about 20% and an effective charge on the metal of only +1.6. Thus even with fluoride ligands it is to be expected that low-spin configurations, with small values of β, will be found if the oxidation state of the metal is high enough. For the 4+ oxidation state, the decreasing stability of the higher valencies toward the end of the first transition series is consistent with the β values found for Mn^{4+} and Ni^{4+}, and further confirmation is provided by our data for CoF_6^{2-} (which also has a low-spin ground state[9]). From our results for Dq and β, Jørgensen's g and k parameters can be deduced: the values are 22.3 and 0.71, respectively, compared with 23.0 and 0.50 for Mn^{4+}. Our data also substantially confirm Jørgensen's predictions[12] of the positions of the $^1T_{1g}$ and $^1T_{2g}$ bands, which were based on the general behavior of Dq and β as functions of oxidation state: his figures of 20 and 28 kK, respectively, slightly overestimate Dq but are in good agreement with the experimental β value.

On the basis of their intensities, the strong bands at 30.8 and 38.9 kK may be assigned to allowed charge-transfer transitions. It seems most likely that these are $\pi \rightarrow e_g$ excitations, corresponding to $t_{1u} \rightarrow e_g$ and $t_{2u} \rightarrow e_g$ in a molecular orbital interpretation, and the predicted absence of other spin-allowed d–d transitions below about 40 kK supports this view.

In view of the uncertainties which are usually experienced in attaching quantitative significance to intensities measured by diffuse reflectance, we have attempted to obtain approximate extinction coefficients for the d–d bands from our F_R values. In order to derive ϵ from the Kubelka–Munk function it is necessary to know s, the scattering coefficient for the given substance, at any required wavelength. Although s does not appear to vary widely from one substance to another, its dependence on wavelength is very sensitive to particle size, especially above about 25 kK. The particle size of our samples is however sufficiently small (20 ± 5 μ) to eliminate any regular reflectance component below 25 kK, so that s is essentially constant in that region, and the observed spectrum is due only to diffuse reflectance. We were therefore able to use the data of Kortum[18] for $KMnO_4$ ($s = 1.73$) to establish an approximate value for s, up to around 25 kK, and thence to derive the values of ϵ and the corresponding oscillator strengths shown in Table I.

It is seen that the intensities of the $^1T_{1g}$ and $^1T_{2g}$ bands are of reasonable magnitude for Laporte-forbidden transitions. Similarly the $^3T_{1g}$ band is about as weak as would be expected for a spin-forbidden transition, and an estimate of its strength relative to the $^1T_{1g}$ band can be made using the spin–orbit matrix elements of Griffith.[13] From the matrix element of $^1T_1$ with the T_1 component of $^3T_1$ $[=(1/2\sqrt{2})\xi]$, we estimate that the intensity stealing of $^3T_{1g}$ from the $^1T_{1g}$ band at about 19 kK should give an oscillator strength for the former of about $^1/_{560}$ of the spin-allowed transition. The experimental value is $^1/_{315}$, but the agreement can be improved if the origin of the $^1T_{1g}$ band lies below 18.4 kK. Similarly the matrix element of $^3T_2$ with the T_1 component of $^1T_1$ is $(^1/_4\sqrt{6})\xi$ which predicts the $^3T_{2g}:{}^1T_{1g}$ intensity ratio to be about $^1/_{30}$. The experimental value is $^1/_{100}$, but here the calculated value is extremely sensitive to the $^3T_{2g} - {}^1T_{1g}$ energy difference.

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Enthalpies of Formation of Some Tungstates, MWO_4

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The enthalpies of formation of the isostructural tungstates MWO_4 (M = Mg, Co, Ni, Cu, Zn, Cd) were determined by solution calorimetry in a $3Na_2O \cdot 4MoO_3$ melt at 970°K. Regularities in the heats of formation are compared with those observed for spinels, sulfates, and carbonates of the same cations.

Introduction

In previous communications,[1,2] we have reported the enthalpies of formation of an extensive series of spinels. The spinel-forming reaction is but one example of the formation of a double oxide from the component acidic and basic oxides.

When one of the constituents is the oxide of a divalent cation, AO, this general reaction may be written

$$a\mathrm{AO} + b\mathrm{BO}_n = \mathrm{A}_a\mathrm{B}_b\mathrm{O}_{(a+bn)} \qquad (1)$$

If the products are isostructural for a series of divalent cations and a given BO_n, regularities in the thermodynamics of reaction 1 may be related to specific properties of the divalent ions, *e.g.*, the ionic radius or the preference of the cation for a particular coordination.

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[1] A. Navrotsky and O. J. Kleppa, *Inorg. Chem.*, **5**, 192 (1966).

[2] A. Navrotsky and O. J. Kleppa, *J. Inorg. Nucl. Chem.*, **30**, 479 (1968).

Examples of reactions of type 1, with A a metal of the first transition series or Mg, Zn, or Cd, include the formation of silicates, spinels, tungstates, sulfates, carbonates, and phosphates. In order to ascertain whether the regularities which we observed in the enthalpies of formation of spinels[2] extend also to other double oxides, we have measured the enthalpies of formation of the tungstates of Mg, Co, Ni, Cu, Zn, and Cd, all of which have the same monoclinic crystal structure. We shall also compare our results with available thermodynamic data for sulfates, carbonates, and silicates.

Experimental Section

The preparation of the calorimetric solvent, $3Na_2O{\cdot}4MoO_3$, and the calorimetric procedures were the same as in our earlier work.[2] All solution experiments were performed at 970 ±2°K.

The oxides AO were the same as those used previously.[2] Baker Analyzed reagent WO_3 was dried for 24 hr at 700° before it was used in calorimetry or sample preparation. The tungstates were prepared by firing stoichiometric mixtures of the two powdered components at 900–1100°. Several cycles of grinding and heating were carried out on each tungstate preparation to ensure complete reaction and homogeneity of product. Powder X-ray diffraction patterns of the products showed the tungstate to be the only detectable phase.

We found that $MgWO_4$ and $NiWO_4$ prepared by the above method dissolved rather slowly in the calorimetric solvent. Samples of these two compounds were also prepared by precipitation from aqueous solutions of sodium tungstate. The precipitates were washed with water, dried at 140°, and ignited at 750–850°. Complete tungstate formation was attained by this treatment. Probably because of their smaller particle size, these samples dissolved more rapidly in the molten molybdate solvent than samples prepared by the dry method. The heats of solution of the two types of samples were the same within experimental error.

Results and Discussion

Table I lists the measured heats of solution of the component oxides and of the tungstates, as well as the calculated enthalpies of the reactions

$$AO + WO_3 = AWO_4 \qquad (2)$$

The uncertainties given for the reported heats of formation are the square roots of the sums of the squares of the standard deviations of the three measured heats of solution used in each computation.

To our knowledge, the only enthalpies of formation of transition metal tungstates reported in the literature are those of Proshina and Rezukhina,[3] obtained by bomb calorimetry. They reported, for $NiWO_4$, $\Delta H_{298} = -12.9$ kcal/mol, which is somewhat more exothermic than our own value, $\Delta H_{970} = -10.6 \pm 0.3$ kcal/mol. Their enthalpy of formation of $MnWO_4$, $\Delta H_{298} = -19.2$ kcal/mol, is comparable to our values for $MgWO_4$ and $CdWO_4$, −17.7 and −18.9 kcal/mol, respectively.

TABLE I

CALORIMETRIC DATA FOR TUNGSTATE FORMATION AT 970°K

AO	$\Delta H_{soln}(AO)$,[a] kcal/mol	$\Delta H_{soln}(AWO_4)$, kcal/mol	$\Delta H_f(AO + WO_3 = AWO_4)$,[c] kcal/mol
MgO	−8.86 ± 0.07 (5)[b]	+16.07 ± 0.25 (6)	−17.69 ± 0.32
CoO	−4.90 ± 0.09 (4)	+16.74 ± 0.11 (4)	−14.40 ± 0.25
NiO	−0.77 ± 0.07 (6)	+17.04 ± 0.22 (5)	−10.57 ± 0.28
CuO	+2.65 ± 0.05 (3)	+16.52 ± 0.20 (6)	−6.63 ± 0.28
ZnO	−3.20 ± 0.06 (6)	+14.11 ± 0.17 (5)	−10.07 ± 0.26
CdO	−9.59 ± 0.07 (4)	+16.58 ± 0.05 (4)	−18.93 ± 0.20

[a] Molar enthalpy of solution in $3Na_2O{\cdot}4MoO_3$, *i.e*, observed heat effect per number of moles of solute. [b] Quoted uncertainties are standard deviations; numbers in parentheses indicate the number of experiments performed. [c] $\Delta H_{soln}(WO_3) = +7.24 \pm 0.18$ (6) kcal/mol.

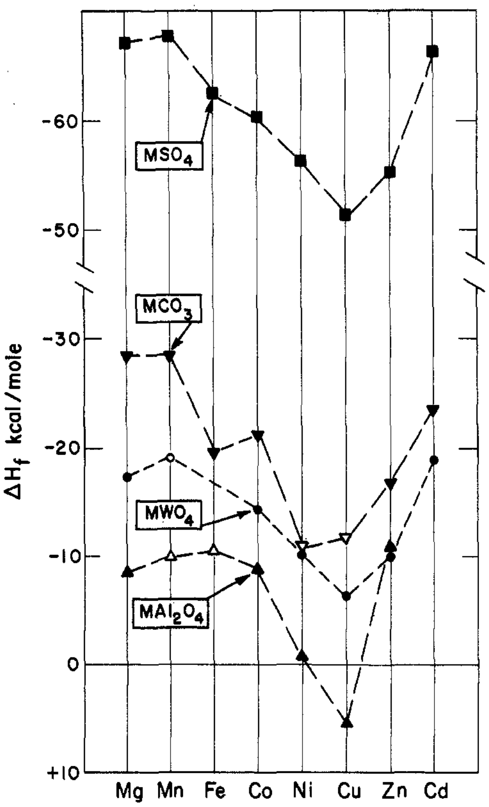

Figure 1.—Enthalpies of formation of interoxidic compounds from binary oxides: aluminates: ref 2 (970°K); tungstates: this work (970°K) and ref 3 (298°K); carbonates: K. K. Kelley and C. T. Anderson, Bureau of Mines Bulletin 601, U. S. Government Printing Office, Washington, D. C., 1962; sulfates: L. H. Adami and E. G. King, Bureau of Mines, Report of Investigation, No. 6617, Mines Bureau, Pittsburgh, Pa., 1965 (298°K); G. N. Lewiz and M. Randall, "Thermodynamics," K. S. Pitzer and L. Brewer, Ed., 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1961. Filled symbols, probably reliable data; open symbols, somewhat uncertain data.

Figure 1 shows the enthalpies of a series of reactions of type 1, with AO = MgO, MnO, FeO, CoO, NiO, ZnO, or CdO, and bBO_n = $2AlO_{1.5}$, WO_3, CO_2, or SO_3. The results for aluminate spinels are generally paralleled by those for ferrites and gallates.[2]

The spinels may be considered an isostructural series if one neglects differences in cation distribution. In an earlier communication,[2] we argued that, once the most stable cation distribution for a particular spinel is assumed, the nature of this distribution (normal, inverse, or intermediate) does not play a major role in determining the enthalpies of formation from the

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(3) Z. V. Proshina and T. N. Rezukhina, *Russ. J. Inorg. Chem.*, **5**, 488 (1960).

oxides. The isostructural tungstates studied in the present work all crystallize in a structure which contains a distorted hexagonal close-packed array of oxide ions, with tungsten in octahedral holes and with the divalent metal ions in two sets of nonequivalent distorted octahedral sites.[4] The carbonates crystallize in the calcite structure, which also contains octahedrally coordinated divalent ions. $NiSO_4$, $MnSO_4$, $FeSO_4$, and the low-temperature forms of $MgSO_4$ and $CoSO_4$ possess the $CuCrO_4$ structure, while $CuSO_4$, $ZnSO_4$, and the high-temperature forms of $MgSO_4$ and $CoSO_4$ possess the $CuSO_4$ structure. These two orthorhombic structures are closely related, with distorted octahedral coordination for the divalent ions.[4] The transition

$$\beta\text{-}CoSO_4\ (CuCrO_4) = \alpha\text{-}CoSO_4\ (CuSO_4) \qquad (3)$$

occurs at 673 ± 10° with a reported enthalpy of transformation of 0.60 kcal/mol.[5] In view of the similarities of the two structures and the small heat of transformation, we shall treat the sulfates as an effectively isostructural series. Thus we shall consider the variations in enthalpy of formation to be related primarily to the nature of the divalent cations rather than to the small differences in structure.

Although the enthalpies of formation from the oxides become markedly more exothermic with increasing acidity of the oxide BO_n, a number of similarities remain evident throughout. Usually the Mg and Mn members of a given series show the most negative enthalpies of formation. Although the Co and Fe spinels have enthalpies of formation comparable to that of Mg, the Co and Fe members show less negative values than the Mg compound in the series involving a more acid oxide BO_n.

The enthalpy of formation of zinc aluminate spinel is comparable to that of cobalt aluminate. In the spinel structure, zinc remains tetrahedrally coordinated as in ZnO, whereas cobalt may assume either octahedral or tetrahedral coordination. On the other hand, in the tungstate, carbonate, and sulfate, zinc is "forced" to assume octahedral coordination. In each of these, the enthalpy of formation of the zinc compound is some 4–5 kcal/mol less negative than that of the corresponding cobalt compound. In a previous discussion of empirical site preference energies of cations in the spinel structure,[6] the difference between the site preference energies of Zn^{2+} and Co^{2+} in spinels was shown to be about 4 kcal/mol. On the basis of these data, it seems reasonable to expect a comparable destabilization whenever 1 mol of zinc ions is forced to assume an octahedral coordination in any oxide structure. Further study of the thermodynamics of oxidic solid solutions which contain zinc would be interesting in this context, particularly of solid solutions in which the pure zinc end member is unstable. For example, note that zinc orthosilicate crystallizes in the phenacite structure rather than in the olivine structure characteristic of the other transition metal orthosilicates. Since the free energy of formation of Co_2SiO_4 olivine is only -3.2 kcal/mol at 1273°K,[7] a 4–5-kcal destabilization per mole of octahedrally coordinated zinc would result in a positive free energy of formation for the hypothetical olivine form of Zn_2SiO_4.

We have commented elsewhere upon the low enthalpies of formation of nickel and copper spinels.[2] In the tungstates, spinels, and sulfates, the enthalpies of formation of the copper compound are also some 4–5 kcal/mol less negative than those of the corresponding nickel compound. Pure anhydrous $NiCO_3$ and $CuCO_3$ may not exist, and the thermodynamic data given in Figure 1 were obtained for compounds which probably contain some water.[8] The lower heats of formation of copper compounds may be attributed to the forced change in coordination of Cu^{2+} ions from almost square planar in the tenorite (CuO) structure to octahedral or distorted octahedral in the interoxidic compounds.[2] The nonexistence of silicates of copper[9] is consistent with this destabilizing factor. The less negative enthalpies of formation of Cu and Ni compounds compared to those of Co seem to be a general feature of the data. It may be related to the loss of some ligand field stabilization energy in the interoxidic compounds because of the competition of more acidic cations (W^{6+}, C^{4+}, etc.) for the oxide ion electrons and to the greater separation between transition metal ions in the complex structures.

As mentioned previously,[2] the stability of cadmium compounds is probably affected by a size factor. In the tungstate, sulfate, and carbonate structures, the octahedral interstices are large enough to accommodate the cadmium ions easily. These compounds show heats of formation comparable to those of the magnesium and manganese counterparts.

In conclusion, it may be said that the observed regularities in the enthalpies of formation of the interoxidic compounds studied here demonstrate that the nature of the divalent oxide, AO, clearly plays an important and quite consistent role in the energetics, even when the second component, BO_n, is allowed to vary. We suggest that further thermodynamic studies, particularly of silicates, titanates, and selected solid solutions, should be useful in clarifying how simple crystal–chemical reasoning may contribute to our understanding of the thermodynamics of complex oxide formation.

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