Free Energies of Formation of WC and W_2C, and the Thermodynamic Properties of Carbon in Solid Tungsten

D.K. Gupta and L.L. Seigle

Abstract

The activity of carbon in the two-phase regions - W + WC and W + W_2C has been obtained from the carbon content of iron rods equilibrated with mixtures of metal plus carbide powders. From this activity data the standard free energies of formation of WC and W_2C have been calculated to be

$$\Delta G_f^o \text{ (WC)} = -10{,}000 + 1.17\ T \pm 100 \text{ cal/mole}$$

$$\Delta G_f^o \text{ (}W_2C\text{)} = -7{,}480 - 0.435\ T \pm 100 \text{ cal/mole}$$

The temperature of the invariant reaction $W_2C = W + WC$ was fixed at 1570 ± 5°K. Using available solubility data for C in solid W, the partial molar free energy of C in the dilute solid solution was calculated to be

$$\Delta\bar{G}_C^\alpha = 23{,}000 - (0.67 - R \ln X_C^\alpha)\ T \pm 3000 \text{ cal/mole}$$

The heat of solution of C in W, $\Delta\bar{H}_C^\alpha = 23{,}000 \pm 5000$ cal/mole and the excess entropy for the interstitial solid solution, $\Delta\bar{S}_C^\alpha$ (xs,i) = -1.5 ± 2 cal/degree mole, assuming that the carbon atoms reside in the octahedral interstices of bcc W.

STATE U. OF N.Y. STONY BROOK

C.S. ?

NGR-33-015-035

(NASA-CR-139406) FREE ENERGIES OF FORMATION OF WC AND W2C AND THE THERMODYNAMIC PROPERTIES OF CARBON IN SOLID TUNGSTEN (State Univ. of New York) 26 p
CSCL 11F G3/17
N74-29983
Unclas
54907

Free Energies of Formation of WC and W_2C, and the Thermodynamic Properties of Carbon in Solid Tungsten

D. K. Gupta and L. L. Seigle

The interstitial elements, C,O, and N play an important role in the technology of the refractory metals Cr, Mo, W, Nb and Ta, since they can have a strong effect upon the low temperature strength and brittleness of these bcc metals. The fundamental properties of the interstitial element - refractory metal solid solutions are therefore of interest, and have been the subjects of many investigations up to the present. As part of a study of the thermodynamic properties of the interstitial elements in the refractory metals we have investigated the behavior of carbon in tungsten. It was our primary goal to establish the thermodynamic properties of C in the terminal solid solution, but in the course of this work the free energies of formation of the carbides of tungsten in equilibrium with the terminal solid solution, namely WC and W_2C, were also determined.

I. Experimental Procedure

The method chosen to determine both the thermodynamic properties of C in the terminal solid solutions, and the free energies of formation of the carbides, was that of equilibration of a mixture of tungsten and tungsten carbide powder with pure iron rods in a sealed quartz capsule containing a trace of oxygen. From the carbon content~~s~~ of the iron at equilibrium, an accurate value of the activity of carbon over the mixture can be obtained, since the concentration-activity relationship for dilute Fe-C alloys is well known.

This activity value can then be used to calculate the thermodynamic parameters for C in the terminal solid solution, with the aid of available solubility data, and also the free energies of formation of the carbides. The method is similar to that used by Heckler and Winchel to determine the activity of C in Fe-Ni-C austenite (1).

Chemical analyses of the as-received W and WC powders, as well as the vacuum-melted iron rod, are given in Table 1. The W and WC powders were intimately mixed in equal proportions by volume and then degassed at 1373°K for 24 hours in a vacuum of 10^{-5} torr. This degassing procedure reduced the oxygen content of the mixture to 59 ppm, and was necessary to prevent explosion of the quartz capsules upon subsequent annealing. The iron rod was reduced from 1/4" to 1/16" diameter by swaging. One and one-half inch lengths of the cleaned and degreased iron rod were sealed with approximately 200 grams of the powder mixture in heavy-walled quartz capsules about 1/2" O.D., 1/4" I.D., and 3" long. An air pressure of 1 torr was left in the capsules to be annealed below 1150°C, while those to be annealed at higher temperatures were sealed under a vacuum of 10^{-5} torr. The capsules were annealed for various lengths of time at temperatures ranging from 1173 - 1658 °K. Temperatures were measured with a calibrated Pt/Pt-10% Rh thermocouple. After annealing, the capsules were quenched into water, the iron rods removed, thoroughly cleaned by filing, and submitted for chemical analysis. Carbon, in the form of CO_2, was determined chromatographically after burning 2 grams of sample in oxygen, with a stated accuracy of ± 2 ppm.

Table 1.

Chemical Analysis of as-received W, WC powders and Iron Rod

Element	W (powder)	WC (powder)	Iron Rod
Fe	<5 ppm	100 ppm max.	99.9+%
W	99.99+%	93.74%	<5 ppm
C	<25 ppm	6.19% total, 0.05% free	<150 ppm
O	<100 ppm	750 ppm	<100 ppm
Si	<5 ppm		<50 ppm
Mn			<50 ppm
Mg	<2 ppm		<20 ppm
Ni	<5 ppm	50 ppm max.	< 5 ppm
Co	<5 ppm	50 ppm max.	< 5 ppm
Mo	<15 ppm	300 ppm max.	< 5 ppm
N	<1 ppm		<100 ppm
others	<5 ppm	200 ppm	<200 ppm

II. Experimental Results

Fig. 1 shows the carbon content of the iron rods after annealing at 1281° and 1483°K, as a function of time. It appears that equilibrium is obtained in approximately 12 hours at the lower, and 6 hours or less at the higher temperature. The equilibrium carbon content at various temperatures is shown in Table II, and the corresponding activity of carbon obtained from Chipman's equation (2)

$$\log a_C^{\gamma} = \frac{2300}{T} - 0.920 + \frac{3860}{T} Y_C + \log \frac{Y_C}{1-Y_C} \qquad (1)$$

in which Y_C = is the atom ratio, n_C/n_{Fe}, and T is in degrees Kelvin. Values of $RT \ln a_C$ are also given in Table II for use in subsequent calculations. No increase in the Si or W content of the iron rods after annealing in quartz in the presence of W + WC at 1483°K was detected by emission spectrographic analysis.

A. Free Energies of Formation of WC and W_2C

The tungsten side of the W-C phase diagram, according to the recent work of Doloff and Sara (3) Rudy, et.al (4), and Orton (5) is shown in Fig. 2. The transitions at ∿2350 and 2650°K, reported by Rudy, et al., are thought to be order-disorder reactions involving only the carbon atoms in W_2C. While WC has been consistently reported to exist as a line compound at the stoichiometric composition, the W_2C phase possesses an appreciable homogeneity range. It may be mentioned at this point that our data fix the $W_2C = W + WC$ invariant reaction at 1570 ± 5° K.

If we designate the terminal solid solution as α, WC as β, W_2C as γ, and let $X_C^{\beta\alpha}$ = mole fraction of C in β which is in equilibrium with α,

Table II

Free Energy of Formation of WC and W_2C

Temperature (^oK)	Carbon Conc. (ppm)	Activity of Carbon	RT ln a_C (cal./mole)
1173	423	0.0242	-8674
1223	645	0.0299	-8529
1273	887	0.0348	-8494
1308	1057	0.0370	-8568
1308	1117	0.0395	-8399
1333	1247	0.0410	-8460
1353	1346	0.0417	-8542
1358	1420	0.0435	-8459
1373	1540	0.0458	-8412
1378	1580	0.0460	-8431
1403	1812	0.0494	-8385
1408	1896	0.0508	-8337
1428	2062	0.0529	-8340
1453	2263	0.0549	-8379
1458	2365	0.0560	-8350
1483	2697	0.0602	-8280
1508	2866	0.0639	-8241
1524	3190	0.0667	-8199
1549	3465	0.0698	-8194
1573	3890	0.0737	-8150
1590	4047	0.0752	-8175
1596	4030	0.0754	-8197
1601	4120	0.0758	-8206
1607	4200	0.0768	-8195
1612	4280	0.0769	-8217
1617	4400	0.0779	-8201
1623	4470	0.0787	-8198
1629	4550	0.0791	-8212
1635	4640	0.0796	-8222
1658	4980	0.0824	-8223

$X_C^{\alpha\beta}$ = mole fraction of C in α which is in equilibrium with β, $\Delta\bar{G}_C^{\beta\alpha}$ = relative partial molar free energy of C in β which is in equilibrium with α, etc., we may write

$$\Delta G^{\beta\alpha} = X_C^{\beta\alpha}\, \Delta\bar{G}_C^{\beta\alpha} + X_W^{\beta\alpha}\, \Delta\bar{G}_W^{\beta\alpha} \tag{2}$$

Since $X_C^{\alpha\beta} \leq 10^{-4}$ below ∿ 1670°K, we may set $\Delta\bar{G}_W^{\beta\alpha} = \Delta\bar{G}_W^{\alpha\beta} \cong RT \ln X_W^{\alpha\beta} \cong 0$. Furthermore, $\Delta\bar{G}_C^{\beta\alpha} = RT \ln a_C^{\beta\alpha}$, where $a_C^{\beta\alpha}$ is the measured activity of C over the two-phase mixture. Therefore,

$$\Delta G^{\beta\alpha} \cong X_C^{\beta\alpha}\, RT \ln a_C^{\beta\alpha} \tag{3}$$

Similarly,

$$\Delta G^{\gamma\alpha} \cong X_C^{\gamma\alpha}\, RT \ln a_C^{\gamma\alpha} \tag{4}$$

According to the literature, WC exists as a closely stoichiometric compound. Precision x-ray diffraction measurements of the lattice parameters of WC equilibrated at ∿ 1570°K with W on the one hand, and C (graphite) on the other revealed slightly (∿ 0.1%) higher "c" and "a" values in the WC equilibrated with C, but it is probably safe to assume $X_C^{\beta\alpha}$ is close to 1/2. Therefore, from equ. 3, $\Delta G^{\beta\alpha} = 1/2\, RT \ln a_C^{\beta\alpha}$, and the standard free energy of formation permole of WC can be obtained from the measured activity values as

$$\Delta G_f^o\ (WC) = RT \ln a_C^{\beta\alpha} \tag{5}$$

Values of $RT \ln a_C^{\beta\alpha}$ vs T are plotted in Fig. 3*. A least squares fit

---

*In Fig. 3, a_C is the activity of C in the two phase mixture and $a_C = a_C^{\beta\alpha} = a_C^{\alpha\beta}$ below 1570°K, $a_C = a_C^{\gamma\alpha} = a_C^{\alpha\gamma}$ above 1570°K.

of the points below 1570°K gives

$$\Delta G_f^o\ (WC) = -10{,}000 + 1.17\ T \pm 100\ \text{cal/mole}$$

$$\Delta H_f^o\ (WC) = -10{,}000 \pm 200\ \text{cal/mole} \qquad (6)$$

$$\Delta S_f^o\ (WC) = -1.17 \pm 0.1\ \text{cal/mole}$$

The discontinuity in the slope of the curve in Fig. 3, occurring at 1570°K, arises, because, according to the phase equilibrium diagram, the terminal solid solution is in equilibrium with W_2C rather than WC above this temperature. In agreement, x-ray diffraction patterns of powder mixtures quenched from 1570°K and lower revealed the presence of only WC, while the diffraction patterns of samples quenched from higher temperatures showed lines from both the W_2C and WC phases. As already mentioned, the W_2C phase possesses an appreciable homogeneity range. The composition in equilibrium with α varies with temperature and $X_C^{\gamma\alpha} < 1/3$, as shown by the data given in Table III from Rudy, et.al (4) and Doloff, et.al (3). It is necessary to take account of these facts in calculating the free energy of formation of the γ phase from our activity data.

The problem may be stated as follows: Given the activities of C and W at a series of compositions along the phase boundary of the γ phase, to calculate ΔG at the stoichiometric composition over the temperature range in question. A good approximation can be obtained by use of the Wagner-Schottky theory of defect compounds as explained in detail in Appendix I, and values of ΔG_f^o for the stoichiometric compound are calculated from our data to be

Table III.

Composition of W_2C (γ) in Equilibrium with Terminal Solid Solution

T°K	$X_C^{\gamma\alpha}$	Reference
2473	0.292	(4)
2733	0.286	(3)
2983	0.256	(4)

$$\Delta G_f^o\ (W_2C) = -7480 - 0.435\ T \pm 100\ \text{cal/mole}$$

$$\Delta H_f^o\ (W_2C) = -7480 \pm 200\ \text{cal/mole} \qquad (7)$$

$$\Delta S_f^o\ (W_2C) = 0.435 \pm 0.1\ \text{cal/degree mole}$$

If we ignore the departure from stoichiometry and simply use equ. (4) with $X_C^{\gamma\alpha} = 1/3$, a value, $\Delta G_f^o\ (\gamma) = 3\Delta G^{\gamma\alpha} = -7300 -0.553\ T$ cal/mole is obtained from a least squares fit of the RT ln $a_C^{\alpha\gamma}$ data of Fig. 3.

B. Thermodynamic Properties of C in Solid W.

The carbon activities over the two-phase metal + carbide mixtures given in Table 2 are also the activities of carbon in the terminal solid solution. It is, therefore, possible to derive the thermodynamic parameters for carbon in the solid solution from these data and a knowledge of the solid solubility.

We may write, in general

$$\Delta\bar{G}_C^\alpha = RT\ \ln\ a_C = \Delta\bar{H}_C^\alpha - T\ \Delta\bar{S}_C^\alpha \qquad (8)$$

If $\Delta\bar{S}_C^\alpha$ is divided into a configurational and non-configurational part, assuming the carbon atoms are randomly distributed in the interstitial sites

$$\Delta\bar{S}_C^\alpha\ (\text{config.}) = -R\ \ln \frac{X_C^\alpha}{\theta(1-X_C^\alpha)-X_C^\alpha} \qquad (9)$$

in which θ = no. of interstitial sites per atom. A partial molar excess free energy for the interstitial solution, $\Delta\bar{G}_C^\alpha$ (xs,i.), may then be defined

$$\Delta\bar{G}_C^\alpha\ (\text{xs,i}) = \Delta\bar{G}_C^\alpha - \Delta\bar{G}_C^\alpha\ (\text{ideal, i}) = \Delta\bar{H}_C^\alpha - T\ \Delta\bar{S}_C^\alpha\ (\text{xs,i}) \qquad (10)$$

where $\Delta\bar{S}^{\alpha}_{C}$ (xs,i) = $\Delta\bar{S}^{\alpha}_{C} + R \ln \dfrac{X^{\alpha}_{C}}{\theta(1-X^{\alpha}_{C})-X^{\alpha}_{C}}$ is the non-configurational or excess entropy of the interstitial solid solution*. Since the C-W solutions are very dilute (the solubility of C in W over the temperature range of our measurements, $X^{\alpha\gamma}_{C} < 10^{-4}$), we may assume $\Delta\bar{H}^{\alpha}_{C}$, $\Delta\bar{S}^{\alpha}_{C}$ (xs,i), and $\Delta\bar{G}^{\alpha}_{C}$ (xs,i) are independent of composition. We may then write

$$\Delta\bar{G}^{\alpha}_{C}\ (xs,i) = \Delta\bar{H}^{\alpha}_{C} - T\,\Delta\bar{S}^{\alpha}_{C}\ (xs,i) = RT\left(\ln a^{\alpha\gamma}_{C} - \ln \frac{X^{\alpha\gamma}_{C}}{\theta(1-X^{\alpha\gamma}_{C})-X^{\alpha\gamma}_{C}}\right)$$

Since $X^{\alpha\gamma}_{C} \ll 1$, this may be written as

$$\Delta\bar{G}^{\alpha}_{C}\ (xs,i) = \ldots \simeq RT \ln \frac{\theta a^{\alpha\gamma}_{C}}{X^{\alpha\gamma}_{C}} \qquad (11)$$

In these expressions $X^{\alpha\gamma}_{C}$ represents the solubility of carbon in the terminal solid solution, and $a^{\alpha\gamma}_{C}$ the activity of carbon over the two phase metal + carbide mixture. The enthalpy and excess entropy terms may then be obtained by the use of standard expressions,

$$\Delta\bar{H}^{\alpha}_{C} = \left[\frac{\partial\left(\frac{\Delta\bar{G}^{\alpha}_{C}\ (xs,i)}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right]_P = \frac{\partial}{\partial\left(\frac{1}{T}\right)}\left(R \ln \frac{\theta a^{\alpha\gamma}_{C}}{X^{\alpha\gamma}_{C}}\right) \qquad (12)$$

$$\Delta\bar{S}^{\alpha}_{C}\ (xs,i) = -\left[\frac{\partial\,\Delta\bar{G}^{\alpha}_{C}\ (xs,i.)}{\partial T}\right]_P = \frac{\partial}{\partial T}\left(RT \ln \frac{\theta a^{\alpha\gamma}_{C}}{X^{\alpha\gamma}_{C}}\right) \qquad (13)$$

The solubility of C in W has been determined by Goldschmid and Brand (11) and Roy (12). Goldschmid and Brand measured the lattice parameters of

---

*It will be noted that we are defining the ideal interstitial solid solution as one in which the relative partial molar free energy of the solute = $RT \ln \dfrac{X}{\theta(1-X)-X}$ rather than RT ln X. This is felt to be more appropriate for the solute in interstitial solution, as mentioned in ref. (14).

carburized and quenched 0.001" tungsten wires, while Roy chemically analyzed the solid solution core of carburized W rods. In Goldschmid and Brand's work the quenching rate of the fine wires was undoubtedly very rapid, but it is not clear that the same was true for the portions of arc-melted ingot used to determine the lattice parameter vs carbon content relationship. If carbide had precipitated from this ingot during quenching from 2773°K, the solubilities reported by Goldschmid and Brand would be systematically low. The method used by Roy was not subject to error due to precipitation of carbide during cooling from the carburizing temperature, since precipitates formed during cooling were automatically included in the chemical analysis. Furthermore, Roy's method has yielded carbon solubilities in Mo, Nb, and Ta in good agreement with those of other workers. There is reason, therefore, to place more reliance on Roy's solubility values than Goldschmid and Brand's.

Roy's data are shown in Fig. 4. In order to calculate the thermodynamic parameters for the solid solution it is necessary to extrapolate the solubility curve down to the temperature range of our activity measurements. The existence, according to Rudy (4), of order-disorder transitions in W_2C at ∿ 2100 and ∿ 2650°K raises a question about how to carry out this extrapolation. Theoretically, the $\ln X_C^{\alpha\gamma}$ vs $\frac{1}{T}$ line should bend downwards and become slightly steeper at lower temperatures. Roy's data seem to indicate, however, a curvature in the other direction, if anything. In view of this discrepancy and the considerable scatter of the lower temperature values, it did not seem possible to make any special allowance for the transitions at 2100 and 2650°K. It was decided therefore to simply accept Roy's straight line for the $\ln_C^{\alpha\gamma}$ vs. $\frac{1}{T}$

relationship and use his expression for the solubility curve, namely

$$\ln X_C^{\alpha\gamma} = 0.06 - \frac{15000}{T} \quad (14)$$

As previously mentioned, a linear fit of the RT ln a_C data above 1570°K (Fig. 3) yields the expression

$$RT \ln a_C^{\alpha\gamma} = -7300 - 0.553\ T \quad (15)$$

When (14) and (15) are substituted into (11), (12) and (13), we obtain, from Roy's solubility data

$$\begin{aligned} \Delta\bar{G}_C^{\alpha}\ (xs,i) &= 23{,}000 - (0.67 - R \ln \theta)\ T \pm 3000 \text{ cal/mole} \\ \Delta\bar{H}_C^{\alpha} &= 23{,}000 \pm 5000 \text{ cal/mole} \\ \Delta\bar{S}_C^{\alpha}\ (xs,i) &= 0.67 - R \ln \theta \pm 2.0 \text{ cal/degree mole} \end{aligned} \quad (16)$$

Assuming the C atoms are in the octahedral interstitial sites, $\theta = 3$, $\Delta\bar{G}_C^{\alpha}\ (xs,i) = 23{,}000 + 1.5\ T$ and $\Delta\bar{S}_C^{\alpha}\ (xs,i) = -1.5$ cal/degree mole. We may also write

$$\begin{aligned} \Delta\bar{G}_C^{\alpha} &= \Delta\bar{G}_C^{\alpha}\ (xs,i) + RT \ln \frac{X_C^{\alpha}}{\theta} = 23{,}000 - (0.67 - R \ln X_C^{\alpha})T \\ \text{and} \quad \Delta\bar{S}_C^{\alpha} &= \Delta\bar{S}_C^{\alpha}\ (xs,i) + \Delta\bar{S}_C^{\alpha}\ (\text{config.}) = 0.67 - R \ln X_C^{\alpha} \end{aligned} \quad (17)$$

It is seen that $\Delta\bar{H}_C^{\alpha}$ and $\Delta\bar{S}_C^{\alpha}$ (xs,i) appear as constants independent of temperature. This is because two-parameter expressions have been accepted for both ln $X_C^{\alpha\gamma}$ and RT ln $a_C^{\alpha\gamma}$.

III. Discussion

A. Thermodynamic Properties of WC and W_2C

Previous determinations of the free energy of formation of WC have been made by Gleiser and Chipman (8), Orton (5) and Alekseev and Schwartzman (15). Gleiser and Chipman report $\Delta G_f^o(WC) = -8340$ cal/mole over the temperature range 1215 - 1266°K, determined by studying the CO-CO_2 equilibrium over mixtures of W and WC. These author's did not attempt to obtain enthalpies and entropies of formation from their data. Over the same temperature range, in reasonably good agreement, our data indicate an average value $\Delta G_f^o(WC) \cong -8570$cal/mole. Both Orton and Alekseev and Schwartzman studied the H_2-CH_4 equilibrium over various tungsten + tungsten carbide mixtures. The data of these authors has been critically reviewed by Storms (9), who points out the uncertainties and inconsistencies in their results.

The high temperature heat capacity of WC has been measured by Chang (19) and Levinson (16). Chang has tabulated the thermal functions of WC from 298 - 3000°K. Our measurements, in conjunction with His data and the JANAF (20) values of the thermal functions of W and C, indicate that $\Delta H_{298}^o(WC) = -10,500$ cal/mole and $\Delta S_{298}^o(WC) = -2.1$ cal/degree mole. The value for the standard heat of formation so obtained is in reasonably good agreement with that determined by Mah (7) and McGraw, et al. (6) using combustion calorimetry, namely, $\Delta H_{298}^o(WC) = -9,700 \pm 400$ cal/mole. It appears quite certain, therefore, that $\Delta S_{298}^o(WC)$ is negative, as indicated by our free energy data. This suggests, in turn, that the heat capacity of WC at low temperatures must be lower than that of a mixture of the elements since the heat capacity of WC at high temperatures, according to the data of Chang (19) and Levinson (16), is greater than that of W+C. A similar conclusion is implied by the calculations of Chang (19).

Our value for the heat of formation of W_2C, $\Delta H_f^o(W_2C)$ = -7480 ±200 cal/mole is in fair agreement with the value $\Delta H^o_{298}(W_2C)$ = -6,300 ±600 cal/mole determined by Mah (7) by combustion calorimetry of a sample containing W and WC in addition to W_2C. (Correction was made for the presence of these substances.) It appears quite certain, therefore, that the entropy of formation of W_2C is slightly positive as indicated by the slope of our free energy vs. temperature curve.

B. Thermodynamic Properties of C in Solid W

The accuracy of the calculated thermodynamic properties of C in W depends upon the accuracy of the solubility data, and it is evident from the scatter of points in Roy's data, Fig. 4, as well as other factors discussed previously, that there is a degree of uncertainty in the extrapolation of the solubility line. Therefore, rather wide limits of error are placed upon the calculated enthalpy and excess entropy of solution ($\Delta\bar{H}_C^\alpha$ = 23,000 ± 5000 cal/mole, $\Delta\bar{S}_C^\alpha$ (xs,i) = -1.5 ± 2 e.u.). It is, nevertheless, clear that the heat of solution is highly positive and the interstitial solution exhibits a very large positive deviation from ideality. For example the activity coefficient $\gamma_C^\alpha = \frac{a_C^\alpha}{X_C^\alpha} > 200$ at 2000°K. This is to be expected from the very low solid solubility of C in W.

The value of the excess entropy of carbon, $\Delta\bar{S}_C^\alpha$ (xs,i) = -1.5 ± 2 e.u. seems rather low for a solution of this type, in which elastic distortion of the metal lattice by the interstitially dissolved atom might be expected to lead to a positive excess entropy. Calculations of the thermodynamic properties of C in solid Mo, Nb, and Ta from solubility data indicate that the excess entropy of C in these bcc metals varies from 5-10 e.u./mole (18) and McLellan (17) has pointed out that the excess entropy of C in α-Fe is about 7 e.u. There is a large element of uncertainty in the interpretation of excess entropy values, however, and it is not clear what significance to attach to the observed differences.

Acknowledgement

This work was supported in part by the NASA Lewis Research Laboratory under grant number NGR-33-015-035. We are also grateful for the comments of Dr. E.K. Storms regarding interpretation of some of the data.

APPENDIX I

The variation of ΔG_f^o (W_2C) with composition and the free energy of formation of the stoichiometric compound can be estimated from the values of carbon activity along the phase boundary, $a_C^{\gamma\alpha}$, with the aid of Wagner's model (10) for the thermodynamic properties of defect compounds. Powder patterns of W_2C have been indexed as L'_3 structure type. In this, the metal atoms form an hcp lattice and the C atoms occupy one-half of the octahedral interstitial sites. At any temperature above absolute zero defects exist on the carbon sublattice, namely, carbon atoms missing from normally occupied (A) sites, called vacancies, and carbon atoms on normally unoccupied (B) sites, called interstitials. Let us designate the following quantities:

N = total number of atoms in the compound

N_S = number of lattice sites

N_A, N_B = number of A and B sites, respectively

N_+, N_- = number of interstitials and vacancies, respectively, on the carbon sublattice

ΔG_f^* = free energy of formation of the compound in a state of perfect order

G_+, G_- = free energies of formation of a mole of interstitial and vacancies, respectively

Also let $n_+ = \frac{N_+}{N}$, $n_- = \frac{N_-}{N}$, $y = \frac{N_S}{N}$,

and let the carbide of variable composition be designated as $W_{1-x}C_x$, and that of stoichiometric composition as $W_{1-x_0}C_{x_0}$. Following Wagner, the free energy of formation of the defect carbide may be written as:

$$\Delta G_f^o = \frac{N_S}{N}\Delta G_f^* + \frac{N_+}{N} G_+ + \frac{N_-}{N} G_- - kT \ln\left\{\frac{N_A!}{(N_A-N_-)!N_-!}\,\frac{N_B!}{(N_B-N_+)!N_+!}\right\} \tag{1}$$

Since $N_A = N_B = x_0N_S$, using Stirling's approximation equation (1) may be written:

$$\Delta G_f^o = y\Delta G_f^* + n_+G_+ + n_-G_- - RT\{2x_0y \ln x_0y - n_+ \ln n_+ - n_-\ln n_- - (x_0y-n_+)\ln(x_0y-n_+) - (x_0y-n_-) \ln(x_0y-n_-)\} \tag{2}$$

Minimizing ΔG_f^o with respect to the concentration of defects under the conservation conditions

$$xN = x_0N + N_+ + N_- \tag{3}$$

and $$(1-x_0)N_S = (1-x)N.$$

It can be shown that at equilibrium:

$$\frac{\partial \Delta G_f^o}{\partial n_+} + \frac{\partial \Delta G_f^o}{\partial n_-} = 0 \tag{4}$$

from which it can then be shown that:

$$n_- = \tfrac{1}{4}\{2x - P[1-x] \pm [8x^2 - 4x - P^2 - (1-x)^2]^{\frac{1}{2}}\} \tag{5}$$

where $P = \dfrac{\exp\left(-\dfrac{\Delta G}{RT}\right) + 1}{\exp\left(-\dfrac{G}{RT}\right) - 1}$, $\Delta G = G_+ + G_-$

If $G_f^o = G_f^o(n_+, n_-, y)$, it may be shown by differentiation of equation (2), and use of equations(3) and (4) that:

$$\frac{d\Delta G_f^o}{dx} = \frac{1}{x_0-1}\left\{G_+ - RT \ln \frac{x_0y-n_+}{n_+} + \Delta G_f^* - RT \ln \frac{x_0^2y^2}{(x_0y-n_+)(x_0y-n_-)}\right\} \tag{6}$$

The partial molar free energy of carbon is given by the standard relationship:

$$\Delta\bar{G}_C^{\gamma} = \Delta G_f^o + (1-x)\frac{d\Delta G_f^o}{dx} \tag{7}$$

from which it may be shown that:

$$G_+ = \frac{1}{(n_+-y-n_-)}\{\Delta G_C^{\gamma} - n_-\Delta G + (n_+-y)[RT\ \ln\left(\frac{x_0y-n_+}{n_+}\right)] + n_-RT\ \ln\left(\frac{x_0y-n_-}{n_-}\right)\} \tag{8}$$

and
$$\Delta G_f^* = \frac{G_+-n_-\Delta G}{3} + \frac{2}{3}RT\{\frac{2x_0}{(1-x_0)}\ \ln x_0y - \frac{(n_++x)}{(1-x_0)}\ln n_+ - n_-\ln n_- - \frac{x_0-x-n_+(1-x_0)}{(1-x_0)}\cdot \ln(x_0y-n_+) - \frac{x_0-n_-(1-x_0)}{(1-x_0)}\ln(x_0y-n_-)\} \tag{9}$$

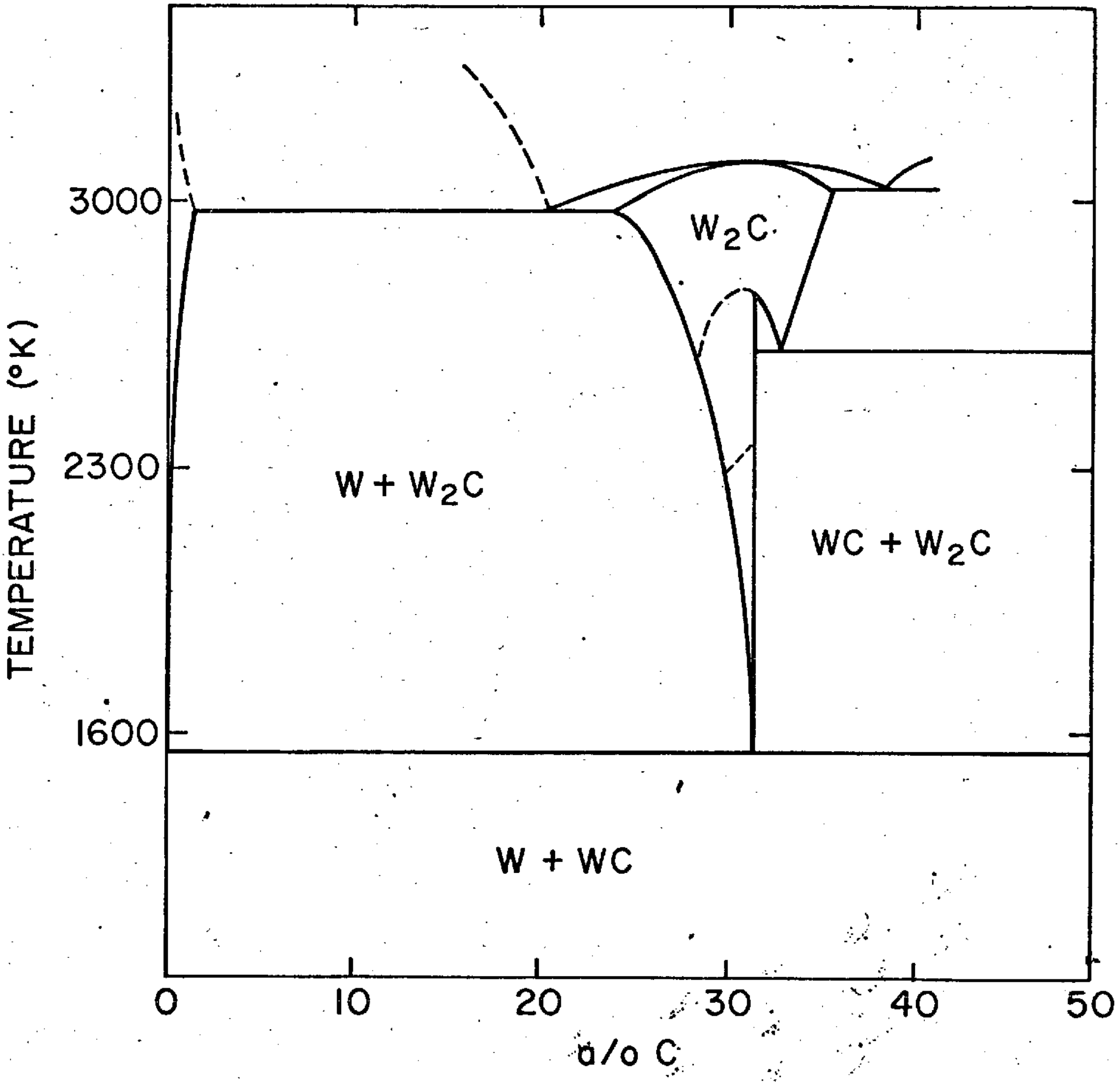
The above equations have been used to calculate $\Delta G_f^o(W_{1-x}C_x)$ as a function of x in the following way: Values of $\Delta\bar{G}_C^{\gamma\alpha}$ at various phase boundary compositions, $x_C^{\gamma\alpha}$, are known from the measured carbon activity values in the two-phase mixture, and values of $x_C^{\gamma\alpha}$ obtained by extrapolating the phase boundary data previously given in Table III. (This has been done by plotting $\ln(x_0-x_C^{\gamma\alpha})$ vs. 1/T). A value of $\Delta G \simeq 2700$ cal/mole was estimated from the temperature of the order - disorder transformation in W_2C, $T_t \cong 2700^oK$. It is assumed that G_+, G_- and ΔG_f^* do not vary with composition in W_2C. Substituting values of $\Delta\bar{G}_C^{\gamma\alpha}$, $x_C^{\gamma\alpha}$ and $\Delta G = 2700$ cal/mole in equations (3), (5), (8) and (9), values for n_-, n_+, G_+, G_-, and ΔG_f^* can be determined at various compositions and temperatures. These can be used in equation (2) to obtain ΔG_f^o $(W_{1-x}C_x)$ as a function of x and T. Figure 5 shows the variation of ΔG_f^o with carbon content so calculated. It was found that changing the value of $\Delta G = G_+ + G_-$ had surprisingly little effect on $\Delta G_f^o(W_2C)$ obtained by this method. For example, varying ΔG from 1000 to 10,000 cal/mole changed ΔG_f^o by less than 5 cal/mole.

References

1. A.J. Heckler and P.J. Winchel: Trans. TMS-AIME, 1963, vol. 227, p.732.
2. J. Chipman: Trans. TMS-AIME, 1972, vol. 3, p.56.
3. R.T. Dolloff and R.V. Sara: WADD Technical Report 60-143, part II, 1961, Wright-Patterson Air Force Base, Ohio.
4. E. Rudy, et.al.: AFML Technical Report 65-2, part I, vol. VI (1966), Part V(1 Wright-Patterson Air Force Base, Ohio.
5. G.W. Orton: Trans. TMS-AIME, 1964, vol. 230, p.600; also Ph.D. Thesis, Ohio State Univ., Columbus, Ohio, 1961, Univ. Microfilm L.C. card no. MIC 61-2839 Dissertation Abstracts, 22, 527.
6. L.D. McGraw, et.al.: J. Am. Chem. Soc., 1947, vol. 69, p.329.
7. A.D. Mah: Bureau of Mines Report of Investigation BM-RI-6337, 1963.
8. M. Gleiser and J. Chipman: Trans. TMS-AIME, 1962, vol. 224, p.1278.
9. E.K. Storms: The Refractory Carbides, Academic Press, N.Y., 1967.
10. C. Wagner: Thermodynamics of Alloys, Addison-Wesley, London, 1952.
11. H.J. Goldschmidt and J.A. Brand: J. Less Common Metals, 1963, vol. 5, p.181.
12. U. Roy: Z. Metallk, 1966, vol. 57, p.732.
13. R.A. Swalin: Thermodynamics of Solids, J. Wiley & Sons, N.Y., 1972.
14. S.C. Srivastava and L.L. Seigle: Trans. TMS-AIME 1974, vol. 5, p.49.
15. V.I. Alekseev and L.A. Schwartzman: Izv. Akad. Nauk, SSSR, Met. i Gorn. Delo Met i Toplivo, 1963, vol. 6, p.171.
16. L.S. Levinson: J. Chem. Phys.,1964, vol. 40, p.1437.
17. R.B. McLellan: Trans. TMS-AIME, 1965, vol. 233, p.1664.
18. A.C. Huang: M.S. Thesis, State Univ. of New York, Stony Brook, N.Y., 4/9/69.
19. Y.A. Chang: Trans. TMS-AIME, 1967 vol. 239, p. 1685.
20. JANAF Thermochemical Tables, 2nd Edition NSRDS-NBS37, U.S. Govt. Printing Office, Wash. D.C., 1971.

LIST OF FIGURES

Fig



W$_2$C
W + W$_2$C
WC + W$_2$C
W + WC
3000
2300
1600
TEMPERATURE (°K)
0
10
20
30
40
50
a/o C

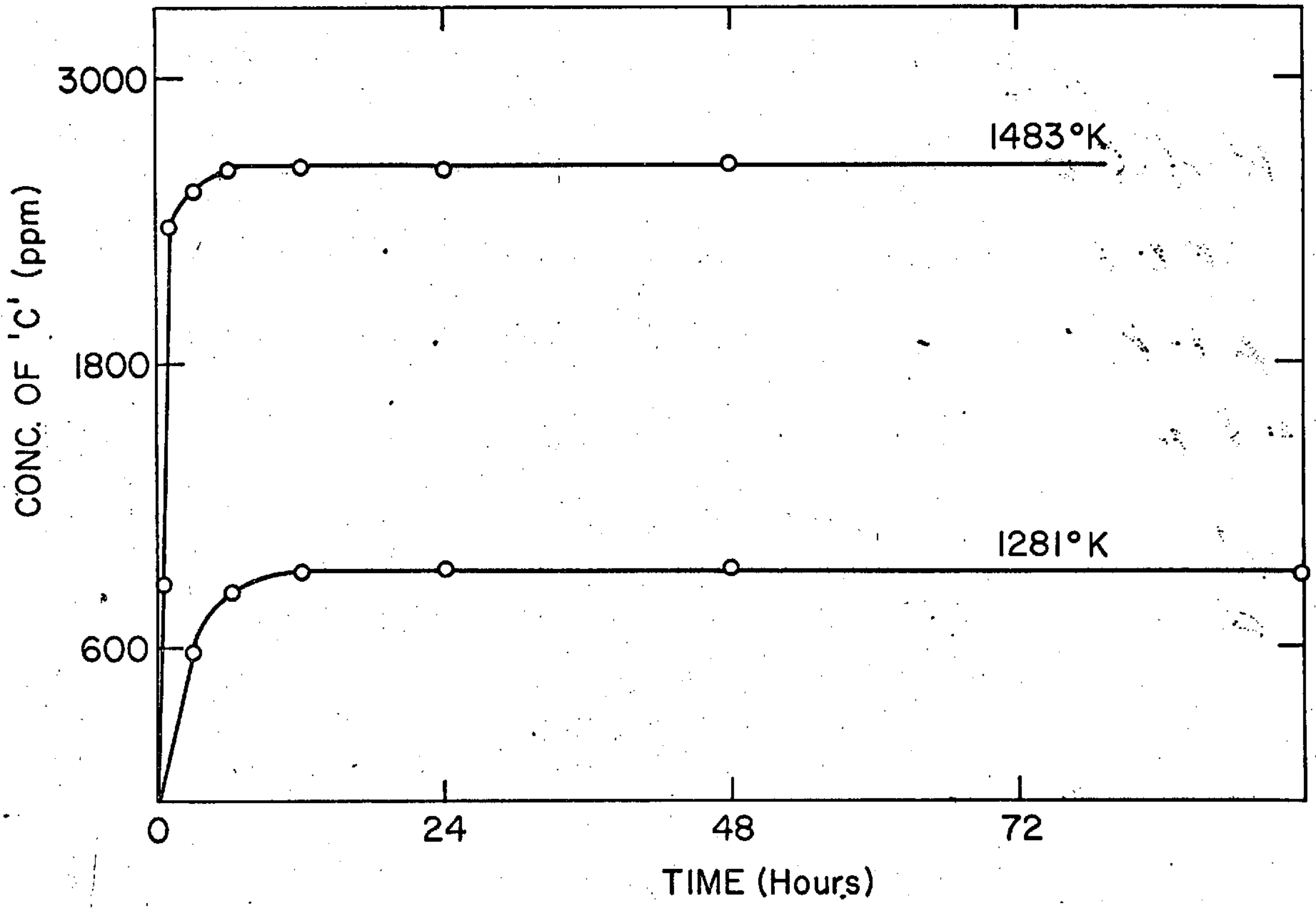
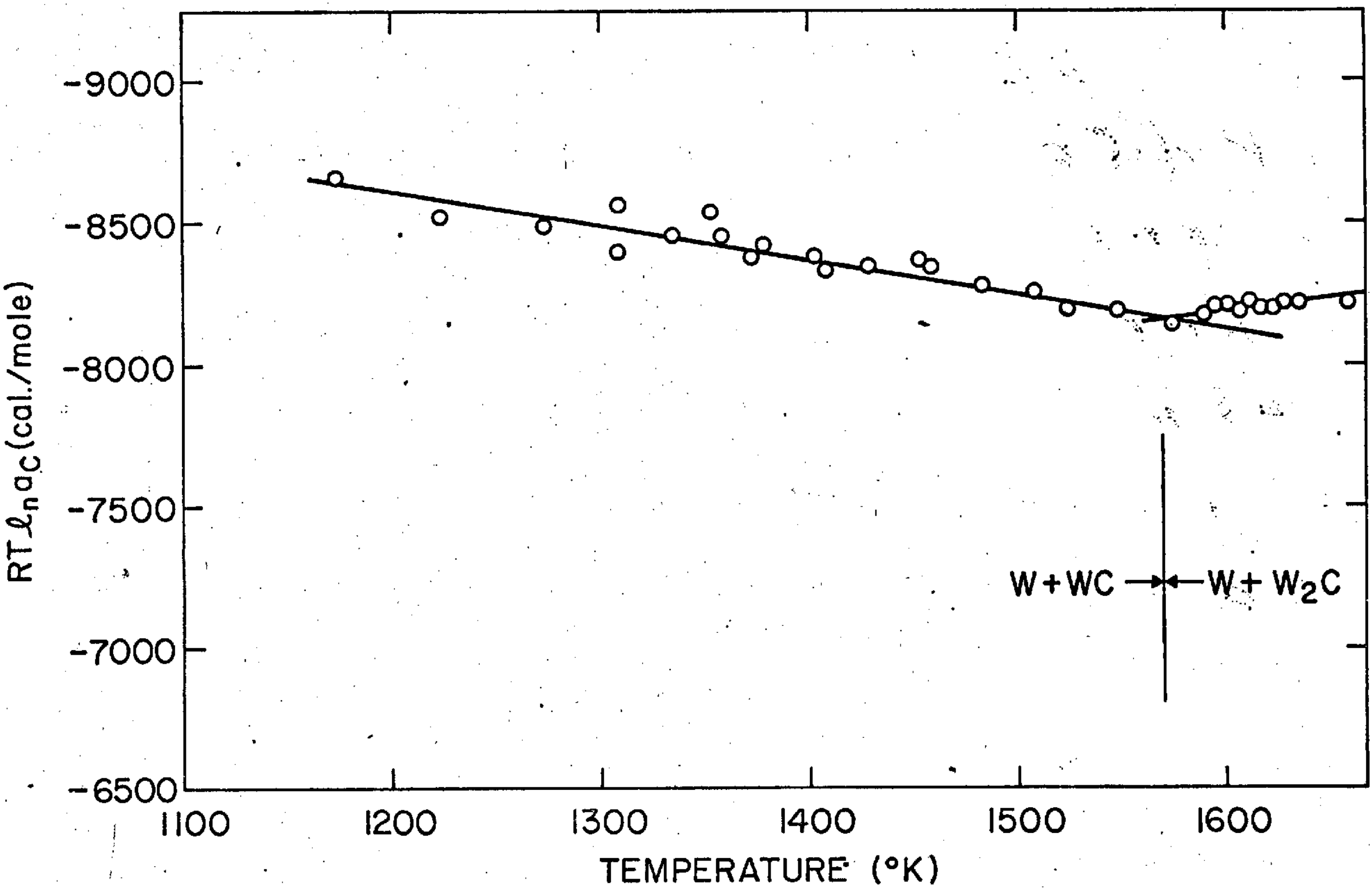


Fig. 2

Fig 3



-9000
-8500
-8000
-7500
-7000
-6500
$RT\,\ell_n a_C$ (cal./mole)
1100
1200
1300
1400
1500
1600
TEMPERATURE (°K)
W + WC
W + W_2C

Fig. 3

Fig 4

Fig. 4

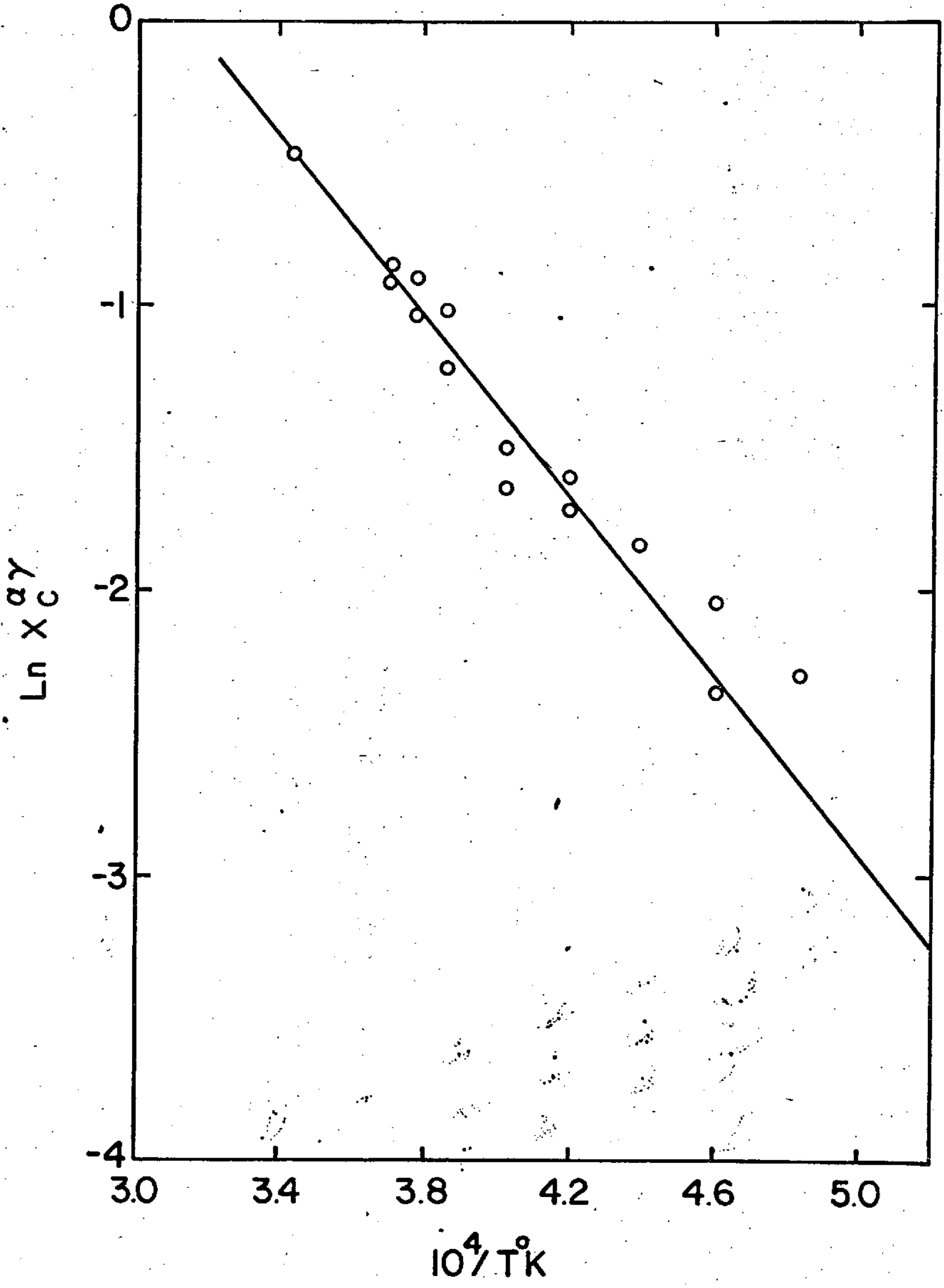
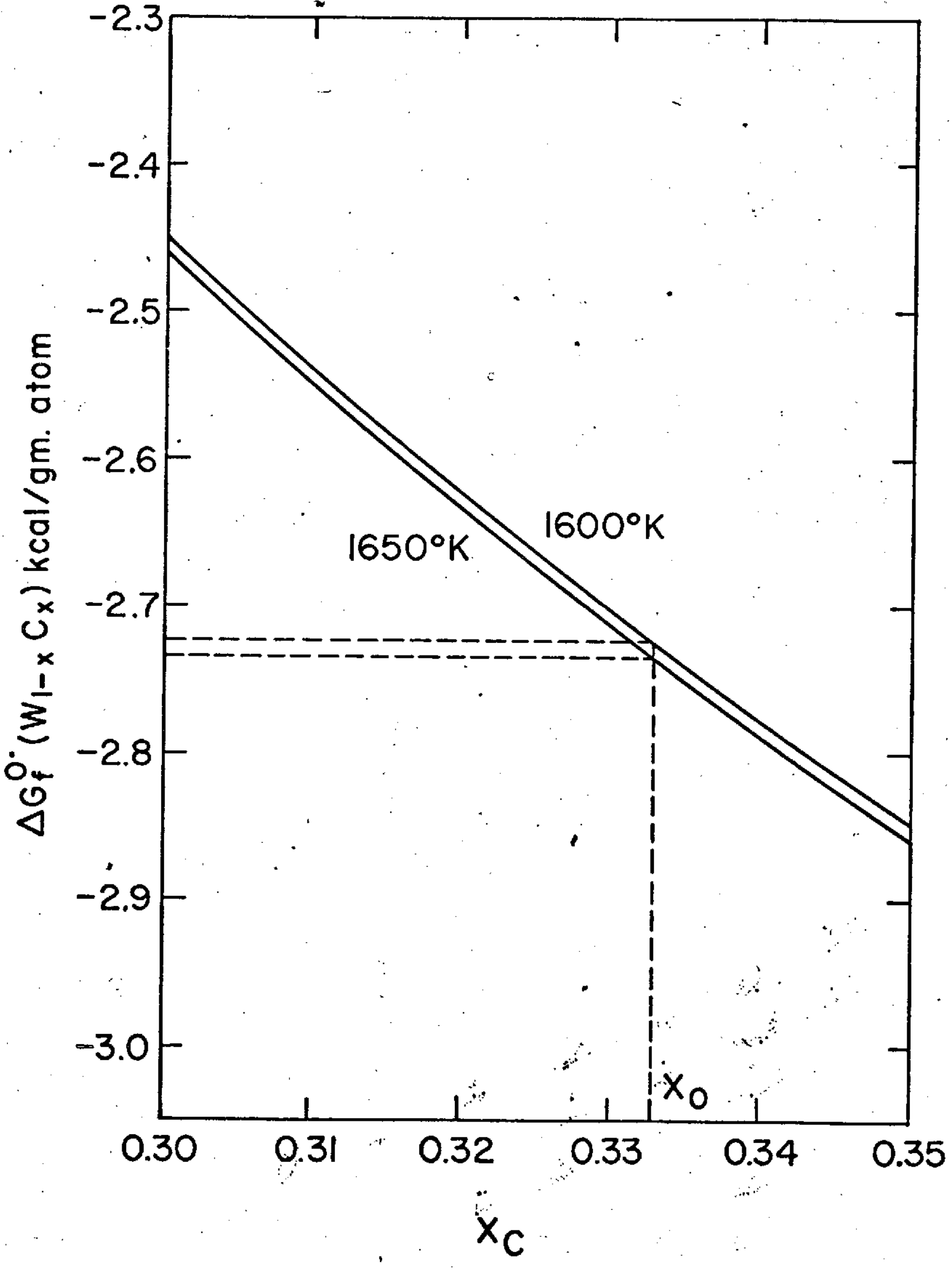


Fig. 5


-2.3
-2.4
-2.5
-2.6
-2.7
-2.8
-2.9
-3.0
$\Delta G_f^{0'}(W_{1-x}C_x)$ kcal/gm. atom
1600°K
1650°K
x_0
0.30
0.31
0.32
0.33
0.34
0.35
x_C