

## Absence of Cr(IV) in the EMF-pH Diagram for Chromium\*

D. C. SILVERMAN\*

Chromium, with its relatively large number of known valence states, forms a complex electrochemical system when combined with water. The complexity of this system and its thermodynamics have been shown in the EMF-pH (Pourbaix) diagram originally derived by Pourbaix.<sup>1</sup> This diagram is reproduced in Figure 1. The diagram was derived by the algorithm written by Froning, Shanley, and Verink<sup>2</sup> in a program modified as previously discussed.<sup>3</sup> The data used to derive Figure 1 are shown in Table 1.

For this diagram, Cr<sub>2</sub>O<sub>3</sub> is the solid Cr(III) compound being considered. There is significant evidence that Cr<sub>2</sub>O<sub>3</sub> is the surface oxide that imparts passivity to chromium for a broad range of potentials and pH.<sup>4,5</sup> The uppermost layer of the Cr<sub>2</sub>O<sub>3</sub> has been predicted to be hydrated. The distance that this hydration extends into the Cr<sub>2</sub>O<sub>3</sub> layers is unclear at present. Activities of 10<sup>-6</sup> and 1 are included in Figure 1. The standard state is the conventional, hypothetical state of one molal concentration, activity coefficient equal to one. An activity of one for the ionic species is included because, as shown in Figure 1, the data of Table 1 predict that a region of stability of CrO<sub>2</sub>-hydr (written as Cr(OH)<sub>4</sub> in the original diagram) exists in the presence of water at high ionic chromium concentrations, moderately low pH, and elevated potentials near but below the breakdown potential of water. At activities of 10<sup>-6</sup> to 10<sup>-2</sup>, CrO<sub>2</sub>-hydr (Cr(OH)<sub>4</sub>) is not predicted to have a region of stability.

Since the original derivation of this diagram, there has been a significant revision of the solid and dissolved species considered to be associated with the dissolution of chromium in water.<sup>6,7</sup> This modern data accounts for all of the known species containing Cr, O, and H that can exist in equilibrium with water at least at atmospheric pressure. One of the conclusions derived from examining this data is that compounds containing Cr(IV) have not been observed to be in equilibrium in the presence of water under conditions used to study chromium hydrolysis. Only the +2, +3, and +6 valence states of chromium are known to exist at equilibrium in water.<sup>6</sup>

This observation is important from the standpoint of chromium passivation for two reasons. First, it seems to contradict the original EMF-pH diagram derived by Pourbaix for the case of high ionic chromium activities. Figure 1 shows a region of stability for Cr(IV) (Cr(OH)<sub>4</sub>) where water is stable. Second, such an absence of a Cr(IV) compound contradicts portions of a chromium passivation theory of Sukhotin, *et al.*<sup>8-10</sup> These authors have hypothesized that CrO<sub>2</sub> could play a role in the passivation of chromium both at relatively low

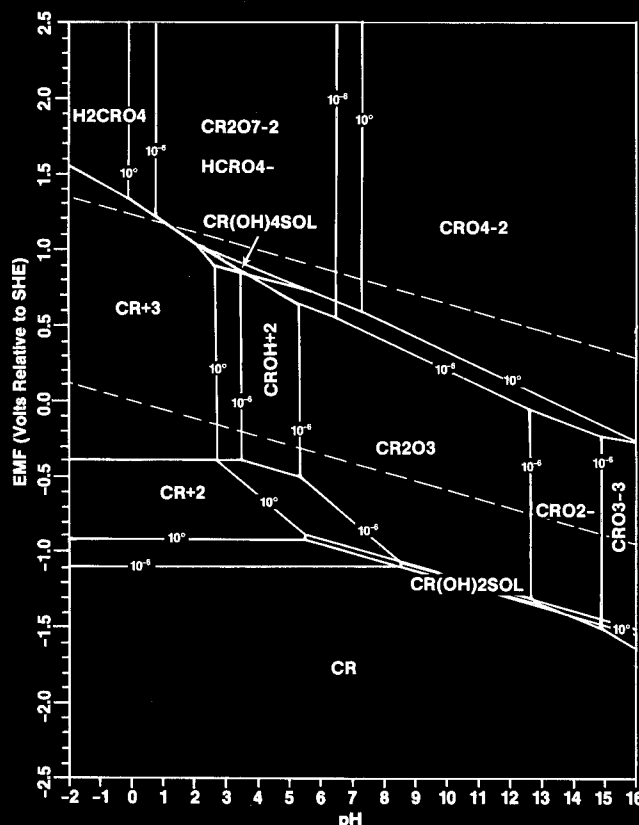


FIGURE 1 — EMF-pH diagram for chromium as derived by Pourbaix<sup>1</sup> at 298K. Ionic activities of 10<sup>-6</sup> and 1 are included. Note that CrO-hydr was defined as Cr(OH)<sub>2</sub> and CrO<sub>2</sub>-hydr was defined as Cr(OH)<sub>4</sub> by Pourbaix.

potentials where Cr<sub>2</sub>O<sub>3</sub> and water are stable and at high potentials, close to the point where Cr(III) would be expected to change to Cr(VI). The validity of this theory itself is questionable. The theory would imply that CrO<sub>2</sub> can be formed and remain thermodynamically stable in the region of stability of water at all chromium ion activities and where Cr<sub>2</sub>O<sub>3</sub> would be stable. Such stability would imply that CrO<sub>2</sub> plays a role in chromium passivation at potentials where Cr<sub>2</sub>O<sub>3</sub> has been shown to be the oxide in the passive surface region.<sup>4,5</sup> Since oxygen was not included in their analysis, Sukhotin, *et al.*, have implicitly assumed that CrO<sub>2</sub> can be stable in the absence of oxygen.

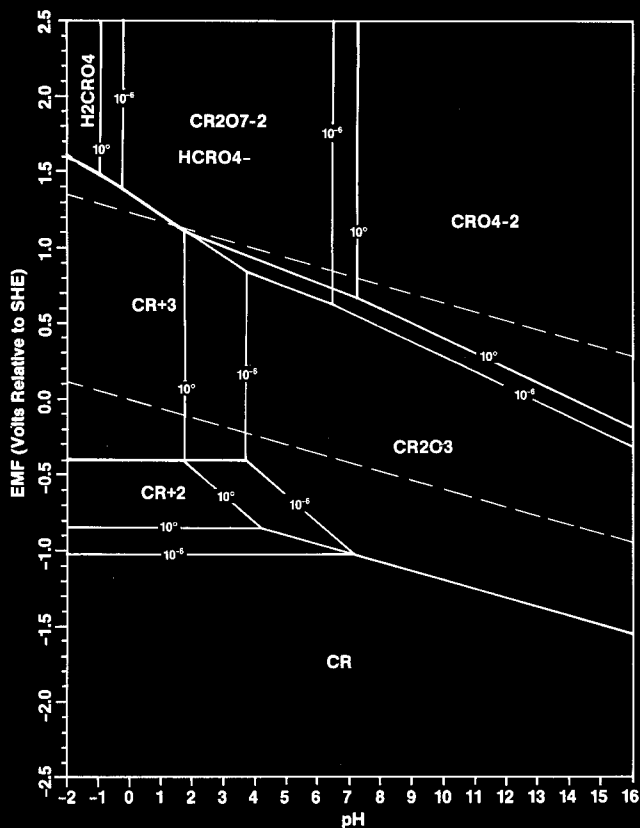
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\* Monsanto Company, St. Louis, Missouri.

**TABLE 1 — Species Considered for Figure 1 (Reference 1)**

Species	Free Energy of Formation, 298K (j/mole)
Cr	0.
CrO-hydr (Cr(OH) <sub>2</sub> )	-3.51 × 10 <sup>5</sup>
Cr <sub>2</sub> O <sub>3</sub> -hydr <sup>(1)</sup> (Cr(OH) <sub>3</sub> )	-1.09 × 10 <sup>6</sup>
Cr <sub>2</sub> O <sub>3</sub>	-1.05 × 10 <sup>6</sup>
Cr <sub>2</sub> O <sub>3</sub> -hydr <sup>(1)</sup> (Cr(OH) <sub>3</sub> ·nH <sub>2</sub> O)	-1.01 × 10 <sup>6</sup>
CrO <sub>2</sub> -hydr (Cr(OH) <sub>4</sub> )	-5.40 × 10 <sup>5</sup>
CrO <sub>3</sub>	-5.02 × 10 <sup>5</sup>
Cr <sup>+2</sup>	-1.76 × 10 <sup>5</sup>
Cr <sup>+3</sup>	-2.15 × 10 <sup>5</sup>
CrOH <sup>+2</sup>	-4.31 × 10 <sup>5</sup>
Cr(OH) <sub>2</sub> <sup>+</sup>	-6.33 × 10 <sup>5</sup>
CrO <sub>2</sub> <sup>-</sup>	-5.36 × 10 <sup>5</sup>
CrO <sub>3</sub> <sup>-3</sup>	-6.03 × 10 <sup>5</sup>
H <sub>2</sub> CrO <sub>4</sub>	-7.78 × 10 <sup>5</sup>
HCrO <sub>4</sub> <sup>-</sup>	-7.74 × 10 <sup>5</sup>
CrO <sub>4</sub> <sup>-2</sup>	-7.37 × 10 <sup>5</sup>
Cr <sub>2</sub> O <sub>7</sub> <sup>-2</sup>	-1.32 × 10 <sup>6</sup>

<sup>(1)</sup>Not considered in Figure 1.



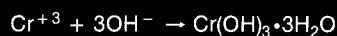
**FIGURE 2 — EMF-pH diagram for chromium as derived from more recent thermodynamic data at 298K. Ionic activities of 10<sup>-6</sup> and 1 are included.**

The possible presence of a Cr(IV) compound in the EMF-pH diagram for chromium has been reinvestigated by using more recent thermodynamic data.<sup>6,7</sup> Table 2 shows the standard free energies of formation of the chromium compounds predicted from this thermodynamic data. As explained in the next paragraph, CrO<sub>2</sub>, not Cr(OH)<sub>4</sub> or CrO<sub>2</sub>-hydr, is the Cr(IV) compound that should be included. The results in Table 2 have been used to construct the EMF-pH diagram shown in Figure 2. Activities of both 10<sup>-6</sup> and 1 are included for the ionic

**TABLE 2 — Species Considered for Figure 2**

Species	Free Energy of Formation, 298K (j/mole)	Ref.
Cr	0.	7
Cr(OH) <sub>2</sub> (SOL)	-5.76 × 10 <sup>5</sup>	6, 7
Cr(OH) <sub>3</sub> (SOL) <sup>(1)</sup>	-8.47 × 10 <sup>5</sup>	6, 7
Cr <sub>2</sub> O <sub>3</sub>	-1.06 × 10 <sup>6</sup>	7
CrO <sub>2</sub>	-5.30 × 10 <sup>5</sup>	See Text
CrO <sub>3</sub>	-5.05 × 10 <sup>5</sup>	7
Cr <sup>+2</sup>	-1.64 × 10 <sup>5</sup>	6, 7
Cr <sup>+3</sup>	-2.03 × 10 <sup>5</sup>	6, 7
Cr(OH) <sup>+2</sup>	-4.18 × 10 <sup>5</sup>	6, 7
Cr(OH) <sub>2</sub> <sup>+</sup>	-6.23 × 10 <sup>5</sup>	6, 7
Cr(OH) <sub>3</sub> (DIS)	-8.13 × 10 <sup>5</sup>	6, 7
Cr(OH) <sub>4</sub> <sup>-</sup>	-9.97 × 10 <sup>5</sup>	6, 7
H <sub>2</sub> CrO <sub>4</sub>	-7.57 × 10 <sup>5</sup>	6, 7
HCrO <sub>4</sub> <sup>-</sup>	-7.58 × 10 <sup>5</sup>	6, 7
CrO <sub>4</sub> <sup>-2</sup>	-7.21 × 10 <sup>5</sup>	6, 7
Cr <sub>2</sub> O <sub>7</sub> <sup>-2</sup>	-1.29 × 10 <sup>6</sup>	6, 7

<sup>(1)</sup>Cr(OH)<sub>3</sub>SOL corresponds to Cr(OH)<sub>3</sub>·3H<sub>2</sub>O. It has a pK of approximately -30 for the reaction



**TABLE 3 — Entropy and Free Energy of Formation Data**

Compound	Enthalpy of Formation (298K) j/mole	Entropy (298K) j/mole-K	Free Energy of Formation (298K) j/mole	Ref.
TiO <sub>2</sub>	-9.12 × 10 <sup>5</sup>	5.02 × 10	-8.53 × 10 <sup>5</sup>	7
VO <sub>2</sub>	-7.40 × 10 <sup>5</sup>	5.15 × 10	-6.65 × 10 <sup>5</sup>	7
CrO <sub>2</sub>	-5.83 × 10 <sup>5</sup>	5.23 × 10	-5.30 × 10 <sup>5</sup>	See Text
MnO <sub>2</sub>	-5.19 × 10 <sup>5</sup>	5.31 × 10	-4.66 × 10 <sup>5</sup>	7

species to compare the new diagram with Figure 1. The major finding is that CrO<sub>2</sub>, the Cr(IV) containing compound included in the derivation, has disappeared from the revised diagram at unit ionic activity for all ionic species. In addition, the ion CrO<sub>2</sub><sup>-</sup> has been included as Cr(OH)<sub>4</sub><sup>-</sup>.<sup>6</sup> No thermodynamic data have been reported for an ion of the form CrO<sub>3</sub><sup>-3</sup> or Cr(OH)<sub>6</sub><sup>-3</sup>.<sup>6,7</sup> This ion has not been reported as a product of chromium ion hydrolysis.<sup>6</sup> Therefore, neither CrO<sub>3</sub><sup>-3</sup> nor Cr(OH)<sub>6</sub><sup>-3</sup> have been included in Table 2 and Figure 2.

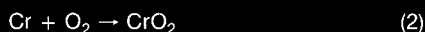
That the appropriate Cr(IV) compound to be included is CrO<sub>2</sub>, not CrO<sub>2</sub>-hydr or Cr(OH)<sub>4</sub>, is based on the following consideration. There is no evidence for the existence of a hydrated Cr(IV) compound, e.g., CrO<sub>2</sub>-hydr or Cr(OH)<sub>4</sub>.<sup>6,7,11</sup> On the other hand, both the existence of and crystal structure of non-hydrated CrO<sub>2</sub> have been verified.<sup>12</sup> The preparation of non-hydrated CrO<sub>2</sub> requires extreme conditions. For example, one method<sup>13</sup> uses high temperatures of 673K to 798K, elevated oxygen pressures (500 to 3000 atm), and supercritical water. Once made, the compound maintains its integrity at room temperature. Therefore, the compound CrO<sub>2</sub>, not Cr(OH)<sub>4</sub>, is a real compound, capable of existing at room temperature but only after being made under appropriate, extreme conditions.

The enthalpy of formation of CrO<sub>2</sub> has been determined to be -5.83 × 10<sup>5</sup> j/mole at 298K.<sup>14</sup> This value could correspond to the defect structure CrO<sub>x</sub> where x ≈ 1.96.<sup>14</sup> No value exists for the standard state entropy of CrO<sub>2</sub>. However, the enthalpies of formation and sublimation have been found to fit within the sequence TiO<sub>2</sub>, VO<sub>2</sub>, CrO<sub>2</sub>, MnO<sub>2</sub>. For example, the enthalpy of formation becomes less negative as metal atomic number increases. This phenomenon is shown in Table 3. This dependency leads to the hypothesis that the entropy may change monotonically with metal atomic number. The estimated standard entropy of CrO<sub>2</sub> at 298K is shown in Table

3. The value of 52.3 j/mole has been estimated by assuming that the entropy increases in a linear fashion with atomic number. Using Equation (1):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (1)$$

for the reaction,



results in a standard free energy of formation for  $\text{CrO}_2$  of  $-5.30 \times 10^5$  j/mole at 298K. As shown in Table 3, this value also fits within the sequence of metal atomic number.

An error of  $\pm 2$  j/mole-K in the entropy, e.g., the difference between the estimated entropy of  $\text{CrO}_2$  and the minimum or maximum entropy in Table 3, leads to a variation in the free energy of  $\pm 600$  j/mole. A free energy of formation for  $\text{CrO}_2$  of approximately  $-5.40 \times 10^5$  j/mole was determined to be required for  $\text{CrO}_2$  to appear in Figure 2 at an ionic activity of 1. This value differs from the estimated value shown in Table 2 by 10000 j/mole, a value far larger than the possible error introduced by the method of estimating the entropy.

Note that when the erroneous value of free energy is used,  $\text{CrO}_2$  appears in Figure 2 at the same position that  $\text{CrO}_2$ -hydr ( $\text{Cr}(\text{OH})_4$ ) appears in Figure 1. This coincidence suggests that the appearance of  $\text{CrO}_2$ -hydr in Figure 1 at unit ionic activity is an artifact of the original free energy of formation data, not the result of an actual region of stability. Thus, the EMF-pH diagram based on revised thermodynamic data predicts that no region of stability exists for  $\text{CrO}_2$ , a Cr(IV) species.

One other major difference in the diagrams is the absence of  $\text{CrO}$ -hydr ( $\text{Cr}(\text{OH})_2$  SOL) in Figure 2. This compound appears between Cr and  $\text{Cr}_2\text{O}_3$  in Figure 1. The support for the absence of this compound is as follows. The data used to generate Figure 2 are calculated from measured equilibrium constants extrapolated to zero ionic strength.<sup>6</sup> The data are internally self-consistent with the value of  $\text{Cr}^{+3}$ <sup>7</sup> as well as consistent with accepted experimental results.<sup>6</sup> Unfortunately, confirming results from controlled potential tests combined with surface analyses are lacking in this pH and potential range.

The absence of a Cr(IV) compound in the EMF-pH diagram for chromium supports the idea that the theory which Sukhotin, *et al.*,<sup>8-10</sup> proposed as a passivation mechanism for chromium is of questionable validity. These workers have proposed that formation of  $\text{CrO}_2$  may play a role in the initial stages of chromium passivation. They hypothesized that this compound may be present within a surface layer of  $\text{Cr}_2\text{O}_3$  at potentials less than 1 V (SHE) including those potentials at which hydrogen would be stable, at least in 1 N  $\text{H}_2\text{SO}_4$ , a fairly low pH.<sup>9</sup> In a later analysis,<sup>15</sup> the proposal was made that in 1 N  $\text{H}_2\text{SO}_4$  and at potentials greater than 1.04 V, the outer surface of  $\text{Cr}_2\text{O}_3$  begins to be oxidized to  $\text{CrO}_2$ . Then, the film will dissolve only after  $\text{CrO}_2$  is transformed to a Cr(VI) compound. Thus, according to this model,  $\text{CrO}_2$  would be expected to be stable over a wide range of potentials. Their proposed Cr(VI) species is  $\text{Cr}_2\text{O}_7^{-2}$ . Note that below ionic chromium activities of  $10^{-2}$ ,  $\text{HCrO}_4^-$  and not  $\text{Cr}_2\text{O}_7^{-2}$  is the expected Cr(VI) dissolution product at this pH.<sup>6</sup> Thus,  $\text{Cr}_2\text{O}_7^{-2}$  cannot be considered to be the only Cr(VI) compound in solution.

The thermodynamic data of Figure 2 do not support the roles of  $\text{CrO}_2$  hypothesized by Sukhotin, *et al.* The compound  $\text{CrO}_2$  is not predicted to be a thermodynamically stable compound when passivation is by  $\text{Cr}_2\text{O}_3$ . This thermodynamic prediction coincides with the ellipsometric results of Genshaw and Sirohi.<sup>4</sup> These workers have shown that in the passive voltage range just above the primary passivation potential of approximately  $-0.4$  V (SHE) at a pH of 1.7 and in the absence of oxygen, ellipsometric results negate the presence of  $\text{CrO}_2$ . Further work by Seo, Saito, and Sato<sup>5</sup> has shown that the passive film on chromium can be characterized as  $\text{Cr}_2\text{O}_3$  for  $1.55 < \text{pH} < 8.43$  for all potentials in the region of stability of water where chromium is passive. Thus, the passive oxide film appears to be chemically unchanged from its formation at fair-

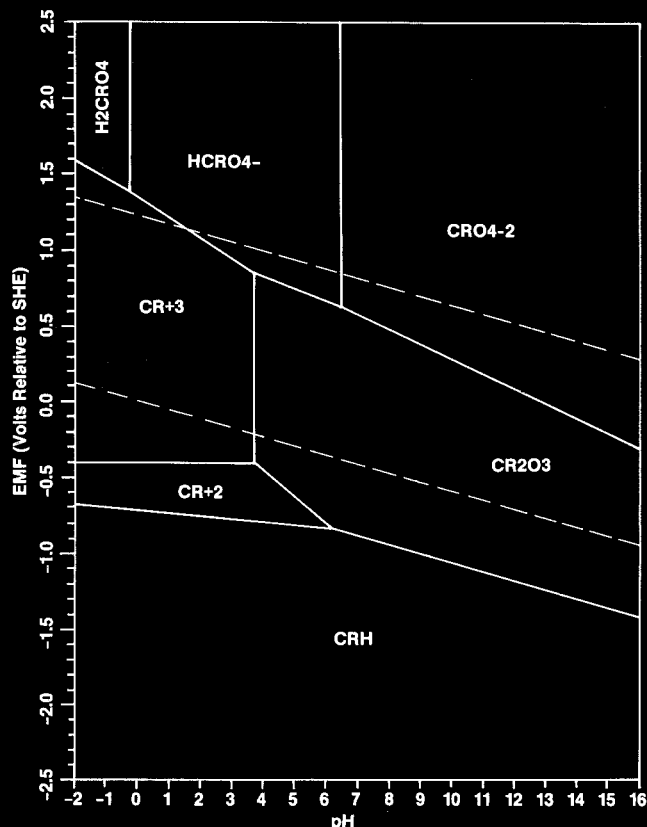


FIGURE 3 — EMF-pH diagram for chromium at 298K with CrH (chrome-hydride) included. Ionic activities are  $10^{-6}$ .

ly cathodic potentials up to its breakdown potential. In fact, the passive current is unchanged until the passive film is destroyed as characterized by a monotonic rise in current. If a transformation of  $\text{Cr}_2\text{O}_3$  to  $\text{CrO}_2$  would occur just below the breakdown potential of the passive film, a current peak or current step might be expected at the transformation potential. The fact that no deviation in the current appears<sup>4,5</sup> supports the absence of  $\text{CrO}_2$  formation, in agreement with the EMF-pH diagrams. The fact that extreme conditions and high oxygen pressures are required for formation of  $\text{CrO}_2$  also supports the absence of this compound from the passivation mechanism of chromium under oxygen free aqueous conditions, those conditions corresponding to the region of stability of water.

One portion of the Sukhotin, *et al.*, theory that is supported by thermodynamics is the possible presence of chrome hydride instead of metallic chromium at cathodic potentials where water breakdown to hydrogen is favored. Chrome hydride as a compound may be written as  $\text{CrH}_x$  ( $0.95 < x < 1$ ).<sup>16</sup> It has a free energy of formation of  $8.64 \times 10^3$  j/mole.<sup>16</sup> Inclusion of this data with that shown in Table 2 results in the EMF-pH diagram shown in Figure 3. The region of stability of metallic chromium has disappeared in favor of chrome hydride. This finding agrees with the thermodynamic analysis of Khoreva and Sukhotin.<sup>15</sup> The ability of chrome hydride to form in acidic solutions under cathodic charging conditions has been verified by X-ray diffraction of chrome exposed to these conditions.<sup>9</sup> That chrome hydride is the stable phase below the primary passivation potential reported by Genshaw and Sirohi<sup>4</sup> or Seo, *et al.*,<sup>5</sup> has yet to be verified.

## References

1. Pourbaix, M., Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd Ed., p. 256, National Association of Corrosion Engineers, Houston, Texas, 1974.
2. Froning, M. H., Shanley, M. E., Verink, E. D., Corros. Sci., Vol. 16, p. 371 (1976).

3. Silverman, D. C., *Corrosion*, Vol. 38, No. 10, p. 541 (1982).
  4. Genshaw, M. A., Sirohi, R. S., *J. Electrochem. Soc.*, Vol. 118, No. 10, p. 1558 (1971).
  5. Seo, M., Saito, R., Sato, N., *J. Electrochem. Soc.*, Vol. 127, No. 9, p. 1910 (1980).
  6. Baes, C. F., Mesmer, R. E., *The Hydrolysis of Cations*, Sec. 10.3, p. 211, John Wiley and Sons, New York, 1976.
  7. Naumov, G. B., Ryzhenko, B. N., Khodakovskiy, I. L., *Handbook of Thermodynamic Data (Eng. Trans.)*, USGS-WRD-74-001, 1974.
  8. Sukhotin, A. M., Antonovskaya, E. I., Pozdeeva, A. A., *Russ. J. Phys. Chem.*, Vol. 36, No. 11, p. 1284 (1962).
  9. Sukhotin, A. M., Borodkina, N. K., *Elektrokhim.*, Vol. 13, No. 2, p. 296 (1976).
  10. Sukhotin, A. M., Khoreva, N. K., Kostikov, Yu. P., Vasil'kova, I. G., Shlepakov, M. N., *Elektrokhim.*, Vol. 16, No. 9, p. 1403 (1979).
  11. Cotton, F. A., Wilkinson, G., *Advanced Inorganic Chemistry*, 4th ed., p. 719, John Wiley and Sons, New York, 1980.
  12. Chamberland, B. L., *Mat. Res. Bull.*, Vol. 2, p. 827 (1967).
  13. Swoboda, T. J., Arthur, P., Cox, N. L., Ingraham, J. N., Oppegard, A. L., Sadler, M. S., *J. Appl. Phys.*, Vol. 32, No. 3, p. 3745 (1961).
  14. Ariya, S. M., Shchukarev, S. A., Glushkova, V. B., *Zhur. Obshch. Khim.*, Vol. 23, p. 1241 (1953).
  15. Khoreva, N. K. and Sukhotin, A. M., *Elektrokhim.*, Vol. 18, No. 1, p. 20 (1982).
  16. Baranowski, B. and Bojarski, K., *Rocz. Chem.*, Vol. 46, p. 1403 (1972).
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