Thermochimica Acta, 204 (1992) 55–60
Elsevier Science Publishers B.V., Amsterdam

Calorimetry and e.m.f. techniques: how they compete and complete each other in determining the enthalpy and entropy of formation of Cr_3C_2 [1]

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(Received 2 September 1991; in final form 9 December 1991)

Abstract

A calorimetric study gave the enthalpy of formation of Cr_3C_2: $\Delta H = -10000 \pm 600$ J mol^{-1}. This value is very far from e.m.f. results: $\Delta_f H = -8400$ or -5800 ± 2900 J mol^{-1}, depending on the computation conditions, illustrated in our paper. It seemed reasonable to consider both the satisfactory value of the Gibbs energy of formation determined by e.m.f. $\delta_f G = -15940 \pm 1000$ J mol^{-1} at 100 K, and the present enthalpy of formation, in order to calculate the entropy of formation ($\Delta_f S = 5.4$ J K^{-1} mol^{-1}).

INTRODUCTION

E.m.f. techniques, as well as chemical equilibrium studies, lead to a complete determination of the thermodynamic properties of formation via partial free enthalpy functions. In contrast, calorimetry, which gives only enthalpies of formation, appears to be considerably limited. Here, we demonstrate the contributions of both techniques, taking as an example the study of Cr_3C_2.

GENERAL SYNOPSIS OF PREVIOUS RESULTS

Numerous papers have been devoted to the carbide Cr_3C_2 which is in equilibrium with carbon. They have been summarized by Du Sichen et al. [1]. A comparison (Fig. 1) of all the results is striking: there is a factor of two between the free enthalpy data reported by different authors. Solid gas

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[1] This paper was presented during the 22nd annual meeting of the French Association of Calorimetry and Thermal Analysis (AFCAT) at Paris-XI–Châtenay-Malabray (27–29 May 1991).

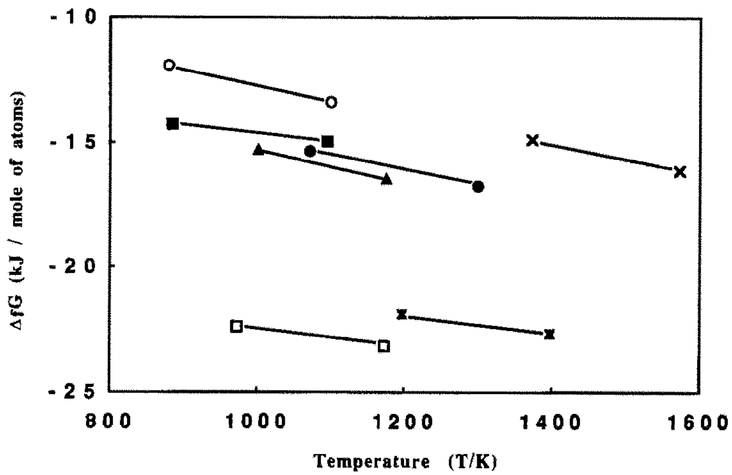

Fig. 1. Some values of the Gibbs energy of formation of Cr_3C_2 obtained by several authors: ○, Kleykamp [2] (e.m.f.; electrolyte, CaF_2); ×, Vintaikin [3] (vapor pressure); ■, Tanaka et al. [4] (e.m.f.; electrolyte, $ThO_2+Y_2O_3$); ▲, Du Sichen et al. [1] (e.m.f.; electrolyte, CaF_2); □, Coltters and Belton [5] (e.m.f.; electrolyte, BaF_2+BaC_2); ●, Mabuchi et al. [6] (e.m.f.; electrolyte, $ThO_2+Y_2O_3$); *, Kelley et al. [7] (Cr_2O_3, CO equilibrium).

equilibria studies have been criticized owing to analyses made on cooled but not efficiently quenched samples, to the incomplete decomposition of Cr_3C_2 during vapor pressure measurements, to ill-defined carbide stoichiometry, etc. E.m.f. measurements, involving oxides or fluorides as solid electrolytes, and their results seem relatively consistent. We consider them to be reliable. The experimental study of Du Sichen et al. [1] was particularly impressive when considering experimental details such as the oxygen elimination. We, therefore, accept their results.

Enthalpies of formation had been measured by calorimetry. The earlier authors used combustion calorimetry: Mah [8] obtained -18.8 kJ mol^{-1} and Dawson and Sale [9] -16.2 kJ mol^{-1} for Cr_3C_2 carbide. Unfortunately, combustion calorimetry relies on very large heats of combustion for the compounds as well as for the elements. When these heats of combustion are changed, the results are dramatically changed. For example Mah's result of -18.8 kJ mol^{-1} becomes -17.1 kJ in the JANAF tables and -15.6 in Kulkarni and Worrell's compilation [10]. More recently, our laboratory has applied direct reaction calorimetry measurements to this problem.

DETERMINATION OF THE Cr_3C_2 ENTHALPY OF FORMATION BY DIRECT REACTION CALORIMETRY

Direct reaction calorimetry has been performed by Berkane et al. [11] using a stoichiometric mixture of C and Cr fine powders. Small pellets of the cold compacted mixture were introduced in the calorimeter which worked at a temperature near 1753 K. The temperature rise inside the samples started the exothermic reaction of formation of Cr_3C_2. The enthalpy of formation at 1753 K is obtained by subtracting the enthalpy increments of the pure components from the total heat effect measured by the calorimeter.

The results are somewhat spread and the relative accuracy is ±6%:

$$\tfrac{3}{5}\mathrm{Cr} + \tfrac{2}{5}\mathrm{C(graphite)} \rightarrow \tfrac{1}{5}\mathrm{Cr_3C_2}$$

$$\Delta_f H(\tfrac{1}{5}\mathrm{Cr_3C_2}, 1753\ \mathrm{K}) = -10.0 \pm 0.6\ \mathrm{kJ\ mol^{-1}}$$

This result seems to indicate that calorimetry gives only one poorly defined value.

E.M.F. DETERMINATION OF THE FREE ENTHALPY, AND THE ENTHALPY AND ENTROPY OF FORMATION OF Cr_3C_2

According to Du Sichen et al., starting from the cell

$$(-)\ \mathrm{Cr, CrF_2, CaF_2 \| CaF_2 \| CaF_2, CrF_2, Cr_3C_2, graphite}\ (+)$$

the authors obtained the e.m.f. values which are reported versus temperature in Fig. 2. The experimental points are not too spread and it seems legitimate to represent them by a straight line giving E versus T

$$E\ (\mathrm{mV}) = 72.9 + 0.0589T\ (K)$$

The above equation is given by a linear regression and this is not usually questioned. But if experimental points are considered as giving T versus E,

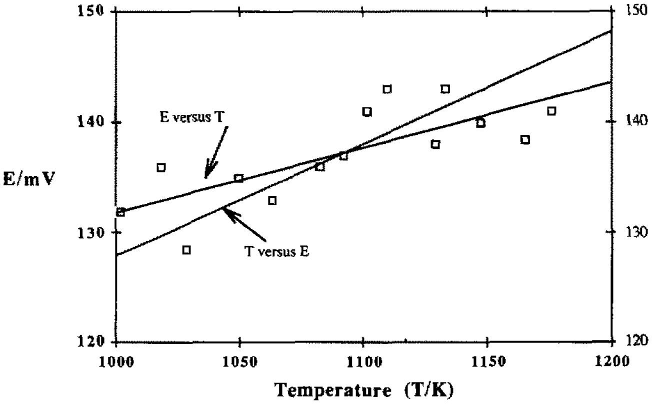

Fig. 2. Experimental points taken from Du Sichen et al. [1] for the cell Cr, CrF_2, $CaF_2 \| CaF_2 \| CaF_2$, CrF_2, Cr_3C_2 and linear regressions of E versus T and of T versus E.

another linear regression line is found (Fig. 2), the equation of which is different from the first

E (mV) $= 26.4 + 0.1014T$ (K)

After both computations, the regression coefficient has the same value, 0.76. The standard derivation of E around one of the straight lines is given by

$$\sigma = \sqrt{\frac{(1-r^2)\sum\left(E_i - \bar{E}\right)^2}{N-2}} \quad \text{or } \sigma = \sqrt{\frac{(1-r^2)\left(\sum E_i^2 - N\bar{E}^2\right)}{N-2}}$$

where N is the number of couples (here $N = 14$).

The 95% confidence range for E is then ±16 mV and the uncertainty range of the E values is about 11.6%. If the degree of confidence which is required is not so high, it is possible to consider just one standard deviation as the uncertainty range and the relative accuracy becomes ±6%, similar to that found by calorimetry.

The free enthalpy of formation which can be deduced is

ΔG J mol$^{-1} = -8440 - 6.82T$ (K) ± 960

in the 1000–1200 K temperature range.

To determine the enthalpy of formation, $\Delta_f H$ is assumed to be constant, and in the experimental domain its value is given by the ordinate of the line for T (K) $= 0$. This is, in fact, an unsound extrapolation, far removed from the experimental data (Fig. 3): the difference between the ordinates of the two lines becomes enormous, about 6 kJ mol^{-1}, and the choice between the two lines is completely arbitrary. It is impossible to agree with Du

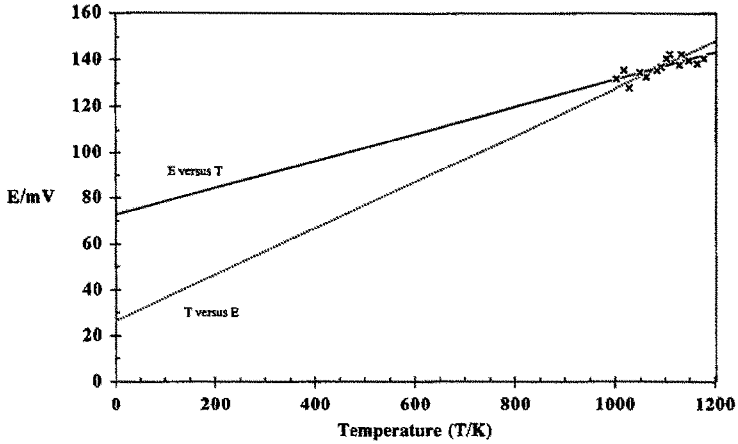

Fig. 3. Extrapolations by linear regressions of the experimental results from Du Sichen et al. [1] to determine the enthalpy of formation.

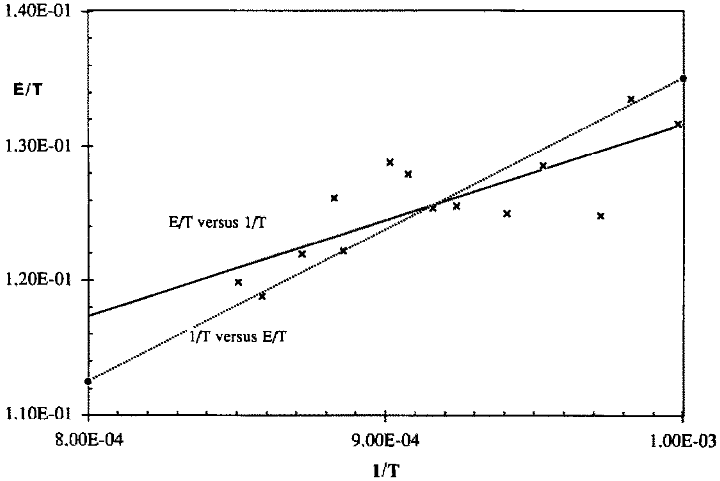

Fig. 4. Representation of E/T versus $1/T$. Experimental points taken from Du Sichen et al. [1] and linear regression of E/T versus $1/T$ and of $1/T$ versus E/T.

Sichen et al. that the part of $\Delta_f G$ independent of T represents $\delta_f H$ with an accuracy of about 5%.

The results which is the most probable is $\Delta_f H$ kJ mol^{-1} = -5.8 ± 2.9.

The e.m.f. determination of $\Delta_f H$ appears to be hazardous, and this also applies to the determination of $\delta_f S$.

The classical representation of E/T versus $1/T$ has the same limitations as that of E versus T (Fig. 4) and the two lines have different slopes.

DETERMINATION OF $\Delta_f S$ BY A COMBINATION OF E.M.F. AND CALORIMETRIC MEASUREMENTS

Considering that $\Delta_f H$ determined by calorimetry and $\Delta_f G$ obtained by e.m.f. measurements are reliable, it becomes possible to write $\Delta_f S = (\Delta_f H - \Delta_f G)/T$.

With $T = 1100$ K, the value of $\Delta_f S$ is $\Delta_f S$ J K^{-1} mol^{-1} = 5.4 ± 1.1. The entropy of formation $\Delta_f S$ is still poorly defined because the uncertainty range is $\pm 20\%$, but at least the order of magnitude can be considered as firmly established.

CONCLUSION

In spite of the fact that the experimental measurements of Gibbs energy are well described by one or other of the regression lines within the temperature range, the extrapolations which yield $\Delta_f H$ and $\Delta_f S$ are very inaccurate and have no meaning, except when the correlation coefficient is equal to 1. It appears that while the Gibbs energy contains simultaneously

TABLE 1

A summary of the recommended results

	$\Delta_f G$ (J mol^{-1}) at 1100 K	$\Delta_f H$ (J mol^{-1})	$\Delta_f S$ (J K^{-1} mol^{-1})
E.m.f. only	−15940 (±1000)	−5800 (±2900)	+9.2 (±2.5)
Calorimetry only		−10000 (±600)	
Combination calorimetry + e.m.f.	−15940 (±1000)	−10000 (±600)	5.4 (±1.1)

the enthalpy and the entropy of formation, it is very dangerous to break it down into its components. Even if the hypothetical thermodynamic $\Delta_f H$ and $\Delta_f S$ values are correct within the experimental range, the mathematical tools which are used during the extrapolation induce such an uncertainty that the results cannot be taken seriously. It is preferable by far to determine $\Delta_f G$ separately by activity measurements, and $\Delta_f H$ by calorimetry. Then the best value for $\Delta_f S$ can be established by a combination of the two experimental values (see Table 1).

REFERENCES

1 Du Sichen, S. Seetharaman and L.I. Staffansson, Metall. Trans. B, 20 (1989) 911.
2 H. Kleykamp, Ber. Bunsenges. Phys. Chem., 73 (1969) 354.
3 Y.Z. Vintaikin, Fiz. Met. Metalloved., 16 (1963) 144.
4 H. Tanaka, Y. Kishida, A. Yamaguchi and J. Moriyama, J. Jpn. Inst. Met., 35 (1971) 523.
5 R.G. Coltters and G.R. Belton, Metall. Trans. B, 15 (1984) 517.
6 H. Mabuchi, N. Sano and Y. Matsushita, Metall. Trans., 2 (1971) 1503.
7 K.K. Kelley, F.S. Boericke, G.E. Huffman and W.M. Bangert, U.S. Bur. Mines, Tech. Paper 662, Washington, DC, 1949.
8 A.D. Mah, U.S. Bur. Mines, RI 7217, Washington, DC, 1969.
9 W.M. Dawson and F.R. Sale, Metall. Trans. A, 8 (1977) 15.
10 A.D. Kulkarni and W.L. Worrell, Metall. Trans., 3 (1972) 2363.
11 R. Berkane, J.C. Gachon, J. Charles and J. Hertz, Calphad, 4 (1987) 375.