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Reviews

Critical Evaluation and Selection of Standard State Thermodynamic Properties for Chromium Metal and Its Aqueous Ions, Hydrolysis Species, Oxides, and Hydroxides

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This review critically evaluates the reported thermodynamic data on chromium metal, oxides, hydroxides, free aqueous ions, and hydrolysis species. Several discrepancies and inconsistencies have been uncovered and resolved to improve equilibrium calculations for chemical modeling and related engineering purposes. A revised set of data is derived from evaluation of electrochemical measurements, silver chromate solubility measurements, and auxiliary post-1980 data, reevaluation of earlier data, and reconsideration of the path for the thermodynamic network. The recommended thermodynamic values for $Cr_{(cr)}$, $Cr^{2+}_{(aq)}$, $Cr^{3+}_{(aq)}$, $CrO^{2-}_{4(aq)}$, $Cr_2O^{2-}_{7(aq)}$, $Cr_2O_{3(cr)}$, $CrO_{3(cr)}$, $FeCr_2O_{4(cr)}$, $CrCl_{2(cr)}$, $CrCl_{3(cr)}$, and $KFe_3(CrO_4)_2(OH)_{6(cr)}$ at 25 °C, 1 bar, and infinite dilution are given.

Introduction

The average concentration of Cr in the earth's crust is about 100 μg/g [88-nri]. Average Cr concentrations in basaltic and ultramafic rocks are 200 and 2400 μg/g, respectively [88-nri]. Dissolved Cr is a trace element in uncontaminated waters, ranging in concentration from 0.05 μg/L in seawater [88-may] to about 500 μg/L in groundwater draining ultramafic rocks in regions with dry climates [75-rob]. The highest known Cr concentration not resulting from human activity, about 7.5 mg/L, occurs in pH 12.5 groundwater near Maqarin, Jordan [92-kho/sal].

Contamination of groundwater with Cr as a result of human activity is widespread and persistent [88-han, 63-per/lie, 94-pul/cla]. Examples of sources of Cr from human activity are electroplating baths, power plant fly ash, leather-tanning and wood-preserving operations, and smelting of Cr ore. Additional references and details may be found elsewhere [96-bal, 88-nri]. Dissolved Cr has been reported in contaminated groundwater at concentrations as high as 27 g/L in India [88-han]. Among all pollutants at hazardous waste sites in the United States, Cr is the third most frequently cited [91-nat, 144−146] and among metallic substances is second only to Pb in frequency of citation [91-nat, 108−109]. Because of the consequent importance of developing useful chemical models for assessing Cr aqueous chemistry and predicting Cr movement in contaminant plumes, there is a critical need for a reliable, up-to-date, internally consistent set of thermodynamic properties for Cr aqueous species and minerals.

The chemical speciation of aqueous dissolved Cr is strongly influenced by redox (reduction−oxidation) conditions and pH. These and other solution conditions such as composition and ionic strength affect the extent of adsorption−desorption and precipitation−dissolution of Cr species. Consequently, it is important to determine the solute speciation of Cr so that the probable movement, eventual fate, and toxicity of Cr in hydrogeological settings can be more reliably calculated.

Ball [96-bal] provided a preliminary compilation and evaluation of Cr thermodynamic properties and primarily discussed $Cr_{(cr)}$, Cr_2O_3, Cr^{2+}/Cr^{3+} redox, and Cr(III) and Cr(VI) hydrolysis. This paper greatly extends the work of Ball, especially for $Cr^{3+}_{(aq)}$ and $CrO^{2-}_{4(aq)}$, to yield a more complete, reliable, and internally consistent set of Cr thermodynamic data.

Numerous references contain data on speciation, solubility, and thermodynamic properties of Cr compounds and aqueous complexes. Only a small fraction of these references addresses the actual measurement of Cr thermodynamic properties. The remainder are compilations of thermodynamic properties or are recalculations of the measurements of others. Among articles reporting the actual measurement of thermodynamic properties, many suffer from inadequately documented methods or inadequately controlled experimental conditions. The only way to determine the reliability of data is to examine the authors' original experimental results, check their calculations, and compare their results with those from independent studies of the same system.

The most comprehensive compilation of standard state thermodynamic properties for Cr species can be found in Wagman et al. [82-wag/eva]. Unfortunately, references are not given, and the decision-making process is not explained. Furthermore, the values are based on literature that is pre-1966, and some of the then-existing aqueous electrolyte data were not refined or used in the evaluation. Slobodov et al. [93-slo/kri] compiled standard state thermodynamic

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properties for Cr oxides, aqueous species, and hydrolysis products. We mathematically tested the thermodynamic parameters selected by Slobodov et al. for internal consistency of the fundamental thermodynamic relations and found several inconsistencies. Schmidt [84-sch] compiled and evaluated thermodynamic properties of Cr aqueous species and minerals for use in geochemical modeling computer codes. This compilation used many secondary sources, and Schmidt did not evaluate the measurements upon which the data are based. The resulting database was incorporated into the MINTEQA2 [91-all/bro] and MINEQL$^+$ [91-sch/mca] computer models. Those databases have since been revised. Dellien et al. [76-del/hal] evaluated and compiled standard state thermodynamic properties for Cr solids and aqueous species. This compilation was the most comprehensive and well-researched of its kind for Cr, but Dellien et al. acknowledged that many of the values were uncertain and that many of their choices were thus arbitrary and subject to large uncertainties.

Since the compilation of Dellien et al. [76-del/hal], many publications have appeared that may impact the thermodynamics of Cr speciation and the solubility of Cr-containing solids. Of particular interest are the CODATA compilation [89-cox/wag] of thermodynamic properties for selected elements, compounds, and aqueous ions, the internally consistent tabulation of Nordstrom and Munoz [94-nor/mun, Appendix D], the paper of Rai et al. [87-rai/sas] which examines the hydrolysis of Cr(III), and that of Palmer et al. [87-pal/wes] which similarly examines the hydrolysis of Cr(VI).

Chemical Modeling of Aqueous Chromium Chemistry

Speciation programs such as MINEQL$^+$ [91-sch/mca], MINTEQA2 [91-all/bro], WATEQ4F [91-bal/nor], EQ3/6 [92-wol], MacWATEQ4F [94-geo], and PHREEQC [95-par] use field measurements of temperature, pH, Eh, and alkalinity, together with the chemical analysis of a water sample as input. They calculate the distribution of aqueous species, ion activities, and mineral saturation indices that indicate the tendency of a water to dissolve or precipitate a set of minerals. The thermodynamic database of the WATEQ4F program has been kept up-to-date by a process of continuing evaluation and revision [84-nor/val, 90-nor/plu, 91-bal/nor, 93-sti/par, 94-nor/mun]. Consequently, it is to this database that we intend to add the Cr reactions resulting from the present study. Speciation models assume homogeneous aqueous phase equilibria, except for redox species. Equilibrium with respect to mineral solubilities is not necessarily assumed. The program results are used primarily to examine the tendency of a water to reach mineral solubility equilibria as a constraint on interpreting the chemistry of natural waters. Computerized chemical models have been widely used in the interpretation of natural water chemistry [93-par/plu, 94-nor/mun].

Complexation Reactions. Chromium aqueous geochemistry has been reviewed recently by Richard and Bourg [91-ric/bou], who discussed conditions under which Cr may form aqueous organic and inorganic complexes, dissolve or precipitate, undergo redox transformations, and exhibit adsorption–desorption behavior. These authors concluded that mobility of Cr is determined by the competition between the above mechanisms and that Cr(III) is mobile under acidic conditions or as dissolved organic complexes. Mobility of Cr(VI) is significantly reduced in the presence of Fe(II) or organic material.

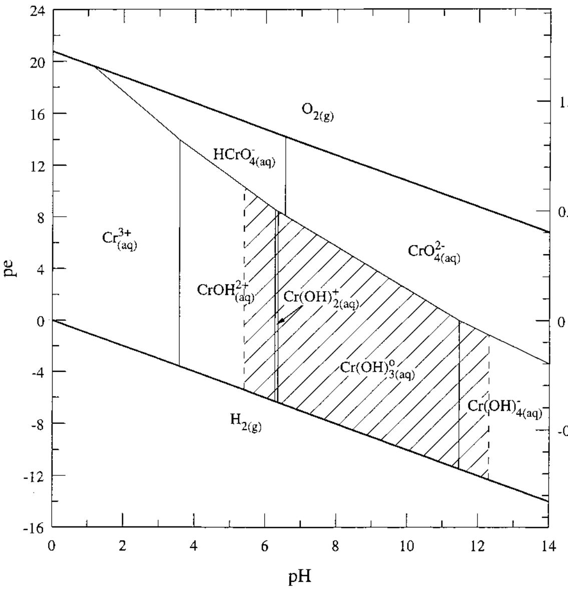

Figure 1. pe–pH diagram for aqueous inorganic chromium hydrolysis species (Cr[III] data, ref 87-rai/sas; Cr[VI] data, ref 87-pal/wes; redox data, ref 71-cha/col). Hatched area indicates predominance region for $Cr(OH)_{3(cr)}$ at $[Cr_{TOT}] = 1 \times 10^{-6}$ M. There are no stability fields for aqueous Cr[II] species within the stability field for $H_2O_{(l)}$.

Chromium reactions in seawater have been studied by Elderfield [70-eld], Nakayama et al. [81-nak/kuw1, 81-nak/kuw2, 81-nak/kuw3], Turner et al. [81-tur/whi], and Pettine and Millero [90-pet/mil]. Elderfield examined Cr speciation by both calculation and analysis and concluded that the thermodynamically favored Cr species are not found by analysis of seawater and that the predominant Cr(III) species should be $Cr(OH)_2^+$. Nakayama et al. tested the hypothesis that most of the apparent discrepancies in valence species distribution of Cr in seawater are the result of complexing of Cr(III) by naturally occurring organic materials. These authors proposed a method for determining the quantities of Cr in organic and inorganic complexes. Turner et al. examined the periodic nature of complexation of 58 elements considered trace constituents of seawater and concluded that the elements can be grouped according to their interactions with the predominant anionic ligands found in seawater. Pettine and Millero determined the kinetics of oxidation of Cr(III) to Cr(VI) with respect to pH and concentration of H_2O_2.

In the absence of elevated concentrations of complexing anions, the predominant forms of dissolved Cr(III) are $Cr(OH)^o_{3(aq)}$ at neutral pH, $CrOH^{2+}_{(aq)}$ at more acidic pH, and $Cr(OH)^-_{4(aq)}$ in the alkaline pH region [87-rai/sas]. Similarly, the predominant forms of dissolved hexavalent Cr are $Cr_2O^{2-}_{7(aq)}$ and $HCrO^-_{4(aq)}$ below pH 6.5, and $CrO^{2-}_{4(aq)}$ at alkaline pH [87-pal/wes].

Oxidation–Reduction Reactions. A pe–pH diagram [97-lan, 94-nor/mun] of aqueous inorganic Cr hydrolysis species based on the results of this study is shown in Figure 1. The right-hand ordinate shows the corresponding Eh scale (EMF based on the standard hydrogen electrode [65-gar/chr]). At a given temperature, Eh and pe differ by a constant [at 298.15 K, pe = Eh(V) × 16.903]. There are no stability fields for aqueous Cr(II) species within the stability field for $H_2O_{(l)}$. Chromium can change redox state in the redox range found in natural waters and is reduced from the hexavalent state (CrO_4^{2-}), a soluble form, to the less soluble trivalent state, which readily forms oxide and hydroxide precipitates [85-hem, 88-ele] and adsorbs to the surface of clay minerals [88-ele, 90-war, 91-war/bas]. At pH values greater than 4, hexavalent Cr is significantly more soluble than trivalent Cr.

Precipitation−Dissolution Reactions. At least four solid phases are likely candidates for providing a solubility limit to the aqueous Cr concentration in natural waters: (1) barite solid solutions, (2) $Cr(OH)_{3(cr)}$, (3) ferrite compounds such as chromite, $FeCr_2O_{4(cr)}$, and (4) chromate jarosite, $KFe_3(CrO_4)_2(OH)_{6(cr)}$. Other insoluble minerals containing sulfate may provide a lattice for which chromate substitution is possible.

Chromium redox, precipitation, and adsorption reactions have been summarized by Rai and Zachara [88-rai/zac], who found that the solid $Ba(S, Cr)O_{4(c)}$ behaved like an ideal solid solution. Thus, in solutions containing Ba, Cr was less soluble than in pure solutions containing only Cr. The concentration of trivalent Cr in solution usually is limited by precipitation of $Cr(OH)_3$, which has a solubility of approximately 10^{-12} M under the chemical conditions found in most uncontaminated surface waters [85-hem]. The solubility of chromite, $FeCr_2O_{4(cr)}$, has been hypothesized to control trivalent Cr concentration in solutions containing significant iron [88-rai/zac]. Baron and Palmer [94-bar/pal, 96-bar/pal] have identified and characterized a chromate jarosite, $KFe_3(CrO_4)_2(OH)_{6(cr)}$, found in soils beneath a leaking chrome-plating bath.

Approach

Techniques and approaches for compiling and evaluating thermodynamic data have been discussed by numerous authors [for example, 76-haa/fis, 88-bal/par, 77-bec, 80-per, 85-mar/mot, 85-cha/dav, 94-nor/mun]. Building an internally consistent thermodynamic database requires that several objectives be met simultaneously. Foremost among these objectives are the choice of an appropriate standard state and an appropriate starting point, since a database of thermodynamic properties is by necessity subject to cumulative uncertainties and is no stronger than its base of primary components. For this compilation, we have chosen the most common standard state conditions conventionally used and accepted by the CODATA Task Group on Key Values for Thermodynamics [89-cox/wag]. These conditions include 1 bar pressure, 298.15 K temperature, pure, perfectly crystalline material for solids, and the hypothetical 1 *m* ideal solution of the solute, with the solvent's standard state chosen to be the real state of the pure solvent.

The following guidelines were used in the present study to achieve consistency and minimize error for the derived thermodynamic values:

(1) Determine the most direct path for a derived thermodynamic quantity.

(2) Determine a thermodynamic path that utilizes measurements of high reliability.

(3) Determine a thermodynamic path that avoids (a) secondary or tertiary sources, (b) circuitous or "incestuous" sources that give consistent results because they come from the same origin, and (c) unpublished or undocumented sources.

(4) Where possible, confirm derived thermodynamic quantities with independent measurements or estimates.

(5) Resolve, as far as possible, discrepancies among measurements or derived thermodynamic quantities.

(6) Maintain thermodynamic relationships.

(7) Reevaluate reliable data in light of improved chemical or mathematical models for system behavior, for example, recalculate speciation and activity coefficients from raw aqueous compositions where possible, if a more primitive model was originally used to reduce the data.

Table 1. Reported Values for Standard Enthalpy of Formation ($\Delta_f H°$) of $Cr_2O_{3(cr)}$ at 298.15 K

$\Delta_f H°/kJ\ mol^{-1}$	reference
-1205.0 ± 2.5	29-rot/bec
-1141.0 ± 1.7	54-mah
-1133.9 ± 7.5	61-gol/chi
-1141.4 ± 1.3	66-nov/len
-1134.7 ± 8.4	85-cha/dav

Four summary tables of thermodynamic properties are presented in Tables 7−10. In the tables, numbers in parentheses are the uncertainties specified by the experimenters. Auxiliary thermodynamic data for the major elemental components and for major ions in aqueous solution are presented in Table 7, and were taken, wherever possible, from the publication of Cox et al. [89-cox/wag]. Any improvements or refinements in these auxiliary data are unlikely to affect calculations made in this report. Actual measurements are always the data of choice, whenever they are available. Thermodynamic properties for Cr solids are presented in Table 8, for Cr aqueous ions in Table 9, and for Cr hydrolysis species in Table 10.

Thermodynamic Properties of Elemental Chromium and Chromium Oxides

Chromium Metal. For the heat capacity of elemental Cr, Slobodov et al. [93-slo/kri] cited five papers [55-wol, 62-clu/fra, 63-clu/fra, 60-bea/chi, and 79-wil/gop] as sources of reliable data. These works, they stated, permit a reliable estimation of $S°(Cr_{(cr)}) = 23.56\ J\ K^{-1}\ mol^{-1}$. Andersson [85-and] also selected $S°(Cr_{(cr)}) = 23.56\ J\ K^{-1}\ mol^{-1}$ from the compilation of Gurvich et al. [82-gur/vei]. Hultgren et al. [73-hul/des] chose $S°(Cr_{(cr)}) = (23.64 \pm 0.21)\ J\ K^{-1}\ mol^{-1}$, a value also adopted by Robie et al. [78-rob/hem]. Chase et al. [85-cha/dav] used graphical techniques to evaluate about 200 heat capacity measurements for Cr metal from 14 studies over a temperature range of 14.1 K−2108 K. These authors noted particularly good agreement below 200 K among the results of Clusius and Franzosini [62-clu/fra], Anderson [37-and], and Kalishevich et al. [65-kal/gel]. Above 298 K, Chase et al. documented typical differences in enthalpy of about 840 $J\ mol^{-1}$ among the various sets of data. Chase et al. recommended a value for $S°(Cr_{(cr)}) = (23.618 \pm 0.21)\ J\ K^{-1}\ mol^{-1}$ from their evaluation. The above values appear to group fairly tightly around 23.6 $J\ K^{-1}\ mol^{-1}$, whereas $S°(Cr_{(cr)}) = (23.77 \pm 0.29)\ J\ K^{-1}\ mol^{-1}$ of Wagman et al. [82-wag/eva], which appears to be based mostly on the work of Anderson, has a mean value that is significantly larger than $S°$ values estimated or chosen by other investigators and a slightly larger uncertainty. On the basis of the closeness of agreement of the three lower values and the thoroughness and care with which Chase et al. evaluated the existing measurements, the values of Chase et al. for $S°(Cr_{(cr)}) = (23.618 \pm 0.21)\ J\ K^{-1}\ mol^{-1}$ and for $C_p°(Cr_{(cr)}) = 23.434\ J\ K^{-1}\ mol^{-1}$ are selected for the present compilation. These values also have been selected by Robie and Hemingway [95-rob/hem].

Chromium(III) Oxide (Cr_2O_3). Several values for $\Delta_f H°(Cr_2O_{3(cr)})$ were found in the literature, and a selection process was necessary. A summary of reported values is given in Table 1. The value of Roth and Becker [29-rot/bec] is inexplicably lower than the others and is assumed to be an outlier. Additional values have been cited by

Dellien et al. [76-del/hal], but all are derived by extrapolation from measurements taken at high temperatures, some up to several hundred degrees above 298.15 K. As such, they may be subject to larger errors than measurements taken closer to 298.15 K. These results could be refined further, but we deem such an undertaking to be beyond the scope of this work. For example, Mazandarany and Pehlke [74-maz/peh] determined $\Delta_f G°(Cr_2O_{3(cr)})$ over a temperature range of about 900 °C−1300 °C in a carefully controlled electrochemical study. These investigators summarized their raw data in tabular form, compared their results to earlier work, and discussed possible reasons for variations in the results of the investigations. However, their recommended equation yields $\Delta_f G°(Cr_2O_{3(cr)}) = -1040.9$ kJ mol^{-1}, which is about 13 kJ mol^{-1} to 18.5 kJ mol^{-1} more positive than $\Delta_f G°(Cr_2O_{3(cr)})$ from other sources [85-cha/dav, 82-wag/eva, this study]. Thus, we find the results of Mazandarany and Pehlke inconsistent with other results. This discrepancy is not uncommon for the extrapolation of very high-temperature electrochemical measurements to 25 °C.

Chase et al. [85-cha/dav] recommended $S°(Cr_2O_{3(cr)}) = (81.15 \pm 1.3)$ J K^{-1} mol^{-1} and $C_p°(Cr_2O_{3(cr)}) = 120.366$ J K^{-1} mol−1, values that we find reliable and also recommend. These authors relied on the results of Anderson [37-and] for their selection of $S°(Cr_2O_{3(cr)})$ and on the results of Kelley et al. [44-kel/boe] for $C_p°(Cr_2O_{3(cr)})$. The $\Delta_f H°(Cr_2O_{3(cr)}) = (-1134.7 \pm 8.4)$ kJ mol^{-1} recommended by Chase et al. represents the average of results from Mah [54-mah] and Golutvin and Chin'k'eui [61-gol/chi] along with three second-law estimates [63-jea/man, 66-nov/len, 74-maz/peh]. Chase et al. used their recommended values for $S°(Cr_2O_{3(cr)})$, $S°(Cr_{(cr)})$, and $\Delta_f H°(Cr_2O_{3(cr)})$ to calculate $\Delta_f G°(Cr_2O_{3(cr)}) = -1053.066$ kJ mol^{-1}. However, the work of Golutvin and Chin'k'eui was not as carefully done as that of Mah. Furthermore, the reduction of chromic oxide to chromium by Novokhatskii and Lenev [66-nov/len] is in excellent agreement with Mah's value.

For the calorimetric determination of $\Delta_f H°(Cr_2O_{3(cr)})$, Mah [54-mah] corrected the results for Fe and Si impurities, which were present in the purified Cr at concentrations of 0.01 and 0.05%, respectively. Results obtained from the combustion, which was carried out at an oxygen fugacity of 30 atm, were additionally corrected to unit oxygen fugacity, to a constant pressure process, and to standard temperature conditions. The $\Delta_f H°(Cr_2O_{3(cr)}) = (-1140.98 \pm 1.67)$ kJ mol^{-1} is in agreement with $\Delta_f H°(Cr_2O_{3(cr)}) = -1139.7$ kJ mol^{-1} in the compilation of Wagman et al. [82-wag/eva] within experimental error, with the small difference possibly attributable to corrections made by Mah using the slightly different thermodynamic data for Fe and Si available at the time the work was done. Hence, Mah's value $\Delta_f H°(Cr_2O_{3(cr)}) = (-1141.0 \pm 1.7)$ kJ mol^{-1} is selected for use in the present study.

Chromium(VI) Oxide (CrO_3). The determination of accurate and precise thermodynamic properties for CrO_3 is less important for geochemical modeling purposes because this strongly oxidizing solid is so soluble in water that its solubility is unlikely to control the concentration of Cr in solution. This solid does play, however, a critical role in evaluating thermodynamic properties of $CrO_{4(aq)}^{2-}$. Wagman et al. [82-wag/eva] recommended $\Delta_f H°(CrO_{3(cr)}) = -589.5$ kJ mol^{-1}. Slobodov et al. [93-slo/kri] recommended $\Delta_f H°(CrO_{3(cr)}) = -586.6$ kJ mol^{-1}, citing the work of Neugebauer and Margrave [57-neu/mar], estimated $S°(CrO_{3(cr)}) = 72.0$ J K^{-1} mol^{-1}, citing Hart [52-har] for the estimation method, and calculated $\Delta_f G°(CrO_{3(cr)}) = -509.1$ kJ mol^{-1}.

Dellien et al. [76-del/hal] cited five works [29-rot/bec, 57-neu/mar, 58-hep, 67-ric/laf, 69-wag/eva] and recommended $\Delta_f H°(CrO_{3(cr)}) = -589.5$ kJ mol^{-1}. Dellien et al. estimated $S°(CrO_{3(cr)}) = 67$ J K^{-1} mol^{-1} and used this value and their recommended $\Delta_f H°(CrO_{3(cr)})$ to calculate $\Delta_f G°(CrO_{3(cr)}) = -510$ kJ mol^{-1}.

Dellien et al. [76-del/mcc] made calorimetric measurements on the reaction:

$$CrO_{3(cr)} + 2OH^-_{(aq)} \rightleftharpoons CrO_{4(aq)}^{2-} + H_2O_{(l)} \qquad (1)$$

for which they obtained $\Delta_r H° = (-120.92 \pm 0.80)$ kJ mol^{-1}. Unfortunately, $\Delta_r H°$(l) cannot be used to evaluate $\Delta_f H°(CrO_{3(cr)})$ because $\Delta_f H°(CrO_{4(aq)}^{2-})$ is required and it is derived from $\Delta_f H°(CrO_{3(cr)})$. Hence, this evaluation path is circular. However, the measurements of Dellien et al. can be used as corroborative evidence for the following argument.

Roth and Becker [29-rot/bec] determined $\Delta_r H° = (-12.8 \pm 0.8)$ kJ mol^{-1} for the reaction

$$^1/_2Cr_2O_{3(cr)} + {}^3/_4O_{2(g)} \rightleftharpoons CrO_{3(cr)} \qquad (2)$$

The value for $\Delta_r H°(2)$ can be combined with Mah's [54-mah] $\Delta_f H°(Cr_2O_{3(cr)}) = (-1141.0 \pm 1.7)$ kJ mol^{-1} according to the following reaction matrix:

reaction	$\Delta_r H°$/ (kJ mol^{-1})	reference
$^1/_2Cr_2O_{3(cr)} + {}^3/_4O_{2(g)} \rightleftharpoons CrO_{3(cr)}$	−12.8 ± 0.8	29-rot/bec
$Cr_{(cr)} + {}^3/_4O_{2(g)} \rightleftharpoons {}^1/_2Cr_2O_{3(cr)}$	−570.5 ± 0.8	54-mah
$Cr_{(cr)} + {}^3/_2O_{2(g)} \rightleftharpoons CrO_{3(cr)}$	−583.3 ± 1.2	

This path is dependent only on $\Delta_f H°(Cr_2O_{3(cr)})$ which we have already established with reasonable precision. While the measurements of Roth and Becker for $\Delta_f H°(Cr_2O_{3(cr)})$ appear inconsistent with those of other investigators, their measurements of $\Delta_r H°(2)$ appear consistent with those of Dellien et al. [76-del/mcc]. Thus, we select $\Delta_f H°(CrO_{3(cr)}) = (-583.3 \pm 1.2)$ kJ mol^{-1} for use in the present study and combine this value with $S°(CrO_{3(cr)}) = 67$ J K^{-1} mol^{-1} from Dellien et al. [76-del/hal] to yield our recommended $\Delta_f G°(CrO_{3(cr)}) = (-504.5 \pm 1.3)$ kJ mol^{-1}.

Chromite ($FeCr_2O_4$). Sack and Ghiorso [91-sac/ghi] developed a model describing the heat capacity of chromite ($FeCr_2O_4$) as a function of temperature. These authors fitted the measurements of Naylor [44-nay] and Shomate [44-sho] to a four-term polynomial that accurately reproduced the data over the temperature range 250 K−1790 K (average absolute deviation <0.2%). On the basis of their model results, Sack and Ghiorso estimated $S°(FeCr_2O_{4(cr)}) = 142.676$ J K^{-1} mol^{-1} and $\Delta_f H°(FeCr_2O_{4(cr)}) = -1445.490$ kJ mol^{-1}. Robie and Hemingway [95-rob/hem] selected $S°(FeCr_2O_{4(cr)}) = (146.0 \pm 1.7)$ J K^{-1} mol^{-1} taken from their earlier compilation (Robie et al. [78-rob/hem], referencing Kelley and King [61-kel/kin], who reference Shomate) and $\Delta_f H°(FeCr_2O_{4(cr)}) = (-1445.5 \pm 5.0)$ kJ mol^{-1} from Sack and Ghiorso. Robie and Hemingway used these data to calculate $\Delta_f G°(FeCr_2O_{4(cr)}) = (-1344.5 \pm 6.0)$ kJ mol^{-1} for this mineral. We arbitrarily select the more recent interpretations of Robie and Hemingway and recommend $\Delta_f H°(FeCr_2O_{4(cr)}) = (-1445.5 \pm 5.0)$ kJ mol^{-1}, $S°(FeCr_2O_{4(cr)}) = (146.0 \pm 1.7)$ J K^{-1} mol^{-1}, and combination of these two values to calculate $\Delta_f G°(FeCr_2O_{4(cr)}) = (-1344.5 \pm 6.0)$ kJ mol^{-1}. These thermodynamic properties can be combined with those for $Fe^{2+}_{(aq)}$ from Parker and Khodakovskii [95-par/kho], $Cr^{3+}_{(aq)}$ from this report, and $H^{+}_{(aq)}$ and $H_2O_{(l)}$ species from Cox et al. [89-cox/wag] to calculate log $K = 16.1$ and $\Delta_r H = -273.7$ kJ mol^{-1} for the reaction

$$FeCr_2O_{4(s)} + 8H^{+}_{(aq)} \rightleftharpoons Fe^{2+}_{(aq)} + 2Cr^{3+}_{(aq)} + 4H_2O_{(l)} \quad (3)$$

To our knowledge, thermodynamic properties for reaction 3 have never been measured. Since most of the economic Cr ore deposits in the world occur in the form of chromite, this reaction would seem to merit further study.

Table 2. Standard Electrochemical Potential ($E°$) for Reactions Involving Results of Electrochemical Measurements

reaction	$E°$/V	reference
$Cr^{2+}_{(aq)} + 2e^{-}_{(aq)} \rightleftharpoons Cr_{(cr)}$	−0.55	26-gru/sch
$Cr^{2+}_{(aq)} + 2e^{-}_{(aq)} \rightleftharpoons Cr_{(cr)}$	−0.557 ± 0.007	27-gru/bre
$Cr^{2+}_{(aq)} + 2e^{-}_{(aq)} \rightleftharpoons Cr_{(cr)}$	−0.86	57-zab[a]
$Cr^{3+}_{(aq)} + e^{-}_{(aq)} \rightleftharpoons Cr^{2+}_{(aq)}$	−0.38 to −0.51	05-maz1, 05-maz2
$Cr^{3+}_{(aq)} + e^{-}_{(aq)} \rightleftharpoons Cr^{2+}_{(aq)}$	−0.38	17-for/ric
$Cr^{3+}_{(aq)} + e^{-}_{(aq)} \rightleftharpoons Cr^{2+}_{(aq)}$	−0.403 ± 0.003	26-gru/sch
$Cr^{3+}_{(aq)} + e^{-}_{(aq)} \rightleftharpoons Cr^{2+}_{(aq)}$	−0.412 ± 0.002	27-gru/bre
$Cr^{3+}_{(aq)} + e^{-}_{(aq)} \rightleftharpoons Cr^{2+}_{(aq)}$	−0.41	57-zab
$Cr^{3+}_{(aq)} + e^{-}_{(aq)} \rightleftharpoons Cr^{2+}_{(aq)}$	−0.38	64-mal/abu
$Cr^{3+}_{(aq)} + e^{-}_{(aq)} \rightleftharpoons Cr^{2+}_{(aq)}$	−0.41	75-bie/rom
$Cr^{3+}_{(aq)} + 3e^{-}_{(aq)} \rightleftharpoons Cr_{(cr)}$	−0.509	27-gru/bre
$Cr^{3+}_{(aq)} + 3e^{-}_{(aq)} \rightleftharpoons Cr_{(cr)}$	−0.71	57-zab[a]
$HCrO^{-}_{4(aq)} + 7H^{+}_{(aq)} + 3e^{-}_{(aq)} \rightleftharpoons Cr^{3+}_{(aq)} + H_2O_{(l)}$	1.195 ± 0.010	39-dur/bro
$Cr_2O^{2-}_{7(aq)} + 14H^{+}_{(aq)} + 6e^{-}_{(aq)} \rightleftharpoons 2Cr^{3+}_{(aq)} + 4H_2O_{(l)}$	1.33	64-lav

[a] 57-zab states that these reactions were not reversible.

Thermodynamic Properties from Electrochemical Measurements

Thermodynamic properties for reactions based on electrochemical measurements are summarized in Table 2.

Chromium Metal−Aqueous Free Ion Redox. (a) Chromium(metal)−Cr^{2+} Aqueous Ion. Although electrode potentials for this equilibrium have been calculated and reported (see Table 2), to our knowledge, this redox couple has never been measured directly.

(b) Chromium(metal)−Cr^{3+} Aqueous Ion. Despite attempts to measure this half-cell reaction [26-gru/sch, 27-gru/bre], no reversible equilibrium measurement was obtained.

(c) Chromium(metal)−CrO_4^{2-} Aqueous Ion. To our knowledge, this redox couple has never been measured, and the electrode potential would not be expected to be reversible.

Aqueous Chromium(II/III) Redox. Charlot et al. [71-cha/col] cited values of E' (formal potential, concentrations of the oxidizing and reducing agents converted to 1 M) from −0.26 to −0.51 V for the reduction of $Cr^{3+}_{(aq)}$ to $Cr^{2+}_{(aq)}$ in various electrolyte solutions at temperatures between 17 and 25 °C. Charlot et al. listed nine values [05-maz1, 05-maz2, 17-for/ric, 26-gru/sch, 27-gru/bre, 39-kal, 50-pek/lin, 57-zab, 64-mal/abu]. These data were not considered in light of the superior electrochemical measurements of Biedermann and Romano [75-bie/rom].

Biedermann and Romano [75-bie/rom] conducted a careful study of the equilibrium for the $Cr^{3+}_{(aq)}/Cr^{2+}_{(aq)}$ couple, in which they exhaustively purified all reagents, employed several measures to ensure the accuracy of their electrochemical apparatus, allowed many hours for their experiments to equilibrate, and repeated their tests 43 times using several concentration ratios of $Cr^{3+}_{(aq)}/Cr^{2+}_{(aq)}$ and several total Cr concentrations. Although these investigators accounted for ion pairing between $Cr^{3+}_{(aq)}$ and $Cl^{-}_{(aq)}$, they defined their standard state so that the activity factors of the reacting species tended to unity as the composition of the solution approached 1 M NaCl and made no corrections for activities. Since this constant ionic medium standard state is not compatible with that chosen for this work, these results must be recalculated to be useful.

Calculations were done with the geochemical simulation computer program PHREEQE [80-par/tho], with Cr reactions added using an initial Cr database obtained from H. Niklaus Waber (University of Bern, Switzerland, electronic communication, June, 1995). For the purposes of this simulation, the PHREEQE database for Cr was modified by disabling all Cr oxidation−reduction reactions and by adding $Cr^{2+}_{(aq)}$ as a master species. Simulations were calculated by providing the computer code with initial concentrations of sodium, chloride, Cr(II), and Cr(III) in mM/L, and an initial guess for the solution pH based on the initial solution [H$^+$] concentration given by the authors. The computer code estimated pH by adding or subtracting protons to charge-balance each solution, and calculated ionic strength, activity coefficients for each of the five ions in the solution, and activities for all species, including $Cr^{2+}_{(aq)}$, $Cr^{3+}_{(aq)}$, and aqueous Cr(III) ion pairs. For initial [H$^+$] between 28.05 and 1.97 mM, respective solution pH values calculated by PHREEQE were between 1.65 and 2.73.

Biedermann and Romano [75-bie/rom] tabulated constant ionic medium $E°$ values for each of their 43 experimental runs. The Nernst equation

$$E = E° - 0.0592 \log\left(\frac{[Cr^{2+}]}{[Cr^{3+}]}\right) \quad (4)$$

(square brackets denote concentration in moles per liter of solution) was used to calculate EMF (E) values from the reported $E°$ and Cr concentration values. Activities of $Cr^{2+}_{(aq)}$ and $Cr^{3+}_{(aq)}$ calculated by PHREEQE were used in the rearranged form of eq 4

$$E° = E + 0.0592 \log\left(\frac{\{Cr^{2+}\}}{\{Cr^{3+}\}}\right) \quad (5)$$

(braces denote activities) to solve for $E°$ at the $I = 0$ standard state.

The 43 $E°$ values obtained in this way were averaged, and the standard deviation and coefficient of variation were calculated. The PHREEQE database for Cr as received contained Debye−Hückel å parameters of 4.5 for $Cr^{2+}_{(aq)}$ and 5.0 for $Cr^{3+}_{(aq)}$. After initial calculations were done, the source of these parameters was consulted (Wolery [92-wol]), and it was found that the B-dot equation (see Wolery and references therein) was specified for calculating activity coefficients, with a value at 25 °C for the b parameter of 0.0410. The PHREEQE database was modified accordingly, and the program was rerun. Results demonstrate that while inclusion of the b term in the activity coefficient calculation significantly changes the activities and activity coefficients for $Cr^{2+}_{(aq)}$ and $Cr^{3+}_{(aq)}$, the effects tend to cancel each other because the $Cr^{2+}_{(aq)}/Cr^{3+}_{(aq)}$ activity ratio is used to calculate $E°$. Specifically, the two mean $E°$ values calcu-

Table 3. Results for Calculation of Standard Electrochemical Potential ($E°$) Using Four Different Methods for Estimating Activity Coefficients (γ)

method of calculating γ	equation	mean $E°$/V	sample standard deviation, s
B-dot, å = 4.5 and 5.0, $b = 0.0410$	$-\log \gamma = (Az^2\sqrt{I})/(1 + Bå\sqrt{I}) + bI$	−0.3734	0.0013
$\gamma_\pm$ estimation (mean salt)	see eqs 6 and 8	−0.3826	0.0015
Debye−Hückel, å = 6.0 and 9.0	$-\log \gamma = (Az^2\sqrt{I})/(1 + Bå\sqrt{I})$	−0.3968	0.0026
Davies equation	$-\log \gamma = Az^2(\sqrt{I}/(1 + \sqrt{I}) + 0.3I)$	−0.4006	0.0012

lated from the modeling results obtained using the two activity coefficient expressions differed by only 0.1 mV.

The table of Kielland [37-kie] reproduced in Nordstrom and Munoz [94-nor/mun] gives an å parameter of 9.0 for $Cr^{3+}_{(aq)}$ and of 5.0 and 6.0 for most divalent transition metals, but no value for $Cr^{2+}_{(aq)}$. On the basis of this information, the PHREEQE simulation was repeated using the extended Debye−Hückel equation with å parameters of 6.0 for $Cr^{2+}_{(aq)}$ and 9.0 for $Cr^{3+}_{(aq)}$, and using the Davies [62-dav] equation.

Because of the discrepancies between the $E°$ values calculated using the three different activity coefficient expressions for $Cr^{2+}_{(aq)}$ and $Cr^{3+}_{(aq)}$, the mean salt method was employed for estimating these activity coefficients, using the best-fit data for $\gamma_\pm$ compiled by Wu and Hamer [69-wu/ham1, 69-wu/ham2]. Since these data were tabulated as a function of molality rather than ionic strength, and since ionic strength of the solutions of Biedermann and Romano [75-bie/rom] varied only slightly, $\gamma_\pm$ values were calculated for molalities equivalent to a constant ionic strength, which was about 1.1 m for the subject solutions. For $CrCl_3$, the total molality of the solutions must be divided by 6 (ionic strength for a tri-univalent electrolyte $I = 6\ m$). For $CrCl_2$, total molality must be divided by 3. No $\gamma_\pm$ data were available for $CrCl_2$ solutions. Therefore, data for $MnCl_2$ and $FeCl_2$ solutions were examined as approximations to $CrCl_2$ solutions.

The value for $\gamma_\pm$ of $CrCl_3$ for this ionic strength is 0.3058; that for KCl is 0.6004. These values were inserted into the equation for calculating $\gamma(Cr^{3+}_{(aq)})$ by the mean salt method [94-nor/mun]:

$$\gamma_{Cr^{3+}} = \frac{\gamma^4_{\pm CrCl_3}}{\gamma^3_{\pm KCl}} \tag{6}$$

Solution of this equation yields $\gamma(Cr^{3+}_{(aq)}) = 0.0404$ at this ionic strength, using the MacInnes [19-mac] assumption:

$$\gamma_{\pm KCl} = \gamma_{K^+} = \gamma_{Cl^-} \tag{7}$$

For this ionic strength, $\gamma_\pm(MnCl_2) = 0.4418$; $\gamma_\pm(FeCl_2) = 0.4538$. These values were inserted into the equation for calculating the activity coefficient for $Cr^{2+}_{(aq)}$:

$$\gamma_{Cr^{2+}} = \frac{\gamma^3_{\pm CrCl_2}}{\gamma^2_{\pm KCl}} \tag{8}$$

Solution of eq 8 yields $\gamma(Cr^{2+}_{(aq)}) = 0.2393$ using $MnCl_2$ mean ionic activity coefficient data and $\gamma(Cr^{2+}_{(aq)}) = 0.2593$ using $FeCl_2$ mean ionic activity coefficient data.

The stoichiometric activities of $Cr^{3+}_{(aq)}$, $Cr^{2+}_{(aq)}$ and $Cl^{-}_{(aq)}$ approximate their corresponding free-ion activities because complexing of $Cr^{3+}_{(aq)}$, $Cr^{2+}_{(aq)}$, and $Cl^{-}_{(aq)}$ are not significant, to a first approximation. For example, the results of the PHREEQE simulation of Biedermann and Romano's [75-bie/rom] first data set indicate that more than 99.95% of the Cl^-, about 100 percent of the Cr(II), and about 91 to 98% of the Cr(III) are present as the free ions. Thus, to obtain activities of $Cr^{3+}_{(aq)}$ and $Cr^{2+}_{(aq)}$ we can multiply the total molalities of Cr(III) and Cr(II) by the activity coefficients obtained above. The resulting activities are inserted into the Nernst equation, which can be solved for additional values of $E°$ for comparison to those calculated by PHREEQE using the Debye−Hückel and Davies equations for activity-coefficient calculations. Results using the four approaches to calculating the activity coefficients are presented in Table 3.

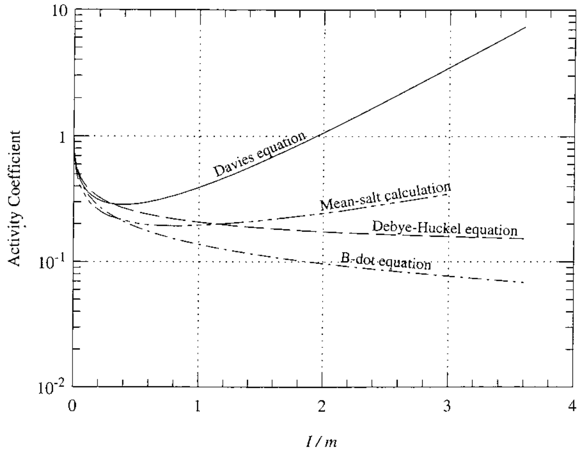

Figure 2. Comparison of $Cr^{2+}_{(aq)}$ activity coefficients calculated using several methods (mean-salt line is $MnCl_2$−$FeCl_2$ average).

The $E°$ value calculated using the $MnCl_2$ data was (−0.3836 ± 0.0011) V, and the $E°$ value calculated using the $FeCl_2$ data was (−0.3816 ± 0.0011) V. Table 3 shows the overall mean obtained by combining results from both data sets. These results are numerically closest to those calculated using PHREEQE and the B-dot equation with a b parameter of 0.0410 and å parameters of 4.5 and 5.0 for $Cr^{2+}_{(aq)}$ and $Cr^{3+}_{(aq)}$, respectively. In this instance $\gamma(Cr^{2+}_{(aq)}) = 0.160$ and $\gamma(Cr^{3+}_{(aq)}) = 0.019$ were calculated. Using PHREEQE and the Debye−Hückel equation with å parameters of 6.0 and 9.0, the respective γ values were about 0.201 and 0.067. Figures 2 and 3 are graphs of $\gamma(Cr^{2+}_{(aq)})$ and $\gamma(Cr^{3+}_{(aq)})$, respectively, calculated by the four methods as a function of ionic strength. The mean-salt data shown in Figure 2 represent the average of the $FeCl_2$ and $MnCl_2$ data. Figures 2 and 3 show that the B-dot method of calculation most closely approximates $\gamma(Cr^{2+}_{(aq)})$ and $\gamma(Cr^{3+}_{(aq)})$ calculated using the mean-salt approach, up to ionic strengths of about 0.6 m and 1 m, respectively. Figure 2 shows that the Debye−Hückel equation most closely approximates the mean-salt $\gamma(Cr^{2+}_{(aq)})$ values above about 0.6 m. In both cases, the Davies equation results in activity coefficients that diverge significantly from the others above an ionic strength of about 0.5 m to 0.8 m. This divergence increases with increasing ionic charge because of the formulation of the Davies equation.

The $E°$ for reduction of $Cr^{3+}_{(aq)}$ to $Cr^{2+}_{(aq)}$ remains somewhat ambiguous, despite the results of calculations done above for the data set of Biedermann and Romano [75-bie/

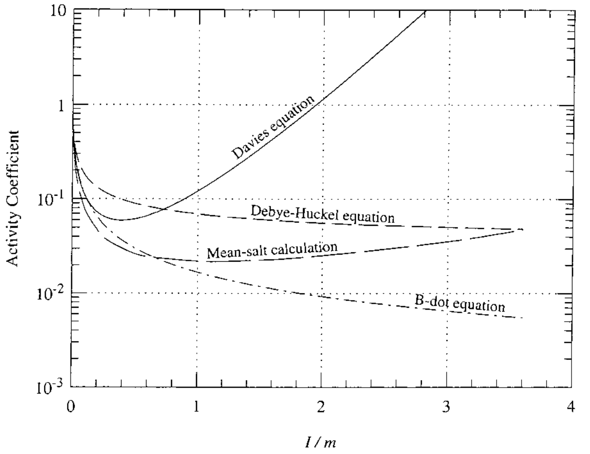

Figure 3. Comparison of $Cr^{3+}_{(aq)}$ activity coefficients calculated using several methods.

rom]. However, it seems unlikely, given the results of the present exercise, that this $E°$ is as negative as −0.41 V at $I = 0$ *m*. Since the Davies equation is known to be increasingly inaccurate for other than monovalent ions at solution concentrations above 0.5 *m*, those results can be discounted when estimating a revised $E°$. Thus, a reasonable value for $E°$ for this reduction, giving equal weight to the two most positive $E°$ values found in Table 3, is about −0.378 V.

On the basis of the results of the foregoing exercise, a few observations can be made about the method of calculating activity coefficients. The mean salt approach is not readily adapted to mixed electrolyte solutions because the data are based on single-salt solutions and significant differences are measured with varying anion identity. The Davies equation appears to be a poor choice because of its progressively worsening accuracy above $I \approx 0.5$ *m*. However, if the application is for solutions of $I \leq 0.2$ *m*, the Davies equation is of equal accuracy and appears unparalleled in simplicity, since no ion-specific parameters are needed. For the most general of applications, neither the Debye−Hückel nor the B-dot equations are sufficiently reliable at $I > 1$ *m*. Thus, in more concentrated solutions a specific-ion interaction approach is needed. Unfortunately, specific-ion interaction parameters are available only for $CrCl_3$ and $Cr(NO_3)_3$ (Pitzer [91-pit], p 107). At $I \leq 1$ *m*, on the basis of the results of the present study, the Debye−Hückel and the B-dot equations appear approximately equivalent, with the B-dot equation yielding a somewhat better overall approximation to the mean salt data.

Aqueous Chromium(III/VI) Redox. Charlot et al. [71-cha/col] reported $E° = +1.20$ V for the reaction

$$HCrO_4^- + 7H^+ + 3e^- \rightleftharpoons Cr^{3+} + 4H_2O \qquad (9)$$

citing their reference number 59.6 [59-tro/mis]. Sillen and Martell [64-sil/mar] listed $E°(9) = 1.195$ V and cited Durban and Brown [39-dur/bro] for the value. (In the references of 71-cha/col the reference numbered "39.6" is 39-dur/bro. Thus, the report of 39-dur/bro is undoubtedly the correct source of this measurement, and what should have been a "3" in the References column of 71-cha/col was entered in error as a "5.") Durban and Brown measured the EMF of a $Cr(ClO_4)_3|CrO_3|HClO_4|Pt$ cell at Cr^{3+}/CrO_3 ratios of 0.001 *m*/0.100 *m*, 0.100 *m*/0.001 *m*, and 0.001 *m*/0.001 *m*, the latter ratio in conjunction with $HClO_4$ concentrations of 1.0 *m*, 0.5 *m*, 0.05 *m*, 0.01 *m*, and 0.001 *m*. These investigators conducted their experiments under an inert gas atmosphere and allowed up to 11 days for the EMF to equilibrate. Rather than correct for nonideality in the solute concentrations, Durban and Brown stated that their activities approached the molalities as the solutions became more dilute and used only results from their more dilute solutions. Durban and Brown proposed a reversible oxidation potential for reaction 9 of (1.195 ± 0.010) V, or $\Delta_f G°(9) = (-345.9 \pm 2.9)$ kJ mol^{-1} and $\log K(9) = (60.60 \pm 0.51)$. Using best values for $\Delta_f G°(Cr^{3+}_{(aq)})$ and $\Delta_f G°(H_2O_{(l)})$ yields $\Delta_f G°(HCrO^-_{4(aq)}) = -828.2$ kJ mol^{-1}. This value is 55 to 60 kJ mol^{-1} more negative than alternative values of −764.7 kJ mol^{-1} selected by Wagman et al. [82-wag/eva], −768.6 kJ mol^{-1} calculated by O'Hare and Boerio [75-oha/boe], and −773.6 kJ mol^{-1} selected by Latimer [52-lat].

Table 4. Summary of Selected Determinations of Standard Enthalpy of Formation ($\Delta_f H°$) of $Cr^{3+}_{(aq)}$

$\Delta_f H°$/ kJ mol^{-1}	reference
−246.5	$Fe^{3/2}/Cr^{2/3}$ using 37-doe and 53-gre/bur
−239.3	49-eva
−256.1	52-ros/wag; 52-lat
−238	76-del/hal
−251.0	76-del/hep
−254.8	77-vas/vas1
−234.8	77-vas/vas1 recalculated
−252.9	77-vas/vas2
−236.5	77-vas/vas2 recalculated
−254.4	80-vas/vas revised weighted mean
−284.1	76-del/hal
−253.6	$Fe^{3/2}/Cr^{2/3}$ using $\Delta_f H°(Cr^{2+}_{(aq)})$ from 82-wag/eva
−256.1	93-slo/kri
−204.7	90-tim/yul + 66-shc/vas
−239.4	this study

Raw EMF values from the two most dilute solutions in Table 4 of Durban and Brown [39-dur/bro] were corrected for ionic strength and hydrolysis using program MINTEQA2 with the database modified to use the hydrolysis and dimerization data from Rai et al. [87-rai/sas] and Palmer et al. [87-pal/wes]. The revised activities of $Cr^{3+}_{(aq)}$ and $HCrO^-_{4(aq)}$ were substituted into the Nernst equation, and new values for $E°$ were calculated. For experiment 4 of Durban and Brown's Table 4, a value for $E°$ of 1.193 V was calculated, compared with the original value of 1.196 V. For experiment 5, a value for $E°$ of 1.186 V was calculated, compared with the original value of 1.194 V. The difference is larger for more dilute solutions because hydrolysis reduces the activity of $Cr^{3+}_{(aq)}$ to a greater extent than the activity of $HCrO^-_{4(aq)}$ at the higher pH. Activity and hydrolysis corrections reduced the difference by a maximum of about 2 kJ mol^{-1}. Using our proposed values for $\Delta_f G°(Cr^{3+}_{(aq)})$, $\Delta_f G°(HCrO^-_{4(aq)})$, and $\Delta_f G°(H_2O_{(l)})$ yields $E°(9) = 1.426$ V. Thus, there appears to be a significant discrepancy between the electrochemical and the calorimetric and solubility measurements. Durban and Brown mentioned that their electrochemical cell was only marginally reversible. Under these circumstances, we believe there is ample justification for selecting the weighted mean of the calorimetric results and ignoring the electrochemical results.

Charlot et al. [71-cha/col] reported $E° = +1.33$ V for the reaction

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad (10)$$

and identified reaction 10 as an equilibrium that has an $E°$ value that has been confirmed by several authors.

Charlot et al. cited the measurements of Lavrenchuk [64-lav] and Willard and Manalo [47-wil/man] and the compilation of Latimer [52-lat] as sources of the reported $E°$ value. Lavrenchuk reported $E°(10) \approx (1.33 \text{ to } 1.38)$ V and found $Cr_2O^{2-}_{7(aq)}$ stable below pH 9.7, $CrO^{2-}_{4(aq)}$ stable above pH 3.7, and both species stable from pH 3.7 to 9.7. Willard and Manalo measured formal potentials in solutions prepared either by mixing equal amounts of oxidized and reduced species or by partial oxidation or reduction of a solution initially containing only one of the species. The solutions were adjusted to NaOH = 1, 3, or 5 F, at which potentials of -0.12, -0.09, and -0.08 V, respectively, were measured. Willard and Manalo compared their results to the molal potential $= -0.12$ V reported by Latimer [38-lat] but stated that temperatures and liquid junction potentials were not carefully controlled, rendering their own potentials no more accurate than ± 0.01 V. Latimer [52-lat] used the results of Evans [49-eva] for the determination of $\Delta_r H°(2Cr^{3+}-Cr_2O_7^{2-}) = 1010.9$ kJ mol^{-1} to recalculate the Cr(VI) thermodynamic properties. From $\Delta_f G°(Cr_2O^{2-}_{7(aq)}) = -1319.6$ kJ mol^{-1}, $\Delta_f G°(Cr^{3+}_{(aq)}) = -215.5$ kJ mol^{-1}, and $\Delta_f G°(H_2O_{(l)}) = -237.19$ kJ mol^{-1}, Latimer [52-lat] calculated $E°(10) = 1.33$ V. From $E°(10)$ we calculate $\Delta_r G°(10) = -769.9$ kJ mol^{-1}, which is equivalent to $\log K(10) = 134.9$. Using our selected $\Delta_f G°(Cr^{3+}_{(aq)}) = -194.8$ kJ mol^{-1} and $\Delta_f G°(H_2O_{(l)}) = -237.14$ kJ mol^{-1} from Cox et al. [89-cox/wag], we calculate $\Delta_f G°(Cr_2O^{2-}_{7(aq)}) = -1279.4$ kJ mol^{-1}. This value is about 16 kJ mol^{-1} more positive than our recommended $\Delta_f G°(Cr_2O^{2-}_{7(aq)}) = -1295.6$ kJ mol^{-1} and 22 to 40 kJ mol^{-1} more positive than $\Delta_f G°(Cr_2O^{2-}_{7(aq)}) = -1301.1$ kJ mol^{-1} [82-wag/eva], -1308.8 kJ mol^{-1} [75-oha/boe], and -1319.6 kJ mol^{-1} [52-lat]. Recalculation of this equilibrium using our recommended, values for $\Delta_f G°(Cr_2O^{2-}_{7(aq)}) = -1295.6$ kJ mol^{-1} and $\Delta_f G°(Cr^{3+}_{(aq)}) = -198.3$ kJ mol^{-1} and $\Delta_f G°(H_2O_{(l)}) = -237.14$ kJ mol^{-1} from Cox et al., yields $\Delta_r G°(10) = -760.94$ kJ mol^{-1}, $E°(10) = 1.31$ V, and $\log K(10) = 133.3$.

Thermodynamic Properties of Chromium Aqueous Ions

Standard State Thermodynamic Properties for $Cr^{3+}_{(aq)}$. There are several pathways for obtaining standard state thermodynamic properties of $Cr^{3+}_{(aq)}$. Unfortunately, few are reliable and none are optimal. The six pathways considered here are dissolution of $CrCl_{3(cr)}$, oxidation of $Cr^{2+}_{(aq)}$ by $Fe^{3+}_{(aq)}$ or $Cu^{2+}_{(aq)}$, and reduction of $Cr_2O^{2-}_{7(aq)}$ by $Fe^{2+}_{(aq)}$, C_2H_5OH, or CH_2O. The network of pathways selected for final consideration is shown in Figure 4.

Dellien et al. [76-del/hal] reviewed and evaluated many earlier determinations of thermodynamic properties of $Cr^{3+}_{(aq)}$. These authors recommended $\Delta_f H°(Cr^{3+}_{(aq)}) = -57$ kcal mol^{-1} (-238 kJ mol^{-1}), $\Delta_f G°(Cr^{3+}_{(aq)}) = -46.5$ kcal mol^{-1} (-194.6 kJ mol^{-1}), and $S°(Cr^{3+}_{(aq)}) = -76$ cal K^{-1} mol^{-1} (-318 J K^{-1} mol^{-1}). Slobodov et al. [93-slo/kri] observed that $Cr^{3+}_{(aq)}$ has been studied very little because of its tendency to be reduced and to hydrolyze, selected $S°(Cr^{3+}_{(aq)}) = -313.8$ J K^{-1} mol^{-1} from Shock and Helgeson [88-sho/hel], and cited three sources [90-tim/yul, 52-lat, 21-lam/fon] for their selected $\Delta_f H°(Cr^{3+}_{(aq)}) = -256.1$ kJ mol^{-1}. Slobodov et al. then calculated $\Delta_f G°(Cr^{3+}_{(aq)}) = -213.9$ kJ mol^{-1}, but inexplicably ignored the work of Dellien and Hepler [76-del/hep] and Vasil'ev et al. [77-vas/vas1, 77-vas/vas2, 78-vas/vas, 80-vas/vas].

Potentially one of the most direct pathways to determining $\Delta_f H°(Cr^{3+}_{(aq)})$ is $\Delta_{soln} H°(CrCl_{3(cr)})$ because $\Delta_f H°(Cl^-_{(aq)})$ is known with good precision and $\Delta_f H°(CrCl_{3(cr)})$ can be determined by reacting the constituent elements in their standard states, making $\Delta_r H°$equal to $\Delta_f H°(CrCl_{3(cr)})$. This pathway is shown in the following reaction matrix:

reaction	$\Delta_f H°$/ (kJ mol^{-1})	reference
$CrCl_{3(cr)} \rightleftharpoons Cr^{3+}_{(aq)} + 3Cl^-_{(aq)}$	-161.5 ± 1.3	66-shc/vas
$Cr_{(cr)} + 1^1/_2Cl_{2(g)} \rightleftharpoons CrCl_{3(cr)}$	-544.4 ± 1.4	90-tim/yul
$3Cl^-_{(aq)} + 3H^+_{(aq)} \rightleftharpoons 1^1/_2Cl_{2(g)} + 1^1/_2H_{2(g)}$	501.24 ± 0.30	89-cox/wag
$Cr_{(cr)} + 3H^+_{(aq)} \rightleftharpoons Cr^{3+}_{(aq)} + 1^1/_2H_{2(g)}$	-204.7 ± 1.9	

Timofeyev and Yuldasheva [90-tim/yul] determined $\Delta_f H°(CrCl_{3(cr)})$ by reacting electrolytic $Cr_{(cr)}$ with $Cl_{2(g)}$. Of the 45 impurities reported, the greatest impurity in the sample of $Cr_{(cr)}$ was C, with a mass fraction of 0.000 04. These investigators repeated their experiment six times, corrected their results for the major impurities, and obtained excellent precision in their results. Timofeyev and Yuldasheva recommended $\Delta_f H°(CrCl_{3(cr)}) = (-544.4 \pm 1.4)$ kJ mol^{-1}.

Doerner [37-doe] conducted high-temperature experiments to measure $\Delta_r H°$ for reduction of $CrCl_{3(cr)}$ to $CrCl_{2(cr)}$, $CrCl_{3(cr)}$ to $Cr_{(cr)}$, and $CrCl_{2(cr)}$ to $Cr_{(cr)}$. Doerner's results can be combined with standard state thermodynamic properties for auxiliary substances from Cox et al. [89-cox/wag] to calculate $\Delta_f H°(CrCl_{3(cr)}) = (-542.5 \pm 1.3)$ kJ mol^{-1}. This value compares favorably with $\Delta_f H°(CrCl_{3(cr)}) = (-544.4 \pm 1.4)$ kJ mol^{-1} of Timofeyev and Yuldasheva [90-tim/yul].

The $S°(CrCl_{3(cr)})$ has been determined by Anderson [37-and] and Hansen and Griffel [58-han/gri], who proposed values of (118.0 ± 4.2) J K^{-1} mol^{-1} and (122.9 ± 0.4) J K^{-1} mol^{-1}, respectively. Hansen and Griffel compared their results to those of earlier investigators and observed that their results agreed with those of Anderson up to 200 K, above which deviations of about 2% were observed. In an electrochemical study, Gee and Shelton [75-gee/she] determined $\Delta_f G°(CrCl_{3(cr)}) = (-484.0 \pm 4.0)$ kJ mol^{-1}. Combining the values proposed by Hansen and Griffel and Gee and Shelton yields $\Delta_f H°(CrCl_{3(cr)}) = -554.1$ kJ mol^{-1}, which is about 9.7 kJ mol^{-1} more negative than $\Delta_f H°(CrCl_{3(cr)}) = -544.4$ kJ mol^{-1} of Timofeyev and Yuldasheva [90-tim/yul]. The above represent a reasonably consistent set of measurements for the standard state thermodynamic properties of $CrCl_{3(cr)}$. The results of Sano [38-san1] were deemed suspicious by Maier [43-mai] because they yielded $S°(CrCl_{3(cr)})$ over 30 J K^{-1} mol^{-1} more positive than entropies determined by other studies. Sano's results yield $\Delta_f H°(CrCl_{3(cr)})$ about 12 kJ mol^{-1} more negative than the above values. Consequently, we choose to exclude Sano's results from further consideration and recommend $\Delta_f H°(CrCl_{3(cr)}) = (-544.4 \pm 1.4)$ kJ mol^{-1} from Timofeyev and Yuldasheva, $S°(CrCl_{3(cr)}) = (122.9 \pm 0.4)$ J K^{-1} mol^{-1} from Hansen and Griffel, and their combination to yield $\Delta_f G°(CrCl_{3(cr)}) = (-474.2 \pm 1.5)$ kJ mol^{-1}.

We have found two measurements of $\Delta_{soln} H°(CrCl_{3(cr)})$ reported in the literature. Shchukarev et al. [66-shc/vas] determined $\Delta_{soln} H°(CrCl_{3(cr)})$ in alkali−chromic chloride compounds of composition M_3CrCl_6 and $M_3Cr_2Cl_9$, where M is Li, Na, K, Rb, or Cs. From the average of seven determinations, these investigators proposed $\Delta_{soln} H°(CrCl_{3(cr)}) = (-161.5 \pm 1.3)$ kJ mol^{-1}. Gregory and Burton [53-gre/bur] determined $\Delta_{soln} H°(CrCl_{3(cr)}) = (-136.9 \pm 1.3)$ kJ mol^{-1} in 1 m KCl but apparently did not correct their data for the effects of complexing and ionic strength. Gee

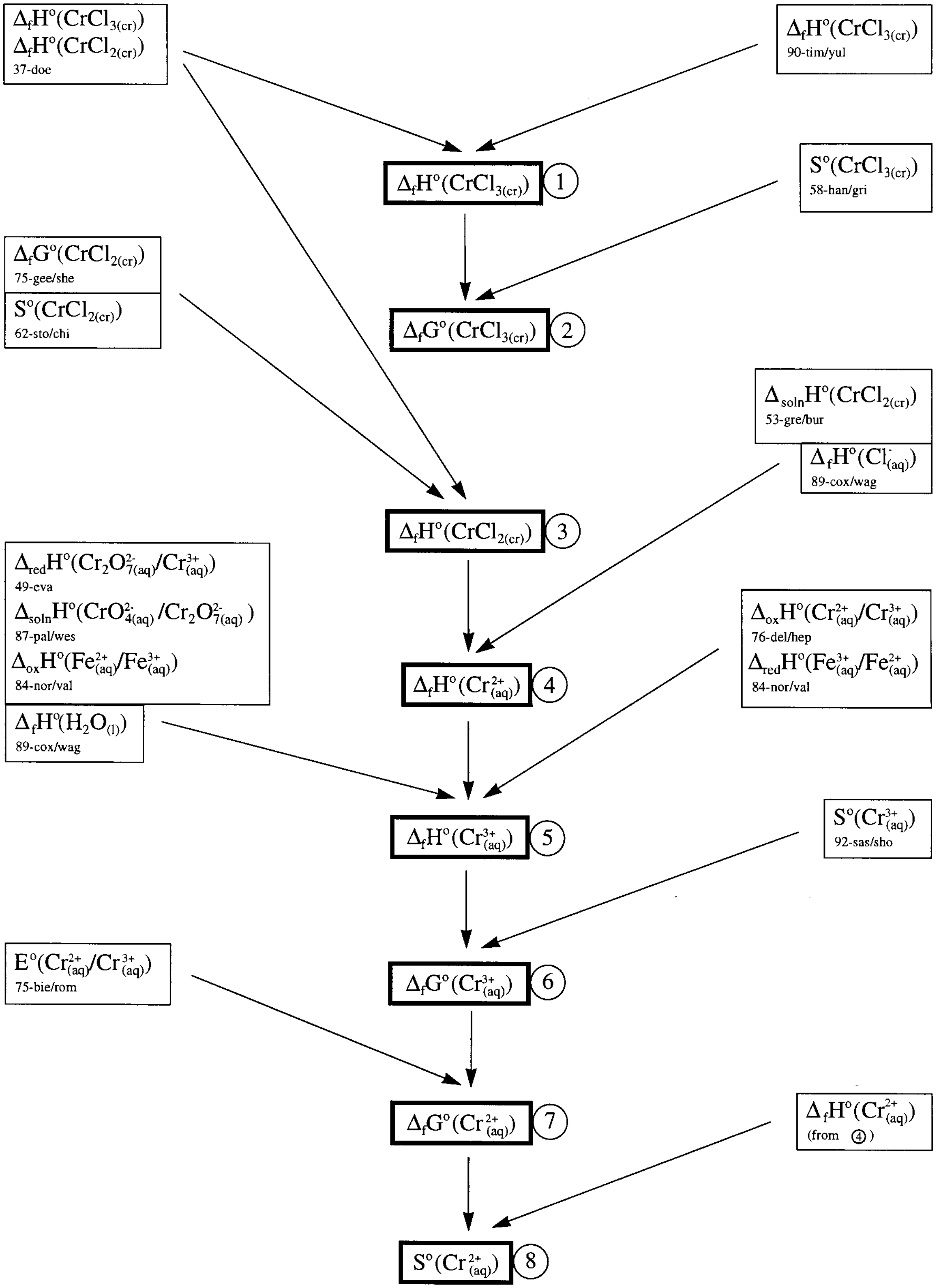

Figure 4. Calculation pathways for obtaining standard state enthalpies, free energies, and entropies of $Cr^{3+}_{(aq)}$.

and Shelton [75-gee/she] and Dellien and Hepler [76-del/hep] discussed these two studies. Dellien and Hepler commented on the difficulty of correcting the results for the presence in the solids of other metal chlorides and eschewed the use of alkali metal chlorides for their calorimetric determinations. Furthermore, Dellien et al. [76-del/hal] noted that assumptions regarding Cr–Cl complexing can introduce significant uncertainty in $\Delta_{soln}H°(CrCl_{3(cr)})$. Recalculation of results of these investigations leads us to $\Delta_fH°(Cr^{2+}_{(aq)})$ and $\Delta_fH°(Cr^{3+}_{(aq)})$ that are not consistent with results using other pathways. Thus, it appears that existing data for $\Delta_{soln}H°(CrCl_{3(cr)})$ cannot be relied upon to yield precise thermodynamic properties of the aqueous ions.

Dellien and Hepler [76-del/hep] determined $\Delta_fH°(Cr^{3+}_{(aq)})$ calorimetrically by measuring the heat of oxidation of

$Cr^{2+}_{(aq)}$ to $Cr^{3+}_{(aq)}$ by $Fe^{3+}_{(aq)}$ in 0.5 M $HClO_4$. This path is illustrated in the following reaction matrix:

reaction	$\Delta_r H°$/ (kJ mol^{-1})	reference
$Cr^{2+}_{(aq)} + Fe^{3+}_{(aq)} \rightleftharpoons Cr^{3+}_{(aq)} + Fe^{2+}_{(aq)}$	−151.9 ± 2.5	76-del/hep
$Fe^{2+}_{(aq)} + H^{+}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + {}^1/_2H_{2(g)}$	41.8 ± 2.1	84-nor/val
$Cr_{(cr)} + 2H^{+}_{(aq)} \rightleftharpoons Cr^{2+}_{(aq)} + H_{2(g)}$	−136.5 ± 2.5	37-doe, 53-gre/bur
$Cr_{(cr)} + 3H^{+}_{(aq)} \rightleftharpoons Cr^{3+}_{(aq)} + 1^1/_2H_{2(g)}$	−246.5 ± 4.1	

Substituting $\Delta_f H°(Cr^{2+}_{(aq)}) = -143.5$ kJ mol^{-1} from Wagman et al. [82-wag/eva] yields $\Delta_f H°(Cr^{3+}_{(aq)}) = -253.6$ kJ mol^{-1}. Unfortunately, this reaction path depends strongly on the choice of $\Delta_f H°(Cr^{2+}_{(aq)})$.

In addition to the above scheme, Dellien and Hepler [76-del/hep] used several alternative methods of determining $\Delta_f H°(Cr^{3+}_{(aq)})$, including oxidation of $Cr^{2+}_{(aq)}$ to $Cr^{3+}_{(aq)}$ by $Cu^{2+}_{(aq)}$, $Ag^{+}_{(aq)}$, and Ce(IV), oxidation of Cr(III) to Cr(VI) by $Fe^{3+}_{(aq)}$, and reduction of Cr(VI) to Cr(III) in acidic solution by H_2O_2. For the Cu path, we note that our recalculated $\Delta_f H°(Cr^{3+}_{(aq)}) = -258.8$ kJ mol^{-1} is 3.8 kJ mol^{-1} more negative than the value actually reported by Dellien and Hepler. Dellien and Hepler excluded the results of their $Ag^{+}_{(aq)}$ and H_2O_2 experiments when they found significant amounts of hydrolytic polymers in the reaction products. These investigators discussed their selection of auxiliary thermodynamic properties for all species used in their determinations and recommended a weighted average of $\Delta_f H°(Cr^{3+}_{(aq)}) = (-60.0 \pm 1.5)$ kcal mol^{-1} [(-251.0 ± 6.3) kJ mol^{-1}]. We prefer to include in our evaluation only Dellien and Hepler's results for oxidation of $Cr^{2+}_{(aq)}$ to $Cr^{3+}_{(aq)}$ by $Fe^{3+}_{(aq)}$, and to use $\Delta_r H°$ for the oxidation of $Fe^{2+}_{(aq)}$ to $Fe^{3+}_{(aq)}$ of (41.8 ± 2.1) kJ mol^{-1} from Nordstrom et al. [84-nor/val] and the alternative $\Delta_f H°(Cr^{2+}_{(aq)}) = -136.5$ kJ mol^{-1} from the $Cr^{3+}_{(aq)}$ reaction matrix above to calculate $\Delta_f H°(Cr^{3+}_{(aq)}) = (-246.5 \pm 4.1)$ kJ mol^{-1}.

Evans [49-eva] measured $\Delta_r H°$ between $Cr_2O^{2-}_{7(aq)}$ and $Fe^{2+}_{(aq)}$. The reaction matrix for this scheme is shown below:

reaction	$\Delta_r H°$/ (kJ mol^{-1})	reference
${}^1/_2Cr_2O^{2-}_{7(aq)} + 3Fe^{2+}_{(aq)} + 7H^{+}_{(aq)} \rightleftharpoons Cr^{3+}_{(aq)} + 3Fe^{3+}_{(aq)} + 3^1/_2H_2O_{(l)}$	−376.1 ± 0.4	49-eva
$Cr_{(cr)} + 1^3/_4O_{2(g)} + {}^1/_2H_{2(g)} \rightleftharpoons {}^1/_2Cr_2O^{2-}_{7(aq)} + H^{+}_{(aq)}$	−738.1 ± 1.4	this study
$3Fe^{3+}_{(aq)} + 1^1/_2H_{2(g)} \rightleftharpoons 3Fe^{2+}_{(aq)} + 3H^{+}_{(aq)}$	−125.4 ± 6.3	84-nor/val
$3^1/_2H_2O_{(l)} \rightleftharpoons 3^1/_2H_{2(g)} + 1^3/_4O_{2(g)}$	1000.405 ± 0.410	89-cox/wag
$Cr_{(cr)} + 3H^{+}_{(aq)} \rightleftharpoons Cr^{3+}_{(aq)} + 1^1/_2H_{2(g)}$	−239.3 ± 6.4	

The resulting $\Delta_f H°(Cr^{3+}_{(aq)})$ is about 12 kJ mol^{-1} more positive than the weighted best value proposed by Dellien and Hepler but is about 7 kJ mol^{-1} more positive than the alternative results of our recalculations for the measurements of Dellien and Hepler. Thus, this result merits additional consideration.

Vasil'ev et al. [77-vas/vas1] evaluated literature values for $\Delta_f H°(Cr^{3+}_{(aq)})$ and reported results of their determination of the enthalpy of reduction of $Na_2Cr_2O_7$ by C_2H_5OH in $HClO_4$ solution. They carefully standardized reaction solutions, accounted for the equilibrium between $HCrO^{-}_{4(aq)}$ and $Cr_2O^{2-}_{7(aq)}$, maintained the reaction at a constant temperature of 25 °C, and conducted many replicate measurements at $I = 2$, 3, and 4 *m*. Vasil'ev et al. evaluated their results in terms of the equilibrium between $HCrO^{-}_{4(aq)}$ and $Cr_2O^{2-}_{7(aq)}$ at $2 \leq I \leq 4$ *m* and used thermodynamic properties for all reactants except Cr^{3+} from the compilation of Glushko [74-glu]. Vasil'ev et al. reported $\Delta_f H°(Cr^{3+}_{(aq)}) = (-60.90 \pm 0.51)$ kcal mol^{-1} [(-254.8 ± 2.1) kJ mol^{-1}] at $I = 0$ *m*.

Vasil'ev et al. [77-vas/vas2] conducted measurements similar to those of Vasil'ev et al. [77-vas/vas1] by reacting $Na_2Cr_2O_7$ with CH_2O in $HClO_4$ solution. The objective of this study was to determine $\Delta_f H°(Cr^{3+}_{(aq)})$ by an independent method to compare with the previous [77-vas/vas1] results. In this set of experiments, the investigators purified $Na_2Cr_2O_7$ by 2-fold recrystallization, used double-distilled H_2O, and conducted measurements at $I = 1.0$, 1.5, and 2.0 *m*. Their results can be evaluated in terms of the following two reaction matrices

reaction	$\Delta_r H°$/ (kJ mol^{-1})	reference
${}^1/_2Cr_2O^{2-}_{7(aq)} + 1^1/_2CH_2O_{(l)} + 4H^{+}_{(aq)} \rightleftharpoons Cr^{3+}_{(aq)} + 1^1/_2HCOOH_{(l)} + 2H_2O_{(l)}$	−449.4 ± 3.2	77-vas/vas2
$Cr_{(cr)} + 1^3/_4O_{2(g)} + {}^1/_2H_{2(g)} \rightleftharpoons {}^1/_2Cr_2O^{2-}_{7(aq)} + H^{+}_{(aq)}$	−738.1 ± 1.4	this study
$1^1/_2C_{(cr)} + 1^1/_2H_{2(g)} + {}^3/_4O_{2(g)} \rightleftharpoons 1^1/_2CH_2O_{(l)}$	−256.05	82-wag/eva
$1^1/_2HCOOH_{(l)} \rightleftharpoons 1^1/_2C_{(cr)} + 1^1/_2H_{2(g)} + 1^1/_2O_{2(g)}$	637.08	82-wag/eva
$2H_2O_{(l)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$	571.7 ± 0.08	89-cox/wag
$Cr_{(cr)} + 3H^{+}_{(aq)} \rightleftharpoons Cr^{3+}_{(aq)} + 1^1/_2H_{2(g)}$	−234.8 ± 3.5	

and:

reaction	$\Delta_r H°$/ (kJ mol^{-1})	reference
$HCrO^{-}_{4(aq)} + 1^1/_2CH_2O_{(l)} + 4H^{+}_{(aq)} \rightleftharpoons Cr^{3+}_{(aq)} + 1^1/_2HCOOH_{(l)} + 2^1/_2H_2O_{(l)}$	−460.8 ± 1.2	77-vas/vas2
$Cr_{(cr)} + 2O_{2(g)} + H_{2(g)} \rightleftharpoons HCrO^{-}_{4(aq)} + H^{+}_{(aq)}$	−873.0 ± 1.4	this study
$1^1/_2C_{(cr)} + 1^1/_2H_{2(g)} + {}^3/_4O_{2(g)} \rightleftharpoons 1^1/_2CH_2O_{(l)}$	−256.05	82-wag/eva
$1^1/_2HCOOH_{(l)} \rightleftharpoons 1^1/_2C_{(cr)} + 1^1/_2H_{2(g)} + 1^1/_2O_{2(g)}$	637.08	82-wag/eva
$2^1/_2H_2O_{(l)} \rightleftharpoons 2^1/_2H_{2(g)} + 1^1/_4O_{2(g)}$	714.58 ± 0.10	89-cox/wag
$Cr_{(cr)} + 3H^{+}_{(aq)} \rightleftharpoons Cr^{3+}_{(aq)} + 3H_2O_{(l)}$	−238.2 ± 1.9	

Vasil'ev et al. [77-vas/vas2] also used auxiliary data from Glushko [74-glu] and reported $\Delta_f H°(Cr^{3+}_{(aq)}) = (-60.44 \pm 0.66)$ kcal mol^{-1} [(-252.9 ± 2.8) kJ mol^{-1}] at $I = 0$. These authors combined results from their two studies and proposed a most probable value for this property of (-60.70 ± 0.20) kcal mol^{-1} [(-254.0 ± 0.8) kJ mol^{-1}]. Our calculations shown in the above matrices using auxiliary data for CH_2O and HCOOH from Wagman et al. [82-wag/eva] yield $\Delta_f H°(Cr^{3+}_{(aq)}) = (-234.8 \pm 3.5)$ kJ mol^{-1} and $\Delta_f H°(Cr^{3+}_{(aq)}) = (-238.2 \pm 1.9)$ kJ mol^{-1} for reaction with $Cr_2O^{2-}_{7(aq)}$ and $HCrO^{-}_{4(aq)}$, respectively.

Vasil'ev et al. [78-vas/vas] measured the enthalpy of reaction between potassium chromium alum ($KCr(SO_4)_2 \cdot 12H_2O$) and NaBrO in alkaline solution to determine $\Delta_f H°(KCr(SO_4)_2 \cdot 12H_2O)$. These investigators then measured the heat of solution of $KCr(SO_4)_2 \cdot 12H_2O$ in $HClO_4$ to obtain $\Delta_f H°(Cr^{3+}_{(aq)})$. The $KCr(SO_4)_2 \cdot 12H_2O$ was purified by double recrystallization from H_2SO_4 and found by titration to have a purity of 99.99%. Experiments were conducted at $I = 0.5$, 1.0, and 1.5 *m*, and enthalpy was extrapolated to $I = 0$ *m*. From these results, the authors proposed a weighted mean value of $\Delta_f H°(Cr^{3+}_{(aq)}) = (-60.72 \pm 0.23)$ kcal mol^{-1} [(-254.1 ± 1.0) kJ mol^{-1}] at $I = 0$ *m* and calculated a weighted mean of results of their three studies [77-vas/

vas1, 77-vas/vas2, 78-vas/vas], proposing a most probable value of $\Delta_f H°(\mathrm{Cr}^{3+}_{(aq)}) = (-60.70 \pm 0.30)$ kcal mol^{-1} [(-254.0 ± 1.3) kJ mol^{-1}]. Vasil'ev et al. noted good agreement between their results and those of Dellien and Hepler [76-del/hep].

Vasil'ev et al. [80-vas/vas] discussed their three previous independent measurements of $\Delta_f H°(\mathrm{Cr}^{3+}_{(aq)})$ (discussed above) and reported a slightly revised weighted mean $\Delta_f H°(\mathrm{Cr}^{3+}_{(aq)}) = (-60.80 \pm 0.30)$ kcal mol^{-1} [(-254.4 ± 1.3) kJ mol^{-1}]. These authors also described in some detail the work of Dellien and Hepler [76-del/hep] and noted that their own $\Delta_f H°(\mathrm{Cr}^{3+}_{(aq)})$ agreed with the weighted mean $\Delta_f H°(\mathrm{Cr}^{3+}_{(aq)}) = (-251.0 \pm 6.3)$ kJ mol^{-1} of Dellien and Hepler within experimental error. Vasil'ev et al. determined the heat of solution in $\mathrm{HClO_4}$ of $\mathrm{NH_4Cr(SO_4)_2{\cdot}12H_2O}$, which they recrystallized and established was 99.94% pure. From these results and literature values [01-loc, 47-smi, 48-smi/len] for the solubility of $\mathrm{NH_4Cr(SO_4)_2{\cdot}12H_2O}$ and its activity and osmotic coefficients in a saturated aqueous solution, the authors were able to calculate $S°(\mathrm{Cr}^{3+}_{(aq)})$. They determined this property at three different ionic strengths, extrapolated their results to $I = 0$ m, and obtained a value for $S°(\mathrm{Cr}^{3+}_{(aq)}) = (-64.4 \pm 1.7)$ cal K^{-1} mol^{-1} [(-269.4 ± 7.1) J K^{-1} mol^{-1}]. With these data, Vasil'ev et al. calculated $\Delta_f G°(\mathrm{Cr}^{3+}_{(aq)}) = (-53.89 \pm 0.58)$ kcal mol^{-1} [(-225.5 ± 2.4) kJ mol^{-1}] and thence $E° = (-0.779 \pm 0.008)$ V for the reduction of $\mathrm{Cr}^{3+}_{(aq)}$ to $\mathrm{Cr_{(cr)}}$.

Sassani and Shock [92-sas/sho] presented revised correlations for estimating partial molal entropies of aqueous ions at 298.15 K and 1 bar. These authors proposed $S°(\mathrm{Cr}^{3+}_{(aq)}) = -77.0$ cal K^{-1} mol^{-1} (-322.2 J K^{-1} mol^{-1}) and noted that this value is consistent with $S°(\mathrm{Cr}^{3+}_{(aq)}) = -318$ J K^{-1} mol^{-1} from Dellien et al. [76-del/hal], with $S°(\mathrm{Cr}^{3+}_{(aq)}) = -307.5$ J K^{-1} mol^{-1} from Latimer [52-lat] and with $S°(\mathrm{Cr}^{3+}_{(aq)}) = -316.3$ J K^{-1} mol^{-1} from Naumov et al. [74-nau/ryz]. We note that $S°(\mathrm{Cr}^{3+}_{(aq)}) = (-269.4 \pm 7.1)$ J K^{-1} mol^{-1} proposed by Vasil'ev et al. [80-vas/vas] is not consistent with these values. Of the standard state thermodynamic properties, we prefer to use estimated $S°$ values because estimation techniques for this parameter should be reasonably constrained and because contributions of uncertainties in $S°$ to errors in the other properties usually are smaller relative to contributions from $\Delta_f H°$ or $\Delta_f G°$.

Latimer [52-lat] used the questionable $\Delta_f H°(\mathrm{Cr}^{3+}_{(aq)}) = -256.1$ kJ mol^{-1} from NBS Circular 500 [52-ros/wag] and an estimated $S°(\mathrm{Cr}^{3+}_{(aq)}) = -280$ J K^{-1} mol^{-1} to obtain $\Delta_f G°(\mathrm{Cr}^{3+}_{(aq)}) = -223.8$ kJ mol^{-1}. Latimer also combined $\Delta_f H°(\mathrm{CrCl}^{+}_{2(aq)}) = -543.9$ kJ mol^{-1} from NBS Circular 500 with an estimated $S°(\mathrm{CrCl}^{+}_{2(aq)}) = 105$ J K^{-1} mol^{-1} to obtain $\Delta_f G°(\mathrm{CrCl}^{+}_{2(aq)}) = -482.0$ kJ mol^{-1}, combining this value with the equilibrium constant for the dissociation of $\mathrm{CrCl}^{+}_{2(aq)}$ measured by Lamb and Fonda [21-lam/fon] to obtain a second estimate for $\Delta_f G°(\mathrm{Cr}^{3+}_{(aq)}) = -208.8$ kJ mol^{-1}. Finally, Latimer calculated a weighted average for $\Delta_f G°(\mathrm{Cr}^{3+}_{(aq)}) = -215.5$ kJ mol^{-1}.

Wagman et al. [82-wag/eva] did not report $S°(\mathrm{Cr}^{3+}_{(aq)})$ or $\Delta_f G°(\mathrm{Cr}^{3+}_{(aq)})$, and their $\Delta_f H°(\mathrm{Cr}^{3+}_{(aq)}) = -284.1$ kJ mol^{-1} is 30 kJ mol^{-1} more negative than those of Dellien and Hepler [76-del/hep] and Vasil'ev et al. [80-vas/vas], and up to 45 kJ mol^{-1} more negative than values we have obtained from our recalculation of the measurements of Evans [49-eva], Dellien and Hepler, and Vasil'ev et al. [77-vas/vas2]. Examination of the publication of Wagman et al. revealed that the chromium thermodynamic properties have not been revised since 1966. Our recalculations of the results of Vasil'ev et al. [77-vas/vas1, 77-vas/vas2] using auxiliary data for the organics from Wagman et al. yielded inconsistent results, suggesting that agreement among compilations is not particularly good. On the basis of our examination of the raw data of Evans and of Dellien and Hepler we propose a $\Delta_f H°(\mathrm{Cr}^{3+}_{(aq)}) = (-242.9 \pm 4.1)$ kJ mol^{-1} that is the average of the recalculated enthalpies for these two sets of measurements. On the basis of our examination of available data and estimates of $S°(\mathrm{Cr}^{3+}_{(aq)})$, we recommend $S°(\mathrm{Cr}^{3+}_{(aq)}) = (-322.2 \pm 7.0)$ J K^{-1} mol^{-1} from Sassani and Shock [92-sas/sho]. Combination of these two properties yields our recommended $\Delta_f G°(\mathrm{Cr}^{3+}_{(aq)}) = (-198.3 \pm 5.0)$ kJ mol^{-1}.

Standard State Thermodynamic Properties for $\mathrm{Cr}^{2+}_{(aq)}$. The $\Delta_f H°(\mathrm{CrCl_{2(cr)}}) = -388.3$ kJ mol^{-1} of Doerner [37-doe] compares favorably with $\Delta_f H°(\mathrm{CrCl_{2(cr)}}) = -388.4$ kJ mol^{-1} calculated by combining $S°(\mathrm{CrCl_{2(cr)}}) = (115.3 \pm 0.2)$ J K^{-1} mol^{-1} of Stout and Chisolm [62-sto/chi] and $\Delta_f G°(\mathrm{CrCl_{2(cr)}}) = (-349.0 \pm 1.5)$ kJ mol^{-1} of Gee and Shelton [75-gee/she]. Thus, we have three independent measurements of standard state thermodynamic properties for $\mathrm{CrCl_{2(cr)}}$ that are in excellent agreement. These data can be combined with the $\Delta_{\mathrm{soln}} H°(\mathrm{CrCl_{2(cr)}}) = -75.3$ kJ mol^{-1} of Gregory and Burton [53-gre/bur] to yield $\Delta_f H°(\mathrm{Cr}^{2+}_{(aq)}) = -129.5$ kJ mol^{-1} uncorrected for dilution enthalpy. Stout and Chisolm proposed corrections to the enthalpy results of Doerner and reconciled them with results from Sano [38-san2] to calculate standard state thermodynamic properties for $\mathrm{CrCl_{2(cr)}}$. Dellien and Hepler [76-del/hep] combined $\Delta_f H°(\mathrm{CrCl_{2(cr)}}) = -395.5$ kJ mol^{-1} from Stout and Chisolm with a $\Delta_{\mathrm{soln}} H°(\mathrm{CrCl_{2(cr)}}) = -75.3$ kJ mol^{-1} of Gregory and Burton corrected for dilution to calculate $\Delta_f H°(\mathrm{Cr}^{2+}_{(aq)}) = -143.5$ kJ mol^{-1}. Thus, half of the 14 kJ mol^{-1} difference between our value and theirs originates from the choice of $\Delta_f H°(\mathrm{CrCl_{2(cr)}})$. The remainder must be their dilution correction to the results of Gregory and Burton. Dellien and Hepler did not describe their method of correcting for dilution. Nevertheless, we shall select Dellien and Hepler's $\Delta_f H°(\mathrm{Cr}^{2+}_{(aq)}) = -143.5$ kJ mol^{-1}.

Combining our proposed $\Delta_f G°(\mathrm{Cr}^{3+}_{(aq)}) = -198.3$ kJ mol^{-1} with our revised $E°(\mathrm{Cr}^{3+}_{(aq)}/\mathrm{Cr}^{2+}_{(aq)}) = -0.378$ discussed previously yields $\Delta_f G°(\mathrm{Cr}^{2+}_{(aq)}) = -161.8$ kJ mol^{-1}. This can be compared with $\Delta_f G°(\mathrm{Cr}^{2+}_{(aq)}) = -176.1$ kJ mol^{-1} deemed questionable by Latimer [52-lat] and $\Delta_f G°(\mathrm{Cr}^{2+}_{(aq)}) = -174.3$ kJ mol^{-1} calculated by Slobodov et al. [93-slo/kri]. To calculate $\Delta_f G°(\mathrm{Cr}^{2+}_{(aq)})$, Slobodov et al. combined $E°(\mathrm{Cr}^{3+}_{(aq)}/\mathrm{Cr}^{2+}_{(aq)}) = -0.41$ V measured in dilute $\mathrm{H_2SO_4}$ solutions by Grube and Breitinger [27-gru/bre], who evidently did not account for $\mathrm{Cr{-}SO_4}$ complexation, and their proposed $\Delta_f G°(\mathrm{Cr}^{3+}_{(aq)}) = -213.9$ kJ mol^{-1}, for which they drew upon the entropy estimation technique of Latimer and the results of Lamb and Fonda [21-lam/fon] and Timofeyev and Yuldasheva [90-tim/yul].

Sassani and Shock [92-sas/sho] estimated $S°(\mathrm{Cr}^{2+}_{(aq)}) = -24.2$ cal K^{-1} mol^{-1} (-101.3 J K^{-1} mol^{-1}), and Dellien et al. [76-del/hal] estimated $S°(\mathrm{Cr}^{2+}_{(aq)}) = -100$ J K^{-1} mol^{-1}. Combining the $\Delta_f H°(\mathrm{Cr}^{2+}_{(aq)}) = -143.5$ kJ mol^{-1} calculated above with $\Delta_f G°(\mathrm{Cr}^{2+}_{(aq)}) = -161.8$ kJ mol^{-1} yields $S°(\mathrm{Cr}^{2+}_{(aq)}) = -45.7$ J K^{-1} mol^{-1}. Thus, there is a 56 J K^{-1} mol^{-1} discrepancy between the calculated and estimated $S°(\mathrm{Cr}^{2+}_{(aq)})$. Using $S°(\mathrm{Cr}^{2+}_{(aq)}) = -101.3$ J K^{-1} mol^{-1} results in a difference between $\Delta_f H°(\mathrm{Cr}^{2+}_{(aq)})$ and $\Delta_f G°(\mathrm{Cr}^{2+}_{(aq)})$ of 1.7 kJ mol^{-1}. The estimates of $S°(\mathrm{Cr}^{2+}_{(aq)}) = -101.3$ J K^{-1} mol^{-1} and $S°(\mathrm{Cr}^{3+}_{(aq)}) = -322.2$ J K^{-1} mol^{-1} by Sassani and Shock appear consistent with the effects of ligand field stabilization energy and other estimates. We have rechecked all the sources of data and the thermodynamic network and cannot find any reasons why the estimated $S°(Cr^{2+}_{(aq)})$ should be so different from our calculated value. On the basis of the evident lack of information on the source for $S°(Cr^{2+}_{(aq)})$ from Sassani and Shock and Dellien et al., we have little choice but to recommend $\Delta_f H°(Cr^{2+}_{(aq)}) = -143.5$ kJ mol^{-1}, $\Delta_f G°(Cr^{2+}_{(aq)}) = -161.8$ kJ mol^{-1}, and $S°(Cr^{2+}_{(aq)}) = -45.7$ J K^{-1} mol^{-1}. The value for $S°(Cr^{2+}_{(aq)})$ is perhaps the weakest link in this network and would benefit from additional measurements. Fortunately, the thermodynamic properties of $Cr^{2+}_{(aq)}$ are of little consequence to chemical modeling of aqueous Cr solutions. They merely indicate an unresolved inconsistency in the thermodynamic network for Cr species.

Standard State Thermodynamic Properties for $CrO^{2-}_{4(aq)}$. Of the numerous pathways for obtaining standard state entropies, enthalpies, and free energies of $CrO^{2-}_{4(aq)}$, errors can be minimized by deriving $\Delta_f H°(CrO^{2-}_{4(aq)})$ and then evaluating several measurements of $Ag_2CrO_{4(cr)}$ to determine $\Delta_f G°(CrO^{2-}_{4(aq)})$. This complex, interconnected network is shown for convenient reference in Figure 5.

(a) $\Delta_f H°(CrO^{2-}_{4(aq)})$. Although there are at least five pathways leading to $\Delta_f H°(CrO^{2-}_{4(aq)})$, only two of these minimize errors, avoid circular reasoning, and are in good agreement. The five pathways are Ag_2CrO_4 dissolution, $PbCrO_4$ dissolution, Cs_2CrO_4 dissolution, CrO_3 dissolution, and $(NH_4)_2Cr_2O_7$ dissolution and decomposition.

Silver chromate dissolution would appear to be a direct path with few uncertainties for finding $\Delta_f H°(CrO^{2-}_{4(aq)})$, if $\Delta_f H°(Ag_2CrO_{4(cr)})$ were known independently of $\Delta_f H°(CrO^{2-}_{4(aq)})$. Unfortunately, this is not the case. The path is given by the following reactions with their associated enthalpies and references:

reaction	$\Delta_r H°$/(kJ mol^{-1})	reference
$Ag_2CrO_{4(cr)} \rightleftharpoons 2Ag^+_{(aq)} + CrO^{2-}_{4(aq)}$	60.45 ± 0.67	37-smi/pit
$2Ag_{(cr)} + Cr_{(cr)} + 2O_{2(g)} \rightleftharpoons Ag_2CrO_{4(cr)}$	−730.44 ± 0.67	76-del/hal
$2Ag^+_{(aq)} + 2e^-_{(aq)} \rightleftharpoons 2Ag_{(cr)}$	−211.58 ± 0.16	89-cox/wag
$Cr_{(cr)} + 2O_{2(g)} + 2e^-_{(aq)} \rightleftharpoons CrO^{2-}_{4(aq)}$	−881.57 ± 0.96	

Enthalpies of formation for $Ag_2CrO_{4(cr)}$ are derived from the temperature dependence of solubility data, electrochemical cell data, and enthalpies for silver and chromate ions. Unfortunately, circular reasoning occurs because Dellien et al. [76-del/hal] used $\Delta_f H°(CrO^{2-}_{4(aq)})$ to derive $\Delta_f H°(Ag_2CrO_{4(cr)})$. Furthermore, the dissolution enthalpy based on solubility data differs by about 2 kJ mol^{-1} from that based on EMF or calorimetric data. It will be argued later that this problem reflects differences in the energy state of the solid phase depending on the preparation procedure. This pathway cannot be used because it is not independent of the property to be derived and it contains unresolved discrepancies.

Lead chromate dissolution is similar to the silver chromate path:

reaction	$\Delta_r H°$/(kJ mol^{-1})	reference
$PbCrO_{4(cr)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO^{2-}_{4(aq)}$	45.7 ± 1.1	10-gol/sto, 28-rot/sch
$Pb_{(cr)} + Cr_{(cr)} + 2O_{2(g)} \rightleftharpoons PbCrO_{4(cr)}$	−927.02 ± 0.80	76-del/mcc
$Pb^{2+}_{(aq)} + 2e^-_{(aq)} \rightleftharpoons Pb_{(cr)}$	−0.92 ± 0.25	89-cox/wag
$Cr_{(cr)} + 2O_{2(g)} + 2e^-_{(aq)} \rightleftharpoons CrO^{2-}_{4(aq)}$	−882.24 ± 1.38	

The difficulty with this path is that the dissolution enthalpy is based on precipitation experiments involving mixtures of salt solutions for which corrections are needed. These corrections are difficult to estimate, the grain size of the solid material is variable, and the results may refer to fine-grained or colloidal material rather than well-crystallized lead chromate. If this suggestion is appropriate then $\Delta_{soln}H°(PbCrO_{4(cr)}) \geq 45$ kJ mol^{-1} because a less negative enthalpy of the solid phase (for a more crystalline solid) would give a less negative $\Delta_{soln}H°$. The value tabulated above is an average of the results of Goldblum and Stoffella [10-gol/sto] and Roth and Schwartz [28-rot/sch]. The error covers the range of final values from the two papers. Corrections for dilution and grain size effects could easily cause a 2 to 3 kJ mol^{-1} increase in $\Delta_{soln}H°$. This hypothesis is consistent with independent data derived below. Hence, the lead chromate dissolution path is used as corroborating evidence, not as a primary pathway.

Cesium chromate dissolution differs from silver chromate and lead chromate dissolutions in one fundamental aspect: the solubility of cesium chromate is much greater. The path for cesium chromate dissolution is shown as follows:

reaction	$\Delta_r H°$/(kJ mol^{-1})	reference
$Cs_2CrO_{4(cr)} \rightleftharpoons 2Cs^+_{(aq)} + CrO^{2-}_{4(aq)}$	31.43 ± 0.12	75-oha/boe
$2Cs_{(cr)} + Cr_{(cr)} + 2O_{2(g)} \rightleftharpoons Cs_2CrO_{4(cr)}$	−1430.01 ± 2.50	80-fre/joh
$2Cs^+_{(aq)} + 2e^-_{(aq)} \rightleftharpoons 2Cs_{(cr)}$	516.00 ± 1.00	89-cox/wag
$Cr_{(cr)} + 2O_{2(g)} + 2e^-_{(aq)} \rightleftharpoons CrO^{2-}_{4(aq)}$	−882.58 ± 2.70	

O'Hare and Boerio [75-oha/boe] reported a solubility for $Cs_2CrO_{4(Cr)}$ of 2.149 mol (kg $H_2O_{(l)}$)$^{-1}$. This high solubility would necessitate correction of the measured $\Delta_{soln}H°$ for hydrolysis. Using a value of about 3 kJ mol^{-1} for the enthalpy of hydrolysis ($CrO^{2-}_{4(aq)} \rightarrow HCrO^-_{4(aq)}$) from Palmer et al. [87-pal/wes] and assuming 50% hydrolyzed $CrO^{2-}_{4(aq)}$, there would be an additional 3 kJ mol^{-1} added to $\Delta_{soln}H°$, resulting in $\Delta_f H°(CrO^{2-}_{4(aq)}) = -879.67$ kJ mol^{-1}. Although this value will be used as corroborating evidence, it contains an error due to self-referencing. The $\Delta_f H°(Cs_2CrO_{4(cr)})$ values reported by Fredrickson et al. [80-fre/joh] were referenced to the 298.15K value of O'Hare and Boerio. The $\Delta_f H°(Cs_2CrO_{4(cr)})$ value was derived from the measured $\Delta_{soln}H°(Cs_2CrO_{4(cr)})$ and $\Delta_f H°(CrO^{2-}_{4(aq)})$ from an internal report not readily accessible. This path suffers from using $\Delta_f H°(CrO^{2-}_{4(aq)})$ to derive $\Delta_f H°(CrO^{2-}_{4(aq)})$ and from use of an inadequately reviewed and unavailable source.

The $\Delta_{soln}H°$ for $CrO_{3(Cr)}$ in alkaline solution was preferred by Dellien et al. [76-del/mcc] as the most direct route to $\Delta_f H°(CrO^{2-}_{4(aq)})$. These authors also noted that this path suffered because of a large uncertainty in $\Delta_f H°(CrO_{3(cr)})$. This pathway can be summarized by the following reaction matrix:

reaction	$\Delta_r H°$/(kJ mol^{-1})	reference
$CrO_{3(cr)} + 2OH^-_{(aq)} \rightleftharpoons CrO^{2-}_{4(aq)} + H_2O_{(l)}$	−120.92 ± 0.80	76-del/mcc
$^1/_2Cr_2O_{3(cr)} + {}^3/_4O_{2(g)} \rightleftharpoons CrO_{3(cr)}$	−12.76 ± 0.80	29-rot/bec
$Cr_{(cr)} + {}^3/_4O_{2(g)} \rightleftharpoons {}^1/_2Cr_2O_{3(cr)}$	−570.49 ± 0.84	54-mah
$H_{2(g)} + O_{2(g)} + 2e^-_{(aq)} \rightleftharpoons 2OH^-_{(aq)}$	−460.03 ± 0.08	89-cox/wag
$H_2O_{(l)} \rightleftharpoons H_{2(g)} + {}^1/_2O_{2(g)}$	285.83 ± 0.04	89-cox/wag
$Cr_{(cr)} + 2O_{2(g)} + 2e^-_{(aq)} \rightleftharpoons CrO^{2-}_{4(aq)}$	−878.37 ± 1.41	

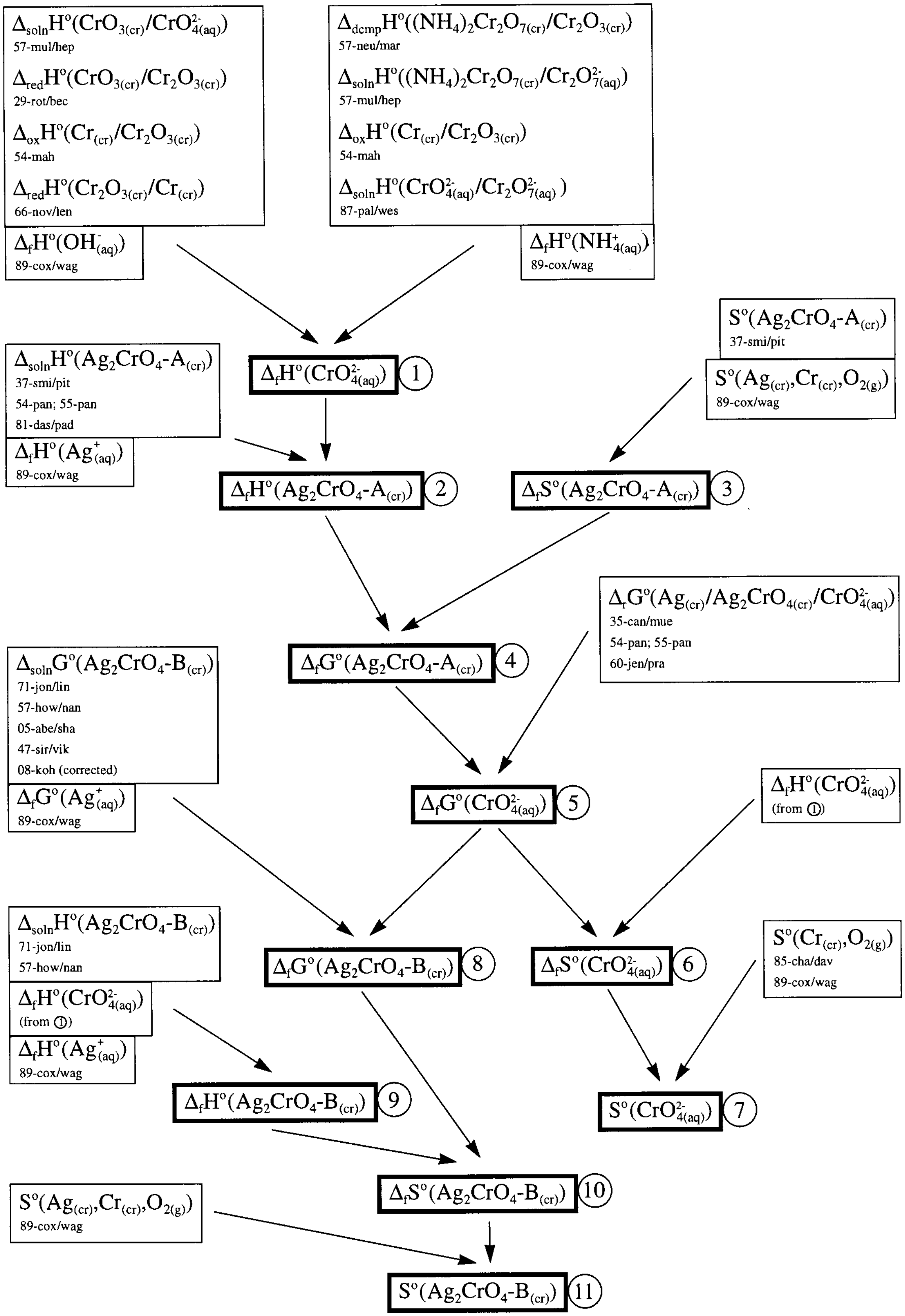

Figure 5. Calculation pathways for obtaining standard state enthalpies, free energies, and entropies of $CrO^{2-}_{4(aq)}$. $Ag_2CrO_{4(cr)}$-A is prepared by electrolysis; $Ag_2CrO_{4(cr)}$-B is prepared by precipitation.

The primary uncertainties involve the first two reactions. Two reported measurements on $\Delta_{soln}H°(CrO_{3(cr)})$, −117.57 kJ mol^{-1} [57-mul/hep] and −120.92 kJ mol^{-1} [76-del/mcc], differ by 3.35 kJ mol^{-1}. This change is not explained, and we assume the more recent value supersedes the earlier one from the same research group. Only one measurement of the oxidation of $Cr_2O_{3(cr)}$ to $CrO_{3(cr)}$ could be found [29-rot/bec], and the reported error is reasonable.

Table 5. Calculation Pathways for Standard Enthalpy of Formation ($\Delta_f H°$) of $CrO^{2-}_{4(aq)}$

$\Delta_f H°$/kJ mol^{-1}	path
-881.57 ± 0.96	Ag_2CrO_4
-882.24 ± 1.38	$PbCrO_4$
-882.58 ± 2.70	Cs_2CrO_4
-878.37 ± 1.41	CrO_3
-879.58 ± 1.41	$(NH_4)_2Cr_2O_7$
-879 ± 1	this study

Finally, the ammonium dichromate pathway is outlined in the following reaction matrix:

reaction	$\Delta_r H°$/ (kJ mol^{-1})	reference
$^1/_2(NH_4)_2Cr_2O_{7(cr)} \rightleftharpoons NH^+_{4(aq)} + {}^1/_2Cr_2O^{2-}_{7(aq)}$	32.0 ± 0.4	57-mul/hep
$^1/_2Cr_2O^{2-}_{7(aq)} + {}^1/_2H_2O_{(l)} \rightleftharpoons CrO^{2-}_{4(aq)} + H^+_{(aq)}$	2 ± 1	87-pal/wes
$NH^+_{4(aq)} + e^-_{(aq)} \rightleftharpoons {}^1/_2N_{2(g)} + 2H_{2(g)}$	133.26 ± 0.25	89-cox/wag
$^1/_2N_{2(g)} + {}^1/_2Cr_2O_{3(cr)} + 2H_2O_{(l)} \rightleftharpoons {}^1/_2(NH_4)_2Cr_2O_{7(cr)}$	238.22 ± 0.19	57-neu/mar
$Cr_{(cr)} + {}^1/_2O_{2(g)} \rightleftharpoons {}^1/_2Cr_2O_{3(cr)}$	-570.49 ± 0.84	54-mah
$1^1/_4O_{2(g)} + 5H^+_{(aq)} + 5e^-_{(aq)} \rightleftharpoons 2^1/_2H_2O_{(l)}$	-714.58 ± 0.10	89-cox/wag
$2H_{2(g)} \rightleftharpoons 4H^+_{(aq)} + 4e^-_{(aq)}$	0	standard state
$Cr_{(cr)} + 2O_{2(g)} + 2e^-_{(aq)} \rightleftharpoons CrO^{2-}_{4(aq)}$	-879.58 ± 1.41	

The primary sources of error in the scheme are the two reactions involving ammonium dichromate. Only one reported value for $\Delta_{soln}H°[(NH_4)_2Cr_2O_{7(cr)}]$ is known, but another confirmatory value for the decomposition of $(NH_4)_2Cr_2O_{7(cr)}$ has been found. Kapustinskii and Shidlovski [56-kap/shi] reported (-430 ± 6) kJ mol^{-1} for the decomposition of $(NH_4)_2Cr_2O_{7(cr)}$, in agreement with (-432.09 ± 0.48) kJ mol^{-1} from Neugebauer and Margrave [57-neu/mar].

The five values for $\Delta_f H°(CrO^{2-}_{4(aq)})$ are given in Table 5. If the corrections described above are considered, the value should lie between -878.4 kJ mol^{-1} and -880 kJ mol^{-1}. The CrO_3 path seems to have the lowest overall error but not the lowest uncertainty. The $(NH_4)_2Cr_2O_7$ path has a low uncertainty but not the lowest error. Our selection of (-879 ± 1) kJ mol^{-1} reflects a compromise between the average (be it mean, median, or mode) and the low error of the CrO_3 path. The stated error encompasses the range of likely values in Table 5 excluding the Ag_2CrO_4 path and uncorrected values.

(b) $Ag_2CrO_{4(cr)}$ and $\Delta_f G°(CrO^{2-}_{4(aq)})$. Two primary types of measurements of Ag_2CrO_4, electrochemical and solubility, provide pathways by which $\Delta_f G°(CrO^{2-}_{4(aq)})$ can be determined. During evaluation of these data a systematic discrepancy between the EMF and the solubility results appeared that was confirmed by enthalpy data derived from EMF, solubility, and calorimetry studies. The exact cause of this discrepancy is not known. Recognition of the discrepancy, however, was instrumental in deriving consistent thermodynamic properties.

A compilation of EMF, solubility, and calorimetric studies on Ag_2CrO_4 is given in Table 6. Jones et al. [71-jon/lin] determined $K_{sp}(Ag_2CrO_{4(cr)})$ from 5 to 80 °C, calculated temperature functions for $\Delta_r H°$ and $\Delta_f S°$, applied ion pairing and activity corrections to their results, and took special care to avoid particle size effects on solubility. Activity coefficients were calculated using the Guntelberg relation, which, lacking B and å terms, is a simplified form of the Debye−Hückel equation. Speciation modeling using program PHREEQC yielded values for log $K_{sp}(Ag_2CrO_{4(cr)})$ that were equivalent to those of Jones et al. within experimental error.

Table 6. Compilation of Electrochemical Potential ($E°$), Solubility, Standard Free Energy of Reaction ($\Delta_r G°$), and Standard Enthalpy of Reaction ($\Delta_r H°$) for $Ag_2CrO_{4(cr)}$

	log K_{sp}[a]				
$E°$/V	reported	this study	$\Delta_r G°$/ kJ mol^{-1}	$\Delta_r H°$/ kJ mol^{-1}	reference
−0.448		−11.77	67.77		04-abe/cox
−0.4504			67.31		26-bol/mac
−0.462			65.07		32-has/jel
−0.4463			68.005		35-can/mue
−0.4472	−11.89		67.91	60.632	54-pan, 55-pan
−0.4468			68.005		60-jen/pra
−0.4491			67.56		81-das/pad
	−11.58		66.10		05-sha/abe
	−11.05		63.07		07-she
	−11.59	−11.56	66.16		08-koh
				60.459	37-smi/pit
	−11.47		65.47	60.88	41-li
	−12.15		69.35		41-mur
	−11.58		66.10		47-sir/vik
		−11.36	64.87		50-gen
	−11.61	−11.62	66.27		55-how/nan, 57-how/nan
	−11.559	−11.553	65.98	58.76	71-jon/lin
				62.41	53-suz

[a] Log K_{sp} = common logarithm of the solubility product constant.

Subsequent to speciation modeling, we rechecked the fit results of Jones et al. [71-jon/lin] by fitting their recalculated results to the expression

$$\log K_{sp} = A - B/T + C \log(T) \qquad (11)$$

yielding the following expression for log $K_{sp}(Ag_2CrO_{4(cr)})$ as a function of temperature:

$$\log K_{sp} = 80.305 - 6676.24/T - 28.073 \log(T) \qquad (12)$$

Figure 6 is a plot of log $K_{sp}(Ag_2CrO_{4(cr)})$ versus 1000/K and illustrates the closeness of the calculated fit to the results of Jones et al. Figure 7 is a deviation plot where the horizontal solid line represents log K_{sp} over the temperature range 0 to 100 °C and the horizontal dashed lines represent 3σ (95% confidence interval) of the maximum deviation of calculated to observed log K_{sp} values from the measured values of Jones et al. Also shown in Figures 6 and 7 are the results of several other investigators whose raw solubility data have been corrected for ion pairing and activity using the PHREEQC simulation program.

The solubility studies of Jones et al. [71-jon/lin] and Howard and Nancollas [57-how/nan] are in excellent agreement and very carefully investigated. Likewise, the EMF studies of Pan [54-pan] and Cann and Mueller [35-can/mue] are carefully done and in excellent agreement. The difference between solubility and EMF values, however, is consistently about 2 kJ mol^{-1} (Figure 8). In examining the reactions, they all contain the same reactants and products: $Ag_2CrO_{4(cr)}$, $Ag^+_{(aq)}$, and $CrO^{2-}_{4(aq)}$. By using $\Delta_f G°(Ag^+_{(aq)})$ from CODATA [89-cox/wag], subtracting the free energy from the reactions, averaging the two solubility results and, separately, the two EMF results, and rearranging, we have two equations in two unknowns that

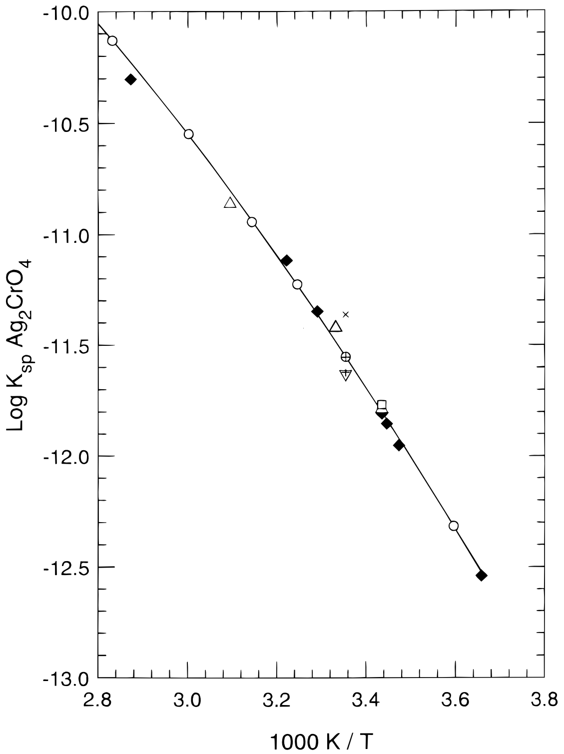

Figure 6. Log $K_{sp}(Ag_2CrO_{4(cr)})$ recalculated using geochemical simulation program PHREEQC as a function of reciprocal Kelvin temperature. Symbols: □, ref 04-abe/cox; ▽, ref 05-sch/abe; ◆, ref 08-koh; △, ref 10-whi; ×, ref 50-gen; +, refs 55-how/nan, 57-how/nan; ○, ref 71-jon/lin; —, best-fit line, calculated using eq 12.

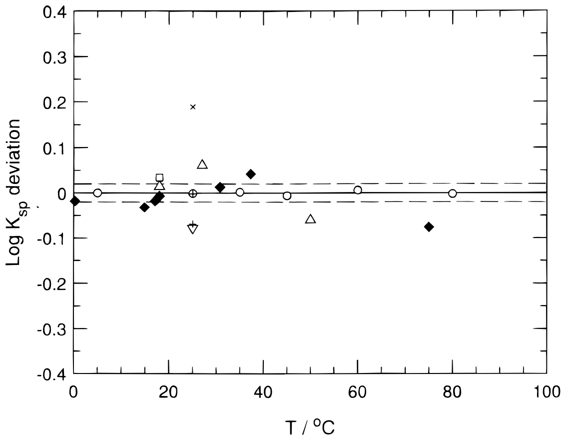

Figure 7. Deviation of log $K_{sp}(Ag_2CrO_{4(cr)})$ as a function of temperature in °C derived from solubility studies compared against refitted data of Jones et al. [71-jon/lin]. Symbols: □, ref 04-abe/cox; ▽, ref 05-sch/abe; ◆, ref 08-koh; △, ref 10-whi; ×, ref 50-gen; +, refs 55-how/nan, 57-how/nan; ○, ref 71-jon/lin; —, zero-deviation line; — —, 95% confidence interval of calculated deviation in measurements of ref 71-jon/lin.

cannot be solved because they contain identical coefficients:

$$\Delta_f G°(CrO^{2-}_{4(aq)}) - \Delta_f G°(Ag_2CrO_{4(cr)}) = -86.22 \text{ kJ mol}^{-1} \quad \text{[EMF]} \quad (13)$$

$$\Delta_f G°(CrO^{2-}_{4(aq)}) - \Delta_f G°(Ag_2CrO_{4(cr)}) = -88.23 \text{ kJ mol}^{-1} \quad \text{[solubility]} \quad (14)$$

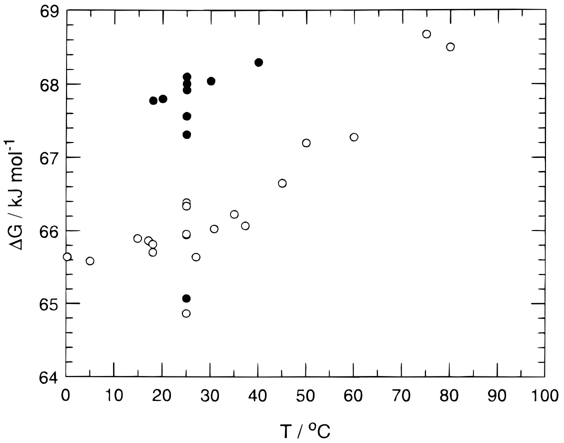

Figure 8. Free energy of reaction for dissolution of $Ag_2CrO_{4(cr)}$ as a function of temperature in °C. Symbols: ○, solubility results; ●, electrochemical results.

When viewed this way it is apparent that since $\Delta_f G°(CrO^{2-}_{4(aq)})$ cannot change, $\Delta_f G°(Ag_2CrO_{4(cr)})$ must differ by 2 kJ mol^{-1}. The Ag_2CrO_4 in the EMF studies were prepared electrolytically by chromic acid reaction with Ag wire, whereas the Ag_2CrO_4 in the solubility studies were prepared by precipitating from solutions of $AgNO_3$ and K_2CrO_4, respectively. Cann and Mueller mentioned that they obtained better results and no contamination from potassium when they used chromic acid instead of K_2CrO_4 for electrolysis. This contamination may well be the source of the 2 kJ mol^{-1} difference. One of the consequences of this hypothesis is that $\Delta_f H°(Ag_2CrO_{4(cr)})$ also should differ by about 2 kJ mol^{-1} depending on its method of preparation. Fortunately, both Pan and Jones et al. did careful measurements of the temperature dependence for the EMF and the solubility, respectively. Deriving parallel equations for enthalpy to those shown above for free energy we have

$$\Delta_f H°(CrO^{2-}_{4(aq)}) - \Delta_f H°(Ag_2CrO_{4(cr)}) = -150.95 \text{ kJ mol}^{-1} \quad \text{[EMF, 54-pan]} \quad (15)$$

$$\Delta_f H°(CrO^{2-}_{4(aq)}) - \Delta_f H°(Ag_2CrO_{4(cr)}) = -152.82 \text{ kJ mol}^{-1} \quad \text{[solubility, 71-jon/lin]} \quad (16)$$

$$\Delta_f H°(CrO^{2-}_{4(aq)}) - \Delta_f H°(Ag_2CrO_{4(cr)}) = -151.12 \text{ kJ mol}^{-1} \quad \text{[calorimetry, 37-smi/pit]} \quad (17)$$

The calorimetric value of Smith et al. [37-smi/pit] is included to show that the Ag_2CrO_4 phase used in the enthalpy of solution measurement is nearly identical to that prepared electrolytically for the EMF studies. It is important to establish this relationship because $\Delta_f G°(CrO^{2-}_{4(aq)})$ can only be derived with internal consistency from reactions involving Ag_2CrO_4 if it is a phase of high purity, crystallinity, and similar energy. Consistent phase properties for the Ag_2CrO_4 used in the EMF and heat of dissolution studies are clearly demonstrated by the close agreement in enthalpies. This relationship also is important because $S°(Ag_2CrO_4)$ is only available from the work of Smith et al. and the entropy is needed to calculate the free energy.

With this hypothesis we can derive the enthalpy and free energy of Ag_2CrO_4 prepared by electrolysis (Ag_2CrO_4-A) and that prepared by precipitation (Ag_2CrO_4-B). The $\Delta_f H°(Ag_2CrO_{4(cr)}\text{-A})$ is obtained by averaging the results of Pan [54-pan] and Smith et al. [37-smi/pit], so that

$$\Delta_f H°(CrO^{2-}_{4(aq)}) - \Delta_f H°(Ag_2CrO_{4(cr)}\text{-A}) = -151.04 \text{ kJ mol}^{-1} \quad (18)$$

Table 7. Thermodynamic Properties for Auxiliary Substances at 100 000 Pa (1 bar)[a]

species or reaction	Δ_fH or Δ_rH/ kJ mol^{-1}	$S°$ or Δ_rS/ J K^{-1} mol^{-1}	C_p or ΔC_p/ J K^{-1} mol^{-1}	Δ_fG or Δ_rG/ kJ mol^{-1}	log K	reference
$H_{2(g)}$	0.0	130.680 (0.003)	28.836 (0.002)	0.0		89-cox/wag
$O_{2(g)}$	0.0	205.152 (0.005)	29.378 (0.003)	0.0		89-cox/wag
$H_2O_{(l)}$	−285.83 (0.04)	69.95 (0.03)	75.351 (0.080)	−237.14 (0.04)		89-cox/wag
$H^+_{(aq)}$	0.0	0.0	0.0	0.0		standard state
$e^-_{(aq)}$	0.0	65.285	0.0	0.0		standard state
$OH^-_{(aq)}$	−230.01 (0.04)	−10.9 (0.2)	−148.5	−157.2 (0.1)		89-cox/wag, 82-wag/eva
$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$	55.82 (0.04)	−80.85 (0.20)	−223.85	79.94 (0.1)	−13.998 (0.002)	89-cox/wag, 82-wag/eva, 77-olo/olo
$K^+_{(aq)}$	−252.14 (0.08)	101.20 (0.20)		−282.1 (0.1)		89-cox/wag
$Fe^{2+}_{(aq)}$	−90.0 (0.5)	−101.6 (3.7)		−90.53 (1.0)		95-par/kho
$Fe^{3+}_{(aq)}$	−49.0 (1.5)	−278.4 (7.7)		−16.28 (1.1)		95-par/kho
$N_{2(g)}$	0.0	191.609 (0.004)		0.0		89-cox/wag
$NH^+_{4(aq)}$	−133.26 (0.25)	111.17 (0.40)				89-cox/wag
$Pb_{(cr)}$	0.0	64.80 (0.30)		0.0		89-cox/wag
$Pb^{2+}_{(aq)}$	0.92 (0.25)	18.5 (1.0)				89-cox/wag
$Ag_{(cr)}$	0.0	42.55 (0.20)		0.0		89-cox/wag
$Ag^+_{(aq)}$	105.79 (0.08)	73.45 (0.40)				89-cox/wag
$Cs_{(cr)}$	0.0	85.23 (0.40)		0.0		89-cox/wag
$Cs^+_{(aq)}$	−258.00 (0.50)	132.1 (0.5)				89-cox/wag

[a] For Tables 7 to 10: Δ_fH or Δ_rH = standard enthalpy of formation or reaction, respectively; $S°$or Δ_rS = third-law entropy or standard entropy of reaction, respectively; C_p or ΔC_p; = standard heat capacity or heat capacity change of the reaction, respectively; Δ_fG or Δ_rG = standard free energy of formation or reaction, respectively; log K = common logarithm of the equilibrium constant for the stated reaction.

Table 8. Thermodynamic Properties for Chromium Metal and Chromium-Containing Solids

species or reaction	Δ_fH or Δ_rH/ kJ mol^{-1}	$S°$ or Δ_rS/ J K^{-1} mol^{-1}	C_p or ΔC_p/ J K^{-1} mol^{-1}	Δ_fG or Δ_rG/ kJ mol^{-1}	log K	reference
$Cr_{(cr)}$	0.0	23.618 (0.21)	23.434	0.0		85-cha/dav
$Cr(OH)_{2(cr)}$				−600.5		this study
$Cr(OH)_{2(cr)} + 2H^+_{(aq)} \rightleftharpoons Cr^{2+}_{(aq)} + 2H_2O_{(l)}$				−62.78 (0.11)	11.00 (0.02)	41-hum/sto
$CrCl_{2(cr)}$	−388.3	115.3 (0.2)	71.2	−349.0 (6.3)		37-doe, 62-sto/chi, 75-gee/she
$Cr(OH)_{3(am)}$	−985.1	95.4 (12.6)		−856.3		74-nau/ryz, this study
$Cr(OH)_{3(am)} + 3H^+_{(aq)} \rightleftharpoons Cr^{3+}_{(aq)} + 3H_2O_{(l)}$	−110.5	−191.7		−53.4	9.35	87-rai/sas, this study
$CrCl_{3(cr)}$	−544.4 (1.4)	122.9 (0.4)		−474.2 (1.5)		90-tim/yul, 58-han/gri, this study
$Cr_2O_{3(cr)}$	−1141.0 (1.7)	81.15 (1.30)	120.366	−1059.3 (1.8)		54-mah
$Cr_2O_{3(cr)} + 6H^+_{(aq)} \rightleftharpoons 2Cr^{3+}_{(aq)} + 3H_2O_{(l)}$	−202.4	−515.8		−48.6	8.52	54-mah, this study
$CrO_{3(cr)}$	−583.3 (1.2)	67.0		−504.5 (1.3)		76-del/hep, 29-rot/bec
$CrO_{3(cr)} + H_2O_{(l)} \rightleftharpoons CrO^{2-}_{4(aq)} + 2H^+_{(aq)}$	−9.87	−92.5		17.7	−3.10	76-del/hep, 29-rot/bec
$FeCr_2O_{4(cr)}$	−1445.5 (5.0)	146.0 (1.7)	133.58	−1344.5 (6.0)		91-sac/ghi, 95-rob/hem
$FeCr_2O_{4(cr)} + 8H^+_{(aq)} \rightleftharpoons Fe^{2+}_{(aq)} + 2Cr^{3+}_{(aq)} + 4H_2O_{(l)}$	−273.7	−608.9		−92.2	16.1	this study
$KFe_3(CrO_4)_2(OH)_{6(cr)}$	−3872 (6)	129 (27)		−3307 (5)		this study
$KFe_3(CrO_4)_2(OH)_{6(cr)} + 6H^+_{(aq)} \rightleftharpoons K^+_{(aq)} + 3Fe^{3+}_{(aq)} + 2CrO^{2-}_{4(aq)} + 6H_2O_{(l)}$	∼0	−352		105.0 (3.4)	−18.4 (0.6)	96-bar/pal, this study
$Ag_2CrO_{4(cr)}$-A	−728.0	216.8 (0.8)		−637.9		37-smi/pit, this study
$Ag_2CrO_{4(cr)}$-B	−726.2	216.8 (0.8)		−636.1		37-smi/pit, this study

Substituting the derived value of $\Delta_fH°(CrO^{2-}_{4(aq)}) = -879.0$ kJ mol^{-1}, we have

$$\Delta_fH°(Ag_2CrO_{4(cr)}\text{-A}) = -728.0 \text{ kJ mol}^{-1} \qquad (19)$$

Combining this value with $S°(Ag_2CrO_4\text{-A}) = 216.8$ J K^{-1} mol^{-1} from Smith et al. we have

$$\Delta_fG°(Ag_2CrO_{4(cr)}\text{-A}) = -637.92 \text{ kJ mol}^{-1} \qquad (20)$$

These results allow the calculation of $\Delta_fH°(Ag_2CrO_{4(cr)}\text{-B})$, $\Delta_fG°(Ag_2CrO_{4(cr)}\text{-B})$, and $S°(Ag_2CrO_{4(cr)}\text{-B})$. These values are listed in Table 8. Now, $\Delta_fG°(CrO^{2-}_{4(aq)})$ and $S°(CrO^{2-}_{4(aq)})$ can be calculated from either the EMF data or the solubility data. Combining results from the two pathways yields mean values of $\Delta_fG°(CrO^{2-}_{4(aq)}) = -724.2$ kJ mol^{-1} and $S°(CrO^{2-}_{4(aq)}) = 45.4$ J K^{-1} mol^{-1}.

Standard state thermodynamic properties for Cr aqueous ions, including oxidation−reduction reactions, are presented in Table 9.

Chromium(II), Chromium(III), and Chromium(VI) Hydrolysis

Chromium(II) Hydrolysis. The difficulties inherent in accurately measuring $E°(Cr^{3+}_{(aq)}/Cr^{2+}_{(aq)})$ are at least as great for determining Cr(II) hydrolysis. Baes and Mesmer [76-bae/mes] stated that nothing is known about Cr(II) hydrolysis. Slobodov et al. [93-slo/kri] stated that a first hydrolysis constant for Cr(II) was obtained by Rossotti and Rossotti [61-ros/ros] but did not mention its value. Slobodov et al. estimated $S°(CrOH^+_{(aq)}) = 25.1$ J K^{-1} mol^{-1} using the technique of Baes and Mesmer [81-bae/mes], and thence $\Delta_fH°(CrOH^+_{(aq)}) = -430.9$ kJ mol^{-1} from the estimated $S°$ and $\Delta_fG°(CrOH^+_{(aq)}) = -373.8$ kJ mol^{-1} derived from the equilibrium constant of Rossotti and Rossotti. Baes and Mesmer [81-bae/mes] correlated measured Δ_rS for the first hydrolysis step for several metal ions with the ratio of their ionic charge to metal−oxygen distance. From regression of the data weighted according to their uncertainties, Baes and Mesmer [81-bae/mes] derived a linear expression for calculating unknown entropies of reaction.

Table 9. Thermodynamic Properties for Chromium Aqueous Ions

species or reaction	Δ_fH or Δ_rH/ kJ mol^{-1}	$S°$ or Δ_rS/ J K^{-1} mol^{-1}	C_p or ΔC_p/ J K^{-1} mol^{-1}	Δ_fG or Δ_rG/ kJ mol^{-1}	log K	reference
$Cr^{3+}_{(aq)}$	−242.9 (4.1)	−322.2 (7.0)		−198.3 (5.0)		49-eva, 76-del/hep, 92-sas/sho
$Cr_{(cr)} \rightleftharpoons Cr^{3+}_{(aq)} + 3e^{-}_{(aq)}$	−242.9 (4.1)	−149.8 (7.0)		−198.3 (5.0)	34.7 (0.4)	49-eva, 76-del/hep
$Cr^{2+}_{(aq)}$	−143.5	−45.7		−161.8		37-doe, 62-sto/chi, 75-gee/she, 53-gre/bur, 75-bie/rom
$Cr^{3+}_{(aq)} + e^{-}_{(aq)} \rightleftharpoons Cr^{2+}_{(aq)}$	106.4	234.7		36.5	−6.39	75-bie/rom, this study
$CrO^{2-}_{4(aq)}$	−879.0 (1.0)	5.4 (0.5)		−724.2 (1.0)		this study
$Cr^{3+}_{(aq)} + 4H_2O_{(l)} \rightleftharpoons CrO^{2-}_{4(aq)} + 8H^{+}_{(aq)} + 3e^{-}_{(aq)}$	651.4	544.6		422.8	−74.1	49-eva, 92-sas/sho, this study
$Cr_2O^{2-}_{7(aq)}$	−1476.2 (2.8)	289.8 (8.2)		−1295.6 (3.0)		87-pal/wes, this study
$2H^{+}_{(aq)} + 2CrO^{2-}_{4(aq)} \rightleftharpoons Cr_2O^{2-}_{7(aq)} + H_2O_{(l)}$	−4 (2)	269 (8)		−83.9 (0.6)	14.7 (0.1)	87-pal/wes

Table 10. Thermodynamic Properties for Chromium Hydrolysis Species

species or reaction	Δ_fH or Δ_rH/ kJ mol^{-1}	$S°$ or Δ_rS/ J K^{-1} mol^{-1}	C_p or ΔC_p/ J K^{-1} mol^{-1}	Δ_fG or Δ_rG/ kJ mol^{-1}	log K	reference
$CrOH^{2+}_{(aq)}$				−415.1		this study
$Cr^{3+}_{(aq)} + H_2O_{(l)} \rightleftharpoons CrOH^{2+}_{(aq)} + H^{+}_{(aq)}$				20.4 (0.5)	−3.57 (0.08)	87-rai/sas
$Cr(OH)^{+}_{2(aq)}$				−616.4		this study
$Cr^{3+}_{(aq)} + 2H_2O_{(l)} \rightleftharpoons Cr(OH)^{+}_{2(aq)} + 2H^{+}_{(aq)}$				56.2	−9.84	87-rai/sas
$Cr(OH)^{\circ}_{3(aq)}$				−817.3		this study
$Cr^{3+}_{(aq)} + 3H_2O_{(l)} \rightleftharpoons Cr(OH)^{\circ}_{3(aq)} + 3H^{+}_{(aq)}$				92.4	−16.19	87-rai/sas
$Cr(OH)^{-}_{4(aq)}$				−989.0		this study
$Cr^{3+}_{(aq)} + 4H_2O_{(l)} \rightleftharpoons Cr(OH)^{-}_{4(aq)} + 4H^{+}_{(aq)}$				157.8 (0.7)	−27.65 (0.12)	87-rai/sas
$Cr_2(OH)^{4+}_{2(aq)}$				−842.3		this study
$2Cr^{3+}_{(aq)} + 2H_2O_{(l)} \rightleftharpoons Cr_2(OH)^{4+}_{2(aq)} + 2H^{+}_{(aq)}$				28.5	−5.0	87-rai/sas
$Cr_3(OH)^{5+}_{4(aq)}$				−1482		this study
$3Cr^{3+}_{(aq)} + 4H_2O_{(l)} \rightleftharpoons Cr_3(OH)^{5+}_{4(aq)} + 2H^{+}_{(aq)}$				61.4 (0.9)	−10.75 (0.15)	87-rai/sas
$HCrO^{-}_{4(aq)}$	−873.0 (1.4)	190.4 (3.2)		−761.4 (1.0)		this study
$H^{+}_{(aq)} + CrO^{2-}_{4(aq)} \rightleftharpoons HCrO^{-}_{4(aq)}$	6 (1)	145 (3)	231 (6)	−37.4 (0.2)	6.55 (0.04)	87-pal/wes
$H_2CrO^{\circ}_{4(aq)}$	−905	90.8		−764		82-mar/smi, 76-bae/mes, this study
$2H^{+}_{(aq)} + CrO^{2-}_{4(aq)} \rightleftharpoons H_2CrO^{\circ}_{4(aq)}$	−23.9	40.6		−36.0	6.31	82-mar/smi, 76-bae/mes

This expression reproduces some observed Δ_rS values within a few percent, but others are in error by over 50%. Thus, this approach may produce values of thermodynamic properties with large uncertainties.

Chromium(III) Hydrolysis. Rai et al. [87-rai/sas] have done a thorough critical review of previous measurements of Cr(III) hydrolysis constants. These investigators observed that Cr(III) hydrolysis data are severely limited and that no good determination of the solubility of $Cr(OH)_3$ had ever been done. In addition, Rai et al. criticized findings that polynuclear Cr(III) species are of major significance at pH values below 7 and presented strong experimental evidence that in dilute solutions polynuclear Cr(III) species do not become dominant at any pH or temperature. Rai et al. also observed that the equilibrium constants proposed for the polynuclear Cr(III) species allow calculated concentrations of Cr(III) in solution in equilibrium with solid $Cr(OH)_3$ several orders of magnitude greater than the known solubility of that solid. Rai et al. carefully measured the solubility of $Cr(OH)_3$ at a constant concentration of 0.01 M $NaClO_4$ or NH_4ClO_4, approaching equilibrium from both undersaturation and supersaturation, and determined new hydrolysis constants for Cr(III). These investigators performed all experiments under an inert gas atmosphere, prepared their own $Cr(OH)_3$ precipitate, filtered samples for analysis through specially preequilibrated 0.0018 μm filters, and analyzed their samples for Cr by UV/visible spectrophotometry, inductively coupled-plasma-optical-emission spectrometry, and graphite-furnace atomic-absorption spectrometry. They allowed some experiments with slow reaction kinetics to proceed for up to 134 days at 65 °C. The study had the following weaknesses: (1) the authors apparently did not attempt rigorous control of temperature and did not determine temperature effects on these equilibria, (2) they conducted their experiments at only one total solution molarity, (3) they presented little of their raw data, (4) accuracy of their data is compromised in the middle-pH region by Cr concentrations very near the detection limits of their analytical techniques, and (5) they presented only circumstantial evidence for their conclusions regarding a possible region of predominance at pH ≤ 4 for $Cr^{3+}_{(aq)}$. Despite these shortcomings, the experimental results of Rai et al. represent a major improvement in the quantification of Cr(III) hydrolysis.

Swaddle and Kong [70-swa/kon] measured log K for the reaction

$$Cr^{3+} + H_2O \rightleftharpoons CrOH^{2+} + H^{+} \qquad (21)$$

at several temperatures and pressures in several different electrolytes at varying ionic strengths. Their data were considered by Baes and Mesmer [76-bae/mes] and Smith and Martell [76-smi/mar] when preparing their respective compilations. Extrapolated to $I = 0\ m$, the log K at 298.15 K is very near −4.0. Rai et al. [87-rai/sas] proposed a log K for this equilibrium of −3.57 but qualified this finding by stating that their statistical treatments indicated that $Cr^{3+}_{(aq)}$ has no region of dominance above pH 2.6.

Rai et al. [87-rai/sas] reported data from which a log K of approximately −9.84 can be calculated for the hydrolysis reaction

$$\mathrm{Cr^{3+} + 2H_2O \rightleftharpoons Cr(OH)_2^{+} + 2H^{+}} \qquad (22)$$

that is only 0.14 more negative than the log $K = -9.7$ proposed by Baes and Mesmer [76-bae/mes].

Prior to the study of Rai et al. [87-rai/sas], few data were found for formation of $\mathrm{Cr(OH)^{\circ}_{3(aq)}}$. Baes and Mesmer [76-bae/mes] suggested an approximate log K value of -18 for the reaction

$$\mathrm{Cr^{3+} + 3H_2O \rightleftharpoons Cr(OH)_3^{\circ} + 3H^{+}} \qquad (23)$$

whereas Rai et al. proposed a log K for reaction 23 of slightly less than -16, a value that is nearly 2 orders of magnitude more positive than the previous value. This revision has the effect of reducing the pH range of predominance for $\mathrm{Cr(OH)^{+}_{2(aq)}}$ to near-extinction (see Figure 1).

Baes and Mesmer [76-bae/mes] proposed log $K = -27.4$ for the reaction

$$\mathrm{Cr^{3+} + 4H_2O \rightleftharpoons Cr(OH)_4^{-} + 4H^{+}} \qquad (24)$$

The log $K = -27.65$ determined by Rai et al. [87-rai/sas] has the effect of enlarging by 0.25 the pH region of dominance for $\mathrm{Cr(OH)^{\circ}_{3(aq)}}$ at the expense of the dominance region for $\mathrm{Cr(OH)^{-}_{4(aq)}}$ (see Figure 1). The more accurate and precise value of Rai et al. now appears to be the most reliable for this equilibrium.

Baes and Mesmer [76-bae/mes] gave log K of reaction of -5.06 and -8.15, respectively, for the reactions

$$\mathrm{2Cr^{3+} + 2H_2O \rightleftharpoons Cr_2(OH)_2^{4+} + 2H^{+}} \qquad (25)$$

$$\mathrm{3Cr^{3+} + 4H_2O \rightleftharpoons Cr_3(OH)_4^{5+} + 4H^{+}} \qquad (26)$$

Rai et al. [87-rai/sas] conducted experiments designed to clarify the importance of reactions 25 and 26, the results of which allowed them to conclude that these species are less prevalent in dilute solutions than previously thought. Rai et al. proposed log K values of -5.0 and -10.75 for reactions 25 and 26, respectively.

Chromium(VI) Hydrolysis. Michel and Machiroux [83-mic/mac] used Raman spectroscopy to demonstrate rather convincingly that $\mathrm{HCrO^{-}_{4(aq)}}$, thought for over 75 years at the time of their writing to exist in acidic chromate solutions, does not exist. These authors presented Raman spectroscopic evidence that $\mathrm{CrO_3Cl^{-}_{(aq)}}$ definitely exists and stated with confidence that additional hexavalent Cr aqueous species, including $\mathrm{HCr_2O^{-}_{7(aq)}}$ and $\mathrm{H_2CrO^{\circ}_{4(aq)}}$, also do not exist. Michel and Machiroux determined log $\beta_{22} = (13.77 \pm 0.02)$ at 20 °C and 0.8 M $\mathrm{KNO_3}$ for the reaction

$$\mathrm{2CrO_4^{2-} + 2H^{+} \rightleftharpoons Cr_2O_7^{2-} + H_2O} \qquad (27)$$

Michel and Machiroux [83-mic/mac] concluded that the presence of $\mathrm{HCrO^{-}_{4(aq)}}$ in acidic solutions of hexavalent Cr is doubtful, stating they were unable to find any spectroscopic and direct argument to support its existence. In addition to $\mathrm{HCrO^{-}_{4(aq)}}$, several authors have postulated the existence of entities such as $\mathrm{H_2CrO^{\circ}_{4(aq)}}$ and $\mathrm{HCr_2O^{-}_{7(aq)}}$ to sustain their arguments but have not presented any direct experimental evidence of their existence.

The papers referred to by Michel and Machiroux [83-mic/mac] include Haight et al. [64-hai/ric], Tong [64-ton], Linge and Jones [68-lin/jon1, 68-lin/jon2], Mason and Kowalak [64-mas/kow], and Davies and Prue [55-dav/pru]. Michel and Machiroux claimed that all the above experimental data are incorrect.

In a subsequent paper, Michel and Cahay [86-mic/cah] used Raman spectroscopy to confirm their earlier [83-mic/mac] conclusions that $\mathrm{HCrO^{-}_{4(aq)}}$, $\mathrm{H_2CrO^{\circ}_{4(aq)}}$, and $\mathrm{HCr_2O^{-}_{7(aq)}}$ do not exist. In addition, Michel and Cahay used Raman spectroscopy to analyze Cr solutions with wider variations in Cr concentration and ionic strength than in the previous [83-mic/mac] paper and determined a thermodynamic equilibrium constant for reaction 27 equal to log $\beta_{22} = (14.85 \pm 0.04)$ at $I = 0$ m and $T = 25$ °C. They concluded that at pH ≈ 6, close to the pK of the hypothetical $\mathrm{HCrO^{-}_{4(aq)}}$–$\mathrm{Cr_2O^{2-}_{7(aq)}}$ equilibrium, Raman spectra show unambiguously that the solutions contain only a mixture of $\mathrm{CrO^{2-}_{4(aq)}}$ and $\mathrm{Cr_2O^{2-}_{7(aq)}}$. Their observations confirmed that $\mathrm{HCrO^{-}_{4(aq)}}$ was not present between pH 1 and pH 11 in dilute solution. They also concluded that $\mathrm{H_2CrO^{\circ}_{4(aq)}}$ was absent in this acidity range.

To correct to $I = 0$ m, Michel and Cahay [86-mic/cah] used a relation derived from the Debye–Hückel equation, suggested by Neuss and Rieman [34-neu/rie], to obtain the reduced form

$$\log \beta_{22} = \log \beta'_{22} + \frac{2\sqrt{\mu}}{1 + 0.7\sqrt{\mu}} \qquad (28)$$

The authors applied a temperature correction derived from the same constants measured at 20 °C and 25 °C by Howlett and Sarsfield [68-how/sar] and Linge and Jones [68-lin/jon1] to arrive at their final value for log $\beta_{22} = (14.85 \pm 0.04)$ at $I = 0$ m and $T = 25$ °C. They stated that the value is comparable to those calculated using hypothetical constants presented by other authors who assumed the presence of $\mathrm{HCrO^{-}_{4(aq)}}$.

Michel and Cahay [86-mic/cah] presented results from Raman spectroscopic measurements in 1 M to 12 M $\mathrm{HNO_3}$ solutions that suggest the formation of $\mathrm{Cr_3O^{2-}_{10(aq)}}$ and $\mathrm{Cr_4O^{2-}_{13(aq)}}$. Finally, they concluded that at $\mathrm{M(HNO_3)} \le 0.5$, only $\mathrm{Cr_2O^{2-}_{7(aq)}}$ is detected.

Palmer et al. [87-pal/wes] reported on a thorough study of hexavalent Cr hydrolysis equilibria. These authors assumed the presence of four equilibria in the hydrolysis of Cr(VI):

$$\mathrm{CrO_4^{2-} + H^{+} \rightleftharpoons HCrO_4^{-}} \qquad (29)$$

$$\mathrm{CrO_4^{2-} + 2H^{+} \rightleftharpoons H_2CrO_4^{\circ}} \qquad (30)$$

$$\mathrm{2CrO_4^{2-} + 2H^{+} \rightleftharpoons Cr_2O_7^{2-} + 2H_2O} \qquad (31)$$

$$\mathrm{CrO_4^{2-} + 2H^{+} + Cl^{-} \rightleftharpoons CrO_3Cl^{-} + H_2O} \qquad (32)$$

These authors noted that the formation quotients for equilibria 29–31 have been determined by potentiometric and spectrophotometric techniques, whereas for equilibrium 32 the quotient was calculated exclusively from spectrophotometric measurements. They tabulated data for several thermodynamic properties (log Q, ΔH, ΔS, and ΔC_p) and noted excellent agreement between their data and the majority of data from other sources. This paper appears to be an excellent summary of existing data on hexavalent Cr hydrolysis reactions.

Palmer et al. [87-pal/wes] conducted careful experiments from 25 to 175 °C and appear to have carefully and thoroughly evaluated their data and compared it with data of earlier workers, as well as fitting it to functions of temperature and ionic strength. Again referring to the work of Michel and Machiroux [83-mic/mac] and Michel and Cahay [86-mic/cah], Palmer et al. found it significant that all their attempts to fit n_0 vs pH data over the pH range 10 to 4 using their ORGLS routine solely in terms of reaction 31 gave inferior fit factors. Palmer et al. gave a generalized nine-parameter equation to which they fitted their data, of which only four parameters had a significant effect on the fit. They presented the parameters obtained for the formation of $HCrO^{-}_{4(aq)}$, $Cr_2O^{2-}_{7(aq)}$, and $CrO_3Cl^{-}_{(aq)}$. Finally, regarding $H_2CrO^{\circ}_{4(aq)}$, they stated that their treatment did not include any possible contribution from reaction 30, which may represent a minor species at higher temperature and lower pH limits. Evidently, Palmer et al. did not consider $H_2CrO^{\circ}_{4(aq)}$ significant but were reluctant to dismiss it entirely.

Palmer et al. [87-pal/wes] also made special mention of the work of Michel and Machiroux [83-mic/mac] and Michel and Cahay [86-mic/cah]. They criticized those findings by stating that the UV/visible spectral assignments from which many of the log Q values they tabulate were derived, as well as the strong evidence provided by the potentiometric titrations of Sasaki [62-sas], are in direct conflict with Michel and Machiroux and Michel and Cahay's interpretation of the Raman spectra. Palmer et al. stated that Sasaki observed a discrete mononuclear wall in titrations of chromate(VI) in 3.49 m $NaClO_4$ (25 °C) at metal concentrations of 1 and 2 × 10^{-4} m where only reaction 29 regulates hydrolysis behavior. The titration curves shifted to higher pH values as the chromate concentration was increased to 0.094 m. Palmer et al. concluded that this phenomenon is only consistent with hydrolysis controlled by at least two equilibria, one involving exclusively mononuclear species and the other involving a polynuclear species. (In a telephone conversation with the first author of this paper (Palmer, D. A., oral communication, January 1996), we learned that attempts by several investigators to duplicate the Raman spectroscopic results [83-mic/mac, 86-mic/cah] have not been successful to date. Dr. Palmer also suggested that the Raman behavior of the various Cr(VI) aqueous species may not be similar to that of the analogous sulfur or other species that form oxyanions in aqueous solution and that therefore the Raman peaks of the Cr hydrolysis species may overlap, thereby obscuring each other.)

Thermodynamic properties for Cr hydrolysis species are presented in Table 10.

Thermodynamic Properties of Chromium Hydroxides and Chromium Jarosite

Chromium(II) and Chromium(III) Hydroxides. Thermodynamic properties for Cr hydroxides and Cr jarosite are presented in Table 8. Hume and Stone [41-hum/sto] determined the solubility of $Cr(OH)_2$ by titrating solutions containing approximately 0.2 M HCl and 0.1 M $CrCl_2$ with KOH. These authors carefully protected their solutions from contact with atmospheric oxygen by preparing and titrating them in an anaerobic titration apparatus. Notwithstanding extreme difficulties with nonreversibility of the equilibrium, Hume and Stone determined $pK_{sp} = (17.00 \pm 0.02)$ for the reaction

$$Cr(OH)_{2(cr)} \rightleftharpoons Cr^{2+} + 2OH^- \qquad (33)$$

The most recent and most accurate and precise determination of the solubility of $Cr(OH)_3$ is by Rai et al. [87-rai/sas], who conducted measurements on the freshly precipitated solid and proposed log $K = (5.78 \pm 0.08)$ for the reaction

$$Cr(OH)_{3(am)} + 2H^+ \rightleftharpoons CrOH^{2+} + 2H_2O \qquad (34)$$

from which, using their estimate for the first hydrolysis constant of Cr^{3+}, log $K = 9.35$ can be calculated for the reaction

$$Cr(OH)_{3(am)} + 3H^+ \rightleftharpoons Cr^{3+} + 3H_2O \qquad (35)$$

The $\Delta_r G°(35)$ can be combined with $\Delta_f G°(Cr^{3+}_{(aq)})$ and $3\Delta_f G°(H_2O_{(l)})$ to calculate $\Delta_f G°(Cr(OH)_{3(am)}) = -856.3$ kJ mol^{-1}. Estimates of $S°(Cr(OH)_3)$ range from 80.3 J K^{-1} mol^{-1} to 95.4 J K^{-1} mol^{-1} [52-lat, 93-slo/kri]. Combining this range of $S°(Cr(OH)_3)$ with $\Delta_f G°(Cr(OH)_{3(am)}) = -856.3$ kJ mol^{-1} yields $\Delta_f H°(Cr(OH)_{3(am)})$ values ranging from −989.6 kJ mol^{-1} to −985.1 kJ mol^{-1}. This strongly suggests that $\Delta_f H°(Cr(OH)_3) = -1064$ kJ mol^{-1} obtained by Wagman et al. [82-wag/eva] recalculating the data of Recoura [1886-rec] is too negative, or that the $Cr(OH)_3$ specimens used by Recoura and Rai et al. are dissimilar. This discrepancy is not unexpected. For example, Baes and Mesmer [76-bae/mes] gave log $K(35) = 12$ for a sample of $Cr(OH)_3$ described as "active". Effects of particle size and degree of crystallinity on solubility of Fe and Al hydroxides have been observed [84-nor/val, 90-nor/plu], and a similarly wide solubility range is expected for Cr hydroxides. Additional determinations of solubility and temperature effects for both freshly precipitated and aged $Cr(OH)_3$ specimens are recommended.

Latimer [52-lat] estimated $\Delta_f H°(Cr(OH)_3) = -989.9$ kJ mol^{-1} for a $Cr(OH)_3$ specimen described as "hydrous". Thus, we recommend $\Delta_f G°(Cr(OH)_{3(am)}) = -856.3$ kJ mol^{-1} derived from the results of Rai et al. [87-rai/sas], $S°(Cr(OH)_{3(am)}) = 95.4$ J K^{-1} mol^{-1} proposed by Naumov et al. [74-nau/ryz] and Slobodov et al. [93-slo/kri], and their combination to yield $\Delta_f H°(Cr(OH)_{3(am)}) = -985.1$ kJ mol^{-1}.

Chromium Jarosite. Recently, chromate jarosite ($KFe_3(CrO_4)_2(OH)_{6(cr)}$) was identified in contaminated soil and its solubility was determined [94-bar/pal, 96-bar/pal]. These investigators synthesized the solid material and characterized it by X-ray diffraction, wet chemical analysis, FTIR analysis, and thermogravimetric analysis. The material was found by all four techniques to be pure chromate jarosite within analytical error. Dissolution experiments of durations 149 to 176 days were run, with equilibrium established in a maximum of 105 days. To obtain a value for the equilibrium solubility of the material, free-ion activities were calculated using a chemical modeling computer code [91-all/bro] with activities corrected using the Davies [62-dav] approximation. Baron and Palmer [96-bar/pal] found it necessary to include formation of the $FeCrO_4^+$ ion pair to obtain a best fit of their data to equilibrium over the pH range of their experiments. Temperature dependence was found to be negligible over the range (4 to 35 °C) studied. These investigators recommended log $K = (-18.4 \pm 0.6)$ for the reaction

$$KFe_3(CrO_4)_2(OH)_{6(cr)} + 6H^+_{(aq)} \rightleftharpoons K^+_{(aq)} + 3Fe^{3+}_{(aq)} + 2CrO^{2-}_{4(aq)} + 6H_2O_{(l)} \qquad (36)$$

The care with which this investigation was conducted suggests that this equilibrium should be accurate and relevant for the interpretation of geochemical conditions in contaminated soils. Thus, it is included in the present set of reactions.

Parker and Khodakovskii [95-par/kho] compiled and evaluated thermodynamic properties for $Fe^{2+}_{(aq)}$ and $Fe^{3+}_{(aq)}$. Combining $\Delta_r G°(36) = (105.0 \pm 3.4)$ kJ mol^{-1} with $\Delta_f G°$-

($Fe^{3+}_{(aq)}$ = (−16.3 ± 1.1) kJ mol^{-1} proposed by Parker and Khodakovskii, $\Delta_f G°(H_2O_{(l)}) = (237.14 \pm 0.04)$ kJ mol^{-1} and $\Delta_f G°(K^+_{(aq)}) = (-282.1 \pm 0.1)$ kJ mol^{-1} from CODATA [89-cox/wag], and $\Delta_f G°(CrO^{2-}_{4(aq)}) = -724.0$ kJ mol^{-1} from this work, $\Delta_f G°(KFe_3(CrO_4)_2(OH)_{6(cr)}) = (-3307.2 \pm 5.2)$ kJ mol^{-1} can be calculated. This value is well within analytical error of the $\Delta_f G°(KFe_3(CrO_4)_2(OH)_{6(cr)}) = (-3305.5 \pm 6.7)$ kJ mol^{-1} proposed by Baron and Palmer [96-bar/pal].

Summary

The results obtained from this study are presented in Tables 8 through 10 in the form of selected Cr thermodynamic properties. Selected thermodynamic properties for Cr metal and other Cr solids appear in Table 8, for Cr aqueous ions in Table 9, and for Cr hydrolysis species in Table 10. The most thoroughly studied, and therefore best known, thermodynamic properties of Cr are the properties of the metal. Thermodynamic properties of chromic oxide, Cr_2O_3, also are known with excellent accuracy and precision. The best determination of the potential for the reduction of Cr^{3+} to Cr^{2+} has been made by Biedermann and Romano [75-bie/rom]. The hydrolysis of the Cr^{3+} and CrO_4^{2-} ions in aqueous solution has been studied recently by Rai et al. [87-rai/sas] and Palmer et al. [87-pal/wes], respectively. These three studies represent major advances in the understanding of these important reactions for Cr in dilute aqueous solution. The equilibrium constants derived from the findings of these three studies provide modelers with much better thermodynamic data for Cr hydrolysis than any previously available.

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