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Note

Thermodynamic Properties of Chromium

J.-O. Andersson[1]

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This paper is intended as a short review of the results of thermodynamic measurements available for pure chromium. The various experimental data are combined and a set of parameters describing the Gibbs energy of each individual phase as a function of temperature and pressure is obtained.

KEY WORDS: chromium; enthalpy; heat capacity; high pressure; high temperature; thermodynamic properties.

1. INTRODUCTION

It is important to have an accurate description of the pure elements before attempting to calculate the thermodynamic properties and phase diagrams of alloy systems. This paper is intended as a short review of the experimental thermodynamic data reported for chromium and as a presentation of an assessment of the Gibbs energy for various modifications of chromium. The resulting expressions yield a reasonable accuracy (5–10%) in the temperature range 298.15–6000 K and for reasonably high pressures (up to 10 GPa).

The thermodynamic data available from the literature can be divided into two groups, i.e., heat capacity (C_P) measurements and enthalpy measurements. The C_P data are usually obtained by measuring the difference in enthalpy at two slightly different temperatures and dividing by the temperature difference. If one of the temperatures is room temperature

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[1] Division of Physical Metallurgy, Royal Institute of Technology, S-100 44 Stockholm, Sweden.

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and the other temperature is appreciably higher, the obtained value is sometimes called the mean C_P. We use such data as information on the enthalpy.

2. GIBBS ENERGY EXPRESSIONS

This report makes use of a temperature polynomial consisting of five terms together with a model for the magnetic transition developed by Inden [1] for the stable region of solid bcc chromium. The knowledge about the liquid phase is limited and a reasonable polynomial should include no more than three terms. A detailed description of the method used to extrapolate C_P of the solid phase above the melting point and the C_P of the liquid phase below the melting point is given by Fernandez Guillermet [2].

The pressure dependencies of Gibbs energy for the phases are included in the final expression using a model for the molar volume described by Fernandez Guillermet [2]. For the gas phase an ideal pressure dependence is assumed. The full expressions for G_m, with numerical values inserted for all the parameters, are given in Table I.

3. MAGNETISM

The contribution to the Gibbs energy due to the magnetic ordering of a phase is evaluated with reference to an ideal paramagnetic state where the magnetic moments are completely disordered. The following formula is given by Hillert and Jarl [3] to represent this magnetic contribution. τ is a normalized temperature, T/T_C, where T_C is the Curie of Néel temperature.

$$G_{\mathrm{m}}^{\mathrm{mo}} = RT\ln(\beta+1)\,f(\tau) \qquad (1)$$

For $\tau < 1$,

$$f(\tau) = 1 - \left[\frac{79\tau^{-1}}{140p} + \frac{474}{497} - \left(\frac{1}{p} - 1\right)\left(\frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600}\right)\right]\Big/ A \qquad (2)$$

For $\tau \geqslant 1$,

$$f() = -\left(\frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500}\right)\Big/ A \qquad (3)$$

where

$$A = \frac{518}{1125} + \frac{11{,}692}{15{,}975}\,(1/p - 1)$$

Table I. Summary of Parameters for Chromium
[All Data in SI Units (J, mol, K)]

Element,	Stable element reference,	Mass,	$H_{298}-H_0$,	S_{298},
Cr	bcc Cr	51.996	4050	23.56

Solid

$G(\text{bcc, Cr}) - H_{298}(\text{bcc, Cr}) =$

$298.15 < T < 311.5$:

$$\begin{aligned} &-8841.93 + 157.48\,T - 26.908\,T\ln(T) + 0.00189435\,T^2 \\ &\quad - 1.47721\times10^{-6}\,T^3 + 139{,}250\,T^{-1} - 15.9112 + 0.0662512\,T \\ &\quad - 26.8922[(T/311.5)^4/6 + (T/311.5)^{10}/135 + (T/311.5)^{16}/600] \\ &\quad + 7.188\times10^{-6}[(1 + 2.6\times10^{-11}\,P)^{0.8} - 1]\exp(1.7\times10^{-6}\,T \\ &\quad + 9.2\times10^{-9}\,T^2)/2.08\times10^{-11} \end{aligned}$$

$311.5 < T < 2180.00$:

$$\begin{aligned} &-8851.93 + 157.48\,T - 26.908\,T\ln(T) + 0.00189435\,T^2 - 1.47721\times10^{-6}\,T^3 \\ &\quad + 139{,}250\,T^{-1} + 7.88\times10^{-6}[(1 + 2.6\times10^{-11}\,P)^{0.8} - 1] \\ &\quad \times\exp(1.7\times10^{-6}\,T + 9.2\times10^{-9}\,T^2)/2.08\times10^{11} \end{aligned}$$

$2180.00 < T < 6000.00$:

$$\begin{aligned} &-34{,}864 + 344.18\,T - 50\,T\ln(T) - 2.88526\times10^{32}\,T^{-9} \\ &\quad + 7.188\times10^{-6}[(1 + 2.6\times10^{-11}\,P)^{0.8} - 1] \\ &\quad \times\exp(1.7\times10^{-6}\,T + 9.2\times10^{-9}\,T^2)/2.08\times10^{-11} \end{aligned}$$

$\beta(\text{bcc, Cr}) = 0.008$
$T_C(\text{bcc, Cr}) = 311.5$

Gas

$G(\text{Gas, Cr}) - H_{298}(\text{bcc, Cr}) =$

$298.15 < T < 800.00$:

$$391{,}905.7 - 130.81\,T - 20.7861\,T\ln(T) + RT\ln(P/101{,}325)$$

$800.00 < T < 1200.00$:

$$\begin{aligned} &391{,}703.8 - 126.821\,T - 21.4288\,T\ln(T) + 8.23558\times10^{4}\,T^2 \\ &\quad - 1.82785\times10^{-7}\,T^3 + 11071.9\,T^{-1} + RT\ln(P/101{,}325) \end{aligned}$$

$1200.00 < T < 2200.00$:

$$\begin{aligned} &401{,}183.5 - 184.883\,T - 13.83336\,T\ln(T) - 0.00108035\,T^2 \\ &\quad - 2.20692\times10^{-7}\,T^3 - 1{,}931{,}730\,T^{-1} + RT\ln(P/101{,}325) \end{aligned}$$

$2200.00 < T < 3600.00$:

$$\begin{aligned} &393{,}019.0 - 198.327\,T - 10.996\,T\ln(T) - 0.00448127\,T^2 \\ &\quad + 1.1658\times10^{-7}\,T + 3{,}710{,}580\,T^{-1} + RT\ln(P/101{,}325) \end{aligned}$$

Table I. *(Continued)*

Element, Cr	Stable element reference, bcc Cr	Mass, 51.996	$H_{298}-H_0$, 4050	S_{298}, 23.56

$3600.00 < T < 4800.00$:

$$304{,}527.7 + 160.8627\,T - 55.8648\,T\ln(T) + 0.0053938\,T^2 - 2.83633\times10^{-7}\,T + 35{,}390{,}400\,T^{-1} + RT\ln(P/101{,}325)$$

$48.00.00 < T < 6000.00$:

$$853{,}670.9 - 1290.85\,T + 115.378\,T\ln(T) - 0.0183853\,T^2 + 3.3669\times10^{-7}\,T - 2.95432\times10^{8}\,T^{-1} + RT\ln(P/101{,}325)$$

Liquid

$G(\text{liquid, Cr}) - H_{298}(\text{bcc, Cr}) =$

$298.15 < T < 2180.00$:

$$+15{,}484 + 146.06\,T - 26.908\,T\ln(T) + 0.00189435\,T^2 - 1.47721\times10^{-6}\,T^3 + 139{,}250\,T^{-1} + 2.37615\times10^{-21}\,T^7 + 7.188\times10^{-6}[(1+4.65\times10^{-11}\,P)^{0.8}-1] \times\exp(1.7\times10^{-6}\,T + 9.2\times10^{-9}\,T^2)/3.72\times10^{-11}$$

$2180.00 < T < 6000.00$:

$$-16{,}459 + 335.618\,T - 50\,T\ln(T) + 7.188\times10^{-6}[(1+4.65\times10^{-11}\,P)^{0.8}-1] \times\exp(1.7\times10^{-6}\,T + 9.2\times10^{-9}\,T^2)/3.72\times10^{-11}$$

The factor p is the fraction of the total magnetic enthalpy absorbed above the critical temperature. For ferromagnetic bcc phases Inden suggested the value of $p = 0.4$. However, bcc chromium is antiferromagnetic and the experimental C_P data for chromium by Beaumont et al. [4] and Williams et al. [5] show that the magnetic contribution above the critical temperature is negligible. It is thus suggested that $p = 0$ should be a reasonable approximation for antiferromagnetic elements and alloys. The maximum value of the magnetic part of the C_P curve predicted by Eq. (3) with a β value of about 0.4 Bohr magneton, obtained from magnetic measurements, is much too large. Instead a hypothetic β value was evaluated to fit the C_P data of Beaumont et al. [4]. It may be called the thermodynamic β.

$$\beta = 0.008 \tag{4}$$

$$T_C = 311.5\ \text{K} \tag{5}$$

4. SELECTED DATA

C_P measurements below 298.15 K were included in this assessment for the sole purpose of obtaining reasonable extrapolations of data to lower temperatures. The data given by Kalsevich et al. [6] and Beaumont et al. [4] were considered. The latter report shows experimental evidence of a magnetic contribution to the C_P curve due to the antiferromagnetic transition at 311.5 K. This value of the Néel temperature was selcted by Gurvich et al. [7] and it is used in the present assessment. In the final stage of this work a report by Williams et al. [5] was found. Their data are in general agreement with those of Beaumont et al. [4] and also with the values calculated from the Gibbs energy expression derived in the present work. As a consequence it was not considered necessary to modify the assessment. Values for the difference in enthalpy and entropy between 0 and 298.15 K were taken from the selected data of Gurvich et al. [7]:

$$H_\mathrm{m}(298.15) - H_\mathrm{m}(0) = 4050 \pm 40\ \mathrm{J \cdot mol^{-1}} \tag{6}$$

$$S_\mathrm{m}(298.15) = 23.56 \pm 0.2\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}} \tag{7}$$

Thermodynamic studies of pure chromium above room temperature have been published by a number of authors. Armstrong and Grayson-Smith [8] have measured C_P between 298 and 1073 K and their results are considered fairly accurate. Other C_P measurements have been made by Krauss [9] (964–1598 K) and Kohlhaas et al. [10] (320–1800 K) and these were also considered. Recent measurements by Bendick and Pepperhoff [11] were disregarded due to the increasing discrepancy with other authors above 1000 K. Enthalpy measurements over a large temperature interval have been published by Chekhovskoy and Zhukova [12] (561.2–2096.2 K) as well as by Conway and Hein [13] (1267–2108 K). The latter report was not available and the values used in the present assessment were values quoted by Hoch [14].

The temperature and enthalpy of melting were assessed by Gurvich et al. [7] and their choice was accepted:

$$T_\mathrm{m} = 2180 \pm 20\ \mathrm{K} \tag{8}$$

$$H_\mathrm{m}(\mathrm{liquid}) - H_\mathrm{m}(\mathrm{solid}) = 21{,}000\ \mathrm{J \cdot mol^{-1}} \tag{9}$$

There are no experimental thermodynamic data for pure liquid chromium in the literature. A constant value of C_P ar zero pressure was thus selected, in accordance with an estimation made by Gurvich et al. [7]:

$$C_P(\mathrm{liquid}) = 50\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}} \tag{10}$$

Table II. Uncertainties Assigned to Experimental Values of Chromium Used in the Optimization Program[a]

Investigator(s)	Ref. No.	Temp. range	Error (%)
Beaumont et al.	4		2.0
Kalsevich	6		2.0
Armstrong and Grayson-Smith	8		1.0
Krauss	9	Low	2.5
Krauss	9	Mid	4.0
Krauss	9	High	6.0
Kohlhaas et al.	10		2.0
Chekhovskoy and Zhukova	12		1.0
Chekhovskoy and Zhukova	12	High	3.0
Conway and Hein	13		1.0

[a] The errors were estimated from claims made by the various investigators.

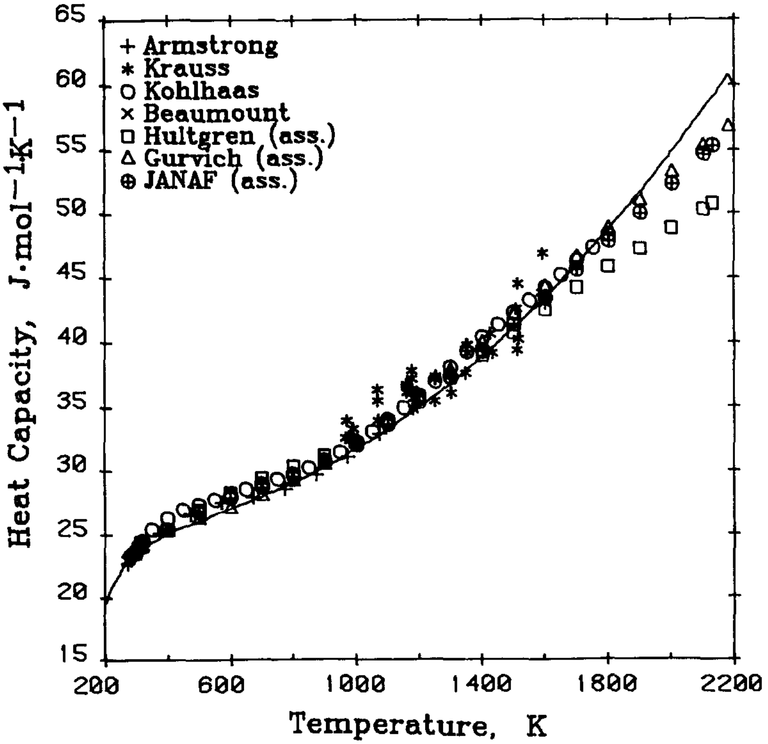

Fig. 1. The calculated and measured heat capacity (C_p) values for bcc chromium. Note that the magnetic contribution is to small to be detected in this plot.

The molar volume of bcc chromium was evaluated by fitting the suggested thermal expansivity given by Touloukian and Ho [15], the compression data of Ming and Manghnani [16], and the molar volume at 298 K and 1 atm given by Pearson [17]. These is very little information on the volume of the liquid phase. The density at the melting point determined by Saito et al. [18] and later confirmed by Waseda and Tamaki [19] was accepted and use as the only experimental value taken into account for the liquid.

C_P values for the chromium gas phase from the *JANAF* tables [20] have been fitted to a set of polynomials valid in different temperature regions by Rand [21]. The Gibbs energy was obtained using the *JANAF* entropy value and gas pressure at 1800 K. The expression is given in Table I.

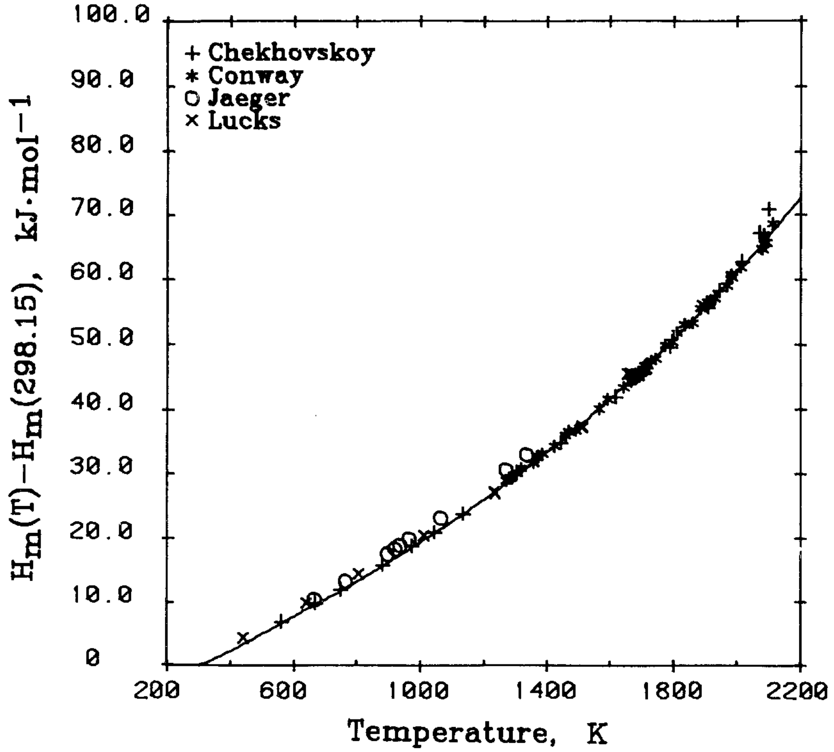

Fig. 2. The calculated and measured enthalpy values for bcc chromium referred to bcc chromium at 298.15 K.

5. RESULTS

The above-mentioned thermodynamic experimental data, altogether 204 pieces of information, weighted with the reltive error given in Table II were optimized to obtain the best possible expression for the Gibbs energy. The sum of squares in the final run was about 180, which indicates that most of the recalculated values fell within the assumed error interval. A comparison with the calculated C_P curve and the experimentally determined points is given in Fig. 1. The diagram also includes the estimated C_P values of Gurvich et al. [7], the *JANAF* tables [20], and Hultgren et al. [22]. It may be of interest to note that the present calculation falls very close to the values of Gurvich et al. [7] except at high temperatures. The obvious reason for this discrepancy can be found in Fig. 2, wgere enthalpy versus temperature is plotted. Gurvich et al. [7] have probably given little attention to the high-temperature measurements of Chekhovskoy and Zhukova [12] and Conway and Hein [13], who have both found an increasing slope of the enthalpy curve. The values in Fig. 2 referring to Jaeger and Rosenbohm [23] and Lucks and Deem [24] were taken from a diagram provided by Rand [21].

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