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Computational thermodynamics of the Zr–N system

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Abstract

Thermodynamic constraints are used to study the thermodynamic functions of the Zr–N system over the temperature range from 1500 K to 3670 K. The results are presented as the nitrogen isobars superimposed on the revised phase diagram. The Gibbs energies of solution of nitrogen dissolution in solid and liquid Zr are also determined with the assumption that nitrogen dissolution in Zr follows Sievert's law.

Keywords: Thermodynamics; Zirconium; Nitrogen

1. Introduction

Thermodynamic constraints relating the integral molal quantities of a compound with its relative partial molal quantities, or relating the relative partial molal quantities themselves, provide a powerful tool for evaluating or generating the thermodynamic functions, sometimes even in regions where no data are available.

At very high temperatures, experimental determination of thermodynamic data becomes increasingly difficult and costly, not only because of reactions between the specimen and the container, but also because of the difficulties in controlling the composition of samples which do not vaporize congruently. Most of the reported thermodynamic data of high temperature compounds have been determined for compositions close to exact stoichiometry. Pressure-composition-temperature (p-C-T) relationships for most of the phases are usually not well established, especially in regions where no experimental data are available. In addition, the integral molal properties such as the enthalpy (entropy) of formation reported from literature are often inconsistent. However, consistent thermodynamic information can be developed using thermodynamic constraints.

The transition-metal nitrides exist over broad composition ranges, and it is necessary to know the variation of the chemical potentials or activities as functions of composition in order to predict the stability of these phases in different environments. The Zr–N system has been chosen not only because of current interest [1] in these compounds, but to demonstrate the utility of the thermodynamic constraint method. Using a similar constraint, Wang and Olander established the full pressure-composition-temperature (p-C-T) spectrum in the Zr–O [2], U–O [2], and Zr–H [3] systems, and Kubachewski et al. evaluated the Ti–O [4] and Zr–O [5] systems.

Nitrogen potentials for the Zr–N system available from the literature are scant and inconsistent. Kaufman and Clougherty [6] proposed the p-C-T relationships for αZr. Kibler et al. [7] and Khromov and Svistunov [8] investigated equilibrium nitrogen pressures in the σZrNC solid solution at temperatures from 1700 K to 2300 K and from 1400 K to 2425 K, respectively. Eropyan and Avarbe [9] analyzed the dependence of the composition of the nitride phase (σZrN_C) on the equilibrium nitrogen pressure over a wide range of temperatures (2480 K–3670 K). The p-C-T relationship in the αZr/σZrN_C two-phase region has been investigated by Kaufman and Clougherty [6] and Khromov and Svistunov [8]. The free energy functions of zirconium nitride have been extensively studied [10–17]. Reported values of $\Delta H_f^0(\mathrm{ZrN})$ at 298 K include -365.1 [10], -336.7 [11], -371.4 [12], -364.7 [13], and -343.8 [14] kJ mole^{-1}. Reported values of $\Delta S_f^0(\mathrm{ZrN})$ at 298 K include -95 [10,13] and -92 [14] J mole^{-1} K^{-1}.

The integral Gibbs energy of formation of the nitride (MN_C) formed by the reaction

$$M+\frac{C}{2}N_{2(g),\,1\,\mathrm{tm}}=MN_C \tag{1}$$

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is related to the relative partial molal free energies of nitrogen over the entire N/M range by

$$\Delta G_f^0(MN_C) = \frac{RT}{2}\int_0^C \ln p dC' \tag{2}$$

where p is the equilibrium nitrogen pressure (atm) of the nitride and R is the gas constant. p depends on C, the N/M ratio. It is worth noting that pure zirconium is used as the standard state for the integral Gibbs energy of formation and 1 atm of N_2 is the reference standard state of the relative partial molal energies in Eq. (2). A relation similar to Eq. (2) can be derived for the relative partial molal enthalpy ($\Delta\bar{H}(N_2)$) and the integral heat of formation of the nitride ($\Delta H_f^0(MN_C)$):

$$\Delta H_f^0(MN_C) = \frac{1}{2}\int_0^C \Delta\bar{H}(N_2)dC' \tag{3}$$

The enthalpy constraint was employed in studying the heat effects in Zircaloy oxidation [18] and in checking the consistency of measured relative partial molal enthalpies of oxygen in both the Zr–O [19] and Ti–O [20] systems.

Speiser [21] showed that three solid phases that coexist at the eutectoid of the Zr–H system imply that the three two-phase equilibria are interrelated. The thermodynamic enthalpy constraint derived by Speiser [21] that applies at the eutectoid of the Zr–H system can also be applied to the Zr–N system at C_μ

$$(C_\epsilon - C_\eta)\Delta\bar{H}^{L/\sigma} = (C_\mu - C_\eta)\Delta\bar{H}^{L/\alpha} + (C_\epsilon - C_\mu)\Delta\bar{H}^{\alpha/\sigma} \tag{4}$$

where $C_\eta = 0.156$, $C_\mu = 0.33$, and $C_\epsilon = 0.66$ are shown in Fig. 1. The superscripts in Eq. (4) refer to the corresponding two-phase regions Zr(L)/σZrN$_C$, Zr(L)/αZrN$_C$, and αZrN$_C$/σZrN$_C$, respectively.

Luo and Flanagan [22] show that the relative partial molal enthalpy of the gas in equilibrium with the two-phase mixture ($\Delta\bar{H}^{2\theta}$) is related to that of the neighboring single-phase ($\Delta\bar{H}$) and the intervening phase boundary (C_{pb}) by

$$\Delta\bar{H}^{2\theta} = \Delta\bar{H} + \left[\frac{\partial(\mu/T)}{\partial C}\right]_T \times \frac{dC_{pb}}{dT^{-1}} \tag{5}$$

where (dC_{pb}/dT^{-1}) refers to the boundary composition change with temperature. Eq. (5) is generally used for qualitative comparison between the two relative partial molal enthalpies. The derivative $[\partial(\mu/T)/\partial C]_T$ must be positive; therefore, whether $\Delta\bar{H}^{2\theta}$ is greater or smaller than $\Delta\bar{H}$ depends on the sign of dC_{pb}/dT^{-1} at the temperature under consideration. Rigorous quantitative comparison of partial molal enthalpies using Eq. (5) is limited owing to the lack of accurate chemical potentials at C_{pb}.

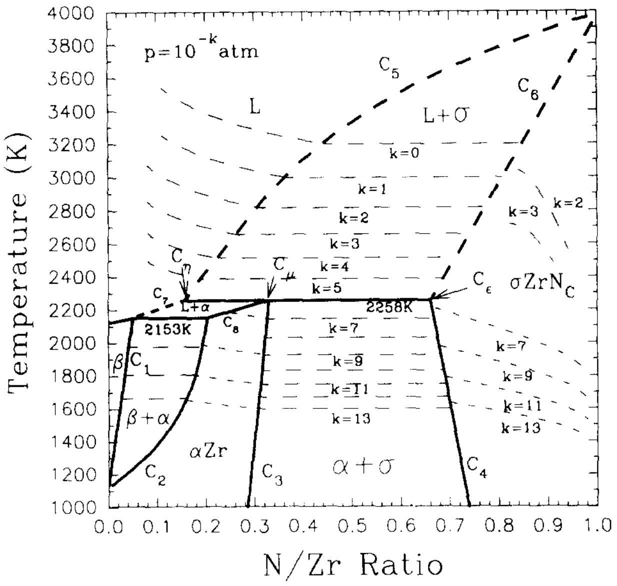

Fig. 1. Revised phase diagram of the Zr–N system. Nitrogen pressure isobars are indicated by the index k in $p = 10^{-k}$ atm.

In the present analysis, Eq. (2) is utilized to establish ΔG_f^0(ZrN) from the available p-C-T spectrum of the Zr–N system. Eq. (3) is used to assess the lower phase boundary of the σZrN$_C$ phase at 298 K. Eq. (4) has been applied to obtain the p-C-T relationship in the two-phase Zr(L)/σZrN$_C$ region. Eq. (5) is used to evaluate the reported partial molal enthalpies from the literature.

2. Zr–N system

2.1. Phase boundaries

The phase boundaries of the Zr–N system in Fig. 1 were compiled from the data of Toth [23] and Hansen [24], and from the present analysis based on data from Kibler et al. [7] and Galbraikh et al. [12].

The solid Zr–N phases including βZr and αZr and their two-phase region are well established [23,24]. C_4 at 298 K is obtained from the data of Galbraikh et al. [12], who measured the heat of formation of zirconium nitride ($\Delta H_f^0(MN_C)$) as a function of composition. Their results show that ($\Delta H_f^0(MN_C)$) is a linear function of the N/Zr ratio that changes slope at $C = 0.78$. According to Eq. (3), this implies that the relative partial molal enthalpy is discontinuously different on the two sides of $C = 0.78$, which then can be characterized as the lower phase boundary of σZrN$_C$ at 298 K. However, the lower phase boundaries of the σZrN$_C$ phase at higher temperatures are not well fixed. Values of C_ϵ reported include 0.5 [23], 0.66 [7], and 0.85 [24]. Yanchur et al. [25] suggested that it should be smaller than 0.77. Khromov and Svistunov [8] found that $C = 0.5$ is a two-phase mixture and $C = 0.79$ is still a single-phase solution. The value of C_ϵ (0.66) adopted by Kibler et al. [7] is therefore chosen in the present study due to its consistency with the analysis of Kaufman and Clougherty [6]. C_4 is calculated by interpolation between 0.78 (at 298 K) and 0.66 (at 2258 K) at any other temperatures. The melting temperature of ZrN reported by Hansen [24] (3253 K) has been disputed by Eropyan and Avarbe [9] with a revised value of 3970 K. The revised phase diagram of the Zr–N system is shown in Fig. 1, where the dotted lines represent the phase boundaries that are not well known. The tentative composition-temperature relationships of the phase boundaries (C_i in Fig. 1) are listed in Table 1.

2.2. σZrN_C

The equilibrium nitrogen pressure over σZrN_C has been measured by Eropyan and Avarbe [9] in the temperature range between 2480 K and 3670 K. Their results are satisfactorily fitted by the following expression

$$\ln p^{\sigma}(E\&A) = 140.5 - 304.2C + 178C^2 + 2\ln\left(\frac{C}{1-C}\right) - \frac{5.62\times10^4}{T} \qquad (6)$$

Eq. (6) is plotted in Fig. 2. The configurational entropy terms in Eq. (6) include a polynomial and a logarithmic term. The latter can be found in the models of Hoch [26–28] and Andrievskii et al. [29] in analogous systems (e.g., ZrC and TiN). Hoch [26–28] applied statistical mechanics to demonstrate that the polynomial term results from the interactions between sublattices, and suggested a linear relationship for the Zr–C system. However, a parabolic polynomial is sometimes required to fit the strong composition dependence of $\ln p^{\sigma}$ away from exact stoichiometry for the Zr–N system. A similar compositional dependence has also been demonstrated in the Zr–H system [3]. Kaufman and Clougherty [6] have extended the Schottky–Wagner [30,31] theory of nonstoichiometric alloys to zirconium nitride to develop a p-C-T relationship analogous to Eq. (6), except that the polynomial term is replaced by a constant. The resulting p-C-T relationship, however, has to be modified slightly in order to better fit the data from Kibler et al. [7] (1700 K–2300 K, $0.709<C<0.957$). The result is plotted in Fig. 3 and expressed by the equation:

$$\ln p^{\sigma}(Kibler) = 17.9 + 8.38C + 2\ln\frac{C}{1-C} - \frac{9.06\times10^4}{T} \qquad (7a)$$

The equilibrium partial nitrogen pressure in this region has also been investigated by Khromov and Svistunov [8] over the temperature range from 1400 K to 2425 K ($0.79<C<0.98$). Fitting of their data yields

$$\ln p^{\sigma}(K\&S) = 13.32 - 27.67C + 35.52C^2 + 2\ln\frac{C}{1-C} - \frac{7.43\times10^4}{T} \qquad (7b)$$

Their data fit well to those of Kibler et al. [7] at $C=0.95$. However, their results at $C=0.88$ and $C=0.79$ are much more negative than those of Kibler et al. [7], as demonstrated (at 2100 K) by the symbols (original data) in Fig. 3. The evaluation of Eqs. (7a) and (7b) will be discussed in the following section.

2.3. αZr, βZr, $Zr(L)/\alpha Zr$, $\alpha Zr/\beta Zr$, and $\alpha Zr/\sigma ZrN_C$, $T<2258$ K

Extending the model developed by Schottky and Wagner [30,31], Kaufman and Clougherty [6] proposed the following expression for p^{α}:

$$\ln p^{\alpha}(K\&C) = 25.5 + 2\ln\left(\frac{C}{1-C}\right) - \frac{8.62\times10^4}{T} \qquad (8a)$$

Eq. (8a) shows a weak dependence on the N/Zr ratio, and extrapolating to the lower phase boundary of αZr (C_2 and C_8 in Fig. 1) should be reasonably accurate. This yields the equilibrium nitrogen pressure in the two-phase ($\alpha Zr/\beta Zr$) region

Table 1
The composition-temperature relationships of the phase boundaries (shown in Fig. 1) expressed as $C_i = a + bT + cT^2 + dT^3$, where T is in Kelvins and C is the N/Zr ratio

N/Zr	a	b	c	d	sources
C1	-5.86×10^{-2}	5.167×10^{-5}	0	0	[23,24]
C2	-1.268	19.517×10^{-4}	-8.889×10^{-7}	13.923×10^{-11}	[23,24]
C3	0.249	3.58×10^{-5}	0	0	[23,24]
C4	0.798	-6.13×10^{-5}	0	0	[7,12,*]
C5	-2.653	28.648×10^{-4}	-1.019×10^{-6}	13.323×10^{-11}	[23,24,*]
C6	0.212	1.986×10^{-4}	0	0	*
C7	-20.676×10^{-1}	98.476×10^{-5}	0	0	[23,24]
C8	-2.444	12.286×10^{-4}	0	0	[23,24]

* This study.

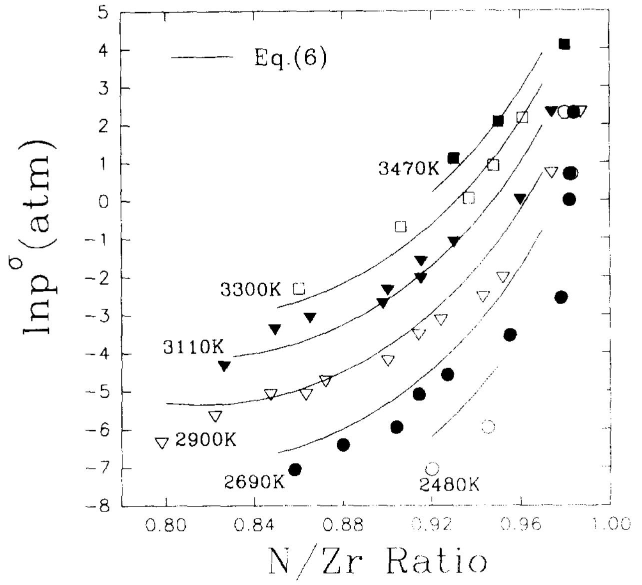

Fig. 2. Comparison of the fit from Eq. (6) and the database of Eropyan and Avarbe [9] (symbols).

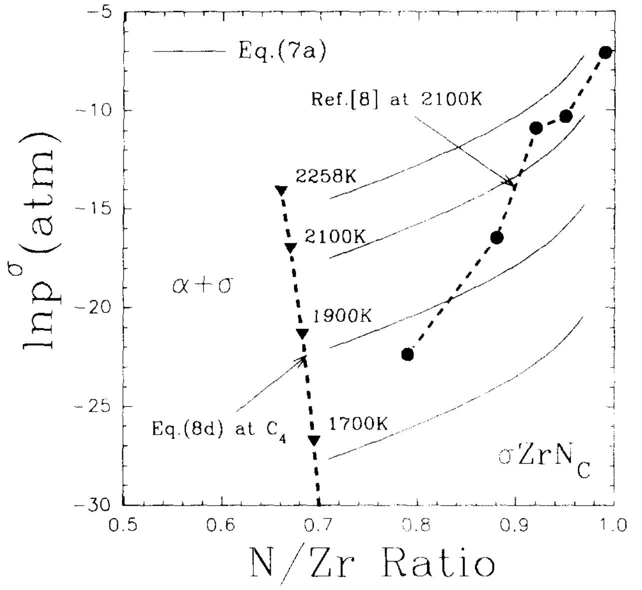

Fig. 3. Comparison of the fit from Eq. (7a) and the data of Khromov and Svitunov [8] (filled circles) at 2100 K. The filled triangles are data from Eq. (8d) at C_4 for 2258 K, 2100 K, 1900 K and 1700 K from top to bottom, respectively.

$$\ln p_{2\theta}^{\alpha/\beta}(K\&C) = 28.03 - \frac{9.64\times10^4}{T} \tag{8b}$$

and in the two-phase (Zr(L)/αZr) region

$$\ln p_{2\theta}^{L/\alpha}(K\&C) = 51.66 - \frac{14.84\times10^4}{T} \tag{8c}$$

Extrapolation of Eq. (8a) to the αZr upper phase boundary (C_3 in Fig. 1) yields the following equilibrium nitrogen pressure in the two-phase ($\alpha Zr/\sigma ZrN_C$) region

$$\ln p_{2\theta}^{\alpha/\sigma}(K\&C) = 24.43 - \frac{8.7\times10^4}{T} \tag{8d}$$

The equilibrium nitrogen pressure over the two-phase ($\alpha Zr/\sigma ZrN_C$) region, however, has also been investigated by Khromov and Svistunov [8], who obtained

$$\ln p_{2\theta}^{\alpha/\sigma}(K\&S) = 34.53 - \frac{12.3\times10^4}{T} \tag{9}$$

Eqs. (8b–d) and (9) are plotted in Fig. 4. The consistency among Eqs. (8b–d) at 2258 K and 2153 K shown in Fig. 4 implies that the database of Kaufman and Clougherty [6] is reliable because of its consistency with the independently-measured phase boundaries (C_2, C_3, and C_8). Investigation of the database of Khromov and Svistunov [8] shows that ($\Delta\bar{H}^{\alpha/\sigma} = -123R = -1023$ kJ mole^{-1}) obtained from Eq. (9) is more negative than ($\Delta\bar{H}^{\sigma} = -74.3R = -618$ kJ mole^{-1} from Eq. (7b)), the relative partial molal enthalpy of nitrogen in equilibrium with the σZrN_C phase. This contradicts the thermodynamic constraint of Eq. (5). The enthalpy constraint of Eq. (5) requires that $\Delta\bar{H}^{\alpha/\sigma}$ should be more positive than $\Delta\bar{H}^{\sigma}$ since the derivative dC_4/dT^{-1} is positive. It is worth noting that Eq. (8d) is consistent with Eq. (7a) at C_4 as shown in Fig. 3 and the corresponding relative partial molal enthalpies also obey the enthalpy constraint of Eq. (5) because ($\Delta\bar{H}^{\alpha/\sigma} = -87R = -723$ kJ mole^{-1}) of Eq. (8d) is more positive than ($\Delta\bar{H}^{\sigma} = -90.6R = -753$ kJ mole^{-1}) of Eq. (7a). This suggests that the data of Kaufman and Clougherty (Eqs.(8a–d)) are consistent with those of Kibler et al. (Eq. (7a)) and the database of Khromov and Svistunov (Eqs. (9) and (7b)) is inconsistent.

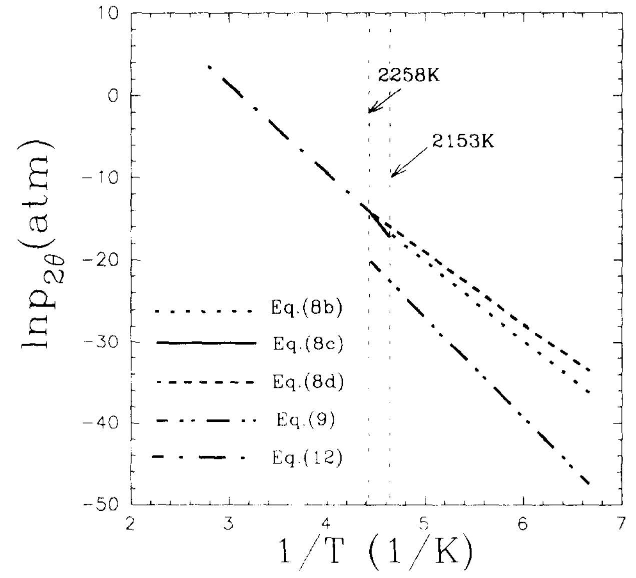

Fig. 4. Equilibrium nitrogen pressures over the univariant two-phase regions (L/σ, L/α, α/σ, α/β) from various sources.

There are no p-C-T data available in the βZr region. However, the p-C-T relationship in these regions can be approximated using the assumption that nitrogen dissolution in zirconium obeys Sievert's law up to the terminal solubility. If so, the equilibrium $1/2N_{2(g)} = N_{diss.}$ yields the mass action law

$$\frac{1}{\gamma_N^0} = \frac{C}{\sqrt{p}} = \frac{C_s}{\sqrt{p^{2\theta}}} \tag{10}$$

where γ_{N0} is the activity coefficient of nitrogen in the metal solution referenced to the standard state (1 atm N_2), C_s is the terminal solubility of nitrogen in the metal, and $p^{2\theta}$ is the equilibrium nitrogen pressure in the nearby univariant two-phase region. Eq. (10) is commonly written using the mole fraction in place of the nitrogen-to-metal ratio. The distinction has been discussed by Wang and Olander [2], Wagner [31], and Lupis [32], all of whom argue that the appropriate concentration unit is the gas-to-metal atom-ratio. The solubility of nitrogen in liquid metals has been compiled extensively by Chang et al. [33], who show that nitrogen dissolution in Cr follows Sievert's law up to the terminal solubility (N/Cr = 0.27). In addition, since phase diagrams of the Zr–N and the Zr–O system are very similar in this region and Eq. (10) has been shown to be valid in the Zr–O system [2], it is assumed that equation above can also be applied to the Zr–N system.

By combining Eq. (10) and Eq. (8b), the p-C-T relationship in the βZr region can be obtained and Gibbs energy of solution of nitrogen dissolution in βZr can be calculated as:

$$RT \ln \gamma_N^0(\beta Zr) = -359 + 0.121T \quad \text{kJ mol}^{-1} \tag{11}$$

The integral Gibbs energy of formation of ZrN, ΔG_f^0(ZrN), can be estimated by using the integral constraint of Eq. (2). The right-hand-side of Eq. (2) can be computed from the complete p-C-T relationship in the temperature range 1500 K $< T <$ 2153 K by Eqs. (7a), (8a,b), (8d), and (10). The results, plotted in Fig. 5, show that ΔH_f^0(ZrN) (-370 kJ mole^{-1}) obtained from the intercept of the regression line is close to the values (-368.6 kJ mole^{-1}) reported by Mah and Gellert [10] and Galbraikh et al. [12] for this temperature range. However, the value of ΔS_f^0(ZrN) (-107.6 J mole^{-1} K^{-1}) obtained from the slope of the line in Fig. 5 is more negative than the reported values of -95 [10,13] and -92 [14] J mole^{-1} K^{-1}).

2.4. Zr(L) and Zr(L)/σZrN$_C$, $T >$ 2258 K

There are no pressure-composition-temperature data available in these regions. However, the p-C-T relationship in these regions can be estimated using the thermodynamic constraint of Eq. (5) and the assumption that nitrogen dissolution in liquid zirconium obeys Sievert's law according to Eq. (10).

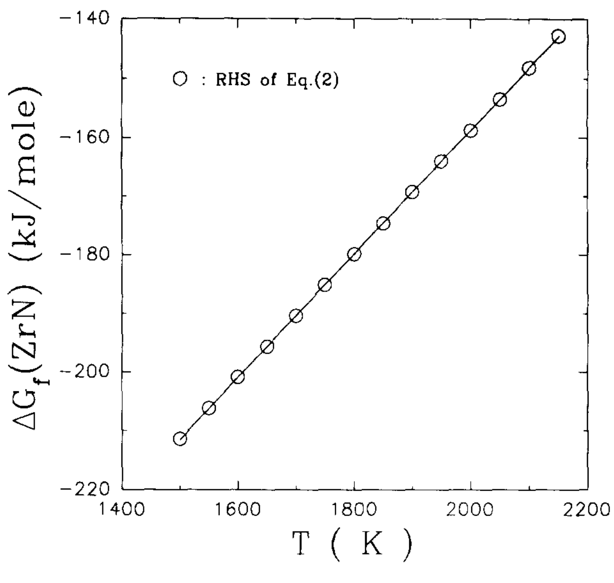

Fig. 5. Integral Gibbs energy of formation of ZrN obtained from Eq. (2).

The pressure-composition-temperature relationship in the Zr(L)/σZrN$_C$ two-phase region can be derived from the thermodynamic constraint of Eq. (4). The relative partial molal enthalpy calculated accordingly is equal to -900 kJ mole^{-1}. The relative partial molal entropy (-281 J mole^{-1} K^{-1}) is determined from the continuity requirement at $T = 2258$ K. Therefore

$$\ln p_{2\theta}^{L/\sigma} = 33.82 - \frac{10.82 \times 10^4}{T} \tag{12}$$

Eq. (12) is plotted in Fig. 4. The extrapolation of the σZrN$_C$ nitrogen pressure data of Eropyan and Avarbe [9](Eq. (6)) to the phase boundary C_6 shows a large discrepancy compared to Eq. (12), as shown in Fig. 1. However, the relative partial molal enthalpies derived from Eqs. (6) and (12) follow the trend predicted by the thermodynamic constraint of Eq. (5) since negative dC_6/dT^{-1} is negative and $\Delta\bar{H}^{\sigma}(= -900$ kJ mole^{-1}) of Eq. (12) is more negative than $\Delta\bar{H}^{L/\sigma}(= -467$ kJ mole^{-1}) of Eq. (6).

The Gibbs energy of solution of nitrogen dissolution in zirconium can be calculated from substituting Eq. (12) into Eq. (10) and replacing C_s with C_5 to yield

$$RT \ln \gamma_N^0(Zr, L) = -374.7 + 0.125T \quad \text{kJ mol}^{-1} \tag{13}$$

It is worth noting that the enthalpy term in Eq. (13) is considered reliable because, due to the large value of $\Delta\bar{H}^{L/\sigma}$, it is not very sensitive to the phase boundary C_5.

2.5. Nitrogen isobars

The p-C-T relationships of nitrogen in equilibrium with the Zr–N system are used to construct the nitrogen isobars superimposed on the phase diagram as shown in Fig. 1. The equations used for $T<2258$ K include (7a), (8a–d), and (10). Eqs. (6), (10), and (12) are used for $T>2258$ K. The slight mismatch in the phase boundary C_4 is acceptable considering the significant uncertainty of this phase boundary. The discontinuity in the phase boundary C_6, however, is yet to be resolved by more experimental data.

3. Conclusions

The phase diagram and the equilibrium N_2 pressures of the Zr–N system are reassessed according to the latest data available. Thermodynamic constraints have been utilized to evaluate the reported data and to establish the pressure-composition-temperature relationships in the Zr(L)/σZrN$_C$ region where no data are available. The results show that the data of Kibler et al. [7] are more reliable than those of Khromov and Svistunov [8] in the σZrN$_C$ region. The data of Kaufman and Clougherty [6] are more reliable than those of Khromov and Svistunov [8] in the αZr/σZrN$_C$ two-phase region. The Gibbs enthalpy of formation of zirconium nitride derived from Eq. (2) is consistent with those of Mah and Gellert [10], Galbraikh et al. [12], and Wagman et al. [13]. The Gibbs energies of solution of nitrogen dissolution in solid and liquid Zr are calculated using the assumption of Sievert's law.

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