An Electrochemical Study of High-Temperature Stability of Compounds between the Rare Earths and Copper Oxide*

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Equilibrium conditions for formation of the compounds $CuLn_2O_4$ (Ln = La, Nd, Sm, Eu, Gd) and $Cu_2R_2O_5$ (R = Tb, Dy, Er, Yb, Y, In) were studied in galvanic cells with solid electrolyte ZrO_2 (Y_2O_3) in the temperature range 950–1150°C. The results, together with results of a study of the equilibrium $CuO–Cu_2O$, were used to calculate the $\Delta G°$ of formation of the double oxides from CuO and the Ln_2O_3 (In_2O_3, Y_2O_3) as listed above. We found a decrease in the stability of the compounds $CuLn_2O_4$ relative to the initial oxides in the sequence La–Gd and an increase in the stability of $Cu_2Ln_2O_5$ in the sequence Tb–Yb. The results are discussed on the basis of special features of the crystalline structure of the compounds examined.

Introduction

Many of the compounds formed by oxides of the transition metals with the rare earth oxides possess remarkable electric, magnetic, optical, catalytic, and other properties that are sensitive to the electron structure (1–4). Rare earth ferrites with garnet and perovskite structure are widely used as magnetic materials (5). However, despite the success of their use and of still greater prospects in this direction, little is known about the equilibrium conditions of formation and the stability of the ternary compounds relative to the initial simple oxides. One measure of this stability is the change in Gibbs' energy in the reaction of the simple oxides to form the ternary compounds. In the present work, an attempt has been made to study the stability of rare earth oxide compounds with cupric oxide. The selection of items for study was determined by the fact that these compounds allow us to trace the regularity of change in thermo-

dynamic properties with electronic structure and dimensions of the lanthanide ions, and also to establish the interconnection of the thermodynamic properties with the crystal structure of the compounds examined.

Three types of compounds are established in the $CuO–Ln_2O_3$ systems. The oxides of the elements La through Gd react with CuO in the mole ratio 1:1 to form isostructural compounds of general formula $CuLn_2O_4$ (3, 4, 6), which crystallize in the K_2NiF_4 structural type. As Longo and Raccah have shown (7), $CuLa_2O_4$ forms a tetragonal lattice of the K_2NiF_4 type, but only at temperatures above 260°C, manifesting strong orthorhombic distortions at lower temperatures.

Compounds of the second type, $Cu_2R_2O_5$ (6, 8), are formed by interaction in a mole ratio of 2:1 of cupric oxide with rare earth element oxides ranging from Tb to Lu (inclusive) and also with oxides of Y, In, and Sc. A detailed X-ray analysis of structures of the type $Cu_2R_2O_5$ was done by Bergerhoff and Kasper (9). During the interaction of Cu_2O and Ln_2O_3 (Ln = La, Pr, Nd, Sm, Eu) com-

TABLE I[a]

La$_2$O$_3$	Nd$_2$O$_3$	Sm$_2$O$_3$	Eu$_2$O$_3$	Gd$_2$O$_3$	Tb$_2$O$_3$	Dy$_2$O$_3$	Er$_2$O$_3$	Yb$_2$O$_3$
A	A	B	C*	C*	C	C	C	C

[a] A, hexagonal; B, monoclinic; C*, cubic metastable; C, cubic.

pounds of $CuLnO_2$ are formed, not one of which, however, exists at $T \geqslant 1000°C$ (_10_).

Synthesis of the Investigated Compounds

All the compounds that were studied ($CuLa_2O_4$, $CuNd_2O_4$, $CuSm_2O_4$, $CuEu_2O_4$, $CuGd_2O_4$; $Cu_2Tb_2O_5$, $Cu_2Dy_2O_5$, $Cu_2Er_2O_5$, $Cu_2Yb_2O_5$; $Cu_2Y_2O_5$, and $Cu_2In_2O_5$) were prepared by mixing cupric oxide with the corresponding sesquioxides of the rare earth elements, yttrium, and indium in high purity (the total amount of impurity in CuO was <0.01 wt%; in the rare earth elements oxides it was <0.1 wt%). The oxides were baked for 2 h at 1000°C in a stream of oxygen, which prevented dissociation of the CuO. The cuprous oxide was prepared from CuO under vacuum at 1000°C. The completeness of the reaction during synthesis of the ternary compounds was confirmed by X-ray analysis. The rare earth element oxides were also subjected to X-ray analysis after firing at 1000°C in order to establish their polymorphic forms. The results of the analysis are presented in Table I.

Methods

The ternary compounds studied break down under equilibrium conditions according to the following schemes:

$$4CuLn_2O_4 \rightarrow 2Cu_2O + 4Ln_2O_3 + O_2 \quad (1)$$

$$2Cu_2R_2O_5 \rightarrow 2Cu_2O + 2R_2O_3 + O_2. \quad (2)$$
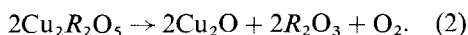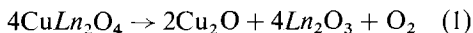
For the compounds $CuLn_2O_4$ ($Ln = $ La–Eu), such a mechanism is true only at temperatures higher than the disintegration temperature of the corresponding compounds of the $CuRO_2$ type.

In agreement with Gibbs' phase rule, the chemical potential for oxygen, μ_{O_2}, over the equilibrium mixture $CuLn_2O_4 + Cu_2O + Ln_2$-

O_3 in reaction (1) is fixed by the temperature and is expressed by the equation

$$\mu_{O_2}^{(1)} = 4\mu_{CuLn_2O_4} - 2\mu_{Cu_2O} - 4\mu_{Ln_2O_3}. \quad (3)$$

Presupposing that the mutual solubility of $CuLn_2O_4$, Cu_2O, and Ln_2O_3 is not very great and that, at equilibrium, each of these phases exists in a pure form, we can rewrite expression (3), using the standard values of the chemical potentials:

$$\mu_{O_2}^{(1)} = 4\mu°_{CuLn_2O_4} - 2\mu°_{Cu_2O} - 4\mu°_{Ln_2O_3}. \quad (4)$$

For the dissociation reaction of cupric oxide,
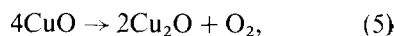
$$4CuO \rightarrow 2Cu_2O + O_2, \quad (5)$$

we can write in analogous fashion

$$\mu_{O_2}^{(5)} = 4\mu°_{CuO} - 2\mu°_{Cu_2O}. \quad (6)$$
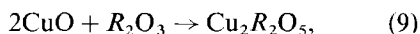
Combining Eqs. (4) and (6), we obtain the expression

$$(\mu_{O_2}^{(1)} - \mu_{O_2}^{(5)})/4 = \mu°_{CuLn_2O_4} - \mu°_{CuO} - \mu°_{Ln_2O_3} \quad (7)$$

the right side of which is $\Delta G°$ of the reaction

$$CuO + Ln_2O_3 \rightarrow CuLn_2O_4. \quad (8)$$
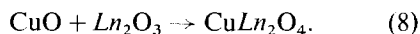
Analogously, we can show that for the reaction

$$2CuO + R_2O_3 \rightarrow Cu_2R_2O_5, \quad (9)$$

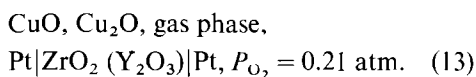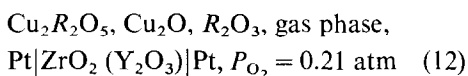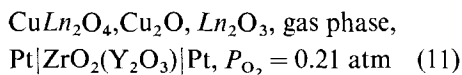the equation is

$$\Delta G°_{(9)} = (\mu_{O_2}^{(2)} - \mu_{O_2}^{(5)})/2. \quad (10)$$

Consequently, for calculating the Gibbs' energy change during formation of the ternary compounds from the simple oxides, it is necessary to determine the equilibrium chemical potential of oxygen in the dissociation of the ternary compounds and the least stable of the reacting simple oxides. For this purpose

we studied electrochemical cells of the following types:

$$CuLn_2O_4, Cu_2O, Ln_2O_3, \text{ gas phase,}$$
$$Pt|ZrO_2(Y_2O_3)|Pt, P_{O_2} = 0.21 \text{ atm} \quad (11)$$

$$Cu_2R_2O_5, Cu_2O, R_2O_3, \text{ gas phase,}$$
$$Pt|ZrO_2(Y_2O_3)|Pt, P_{O_2} = 0.21 \text{ atm} \quad (12)$$

$$CuO, Cu_2O, \text{ gas phase,}$$
$$Pt|ZrO_2(Y_2O_3)|Pt, P_{O_2} = 0.21 \text{ atm.} \quad (13)$$

In accord with Wagner's fundamental equation for each of these cells the expression

$$E = \frac{1}{4F}(\mu_{O_2}^R - \mu_{O_2}^L) \quad (14)$$

is correct, where E = electromotive force of the cell, F = the Faraday constant, $\mu_{O_2}^R$ = the chemical potential of oxygen at the right electrode (i.e., the reference electrode), and $\mu_{O_2}^L$ = the chemical potential of oxygen at the electrode made of the mixture under study.

From Eqs. (14) and (7) we obtain

$$\Delta G^{\circ}_{(8)} = -F[E_{(11)} - E_{(13)}], \quad (15)$$

while Eqs. (14) and (9) give

$$\Delta G^{\circ}_{(9)} = -2F[E_{(12)} - E_{(13)}]. \quad (16)$$

The construction of the galvanic cell used is traditional as is clear from Fig. 1. The ternary compounds studied were carefully mixed in an agate mortar with the cuprous oxide and the corresponding rare earth oxide in molar proportions corresponding to the stoichiometric coefficients of the dissociation equations (1) and (2). The triphase mixture was loaded into a crucible of ZrO_2 (Y_2O_3) or Al_2O_3, which in turn was placed in a platinum, current-lead container. The elimination of direct contact between the mixture under study and the current-lead helped to avoid any complications arising from volatility of cuprous oxide, which is observed at temperatures higher than 1000°C and which leads to surface depletion of the specimen. The diffusion of copper ions from the depth of the specimen to the surface compensates for this effect at high temperatures, but when the temperature is lowered, the diffusion speed falls sharply and an insufficiency of Cu_2O is perceived at the surface. An X-ray analysis of the surface layer of the specimen indicates presence in it only of the compound under study and the rare earth oxide. By eliminating direct contact of the specimen with platinum, the chemical potential of the oxygen is given throughout the gas phase and this surface effect develops at a lower temperature.

A careful degassing at $T \sim 200$°C in a vacuum of $\sim 5 \times 10^{-2}$ mm Hg preceded the experiments. After this, the cell was filled with spectrally pure Ar (1 atm) and heated to the operative temperature.

Measurements of the EMF and temperature were carried out by means of a compensation circuit. Temperature constancy within ± 1°C was maintained automatically. Equilibrium in the system was considered attained if the changes in the magnitude of the EMF were not monotonic and did not exceed ± 0.1 mV at a fixed temperature. The basic criterion for successful execution of the experiment was agreement of data on passage in both directions through the temperature interval studied.
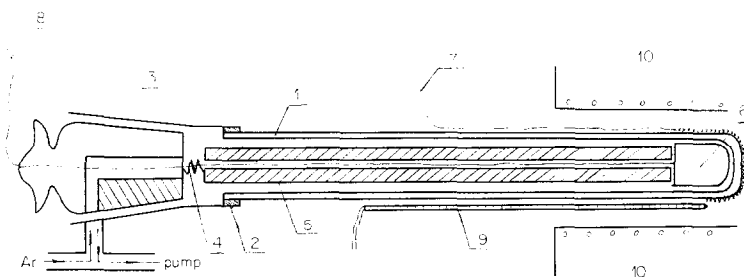

FIG. 1. Construction of the galvanic cell with a divided electrode space (the reference electrode is air with $P_{O_2} = 0.21$ atm): 1, solid electrolyte; 2, vacuum tight connection; 3, glass tap; 4, spring; 5, quartz rod; 6, platinum container; 7, 8, current leads; 9, thermocouple; 10, furnace.

TABLE II

RESULTS OF THE STUDY OF CELLS OF TYPE (11) AND (12)

Compounds	Temperature range (°K)	$E \pm \sigma$ (mV) $= A - BT$ (°K)		$\sigma = f(T)$
		A	B	
$CuLa_2O_4$	1220–1340	766.9	0.434	$[0.16 + 3.78 \times 10^{-4}(T-1285)^2]^{1/2}$
$CuNd_2O_4$	1220–1340	773.0	0.468	$[0.92 + 6.01 \times 10^{-4}(T-1231)^2]^{1/2}$
$CuSm_2O_4$	1173–1340	778.4	0.508	$[0.04 + 0.91 \times 10^{-4}(T-1289)^2]^{1/2}$
$CuEu_2O_4$	1173–1360	623.3	0.418	$[0.08 + 0.38 \times 10^{-4}(T-1315)^2]^{1/2}$
$CuGd_2O_4$	1220–1360	607.3	0.418	$[0.17 + 1.49 \times 10^{-4}(T-1267)^2]^{1/2}$
$Cu_2Tb_2O_5$	1173–1340	614.7	0.455	$[0.23 + 26.50 \times 10^{-6}(T-1244)^2]^{1/2}$
$Cu_2Dy_2O_5$	1173–1340	616.7	0.452	$[0.09 + 34.03 \times 10^{-6}(T-1259)^2]^{1/2}$
$Cu_2Er_2O_5$	1173–1340	593.2	0.427	$[0.11 + 32.29 \times 10^{-6}(T-1274)^2]^{1/2}$
$Cu_2Yb_2O_5$	1173–1340	633.8	0.454	$[0.11 + 27.70 \times 10^{-6}(T-1260)^2]^{1/2}$
$Cu_2In_2O_5$	1173–1340	672.3	0.496	$[0.05 + 18.40 \times 10^{-6}(T-1284)^2]^{1/2}$
$Cu_2Y_2O_5$	1173–1340	590.8	0.422	$[0.09 + 71.44 \times 10^{-6}(T-1291)^2]^{1/2}$

Results and Discussion

Results of measuring the EMF of cells type (11) and (12), which were worked out using the least-squares method, are presented in Table II. Results of the experiment on cell (13), which are expressed by the equation $E_{(13)}$ (mV) $= 698.2 - 0.540\ T$ (°K) $\pm [0.024 + 13.2$ $(T-1235)^2 \times 10^{-6}]^{1/2}$, are presented in Fig. 2, from which one can also see the good agreement with data from the literature (12, 13). The changes in Gibbs' energy for the formation reactions of the ternary oxides from CuO and
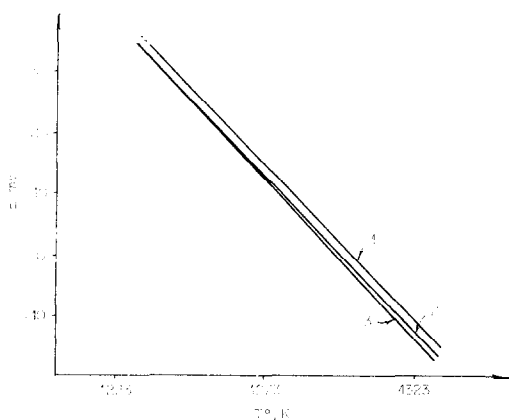

FIG. 2. A comparison of the results of the investigation of the equilibrium $CuO-Cu_2O$ in cell (13) with data in the literature 1, Ref. (12); 2, Ref. (13); 3, our data.

Ln_2O_3 (R_2O_3) calculated by Eqs. (15) and (16) are presented in Table III. Table IV shows the $\Delta H°$ and $\Delta S°$ of these reactions, which, in the first approximation, are independent of temperature in the range studied and are determined as coefficients of the linear equations $\Delta G° = A - BT$.

Analysis of the results allows us to draw a series of conclusions. Above all, we can confirm that, in the entire series investigated, only three compounds, corresponding to La, Nd, and Sm, are exothermic, whereas all the rest are endothermic and are stabilized in proportion to the temperature rise because of significant entropy term. Table IV presents the minimum temperatures for stable existence of the ternary compounds, below which they become metastable. These temperatures are obtained by extrapolating the dependence $\Delta G° = f(T)$ to the condition $\Delta G° = 0$.

The entropy change in solid-state reactions is sometimes related to magnetic ordering of the participants in the reaction or related to significant intrinsic disorder in the product (14).

In the temperature range of our investigation, magnetic contribution to the entropy is evidently negligible, and as yet there are no data indicating strong natural disorder in the ternary oxides. However, an alternate purely crystallochemical interpretation of entropy

TABLE III

STANDARD GIBBS' ENERGY CHANGES IN THE REACTIONS $nCuO + R_2O_3 \rightarrow nCuO \cdot R_2O_3$ $(n = 1, 2)$

Compounds	ΔG° ($\pm$) (kcal/mole)	$\Delta G^\circ_{1273°K}$ (kcal/mole)
$CuLa_2O_4$	$-1.58 - 2.44 \times 10^{-3}T \pm [3.50 \times 10^{-4} + 0.21 \times 10^{-6}(T-1283)^2]^{1/2}$	-4.70 ± 0.02
$CuNd_2O_4$	$-1.73 - 1.64 \times 10^{-3}T \pm [7.43 \times 10^{-4} + 0.33 \times 10^{-6}(T-1231)^2]^{1/2}$	-3.8 ± 0.04
$CuSm_2O_4$	$-1.85 - 0.72 \times 10^{-3}T \pm [2.96 \times 10^{-4} + 0.06 \times 10^{-6}(T-1282)^2]^{1/2}$	-2.77 ± 0.02
$CuEu_2O_4$	$+1.73 - 2.81 \times 10^{-3}T \pm [2.20 \times 10^{-4} + 0.03 \times 10^{-6}(T-1294)^2]^{1/2}$	-1.85 ± 0.02
$CuGd_2O_4$	$+2.10 - 2.81 \times 10^{-3}T \pm [4.37 \times 10^{-4} + 0.09 \times 10^{-6}(T-1264)^2]^{1/2}$	-1.48 ± 0.02
$Cu_2Tb_2O_5$	$+3.85 - 3.92 \times 10^{-3}T \pm [15.14 \times 10^{-4} + 0.08 \times 10^{-6}(T-1241)^2]^{1/2}$	-1.14 ± 0.04
$Cu_2Dy_2O_5$	$+3.66 - 4.04 \times 10^{-3}T \pm [12.34 \times 10^{-4} + 0.10 \times 10^{-6}(T-1252)^2]^{1/2}$	-1.48 ± 0.04
$Cu_2Er_2O_5$	$+4.84 - 5.18 \times 10^{-3}T \pm [13.00 \times 10^{-4} + 0.10 \times 10^{-6}(T-1263)^2]^{1/2}$	-1.75 ± 0.04
$Cu_2Yb_2O_5$	$+2.97 - 5.95 \times 10^{-3}T \pm [12.78 \times 10^{-4} + 0.09 \times 10^{-6}(T-1252)^2]^{1/2}$	-2.06 ± 0.04
$Cu_2In_2O_5$	$+1.20 - 1.99 \times 10^{-3}T \pm [11.57 \times 10^{-4} + 0.07 \times 10^{-6}(T-1264)^2]^{1/2}$	-1.33 ± 0.03
$Cu_2Y_2O_5$	$+4.95 - 5.44 \times 10^{-3}T \pm [14.00 \times 10^{-4} + 0.18 \times 10^{-6}(T-1282)^2]^{1/2}$	-1.98 ± 0.04

TABLE IV

STANDARD ENTHALPY AND ENTROPY FOR THE REACTIONS $nCuO + R_2O_3 \rightarrow nCuO \cdot R_2O_3$ $(n = 1, 2)$

Compound	ΔH° (kcal/mole)	ΔS° (entropy units)	Minimum temperature for stability of compound (°K)
$CuLa_2O_4$	-1.6 ± 0.6	2.4 ± 0.5	—
$CuNd_2O_4$	$-1.7 + 0.7$	1.6 ± 0.6	—
$CuSm_2O_4$	-1.9 ± 0.3	0.7 ± 0.2	—
$CuEu_2O_4$	1.7 ± 0.3	2.8 ± 0.2	616
$CuGd_2O_4$	2.1 ± 0.4	2.8 ± 0.3	746
$Cu_2Tb_2O_5$	3.9 ± 0.4	3.9 ± 0.3	983
$Cu_2Dy_2O_5$	3.7 ± 0.4	4.1 ± 0.3	902
$Cu_2Er_2O_5$	4.8 ± 0.4	5.2 ± 0.2	940
$Cu_2Yb_2O_5$	3.0 ± 0.4	4.0 ± 0.3	752
$Cu_2In_2O_5$	1.2 ± 0.3	2.0 ± 0.2	602
$Cu_2Y_2O_5$	5.0 ± 0.6	5.4 ± 0.4	910

change in solid-state reactions is possible. Knowing the entropy is a measure of randomness in the system, we can say that the less ordered the crystalline structure of a compound is (the lower its symmetry), the larger (for a given formula composition) is its entropy. It is evident that this can be applied not only to the absolute size of the entropy of the compound, but also to its change in the reaction of crystalline materials—the less ordered the phases formed from the same initial materials, the larger is the ΔS of reaction. A comparison of ΔS for the formation reactions as distinct from the absolute size of the entropy evidently can apply in first approximation even to compounds of different composition, since the inclusion of individual masses (atoms or ions) in the entropy of the product is cancelled by subtraction of the entropies of the initial materials. In our investigation, we draw attention to the fact that the formation reactions of $CuLn_2O_4$ from the oxides are characterized by ΔS° of the order of 1.6–2.8 entropy units whereas for compounds of the type $Cu_2R_2O_5$ the magnitude is substantially larger: ~4–5 entropy units. In conformity with the above, such a difference can be explained by a lesser ordering of the compounds of type $Cu_2R_2O_5$. Actually, the crystal lattice of the compounds $Cu_2R_2O_5$ is of the orthorhombic type with primitive cell parameters $a' \simeq 25$ Å, $b' \simeq 10.8$ Å, $c' \simeq 3.5$ Å (9). Compounds of the type CuR_2O_4 crystallize in the tetragonal class with primitive cell parameters $a = b \simeq 3.9$ Å and $c \simeq 12$ Å (4). It is evident that the symmetry of the compounds of the $Cu_2R_2O_5$ type is lower than of the type CuR_2O_4, which finds reflection in the large magnitude of ΔS° for the formation reactions of compounds of the first type.

It is curious that for $CuSm_2O_4$ the magnitude $\Delta S^\circ = 0.7 \pm 0.2$ entropy units is minimal compared to the other phases of CuR_2O_4. This fact apparently means that Sm_2O_3 (as distinct from the other oxides Ln_2O_3) has a natural crystalline structure more similar to the ternary compounds; therefore, the transition from Sm_2O_3 to $CuSm_2O_4$ is accompanied by a much smaller restructuring of the crystalline lattice. As is seen in Table I, only Sm_2O_3 occurs in the monoclinic form. This observation, although it does not prove real proximity of the structures of Sm_2O_3 and $CuSm_2O_4$, nevertheless does attest to the fact that Sm_2O_3 is not completely analogous to the other oxides of the rare earth elements that form compounds of the type $CuLn_2O_4$ and occupies a special position among them.

Comparison of the values for $\Delta G^\circ_{1273°K}$ clearly indicates that for the compounds CuR_2O_4 (R = La, Nd, Sm, Eu, Gd), when compared with the lanthanide contraction, a steady decrease of stability is observed, whereas for compounds of the type $Cu_2R_2O_5$ (R = Tb, Dy, Er, Yb), decrease of the lanthanide ionic radius is accompanied by monotonic increase in stability (Table III, Fig. 3).

The difference we have observed in the change of thermodynamic stability of the compounds of the two types with the lanthanide contraction is explained in an examination of the crystalline structure. It is well known that the compounds $CuLn_2O_4$ belong to the structural type K_2NiF_4 and that the copper ions in them are octahedrally surrounded by oxygen ions. The octahedral crystal field, interacting with electrons of the Cu^{2+} ion, configuration $t_{2g}^6 e_g^3$, experiences a perturbation which leads to elongation or compression of the octahedron [$Cu^{2+}O_6^{2-}$] along one of its axes (Jahn–Teller effect). It is evident that the deformation of the octahedra is more pronounced when the electrostatic interaction of the ion-ligands with the electrons of the complexing ion is stronger. For given ligands, the interaction, and consequently the deformation, should increase with decrease in the distance ligand-complexing ion (in our case, Cu^{2+}–O^{2-}). A decrease in the size of the lanthanides in the series La–Gd brings about a decrease in the parameters of the primitive
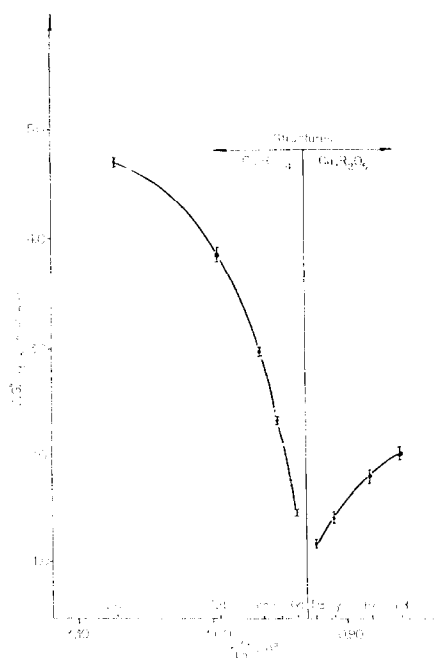

FIG. 3. Change of free energy of formation of the ternary compounds from oxides (at 1273°K) as a function of the ionic radius of the lanthanide.

cells of the compounds of type $CuLn_2O_4$ (4) and, as a result, a decrease in the distance Cu^{2+}–O^{2-}. This increases the degree of deformation of the Cu^{2-}–O_6^{2-} octahedra and finds thermodynamic expression in the fall of absolute thermal stability of the compounds $CuLn_2O_4$ and their stability with respect to the initial oxides.

The coordination polyhedron of the oxygen around the copper ion in compounds of the type $Cu_2R_2O_5$ can be viewed as an extremely deformed octahedron in which the interaction of the Cu^{2+} with the two remote oxygen ions is weakened. Therefore, a decrease in the primitive cell parameters for compounds of this type in the series Tb ~ Yb does not cause strong changes in the interaction energy of Cu^{2+}–O^{2-}. The increase of thermal stability observed in the series (also the increase of stability with respect to initial oxides) of the compounds $Cu_2R_2O_5$ can be explained by the reduction of the distances and the increase of the electrostatic attraction of the ions in the $R^{3+}O_6^{2-}$ octahedra.

Summarizing the discussion of regularity in the change of magnitude of $\Delta G°$ for the formation reactions of the compounds in the Cu^{2+}–R–O systems, one should note that the change of structural type is in logical correspondence with the fall in stability of the compounds observed when gadolinium is approached both from the right and from the left.

The study of thermodynamic stability of the compounds $Cu_2In_2O_5$ and $Cu_2Y_2O_5$ is of interest inasmuch as these elements are in the same group as the rare earth elements (yttrium is in the same IIIa subgroup) and their properties should be similar.

In fact, the stability of the compounds $Cu_2In_2O_5$ and $Cu_2Y_2O_5$ in the temperature range studied is very close to the stability of the analogous compounds of the rare earth elements. However, a complete analogy of properties, especially in the case of $Cu_2In_2O_5$, has not been observed (cf. Table III).

Ternary compounds from Ho_2O_3, Tm_2O_3, and Lu_2O_3 were not investigated, only because of lack of these oxides. Investigation of $CuPr_2O_4$ runs up against major difficulties. From our data, $\Delta G°_{1273°K}$ for the reaction

$$4CuLa_2O_4 \rightarrow 2Cu_2O + 4La_2O_3 + O_2 \quad (17)$$
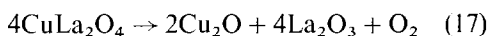
is equal to 23 kcal. Based on closeness of the thermodynamic properties of isostructural compounds of the rare earth oxides, it is natural to suggest that $\Delta G°_{1273°K}$ for the analogous reaction

$$4CuPr_2O_4 \rightarrow 2Cu_2O + 4Pr_2O_3 + O_2 \quad (18)$$
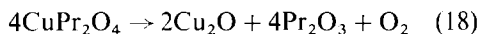
is close to 23 kcal. The magnitude of $\Delta G°_{1273°K}$ for the reaction evaluated in (15),

$$3Pr_2O_3 + O_2 \rightarrow Pr_6O_{11}, \quad (19)$$

consists of ~–25 kcal. Comparing $\Delta G°_{1273°K}$ of reactions (18) and (19), it can be determined that in equilibrium with $CuPr_2O_4$ during dissociation we will find not Pr_2O_3, but a more oxidized form of oxide. In view of the indefiniteness of the composition of the latter, an exact calculation of $\Delta G°$ (18) was impossible and a study of $CuPr_2O_4$ in a cell of type (II) made no sense.

Still, the thermodynamic picture of the interactions in the CuO–Ln_2O_3 systems allows us to propose that: (1) the formation reactions of the compounds $CuPr_2O_4$ and $CuPm*_2O_4$ from oxides are exothermal processes, in which $\Delta H° = -(1.5–2)$ kcal/mole and $\Delta S° \simeq 2$ entropy units; (2) the oxides of Ho, Tm, and Lu react with cupric oxide to form endothermic compounds of composition $Cu_2Ln_2O_5$ which stabilize at increased temperatures because of an appreciable entropy contribution. In the range 950–1100°C, the values $\Delta H° = 3$–5 kcal/mole and $\Delta S° = 4$–5 entropy units are probable.

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