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# A thermodynamic evaluation of the titanium–oxygen system from O/Ti = 0 to 3/2

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**Abstract**

Evaluation of the partial thermodynamic functions of the Ti–O system (up to O/Ti = 1.5) from 1000 to 2000 K, using a methodology previously developed for other M–O, M–H and M–N systems, is presented. Satisfactory pressure–composition–temperature relationships for each phase have been obtained even in regions where no data are available. The results are presented as oxygen isobars superimposed on the phase diagram. The Gibbs energy of oxygen dissolution in solid titanium is also calculated. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The titanium–oxygen system, one of the most important and yet most complicated oxides, is still not fully understood. Reviews on this system have been carried out by Murray and Wriedt [1], Kubaschewski [2], Pajunen and Kivilahti [3], and Kaufman and Clougherty [4]. Murray and Wriedt [1] critically evaluated the phase boundaries. Kubaschewski [2] compiled the oxygen potential databases up to 1982. Kaufman and Clougherty [4] proposed the *p–C–T* relationships for αTi and γTi without comparing them with the experimental data. However, no comprehensive evaluation of the pressure–composition–temperature relationships is available for the Ti–O system.

This study investigates extensively the partial molar free energies of oxygen in the Ti–O system from O/Ti = 0 to O/Ti = 1.5 between 1000 and 2000 K. The techniques applied in this study, which have been previously developed [5–13], are summarized briefly in the following section.

### 1.1. Thermodynamic constraints and a modified form of Sieverts law

Analytical methods introduced in the following sections have been applied by Wang and Olander [5–13] to many M–X (M = U, Th, U, Zr, Ti, Y, X = O, N, H) systems successfully.

#### 1.1.1. Integral constraint

The integral Gibbs energy of formation of the oxide ($\mathrm{TiO}_C$) formed by the reaction

$$\mathrm{Ti} + \frac{C}{2}\mathrm{O}_{2(\mathrm{g}),1\mathrm{atm}} = \mathrm{TiO}_C$$

is related to the relative partial molar free energies of oxygen ($\Delta\overline{G} = RT \ln p$ over the entire O/Ti range by Eq. (1) [14]

$$\Delta G_\mathrm{f}^0(\mathrm{TiO}_C) = \frac{RT}{2}\int_0^C \ln p \, \mathrm{d}C', \qquad (1)$$

where $R$ is the universal gas constant and $p$, a function of $C$ and $T$, is the equilibrium oxygen pressure (in atm) over the oxide. Pure titanium is used as the standard state for the integral Gibbs energy of formation and 1 atm of $\mathrm{O}_2$ is the reference standard state of the relative partial molar energies in Eq. (1). This equation has been applied to the Y–O, U–O, Zr–O, Th–O, Zr–N, Zr–H, U–N, Ti–N, and Ti–H systems [5–13]. Equations analogous to Eq. (1) have also been applied by Kubaschewski [14], Kubaschewski et al. [15] and Kubaschewski and Dench [16] and by Boureau and Gerdanian [17] to the Ti–O system.

#### 1.1.2. Sieverts law

If we assume that Sieverts law behavior is obeyed for oxygen dissolution up to the terminal solubility in the metal, then the corresponding equilibrium: $\frac{1}{2}\mathrm{O}_2 = \mathrm{O}_{\mathrm{diss.}}$ yields the following mass action law

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$$\frac{C}{\sqrt{p}} = \frac{C_{\text{sat}}}{\sqrt{p_{2\theta}}} = k_S, \tag{2}$$

where $C_{\text{sat}}(= C_{\beta/(\alpha+\beta)})$ is the terminal solubility of oxygen in the metal, $p_{2\theta}$ is the equilibrium pressure of the αTi + βTi two-phase region, and $k_S$ is the corresponding Sieverts law constant. Eq. (2) is commonly written using the mole fraction in place of the oxygen-to-metal ratio. The distinction has been discussed by Wang and Olander [7] and Lupis [18], all of whom argue that the appropriate concentration unit is the gas-to-metal atom ratio.

The relationship between $\Delta\overline{H}$ and $\Delta\overline{H}_{2\theta}$ in the adjoining two-phase region can be derived using Eq. (2) [7], which yields

$$\Delta\overline{H} = \Delta\overline{H}_{2\theta} - 2R\frac{\mathrm{d}\ln C_{\text{sat}}}{\mathrm{d}T^{-1}}. \tag{3}$$

It can be shown that $\Delta\overline{H}$ is more positive than $\Delta\overline{H}_{2\theta}$ if the second term on the right-hand side of the above equation is negative.

Eq. (2) provides an interrelationship among $C_{\text{sat}}$, $p_{2\theta}$, and $k_S$, which are usually measured independently. Eq. (3) is useful in evaluating partial molar enthalpies measured in these regions. An analogous relation has also been derived by Luo and Flanagan [19]. This interrelationship has been applied successfully to the analysis of the Zr–H [8], the Zr–O [7], and the Ti–H [6] systems. It is assumed that it also can be applied to the analogous Ti–O system.

### 1.1.3. A modified form of Sieverts law

A more generalized form for describing gas in equilibrium with its compound can usually be expressed by the following *p–C–T* relationship [6,8,20,21]:

$$\ln p = f(C) + 2\ln g(C) + \frac{h}{T}, \tag{4}$$

where $\Delta\overline{H} = h \times R$ can be obtained from the above equation. The first and second terms on the right-hand side of Eq. (4) result from thermal and configurational entropy. There are extensive theoretical works in predicting the *p–C–T* relationship of the M–X systems. Libowitz's [20] review for the M–H systems proposed that the $h(C)$ could be a strong linear function of $C$, $f(C)$ equals a constant, and $g(C) = C/(\xi - C)$ where $\xi$ is usually related to the stoichiometry of the compound. Eq. (4) reduces to Eq. (2) with $g(C) = C$, and both $h(C)$ and $f(C)$ constants. However, Lupis [18] and Flanagan and Oates [21] suggested that even if $g(C) = C/(2 - C)$ (with both $h(C)$ and $f(C)$ constant) in Eq. (4), a gas solution still follows Sieverts law from the statistical thermodynamic point of view.

### 1.2. Application

In the present analysis, Eq. (2) is used to calculate the Gibbs energy of solution of oxygen dissolved in solid titanium. Eqs. (1), (3) and (4) are used to evaluate the extensive and yet inconsistent databases. In addition, they have also been utilized to establish the *p–C–T* relationships in regions where no data are available.

## 2. Regions in the titanium–oxygen system

The phase diagram of the Ti–O system, shown in Fig. 1, is obtained from the compilation of Murray and Wriedt [1].

### 2.1. βTi and αTi + βTi, 1200 K < T < 2000 K

The *p–C–T* relationships in these regions have been studied extensively [17,22–27]. Okabe et al. [22] proposed the following *p–C–T* relationship for the βTi region

$$\ln p_\beta(\text{Oka.}) = 30.55 + 2\ \ln\frac{C}{(3-4C)} - \frac{14\times10^4}{T}. \tag{5}$$

Boureau and Gerdanian [17] suggested a similar relationship

$$\ln p_\beta(\text{B\&G}) = 24.96 + 2\ \ln\frac{C}{(3-C)} - \frac{13.07\times10^4}{T}. \tag{6}$$

Fitting the database of Reznichenko and Khalimov [23] ($C < 0.006$) to Eq. (4), we obtain (with 98% confidence)

$$\ln p_\beta(\text{R\&K}) = 27.66 + 5747.5C - 6.746\times10^5C^2 + 2\ \ln\frac{C}{3-C} - \frac{14.68\times10^4}{T}. \tag{7}$$

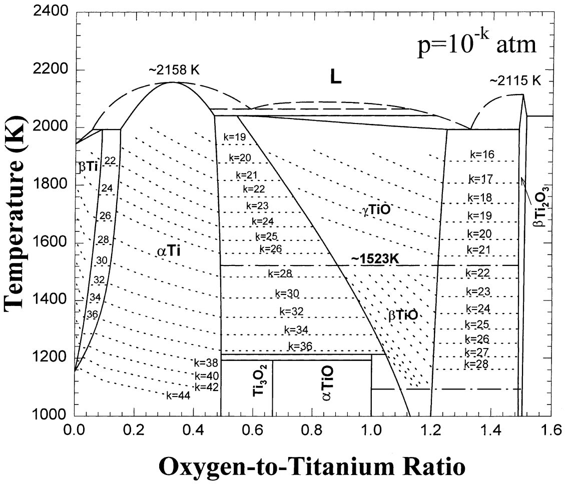

Fig. 1. Revised phase diagram of the Ti–O system [1]. Oxygen pressure isobars are indicated by the index $k$ in $p = 10^{-k}$ atm.

It is worth noting that a second-order polynomial for $f(C)$ is required to fit this database. Fitting the database of Mah et al. [24] ($C < 0.06$) to Eq. (4), we obtain (with 99% confidence)

$$\ln p_{\beta}(\mathrm{Mah}) = 22.74 + 2\ \ln\frac{C}{(3-C)} - \frac{12.82 \times 10^4}{T}. \qquad (8)$$

The equilibrium oxygen pressure at the αTi + βTi two-phase region $p_{(\alpha+\beta)}$ measured by Mah et al. [24] yields

$$\ln p_{(\alpha+\beta)} = 30.43 - \frac{15.14 \times 10^4}{T}. \qquad (9)$$

Eqs. (7) and (8) are only valid for limited concentrations. The databases of Boureau and Gerdanian [17] and Okabe et al. [22], however, can be evaluated by extrapolating Eqs. (5) and (6) to the terminal solubility of βTi($= C_{\alpha/(\alpha+\beta)}$) and comparing it to that of Mah et al. [24] (Eq. (9)). The result obtained shows that these three databases are quite consistent.

$\Delta\overline{H}_{\beta}$ (−1068 kJ/mol $O_2$) suggested by Mah et al. [24] is close to that of Boureau and Gerdanian [17] (−1087 kJ/mol $O_2$). $\Delta\overline{H}_{\beta}$ of Boureau and Gerdanian [17], however, have been disputed by Tetot et al. [25–27] who proposed a much higher value (−1278 ± 25 kJ/mol $O_2$). $\Delta\overline{H}_{\beta}$ can also be calculated using Eq. (3) and $\Delta\overline{H}(\alpha+\beta)$ (−1292 kJ/mol $O_2$) from Eq. (9), which yields −1214 ± 7 kJ/mol $O_2$. This value lies between that of Boureau and Gerdanian [17] and Tetot et al. [25–27] and is close to that of Reznichenko and Khalimov [23] (−1220 kJ/mol $O_2$). Kubaschewski [14] and Kubaschewski et al. [15] suggested a value of −1121 kJ/mol $O_2$ which lies between the value of Boureau and Gerdanian [17] and of Okabe et al. [22] (−1164 kJ/mol $O_2$). These discrepancies, however, can only be resolved with further experimental investigation.

No measurements of the Gibbs energy of solution (defined as $-RT \ln k_S$ according to Chang et al. [28]) for oxygen dissolution in solid titanium are available. However, its value can be calculated by substituting Eq. (9) and $C_{\beta(\alpha+\beta)}$ into Eq. (2), which yields

$$\begin{aligned} -RT\ \ln k_S &= RT\left[\frac{1}{2}\ln p_{(\alpha+\beta)} - \ln(C_{\beta/(\alpha+\beta)})\right] \\ &= -609 + 0.126T \quad \mathrm{kJ/mol}. \end{aligned} \qquad (10)$$

The enthalpy of solution of oxygen dissolution in solid titanium from the above equation (−609 kJ/mol) is very close to that of the analogous Y–O system [5].

### 2.2. αTi and αTi + γTiO, 1000 K < T < 2000 K

Among all the phases in the Ti–O system, αTi is most extensively studied [4,24–27,29–32]. Original experimental data from Komarek and Silver [29] are used to fit Eq. (4) and the fitting, shown in Fig. 2, yields (with 99% confidence)

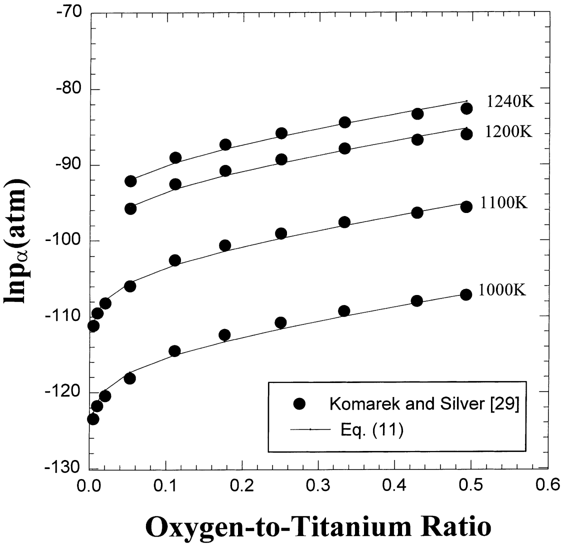

Fig. 2. Comparison between Eq. (11) (solid lines) and the database of Komarek and Silver [29] (symbols).

$$\begin{aligned} \ln p_{\alpha}(\mathrm{K\&S}) = 21.24 + 12.45C + 2\ \ln\frac{C}{3-C} \\ - \frac{13.12 \times 10^4}{T}. \end{aligned} \qquad (11)$$

$f(C)$ of Eq. (4) must at least be a linear function of $C$ in order to fit the complete range of this database. This type of fitting has also been applied successfully in the βTi (Ti–H) [6] and the βZr (Zr–H) [8] phases.

A complicated $p$–$C$–$T$ relationship proposed by Kaufman and Clougherty [4] is given in Eq. (12)

$$\begin{aligned} \ln p_{\alpha}(\mathrm{K\&C}) = 4.248\ \ln\frac{T}{2.74} + 6\ \ln\frac{632}{T} \\ - \frac{(12.48 + 2.472(1 - 4x + 2x^2)) \times 10^4}{T} \\ + 2\ \ln\frac{x}{1-2x} + 6\left\{\ln\left[(1+2x)(1-x)\right]\right. \\ \left. + \frac{1-4x}{1+2x}\right\}. \end{aligned} \qquad (12)$$

where $x = 1/(1 + C)$. The evaluation of Eqs. (11) and (12) can be carried out by extrapolating these equations to $C_{(\beta+\alpha)/\alpha}$ and comparing to the direct measurement of Eq. (9). The results show that these databases are consistent at low temperatures with slight mismatch at high temperatures.

The equilibrium oxygen partial pressure over the αTi + γTiO two-phase region can be calculated by extrapolating Eq. (11) to the αTi upper phase boundary, which yields

$$\ln p_{(\alpha+\gamma)} = 23.27 - \frac{13.01 \times 10^4}{T}. \qquad (13)$$

### 2.3. $\gamma$TiO and $\gamma$TiO + $\beta Ti_2O_3$, 1523 K < T < 2000 K

The databases available [4,30–35] for this region are less consistent than those in the $\alpha$TiO region. Kaufman and Clougherty [4] proposed the following *p–C–T* relationships for the $\gamma$TiO region:

$$\ln p_\gamma(\mathrm{K\&C}) = 20.03 + 2\ \ln\frac{C}{1-C} - \frac{12.06\times 10^4}{T} \qquad (14a)$$

for $C < 1$,

$$\ln p_\gamma(\mathrm{K\&C}) = 20.03 + 2\ \ln\frac{C-1}{4C} - \frac{10.53\times 10^4}{T} \qquad (14b)$$

for $C > 1$.

Fitting the original experimental results obtained by Suzuki and Sambongi [32] with Eq. (4), we obtain (with 99% confidence)

$$\ln p_\gamma(\mathrm{S\&S}) = 5.27 + 9.96C + 2\ \ln\frac{C}{3-C} - \frac{10.02\times 10^4}{T}. \qquad (15)$$

Eq. (15), together with the database of Gilles et al. [33–35] at O/Ti = 1 and Kaufman and Clougherty [4], is plotted in Fig. 3. Comparison between Eq. (14a) Eqs. (14b) and (15) shows that $p_\gamma$ calculated from Eq. (14a) agrees fairly well with that obtained from Eq. (15) for $C < 0.95$. However, the unrealistic large values at $C$ close to unity and the abrupt change of oxygen partial pressures across $C = 1$ for Eqs. (14a) and (14b) have not been observed in the experimental databases. This implies that the database of Suzuki and Sambongi [32] is more reliable than that of Kaufman and Clougherty [4] in the $\gamma$TiO region. Therefore, the former (Eq. (15)) is used to extrapolate the equilibrium oxygen pressure over the $\gamma\mathrm{TiO} + \beta\mathrm{Ti_2O_3}(\gamma+\beta)$ two-phase region, which yields

$$\ln p_{(\alpha+\gamma)} = 18.08 - \frac{10.34\times 10^4}{T}. \qquad (16)$$

The evaluation of database of Suzuki and Sambongi [32] is carried out using the integral constraint of Eq. (1), which is rewritten as

$$\Delta G_f^0(\mathrm{TiO_{1.5}}) \approx \frac{RT}{2}\left(\int_0^{C_{\beta/(\beta+\alpha)}} \ln p_\beta\, \mathrm{d}C' + \int_{C_{\beta/(\beta+\alpha)}}^{C_{(\beta+\alpha)/\alpha}} \ln p_{(\alpha+\beta)}\mathrm{d}C' + \int_{C_{(\beta+\alpha)/\alpha}}^{C_{\alpha/(\alpha+\gamma)}} \ln p_\alpha \mathrm{d}C' + \int_{C_{\alpha/(\alpha+\gamma)}}^{C_{(\alpha+\gamma)/\gamma}} \ln p_{(\alpha+\gamma)}\mathrm{d}C' + \int_{C_{(\alpha+\gamma)/\gamma}}^{C_{\gamma/(\gamma+\beta)}} \ln p_\gamma \mathrm{d}C' + \int_{C_{\gamma/(\gamma+\beta)}}^{C_{(\gamma+\beta)/\beta}} \ln p_{(\gamma+\beta)}\mathrm{d}C'\right), \qquad (17)$$

where the extreme narrow homogeneous region of $\beta Ti_2O_3$ is neglected in the above equation. The results, plotted in Fig. 4, show that $\Delta G_f^0(\mathrm{TiO_{1.5}})$ calculated from Eq. (17) ($-7.47\times 10^2 + 12.70\times 10^{-2}T$ kJ/mol) using Eqs. (5), (9), (11), (13), (15) and (16) is close to that suggested by Chase et al. [36] ($-7.50\times 10^2 + 12.95\times 10^{-2}\ T$ kJ/mol) and Kubaschewski [14]

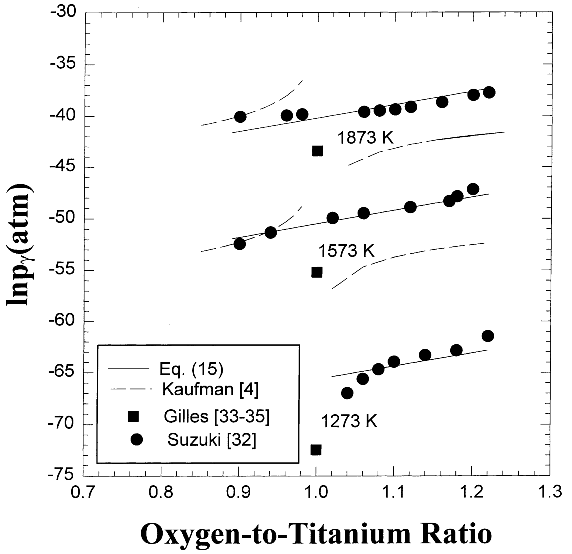

Fig. 3. Comparison among Eq. (15) (solid lines), the databases of Suzuki and Sambongi [32] (filled circles), the database of Gilles[33], Sheldon and Gilles[34] and Gernier and Gilles[35] at $C = 1$ (filled squares), and Kaufman and Clougherty [4] (dashed lines), at 1873, 1573, and 1273 K, respectively.

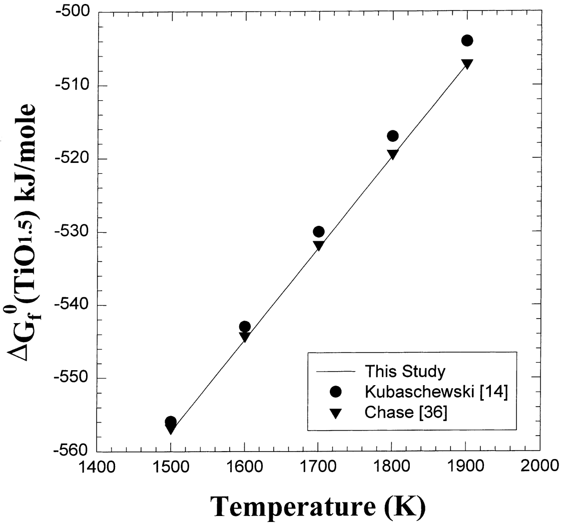

Fig. 4. Comparison of calculated $\Delta G_f^0(\mathrm{TiO_{1.5}})$ from Eq. (17) (solid lines) and those of Chase et al. [36], and Kubaschewski [14].

($-7.50 \times 10^2 + 12.90 \times 10^{-2}\ T$ kJ/mol). This implies that the databases selected, including Okabe et al. [22], Mah et al. [24], Komarek and Silver [29], and Suzuki and Sambongi [32], are not only consistent among themselves, but also agree well with the independently measured values of $\Delta G_f^0(\mathrm{TiO}_{1.5})$.

### 2.4. βTiO and βTiO + βTi₂O₃, 1100 K < T < 1523 K

The inconsistency between the database of Tetot et al. [25–27] and that of Suzuki and Sambongi [32] in this region is demonstrated in Fig. 5. $p_{\beta'}$ of Tetot et al. [25–27] should be more positive (shown as more negative in Fig. 5) than those of Suzuki and Sambongi [32] since the formers are at a higher temperature. However, both of these two databases do not fulfill the integral constraint of Eq. (1) when applied. Subsequently, no reliable *p–C–T* relationships are available in the βTiO region. Nevertheless, the following linear *p–C–T* relationship is suggested

$$\ln p_{\beta'} = \ln p_{(\alpha+\beta')} + \frac{C - C_{(\alpha+\beta')/\beta'}}{C_{\beta'/(\alpha+\beta')} - C_{(\alpha+\beta')/\beta'}} \times (\ln p_{(\beta+\beta')} - \ln p_{(\alpha+\beta')}), \qquad (18)$$

where $p_{(\beta+\beta')}$ is the equilibrium oxygen pressure at the $\beta\mathrm{Ti}_2\mathrm{O}_3 + \beta\mathrm{TiO}(\beta + \beta')$ two-phase region. It is also assumed that $p_{(\alpha+\beta')} \approx p_{(\alpha+\gamma)}$ of Eq. (13). $p_{(\beta+\beta')}$ can be calculated using the integral constraint of Eq. (17) by substituting $p_\gamma$ with $p_{\beta'}$ and $p_{(\gamma+\beta)}$ with $p_{(\beta+\beta')}$, together with Eqs. (5), (9), (11) and (13) and $\Delta G_f^0(\mathrm{TiO}_{1.5})$ from Chase et al. [36].$p_{(\beta+\beta')}$ obtained this way yields

$$\ln p_{(\beta+\beta')} = 0.16 - \frac{7.51 \times 10^4}{T}. \qquad (19)$$

As a comparison, $p_{\beta'}$ at 1323 and 1273 K are also plotted in Fig. 5. Even though values of $p_{\beta'}$ from Eq. (18) fulfill the integral constraint of Eq. (1) but they mismatch slightly with $p_{(\alpha+\beta')}$ at the lower phase boundary of βTiO. This is due to the fact that $p_{\beta'}$ computed using the integral constraint of Eq. (1) also inherits all the uncertainties of the databases used. This implies that $p_{\beta'}$ from Eq. (18) may be no more reliable than those of Tetot et al. [25–27] and Suzuki and Sambongi [32]. The inconsistencies among Eq. (18) and those of Tetot et al. [25–27] and that of Suzuki and Sambongi [32], shown in Fig. 5, could only be resolved with further experimental investigation.

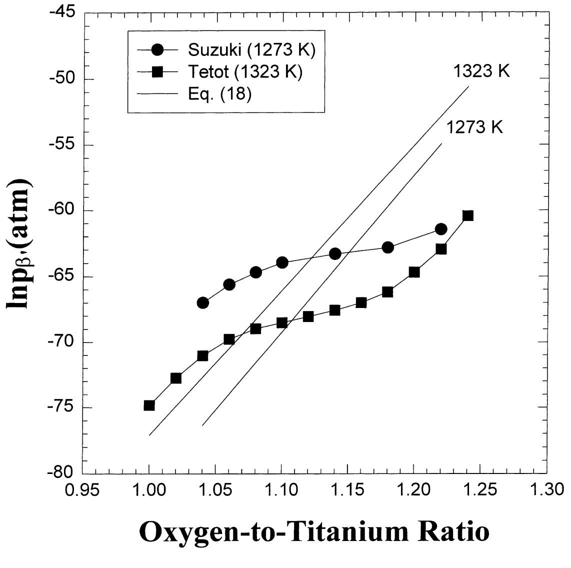

Fig. 5. Comparison of Eq. (18) and the databases of Tetot et al. [25–27] and Suzuki and Sambongi [32].

### 2.5. Oxygen isobars and the analysis of uncertainties

The *p–C–T* relationships of oxygen in equilibrium with the Ti–O system from Eqs. (5), (9), (11), (13), (15), (16), (18) and (19) are used to construct the oxygen isobars superimposed on the phase diagram shown in Fig. 1. The results obtained are satisfactory in general. However, even though the methodology applied in the approach is based on several valid thermodynamic relations, certain uncertainties are expected. For instance, the discontinuities of oxygen isobars at $C > 0.9$ around 1523 K and at $C_{(\alpha+\gamma)/\gamma}$ at low temperatures, and the slight mismatches at $C_{(\alpha+\beta)/\beta}$ at high temperatures, shown in Fig. 1, are indications of uncertainties for the oxygen pressure databases in these regions. These inconsistencies can only be resolved by further experimental investigation.

## 3. Conclusions

The partial free energy functions of the Ti–O system have been reviewed using the thermodynamic constraint methods. Consistency among the databases in the αTi, βTi, and βTi + αTi phases has been demonstrated. Sieverts law constant for the βTi phase, together with the Gibbs energy of oxygen dissolution in solid titanium, has been calculated. The databases for the γTiO region and βTiO region are less consistent. However, satisfactory *p–C–T* relationships are obtained using the available experimental results and the integral constraint of Eq. (1).

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