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Standard enthalpies of formation of Sr_2CuO_3 and Ca_2CuO_3

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Abstract

The enthalpies of reactions between alkaline-earth cuprates M_2CuO_3 (M = Ca, Sr) and hydrochloric acid were measured in a hermetic swinging calorimeter at 298.15 K. The M_2CuO_3 samples were prepared by solid-phase synthesis from calcium or strontium carbonate and copper oxide and characterized by X-ray powder diffraction, EDX and wet analysis. The standard enthalpies of formation obtained for the cuprates, $-1431 \pm 4\,\mathrm{kJ\,mol^{-1}}$ for Ca_2CuO_3 and $-1374 \pm 3\,\mathrm{kJ\,mol^{-1}}$ for Sr_2CuO_3, are discussed and compared with previous experimental and assessed values.

Keywords: Solution calorimetry; Enthalpy of reaction; Enthalpy of formation; Alkaline-earth cuprates; Ca_2CuO_3; Sr_2CuO_3

1. Introduction

Alkaline-earth cuprates are a subject of broad experimental and theoretical interest because of the discovery of high-temperature superconductors in the multi-component Hg–(Ba, Sr)–Ca–Cu–O system. Reliable thermodynamic data are indispensable for construction of phase diagrams and for the preparation of single-phase superconducting oxides.

Two types of experiments on the thermochemical study of Sr_2CuO_3 and Ca_2CuO_3 can be found in the literature; calorimetric investigations [1] and EMF measurements [2–7]. The available experimental data and resulting thermodynamic values are summarized in a review [8]. The calculated values are also presented in [9–11]. The literature data vary considerably, values of standard enthalpy of formation for Ca_2CuO_3 by $\sim 7\,\mathrm{kJ\,mol^{-1}}$ and by $\sim 45\,\mathrm{kJ\,mol^{-1}}$ for Sr_2CuO_3.

The purpose of this work was to carry out an independent calorimetric determination for standard enthalpies of formation of Ca_2CuO_3 and Sr_2CuO_3 by calorimetry on carefully characterized substances.

2. Experimental

2.1. Sample preparation and characterization

Single-phase Ca_2CuO_3 and Sr_2CuO_3 samples were synthesized by annealing a fine mixture of calcium or strontium carbonate and copper oxide in alumina crucibles, calcium cuprate at 1000 °C for 72 h in air, and strontium cuprate at 1050 °C for 24 h in a dry oxygen flow. These substances are hygroscopic and, therefore, were protected from contact with moist air and carbon dioxide by storage in desiccators. All preparative handlings were carried out in a nitrogen-filled glove box.

The phase composition and lattice constants were determined by X-ray powder diffraction using a Guinier-camera FR-552 (Cu Kα_1 radiation, $\lambda = 1.54056$ Å) with germanium as an internal standard. The scanning electronic microscope JEOL JSM 820 with LINK AN 10000 additional device was used for EDX study.

The X-ray examination showed only Ca_2CuO_3 or Sr_2CuO_3 single phases with cell parameters $a = 12.232(2)$ Å, $b = 3.7777(8)$ Å, $c = 3.2580(9)$ Å for Ca_2CuO_3 and $a = 12.685(3)$ Å, $b = 3.9054(11)$ Å, $c = 3.4959(8)$ Å for Sr_2CuO_3

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which are close to the reference data [12]. The EDX study of Ca_2CuO_3 did not reveal any contamination. The copper content and formal copper valence in the samples were determined by iodometric titration. The alkaline-earth oxide content was calculated as a difference between total sample mass and mass of the copper oxide. According to the chemical analysis the composition of the studied phases may be described as $Ca_{2.00(3)}Cu_{1.00(2)}O_{3.00(2)}$ and $Sr_{1.99(3)}Cu_{1.01(2)}O_{3.01(2)}$ with the stoichiometric composition and formal copper oxidation degree +2 within the experimental errors. In further thermochemical calculation these phases are considered to be stoichiometric Ca_2CuO_3 and Sr_2CuO_3.

The hydrochloric acid solution (1.07 mol dm^{-3}) was prepared by diluting high purity concentrated HCl by distilled water (electrical conductivity 6×10^{-4} S m^{-1}).

2.2. Calorimetric technique

The measurements were performed at 298.15 K in a sealed swinging calorimeter with an isothermal jacket, similar to that described in Refs. [13,14]. The calorimeter consists of a thin-walled titanium reaction vessel fitted with a copper resistance thermometer, a calibration heater and a holder for spherical glass bulbs. The calorimeter is contained within a chromium-plated brass case. The resistance thermometer forms one arm of a Wheanstone bridge with a thermometric detection limit of 3×10^{-5} K. The chromium plated brass case is submerged in a thermostatically controlled water bath with thermal stability better than 10^{-3} K. Blank experiments showed the material of the calorimeter vessel and the ampoule holder did not react with the acid used. The energy equivalent of the calorimeter is determined by electric heating. The potentiometric circuit used for this purpose provides an accuracy of a few hundredths of a percent. The energy equivalent of the calorimetric system filled with 1.07 mol dm^{-3} HCl to the mass of (55.000 ± 0.003) g is equal to (344.55 ± 0.19) J Ω^{-1}.

The calorimeter has been tested several times by dissolution of KCl in water (the molality of the final solution was 0.028 mol kg^{-1} at 298.15 K). The most recent set of KCl dissolution measurements yielded (17.40 ± 0.04) kJ mol^{-1}. The critically evaluated value is (17.43 ± 0.02) kJ mol^{-1} [15].

2.3. Determination of the molar enthalpies of reactions

Freshly prepared samples of alkaline-earth cuprates were placed in thin-walled glass bulbs and sealed in an atmosphere of dry nitrogen. Then the ampoules were broken inside the calorimetric vessel filled 55.000(3) g of 1.07 mol dm^{-3} HCl. The results for the direct calorimetric measurements of the enthalpy of reaction of Ca_2CuO_3 and Sr_2CuO_3 with the hydrochloric acid are presented in Table 1. The correction for the enthalpy of breaking the calorimetric bulbs and the temperature correction of the thermal effect to 298.15 K were negligible and were not included in the calculation.

Table 1
Results of measurements of the enthalpy of reaction of Ca_2CuO_3 and Sr_2CuO_3 in 1.07 mol dm^{-3} HCl at 298.15 K

	ΔR (Ω)	Q (J)	Mass (g)	$-\Delta_r H^\circ_m$ (kJ mol^{-1})
Ca_2CuO_3[a]				
1	0.51517	177.50	0.07695	442.20
2	0.48420	166.83	0.07114	449.56
3	0.35078	120.86	0.05146	450.23
4	0.33546	115.58	0.04948	447.79
5	0.27618	95.158	0.04101	444.82
Sr_2CuO_3[b]				
1	0.31853	109.75	0.06119	514.38
2	0.23017	79.304	0.04443	511.89
3	0.33927	116.90	0.06484	517.05
4	0.13314	45.873	0.02554	515.10

ΔR is the corrected temperature rise, Q the energy evolved in each experiment, m the sample mass, $\Delta_r H^\circ_m$ the molar enthalpy change of the reaction, $\langle \Delta_r H^\circ_m \rangle$ the average enthalpy of reaction, σ the standard deviation of the mean value, $\sigma(t_{0.05})$ the confidence limits given by Student's t-test.

[a] $\langle \Delta_r H^\circ_m \rangle = (-446.9 \pm 4.2)$ kJ mol^{-1}.

[b] $\langle \Delta_r H^\circ_m \rangle = (-514.6 \pm 3.4)$ kJ mol^{-1}.

3. Calculation of the standard molar enthalpies of formation of Sr_2CuO_3 and Ca_2CuO_3

The standard enthalpies of formation of Sr_2CuO_3 and Ca_2CuO_3 from oxides ($\Delta_{f,ox} H^\circ_{298.15}$) and the elements ($\Delta_f H^\circ_{298.15}$) were calculated by two alternative schemes via oxides (Cycle 1) and via chlorides (Cycle 2) (see Table 2).

In Cycle 1, ΔH_1 is the enthalpy of the reaction between M_2CuO_3 (M = Ca, Sr) and 1.07 mol dm^{-3} HCl measured in this work, and ΔH_2 and ΔH_3 are the reliable literature data necessary for the calculations. In all reactions, the term "solution" (sln) refers to the state of solutions of the corresponding compounds in excess 1.07 mol dm^{-3} hydrochloric acid. It was taken into account in the calculation that the enthalpy of formation of the final solution in reaction (1) equaled the sum of the enthalpies of formation of the final solutions in reactions (2) and (3). The enthalpy of mixing of hydrochloric acid solutions of calcium (strontium) and copper chlorides can be ignored, because the amount of these salts in the solutions is insignificant against the large excess of hydrochloric acid. The overall errors of the enthalpies of formation in all thermochemical cycles were calculated by the formula $\sigma = \left(\sum \sigma_i^2\right)^{1/2}$, where σ_i are the standard errors of the values used in the calculations.

The standard enthalpies of formation of M_2CuO_3 (M = Ca, Sr) phases from the elements were calculated using the obtained $\Delta_{f,ox} H^\circ_{298.15}$ values and the reliable reference data on the enthalpies of formation of calcium oxide (−635.09 ± 0.96) kJ mol^{-1} [15], strontium oxide (−592.15 ± 0.86) kJ mol^{-1} [17] and copper oxide (−157.07 ± 0.84) kJ mol^{-1} [26].

In Cycle 2, ΔH_2 and ΔH_5 are the reference data necessary for the calculation. The standard enthalpies of formation of M_2CuO_3 (M = Ca, Sr) from the oxides were calculated using the obtained $\Delta_f H^\circ_{298.15}$ values and the same reference data

Table 2
Thermochemical cycles for calculation of the enthalpies of formation of Ca_2CuO_3 and Sr_2CuO_3

Number	Equations of the reactions	Enthalpies of the reactions
Cycle 1 (the set of thermochemical equations for calculation of the enthalpies of formation of M_2CuO_3 (M = Ca, Sr) via oxides)		
(1)	$M_2CuO_3(cr) + 6HCl(sln) = 2MCl_2(sln) + CuCl_2(sln) + 3H_2O(sln)$	$\Delta H_1 = (-446.92 \pm 4.2)\,kJ\,mol^{-1}$ for (M = Ca) and $(-514.61 \pm 3.39)\,kJ\,mol^{-1}$ for M = Sr [this work]
(2)	$MO(cr) + 2HCl(sln) = MCl_2(sln) + H_2O(sln)$	$\Delta H_2 = (-194.68 \pm 0.25)\,kJ\,mol^{-1}$ for CaO [16] and $(-243.93 \pm 0.33)\,kJ\,mol^{-1}$ for SrO [17]
(3)	$CuO(cr) + 2HCl(sln) = CuCl_2(sln) + H_2O(sln)$	$\Delta H_3 = (-60.59 \pm 2.32)\,kJ\,mol^{-1}$ [18]
(4)	$2MO(cr) + CuO(cr) = M_2CuO_3(cr)$	$\Delta H_4 = \Delta_{f,ox}H^\circ_{298.15}$ $(M_2CuO_3) = 2\Delta H_2 + \Delta H_3 - \Delta H_1 = (-3.0 \pm 4.8)\,kJ\,mol^{-1}$ for M = Ca and $(-33.8 \pm 4)\,kJ\,mol^{-1}$ for M = Sr
Cycle 2 (the set of thermochemical equations for calculation of the enthalpies of formation of M_2CuO_3 (M = Ca, Sr) via chlorides)		
(1)	$M_2CuO_3(cr) + 6HCl(sln) = 2MCl_2(sln) + CuCl_2(sln) + 3H_2O(sln)$	$\Delta H_1 = (-446.92 \pm 4.2)\,kJ\,mol^{-1}$ for M = Ca and $(-514.61 \pm 3.39)\,kJ\,mol^{-1}$ for M = Sr [this work]
(2)	$M(cr) + Cl_2(g) + [HCl(sln)] = MCl_2\ (sln)$	$\Delta H_2 = (-875.3 \pm 2.0)\,kJ\,mol^{-1}$ for Ca [19,20] and $(-879.79 \pm 0.65)\,kJ\,mol^{-1}$ for Sr [21–23]
(3)	$Cu(cr) + Cl_2(g) + [HCl(sln)] = CuCl_2(sln)$	$\Delta H_3 = (-256.63 \pm 1.62)\,kJ\,mol^{-1}$ [15,24]
(4)	$(1/2)H_2(g) + (1/2)Cl_2(g) + [H_2O(aq)] = HCl(sln)$	$\Delta H_4 = (-164.4 \pm 0.2)\,kJ\,mol^{-1}$ [25]
(5)	$H_2(g) + (1/2)O_2(g) + [HCl(sln)] = H_2O(sln)$	$\Delta H_5 = (-285.85 \pm 0.04)\,kJ\,mol^{-1}$ [25]
(6)	$2M(cr) + Cu(cr) + (3/2)O_2(g) = M_2CuO_3(cr)$	$\Delta H_6 = \Delta_f H^\circ_{298.15}(M_2CuO_3) = 2\Delta H_2 + \Delta H_3 - 6\Delta H_4 + 3\Delta H_5 - \Delta H_1$ $= (-1431.5 \pm 6)\,kJ\,mol^{-1}$ for M = Ca and $(-1372.7 \pm 4)\,kJ\,mol^{-1}$ for M = Sr

$\Delta_f H^\circ_{298.15}$ $(M_2CuO_3) = \Delta_f H^\circ_{298.15}(CuO) + 2\Delta_f H^\circ_{298.15}(MO) + \Delta H_4 = (-1430.3 \pm 5)\,kJ\,mol^{-1}$ for M = Ca and $(-1375.1 \pm 5)\,kJ\,mol^{-1}$ for M = Sr.
$\Delta_{f,ox}H^\circ_{298.15}(M_2CuO_3) = \Delta H_6 - \Delta_f H^\circ_{298.15}(CuO) - 2\Delta_f H^\circ_{298.15}$ $(MO) = (-4.3 \pm 6.4)\,kJ\,mol^{-1}$ for M = Ca and $(-31.3 \pm 4.6)\,kJ\,mol^{-1}$ for M = Sr.

Table 3
Standard enthalpies of formation of Ca_2CuO_3 and Sr_2CuO_3 from oxides ($\Delta_{f,ox}H^\circ_{298.15}$) and elements ($\Delta_f H^\circ_{298.15}$)

Substance	$\Delta_{f,ox}H^\circ_{298.15}$ $(kJ\,mol^{-1})$		$\Delta_f H^\circ_{298.15}$ $(kJ\,mol^{-1})$	
	Cycle 1	Cycle 2	Cycle 1	Cycle 2
Ca_2CuO_3	-3.0 ± 4.8	-4.3 ± 6.4	-1430.3 ± 5	-1431.5 ± 6
Sr_2CuO_3	-33.8 ± 4.2	-31.3 ± 4.6	-1375.1 ± 5	-1372.7 ± 4

	$\Delta_{f,ox}H^\circ_{298.15}$ $(kJ\,mol^{-1})$	$\Delta_f H^\circ_{298.15}$ $(kJ\,mol^{-1})$
Recommended values		
Ca_2CuO_3	-3.5 ± 3.8	-1431 ± 4
Sr_2CuO_3	-32.7 ± 3.1	-1374 ± 3

on the enthalpies of formation of calcium oxide, strontium oxide and copper oxide (see Cycle 1).

The results show that the values for the enthalpies of formation of M_2CuO_3 (M = Ca, Sr) calculated by two alternative ways coincide within the error of the measurements. Therefore, the weighed mean of the two determinations is recommended for the further thermodynamic calculations (see Table 3).

4. Discussion and conclusion

The currently available data on the enthalpies of formation of M_2CuO_3 (M = Ca, Sr) are summarized in Table 4 . The results obtained in the present work coincide within the experimental errors with the data for Ca_2CuO_3 resulting from the previous calorimetric study [1] and differ from the data for Sr_2CuO_3. Our measurements on Sr_2CuO_3 cannot be strictly correlated with the results of Idemoto et al. [1] as the samples under investigation differ in composition.

For comparison with the literature EMF data presented in Table 4 the results obtained in the present work were converted from 298.15 to 1000 K and the following values of $\Delta_{f,ox}H^\circ$ were obtained

$$\Delta_{f,ox}H^\circ_{1000} = (-1.9 \pm 3.8)\,kJ\,mol^{-1} \quad \text{for } Ca_2CuO_3$$

and

$$\Delta_{f,ox}H^\circ_{1000} = (-26.6 \pm 3.9)\,kJ\,mol^{-1} \quad \text{for } Sr_2CuO_3$$

The reliable reference data on the heat capacity of CuO(cr), $O_2(g)$ [27] and assessed value of the heat capacities of Ca_2CuO_3 and Sr_2CuO_3 [28] were used in calculations. Table 4 shows some discrepancy in the EMF data obtained in different works. The results of the present work, converted to 1000 K, coincide within the experimental errors with the results of Mathews et al. [2,7]. The assessed values recommended in [8–11] are in good agreement with the data of the present calorimetric study.

In the present work and in [1] the standard enthalpies of formation of the cuprates were obtained by solution calorime-

Table 4
The comparison of reference and our values for the standard molar enthalpies of formation of Ca_2CuO_3 and Sr_2CuO_3 from oxides

Substance composition	EMF technique		Solution calorimetry, $HClO_4$ as a solvent [1]	Solution calorimetry, HCl as a solvent [obtained in this work]	Assessed values
	$\Delta_{f,ox}H^\circ_T$ (kJ mol^{-1})	Temperature (K)	$\Delta_{f,ox}H^\circ_{298.15}$ (kJ mol^{-1})	$\Delta_{f,ox}H^\circ_{298.15}$ (kJ mol^{-1})	$\Delta_{f,ox}H^\circ_{298.15}$ (kJ mol^{-1})
Ca_2CuO_3	−4.8 ± 0.1 [2]	1110–1260			−5.2[8]
	−4.9 ± 0.1 [2]	925–1250		−3.5 ± 3.8	
	−3.3 ± 2.2 [3][a]	1000–1220			−3.2[9]
$Ca_{2.01}Cu_{1.00}O_{3.01}$			−7.8 ± 2.7[b]		
Sr_2CuO_3	−67.12 ± 1.2 [4]	1050–1150			−31.4[8]
	−31.8 ± 1.1 [5]	1030–1260			
	−32.22 ± 0.25 [6]	975–1260		−32.7 ± 3.1	−27.8[10]
	−31.84 ± 0.31 [6]	900–1280			
	−23.08 ± 0.43 [7][a]	923–1223			
					−26.1[11]
$Sr_{1.90}Cu_{1.10}O_{3.01}$			−70.5 ± 3.8[b]		

[a] Re-calculated in this work.

[b] The total error is re-calculated in this work according to the propagation law.

try with two different calorimeters, in two different solvents and with different enthalpies of the reactions involved in the calculations via the thermochemical cycles. The good agreement in the values for the samples of Ca_2CuO_3 with the same approximate composition provides a convincing proof of the reliability of the calorimetric method, and the obtained values of standard enthalpies of formation of Ca_2CuO_3 and Sr_2CuO_3 can be recommended as the reference ones.

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