Properties of Materials and Systems of Importance to Environmental Fates and Remediation. III. Review of Previous Thermodynamic Property Values for Chromium and Some of its Compounds

Duane R. Kirklin[a)]

Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received February 4, 1999; final revision received April 28, 1999

Twenty-seven (27) crystalline and aqueous chromium species from the NBS Tables of Chemical Thermodynamic Properties were selected based upon their possible importance to environmental fate and remediation processes. Their NBS files were studied to determine the sources of information and the methodology used to determine the NBS selected thermodynamic values. The NBS tables for chromium were compiled in 1966. A literature search was performed to determine the existence of additional data for these species. Documentary data are presented for the thermodynamic properties of these twenty-seven (27) species. © *1999 American Institute of Physics and American Chemical Society.* [S0047-2689(99)00205-6]

Key words: aqueous solutions, chromium, thermodynamic properties.

Contents

1. Introduction.................................. 1675
   1.1. Environmental Considerations of Chromium. 1676
   1.2. Uncertainty Considerations................ 1676
   1.3. Acknowledgments........................ 1678
   1.4. References for the Introduction............ 1678
2. Cr(cr).. 1679
3. Cr^{2+}(aq).................................... 1679
4. $[Cr(H_2O)_6]^{3+}$(aq, violet)...................... 1680
5. CrO_4^{2-}(aq).................................. 1682
6. $HCrO_4^-$(aq)................................... 1684
7. $Cr_2O_7^{2-}$(aq)................................. 1687
8. Cr_2O_3(cr)...................................... 1690
9. $Cr_2O_3\cdot H_2O$(cr)............................. 1691
10. $Cr_2O_3\cdot 2H_2O$(cr)............................ 1692
11. $Cr_2O_3\cdot 3H_2O$(cr)............................ 1692
12. Cr_3O_4(cr)..................................... 1693
13. CrO_2(cr)...................................... 1693
14. CrO_3(cr)...................................... 1694
15. $CrO_3\cdot 80H_2O$................................ 1694
16. $[Cr(H_2O)_6]_2(SO_4)_3$(aq, violet).................. 1695
17. $[Cr_2(H_2O)_6](SO_4)_3$(aq, green).................. 1696
18. $[Cr_2(H_2O)_8(SO_4)_2](SO_4)$(aq).................. 1696
19. $[Cr_2(H_2O)_{10}SO_4](SO_4)_2$(aq).................. 1697
20. $CrCl_2$(cr)..................................... 1697
21. $CrCl_2$(aq)..................................... 1698
22. $CrCl_2\cdot 2H_2O$(cr, light green)................... 1698
23. $CrCl_2\cdot 3H_2O$(cr, pale blue)..................... 1699
24. $CrCl_2\cdot 4H_2O$(cr, dark blue).................... 1699
25. $CrCl_3$(cr)..................................... 1700
26. $[Cr(H_2O)_6]Cl_3$(aq, violet)...................... 1702
27. $Cr(OH)_3$(cr)................................... 1703
28. $PbCrO_4$(cr).................................... 1703

1. Introduction

The fate of many heavy metal species in aqueous environments is often determined by thermodynamic and mathematical modeling techniques. However, the reliability of the results obtained by these methods depends upon the reliability of the thermodynamic properties of the chemical species under investigation. The existing thermodynamic data for many chemical species of interest is often incomplete or unreliable. The NBS Tables of Chemical Thermodynamic Properties, 82WAG/EVA data compilation, is often used as a source for the initial thermodynamic data used. The Congress of the United States of America changed the name of the National Bureau of Standards (NBS; founded in 1901) to the National Institute of Standards and Technology (NIST; name changed in January 1989). However, the NBS tables, not the NIST tables, will be used throughout this document since the data compilation is named the NBS Tables of Chemical Thermodynamic Properties. This paper provides some additional documentation for the data in the 82WAG/EVA compilation for chromium species of interest.

The following information is arranged by chemical species. There are six (6) sections for each chemical species of interest. Section A lists the NBS selected values and the source of the thermodynamic data used. Section A also describes how the selected values were derived. Section B contains the personal comments of this reviewer about any readily apparent discrepancies in how the selected values were obtained. Section C lists the auxiliary thermodynamic parameters needed to calculate the selected thermodynamic

---

[a)]Electronic mail: duane.kirklin@nist.gov

Reprints available from ACS; see Reprints List at back of issue.

values. The NBS evaluators considered several pieces of existing thermodynamic data but often the selected values were derived from just a few of the existing data. Section D identifies the references of thermodynamic data that the NBS evaluators considered but did not actually use to derive the selected values. A literature search of the Chemical Abstract files from 1967–1997 was done to find any references of thermodynamic data on chromium species of interest since the NBS selected values for chromium were compiled in 1966. Some more recent compilations also listed experimental data prior to 1966 that were not considered in the NBS compilation. Section E contains additional references that can possibly be used to derive a more consistent set of thermodynamic data for chromium species. The references in section E came from the literature search and published compilations of thermodynamic data for chromium species, 93SLO/KRI and 98BAL/NOR. Section F is a list of all the cited thermodynamic data for the chromium species of interest.

There is a lack of very recent data for many of the chromium species. The author can only speculate on the reason for this. Some species which seem to be very similar in composition had distinctly different colors. Therefore, even before the advent of modern spectroscopic techniques, several different chromium species were known to exist with very similar chemical compositions. Many of these can be explained by the coordination sphere around the chromium metal. The classical thermodynamic measurements have become less active as new instrumental methods have evolved. But it is clear that interest must be rejuvenated in this area since some of the ''old'' classical data fails to predict the fate of various chemical species by the present day thermodynamic modeling programs.

The data presented here are not evaluated since it is assumed that the original NBS tables evaluators had some criteria for selection of the ''best'' value. The author could choose different criteria and hence would probably select a different ''best'' value. Instead, the author has chosen to accept the NBS values and provide the information that was used to calculate the selected values. This paper documents the sources of the data used to obtain the NBS selected values of 82WAG/EVA. The chromium data presented in 82WAG/EVA is a collection of the selected values published in Technical Note (TN) 270-4, 69WAG/EVA, using some data from TN 270-3, 68WAG/EVA, and is presented in SI units. The chromium data published in TN 270-4, 69WAG/EVA, was compiled in 1966. These data used the energy unit of calorie at the standard conditions of 298.15 K and 1 atm. of pressure. The TN270-4 worksheets and data were used to arrive at the NBS selected values. The calculations presented here document how the selected values were derived. The chromium data presented herein uses the energy unit Joule at the standard conditions of 298.15 K and 1 atm of pressure. 82WAG/EVA uses the standard pressure of 1 bar. The entropies of gases and the Gibbs energies of formation presented here may be slightly different from the values in 82WAG/EVA due to the different standard pressure. In addition, 82WAG/EVA converts from non-SI units to SI units. Sometimes, due to rounding errors, the 82WAG/EVA values cannot be calculated exactly if the experimental values are converted to SI units and all the calculations are carried out in SI units. (See Section B, the comment section, for the last species in this group, $PbCrO_4$.) The data contained herein should be useful for data evaluators and thermodynamic modelers to obtain a self consistent set of selected thermodynamic values for chromium species of interest.

1.1. Environmental Considerations of Chromium

Chromium is the seventh most abundant element in the earth. The natural process of chemical weathering is responsible for the natural concentrations of chromium in our waters, soils and air. However, several of our human activities have altered the natural distribution of chromium. Although the chromium contents of fossil fuels are very low, the tremendous quantities of fossil fuels used by man have contributed significantly to the redistribution of chromium into our atmosphere and soils. Chemical manufacturing facilities, cooling towers, steel mills, and chrome plating facilities are just a few of the many activities that man has used to redistribute chromium in our environment. The environmental fate of chromium is controlled by several processes that include oxidation–reduction, precipitation–dissolution, and adsorption–desorption. The danger of environmental contamination depends upon the oxidation state of the chromium. The chromium literature suggests that the hexavalent species are more toxic than most common trivalent species. Chromium compounds are known to reduce plant growth and cause skin inflammation and eczemas in fish, mammals, and humans and after a longer latent time, they also are known to produce lung cancer.

The information included here covers chromium species of several oxidation states. There are considerable data on the hexavalent state. Many of the studies are concerned with the determination of the hexavalent chromium speciation. The number of studies suggests that there is some doubt concerning the methods used to determine the speciation. There is also not complete certainty of the structure of many of the trivalent chromium species. Most of these uncertainties seem to be focused on the coordination of species around the trivalent chromium ion. Although we have some data on the thermodynamics of the various oxidation states of chromium, it appears that there is a lack of certainty in the thermodynamic data due to lack of understanding about the correct speciation.

1.2. Uncertainty Considerations

All of the NBS selected values have an uncertainty associated with it which is indicated by the number of significant figures. Since the selected values were often derived from several different reactions, it is appropriate that we discuss uncertainty and what does it really mean for the selected values. Examination of the pedigree of the NBS Tables of

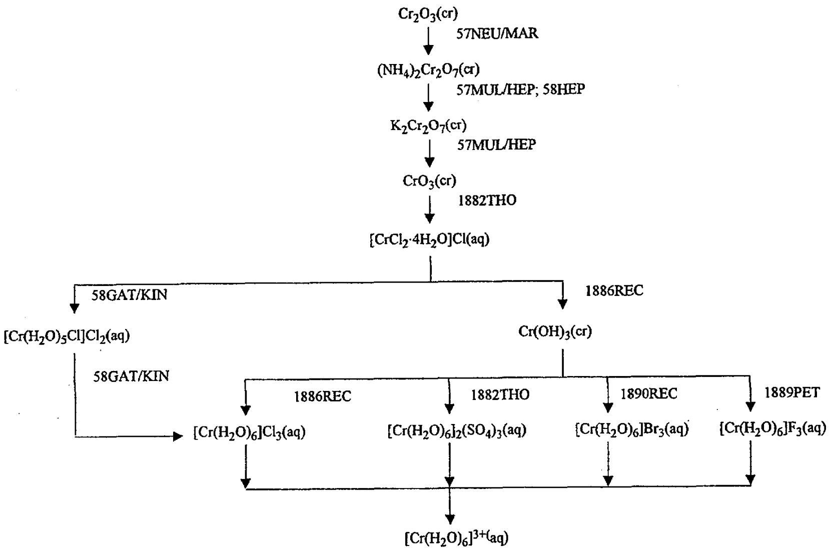

FIG. 1. Sequential pathway used to determine the enthalpy of formation of $Cr(H_2O)_6^{3+}$(aq).

Enthalpy of Formation of the hexaaqua Cr(III) ion is informative for heuristic reasons described here. Figure 1 shows a series of reactions that lead to the enthalpy of formation of $[Cr(H_2O)_6]^{3+}$(aq). The first reaction is the combustion of chromium to obtain Cr_2O_3(cr). The sequential pathway in Fig. 1 begins with this reaction. The next step in the pathway utilized by 57NEU/MAR's autocombustion of ammonium dichromate, $(NH_4)_2Cr_2O_7$(cr), for which the assumed reaction products were Cr_2O_3(cr), H_2O(l), and N_2(g). The next step involved measurement of the dissolution enthalpy of $(NH_4)_2Cr_2O_7$(cr) into water with adjustment for hydrolysis reactions (57MUL/HEP, 58HEP) to obtain the enthalpy of formation of the dichromate ion. The enthalpy of solution of $K_2Cr_2O_7$(cr) into water was then used to calculate the enthalpy of formation of crystalline potassium dichromate. 57MUL/HEP measured the enthalpy of dissolving potassium dichromate into an aqueous hydroxide to obtain the enthalpy of formation of K_2CrO_4(aq). This value was then combined with the enthalpy of solution of CrO_3(cr) into aqueous base, which was assumed to produce aqueous chromate, in order to obtain the enthalpy of formation of CrO_3(cr). The enthalpy of solution of CrO_3(cr) into water was then used to determine the enthalpy of formation of CrO_3(aq). The enthalpy of formation of CrO_3(aq) was then combined with the enthalpies of formation of $SnCl_2$(aq), $SnCl_4$(aq), H_2O(l), and HCl(aq); and the enthalpy of the reaction:

$$2CrO_3(aq)+12HCl(aq)+3SnCl_2(aq)+2H_2O(l)$$
$$=3SnCl_4(aq)+2[CrCl_2(H_2O)_4]Cl(qa) \qquad (1)$$

determined by 1882THO to calculate the enthalpy of formation for $[CrCl_2(H_2O)_4]Cl$(aq). From this point, there are different possible pathways for calculation of $\Delta_f H_m^\circ$ for $[Cr(H_2O)_6]^{3+}$(aq). As discussed later in this article, the pathway chosen for the NBS tabulated value proceeded through the calculation of the enthalpy of formation of $Cr(OH)_3$(cr). This value was calculated from 1886REC's measurement of the enthalpy change for the reaction:

$$[CrCl_2(H_2O)_4]Cl(aq)+3NaOH(aq)$$
$$=Cr(OH)_3(cr)+3NaCl(aq)+4H_2O(l). \qquad (2)$$

From a starting point of $Cr(OH)_3$(cr), the measurement of the enthalpies of formation of several reactions of the prototype:

$$Cr(OH)_3(cr)+3HCl(aq)+3H_2O(l)=[Cr(H_2O)_6]Cl_3(aq) \quad (3)$$

were then examined in order to arrive at $\Delta_f H_m^\circ$ for $[Cr(H_2O)_6]^{3+}$(aq). All of these measurements were obtained prior to 1900. The alternate pathway, which does not involve the enthalpy of formation of $Cr(OH)_3$(cr) [reaction (2)], was examined but not used in the calculation of the enthalpy of formation of $[Cr(H_2O)_6]^{3+}$(aq). This pathway, which utilized measurements in 58GAT/KIN, yields a $\Delta_f H_m^\circ$ for $[Cr(H_2O)_6]^{3+}$(aq) that was different from the other pathway by approximately 7 $kJ\cdot mol^{-1}$.

Some comments regarding some of the above-mentioned reactions are germane at this point. Of the large number of reaction enthalpies used to determine the $\Delta_f H_m^\circ$ for $[Cr(H_2O)_6]^{3+}$(aq) almost none are confidently known to 1 $kJ\cdot mol^{-1}$ or better. Specific details on each of the reactions can be found below. We note the following as examples: (1) Enthalpies of formation for Cr_2O_3(cr) are spread over the range of (1120–1140) $kJ\cdot mol^{-1}$, the minimum uncertainty in this value, assuming that 54MAH was in fact the most accurate value, would be that claimed by 54MAH, ± 1.7 $kJ\cdot mol^{-1}$. (2) The autocombustion of ammonium dichromate is uncertain by an unknown amount. This is because it was assumed that the reaction products included pure Cr_2O_3(cr) and H_2O(l). However, the mono-, di-, and trihydrates of Cr_2O_3(cr) are known to exist. The Gibbs energy of the reaction:

$$Cr_2O_3(cr)+H_2O(l)=Cr_2O_3\cdot H_2O(cr) \qquad (4)$$

can be calculated from the enthalpies of formation of $Cr_2O_3(cr)$, $H_2O(l)$, and $Cr_2O_3\cdot H_2O(cr)$ and an estimate of the entropy change for forming the monohydrate ($-23\ J\cdot K^{-1}\cdot mol^{-1}$). From these values, $\Delta_{rxn}G_m^\circ = -74\ kJ\cdot mol^{-1}$. This value of the Gibbs energy of reaction implies that hydrated chromium oxides, not the anhydrous chromium oxide, are the thermodynamically stable material for 298.15 K. What actually formed in the process, therefore, depends on the kinetics of the process. 57NEU/MAR did not describe determination of which material was formed in the autocombustion reaction. (3) Uncertainties in the 57MUL/HEP reactions are not known and are most likely larger than those claimed by them; this is discussed separately below. (4) The uncertainty of the enthalpy of reaction (1) must be considered large, due to the multiplying effect of the large stoichiometric numbers of molecules involved in the reaction and due to uncertainties in the formation properties of the aqueous stannous and stannic chlorides.

What then is the ''uncertainty'' of the calculated enthalpy of formation for $[Cr(H_2O)_6]^{3+}(aq)$? One could attempt to assign uncertainties to all of the reactions involved in its determination and calculate a final uncertainty through usual formulas for propagation of error. Clearly, such a value, call it u, based on the information given above and in sections below, would have to be larger than $20\ kJ\cdot mol^{-1}$; $u > 20\ kJ\cdot mol^{-1}$. This type of treatment overestimates the uncertainty. Consider the 58GAT/KIN reaction:

$$[CrCl_2(H_2O)_4]Cl(aq)=[CrCl(H_2O)_5]Cl_2(aq). \qquad (5)$$

The uncertainty in the enthalpy of formation of $[CrCl_2(H_2O)_4]Cl(aq)$ could be calculated as the propagation of the uncertainties of all the preceding reactions that were combined to lead to its value. Call this uncertainty u_0 and recognize that its value would be greater than $10\ kJ\cdot mol^{-1}$. The uncertainty in $\Delta_f H_m^\circ$ for $[CrCl(H_2O)_5]Cl_2(aq)$ would be the propagation of u_0 and the uncertainty in the enthalpy for reaction (5), given by 58GAT/KIN as $1\ kJ\cdot mol^{-1}$. Therefore the tabulated enthalpies of formation would have tabulated uncertainties of u_0 and $(u_0^2+1\ kJ^2\cdot mol^{-2})^{1/2}$. Now, consider if one takes tabulated values for the enthalpies of formation and attempts to calculate the enthalpy of reaction (5) and its uncertainty. Then the calculated uncertainty would be $(2u_0^2 + 1\ kJ\cdot mol^{-1})^{1/2}$, or approximately $1.4u_0$. Thus, the calculated uncertainty in reaction (5) would be greater than $14\ kJ\cdot mol^{-1}$, which is not the correct value; its correct value is only $1\ kJ\cdot mol^{-1}$. The end result then is that the wrong uncertainty, wrong by at least an order of magnitude, was calculated.

Whether tabulated uncertainties for thermodynamic values, where the thermodynamic values were obtained in a sequential analysis, result in correct calculated uncertainties for a reaction depend upon how much of the sequential analysis is *not* in common for the substances involved in the reaction. In other words, the calculated uncertainty will be correct only if the sequential pathways for all members of the reaction have no preceding reactions in common with each other. 82WAG/EVA cautions that calculation of uncertainty limits as the square root of the sum of the squares of the individual uncertainties will lead to gross overestimates of the uncertainty of the value for the given reaction.

One of the more important considerations for prediction of chromium migration through the environment is the reduction of Cr(VI) to Cr(III) in aqueous solution. All of the enthalpy of formation and entropy values for aqueous oxoanions of Cr(VI) depend on calorimetric measurements reported by Muldrow and Hepler (57MUL/HEP). One of the calorimetrically studied reactions was:

$$CrO_3(cr)+2OH^-(aq)=CrO_4^{2-}(aq)+H_2O(aq). \qquad (6)$$

57MUL/HEP reported that the enthalpy of reaction (6) was $(-117.1\pm0.8)\ kJ\cdot mol^{-1}$. Subsequent to that measurement, Hepler and coauthors (76DEL/HEP) reported that measurement of the enthalpy of reaction (6) gave $(-120.9 \pm 0.8)\ kJ\cdot mol^{-1}$. These two measurements from the same laboratory, but performed with different calorimeters, differ by $3.8\ kJ\cdot mol^{-1}$. This difference is much more than the claimed uncertainties. It is certainly reasonable to expect that the difference reflects calorimetric biases of one or both of Hepler's studies. If not, then the preparation of materials and/or the nature of reactions are in doubt in one or the other article. There is no *a priori* reason to expect that the 3.8 $kJ\cdot mol^{-1}$ must be a relative error, i.e., a percentage of the measured enthalpy. If the earlier calorimetric results from 57MUL/HEP are in error, then these calorimetric errors put into doubt all of the enthalpies of reaction in that study. Errors in those enthalpies of reaction would directly translate into errors of unknown amounts in the tabulated enthalpies of formation and entropies of $Cr_2O_7^{2-}(aq)$, $CrO_4^{2-}(aq)$, $HCrO_4^-(aq)$, $K_2Cr_2O_7(cr)$, as well as several other substances.

1.3. Acknowledgments

The author wishes to recognize the efforts of Rhoda Levin and Tamar Thorne in the collection of many of the literature articles and some of the formatting for this article. The author especially wants to thank Dr. Donald G. Archer for his many suggestions and encouragements during the preparation of this article.

1.4. References for the Introduction

1882THO Thomsen, J., *Thermochemische Untersuchungen von Julius Thomsen* (J. Barth Verlag, Leipzig, 1882–1886).
1886REC Recoura, A., Compt. Rend. **102**, 865 (1886).
1890RECa Recoura, A., Compt. Rend. **110**j, 1029-1032 (1890)
1890RECb Recoura, A., Compt. Rend. **110**, 1193-1196 (1890).
1889PET Petersen, E., Z. Physik. Chem. **4**, 384-412 (1889).

54MAH	Mah, A. D., J. Am. Chem. Soc. **76**, 3363 (1954).
57MUL/HEP	Muldrow, O. N., Hepler, L. G., J. Am. Chem. Soc. **79**, 4095 (1957).
57NEU/MAR	Neugebauer, C. A., Margrave, J. L., J. Phys. Chem. **61**, 1429 (1957).
58GAT/KIN	Gates, H. S., King, E. L., J. Am. Chem. Soc. **80**, 5011 (1958).
58HEP	Hepler, L. G., J. Am. Chem. Soc. **80**, 6181 (1958).
68WAG/EVA	Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., Schumm, R. H., Natl. Bur. Stand. (U.S.) Tech. Note 270-3 (1968).
69WAG/EVA	Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., Schumm, R. H., Natl. Bur. Stand. (U.S.) Tech. Note 270-4 (1969).
76DEL/HEP	Dellien, I., Hepler, L. G., Can. J. Chem. **54**, 1383 (1976).
82WAG/EVA	Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., Nuttall, R. L., J. Phys. Chem. Ref. Data **11**, (2) (1982).
93SLO/KRI	Slobodov, A. A., Kritskii, A. V., Zarembo, V. I., Puchkov, L. V., Russ. J. Appl. Chem. **66**, 39 (1993) [Translated from Zhurnal Prikladnoi Khimii **66**, 47 (1993)].
98BAL/NOR	Ball, J. W., Nordstrom, D. K., J. Chem. Eng. Data **43**, 895 (1998).

2. Cr(cr)

A. Selected Values, NBS Tables

The NBS tables have selected values for three (3) thermodynamic properties of the crystalline chromium metal. The thermodynamic functions and their selected values are:

$H^\circ_m(298.15\ \text{K})$

$-H^\circ_m(0\ \text{K}){:}4.058\ \text{kJ}\cdot\text{mol}^{-1}\ (0.970\ \text{kcal}\cdot\text{mol}^{-1})$

$S^\circ_m(298.15\ \text{K}){:}23.77\ \text{J}\cdot\text{K}^{-1}\text{mol}^{-1}\ (5.68\ \text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$

$C^\circ_{p,m}(298.15\ \text{K}){:}23.35\ \text{J}\cdot\text{K}^{-1}\text{mol}^{-1}\ (5.58\ \text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$.

The actual data used was from 37AND, which reported measurements of $C^\circ_{p,m}$ from 56 to 291 K.

B. Comments on NBS Selected Values

NBS values selected were the same values selected by 63HUL/ORR. However, 73HUL/DES, which is an update of 63HUL/ORR, uses 5.65 $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for S°_m while in 1963 they used 5.68 $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The original compilation of chromium data was from 61KEL/KIN.

C. Auxiliary Values Required for Data Pathway

None.

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

55WOL measured the low temperature heat capacity of chromium from 1.20 to 20 K.

60BEA/CHI measured the heat capacity on a 99.998% pure sample of chromium from 268 to 324 K.

73HUL/DES contains a bibliography that includes some more recent papers and lists the authors from whom the earlier data were selected.

79WIL/GOP measured the heat capacity of chromium above 200–400 K.

F. Bibliography

37AND	Anderson C. T., J. Am. Chem. Soc. **59**, 488 (1937).
55WOL	Wolcott, N. M., Proceedings Conference on Physics Des Basses Temperature, Institute Internationale Froid, 1995, pp. 286–289.
60BEA/CHI	Beaumont, R. H., Chihara, H., Morrison, J. A., Philos, Mag. **5**, 188 (1960).
61KEL/KIN	Kelley, K. K., King, E. G., U.S. Bur. Mines Bull. **592**, 149pp. (1961).
63HUL/ORR	Hultgren, R. R., Orr, R. L., Anderson, P. D., Kelley, K. K., *Selected Values of Thermodynamic Properties of Metals and Alloys* (Wiley, New York, 1963).
73HUL/DES	Hultgren, R. R., Desai, P. D., Hawkins, D. T., Gleiser, M., Kelley, K. K., Wagman, D. D., *Selected Values of the Thermodynamic Properties of the Elements* (American Society of Metals, Metals Park, OH, 1973).
79WIL/GOP	Williams, I. S., Gopal, E. S. R., Street, R., J. Phys. F **9**, 431 (1979).

3. Cr^{2+}(aq)

A. Selected Values, NBS Tables

The NBS tables have selected values for only one (1) thermodynamic property of the aqueous chromium (II) ion. The thermodynamic function and its selected value is:

$\Delta_f H^\circ_m(298.15\ \text{K}){:}-143.5\ \text{kJ}\cdot\text{mol}^{-1}\ (-34.3\ \text{kcal}\cdot\text{mol}^{-1})$.

The NBS selected value was calculated as

$$\begin{aligned}\Delta_f H^\circ_m(\mathrm{Cr}^{2+},\mathrm{aq}) &= \Delta_f H^\circ_m(\mathrm{CrCl_2},\mathrm{aq}) - 2\times\Delta_f H^\circ_m(\mathrm{Cl}^-,\mathrm{aq})\\ &= [(-477.8\ \mathrm{kJ\cdot mol^{-1}}) - 2\times(-167.159\ \mathrm{kJ\cdot mol^{-1}})]\\ &= -143.5\ \mathrm{kJ\cdot mol^{-1}}(-34.3\ \mathrm{kcal\cdot mol^{-1}}),\end{aligned}$$

from the data of 1886REC based on reaction (1):

$$\mathrm{CrCl_2(aq)} = \mathrm{Cr^{2+}(aq)} + 2\mathrm{Cl^-(aq)}. \qquad (1)$$

B. Comments on NBS Selected Values

The NBS selected value was derived with the $\Delta_f H^\circ_m(\mathrm{CrCl_2},\mathrm{aq})$ which appears to have a transcription error of +4.6 $\mathrm{kJ\cdot mol^{-1}}$ (+1.1 $\mathrm{kcal\cdot mol^{-1}}$). The $\Delta_f H^\circ_m(\mathrm{CrCl_2},\mathrm{aq})$ value should have been −473.2 $\mathrm{kJ\cdot mol^{-1}}$ (−113.1 $\mathrm{kcal\cdot mol^{-1}}$) and not the −477.8 $\mathrm{kJ\cdot mol^{-1}}$ (−114.2 $\mathrm{kcal\cdot mol^{-1}}$) used in the 1966 calculations. Therefore, $\Delta_f H^\circ_m(\mathrm{Cr^{2+}},\mathrm{aq}) = -138.9$ $\mathrm{kJ\cdot mol^{-1}}$ (−33.2 $\mathrm{kcal\cdot mol^{-1}}$) should have been the calculated value.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f H^\circ_m(\mathrm{CrCl_2},\mathrm{aq})$$

$$\Delta_f H^\circ_m(\mathrm{Cl^-},\mathrm{aq})$$

D. Other Thermodynamic Measurements Considered

53GRE/BUR measured the $\Delta_{\mathrm{sol}} H^\circ_m$ of

$$\mathrm{CrCl_2(cr)} = -77.8\ \mathrm{kJ\cdot mol^{-1}}(-18.6\ \mathrm{kcal\cdot mol^{-1}}).$$

The $\Delta_f H^\circ_m(\mathrm{CrCl_2},\mathrm{aq})$ would be equal to −475.0 $\mathrm{kJ\cdot mol^{-1}}$ that would lead to a $\Delta_f H^\circ_m(\mathrm{Cr^{2+}},\mathrm{aq}) = -140.7$ $\mathrm{kJ\cdot mol^{-1}}$ (−33.6 $\mathrm{kcal\cdot mol^{-1}}$).

E. Additional Determinations of the Thermodynamic Properties

27GRU/BRE made electromotive force (EMF) measurements of $\mathrm{Cr^{2+}/Cr^{3+}}$ potentials in sulfate solutions at 19 °C. Their standard potential for $\mathrm{Cr^{2+}/Cr^{3+}}$ reaction was −0.412 Vs.

F. Bibliography

1886REC Recoura, A., Compt. Rend. **102**, 865 (1886).
27GRU/BRE Grube, G., Breitinger, G., Z. Electrochem. **33**, 112 (1927).
53GRE/BUR Gregory, N. W., Burton, T. M., J. Am. Chem. Soc. **75**, 6053 (1953).

4. $[\mathrm{Cr(H_2O)_6}]^{3+}$(aq,violet)

A. Selected Values, NBS Tables

The NBS tables have a selected value for only one (1) thermodynamic property of the aqueous chromium (III) hexahydrate ion. The thermodynamic function and its selected value is:

$$\Delta_f H^\circ_m(298.15\ \mathrm{K}): -1999.1\ \mathrm{kJ\cdot mol^{-1}}\ (-477.8\ \mathrm{kcal\cdot mol^{-1}}).$$

Nine enthalpies of formation, $\Delta_f H^\circ_m$, were considered during the selection of the NBS selected value. The enthalpies of formation of five aqueous compounds and the enthalpies of formation of the accompanying anions were used to calculate an enthalpy of formation for the aqueous chromium (III) hexahydrate ion. The sulfate, chloride, bromide, fluoride, and the monohydrogen difluoride compounds produced $\Delta_f H^\circ_m = [(-1994.9),(-1999.74),(-1998.49),(-1990.3),(-1998.7)\ \mathrm{kJ\cdot mol^{-1}}]$; [(−476.8), (−477.95), (−477.65), (−475.7), and (−477.7) $\mathrm{kcal\cdot mol^{-1}}$], respectively, for the aqueous chromium (III) hexahydrate ion.

58GAT/KIN presented data for the $\Delta_{rxn} H^\circ_m = 27.6$ $\mathrm{kJ\cdot mol^{-1}}$ (6.6 $\mathrm{kcal\cdot mol^{-1}}$) for the following reaction:

$$\mathrm{Cr(H_2O)_6^{3+}(aq) + Cl^-(aq) = Cr(H_2O)_5Cl^{2+}(aq) + H_2O}, \quad (1)$$

which yielded a $\Delta_f H^\circ_m(\mathrm{Cr(H_2O)_6^{3+}},\mathrm{aq}) = -2006.2$ $\mathrm{kJ\cdot mol^{-1}}$ (−479.5 $\mathrm{kcal\cdot mol^{-1}}$).

58SCH/KIN presented data for the $\Delta_{rxn} H^\circ_m = -45.31$ $\mathrm{kJ\cdot mol^{-1}}$ (−10.83 $\mathrm{kcal\cdot mol^{-1}}$) for the following reaction:

$$\mathrm{Cr(H_2O)_6Cl_3(cr) = Cr(H_2O)_6^{3+}(cr) + 3Cl^-(aq)}, \quad (2)$$

which yielded a $\Delta_f H^\circ_m(\mathrm{Cr(H_2O)_6^{3+}},\mathrm{aq}) = -1996.6$ $\mathrm{kJ\cdot mol^{-1}}$ (−477.2 $\mathrm{kcal\cdot mol^{-1}}$).

47EVA presented data for the $\Delta_{rxn} H^\circ_m = -746.63$ $\mathrm{kJ\cdot mol^{-1}}$ (−178.45 $\mathrm{kcal\cdot mol^{-1}}$) for the following reaction:

$$\mathrm{Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ = 2Cr^{3+} + 6Fe^{3+} + 7H_2O}, \quad (3)$$

which yielded a $\Delta_f H^\circ_m(\mathrm{Cr^{3+}},\mathrm{aq})$ which when combined with the $\Delta_f H^\circ_m$ of 6 moles of $\mathrm{H_2O}$ to yield a $\Delta_f H^\circ_m(\mathrm{Cr(H_2O)_6^{3+}},\mathrm{aq}) = -1953.9$ $\mathrm{kJ\cdot mol^{-1}}$ (−467.0 $\mathrm{kcal\cdot mol^{-1}}$).

49EVA presented data for the $\Delta_{rxn} H^\circ_m = -740.99$ $\mathrm{kJ\cdot mol^{-1}}$ (−177.10 $\mathrm{kcal\cdot mol^{-1}}$) for the same reaction in 47EVA that yielded a $\Delta_f H^\circ_m(\mathrm{Cr^{3+}},\mathrm{aq}) = -245.6$ $\mathrm{kJ\cdot mol^{-1}}$ (−58.7 $\mathrm{kcal\cdot mol^{-1}}$). When six (6) $\Delta_f H^\circ_m(\mathrm{H_2O},\mathrm{l}) = -285.83$ $\mathrm{kJ\cdot mol^{-1}}$ (−68.315 $\mathrm{kcal\cdot mol^{-1}}$) are added to this value, they obtained $\Delta_f H^\circ_m(\mathrm{Cr(H_2O)_6^{3+}},\mathrm{aq}) = -1960.6$ $\mathrm{kJ\cdot mol^{-1}}$(−468.6 $\mathrm{kcal\cdot mol^{-1}}$).

The average of these eight (49EVA was a correction for the 47EVA value) values is −1993.2 $\mathrm{kJ\cdot mol^{-1}}$ (−476.4 $\mathrm{kcal\cdot mol^{-1}}$). However, the NBS selected value is −1999.1 $\mathrm{kJ\cdot mol^{-1}}$ (−477.8 $\mathrm{kcal\cdot mol^{-1}}$).

B. Comments on NBS Selected Values

In the consideration of values used to decide the NBS selected value, the NBS evaluators considered measurements of 47EVA and 49EVA that dealt with the aqueous Cr^{3+} ion and not the hexahydrated Cr^{3+} ion. 49EVA was a recalculation of the 47EVA results and thus should be considered as only one value. The NBS sheet showed the addition of six $\Delta_f H^\circ_m(H_2O,l)$ to the $\Delta_f H^\circ_m(Cr^{3+},aq)$ to yield the hexahydrated value, $\Delta_f H^\circ_m(Cr(H_2O)_6^{3+},aq)$. While this method does not consider the increased stability of the bonded hexahydrated complex, the bonding energy is probably small and the result should have a slightly more positive value. However, this method should give support for the other values considered.

There are several ways to calculate $-1999.1\ kJ\cdot mol^{-1}$ ($-477.8\ kcal\cdot mol^{-1}$). One is to average just the bromide and chloride. Another is to average (-476.8, -477.95, -477.65, -477.7, -479.5, and -477.2) $kcal\cdot mol^{-1}$. There is no information that suggests either of these alternatives over the other, or over any other method. Also, all of these values are not independent since all of the calculated values depended on the enthalpy of formation of $[CrCl_2(H_2O)_4]Cl(aq)$ that was calculated from a reaction enthalpy measured by 1882THO [see Section B of $Cr(OH)_3(cr)$]. Additionally most of the values depended on the enthalpy of formation of $Cr(OH)_3(cr)$ that also was calculated from a measurement made by 1882THO.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H^\circ_m([Cr(H_2O)_6]_2(SO_4)_3,aq)$

$\Delta_f H^\circ_m([Cr(H_2O)_6]Cl_3,aq)$

$\Delta_f H^\circ_m([Cr(H_2O)_6]Br_3,aq)$

$\Delta_f H^\circ_m(Cr(H_2O)_5Cl^{2+},aq)$

$\Delta_f H^\circ_m(H_2O,l)$

$\Delta_f H^\circ_m(SO_4^{2-},aq)$

$\Delta_f H^\circ_m(Cl^-,aq)$

$\Delta_f H^\circ_m(Br^-,aq)$

$\Delta_f H^\circ_m(F^-,aq)$

$\Delta_f H^\circ_m(HF_2^-,aq)$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

The NBS Thermodynamic Tables do not have a selected value for the $Cr^{3+}(aq)$ ion. However, many thermodynamic studies deal with the aqueous Cr^{3+} ion and in the interest of thermodynamic consistency, several thermodynamic measurements that represent the unhydrated Cr^{3+} ion are presented next.

76DEL/HEP measured the enthalpy of reaction for the oxidation of $Cr^{2+}(aq)$ with $Fe^{3+}(aq)$ with $\Delta_r H^\circ_m = -151.9\ kJ\cdot mol^{-1}$ for reaction (2):

$$Cr^{2+}(aq)+Fe^{3+}(aq)=Cr^{3+}(aq)+Fe^{2+}(aq) \qquad (4)$$

in perchloric acid. The measured enthalpy, $-150.6\ kJ\cdot mol^{-1}$, was corrected for the enthalpy of dilution, $+1.30\ kJ\cdot mol^{-1}$, of the ferric perchlorate solution. The authors wanted to calculate the enthalpy of formation for $Cr^{3+}(aq)$ but needed the enthalpy of formation for $Cr^{2+}(aq)$. They chose a $\Delta_f H^\circ_m$ of $Cr^{2+}(aq) = -143.5\ kJ\cdot mol^{-1}$ that was calculated using the $\Delta_f H^\circ_m$ of $CrCl_2(cr)$. These $\Delta_f H^\circ_m$s and the $\Delta_f H^\circ_m$s of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ from the NBS tables gave a $\Delta_f H^\circ_m$ of $Cr^{3+}(aq) = -254.8\ kJ\cdot mol^{-1}$. Because the $\Delta_f H^\circ_m$ value used in their calculations included an arithmetic error, their value for Cr^{3+} would also include this error.

Depending upon the pH, the Cr^{3+}/H_2O equilibrium can produce hydrolyzed Cr^{3+} species with the general formula of $Cr(OH)_x^{3-x}$. Although these species are also not present in the NBS Thermodynamic Tables, several thermodynamic measurements that represent the hydrolysis of the Cr^{3+} ion are also presented here.

81BAE/MES correlated $\Delta_r S^\circ_m$ for the first hydrolysis step for several metal ions with the ratio of their ionic charge to metal–oxygen distance. Their derived linear expression allows the calculation of unknown entropies of reaction. Their expression reproduces some observed entropies of reaction values to within a few percent, while others are in error by more than 50%.

55POS/KIN made spectrophotometric measurements in perchlorate and thiocyanate solutions of Cr^{3+} ions to obtain $\Delta_r H^\circ_m = 39.3 \pm 1.7\ kJ\cdot mol^{-1}$. $\Delta_r S^\circ_m = 59.0\ J\cdot mol^{-1}\cdot K^{-1}$ and $pK_1 = 3.82$ for the first hydrolysis of Cr^{3+} according to the reaction: $Cr^{3+}+H_2O=CrOH^{2+}+H^+$.

76BAE/MES modified the data of 55POS/KIN by introducing a correction for infinite dilution and extrapolated the data of 55POS/KIN to obtain a $pK_1 = 3.4$.

70SWA/KON made spectrophotometric measurements at several temperatures and at various ionic strengths to obtain K_1 as a function of temperature and ionic strength for the reaction: $Cr^{3+}+H_2O=CrOH^{2+}+H^+$.

72KLA/KUB made potentiometric measurements to determine $pK_1 = 3.3$ for the first hydrolysis of the Cr^{3+} ion, $Cr^{3+}+H_2O=CrOH^{2+}+H^+$. They did not consider the possibility of the formation of chromate hydroxy polymers and complexes in the $3.75\ mol\cdot l^{-1}$ $(NH_4)_2SO_4$ medium used in their study and therefore their result may be too low.

73MEY/SIR determined the first three (3) hydrolysis constants of the Cr^{3+} ion, however, their calculations were only crude estimates. Their data suggest that all steps in the hydrolysis of Cr^{3+} can occur in an extremely small pH range of approximately 0.4 and this consideration may not be reliable.

68KON/KON made measurements similar to 73MEY/SIR in an extremely small pH range of approximately 0.4. The validity of these results in this small pH range is questionable.

67SAN/KRY made spectrophotometric measurements to determine the degree of polymerization and hydrolysis of Cr^{3+} in perchlorate solutions. The value of this work is questionable due to their assumption that only one (1) polymeric hydroxy form of Cr^{3+} predominates in solution.

68MOR/LEV made a study very similar to that of 67SAN/KRY in $1\ mol \cdot l^{-1} NaClO_4$. They suggest that only monomeric and dimeric particles are present in solution.

64THO made measurements in the temperature range of 310–340 K and considered the possible existence of several polymeric hydroxy forms of Cr^{3+} in solution. Their data were extrapolated by 76BAE/MES to standard conditions for the reactions:

$$2Cr^{3+} + 2H_2O = Cr_2(OH)_2^{4+} + 2H^+$$

and

$$3Cr^{3+} + 4H_2O = Cr_3(OH)_4^{5+} + 4H^+$$

to obtain pKs equal to 5.06 and 8.13, respectively. The $\Delta_r H_m^\circ = 51.9$ and $104.6\ kJ \cdot mol^{-1}$, respectively, were calculated for these two reactions.

87RAI/SAS performed a critical review of the hydrolysis constants of Cr^{3+}. Their review contains all of the previously mentioned measurements. They also carefully measured the solubility of $Cr(OH)_3$ at a constant concentration of $0.01\ mol \cdot l^{-1}$ of sodium or ammonium perchlorate. Their measurements approached the equilibrium from undersaturation and also from supersaturation and determined hydrolysis constants for the Cr^{3+} ion. They proposed a $\log K_1 = -3.57$ for the first hydrolysis of the Cr^{3+} ion. For the second hydrolysis constant they proposed $\log K_2 = -9.84$. The $\log K_3$ for the third hydrolysis constant with the formation of the neutral species was calculated as slightly less than −16. A $pK_4 = -27.65$ was determined for the fourth hydrolysis constant. The authors also conducted experiments to clarify the importance of polymeric forms of Cr^{3+}. 76BAE/MES had obtained earlier pKs equal to 5.06 and 8.13 for the reactions:

$$2Cr^{3+} + 2H_2O = Cr_2(OH)_2^{4+} + 2H^+$$

and

$$3Cr^{3+} + 4H_2O = Cr_3(OH)_4^{5+} + 4H^+,$$

respectively. 87RAI/SAS obtained the values of 5.0 and 10.75 and concluded that these polymeric species are not very prevalent in dilute solutions.

F. Bibliography

1882THO	Thomsen, J., *Thermochemische Untersuchungen von Julius Thomsen* (J. Barth Verlag, Leipzig, 1882–1886).
47EVA	Evans, M. W., U.S. AEC MDDC, 1206 (1947).
49EVA	Evans, M. W. in *The Transuranium Elements*, edited by G. T. Seaborg, J. J. Katz, and W. M. Manning, National Nuclear Energy, Series 2nd 14B, (McGraw Hill, New York, 1949) pp. 282–294.
55POS/KIN	Postmus, C., King, E. L., J. Phys. Chem. **59**, 1208 (1955).
58GAT/KIN	Gates, H. S., King, E. L., J. Am. Chem. Soc. **80**, 5011 (1958).
58SCH/KIN	Schug, K., King, E. L., J. Am. Chem. Soc. **80**, 1089 (1958).
64THO	Thompson, G., UCRL-11410, Lawrence Radiation Laboratory (1964).
67SAN/KRY	Sannikov, Yu, I., Krylov, E. I., Vinogradov, V. M., Zh. Neorg. Khim. **12**, 2651 (1967).
68KON/KON	Kondratov, P. I., Kondratov, T. S., Surkov, K. K., Tr. Voronezh. Tekhnol. Inst, **17**, 102 (1968).
68MOR/LEV	Morrow, J. I., Levy, J., J. Phys. Chem. **72**, 885 (1968).
70SWA/KON	Swaddle, T. W., Kong, P. C., Can. J. Chem. **48**, 3223 (1970).
72KLA/KUB	Kladnitskaya, K. B., Kublanovskii, V. S., Zosimovich, D. P., Ukr. Khim. Zh. **38**, 104–106 (1972).
73MEY/SIR	Meyenburg, U., Siroky, O., Schwarzenbach, G., Helv. Chim. Acta, **56**, 1099 (1973).
76BAE/MES	Baes, C. F., Mesmer, R. E., *Hydrolysis of Cations* (Academic, New York, 1976).
76DEL/HEP	Dellien, I., Hepler, L. G., Can. J. Chem. **54**, 1383 (1976).
81BAE/MES	Baes, C. F., Mesmer, R. E., Am. J. Sci. **281**, 935 (1981).
87RAI/RAS	Rai, D., Sass, B. M., Moore, D. A., Inorg. Chem. **26**, 345 (1987).

5. CrO_4^{2-}(aq)

A. Selected Values, NBS Tables

The NBS tables have selected values for three (3) thermodynamic properties of the aqueous chromate ion. The thermodynamic functions and their selected values are:

$\Delta_f H_m^\circ$(298.15 K):

$-881.15\ kJ \cdot mol^{-1}\ (-210.60\ kcal \cdot mol^{-1})$

$\Delta_f G_m^\circ$(298.15 K):

$-727.85\ kJ \cdot mol^{-1}\ (-173.96\ kcal \cdot mol^{-1})$

S°_m(298.15 K):

$50.21\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ ($12.00\ \mathrm{kcal\cdot mol^{-1}\cdot K^{-1}}$).

Several sets of potassium chromate data were considered, however, the selected NBS value came from the plot of the 1886SAB data extrapolated to $m^{1/2}=0$ to obtain the value for $\Delta_f H^\circ_m(\mathrm{K_2CrO_4,aq})=-1385.91\ \mathrm{kJ\cdot mol^{-1}}$ ($-331.24\ \mathrm{kcal\cdot mol^{-1}}$). When twice the $\Delta_f H^\circ_m(\mathrm{K^+,aq})$, $-252.38\ \mathrm{kJ\cdot mol^{-1}}$ ($-60.32\ \mathrm{kcal\cdot mol^{-1}}$), is subtracted from $\Delta_f H^\circ_m(\mathrm{K_2CrO_4,aq})$, $-1385.91\ \mathrm{kJ\cdot mol^{-1}}$ ($-331.24\ \mathrm{kcal\cdot mol^{-1}}$), one obtains the NBS selected value for $\Delta_f H^\circ_m(\mathrm{CrO_4^{2-},aq})=(-1385.91)-2\times(-252.38)=-881.15\ \mathrm{kJ\cdot mol^{-1}}$ for the chromate ion.

S°_m for chromate ion was calculated from $\mathrm{Ag_2CrO_4}$ (cr) data of 54PAN. 54PAN measured the emf for a cell at four temperatures that corresponded to reaction (1).

$$2\mathrm{Ag^+CrO_4^{2-}}=\mathrm{Ag_2CrO_4(cr)}. \tag{1}$$

The emf data at the four temperatures were used to plot E°/T vs $1/T$. A $\Delta_{rxn}H^\circ=-61.455\ \mathrm{kJ\cdot mol^{-1}}$ ($-14.688\ \mathrm{kcal\cdot mol^{-1}}$) was calculated from the slope of the plot. $\Delta_{rxn}G^\circ_m=-nFE^\circ$ was used to calculate a $\Delta G^\circ_m=-67.91\ \mathrm{kJ\cdot mol^{-1}}$ ($-16.23\ \mathrm{kcal\cdot mol^{-1}}$) for the cell reaction from the measured E° at 25 °C. A $\Delta S^\circ_m=21.8\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ ($5.2\ \mathrm{cal\cdot mol^{-1}\cdot K^{-1}}$) was calculated for the cell reaction using $\Delta G^\circ_m=\Delta H^\circ_m-T\Delta S^\circ_m$ at $T=298.15$ K. $S^\circ_m(\mathrm{CrO_4^{2-},aq})$ was calculated from the ΔS°_m of reaction (1) and the NBS values for S°_m of $\mathrm{Ag_2CrO_4(cr)}$ and $\mathrm{Ag^+(aq)}$. $\Delta S^\circ_m=S^\circ_m(\mathrm{Ag_2CrO_4})-2\times S^\circ_m(\mathrm{Ag^+})-S^\circ_m(\mathrm{CrO_4^{2-}})$. Therefore, $S^\circ_m(\mathrm{CrO_4^{2-}})=[-21.8+217.6-2\times72.8]\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}=50.2\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$.

$\Delta_f G^\circ_m=\Delta_f H^\circ_m-T\Delta_f S^\circ_m$ was used to calculate the Gibbs free energy change at 298.15 K using the NBS selected standard enthalpy and standard entropy changes that were calculated using the molar entropy of the aqueous chromate ion. The standard molar entropy change was calculated for the following reaction (2):

$$\mathrm{Cr(cr)+2O_2(g)+H_2(g)=2H^++CrO_4^{2-}} \tag{2}$$

as $\Delta_f S^\circ_m=50.2-23.77-2\times(204.999)-130.574=-514.13\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$. Therefore,

$$\begin{aligned}\Delta_f G^\circ_m&=\Delta_f H^\circ_m-T\Delta S^\circ_m\\&=[(-881.15)-(298.15)(-0.51413)]\ \mathrm{kJ\cdot mol^{-1}}\\&=-727.85\ \mathrm{kJ\cdot mol^{-1}}.\end{aligned}$$

B. Comments on NBS Selected Values

The NBS worksheets listed a second pathway that leads to $\Delta_f H^\circ_m$ based upon the enthalpy of the reaction:

$$\mathrm{CrO_4^{2-}(aq)+H^+(aq)=HCrO_4^-(aq)} \tag{3}$$

given by 58HEP that was $2.93\pm1.67\ \mathrm{kJ\cdot mol^{-1}}$($0.7\pm0.4\ \mathrm{kcal\cdot mol^{-1}}$). Combination with $\Delta_f H^\circ_m=-878.2\ \mathrm{kJ\cdot mol^{-1}}$ ($-209.9\ \mathrm{kcal\cdot mol^{-1}}$) for $\mathrm{HCrO_4^-(aq)}$ gave $-881.2\ \mathrm{kJ\cdot mol^{-1}}$ ($-210.6\ \mathrm{kcal\cdot mol^{-1}}$) for $\mathrm{CrO_4^{2-}(aq)}$. This pathway also supports the NBS selected value.

Crystalline $\mathrm{K_2CrO_4}$ is not listed in any of the above pathways but the enthalpy of formation of the aqueous $\mathrm{K_2CrO_4}$ is not independent of the enthalpy of formation of crystalline $\mathrm{K_2CrO_4}$.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H^\circ_m(\mathrm{K_2CrO_4,aq})$

$\Delta_f H^\circ_m(\mathrm{K^+,aq})$

$S^\circ_m(\mathrm{Ag_2CrO_4,cr})$

$S^\circ_m(\mathrm{Ag^+,aq})$

$S^\circ_m(\mathrm{Cr,cr})$

$S^\circ_m(\mathrm{O_2,g})$

$S^\circ_m(\mathrm{H_2,g})$

$S^\circ_m(\mathrm{CrO_4^{2-},aq})$

D. Other Thermodynamic Measurements Considered

57MUL/HEP determined the enthalpies of solution of crystalline $\mathrm{K_2CrO_4}$, $\mathrm{K_2Cr_2O_7}$, and $\mathrm{(NH_4)_2Cr_2O_7}$ and the enthalpies of reaction of crystalline $\mathrm{K_2Cr_2O_7}$ and $\mathrm{CrO_3}$ with aqueous alkali and of $\mathrm{K_2CrO_4}$ with aqueous acid. The enthalpies of formation of crystalline $\mathrm{K_2CrO_4}$, $\mathrm{K_2Cr_2O_7}$, and $\mathrm{(NH_4)_2Cr_2O_7}$ and aqueous $\mathrm{CrO_4^{2-}}$ and $\mathrm{Cr_2O_7^{2-}}$ were calculated to be -1388.7, -2035.1, -1778.2, -868.6, and $-1444.3\ \mathrm{kJ\cdot mol^{-1}}$, respectively. Using the literature K_{eq} and entropy data they calculated the entropies of the aqueous dichromate and bichromate ions to be 295.0 and 200.0 $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$, respectively. The $\Delta_f G^\circ_m$ of the aqueous chromate, dichromate, and bichromate were calculated to be -711.7, -1269.4, and $-748.9\ \mathrm{kJ\cdot mol^{-1}}$, respectively.

In many of the following studies, $\Delta_f H^\circ_m$ of aqueous $\mathrm{K_2CrO_4}$ was measured and the $\Delta_f H^\circ_m(\mathrm{CrO_4^{2-},aq})$ was calculated by subtraction of two $\Delta_f H^\circ_m(\mathrm{K^+,aq})$, $-252.38\ \mathrm{kJ\cdot mol^{-1}}$.

40PER measured enthalpies of solution of $\mathrm{K_2CrO_4}$ from which a $\Delta_f H^\circ_m$ of aqueous $\mathrm{K_2CrO_4}$ was calculated to be $-1385.0\ \mathrm{kJ\cdot mol^{-1}}$. Using the $\Delta_f H^\circ_m(\mathrm{K^+,aq})$, one obtains a value for $\Delta_f H^\circ_m(\mathrm{CrO_4^{2-},aq})=-880.24\ \mathrm{kJ\cdot mol^{-1}}$.

1876MAR measured enthalpies of solution of $\mathrm{K_2CrO_4}$ from which a $\Delta_f H^\circ_m$ of aqueous $\mathrm{K_2CrO_4}$ was calculated to be $-1383.6\ \mathrm{kJ\cdot mol^{-1}}$. Using the $\Delta_f H^\circ_m(\mathrm{K^+,aq})$, one obtains a value for $\Delta_f H^\circ_m(\mathrm{CrO_4^{2-},aq})=-878.8\ \mathrm{kJ\cdot mol^{-1}}$.

56YAT/VAS measured enthalpies of solution of $\mathrm{K_2CrO_4}$ in aqueous $\mathrm{H_2SO_4}$ from which a $\Delta_f H^\circ_m$ of aqueous $\mathrm{K_2CrO_4}$

was calculated to be $-1385.4\ \mathrm{kJ\cdot mol^{-1}}$. Using the $\Delta_f H_m^\circ(\mathrm{K^+,aq})$, one obtains a value for $\Delta_f H_m^\circ(\mathrm{CrO_4^{2-},aq}) = -880.6\ \mathrm{kJ\cdot mol^{-1}}$.

57TER measured enthalpies of solution of K_2CrO_4 from which a $\Delta_f H_m^\circ$ of aqueous K_2CrO_4 was calculated to be $-1387.1\ \mathrm{kJ\cdot mol^{-1}}$. Using the $\Delta_f H_m^\circ(\mathrm{K^+,aq})$, one obtains a value for $\Delta_f H_m^\circ(\mathrm{CrO_4^{2-},aq}) = -882.3\ \mathrm{kJ\cdot mol^{-1}}$.

34KOL/GUS measured enthalpies of solution of K_2CrO_4 from which a $\Delta_f H_m^\circ$ of aqueous K_2CrO_4 was calculated to be $-1384.8\ \mathrm{kJ\cdot mol^{-1}}$. Using the $\Delta_f H_m^\circ(\mathrm{K^+,aq})$, one obtains a value for $\Delta_f H_m^\circ(\mathrm{CrO_4^{2-},aq}) = -880.0\ \mathrm{kJ\cdot mol^{-1}}$.

1878MOR measured the enthalpy of formation of aqueous K_2CrO_4 by the reaction of aqueous CrO_3 and KOH. The $\Delta_f H_m^\circ$ of aqueous K_2CrO_4 was calculated to be $-1383.6\ \mathrm{kJ\cdot mol^{-1}}$. Using the $\Delta_f H_m^\circ(\mathrm{K^+,aq})$, one obtains a value for $\Delta_f H_m^\circ(\mathrm{CrO_4^{2-},aq}) = -878.8\ \mathrm{kJ\cdot mol^{-1}}$.

28ROT/SCH measured enthalpies of solution of K_2CrO_4 from which a $\Delta_f H_m^\circ$ of aqueous K_2CrO_4 was calculated to be $-1385.2\ \mathrm{kJ\cdot mol^{-1}}$. Using the $\Delta_f H_m^\circ(\mathrm{K^+,aq})$, one obtains a value for $\Delta_f H_m^\circ(\mathrm{CrO_4^{2-},aq}) = -880.4\ \mathrm{kJ\cdot mol^{-1}}$.

60JEN/PRA measured emf data on Ag_2CrO_4 at 35 °C. They had an emf $= -0.4468$ V.

37SMI/PIT measured heat capacity, entropy, and free energy of formation for Ag_2CrO_4 from which $S^\circ = 43.9\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ was calculated for CrO_4^{2-}.

E. Additional Determinations of the Thermodynamic Properties

75OHA/BOE measured the $\Delta_{sol} H_m^\circ$ of Cs_2CrO_4 and recomputed and tabulated the thermodynamic data for the formation of the other alkali metal chromates. These thermochemical data were combined with solubility and equilibrium data to recalculate the thermodynamic properties of the aqueous chromate, bichromate, and dichromate ions. The $\Delta_f H_m^\circ$ of the chromate ion was taken from 58HEP. The following values were selected:

	$S^\circ/$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	$\Delta_f H_m^\circ/$ $\mathrm{kJ\cdot mol^{-1}}$	$\Delta_f G_m^\circ/$ $\mathrm{kJ\cdot mol^{-1}}$
CrO_4^{2-}(aq)	57.7 ± 2.1	-882.53 ± 1.88	-731.4 ± 2.1
$HCrO_4^-$(aq)	195.0 ± 7.5	-878.6 ± 2.9	-768.6 ± 2.1
$Cr_2O_7^{2-}$(aq)	241.4 ± 8.8	-1492.0 ± 6.3	-1308.8 ± 4.2

F. Bibliography

1876MAR	Marignac, C., Ann. Chim. Phys. **8**, 410 (1876).
1878MOR	Morges, F., Compt. Rend. **86**, 1443 (1878).
1886SAB	Sabatier, P., Comp. Rend. **103**, 267 (1886).
28ROT/SCH	Roth, W. A., Schwartz, O., Ber. **61B**, 1539 (1928).
34KOL/GUS	Kolosovskii, N., Gushkun, B. V., Zh. Obschchei Khim. **4**, 1289 (1934).
37SMI/PIT	Smith, W. V., Pitzer, K. S., Latimer, W. M., J. Am. Chem. Soc. **59**, 2642 (1937).
40PER	Perreu, J., Compt. Rend. **211**, 136 (1940).
54PAN	Pan, K., J. Chin. Chem. Soc. Taiwan **1**, 1 (1954).
56YAT/VAS	Yatsimirskii, K. B., Vasil'eva, V. N., Zh. Neorg. Khim **1**, 984 (1956).
57MUL/HEP	Muldrow, C. N., Hepler, I. G., J. Am. Chem. Soc. **79**, 4045 (1957).
57TER	Terasaki, Y., Nippon Kagaku Zasshi **78**, 1774 (1957).
58HEP	Hepler, L. G., J. Am. Chem. Soc. **80**, 6181 (1958).
60JEN/PRA	Jena, P. K., Prasad, B., J. Indian Chem. Soc. **37**, 634 (1960).
75OHA/BOE	O'Hare, P. A. G., Boerio, J., J. Chem. Thermodyn. **7**, 1195 (1975).

6. $HCrO_4^-$(aq)

A. Selected Values, NBS Tables

The NBS tables have selected values for three (3) thermodynamic properties of the hydrogen chromate ion, bichromate ion. The thermodynamic functions and their selected values are:

$\Delta_f H_m^\circ(298.15\ \mathrm{K}){:}-878.2\ \mathrm{kJ\cdot mol^{-1}}-(209.9\ \mathrm{kcal\cdot mol^{-1}})$

$\Delta_f G_m^\circ(298.15\ \mathrm{K}){:}-764.8\ \mathrm{kJ\cdot mol^{-1}}-(182.8\ \mathrm{kcal\cdot mol^{-1}})$

$S_m^\circ(298.15\ \mathrm{K}){:}184.1\ \mathrm{J\cdot mol^{-1}K}\ (44.0\ \mathrm{cal\cdot mol^{-1}K})$.

Enthalpies of reaction were calculated for three (3) reactions containing the bichromate ion in 58HEP using experimental enthalpies of reaction determined in 57MUL/HEP and equilibrium constants determined in 53TON/KIN. Three standard molar enthalpies of formation, $\Delta_f H_m^\circ$, were calculated using these three equations:

$$K_2Cr_2O_2(\mathrm{cr})+H_2O(\mathrm{l})=2K^+ + 2HCrO_4^-$$

$$\Delta_{rxn} H_m^\circ = 86.6\ \mathrm{kJ\cdot mol^{-1}}\ (20.7\ \mathrm{kcal\cdot mol^{-1}}), \tag{1}$$

$$(NH_4)_2Cr_2O_7(\mathrm{cr})+H_2O(\mathrm{l})=2NH_4^+ + 2HCrO_4^-,$$

$$\Delta_{rxn} H_m^\circ = 69.9\ \mathrm{kJ\cdot mol^{-1}}\ (16.7\ \mathrm{kcal\cdot mol^{-1}}), \tag{2}$$

$$K_2CrO_4(\mathrm{cr})+H^+ = 2K^+ + 2HCrO_4^-$$

$$\Delta_{rxn} H_m^\circ = 20.9\ \mathrm{kJ\cdot mol^{-1}}\ (5.0\ \mathrm{kcal\cdot mol^{-1}}). \tag{3}$$

The enthalpy of formation values of -2061.9, -1403.3, and $-1806.7\ \mathrm{kJ\cdot mol^{-1}}$ (-492.8, -335.4, and $-431.8\ \mathrm{kcal\cdot mol^{-1}}$) for $K_2Cr_2O_7$(cr), K_2CrO_4(cr), and $(NH_4)Cr_2O_7$(cr), respectively, were used to calculate the enthalpy of formation of the bichromate ion from these reactions. The three values calculated, -878.18, -878.81, and $-877.64\ \mathrm{kJ\cdot mol^{-1}}$ (-209.89, -210.04, and $-209.76\ \mathrm{kcal\cdot mol^{-1}}$) were averaged to yield the selected value of $-878.2\ \mathrm{kJ\cdot mol^{-1}}$ ($-209.9\ \mathrm{kcal\cdot mol^{-1}}$).

A free energy of dissociation was calculated for the bichromate ion in 58HEP.

$$\mathrm{HCrO_4^-(aq)=CrO_4^{2-}(aq)+H^+(aq)}$$

$$\Delta_{rxn}G^\circ_m=37.07\ \mathrm{kJ\cdot mol^{-1}}\ (8.86\ \mathrm{kcal\cdot mol^{-1}}). \quad (4)$$

This value was used with the standard molar free energy of formation of the chromate ion, $-727.85\ \mathrm{kJ\cdot mol^{-1}}$ ($-173.96\ \mathrm{kcal\cdot mol^{-1}}$), to calculate the standard molar free energy of formation of the bichromate ion, $\mathrm{HCrO_4^-}$, equal to $-764.8\ \mathrm{kJ\cdot mol^{-1}}$ ($-182.8\ \mathrm{kcal\cdot mol^{-1}}$).

$\Delta_fG^\circ_m=\Delta_fH^\circ_m-T\Delta S^\circ_m$ was used to calculate $\Delta S^\circ_m=-380.28\ \mathrm{J\cdot mol^{-1}}$ ($-90.89\ \mathrm{cal\cdot mol^{-1}}$) for the formation of the bichromate ion from its elements at 298.15 K

$$\mathrm{Cr(cr)+2O_2(g)+H_2(g)=H^+(aq)+HCrO_4^-(aq)}. \quad (5)$$

Using this ΔS°_m and the standard entropies of Cr, O_2, and H_2, the standard entropy of $184.1\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ was calculated for the bichromate ion. The $S^\circ_m(\mathrm{HCrO_4^-})=\Delta S^\circ_m+S^\circ_m(\mathrm{Cr})+2\times S^\circ_m(\mathrm{O_2})+S^\circ_m(\mathrm{H_2})=[-380.28+23.77+2\times(204.999)+(130.574)]\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}=184.1\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$.

B. Comments on NBS Selected Values

58HEP had a $\Delta_{rxn}S^\circ_m$ of $-134.3\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ for reaction (6):

$$\mathrm{HCrO_4^-(aq)=CrO_4^{2-}(aq)+H^+(aq)}. \quad (6)$$

Using this value and Eq. (5), $S^\circ_m(\mathrm{HCrO_4^-,aq})=184.5\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$. This value supports the selected value of $184.1\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$.

Values of $\Delta_fH^\circ_m$ for $\mathrm{K_2Cr_2O_7(cr)}$ and $\mathrm{K_2CrO_4(cr)}$ used in the calculations did not match the values tabulated -2061.5 and $-1403.7\ \mathrm{kJ\cdot mol^{-1}}$, respectively. The differences were not due to rounding error but due instead to the method of calculation, because values for these two substances were calculated once on worksheets for chromium compounds and then again some time later on worksheets for potassium compounds. The calculations on the two different worksheets were not the same.

The $\Delta_fH^\circ_m$ value for $\mathrm{K_2Cr_2O_7(cr)}$ in reaction (1) was obtained from subtraction of the enthalpies for the reactions:

$$\mathrm{K_2Cr_2O_7(cr)+H_2O(l)=2K^+(aq)+2HCrO_4^-(aq)}, \quad (7)$$

$$\mathrm{(NH_4)_2Cr_2O_7(cr)+H_2O(l)=2NH_4^+(aq)+2HCrO_4^-(aq)} \quad (8)$$

given by 58HEP to obtain the enthalpy change for the hypothetical reaction:

$$\mathrm{K_2Cr_2O_7(cr)+2NH_4^+(aq)=2K^+(aq)+(NH_4)_2Cr_2O_7(cr)}. \quad (9)$$

The enthalpy for reaction (9) was combined with the enthalpy change for:

$$\mathrm{(NH_4)_2Cr_2O_7(cr)+O_2(g)=Cr_2O_3(cr)+N_2(g)+4H_2O(l)} \quad (10)$$

determined by 57NEU/MAR and the tabulated enthalpy of formation for $\mathrm{Cr_2O_3(cr)}$ to obtain $\Delta_fH^\circ_m$ for $\mathrm{K_2Cr_2O_7(cr)}$. Because the enthalpy change for reaction (7) was used to determine $\Delta_fH^\circ_m$ for $\mathrm{K_2Cr_2O_7(cr)}$ it cannot also give an independent value of $\Delta_fH^\circ_m$ for $\mathrm{HCrO_4^-(aq)}$ and should not have been included in the average.

The $\Delta_fH^\circ_m$ for $\mathrm{K_2CrO_4(cr)}$ was obtained in a similar fashion in which the enthalpy change for

$$\mathrm{K_2CrO_4(cr)+H_2O(l)=2K^+(aq)+HCrO_4^-(aq)} \quad (11)$$

was combined with enthalpy changes for reactions (7)–(10) and the $\Delta_fH^\circ_m$ for $\mathrm{Cr_2O_3(cr)}$ to obtain $\Delta_fH^\circ_m$ for $\mathrm{K_2CrO_4(cr)}$. Thus reaction (3) is also not an independent equation for determination of $\Delta_fH^\circ_m$ for $\mathrm{HCrO_4^-(cr)}$. Because neither of reactions (1) and (3) were independent, only reaction (2) should have been used for determination of the enthalpy of formation. This would change $\Delta_fH^\circ_m$ to $-878.8\ \mathrm{kJ\cdot mol^{-1}}$ ($-210.04\ \mathrm{kcal\cdot mol^{-1}}$) and the entropy to $181.95\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

The Gibbs energy of reaction (4) given by 58HEP was calculated in an unspecified way from values given in 53TON/KIN, 34NEU/RIE, and 55DAV/PRU. The enthalpy of formation is dependent on the Gibbs energy of reaction (4).

C. Auxiliary Values Required for Data Pathway

$\Delta_fH^\circ_m(\mathrm{K_2Cr_2O_7,\ cr})$

$\Delta_fH^\circ_m(\mathrm{H_2O,\ l})$

$\Delta_fH^\circ_m(\mathrm{K^+,\ aq})$

$\Delta_fH^\circ_m(\mathrm{(NH_4)_2Cr_2O_7,\ cr})$

$\Delta_fH^\circ_m(\mathrm{NH_4^+,\ aq})$

$\Delta_fH^\circ_m(\mathrm{K_2CrO_4,\ cr})$

$\Delta_fH^\circ_m(\mathrm{H^+,\ aq})$

$\Delta_fG^\circ_m(\mathrm{CrO_4^{2-}})$

$\Delta_fH^\circ_m(\mathrm{HCrO_4^-})$

$\Delta_fG^\circ_m(\mathrm{HCrO_4^-})$

$S^\circ_m(\mathrm{Cr,\ cr})$

$S^\circ_m(\mathrm{O_2,\ g})$

$S^\circ_m(\mathrm{H_2,\ g})$

$S^\circ_m(\mathrm{H^+,\ aq})$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

The speciation of the Cr^{6+} species is largely dependent upon the reaction conditions. Many of the following studies were performed to determine which chromium species are present under certain experimental conditions. The following studies present K_{eq}, to adequately identify the proper chemical reaction that corresponds to the measured thermal energy. These speciation studies deal with several Cr^{6+} species. Although they are referenced with respect to $HCrO_4^-$, much of the data are also relevant to other Cr^{6+} species.

28SAA studied the dichromate to chromate reaction under alkaline, neutral, and acidic conditions. The reactions studied were:

$$Cr_2O_7^{2-}+OH^-=CrO_4^{2-} \quad \text{(alkaline)}$$

$$Cr_2O_7^{2-}+H_2O=2HCrO_4^- \quad \text{(neutral)}$$

$$Cr_2O_7^{2-}+H^++H_2O=HCr_2O_7^-+H_2O \quad \text{(acidic)}$$

$$HCr_2O_7^-+H_2O=2HCrO_4^-+H^+ \quad \text{(acidic)}$$

The usual reaction of interest is:

$$Cr_2O_7^{2-}+H_2O=2HCrO_4^- \quad K_{eq}=0.019.$$

This study indicated that the chromium equilibrium reactions can contain four possible species and that a clear understanding of the speciation is needed to adequately describe Cr^{6+} systems.

36KOR studied the validity of Lambert–Beer's law in determining the speciation of aqueous solutions of inorganic salts. Since solution characterization is often determined by optical methods, the validity of Beer's law was studied by making photoelectric measurements on several aqueous solutions, two of which were K_2CrO_4 and $K_2Cr_2O_7$. Beer's law was not found to be valid over the complete absorption region. At high dilutions, the extinction coefficient was found to approach a constant limiting value.

53TON/KIN spectrophotometrically determined the equilibrium constant for the dissociation of chromic acid, $H_2CrO_4=H^++HCrO_4^-$, equal to $K_{eq}=1.21$ at unit ionic strength. The bichromate is thought to further dissociate by two possible pathways: $HCrO_4^-=H^++CrO_4^{2-}$ and $2HCrO_4^-=Cr_2O_7^{2-}+H_2O$. The correct equilibrium constant is needed to determine the correct Cr^{6+} speciation. They also determined a $K_{eq}=0.028_2$ for the reaction: $Cr_2O_7^{2-}+H_2O=2HCrO_4^-$.

58HOW/NAI made potentiometric and spectrophotometric measurements of the $HCrO_4^-=H^++CrO_4^{2-}$ equilibrium reaction. A thermodynamic dissociation constant $=3.0\times10^{-7}$ $\text{mole}\cdot l^{-1}$ at 25 °C and 0.002 ionic strength was calculated.

62SAS measured emf and spectrophotometric data on the reaction of CrO_4^{2-} with the H^+ that indicated the presence of $Cr_2O_7^{2-}$ and $HCrO_4^-$. Spectrophotometric data yielded $\log K_1=5.90$ for $H^++CrO_4^{2-}=HCrO_4^-$ and $\log K_{22}=2.19$ for $2HCrO_4^-=Cr_2O_7^{2-}+H_2O$.

64LEE/STE made a spectroscopic study of the variation of the apparent pK_a of the protonation of the bichromate ion $HCrO_4^-+H^+=H_2CrO_4$, in several different acids. A $K_{eq}=10.23$ was calculated at 25 °C and unit ionic strength.

64HAI/RIC spectroscopically studied the reaction of the bichromate ion with the hydrogen ion. An equilibrium constant equal to 4.35 was calculated for the protonation of the bichromate at 25 °C and unit ionic strength.

64TON revaluated the 53TON/KIN equilibrium constant data for the dissociation of chromic acid, $H_2CrO_4=H^++HCrO_4^-$. In the earlier paper they postulated the existence of the $HCr_2O_7^-$ ion. 64TON now calculates a $K_{eq}=4.21$ $\text{mole}\cdot l^{-1}$ at unit ionic strength instead of the earlier 1.21 $\text{mole}\cdot l^{-1}$ value. The bichromate is thought to further dissociate by two possible pathways: $HCrO_4^-=H^++CrO_4^{2-}$ and $2HCrO_4^-=Cr_2O_7^{2-}+H_2O$. The correct equilibrium constant is needed to determine the correct Cr^{6+} speciation.

66TON/JOH spectrophotometrically determined the equilibrium constant for the reactions:

$$CrO_3Cl+H_2O=HCrO_4^-+Cl^-+H^+$$

$$H_2CrO_4=HCrO_4^-+H^+$$

at three (3) wavelengths (320, 330, and 340 nm) and three temperatures, 15.0, 25.0, and 35 °C at unit ionic strength. The ΔH and ΔS for the dissociation of CrO_3Cl^- were found to be -4.73 $\text{kJ}\cdot\text{mol}^{-1}$ and -36.0 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively. The same thermodynamic quantities for the dissociation of H_2CrO_4 were -35.6 $\text{kJ}\cdot\text{mol}^{-1}$ and -108.8 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively.

67LUK determined the first ionization constant of chromic acid, $K_1=6.3$, at unit ionic strength in a spectrophotometric study of the equilibria of Cr^{6+} species in acid solutions of varying chloride ion content. The molar absorptivities of the bichromate and dichromate ions were determined at wavelengths from 220 to 400 nm using an approximate dimerization constant K_d of the bichromate ion. At $I<1$ and $K_d=1.54+(1.01\sqrt{I}(1+1.60\sqrt{I}))+0.06\times I$, the molar absorptivities were redetermined at varying acidities but the only polymeric ion found was the dichromate. At high acidities and high chloride ion concentrations, there was a high concentration of the chlorochromate ion. The equilibrium constant for the formation of the chlorochromate ion was $K_e=10.7\pm0.07$.

70LUKa spectrophotometrically determined the total Cr^{6+} concentrations, 4×10^{-4} $\text{mol}\cdot l^{-1}$ to 4×10^{-3} $\text{mol}\cdot l^{-1}$, in aqueous solutions that did or did not contain $NaClO_4$, $NaNO_3$, NaCl, or Na_2SO_4.

70LUKb measured the first dissociation constant of chromic acid in 0.17–1.0 $\text{mol}\cdot l^{-1}$ $HClO_4$. A thermodynamic dissociation constant of 1.50 was obtained by fitting the spectral data at 20 °C to an extended Debye–Hückel equation.

68LIN/JONa studied the equilibrium reaction $Cr_2O_7^{2-}+H_2O=2HCrO_4^-$ in an acid solution, spectrophotometrically. Values of $(2.3_0\pm0.1_7, 2.9_4\pm0.2_2, 4.0_0\pm0.4_0, \text{and } 4.9_7\pm0.4_0)\times10^{-2}$ $mol\cdot l^{-1}$ were obtained for the thermodynamic equilibrium constant at 15, 25, 35, and 45 °C, respectively.

In 68LIN/JONb the equilibrium reaction $HCrO_4^-=H^++CrO_4^{2-}$ was studied in H_2O by potentiometric and independent spectrophotometric methods at 5–60 °C. The thermodynamic quantities $\Delta S^\circ=(-34_{.4}\pm1_{.00})-(80\pm20)\times(\log T-2.474)$ $cal\cdot mol^{-1}\cdot K^{-1}$ and $\Delta H^\circ=(-1_{.3}\pm0.5)-(0.03_5\pm0.01)\times(T-298)$ $kcal\cdot mol^{-1}$ were determined as a function of temperature, for the specified reaction. The $\Delta C_p=(3_5\pm1_0)$ $cal\cdot mol^{-1}$ was calculated and found to be independent of temperature within the accuracy of their data.

86MIC/CAH made a Raman spectroscopic investigation to determine the influence of ionic strength and the chromate–dichromate equilibrium constant on the species present in the Cr^{6+} equilibria. Five species are usually believed to be present in Cr^{6+} aqueous solutions, namely, CrO_4^{2-}, $Cr_2O_7^{2-}$, H_2CrO_4, $HCrO_4^-$, and $HCr_2O_7^-$. The Raman spectra of dilute Cr^{6+} solutions contained no evidence for the presence of the H_2CrO_4, $HCrO_4^-$, and $HCr_2O_7^-$ species when Cr^{6+} concentrations were in the range of 0.1–0.003 $mol\cdot l^{-1}$. The $2CrO_4^{2-}+2H^+=2HCrO_4$ equilibrium was the only one existing between pH1 and 11. The equilibrium constant for the proposed equilibrium was found to be $K_{eq}=14.85\pm0.04$ at 25 °C and $I=1.0$. In more acidic solutions, up to 12 $mol\cdot l^{-1}$ in HNO_3, the trichromate and tetrachromate species were observed.

87PAL/WES studied the hydrolysis of the chromate ion potentiometrically with H electrodes in a concentration cell by titrating basic $NaCl–Na_2CrO_4$ solutions with standardized HCl against a NaOH reference solution. The temperature was varied from 25 to 175 °C at 25 °C intervals at ionic strengths of 0.1140–5.239 (NaCl). Depending on the ionic strength, the molality of total Cr was varied from 0.001 to 0.100. The titration curves were best resolved in terms of three (3) equilibriums involving the formation of the aqueous $HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_3Cl^- ions. The equilibrium constants were fitted as functions of temperature and ionic strength. The molal thermodynamic parameters were calculated and presented in tabular form at specific ionic strengths over the experimental temperature range.

F. Bibliography

28SAA Saal, R. N. J., Recl. Trav. Chim. Pays Bas **47**, 264 (1928).
34NEU/RIE Neuss, J. D., Rieman, W. III, J. Am. Chem. Soc. **56**, 2238 (1934).
36KOR Kortum, G., Z. Phys. Chem., Apt. B **33**, 243 (1936).
53TON/KIN Tong, J. Y., King, E. L., J. Am. Chem. Soc. **75**, 6180 (1953).
55DAV/PRU Davies, W. G., Prue, J. B., Trans. Faraday Soc. **51**, 1045 (1955).
57MUL/HEP Muldrow, C. N., Jr., Hepler, L. G., J. Am. Chem. Soc. **79**, 4045 (1957).
57NEU/MAR Neugebauer, C. A., Margrave, J. L., J. Phys. Chem. **61**, 1429 (1957).
58HEP Hepler, L. G., J. Am. Chem. Soc. **80**, 6181 (1958).
58HOW/NAI Howard, J. R., Nair, V. S. K., Nancollas, G. H., Trans. Faraday Soc. **54**, 1034 (1958).
62SAS Sasaki, Y., Acta Chem. Scand. **16**, 719 (1962).
64HAI/RIC Haight, G. P., Richardson, D. C., Coburn, N. H., J. Inorg. Chem. **3**, 1777 (1964).
64LEE/STE Lee, D. W., Steward, R., J. Am. Chem. Soc. **86**, 3051 (1964).
64TON Tong, J. Y., J. Inorg. Chem. **3**, 1804 (1964).
66TON/JOH Tong, J. Y., Johnson, R. L., J. Inorg. Chem. **5**, 1902 (1966).
67LUK Lukkari, O., Ann. Univ. Turku, Ser. A **I100**, 57pp. (1967).
68LIN/JONa Linge, H. G., Jones, A. L., J. Aust. Chem. Soc. **21**, 1445 (1968).
68LIN/JONb Linge, H. G., Jones, A. L., J. Aust. Chem. Soc. **21**, 2189 (1968).
70LUKa Lukkari, O., Suom. Kemistil. B **43**, 336 (1970).
70LUKb Lukkari, O., Suom. Kemistil. B **43**, 347 (1970).
86MIC/CAH Michel, G., Cahay, R., J. Raman Spectrosc. **17**, 79 (1986).
87PAL/WES Palmer, D. A., Wesolowski, D., Mesmer, R. E., J. Soln. Chem. **16**, 443 (1987).

7. $Cr_2O_7^{2-}$(aq)

A. Selected Values, NBS Tables

The NBS tables have selected values for three (3) thermodynamic properties of the aqueous dichromate ion. The thermodynamic functions and their selected values are:

$\Delta_f H_m^\circ$(298.15 K):

-1490.3 $kJ\cdot mol^{-1}$ (-356.2 $kcal\cdot mol^{-1}$)

$\Delta_f G_m^\circ$(298.15 K):

-1301.2 $kJ\cdot mol^{-1}$ (-311.0 $kcal\cdot mol^{-1}$)

S_m°(298.15 K):261.9 $J\cdot mol^{-1}K^{-1}$ (62.6 $cal\cdot mol^{-1}K^{-1}$).

The standard molar enthalpy of formation, $\Delta_f H_m^\circ$, was calculated for the dichromate ion using a reaction from 58HEP:

$$Cr_2O_7^{2-}(aq)+H_2O(l)=2HCrO_4^-(aq), \qquad (1)$$

where the $\Delta_{rxn}H=19.7\ kJ\cdot mol^{-1}$ ($4.7\ kcal\cdot mol^{-1}$). The NBS selected value for the hydrogen chromate ion is $-878.2\ kJ\cdot mol^{-1}$. The enthalpy of formation for the dichromate was calculated as $\Delta_f H^\circ_m$, $(Cr_2O_7^{2-},aq)=-19.7\ kJ\cdot mol^{-1}+2\times\Delta_f H^\circ_m$, $(HCrO_4^-,aq)-\Delta_f H^\circ_m$, $(H_2O,l)=(-19.7\ kJ\cdot mol^{-1})+2\times(-878.2 kJ\cdot mol^{-1})-(-285.823\ kJ\cdot mol^{-1})=-1490.3\ kJ\cdot mol^{-1}$ ($-356.2\ kcal\cdot mol^{-1}$).

The Gibbs free energy of formation for the aqueous dichromate ion was also calculated using the 58HEP reaction, reaction (1). 58HEP chose 0.029 for the equilibrium constant based upon the data of 34NEU/RIE, 53TON/KIN, and 55DAV/PRU. The $\Delta_{rxn}G^\circ=8.83\ kJ\cdot mol^{-1}$ ($2.11\ kcal\cdot mol^{-1}$) for reaction (1) was calculated using this K_{eq}. The molar free energies of the aqueous hydrogen chromate ion and liquid water were used to calculate $\Delta_f G^\circ_m(Cr_2O_7^{2-})$ from the following relationship:

$$\Delta_{rxn}G^\circ=2\times\Delta_f G^\circ_m(HCrO_4)-\Delta_f G^\circ_m(Cr_2O_7^{2-})$$
$$-\Delta_f G^\circ_m(H_2O).$$

Therefore,

$$8.83\ kJ\cdot mol^{-1}=2\times(-764.8\ kJ\cdot mol^{-1})-\Delta_f G^\circ_m(Cr_2O_7^{2-})$$
$$-(-237.183\ kJ\cdot mol^{-1})$$

and

$$\Delta_f G^\circ_m(Cr_2O_7^{2-})=[(-8.83)+2\times(-764.8)$$
$$-(-237.183)]\ kJ\cdot mol^{-1}$$
$$=-1301.2\ kJ\cdot mol^{-1}.$$

The standard molar entropy change of $\Delta S^\circ_m=-634.3\ J\cdot mol^{-1}\cdot K^{-1}$ ($-151.6\ cal\cdot mol^{-1}\cdot K^{-1}$) was calculated for the following reaction:

$$2Cr(cr)+7/2O_2(g)+H_2(g)=2H^++Cr_2O_7^{-2} \qquad (2)$$

using the relation of $\Delta_f G^\circ_m=\Delta_f H^\circ_m-T\Delta_f S^\circ_m$ at 298.15 K and the standard free energy and enthalpy changes. The molar entropy of the aqueous dichromate ion was then calculated from the following relationship:

$$S^\circ_m(Cr_2O_7^{2-})=\Delta S^\circ_m-2\times S^\circ_m(H^+)+2\times S^\circ_m(Cr)+7/2$$
$$\times S^\circ_m(O_2)+S^\circ_m(H_2).$$

$$S^\circ_m(Cr_2O_7^{2-})=[-634.3-2\times(0)+2\times(23.8)+7/2$$
$$\times(204.999)+130.574]\ J\cdot mol^{-1}\cdot K^{-1}$$

to yield a value of $261.9\ J\cdot mol^{-1}\cdot K^{-1}$ ($62.6\ cal\cdot mol^{-1}\cdot K^{-1}$), the NBS selected value.

B. Comments on NBS Selected Values

The Gibbs free energy of formation for the aqueous dichromate ion was calculated using the 58HEP reaction, reaction (1). 53TON/KIN, 34NEU/RIE and 55DAV/PRU had measured K_{eq} at 298 K that all were in fairly good agreement. However, 58HEP chose 0.029 for the equilibrium constant. 34NEU/RIE gave 0.023, 53TON/KIN gave 0.028_2, and 55DAV/PRU gave 0.030_3. The value used in 58HEP is apparently the average of the 53TON/KIN and 55DAV/PRU values with no contribution in 34NEU/RIE.

Crystalline $K_2Cr_2O_7$ is not listed in any of the above pathways but the enthalpy of formation of the aqueous $K_2Cr_2O_7$ is not independent of the enthalpy of formation of crystalline $K_2Cr_2O_7$.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H^\circ_m(HCrO_4^-,\ aq)$

$\Delta_f H^\circ_m(H_2O,\ l)$

$\Delta_f G^\circ_m(H_2O,\ l)$

$\Delta_f G^\circ_m(HCrO_4^-,\ aq)$

$\Delta_f G^\circ_m(Cr_2O_7^{-2},\ aq)$

$\Delta_f H^\circ_m(Cr_2O_7^{2-},\ aq)$

$S^\circ_m(Cr,\ cr)$

$S^\circ_m(O_2,\ g)$

$S^\circ_m(H_2,\ g)$

$S^\circ_m(H^+,\ aq)$

D. Other Thermodynamic Measurements Considered

The NBS table value for the molar enthalpy change was derived purely from the results of 58HEP, 57MUL/HEP, and 53TON/KIN. The selected value agrees quite well with the average value obtained from the $K_2Cr_2O_7$ studies of 56YAT/VAS ($-1990.29\ kJ\cdot mol^{-1}$), 1882THO ($-1994.89\ kJ\cdot mol^{-1}$), 1886SAB ($-1997.11\ kJ\cdot mol^{-1}$), and 40PER ($-1997.86\ kJ\cdot mol^{-1}$). Where the $\Delta_f H^\circ_m(Cr_2O_7^{2-},aq)=\Delta_f H^\circ_m(K_2Cr_2O_7,aq)-2\times\Delta_f H^\circ_m$, $(K^+,aq)=[(-1995.05)-2\times(-252.38)]\ kJ\cdot mol^{-1}=-1490.3\ kJ\cdot mol^{-1}$. Many $Na_2Cr_2O_7$ and $(NH_4)_2Cr_2O_7$ studies were also considered but not used. The following is a list of other measurements and the species that were studied.

The calculation of the $\Delta_f H^\circ_m(Cr_2O_7^{2-},aq)$ was performed with methods similar to those used to calculate the $\Delta_f H^\circ_m(CrO_4^{2-},aq)$. The enthalpy of formation of the aqueous alkali dichromate salt was determined and the enthalpy of formation of the aqueous alkali ion was subtracted to obtain the desired quantity.

56YAT/VAS measured the enthalpy of solution of $K_2Cr_2O_7$ in aqueous H_2SO_4 that resulted in a $\Delta_f H^\circ_m = -1990.29\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $K_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1485.5\,\mathrm{kJ\cdot mol^{-1}}$.

1882THO measured the enthalpy of solution of $K_2Cr_2O_7$ in H_2O that resulted in a $\Delta_f H^\circ_m = -1994.89\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $K_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1490.1\,\mathrm{kJ\cdot mol^{-1}}$. They also measured the enthalpy of solution of $Na_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -1990.29\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $Na_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1493.1\,\mathrm{kJ\cdot mol^{-1}}$.

1886SAB measured the enthalpy of solution of $K_2Cr_2O_7$ in aqueous KOH that resulted in a $\Delta_f H^\circ_m = -1997.11\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $K_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1492.4\,\mathrm{kJ\cdot mol^{-1}}$.

40PER measured the enthalpy of solution of $K_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -1997.86\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $K_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1493.1\,\mathrm{kJ\cdot mol^{-1}}$.

1878MOR measured the enthalpy of solution of $K_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -1994.4\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $K_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1489.7\,\mathrm{kJ\cdot mol^{-1}}$. They also measured the enthalpy of solution of $Na_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -1965.2\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $Na_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1485.0\,\mathrm{kJ\cdot mol^{-1}}$. They also measured the enthalpy of solution of $(NH_4)_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -1757.3\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $(NH_4)_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1492.3\,\mathrm{kJ\cdot mol^{-1}}$.

1898VON measured the enthalpy of solution of $K_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -1996.9\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $K_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1492.1\,\mathrm{kJ\cdot mol^{-1}}$.

1884BER measured the enthalpy of solution of $K_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -1998.5\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $K_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1493.8\,\mathrm{kJ\cdot mol^{-1}}$. They also measured the enthalpy of solution of $(NH_4)_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -1757.3\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $(NH_4)_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1492.3\,\mathrm{kJ\cdot mol^{-1}}$.

34KOL/GRI measured the enthalpy of solution of $K_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -1997.3\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $K_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1492.5\,\mathrm{kJ\cdot mol^{-1}}$.

60NEL/MOS measured the enthalpy of solution of $Na_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -1979.0\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $Na_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1498.8\,\mathrm{kJ\cdot mol^{-1}}$.

54HER/LAU measured the enthalpy of solution of $Na_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -1965.6\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $Na_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1485.4\,\mathrm{kJ\cdot mol^{-1}}$.

30LAM/REA measured the enthalpy of solution of $Na_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -2003.7\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $Na_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1523.5\,\mathrm{kJ\cdot mol^{-1}}$.

61SHI/VAL measured the enthalpy of solution of $Na_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -1964.4\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $Na_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1484.1\,\mathrm{kJ\cdot mol^{-1}}$.

57NEU/MAR measured the enthalpy of decomposition of $((NH_4)_2Cr_2O_7,\mathrm{cr})$ from which they calculated the enthalpy of formation of $((NH_4)_2Cr_2O_7,\mathrm{cr})$, $\Delta_f H^\circ_m = -1806.6\,\mathrm{kJ\cdot mol^{-1}}$ from the following reaction: $(NH_4)_2Cr_2O_7(\mathrm{cr}) = Cr_2O_3(\mathrm{cr}) + N_2(\mathrm{g}) + 4H_2O(\mathrm{l})$. This value is used to determine the enthalpy of formation of crystalline $Na_2Cr_2O_7$ that was then used in the calculation of the value for the aqueous $Na_2Cr_2O_7$.

55KAP/SHI measured the enthalpy of decomposition of crystalline $(NH_4)_2Cr_2O_7$ based on the same reaction as 57NEU/MAR. A $\Delta_f H^\circ_m = -1812.5\,\mathrm{kJ\cdot mol^{-1}}$ was calculated for crystalline $Na_2Cr_2O_7$.

41PER measured the enthalpy of solution of $(NH_4)_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -1757.8\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $(NH_4)_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1492.8\,\mathrm{kJ\cdot mol^{-1}}$.

23MOL/GON measured the enthalpy of solution of $(NH_4)_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -1754.8\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $(NH_4)_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1489.8\,\mathrm{kJ\cdot mol^{-1}}$.

57MUL/HEP measured the enthalpy of solution of $(NH_4)_2Cr_2O_7$ that resulted in a $\Delta_f H^\circ_m = -1745.6\,\mathrm{kJ\cdot mol^{-1}}$ for aqueous $(NH_4)_2Cr_2O_7$. This resulted in a $\Delta_f H^\circ_m(Cr_2O_7^{2-},\mathrm{aq}) = -1480.3\,\mathrm{kJ\cdot mol^{-1}}$.

64SHA/GER used a Cu/CuO electrode to determine O^{2-} ion concentration in molten KNO_3. The CuO electrode was used to titrate $K_2Cr_2O_7$ with Na_2O_2 in molten KNO_3. Sharp potential drops were recorded at the equivalence point. The equilibrium constant of the reaction: $Cr_2O_7^{2-} + O^{2-} = 2CrO_4^{2-}$ was calculated as $K_{\mathrm{eq}} = 1.8\times 10^{12}$.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

1878MOR Morges, F., Compt. Rend. **86**, 1443 (1878).
1882THO Thomsen, J., *Thermochemische Untersuchungen von Julius Thomsen* (J. Barth Verlag, Leipzig, 1882–1886).
1884BER Berthelot, M., Ann. Chim. Phys. **1**, 92 (1884).

1886SAB Sabatier P., Compt. Rend. **103**, 267 (1886).
1898VON von Stackelberg, E., Z. Phys. Chem. **26**, 533 (1898).
23MOL/GON Moles, B., Gonzales, P., Anales. Soc. Espan. Fis. Quim. **21**, 204 (1923).
30LAM/REA La Mer, V. K., Read, C. L., J. Am. Chem. Soc. **52**, 3098 (1930).
34KOL/GRI Kolosovskii, N., Grishkun, E. V., Zh. Obshch. Khim. **4**, 1289 (1934).
34NEU/RIE Neuss, J. D., Rieman, W. III, J. Am. Chem. Soc. **56**, 2238 (1934).
40PER Perreu, J., Compt. Rend. **211**, 136 (1940).
41PER Perreu, J., Compt. Rend. **212**, 442 (1941).
53TON/KIN Tong, J. Y., King, E. L., J. Am. Chem. Soc. **75**, 6180 (1953).
54HER/LAU Herman, M. A., Lauryssens, M. G., Med. Koninkl. Vlaam. Acad. Wetenschap. Belg. **16**, 3 (1954).
55DAV/PRU Davies, W. G., Prue, J. B., Trans. Faraday Soc. **51**, 1045 (1955).
55KAP/SHI Kapustinskii, A. F., Shidlovskii, A. A., Izvesxt. Sektora Platiny I Drug. Blagorod. Metal., Inst. Obshchei I Neorg. Khim., Akad. Nauk S.S.S.R. **30**, 31 (1955).
56YAT/VAS Yatsimirskii, K. B., Vasil'eva, V. N., Zh. Neorg. Khim. **1**, 984 (1956).
57MUL/HEP Muldrow, O. N., Hepler, L. G., J. Am. Chem. Soc. **79**, 4095 (1957).
57NEU/MAR Neugebauer, C. A., Margrave, J. L., J. Phys. Chem. **61**, 1429 (1957).
58HEP Hepler, L. G., J. Am. Chem. Soc. **80**, 6181 (1958).
60NEL/MOS Nelson, T., Moss, C., Hepler, L. G., J. Phys. Chem. **64**, 376 (1960).
61SHI/VAL Shidlovskii, A. A., Valkina, K. V., Zh. Fiz. Khim. **35**, 294 (1961).
64SHA/GER Shams El Din, A. M., Gerges, A. A. A., Electrochim. Acta **9**, 613 (1964).

8. $\mathrm{Cr_2O_3}$(cr)

A. Selected Values, NBS Tables

The NBS tables have selected values for four (4) thermodynamic properties of crystalline chromium (III) oxide. The thermodynamic functions and their selected values are

$\Delta_f H^\circ_m$(298.15 K):

-1139.7 kJ·mol^{-1} (-272.4 kcal·mol-1)

$\Delta_f G^\circ_m$(298.15 K):

-1058.1 kJ·mol^{-1} (-252.9 kcal·mol^{-1})

S°_m(298.15 K): 81.2 J·mol^{-1}·K^{-1} (19.4 cal·mol^{-1}·K^{-1})

$C^\circ_{p,m}$(298.15 K):

118.74 J·mol^{-1}·K^{-1} (28.38 cal·mol^{-1}·K^{-1}).

It was not clear upon which data the NBS selected value was determined. However, based upon the notes around the combustion measurements of 54MAH, it appears that the selected value came from this study. The selected NBS table value was -1139.7 kJ·mol^{-1}.

37AND measured the heat capacity of $\mathrm{Cr_2O_3}$, the $S^\circ_m(\mathrm{Cr_2O_3,cr})=81.2$ J·mol^{-1}·K^{-1} and $C^\circ_{p,m}(\mathrm{Cr_2O_3,cr})=118.74$ J·mol^{-1}·K^{-1} came directly from their measurement data.

$\Delta_f G^\circ_m(\mathrm{Cr_2O_3,cr})$ was calculated using: $\Delta_f G^\circ_m=\Delta_f H^\circ_m-T\Delta_f S^\circ_m$. The $\Delta_f S^\circ_m$ was calculated as $\Delta_f S^\circ_m=[81.2-2\times(23.77)-3/2\times(204.999)]$ J·mol^{-1}·K^{-1} $=-273.86$ J·mol^{-1}·K^{-1} based upon the formation reaction, $2\mathrm{Cr(cr)}+3/2\mathrm{O_2(g)}=\mathrm{Cr_2O_3(cr)}$. Therefore, $\Delta_f G^\circ_m=[-1139.7-298.15\times(-0.27386)]$ kJ·mol^{-1}$=-1058.1$ kJ·mol^{-1}.

B. Comments on NBS Selected Values

54MAH reported the enthalpy of formation as -1141.0 kJ·mol^{-1} (-272.7 kcal·mol^{-1}). The value on the worksheets was -1140.6 kJ·mol^{-1} (-272.6 kcal·mol^{-1}), the difference apparently due to a difference in atomic weight of chromium. The value tabulated was -1139.7 kJ·mol^{-1} (-272.4 kcal·mol^{-1}), which is smaller than the value identified for 54MAH. Other than the descriptions of other measurements considered, found in Section D below, no additional information as to the origin of this value was available. This is a key quantity because the enthalpy of formation of $\mathrm{Cr_2O_3}$ is contained within the pedigrees of at least the following substances $\mathrm{CrO_4^{2-}}$(aq), $\mathrm{Cr_2O_7^{2-}}$(aq), $\mathrm{HCrO_4^-}$(aq), $\mathrm{CrO_3}$(cr), $\mathrm{CrO_3}$(aq), $\mathrm{K_2CrO_4}$(cr), $\mathrm{K_2Cr_2O_7}$(cr), $\mathrm{Cr(OH)_3}$(cr), and all Cr(III)(aq) species.

C. Auxiliary Values Required for Data Pathway

$C^\circ_{p,m}$(Cr,cr)

$C_{p,m}(\mathrm{O_2},\mathrm{g})$

$S^\circ_m(\mathrm{O_2},\mathrm{g})$

S°_m(Cr,cr)

D. Other Thermodynamic Measurements Considered

29ROT/BEC also measured the enthalpy of combustion of chromium to form $\mathrm{Cr_2O_3}$(cr) at 292.15 K. Conversion to 298.15 K yielded a value of -1208.8 kJ·mol^{-1}.

39GRU/FLA measured the oxygen vapor pressure over $\mathrm{Cr_2O_3}$ at temperatures of 1168–1275 K. The reaction $\mathrm{Cr_2O_3}=2\mathrm{Cr}+1.5\mathrm{O_2}$ was assumed to occur. The enthalpy of formation for 298.15 K, calculated as an average from these measurements, was -1118 kJ·mol^{-1}, with a range of ≈ 2 kJ·mol^{-1}.

40ROT/WOL measured the enthalpy of combustion of chromium to form Cr_2O_3(cr) at 294.15 K. Conversion to 298.15 K yielded a value of -1125.1 $kJ \cdot mol^{-1}$.

61GOL/TSZ measured the enthalpy of combustion at 298.15 K and obtained (-1137.6 ± 7.5) $kJ \cdot mol^{-1}$.

55ROB/JEN measured the enthalpy of the reaction: $Cr_2O_3(cr)+2Al(cr)=2Cr(cr)+Al_2O_3(cr)$ as -540 $kJ \cdot mol^{-1}$. Combination with the enthalpy of formation of Al_2O_3(cr), -1675.7 $kJ \cdot mol^{-1}$, gave $\Delta_f H^\circ = -1135$ $kJ \cdot mol^{-1}$.

27VON/AOY measured the reduction equilibrium of Cr_2O_3:

$$Cr_2O_3(cr)+H_2(g)=2/3\ Cr(cr)+H_2O(g) \qquad (1)$$

at temperatures from 873 to 1653 K. Their calculated value at 298 K for $\Delta_f H^\circ$ was -1120.5 $kJ \cdot mol^{-1}$.

34AOY/KAN also measured the equilibrium of reaction (2) from 718 to 1409 K. Their calculated value at 298 K for $\Delta_f H^\circ$ was -1136.0 $kJ \cdot mol^{-1}$, 16 $kJ \cdot mol^{-1}$ different from their earlier measurements (27VON/AOY).

43OKA also measured the equilibrium of reaction (2) from 1212 to 1583 K. Their calculated value at 298 K for $\Delta_f H^\circ$ was -1128.4 $kJ \cdot mol^{-1}$.

46GRU/FLA also measured the equilibrium of reaction (2) from 1053 to 1573 K. Their calculated at 298 K value for $\Delta_f H^\circ$ was -1119.2 $kJ \cdot mol^{-1}$.

44KEL/BOE measured the enthalpy of the reaction $Cr_2O_3+3C=2Cr+3CO$ to be -801.32 $kJ \cdot mol^{-1}$. Combination with the enthalpy of formation of CO(g), 110.52 $kJ \cdot mol^{-1}$, gave a $\Delta_f H^\circ = -1132.9$ $kJ \cdot mol^{-1}$.

E. Additional Determinations of the Thermodynamic Properties

66NOV/LEN studied the reaction between H_2 and Cr_2O_3 at temperatures of 1220–1500 °C from which was calculated the thermodynamic properties associated with the formation of Cr_2O_3 according to the reaction: $2Cr+1\frac{1}{2}O_2=\beta-Cr_2O_3$. $\Delta_f G_T^\circ = 270.780+0.06172 \times T(\pm 0.700)$ $kcal \cdot mol^{-1}$ and $P_{O_2} = 39453/T - 8.994$ were calculated for the reaction.

74MAZ/PEH have calculated $\Delta_f G_m^\circ = -1115.5+250.1 \times T \pm 1.46$ $kJ \cdot mol^{-1}$ of crystalline Cr_2O_3 as a function of temperature in the temperature region of 1150–1540 K from electrochemical measurements using a ThO_2–Y_2O_3 solid electrolyte.

77BRU/CAN have made precise measurements of the heat capacity of crystalline Cr_2O_3 from 291 to 323 K.

F. Bibliography

27VON/AOY von Wartenberg, H., Aoyama, S., Z. Elektrochem. **33**, 144 (1927).
29ROT/BEC Roth, W. A., Becker, G., Z. Phys. Chem. **145**, 461 (1929).
34AOY/KAN Aoyama, S., Kanda, B., J. Chem. Soc. Jpn. **55**, 1174 (1934).
37AND Anderson, C. T., J. Am. Chem. Soc. **59**, 488 (1937).
39GRU/FLA Grube, G., Flad, M., Z. Electrochem. **45**, 835 (1939).
40ROT/WOL Roth, W. A., Wolf, U., Z. Elektrochem. **46**, 45 (1940).
43OKA Okaka, S., Kogyo Kwagaku Zasshi **46**, 324 (1943).
44KEL/BOE Kelley, K. K., Boericke, F. S., Moore, G. E., Huffman, E. H., and Bangert, W. M., U.S. Bur. Mines Tech. Papers 662 (1944).
46GRU/FLA Grube, G., Flad, M., Z. Electrochem. **48**, 377 (1946).
54MAH Mah, A. D., J. Am. Chem. Soc. **76**, 3363 (1954).
55ROB/JEN Robins, D. A., Jenkins, I., Acta Metall. **3**, 598 (1955).
61GOL/TSZ Golutvin, Yu. M., Tszin'-Kui, I., Zh. Phys. Khim. **35**, 129 (1961).
66NOV/LEN Novokhvatskii, I. A., Lenev, L. M., Zh. Neorg. Khim. **11**, 2014 (1966).
74MAZ/PEH Mazandarany, F. N., Pehlke, R. D., J. Electrochem. Soc. **121**, 711 (1974).
77BRU/CAN Bruce, R. H., Cannell, D. S., Phys. Rev. **15**, 4451 (1977).

9. $Cr_2O_3 \cdot H_2O$ (cr)

A. Selected Values, NBS Tables

The NBS tables have a selected value for only one (1) thermodynamic property of the crystalline chromium (III) oxide monohydrate. The thermodynamic function and its selected value is:

$\Delta_f H_m^\circ(298.15\ K)$: $-1506.$ $kJ \cdot mol^{-1}$ ($-360.$ $kcal \cdot mol^{-1}$).

29SIM/FIS measured pressure against temperature for hydrated crystalline chromium (III) oxide. Their measurements were used to calculate the enthalpy of hydration for three (3) successive hydrations with one mole of water each. The monohydrate was formed according to the reaction $Cr_2O_3(cr)+H_2O(g)=Cr_2O_3 \cdot H_2O(cr)$. The enthalpy of hydration was $\Delta_{rxn} H^\circ = -124.60$ $kJ \cdot mol^{-1}$.

$$\begin{aligned}
&\Delta_f H_m^\circ(Cr_2O_3 \cdot H_2O,cr) \\
&\quad = \Delta_{rxn} H^\circ + \Delta_f H_m^\circ(Cr_2O_3,cr) + \Delta_f H_m^\circ(H_2O,g) \\
&\quad = [-124.60+(-1139.7)+(-241.82)]\ kJ \cdot mol^{-1} \\
&\quad = -1506.1 kJ \cdot mol^{-1},
\end{aligned}$$

which was rounded to -1506.0 $kJ \cdot mol^{-1}$ for the NBS selected value.

B. Comments on NBS Selected Values

None.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m^\circ(Cr_2O_3,cr)$$

$$\Delta_f H_m^\circ(H_2O,g)$$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

29SIM/FIS	Simon, A., Fischer, O., Schmidt, J., Z. Anorg. Allgem. Chem. **185**, 107 (1929).

10. $Cr_2O_3 \cdot 2H_2O(cr)$

A. Selected Values, NBS Tables

The NBS tables have a selected value for only one (1) thermodynamic property of the crystalline chromium (III) oxide dihydrate. The thermodynamic function and its selected value is:

$\Delta_f H_m^\circ(298.15\ K)$:

$-1845.\ kJ \cdot mol^{-1}\ (-441.\ kcal \cdot mol^{-1})$.

29SIM/FIS measured pressure against temperature for hydrated crystalline chromium (III) oxide. Their measurements were used to calculate the enthalpy of hydration for three (3) successive hydrations with one mole of water each. The dihydrate was formed according to the reaction, $Cr_2O_3 \cdot H_2O(cr)+H_2O(g)=Cr_2O_3 \cdot 2H_2O(cr)$. The enthalpy of hydration was $\Delta_{rxn}H_m^\circ=-96.2\ kJ \cdot mol^{-1}$.

$$\begin{aligned}\Delta_f H_m^\circ(Cr_2O_3 \cdot 2H_2O,cr) &= \Delta_{rxn}H_m^\circ+\Delta_f H_m^\circ(Cr_2O_3 \cdot H_2O,cr)+\Delta_f H_m^\circ(H_2O,g)\\ &=[-96.2+(-1506.)+(-241.82)]\ kJ \cdot mol^{-1}\\ &=-1844.3\ kJ \cdot mol^{-1}.\end{aligned}$$

The NBS selected value is $-1845.\ kJ \cdot mol^{-1}$.

B. Comments on NBS Selected Values

None.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m^\circ(Cr_2O_3 \cdot H_2O,cr)$$

$$\Delta_f H_m^\circ(H_2O,g)$$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

29SIM/FIS	Simon, A., Fischer, O., Schmidt, J., Z. Anorg. Allgem. Chem. **185**, 107 (1929).

11. $Cr_2O_3 \cdot 3H_2O(cr)$

A. Selected Values, NBS Tables

The NBS tables have a selected value for only one (1) thermodynamic property of the crystalline chromium (III) oxide trihydrate. The thermodynamic function and its selected value is:

$\Delta_f H_m^\circ(298.15\ K)$: $-2171.\ kJ \cdot mol^{-1}\ (-519.\ kcal \cdot mol^{-1})$.

29SIM/FIS measured pressure against temperature for hydrated crystalline chromium (III) oxide. Their measurements were used to calculate the enthalpy of hydration for three (3) successive hydrations with 1 mole of water each. The trihydrate was formed according to the reaction, $Cr_2O_3 \cdot 2H_2O(cr)+H_2O(g)-Cr_2O_3 \cdot 3H_2O(cr)$. The enthalpy of hydration was $\Delta_{rxn}H_m^\circ=-85.8\ kJ \cdot mol^{-1}$. $\Delta_f H_m^\circ(Cr_2O_3 \cdot 3H_2O,cr)=\Delta_{rxn}H_m^\circ+\Delta_f H_m^\circ(Cr_2O_3 \cdot 2H_2O,cr)+\Delta_f H_m^\circ(H_2O,g)=[-85.8+(-1845.)+(-241.82)]\ kJ \cdot mol^{-1}=-2172.7\ kJ \cdot mol^{-1}$. The NBS selected value is $-2171.\ kJ \cdot mol^{-1}$.

B. Comments on NBS Selected Values

None.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m^\circ(Cr_2O_3 \cdot 2H_2O,cr)$$

$$\Delta_f H_m^\circ(H_2O,g)$$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

29SIM/FIS	Simon, A., Fischer, O., Schmidt, J., Z. Anorg. Allgem. Chem. **185**, 107 (1929).

12. Cr_3O_4(cr)

A. Selected Values, NBS Tables

The NBS tables have a selected value for only one (1) thermodynamic property of the crystalline mixed chromium (II) and chromium (III) oxide, $CrO\cdot Cr_2O_3$. The thermodynamic function and its selected value is:

$$\Delta_f H^\circ_m(298.15\ \text{K}):$$

$$-1531.\ \text{kJ}\cdot\text{mol}^{-1}\ (-366.\ \text{kcal}\cdot\text{mol}^{-1}).$$

The $\Delta_f H^\circ_m$ of crystalline mixed chromium (II) and chromium (III) oxide, $CrO\cdot Cr_2O_3$, was selected from the work of 61DAN/MOR. An enthalpy of reaction of $\Delta_{rxn}H^\circ_m=550.6$ kJ·mol^{-1} was measured for the following reaction at 1700 °C:

$$Cr_3O_4(\text{cr})+4H_2(\text{g})=3Cr+4H_2O(\text{g}). \qquad (1)$$

The $\Delta_{rxn}H^\circ_m=564.8$ kJ·mol^{-1} at 25 °C.

$$\begin{aligned}\Delta_f H^\circ_m&(Cr_2O_3,\text{cr})\\ &=-(\Delta_{rxn}H^\circ_m)+4\Delta_f H^\circ_m(H_2O,\text{g})\\ &=[-564.8+4(-241.82)]\text{kJ}\cdot\text{mol}^{-1}\\ &=-1531.\text{kJ}\cdot\text{mol}^{-1}.\end{aligned}$$

B. Comments on NBS Selected Values

None.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f H^\circ_m(H_2O,\text{g})$$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

61DAN/MOR Danilovich, Yu. A., Morozov, A. N., Fiz. Khim. Osnovy Proizv. Stali., Akad. Nauk S.S.S.R., Inst. Met., Tr. 6th Konf. Moscow, 223 (1961).

13. CrO_2(cr)

A. Selected Values, NBS Tables

The NBS tables gives a selected value for only one (1) thermodynamic property of the crystalline chromium (IV) oxide:

$$\Delta_f H^\circ_{m,298.15\ \text{K}}:=-598.\ \text{kJ}\cdot\text{mol}^{-1}\ (-143.\ \text{kcal}\cdot\text{mol}^{-1}).$$

The $\Delta_f H^\circ_m(CrO_2,\text{cr})$ was obtained as the average of two literature values, 61KUB and 53ARI/SHC. 61KUB determined the $\Delta_{rxn}H^\circ_m=110.0$ kJ·mol^{-1} at a mean temperature of 500 °C for the decomposition of CrO_2(cr) over the temperature range from 450 to 550 °C according to the following reaction:

$$2CrO_2(\text{cr})=Cr_2O_3(\text{cr})+1/2O_2(\text{g}). \qquad (1)$$

A $\Delta C^\circ_p=29$ J·mol^{-1}·K^{-1} was calculated using an estimated heat capacity for CrO_2(cr) of 52.3 J·mol^{-1}·K^{-1}. The $\Delta C^\circ_p=[118.7+\frac{1}{2}(29.4)-2(52.3)]$ J·mol^{-1}·K^{-1}=29 J·mol^{-1}·K^{-1}. The $\Delta_{rxn}H^\circ_m=110.0$ kJ·mol^{-1} reduces to 96.2 kJ·mol^{-1} when corrected from 500 to 25 °C. Therefore,

$$\begin{aligned}\Delta_f H^\circ_m(CrO_2)&=[-(\Delta_{\text{rxn}}H^\circ_m)+\Delta_f H^\circ_m(Cr_2O_3,\text{cr})]/2\\ &=[-(96.2)+(-1139.7)]/2\\ &=-618.0\ \text{kJ}\cdot\text{mol}^{-1}.\end{aligned}$$

53 ARI/SHC determined a $\Delta_{rxn}H^\circ_m=-250.2$ kJ·mol^{-1} at 25 °C for the following reaction:

$$2CrO_{1.98}(\text{cr})+0.96H_2=Cr_2O_3(\text{cr})+0.96H_2O(\text{l}) \qquad (2)$$

and

$$\begin{aligned}\Delta_f H^\circ_m(CrO_2)&=[-(\Delta_{rxn}H^\circ_m)+\Delta_f H^\circ_m(Cr_2O_3,\text{cr})+0.96\\ &\quad\times\Delta_f H^\circ_m(H_2O,\text{l})]/2\\ &=[-(-250.2)+(-1139.7)\\ &\quad+0.96\times(-285.83)]/2\\ &=-582.0\ \text{kJ}\cdot\text{mol}^{-1}.\end{aligned}$$

The average of −618.0 kJ·mol^{-1} and −582.0 kJ·mol^{-1} is −600.0 kJ·mol^{-1}. The NBS selected value is −598 kJ·mol^{-1} (−143 kcal·mol^{-1}). The NBS selected value was derived as −143.4 kcal·mol^{-1} that was rounded to −143 kcal·mol^{-1} and when converted to kJ·mol^{-1} produced the selected value of 598 kJ·mol^{-1}.

B. Comments on NBS Selected Values

The average of −618.0 and −582.0 kJ·mol^{-1} (−147.7 and −139.1 kcal·mol^{-1}) is −600.0 kJ·mol^{-1} (−143.4 kcal·mol^{-1}). The NBS selected value is −598 kJ·mol^{-1} (−143 kcal·mol^{-1}). The NBS selected value was derived from the rounded kcal·mol^{-1} value and thus the selection of 598 instead of 600 kJ·mol^{-1}.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f H^\circ_m(Cr_2O_3,\text{cr})$$

$$\Delta_f H^\circ_m(H_2O,\text{liq})$$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

53ARI/SHC	Ariya, S. M., Shchukarev, S. A., Glushkova, V. B., Zh. Obshchei. Khim. **23**, 1241 (1953).
61KUB	Kubota, B., J. Am. Ceram. Soc. **44**, 239 (1961).

14. $CrO_3(cr)$

A. Selected Values, NBS Tables

The NBS tables have a selected value for only one (1) thermodynamic property of the crystalline chromium (VI) oxide. The thermodynamic function and its selected value is:

$\Delta_f H^\circ_m(298.15\ \mathrm{K})$:

$-589.5\ \mathrm{kJ{\cdot}mol^{-1}}\ (-140.9\ \mathrm{kcal{\cdot}mol^{-1}})$.

57MUL/HEP gave enthalpies for the two reactions:

$$K_2Cr_2O_7(cr)+2OH^-(aq)=2K^+(aq)+2CrO_4^{2-}(aq)+H_2O(l)$$

$$\Delta_{rxn}H^\circ_m=-30.5\ \mathrm{kJ{\cdot}mol^{-1}}\ (-7.3\ \mathrm{kcal{\cdot}mol^{-1}})$$

and

$$CrO_3(cr)+2OH^-(aq)=CrO_4^{2-}(aq)+H_2O(l)$$

$$\Delta_{rxn}H^\circ_m=-117.2\ \mathrm{kJ{\cdot}mol^{-1}}\ (-28.0\ \mathrm{kcal{\cdot}mol^{-1}}).$$

Subtraction of these two reactions gave

$$K_2Cr_2O_7(cr)+H_2O(l)=2KOH(aq)+2CrO_3$$

$$\Delta_{rxn}H^\circ_m=203.8\ \mathrm{kJ{\cdot}mol^{-1}}\ (48.7\ \mathrm{kcal{\cdot}mol^{-1}}),$$

which then led to $\Delta_f H^\circ_m(CrO_3(cr))=-589.5\ \mathrm{kJ{\cdot}mol^{-1}}$ $(-140.9\ \mathrm{kcal{\cdot}mol^{-1}})$, using the $\Delta_f H^\circ_m$ of crystalline $K_2Cr_2O_7$, described under $HCrO_4^-(aq)$.

B. Comments on NBS Selected Values

The value of $\Delta_f H^\circ_m(K_2Cr_2O_7,cr)$ used in the calculation did not match that tabulated; see $HCrO_4^-(aq)$ Section B.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H^\circ_m(K_2Cr_2O_7,cr)$

$\Delta_f H^\circ_m(H_2O,l)$

$\Delta_f H^\circ_m(KOH,aq)$

D. Other Thermodynamic Measurements Considered

29ROT/BEC measured the enthalpy change for the reaction:

$$2CrO_3(cr)=Cr_2O_3(cr)+3/2O_2(g)$$

as 29.3 kJ·mol^{-1}. Combination with the tabulated $\Delta_f H^\circ_m$ for $Cr_2O_3(cr)$, -1139.7 kJ·mol^{-1}, gave $\Delta_f H^\circ_m$ for $CrO_3(cr)$, -584.5 kJ·mol^{-1}.

08MIX measured the enthalpy changes for the reactions:

$$CrO_3(cr)+Na_2O(cr)=Na_2CrO_4(cr)$$

and

$$Cr(cr)+3Na_2O_2(cr)=Na_2CrO_4(cr)+2Na_2O(cr)$$

as -322.2 kJ·mol^{-1} and -664.4 kJ·mol^{-1}. Combination of the two reactions yields

$$Cr+3Na_2O_2(cr)=CrO_3(cr)+3Na_2O(cr)$$

with a calculated enthalpy change of -342.2 kJ·mol^{-1}. This was combined with $\Delta_f H^\circ_m$s for $Na_2O_2(cr)$ and $Na_2O(cr)$ of -504.6 and -415.9 kJ·mol^{-1} to give $\Delta_f H^\circ_m(CrO_3)=-608.4$ kJ·mol^{-1}. The $\Delta_f H^\circ_m$ used for $Na_2O(cr)$ and $Na_2O_2(cr)$ did not match the values tabulated: -414.22 and -510.87 kJ·mol^{-1}. Use of these values gives $\Delta_f H^\circ_m(CrO_3)=-632.2$ kJ·mol^{-1}.

E. Additional Determinations of the Thermodynamic Properties

52HAR made an extensive study of the periodicity of chemical thermodynamic functions. A family of straight lines, based upon the periodic table grouping, was observed when the standard molar entropies were plotted against the log of the molecular weight. Making use of all the curves, entropies were estimated for several oxides where data were missing. 52HAR estimated the entropy for CrO_3 to be 63.6 J·mol^{-1}·K^{-1} (15.2 cal·mol^{-1}·K^{-1}). However, Table I in the paper contains the value of 72.0 J·mol^{-1}·K^{-1} (17.2 cal·mol^{-1}·K^{-1}).

F. Bibliography

08MIX	Mixter, W. G., Am. J. Sci. **26**, 125 (1908).
29ROT/BEC	Roth, W. A., Becker, G., Z. Phys. Chem. **145**, 461 (1929).
52HAR	Hart, D., J. Phys. Chem. **56**, 202 (1952).
57MUL/HEP	Muldrow, O. N., Hepler, L. G., J. Am. Chem. Soc. **79**, 4095 (1957).

15. $CrO_3{\cdot}80H_2O$

A. Selected Values, NBS Tables

The NBS tables have a selected value for only one (1) thermodynamic property of the chromium (VI) oxide in 80 mole of water. The thermodynamic function and its selected value is:

$\Delta_f H^\circ_m(298.15\ \mathrm{K})$:

$-601.2\ \mathrm{kJ{\cdot}mol^{-1}}\ (-143.7\ \mathrm{kcal{\cdot}mol^{-1}})$.

12BUC/PRI measured the enthalpy of solution of crystalline chromium (VI) oxide in 80 mole of water as $\Delta_{rxn}H^\circ_m=-10.3$ kJ·mol^{-1} at 15 °C that was calculated to be

$\Delta_{rxn}H^\circ_m = -11.7\,\mathrm{kJ\cdot mol^{-1}}$ at 25 °C. An enthalpy of formation of the crystalline substance of $\Delta_f H^\circ_m = -589.5\,\mathrm{kJ\cdot mol^{-1}}$ was used from the work of 57MUL/HEP. 1878MOR measured enthalpies of solution at several concentrations using from 2 to 50 mole of H_2O. Therefore the NBS table has entries for the enthalpy of formation of aqueous chromium (VI) oxide with from 2 to 80 mole of H_2O.

B. Comments on NBS Selected Values

None.

C. Auxiliary Values Required for Data Pathway

$C^\circ_{p,m}(\mathrm{CrO_3,cr})$

$C^\circ_{p,m}(\mathrm{CrO_3,aq})$

$C^\circ_{p,m}(\mathrm{H_2O,l})$

D. Other Thermodynamic Measurements Considered

None.

E. More Recent Determinations of the Thermodynamic Properties

None.

F. Bibliography

1878MOR	Morges, F., Compt. Rend. **86**, 1443 (1878).
12BUC/PRI	Buchner, E. B., Prins, A., Z. Phys. Chem. **81**, 113 (1912).
57MUL/HEP	Muldrow, O. N., Hepler, L. G., J. Am. Chem. Soc. **79**, 4095 (1957).

16. $[\mathrm{Cr(H_2O)_6}]_2(\mathrm{SO_4})_3$ (aq,violet)

A. Selected Values, NBS Tables

The NBS tables have a selected value for only one (1) thermodynamic property of the aqueous chromium (III) sulfate dodecahydrate. The thermodynamic function and its selected value is:

$\Delta_f H^\circ_m(298.15\ \mathrm{K})$:

$-6717.4\ \mathrm{kJ\cdot mol^{-1}}\ (-1605.5\ \mathrm{kcal\cdot mol^{-1}})$.

The $\Delta_f H^\circ_m$ of this hexahydrated chromium sulfate complex, $[\mathrm{Cr(H_2O)_6}]_2(\mathrm{SO_4})_3$, was determined as the average of three (3) measurements reported in the literature. The first value was reported in 07COL as $[\mathrm{Cr(H_2O)_6}]_2[\mathrm{SO_4}]_3(\mathrm{aq}) = -6714.1\ \mathrm{kJ\cdot mol^{-1}}(-1604.7\ \mathrm{kcal\cdot mol^{-1}})$. This value was determined from the enthalpy of the following reaction:

$$[\mathrm{Cr(H_2O)_6}]_2[\mathrm{SO_4}]_3(\mathrm{aq}) + 6\mathrm{HCl\cdot 1500H_2O} = 2[\mathrm{Cr(H_2O)_6}]\mathrm{Cl_3(aq)} + 3\mathrm{H_2SO_4\cdot 1000\ H_2O} \quad (1)$$

with $\Delta_{rxn}H^\circ_m = 35.6\ \mathrm{kJ\cdot mol^{-1}}(+8.5\ \mathrm{kcal\cdot mol^{-1}})$. $\Delta_f H^\circ_m = [-35.6 + 2(-2501.2) + 3(-892.36) - 6(-166.82)]\ \mathrm{kJ\cdot mol^{-1}} = -6714.1\ \mathrm{kJ\cdot mol^{-1}}(-1604.7\ \mathrm{kcal\cdot mol^{-1}})$. A second value of $\Delta_f H^\circ_m = -6719.5\ \mathrm{kJ\cdot mol^{-1}}(-1606.0\ \mathrm{kcal\cdot mol^{-1}})$ came from 1882THO. 1882THO had an enthalpy of reaction of $\Delta_{rxn}H^\circ_m = -186.372\ \mathrm{kJ\cdot mol^{-1}}$ $(-44.544\ \mathrm{kcal\cdot mol^{-1}})$ for the following reaction:

$$[\mathrm{Cr(H_2O)_6}]_2[\mathrm{SO_4}]_3(\mathrm{aq}) + 6\mathrm{KOH} = 3\mathrm{K_2SO_4} + 2\mathrm{Cr(OH)_3(cr)} + 12\mathrm{H_2O}. \quad (2)$$

The $\Delta_f H^\circ_m[\mathrm{Cr(H_2O)_6}]_2(\mathrm{SO_4})_3,\mathrm{aq}] = [186.372 + 3(-1414.02) + 2(-1064.0) + 12(-285.830) - 6(-482.37)]\ \mathrm{kJ\cdot mol^{-1}} = -6719.5\ \mathrm{kJ\cdot mol^{-1}}(-1606.0\ \mathrm{kcal\cdot mol^{-1}})$. The third value of $\Delta_f H^\circ_m = 6719.1\ \mathrm{kJ\cdot mol^{-1}}\ (-1605.9\ \mathrm{kcal\cdot mol^{-1}})$ also came from 1882THO. The reaction

$$2\mathrm{Cr(OH)_3} + 3\mathrm{H_2SO_4\cdot 400H_2O} + 6\mathrm{H_2O} = [\mathrm{Cr(H_2O)_6}]_2[\mathrm{SO_4}]_3 \quad (3)$$

had an enthalpy of reaction of $\Delta_{rxn}H^\circ_m = -206.3\ \mathrm{kJ\cdot mol^{-1}}$ $(-49.3\ \mathrm{kcal\cdot mol^{-1}})$. The $\Delta_f H^\circ_m[(\mathrm{Cr(H_2O)_6})_2(\mathrm{SO_4})_3,\mathrm{aq}] = [-206.3 + 2(-1064.0) + 3(-889.974)_{400} + 6(-285.830)]\ \mathrm{kJ\cdot mol^{-1}} = -6719.1\ \mathrm{kJ\cdot mol^{-1}}\ (-1605.9\ \mathrm{kcal\cdot mol^{-1}})$. The average of these three values, $-(6714.1 + 6719.5 + 6719.1)\ \mathrm{kJ\cdot mol^{-1}}/3 = -6717.4\ \mathrm{kJ\cdot mol^{-1}}$ $(-1605.5\ \mathrm{kcal\cdot mol^{-1}})$, was chosen as the NBS selected value.

B. Comments on NBS Selected Values

The $-6714.1\ \mathrm{kJ\cdot mol^{-1}}\ (-1604.7\ \mathrm{kcal\cdot mol^{-1}})$ value used in the average came from the work of 07COL. The calculations used $\mathrm{HCl\cdot 1500H_2O}$ and $\mathrm{H_2SO_4\cdot 1000H_2O}$ while the reactions reported in 07COL used $\mathrm{HCl\cdot 400H_2O}$ and $\mathrm{H_2SO_4\cdot 400H_2O}$. The correction to a lower degree of hydration only amounts to less than $2\ \mathrm{kJ\cdot mol^{-1}}$ and with the other uncertainties involved, this quantity is negligible.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H^\circ_m[\mathrm{HCl\cdot 1500H_2O,aq}]$

$\Delta_f H^\circ_m[\mathrm{H_2SO_4\cdot 1000H_2O,aq}]$

$\Delta_f H^\circ_m[\mathrm{H_2SO_4\cdot 400H_2O,aq}]$

$\Delta_f H^\circ_m[(\mathrm{Cr(H_2O)_6})\mathrm{Cl_3,aq}]$

$\Delta_f H^\circ_m[\mathrm{KOH,aq}]$

$\Delta_f H^\circ_m[\mathrm{K_2SO_4,aq}]$

$\Delta_f H^\circ_m[\mathrm{H_2O,l}]$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

1882THO Thomsen, J., *Thermochemische Untersuchungen von Julius Thomsen* (J. Barth Verlag, Leipzig, 1882–1886).
07COL Colson, A., Ann. Chim. Phys. **12**, 433 (1907).

17. $[Cr_2(H_2O)_6](SO_4)_3$ (aq, green)

A. Selected Values, NBS Tables

The NBS tables have a selected value for only one (1) thermodynamic property of the aqueous chromium (III) sulfate hexahydrate. The thermodynamic function and its selected value is:

$$\Delta_f H^\circ_m(298.15\ \mathrm{K}):$$

$$-4935.0\ \mathrm{kJ\cdot mol^{-1}}\ (-1179.5\ \mathrm{kcal\cdot mol^{-1}}).$$

The $\Delta_f H^\circ_m$ of this hexahydrated chromium sulfate complex, $[Cr_2(H_2O)_6](SO_4)_3$, was determined from the work of 07COL. The following chemical reaction was used:

$$[Cr_2(H_2O)_6](SO_4)_3(aq)+6KOH(aq)$$
$$=2Cr(OH)_3+3K_2SO_4(aq)+6H_2O(l) \qquad (1)$$

with an enthalpy of reaction, $\Delta_{rxn}H^\circ_m=-1069.4$ kcal·mol^{-1}. The

$$\Delta_f H^\circ_m([Cr_2(H_2O)_6](SO_4)_3,aq)$$
$$=(-\Delta_{rxn}H^\circ_m)+2\times\Delta_f H^\circ_m(Cr(OH)_3,cr)$$
$$+3\Delta_f H^\circ_m(K_2SO_4,aq)+6\times\Delta_f H^\circ_m(H_2O,l)$$
$$-6\Delta_f H^\circ_m(KOH,aq)$$
$$=[-(-1069.4)+2\times(-1064.0)+3\times(-1414.0)$$
$$+6\times(-285.83)-6\times(-482.37)]\ \mathrm{kJ\cdot mol^{-1}}$$
$$=-4935.0\ \mathrm{kJ\cdot mol^{-1}}\ (-1179.5\ \mathrm{kcal\cdot mol^{-1}}).$$

B. Comments on NBS Selected Values

None.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H^\circ_m(KOH,aq)$

$\Delta_f H^\circ_m(Cr(OH)_3,cr)$

$\Delta_f H^\circ_m(K_2SO_4,aq)$

$\Delta_f H^\circ_m(H_2O,l)$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

07COL Colson, A., Ann. Chim. Phys. **12**, 433 (1907).

18. $[Cr_2(H_2O)_8(SO_4)_2](SO_4)(aq)$

A. Selected Values, NBS Tables

The NBS tables have a selected value for only one (1) thermodynamic property of the aqueous chromium (III) sulfate octahydrate. The thermodynamic function and its selected value is:

$$\Delta_f H^\circ_m(298.15\ \mathrm{K}):$$

$$-5521.6\ \mathrm{kJ\cdot mol^{-1}}\ (-1319.7\ \mathrm{kcal\cdot mol^{-1}}).$$

The $\Delta_f H^\circ_m$ of this octahydrated chromium sulfate complex, $[Cr_2(H_2O)_8(SO_4)_2]SO_4$, was determined from the work of 07COL. The following chemical reaction was used:

$$[Cr_2(H_2O)_8(SO_4)_2]SO_4(aq)+6KOH(aq)$$
$$=2Cr(OH)_3+3K_2SO_4(aq)+8H_2O(l) \qquad (1)$$

with an enthalpy of reaction, $\Delta_{rxn}H^\circ_m=-241.0$ kJ·mol^{-1} (−57.6 kcal·mol^{-1}). The $\Delta_f H^\circ_m([Cr_2(H_2O)_8(SO_4)_2]SO_4,aq)$ $=-\Delta_{rxn}H^\circ_m+2\times\Delta_f H^\circ_m(Cr(OH)_3,cr)+3\times\Delta_f H^\circ_m$ $\times(K_2SO_4,aq)+6\times\Delta_f H^\circ_m(H_2O,l)-6\times\Delta_f H^\circ_m(KOH,aq)$ $=[-(-241.0)+2\times(-1064.0)+3\times(-1414.02)$ $+8\times(-285.830)-6\times(-482.37)]$ kJ·mol^{-1}=−5521.6 kJ·mol^{-1} (−1319.7 kcal·mol^{-1}).

B. Comments on NBS Selected Values

None.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H^\circ_m(KOH,aq)$

$\Delta_f H^\circ_m(Cr(OH)_3,cr)$

$\Delta_f H^\circ_m(K_2SO_4,aq)$

$\Delta_f H^\circ_m(H_2O,l)$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

07COL Colson, A., Ann. Chim. Phys. **12**, 433 (1907).

19. $[Cr_2(H_2O)_{10}SO_4](SO_4)_2(aq)$

A. Selected Values, NBS Tables

The NBS tables have a selected value for only one (1) thermodynamic property of the aqueous chromium (III) sulfate decahydrate. The thermodynamic function and its selected value is:

$\Delta_f H_m^\circ(298.15\ \mathrm{K})$:

$-6123.3\ \mathrm{kJ\cdot mol^{-1}}\ (-1463.5\ \mathrm{kcal\cdot mol^{-1}})$.

The $\Delta_f H^\circ_{m,298.15\ \mathrm{K}}$ of this decahydrated chromium sulfate complex, $[Cr_2(H_2O)_{10}SO_4](SO_4)_2$, was determined from the work of 07COL. The following chemical reaction was used:

$$2Cr(OH)_3+3H_2SO_4(aq)+4H_2O = [Cr_2(H_2O)_{10}SO_4](SO_4)_2(aq) \qquad (1)$$

with an enthalpy of reaction, $\Delta_{rxn}H_m^\circ(298.15\ \mathrm{K}) = -182.0\ \mathrm{kJ\cdot mol^{-1}}\ (-43.5\ \mathrm{kcal\cdot mol^{-1}})$. The $\Delta_f H_m^\circ(298.15\ \mathrm{K})([Cr_2(H_2O)_{10}SO_4](SO_4)_2,\mathrm{aq}) = \Delta_{rxn}H_m^\circ + 2\times\Delta_f H_m^\circ(298.15\ \mathrm{K})(Cr(OH)_3,\mathrm{cr}) + 3\times\Delta_f H_m^\circ(298.15\ \mathrm{K})(H_2SO_4,\mathrm{aq}) + 4\times\Delta_f H_m^\circ(298.15\ \mathrm{K})(H_2O,\mathrm{l}) = [(-182.0)+2\times(-1064.0)+3\times(-889.98)+4\times(-285.830)]\ \mathrm{kJ\cdot mol^{-1}} = -6123.3\ \mathrm{kJ\cdot mol^{-1}}\ (-1463.5\ \mathrm{kcal\cdot mol^{-1}})$.

B. Comments on NBS Selected Values

None.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H_m^\circ(298.15\ \mathrm{K})(Cr(OH)_3,\mathrm{cr})$

$\Delta_f H_m^\circ(298.15\ \mathrm{K})(H_2SO_4,\mathrm{aq})$

$\Delta_f H_m^\circ(298.15\ \mathrm{K})(H_2O,\mathrm{l})$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

07COL Colson, A., Ann. Chim. Phys. **12**, 433 (1907).

20. $CrCl_2(cr)$

A. Selected Values, NBS Tables

The NBS tables have selected values for six (6) thermodynamic properties of the crystalline chromium (II) chloride. The thermodynamic functions and their selected values are:

$\Delta_f H_m^\circ(0\ \mathrm{K}): -397.19\ \mathrm{kJ\cdot mol^{-1}}\ (-94.93\ \mathrm{kcal\cdot mol^{-1}})$

$\Delta_f H_m^\circ(298.15\ \mathrm{K}): -395.4\ \mathrm{kJ\cdot mol^{-1}}\ (-94.5\ \mathrm{kcal\cdot mol^{-1}})$

$\Delta_f G_m^\circ(298.15\ \mathrm{K}): -356.0\ \mathrm{kJ\cdot mol^{-1}}\ (-85.1\ \mathrm{kcal\cdot mol^{-1}})$

$H_m^\circ(298.15\ \mathrm{K}) - H_m^\circ(0\ \mathrm{K})$:

$15.033\ \mathrm{kJ\cdot mol^{-1}}\ (3.593\ \mathrm{kcal\cdot mol^{-1}})$

$S_m^\circ(298.15\ \mathrm{K})$:

$115.31\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}\ (27.56\ \mathrm{cal\cdot mol^{-1}\cdot K^{-1}})$

$C_{p,m}^\circ(298.15\ \mathrm{K})$:

$71.17\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}\ (17.01m\ \mathrm{cal\cdot mol^{-1}\cdot K^{-1}})$.

62STO/CHI measured the heat capacity of crystalline $CrCl_2$ between 11 and 300 K. Their measurement data were used to derive most of the selected thermodynamic properties of crystalline $CrCl_2$. The heat capacity, entropy, and enthalpy increment from 0 to 298 K came directly from their measurement data.

The equilibrium data of 37DOE and that of 38SAN were also used to derive the standard molar enthalpy of formation. 62STO/CHI recalculated the enthalpy of the reaction studied by both 37DOE and 38SAN. A $\Delta_{rxn}H_m^\circ = 210.87\ \mathrm{kJ\cdot mol^{-1}}$ was obtained for the reduction of $CrCl_2$ according to the following reaction:

$$CrCl_2(cr)+H_2(g)=Cr(cr)+2HCl(g)$$

$$\begin{aligned}\Delta_f H_m^\circ(CrCl_2,\mathrm{cr}) &= -\Delta_{rxn}H_m^\circ + 2\times\Delta_f H_m^\circ(HCl,\mathrm{g})\\ &= [-210.87+2\times(-92.307)]\ \mathrm{kJ\cdot mol^{-1}}\\ &= -395.48\ \mathrm{kJ\cdot mol^{-1}}. \qquad (1)\end{aligned}$$

The $\Delta_f H^\circ(0\ \mathrm{K})$ was calculated using $\Delta_f H^\circ(298\ \mathrm{K})$ minus the $[H^\circ(298\ \mathrm{K}) - H^\circ(0\ \mathrm{K})]$ of $CrCl_2$, Cr, and Cl_2 based upon reaction (2):

$$Cr(cr)+Cl_2(g)=CrCl_2(cr) \qquad (2)$$

as $\Delta_f H_0^\circ = -395.5-[15.033-4.058-9.176] = -397.19\ \mathrm{kJ\cdot mol^{-1}}$.

The relation $\Delta_f G_m^\circ = \Delta_f H_m^\circ - T\times\Delta_f S_m^\circ$ was used to calculate $\Delta_f G_m^\circ$. $\Delta_f S_m^\circ$ was calculated based upon reaction (2) as $\Delta_f S_m^\circ = S_m^\circ(CrCl_2) - S_m^\circ(Cr) - S_m^\circ(Cl_2) = [115.31-23.77-222.957]\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}} = -131.411\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$. Then $\Delta_f G_m^\circ = [-395.4-298.15\times(-0.131411)]\ \mathrm{kJ\cdot mol^{-1}} = -356.1\ \mathrm{kJ\cdot mol^{-1}}$.

B. Comments on NBS Selected Values

None.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H^\circ_m(\mathrm{HCl,g})$

$[H^\circ(298\ \mathrm{K})-H^\circ(0\ \mathrm{K})](\mathrm{Cr,cr})$

$[H^\circ(298\ \mathrm{K})-H^\circ(0\ \mathrm{K})](\mathrm{Cl_2,g})$

$S^\circ(\mathrm{Cr,cr})$

$S^\circ(\mathrm{Cl_2,g})$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

76GEE/SHE calculated a $\Delta_f H^\circ_m = -396.72 \pm 0.30$ $\mathrm{kJ \cdot mol^{-1}}$ for crystalline $\mathrm{CrCl_2}$ from emf measurements of solid electrolyte galvanic cells containing the Cr, $\mathrm{CrCl_2}$ electrode. The cell utilized was

$$\mathrm{Pt|Cr,CrCl_2|BaCl_2|Fe,FeCl_2|Pt}$$

over the temperature range of 530–800 K. The emf measurements produced a $\Delta_f G^\circ_m = (-380.210 + 0.10458 \times T)$ $\mathrm{kJ \cdot mol^{-1}}$ for the formation of $\mathrm{CrCl_2}$ according to the reaction: $\mathrm{Cr(cr)+Cl_2(g)=CrCl_2(cr)}$. The $\Delta_f H^\circ_m$ of crystalline $\mathrm{CrCl_2}$ was calculated from the $\Delta_f G^\circ_m$ for the formation of crystalline $\mathrm{CrCl_2}$ and tabulated standard entropies and heat capacities.

F. Bibliography

37DOE Doerner, H. A., U.S. Bur. Mines. Tech. Papers No. 577 (1937).
38SAN Sano, J. Chim. Soc. Jpn. **59**, 937 (1938).
62STO/CHI Stout, J. W., Chisholm, R. C., J. Chem. Phys. **36**, 979 (1962).
76GEE/SHE Gee, R., Shelton, R. A. J., Trans. Inst. Min. Metall. **85**, 208 (1976).

21. $\mathrm{CrCl_2(aq)}$

A. Selected Values, NBS Tables

The NBS tables have selected values for one (1) thermodynamic property of aqueous chromium (II) chloride. The thermodynamic function and its selected value is:

$\Delta_f H^\circ_m(298.15\ \mathrm{K})$: $-477.8\ \mathrm{kJ \cdot mol^{-1}}$ $(-114.2\ \mathrm{kcal \cdot mol^{-1}})$.

1886REC determined the enthalpy of solution of crystalline chromium (II) chloride. The NBS tables value for the enthalpy of formation of aqueous chromium (II) chloride was calculated as the sum of the enthalpies of formation and solution of crystalline chromium (II) chloride. Therefore, $\Delta_f H^\circ_m(\mathrm{CrCl_2,aq}) = \Delta_f H^\circ_m(\mathrm{CrCl_2,cr}) + \Delta_{\mathrm{soln}} H^\circ_m(\mathrm{CrCl_2,cr})$ $= [(-395.64)+(-77.8)]$ $\mathrm{kJ \cdot mol^{-1}} = -473.46$ $\mathrm{kJ \cdot mol^{-1}}$ $(-113.16\ \mathrm{kcal \cdot mol^{-1}})$ which would round to -473.5 $\mathrm{kJ \cdot mol^{-1}}$ $(113.2\ \mathrm{kcal \cdot mol^{-1}})$. The NBS tables selected a value of $-477.8\ \mathrm{kJ \cdot mol^{-1}}$ $(-114.2\ \mathrm{kcal \cdot mol^{-1}})$ and not the calculated value of $-473.5\ \mathrm{kJ \cdot mol^{-1}}$ $(-113.2\ \mathrm{kcal \cdot mol^{-1}})$.

B. Comments on NBS Selected Values

The $\Delta_f H^\circ_m(\mathrm{CrCl_2,cr}) = -395.64$ $\mathrm{kJ \cdot mol^{-1}}$ $(-94.56$ $\mathrm{kcal \cdot mol^{-1}})$ is an earlier NBS value but the selected value that was derived from 62STO/CHI and $\Delta_f H^\circ_m(\mathrm{CrCl_2,cr})$ $= -395.47\ \mathrm{kJ \cdot mol^{-1}}$ $(-94.52\ \mathrm{kcal \cdot mol^{-1}})$ should have been used. The result would be $-473.29\ \mathrm{kJ \cdot mol^{-1}}$ $(-113.12$ $\mathrm{kcal \cdot mol^{-1}})$ which would round off to $-473.3\ \mathrm{kJ \cdot mol^{-1}}$ $(-113.1\ \mathrm{kcal \cdot mol^{-1}})$. The NBS selected value of -477.8 $\mathrm{kJ \cdot mol^{-1}}$ $(-114.2\ \mathrm{kcal \cdot mol^{-1}})$ seems to have been a transcription error that was discussed earlier under the aqueous $\mathrm{Cr^{2+}}$ species.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H^\circ_m(\mathrm{CrCl_2,cr})$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

1886REC Recoura, A., Compt. Rend. **102**, 865 (1886).
62STO/CHI Stout, J. W., Chisholm, R. C., J. Chem. Phys. **36**, 979 (1962).

22. $\mathrm{CrCl_2 \cdot 2H_2O}$ (cr, light green)

A. Selected Values, NBS Tables

The NBS tables have selected values for one (1) thermodynamic property of crystalline chromium (II) chloride dihydrate. The thermodynamic function and its selected value is:

$\Delta_f H^\circ_m(298.15\ \mathrm{K})$: $-992.0\ \mathrm{kJ \cdot mol^{-1}}$ $(-237.1\ \mathrm{kcal \cdot mol^{-1}})$.

11KNI/RIC measured the vapor pressure of water over the dehydration reaction:

$$\mathrm{CrCl_2 \cdot 3H_2O(cr,\ pale\ blue)} \\ \mathrm{=CrCl_2 \cdot 2H_2O(cr,\ pale\ green)+H_2O(g).} \qquad (1)$$

From a van't Hoff plot they calculated $\Delta_{rxn} H^\circ_m$ $= 58.6\ \mathrm{kJ \cdot mol^{-1}}$ $(14.0\ \mathrm{kcal \cdot mol^{-1}})$ from the slope. The

$$\begin{aligned}&\Delta_f H^\circ_m(\mathrm{CrCl_2{\cdot}2H_2O,cr})\\&\quad=\Delta_{rxn}H^\circ_m-\Delta_f H^\circ_m(\mathrm{H_2O,g})+\Delta_f H^\circ_m(\mathrm{CrCl_2{\cdot}3H_2O,cr})\\&\quad=[58.6-(-241.84)+(-1292.4)]\mathrm{kJ{\cdot}mol^{-1}}\\&\quad=-992.0\ \mathrm{kJ{\cdot}mol^{-1}}\ (-237.1\mathrm{kcal{\cdot}mol^{-1}}).\end{aligned}$$

B. Comments on NBS Selected Values

None.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H^\circ_m(\mathrm{CrCl_2{\cdot}3H_2O,cr})$

$\Delta_f H^\circ_m(\mathrm{H_2O,g})$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

11KNI/RIC Knight, W. A., Rich, E. M., J. Chem. Soc. **99**, 87 (1911).

23. $\mathrm{CrCl_2{\cdot}3H_2O}$ (cr, pale blue)

A. Selected Values, NBS Tables

The NBS tables have selected values for one (1) thermodynamic property of crystalline chromium (II) chloride trihydrate. The thermodynamic function and its selected value is

$\Delta_f H^\circ_m(298.15\ \mathrm{K})$:

$-1292.4\ \mathrm{kJ{\cdot}mol^{-1}}\ (-308.9\ \mathrm{kcal{\cdot}mol^{-1}})$.

11KNI/RIC measured the vapor pressure of water over the dehydration reaction

$$\begin{aligned}&\mathrm{CrCl_2{\cdot}4H_2O(cr,\ dark\ blue)}\\&\quad=\mathrm{CrCl_2{\cdot}3H_2O(cr,\ pale\ blue)+H_2O(g)}.\qquad(1)\end{aligned}$$

From a van't Hoff plot they calculated $\Delta_{rxn}H^\circ_m=74.1\ \mathrm{kJ{\cdot}mol^{-1}}(17.7\ \mathrm{kcal{\cdot}mol^{-1}})$ from the slope. The

$$\begin{aligned}&\Delta_f H^\circ_m(\mathrm{CrCl_2{\cdot}3H_2O,cr})\\&\quad=\Delta_{rxn}H^\circ_m-\Delta_f H^\circ_m(\mathrm{H_2O,g})+\Delta_f H^\circ_m(\mathrm{CrCl_2{\cdot}4H_2O,cr})\\&\quad=[74.1-(-241.84)+(-1608.3)]\ \mathrm{kJ{\cdot}mol^{-1}}\\&\quad=-1292.4\mathrm{kJ{\cdot}mol^{-1}}\ (-308.9\ \mathrm{kcal{\cdot}mol^{-1}}).\end{aligned}$$

B. Comments on NBS Selected Values

None.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H^\circ_m(\mathrm{CrCl_2{\cdot}4H_2O,cr})$

$\Delta_f H^\circ_m(\mathrm{H_2O,g})$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

11KNI/RIC Knight, W. A., Rich, E. M., J. Chem. Soc. **99**, 87 (1911).

24. $\mathrm{CrCl_2{\cdot}4H_2O}$ (cr, dark blue)

A. Selected Values, NBS Tables

The NBS tables have selected a value for one (1) thermodynamic property of crystalline chromium (II) chloride tetrahydrate. The thermodynamic function and its selected value is

$\Delta_f H^\circ_m(298.15\ \mathrm{K})$:

$-1608.3\ \mathrm{kJ{\cdot}mol^{-1}}\ (-384.4\ \mathrm{kcal{\cdot}mol^{-1}})$.

The NBS table value was calculated two (2) ways from the results of 1886REC. In the first method, 1886REC measured the enthalpy of solution of crystalline chromium (II) chloride, $\Delta_{rxn}H^\circ_m=-8.4\ \mathrm{kJ{\cdot}mol^{-1}}\ (-2.0\ \mathrm{kcal{\cdot}mol^{-1}})$, for the following reaction:

$$\mathrm{CrCl_2{\cdot}4H_2O(cr)=CrCl_2(aq)+4H_2O(l)}.\qquad(1)$$

The

$$\begin{aligned}&\Delta_f H^\circ_m(\mathrm{CrCl_2,aq})\\&\quad=-\Delta_{rxn}H^\circ_m+4\times\Delta_f H^\circ_m(\mathrm{H_2O,l})\\&\qquad-\Delta_f H^\circ_m(\mathrm{CrCl_2{\cdot}4H_2O,cr})\\&\quad=[+8.37+(-473.6)+4\times(-285.83)]\ \mathrm{kJ{\cdot}mol^{-1}}\\&\quad=-1608.3\ \mathrm{kJ{\cdot}mol^{-1}}\ (-384.4\mathrm{kcal{\cdot}mol^{-1}}).\end{aligned}$$

In the second method, also from 1886REC, the measured enthalpy of reaction, $\Delta_{rxn}H^\circ_m=-69.5\ \mathrm{kJ{\cdot}mol^{-1}}\ (-16.6\ \mathrm{kcal{\cdot}mol^{-1}})$ was used based upon the following reaction:

$$\mathrm{CrCl_2(cr)+4H_2O(l)=CrCl_2{\cdot}4H_2O(cr)}.\qquad(2)$$

$$\begin{aligned}&\Delta_f H^\circ_m(\mathrm{CrCl_2{\cdot}4H_2O,cr})\\&\quad=\Delta_{rxn}H^\circ_m+\Delta_f H^\circ_m(\mathrm{CrCl_2,aq})+4\times\Delta_f H^\circ_m(\mathrm{H_2O,l})\\&\quad=[-69.5+(-395.4)+4\times(-285.830)]\ \mathrm{kJ{\cdot}mol^{-1}}\end{aligned}$$

$$= -1608.3\ \mathrm{kJ\cdot mol^{-1}}\ (-384.4\mathrm{kcal\cdot mol^{-1}}).$$

The two methods produced identical results.

B. Comments on NBS Selected Values

The second calculation, which yielded the -1608 kJ·mol^{-1} (-384.4 kcal·mol^{-1}), should have used the enthalpy of formation for gaseous water, $\Delta_f H^\circ_m = -241.84$ kJ·mol^{-1} (-57.80 kcal·mol^{-1}), and not the enthalpy of formation for liquid water, $\Delta_f H^\circ_m = -285.83$ kJ·mol^{-1} (-68.315 kcal·mol^{-1}) and thus would have produced a different result.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f H^\circ_m(\mathrm{CrCl_2,cr})$$

$$\Delta_f H^\circ_m(\mathrm{CrCl_2,aq})$$

$$\Delta_f H^\circ_m(\mathrm{H_2O,liq})$$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

1886REC Recoura, A., Compt. Rend. **102**, 865 (1886).

25. $\mathrm{CrCl_3}$ (cr)

A. Selected Values, NBS Tables

The NBS tables have selected values for six (6) thermodynamic properties of the crystalline chromium (III) chloride. The thermodynamic functions and their selected values are

$\Delta_f H^\circ_m(0\ \mathrm{K})$: -556.30 kJ·mol^{-1} (-132.96 kcal·mol^{-1})

$\Delta_f H^\circ_m(298.15\ \mathrm{K})$: -556.5 kJ·mol^{-1} (-133.0 kcal·mol^{-1})

$\Delta_f G^\circ_m(298.15\ \mathrm{K})$: -486.1 kJ·mol^{-1} (-116.2 kcal·mol^{-1})

$H^\circ_m(298.15\ \mathrm{K}) - H^\circ_m(0\ \mathrm{K})$:

17.66 kJ·mol^{-1} (4.22 kcal·mol^{-1})

$S^\circ_m(298.15\ \mathrm{K})$: 123.0 J·mol^{-1}·K^{-1} (29.4 cal·mol^{-1}·K^{-1})

$C^\circ_{p,m}(298.15\ \mathrm{K})$:

91.80 J·mol^{-1}·K^{-1} (21.94 cal·mol^{-1}·K^{-1}).

The values for $[H^\circ_m(298.15\,\mathrm{K}) - H^\circ_m(0\,\mathrm{K})]$, $C^\circ_{p,m}$ and S°_m came from 58HAN/GRI that reported heat capacity measurements from 15 to 300 K. This work expanded on the work in 37AND which contained measurements from 54 to 297 K.

$\Delta_f H^\circ_m$ was determined by six (6) investigators. Most used a series of reactions to obtain the enthalpy of reaction for one of two reactions: reaction (1): the oxidation of chromium (II) chloride with chlorine to obtain chromium (III) chloride

$$2\mathrm{CrCl_2(cr)} + \mathrm{Cl_2(g)} = 2\mathrm{CrCl_3(cr)} \tag{1}$$

or reaction (2): the reduction of chromium (III) chloride with hydrogen to produce chromium (II) chloride and hydrogen chloride,

$$2\mathrm{CrCl_3(cr)} + \mathrm{H_2(g)} = 2\mathrm{CrCl_2(cr)} + 2\mathrm{HCl(g)}. \tag{2}$$

1887REC determined a $\Delta_{rxn} H^\circ_m = -164.8$ kJ·mol^{-1} per mole of $\mathrm{CrCl_3}$ for the oxidation in reaction (1). No correction was used to correct the measured enthalpy to 25 °C. $\Delta_f H^\circ_m(\mathrm{CrCl_3,cr}) = \Delta_{rxn} H^\circ_m + \Delta_f H^\circ_m(\mathrm{CrCl_2,cr}) = [(-164.8) + (-395.4)]$ kJ·mol^{-1} $= -560.2$ kJ·mol^{-1}.

39SAN determined the K_{eq} from partial pressures of HCl and $\mathrm{H_2}$ gases at several temperatures between 600 and 700 °C for the reduction in reaction (2). His $\Delta_{rxn} H^\circ_m = 93.01$ kJ·mol^{-1} at 650 °C from the slope of his fitted data was calculated to be $\Delta_{rxn} H^\circ_m = 97.5$ kJ·mol^{-1} at 25 °C. The $\Delta C^\circ_{p,m}$ was calculated as -12.6 J·mol^{-1}·K^{-1} for reaction (2). Therefore,

$$\begin{aligned}\Delta_f H^\circ_m(\mathrm{CrCl_3,cr}) &= [-\Delta_{rxn} H^\circ_m + 2\times\Delta_f H^\circ_m(\mathrm{CrCl_2,cr}) \\ &\quad + 2\times\Delta_f H^\circ_m(\mathrm{HCl,g})]/2 \\ &= \{[(-97.5) + 2\times(-395.4) \\ &\quad + 2\times(-92.307)]/2\}\ \mathrm{kJ\cdot mol^{-1}} \\ &= -536.4\ \mathrm{kJ\cdot mol^{-1}}.\end{aligned}$$

29JEL/KOO determined a $\Delta_{rxn} H^\circ_m = -280.12$ kJ·mol^{-1} for the oxidation of reaction (1) at 736 K. This was corrected to $\Delta_{rxn} H^\circ_m = -285.62$ kJ·mol^{-1} of $\mathrm{Cl_2}$ at 298 K using a $\Delta C^\circ_{p,m} = 12.6$ J·mol^{-1}·K^{-1}. This produced a $\Delta_f H^\circ_m(\mathrm{CrCl_3,cr}) = -538.1$ kJ·mol^{-1}.

37DOE determined a $\Delta_{rxn} H^\circ_m = -307.9$ kJ·mol^{-1} of $\mathrm{Cl_2}$ for the oxidation of reaction (1) at 298 K. This produced a $\Delta_f H^\circ_m(\mathrm{CrCl_3,cr}) = -549.4$ kJ·mol^{-1}.

58FLE/ING measured the electrode potential in two cells from 973 to 1173 K. The overall reaction was $\mathrm{CrCl_2(cr)} + \mathrm{AgCl(cr)} = \mathrm{CrCl_3(cr)} + \mathrm{Ag(cr)}$. The $\Delta_{rxn} H^\circ_m = -49.54$ kJ·mol^{-1} at 1073 K corrected to $\Delta_{rxn} H^\circ_m = -46.28$ kJ·mol^{-1} at 298 K and yielded a $\Delta_f H^\circ_m(\mathrm{CrCl_3,cr}) = -568.6$ kJ·mol^{-1}.

42MAI measured the vapor pressure of $\mathrm{Cl_2}$ for the reverse of reaction (1)

$$2\mathrm{CrCl_3(cr)} = 2\mathrm{CrCl_2(cr)} + \mathrm{Cl_2(g)}. \tag{3}$$

The $\Delta_{rxn} H^\circ_m = 294.68$ kJ·mol^{-1} at 298 K yielded a $\Delta_f H^\circ_m(\mathrm{CrCl_3,cr}) = -542.7$ kJ·mol^{-1}.

The selected value was $\Delta_f H^\circ_m(\mathrm{CrCl_3,cr}) = -556.5$ kJ·mol^{-1}. The only way that this selected value can be obtained from the above six (6) values is to use only the results of 1887REC and 37DOE with the former being given double weight. This would imply that the high value of -568.6 $\mathrm{kJ\cdot mol^{-1}}$ and all values less than -544 $\mathrm{kJ\cdot mol^{-1}}$ were rejected. However, there is no evidence on the worksheets to support this hypothesis or to indicate how this value was obtained.

The $\Delta_f H^\circ_0 = -556.30\ \mathrm{kJ\cdot mol^{-1}}$ was calculated as $\Delta_f H^\circ_0 = \Delta_f H^\circ_m(298.15\ \mathrm{K}) - \Delta(H^\circ_{298\ \mathrm{K}} - H^\circ_{0\ \mathrm{K}})$ for the formation reaction,

$$\mathrm{Cr(cr)} + 1.5\ \mathrm{Cl_2(g)} = \mathrm{CrCl_3(cr)}. \tag{4}$$

Therefore, $\Delta_f H^\circ_0 = \Delta_f H^\circ_m(298.15\ \mathrm{K}) - \Delta(H^\circ_{298\ \mathrm{K}} - H^\circ_{0\ \mathrm{K}}) = \{-556.5 - [17.66 - 4.058 - 1.5\times 9.176]\}$ $\mathrm{kJ\cdot mol^{-1}} = -556.30\ \mathrm{kJ\cdot mol^{-1}}$.

The $\Delta_f G^\circ_{298\ \mathrm{K}} = -486.2\ \mathrm{kJ\cdot mol^{-1}}$ was calculated from the relation of $\Delta G^\circ_m = \Delta_f H^\circ_m - T\Delta_f S^\circ_m$. The $\Delta_f S^\circ_m$ was calculated from the formation reaction, reaction (4), as $\Delta_f S^\circ_m = \Delta(S^\circ)$. Therefore,

$$\Delta_f S^\circ_m = [123.0 - 23.7 - 1.5\times 222.96]\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$$

$$= -235.19\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}.$$

Then

$$\Delta_f G^\circ_{298\ \mathrm{K}}$$

$$= [-556.5 - 298.15\times(-0.235\,19)]\ \mathrm{kJ\cdot mol^{-1}}$$

$$= -486.2\ \mathrm{kJ\cdot mol^{-1}}.$$

B. Comments on NBS Selected Values

The actual method used to select the $\Delta_f H^\circ_m(\mathrm{CrCl_3,cr})$ was not clearly identified. See the comments under Section A.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H^\circ_m(\mathrm{CrCl_2,cr})$

$\Delta_f H^\circ_m(\mathrm{HCl,g})$

$\Delta_f H^\circ_m(\mathrm{AgCl,cr})$

$[H^\circ_{298\ \mathrm{K}} - H^\circ_{0\ \mathrm{K}}](\mathrm{Cr,cr})$

$[H^\circ_{298\ \mathrm{K}} - H^\circ_{0\ \mathrm{K}}](\mathrm{Cl_2,g})$

$[H^\circ_{298\ \mathrm{K}} - H^\circ_{0\ \mathrm{K}}](\mathrm{CrCl_3,g})$

$S^\circ_m(\mathrm{Cr,cr})$

$S^\circ_m(\mathrm{Cl_2,g})$

$S^\circ_m(\mathrm{CrCl_3,cr})$

D. Other Thermodynamic Measurements Considered

37AND measured the heat capacity measurements from 54 to 297 K, however, the 58HAN/GRI data were more recent and were made from 15 to 300 K.

42VON measured the enthalpy of solution of $\mathrm{CrCl_3}$ in aqueous HCl and the enthalpy of formation of aqueous $\mathrm{CrCl_3}$ by reacting Cr with HCl. These reactions were combined to obtain the enthalpy of formation of crystalline $\mathrm{CrCl_3}$. A $\Delta_f H^\circ_m = -564.8\ \mathrm{kJ\cdot mol^{-1}}$ was calculated.

E. Additional Determinations of the Thermodynamic Properties

68KOS made heat capacity measurements of anhydrous $\mathrm{CrCl_3}$ from 2 to 4 K. The experimental data fit the equation $C = 0.051\times T + 7.1\times 10^{-4}\times T^3$, where C was expressed in $\mathrm{cal\cdot mol^{-1}\cdot K^{-1}}$.

73KOS/LUK made heat capacity measurements of anhydrous $\mathrm{CrCl_3}$ from 4.5 to 20 K in magnetic fields of 0, 870, 5800, and 8100 H. At $T < 12$ K, the heat capacity was independent of the magnetic field. At $T \leqslant 10$ K, the experimental data fit the equation $C = 0.0535\times T + 5.11\times 10^{-4}\times T^3$, where C was expressed in $\mathrm{cal\cdot mol^{-1}\cdot K^{-1}}$.

75GEE/SHE used a mixture of crystalline $\mathrm{CrCl_2}$ and $\mathrm{CrCl_3}$ as a chlorine electrode to obtain the Gibbs energy of formation $\mathrm{CrCl_3}$ by the emf method. $\mathrm{emf} = -217.6 + 0.617\times T$ was obtained from 570 to 680 K for the cell: $\mathrm{Pt|Ni, NiCl_2|PbCl_2|CrCl_2, CrCl_3|Pt}$. They calculated for the cell reaction:

$$\mathrm{Ni(cr)} + 2\mathrm{CrCl_3(cr)} = \mathrm{NiCl_2(cr)} + 2\mathrm{CrCl_2(cr)}$$

$$\Delta_{rxn} G^\circ_m = (42.000 - 0.119\times T)\ \mathrm{kJ\cdot mol^{-1}}.$$

The same authors, 76GEE/SHE, made other emf measurements to determine $\Delta_{rxn} G^\circ_m$ for the formation of $\mathrm{NiCl_2(cr)}$ and $\mathrm{CrCl_2}$ according to the reactions:

$$\mathrm{Ni(cr)} + \mathrm{Cl_2(g)} = \mathrm{NiCl_2(cr)}$$

$$\Delta_{rxn} G^\circ_m = (-310.110 + 0.156\,85\times T)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\mathrm{Cr(cr)} + \mathrm{Cl_2(g)} = \mathrm{CrCl_2(cr)}$$

$$\Delta_{rxn} G^\circ_m = (-380.210 + 0.104\,58\times T)\ \mathrm{kJ\cdot mol^{-1}}.$$

Addition and subtraction of the three reactions produced:

$$\mathrm{Cr(cr)} + 1\tfrac{1}{2}\mathrm{Cl_2(g)} = \mathrm{CrCl_3(cr)}$$

$$\Delta_{rxn} G^\circ_m = (-556.260 + 0.242\,38\times T)\ \mathrm{kJ\cdot mol^{-1}}.$$

A third law $\Delta_f H^\circ_m = -553.0 \pm 5.0\ \mathrm{kJ\cdot mol^{-1}}$ for $\mathrm{CrCl_3(cr)}$ was calculated using tabulated standard entropies and heat capacities. However, the emf measurements were done at elevated temperatures and they may not be valid at 298.15 K.

90TIM/YUL chlorinated a heated Cr sample inside a bomb calorimeter. A $\Delta_f H^\circ_m = -544.4 \pm 10.5\ \mathrm{kJ\cdot mol^{-1}}$ was determined for chromium (III) chloride according to the following reaction: $\mathrm{Cr(cr,cubic)} + 1.5\ \mathrm{Cl_2(g)} = \mathrm{CrCl_3(cr,hexagonal)}$.

F. Bibliography

1887REC Recoura, A., Ann. Chim. Phys. **10**, 68 (1887).

29JEL/KOO Jellinek, R., Koop, R., Z. Phys. Chem. **A145**, 305 (1929).
37AND Anderson, C. T., J. Am. Chem. Soc. **59**, 488 (1937).
37DOE Doerner, H. A., U.S. Bur. Mines **TP577**, 51pp (1937).
39SAN Sano, K., J. Chem. Soc. Jpn. **59**, 17 (1939).
42MAI Maier, C. G., U.S. Bur. Mines, Bull. **436**, 109pp (1942).
42VON von Wartenberg, H., Z. Anorg. Allgem. Chem. **249**, 100 (1942).
58FLE/ING Flengras, S. N., Ingraham, T. R., Can. J. Chem. **36**, 1003 (1958).
58HAN/GRI Hansen, W. N., Griffel, M., J. Chem. Phys. **28**, 902 (1958).
68KOS Kostryukova, M. O., Zh. Eksp. Teor. Fiz., Pis'ma Red. **8**, 231 (1968).
73KOS/LUK Kostryukova, M. O., Luk'yanova, L. V., Pis'ma Zh. Eksp. Teor. Fiz. **17**, 78 (1973).
75GEE/SHE Gee, R., Shelton, R. A. J., J. Less-Common Met. **41**, 347 (1975).
76GEE/SHE Gee, R., Shelton, R. A. J., Trans. Inst. Min. Metall. **85**, 208 (1976).
90TIM/YUL Timofeyev, B. I., Yuldasheva, V. M., I. Chem. Thermodyn. **22**, 417 (1990).

26. $[Cr(H_2O)_6]Cl_3$(aq,violet)

A. Selected Values, NBS Tables

The NBS tables have selected a value for one (1) thermodynamic property of aqueous chromium hexahydrate (III) chloride. The thermodynamic function and its selected value is:

$$\Delta_f H^\circ_m(298.15\ \text{K}):$$

$$-2501.2\ \text{kJ}\cdot\text{mol}^{-1}\ (-597.8\ \text{kcal}\cdot\text{mol}^{-1}).$$

$\Delta_f H^\circ_m$ came from the average of two (2) sets of 15 °C measurements as described in 1886REC. A $\Delta_{rxn}H^\circ_m = -86.6\ \text{kJ}\cdot\text{mol}^{-1}$ $(-20.7\ \text{kcal}\cdot\text{mol}^{-1})$ which adjusted to $-85.4\ \text{kJ}\cdot\text{mol}^{-1}$ $(-20.4\ \text{kcal}\cdot\text{mol}^{-1})$ at 298 K was used for reaction (1)

$$\begin{aligned}&\text{Cr(OH)}_3(\text{cr})+3\text{HCl(aq)}+3\text{H}_2\text{O(l)}\\&\quad=[\text{Cr(H}_2\text{O)}_6]\text{Cl}_3(\text{aq, violet}).\end{aligned}\tag{1}$$

$$\begin{aligned}&\Delta_f H^\circ_m([\text{Cr(H}_2\text{O)}_6]\text{Cl}_3,\text{aq})\\&\quad=\Delta_{rxn}H^\circ_m+3\Delta_f H^\circ_m(\text{H}_2\text{O,l})\\&\qquad+3\Delta_f H^\circ_m(\text{HCl,aq})+\Delta_f H^\circ_m(\text{Cr(OH)}_3,\text{cr})\\&\quad=[-85.4+3(-285.830)\\&\qquad+3(-165.94)_{100}+(-1064.0)]\ \text{kJ}\cdot\text{mol}^{-1}\\&\quad=-2504.7\ \text{kJ}\cdot\text{mol}^{-1}\ (-598.6\text{kcal}\cdot\text{mol}^{-1}),\end{aligned}$$

where HCl in 100 mole of water was used for $\Delta_f H^\circ_m$(HCl,aq). A $\Delta_{rxn}H^\circ_m = -92.9\ \text{kJ}\cdot\text{mol}^{-1}$ $(-22.2\ \text{kcal}\cdot\text{mol}^{-1})$ for reaction (2) was used to calculate the second value:

$$\begin{aligned}&[\text{Cr(H}_2\text{O)}_6]\text{Cl}_3(\text{aq})+3\text{NaOH(aq)}\\&\quad=\text{Cr(OH)}_3(\text{cr})+3\text{NaCl(aq)}+6\text{H}_2\text{O(l)}.\end{aligned}\tag{2}$$

$$\begin{aligned}&\Delta_f H^\circ_m(\text{Cr(H}_2\text{O)}_6]\text{Cl}_3,\text{aq})\\&\quad=(-\Delta_{rxn}H^\circ_m)+\Delta_f H^\circ_m(\text{CrOH}_3,\text{cr})\\&\quad+3\Delta_f H^\circ_m(\text{NaCl,aq})+6\Delta_f H^\circ_m(\text{H}_2\text{O,1})\\&\qquad-3H\Delta_f H^\circ_m(\text{NaOH,aq})\\&\quad=[+92.9+(-1064.0)+3(-406.98)\\&\qquad+6(-285.830)-3(-469.78)]\ \text{kJ}\cdot\text{mol}^{-1}\\&\quad=-2497.7\ \text{kJ}\cdot\text{mol}^{-1}\ (-597.0\ \text{kcal}\cdot\text{mol}^{-1}).\end{aligned}$$

Therefore the average value of $-2504.7\ \text{kJ}\cdot\text{mol}^{-1}$ $(-598.6\ \text{kcal}\cdot\text{mol}^{-1})$ and $-2497.7\ \text{kJ}\cdot\text{mol}^{-1}$ $(-597.0\ \text{kcal}\cdot\text{mol}^{-1})=-2501.2\ \text{kJ}\cdot\text{mol}^{-1}$ $(-597.8\ \text{kcal}\cdot\text{mol}^{-1})$.

B. Comments on NBS Selected Values

In the calculations using reaction (1), the $\Delta_{rxn}H^\circ_m = -86.6\,\text{kJ}\cdot\text{mol}^{-1}$ $(-20.7\ \text{kcal}\cdot\text{mol}^{-1})$ at 15 °C and was adjusted to $-85.4\,\text{kJ}\cdot\text{mol}^{-1}$ $(-20.4\ \text{kcal}\cdot\text{mol}^{-1})$ at 25 °C. In the calculations with reaction (2), the literature value for $\Delta_{rxn}H^\circ_m$ was used with no adjustment for the temperature change. In both sets of measurements, the reactions were referenced to 15 °C and only the value for reaction (1) was adjusted to the corresponding value at 25 °C.

In the calculations for reaction (2), a value of $-469.78\ \text{kJ}\cdot\text{mol}^{-1}$ $(-112.28\ \text{kcal}\cdot\text{mol}^{-1})$ was used for $\Delta_f H^\circ_m$(NaOH,aq) while the NBS table value is $-470.11\ \text{kJ}\cdot\text{mol}^{-1}$ $(-112.36\ \text{kcal}\cdot\text{mol}^{-1})$.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H^\circ_m(\text{HCl}\cdot 100\ \text{H}_2\text{O})$

$\Delta_f H^\circ_m(\text{H}_2\text{O,l})$,

$\Delta_f H^\circ_m(\text{Cr(OH)}_3,\text{cr})$

$\Delta_f H^\circ_m(\text{NaCl,aq})$

$\Delta_f H^\circ_m(\text{NaOH,aq})$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

1886REC Recoura, A., Compt. Rend. **102**, 515 (1886).

27. $Cr(OH)_3(cr)$

A. Selected Values, NBS Tables

The NBS tables have a selected value for only one (1) thermodynamic property of the crystalline chromium (III) hydroxide. The thermodynamic function and its selected value is

$$\Delta_f H^\circ_m(298.15\ \mathrm{K}):$$

$$-1064.0\ \mathrm{kJ\cdot mol^{-1}}\ (-254.3\ \mathrm{kcal\cdot mol^{-1}}).$$

The enthalpy of formation value was calculated from an experimentally determined enthalpy of reaction for the precipitation of $Cr(OH)_3$. 1886REC had a $\Delta_{rxn}H^\circ_m = -131.8\ \mathrm{kJ\cdot mol^{-1}}$ ($-31.5\ \mathrm{kcal\cdot mol^{-1}}$) for the following reaction:

$$[\mathrm{CrCl_2{:}4H_2O}]\mathrm{Cl(aq)} + 3\mathrm{NaOH(aq)} = \mathrm{Cr(OH)_3(cr)} + 3\mathrm{NaCl(aq)} + 4\mathrm{H_2O(l)}. \tag{1}$$

$$\begin{aligned}
\Delta_f H^\circ_m(\mathrm{Cr(OH)_3,cr}) &= \Delta_{rxn}H^\circ_m - 3\times\Delta_f H^\circ_m(\mathrm{NaCl,aq}) \\
&\quad -4\times\Delta_f H^\circ_m(\mathrm{H_2O,l}) \\
&\quad +3\times\Delta_f H^\circ_m(\mathrm{NaOH,aq}) \\
&\quad +\Delta_f H^\circ_m([\mathrm{CrCl_2\cdot 4H_2O}]\mathrm{Cl,aq}) \\
&= [-131.8-3\times(-407.0)-4\times(-285.830) \\
&\quad +3\times(-469.7)+(-1887.4)]\ \mathrm{kJ\cdot mol^{-1}} \\
&= -1064.0\ \mathrm{kJ\cdot mol^{-1}}(-254.3\ \mathrm{kcal\cdot mol^{-1}}).
\end{aligned}$$

B. Comments on NBS Selected Values

Equation (1) contained $\Delta_f H^\circ_m = -1887.4\ \mathrm{kJ\cdot mol^{-1}}$ for $[\mathrm{CrCl_2\cdot 4H_2O}]\mathrm{Cl(aq)}$. This value was obtained from 1882THO's enthalpy change for the reaction $2\mathrm{CrO_3(aq)} + 12\mathrm{HCl(aq)} + 3\mathrm{SnCl_2(aq)} + 2\mathrm{H_2O(l)} = 3\mathrm{SnCl_4(aq)} + 2[\mathrm{CrCl_2\cdot 4H_2O}]\mathrm{Cl(aq)}$; $\Delta_{rxn}H^\circ_m = -219.6\ \mathrm{kJ\cdot mol^{-1}}$. $\Delta_f H^\circ_m$ values for $CrO_3(aq)$, HCl(aq), $SnCl_2(aq)$, $H_2O(l)$, $SnCl_4(aq)$ were −602.1, −166.56, −331.8, −285.830, and −638.1 $\mathrm{kJ\cdot mol^{-1}}$, respectively. Measurements from 32NEU/KRO and V42NON that resulted in values of $\Delta_f H^\circ_m$ of −1835.1 and −1825.9 $\mathrm{kJ\cdot mol^{-1}}$, respectively, for $[\mathrm{CrCl_2\cdot 4H_2O}]\mathrm{Cl(aq)}$, from determinations of $\Delta_{rxn}H_m$ for

$$\mathrm{Cr} + 3\mathrm{HCl(g)} + 4\mathrm{H_2O} = [\mathrm{CrCl_2\cdot 4H_2O}]\mathrm{Cl(aq)}$$

and

$$\mathrm{Cr} + \mathrm{HCl(20\%\ aq)} + 4\mathrm{H_2O(l)} = [\mathrm{CrCl_2\cdot 4H_2O}]\mathrm{Cl(aq)}$$

of −211.7 and −202.5 $\mathrm{kJ\cdot mol^{-1}}$. Clearly, the enthalpy of formation of $[\mathrm{CrCl_2\cdot 4H_2O}]\mathrm{Cl(aq)}$ was not well determined, ±60 $\mathrm{kJ\cdot mol^{-1}}$, and so the tabulated enthalpy of formation of $Cr(OH)_3(cr)$, calculated this way, could be considered uncertain by about this amount.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f H^\circ_m(\mathrm{NaCl,aq})$$

$$\Delta_f H^\circ_m(\mathrm{H_2O,l})$$

$$\Delta_f H^\circ_m([\mathrm{CrCl_2\cdot 4H_2O}]\mathrm{Cl,aq})$$

$$\Delta_f H^\circ_m(\mathrm{NaOH,aq})$$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

None.

F. Bibliography

1882THO Thomsen, J., *Thermochemische Untersuchungen von Julius Thomsen* (J. Barth Verlag, Leipzig, 1882–1886).
1886REC Recoura, A., Compt. Rend. **102**, 515 (1886).
32NEU/KRÖ Neumann, E., Kröger, C., Kunz, H., Z. Anorg. Allgem. Chem. **207**, 133 (1932).
42VON von Wartenberg, H., Z. Anorg. Allgem. Chem. **249**, 100 (1942).

28. $PbCrO_4(cr)$

A. Selected Values, NBS Tables

The NBS tables have a selected value for only one (1) thermodynamic property of the crystalline lead chromate. The thermodynamic function and its selected value is

$$\Delta_f H^\circ_m(298.15\ \mathrm{K}):$$

$$-930.9\ \mathrm{kJ\cdot mol^{-1}}\ (-222.5\ \mathrm{kcal\cdot mol^{-1}}).$$

Enthalpy of formation values were calculated from two experimentally determined heats of reaction for the precipitation of $PbCrO_4$ by 10GOL/STO. Either lead chloride or lead nitrate was reacted with potassium chromate to produce the corresponding potassium salt and lead chromate. 28ROT/SCH had a $\Delta_{rxn}H^\circ_m = -46.69\ \mathrm{kJ\cdot mol^{-1}}$ for the following reaction:

$$\mathrm{PbCl_2(aq)} + \mathrm{K_2CrO_4(aq)} = 2\mathrm{KCl(aq)} + \mathrm{PbCrO_4(cr)}, \tag{1}$$

$$\begin{aligned}\Delta_f H^\circ_m(\mathrm{PbCrO_4,cr}) &= \Delta_{rxn}H^\circ_m - 2\times\Delta_f H^\circ_m(\mathrm{KCl,aq}) + \Delta_f H^\circ_m(\mathrm{PbCl_2,aq}) \\ &\quad + \Delta_f H^\circ_m(\mathrm{K_2CrO_4,aq}) = [-46.69 - 2\times(-167.15) \\ &\quad + (-336.0) + (-881.15)]\ \mathrm{kJ\cdot mol^{-1}} \\ &= -929.54\ \mathrm{kJ\cdot mol^{-1}}\ (-222.17\ \mathrm{kcal\cdot mol^{-1}}).\end{aligned}$$

10GOL/STO had a $\Delta_{rxn}H^\circ_m = -44.4\ \mathrm{kJ\cdot mol^{-1}}$ for the following reaction:

$$\mathrm{Pb(NO_3)_2(aq) + K_2CrO_4(aq) = 2KNO_3(aq) + PbCrO_4(cr)}, \tag{2}$$

$$\begin{aligned}\Delta_f H^\circ_m(\mathrm{PbCrO_4,cr}) &= \Delta_{rxn}H^\circ_m - 2\times\Delta_f H^\circ_m(\mathrm{KNO_3,aq}) \\ &\quad + \Delta_f H^\circ_m(\mathrm{Pb(NO_3)_2,aq}) + \Delta_f H^\circ_m(\mathrm{K_2CrO_4,aq}) \\ &= [-44.4 - 2\times(-207.4) + (-421.3) \\ &\quad + (-881.15)]\ \mathrm{kJ\cdot mol^{-1}} \\ &= -932.05\ \mathrm{kJ\cdot mol^{-1}}\ (-222.77\ \mathrm{kcal\cdot mol^{-1}}).\end{aligned}$$

The average of these two values, $\Delta_f H^\circ_m(\mathrm{PbCrO_4,cr}) = -930.9\ \mathrm{kJ\cdot mol^{-1}}$ $(-222.5\ \mathrm{kcal\cdot mol^{-1}})$, was chosen as the NBS selected value.

B. Comments on NBS Selected Values

Calculation of the NBS selected value, using the original experimental values in $\mathrm{kJ\cdot mol^{-1}}$, produced $-930.80\ \mathrm{kJ\cdot mol^{-1}}$, not $-930.9\ \mathrm{kJ\cdot mol^{-1}}$. Conversion of $-930.80\ \mathrm{kJ\cdot mol^{-1}}$ into $-222.47\ \mathrm{kcal\cdot mol^{-1}}$ rounds to $-222.5\ \mathrm{kcal\cdot mol^{-1}}$ which originally was the NBS selected value in 1966. The 1966 value was in $\mathrm{kcal\cdot mol^{-1}}$ at the standard conditions of 298.15 K and 1 atm of pressure. The 82WAG/EVA value was in $\mathrm{kJ\cdot mol^{-1}}$ at the standard conditions of 298.15 K and 1 bar of pressure. The change from 1 atm to 1 bar of pressure did not affect the numerical value of the $\Delta_f H^\circ_m(\mathrm{PbCrO_4,cr})$. The use of the (4.184J/1 cal) conversion factor, converts $-222.5\ \mathrm{kcal\cdot mol^{-1}}$ to $-930.9\ \mathrm{kJ\cdot mol^{-1}}$ which is the value represented in the 82WAG/EVA compilation. The rounding of the selected $\mathrm{kcal\cdot mol^{-1}}$ value was done and then converted to the selected $\mathrm{kJ\cdot mol^{-1}}$ value. Throughout this manuscript, discrepancies may exist between the values in 82WAG/EVA and those values calculated herein by using the original experimental values in $\mathrm{kJ\cdot mol^{-1}}$.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H^\circ_m(\mathrm{PbCl_2,aq})$

$\Delta_f H^\circ_m(\mathrm{Pb(NO_3)_2,aq})$

$\Delta_f H^\circ_m(\mathrm{K_2CrO_4,aq})$

$\Delta_f H^\circ_m(\mathrm{KCl,aq})$

$\Delta_f H^\circ_m(\mathrm{KNO_3,aq})$

D. Other Thermodynamic Measurements Considered

None.

E. Additional Determinations of the Thermodynamic Properties

76DEL/MCC measured enthalpies of reaction for eight (8) reactions, three (3) of which could be directly linked to the formation of $\mathrm{PbCrO_4}$ from its elements. The results of these measurements allowed the calculation of $\Delta_f H^\circ_m = -1052.66\ \mathrm{kJ\cdot mol^{-1}}$ for $\mathrm{PbCrO_4}$ which differs greatly from the NBS selected value of $-930.9\ \mathrm{kJ\cdot mol^{-1}}$.

F. Bibliography

10GOL/STO	Goldblum, H., Stoffella, G., J. Chim. Phys. **8**, 135 (1910).
28ROT/SCH	Roth, W. A., Schwartz, O., Büchner, A., Ber. **61**, 1539 (1928).
76DEL/MCC	Dellien, I., McCurdy, K. G., Hepler, L. G., J. Chem. Thermodyn. **8**, 203 (1976).
82WAG/EVA	Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., Nuttall, R. L., J. Phys. Chem. Ref. Data **11**, (2) (1982).