ELSEVIER

Journal of Alloys and Compounds 321 (2001) 138–145

Journal of ALLOYS AND COMPOUNDS

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Thermodynamic studies on chromium carbides by the electromotive force (emf) method[☆]

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Received 16 January 2001; accepted 1 February 2001

Abstract

The Gibbs energies of formation $\Delta_f G^\circ$ of the three carbides Cr_3C_2, Cr_7C_3 and $Cr_{23}C_6$ existing in the Cr–C system were re-determined by electromotive force (emf) measurements between 930 and 1120 K using the galvanic cells Cr, $CrF_2|CaF_2|CrF_2$, Cr_mC_n, Cr_pC_q which give at 1100 K: $\Delta_f G^\circ \langle Cr_3C_2 \rangle = -84.3$ kJ/mol, $\Delta_f G^\circ \langle Cr_7C_3 \rangle = -177$ kJ/mol and $\Delta_f G^\circ \langle Cr_{23}C_6 \rangle = -407$ kJ/mol. The third-law enthalpies of formation $\Delta_f H^\circ$ at 298 K were evaluated to be $\Delta_f H^\circ \langle Cr_3C_2 \rangle = -72.3$ kJ/mol, $\Delta_f H^\circ \langle Cr_7C_3 \rangle = -144$ kJ/mol and $\Delta_f H^\circ \langle Cr_{23}C_6 \rangle = -344$ kJ/mol. Previous investigations by other authors diverge from these results up to ±50%. Obsolete thermodynamic data of Cr_2O_3 used in oxygen combustion calorimetry and in CO equilibrium pressure measurements as well as an oxycarbide formation may be the reasons. The experimental difficulties of emf measurements using a CaF_2 electrolyte are outlined. Recommended $\Delta_f G^\circ$ values of the chromium carbides are given. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Transition metal compounds; Electromotive force; Thermodynamic properties; Enthalpy

1. Introduction

The chromium–carbon system is characterised by three intermediate compounds, $Cr_{23}C_6$, Cr_7C_3 and Cr_3C_2, with narrow homogeneity ranges. Accurate investigations of the phase boundaries of the system have not yet been carried out. However, the homogeneity ranges of the carbides were recently determined between 1200 and 1400°C by X-ray microanalysis [1]. Assessments of the phase diagram of the Cr–C system are reported by Storms [2] and by Massalski [3]. The latter is essentially based on the experimental work of Rudy [4], which is confirmed in all details by Knotek et al. [5]. Further references on the phase diagram of the Cr–C system are quoted by Schuster and Yong Du [6]. Chromium melting points are reported at 1907°C [7], 1903°C [2], 1863°C [3] and 1857°C [8–10], respectively. $Cr_{23}C_6$ melts peritectically at 1520°C [2] and 1577°C [3], respectively. Cr_7C_3 melts peritectically at 1780°C [2]; a congruent melting point at 1768°C (more probable) was quoted by Massalski [3]. Cr_3C_2 melts peritectically at 1895°C [2] and 1813°C [3], respectively.

Heat capacity results of the chromium carbides were published only by Kelley et al. [11] in 1944. All subsequent assessments refer to this report, but quote an incorrect year of publication (1949). The heat capacity of Cr_3C_2 was measured further by DeSorbo [12] and by Oriani and Murphy [13], however, the results were not taken into account in recent assessments.

The enthalpy of formation of Cr_3C_2 was measured by oxygen bomb calorimetry [14,15]. The quoted values given in Table 1 depend on the selection of the enthalpy of formation data of the reaction product Cr_2O_3 which are −1141.0 kJ/mol [16] and −1129.7 kJ/mol at 298 K [17]. Recently, assessed data of Cr_2O_3 at 298 K were reported: −1139.7 kJ/mol [9] and −1134.7 kJ/mol [10]. The enthalpy of formation of Cr_3C_2 was determined further by reaction calorimetry between Cr and C at 1753 K [18]. The result at 298 K is also given in Table 1. The enthalpies of formation of Cr_7C_3 and $Cr_{23}C_6$ were measured likewise by oxygen bomb calorimetry [14,15] and by reaction calorimetry [18,19]. The results are compiled in Tables 2 and 3, respectively.

The Gibbs energies of formation of the chromium carbides were determined by various gas phase equilibria, e.g. isopiestic methods [20], H_2/CH_4 equilibria [21–23] and C/CO equilibria [11,24–26], by Knudsen cell vapour pressure measurements using the mass loss effect [27,28]

[☆] Presented at the Discussion Meeting on Thermodynamics of Alloys, Stockholm, Sweden, 8–11 May, 2000.

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PII: S0925-8388(01)01012-X

Table 1
Gibbs energy of formation $\Delta_f G^\circ_T$ at temperature T and temperature range of measurements, and third-law evaluation of the enthalpy of formation $\Delta_f H^\circ_{298}$ at 298 K of Cr_3C_2

Method	Temp. range (K)	$\Delta_f G^\circ_T$ (kJ/mol)	T (K)	$\Delta_f H^\circ_{298}$ [a] (kJ/mol)	Author (year)	Ref.
CO pressure	1160–1370	−126.7	1300	−110.9	Heusler (1926)	[24]
CO pressure	1243–1381	−99.3	1300	−83.5	Kelley (1944)	[11]
Knudsen cell	1900–2240	−131.7	2100	−102.8	Fujishiro (1961)	[27]
Knudsen cell	1370–1570	−77.8	1500	−58.4	Vintaikin (1963)	[29]
H_2/CH_4 equil.	1070–1310	−81.1	1300	−65.3	Alekseev (1964)	[22]
CO pressure	1300–1380	−129.6	1300	−113.8	Gleiser (1965)	[25]
Knudsen cell	1800–2050	–	–	(−97.9)	Bolgar (1966)	[28]
EMF (CaF_2)	880–1110	−66.9	1100	−55.0	Kleykamp (1969)	[30]
EMF (CaF_2)	880–1100	−74.7	1100	−62.7	Tanaka (1971)	[31]
EMF (ThO_2)	1070–1300	−77.3	1100	−65.3	Mabuchi (1971)	[34]
CO pressure	1300–1500	−92.5	1300	−76.5	Kulkarni (1972)	[26]
EMF (BaF_2)	970–1170	−114.2	1100	−102.2	Coltters (1984)	[33]
EMF (CaF_2)	1000–1180	−79.1	1100	−67.1	Du Sichen (1989)	[32]
H_2/CH_4 equil.	973–1173	−75.9	1100	−63.9	Anthonysamy (1996)	[23]
EMF (CaF_2)	930–1120	−84.3	1100	−72.3	Kleykamp (2000)	–
Oxygen combustion calorimetry				−94.1[b]	Mah (1969)	[14]
Oxygen combustion calorimetry				−81.1[c]	Dawson (1977)	[15]
Reaction calorimetry at 1753 K				−54.5	Berkane (1987)	[18]

[a] Third-law evaluations of Cr_3C_2 with Gibbs energy functions of Barin [9] by the present author.
[b] $\Delta_f H^\circ$ of Cr_3C_2 was calculated with Cr_2O_3 data of Mah [16].
[c] $\Delta_f H^\circ$ of Cr_3C_2 was calculated with Cr_2O_3 data of Jeannin [17].

or radioactive tracers [29], and by the electromotive force technique using solid electrolytes, e.g. CaF_2 [30–32], BaF_2–BaC_2 [33] or ThO_2 [34]. Further, thermodynamic calculations were published on the Gibbs energies of formation [35] and on experimental results of the relative partial molar enthalpies of carbon [36] in the Cr–C melts. The accuracy of the thermodynamic data of the chromium carbides can be influenced by inexact data (i) of the enthalpy of sublimation of Cr used with the Knudsen cell method; (ii) the Gibbs energy of formation of Cr_2O_3 used with combustion calorimetry; and (iii) with the CO equilibrium method according to the reaction

$$CrC_x + Cr_2O_3 = CrC_y + CO, \quad x > y \tag{1}$$

An uncertainty is also given by the unknown solubility of oxygen in the chromium carbides [35] and by the formation of chromium oxycarbides [37]. Lux and Ignatowicz reported a cubic phase of the composition $Cr_{0.60}O_{0.13}C_{0.27}$ which would prevent the equilibrium of

Table 2
Gibbs energy of formation $\Delta_f G^\circ_T$ at temperature T and temperature range of measurements, and third-law evaluation of the enthalpy of formation $\Delta_f H^\circ_{298}$ at 298 K of Cr_7C_3

Method	Temp. range (K)	$\Delta_f G^\circ_T$ (kJ/mol)	T (K)	$\Delta_f H^\circ_{298}$ [a] (kJ/mol)	Author (year)	Ref.
CO pressure	1306–1495	−210.6	1400	−166.8	Kelley (1944)	[11]
H_2/CH_4 equil.	970–1220	−163.1	1100	−130.8	Alekseev (1964)	[22]
EMF (CaF_2)	920–1080	−134.9	1000	−106.5	Kleykamp (1969)	[30]
EMF (CaF_2)	880–1023	−152.6	1000	−124.2	Tanaka (1971)	[31]
CO pressure	1100–1720	−198.2[b]	1400	−154.4	Kulkarni (1972)	[26]
calculated	600–973	−134.2	800	−113.4	Small (1981)	[35]
EMF (BaF_2)	900–1250	−191.2	1000	−162.8	Coltters (1984)	[33]
EMF (CaF_2)	990–1150	−156.1	1000	−127.7	Du Sichen (1989)	[32]
isopiestic	1100–1470	−142	1200	−106	Bhatt (1989)	[20]
H_2/CH_4 equil.	973–1173	−137.7	1100	−105.4	Anthonysamy (1996)	[23]
EMF (CaF_2)	980–1110	−176.7	1100	−144.4	Kleykamp (2000)	–
Oxygen combustion calorimetry				−181.2[c]	Mah (1969)	[14]
Oxygen combustion calorimetry				−149.2[b]	Dawson (1977)	[15]
Reaction calorimetry at 1753 K				−105.0	Berkane (1987)	[18]
Reaction calorimetry at 1473 K				−141	Meschel (1997)	[19]

[a] Third-law evaluations of Cr_7C_3 with Gibbs energy functions of Barin [9] by the present author.
[b] $\Delta_f G^\circ$ and $\Delta_f H^\circ$ of Cr_7C_3 were calculated with Cr_2O_3 data of Jeannin [17].
[c] $\Delta_f H^\circ$ of Cr_7C_3 was calculated with Cr_2O_3 data of Mah [16].

Table 3
Gibbs energy of formation $\Delta_f G^\circ_T$ at temperature T and temperature range of measurements, and third-law evaluation of the enthalpy of formation $\Delta_f H^\circ_{298}$ at 298 K of $Cr_{23}C_6$

Method	Temp. range (K)	$\Delta_f G^\circ_T$ (kJ/mol)	T (K)	$\Delta_f H^\circ_{298}$ [a] (kJ/mol)	Author (year)	Ref.
CO pressure	1503–1721	−468.7[b]	1600	−370.7	Kelley (1944)	[11]
H_2/CH_4 equil.	970–1220	−346.9	1100	−283.4	Alekseev (1961)	[21]
CO pressure	1150–1310	−414.0[c]	1200	−342.9	Kulkarni (1972)	[26]
calculated	600–973	−305.2	800	−264.7	Small (1981)	[35]
EMF (CaF_2)	980–1230	−357.6	1100	−294.1	Du Sichen (1989)	[32]
isopiestic	1100–1470	−339	1200	−268	Bhatt (1989)	[20]
H_2/CH_4 equil.	973–1173	−331.2	1100	−267.7	Anthonysamy (1996)	[23]
EMF (CaF_2)	1030–1110	−407.4	1100	−343.9	Kleykamp (2000)	–
Oxygen combustion calorimetry				−396.2[d]	Mah (1969)	[14]
Oxygen combustion calorimetry				−295.0[c]	Dawson (1977)	[15]
Reaction calorimetry at 1753 K				−249.0	Berkane (1987)	[18]

[a] Third-law evaluations of $Cr_{23}C_6$ with Gibbs energy functions of Barin [9] by the present author.
[b] $6\cdot\Delta_f G^\circ\langle Cr_4C\rangle$.
[c] $\Delta_f G^\circ$ and $\Delta_f H^\circ$ of $Cr_{23}C_6$ were calculated with Cr_2O_3 data of Jeannin [17].
[d] $\Delta_f H^\circ$ of $Cr_{23}C_6$ was calculated with Cr_2O_3 data of Mah [16].

the binary carbides with Cr_2O_3. Consequently, Eq. (1) would be unsuitable for the $\Delta_f G^\circ$ determination.

The evaluated thermodynamic data of Cr_3C_2, Cr_7C_3 and $Cr_{23}C_6$ based on Gibbs energy measurements are compiled in Tables 1, 2 and 3, respectively. They comprise the method and the temperature range of investigation as well as the measured Gibbs energies of formation at one intermediate temperature. These data were taken for a third-law evaluation of the enthalpies of formation at 298 K using exclusively the Gibbs energy function data ϕ°_T compiled by Barin [9].

Though many experimental investigations by calorimetry, vapour pressure and gas phase equilibration methods and by galvanic cell measurements were published on the thermodynamic properties of the chromium carbides no definite decision can be taken on the most probable data of the Gibbs energy of formation and enthalpy of formation. Possible reasons for the large scattering of the emf results of the numerous galvanic cell measurements were already discussed in the respective contributions, e.g. the use of polycrystalline CaF_2 instead of a single-crystal CaF_2 electrolyte, some electronic conduction in the electrolyte [23,33,34] and 'high' oxygen partial pressures in the galvanic cell system [32]. In order to eliminate these ideas, the former emf measurements of the author [30] were started again on Cr_3C_2 and Cr_7C_3 and were complemented by experiments on $Cr_{23}C_6$.

2. Experimental

2.1. Cell arrangement

The Gibbs energies of formation of Cr_3C_2, Cr_7C_3 and $Cr_{23}C_6$ were determined by the electromotive force of second kind galvanic cells using a fluorine ion conducting single-crystal CaF_2 electrolyte. Electronic contributions are expected only below the partial pressure $p(F_2)\simeq 10^{-50}$ bar [38]. The Cr–CrF_2 mixture presents the reference electrode, two phases co-existing in the Cr–C system in equilibrium with the auxiliary electrolyte CrF_2 form the working electrode. The arrangement of the cells (the cathode is on the right-hand side), the reactions in the left and in the right electrode, the total cell reactions and the Gibbs energies of the respective cell reactions ($\underline{F}$ is the Faraday constant) are formulated by the following schemes:

Cell (I)

$$\mathrm{Cr,\ CrF_2|CaF_2|CrF_2,Cr_3C_2,C} \tag{2}$$

$$\begin{array}{l} \mathrm{l.{:}3Cr + 6F^- = 3CrF_2 + 6e^-} \\ \underline{\mathrm{r.{:}6e^- + 3CrF_2 + 2C = Cr_3C_2 + 6F^-}} \\ \qquad\qquad \mathrm{3Cr + 2C = Cr_3C_2} \end{array} \tag{3}$$

$$\Delta_r G^\circ = 6\cdot\underline{F}\cdot E_I = \Delta_f G^\circ\langle Cr_3C_2\rangle \tag{4}$$

Cell (II):

$$\mathrm{Cr,CrF_2|CaF_2|CrF_2,Cr_7C_3,Cr_3C_2} \tag{5}$$

$$\begin{array}{l} \mathrm{l.{:}5Cr + 10F^- = 5CrF_2 + 10e -} \\ \underline{\mathrm{r.{:}5CrF_2 + 3Cr_3C_2 + 10e^- = 2Cr_7C_3 + 10F^-}} \\ \qquad\qquad \mathrm{5Cr + 3Cr_3C_2 = 2Cr_7C_3} \end{array} \tag{6}$$

$$\begin{aligned} \Delta_f G^\circ &= -10\cdot\underline{F}\cdot E_{II} \\ &= 2\cdot\Delta_f G^\circ\langle Cr_7C_3\rangle - 3\cdot\Delta_f G^\circ\langle Cr_3C_2\rangle \end{aligned} \tag{7}$$

Cell (III):

$$\mathrm{Cr,CrF_2|CaF_2|CrF_2,Cr_{23}C_6,Cr_7C_3} \tag{8}$$

$$\begin{array}{c}\text{l.:}\,9Cr + 18F^{-} = 9CrF_2 + 18e^{-}\\ \underline{\text{r.:}\,18e^{-} + 9CrF_2 + 2Cr_7C_3 = Cr_{23}C_6 + 18F^{-}}\\ 9Cr + 2Cr_7C_3 = Cr_{23}C_6\end{array} \qquad (9)$$

$$\begin{aligned}\Delta_r G^\circ &= -18 \cdot \underline{F} \cdot E_{\mathrm{III}}\\ &= \Delta_f G^\circ \langle Cr_{23}C_6\rangle - 2 \cdot \Delta_f G^\circ \langle Cr_7C_3\rangle\end{aligned} \qquad (10)$$

2.2. Materials

Chromium granules (99.995% purity, Alfa Aesar, Karlsruhe) and graphite (spectropure, Ringsdorff, Köln) were weighed in two-phase $Cr_{23}C_6$–Cr_7C_3, Cr_7C_3–Cr_3C_2 and Cr_3C_2–C compositions, compacted and arc melted together under reduced argon pressure by repeated turnover of the buttons. The material was crushed, re-compacted and annealed at 1000°C for 11 days under argon. The two-phase character was checked by X-ray diffraction. The CrF_2 auxiliary electrolyte powder ($T_m = 894$°C, 99.5% purity, Schuchardt, München) was used for the preparation of the Cr–CrF_2 reference electrode and the $Cr_{23}C_6$–Cr_7C_3–CrF_2, Cr_7C_3–Cr_3C_2–CrF_2 and Cr_3C_2–C–CrF_2 working electrodes by pressing of pellets from the crushed carbides. The material was annealed in evacuated quartz ampoules at 800°C for 11 days. The phases were again checked by X-ray diffraction. Single-crystal CaF_2 disks (Steeg and Reuter, Gießen) with 10 mm diameter and about 3 mm thickness operated as the electrolyte of the galvanic cells.

2.3. Cell operation

The cells were operated under flowing argon (5 N) with about one bubble per second. The gas was additionally purified by zirconium sponges heated at 600°C to remove oxygen, nitrogen and water vapour residues. The emf was measured with an electrometer (Keithley) instead of a high-impedance voltmeter applied previously.

The dynamic equilibrium of the cells was influenced by external polarisation of the electrodes. Equilibrium was again attained after 6 h at 660°C for galvanic cell (2), at 710°C for cell (5) and at 760°C for cell (8), which are by definition the minimum operation temperatures. Polarisation tests are indications of the reversibility of the cells. Details are reported in [39]. The upper temperature limits of the cell operation are caused by distinct and detrimental gas phase reactions and re-condensation of the products. As a consequence, the emf is reduced and tends occasionally to zero emf. An opacity of the quartz apparatus was observed above 840°C in these experiments and Cr_2O_3 could be detected in the electrodes by X-ray diffraction. The following reactions are possible between the quartz container and the CrF_2 auxiliary electrolyte; ⟨solid⟩, (gaseous):

$$\begin{aligned}\langle SiO_2\rangle + 2(CrF_2) &= (SiF_4) + 2(CrO)\\ 2(CrO) &= 2/3\langle Cr_2O_3\rangle + 2/3\langle Cr\rangle\end{aligned} \qquad (11)$$

or

$$\begin{aligned}\langle SiO_2\rangle + 2(F_2) &= (SiF_4) + (O_2)\\ 3/2\,(O_2) + 2\langle Cr\rangle &= \langle Cr_2O_3\rangle\\ (O_2) + \langle CrC_x\rangle &\rightarrow \langle Cr_2O_3\rangle + (CO)\end{aligned} \qquad (12)$$

3. Results

The measurements of emf E_{I} on the galvanic cell, Eq. (2) were performed between about 930 and 1120 K; the results are illustrated in Fig. 1. A linear regression analysis of E_{I} as a function of temperature T (in K)

$$E_{\mathrm{I}} = 143.7 + 0.0017 \cdot T \pm 1.7\ \mathrm{mV} \qquad (13)$$

results in the Gibbs energy of formation of Cr_3C_2 using Eq. (4)

$$\Delta_f G^\circ \langle Cr_3C_2\rangle = -83189 - 0.967 \cdot T\ \mathrm{J/mol} \qquad (14)$$

which is presented in Fig. 2. A third-law evaluation of the enthalpy of formation of Cr_3C_2 at 298 K in Table 1 was made by use of the Gibbs energy functions of Cr, C and Cr_3C_2 at 1100 K compiled by Barin [9] which yields

$$(15)\Delta_f H^{\circ}_{298} \langle Cr_3C_2\rangle = -72.3\ \mathrm{kJ/mol}$$

The measurements of emf E_{II} on the galvanic cell, Eq. (5) were carried out between about 980 and 1110 K; the results are illustrated in Fig. 1. A linear regression analysis of E_{II} as a function of temperature T (in K)

$$E_{\mathrm{II}} = 37.1 + 0.0611 \cdot T \pm 2.2\ \mathrm{mV} \qquad (16)$$

results in the Gibbs energy of formation of Cr_7C_3 using Eq. (7)

$$\Delta_f G^\circ \langle Cr_7C_3\rangle = -142666 - 30.92 \cdot T\ \mathrm{J/mol} \qquad (17)$$

which is presented in Fig. 3. A third-law evaluation of the enthalpy of formation of Cr_7C_3 at 298 K was made by use of the Gibbs energy functions of Cr, C and Cr_7C_3 at 1100 K compiled by Barin [9] which yields

$$\Delta_f H^{\circ}_{298} \langle Cr_7C_3\rangle = -144.4\ \mathrm{kJ/mol} \qquad (18)$$

The measurements of emf E_{III} on the galvanic cell, Eq. (8) were taken between about 1030 and 1110 K; the results are illustrated in Fig. 1. A linear regression analysis of E_{III} as a function of temperature T (in K)

$$E_{\mathrm{III}} = 2.75 + 0.02578 \cdot T \pm 0.4\ \mathrm{mV} \qquad (19)$$

results in the Gibbs energy of formation of $Cr_{23}C_6$ using Eq. (10)

$$\Delta_f G^\circ \langle Cr_{23}C_6\rangle = -290108 - 106.65 \cdot T\ \mathrm{J/mol} \qquad (20)$$

which is presented in Fig. 4. A third-law evaluation of the

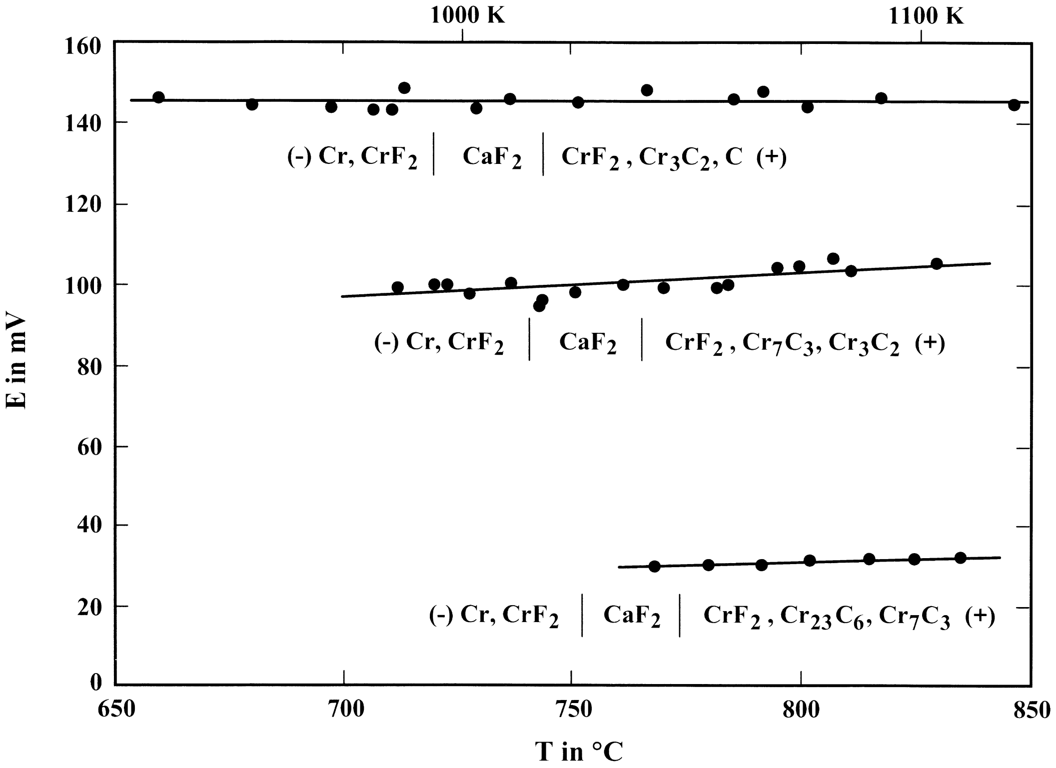

Fig. 1. Electromotive force E of the galvanic cells, I, II and III, as a function of temperature.

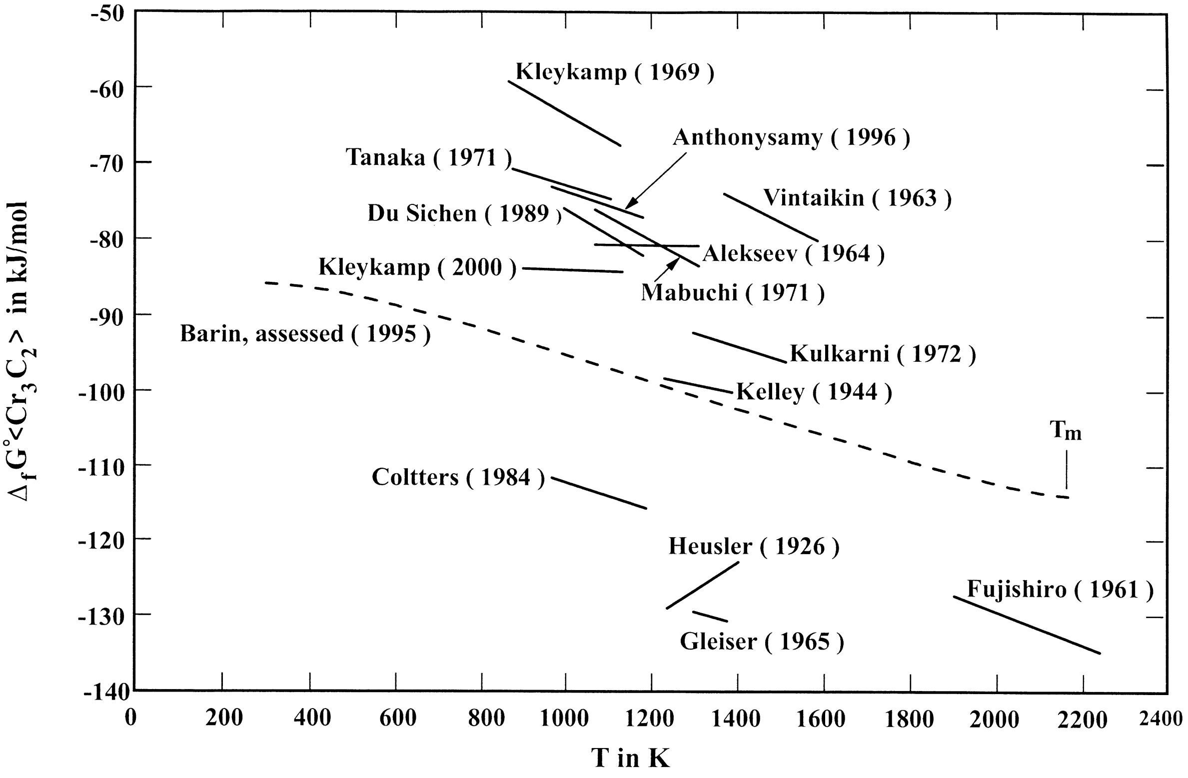

Fig. 2. Gibbs energy of formation $\Delta_f G^\circ$ of Cr_3C_2 as a function of temperature.

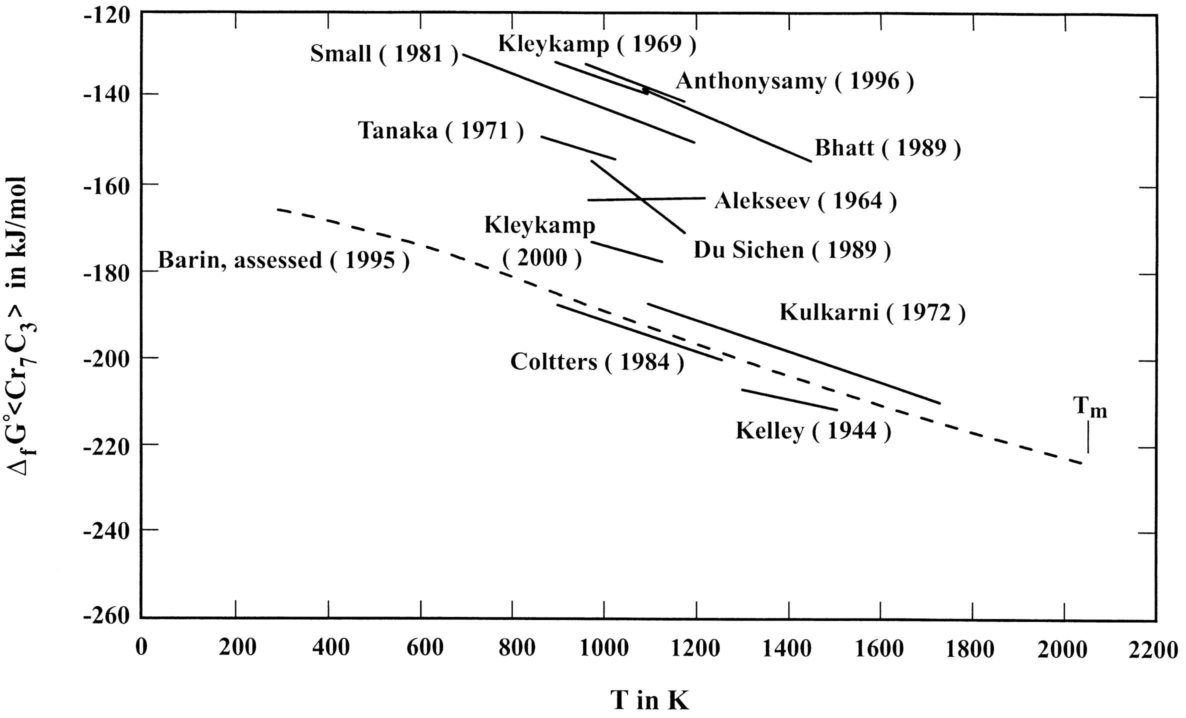

Fig. 3. Gibbs energy of formation $\Delta_f G°$ of Cr_7C_3 as a function of temperature.

enthalpy of formation of $Cr_{23}C_6$ at 298 K was made by use of the Gibbs energy functions of Cr, C and $Cr_{23}C_6$ at 1100 K compiled by Barin [9] which yields

$$\Delta_f H^o_{298}\langle Cr_{23}C_6\rangle = -343.9 \text{ kJ/mol} \quad (21)$$

The relative partial molar Gibbs energies $\Delta\bar{G}_{Cr}$ and $\Delta\bar{G}_C$

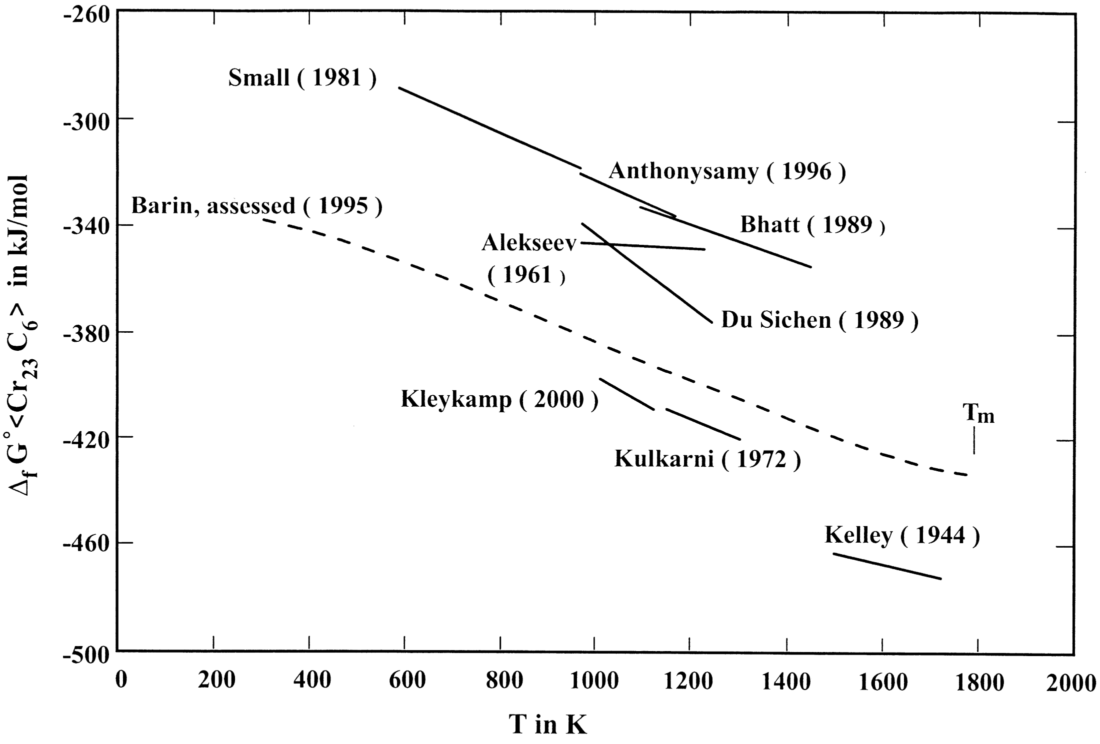

Fig. 4. Gibbs energy of formation $\Delta_f G°$ of $Cr_{23}C_6$ as a function of temperature.

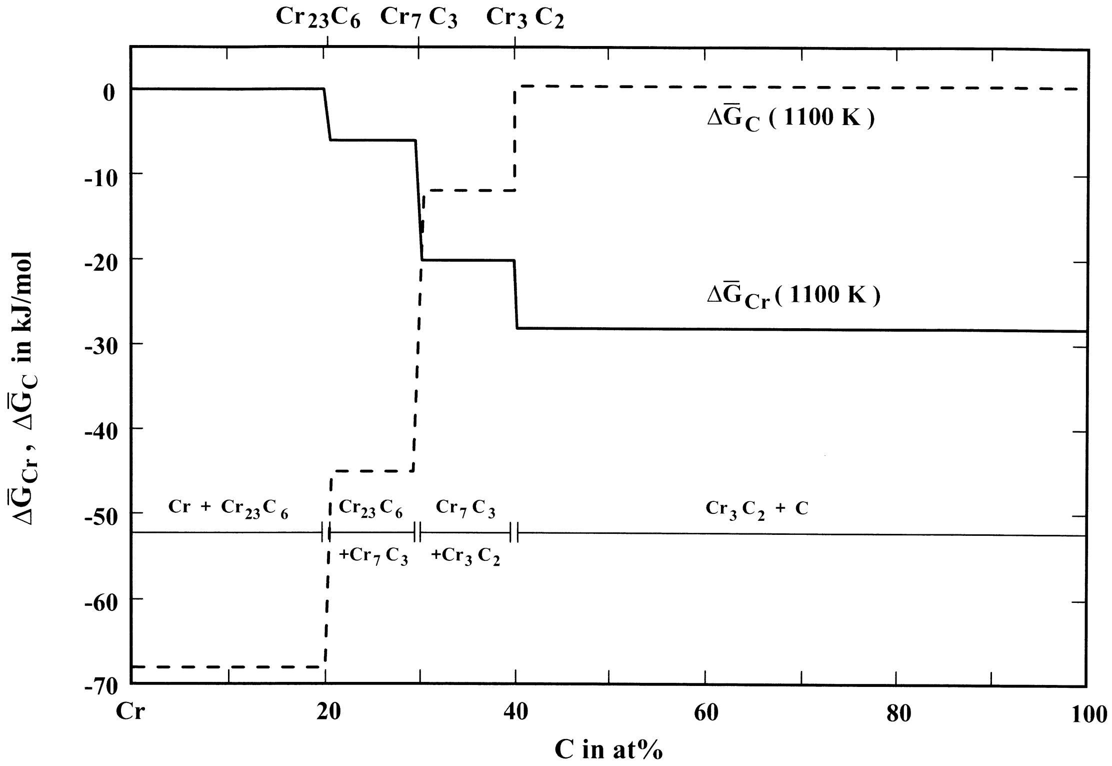

Fig. 5. Relative partial molar Gibbs energies $\Delta\bar{G}_{\mathrm{Cr}}$ and $\Delta\bar{G}_{\mathrm{C}}$ at 1100 K in the chromium–carbon system.

of the Cr–C system at 1100 K are illustrated in Fig. 5. Numerical results are $\Delta\bar{G}_{\mathrm{C}} = -67900$ J/mol in the Cr–$Cr_{23}C_6$ two-phase field, $\Delta\bar{G}_{\mathrm{Cr}} = -6000$ J/mol and $\Delta\bar{G}_{\mathrm{C}} = -44900$ J/mol in the $Cr_{23}C_6$–Cr_7C_3 two-phase field, $\Delta\bar{G}_{\mathrm{Cr}} = -20100$ J/mol and $\Delta\bar{G}_{\mathrm{C}} = -11900$ J/mol in the Cr_7C_3–Cr_3C_2 two-phase field and $\Delta\bar{G}_{\mathrm{Cr}} = -28100$ J/mol in the Cr_3C_2–C two-phase field.

4. Discussion

The literature survey demonstrates a wide spread of the enthalpies of formation of the three chromium carbides. The 1σ-standard deviation of 18 individual results of Cr_3C_2 is about 25% compared to the average value. The CO equilibrium pressure measurements give largely too negative enthalpies of formation compared to the average value. This behaviour could be influenced by the formation of chromium oxycarbides which control the thermodynamic activities of the components and, consequently, the CO partial pressure. The emf measurements give in general too positive enthalpies of formation. The calorimetry yields an unspecific scatter. These trends are also observed for the enthalpies of formation of Cr_7C_3 and $Cr_{23}C_6$. The standard deviation of 15 individual results of Cr_7C_3 is about 19%, that of 11 individual results of $Cr_{23}C_6$ is about 16%; both are less than that for Cr_3C_2. The reasons for the wide spread of the results are speculative. The enthalpy of formation from CO equilibrium measurements and oxygen combustion calorimetry follows from the difference of two large quantities. Furthermore, different and partly obsolete Gibbs energies of formation of Cr_2O_3 were used for the evaluation of the enthalpies of formation of the chromium carbides. Finally, the problems of the solubility of oxygen and a possible oxycarbide formation are still open.

The scattered results gained by emf measurements using fluorine ion conducting electrolytes are based on a quite different level. In the first instance, the composition of that auxiliary electrolyte fluoride phase should be known which is in thermodynamic equilibrium with the metallic phases AB_n of which the Gibbs energies of formation and the thermodynamic activities, respectively, are determined by emf measurements. Therefore, the knowledge of the phase diagrams of the respective ternary A–B–F systems is necessary. Oxygen contaminations have to be avoided in the galvanic cells before and during the emf measurements. This problem has been already discussed earlier [39]. The first condition can be fulfilled by use of very pure substances for electrolyte, electrodes, electric leads, container and protection gas. The second condition is more difficult to meet because the constituent parts of the galvanic cells inclusive the containers can react via the solid and the gas phase at high temperatures. There is positive proof that the vapour species of the auxiliary electrolyte CrF_2 react with the SiO_2 container by formation of a gaseous oxygen carrier which oxidises Cr metal and Cr carbides in the electrodes above a definite temperature and partial pressure level, respectively.

5. Conclusion

New experimental results of the Gibbs energies of formation of chromium carbides were generated by emf measurements which avoid experimental deficiencies possibly made in previous experiments [39]. The enthalpies of formation of the chromium carbides of this paper and earlier investigations were evaluated by use of the heat capacities of Kelley [11] which are the sole results available and used in subsequent original contributions and assessments. The author of this paper eliminated all identifiable experimental sources of error. However, the general situation remains unsatisfactory that the scatter of the total of results of all authors is extraordinarily high. The assessed thermodynamic data [9] are based on previous evaluations made by experts in the early seventies; they cause a discomfort to the user. For this reason, the present author dares to give a recommendation of the Gibbs energies of formation of the chromium carbides founded on his personal experimental experience and on the judgement of the different experimental methods and laboratories. The results of Kelley et al. [1] who did not directly use the thermodynamic data of Cr_2O_3 for their calculations and those of Kulkarni and Worrell [26], Du Sichen et al. [32] and the present work were selected for a recommendation of the Gibbs energy of formation of Cr_3C_2, $\Delta_f G^\circ = -63000 - 23.5 \cdot T$ J/mol, 298–2000 K, $\Delta_f S^\circ = +4.7$ J/K·g-atom. The results of Kelley et al. [11], of Kulkarni and Worrell [26], of the present work and of the enthalpy of formation through reaction calorimetry by Meschel and Kleppa [19] were selected for a recommendation of the Gibbs energy of formation of Cr_7C_3: $\Delta_f G^\circ = -132000 - 44.1 \cdot T$ J/mol, 298–2000 K, $\Delta_f S^\circ = +4.4.$ J/K·g-atom. The results of Kelley et al. [11], of Kulkarni and Worrell [26] and of the present author were chosen for a recommendation of the Gibbs energy of formation of $Cr_{23}C_6$: $\Delta_f G^\circ = -288000 - 106 \cdot T$ J/mol, 298–1800 K, $\Delta_f S^\circ = +3.7$ J/K·g-atom.

Acknowledgements

This work was crowned with success by years of experience of Mr Werner Laumer. The author acknowledges the discussions and advises of Professor Dr H. Ipser, Institute of Inorganic Chemistry and Professor Dr J. Schuster, Institute of Physical Chemistry of the University of Vienna.

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