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Abstract

The solubility behavior of transition metal oxides in high temperature water is interpreted by recognizing three types of chemical reaction equilibria: metal oxide hydration/dehydration, metal oxide dissolution and metal ion hydroxocomplex formation. The equilibria are quantified using thermodynamic concepts and the thermochemical properties of the metal oxides/ions representative of the most common constituents of construction metal alloys, i.e., elements having atomic numbers between Z=22 (Ti) and Z=30 (Zn), are summarized on the basis of metal oxide solubility studies conducted in our laboratory. Particular attention is devoted to the uncharged metal ion hydroxocomplex, $M^{z}(OH)_{z}$ (aq), since its thermochemical properties define minimum solubilities of the metal oxide at a given temperature. Experimentally-extracted values of standard partial molal entropy (S^{o}) for the transition metal ion neutral hydroxocomplex are shown to be influenced by ligand field stabilization energies and complex symmetry.

KEY WORDS: Aqueous solutions, transition metal oxides, metal ion hydrolysis, hydroxocomplexes, hydrothermal solutions, corrosion, rutile, chromium(III) oxide hydroxide, magnetite, hematite, cobalt(II) oxide, bunsenite, copper(II) oxide, zincite

1. Introduction

Alloys of the transition metals, i.e., elements having atomic numbers between Z=22 (titanium) and Z=30 (zinc), are employed in various regions of thermal power plants. Athough these materials have been selected for their high strength and inertness in the aqueous media used for heat transport, the successful coolant chemist must deal with the consequences of chemical interactions, such as metal oxide formation, solubilization and crystallization, which may result in: (a) fouling or corrosion of heat transfer surfaces, or (b) the hydrothermal transport and activation of dissolved impurities in water-cooled nuclear reactors.

The unsatisfied need for fundamental knowledge on metal oxide solubility behavior is evident by the many and continuing series of conferences on this topic: 13th International Conference on the Properties of Water and Steam (1999), 5th International Symposium on Hydrothermal Reactions (1997), Water Chemistry of Nuclear Reactor Systems 7, BNES (1996), 9th International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors (1999), etc. Presently our attention is focused on the thermochemical database upon which metal oxide solubilities may be predicted in aqueous solutions. At the 2nd International Symposium on Chemistry in High Temperature Aqueous Solutions (1992), we summarized the results of our work in this area and provided experimentally-based thermochemical properties for the transition metal cations and their hydrolysis products [1]. These properties were then applied to describe metal oxide solubility behavior in near-neutral, deoxygenated water at sub- and super-critical temperatures. Subsequently, we have provided the results of our solubility studies, conducted over the temperature range 25 to 285°C, for ZnO [2], TiO_2 [3], Fe_3O_4 [4], Cr_2O_3 [5], and CoO [6], to complement our previous results on CuO [7] and NiO [8]. Although the possibility of unknown experimental errors exists, we have either shown consistency with other solubility data where possible, or have resolved experimental differences when they arose.

In this paper, the conclusions of these solubility studies with regard to metal oxide phase stability are highlighted. It is also demonstrated that the thermodynamic properties of the resulting metal cation hydrolysis products, which are intimately related to their structural features, are quantitatively affected by the existence of an incomplete 3*d* electron shell: octahedral vs. tetrahedral coordination and ligand field stabilization. It is expected that the availability of reliable, experimentally-based thermochemical properties for hydroxocomplexes of the transition metal cations (such as standard partial molar entropies) will lead to improved metal oxide solubility predictions, especially for the tri- and tetra-valent transition metal oxides in high temperature, alkaline solutions.

2. Summary of Results

Table I provides a summary of thermodynamic properties for the various solid and aqueous species observed in the above metal oxide-water binaries. Note that the formation reaction for ions in solution is defined in terms of an oxidation-reduction reaction involving hydrogen and its aqueous ion:

$$M(s) + zH^{+}(aq) = M^{z+}(aq) + (z/2)\,H_2(g)$$

The normal thermodynamic convention is to take $\Delta G_f^{o} = \Delta H_f^{o} = S^{o} = C_p^{o} = 0$ for $H^{+}(aq)$. However, in the present paper we prefer to reference thermodynamic properties for aqueous ions to an 'absolute' scale in which $H^{+}(aq)$ has $S^{o} = -22.2$ J/mol-K [32] and $C_p^{o} = -71$ J/mol-K [23], while ΔG_f^{o} and ΔH_f^{o} remain zero. This change is made to provide a closer link between entropy and structure. Conventional (i.e., NBS/NIST-tabulated) properties are readily converted to absolute properties by adding -22.2z and -71z J/mol-K to S^{o} and C_p^{o}, respectively.

A. Titanium (IV) Oxide-Water System

The tetravalent oxide of titanium is stable in deoxygenated aqueous solutions. Although three crystal variations, rutile, anatase and brookite, are known, the latter two transform exothermally and irreversibly to rutile over a wide range of temperatures. Either of two formulas is generally used to designate hydrous titanium(IV) oxide: $Ti(OH)_4$ or $TiO_2 \cdot 2H_2O$, the exact composition and crystal structure remain to be determined. Hydrous Ti(IV) oxide, however, does not play a role in the solubility behavior of hydrothermally-grown corrosion films formed on titanium metal. Solubility behavior is controlled solely by equilibria with rutile.

Minimum Ti(IV) ion solubilities, due to the formation of the $Ti(OH)_4(aq)$ species, are around one nanomolal and are nearly insensitive to temperature changes, see Fig. 1 (a).

B. Chromium(III) Oxide-Water System

The trivalent oxide of chromium is the stable oxide form in deoxygenated waters, although accidental air incursions may cause oxidation to Cr(VI). The stability of chromium(III) oxide in aqueous solutions is such that only hydrous forms exist at sub-critical temperatures. Below about 50°C, crystalline chromium(III) hydroxide hydrate, $Cr(OH)_3 \cdot 3H_2O$, is stable. Above this temperature, transformation to chromium(III) oxide hydroxide, CrOOH, occurs. Three polymorphs of CrOOH have been synthesized hydrothermally: α-, β- and γ-. The α- and β- forms, whose structures are characterized by shorter hydrogen bonds, are the stable high temperature forms. These compounds occur in nature as the minerals grimaldiite and guyanaite, respectively.

Although γ-CrOOH has no known mineral counterpart, it is believed to be isostructural with lepidocrocite (γ-FeOOH) and boehmite (γ-AlOOH). γ-CrOOH is believed to be the saturating solid phase of chromium(III) oxide in saturated aqueous solutions at temperatures between 50 and 295°C. A transformation from the γ- to the α-CrOOH form is believed to occur around 295°C, since hydrothermal decomposition of aqueous chromic acid is known to yield grimaldiite at solution temperatures as low as 300°C. Only at supercritical conditions (510°C, 670 bars) does dehydration to eskolaite (Cr_2O_3) occur.

Minimum Cr(III) ion solubilities, due to the formation of the $Cr(OH)_3(aq)$ species, are around 0.1 nanomolal and decrease slightly with temperature, see Fig. 1(b).

C. Iron(II, III) Oxide-Water System

Complexities exist in the iron oxide-water system due to the stability of hydrous oxide phases and the relative ease with which the Fe(II)-Fe(III) redox reaction occurs. For example, at least two iron(III) oxide hydroxide compounds have been identified in the lower temperature (condensate/feed) regions of steel-tubed, fossil-fired power plants, i.e., α-FeOOH (goethite) and γ-FeOOH (lepidocrocite). Lepidocrocite appears to be associated with lower oxygen levels. In non-deaerated waters at elevated temperatures, goethite dehydrates to α-Fe_2O_3 (hematite), the transformation temperature in water at its saturation vapor pressure being around 70°C.

Hydrogen is added to reactor coolant in the world's pressurized water reactors to prevent radiolytic phenomena from creating a net oxidizing environment. As a result, the stable iron oxide form is Fe_3O_4 (magnetite), which reflects a partial reduction of Fe(III) to Fe(II), i.e., $Fe(II)Fe(III)_2O_4$. Our magnetite solubility study has also shown that the use of hydrogen causes magnetite to transform to hydrous iron(II) oxide at lower temperatures. For a one atmosphere blanket of hydrogen cover gas (at 25°C), the transformation occurs at 116°C.

In addition to our magnetite solubility study, two other fairly comprehensive magnetite solubility studies have been conducted in hydrogenated waters: Sweeton and Baes [33] and Tremaine and Leblanc [34]; the former work being the most widely-quoted geochemical reference for magnetite solubility behavior. Unfortunately, both studies did not allow for the magnetite surface hydration reaction, which was shown in our study to occur at 116°C when one atmosphere of hydrogen was used: Tremaine and Leblanc reported finding a ferrous hydroxide surface layer, but could not establish when it formed, while the bulk characterizations employed by Sweeton and Baes were insensitive to surface transformations. Therefore, it is probable that the 50 and 100°C data (28 points) of Sweeton and Baes and the 100°C data (43 points) of Tremaine and Leblanc do not represent true magnetite solubilities.

On the other hand, it is encouraging that all three magnetite solubility studies provide nearly the same minimum solubilities. Our measurements, as shown in Fig. 2(a), indicate minimum iron concentrations around 0.03 micromolal which are relatively insensitive to temperature changes. The minimum levels of Sweeton and Baes (0.1 micromolal) are slightly higher, while those of Tremaine and Leblanc (0.01 micromolal) are slightly lower. The positive partial molar entropy values extracted for $Fe(OH)_2(aq)$ from these two investigations (40.3 and 36.5 J/mol-K, respectively) are believed to be biased by inclusion of non-representative, lower temperature data. Therefore, our lower S^0 value (-29.2 J/mol-K) is preferred.

As solution alkalinity increases, it is generally accepted that anionic hydroxocomplexes begin to control solubility behavior. Our results and those of Tremaine and Leblanc conclusively demonstrate that $Fe(OH)_4^-$ is formed in preference to $Fe(OH)_3^-$ at lower solution alkalinities, despite the presence of hydrogen. Therefore, the thermodynamic analysis of Sweeton and Baes, which assumes that $Fe(OH)_3^-$ is the only anionic hydrolysis product, is in error, so that the thermochemical properties that were extracted for $Fe(OH)_3^-$ should be disregarded.

The inferred minimum solubility of hematite, per Table I, is 0.05 ppb at 300°C. Such a low value is consistent with power plant operational experience with once-through boilers. These units operate with oxygenated treatment (OT), which is essentially pure water having small additions of oxygen, in order to minimize iron transport (solubility).

An independent source of information is available as a check on the extracted thermochemical properties of the anionic hydroxocomplex of the iron(III) ion. In a poster at the 5th ISHR, Khodakovsky et al. [35] presented preliminary results of a hematite solubility study conducted in sodium hydroxide solutions (0.02 - 0.1 m) under an oxygen cover gas. Equilibrium constants were reported for the hematite dissolution reaction

$$1/2\,Fe_2O_3(s,\alpha-) + 5/2\,H_2O = Fe(OH)_4^-(aq) + H^+(aq)$$

at five temperatures between 110 and 300°C. We extracted thermochemical properties for $Fe(OH)_4^-$ from these data after accounting for their expected non-linearity by fitting a constrained three-parameter model (i.e., $\Delta G = A - BT - CT\ln T$, where C was fixed at its expected isocoulombic value -223.8 J/mol-K): $\Delta G_f^\circ(298) = -841.68$ kJ/mol, $S^\circ(298) = 163.8$ J/mol-K and $C_p^\circ(298) = 87.4$ J/mol-K. The standard Gibbs energy of formation agrees quite well with the Table I value, while the higher value for standard partial molar entropy indicates that $Fe(OH)_4^-$ is an even more important hydrolysis product at elevated temperatures than we found in our constrained analysis of magnetite solubility behavior.

D. Cobalt(II) Oxide-Water System

The divalent oxide of cobalt is stable in high temperature aqueous solutions. Hydrous cobalt(II) oxide is expected to be thermodynamically stable at lower temperatures. Two polymorphs are known: α-$Co(OH)_2$ (blue) and β-$Co(OH)_2$ (pink), although only the pink form is expected to remain stable in aged solutions at room temperature. Based on thermochemical properties of β-$Co(OH)_2$ extracted from our cobalt(II) oxide solubility study, and those of CoO listed in Table I, hydrous cobalt(II) oxide is expected to dehydrate to CoO in saturated aqueous solutions at temperatures above 80°C.

Our study also demonstrated that hydrogen affects cobalt(II) ion solubility. For feed solutions saturated with a one-atmosphere blanket of hydrogen cover gas, the solubility equilibria were usually controlled by an oxidative dissolution reaction of *metallic* cobalt:

$$Co(s) + 2H^+(aq) = Co^{2+}(aq) + H_2(g)$$

Based on Table I thermodynamic properties, cobalt(II) ion solubility behavior will be controlled by equilibria with CoO only at solution temperatures >250°C when this level of dissolved hydrogen is present.

Formation of the anionic hydroxocomplex $Co(OH)_3^-$ occurred with relative difficulty, since our study found no evidence for $Co(OH)_3^-$ formation at sodium hydroxide concentrations as high as two millimolal (pH at 25°C = 11.3). Based on Table I, cobalt(II) ion hydrolysis to $Co(OH)_3^-$ is not expected until pH (at 25°C) = 11.7.

E. Nickel(II) Oxide-Water System

The divalent oxide of nickel (bunsenite) is stable in typical power plant waters. It is isostructural with CoO and is known to hydrate to β-$Ni(OH)_2$ (theophrastite) which is isostructural with β-$Co(OH)_2$. The transformation threshold for the hydrous nickel(II) oxide dehydration reaction, consistent with our solubility results (and Table I), is 195°C in aqueous solutions maintained at their saturation vapor pressure.

Minimum solubilities of bunsenite are found to be around 0.01 micromolal at 300°C, see Fig. 2(c). Our results are slightly higher than the minimum 0.003 micromolal solubility reported by Tremaine and Leblanc [36], a widely-quoted geochemical reference on bunsenite solubility behavior. Given the degree of data scatter present in both data sets at these low solubility levels, the difference may not be significant.

More importantly, however, it is noted that the solubility measurements of Tremaine and Leblanc at 100 and 150°C may be invalid, since we observed NiO to be unstable relative to β-$Ni(OH)_2$ in this temperature region. Extraction of thermochemical properties for $Ni(OH)_3^-$ using our NiO solubility database and the portion of Tremaine and Leblanc's database where $Ni(OH)_3^-$ is expected to be present (NaOH > 1 millimolal and T ≥ 200°C), yields essentially the same results as provided in Table I. Therefore, we conclude that the thermochemical properties of $Ni(OH)_3^-$ claimed by Tremaine and Leblanc are in error, since they indicate that hydrolysis of $Ni(OH)_2(aq)$ to $Ni(OH)_3^-$ occurs at a room temperature pH of 9.5, rather than >11 as suggested by our results in Table I. Thus our results indicate that the standard Gibbs energy change involved in the creation of the $M(OH)_3^-$ anionic hydroxocomplex from the neutral hydroxocomplex via

$$M(OH)_2(aq) + H_2O = M(OH)_3^-(aq) + H^+(aq)$$

is nearly the same for M = Fe(II), Co(II) and Ni(II), i.e., $\Delta G°(298) = 68.6$ kJ/mol.

Nickel(II) ion solubility behavior is also affected by dissolved hydrogen. In solutions saturated with one atmosphere of hydrogen (at 25°C), solubility equilibria will be controlled by oxidative dissolution of metallic nickel, rather than by theophrastite or bunsenite. Only at solution temperatures >306°C will nickel(II) ion solubility be controlled by equilibria with bunsenite when this level of hydrogen is present.

F. Copper(II) Oxide-Water System

Being the most 'noble' of the transition metals, redox behavior of the trio Cu(0)-Cu(I)-Cu(II) is expected to contribute significantly to the hydrothermally-induced transport of copper in the water-steam circuit of power plants. Our solubility study, however, was devoted only to copper(II) oxide (tenorite). Hydrous copper(II) oxide (spertiniite) is known, although it is unstable in room temperature aqueous solutions and dehydrates to CuO.

The solubility behavior of tenorite in neutral pH and alkaline solutions differs relative to that of the other divalent transition metal oxides in that the slopes (vs. temperature) are relatively insensitive to changes in alkalinity, see Fig. 3(a). Steep increases in copper solubility with temperature are observed, the entire curve shifting (to the left or right) as solution alkalinity increases. Our study included solution pH values >11, which was adequate to determine the thermochemical properties for the anionic hydroxocomplexes $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$. The Table I entry for $Cu(OH)^+$ was obtained from a regression analysis of tenorite solubility data in pure, sub- and super-critical water reported by Hearn et al. [28].

Thermochemical properties for the neutral hydroxocomplex $Cu(OH)_2(aq)$ are included in Table I based on unpublished tenorite solubility measurements taken in our laboratory. They are intended as estimates until the results from a tenorite solubility study become formally available over the pH region 8 - 10.

G. Zinc(II) Oxide-Water System

Only the divalent oxide form of zinc exists. Although zinc is not a transition metal, its behavior is included here as a 'reference case' to support the seemingly anomalous results exhibited by CuO. Zinc(II) oxide (zincite) is stable in most power plant waters. A hydrous zinc(II) oxide, ϵ-$Zn(OH)_2$ (wuelfingite), is known, but is thermodynamically unstable in water at room temperature and dehydrates to ZnO. Similarities between the ZnO and CuO solubility curves, particularly in magnitude and shape, are readily apparent, compare Figs. 3(b) and (a).

Our zincite solubility study included pH (at 25°C) values as low as 10.2, which was sufficient to allow thermochemical properties to be extracted for $Zn(OH)_2(aq)$, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$. A subsequent zincite solubility study at lower alkalinities, conducted by Hanzawa et al. [31], provided the $Zn(OH)^+$ properties listed in Table I. Their results for the neutral hydroxocomplex $Zn(OH)_2(aq)$

ΔG_f^o (298) = -514.0 kJ/mol and $S°(298) = 86.8$ J/mol-K, provide free energies of hydrolysis that deviate from ours by an average of 2.4 kJ/mol throughout the applicable temperature range (100 to 250°C). This difference is not considered significant.

3. Discussion

Within the expected accuracy and applicable temperature range of our measured solubilities, the Gibbs energy of each hydroxocomplex may be determined at any temperature using two properties: $\Delta G_f^o(298)$ and $S°(298)$. As discussed above, the Table I values for ΔG_f^o are in good agreement with consensus values recommended by Baes and Mesmer [13]. More importantly, our results provide experimental entries for many estimated ΔG_f^o values and serve as a source for S^o values needed to make metal oxide calculations at elevated temperatures.

The Table I database also provides an opportunity to advance basic understanding of hydrolytic behavior. Previously, the thermodynamic properties of solubilized metal cations in aqueous solutions were quantified in two stages: (1) predict properties of the unhydrolyzed metal cation (aquocomplex) from those of the gaseous metal cation, and (2) predict properties of the hydrolyzed metal cations (hydroxocomplexes) from those of the unhydrolyzed metal cation. For example, the phenomenological model developed by Marcus [37] predicts/correlates standard Gibbs energy and entropy (ΔG_f^o and S^o) for unhydrolyzed metal cations based on charge (Z) and size (r), while Brown et al. [38] successfully correlated $\Delta G_f^o(298)$ for the first hydrolysis reaction based on Z, r and two electron screening functions. Recently, Shock et al. [39] developed empirical correlations to predict S^o values for metal ion hydroxocomplexes from those of the unhydrolyzed metal cation based on Z and the number of hydroxide ligands (n).

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A. Neutral Hydroxocomplexes

Presently, our attention is directed at the neutral metal cation hydroxocomplex, since it possesses special significance: it is the metal cation hydrolytic state present in solution when a minimum solubility of the metal oxide occurs. Therefore, determination of the thermochemical properties of this species takes on practical engineering importance. When the special case of a neutral hydroxocomplex of a hydrolyzed metal cation, i.e., an uncharged complex, is considered within the context of the Marcus model, it is seen that all of the charge-dependent terms disappear and only two contributions remain: (1) one due to cavity formation (size dependent), as represented by S values for the monatomic, inert gases, and (2) one due to the effect that the hydroxocomplex has on the structure of water in the surrounding environment. Negative contributions are associated with structure-making properties, while positive contributions are associated with structure-breaking properties.

A summary of experimentally-determined $S^o(298)$ values for the neutral hydroxocomplexes of the hydrolyzed metal cations in Period 4 (Ar to Kr, $Z \leq 4$) is provided in Table II. Values given in parentheses are S^o values calculated using the algorithms recommended by Shock et al. Agreement between the two is considered to be unsatisfactory, especially for $Fe(OH)_3(aq)$, $Cr(OH)_3(aq)$ and $Ca(OH)_2(aq)$. Using the S^o predictions and the Table I ΔG_f^o values produces minimum solubilities for hematite and γ-CrOOH at 300°C that are more than two orders of magnitude too high. A direct comparison for the Period 4 tetravalent cations, Ti(IV) and Ge(IV), is not possible, since Shock et al. chose to omit these predictions. In the case of $Ge(OH)_4(aq)$, predictions were not possible, since no cationic aquohydroxocomplexes were known. Discussion of $Ti(OH)_4(aq)$ properties was deferred to a paper in preparation, which has not been issued.

Table II reveals that the S^o values occur within a range between -80 and 200 J/mol-K; the inert gas values falling approximately mid-way, S^o = 60 J/mol-K. Furthermore, the group of neutral

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hydroxocomplexes having higher standard partial molar entropies is associated with metal cations that prefer C.N. = 4 (i.e., tetrahedral symmetry), while those having S^{o} values less than the inert gases are known to have aquocomplexes with C.N. = 6.

The hydrolysis phenomenon, i.e., replacement of a water molecule ligand with a hydroxide ligand, is known to destabilize octahedral bonding symmetry. Although it has not yet been determined how many hydroxide ion substitutions are required to cause a transformation in coordination number from six to four, it is known that transition metal cations are subject to a phenomenon known as ligand field stabilization, which tends to stabilize octahedral bonding symmetry.

The results of the hypothesized competition between hydrolysis and ligand field stabilization are illustrated in Fig. 4, where a plot of S^{o} versus ligand field stabilization energy [43] is provided for the neutral hydroxocomplexes of the divalent metal cations in Period 4. A fairly consistent trend is noted except for two deviations: Cu(II) and Ca(II). Octahedral coordination is expected to be destabilized in Cu(II) complexes by an additional amount due to the Jahn-Teller distortion effect. This effect displaces the two ligand positions above and below the four planar positions. With regard to the non-transition element cations, octahedral coordination of Ca(II) complexes is stabilized by *sd*^{5} bonding, while tetrahedral coordination of Zn(II) complexes is stabilized by *sp*^{3} bonding (since its 3*d* electron shell is complete). Thus, both deviations may be rationalized.

With regard to trivalent ion hydrolysis, neutral hydroxocomplexes of the non-transition metal cations exhibit S^{o} values that approach 200 J/mol-K, a value probably indicative of tetrahedral symmetry: $Ga(OH)_3(aq)$ and $As(OH)_3(aq)$ have S^{o} values of 133 and 200 J/mol-K, respectively. Based on a negative S^{o} value observed for $Cr(OH)_3(aq)$, we conclude that the extremely large ligand field stabilization energy for Cr(III) is able to delay the octahedral-to-tetrahedral complex transformation to beyond the third stepwise hydrolysis reaction. On the other hand, the S^{o} value for the neutral

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hydroxocomplex of Fe(III) (LFSE = 0), is more than 50 J/mol-K greater than that of $Cr(OH)_3(aq)$. This value is approximately equal to that possessed by aquocomplexes of the solvated inert gas atoms and indicates the balancing (or absence) of structure-making and -breaking forces.

Finally, it is noted that $Ti(OH)_4(aq)$ and $Fe(OH)_3(aq)$ possess nearly equivalent S^o values and that LFSE is zero for both of their unhydrolyzed metal ion aquocomplexes. The neutral hydroxocomplex of Ge(IV) (the other tetravalent, Period 4, non-transition metal cation) is believed to possess tetrahedral symmetry, as indicated by its large standard partial molar entropy, $S^o = 200$ J/mol-K. Thus, the poor predictive capability demonstrated by the Shock et al. model for neutral hydroxocomplexes of the tri- and tetra-valent transition metal cations appears to be due to the inability to account for ligand field stabilization and specific structure-making/breaking tendencies of the metal cation.

B. First Anionic Hydroxocomplexes

Table III summarizes the experimentally-based $S^o(298)$ values for the first anionic hydroxocomplexes of hydrolyzed metal cations in Period 4 (Ti to Ge, $Z \leq 4$). Values given in parentheses are predictions based on the Shock et al. correlations. These algorithms are seen to predict S^o values for the divalent metal ion complexes to within 40 J/mol-K, due to the availability of a more-inclusive database. This degree of agreement is considered to be satisfactory. On the other hand, the Shock correlations tended to significantly over-predict S^o values for transition metal ion complexes having higher oxidation states. Unfortunately, the algorithms were inapplicable to the two Period 4 tetravalent cations of interest.

The trends in experimental S^o values established previously for the neutral hydroxocomplexes continues: complexes of the divalent transition metal cations exhibit a range of S^o values between -100 and 100 J/mol-K, with those having LFSEs ($Fe(OH)_3^-$ and $Ni(OH)_3^-$ exhibiting lower S^o values than those that do not ($Cu(OH)_3^-$ and $Zn(OH)_3^-$). A correlation of S° versus LSFE was not attempted, however, due to the lack of data for $Co(OH)_3^-$ and $Mn(OH)_3^-$.

Relative to the trivalent cation hydroxocomplexes, S^o values for $Fe(OH)_4^-$, which has no LFSE, and $Ga(OH)_4^-$, which represents a non-transition element, are about equal. As mentioned earlier, the Table I S^o value for $Fe(OH)_4^-$ may be biased because of an inappropriately(?) constrained fit of our magnetite solubility data. On the other hand, $Cr(OH)_4^-$, whose cation possesses the highest LFSE, has an S^o value lower by about 70 J/mol-K.

The anionic hydroxocomplexes of the two tetravalent cations in Table III show a difference in S^o values of about 100 J/mol-K, the complex of the transition metal cation having the lower value (even though Ti(IV) has no LFSE). It is interesting to note that Pokrovski and Schott [41] concluded that the Ge(IV) anionic hydroxocomplex should actually be written as an oxohydroxocomplex, $GeO(OH)_3^-$, because Ge(IV) tends to exhibit C.N. = 4. Thus, the difference in S^o values may be due to a difference in the structure-making/breaking contribution caused by octahedral vs. tetrahedral coordination in the two anionic complexes.

4. Conclusions/Significance

On the basis of transition metal oxide solubility studies, thermodynamic properties (ΔG_f^o, ΔH_f^o, and S^o) have been extracted for solubilized metal cation aquocomplexes and their series of hydroxocomplexes. Use of alkaline pH conditions and a broad temperature range (25 to 285°C) permitted reliable values for partial molar entropy (S^o) to be extracted for many neutral hydroxocomplexes, $M^z(OH)_z(aq)$, for the first time.

S^o values for the Period 4 neutral hydroxocomplexes were shown to fall in a range between -80 and +200 J/mol-K. These values were shown to be affected by differences in water structure-making/

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breaking properties, which were caused by octahedral vs. tetrahedral complex symmetry and by ligand field stabilization, a phenomenon that stabilizes octahedral coordination and is specific to cations of the transition elements. It was also concluded that empirical correlations of thermodynamic properties, developed by regression of data that under-represents transition metal cation contributions, such as Shock et al., will provide unreliable estimates for the thermodynamic properties of hydrolysis products of the transition metal cations because the above effects have not been taken into account.

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Table I

Thermochemical Parameters for Species in
Various Transition Metal Oxide-Water Systems

Species	C_p° (298) ($J\text{-}mol^{-1}\text{-}K^{-1}$)	S° (298) ($J\text{-}mol^{-1}\text{-}K^{-1}$)	ΔH_f° (298) ($kJ\text{-}mol^{-1}$)	ΔG_f° (298) ($kJ\text{-}mol^{-1}$)	Ref.
A. TiO_2 - H_2O System (Ref. 3)					
Ti(s)	25.02	30.63± 0.21	0	0	9, 10
TiO_2(s)	55.02	50.33±0.2	-944.7±1.7	-889.5	9,10
Ti^{4+}(aq)	--	-664.1	-457.00±4.8	-354.18±3.85	11,12
$Ti(OH)^{3+}$(aq)	--	--	--	-614.00±3.85	11
$Ti(OH)_2^{2+}$(aq)	--	-190.5	-976.02±3.3	-862.16	13, 14
$Ti(OH)_3^{+}$(aq)	--	--	--	-1086.21	13
$Ti(OH)_4$(aq)	--	21.6	-1515.28	-1312.48	3
$Ti(OH)_5^{-}$(aq)	--	103.0	-1733.86	-1479.20	3
B. Cr_2O_3 - H_2O System (Ref. 5)					
Cr(s)	23.35	23.77	0	0	10
$Cr(OH)_3 \cdot 3H_2O$(s)	--	328.0	-1880.54	-1612.46	5
γ-CrO(OH)(s)	98.6	130.7	-710.64	-661.90	5
α-CrOOH(s)	--	110.8	-722.10	-667.40	15, 5
Cr_2O_3(s)	118.7	81.15	-1139.70	-1058.07	10, 16
Cr^{3+}(aq)	--	-367.8	-253.97	-215.48	17, 18
$Cr(OH)^{2+}$(aq)	--	-208.2	-497.96	-430.96	19
$Cr(OH)_2^{+}$(aq)	--	-140.6	-751.15	-628.15	19
$Cr(OH)_3$(aq)	--	-18.3	-1007.09	-844.40	5
$Cr(OH)_4^{-}$(aq)	--	89.3	-1214.54	-1007.75	5
C. Fe_3O_4 - H_2O System (Ref. 4)					
Fe(s)	24.98	27.28	0	0	16
$Fe(OH)_2$(s)	--	84.0	-583.39	-500.16	4
α-FeOOH(s)	74.33	60.38	-562.92	-492.1	20
γ-FeOOH(s)	76.2	62.5	-556.4	-486.3	21
Fe_3O_4(s)	150.73	146.15	-1118.38	-1015.23	16
α-Fe_2O_3(s)	103.87	87.40	-824.25	-742.29	16
Fe^{2+}(aq)	-51.2	-149.6	-88.69	-88.14	4
$Fe(OH)^{+}$(aq)	--	-162.9	-354.83	-274.18	4
$Fe(OH)_2$(aq)	--	-29.2	-563.08	-446.13	4
$Fe(OH)_3^{-}$(aq)	--	-28.7	-806.40	-613.42	4
Fe^{3+}(aq)	--	-346.9	-50.21	-16.74	22
$Fe(OH)^{2+}$(aq)	--	-150.6	-292.55	-241.58	13
$Fe(OH)_2^{+}$(aq)	--	--	--	-458.82	13
$Fe(OH)_3$(aq)	--	38.1	-804.81	-657.86	4
$Fe(OH)_4^{-}$(aq)	--	10.9	-1071.46	-840.22	4

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Table I (Cont'd)

Species	C_p° (298) ($J\text{-}mol^{-1}\text{-}K^{-1}$)	S° (298) ($J\text{-}mol^{-1}\text{-}K^{-1}$)	ΔH_f° (298) ($kJ\text{-}mol^{-1}$)	ΔG_f° (298) ($kJ\text{-}mol^{-1}$)	Ref.
D. CoO - H_2O System (Ref. 6)					
Co(s)	24.81	30.04	0	0	16
β-$Co(OH)_2$(s)	97.1	97.2	-534.17	-453.07	6, 16
CoO(s)	55.06	52.97	-237.94	-214.20	16
Co^{2+}(aq)	-169	-149.9	-56.67	-55.23	6, 23
$Co(OH)^+$(aq)	-23	-78.4	-291.77	-235.49	6
$Co(OH)_2$(aq)	124	-3.6	-520.91	-410.76	6
$Co(OH)_3^-$(aq)	--	--	--	-581.21	6, 24
$Co(OH)_4^{2-}$(aq)	--	--	--	-739.49	25, 26
E. NiO - H_2O System (Ref. 8)					
Ni(s)	26.07	29.87	0	0	10
β-$Ni(OH)_2$(s)	162.5	52.9	-549.51	-456.25	8
NiO(s)	44.31	37.99	-239.7	-211.54	16
Ni^{2+}(aq)	-184	-176.6	-53.6	-43.9	22, 23
$Ni(OH)^+$(aq)	--	-93.2	-287.9	-227.6	10
$Ni(OH)_2$(aq)	--	-77.1	-542.37	-410.36	8
$Ni(OH)_3^-$(aq)	--	-100.6	-793.47	-578.28	8
F. CuO - H_2O System (Ref. 7)					
Cu(s)	24.43	33.14±0.21	0	0	9
$Cu(OH)_2$(s)	87.85	87.03	-444.09	-359.02	16
CuO(s)	42.25	42.59±0.4	-156.06±2.1	-128.29	27
Cu^{2+}(aq)	-162	-142.4±4.0	64.9±1.0	65.04	22, 23
$Cu(OH)^+$(aq)	-82.1	113.9	-115.87	-116.00	7, 28
$Cu(OH)_2$(aq)	--	59.3	-408.32	-315.98	29
$Cu(OH)_3^-$(aq)	213	86.1	-659.28	-498.98	7
$Cu(OH)_4^{2-}$(aq)	--	8.5	-917.96	-658.35	7
G. ZnO - H_2O System (Ref. 2)					
Zn(s)	25.40	41.63±0.21	0	0	9
ϵ-$Zn(OH)_2$(s)	72.4	76.99±0.21	-645.47	-555.93±0.21	30
ZnO(s)	40.25	43.64±0.42	-350.83±0.21	-320.91±0.25	9
Zn^{+2}(aq)	-164	-154.8±1.3	-153.64±0.42	-147.23	23, 30
$Zn(OH)^+$(aq)	--	1.1	-368.42	-352.39	31
$Zn(OH)_2$ (aq)	-3.8	67.7	-611.95	-519.67	2
$Zn(OH)_3^-$(aq)	--	52.4	-871.97	-699.02	2
$Zn(OH)_4^{2-}$(aq)	--	7.9	-1125.64	-863.30	2
H. Key Parameters					
H_2(g)	28.84	130.68	0	0	16
O_2(g)	29.38	205.15	0	0	16
H_2O(aq)	75.29	69.95	-285.83	-237.14	16
H^+(aq)	-71	-22.2	0	0	23, 32

Table II

Standard Partial Molar Entropies (S^o) for Neutral Hydroxocomplexes of Hydrolyzed Metal Cations in Period 4

Atomic Number/ Element	Oxidation State	S^o(298) J/mol-K	Ref.
18 Ar	0	59.4	10
19 K	I	91.6 (108.4)	10
20 Ca	II	-74.5 (75.5)	10
22 Ti	IV	21.6 (--)	Table 1
24 Cr	III	-18.3 (95.0)	Table 1
26 Fe	III	38.1 (162.8)	Table 1
26 Fe	II	-29.2 (28.1)	Table 1
27 Co	II	-3.6 (-4.6)	Table 1
28 Ni	II	-77.1 (-34.7)	Table 1
29 Cu	II	59.3 (18.0)	Table 1
30 Zn	II	67.7 (61.5)	Table 1
31 Ga	III	132.6 (82.0)	40
32 Ge	IV	200.1 (--)	41
33 As	III	200.0	42
36 Kr	0	61.5	10

( ) Denotes Ref. 39 prediction, Table 10

Table III

Standard Partial Molar Entropies (S^o) for First Anionic Hydroxocomplex, $M(OH)_{z+1}^-$ of Hydrolyzed Period 4 Metal Cations

Element/ Oxidation State	**$S^o(298)$ J/mol-K**	**Ref.**
Ti (IV)	103.0 (--)	Table 1
Cr (III)	89.3 (134.1)	Table 1
Fe (III)	163.8 (206.5)	35
Fe (II)	-28.7 (29.4)	Table 1
Co(II)	-- (-14.5)	--
Ni (II)	-100.6 (-58.5)	Table 1
Cu (II)	86.1 (93.4)	Table 1
Zn (II)	52.4 (52.3)	Table 1
Ga (III)	158.9 (120.3)	40
Ge (IV)	205.7 (--)	41

( ) Denotes Ref. 39 prediction, Table 10

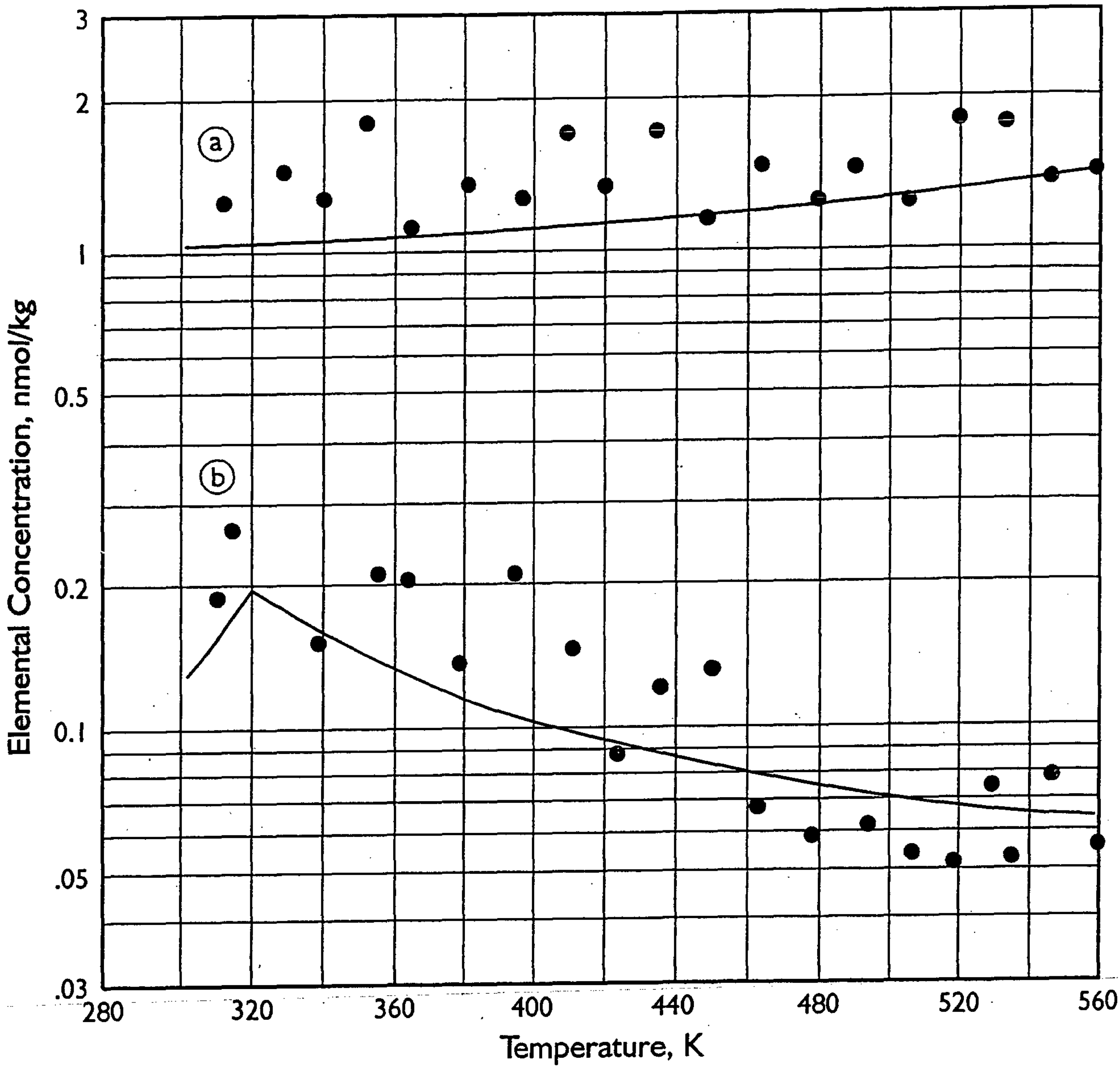
List of Figure Captions

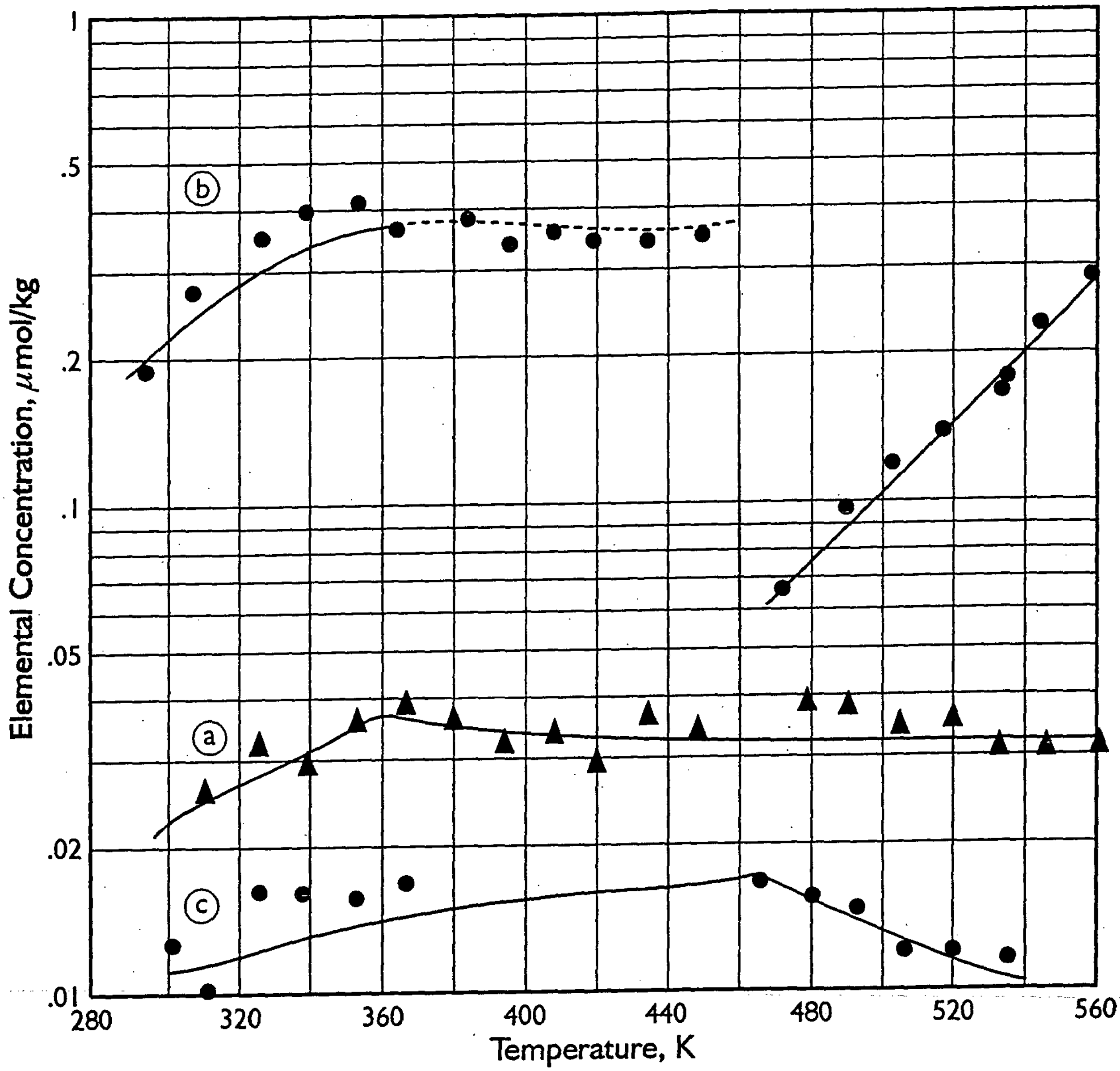
Fig. 1. Minimum solubility of: (a) titanium(IV) oxide and (b) chromium(III) oxide hydroxide; both in 0.07 millimolal ammonia.

Fig. 2. Measured solubility behavior of magnetite, cobalt(II) oxide and nickel(II)oxide at near-minimum conditions: (a) $Fe(OH)_2/Fe_3O_4$ in 0.70 millimolal ammonia ($H_2 = 5.3$ cm^3-kg^{-1}), (b) $Co(OH)_2$ and Co ($H_2 = 17.7$ cm^3-kg^{-1}) in 0.19 millimolal NaOH and (c) $Ni(OH)_2/NiO$ in 0.54 millimolal phosphate (Na/P = 2.36).

Fig. 3. Measured solubility behavior of copper(II) oxide and zinc(II) oxide at near-minimum conditions*: (a) CuO in 0.07 millimolal ammonia [29] and (b) ZnO in 0.18 millimolal NaOH [29]. *Measured solubilities include significant contributions from $M(OH)^+$ and $M(OH)_3^-$ hydrolytic species.

Fig. 4. Variation in partial molar entropy of neutral hydroxocomplex (S°) with ligand field stabilization energy (LFSE).


Elemental Concentration, nmol/kg
3
2
1
0.5
0.2
0.1
.05
.03
280
320
360
400
440
480
520
560
Temperature, K
ⓐ
ⓑ


Elemental Concentration, μmol/kg
1
.5
.2
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.02
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ⓒ
280
320
360
400
440
480
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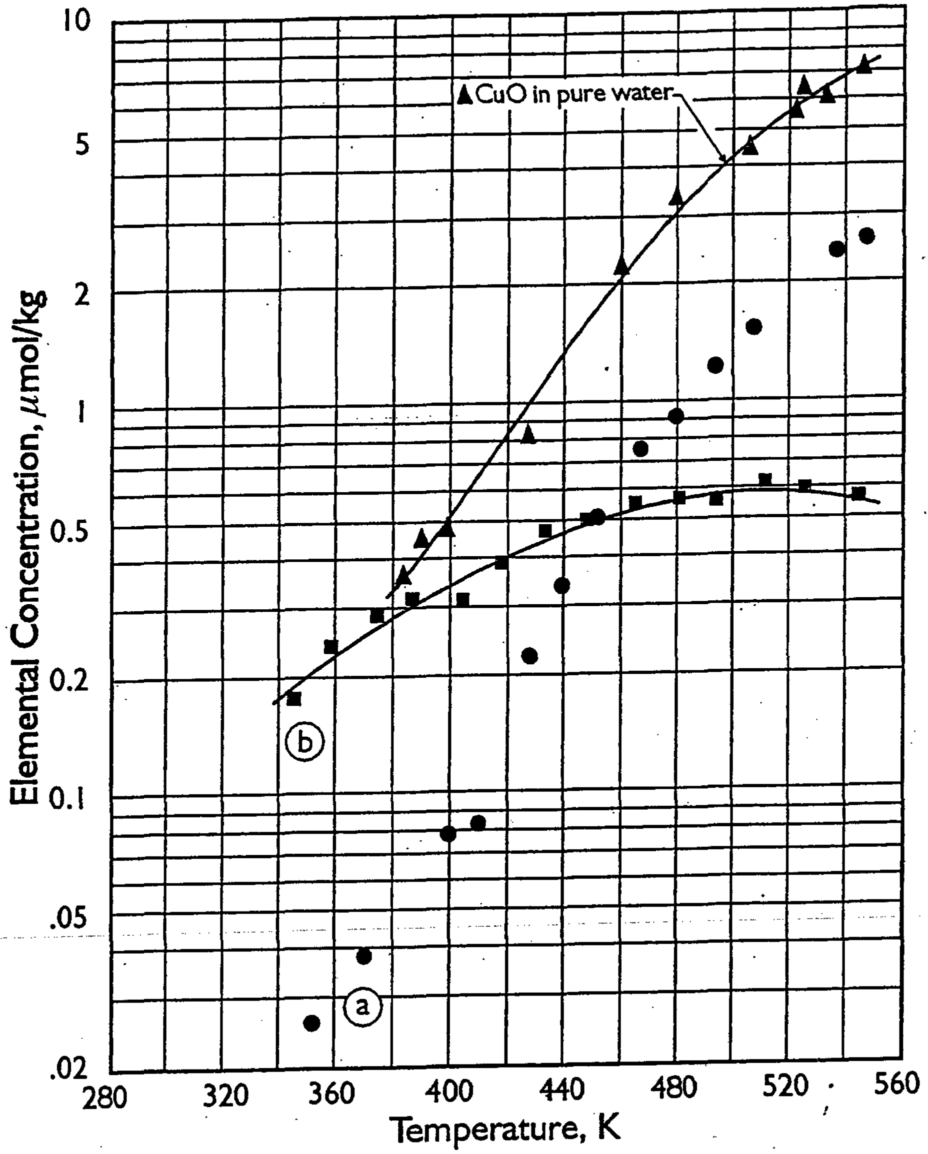
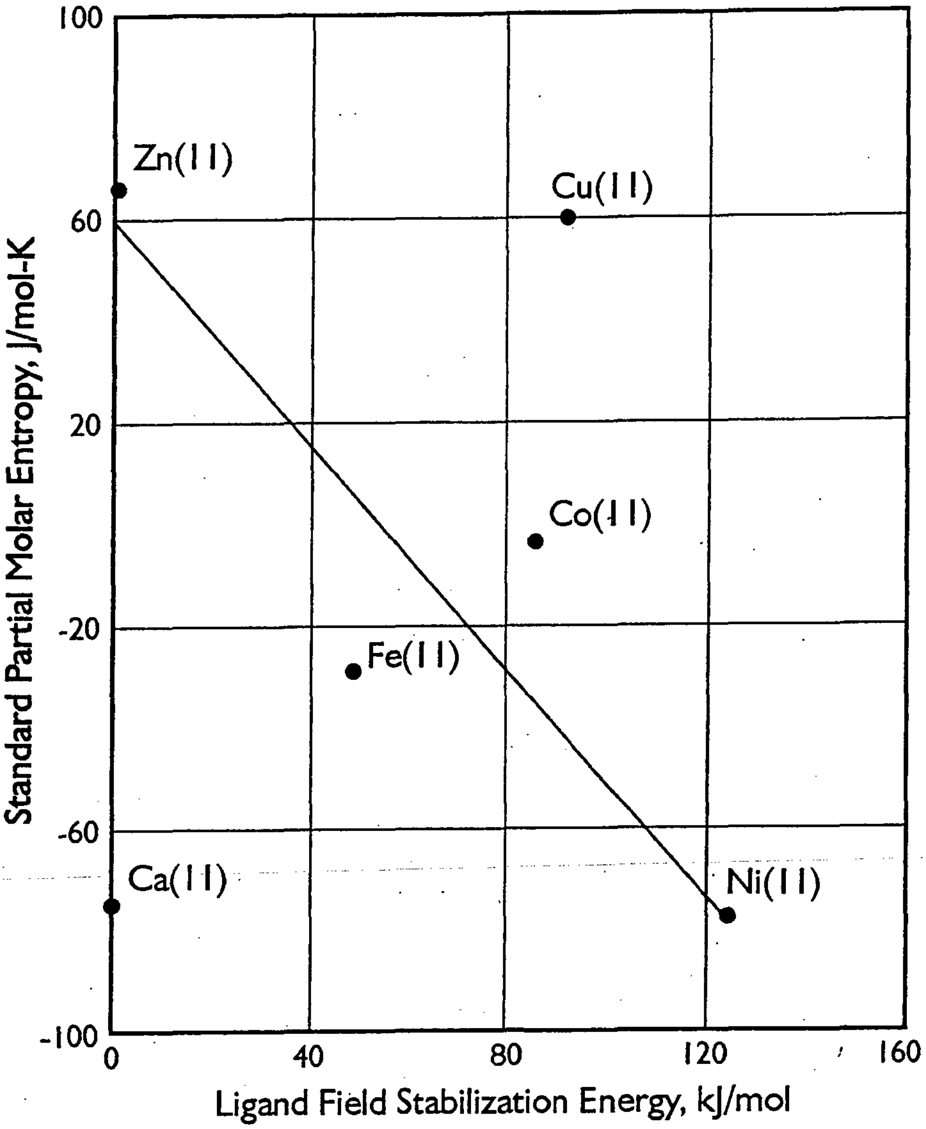
560
Temperature, K


▲CuO in pure water
ⓑ
ⓐ
10
5
2
1
0.5
0.2
0.1
.05
.02
280
320
360
400
440
480
520
560
Elemental Concentration, μmol/kg
Temperature, K


100
60
20
-20
-60
-100
0
40
80
120
160
Standard Partial Molar Entropy, J/mol-K
Ligand Field Stabilization Energy, kJ/mol
Zn(II)
Cu(II)
Co(II)
Fe(II)
Ca(II)
Ni(II)