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Abstract

Full Text

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CALORIMETRIC DETERMINATION OF THE HEATS OF FORMATION OF FERRITES

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There are comparatively few works in the literature whose purpose has been to determine the thermodynamic functions of ferrites. For practical purposes in the synthesis of ferrites it is necessary to determine the free energies and heats of formation of ferrites. The heats of formation of copper, zinc, and calcium ferrites were determined from the difference between the heats of interaction of mixtures of oxides and ferrites at 413° K with a mixture of sulfuric and phosphoric acids, as described earlier in determining the heat of formation of magnesium ferrite.

Copper and zinc ferrites were prepared by thermal decomposition of isomorphous chenites of composition: $^{1}/_{3}MSO_4 \cdot {}^{2}/_{3}FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, where M = Cu or Zn. Calcium ferrite was obtained by the ceramic method from $CaCO_3$ and Fe_2O_3, by calcination at 1100°. In all series of experiments, equal weighed portions of ferrites and of the corresponding mixtures of ferrite-forming oxides were taken, so that the final solutions would have the same dilution. Table 1 summarizes the results of experiments on determining the enthalpy of dissolution of mixtures of oxides and ferrites in acid at 413° K.

Table 1

	$CuO + Fe_2O_3$, $9.005 \cdot 10^{-4}$ mole	$CuFe_2O_4$, $9.005 \cdot 10^{-4}$ mole	$ZnO + Fe_2O_3$, $8.1 \cdot 10^{-4}$ mole	$ZnFe_2O_4$, $8.1 \cdot 10^{-4}$ mole	$CaO + Fe_2O_3$, $5.65 \cdot 10^{-4}$ mole	$CaFe_2O_4$, $5.65 \cdot 10^{-4}$ mole
Enthalpy of dissolution $-\Delta H$, kcal/mole	61.5 ± 0.9	59.9 ± 0.4	62.8 ± 0.3	55.8 ± 0.5	87.7 ± 0.8	68.6 ± 0.9

	$CuO + Fe_2O_3$, $9.005 \cdot 10^{-4}$ mole	$CuFe_2O_4$, $9.005 \cdot 10^{-4}$ mole	$ZnO + Fe_2O_3$, $8.1 \cdot 10^{-4}$ mole	$ZnFe_2O_4$, $8.1 \cdot 10^{-4}$ mole	$CaO + Fe_2O_3$, $5.65 \cdot 10^{-4}$ mole	$CaFe_2O_4$, $5.65 \cdot 10^{-4}$ mole
Enthalpy of formation of ferrite from oxides $-\Delta H$, kcal/mole		1.6		7.0		19.1

Taking into account the previously determined heat of formation of $MgFe_2O_4$ from MgO and Fe_2O_3–ΔH_{413} = 9.2 kcal/mole–it may be concluded that the heat of formation of ferrites from oxides decreases along the series Ca—Mg—Zn—Cu, which coincides with the electromotive series of the metals. The very small exothermic effect in the formation of $CuFe_2O_4$ from oxides agrees well with the thermal instability of $CuFe_2O_4$ above 1100°, when dissociation is observed:

$$4CuFe_2O_4 = 2Cu_2O + 4Fe_2O_3 + O_2.$$

To calculate the heats of formation of $CuFe_2O_4$ and $ZnFe_2O_4$ from the elements at 413° K, the equations for C_p and the values of ΔH_{298} for the oxides ([1,2]) were used. From these data, using the values determined in the present

the heats of formation from the oxides were calculated as $\Delta H_{413}CuFe_2O_4$ = −233.7 kcal/mole and $\Delta H_{413}ZnFe_2O_4$ = −284.9 kcal/mole. For magnesium and calcium ferrites it is possible to recalculate the thermodynamic data to 298° K, since their heat capacities and entropies were determined by King and Bonnickson ([3,4]). We give the values of the heats of formation and free energies of formation of magnesium and calcium ferrites.

	$-\Delta H_{298}$, kcal/mole	$-\Delta Z_{298}$, kcal/mole
$MgFe_2O_4$	349.9	322.9
$CaFe_2O_4$	365.9	340.2

Two papers describing the determination of the heat of formation of calcium ferrite have been reported in the literature. Marshall ([5]) estimated the heat of formation of $CaFe_2O_4$ as ΔH = −398 kcal/mole. Later, Honus ([6]) found

$\Delta H_{298} = -364.5$ kcal/mole. Honus' s data agree with our determination ($\Delta H_{298} = -365.9$ kcal/mole).

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Note: Figure translations are in progress. See original paper for figures.