

# 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

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# 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

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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.

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## 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

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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,  $\text{PbCrO}_4$ .) 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

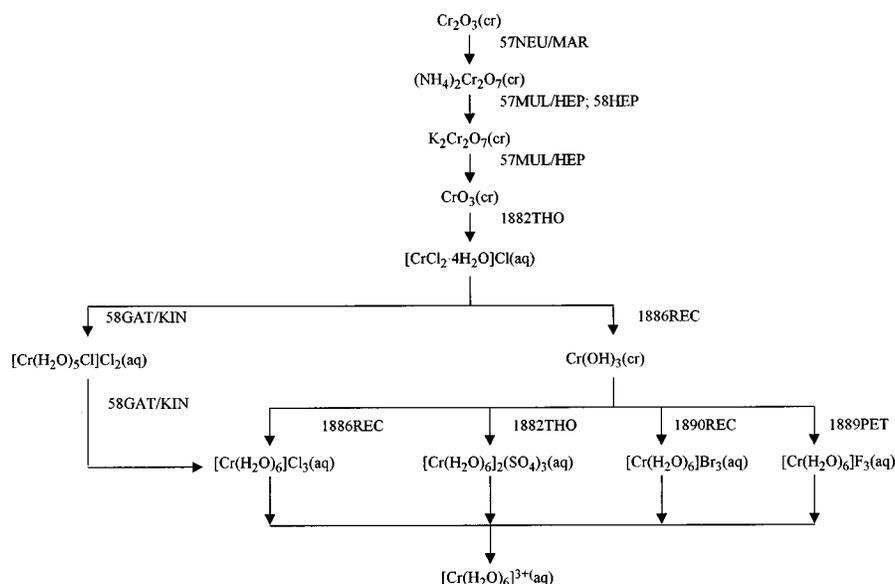
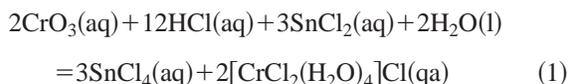


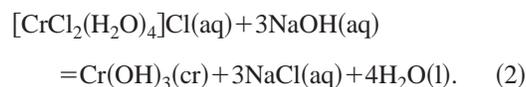
FIG. 1. Sequential pathway used to determine the enthalpy of formation of  $\text{Cr}(\text{H}_2\text{O})_6^{3+}(\text{aq})$ .

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  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ . The first reaction is the combustion of chromium to obtain  $\text{Cr}_2\text{O}_3(\text{cr})$ . 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,  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(\text{cr})$ , for which the assumed reaction products were  $\text{Cr}_2\text{O}_3(\text{cr})$ ,  $\text{H}_2\text{O}(\text{l})$ , and  $\text{N}_2(\text{g})$ . The next step involved measurement of the dissolution enthalpy of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(\text{cr})$  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  $\text{K}_2\text{Cr}_2\text{O}_7(\text{cr})$  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  $\text{K}_2\text{CrO}_4(\text{aq})$ . This value was then combined with the enthalpy of solution of  $\text{CrO}_3(\text{cr})$  into aqueous base, which was assumed to produce aqueous chromate, in order to obtain the enthalpy of formation of  $\text{CrO}_3(\text{cr})$ . The enthalpy of solution of  $\text{CrO}_3(\text{cr})$  into water was then used to determine the enthalpy of formation of  $\text{CrO}_3(\text{aq})$ . The enthalpy of formation of  $\text{CrO}_3(\text{aq})$  was then combined with the enthalpies of formation of  $\text{SnCl}_2(\text{aq})$ ,  $\text{SnCl}_4(\text{aq})$ ,  $\text{H}_2\text{O}(\text{l})$ , and  $\text{HCl}(\text{aq})$ ; and the enthalpy of the reaction:



determined by 1882THO to calculate the enthalpy of formation for  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}(\text{aq})$ . From this point, there are different possible pathways for calculation of  $\Delta_f H_m^\circ$  for  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ . As discussed later in this article, the pathway chosen for the NBS tabulated value proceeded through

the calculation of the enthalpy of formation of  $\text{Cr}(\text{OH})_3(\text{cr})$ . This value was calculated from 1886REC's measurement of the enthalpy change for the reaction:



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



were then examined in order to arrive at  $\Delta_f H_m^\circ$  for  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ . All of these measurements were obtained prior to 1900. The alternate pathway, which does not involve the enthalpy of formation of  $\text{Cr}(\text{OH})_3(\text{cr})$  [reaction (2)], was examined but not used in the calculation of the enthalpy of formation of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ . This pathway, which utilized measurements in 58GAT/KIN, yields a  $\Delta_f H_m^\circ$  for  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$  that was different from the other pathway by approximately  $7 \text{ kJ} \cdot \text{mol}^{-1}$ .

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  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$  almost none are confidently known to  $1 \text{ kJ} \cdot \text{mol}^{-1}$  or better. Specific details on each of the reactions can be found below. We note the following as examples: (1) Enthalpies of formation for  $\text{Cr}_2\text{O}_3(\text{cr})$  are spread over the range of  $(1120-1140) \text{ kJ} \cdot \text{mol}^{-1}$ , the minimum uncertainty in this value, assuming that 54MAH was in fact the most accurate value, would be that claimed by 54MAH,  $\pm 1.7 \text{ kJ} \cdot \text{mol}^{-1}$ . (2) The autocombustion of ammonium dichromate is uncertain by an unknown amount. This is because it was assumed that the reaction products included pure  $\text{Cr}_2\text{O}_3(\text{cr})$  and  $\text{H}_2\text{O}(\text{l})$ . However, the mono-, di-, and trihydrates of  $\text{Cr}_2\text{O}_3(\text{cr})$  are known to exist. The Gibbs energy of the reaction:



can be calculated from the enthalpies of formation of  $\text{Cr}_2\text{O}_3(\text{cr})$ ,  $\text{H}_2\text{O}(\text{l})$ , and  $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{cr})$  and an estimate of the entropy change for forming the monohydrate ( $-23 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ). From these values,  $\Delta_{\text{rxn}} G_m^\circ = -74 \text{ kJ} \cdot \text{mol}^{-1}$ . 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  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ ? 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  $20 \text{ kJ} \cdot \text{mol}^{-1}$ ;  $u > 20 \text{ kJ} \cdot \text{mol}^{-1}$ . This type of treatment overestimates the uncertainty. Consider the 58GAT/KIN reaction:



The uncertainty in the enthalpy of formation of  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}(\text{aq})$  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  $10 \text{ kJ} \cdot \text{mol}^{-1}$ . The uncertainty in  $\Delta_f H_m^\circ$  for  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2(\text{aq})$  would be the propagation of  $u_0$  and the uncertainty in the enthalpy for reaction (5), given by 58GAT/KIN as  $1 \text{ kJ} \cdot \text{mol}^{-1}$ . Therefore the tabulated enthalpies of formation would have tabulated uncertainties of  $u_0$  and  $(u_0^2 + 1 \text{ kJ}^2 \cdot \text{mol}^{-2})^{1/2}$ . 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  $(2u_0^2 + 1 \text{ kJ} \cdot \text{mol}^{-1})^{1/2}$ , or approximately  $1.4u_0$ . Thus, the calculated uncertainty in reaction (5) would be greater than  $14 \text{ kJ} \cdot \text{mol}^{-1}$ , which is not the correct value; its correct value is only  $1 \text{ kJ} \cdot \text{mol}^{-1}$ . 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:



57MUL/HEP reported that the enthalpy of reaction (6) was  $(-117.1 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$ . Subsequent to that measurement, Hepler and coauthors (76DEL/HEP) reported that measurement of the enthalpy of reaction (6) gave  $(-120.9 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$ . These two measurements from the same laboratory, but performed with different calorimeters, differ by  $3.8 \text{ kJ} \cdot \text{mol}^{-1}$ . 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  $3.8 \text{ kJ} \cdot \text{mol}^{-1}$  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  $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ ,  $\text{CrO}_4^{2-}(\text{aq})$ ,  $\text{HCrO}_4^-(\text{aq})$ ,  $\text{K}_2\text{Cr}_2\text{O}_7(\text{cr})$ , 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.

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## 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:

$$H_m^\circ(298.15 \text{ K})$$

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

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

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

The actual data used was from 37AND, which reported measurements of  $C_{p,m}^\circ$  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  $S_m^\circ$  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.

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- 79WIL/GOP Williams, I. S., Gopal, E. S. R., Street, R., *J. Phys. F* **9**, 431 (1979).

## 3. Cr<sup>2+</sup>(aq)

### A. Selected Values, NBS Tables

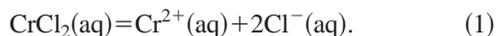
The NBS tables have selected values for only one (1) thermodynamic property of the aqueous chromium (II) ion. The thermodynamic function and its selected value is:

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

The NBS selected value was calculated as

$$\begin{aligned}\Delta_f H_m^\circ(\text{Cr}^{2+}, \text{aq}) &= \Delta_f H_m^\circ(\text{CrCl}_2, \text{aq}) - 2 \times \Delta_f H_m^\circ(\text{Cl}^-, \text{aq}) \\ &= [(-477.8 \text{ kJ}\cdot\text{mol}^{-1}) - 2 \times (-167.159 \text{ kJ}\cdot\text{mol}^{-1})] \\ &= -143.5 \text{ kJ}\cdot\text{mol}^{-1} (-34.3 \text{ kcal}\cdot\text{mol}^{-1}),\end{aligned}$$

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



### B. Comments on NBS Selected Values

The NBS selected value was derived with the  $\Delta_f H_m^\circ(\text{CrCl}_2, \text{aq})$  which appears to have a transcription error of  $+4.6 \text{ kJ}\cdot\text{mol}^{-1}$  ( $+1.1 \text{ kcal}\cdot\text{mol}^{-1}$ ). The  $\Delta_f H_m^\circ(\text{CrCl}_2, \text{aq})$  value should have been  $-473.2 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-113.1 \text{ kcal}\cdot\text{mol}^{-1}$ ) and not the  $-477.8 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-114.2 \text{ kcal}\cdot\text{mol}^{-1}$ ) used in the 1966 calculations. Therefore,  $\Delta_f H_m^\circ(\text{Cr}^{2+}, \text{aq}) = -138.9 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-33.2 \text{ kcal}\cdot\text{mol}^{-1}$ ) should have been the calculated value.

### C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m^\circ(\text{CrCl}_2, \text{aq})$$

$$\Delta_f H_m^\circ(\text{Cl}^-, \text{aq})$$

### D. Other Thermodynamic Measurements Considered

53GRE/BUR measured the  $\Delta_{\text{sol}} H_m^\circ$  of



The  $\Delta_f H_m^\circ(\text{CrCl}_2, \text{aq})$  would be equal to  $-475.0 \text{ kJ}\cdot\text{mol}^{-1}$  that would lead to a  $\Delta_f H_m^\circ(\text{Cr}^{2+}, \text{aq}) = -140.7 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-33.6 \text{ kcal}\cdot\text{mol}^{-1}$ ).

### E. Additional Determinations of the Thermodynamic Properties

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

### F. Bibliography

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 27GRU/BRE Grube, G., Breiting, G., *Z. Electrochem.* **33**, 112 (1927).  
 53GRE/BUR Gregory, N. W., Burton, T. M., *J. Am. Chem. Soc.* **75**, 6053 (1953).

## 4. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq}, \text{violet})$

### 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:

$$\Delta_f H_m^\circ(298.15 \text{ K}): -1999.1 \text{ kJ}\cdot\text{mol}^{-1} (-477.8 \text{ kcal}\cdot\text{mol}^{-1}).$$

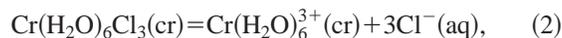
Nine enthalpies of formation,  $\Delta_f H_m^\circ$ , were considered during the selection of the NBS selected value. The enthalpies of formation of five aqueous compounds and the enthalpies of formation of the accompanying anions were used to calculate an enthalpy of formation for the aqueous chromium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

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



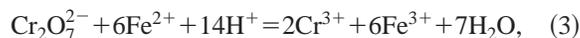
which yielded a  $\Delta_f H_m^\circ(\text{Cr}(\text{H}_2\text{O})_6^{3+}, \text{aq}) = -2006.2 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-479.5 \text{ kcal}\cdot\text{mol}^{-1}$ ).

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



which yielded a  $\Delta_f H_m^\circ(\text{Cr}(\text{H}_2\text{O})_6^{3+}, \text{aq}) = -1996.6 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-477.2 \text{ kcal}\cdot\text{mol}^{-1}$ ).

47EVA presented data for the  $\Delta_{\text{rxn}} H_m^\circ = -746.63 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-178.45 \text{ kcal}\cdot\text{mol}^{-1}$ ) for the following reaction:



which yielded a  $\Delta_f H_m^\circ(\text{Cr}^{3+}, \text{aq})$  which when combined with the  $\Delta_f H_m^\circ$  of 6 moles of  $\text{H}_2\text{O}$  to yield a  $\Delta_f H_m^\circ(\text{Cr}(\text{H}_2\text{O})_6^{3+}, \text{aq}) = -1953.9 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-467.0 \text{ kcal}\cdot\text{mol}^{-1}$ ).

49EVA presented data for the  $\Delta_{\text{rxn}} H_m^\circ = -740.99 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-177.10 \text{ kcal}\cdot\text{mol}^{-1}$ ) for the same reaction in 47EVA that yielded a  $\Delta_f H_m^\circ(\text{Cr}^{3+}, \text{aq}) = -245.6 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-58.7 \text{ kcal}\cdot\text{mol}^{-1}$ ). When six (6)  $\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) = -285.83 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-68.315 \text{ kcal}\cdot\text{mol}^{-1}$ ) are added to this value, they obtained  $\Delta_f H_m^\circ(\text{Cr}(\text{H}_2\text{O})_6^{3+}, \text{aq}) = -1960.6 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-468.6 \text{ kcal}\cdot\text{mol}^{-1}$ ).

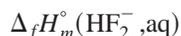
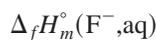
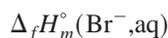
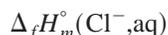
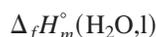
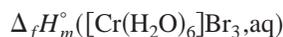
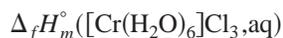
The average of these eight (49EVA was a correction for the 47EVA value) values is  $-1993.2 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-476.4 \text{ kcal}\cdot\text{mol}^{-1}$ ). However, the NBS selected value is  $-1999.1 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-477.8 \text{ kcal}\cdot\text{mol}^{-1}$ ).

### 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  $\text{Cr}^{3+}$  ion and not the hexahydrated  $\text{Cr}^{3+}$  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  $\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l})$  to the  $\Delta_f H_m^\circ(\text{Cr}^{3+}, \text{aq})$  to yield the hexahydrated value,  $\Delta_f H_m^\circ(\text{Cr}(\text{H}_2\text{O})_6^{3+}, \text{aq})$ . 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  $-1999.1 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-477.8 \text{ kcal}\cdot\text{mol}^{-1}$ ). One is to average just the bromide and chloride. Another is to average ( $-476.8$ ,  $-477.95$ ,  $-477.65$ ,  $-477.7$ ,  $-479.5$ , and  $-477.2$ )  $\text{kcal}\cdot\text{mol}^{-1}$ . 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  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}(\text{aq})$  that was calculated from a reaction enthalpy measured by 1882THO [see Section B of  $\text{Cr}(\text{OH})_3(\text{cr})$ ]. Additionally most of the values depended on the enthalpy of formation of  $\text{Cr}(\text{OH})_3(\text{cr})$  that also was calculated from a measurement made by 1882THO.

### C. Auxiliary Values Required for Data Pathway



### D. Other Thermodynamic Measurements Considered

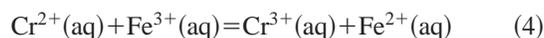
None.

### E. Additional Determinations of the Thermodynamic Properties

The NBS Thermodynamic Tables do not have a selected value for the  $\text{Cr}^{3+}(\text{aq})$  ion. However, many thermodynamic

studies deal with the aqueous  $\text{Cr}^{3+}$  ion and in the interest of thermodynamic consistency, several thermodynamic measurements that represent the unhydrated  $\text{Cr}^{3+}$  ion are presented next.

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



in perchloric acid. The measured enthalpy,  $-150.6 \text{ kJ}\cdot\text{mol}^{-1}$ , was corrected for the enthalpy of dilution,  $+1.30 \text{ kJ}\cdot\text{mol}^{-1}$ , of the ferric perchlorate solution. The authors wanted to calculate the enthalpy of formation for  $\text{Cr}^{3+}(\text{aq})$  but needed the enthalpy of formation for  $\text{Cr}^{2+}(\text{aq})$ . They chose a  $\Delta_f H_m^\circ$  of  $\text{Cr}^{2+}(\text{aq}) = -143.5 \text{ kJ}\cdot\text{mol}^{-1}$  that was calculated using the  $\Delta_f H_m^\circ$  of  $\text{CrCl}_2(\text{cr})$ . These  $\Delta_f H_m^\circ$ s and the  $\Delta_f H_m^\circ$ s of  $\text{Fe}^{2+}(\text{aq})$  and  $\text{Fe}^{3+}(\text{aq})$  from the NBS tables gave a  $\Delta_f H_m^\circ$  of  $\text{Cr}^{3+}(\text{aq}) = -254.8 \text{ kJ}\cdot\text{mol}^{-1}$ . Because the  $\Delta_f H_m^\circ$  value used in their calculations included an arithmetic error, their value for  $\text{Cr}^{3+}$  would also include this error.

Depending upon the pH, the  $\text{Cr}^{3+}/\text{H}_2\text{O}$  equilibrium can produce hydrolyzed  $\text{Cr}^{3+}$  species with the general formula of  $\text{Cr}(\text{OH})_x^{3-x}$ . Although these species are also not present in the NBS Thermodynamic Tables, several thermodynamic measurements that represent the hydrolysis of the  $\text{Cr}^{3+}$  ion are also presented here.

81BAE/MES correlated  $\Delta_r S_m^\circ$  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  $\text{Cr}^{3+}$  ions to obtain  $\Delta_r H_m^\circ = 39.3 \pm 1.7 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_r S_m^\circ = 59.0 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  and  $pK_1 = 3.82$  for the first hydrolysis of  $\text{Cr}^{3+}$  according to the reaction:  $\text{Cr}^{3+} + \text{H}_2\text{O} = \text{CrOH}^{2+} + \text{H}^+$ .

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:  $\text{Cr}^{3+} + \text{H}_2\text{O} = \text{CrOH}^{2+} + \text{H}^+$ .

72KLA/KUB made potentiometric measurements to determine  $pK_1 = 3.3$  for the first hydrolysis of the  $\text{Cr}^{3+}$  ion,  $\text{Cr}^{3+} + \text{H}_2\text{O} = \text{CrOH}^{2+} + \text{H}^+$ . They did not consider the possibility of the formation of chromate hydroxy polymers and complexes in the  $3.75 \text{ mol}\cdot\text{l}^{-1}$   $(\text{NH}_4)_2\text{SO}_4$  medium used in their study and therefore their result may be too low.

73MEY/SIR determined the first three (3) hydrolysis constants of the  $\text{Cr}^{3+}$  ion, however, their calculations were only crude estimates. Their data suggest that all steps in the hy-

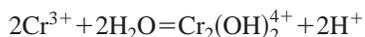
drololysis of  $\text{Cr}^{3+}$  can occur in an extremely small  $p\text{H}$  range of approximately 0.4 and this consideration may not be reliable.

68KON/KON made measurements similar to 73MEY/SIR in an extremely small  $p\text{H}$  range of approximately 0.4. The validity of these results in this small  $p\text{H}$  range is questionable.

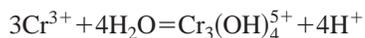
67SAN/KRY made spectrophotometric measurements to determine the degree of polymerization and hydrolysis of  $\text{Cr}^{3+}$  in perchlorate solutions. The value of this work is questionable due to their assumption that only one (1) polymeric hydroxy form of  $\text{Cr}^{3+}$  predominates in solution.

68MOR/LEV made a study very similar to that of 67SAN/KRY in  $1 \text{ mol}\cdot\text{l}^{-1}\text{NaClO}_4$ . 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  $\text{Cr}^{3+}$  in solution. Their data were extrapolated by 76BAE/MES to standard conditions for the reactions:

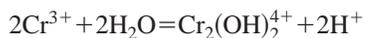


and

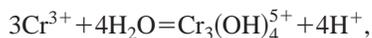


to obtain  $pK$ s equal to 5.06 and 8.13, respectively. The  $\Delta_f H_m^\circ = 51.9$  and  $104.6 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively, were calculated for these two reactions.

87RAI/SAS performed a critical review of the hydrolysis constants of  $\text{Cr}^{3+}$ . Their review contains all of the previously mentioned measurements. They also carefully measured the solubility of  $\text{Cr}(\text{OH})_3$  at a constant concentration of  $0.01 \text{ mol}\cdot\text{l}^{-1}$  of sodium or ammonium perchlorate. Their measurements approached the equilibrium from undersaturation and also from supersaturation and determined hydrolysis constants for the  $\text{Cr}^{3+}$  ion. They proposed a  $\log K_1 = -3.57$  for the first hydrolysis of the  $\text{Cr}^{3+}$  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  $\text{Cr}^{3+}$ . 76BAE/MES had obtained earlier  $pK$ s equal to 5.06 and 8.13 for the reactions:



and



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

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## 5. $\text{CrO}_4^{2-}(\text{aq})$

### 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:

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

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

$$\Delta_f G_m^\circ(298.15 \text{ K}):$$

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

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

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

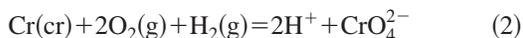
Several sets of potassium chromate data were considered, however, the selected NBS value came from the plot of the 1886SAB data extrapolated to  $m^{1/2}=0$  to obtain the value for  $\Delta_f H_m^\circ(\text{K}_2\text{CrO}_4, \text{aq}) = -1385.91 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-331.24 \text{ kcal}\cdot\text{mol}^{-1}$ ). When twice the  $\Delta_f H_m^\circ(\text{K}^+, \text{aq})$ ,  $-252.38 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-60.32 \text{ kcal}\cdot\text{mol}^{-1}$ ), is subtracted from  $\Delta_f H_m^\circ(\text{K}_2\text{CrO}_4, \text{aq})$ ,  $-1385.91 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-331.24 \text{ kcal}\cdot\text{mol}^{-1}$ ), one obtains the NBS selected value for  $\Delta_f H_m^\circ(\text{CrO}_4^{2-}, \text{aq}) = (-1385.91) - 2 \times (-252.38) = -881.15 \text{ kJ}\cdot\text{mol}^{-1}$  for the chromate ion.

$S_m^\circ$  for chromate ion was calculated from  $\text{Ag}_2\text{CrO}_4(\text{cr})$  data of 54PAN. 54PAN measured the emf for a cell at four temperatures that corresponded to reaction (1).



The emf data at the four temperatures were used to plot  $E^\circ/T$  vs  $1/T$ . A  $\Delta_{rxn} H^\circ = -61.455 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-14.688 \text{ kcal}\cdot\text{mol}^{-1}$ ) was calculated from the slope of the plot.  $\Delta_{rxn} G_m^\circ = -nFE^\circ$  was used to calculate a  $\Delta G_m^\circ = -67.91 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-16.23 \text{ kcal}\cdot\text{mol}^{-1}$ ) for the cell reaction from the measured  $E^\circ$  at  $25^\circ\text{C}$ . A  $\Delta S_m^\circ = 21.8 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  ( $5.2 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) was calculated for the cell reaction using  $\Delta G_m^\circ = \Delta H_m^\circ - T\Delta S_m^\circ$  at  $T = 298.15 \text{ K}$ .  $S_m^\circ(\text{CrO}_4^{2-}, \text{aq})$  was calculated from the  $\Delta S_m^\circ$  of reaction (1) and the NBS values for  $S_m^\circ$  of  $\text{Ag}_2\text{CrO}_4(\text{cr})$  and  $\text{Ag}^+(\text{aq})$ .  $\Delta S_m^\circ = S_m^\circ(\text{Ag}_2\text{CrO}_4) - 2 \times S_m^\circ(\text{Ag}^+) - S_m^\circ(\text{CrO}_4^{2-})$ . Therefore,  $S_m^\circ(\text{CrO}_4^{2-}) = [-21.8 + 217.6 - 2 \times 72.8] \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 50.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .

$\Delta_f G_m^\circ = \Delta_f H_m^\circ - T\Delta_f S_m^\circ$  was used to calculate the Gibbs free energy change at  $298.15 \text{ K}$  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):

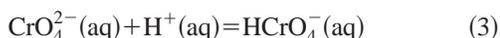


as  $\Delta_f S_m^\circ = 50.2 - 23.77 - 2 \times (204.999) - 130.574 = -514.13 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . Therefore,

$$\begin{aligned} \Delta_f G_m^\circ &= \Delta_f H_m^\circ - T\Delta_f S_m^\circ \\ &= [(-881.15) - (298.15)(-0.51413)] \text{ kJ}\cdot\text{mol}^{-1} \\ &= -727.85 \text{ kJ}\cdot\text{mol}^{-1}. \end{aligned}$$

## B. Comments on NBS Selected Values

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



given by 58HEP that was  $2.93 \pm 1.67 \text{ kJ}\cdot\text{mol}^{-1}$  ( $0.7 \pm 0.4 \text{ kcal}\cdot\text{mol}^{-1}$ ). Combination with  $\Delta_f H_m^\circ = -878.2 \text{ kJ}\cdot\text{mol}^{-1}$

( $-209.9 \text{ kcal}\cdot\text{mol}^{-1}$ ) for  $\text{HCrO}_4^-(\text{aq})$  gave  $-881.2 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-210.6 \text{ kcal}\cdot\text{mol}^{-1}$ ) for  $\text{CrO}_4^{2-}(\text{aq})$ . This pathway also supports the NBS selected value.

Crystalline  $\text{K}_2\text{CrO}_4$  is not listed in any of the above pathways but the enthalpy of formation of the aqueous  $\text{K}_2\text{CrO}_4$  is not independent of the enthalpy of formation of crystalline  $\text{K}_2\text{CrO}_4$ .

## C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m^\circ(\text{K}_2\text{CrO}_4, \text{aq})$$

$$\Delta_f H_m^\circ(\text{K}^+, \text{aq})$$

$$S_m^\circ(\text{Ag}_2\text{CrO}_4, \text{cr})$$

$$S_m^\circ(\text{Ag}^+, \text{aq})$$

$$S_m^\circ(\text{Cr}, \text{cr})$$

$$S_m^\circ(\text{O}_2, \text{g})$$

$$S_m^\circ(\text{H}_2, \text{g})$$

$$S_m^\circ(\text{CrO}_4^{2-}, \text{aq})$$

## D. Other Thermodynamic Measurements Considered

57MUL/HEP determined the enthalpies of solution of crystalline  $\text{K}_2\text{CrO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ , and  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  and the enthalpies of reaction of crystalline  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{CrO}_3$  with aqueous alkali and of  $\text{K}_2\text{CrO}_4$  with aqueous acid. The enthalpies of formation of crystalline  $\text{K}_2\text{CrO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ , and  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  and aqueous  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  were calculated to be  $-1388.7$ ,  $-2035.1$ ,  $-1778.2$ ,  $-868.6$ , and  $-1444.3 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively. Using the literature  $K_{\text{eq}}$  and entropy data they calculated the entropies of the aqueous dichromate and bichromate ions to be  $295.0$  and  $200.0 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , respectively. The  $\Delta_f G_m^\circ$  of the aqueous chromate, dichromate, and bichromate were calculated to be  $-711.7$ ,  $-1269.4$ , and  $-748.9 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively.

In many of the following studies,  $\Delta_f H_m^\circ$  of aqueous  $\text{K}_2\text{CrO}_4$  was measured and the  $\Delta_f H_m^\circ(\text{CrO}_4^{2-}, \text{aq})$  was calculated by subtraction of two  $\Delta_f H_m^\circ(\text{K}^+, \text{aq})$ ,  $-252.38 \text{ kJ}\cdot\text{mol}^{-1}$ .

40PER measured enthalpies of solution of  $\text{K}_2\text{CrO}_4$  from which a  $\Delta_f H_m^\circ$  of aqueous  $\text{K}_2\text{CrO}_4$  was calculated to be  $-1385.0 \text{ kJ}\cdot\text{mol}^{-1}$ . Using the  $\Delta_f H_m^\circ(\text{K}^+, \text{aq})$ , one obtains a value for  $\Delta_f H_m^\circ(\text{CrO}_4^{2-}, \text{aq}) = -880.24 \text{ kJ}\cdot\text{mol}^{-1}$ .

1876MAR measured enthalpies of solution of  $\text{K}_2\text{CrO}_4$  from which a  $\Delta_f H_m^\circ$  of aqueous  $\text{K}_2\text{CrO}_4$  was calculated to be  $-1383.6 \text{ kJ}\cdot\text{mol}^{-1}$ . Using the  $\Delta_f H_m^\circ(\text{K}^+, \text{aq})$ , one obtains a value for  $\Delta_f H_m^\circ(\text{CrO}_4^{2-}, \text{aq}) = -878.8 \text{ kJ}\cdot\text{mol}^{-1}$ .

56YAT/VAS measured enthalpies of solution of  $\text{K}_2\text{CrO}_4$  in aqueous  $\text{H}_2\text{SO}_4$  from which a  $\Delta_f H_m^\circ$  of aqueous  $\text{K}_2\text{CrO}_4$

was calculated to be  $-1385.4 \text{ kJ}\cdot\text{mol}^{-1}$ . Using the  $\Delta_f H_m^\circ(\text{K}^+, \text{aq})$ , one obtains a value for  $\Delta_f H_m^\circ(\text{CrO}_4^{2-}, \text{aq}) = -880.6 \text{ kJ}\cdot\text{mol}^{-1}$ .

57TER measured enthalpies of solution of  $\text{K}_2\text{CrO}_4$  from which a  $\Delta_f H_m^\circ$  of aqueous  $\text{K}_2\text{CrO}_4$  was calculated to be  $-1387.1 \text{ kJ}\cdot\text{mol}^{-1}$ . Using the  $\Delta_f H_m^\circ(\text{K}^+, \text{aq})$ , one obtains a value for  $\Delta_f H_m^\circ(\text{CrO}_4^{2-}, \text{aq}) = -882.3 \text{ kJ}\cdot\text{mol}^{-1}$ .

34KOL/GUS measured enthalpies of solution of  $\text{K}_2\text{CrO}_4$  from which a  $\Delta_f H_m^\circ$  of aqueous  $\text{K}_2\text{CrO}_4$  was calculated to be  $-1384.8 \text{ kJ}\cdot\text{mol}^{-1}$ . Using the  $\Delta_f H_m^\circ(\text{K}^+, \text{aq})$ , one obtains a value for  $\Delta_f H_m^\circ(\text{CrO}_4^{2-}, \text{aq}) = -880.0 \text{ kJ}\cdot\text{mol}^{-1}$ .

1878MOR measured the enthalpy of formation of aqueous  $\text{K}_2\text{CrO}_4$  by the reaction of aqueous  $\text{CrO}_3$  and  $\text{KOH}$ . The  $\Delta_f H_m^\circ$  of aqueous  $\text{K}_2\text{CrO}_4$  was calculated to be  $-1383.6 \text{ kJ}\cdot\text{mol}^{-1}$ . Using the  $\Delta_f H_m^\circ(\text{K}^+, \text{aq})$ , one obtains a value for  $\Delta_f H_m^\circ(\text{CrO}_4^{2-}, \text{aq}) = -878.8 \text{ kJ}\cdot\text{mol}^{-1}$ .

28ROT/SCH measured enthalpies of solution of  $\text{K}_2\text{CrO}_4$  from which a  $\Delta_f H_m^\circ$  of aqueous  $\text{K}_2\text{CrO}_4$  was calculated to be  $-1385.2 \text{ kJ}\cdot\text{mol}^{-1}$ . Using the  $\Delta_f H_m^\circ(\text{K}^+, \text{aq})$ , one obtains a value for  $\Delta_f H_m^\circ(\text{CrO}_4^{2-}, \text{aq}) = -880.4 \text{ kJ}\cdot\text{mol}^{-1}$ .

60JEN/PRA measured emf data on  $\text{Ag}_2\text{CrO}_4$  at  $35^\circ\text{C}$ . They had an emf =  $-0.4468 \text{ V}$ .

37SMI/PIT measured heat capacity, entropy, and free energy of formation for  $\text{Ag}_2\text{CrO}_4$  from which  $S^\circ = 43.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  was calculated for  $\text{CrO}_4^{2-}$ .

### E. Additional Determinations of the Thermodynamic Properties

75OHA/BOE measured the  $\Delta_{\text{sol}} H_m^\circ$  of  $\text{Cs}_2\text{CrO}_4$  and re-computed 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:

	$S^\circ /$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f H_m^\circ /$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f G_m^\circ /$ $\text{kJ}\cdot\text{mol}^{-1}$
$\text{CrO}_4^{2-}(\text{aq})$	$57.7 \pm 2.1$	$-882.53 \pm 1.88$	$-731.4 \pm 2.1$
$\text{HCrO}_4^-(\text{aq})$	$195.0 \pm 7.5$	$-878.6 \pm 2.9$	$-768.6 \pm 2.1$
$\text{Cr}_2\text{O}_7^{2-}(\text{aq})$	$241.4 \pm 8.8$	$-1492.0 \pm 6.3$	$-1308.8 \pm 4.2$

### F. Bibliography

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- 37SMI/PIT Smith, W. V., Pitzer, K. S., Latimer, W. M., J. Am. Chem. Soc. **59**, 2642 (1937).  
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 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).  
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## 6. $\text{HCrO}_4^-(\text{aq})$

### 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:

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

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

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

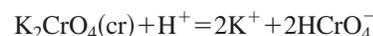
Enthalpies of reaction were calculated for three (3) reactions containing the bichromate ion in 58HEP using experimental enthalpies of reaction determined in 57MUL/HEP and equilibrium constants determined in 53TON/KIN. Three standard molar enthalpies of formation,  $\Delta_f H_m^\circ$ , were calculated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



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



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



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

The enthalpy of formation values of  $-2061.9$ ,  $-1403.3$ , and  $-1806.7 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-492.8$ ,  $-335.4$ , and  $-431.8 \text{ kcal}\cdot\text{mol}^{-1}$ ) for  $\text{K}_2\text{Cr}_2\text{O}_7(\text{cr})$ ,  $\text{K}_2\text{CrO}_4(\text{cr})$ , and  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(\text{cr})$ , 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  $-877.64 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-209.89$ ,  $-210.04$ , and  $-209.76 \text{ kcal}\cdot\text{mol}^{-1}$ ) were averaged to yield the selected value of  $-878.2 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-209.9 \text{ kcal}\cdot\text{mol}^{-1}$ ).

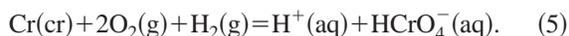
A free energy of dissociation was calculated for the bichromate ion in 58HEP.



$$\Delta_{rxn} G_m^\circ = 37.07 \text{ kJ}\cdot\text{mol}^{-1} \text{ (8.86 kcal}\cdot\text{mol}^{-1}). \quad (4)$$

This value was used with the standard molar free energy of formation of the chromate ion,  $-727.85 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-173.96 \text{ kcal}\cdot\text{mol}^{-1}$ ), to calculate the standard molar free energy of formation of the bichromate ion,  $\text{HCrO}_4^-$ , equal to  $-764.8 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-182.8 \text{ kcal}\cdot\text{mol}^{-1}$ ).

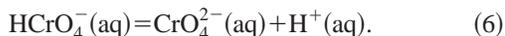
$\Delta_f G_m^\circ = \Delta_f H_m^\circ - T\Delta S_m^\circ$  was used to calculate  $\Delta S_m^\circ = -380.28 \text{ J}\cdot\text{mol}^{-1}$  ( $-90.89 \text{ cal}\cdot\text{mol}^{-1}$ ) for the formation of the bichromate ion from its elements at 298.15 K



Using this  $\Delta S_m^\circ$  and the standard entropies of Cr, O<sub>2</sub>, and H<sub>2</sub>, the standard entropy of  $184.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  was calculated for the bichromate ion. The  $S_m^\circ(\text{HCrO}_4^-) = \Delta S_m^\circ + S_m^\circ(\text{Cr}) + 2 \times S_m^\circ(\text{O}_2) + S_m^\circ(\text{H}_2) = [-380.28 + 23.77 + 2 \times (204.999) + (130.574)] \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 184.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .

## B. Comments on NBS Selected Values

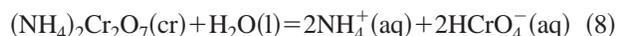
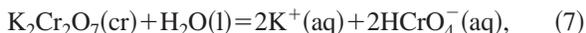
58HEP had a  $\Delta_{rxn} S_m^\circ$  of  $-134.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  for reaction (6):



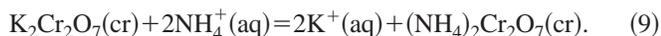
Using this value and Eq. (5),  $S_m^\circ(\text{HCrO}_4^-)$ ,  $\text{aq} = 184.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . This value supports the selected value of  $184.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .

Values of  $\Delta_f H_m^\circ$  for  $\text{K}_2\text{Cr}_2\text{O}_7(\text{cr})$  and  $\text{K}_2\text{CrO}_4(\text{cr})$  used in the calculations did not match the values tabulated  $-2061.5$  and  $-1403.7 \text{ kJ}\cdot\text{mol}^{-1}$ , 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.

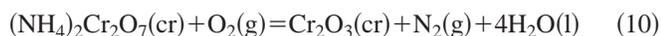
The  $\Delta_f H_m^\circ$  value for  $\text{K}_2\text{Cr}_2\text{O}_7(\text{cr})$  in reaction (1) was obtained from subtraction of the enthalpies for the reactions:



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



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



determined by 57NEU/MAR and the tabulated enthalpy of formation for  $\text{Cr}_2\text{O}_3(\text{cr})$  to obtain  $\Delta_f H_m^\circ$  for  $\text{K}_2\text{Cr}_2\text{O}_7(\text{cr})$ . Because the enthalpy change for reaction (7) was used to

determine  $\Delta_f H_m^\circ$  for  $\text{K}_2\text{Cr}_2\text{O}_7(\text{cr})$  it cannot also give an independent value of  $\Delta_f H_m^\circ$  for  $\text{HCrO}_4^-(\text{aq})$  and should not have been included in the average.

The  $\Delta_f H_m^\circ$  for  $\text{K}_2\text{CrO}_4(\text{cr})$  was obtained in a similar fashion in which the enthalpy change for



was combined with enthalpy changes for reactions (7)–(10) and the  $\Delta_f H_m^\circ$  for  $\text{Cr}_2\text{O}_3(\text{cr})$  to obtain  $\Delta_f H_m^\circ$  for  $\text{K}_2\text{CrO}_4(\text{cr})$ . Thus reaction (3) is also not an independent equation for determination of  $\Delta_f H_m^\circ$  for  $\text{HCrO}_4^-(\text{cr})$ . 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  $\Delta_f H_m^\circ$  to  $-878.8 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-210.04 \text{ kcal}\cdot\text{mol}^{-1}$ ) and the entropy to  $181.95 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

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

$\Delta_f H_m^\circ(\text{K}_2\text{Cr}_2\text{O}_7, \text{cr})$
$\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l})$
$\Delta_f H_m^\circ(\text{K}^+, \text{aq})$
$\Delta_f H_m^\circ((\text{NH}_4)_2\text{Cr}_2\text{O}_7, \text{cr})$
$\Delta_f H_m^\circ(\text{NH}_4^+, \text{aq})$
$\Delta_f H_m^\circ(\text{K}_2\text{CrO}_4, \text{cr})$
$\Delta_f H_m^\circ(\text{H}^+, \text{aq})$
$\Delta_f G_m^\circ(\text{CrO}_4^{2-})$
$\Delta_f H_m^\circ(\text{HCrO}_4^-)$
$\Delta_f G_m^\circ(\text{HCrO}_4^-)$
$S_m^\circ(\text{Cr}, \text{cr})$
$S_m^\circ(\text{O}_2, \text{g})$
$S_m^\circ(\text{H}_2, \text{g})$
$S_m^\circ(\text{H}^+, \text{aq})$

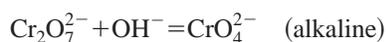
## D. Other Thermodynamic Measurements Considered

None.

### E. Additional Determinations of the Thermodynamic Properties

The speciation of the  $\text{Cr}^{6+}$  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  $K_{\text{eq}}$ , to adequately identify the proper chemical reaction that corresponds to the measured thermal energy. These speciation studies deal with several  $\text{Cr}^{6+}$  species. Although they are referenced with respect to  $\text{HCrO}_4^-$ , much of the data are also relevant to other  $\text{Cr}^{6+}$  species.

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



The usual reaction of interest is:



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  $\text{Cr}^{6+}$  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  $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ . 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,  $\text{H}_2\text{CrO}_4 = \text{H}^+ + \text{HCrO}_4^-$ , equal to  $K_{\text{eq}} = 1.21$  at unit ionic strength. The bichromate is thought to further dissociate by two possible pathways:  $\text{HCrO}_4^- = \text{H}^+ + \text{CrO}_4^{2-}$  and  $2\text{HCrO}_4^- = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ . The correct equilibrium constant is needed to determine the correct  $\text{Cr}^{6+}$  speciation. They also determined a  $K_{\text{eq}} = 0.028_2$  for the reaction:  $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} = 2\text{HCrO}_4^-$ .

58HOW/NAI made potentiometric and spectrophotometric measurements of the  $\text{HCrO}_4^- = \text{H}^+ + \text{CrO}_4^{2-}$  equilibrium reaction. A thermodynamic dissociation constant  $= 3.0 \times 10^{-7} \text{ mole} \cdot \text{l}^{-1}$  at  $25^\circ\text{C}$  and 0.002 ionic strength was calculated.

62SAS measured emf and spectrophotometric data on the reaction of  $\text{CrO}_4^{2-}$  with the  $\text{H}^+$  that indicated the presence of

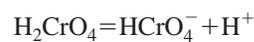
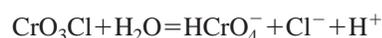
$\text{Cr}_2\text{O}_7^{2-}$  and  $\text{HCrO}_4^-$ . Spectrophotometric data yielded  $\log K_1 = 5.90$  for  $\text{H}^+ + \text{CrO}_4^{2-} = \text{HCrO}_4^-$  and  $\log K_{22} = 2.19$  for  $2\text{HCrO}_4^- = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ .

64LEE/STE made a spectroscopic study of the variation of the apparent  $pK_a$  of the protonation of the bichromate ion  $\text{HCrO}_4^- + \text{H}^+ = \text{H}_2\text{CrO}_4$ , in several different acids. A  $K_{\text{eq}} = 10.23$  was calculated at  $25^\circ\text{C}$  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  $25^\circ\text{C}$  and unit ionic strength.

64TON reevaluated the 53TON/KIN equilibrium constant data for the dissociation of chromic acid,  $\text{H}_2\text{CrO}_4 = \text{H}^+ + \text{HCrO}_4^-$ . In the earlier paper they postulated the existence of the  $\text{HCr}_2\text{O}_7^-$  ion. 64TON now calculates a  $K_{\text{eq}} = 4.21 \text{ mole} \cdot \text{l}^{-1}$  at unit ionic strength instead of the earlier  $1.21 \text{ mole} \cdot \text{l}^{-1}$  value. The bichromate is thought to further dissociate by two possible pathways:  $\text{HCrO}_4^- = \text{H}^+ + \text{CrO}_4^{2-}$  and  $2\text{HCrO}_4^- = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ . The correct equilibrium constant is needed to determine the correct  $\text{Cr}^{6+}$  speciation.

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



at three (3) wavelengths (320, 330, and 340 nm) and three temperatures, 15.0, 25.0, and  $35^\circ\text{C}$  at unit ionic strength. The  $\Delta H$  and  $\Delta S$  for the dissociation of  $\text{CrO}_3\text{Cl}^-$  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  $\text{H}_2\text{CrO}_4$  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  $\text{Cr}^{6+}$  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  $K_e = 10.7 \pm 0.07$ .

70LUKa spectrophotometrically determined the total  $\text{Cr}^{6+}$  concentrations,  $4 \times 10^{-4} \text{ mol} \cdot \text{l}^{-1}$  to  $4 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ , in aqueous solutions that did or did not contain  $\text{NaClO}_4$ ,  $\text{NaNO}_3$ ,  $\text{NaCl}$ , or  $\text{Na}_2\text{SO}_4$ .

70LUKb measured the first dissociation constant of chromic acid in  $0.17$ – $1.0 \text{ mol} \cdot \text{l}^{-1}$   $\text{HClO}_4$ . A thermodynamic dis-

sociation 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  $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} = 2\text{HCrO}_4^-$  in an acid solution, spectrophotometrically. Values of  $(2.3_0 \pm 0.1_7, 2.9_4 \pm 0.2_2, 4.0_0 \pm 0.4_0, \text{ and } 4.9_7 \pm 0.4_0) \times 10^{-2} \text{ mol} \cdot \text{l}^{-1}$  were obtained for the thermodynamic equilibrium constant at 15, 25, 35, and 45 °C, respectively.

In 68LIN/JONb the equilibrium reaction  $\text{HCrO}_4^- = \text{H}^+ + \text{CrO}_4^{2-}$  was studied in  $\text{H}_2\text{O}$  by potentiometric and independent spectrophotometric methods at 5–60 °C. The thermodynamic quantities  $\Delta S^\circ = (-34.4 \pm 1.00) - (80 \pm 20) \times (\log T - 2.474) \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  and  $\Delta H^\circ = (-1.3 \pm 0.5) - (0.03_5 \pm 0.01) \times (T - 298) \text{ kcal} \cdot \text{mol}^{-1}$  were determined as a function of temperature, for the specified reaction. The  $\Delta C_p = (3_5 \pm 1_0) \text{ cal} \cdot \text{mol}^{-1}$  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  $\text{Cr}^{6+}$  equilibria. Five species are usually believed to be present in  $\text{Cr}^{6+}$  aqueous solutions, namely,  $\text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{H}_2\text{CrO}_4$ ,  $\text{HCrO}_4^-$ , and  $\text{HCr}_2\text{O}_7^-$ . The Raman spectra of dilute  $\text{Cr}^{6+}$  solutions contained no evidence for the presence of the  $\text{H}_2\text{CrO}_4$ ,  $\text{HCrO}_4^-$ , and  $\text{HCr}_2\text{O}_7^-$  species when  $\text{Cr}^{6+}$  concentrations were in the range of 0.1–0.003  $\text{mol} \cdot \text{l}^{-1}$ . The  $2\text{CrO}_4^{2-} + 2\text{H}^+ = 2\text{HCrO}_4^-$  equilibrium was the only one existing between pH 1 and 11. The equilibrium constant for the proposed equilibrium was found to be  $K_{\text{eq}} = 14.85 \pm 0.04$  at 25 °C and  $I = 1.0$ . In more acidic solutions, up to 12  $\text{mol} \cdot \text{l}^{-1}$  in  $\text{HNO}_3$ , 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  $\text{NaCl} - \text{Na}_2\text{CrO}_4$  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) equilibria involving the formation of the aqueous  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , and  $\text{CrO}_3\text{Cl}^-$  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.

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 70LUKa Lukkari, O., Suom. Kemistil. B **43**, 336 (1970).  
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 86MIC/CAH Michel, G., Cahay, R., J. Raman Spectrosc. **17**, 79 (1986).  
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## 7. $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$

### 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:

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

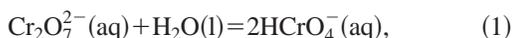
$$-1490.3 \text{ kJ} \cdot \text{mol}^{-1} \quad (-356.2 \text{ kcal} \cdot \text{mol}^{-1})$$

$$\Delta_f G_m^\circ(298.15 \text{ K}):$$

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

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

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



where the  $\Delta_{rxn}H = 19.7 \text{ kJ}\cdot\text{mol}^{-1}$  ( $4.7 \text{ kcal}\cdot\text{mol}^{-1}$ ). The NBS selected value for the hydrogen chromate ion is  $-878.2 \text{ kJ}\cdot\text{mol}^{-1}$ . The enthalpy of formation for the dichromate was calculated as  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -19.7 \text{ kJ}\cdot\text{mol}^{-1} + 2 \times \Delta_f H_m^\circ(\text{HCrO}_4^-, \text{aq}) - \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) = (-19.7 \text{ kJ}\cdot\text{mol}^{-1}) + 2 \times (-878.2 \text{ kJ}\cdot\text{mol}^{-1}) - (-285.823 \text{ kJ}\cdot\text{mol}^{-1}) = -1490.3 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-356.2 \text{ kcal}\cdot\text{mol}^{-1}$ ).

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  $\Delta_{rxn}G^\circ = 8.83 \text{ kJ}\cdot\text{mol}^{-1}$  ( $2.11 \text{ kcal}\cdot\text{mol}^{-1}$ ) 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  $\Delta_f G_m^\circ(\text{Cr}_2\text{O}_7^{2-})$  from the following relationship:

$$\Delta_{rxn}G^\circ = 2 \times \Delta_f G_m^\circ(\text{HCrO}_4^-) - \Delta_f G_m^\circ(\text{Cr}_2\text{O}_7^{2-}) - \Delta_f G_m^\circ(\text{H}_2\text{O}).$$

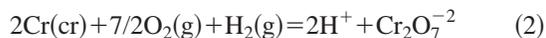
Therefore,

$$8.83 \text{ kJ}\cdot\text{mol}^{-1} = 2 \times (-764.8 \text{ kJ}\cdot\text{mol}^{-1}) - \Delta_f G_m^\circ(\text{Cr}_2\text{O}_7^{2-}) - (-237.183 \text{ kJ}\cdot\text{mol}^{-1})$$

and

$$\begin{aligned} \Delta_f G_m^\circ(\text{Cr}_2\text{O}_7^{2-}) &= [(-8.83) + 2 \times (-764.8) \\ &\quad - (-237.183)] \text{ kJ}\cdot\text{mol}^{-1} \\ &= -1301.2 \text{ kJ}\cdot\text{mol}^{-1}. \end{aligned}$$

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



using the relation of  $\Delta_f G_m^\circ = \Delta_f H_m^\circ - T\Delta_f S_m^\circ$  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:

$$\begin{aligned} S_m^\circ(\text{Cr}_2\text{O}_7^{2-}) &= \Delta S_m^\circ - 2 \times S_m^\circ(\text{H}^+) + 2 \times S_m^\circ(\text{Cr}) + 7/2 \\ &\quad \times S_m^\circ(\text{O}_2) + S_m^\circ(\text{H}_2). \\ S_m^\circ(\text{Cr}_2\text{O}_7^{2-}) &= [-634.3 - 2 \times (0) + 2 \times (23.8) + 7/2 \\ &\quad \times (204.999) + 130.574] \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \end{aligned}$$

to yield a value of  $261.9 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  ( $62.6 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ), 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<sub>2</sub>, and 55DAV/PRU gave 0.030<sub>3</sub>. The value used in 58HEP is apparently the average of the 53TON/KIN and 55DAV/PRU values with no contribution in 34NEU/RIE.

Crystalline  $\text{K}_2\text{Cr}_2\text{O}_7$  is not listed in any of the above pathways but the enthalpy of formation of the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  is not independent of the enthalpy of formation of crystalline  $\text{K}_2\text{Cr}_2\text{O}_7$ .

## C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m^\circ(\text{HCrO}_4^-, \text{aq})$$

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

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

$$\Delta_f G_m^\circ(\text{HCrO}_4^-, \text{aq})$$

$$\Delta_f G_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq})$$

$$\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq})$$

$$S_m^\circ(\text{Cr}, \text{cr})$$

$$S_m^\circ(\text{O}_2, \text{g})$$

$$S_m^\circ(\text{H}_2, \text{g})$$

$$S_m^\circ(\text{H}^+, \text{aq})$$

## 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  $\text{K}_2\text{Cr}_2\text{O}_7$  studies of 56YAT/VAS ( $-1990.29 \text{ kJ}\cdot\text{mol}^{-1}$ ), 1882THO ( $-1994.89 \text{ kJ}\cdot\text{mol}^{-1}$ ), 1886SAB ( $-1997.11 \text{ kJ}\cdot\text{mol}^{-1}$ ), and 40PER ( $-1997.86 \text{ kJ}\cdot\text{mol}^{-1}$ ). Where the  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = \Delta_f H_m^\circ(\text{K}_2\text{Cr}_2\text{O}_7, \text{aq}) - 2 \times \Delta_f H_m^\circ(\text{K}^+, \text{aq}) = [(-1995.05) - 2 \times (-252.38)] \text{ kJ}\cdot\text{mol}^{-1} = -1490.3 \text{ kJ}\cdot\text{mol}^{-1}$ . Many  $\text{Na}_2\text{Cr}_2\text{O}_7$  and  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  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  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq})$  was performed with methods similar to those used to calculate the  $\Delta_f H_m^\circ(\text{CrO}_4^{2-}, \text{aq})$ . The enthalpy of formation of the aqueous

ous 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  $\text{K}_2\text{Cr}_2\text{O}_7$  in aqueous  $\text{H}_2\text{SO}_4$  that resulted in a  $\Delta_f H_m^\circ = -1990.29 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1485.5 \text{ kJ}\cdot\text{mol}^{-1}$ .

1882THO measured the enthalpy of solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  in  $\text{H}_2\text{O}$  that resulted in a  $\Delta_f H_m^\circ = -1994.89 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1490.1 \text{ kJ}\cdot\text{mol}^{-1}$ . They also measured the enthalpy of solution of  $\text{Na}_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -1990.29 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $\text{Na}_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1493.1 \text{ kJ}\cdot\text{mol}^{-1}$ .

1886SAB measured the enthalpy of solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  in aqueous  $\text{KOH}$  that resulted in a  $\Delta_f H_m^\circ = -1997.11 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1492.4 \text{ kJ}\cdot\text{mol}^{-1}$ .

40PER measured the enthalpy of solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -1997.86 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1493.1 \text{ kJ}\cdot\text{mol}^{-1}$ .

1878MOR measured the enthalpy of solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -1994.4 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1489.7 \text{ kJ}\cdot\text{mol}^{-1}$ . They also measured the enthalpy of solution of  $\text{Na}_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -1965.2 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $\text{Na}_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1485.0 \text{ kJ}\cdot\text{mol}^{-1}$ . They also measured the enthalpy of solution of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -1757.3 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1492.3 \text{ kJ}\cdot\text{mol}^{-1}$ .

1898VON measured the enthalpy of solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -1996.9 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1492.1 \text{ kJ}\cdot\text{mol}^{-1}$ .

1884BER measured the enthalpy of solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -1998.5 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1493.8 \text{ kJ}\cdot\text{mol}^{-1}$ . They also measured the enthalpy of solution of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -1757.3 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1492.3 \text{ kJ}\cdot\text{mol}^{-1}$ .

34KOL/GRI measured the enthalpy of solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -1997.3 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1492.5 \text{ kJ}\cdot\text{mol}^{-1}$ .

60NEL/MOS measured the enthalpy of solution of  $\text{Na}_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -1979.0 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $\text{Na}_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1498.8 \text{ kJ}\cdot\text{mol}^{-1}$ .

54HER/LAU measured the enthalpy of solution of

$\text{Na}_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -1965.6 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $\text{Na}_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1485.4 \text{ kJ}\cdot\text{mol}^{-1}$ .

30LAM/REA measured the enthalpy of solution of  $\text{Na}_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -2003.7 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $\text{Na}_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1523.5 \text{ kJ}\cdot\text{mol}^{-1}$ .

61SHI/VAL measured the enthalpy of solution of  $\text{Na}_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -1964.4 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $\text{Na}_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1484.1 \text{ kJ}\cdot\text{mol}^{-1}$ .

57NEU/MAR measured the enthalpy of decomposition of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7, \text{cr}$  from which they calculated the enthalpy of formation of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7, \text{cr}$ ,  $\Delta_f H_m^\circ = -1806.6 \text{ kJ}\cdot\text{mol}^{-1}$  from the following reaction:  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7, \text{cr} = \text{Cr}_2\text{O}_3, \text{cr} + \text{N}_2, \text{g} + 4\text{H}_2\text{O}, \text{l}$ . This value is used to determine the enthalpy of formation of crystalline  $\text{Na}_2\text{Cr}_2\text{O}_7$  that was then used in the calculation of the value for the aqueous  $\text{Na}_2\text{Cr}_2\text{O}_7$ .

55KAP/SHI measured the enthalpy of decomposition of crystalline  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  based on the same reaction as 57NEU/MAR. A  $\Delta_f H_m^\circ = -1812.5 \text{ kJ}\cdot\text{mol}^{-1}$  was calculated for crystalline  $\text{Na}_2\text{Cr}_2\text{O}_7$ .

41PER measured the enthalpy of solution of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -1757.8 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1492.8 \text{ kJ}\cdot\text{mol}^{-1}$ .

23MOL/GON measured the enthalpy of solution of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -1754.8 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1489.8 \text{ kJ}\cdot\text{mol}^{-1}$ .

57MUL/HEP measured the enthalpy of solution of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  that resulted in a  $\Delta_f H_m^\circ = -1745.6 \text{ kJ}\cdot\text{mol}^{-1}$  for aqueous  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ . This resulted in a  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_7^{2-}, \text{aq}) = -1480.3 \text{ kJ}\cdot\text{mol}^{-1}$ .

64SHA/GER used a  $\text{Cu}/\text{CuO}$  electrode to determine  $\text{O}^{2-}$  ion concentration in molten  $\text{KNO}_3$ . The  $\text{CuO}$  electrode was used to titrate  $\text{K}_2\text{Cr}_2\text{O}_7$  with  $\text{Na}_2\text{O}_2$  in molten  $\text{KNO}_3$ . Sharp potential drops were recorded at the equivalence point. The equilibrium constant of the reaction:  $\text{Cr}_2\text{O}_7^{2-} + \text{O}^{2-} = 2\text{CrO}_4^{2-}$  was calculated as  $K_{\text{eq}} = 1.8 \times 10^{12}$ .

## E. Additional Determinations of the Thermodynamic Properties

None.

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## 8. Cr<sub>2</sub>O<sub>3</sub>(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

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

$$-1139.7 \text{ kJ}\cdot\text{mol}^{-1} \text{ } (-272.4 \text{ kcal}\cdot\text{mol}^{-1})$$

$$\Delta_f G_m^\circ(298.15 \text{ K}):$$

$$-1058.1 \text{ kJ}\cdot\text{mol}^{-1} \text{ } (-252.9 \text{ kcal}\cdot\text{mol}^{-1})$$

$$S_m^\circ(298.15 \text{ K}): 81.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \text{ } (19.4 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$$

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

$$118.74 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \text{ } (28.38 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}).$$

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  $-1139.7 \text{ kJ}\cdot\text{mol}^{-1}$ .

37AND measured the heat capacity of Cr<sub>2</sub>O<sub>3</sub>, the  $S_m^\circ(\text{Cr}_2\text{O}_3, \text{cr}) = 81.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  and  $C_{p,m}^\circ(\text{Cr}_2\text{O}_3, \text{cr}) = 118.74 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  came directly from their measurement data.

$\Delta_f G_m^\circ(\text{Cr}_2\text{O}_3, \text{cr})$  was calculated using:  $\Delta_f G_m^\circ = \Delta_f H_m^\circ - T\Delta_f S_m^\circ$ . The  $\Delta_f S_m^\circ$  was calculated as  $\Delta_f S_m^\circ = [81.2 - 2 \times (23.77) - 3/2 \times (204.999)] \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = -273.86 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  based upon the formation reaction,  $2\text{Cr}(\text{cr}) + 3/2\text{O}_2(\text{g}) = \text{Cr}_2\text{O}_3(\text{cr})$ . Therefore,  $\Delta_f G_m^\circ = [-1139.7 - 298.15 \times (-0.27386)] \text{ kJ}\cdot\text{mol}^{-1} = -1058.1 \text{ kJ}\cdot\text{mol}^{-1}$ .

### B. Comments on NBS Selected Values

54MAH reported the enthalpy of formation as  $-1141.0 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-272.7 \text{ kcal}\cdot\text{mol}^{-1}$ ). The value on the worksheets was  $-1140.6 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-272.6 \text{ kcal}\cdot\text{mol}^{-1}$ ), the difference apparently due to a difference in atomic weight of chromium. The value tabulated was  $-1139.7 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-272.4 \text{ kcal}\cdot\text{mol}^{-1}$ ), 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 Cr<sub>2</sub>O<sub>3</sub> is contained within the pedigrees of at least the following substances CrO<sub>4</sub><sup>2-</sup>(aq), Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>(aq), HCrO<sub>4</sub><sup>-</sup>(aq), CrO<sub>3</sub>(cr), CrO<sub>3</sub>(aq), K<sub>2</sub>CrO<sub>4</sub>(cr), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>(cr), Cr(OH)<sub>3</sub>(cr), and all Cr(III)(aq) species.

### C. Auxiliary Values Required for Data Pathway

$$C_{p,m}^\circ(\text{Cr}, \text{cr})$$

$$C_{p,m}^\circ(\text{O}_2, \text{g})$$

$$S_m^\circ(\text{O}_2, \text{g})$$

$$S_m^\circ(\text{Cr}, \text{cr})$$

### D. Other Thermodynamic Measurements Considered

29ROT/BEC also measured the enthalpy of combustion of chromium to form Cr<sub>2</sub>O<sub>3</sub>(cr) at 292.15 K. Conversion to 298.15 K yielded a value of  $-1208.8 \text{ kJ}\cdot\text{mol}^{-1}$ .

39GRU/FLA measured the oxygen vapor pressure over Cr<sub>2</sub>O<sub>3</sub> at temperatures of 1168–1275 K. The reaction  $\text{Cr}_2\text{O}_3 = 2\text{Cr} + 1.5\text{O}_2$  was assumed to occur. The enthalpy of formation for 298.15 K, calculated as an average from these measurements, was  $-1118 \text{ kJ}\cdot\text{mol}^{-1}$ , with a range of  $\approx 2 \text{ kJ}\cdot\text{mol}^{-1}$ .

40ROT/WOL measured the enthalpy of combustion of chromium to form  $\text{Cr}_2\text{O}_3(\text{cr})$  at 294.15 K. Conversion to 298.15 K yielded a value of  $-1125.1 \text{ kJ}\cdot\text{mol}^{-1}$ .

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

55ROB/JEN measured the enthalpy of the reaction:  $\text{Cr}_2\text{O}_3(\text{cr}) + 2\text{Al}(\text{cr}) = 2\text{Cr}(\text{cr}) + \text{Al}_2\text{O}_3(\text{cr})$  as  $-540 \text{ kJ}\cdot\text{mol}^{-1}$ . Combination with the enthalpy of formation of  $\text{Al}_2\text{O}_3(\text{cr})$ ,  $-1675.7 \text{ kJ}\cdot\text{mol}^{-1}$ , gave  $\Delta_f H^\circ = -1135 \text{ kJ}\cdot\text{mol}^{-1}$ .

27VON/AOY measured the reduction equilibrium of  $\text{Cr}_2\text{O}_3$ :



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

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  $-1136.0 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $16 \text{ kJ}\cdot\text{mol}^{-1}$  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  $-1128.4 \text{ kJ}\cdot\text{mol}^{-1}$ .

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  $-1119.2 \text{ kJ}\cdot\text{mol}^{-1}$ .

44KEL/BOE measured the enthalpy of the reaction  $\text{Cr}_2\text{O}_3 + 3\text{C} = 2\text{Cr} + 3\text{CO}$  to be  $-801.32 \text{ kJ}\cdot\text{mol}^{-1}$ . Combination with the enthalpy of formation of  $\text{CO}(\text{g})$ ,  $110.52 \text{ kJ}\cdot\text{mol}^{-1}$ , gave a  $\Delta_f H^\circ = -1132.9 \text{ kJ}\cdot\text{mol}^{-1}$ .

### E. Additional Determinations of the Thermodynamic Properties

66NOV/LEN studied the reaction between  $\text{H}_2$  and  $\text{Cr}_2\text{O}_3$  at temperatures of 1220–1500 °C from which was calculated the thermodynamic properties associated with the formation of  $\text{Cr}_2\text{O}_3$  according to the reaction:  $2\text{Cr} + 1\frac{1}{2}\text{O}_2 = \beta\text{-Cr}_2\text{O}_3$ .  $\Delta_f G_T^\circ = 270.780 + 0.06172 \times T (\pm 0.700) \text{ kcal}\cdot\text{mol}^{-1}$  and  $P_{\text{O}_2} = 39453/T - 8.994$  were calculated for the reaction.

74MAZ/PEH have calculated  $\Delta_f G_m^\circ = -1115.5 + 250.1 \times T \pm 1.46 \text{ kJ}\cdot\text{mol}^{-1}$  of crystalline  $\text{Cr}_2\text{O}_3$  as a function of temperature in the temperature region of 1150–1540 K from electrochemical measurements using a  $\text{ThO}_2\text{-Y}_2\text{O}_3$  solid electrolyte.

77BRU/CAN have made precise measurements of the heat capacity of crystalline  $\text{Cr}_2\text{O}_3$  from 291 to 323 K.

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## 9. $\text{Cr}_2\text{O}_3\cdot\text{H}_2\text{O}(\text{cr})$

### 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:

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

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  $\text{Cr}_2\text{O}_3(\text{cr}) + \text{H}_2\text{O}(\text{g}) = \text{Cr}_2\text{O}_3\cdot\text{H}_2\text{O}(\text{cr})$ . The enthalpy of hydration was  $\Delta_{rxn} H^\circ = -124.60 \text{ kJ}\cdot\text{mol}^{-1}$ .

$$\begin{aligned} \Delta_f H_m^\circ (\text{Cr}_2\text{O}_3\cdot\text{H}_2\text{O}, \text{cr}) \\ &= \Delta_{rxn} H^\circ + \Delta_f H_m^\circ (\text{Cr}_2\text{O}_3, \text{cr}) + \Delta_f H_m^\circ (\text{H}_2\text{O}, \text{g}) \\ &= [-124.60 + (-1139.7) + (-241.82)] \text{ kJ}\cdot\text{mol}^{-1} \\ &= -1506.1 \text{ kJ}\cdot\text{mol}^{-1}, \end{aligned}$$

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

### B. Comments on NBS Selected Values

None.

**C. Auxiliary Values Required for Data Pathway**

$$\Delta_f H_m^\circ(\text{Cr}_2\text{O}_3, \text{cr})$$

$$\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{g})$$

**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<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O(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:

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

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

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,  $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{cr}) + \text{H}_2\text{O}(\text{g}) = \text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$ . The enthalpy of hydration was  $\Delta_{rxn} H_m^\circ = -96.2 \text{ kJ}\cdot\text{mol}^{-1}$ .

$$\Delta_f H_m^\circ(\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}, \text{cr})$$

$$= \Delta_{rxn} H_m^\circ + \Delta_f H_m^\circ(\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}, \text{cr}) + \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{g})$$

$$= [-96.2 + (-1506.) + (-241.82)] \text{ kJ}\cdot\text{mol}^{-1}$$

$$= -1844.3 \text{ kJ}\cdot\text{mol}^{-1}.$$

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

**B. Comments on NBS Selected Values**

None.

**C. Auxiliary Values Required for Data Pathway**

$$\Delta_f H_m^\circ(\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}, \text{cr})$$

$$\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{g})$$

**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<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O(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:

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

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,  $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}(\text{cr}) + \text{H}_2\text{O}(\text{g}) = \text{Cr}_2\text{O}_3 \cdot 3\text{H}_2\text{O}(\text{cr})$ . The enthalpy of hydration was  $\Delta_{rxn} H_m^\circ = -85.8 \text{ kJ}\cdot\text{mol}^{-1}$ .  $\Delta_f H_m^\circ(\text{Cr}_2\text{O}_3 \cdot 3\text{H}_2\text{O}, \text{cr}) = \Delta_{rxn} H_m^\circ + \Delta_f H_m^\circ(\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}, \text{cr}) + \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{g}) = [-85.8 + (-1845.) + (-241.82)] \text{ kJ}\cdot\text{mol}^{-1} = -2172.7 \text{ kJ}\cdot\text{mol}^{-1}$ . The NBS selected value is  $-2171. \text{ kJ}\cdot\text{mol}^{-1}$ .

**B. Comments on NBS Selected Values**

None.

**C. Auxiliary Values Required for Data Pathway**

$$\Delta_f H_m^\circ(\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}, \text{cr})$$

$$\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{g})$$

**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<sub>3</sub>O<sub>4</sub>(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·Cr<sub>2</sub>O<sub>3</sub>. The thermodynamic function and its selected value is:

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

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

The  $\Delta_f H_m^\circ$  of crystalline mixed chromium (II) and chromium (III) oxide, CrO·Cr<sub>2</sub>O<sub>3</sub>, was selected from the work of 61DAN/MOR. An enthalpy of reaction of  $\Delta_{rxn} H_m^\circ = 550.6 \text{ kJ}\cdot\text{mol}^{-1}$  was measured for the following reaction at 1700 °C:



The  $\Delta_{rxn} H_m^\circ = 564.8 \text{ kJ}\cdot\text{mol}^{-1}$  at 25 °C.

$$\Delta_f H_m^\circ(\text{Cr}_2\text{O}_3, \text{cr})$$

$$= -(\Delta_{rxn} H_m^\circ) + 4\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{g})$$

$$= [-564.8 + 4(-241.82)] \text{ kJ}\cdot\text{mol}^{-1}$$

$$= -1531. \text{ kJ}\cdot\text{mol}^{-1}.$$

### B. Comments on NBS Selected Values

None.

### C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{g})$$

### 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).

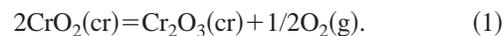
## 13. CrO<sub>2</sub>(cr)

### A. Selected Values, NBS Tables

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

$$\Delta_f H_m^\circ, 298.15 \text{ K} := -598. \text{ kJ}\cdot\text{mol}^{-1} \quad (-143. \text{ kcal}\cdot\text{mol}^{-1}).$$

The  $\Delta_f H_m^\circ(\text{CrO}_2, \text{cr})$  was obtained as the average of two literature values, 61KUB and 53ARI/SHC. 61KUB determined the  $\Delta_{rxn} H_m^\circ = 110.0 \text{ kJ}\cdot\text{mol}^{-1}$  at a mean temperature of 500 °C for the decomposition of CrO<sub>2</sub>(cr) over the temperature range from 450 to 550 °C according to the following reaction:



A  $\Delta C_p^\circ = 29 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  was calculated using an estimated heat capacity for CrO<sub>2</sub>(cr) of  $52.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . The  $\Delta C_p^\circ = [118.7 + \frac{1}{2}(29.4) - 2(52.3)] \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 29 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . The  $\Delta_{rxn} H_m^\circ = 110.0 \text{ kJ}\cdot\text{mol}^{-1}$  reduces to  $96.2 \text{ kJ}\cdot\text{mol}^{-1}$  when corrected from 500 to 25 °C. Therefore,

$$\Delta_f H_m^\circ(\text{CrO}_2) = [-(\Delta_{rxn} H_m^\circ) + \Delta_f H_m^\circ(\text{Cr}_2\text{O}_3, \text{cr})]/2$$

$$= [-96.2 + (-1139.7)]/2$$

$$= -618.0 \text{ kJ}\cdot\text{mol}^{-1}.$$

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



and

$$\Delta_f H_m^\circ(\text{CrO}_2) = [-(\Delta_{rxn} H_m^\circ) + \Delta_f H_m^\circ(\text{Cr}_2\text{O}_3, \text{cr}) + 0.96$$

$$\times \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l})]/2$$

$$= [-(-250.2) + (-1139.7)$$

$$+ 0.96 \times (-285.83)]/2$$

$$= -582.0 \text{ kJ}\cdot\text{mol}^{-1}.$$

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

### B. Comments on NBS Selected Values

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

### C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m^\circ(\text{Cr}_2\text{O}_3, \text{cr})$$

$$\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{liq})$$

### 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<sub>3</sub>(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:

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

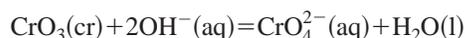
$$-589.5 \text{ kJ}\cdot\text{mol}^{-1} \text{ } (-140.9 \text{ kcal}\cdot\text{mol}^{-1}).$$

57MUL/HEP gave enthalpies for the two reactions:



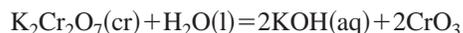
$$\Delta_{rxn} H_m^\circ = -30.5 \text{ kJ}\cdot\text{mol}^{-1} \text{ } (-7.3 \text{ kcal}\cdot\text{mol}^{-1})$$

and



$$\Delta_{rxn} H_m^\circ = -117.2 \text{ kJ}\cdot\text{mol}^{-1} \text{ } (-28.0 \text{ kcal}\cdot\text{mol}^{-1}).$$

Subtraction of these two reactions gave



$$\Delta_{rxn} H_m^\circ = 203.8 \text{ kJ}\cdot\text{mol}^{-1} \text{ } (48.7 \text{ kcal}\cdot\text{mol}^{-1}),$$

which then led to  $\Delta_f H_m^\circ(\text{CrO}_3(\text{cr})) = -589.5 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-140.9 \text{ kcal}\cdot\text{mol}^{-1}$ ), using the  $\Delta_f H_m^\circ$  of crystalline  $\text{K}_2\text{Cr}_2\text{O}_7$ , described under  $\text{HCrO}_4^-(\text{aq})$ .

### B. Comments on NBS Selected Values

The value of  $\Delta_f H_m^\circ(\text{K}_2\text{Cr}_2\text{O}_7, \text{cr})$  used in the calculation did not match that tabulated; see  $\text{HCrO}_4^-(\text{aq})$  Section B.

### C. Auxiliary Values Required for Data Pathway

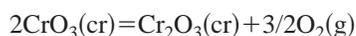
$$\Delta_f H_m^\circ(\text{K}_2\text{Cr}_2\text{O}_7, \text{cr})$$

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

$$\Delta_f H_m^\circ(\text{KOH}, \text{aq})$$

### D. Other Thermodynamic Measurements Considered

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



as  $29.3 \text{ kJ}\cdot\text{mol}^{-1}$ . Combination with the tabulated  $\Delta_f H_m^\circ$  for  $\text{Cr}_2\text{O}_3(\text{cr})$ ,  $-1139.7 \text{ kJ}\cdot\text{mol}^{-1}$ , gave  $\Delta_f H_m^\circ$  for  $\text{CrO}_3(\text{cr})$ ,  $-584.5 \text{ kJ}\cdot\text{mol}^{-1}$ .

08MIX measured the enthalpy changes for the reactions:



and



as  $-322.2 \text{ kJ}\cdot\text{mol}^{-1}$  and  $-664.4 \text{ kJ}\cdot\text{mol}^{-1}$ . Combination of the two reactions yields



with a calculated enthalpy change of  $-342.2 \text{ kJ}\cdot\text{mol}^{-1}$ . This was combined with  $\Delta_f H_m^\circ$ s for  $\text{Na}_2\text{O}_2(\text{cr})$  and  $\text{Na}_2\text{O}(\text{cr})$  of  $-504.6$  and  $-415.9 \text{ kJ}\cdot\text{mol}^{-1}$  to give  $\Delta_f H_m^\circ(\text{CrO}_3) = -608.4 \text{ kJ}\cdot\text{mol}^{-1}$ . The  $\Delta_f H_m^\circ$  used for  $\text{Na}_2\text{O}(\text{cr})$  and  $\text{Na}_2\text{O}_2(\text{cr})$  did not match the values tabulated:  $-414.22$  and  $-510.87 \text{ kJ}\cdot\text{mol}^{-1}$ . Use of these values gives  $\Delta_f H_m^\circ(\text{CrO}_3) = -632.2 \text{ kJ}\cdot\text{mol}^{-1}$ .

### 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  $\text{CrO}_3$  to be  $63.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  ( $15.2 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ). However, Table I in the paper contains the value of  $72.0 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  ( $17.2 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ).

### F. Bibliography

- 08MIX Mixer, 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<sub>3</sub>·80H<sub>2</sub>O

### 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:

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

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

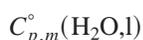
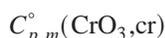
12BUC/PRI measured the enthalpy of solution of crystalline chromium (VI) oxide in 80 mole of water as  $\Delta_{rxn} H_m^\circ = -10.3 \text{ kJ}\cdot\text{mol}^{-1}$  at  $15^\circ\text{C}$  that was calculated to be

$\Delta_{rxn}H_m^\circ = -11.7 \text{ kJ}\cdot\text{mol}^{-1}$  at 25 °C. An enthalpy of formation of the crystalline substance of  $\Delta_fH_m^\circ = -589.5 \text{ kJ}\cdot\text{mol}^{-1}$  was used from the work of 57MUL/HEP. 1878MOR measured enthalpies of solution at several concentrations using from 2 to 50 mole of  $\text{H}_2\text{O}$ . Therefore the NBS table has entries for the enthalpy of formation of aqueous chromium (VI) oxide with from 2 to 80 mole of  $\text{H}_2\text{O}$ .

### B. Comments on NBS Selected Values

None.

### C. Auxiliary Values Required for Data Pathway



### 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. $[\text{Cr}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3$ (aq, violet)

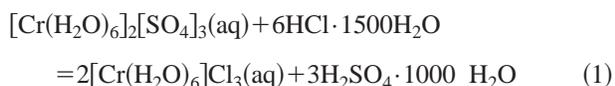
### A. Selected Values, NBS Tables

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:

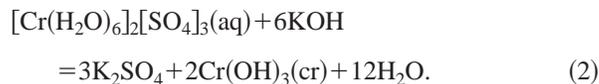
$$\Delta_fH_m^\circ(298.15 \text{ K}):$$

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

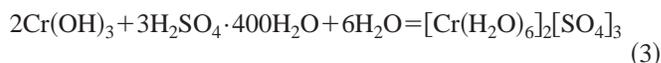
The  $\Delta_fH_m^\circ$  of this hexahydrated chromium sulfate complex,  $[\text{Cr}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3$ , was determined as the average of three (3) measurements reported in the literature. The first value was reported in 07COL as  $[\text{Cr}(\text{H}_2\text{O})_6]_2[\text{SO}_4]_3(\text{aq}) = -6714.1 \text{ kJ}\cdot\text{mol}^{-1} (-1604.7 \text{ kcal}\cdot\text{mol}^{-1})$ . This value was determined from the enthalpy of the following reaction:



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



The  $\Delta_fH_m^\circ[\text{Cr}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3, \text{aq}] = [186.372 + 3(-1414.02) + 2(-1064.0) + 12(-285.830) - 6(-482.37)] \text{ kJ}\cdot\text{mol}^{-1} = -6719.5 \text{ kJ}\cdot\text{mol}^{-1} (-1606.0 \text{ kcal}\cdot\text{mol}^{-1})$ . The third value of  $\Delta_fH_m^\circ = 6719.1 \text{ kJ}\cdot\text{mol}^{-1} (-1605.9 \text{ kcal}\cdot\text{mol}^{-1})$  also came from 1882THO. The reaction

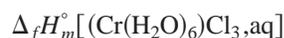
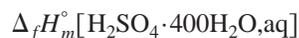
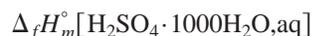
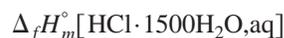


had an enthalpy of reaction of  $\Delta_{rxn}H_m^\circ = -206.3 \text{ kJ}\cdot\text{mol}^{-1} (-49.3 \text{ kcal}\cdot\text{mol}^{-1})$ . The  $\Delta_fH_m^\circ[[\text{Cr}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3, \text{aq}] = [-206.3 + 2(-1064.0) + 3(-889.974)_{400} + 6(-285.830)] \text{ kJ}\cdot\text{mol}^{-1} = -6719.1 \text{ kJ}\cdot\text{mol}^{-1} (-1605.9 \text{ kcal}\cdot\text{mol}^{-1})$ . The average of these three values,  $-(6714.1 + 6719.5 + 6719.1) \text{ kJ}\cdot\text{mol}^{-1}/3 = -6717.4 \text{ kJ}\cdot\text{mol}^{-1} (-1605.5 \text{ kcal}\cdot\text{mol}^{-1})$ , was chosen as the NBS selected value.

### B. Comments on NBS Selected Values

The  $-6714.1 \text{ kJ}\cdot\text{mol}^{-1} (-1604.7 \text{ kcal}\cdot\text{mol}^{-1})$  value used in the average came from the work of 07COL. The calculations used  $\text{HCl}\cdot 1500\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4\cdot 1000\text{H}_2\text{O}$  while the reactions reported in 07COL used  $\text{HCl}\cdot 400\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4\cdot 400\text{H}_2\text{O}$ . The correction to a lower degree of hydration only amounts to less than  $2 \text{ kJ}\cdot\text{mol}^{-1}$  and with the other uncertainties involved, this quantity is negligible.

### C. Auxiliary Values Required for Data Pathway



### 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<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>](SO<sub>4</sub>)<sub>3</sub> (aq, green)

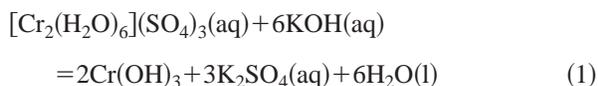
### A. Selected Values, NBS Tables

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:

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

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

The  $\Delta_f H_m^\circ$  of this hexahydrated chromium sulfate complex, [Cr<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>](SO<sub>4</sub>)<sub>3</sub>, was determined from the work of 07COL. The following chemical reaction was used:



with an enthalpy of reaction,  $\Delta_{rxn} H_m^\circ = -1069.4 \text{ kcal}\cdot\text{mol}^{-1}$ . The

$$\Delta_f H_m^\circ([\text{Cr}_2(\text{H}_2\text{O})_6](\text{SO}_4)_3, \text{aq})$$

$$= (-\Delta_{rxn} H_m^\circ) + 2 \times \Delta_f H_m^\circ(\text{Cr}(\text{OH})_3, \text{cr})$$

$$+ 3 \Delta_f H_m^\circ(\text{K}_2\text{SO}_4, \text{aq}) + 6 \times \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l})$$

$$- 6 \Delta_f H_m^\circ(\text{KOH}, \text{aq})$$

$$= [ -(-1069.4) + 2 \times (-1064.0) + 3 \times (-1414.0)$$

$$+ 6 \times (-285.83) - 6 \times (-482.37) ] \text{ kJ}\cdot\text{mol}^{-1}$$

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

### B. Comments on NBS Selected Values

None.

### C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m^\circ(\text{KOH}, \text{aq})$$

$$\Delta_f H_m^\circ(\text{Cr}(\text{OH})_3, \text{cr})$$

$$\Delta_f H_m^\circ(\text{K}_2\text{SO}_4, \text{aq})$$

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

### 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<sub>2</sub>(H<sub>2</sub>O)<sub>8</sub>(SO<sub>4</sub>)<sub>2</sub>](SO<sub>4</sub>)(aq)

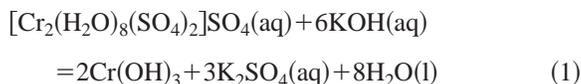
### A. Selected Values, NBS Tables

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:

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

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

The  $\Delta_f H_m^\circ$  of this octahydrated chromium sulfate complex, [Cr<sub>2</sub>(H<sub>2</sub>O)<sub>8</sub>(SO<sub>4</sub>)<sub>2</sub>](SO<sub>4</sub>), was determined from the work of 07COL. The following chemical reaction was used:



with an enthalpy of reaction,  $\Delta_{rxn} H_m^\circ = -241.0 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-57.6 \text{ kcal}\cdot\text{mol}^{-1}$ ). The  $\Delta_f H_m^\circ([\text{Cr}_2(\text{H}_2\text{O})_8(\text{SO}_4)_2]\text{SO}_4, \text{aq})$   
 $= -\Delta_{rxn} H_m^\circ + 2 \times \Delta_f H_m^\circ(\text{Cr}(\text{OH})_3, \text{cr}) + 3 \times \Delta_f H_m^\circ$   
 $\times (\text{K}_2\text{SO}_4, \text{aq}) + 6 \times \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) - 6 \times \Delta_f H_m^\circ(\text{KOH}, \text{aq})$   
 $= [ -(-241.0) + 2 \times (-1064.0) + 3 \times (-1414.02)$   
 $+ 8 \times (-285.830) - 6 \times (-482.37) ] \text{ kJ}\cdot\text{mol}^{-1} = -5521.6$   
 $\text{kJ}\cdot\text{mol}^{-1} \quad (-1319.7 \text{ kcal}\cdot\text{mol}^{-1}).$

### B. Comments on NBS Selected Values

None.

### C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m^\circ(\text{KOH}, \text{aq})$$

$$\Delta_f H_m^\circ(\text{Cr}(\text{OH})_3, \text{cr})$$

$$\Delta_f H_m^\circ(\text{K}_2\text{SO}_4, \text{aq})$$

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

### 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).

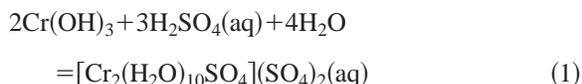
**19. [Cr<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub>SO<sub>4</sub>](SO<sub>4</sub>)<sub>2</sub>(aq)**
**A. Selected Values, NBS Tables**

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:

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

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

The  $\Delta_f H_m^\circ(298.15 \text{ K})$  of this decahydrated chromium sulfate complex, [Cr<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub>SO<sub>4</sub>](SO<sub>4</sub>)<sub>2</sub>, was determined from the work of 07COL. The following chemical reaction was used:



with an enthalpy of reaction,  $\Delta_{rxn} H_m^\circ(298.15 \text{ K}) = -182.0 \text{ kJ}\cdot\text{mol}^{-1} \text{ } (-43.5 \text{ kcal}\cdot\text{mol}^{-1})$ . The  $\Delta_f H_m^\circ(298.15 \text{ K})$  ([Cr<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub>SO<sub>4</sub>](SO<sub>4</sub>)<sub>2</sub>,aq) =  $\Delta_{rxn} H_m^\circ + 2 \times \Delta_f H_m^\circ(298.15 \text{ K})$  (Cr(OH)<sub>3</sub>,cr) +  $3 \times \Delta_f H_m^\circ(298.15 \text{ K})$  (H<sub>2</sub>SO<sub>4</sub>,aq) +  $4 \times \Delta_f H_m^\circ(298.15 \text{ K})$  (H<sub>2</sub>O,l) =  $[(-182.0) + 2 \times (-1064.0) + 3 \times (-889.98) + 4 \times (-285.830)] \text{ kJ}\cdot\text{mol}^{-1} = -6123.3 \text{ kJ}\cdot\text{mol}^{-1} \text{ } (-1463.5 \text{ kcal}\cdot\text{mol}^{-1})$ .

**B. Comments on NBS Selected Values**

None.

**C. Auxiliary Values Required for Data Pathway**

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

$$\Delta_f H_m^\circ(298.15 \text{ K})(\text{H}_2\text{SO}_4, \text{aq})$$

$$\Delta_f H_m^\circ(298.15 \text{ K})(\text{H}_2\text{O}, \text{l})$$

**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<sub>2</sub>(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:

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

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

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

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

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

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

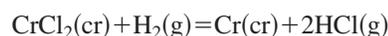
$$115.31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \text{ } (27.56 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$$

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

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

62STO/CHI measured the heat capacity of crystalline CrCl<sub>2</sub> between 11 and 300 K. Their measurement data were used to derive most of the selected thermodynamic properties of crystalline CrCl<sub>2</sub>. 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  $\Delta_{rxn} H_m^\circ = 210.87 \text{ kJ}\cdot\text{mol}^{-1}$  was obtained for the reduction of CrCl<sub>2</sub> according to the following reaction:



$$\Delta_f H_m^\circ(\text{CrCl}_2, \text{cr}) = -\Delta_{rxn} H_m^\circ + 2 \times \Delta_f H_m^\circ(\text{HCl}, \text{g})$$

$$= [-210.87 + 2 \times (-92.307)] \text{ kJ}\cdot\text{mol}^{-1}$$

$$= -395.48 \text{ kJ}\cdot\text{mol}^{-1}. \quad (1)$$

The  $\Delta_f H^\circ(0 \text{ K})$  was calculated using  $\Delta_f H^\circ(298 \text{ K})$  minus the [ $H^\circ(298 \text{ K}) - H^\circ(0 \text{ K})$ ] of CrCl<sub>2</sub>, Cr, and Cl<sub>2</sub> based upon reaction (2):



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

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  $\Delta_f S_m^\circ = S_m^\circ(\text{CrCl}_2) - S_m^\circ(\text{Cr}) - S_m^\circ(\text{Cl}_2) = [115.31 - 23.77 - 222.957] \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = -131.411 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . Then  $\Delta_f G_m^\circ = [-395.4 - 298.15 \times (-0.131411)] \text{ kJ}\cdot\text{mol}^{-1} = -356.1 \text{ kJ}\cdot\text{mol}^{-1}$ .

**B. Comments on NBS Selected Values**

None.

**C. Auxiliary Values Required for Data Pathway**

$$\Delta_f H_m^\circ(\text{HCl}, \text{g})$$

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

$$[H^\circ(298 \text{ K}) - H^\circ(0 \text{ K})](\text{Cl}_2, \text{g})$$

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

$$S^\circ(\text{Cl}_2, \text{g})$$

**D. Other Thermodynamic Measurements Considered**

None.

**E. Additional Determinations of the Thermodynamic Properties**

76GEE/SHE calculated a  $\Delta_f H_m^\circ = -396.72 \pm 0.30$  kJ·mol<sup>-1</sup> for crystalline CrCl<sub>2</sub> from emf measurements of solid electrolyte galvanic cells containing the Cr, CrCl<sub>2</sub> electrode. The cell utilized was



over the temperature range of 530–800 K. The emf measurements produced a  $\Delta_f G_m^\circ = (-380.210 + 0.10458 \times T)$  kJ·mol<sup>-1</sup> for the formation of CrCl<sub>2</sub> according to the reaction: Cr(cr) + Cl<sub>2</sub>(g) = CrCl<sub>2</sub>(cr). The  $\Delta_f H_m^\circ$  of crystalline CrCl<sub>2</sub> was calculated from the  $\Delta_f G_m^\circ$  for the formation of crystalline CrCl<sub>2</sub> 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. CrCl<sub>2</sub>(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:

$$\Delta_f H_m^\circ(298.15 \text{ K}): -477.8 \text{ kJ}\cdot\text{mol}^{-1} (-114.2 \text{ kcal}\cdot\text{mol}^{-1}).$$

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 so-

lution of crystalline chromium (II) chloride. Therefore,  $\Delta_f H_m^\circ(\text{CrCl}_2, \text{aq}) = \Delta_f H_m^\circ(\text{CrCl}_2, \text{cr}) + \Delta_{\text{soln}} H_m^\circ(\text{CrCl}_2, \text{cr}) = [(-395.64) + (-77.8)] \text{ kJ}\cdot\text{mol}^{-1} = -473.46 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-113.16 \text{ kcal}\cdot\text{mol}^{-1}$ ) which would round to  $-473.5 \text{ kJ}\cdot\text{mol}^{-1}$  ( $113.2 \text{ kcal}\cdot\text{mol}^{-1}$ ). The NBS tables selected a value of  $-477.8 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-114.2 \text{ kcal}\cdot\text{mol}^{-1}$ ) and not the calculated value of  $-473.5 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-113.2 \text{ kcal}\cdot\text{mol}^{-1}$ ).

**B. Comments on NBS Selected Values**

The  $\Delta_f H_m^\circ(\text{CrCl}_2, \text{cr}) = -395.64 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-94.56 \text{ kcal}\cdot\text{mol}^{-1}$ ) is an earlier NBS value but the selected value that was derived from 62STO/CHI and  $\Delta_f H_m^\circ(\text{CrCl}_2, \text{cr}) = -395.47 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-94.52 \text{ kcal}\cdot\text{mol}^{-1}$ ) should have been used. The result would be  $-473.29 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-113.12 \text{ kcal}\cdot\text{mol}^{-1}$ ) which would round off to  $-473.3 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-113.1 \text{ kcal}\cdot\text{mol}^{-1}$ ). The NBS selected value of  $-477.8 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-114.2 \text{ kcal}\cdot\text{mol}^{-1}$ ) seems to have been a transcription error that was discussed earlier under the aqueous Cr<sup>2+</sup> species.

**C. Auxiliary Values Required for Data Pathway**

$$\Delta_f H_m^\circ(\text{CrCl}_2, \text{cr})$$

**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. CrCl<sub>2</sub>·2H<sub>2</sub>O (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:

$$\Delta_f H_m^\circ(298.15 \text{ K}): -992.0 \text{ kJ}\cdot\text{mol}^{-1} (-237.1 \text{ kcal}\cdot\text{mol}^{-1}).$$

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



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

$$\begin{aligned}\Delta_f H_m^\circ(\text{CrCl}_2 \cdot 2\text{H}_2\text{O}, \text{cr}) &= \Delta_{rxn} H_m^\circ - \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{g}) + \Delta_f H_m^\circ(\text{CrCl}_2 \cdot 3\text{H}_2\text{O}, \text{cr}) \\ &= [58.6 - (-241.84) + (-1292.4)] \text{kJ} \cdot \text{mol}^{-1} \\ &= -992.0 \text{ kJ} \cdot \text{mol}^{-1} \quad (-237.1 \text{ kcal} \cdot \text{mol}^{-1}).\end{aligned}$$

### B. Comments on NBS Selected Values

None.

### C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m^\circ(\text{CrCl}_2 \cdot 3\text{H}_2\text{O}, \text{cr})$$

$$\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{g})$$

### 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).

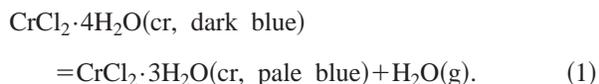
## 23. CrCl<sub>2</sub>·3H<sub>2</sub>O (cr, pale blue)

### 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

$$\begin{aligned}\Delta_f H_m^\circ(298.15 \text{ K}): \\ -1292.4 \text{ kJ} \cdot \text{mol}^{-1} \quad (-308.9 \text{ kcal} \cdot \text{mol}^{-1}).\end{aligned}$$

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



From a van't Hoff plot they calculated  $\Delta_{rxn} H_m^\circ = 74.1 \text{ kJ} \cdot \text{mol}^{-1}$  (17.7 kcal·mol<sup>-1</sup>) from the slope. The

$$\begin{aligned}\Delta_f H_m^\circ(\text{CrCl}_2 \cdot 3\text{H}_2\text{O}, \text{cr}) \\ = \Delta_{rxn} H_m^\circ - \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{g}) + \Delta_f H_m^\circ(\text{CrCl}_2 \cdot 4\text{H}_2\text{O}, \text{cr}) \\ = [74.1 - (-241.84) + (-1608.3)] \text{kJ} \cdot \text{mol}^{-1} \\ = -1292.4 \text{ kJ} \cdot \text{mol}^{-1} \quad (-308.9 \text{ kcal} \cdot \text{mol}^{-1}).\end{aligned}$$

### B. Comments on NBS Selected Values

None.

### C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m^\circ(\text{CrCl}_2 \cdot 4\text{H}_2\text{O}, \text{cr})$$

$$\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{g})$$

### 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).

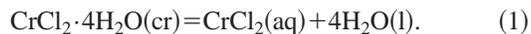
## 24. CrCl<sub>2</sub>·4H<sub>2</sub>O (cr, dark blue)

### 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

$$\begin{aligned}\Delta_f H_m^\circ(298.15 \text{ K}): \\ -1608.3 \text{ kJ} \cdot \text{mol}^{-1} \quad (-384.4 \text{ kcal} \cdot \text{mol}^{-1}).\end{aligned}$$

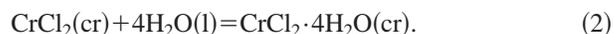
The NBS table value was calculated two (2) ways from the results of 1886REC. In the first method, 1886REC measured the enthalpy of solution of crystalline chromium (II) chloride,  $\Delta_{rxn} H_m^\circ = -8.4 \text{ kJ} \cdot \text{mol}^{-1}$  (-2.0 kcal·mol<sup>-1</sup>), for the following reaction:



The

$$\begin{aligned}\Delta_f H_m^\circ(\text{CrCl}_2, \text{aq}) \\ = -\Delta_{rxn} H_m^\circ + 4 \times \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) \\ - \Delta_f H_m^\circ(\text{CrCl}_2 \cdot 4\text{H}_2\text{O}, \text{cr}) \\ = [+8.37 + (-473.6) + 4 \times (-285.83)] \text{kJ} \cdot \text{mol}^{-1} \\ = -1608.3 \text{ kJ} \cdot \text{mol}^{-1} \quad (-384.4 \text{ kcal} \cdot \text{mol}^{-1}).\end{aligned}$$

In the second method, also from 1886REC, the measured enthalpy of reaction,  $\Delta_{rxn} H_m^\circ = -69.5 \text{ kJ} \cdot \text{mol}^{-1}$  (-16.6 kcal·mol<sup>-1</sup>) was used based upon the following reaction:



$$\begin{aligned}\Delta_f H_m^\circ(\text{CrCl}_2 \cdot 4\text{H}_2\text{O}, \text{cr}) \\ = \Delta_{rxn} H_m^\circ + \Delta_f H_m^\circ(\text{CrCl}_2, \text{aq}) + 4 \times \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) \\ = [-69.5 + (-395.4) + 4 \times (-285.830)] \text{kJ} \cdot \text{mol}^{-1}\end{aligned}$$

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

The two methods produced identical results.

### B. Comments on NBS Selected Values

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

### C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m^\circ(\text{CrCl}_2, \text{cr})$$

$$\Delta_f H_m^\circ(\text{CrCl}_2, \text{aq})$$

$$\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{liq})$$

### 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. CrCl<sub>3</sub> (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

$$\Delta_f H_m^\circ(0 \text{ K}): -556.30 \text{ kJ}\cdot\text{mol}^{-1} \text{ } (-132.96 \text{ kcal}\cdot\text{mol}^{-1})$$

$$\Delta_f H_m^\circ(298.15 \text{ K}): -556.5 \text{ kJ}\cdot\text{mol}^{-1} \text{ } (-133.0 \text{ kcal}\cdot\text{mol}^{-1})$$

$$\Delta_f G_m^\circ(298.15 \text{ K}): -486.1 \text{ kJ}\cdot\text{mol}^{-1} \text{ } (-116.2 \text{ kcal}\cdot\text{mol}^{-1})$$

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

$$17.66 \text{ kJ}\cdot\text{mol}^{-1} \text{ } (4.22 \text{ kcal}\cdot\text{mol}^{-1})$$

$$S_m^\circ(298.15 \text{ K}): 123.0 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \text{ } (29.4 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$$

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

$$91.80 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \text{ } (21.94 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}).$$

The values for  $[H_m^\circ(298.15 \text{ K}) - H_m^\circ(0 \text{ K})]$ ,  $C_{p,m}^\circ$  and  $S_m^\circ$  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.

$\Delta_f H_m^\circ$  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



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



1887REC determined a  $\Delta_{rxn} H_m^\circ = -164.8 \text{ kJ}\cdot\text{mol}^{-1}$  per mole of  $\text{CrCl}_3$  for the oxidation in reaction (1). No correction was used to correct the measured enthalpy to 25 °C.  $\Delta_f H_m^\circ(\text{CrCl}_3, \text{cr}) = \Delta_{rxn} H_m^\circ + \Delta_f H_m^\circ(\text{CrCl}_2, \text{cr}) = [(-164.8) + (-395.4)] \text{ kJ}\cdot\text{mol}^{-1} = -560.2 \text{ kJ}\cdot\text{mol}^{-1}$ .

39SAN determined the  $K_{eq}$  from partial pressures of HCl and  $\text{H}_2$  gases at several temperatures between 600 and 700 °C for the reduction in reaction (2). His  $\Delta_{rxn} H_m^\circ = 93.01 \text{ kJ}\cdot\text{mol}^{-1}$  at 650 °C from the slope of his fitted data was calculated to be  $\Delta_{rxn} H_m^\circ = 97.5 \text{ kJ}\cdot\text{mol}^{-1}$  at 25 °C. The  $\Delta C_{p,m}^\circ$  was calculated as  $-12.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  for reaction (2). Therefore,

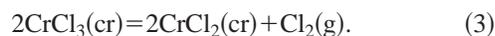
$$\begin{aligned} \Delta_f H_m^\circ(\text{CrCl}_3, \text{cr}) &= [-\Delta_{rxn} H_m^\circ + 2 \times \Delta_f H_m^\circ(\text{CrCl}_2, \text{cr}) \\ &\quad + 2 \times \Delta_f H_m^\circ(\text{HCl}, \text{g})] / 2 \\ &= \{ [(-97.5) + 2 \times (-395.4) \\ &\quad + 2 \times (-92.307)] / 2 \} \text{ kJ}\cdot\text{mol}^{-1} \\ &= -536.4 \text{ kJ}\cdot\text{mol}^{-1}. \end{aligned}$$

29JEL/KOO determined a  $\Delta_{rxn} H_m^\circ = -280.12 \text{ kJ}\cdot\text{mol}^{-1}$  for the oxidation of reaction (1) at 736 K. This was corrected to  $\Delta_{rxn} H_m^\circ = -285.62 \text{ kJ}\cdot\text{mol}^{-1}$  of  $\text{Cl}_2$  at 298 K using a  $\Delta C_{p,m}^\circ = 12.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . This produced a  $\Delta_f H_m^\circ(\text{CrCl}_3, \text{cr}) = -538.1 \text{ kJ}\cdot\text{mol}^{-1}$ .

37DOE determined a  $\Delta_{rxn} H_m^\circ = -307.9 \text{ kJ}\cdot\text{mol}^{-1}$  of  $\text{Cl}_2$  for the oxidation of reaction (1) at 298 K. This produced a  $\Delta_f H_m^\circ(\text{CrCl}_3, \text{cr}) = -549.4 \text{ kJ}\cdot\text{mol}^{-1}$ .

58FLE/ING measured the electrode potential in two cells from 973 to 1173 K. The overall reaction was  $\text{CrCl}_2(\text{cr}) + \text{AgCl}(\text{cr}) = \text{CrCl}_3(\text{cr}) + \text{Ag}(\text{cr})$ . The  $\Delta_{rxn} H_m^\circ = -49.54 \text{ kJ}\cdot\text{mol}^{-1}$  at 1073 K corrected to  $\Delta_{rxn} H_m^\circ = -46.28 \text{ kJ}\cdot\text{mol}^{-1}$  at 298 K and yielded a  $\Delta_f H_m^\circ(\text{CrCl}_3, \text{cr}) = -568.6 \text{ kJ}\cdot\text{mol}^{-1}$ .

42MAI measured the vapor pressure of  $\text{Cl}_2$  for the reverse of reaction (1)



The  $\Delta_{rxn} H_m^\circ = 294.68 \text{ kJ}\cdot\text{mol}^{-1}$  at 298 K yielded a  $\Delta_f H_m^\circ(\text{CrCl}_3, \text{cr}) = -542.7 \text{ kJ}\cdot\text{mol}^{-1}$ .

The selected value was  $\Delta_f H_m^\circ(\text{CrCl}_3, \text{cr}) = -556.5 \text{ kJ}\cdot\text{mol}^{-1}$ . 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  $-568.6 \text{ kJ}\cdot\text{mol}^{-1}$  and all values less than  $-544 \text{ kJ}\cdot\text{mol}^{-1}$  were rejected. However, there is no evidence on the worksheets to support this hypothesis or to indicate how this value was obtained.

The  $\Delta_f H_0^\circ = -556.30 \text{ kJ}\cdot\text{mol}^{-1}$  was calculated as  $\Delta_f H_0^\circ = \Delta_f H_m^\circ(298.15 \text{ K}) - \Delta(H_{298 \text{ K}}^\circ - H_{0 \text{ K}}^\circ)$  for the formation reaction,



Therefore,  $\Delta_f H_0^\circ = \Delta_f H_m^\circ(298.15 \text{ K}) - \Delta(H_{298 \text{ K}}^\circ - H_{0 \text{ K}}^\circ) = \{-556.5 - [17.66 - 4.058 - 1.5 \times 9.176]\} \text{ kJ}\cdot\text{mol}^{-1} = -556.30 \text{ kJ}\cdot\text{mol}^{-1}$ .

The  $\Delta_f G_{298 \text{ K}}^\circ = -486.2 \text{ kJ}\cdot\text{mol}^{-1}$  was calculated from the relation of  $\Delta G_m^\circ = \Delta_f H_m^\circ - T\Delta_f S_m^\circ$ . The  $\Delta_f S_m^\circ$  was calculated from the formation reaction, reaction (4), as  $\Delta_f S_m^\circ = \Delta(S^\circ)$ . Therefore,

$$\begin{aligned} \Delta_f S_m^\circ &= [123.0 - 23.7 - 1.5 \times 222.96] \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \\ &= -235.19 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}. \end{aligned}$$

Then

$$\begin{aligned} \Delta_f G_{298 \text{ K}}^\circ &= [-556.5 - 298.15 \times (-0.23519)] \text{ kJ}\cdot\text{mol}^{-1} \\ &= -486.2 \text{ kJ}\cdot\text{mol}^{-1}. \end{aligned}$$

### B. Comments on NBS Selected Values

The actual method used to select the  $\Delta_f H_m^\circ(\text{CrCl}_3, \text{cr})$  was not clearly identified. See the comments under Section A.

### C. Auxiliary Values Required for Data Pathway

$$\begin{aligned} &\Delta_f H_m^\circ(\text{CrCl}_2, \text{cr}) \\ &\Delta_f H_m^\circ(\text{HCl}, \text{g}) \\ &\Delta_f H_m^\circ(\text{AgCl}, \text{cr}) \\ &[H_{298 \text{ K}}^\circ - H_{0 \text{ K}}^\circ](\text{Cr}, \text{cr}) \\ &[H_{298 \text{ K}}^\circ - H_{0 \text{ K}}^\circ](\text{Cl}_2, \text{g}) \\ &[H_{298 \text{ K}}^\circ - H_{0 \text{ K}}^\circ](\text{CrCl}_3, \text{g}) \\ &S_m^\circ(\text{Cr}, \text{cr}) \\ &S_m^\circ(\text{Cl}_2, \text{g}) \\ &S_m^\circ(\text{CrCl}_3, \text{cr}) \end{aligned}$$

### 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.

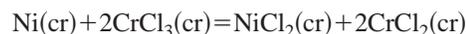
42VON measured the enthalpy of solution of  $\text{CrCl}_3$  in aqueous HCl and the enthalpy of formation of aqueous  $\text{CrCl}_3$  by reacting Cr with HCl. These reactions were combined to obtain the enthalpy of formation of crystalline  $\text{CrCl}_3$ . A  $\Delta_f H_m^\circ = -564.8 \text{ kJ}\cdot\text{mol}^{-1}$  was calculated.

### E. Additional Determinations of the Thermodynamic Properties

68KOS made heat capacity measurements of anhydrous  $\text{CrCl}_3$  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  $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .

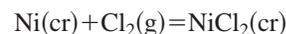
73KOS/LUK made heat capacity measurements of anhydrous  $\text{CrCl}_3$  from 4.5 to 20 K in magnetic fields of 0, 870, 5800, and 8100 H. At  $T < 12 \text{ K}$ , the heat capacity was independent of the magnetic field. At  $T \leq 10 \text{ K}$ , the experimental data fit the equation  $C = 0.0535 \times T + 5.11 \times 10^{-4} \times T^3$ , where  $C$  was expressed in  $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .

75GEE/SHE used a mixture of crystalline  $\text{CrCl}_2$  and  $\text{CrCl}_3$  as a chlorine electrode to obtain the Gibbs energy of formation  $\text{CrCl}_3$  by the emf method.  $\text{emf} = -217.6 + 0.617 \times T$  was obtained from 570 to 680 K for the cell:  $\text{Pt}|\text{Ni}, \text{NiCl}_2|\text{PbCl}_2|\text{CrCl}_2, \text{CrCl}_3|\text{Pt}$ . They calculated for the cell reaction:

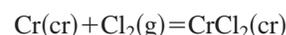


$$\Delta_{rxn} G_m^\circ = (42.000 - 0.119 \times T) \text{ kJ}\cdot\text{mol}^{-1}.$$

The same authors, 76GEE/SHE, made other emf measurements to determine  $\Delta_{rxn} G_m^\circ$  for the formation of  $\text{NiCl}_2(\text{cr})$  and  $\text{CrCl}_2$  according to the reactions:

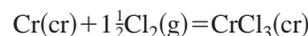


$$\Delta_{rxn} G_m^\circ = (-310.110 + 0.15685 \times T) \text{ kJ}\cdot\text{mol}^{-1}$$



$$\Delta_{rxn} G_m^\circ = (-380.210 + 0.10458 \times T) \text{ kJ}\cdot\text{mol}^{-1}.$$

Addition and subtraction of the three reactions produced:



$$\Delta_{rxn} G_m^\circ = (-556.260 + 0.24238 \times T) \text{ kJ}\cdot\text{mol}^{-1}.$$

A third law  $\Delta_f H_m^\circ = -553.0 \pm 5.0 \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{CrCl}_3(\text{cr})$  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  $\Delta_f H_m^\circ = -544.4 \pm 10.5 \text{ kJ}\cdot\text{mol}^{-1}$  was determined for chromium (III) chloride according to the following reaction:  $\text{Cr}(\text{cr}, \text{cubic}) + 1.5 \text{ Cl}_2(\text{g}) = \text{CrCl}_3(\text{cr}, \text{hexagonal})$ .

### F. Bibliography

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

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- 39SAN Sano, K., J. Chem. Soc. Jpn. **59**, 17 (1939).
- 42MAI Maier, C. G., U.S. Bur. Mines, Bull. **436**, 109pp (1942).
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- 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. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3(\text{aq}, \text{violet})$

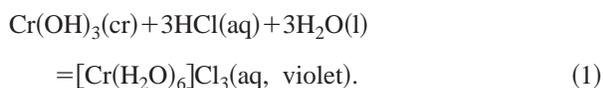
### A. Selected Values, NBS Tables

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:

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

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

$\Delta_f H_m^\circ$  came from the average of two (2) sets of 15 °C measurements as described in 1886REC. A  $\Delta_{rxn} H_m^\circ = -86.6 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-20.7 \text{ kcal}\cdot\text{mol}^{-1}$ ) 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)



$$\Delta_f H_m^\circ([\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3, \text{aq})$$

$$= \Delta_{rxn} H_m^\circ + 3 \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l})$$

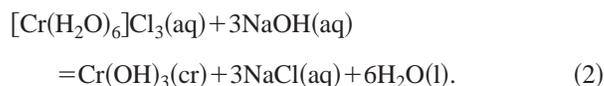
$$+ 3 \Delta_f H_m^\circ(\text{HCl}, \text{aq}) + \Delta_f H_m^\circ(\text{Cr}(\text{OH})_3, \text{cr})$$

$$= [-85.4 + 3(-285.830)$$

$$+ 3(-165.94)_{100} + (-1064.0)] \text{ kJ}\cdot\text{mol}^{-1}$$

$$= -2504.7 \text{ kJ}\cdot\text{mol}^{-1} \quad (-598.6 \text{ kcal}\cdot\text{mol}^{-1}),$$

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



$$\Delta_f H_m^\circ([\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3, \text{aq})$$

$$= (-\Delta_{rxn} H_m^\circ) + \Delta_f H_m^\circ(\text{Cr}(\text{OH})_3, \text{cr})$$

$$+ 3 \Delta_f H_m^\circ(\text{NaCl}, \text{aq}) + 6 \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l})$$

$$- 3H \Delta_f H_m^\circ(\text{NaOH}, \text{aq})$$

$$= [+92.9 + (-1064.0) + 3(-406.98)$$

$$+ 6(-285.830) - 3(-469.78)] \text{ kJ}\cdot\text{mol}^{-1}$$

$$= -2497.7 \text{ kJ}\cdot\text{mol}^{-1} \quad (-597.0 \text{ kcal}\cdot\text{mol}^{-1}).$$

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  $\Delta_{rxn} H_m^\circ = -86.6 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-20.7 \text{ kcal}\cdot\text{mol}^{-1}$ ) 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  $\Delta_{rxn} H_m^\circ$  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  $\Delta_f H_m^\circ(\text{NaOH}, \text{aq})$  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

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

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

$$\Delta_f H_m^\circ(\text{Cr}(\text{OH})_3, \text{cr})$$

$$\Delta_f H_m^\circ(\text{NaCl}, \text{aq})$$

$$\Delta_f H_m^\circ(\text{NaOH}, \text{aq})$$

### 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)<sub>3</sub>(cr)

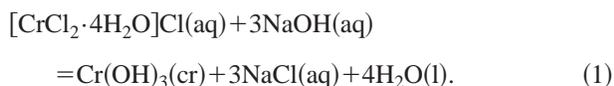
### A. Selected Values, NBS Tables

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

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

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

The enthalpy of formation value was calculated from an experimentally determined enthalpy of reaction for the precipitation of Cr(OH)<sub>3</sub>. 1886REC had a  $\Delta_{rxn} H_m^\circ = -131.8 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-31.5 \text{ kcal}\cdot\text{mol}^{-1}$ ) for the following reaction:



$$\Delta_f H_m^\circ(\text{Cr}(\text{OH})_3, \text{cr})$$

$$= \Delta_{rxn} H_m^\circ - 3 \times \Delta_f H_m^\circ(\text{NaCl}, \text{aq})$$

$$- 4 \times \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l})$$

$$+ 3 \times \Delta_f H_m^\circ(\text{NaOH}, \text{aq})$$

$$+ \Delta_f H_m^\circ([\text{CrCl}_2\cdot 4\text{H}_2\text{O}]\text{Cl}, \text{aq})$$

$$= [-131.8 - 3 \times (-407.0) - 4 \times (-285.830)$$

$$+ 3 \times (-469.7) + (-1887.4)] \text{ kJ}\cdot\text{mol}^{-1}$$

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

### B. Comments on NBS Selected Values

Equation (1) contained  $\Delta_f H_m^\circ = -1887.4 \text{ kJ}\cdot\text{mol}^{-1}$  for  $[\text{CrCl}_2\cdot 4\text{H}_2\text{O}]\text{Cl}(\text{aq})$ . This value was obtained from 1882THO's enthalpy change for the reaction  $2\text{CrO}_3(\text{aq}) + 12\text{HCl}(\text{aq}) + 3\text{SnCl}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) = 3\text{SnCl}_4(\text{aq}) + 2[\text{CrCl}_2\cdot 4\text{H}_2\text{O}]\text{Cl}(\text{aq})$ ;  $\Delta_{rxn} H_m^\circ = -219.6 \text{ kJ}\cdot\text{mol}^{-1}$ .  $\Delta_f H_m^\circ$  values for  $\text{CrO}_3(\text{aq})$ ,  $\text{HCl}(\text{aq})$ ,  $\text{SnCl}_2(\text{aq})$ ,  $\text{H}_2\text{O}(\text{l})$ ,  $\text{SnCl}_4(\text{aq})$  were  $-602.1$ ,  $-166.56$ ,  $-331.8$ ,  $-285.830$ , and  $-638.1 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively. Measurements from 32NEU/KRO and V42NON that resulted in values of  $\Delta_f H_m^\circ$  of  $-1835.1$  and  $-1825.9 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively, for  $[\text{CrCl}_2\cdot 4\text{H}_2\text{O}]\text{Cl}(\text{aq})$ , from determinations of  $\Delta_{rxn} H_m^\circ$  for



and



of  $-211.7$  and  $-202.5 \text{ kJ}\cdot\text{mol}^{-1}$ . Clearly, the enthalpy of formation of  $[\text{CrCl}_2\cdot 4\text{H}_2\text{O}]\text{Cl}(\text{aq})$  was not well determined,  $\pm 60 \text{ kJ}\cdot\text{mol}^{-1}$ , and so the tabulated enthalpy of formation of  $\text{Cr}(\text{OH})_3(\text{cr})$ , calculated this way, could be considered uncertain by about this amount.

### C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m^\circ(\text{NaCl}, \text{aq})$$

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

$$\Delta_f H_m^\circ([\text{CrCl}_2\cdot 4\text{H}_2\text{O}]\text{Cl}, \text{aq})$$

$$\Delta_f H_m^\circ(\text{NaOH}, \text{aq})$$

### 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<sub>4</sub>(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

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

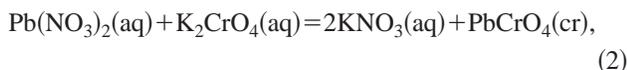
$$-930.9 \text{ kJ}\cdot\text{mol}^{-1} \quad (-222.5 \text{ kcal}\cdot\text{mol}^{-1}).$$

Enthalpy of formation values were calculated from two experimentally determined heats of reaction for the precipitation of PbCrO<sub>4</sub> 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  $\Delta_{rxn} H_m^\circ = -46.69 \text{ kJ}\cdot\text{mol}^{-1}$  for the following reaction:



$$\begin{aligned} \Delta_f H_m^\circ(\text{PbCrO}_4, \text{cr}) &= \Delta_{rxn} H_m^\circ - 2 \times \Delta_f H_m^\circ(\text{KCl}, \text{aq}) + \Delta_f H_m^\circ(\text{PbCl}_2, \text{aq}) \\ &\quad + \Delta_f H_m^\circ(\text{K}_2\text{CrO}_4, \text{aq}) = [-46.69 - 2 \times (-167.15) \\ &\quad + (-336.0) + (-881.15)] \text{ kJ} \cdot \text{mol}^{-1} \\ &= -929.54 \text{ kJ} \cdot \text{mol}^{-1} \quad (-222.17 \text{ kcal} \cdot \text{mol}^{-1}). \end{aligned}$$

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



$$\begin{aligned} \Delta_f H_m^\circ(\text{PbCrO}_4, \text{cr}) &= \Delta_{rxn} H_m^\circ - 2 \times \Delta_f H_m^\circ(\text{KNO}_3, \text{aq}) \\ &\quad + \Delta_f H_m^\circ(\text{Pb}(\text{NO}_3)_2, \text{aq}) + \Delta_f H_m^\circ(\text{K}_2\text{CrO}_4, \text{aq}) \\ &= [-44.4 - 2 \times (-207.4) + (-421.3) \\ &\quad + (-881.15)] \text{ kJ} \cdot \text{mol}^{-1} \\ &= -932.05 \text{ kJ} \cdot \text{mol}^{-1} \quad (-222.77 \text{ kcal} \cdot \text{mol}^{-1}). \end{aligned}$$

The average of these two values,  $\Delta_f H_m^\circ(\text{PbCrO}_4, \text{cr}) = -930.9 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-222.5 \text{ kcal} \cdot \text{mol}^{-1}$ ), 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  $\text{kJ} \cdot \text{mol}^{-1}$ , produced  $-930.80 \text{ kJ} \cdot \text{mol}^{-1}$ , not  $-930.9 \text{ kJ} \cdot \text{mol}^{-1}$ . Conversion of  $-930.80 \text{ kJ} \cdot \text{mol}^{-1}$  into  $-222.47 \text{ kcal} \cdot \text{mol}^{-1}$  rounds to  $-222.5 \text{ kcal} \cdot \text{mol}^{-1}$  which originally was the NBS selected value in 1966. The 1966 value was in  $\text{kcal} \cdot \text{mol}^{-1}$  at the standard conditions of 298.15 K and 1 atm of pressure. The 82WAG/EVA value was in  $\text{kJ} \cdot \text{mol}^{-1}$  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  $\Delta_f H_m^\circ(\text{PbCrO}_4, \text{cr})$ . The use of the (4.184J/1 cal) conversion factor, converts  $-222.5 \text{ kcal} \cdot \text{mol}^{-1}$  to  $-930.9 \text{ kJ} \cdot \text{mol}^{-1}$  which is the value represented in the 82WAG/EVA compilation. The rounding of the selected  $\text{kcal} \cdot \text{mol}^{-1}$  value was

done and then converted to the selected  $\text{kJ} \cdot \text{mol}^{-1}$  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  $\text{kJ} \cdot \text{mol}^{-1}$ .

### C. Auxiliary Values Required for Data Pathway

$$\begin{aligned} \Delta_f H_m^\circ(\text{PbCl}_2, \text{aq}) \\ \Delta_f H_m^\circ(\text{Pb}(\text{NO}_3)_2, \text{aq}) \\ \Delta_f H_m^\circ(\text{K}_2\text{CrO}_4, \text{aq}) \\ \Delta_f H_m^\circ(\text{KCl}, \text{aq}) \\ \Delta_f H_m^\circ(\text{KNO}_3, \text{aq}) \end{aligned}$$

### 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  $\text{PbCrO}_4$  from its elements. The results of these measurements allowed the calculation of  $\Delta_f H_m^\circ = -1052.66 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{PbCrO}_4$  which differs greatly from the NBS selected value of  $-930.9 \text{ kJ} \cdot \text{mol}^{-1}$ .

### F. Bibliography

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