
Thermodynamic Properties and Environmental Chemistry of Chromium

R. L. Schmidt

July 1984

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SUMMARY

Values of standard entropy, standard enthalpy of formation, and standard free energy of formation for Cr and its solid and aqueous species are tabulated in this report. These values were selected or recalculated after careful evaluation of the best available current thermochemical data. The basis for selection of data centered on conformation with the recent studies of Vasil'ev et al. (1977a,b, 1978, 1980, 1981) for Cr^{3+} data and O'Hare and Boerio (1975) for CrO_4^{2-} data. The thermodynamic data presented in this report will be incorporated into the data base of the geochemical computer model, MINTEQ.

The distribution of Cr in the environment among its aqueous inorganic species is, according to the thermodynamic data, highly dependent upon pH and Eh and the presence of complexing ligands. The speciation of Cr in natural waters is also controlled by reduction and complexation by organic matter, adsorption and oxidation by Mn-oxide in suspended particulate matter and sediment, and reduction by H_2S released from anoxic sediments.

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THERMODYNAMIC PROPERTIES AND ENVIRONMENTAL CHEMISTRY OF CHROMIUM

INTRODUCTION

The thermodynamic properties and environmental behavior of chromium are of concern because of implied adverse effects on human health. Chromium is apparently absorbed by organisms in the hexavalent form and reduced to the trivalent state, likely by reaction with ascorbic acid (Beliles, 1979). Trivalent chromium is an essential element for glucose and lipid metabolism, perhaps through potentiation of insulin activity (Shamberger, 1979). However, inhaled chromium has been implicated as a cause of lung cancer through industrial exposure, and chromium in cement, paint and detergent is responsible for allergic dermatitis (Beliles, 1979).

The predominant mineral form of chromium in rocks is chromite, FeCr_2O_4 . Other spinel structures, such as magnesiochromite, MgCr_2O_4 , are also found (Bowen, 1979). Compared to other mineral constituents of soils or sediments, chromium minerals appear to be resistant to weathering. For example, chemical extraction of deep-sea pelagic clay removed 80% of the total manganese, 90% of the copper, 40% of the zinc and 50% of the nickel, but only 7% of the total sediment chromium (Schmidt, 1982).

The largest sources of chromium to the environment are mining and smelting, which account for over 75% of the annual transfer of the element (Bowen, 1979). Weathering, runoff, and combustion constitute other sources that contribute to concentrations in the environment.

The geochemical behavior of trace elements in the environment can be estimated with a multicomponent predictive model having an extensive thermodynamic data base (Ball et al., 1979). This report contains thermodynamic data for chromium selected from the literature as input to the geochemical computer model, MINTEQ, which is being developed at the Pacific

Northwest Laboratory (Felmy et al., 1983). From the published thermochemical data for chromium, I selected or recalculated values to provide a consistently accurate set of thermodynamic values for the model. The relationship for the formation reaction,

$$\Delta G_{f298}^{\circ} = \Delta H_{f298}^{\circ} - T\Delta S_{f298}^{\circ}$$

was used to verify internal consistency. As much as practicable, ΔG° and ΔH° were assumed to be correct for aqueous species and S° was computed. For solid species I generally took ΔH° and S° as correct and recalculated ΔG° . However, for many solids, ΔG° and ΔH° were reported from solubility determinations and S° was derived. The calculations were made, arbitrarily in many cases, to three decimal places and rounded to two places to maintain consistency within the data.

This report also reviews several studies on the effects that pH, redox potential, and organic and inorganic materials have on the behavior of chromium. Examples are cited to illustrate the importance of the ability of geochemical modeling to predict the environmental behavior of pollutants.

ESTIMATION OF UNKNOWN THERMODYNAMIC VALUES

For some important chromium compounds, thermodynamic data were not available in the literature reviewed. However, values can be estimated by employing the relationship of another known variable to the thermodynamic properties. Langmuir (1979) suggested that the thermodynamic properties of compounds of cations and a common ligand will vary linearly with cation valence and cation radius. This approach was successfully employed by Turner et al. (1981) to estimate the speciation of 58 trace elements in model sea and fresh waters.

Using an approach similar to the Fuoss model (Langmuir, 1979), I developed an equation that relates ΔS_{298}° for the dissolution of BaCrO_4 and

SrCrO_4 to the ionic radii of the cation. A value of ΔS_{298}° for the dissolution of CaCrO_4 was then estimated from this relationship that conforms quite closely to another model that also relates thermodynamic properties directly to ionic radii (see Figure 1).

Shidlovskii et al. (1971a) demonstrated that the sum of the differences between the heats of formation and solution of the sulfates and chromates of the alkaline earths are similar. Using this approach for the chromates and tungstates (in Table 1), I found that the differences between

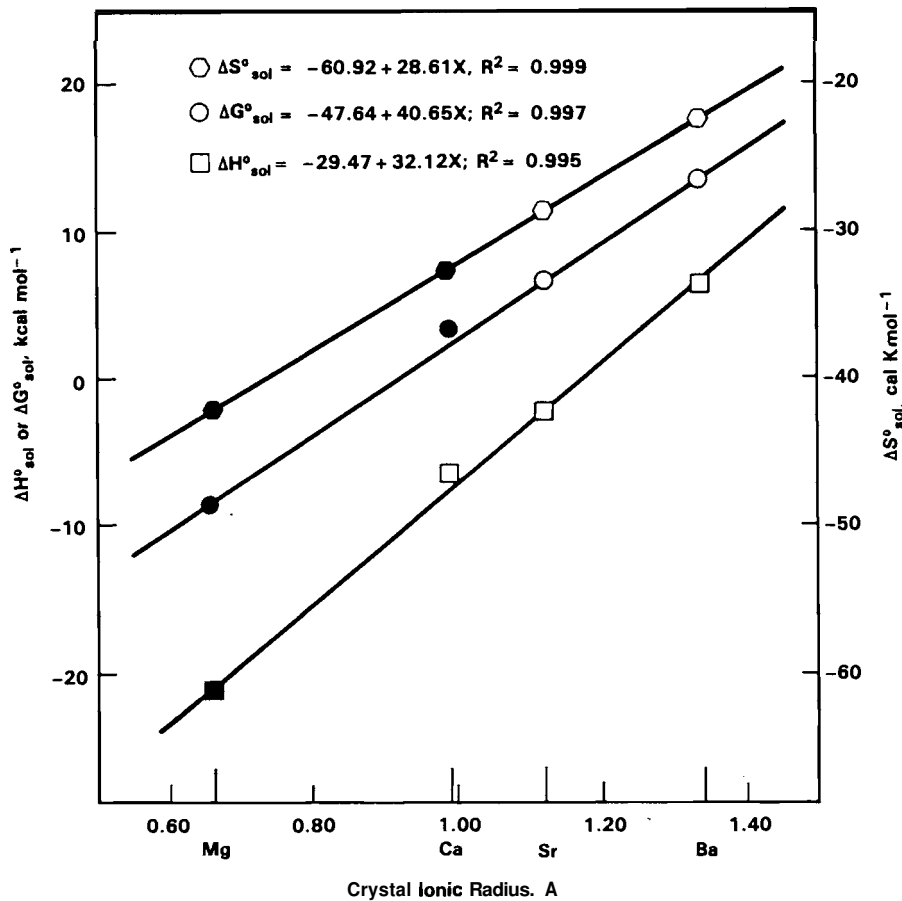


FIGURE 1. Thermodynamic Data for the Dissolution of Ba, Sr, Ca and Mg Chromates
 Open Symbols: data derived from literature values
 Solid Symbols: estimated values.

TABLE 1. Heats of Formation and Heats of Solution in Water of Ba, Sr, Ca and Mg Chromates and Tungstates. Figures in parentheses indicate estimated values.

Cation	Ionic Radius, Å ^o (a)	ΔH_{f298}° , kcal mol ⁻¹			ΔH_{sol}° , kcal mol ⁻¹			$\Delta' + \Delta''$
		CrO ₄ ²⁻ (b)	WO ₄ ²⁻ (c)	Δ'	CrO ₄ ²⁻ (b)	WO ₄ ²⁻ (c)	Δ''	
Ba ²⁺	1.34	-345.82	-390.5	44.58	6.40	8.71	-2.31	42.27
Sr ²⁺	1.12	-338.96	-395.9	56.94	-2.11	6.26	-8.37	48.57
Ca ²⁺	0.99	-334.23	-392.2	57.97	-6.50	5.66	-12.16	45.81
Mg ²⁺	0.66	-321.10	-366.8	45.70	-1.42	0.10	-1.52	44.18
Mg ²⁺	0.66	(-301.25)	-366.8	65.50	(-21.27)	0.10	(-21.37) (d)	44.18

(a) Weast 1972.

(b) From various sources (see next section).

(c) From Naumov et al. (1974).

(d) Derived from $\Delta'' = -39.91 + 28.08$ (ionic radius of cation); $R^2 = 0.9998$.

the heats of solution of the chromates and tungstates for Ba, Sr and Ca, Δ'' , were very nearly perfectly correlated ($R = 0.9999$) to the crystal ionic radii of the cations. However, the literature value given for ΔH_{f298}° for $MgCrO_4$ leads to a quality for ΔH_{sol}° that fails to conform to this pattern. Thus, a value for ΔH_{sol}° of $MgCrO_4$ was estimated from the ionic radius relationship and a new value for ΔH_{f298}° was calculated. The ΔS_{sol}° for $MgCrO_4$ was also estimated from the apparent constant difference between ΔS_{sol}° of the chromates and tungstates of Ba, Sr and Ca, as shown in Table 2.

When the estimated value of ΔS_{sol}° for $MgCrO_4$ is applied to the values of ΔH_{sol}° calculated from the literature or estimated by the method of Table 1, contrasting values of $\log K_{SP}$ are generated (Table 3). Since $MgCrO_4$ is very soluble (Weast, 1972), $\log K_{SP} = 6.39$, based on ΔH_{sol}° as estimated above, is the most likely value. The relationships of the estimates of the thermodynamic properties of $MgCrO_4$ to those of $BaCrO_4$,

TABLE 2. Entropies of Solution in Water of Ba, Sr, Ca and Mg Chromates and Tungstates. Figures in parentheses indicate estimated values.

Cation	$\Delta S_{\text{sol}}^{\circ}$, cal K ⁻¹ mol ⁻¹		
	CrO ₄ ²⁻	WO ₄ ²⁻ (c)	Δ
Ba ²⁺	-22.78(a)	-10.9	-12.88
Sr ²⁺	-28.47(a)	-16.1	-12.37
Ca ²⁺	-32.73(b)	-20.2	-12.53
Mg ²⁺	(-42.09)	-29.5	-12.59(d)

(a) From literature (see next section).

(b) From Fuoss model (Langmuir, 1979).

(c) From Naumov et al. (1974).

(d) Mean A.

TABLE 3. Thermodynamic Values for the Dissolution of MgCrO₄.

	$\Delta S_{\text{sol}}^{\circ}$, cal K ⁻¹ mol ⁻¹	$\Delta H_{\text{sol}}^{\circ}$, kcal mol ⁻¹	Log KSP
From estimated $\Delta H_{\text{f}298}^{\circ}$	-42.09	-21.27	6.39
From literature $\Delta H_{\text{f}298}^{\circ}$	-42.09	-1.42	-8.16

SrCrO₄ and CaCrO₄ can be seen in Figure 1, which relates $\Delta S_{\text{sol}}^{\circ}$, $\Delta H_{\text{sol}}^{\circ}$ and $\Delta G_{\text{sol}}^{\circ}$ to the crystal ionic radii of the alkaline earth cations.

As shown in Table 4, the sum of the differences between $\Delta H_{\text{f}298}^{\circ}$ and $\Delta H_{\text{sol}}^{\circ}$ of alkali metal and NH₄⁺ chromates and sulfates is very nearly

TABLE 4. Heats of Formation and Heats of Solution in Water of Li, Na, K, NH₄, Rb and Cs Chromates and Sulfates.

Cation	Ionic Radius, Å°	ΔH_{f298}° , kcal mol ⁻¹			ΔH_{sol}° , kcal mol ⁻¹			$\Delta' + \Delta''$
		CrO ₄ ²⁻	SO ₄ ²⁻	Δ'	CrO ₄ ²⁻	SO ₄ ²⁻	Δ''	
		(a)	(b)		(a)	(b)		
Li ⁺	0.68	-333.23	-343.18	9.95	-10.80	-7.32	-3.48	6.47
Na ⁺	0.97	-321.18	-331.71	10.53	-4.57	-0.56	-4.01	6.52
K ⁺	1.33	-335.72	-343.62	7.90	4.25	5.68	-1.43	6.47
NH ₄ ⁺	1.43	-267.82	-282.03	5.21	2.19	0.93	1.26	6.47
Rb ⁺	1.47	-336.86	-343.09	6.23	5.90	5.65	0.25	6.48
Cs ⁺	1.67	-341.78	-344.81	3.03	7.51	4.06	3.45	6.48

(a) From various sources (see next section).

(b) From Naumov et al. (1974).

TABLE 5. Standard Entropies and Entropies of Solution in Water of Li, Na, K, NH₄, Rb and Cs Chromates and Sulfates. Figures in parentheses indicate estimated values.

Cation	Ionic Radius, Å°	S_{298}° , kcal mol ⁻¹			ΔS_{sol}° , kcal mol ⁻¹			$\Delta' + \Delta''$
		CrO ₄ ²⁻	SO ₄ ²⁻	Δ'	CrO ₄ ²⁻	SO ₄ ²⁻	Δ''	
		(a)	(b)		(a)	(b)		
Li ⁺	0.68	34.29	27.24	7.05	-15.70	-17.34	1.64	8.69
Na ⁺	0.97	42.21	35.73	6.48	-0.57	-3.31	2.74	9.22
K ⁺	1.33	47.76	41.96	5.80	14.31	10.84	3.47	9.27
NH ₄ ⁺	1.43	(57.68)	52.60	(5.08) (c)	(9.20)	5.04	(4.16) (c)	(9.24)
Rb ⁺	1.47	52.01	47.19	4.82	19.40	14.89	4.51	9.33
Cs ⁺	1.67	54.63	50.65	3.98	22.64	17.35	5.29	9.27

(a) From various sources (see text).

(b) From Naumov et al. (1974).

(c) Estimated from relationship between Δ and the squares of the crystal ionic radii.

constant at about $6.5 \text{ kcal mol}^{-1}$. With this in mind, ■ derived the standard entropy of $(\text{NH}_4)_2\text{CrO}_4$ from the relationship between S_{298}° and $\Delta S_{\text{sol}}^\circ$ for these same sulfates and chromates (Table 5).

DERIVATION OF THERMODYNAMIC DATA

ELEMENTAL Cr

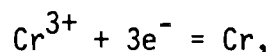
The value ■ selected for the standard entropy of elemental Cr at 25°C , $5.68 \pm 0.07 \text{ cal K}^{-1} \text{ mol}^{-1}$, is based on heat capacity measurements reviewed by Kelley (1960). This value is reported by Wagman et al. (1982), Naumov et al. (1974) and Dellien et al. (1976a). Other compilations give 5.65 ± 0.05 (Robie et al., 1979) and $5.645 \pm 0.05 \text{ cal K}^{-1} \text{ mol}^{-1}$ (Chase et al., 1975).

Cr³⁺(aq)

The standard enthalpy of formation of Cr^{3+} in aqueous solution was determined by Vasil'ev and associates (1977, 1978, 1980) using three independent calorimetric methods. ■ selected the mean value of their determinations at 25°C , $-60.80 \pm 0.30 \text{ kcal mol}^{-1}$, which agrees, within experimental error, with the calorimetric measurements of Dellien and Hepler (1976) of $-60.0 \pm 1.5 \text{ kcal mol}^{-1}$.

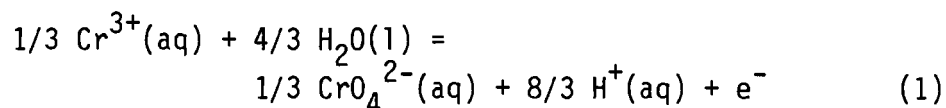
Several different values for the standard free energy of formation of $\text{Cr}^{3+}(\text{aq})$ are represented in the literature. The value given by Naumov et al. (1974), $-48.74 \text{ kcal mol}^{-1}$, is questionable, because it is not internally consistent with the reported values for standard enthalpy and entropy. Garrels and Christ (1965) based their thermodynamic values on Latimer's review (1952) and these values are not considered to be authoritative (Naumov et al., 1974). Dellien et al. (1976a) arbitrarily selected values of ΔG_{f298}° and S_{298}° , apparently based on the works of Naumov et al. (1974) and Garrels and Christ (1965) for which they later express

reservation (Dellien and Hepler, 1976). Cotton and Wilkinson (1972) listed -0.74v for the electrode potential of



which yields a value for ΔG_{f298}° of $-51.20 \text{ kcal mol}^{-1}$ for Cr^{3+} .

Bartlett and James (1979) listed values for log K of several oxidation reactions from which I computed ΔG_{f298}° for Cr^{3+} . For example, log K for the reaction,



is given as -25.0 (Bartlett and James, 1979) and thus $\Delta G^{\circ}(1) = 34.10 \text{ kcal mol}^{-1}$. Coupled with ΔG_{f298}° for $\text{CrO}_4^{2-}(\text{aq})$ measured by O'Hare and Boerio (1975), ΔG_{f298}° for $\text{Cr}^{3+}(\text{aq})$ is computed to be $-50.36 \text{ kcal mol}^{-1}$. However, since Bartlett and James (1979) used data from Garrels and Christ (1965) to derive log K, this value may not be authoritative.

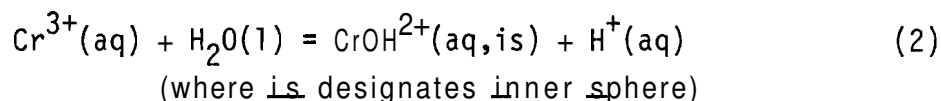
Thermodynamic values from another set of oxidation equations were given by Benson and Teague (1980), apparently based on data in Sillen and Martell (1969). The log K for Equation (1) is listed as -22.36. From this I compute a value of $-39.56 \text{ kcal mol}^{-1}$ for ΔG_{f298}° for Cr^{3+} . Using $\Delta H_{f298}^{\circ} = -60.8 \text{ kcal mol}^{-1}$, I found the standard entropy for Cr^{3+} to be $-112.37 \text{ cal K}^{-1} \text{ mol}^{-1}$. This is about twice the values listed by Naumov et al. (1974) for S_{298}° for other trivalent cations in the fourth row of the periodic table. Thus, the data of Benson and Teague (1980) cannot be considered a reliable basis for determining the standard free energy of formation of $\text{Cr}^{3+}(\text{aq})$.

Finally, Vasil'ev et al. (1980) measured the enthalpy of solution of $\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}(\text{c})$ and derived $S_{298}^{\circ} = -64.4 \pm 1.7 \text{ cal K}^{-1} \text{ mol}^{-1}$ for Cr^{3+} . This entropy and $\Delta H_{f298}^{\circ} = -60.80 \text{ kcal mol}^{-1}$ yield $\Delta G_{f298}^{\circ} = -53.89 \text{ kcal mol}^{-1}$

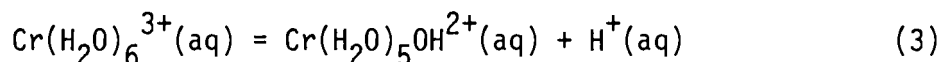
for $\text{Cr}^{3+}(\text{aq})$. On the basis of these values ■ selected $S_{298}^{\circ} = -64.31 \text{ cal K}^{-1} \text{ mol}^{-1}$, which is internally consistent with the entropy ■ selected for $\text{Cr}(\text{c})$ and compares well with the values listed by Naumov et al. (1974) for $\text{Sc}^{3+}(\text{aq})$, $\text{V}^{3+}(\text{aq})$, $\text{Mn}^{3+}(\text{aq})$, and $\text{Fe}^{3+}(\text{aq})$. These values are, respectively, -63.2, -57.0, -51.0, and -66.7 $\text{cal K}^{-1} \text{ mol}^{-1}$.

Cr(III) AQUEOUS IONS AND COMPLEXES

The thermodynamic quantities derived for the aqueous species of Cr(III) are for those of the inner sphere complexes in which the complexing ligand has replaced a solvent molecule from the solvated ion (Wilkins, 1974). Thus $\text{Cr}^{3+}(\text{aq})$ is more accurately $\text{Cr}(\text{H}_2\text{O})_6^{3+}(\text{aq})$ and a reaction such as

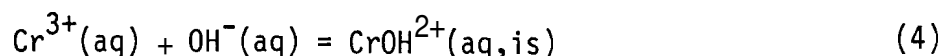


is better represented as



Dellien et al. (1976a) estimated the thermodynamic values for the solvated species by simply adding the required quantities of the respective values for the number of associated water molecules to the values of the unsolvated species. In computing thermodynamic quantities in this report, all aqueous species are assumed to be inner sphere complexes unless otherwise specified and the thermodynamic values of the waters of solvation are ignored.

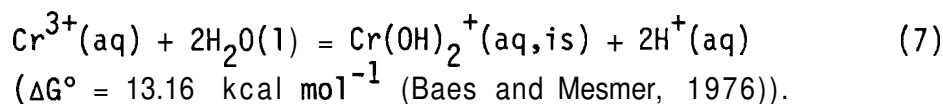
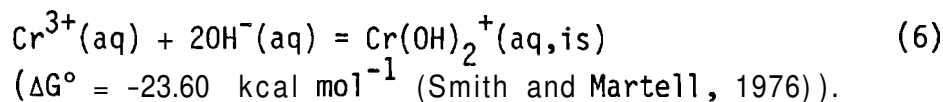
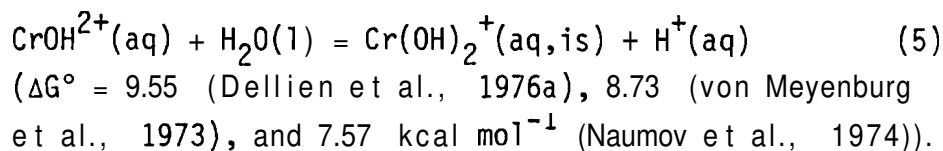
The first hydroxy complex of Cr^{3+} , CrOH^{2+} , is formed in the reaction,



The free energy for this reaction is given as $-13.74 \text{ kcal mol}^{-1}$ (Smith and Martell, 1976). From this relationship is derived the standard free energy

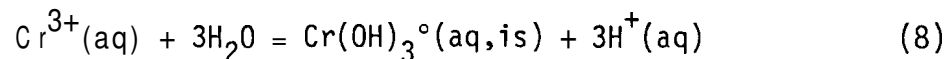
of formation for CrOH^{2+} , $\Delta G_{f298}^{\circ} = -105.23 \text{ kcal mol}^{-1}$. When this value is applied to reaction (2), the $\log K^{\circ}(2) = -3.92$ and compares well with listed values of -3.95 (Naumov et al., 1974), -3.80 (Dellien et al., 1976a), -4.1 (Baes and Mesmer, 1976), -4.00 (von Meyenburg et al., 1973), and -3.83 (Thompson, 1964), which have a mean of -3.94 . Equation (2) can be used to estimate ΔH_{f298}° by applying $\Delta H^{\circ} = -1.0 \text{ kcal mol}^{-1}$ (Smith and Martell, 1976), which yields $\Delta H_{f298}^{\circ} = -116.78 \text{ kcal mol}^{-1}$ for $\text{CrOH}^{2+}(\text{aq})$. This compares well $\Delta H_{f298}^{\circ} = -115 \text{ kcal mol}^{-1}$ estimated by Dellien et al. (1976a). I derive $S_{298}^{\circ} = -24.14 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{CrOH}^{2+}(\text{aq})$.

The free energy of formation of the complex, $\text{Cr}(\text{OH})_2^{+}(\text{aq})$, is derived from the mean ΔG_{f298}° computed from the following reactions:



From these reactions, I calculate $\Delta G_{f298}^{\circ} = -153.35 \text{ kcal mol}^{-1}$ for $\text{Cr}(\text{OH})_2^{+}(\text{aq, is})$. This yields $\Delta G^{\circ}(5) = 8.58$, $\Delta G^{\circ}(6) = -24.25$, and $\Delta G^{\circ}(7) = 13.92 \text{ kcal mol}^{-1}$. The enthalpy of reaction (5) is given by Dellien et al. (1976a) as $7.8 \text{ kcal mol}^{-1}$, which leads to $\Delta H_{f298}^{\circ} = -177.29 \text{ kcal mol}^{-1}$ for $\text{Cr}(\text{OH})_2^{+}(\text{aq, is})$. The computed S_{298}° is $-10.03 \text{ cal K}^{-1} \text{ mol}^{-1}$.

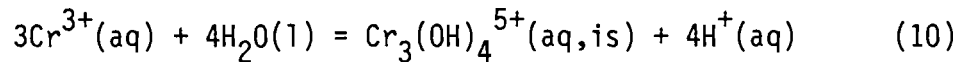
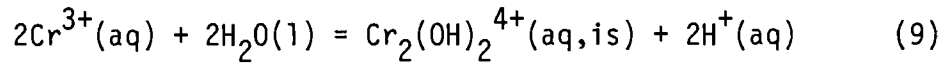
The uncharged hydroxy complex, $\text{Cr}(\text{OH})_3^{\circ}(\text{aq, is})$ may be formed by the reaction,



When the given ΔG° , $24.55 \text{ kcal mol}^{-1}$ (Baes and Mesmer, 1976), is applied, $\Delta G_{f298}^\circ = -199.41 \text{ kcal mol}^{-1}$ for $\text{Cr}(\text{OH})_3^\circ(\text{aq, is})$.

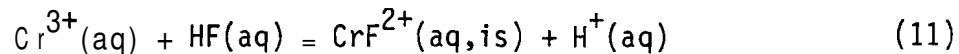
In the presence of excess OH^- , $\text{Cr}(\text{OH})_3^\circ(\text{c})$ dissolves to yield an anion containing Cr(III). In simplistic terms the anion may be represented as $\text{Cr}(\text{OH})_4^{-4}(\text{aq})$ (Dellien et al., 1976), which has a $\Delta G_{f298}^\circ = -243.28 \text{ kcal mol}^{-1}$ (Baes and Mesmer, 1976a).

Other hydroxy complexes may include $\text{Cr}_2(\text{OH})_2^{4+}(\text{aq, is})$ and $\text{Cr}_3(\text{OH})_4^{5+}(\text{aq, is})$. However these polymeric species may form only at elevated temperatures and at relatively high Cr concentrations. Their importance under usual environmental conditions is not clear. Baes and Mesmer (1976) and Thompson (1964) reported thermodynamic values of $\Delta G^\circ = 6.90$ and $11.12 \text{ kcal mol}^{-1}$, respectively, for the reactions,



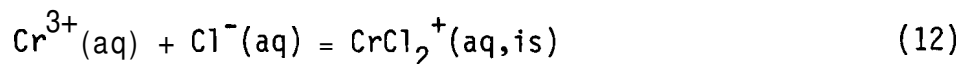
Application of the reported values yields $\Delta G_{f298}^\circ = -214.26 \text{ kcal mol}^{-1}$, $\Delta H_{f298}^\circ = -245.83 \text{ kcal mol}^{-1}$, and $S_{298}^\circ = -76.77 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{Cr}_2(\text{OH})_2^{4+}(\text{aq, is})$. Similarly for $\text{Cr}_3(\text{OH})_4^{5+}(\text{aq, is})$, $\Delta G_{f298}^\circ = -377.31 \text{ kcal mol}^{-1}$, $\Delta H_{f298}^\circ = -430.66 \text{ kcal mol}^{-1}$, and $S_{298}^\circ = -79.51 \text{ cal K}^{-1} \text{ mol}^{-1}$. I derive the free energy of formation of the ion, $\text{CrO}_2^-(\text{aq})$, from data presented by Naumov et al. (1974) to be $-129.14 \text{ kcal mol}^{-1}$.

For the reaction,

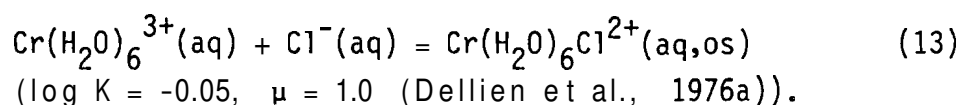


$\Delta G^\circ = 4.92 \text{ kcal mol}^{-1}$ (Thusius, 1971) and $\Delta H^\circ = 3.35 \text{ kcal mol}^{-1}$ (Hale and King, 1967). From these data is derived the following thermodynamic values for $\text{CrF}^{2+}(\text{aq, is})$: $\Delta G_{f298}^\circ = -127.15 \text{ kcal mol}^{-1}$, $\Delta H_{f298}^\circ = -137.60 \text{ kcal mol}^{-1}$ and $S_{298}^\circ = -36.34 \text{ cal K}^{-1} \text{ mol}^{-1}$.

Based on data presented by Thusius (1971), Hale and King (1967), and Dellien and Hepler (1976), I estimate that $\Delta G^\circ = 1.14 \text{ kcal mol}^{-1}$, $\Delta H^\circ = 6.29 \text{ kcal mol}^{-1}$ and $\Delta S^\circ = 17.28 \text{ cal K}^{-1} \text{ mol}^{-1}$ for the reaction,

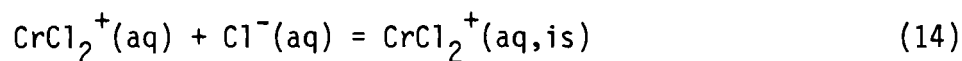


These data lead to $\Delta G_{f298}^\circ = -84.13 \text{ kcal mol}^{-1}$, $\Delta H_{f298}^\circ = -94.44 \text{ kcal mol}^{-1}$ and $S_{298}^\circ = -33.47 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{CrCl}_2^{+}(\text{aq, is})$. The outer sphere complex forms in the reaction,



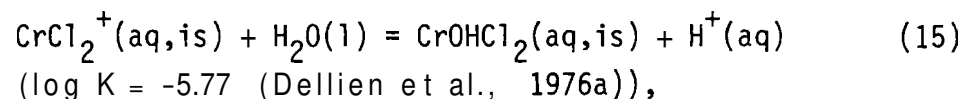
This leads to $\Delta G_{f298}^\circ = -425 \text{ kcal mol}^{-1}$ for $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}^{2+}(\text{aq, os})$.

From Naumov et al. (1974) and Dellien et al. (1976a) $\Delta G^\circ = 0.97 \text{ kcal mol}^{-1}$, $\Delta H^\circ = 4.48 \text{ kcal mol}^{-1}$ and $\Delta S^\circ = 11.78 \text{ cal K}^{-1} \text{ mol}^{-1}$ for the reaction,



From these data I compute $\Delta G_{f298}^\circ = -114.54 \text{ kcal mol}^{-1}$, $\Delta H_{f298}^\circ = -129.90 \text{ kcal mol}^{-1}$, and $S_{298}^\circ = -8.12 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{CrCl}_2^{+}(\text{aq, is})$.

The chlorohydroxy complex, CrOHCl_2 may form under basic conditions in the reaction,

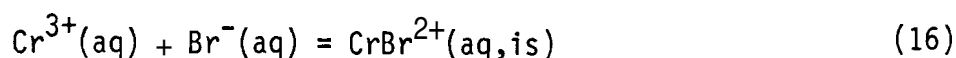


yielding $\Delta G_{f298}^\circ = -163.46 \text{ kcal mol}^{-1}$ for $\text{CrOHCl}_2(\text{aq, is})$.

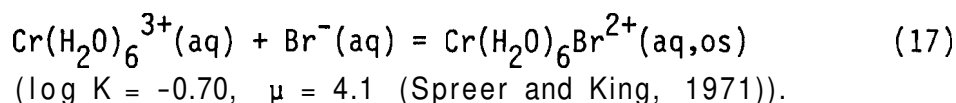
The solvated species of the inner sphere complex, $\text{CrCl}_2^{+}(\text{aq, is})$, represented by $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^{+}(\text{aq})$, exists in cis and trans forms with

$\log K = -0.3$ for cis = trans (Dellien et al., 1976a). Thus, the cis form is slightly more stable by $0.4 \text{ kcal mol}^{-1}$ than the trans form.

Dellien and Hepler (1976) measured $\Delta H^\circ = 8.93 \text{ kcal mol}^{-1}$ for the reaction,



The free energy change of this reaction is reported by Thusius (1971) to be $3.62 \text{ kcal mol}^{-1}$. These data yield $\Delta G_{f298}^\circ = -75.14 \text{ kcal mol}^{-1}$, $\Delta H_{f298}^\circ = -80.91 \text{ kcal mol}^{-1}$ and $S_{298}^\circ = -26.69 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{CrBr}^{2+}(\text{aq, is})$. An outer sphere complex may form as follows:

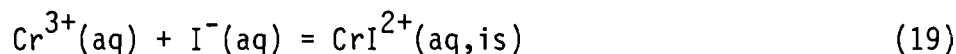


For $\text{Cr}(\text{H}_2\text{O})_6\text{Br}^{2+}(\text{aq, os})$, ■ found that $\Delta G_{f298}^\circ = -418 \text{ kcal mol}^{-1}$.

The Debye-Hueckel relationship,

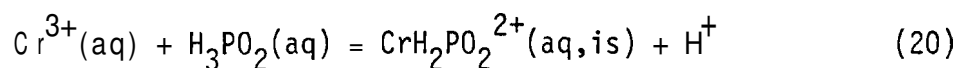
$$-\log q_i = \frac{AZ_i^2 I^{0.5}}{1 + Ba_i I^{0.5}} \quad (18)$$

is used to correct activity coefficients and, thus, to determine $\log K$ at zero ionic strength (Stumm and Morgan, 1970). In this manner, I corrected data from Swaddle and Guastalla (1968) to give $\log K = -5.38$ for the reaction,

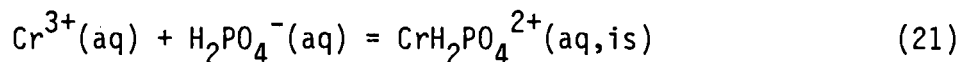


From this I compute $\Delta G_{f298}^\circ = 58.97 \text{ kcal mol}^{-1}$ for CrI^{2+} .

For the reaction,

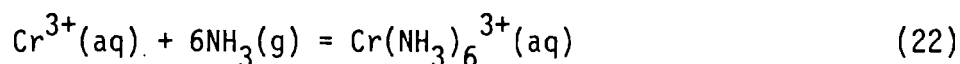


■ extrapolated the kinetic data of Espenson and Binau (1966) to 25°C and determined that $\log K = 0.26$. This value gives $\Delta G_{f298}^{\circ} = -179 \text{ kcal mol}^{-1}$ for $\text{CrH}_2\text{PO}_4^{2+}(\text{aq, is})$. The inner sphere complex $\text{CrH}_2\text{PO}_4^{2+}$ is formed by the reaction between $\text{Cr}(\text{NO}_3)_3$ and H_3PO_4 :

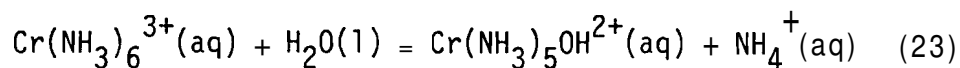


The estimated ΔG° for this reaction is about $-2.7 \text{ kcal mol}^{-1}$ (Aleshechkina et al., 1976), which leads to $\Delta G_{f298}^{\circ} = -327 \text{ kcal mol}^{-1}$ for $\text{CrH}_2\text{PO}_4^{2+}(\text{aq, is})$.

Anderson et al. (1975) estimated $\log B_6 = 12.75$ for the ammination reaction,

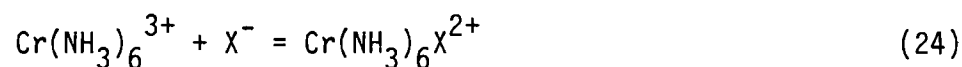


from which I derive $\Delta G_{f298}^{\circ} = -109.48 \text{ kcal mol}^{-1}$ from $\text{Cr}(\text{NH}_3)_6^{3+}(\text{aq})$. The hydrolysis of $\text{Cr}(\text{NH}_3)_6^{3+}$,



has $\log K = 2.29$ (Anderson et al., 1975) and, thus, $\Delta G_{f298}^{\circ} = -150.31 \text{ kcal mol}^{-1}$ for $\text{Cr}(\text{NH}_3)_5\text{OH}^{2+}(\text{aq})$. Hydrolysis of the preceding complex leads to $\text{Cr}(\text{NH}_3)_4\text{OH}^{2+}(\text{aq})$, which exists in cis and trans forms. The ratio of cis- $\text{Cr}(\text{NH}_3)_4(\text{OH})^{2+}$ to trans- $\text{Cr}(\text{NH}_3)_4(\text{OH})^{2+}$ is 4.9 and $\Delta G_{f298}^{\circ} = -197.63 \text{ kcal mol}^{-1}$ for cis- $\text{Cr}(\text{NH}_3)_4(\text{OH})^{2+}(\text{aq})$ (Anderson et al., 1975).

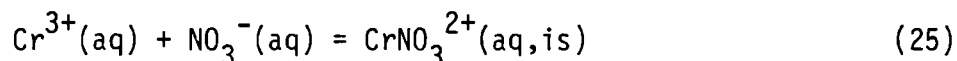
I reevaluated data for the association of $\text{Cr}(\text{NH}_3)_6^{3+}(\text{aq})$ with halide ions presented by Mironov et al. (1977) using the Debye-Hueckel equation (Stumm and Morgan, 1970). Although Mironov et al. (1977) did not give explicit details, I assumed that the outer sphere complex is formed:



I estimate the standard free energies of formation at 298.15 K for

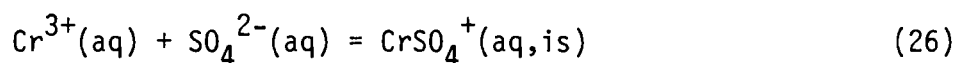
$\text{Cr}(\text{NH}_3)_6\text{X}^{2+}(\text{aq})$, where X^- is Cl^- , Br^- , and I^- , to be, respectively, -141.92, -135.28, and -122.66 $\text{kcal}\cdot\text{mol}^{-1}$.

The investigation of Ardon and Sutin (1967) of the reaction,



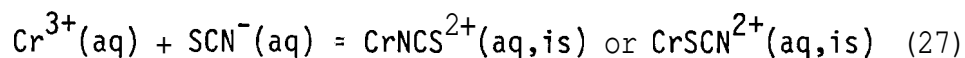
produced $\Delta\text{H}^\circ = 4.5 \pm 0.2 \text{ kcal mol}^{-1}$, $\Delta\text{S}^\circ = 5.9 \pm 0.6 \text{ cal K}^{-1} \text{ mol}^{-1}$ and $\log K = -2.013$ at 25°C . From these data, I estimate the following thermodynamic values for $\text{Cr}(\text{NO}_3)_2^{2+}(\text{aq, is})$: $\Delta\text{G}_{f298}^\circ = -77.78 \text{ kcal mol}^{-1}$, $\Delta\text{H}_{f298}^\circ = -105.86 \text{ kcal mol}^{-1}$, and $\text{S}_{298}^\circ = -23.30 \text{ cal K}^{-1} \text{ mol}^{-1}$.

After correcting for temperature and ionic strength, ΔG° for the reaction,



is estimated to be $-1.08 \text{ kcal mol}^{-1}$ (Fogel et al., 1962). From this value and $\Delta\text{H}^\circ(26) = 7.6 \text{ kcal mol}^{-1}$ measured by Dellien and Hepler (1976), $\Delta\text{G}_{f298}^\circ = -232.90 \text{ kcal mol}^{-1}$, $\Delta\text{H}_{f298}^\circ = -270.60 \text{ kcal mol}^{-1}$ and $\text{S}_{298}^\circ = -30.70 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{CrSO}_4^+(\text{aq, is})$. Masalovich et al. (1975) studied the formation of the complexes arising between CrOH^{2+} and SO_4^{2-} and concluded that two outer-sphere complexes, $[\text{CrOH}]\text{SO}_4$ and $[\text{Cr}_2(\text{OH})_2\text{SO}_4]\text{SO}_4$, and two inner-sphere complexes, $[\text{Cr}_2(\text{OH})_2\text{SO}_4]^{2+}$ and $[\text{Cr}_2(\text{OH})_2(\text{SO}_4)_2]$, are formed. From their data, I obtain the following $\Delta\text{G}_{f298}^\circ$ values: $[\text{CrOH}]\text{SO}_4$, -285.92; $[\text{Cr}_2(\text{OH})_2\text{SO}_4]\text{SO}_4$, -569.08; $[\text{Cr}_2(\text{OH})_2\text{SO}_4]^{2+}$, -393.33; and $[\text{Cr}_2(\text{OH})_2(\text{SO}_4)_2]$, -573.72 kcal mol^{-1} .

The reaction of thiocyanate ion with Cr^{3+} produces both CrSCN^{2+} and CrNCS^{2+} inner-sphere complexes:

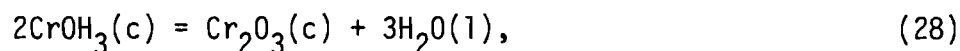


Using data from Armor and Haim (1971), Espenson (1969), Haim and Sutin (1965), Orhanovic and Sutin (1968), Postmus and King (1955), and Thusis

(1971), I find ΔG_{f298}° for CrSCN^{2+} and CrNCS^{2+} to be -27.18 and -34.47 kcal mol^{-1} , respectively.

Cr(III) SOLID PHASES

From data presented by Amacher and Baker (1980), I estimate a value of log K for the reaction,



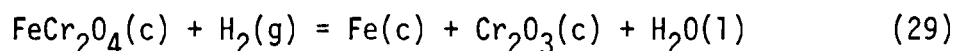
which leads to $\Delta G_{f298}^{\circ} = -254.64$ kcal mol^{-1} for Cr_2O_3 . The reported values are -252.9 (Wagman et al., 1982), -253.2 (Naumov et al., 1974), and -251.69 ± 2.01 kcal mol^{-1} (Robie et al., 1979; Chase et al., 1975). Using $S_{298}^{\circ} = 19.46$ cal K^{-1} mol^{-1} (Robie et al., 1979), $\Delta H_{f298}^{\circ} = -274.14$ kcal mol^{-1} for $\text{Cr}_2\text{O}_3(\text{c})$, which compares with published data of -272.4 (Wagman et al., 1982), -272.7 ± 0.4 (Naumov et al., 1974; Barnes et al., 1974) and -271.2 ± 2.0 kcal mol^{-1} (Robie et al., 1979; Chase et al., 1975).

The standard free energy of formation of $\text{Cr}(\text{OH})_3(\text{c})$, computed from the solubility product, $\log K_{\text{sp}} = -30.07$, reported by von Meyenburg et al. (1973), together with $\Delta G_{f298}^{\circ} = 53.89$ kcal mol^{-1} for $\text{Cr}^{3+}(\text{aq})$ (Vasil'ev et al., 1980), is $\Delta G_{f298}^{\circ} = -207.72$ kcal mol^{-1} . Naumov et al. (1974) list ΔG_{f298}° for this species as -202.4 ± 2.0 kcal mol^{-1} . The data reported for ΔH_{f298}° for $\text{Cr}(\text{OH})_3(\text{c})$ range between -233.2 ± 3 (Naumov et al., 1974) to -254.3 kcal mol^{-1} (Wagman et al., 1982). Naumov et al. (1974) give $S_{298}^{\circ} = 22.8 \pm 3$ cal K^{-1} mol^{-1} which, with ΔG_{f298}° computed above, lead to $\Delta H_{f298}^{\circ} = -238.49$ kcal mol^{-1} for $\text{Cr}(\text{OH})_3(\text{c})$.

The thermodynamic values for $\text{CrF}_3(\text{c})$ given in the literature (Wagman et al., 1982; Naumov et al., 1974; Dellien et al., 1976a; Barnes et al., 1974) generally agree and appear consistent with the values I adopted for $\text{Cr}^{3+}(\text{aq})$. For $\text{CrF}_3(\text{c})$, I accept $\Delta G_{f298}^{\circ} = -260.08$ kcal mol^{-1} , $\Delta H_{f298}^{\circ} = -276.75$ kcal mol^{-1} , and $S_{298}^{\circ} = 22.44$ cal K^{-1} mol^{-1} . Gee and Shelton (1975) produced the following data for $\text{CrCl}_3(\text{c})$: $\Delta G_{f298}^{\circ} = -115.68 \pm 0.96$ kcal mol^{-1} , $\Delta H_{f298}^{\circ} = -132.95 \pm 0.96$ kcal mol^{-1} , $S_{298}^{\circ} = 27.68$ cal K^{-1} mol^{-1} . The

values of ΔH_{f298}° from other compilations or investigations (Wagman et al., 1982; Dellien et al., 1976a; Barnes et al., 1974; Kubaschewski et al., 1967) range from -129.5 to -135.06 kcal mol⁻¹ with mean $\pm 1s = -132.49 \pm 1.81$ kcal mol⁻¹. Thus, Gee and Shelton's (1975) values are within the range of other published data. Using $S_{298}^{\circ} = 38.16$ cal K⁻¹ mol⁻¹ (Naumov et al., 1974) and $\Delta H_{f298}^{\circ} = -94.00$ kcal mol⁻¹ (Barnes et al., 1974) for CrBr₃(c), I derive $\Delta G_{f298}^{\circ} = -87.41$ kcal mol⁻¹. Similarly, for CrI₃, $\Delta S_{298}^{\circ} = 47.10$ cal K⁻¹ mol⁻¹ (Shieh and Gregory, 1973) and $\Delta H_{f298}^{\circ} = -49.33$ kcal mol⁻¹ (Barnes et al., 1974), thus $\Delta G_{f298}^{\circ} = -49.27$ kcal mol⁻¹.

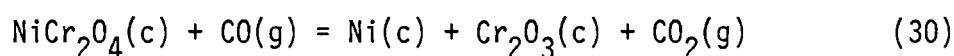
For chromite, FeCr₂O₄(c), $S_{298}^{\circ} = 34.9 \pm 0.4$ cal K⁻¹ mol⁻¹ (Dellien et al., 1976a; Naumov et al., 1974; Robie et al., 1979; Wagman et al., 1982) and the published values of ΔH_{f298}° range between -345.3 (Wagman et al., 1982) to 349.3 ± 0.90 kcal mol⁻¹ (Barnes et al., 1974). For the following equation, $\Delta G^{\circ} = 15.45 \pm 0.46$ kcal mol⁻¹ (Naumov et al., 1974),



Applying $\Delta G_{f298}^{\circ} = -254.64$ kcal mol⁻¹ for Cr₂O₃, as defined above, to this equilibrium produces $\Delta G_{f298}^{\circ} = -326.78$ kcal mol⁻¹ for FeCr₂O₄. Using the published S_{298}° , $\Delta H_{f298}^{\circ} = -351.02$ kcal mol⁻¹.

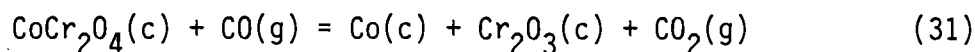
Data presented by Robie et al. (1979) for the spinel, magnesiochromite, MgCr₂O₄, which conform well with values from other sources (Naumov et al., 1974; Dellien et al., 1976a; Parker et al., 1971), are $\Delta G_{f298}^{\circ} = -398.92 \pm 0.20$ kcal mol⁻¹, $\Delta H_{f298}^{\circ} = -4.26.30 \pm 0.20$ kcal mol⁻¹, and $S_{298}^{\circ} = 25.34$ cal K⁻¹ mol⁻¹.

Naumov et al. (1974) give $\Delta G^{\circ} = 1.2 \pm 0.3$ kcal mol⁻¹ and $\Delta H^{\circ} = 2.7 \pm 0.2$ kcal mol⁻¹ for the reaction,



Using these data, $\Delta G_{f298}^{\circ} = -254.64$ kcal mol⁻¹, $\Delta H_{f298}^{\circ} = -274.14$ kcal mol⁻¹ and $S_{298}^{\circ} = 28.80$ cal K⁻¹ mol⁻¹ for NiCr₂O₄(c).

For the reaction,

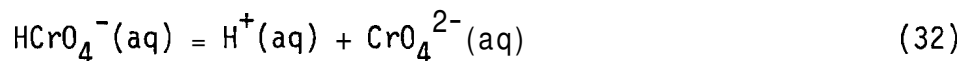


Naumov et al. (1974) report $\Delta G^\circ = 2.6 \pm 0.4 \text{ kcal mol}^{-1}$ and $\Delta H^\circ = 1.8 \pm 0.3 \text{ kcal mol}^{-1}$. From these data I calculate $\Delta G_{f298}^\circ = -318.72 \text{ kcal mol}^{-1}$ and $\Delta H_{f298}^\circ = -343.58 \text{ kcal mol}^{-1}$ for $\text{CoCr}_2\text{O}_4(\text{c})$.

Cr(VI) AQUEOUS IONS AND COMPLEXES

The standard enthalpy of formation of $\text{CrO}_4^{2-}(\text{aq})$ is listed in the literature as -210.60 (Wagman et al., 1982), -209.23 ± 0.4 (Naumov et al., 1974), -210.60 (Dellien et al., 1976a), -210.73 ± 0.44 (Vasil'ev et al., 1981), and $-210.93 \pm 0.45 \text{ kcal mol}^{-1}$ (O'Hare and Boerio, 1975; Barnes et al., 1974). The latter value conforms most closely with the thermodynamic data ■ selected for $\text{Cr}^{3+}(\text{aq})$. O'Hare and Boerio (1975) present data updating the thermodynamic properties of the alkali metal chromates from which they selected K_2CrO_4 and Cs_2CrO_4 , as well as Ag_2CrO_4 , to deduce a value for S_{298}° for $\text{CrO}_4^{2-}(\text{aq})$. The mean value of their calculations is $13.78 \pm 0.46 \text{ cal K}^{-1} \text{ mol}^{-1}$. This value is 1 or 2 $\text{cal K}^{-1} \text{ mol}^{-1}$ higher than values previously published, but the earlier data were generally based on Ag_2CrO_4 solubility studies conducted in 1935 (Dellien et al., 1976a). Using the selected values of ΔH_{f298}° and S_{298}° , ■ compute $\Delta G_{f298}^\circ = -174.81 \text{ kcal mol}^{-1}$ for CrO_4^{2-} .

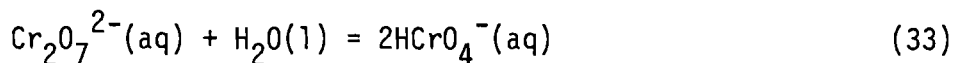
The equilibrium constant for the reaction,



is well established in the literature. For $\log K_{298}^\circ$, values of -6.48 (Dellien et al., 1976a; Benson and Teague, 1980), -6.50 (Naumov et al., 1974; Linge and Jones, 1968a), -6.51 (O'Hare and Boerio, 1975; Smith and Martell, 1976; Baes and Mesmer, 1976), and -6.52 (Hepler, 1958) are published. Selecting $\log K_{298}^\circ = -6.51$, $\Delta G^\circ(32) = 8.88 \text{ kcal mol}^{-1}$. This value, combined with $\Delta G_{f298}^\circ = -174.81 \text{ kcal mol}^{-1}$ for $\text{CrO}_4^{2-}(\text{aq})$ yields

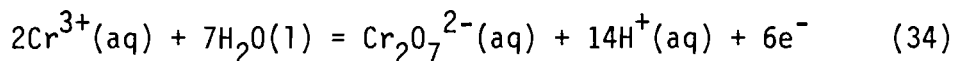
$\Delta G_{f298}^{\circ} = -183.69 \text{ kcal mol}^{-1}$ for HCrO_4^- . Hepler (1958) lists values for $\Delta H^{\circ}(32) = -0.6$ and $-0.8 \text{ kcal mol}^{-1}$ based on measurements of the solubility of $\text{K}_2\text{CrO}_4(\text{c})$. Linge and Jones (1968a) determined acidity constants for reaction (32) at different temperatures and derived $\Delta H^{\circ}(32) = -1.3 \pm 0.5 \text{ kcal mol}^{-1}$. Using the mean of these three values, $-0.9 \text{ kcal mol}^{-1}$ (O'Hare and Boerio, 1975), I derive $\Delta H_{f298}^{\circ} = -210.03 \text{ kcal mol}^{-1}$ for $\text{HCrO}_4^-(\text{aq})$. From these values for ΔG_{f298}° and ΔH_{f298}° , I find $S_{298}^{\circ} = 46.58 \text{ cal K}^{-1} \text{ mol}^{-1}$.

For the equilibrium,

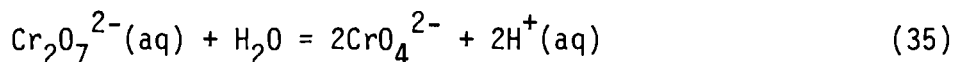


Linge and Jones (1968b), through spectrophotometric measurements, found $K = (2.94 \pm 0.22) \times 10^{-2} \text{ mol kg}^{-1}$ at 25°C . From this I calculate $\Delta G^{\circ}(33) = 2.09 \pm 0.05 \text{ kcal mol}^{-1}$ and $\Delta G_{f298}^{\circ} = -312.79 \text{ kcal mol}^{-1}$ for $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$. For reaction (33), $\Delta H^{\circ} = 4.80 \text{ kcal mol}^{-1}$, based on the work of Linge and Jones (1968b), Hepler (1958), and Vasil'ev et al. (1981, 1977) and, thus, $\Delta H_{f298}^{\circ} = -356.54 \text{ kcal mol}^{-1}$. Combining this value with ΔG_{f298}° , $S_{298}^{\circ} = 67.35 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$.

Naumov et al. (1974) give $\Delta H^{\circ} = 241.6 \text{ kcal mol}^{-1}$ for the reaction,

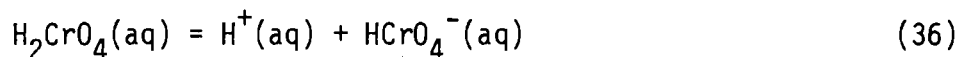


The thermodynamic values selected in this review lead to $\Delta H^{\circ}(34) = 243.27 \text{ kcal mol}^{-1}$, a discrepancy of less than 1%. Similarly for the equilibrium,



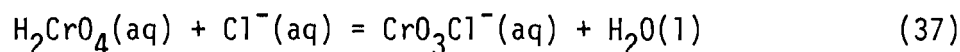
the calculated value of ΔG° , $19.94 \text{ kcal mol}^{-1}$, yields $\log K^{\circ}(35) = -14.62$, which compares favorably with $\log K^{\circ} = -14.49$ reported by Benson and Teague (1980). Arnek (1970) gives $\Delta S^{\circ}(35) = -(55 \pm 0.2) \text{ cal K}^{-1} \text{ mol}^{-1}$ whereas the computed value is $-56.51 \text{ cal K}^{-1} \text{ mol}^{-1}$ from data selected for this report.

Literature values for $\log K^\circ$ for the reaction,



range between 0.70 (Haight et al., 1964) and 0.98 (Naumov et al., 1974). After extrapolating spectrophotometric data given by Haight et al. (1964) to zero ionic strength, $\log K^\circ(36) = 0.86$ or $\Delta G^\circ = -1.17 \text{ kcal mol}^{-1}$. From this value, I obtain $\Delta G_{f298}^\circ = -182.52 \text{ kcal mol}^{-1}$ for $\text{H}_2\text{CrO}_4(\text{aq})$.

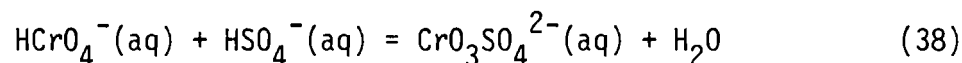
Other aqueous ions of Cr(VI) reported in the literature include CrO_3Cl^- , $\text{CrO}_3\text{H}_2\text{PO}_4^-$, $\text{CrO}_3\text{HPO}_4^{2-}$, and $\text{CrO}_3\text{SO}_4^{2-}$ (Haight et al., 1964; 1974). The chlorochromate species is formed by the reaction of Cl^- with chromic acid:



I used data from Haight et al. (1964) to determine that $\Delta G^\circ(37) = -2.25 \text{ kcal mol}^{-1}$. Thence, $\Delta G_{f298}^\circ = -159.47 \text{ kcal mol}^{-1}$ for $\text{CrO}_3\text{Cl}^-(\text{aq})$.

The free energy of formation of the phosphatochromates, $\text{CrO}_3\text{H}_2\text{PO}_4^-$ and $\text{CrO}_3\text{HPO}_4^{2-}$, is estimated to be -401.68 and $-398.02 \text{ kcal mol}^{-1}$, respectively (Haight et al., 1964, 1974). The acid ionization constant between these two species, $\log K_{a2} = -2.7$, is similar to that ($\log K_a = -2.4$) for the polyphosphate, $\text{H}_3\text{P}_2\text{O}_7^{2-}$ (Snoeyink and Jenkins, 1980).

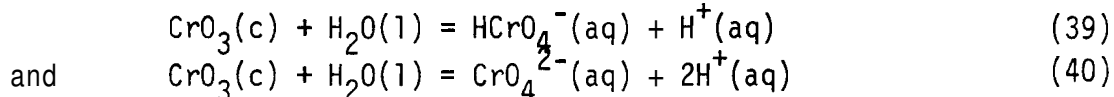
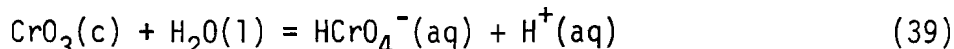
The reaction between bichromate and bisulfate,



was investigated by Haight et al. (1964). They found $\log K^\circ(38) = 0.61$ at ionic strength = 3.0 and 25° . I estimate that $\log K^\circ(38) = 0.51$ at zero ionic strength, and thence $\Delta G_{f298}^\circ = -308.36 \text{ kcal mol}^{-1}$ for $\text{CrO}_3\text{SO}_4^{2-}$.

Cr(VI) SOLID PHASES

The oxide of Cr(VI), CrO_3 , hydrolyzes to form bichromate or chromate in the reactions,



Using data presented by Muldrow and Hepler (1957) and Naumov et al. (1974), $\Delta G_{\text{f}298}^\circ = -122.50 \text{ kcal mol}^{-1}$ for $\text{CrO}_3(\text{c})$.

The solubility data for Ag_2CrO_4 given by Jones et al. (1971) indicates that $\log K_{\text{SP}} = -11.57 \pm 0.01$. From this, $\Delta G_{\text{f}298}^\circ = -153.73 \text{ kcal mol}^{-1}$ for $\text{Ag}_2\text{CrO}_4(\text{c})$. From the variability of K_{SP} with temperature, Jones et al. (1971) determined that $\Delta H_{\text{f}298}^\circ = -175.42 \text{ kcal mol}^{-1}$, which leads to $S_{298}^\circ = 54.63 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{Ag}_2\text{CrO}_4(\text{c})$. The literature values (Wagman et al., 1982) for this compound are $\Delta G_{\text{f}298}^\circ = -153.38 \text{ kcal mol}^{-1}$, $\Delta H_{\text{f}298}^\circ = -174.89 \text{ kcal mol}^{-1}$, and $S_{298}^\circ = 52.0 \text{ cal K}^{-1} \text{ mol}^{-1}$.

Naumov et al. (1974) report the heat of solution of BaCrO_4 as $6.398 \pm 0.018 \text{ kcal mol}^{-1}$ that leads to $\Delta H_{\text{f}298}^\circ = -345.82 \text{ kcal mol}^{-1}$. The solubility product given in the literature (O'Hare and Boerio, 1975; Smith and Martell, 1976), $2.14 \times 10^{-10} \text{ mol}^2 \text{ kg}^{-2}$, yields $\Delta G_{\text{f}298}^\circ = -322.02 \text{ kcal mol}^{-1}$. These data combine to give $S_{298}^\circ = 38.86 \text{ cal K}^{-1} \text{ mol}^{-1}$ for BaCrO_4 .

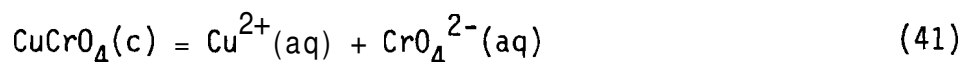
Shidlovskii et al. (1971a) give the heat of solution for CaCrO_4 as $-6.5 \text{ kcal mol}^{-1}$. From this value, $\Delta H_{\text{f}298}^\circ = -334.23 \text{ kcal mol}^{-1}$. ■ estimate $S_{298}^\circ = 32.44 \text{ cal K}^{-1} \text{ mol}^{-1}$ (see page 3 of this report) and thus $\Delta G_{\text{f}298}^\circ = -310.20 \text{ kcal mol}^{-1}$ for $\text{CaCrO}_4(\text{c})$.

An extensive amount of work has been published on the thermodynamic properties of various chromates of Cs (O'Hare and Boerio, 1975; Lyon et al., 1975, 1976; Frederickson et al., 1980; Shidlovskii et al., 1971; Denielou et al., 1975). The enthalpy of solution of Cs_2CrO_4 , given by

O'Hare and Boerio (1975), is $7.51 \pm 0.03 \text{ kcal mol}^{-1}$, which leads to $\Delta H_{f298}^{\circ} = -341.78 \text{ kcal mol}^{-1}$ for $\text{Cs}_2\text{CrO}_4(\text{c})$. From a series of heat capacity measurements, Lyon et al. (1975) were able to derive the standard entropy of $\text{Cs}_2\text{CrO}_4(\text{c})$: $S_{298}^{\circ} = 54.63 \pm 0.05 \text{ cal } ^{\circ}\text{K}^{-1} \text{ mol}^{-1}$. This value is confirmed by Frederickson et al. (1980). From these data, I calculate the standard free energy of formation to be $\Delta G_{f298}^{\circ} = -315.01 \text{ kcal mol}^{-1}$. This is in excellent agreement with the value published by O'Hare and Boerio (1975): $-315.04 \pm 0.46 \text{ kcal mol}^{-1}$.

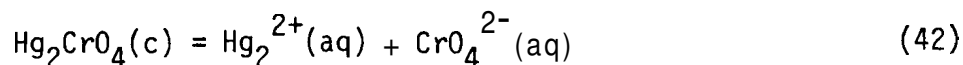
Two separate series of calorimetric measurements, conducted by O'Hare et al. (1976), determined the standard enthalpy of formation of $\text{Cs}_2\text{Cr}_2\text{O}_7(\text{c})$ to be $\Delta H_{f298}^{\circ} = -499.79 \pm 0.68 \text{ kcal mol}^{-1}$. Heat capacity experiments by Lyon et al. (1976) led to the standard entropy for $\text{Cs}_2\text{Cr}_2\text{O}_7$ of $S_{298}^{\circ} = 78.89 \pm 0.08 \text{ cal K}^{-1} \text{ mol}^{-1}$. Using these data I find $\Delta G_{f298}^{\circ} = -456.63 \text{ kcal mol}^{-1}$, which conforms well with $\Delta G_{f298}^{\circ} = -456.67 \pm 0.67 \text{ kcal mol}^{-1}$ determined by Lyon et al. (1976).

Naumov et al. (1974) give a value of $\log K_{\text{SP}} = -5.44$ for the reaction,



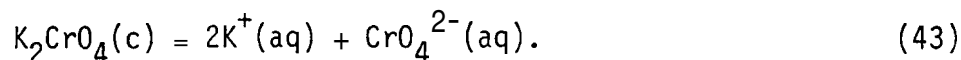
which leads to $\Delta G_{f298}^{\circ} = -166.56 \text{ kcal mol}^{-1}$ for $\text{CuCrO}_4(\text{c})$.

For the dissolution of $\text{Hg}_2\text{CrO}_4(\text{c})$,



$\log K_{\text{SP}}$ is reported to be -8.70 (Naumov et al., 1974; Smith and Martell, 1976). From this I derive $\Delta G_{f298}^{\circ} = -149.97 \text{ kcal mol}^{-1}$ for $\text{Hg}_2\text{CrO}_4(\text{c})$.

Using the Debye-Hueckel equation and coefficients presented by Vasil'ev and Yasinskii (1978), I recalculated the enthalpy data of Muldrow and Hepler (1957) for the reaction,



At infinite dilution they report $\Delta H^\circ(43) = 4.2 \pm 0.1 \text{ kcal mol}^{-1}$, the value quoted by a number of authors (Naumov et al., 1974; O'Hare and Boerio, 1975; Barnes et al., 1974; Hepler, 1958; Shidlovskii et al., 1971b). The recalculated value, $4.25 \text{ kcal mol}^{-1}$, is within the limits of experimental error. From this value, $\Delta H_{f298}^\circ = -335.72 \text{ kcal mol}^{-1}$ for K_2CrO_4 , which agrees closely with O'Hare and Boerio (1975) who report $\Delta H_{f298}^\circ = -335.67 \pm 0.46 \text{ kcal mol}^{-1}$. Popov and Kolesov (1956) measured $\Delta S_{f298}^\circ = -86.3 \pm 1.3 \text{ cal K}^{-1} \text{ mol}^{-1}$ and quote a value of $-87.4 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{K}_2\text{CrO}_4(\text{c})$. The mean of these data leads to $S_{298}^\circ = 47.76 \text{ cal K}^{-1} \text{ mol}^{-1}$ and, thence, $\Delta G_{f298}^\circ = -309.82 \text{ kcal mol}^{-1}$ for $\text{K}_2\text{CrO}_4(\text{c})$.

Vasil'ev et al. (1981) investigated the enthalpy of solution of $\text{K}_2\text{Cr}_2\text{O}_7(\text{c})$ employing calorimetry at 25°C . From their data I calculate $\Delta G_{f298}^\circ = -492.21 \text{ kcal mol}^{-1}$ for $\text{K}_2\text{Cr}_2\text{O}_7(\text{c})$. The standard entropy of formation of this compound is reported to be $\Delta S_{f298}^\circ = -143.8 \pm 2.3 \text{ cal K}^{-1} \text{ mol}^{-1}$ (Popov and Kolesov, 1956), which yields $\Delta S_{298}^\circ = 70.00 \text{ cal K}^{-1} \text{ mol}^{-1}$. I compute the standard free energy of formation to be $\Delta G_{f298}^\circ = -449.33 \text{ kcal mol}^{-1}$.

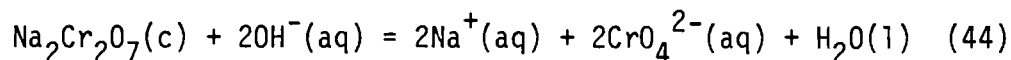
The heat of solution of $\text{Li}_2\text{CrO}_4(\text{c})$ is $-10.8 \pm 0.1 \text{ kcal mol}^{-1}$ according to Shidlovskii et al. (1971b). From this value I derive $\Delta H_{f298}^\circ = -333.23 \text{ kcal mol}^{-1}$. O'Hare and Boerio (1975) selected $\Delta S_{f298}^\circ = -82.7 \pm 2.2 \text{ cal K}^{-1} \text{ mol}^{-1}$ for Li_2CrO_4 . However, from analysis of their data I chose $-83.32 \text{ cal K}^{-1} \text{ mol}^{-1}$ for this value, and thence $S_{298}^\circ = 34.29 \text{ cal K}^{-1} \text{ mol}^{-1}$. From these data I derive $\Delta G_{f298}^\circ = -308.39 \text{ kcal mol}^{-1}$ for Li_2CrO_4 .

The heat of formation of $\text{MgCrO}_4(\text{c})$, $\Delta H_{298}^\circ = -301.25 \text{ kcal mol}^{-1}$, is estimated earlier in this report (Table 1) based on the relationships between analogous chromates and tungstates of the alkaline earth metals. The entropy of solution is similarly computed (Table 2), which leads to $S_{298}^\circ = 27.41 \text{ cal K}^{-1} \text{ mol}^{-1}$. From these data I find that $\Delta G_{f298}^\circ = -276.17 \text{ kcal mol}^{-1}$ for $\text{MgCrO}_4(\text{c})$.

The heat of formation of $(\text{NH}_4)_2\text{CrO}_4(\text{c})$ is given by Barnes et al. (1974) as $-276.82 \pm 3.01 \text{ kcal mol}^{-1}$. From data presented in Table 5, I

estimate $S_{298}^{\circ} = 57.68 \text{ cal K}^{-1} \text{ mol}^{-1}$ that leads to $\Delta G_{f298}^{\circ} = -212.24 \text{ kcal mol}^{-1}$ for $(\text{NH}_4)_2\text{CrO}_4(\text{c})$.

The enthalpy of solution for $\text{Na}_2\text{CrO}_4(\text{c})$ listed in the literature (Naumov et al., 1974; O'Hare and Boerio, 1975; Nelson et al., 1960) is $-4.57 \pm 0.10 \text{ kcal mol}^{-1}$. From this $\Delta H_{f298}^{\circ} = -321.18 \text{ kcal mol}^{-1}$. Ferrante et al. (1972) determined $S_{298}^{\circ} = 42.21 \text{ cal K}^{-1} \text{ mol}^{-1}$, thence I compute $\Delta G_{f298}^{\circ} = -295.54 \text{ kcal mol}^{-1}$. These values are within the experimental error of O'Hare and Boerio (1975), who list $\Delta H_{f298}^{\circ} = -321.22 \pm 0.46 \text{ kcal mol}^{-1}$ and $\Delta G_{f298}^{\circ} = -295.61 \pm 0.46 \text{ kcal mol}^{-1}$ for $\text{Na}_2\text{CrO}_4(\text{c})$. The calorimetric measurements of Nelson et al. (1960) for the reaction,



yield $\Delta H^{\circ} = -21.37 \pm 0.18 \text{ kcal mol}^{-1}$. From this value I derive $\Delta H_{f298}^{\circ} = -473.71 \text{ kcal mol}^{-1}$ for $\text{Na}_2\text{Cr}_2\text{O}_7(\text{c})$. I compute $\Delta G_{f298}^{\circ} = -431.61 \text{ kcal mol}^{-1}$ from $S_{298}^{\circ} = 66.20 \text{ cal K}^{-1} \text{ mol}^{-1}$ given by Naumov et al. (1974).

Dellien et al. (1976b) determined calorimetrically that $\Delta H_{f298}^{\circ} = -221.56 \text{ kcal mol}^{-1}$ for $\text{PbCrO}_4(\text{c})$. This value when combined with $\log K_{\text{sp}} = -13.75$ (O'Hare and Boerio, 1915) yields $S_{298}^{\circ} = -44.54 \text{ cal K}^{-1} \text{ mol}^{-1}$ and $\Delta G_{f298}^{\circ} = -199.31 \text{ kcal mol}^{-1}$ for $\text{PbCrO}_4(\text{c})$.

The heat of solution of $\text{Rb}_2\text{CrO}_4(\text{c})$ is $5.90 \pm 0.10 \text{ kcal mol}^{-1}$ according to Shidlovskii et al. (1971b), which yields $\Delta H_{f298}^{\circ} = -336.86 \text{ kcal mol}^{-1}$. Lyon et al. (1975) estimate $S_{298}^{\circ} = 52.01 \text{ cal K}^{-1} \text{ mol}^{-1}$ and I determine $\Delta G_{f298}^{\circ} = -310.51 \text{ kcal mol}^{-1}$ for $\text{Rb}_2\text{CrO}_4(\text{c})$.

The entropy of $\text{SrCrO}_4(\text{c})$ is estimated by O'Hare and Boerio (1975) to be $35.5 \pm 1.3 \text{ cal K}^{-1} \text{ mol}^{-1}$. $\log K_{\text{sp}}$ is given in the literature as -4.65 ± 0.1 (Naumov et al., 1974) and -4.70 (O'Hare and Boerio, 1975). The mean of these values corresponds to $\Delta G_{\text{sol}}^{\circ} = 6.38 \text{ kcal mol}^{-1}$ and thus $\Delta G_{f298}^{\circ} = -314.90 \text{ kcal mol}^{-1}$. Using these data, I derive $\Delta H_{f298}^{\circ} = -338.96 \text{ kcal mol}^{-1}$ for $\text{SrCrO}_4(\text{c})$.

The log solubility product for $\text{Ti}_2\text{CrO}_4(\text{c})$, given as -12.01 (Naumov et al., 1974; Dellien et al., 1976a; Smith and Martell, 1976), yields $\Delta G_{\text{f}298}^{\circ} = -206.68 \text{ kcal mol}^{-1}$. The literature lists $S_{298}^{\circ} = 67.5 \text{ cal K}^{-1} \text{ mol}^{-1}$ (Wagman et al., 1982) which Dellien et al. (1976a), suspecting an error in the reported data, consider too high. Dellien et al. (1976a) estimate $S_{298}^{\circ} = 61 \text{ cal K}^{-1} \text{ mol}^{-1}$ in line with analogous compounds. These values yield $\Delta H_{\text{f}298}^{\circ} = -233.68 \text{ kcal mol}^{-1}$ compared to reported values of about $-226 \text{ kcal mol}^{-1}$ (Wagman et al., 1982; Dellien et al., 1976a).

THERMODYNAMIC PROPERTIES OF Cr AND ITS SOLID
COMPOUNDS AND AQUEOUS SPECIES

The values of standard entropy, standard enthalpy of formation, and standard free energy of formation for Cr and its solid and aqueous species are selected after evaluation of available data as presented in the previous section. The data for ancillary elements and species relevant to this study, given in Tables 6 and 7, are primarily based on the CODATA report of 1977 (CODATA Task Group, 1978) which is the accepted international source of recommended values for thermodynamics. ■ used data from the National Bureau of Standards (Wagman et al., 1982) to supplement CODATA with occasional reference to other sources (Naumov et al., 1974; O'Hare and Boerio, 1975; Smith and Martell, 1976).

The data for Cr in Tables 8 and 9 are based, as much as possible, on the best available current information. Values that were repeatedly cited by recent compilations, and for which no current measurements were available, were accepted providing they did not conflict when combined with recent measurements of other species. In case of conflict, ■ combined original measurements of log K, heat of reaction, or other available data with more recent determinations of standard thermodynamic values of formation to yield the listed values. In some cases, averages of two similar but separately reported quantities were used or ■ selected the most appropriate value to conform to current data. The basis for selection of data centered on conformation with the recent studies of Vasil'ev et al. (1977a,b, 1978, 1980, 1981) for Cr^{3+} data and O'Hare and Boerio (1975) for CrO_4^{4-} data.

TABLE 6. Entropies of Ancillary Elements Relevant to This Study.

Element	S_{298}° , cal K ⁻¹ mol ⁻¹	Reference
H ₂ (g)	31.207	CODATA 1978
O ₂ (g)	49.005	CODATA 1978
Ag(c)	10.17	CODATA 1978
Ba	(15.0)	O'Hare & Boerio, 1975
Br ₂ (l)	36.379	CODATA 1978
Ca(c)	9.93	CODATA 1978
Cl ₂ (g)	53.290	CODATA 1978
Cs(c)	20.37	CODATA 1978
Cu(c)	7.92	CODATA 1978
F ₂ (g)	48.443	CODATA 1978
Fe(c)	6.520	Wagman et al., 1982
Hg(l)	18.14	CODATA 1978
I ₂ (c)	27.758	CODATA 1978
K(c)	15.46	CODATA 1978
Li(c)	6.96	CODATA 1978
Mg(c)	7.81	CODATA 1978
Na(c)	12.26	CODATA 1978
Pb(c)	15.49	CODATA 1978
Rb(c)	18.35	CODATA 1978
Sr(c)	12.5	Wagman et al., 1982

TABLE 7. Thermodynamic Data for Ancillary Aqueous Species Relevant to This Study.

Species	ΔG_{f298}° , kcal mol ⁻¹	ΔH_{f298}° , kcal mol ⁻¹	S_{298}° , cal K ⁻¹ mol ⁻¹	Reference
H ₂ O(l)	-56.690	-68.315	16.718	CODATA 1978
e ⁻	0	0	15.6035	Wagman et al., 1982
H ⁺	0	0	0	CODATA 1978
OH ⁻	-37.60	-54.977	-2.56	CODATA 1978
Ag ⁺	18.43	25.275	17.53	CODATA 1978
Ba ²⁺	-134.02	-128.50	2.30	Wagman et al., 1982
Br ⁻	-24.87	-29.04	19.80	CODATA 1978
Ca ²⁺	-132.12	-129.80	-13.5	CODATA 1978
Cl ⁻	-31.38	-39.933	13.56	CODATA 1978
CNS ⁻	22.11	18.27	34.46	Wagman et al., 1982
Cs ⁺	-69.72	-61.76	31.75	CODATA 1978
Cu ²⁺	15.68	15.70	-23.2	CODATA 1978
F ⁻	-67.34	-80.15	-3.15	CODATA 1978
Fe ²⁺	-18.85	-21.3	32.9	Wagman et al., 1982
Hg ₂ ²⁺	36.72	39.87	15.66	CODATA 1978
Hg ²⁺	39.36	40.67	-8.68	CODATA 1978
I ⁻	-12.41	-13.60	25.50	CODATA 1978
K ⁺	-67.51	-60.27	24.15	CODATA 1978
Li ⁺	-69.93	-66.552	2.70	CODATA 1978
Mg ²⁺	-108.70	-111.58	-33.01	Wagman et al., 1982
NH ₄ ⁺	-19.00	-31.85	26.57	CODATA 1978
NH ₃ (g)	-3.93	-10.98	46.05	CODATA 1978
Na ⁺	-62.59	-57.433	13.96	CODATA 1978
NO ₃ ⁻	-26.63	-49.56	35.12	CODATA 1978 Wagman et al., 1982
H ₂ PO ₄ ⁻	-270.16	--	--	Smith & Martell, 1976
HPO ₄ ²⁻	-260.34	--	--	Wagman et al., 1982
Pb ²⁺	-5.73	0.22	4.2	CODATA 1978
Rb ⁺	-67.78	-60.02	28.79	CODATA 1978
SO ₄ ²⁻	-177.93	-217.40	4.50	CODATA 1978
HSO ₄ ⁻	-180.48	--	--	Naumov et al., 1974
Sr ²⁺	-133.71	-130.45	-7.80	Wagman et al., 1982
Tl ⁺	-7.74	1.28	30.00	Wagman et al., 1982

TABLE 8. Thermodynamic Values for Solid Compounds Containing Cr.

Species	ΔG_{f298}° , kcal mol ⁻¹	ΔH_{f298}° , kcal mol ⁻¹	S_{298}° , cal K ⁻¹ mol ⁻¹	Reference
Cr (metal)	0	0	5.68	Wagman et al., 1982
Cr ₂ O ₃ (escolaitite)	-254.64	-274.14	19.40	Postmus and King, 1955
CrO ₃	-122.50	-141.37	15.9	Muldrow and Hepler, 1957
Cr(OH) ₂	-142.61	-162.42	19.4	Naumov et al., 1974
Cr(OH) ₃	-207.72	-238.49	22.8	Naumov et al., 1974
CrBr ₃	-87.14	-97.00	38.16	Naumov et al., 1974
CrCl ₂	-85.1	-94.5	27.56	Wagman et al., 1982
CrCl ₃	-115.68	-132.95	27.68	Gee & Shelton, 1975
CrF ₃	-260.08	-276.75	22.44	Wagman et al., 1982
CrI ₃	-49.27	-49.33	47.10	Shieh and Gregory, 1973
Ag ₂ CrO ₄	-153.73	-174.42	54.63	Muldrow and Hepler, 1957
BaCrO ₄	-321.02	-345.82	38.86	O'Hare and Boerio, 1975
CaCrO ₄	-310.20	-334.23	32.44	Shidlovskii et al., 1971
Cs ₂ CrO ₄	-315.01	-341.78	54.63	O'Hare and Boerio, 1975
Cs ₂ Cr ₂ O ₇	-456.63	-499.789	78.89	O'Hare et al., 1976
CuCrO ₄	-166.56	--	--	Naumov et al., 1974
Hg ₂ CrO ₄	-149.97	--	--	Naumov et al., 1974
K ₂ CrO ₄ (tarapacacite)	-309.82	-335.72	47.76	Muldrow and Hepler, 1957 Popov and Kolesov, 1956
K ₂ Cr ₂ O ₇ (lopezite)	-449.33	-492.21	70.00	Vasil'ev et al., 1977b
Li ₂ CrO ₄	-308.39	-333.23	34.29	O'Hare and Boerio, 1975 Shidlovskii et al., 1971
MgCrO ₄	-276.17	-301.25	27.41	Estimated
(NH ₄) ₂ CrO ₄	-212.26	-282.82	57.68	Barnes et al., 1974 Estimated
Na ₂ CrO ₄	-295.54	-321.18	42.21	O'Hare and Boerio, 1975
Na ₂ Cr ₂ O ₇	-431.61	-473.71	66.20	Nelson et al., 1960
PbCrO ₄ (crocoite)	-199.31	-221.56	44.54	O'Hare and Boerio, 1975
Rb ₂ CrO ₄	-310.51	-336.86	52.01	Lyon et al., 1975
SrCrO ₄	-314.90	-343.81	35.5	O'Hare and Boerio, 1975
Tl ₂ CrO ₄	-206.68	-233.68	61.00	Dellien et al., 1976a
FeCr ₂ O ₄ (chromite)	-326.78	-351.02	34.9	Wagman et al., 1982
MgCr ₂ O ₄ (magnesi- chromite)	-398.92	-426.30	25.34	Robie et al., 1979

TABLE 9. Thermodynamic Values for Aqueous Species and Complexes of Cr.

Species	ΔG_{f298}° , kcal mol ⁻¹	ΔH_{f298}° , kcal mol ⁻¹	S_{298}° , cal K ⁻¹ mol ⁻¹	Reference
Cr ²⁺	-43.99	-34.30	6.97	Cotton and Wilkinson, 1972 Barnes et al., 1974
Cr ³⁺	-53.89	-60.80	-64.31	Vasil'ev et al., 1977a, 1978, 1980
CrOH ²⁺	-105.23	-116.78	-24.14	Smith and Martell, 1976
Cr(OH) ₂ ⁺	-153.35	-177.29	-10.03	von Meyenburg et al., 1973 Baes and Mesmer, 1976
Cr(OH) ₃ [°]	-199.41	--	--	Baes and Mesmer, 1976
Cr ₂ (OH) ₂ ⁴⁺	-214.26	-245.83	-76.77	Baes and Mesmer, 1976 Thompson, 1964
Cr ₃ (OH) ₄ ⁵⁺	-377.31	-430.66	-79.51	Baes and Mesmer, 1976 Thompson, 1964
Cr(OH) ₄ ⁻	-243.28	--	--	Baes and Mesmer, 1976
CrO ₂ ⁻	-129.14	--	--	Naumov et al., 1974
CrBr ²⁺	-75.14	-80.91	-26.69	Dellien and Hepler, 1976 Thusius, 1971
CrCl ²⁺	-84.13	-94.44	-33.47	Dellien and Hepler, 1976 Thusius, 1971 Hale and King, 1967
CrCl ₂ ⁺	-114.54	-129.90	-8.12	Naumov et al., 1974 Dellien et al., 1976a
CrOHC1 ₂	-163.46	--	--	Dellien et al., 1976a
CrNCS ²⁺	-34.47	--	--	Armor and Haim, 1965 Espenson, 1969 Haim and Sutin, 1965 Orhanovic and Sutin, 1968
CrSCN ²⁺	-27.18	--	--	Postmus and King, 1955 Thusius, 1971
CrF ²⁺	-127.15	-137.60	-36.34	Dellien and Hepler, 1976 Thusius, 1971
CrI ²⁺	-58.97	--	--	Swaddle and Cuastalla, 1968
Cr(NH ₃) ₆ ³⁺	-109.48	--	--	Anderson et al., 1975
Cr(NH ₃) ₅ (OH) ²⁺	-150.31	--	--	Anderson et al., 1975
<i>cis</i> - Cr(NH ₃) ₄ (OH) ₂ ⁺	-188.58	--	--	Anderson et al., 1975
<i>trans</i> - Cr(NH ₃) ₄ (OH) ₂ ⁺	-187.63	--	--	Anderson et al., 1975
Cr(NH ₃) ₆ Cl ²⁺	-141.92	--	--	Mironov et al., 1977

TABLE 9. (Continued)

Species	ΔG_{f298}° , kcal mol ⁻¹	ΔH_{f298}° , kcal mol ⁻¹	S_{298}° , cal K ⁻¹ mol ⁻¹	Reference
Cr(NH ₃) ₆ Br ²⁺	-135.28	--	--	Mironov et al., 1977
Cr(NH ₃) ₆ I ²⁺	-122.66	--	--	Mironov et al., 1977
Cr(NO ₃) ₃ ²⁺	-77.78	-105.86	-23.30	Ardon and Sutin, 1967
CrH ₂ PO ₄ ²⁺	-327.00	--	--	Aleshechkina et al., 1976
CrSO ₄ ⁺	-232.90	-270.60	-30.70	Dellien and Hepler, 1976 Fogel et al., 1962
[CrOH]SO ₄	-285.92	--	--	Masalovich et al., 1975
[Cr ₂ (OH) ₂ SO ₄] ₂ SO ₄	-569.08	--	--	Masalovich et al., 1975
[Cr ₂ (OH) ₂ SO ₄] ²⁺	-393.33	--	--	Masalovich et al., 1975
[Cr ₂ (OH) ₂ (SO ₄) ₂]	-573.72	--	--	Masalovich et al., 1975
CrO ₄ ²⁻	-174.81	-210.93	13.78	O'Hare and Boerio, 1975
HCrO ₄ ⁻	-183.69	-210.03	46.58	O'Hare and Boerio, 1975 Linge and Jones, 1968 Hepler, 1958
H ₂ CrO ₄ ^o	-182.52	--	--	Naumov et al., 1974 Haight et al., 1964
Cr ₂ O ₇ ²⁻	-312.79	-356.54	67.35	O'Hare and Boerio, 1975
CrO ₃ Cl ⁻	-159.47	--	--	Haight et al., 1964 Haight et al., 1974
CrO ₃ H ₂ PO ₄ ⁻	-401.68	--	--	Haight et al., 1964 Haight et al., 1974
CrO ₃ HPO ₄ ²⁻	-398.02	--	--	Haight et al., 1964 Haight et al., 1974
CrO ₃ SO ₄ ²⁻	-308.36	--	--	Haight et al., 1964
NaCrO ₄ ⁻	-238.35	--	--	Turner et al., 1981
KCrO ₄ ⁻	-243.41	--	--	Turner et al., 1981

For the data in Tables 10 and 11, compilations of the thermodynamics of reactions of Cr species, I focus on two environmentally important species, $\text{Cr(OH)}_2^{\text{t}}$ and CrO_4^{2-} . As discussed in the next section, these two species appear to predominate in most natural waters between pH 6 and 8. In writing the equations in Tables 10 and 11, I consider either $\text{Cr(OH)}_2^{\text{t}}$ or CrO_4^{2-} to be the product species. Also, I consistently include any H_2O as a reactant and the appropriate dissociation product, H^+ or OH^- , as a product. Any reactions between product species, such as Fe^{2+} with OH^- , are not considered. I limit oxidation-reduction reactions to a few solids and to the major aqueous species.

CHROMIUM IN THE ENVIRONMENT

The distribution of Cr among its aqueous inorganic species in the environment is, according to **thermodynamic** considerations demonstrated by the data in Tables 8-11, highly dependent upon pH and Eh and, to a lesser degree, the presence of complexing ligands. The dramatic effect of pH can be seen in Figure 2, which shows the relative amounts of various species of Cr(III) with respect to $\text{Cr(OH)}_2^{\text{t}}$ as a function of pH. This figure omits the Cr(VI) species, CrO_4^{2-} and HCrO_4^- , which predominate at $\text{pE} > 3$ at pH 10 to $\text{pE} > 15$ at pH 4. To better illustrate the effect of redox potential, plots are constructed for pH 6 and 8 of $\log [x]/[\text{Cr(OH)}_2^{\text{t}}]$ as a function of pE (Figure 3). These plots show that in distilled water at pH 6, $\text{Cr(OH)}_2^{\text{t}}$ and HCrO_4^- are the dominant Cr(III) and Cr(VI) species, respectively, whereas the principal species at pH 8 are Cr(OH)_3° and CrO_4^{2-} .

Another perspective on the distribution of aqueous inorganic Cr species is shown in Figures 4-6, which illustrate the abrupt change in percent distribution among Cr species that theoretically occurs at a critical redox potential. Figures 4 and 5 are distributions in freshwater at pH 6 and 9, respectively. Before plotting Figure 6, the distribution of Cr in seawater at pH 8, I recalculated log K values to account for the ionic strength of seawater. As can be seen, NaCrO_4^- may be an important species in seawater. These values conform well with the model of Turner et al. (1981) for freshwater, who predict 74% HCrO_4^- at pH 6 and 100%

TABLE 10. Thermodynamic Values for Reactions Involving Solid Cr Compounds.

Reaction	ΔH° kcal mol ⁻¹	ΔG° kcal mol ⁻¹	log K
Cr(metal) = Cr ³⁺ + 3e ⁻	-60.80	-53.89	39.51
CrO ₃ + 3H ₂ O + 3e ⁻ = Cr(OH) ₂ ⁺ + 4OH ⁻	-50.88	-11.18	8.20
1/2Cr ₂ O ₃ + 3/2H ₂ O = Cr(OH) ₂ ⁺ + OH ⁻	7.27	21.40	-15.69
Cr(OH) ₃ (c) = Cr(OH) ₂ ⁺ + OH ⁻	6.22	16.77	-12.29
Cr(OH) ₂ = Cr(OH) ₂ ⁺ + e ⁻	-14.87	-10.74	7.87
CrBr ₃ + 2H ₂ O = Cr(OH) ₂ ⁺ + 3Br ⁻ + 2H ⁺	-33.78	-27.44	20.12
CrCl ₂ + 2H ₂ O = Cr(OH) ₂ ⁺ + 2Cl ⁻ + 2H ⁺ + e ⁻	-26.02	-17.63	12.92
CrCl ₃ + 2H ₂ O = Cr(OH) ₂ ⁺ + 3Cl ⁻ + 2H ⁺	-27.50	-18.43	13.51
CrF ₃ + 2H ₂ O = Cr(OH) ₂ ⁺ + 3F ⁻ + 2H ⁺	-4.36	-18.09	-13.26
CrI ₃ + 2H ₂ O = Cr(OH) ₂ ⁺ + 3I ⁻ + 2H ⁺	-32.13	-27.93	20.48
1/2FeCr ₂ O ₄ + 2H ₂ O = Cr(OH) ₂ ⁺ + 1/2Fe ²⁺ + 2OH ⁻	14.25	38.80	-28.44
1/2MgCr ₂ O ₄ + 2H ₂ O = Cr(OH) ₂ ⁺ + 1/2Mg ²⁺ + 2OH ⁻	6.75	29.94	-21.95
1/2Cr ₂ O ₃ + 5/2H ₂ O = CrO ₄ ²⁻ + 5H ⁺ + 3e ⁻	96.93	94.24	-69.08
CrO ₃ + H ₂ O = CrO ₄ ²⁻ + 2H ⁺	-1.24	4.38	-3.21
Cr(OH) ₂ + 2H ₂ O = CrO ₄ ²⁻ + 6H ⁺ + 4e ⁻	88.12	81.18	-59.51
Cr(OH) ₃ + H ₂ O = CrO ₄ ²⁻ + 5H ⁺ + 3e ⁻	95.88	89.60	-65.69
Ag ₂ CrO ₄ = CrO ₄ ²⁻ + 2Ag ²⁺	14.04	15.78	-11.57
BaCrO ₄ = CrO ₄ ²⁻ + Ba ²⁺	6.39	12.19	-8.94
CaCrO ₄ = CrO ₄ ²⁻ + Ca ²⁺	-6.50	3.27	-2.40
Cs ₂ CrO ₄ = CrO ₄ ²⁻ + 2Cs ⁺	7.33	0.76	-0.56
1/2Cs ₂ Cr ₂ O ₇ + 1/2H ₂ O = CrO ₄ ²⁻ + Cs ⁺ + H ⁺	11.40	12.13	-8.89
CuCrO ₄ = CrO ₄ ²⁻ + Cu ²⁺	--	-7.43	-5.45
Hg ₂ CrO ₄ = CrO ₄ ²⁻ + Hg ₂ ²⁺	--	-11.88	-8.71
K ₂ CrO ₄ = CrO ₄ ²⁻ + 2K ⁺	4.25	-0.01	0.01
1/2K ₂ Cr ₂ O ₇ + 1/2H ₂ O = CrO ₄ ²⁻ + K ⁺ + H ⁺	9.06	10.69	7.84
Li ₂ CrO ₄ = CrO ₄ ²⁻ + 2Li ²⁺	-10.80	-6.28	4.60
MgCrO ₄ = CrO ₄ ²⁻ + Mg ²⁺	-21.27	-8.72	6.39
(NH ₄) ₂ CrO ₄ = CrO ₄ ²⁻ + 2NH ₄ ⁺	8.19	-0.55	0.40
Na ₂ CrO ₄ = CrO ₄ ²⁻ + 2Na ⁺	-4.62	-4.45	3.26
1/2Na ₂ Cr ₂ O ₇ + 1/2H ₂ O = CrO ₄ ²⁻ + Na ⁺ + H ⁺	2.65	6.75	-4.95
PbCrO ₄ = CrO ₄ ²⁻ + Pb ²⁺	10.85	18.77	-13.76
Rb ₂ CrO ₄ = CrO ₄ ²⁻ + 2Rb ⁺	5.89	0.14	-0.10
SrCrO ₄ = CrO ₄ ²⁻ + Sr ²⁺	2.43	6.38	-4.68
Tl ₂ CrO ₄ = CrO ₄ ²⁻ + 2Tl ⁺	25.31	16.39	-12.02

TABLE 11. Thermodynamic Values for Reactions Involving Aqueous Species of Cr.

Reaction	ΔH°	ΔG°	log K
	kcal mol ⁻¹	kcal mol ⁻¹	
$\text{Cr}^{2+} + 2\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + 2\text{H}^+ + \text{e}^-$	-6.36	4.02	-2.95
$\text{Cr}^{3+} + 2\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + 2\text{H}^+$	20.14	13.92	-10.20
$\text{CrOH}^{2+} + \text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{H}^+$	7.80	8.57	-6.28
$\text{Cr}(\text{OH})_2^+ + \text{H}_2\text{O} = \text{Cr}(\text{OH})_3^\circ + \text{H}^+$	--	10.63	-7.79
$1/2\text{Cr}_2(\text{OH})_2^{4+} + \text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{H}^+$	13.94	10.47	-7.68
$1/3\text{Cr}_3(\text{OH})_4^{5+} + 2/3\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + 2/3\text{H}^+$	11.81	10.21	-7.48
$\text{Cr}(\text{OH})_4^- = \text{Cr}(\text{OH})_2^+ + 2\text{OH}^-$	--	14.73	-10.80
$\text{CrO}_2^- + 2\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + 2\text{OH}^-$	--	13.97	-10.24
$\text{CrBr}^{2+} + 2\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{Br}^- + 2\text{H}^+$	11.21	10.30	-7.55
$\text{CrCl}^{2+} + 2\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{Cl}^- + 2\text{H}^+$	13.85	12.78	-9.37
$\text{CrCl}_2^+ + 2\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + 2\text{Cl}^- + 2\text{H}^+$	9.37	11.81	-8.66
$\text{CrOHC1}_2(\text{aq}) + \text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + 2\text{Cl}^- + \text{H}^+$	--	4.04	-2.96
$\text{CrNCS}^{2+} + 2\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{CNS}^- + 2\text{H}^+$	--	16.65	-12.21
$\text{CrSCN}^{2+} + 2\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{CNS}^- + 2\text{H}^+$	--	9.36	-6.86
$\text{CrF}^{2+} + 2\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{F}^- + 2\text{H}^+$	16.79	19.84	-14.54
$\text{CrI}^{2+} + 2\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{I}^- + 2\text{H}^+$	--	6.59	-4.83
$\text{Cr}(\text{NH}_3)_6^{3+} + 6\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + 6\text{NH}_4^+ + 4\text{OH}^-$	--	31.87	-23.36
$\text{Cr}(\text{NH}_3)_5(\text{OH})^{2+} + 5\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + 5\text{NH}_4^+ + 4\text{OH}^-$	--	35.01	-25.67
$\text{cis-Cr}(\text{NH}_3)_4(\text{OH})_2^+ + 4\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + 4\text{NH}_4^+ + 4\text{OH}^-$	--	35.59	-26.09
$\text{trans-Cr}(\text{NH}_3)_4(\text{OH})_2^+ + 4\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + 4\text{NH}_4^+ + 4\text{OH}^-$	--	34.64	-25.39
$\text{Cr}(\text{NH}_3)_6\text{Cl}^{2+} + 6\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + 6\text{NH}_4^+ + \text{Cl}^- + 4\text{OH}^-$	--	32.93	-24.14
$\text{Cr}(\text{NH}_3)_6\text{Br}^{2+} + 6\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + 6\text{NH}_4^+ + \text{Br}^- + 4\text{OH}^-$	--	32.80	-24.05
$\text{Cr}(\text{NH}_3)_6\text{I}^{2+} + 6\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + 6\text{NH}_4^+ + \text{I}^- + 4\text{OH}^-$	--	32.64	-23.93
$\text{Cr}(\text{NO}_3)^{2+} + 2\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{NO}_3^- + 2\text{H}^+$	15.64	11.18	-8.20

TABLE 11. (Continued)

Reaction	ΔH°	ΔG°	log K
	kcal mol ⁻¹	kcal mol ⁻¹	
$\text{CrH}_2\text{PO}_4^{2+} + 2\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{H}_2\text{PO}_4^- + 2\text{H}^+$	--	16.86	-12.36
$\text{Cr}(\text{SO}_4)^+ + 2\text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{SO}_4^{2-} + 2\text{H}^+$	12.54	15.00	-11.00
$\text{Cr}(\text{OH})\text{SO}_4 + \text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{SO}_4^{2-} + \text{H}^+$	--	11.33	-8.31
$1/2[\text{Cr}_2(\text{OH})_2\text{SO}_4]\text{SO}_4 + \text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{SO}_4^{2-} + \text{H}^+$	--	9.95	-7.29
$1/2[\text{Cr}_2(\text{OH})_2\text{SO}_4]^{2+} + \text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + 1/2\text{SO}_4^{2-} + \text{H}^+$	--	11.04	-8.09
$1/2[\text{Cr}_2(\text{OH})_2(\text{SO}_4)_2] + \text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{SO}_4^{2-} + \text{H}^+$	--	12.27	-9.00
$\text{CrO}_4^{2-} + 6\text{H}^+ + 3\text{e}^- = \text{Cr}(\text{OH})_2^+ + 2\text{H}_2\text{O}$	-102.99	-91.92	67.39
$\text{HCrO}_4^- + 5\text{H}^+ + 3\text{e}^- = \text{Cr}(\text{OH})_2^+ + 2\text{H}_2\text{O}$	-103.89	-83.04	60.88
$\text{H}_2\text{CrO}_4^\circ + 4\text{H}^+ + 3\text{e}^- = \text{Cr}(\text{OH})_2^+ + 2\text{H}_2\text{O}$	--	-84.21	61.74
$1/2\text{Cr}_2\text{O}_7^{2-} + 5\text{H}^+ + 3\text{e}^- = \text{Cr}(\text{OH})_2^+ + 3/2\text{H}_2\text{O}$	-101.49	-81.99	60.11
$\text{HCrO}_4^- = \text{CrO}_4^{2-} + \text{H}^+$	-0.90	8.88	-6.51
$\text{H}_2\text{CrO}_4^\circ = \text{CrO}_4^{2-} + 2\text{H}^+$	--	7.71	-5.65
$1/2\text{Cr}_2\text{O}_7^{2-} + 1/2\text{H}_2\text{O} = \text{CrO}_4^{2-} + \text{H}^+$	1.50	9.93	-7.28
$\text{CrO}_3\text{Cl}^- + \text{H}_2\text{O} = \text{CrO}_4^{2-} + \text{Cl}^- + 2\text{H}^+$	--	9.97	-7.31
$\text{CrO}_3\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} = \text{CrO}_4^{2-} + \text{H}_2\text{PO}_4^- + 2\text{H}^+$	--	13.39	-9.82
$\text{CrO}_3\text{HPO}_4^{2-} + \text{H}_2\text{O} = \text{CrO}_4^{2-} + \text{HPO}_4^{2-} + 2\text{H}^+$	--	19.56	-14.34
$\text{CrO}_3\text{SO}_4^{2-} + \text{H}_2\text{O} = \text{CrO}_4^{2-} + \text{SO}_4^{2-} + 2\text{H}^+$	--	12.31	-9.02
$\text{NaCrO}_4^- = \text{CrO}_4^{2-} + \text{Na}^+$	--	0.95	-0.70
$\text{KCrO}_4^- = \text{CrO}_4^{2-} + \text{K}^+$	--	1.09	-0.80

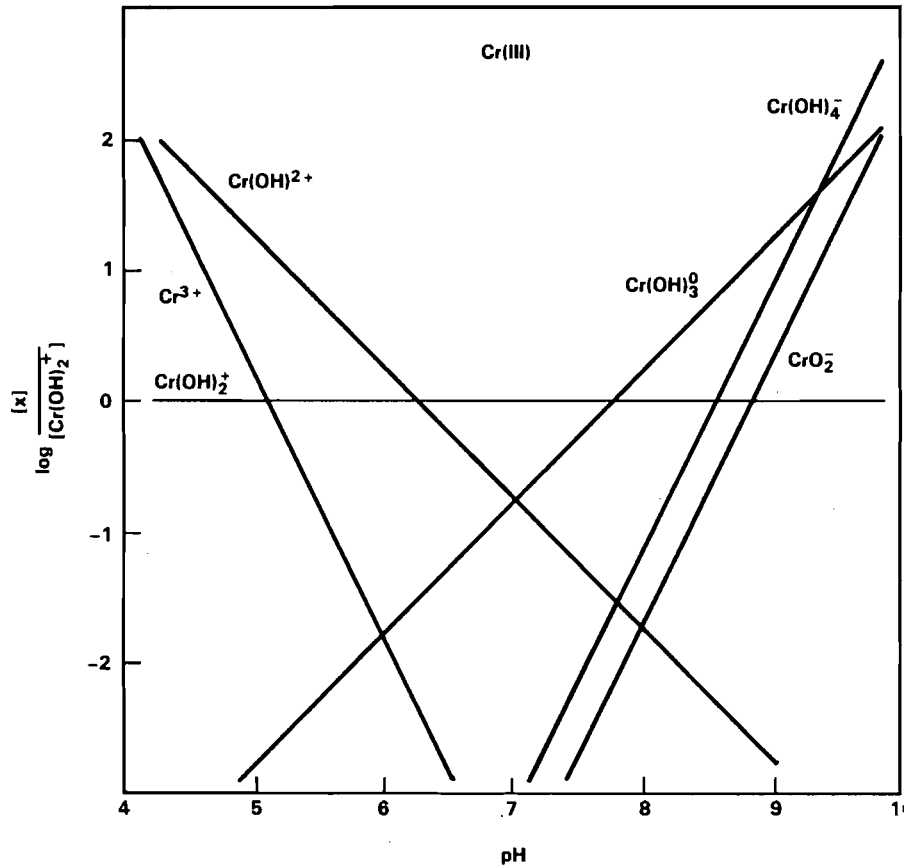


FIGURE 2. Distribution of Aqueous Inorganic Cr(III) Species as a Function of pH.

CrO_4^{2-} at pH 9. However, their model for seawater at pH 8.2 gives 71% CrO_4^{2-} and 28% NaCrO_4^- while I calculate 85 and 14%, respectively. A difference in a log K value of -0.4 could account for this discrepancy.

In Figure 7, the range of pH and pE is illustrated in which various aqueous inorganic species of Cr are dominant. As shown, the major inorganic Cr species in natural waters should be CrO_4^{2-} and Cr(OH)_2^+ with CrO_4^{2-} dominating strongly at the theoretical pE of aerated seawater (8.5 to 12.5). The polynuclear species, $\text{Cr}_2(\text{OH})_2^{4+}$ and $\text{Cr}_3(\text{OH})_4^{5+}$, which could be dominant species according to thermodynamic considerations (Baes and Mesmer, 1976), are omitted because they likely form only at elevated temperatures or concentrations (Thompson, 1964).

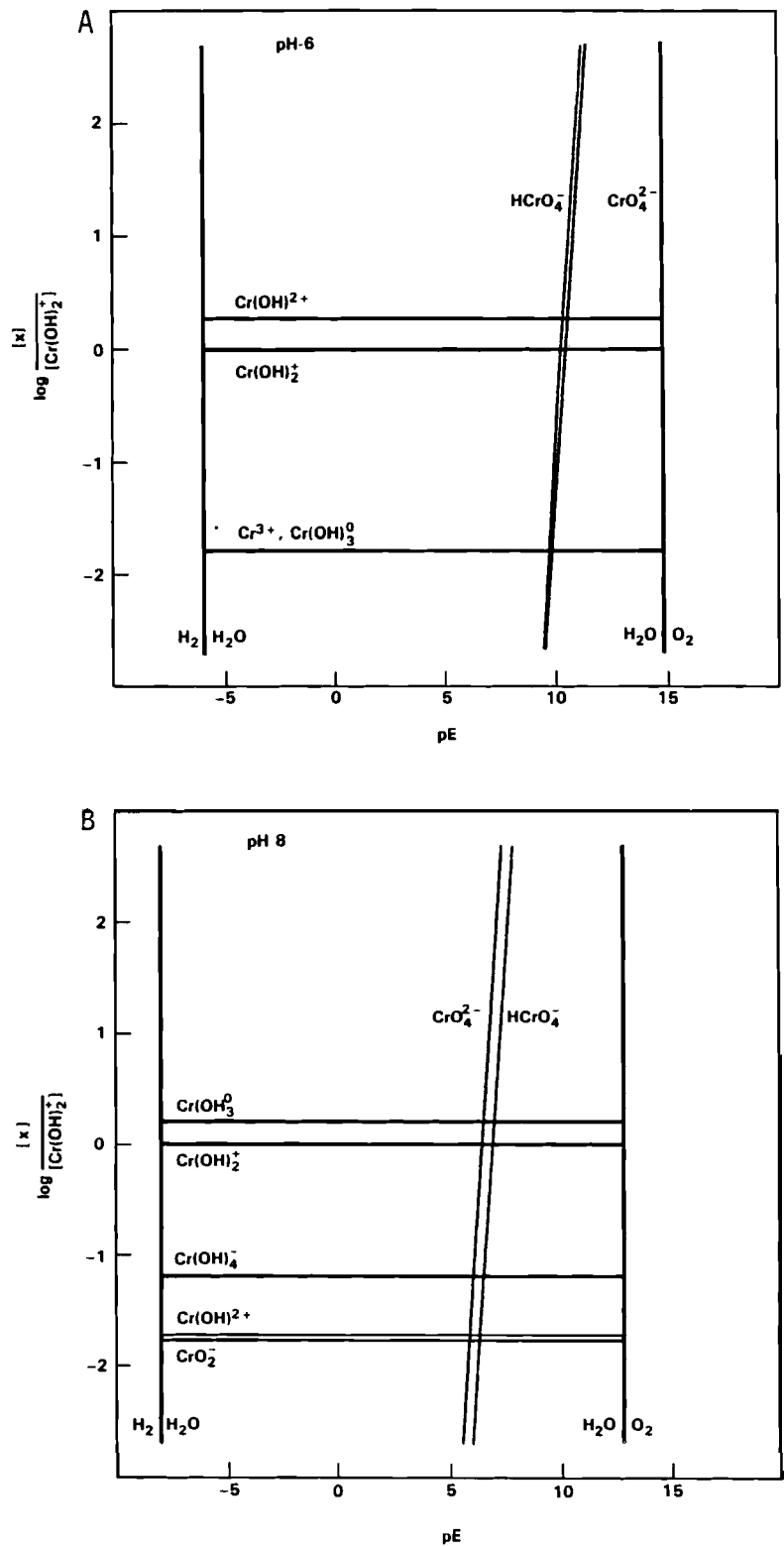


FIGURE 3. Distribution of Aqueous Inorganic Cr Species at (A) pH 6 and at (B) pH 8.

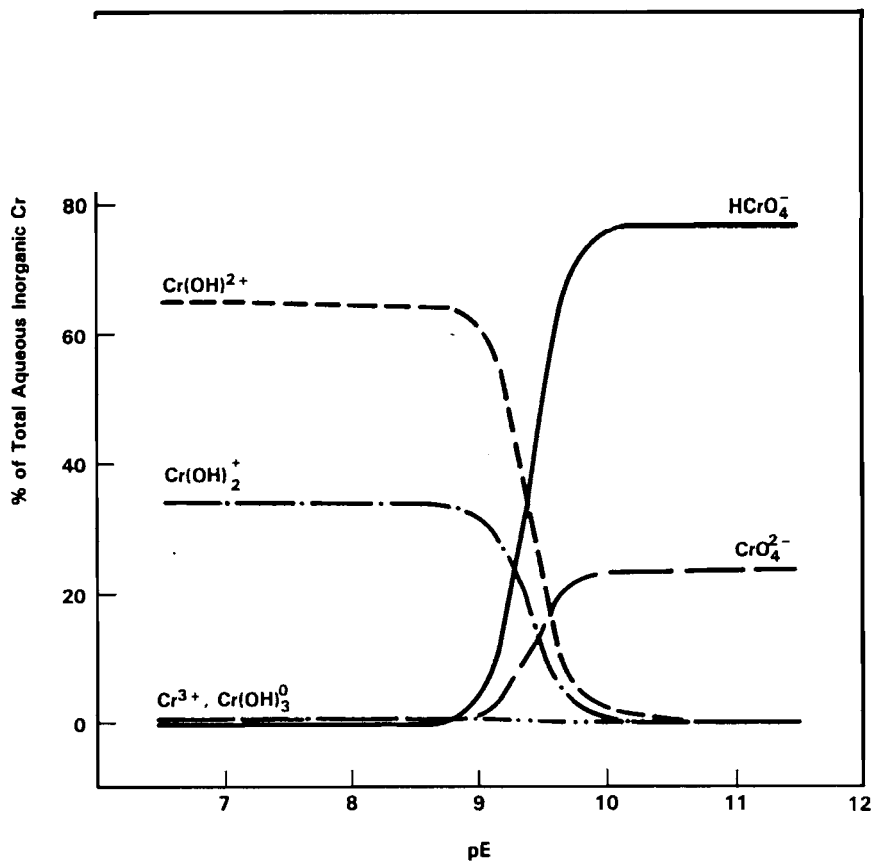


FIGURE 4. Distribution of Aqueous Inorganic Cr Species in Freshwater at pH 6.

Now the question arises, "Does the measured distribution of chromium species in natural waters conform to predictions based on known thermodynamic considerations?" and, "If not, why not?" Early analyses of seawater for Cr led to contradictory conclusions. Brewer (1975) cites studies made during the late 1960s which found that Cr(VI) is, indeed, generally the major form in seawater from the Mediterranean, as might be predicted from the pE/pH diagram (Figure 7). Cranston and Murray (1978) measured chromium species in several types of waters and also found that Cr(VI) is the dominant form under oxic conditions, while Cr(III) is found in anoxic waters. However, Elderfield (1970) found that Cr(III) predominates in waters off the coast of Wales. Brewer (1975) cites other similarly conflicting studies and concludes that the Cr(III)-Cr(VI) redox couple is not at equilibrium in seawater and that local processes are likely controlling the distribution of chromium among its aqueous species.

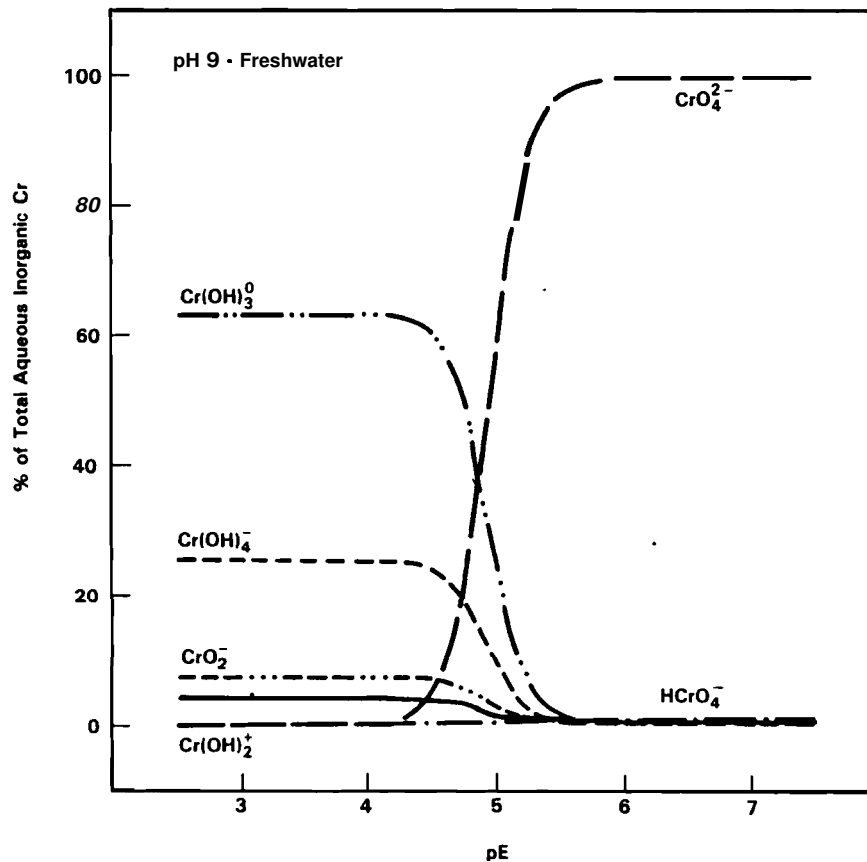


FIGURE 5. Distribution of Aqueous Inorganic Cr Species in Freshwater at pH 9.

A major factor influencing the distribution of chromium species in seawater appears to be the formation of Cr-organic complexes. Nakayama et al. (1981a) tested a wide variety of organic and amino acids and found that the presence of ascorbic and citric acids in seawater markedly affects the behavior of Cr(III). They conclude that Cr(III) becomes stabilized to a large degree by complex formation with natural organic materials present in seawater, such as amino and polybasic organic acids.

These same investigators (Nakayama et al., 1981b), by means of selective extraction methods, were able to successfully determine the amounts of Cr(III), Cr(VI) and organically complexed Cr in seawater. Their data indicate that seawater from the Pacific Ocean and the Sea of Japan contains ca. 9×10^{-9} M soluble Cr of which about 15% is inorganic Cr(III),

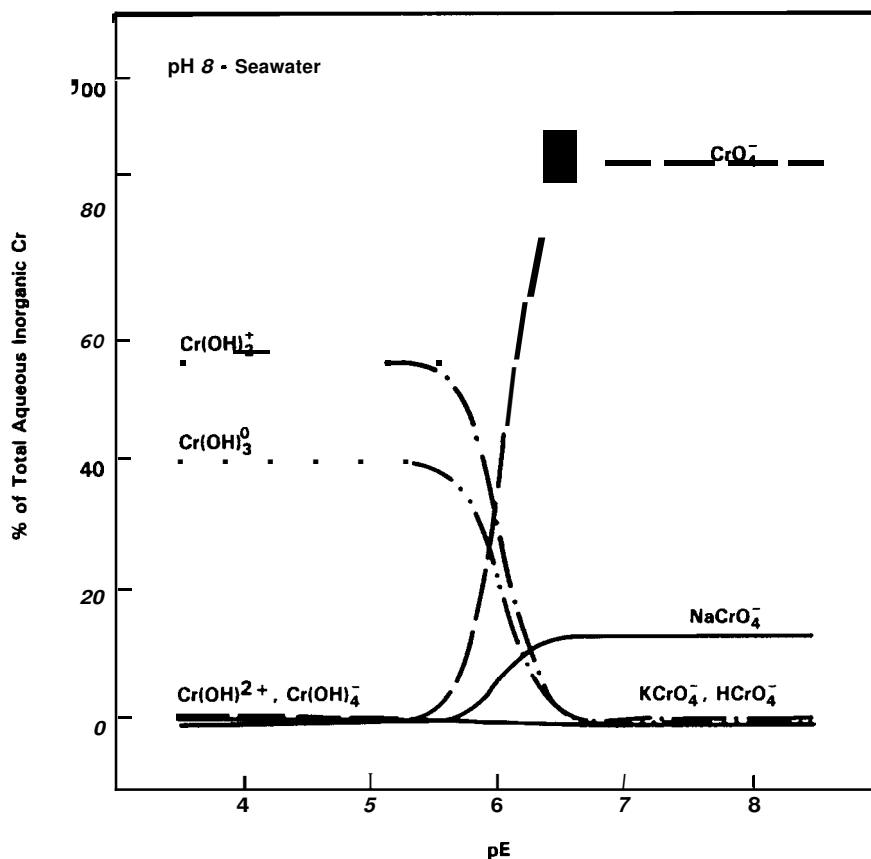


FIGURE 6. Distribution of Aqueous Inorganic Cr Species in Seawater at pH 8.

25% inorganic Cr(VI) and 60% organically bound Cr. Assuming that seawater reasonably contains about 10^{-6} M metal-binding organic ligands at pH 8, log K for the formation of CrL_2^- should be about 11.8 to 12.0. Nakayama et al. (1981a) cite a study reporting the log K value for Cr(III) 1-phenylbiguanide to be 12.02 and Cr(III) iminodiacetate has a log K of 10.9 (Martell and Smith, 1974).

Using the ratio of inorganic Cr(III) to inorganic Cr(VI) reported by Nakayama et al. (1981b), ■ calculate that pE must be 5.8 to 5.9 at pH 8 for equilibrium among inorganic species to be attained. For open ocean water pE is generally greater than 8.5 (Breck, 1974). However, Nakayama et al. (1981c) report that oxidation of Cr(III) to Cr(VI) does not occur rapidly in seawater; in fact, no Cr(VI) could be detected after bubbling air

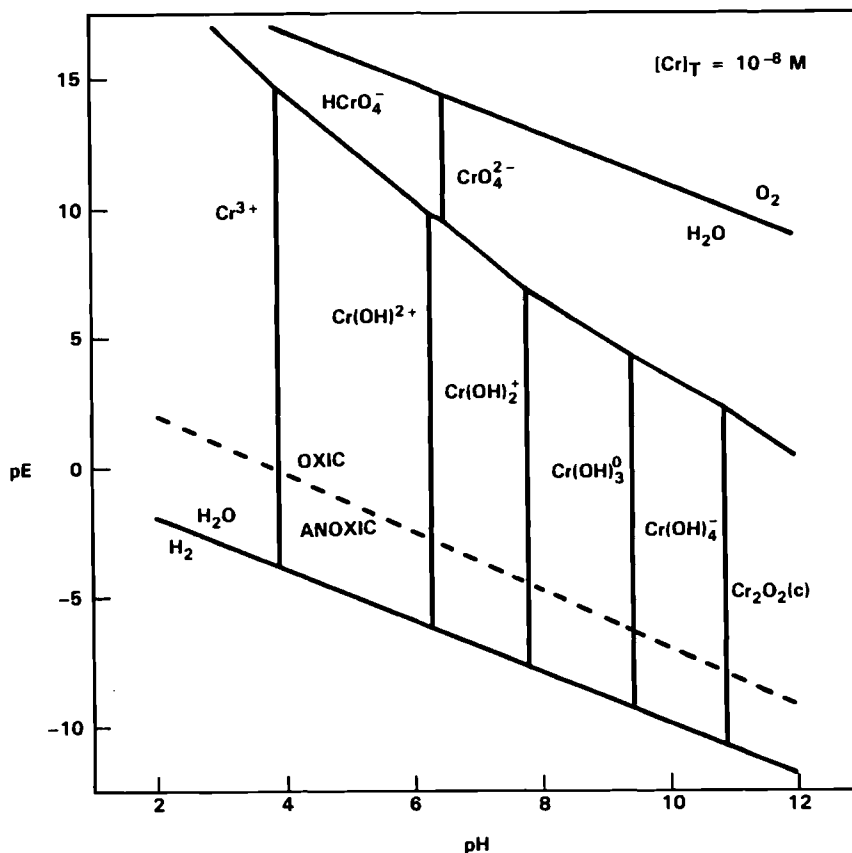


FIGURE 7. pE-pH Diagram of Aqueous Inorganic Cr Species at Total Cr Concentration of 10^{-8} M.

through seawater containing Cr(III) after almost two weeks. Thus, it is doubtful that equilibrium between Cr(III) and Cr(VI) is ever achieved in seawater. However, the presence of Mn oxides catalyzes the rapid oxidation of Cr(III) to Cr(VI) while Cr(VI) is reduced to Cr(III) by reducible organic materials (Nakayama et al., 1981c). In addition, H_2S diffusing from some sediments into overlying water will rapidly convert Cr(VI) to Cr(III). Smillie et al. (1981) found that 40 to 60% of Cr(VI) is reduced to Cr(III) in 24 hours by H_2S produced from a harbor sediment or from SO_4^{2-} -reducing bacteria in seawater.

A steady-state condition controlling the speciation of Cr in natural waters appears to exist and the distribution of Cr among inorganic Cr(III), inorganic Cr(VI), and organically bound Cr(III) species depends on the

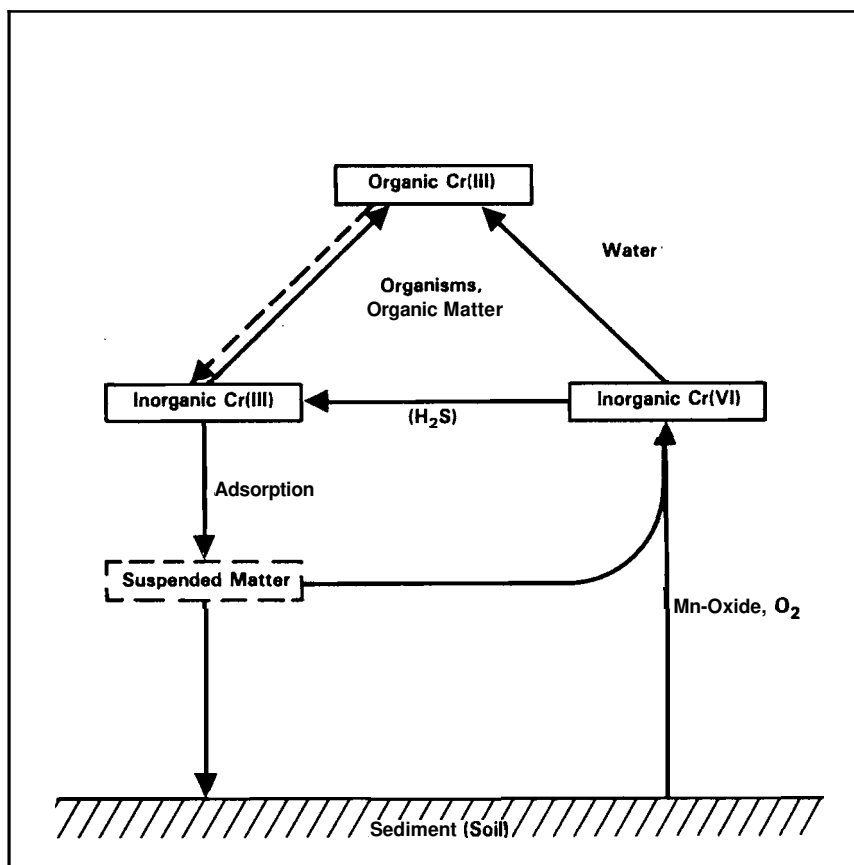


FIGURE 8. Model of Processes Controlling the Distribution of Cr in the Environment (After Nakayama et al. 1981C).

presence of Mn-oxide in suspended particulate matter, H_2S released from anoxic sediments, or possibly, reducible organic materials at a particular location.

The effects of Mn-oxides, H_2S and organic matter on the speciation of Cr are dramatically demonstrated by Emerson et al. (1979). A profile of Cr-species distribution with depth in Saanich Inlet, B.C., an anoxic fjord, shows that the log of the ratio of CrO_4^{2-} to $Cr(OH)_2^-$ in the surface waters is about 1.0 but decreases to <-2.0 at the O_2/H_2S boundary and then increases again to -0.4 to -0.7 near the bottom. Emerson et al. (1979) postulate that Mn^{2+} , which diffuses out of the anoxic layer is oxidized at the O_2/H_2S boundary with the simultaneous reduction of CrO_4^{2-} . Then as MnO_2 settles into the anoxic zone, it becomes reduced, partially through

the oxidation of adsorbed Cr(III). When reaction kinetics are considered, such a scenario may be possible. Emerson et al. (1979) found that the residence time for Cr(III) is 6 to 20 days in the oxic zone while the oxidation of Mn^{2+} is more rapid: the residence time of Mn^{2+} is about 2 days.

The behavior of Cr in soils, reported by Bartlett and Kimble (1976a,b) and Bartlett and James (1979), is also strongly influenced by the presence of organic matter which leads to the reduction of Cr(VI), and Mn-oxides which oxidize Cr(III).

Out of the above studies, a steady-state model for the speciation of Cr can be developed patterned after that of Nakayama et al. (1981c) and shown in Figure 8. This model presents the probable environmental behavior of Cr under the influence of various factors. The major processes include reduction and complexation by organic matter, adsorption and oxidation by Mn-oxides in suspended matter and sediment (soil), and reduction by H_2S . While it appears that these mechanisms do not lead to a state of equilibrium, equilibrium thermodynamics help in understanding the outcome of these processes.

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