthetic air (Linde, Germany), which was virtually water-free, flowed continuously through the cell vessel. The e.m.f. was measured with a Keithley 197A electrometer. The equilibrium e.m.f. values were attained in a period of time ranging from 10 to 3 h depending on temperature. Then, the e.m.f. value was constant with time. The cell resistance was of the order of 0.3 MΩ in the temperature range from 873 K to about 1100 K.

The variation of e.m.f. with temperature for cell IV is shown in Fig. 5. The linear relation between e.m.f. and temperature obtained from the least-squares fit is

$$E_{\mathrm{IV}} = -0.1453 + 0.0001734\,T \qquad (15)$$

Since the half-cell reactions at the left hand site

$$\text{Y}_2\text{O}_3 + 2\,\text{F}^{1-} = 2\,\text{YOF} + 1/2\,\text{O}_2 + 2\text{e} \qquad (16)$$

and the right hand site electrode

$$2\,\text{YOF} + 2\,\text{CuO} + 1/2\,\text{O}_2 + 2\text{e} = \text{Cu}_2\text{Y}_2\text{O}_5 + 2\text{F}^{1-} \qquad (17)$$

yield the net cell reaction of cell IV in the form:

$$2\,\text{CuO} + \text{Y}_2\text{O}_3 = \text{Cu}_2\text{Y}_2\text{O}_5 \qquad (18)$$

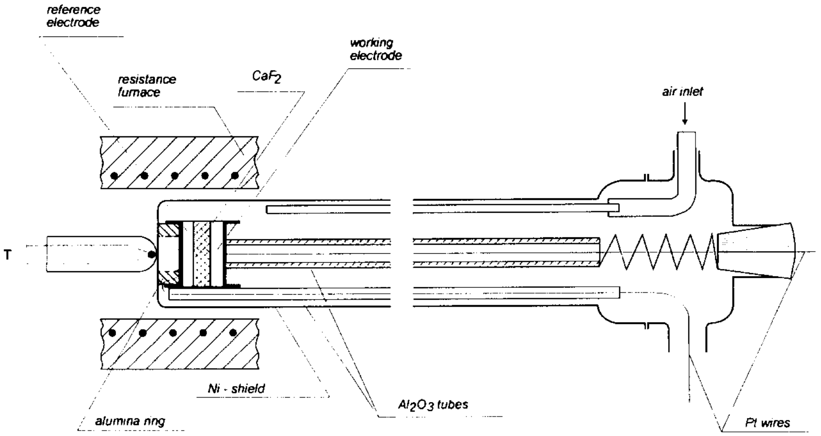

Fig. 4. Schematic cell assembly with CaF_2 electrolyte.

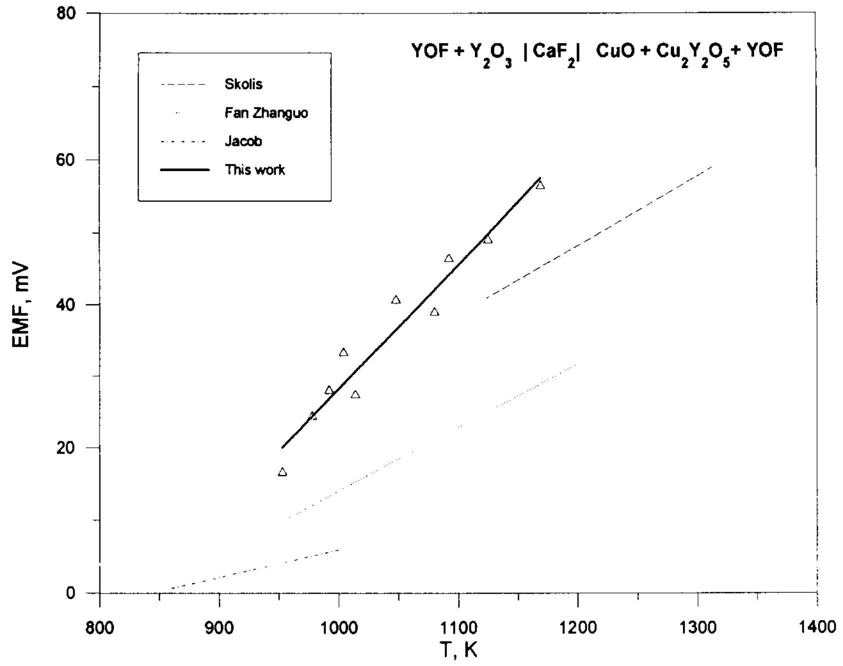

Fig. 5. Variation of e.m.f. with temperature for cell IV.

(which is identical with reaction (12)), the Gibbs free energy change of reaction (18) can be obtained directly from the experimental results. Based on Eq. (15), one can obtain for reaction (18)

$$\Delta G^\ominus_T = \Delta G^\ominus_{f,ox} = 2\,FE_{IV} = 28040 - 33.48\,T \tag{19}$$

4. Discussion

Using experimental data obtained in this study, we derived the Gibbs free energy of formation of solid $Cu_2Y_2O_5$ and $CuYO_2$ from the respective oxides. For this purpose, the oxygen pressure for the Cu + Cu_2O and Cu_2O + CuO equilibria determined by reactions (9) and (10) must be known, because $\Delta G^\ominus_{f,ox}$ cannot be obtained directly from the measured e.m.f.s. It is easy to demonstrate that by accepting free energy values from different literature sources, one may derive different results for the reactions (11) and (12) using the same experimental data produced by cells II and III. The results of such calculations are shown in Table 1 and in Fig. 6. Different literature data for reactions (9) and (10) used in these calculations were taken from the thermochemical tables of Turkdogan [11], Barin and Knacke [12], Kubaschewski and Alcock [13] and Chang and Hsieh [14], respectively. The entire set of $\Delta H^\ominus_{f,ox}$ and $\Delta S^\ominus_{f,ox}$ values was generated. This demonstrates that one reason for obtaining the diverse results observed in the literature may be simply the choice of the data for reactions (9) and (10). Therefore in

Table 1
Enthalpy and entropy terms calculated for reactions (11) and (12) according to different literature data accepted for reactions (9) and (10) (in J mol^{-1} and J K^{-1} mol^{-1}, respectively)

Author	$Cu_2O + Y_2O_3 \Leftrightarrow 2CuYO_2$		$2CuO + Y_2O_3 \Leftrightarrow Y_2Cu_2O_5$	
	$\Delta H^{\ominus}_{f,ox}$	$\Delta S^{\ominus}_{f,ox}$	$\Delta H^{\ominus}_{f,ox}$	$\Delta S^{\ominus}_{f,ox}$
Turkdogan, Ref. [11]	−13 470	−17.49	12 760	11.01
Barin, Knacke, Ref. [12]	−17 240	−20.27	2560	1.64
Kubaschewski, Alcock, Ref. [13]	−20 380	−22.45	3620	3.03
Chang, Hsieh, Ref. [14]	−12 540	−15.38	14 590	12.77
Onderka, Fitzner, Ref. [8]	−14 530	−16.62	6670	7.05

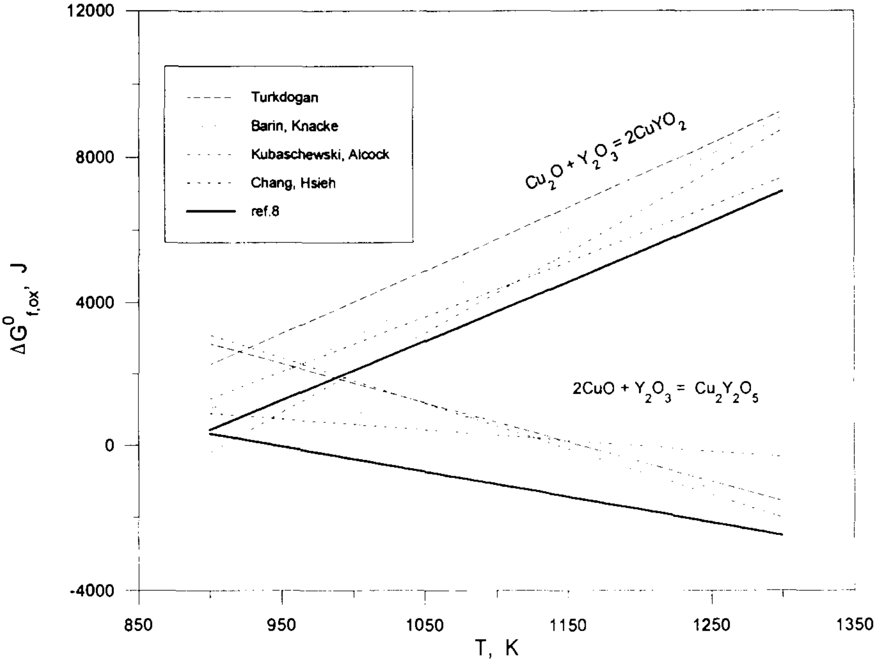

Fig. 6. Comparison of $\Delta G^{\ominus}_{f,ox}$ derived from the EMF's of cells II and III using different literature sources for reactions (9) and (10).

this case, it seems advisable to use the data produced by the same experimental setup for reactions (9) and (10). Also, it indicates the importance of the data evaluation for these reactions because of their further applications.

Of course, the observed influence of the choice of data for reactions (9) and (10) on the obtained result is not the only cause of the existing discrepancies. Using galvanic cells of type I, Tretyakov et al. [15], Pankajavalli and Sreedharan [16], Borowiec and Kolbrecka [17], Shimpo and Nakamura [18], and Fitzner and Chang [19], assumed equilibrium among Y_2O_3, Cu_2O and $Cu_2Y_2O_5$ at the working electrode. Unfortunately, such an equilibrium does not exist under experimental conditions as it demonstrates the performance of cell I. Therefore, taking into account the fact that the oxygen pressure is in fact established by the $Cu_2Y_2O_5+CuYO_2$ equilibrium, a number of studies were carried out to determine the Gibbs free energies of formation of both $Cu_2Y_2O_5$ and $CuYO_2$. Consequently, Wiesner et al. [20], Kale and Jacob [21], Mudretslova et al. [22], Suzuki et al. [23], and Borowiec and Kolbrecka [24] determined the equilibrium oxygen pressure over the proper three-phase fields. However, these results are still diverse. For both compounds, $\Delta H^{\ominus}_{f,ox}$ and $\Delta S^{\ominus}_{f,ox}$ show either positive or negative signs. As far as $Cu_2Y_2O_5$ is concerned, the studies of Kale and Jacob [21], Suzuki et al. [23], and also this work, indicate positive values of $\Delta H^{\ominus}_{f,ox}$ (11.2, 28.7, 6.7 kJ mol^{-1}, respectively) and $\Delta S^{\ominus}_{f,ox}$ (15.1, 31.6, 7.1 J K^{-1} mol^{-1}, respectively). Those of Wiesner et al. [20] and Borowiec and Kolbrecka [24] give negative values. Taking into account the results of e.m.f. studies performed with CaF_2 solid electrolyte on the one hand [25–27], and the calorimetric results obtained by Zhou and Navrotsky [7] ($\Delta H^{\ominus}_{f,ox} = 5.1 \pm 2.2$ kJ mol^{-1} at 977 K) on the other, we think that positive values give the right answer. This means that $Cu_2Y_2O_5$ is an entropy-stabilized compound. Its temperature of decomposition calculated from Eqs. (14) and (19) varies from 947 to 838 K. A similar difference, about one hundred degrees, in calculated decomposition temperature is observed between the results of Jacob and coworkers [21, 27], who also used both cells with zirconia and CaF_2 solid electrolytes.

In the case of $CuYO_2$ however, the situation is less clear. Our results are close to those obtained by Kale and Jacob [21] ($\Delta H^{\ominus}_{f,ox} = -5.8$ kJ mol, $\Delta S^{\ominus}_{f,ox} = -3.9$ J K^{-1} mol^{-1}) while $\Delta G^{\ominus}_{f,ox}$ values derived from the studies of Mudretslova et al. [22], and Suzuki et al. [23], although close as well, indicate different temperature dependences. The results derived from Refs. [20, 23, 24] seem to be too diverse. Since the obtained result is sensitive to both e.m.f. temperature dependences, and the accepted value of $\Delta G^{\ominus}_{T}(9)$, more work is still needed to resolve this discrepancy. Again, we think that in this case negative values give the right answer simply because it is very difficult to synthesize $CuYO_2$ from the respective oxides at high temperature.

Another technique which assures a direct determination of the Gibbs free energy change of reaction (12) is the electrochemical method based on the application of CaF_2 solid electrolyte. Eq. (19) demonstrates that the measured EMF is directly related to $\Delta G^{\ominus}_{f,ox}$ of reaction (12). Cells with CaF_2 single crystals were used by Skolis and Kitsenko [25], Fan Zhanguo et al. [26] and Azad et al. [27] for the determination of the Gibbs free energy of formation of $Cu_2Y_2O_5$ phase. Their e.m.f. vs. temperature dependence is compared with the performance of our cell IV in Fig. 5. Although all the results indicate different temperature dependences, calculated values of $\Delta G^{\ominus}_{f,ox}$ show positive values of $\Delta H^{\ominus}_{f,ox}$ and $\Delta S^{\ominus}_{f,ox}$ in all cases. The observed differences in temperature dependence can probably be related to addition of either YF_3 (Azad et al. [27]) or YOF (other studies) to the working and reference electrodes. Also, the temperature range used in the experiments of Skolis and Kitsenko [25] is high enough (1123–1313 K) for the formation of $Cu_2YO_{2.5}$ at the working electrode above 1263 K [4]. This reaction may affect the slope of their EMF vs. temperature dependence. It is still difficult, however, to explain the differences between the results produced by the cells with zirconia and CaF_2

electrolytes in the case of the $Cu_2Y_2O_5$ phase. In general, cells with CaF_2 electrolyte have a higher resistance (of the order $10^5\,\Omega$) than those with zirconia. Also, an equilibrium state at both electrodes may be more difficult to attain. This may be the main reason for the observed differences in the results produced by cells II, III and IV.

Acknowledgements

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