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# Thermodynamics of gas dissolution in liquid metals with extensive solubility; the U(L)–N, Zr(L)–O, and Th(L)–O systems

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## Abstract

The pressure–composition–temperature ( $p$ – $C$ – $T$ ) relationships of the systems U(L)–N, Zr(L)–O, and Th(L)–O are derived using thermodynamic constraints and a modified form of Sievert's law. The results are used to evaluate the thermodynamic functions of each system: The integral Gibbs enthalpy of formation of UN and the Gibbs energy of solution of nitrogen in liquid uranium are determined. Inconsistency in the literature concerning the Th(L)–O system is resolved. The equilibrium oxygen pressure in the two-phase  $\alpha$ Th(L)/ $\sigma$ ThO<sub>c</sub> region is reassessed and the corresponding Gibbs energy of solution is determined.

*Keywords:* Gas dissolution; Liquid metals; Thermodynamics; Solubility; Uranium; Thallium; Zirconium

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## 1. Introduction

Thermodynamics of gas dissolution in liquid metals is crucial not only to many industrial applications, but also in evaluating the complete pressure–temperature–composition ( $p$ – $C$ – $T$ ) relationships of compounds throughout the composition fields at high temperatures. However, the databases available usually suffered from significant uncertainties owing to the difficulties of the experiments, as demonstrated by the extensive compilation of Chang et al. [1].

The thermodynamics of gas dissolution in liquid metal has been studied extensively. Chang et al. [1] proposed to interpret the gas dissolution in liquid metal by the reaction  $\frac{1}{2}X_2(g) = X_{\text{diss}}$ , with the following classical Sievert's law:

$$\frac{n}{\sqrt{p^\alpha}} = \frac{1}{\gamma_X^0} = k_s \quad (1)$$

where  $p^\alpha$  (in atm) is the gas pressure in equilibrium with the liquid metal,  $n$  is the mole fraction of the dissolved gas,  $\gamma_X^0$  is the activity coefficient of gas atom X in the solution referenced to 1 atm of X<sub>2</sub>, and  $k_s$  is the classical Sievert's law constant. Eq. (1) is usually valid for very dilute solutions. Lupis [2], Oates and

Flanagan [3], and Chipman [4] pointed out the inadequacy of applying Eq. (1) to gas dissolved interstitially in metal, which can be better approached from statistical thermodynamics. Mclellan [5] also showed that the composition dependence of  $p^\alpha$  is usually more complicated than suggested by Eq. (1). For those gases which dissolve extensively in the liquid metal, Eq. (1) is often inadequate for describing dissolution behavior.

To account for the extensive and complex hydrogen dissolution behavior in  $\beta$ Zr, Wang and Olander [6] proposed the following modified Sievert's law:

$$\frac{f(C)}{\sqrt{p^\alpha}} = \frac{f(C_s)}{\sqrt{p^{2\theta}}} = k'_s \quad (2)$$

where  $p^{2\theta}$  is the equilibrium pressure over the adjoining two-phase region, and  $k'_s$  is the corresponding modified Sievert's law constant.  $C = n/(1 - n)$  is the gas-to-metal atom ratio and  $C_s$  is its terminal solubility. Complicated functional forms of  $f(C)$  have been proposed by Boureau [7,8]. In this study, the logarithm of  $f(C)$  is assumed to be expressed by  $g^*(C) + 2\ln[C/(m - C)]$ , where  $g^*(C)$  is a polynomial in  $C$  and  $m$  is a constant. The logarithmic term results from the configurational entropy owing to random arrangements of gas atoms in the available interstitial sites and  $m$  is an integer usually chosen as the stoichiometric ratio of the compound under considera-

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tion ( $m = 1$  for UN and  $m = 2$  for  $ZrO_2$  and  $ThO_2$ ). The polynomial term  $g^*(C)$  is used to fit the strong composition dependency in regions far away from  $C = 0$  or  $C = m$ . The  $p$ - $C$ - $T$  relationship of gas dissolution in liquid metal can be obtained according to:

$$\ln p^\alpha = g(C) + 2 \ln \frac{C}{m-C} + \frac{h}{RT} \quad (3)$$

where  $g(C)$  is a polynomial of  $C$ , and  $h$  is the relative partial molal enthalpy of gas dissolution in the metal. Eq. (3) has been successfully applied in the Zr-H [6], Ti-O [9], and Ti-H [10] systems with the assumption that the enthalpy of gas dissolution is a constant, an assumption that is retained. Deviation from constant enthalpy has been observed by Boureau and Gerdanian in the solid  $\alpha$ Zr phase of the Zr-O and Hf-O systems [11], in the solid  $\alpha/\beta$  phase of the Zr-H system [12,13], and in the solid  $\alpha$  phase of the Ti-O system [9]. Indirect evidence of non-constant enthalpy has been observed in systems with extensive miscibility gaps, such as the Pd-H [14] and Li-H [15] systems. Rudman [16] has also given a detailed discussion of this subject. However, no direct experimental dissolution enthalpy data on systems similar to those in this study are available.

The integral Gibbs energy of formation of the compound ( $MX_C$ ) for the reaction



is related to the relative partial molal free energies of  $X_2$  over the entire X/M range by

$$\Delta G_f^0(MX_C) = \frac{RT}{2} \int_0^C \ln p \, dC' \quad (5)$$

where  $p$  is the equilibrium gas pressure (in atm) at the specified composition  $C$ . The pure liquid metal is used as the standard state of the Gibbs energy of formation in Eq. (5) and  $C$  does not need to be at exact stoichiometry. Application of Eq. (5) has been demonstrated by Wang and Olander for the Zr-N [17], Zr-O [18], U-O [18], and Zr-H [6] systems, by Kubaschewski and Dench [19] for the Zr-O system, and by Veleckis et al. [15] for the Li-H system.

Substituting Eq. (3) into Eq. (5), letting  $g(C)$  be a linear function of  $C$  ( $g(C) = a + bC$ ), and integrating Eq. (5) from  $C = 0$  to  $C = C_{upb}$  (the upper phase boundary of the two-phase M(L)/ $MX_C$  region), we obtain

$$\frac{\Delta G_f^0(MX_{C_{upb}})}{RT} = \int_0^{C_s} \ln \frac{C}{m-C} dC' + \frac{1}{2} \left( aC_s + \frac{b}{2} C_s^2 \right) + \frac{hC_s}{2RT} + \frac{(C_{upb} - C_s)}{2} \ln p^{2\theta} \quad (6)$$

where  $\Delta G_f^0(MX_{C_{upb}})$  is the integral Gibbs energy formation of the compound at  $C_{upb}$ . Values of  $a$  and  $b$  in Eq. (6) can be obtained by fitting Eq. (6) to the known values of  $\Delta G_f^0(MX_{C_s})$ ,  $\Delta G_f^0(MX_{C_{upb}})$ ,  $C_s$ , and  $C_{upb}$  over the corresponding temperature ranges. Two sets of  $p^\alpha$  result with two possible fittings: the first fitting sets  $b = 0$  and the second fitting lets  $b \neq 0$ . Nevertheless,  $p^\alpha$  must obey the following continuity relation:

$$p^\alpha(C_s(T)) = p^{2\theta}(T) \quad (7)$$

Luo and Flanagan [20] show that the partial molal enthalpy of a two-phase region ( $\Delta \bar{H}^{2\theta}$ ) is related to that of the neighboring single-phase region ( $\Delta \bar{H}^\alpha$ ) and the intervening terminal solubility ( $C_s$ ) by

$$\Delta \bar{H}^{2\theta} = \Delta \bar{H}^\alpha + \left[ \frac{\partial(\mu/T)}{\partial C} \right]_T \frac{dC_s}{dT^{-1}} \quad (8)$$

where  $\partial C_s / \partial T^{-1}$  refers to the boundary composition change with temperature. Eq. (8) is generally used for qualitative comparison between these two relating relative partial molal enthalpies ( $\Delta \bar{H}^{2\theta}$  and  $\Delta \bar{H}^\alpha$ ). The derivative  $[(\partial(\mu/T))/(\partial C)]_T$  must be positive; therefore, whether  $|\Delta \bar{H}^{2\theta}|$  is greater or smaller than  $|\Delta \bar{H}^\alpha|$  depends on the sign of  $dC_s/dT^{-1}$  at the temperature under consideration. Rigorous quantitative comparison of partial molal enthalpies using Eq. (8) is limited owing to the lack of accurate thermodynamic potentials ( $\mu$ ) at  $C_s$ . In this study,  $|\Delta \bar{H}^{2\theta}|$  should be more negative than  $|\Delta \bar{H}^\alpha|$  since  $dC_s/dT^{-1}$  is always negative.

In this paper, the  $p$ - $C$ - $T$  relationships over the liquid metal regions of the systems Zr-O, U-N, and Th-O are derived according to Eq. (6), and the results are evaluated with the constraints of Eqs. (7) and (8).

## 2. The U-N, Zr-O, and Th-O systems

Partial phase diagrams of U(L)-N, Zr(L)-O, and Th(L)-O are shown in Fig. 1. These systems exhibit extensive terminal solubilities which are obtained from Tagawa [21], Abriata et al. [22], Benz [23], and Ackermann and Tetenbaum [24], respectively.

### 2.1. U(L)-N

The thermodynamics of the U(L)-N system has been studied extensively by Tagawa [21], who also measured the following equilibrium nitrogen pressure over the U(L)/UN two-phase region:

$$\ln p^{2\theta} = 22.68 - \frac{7.36 \times 10^4}{T} \quad (9)$$

The Gibbs energy of formation of uranium nitride

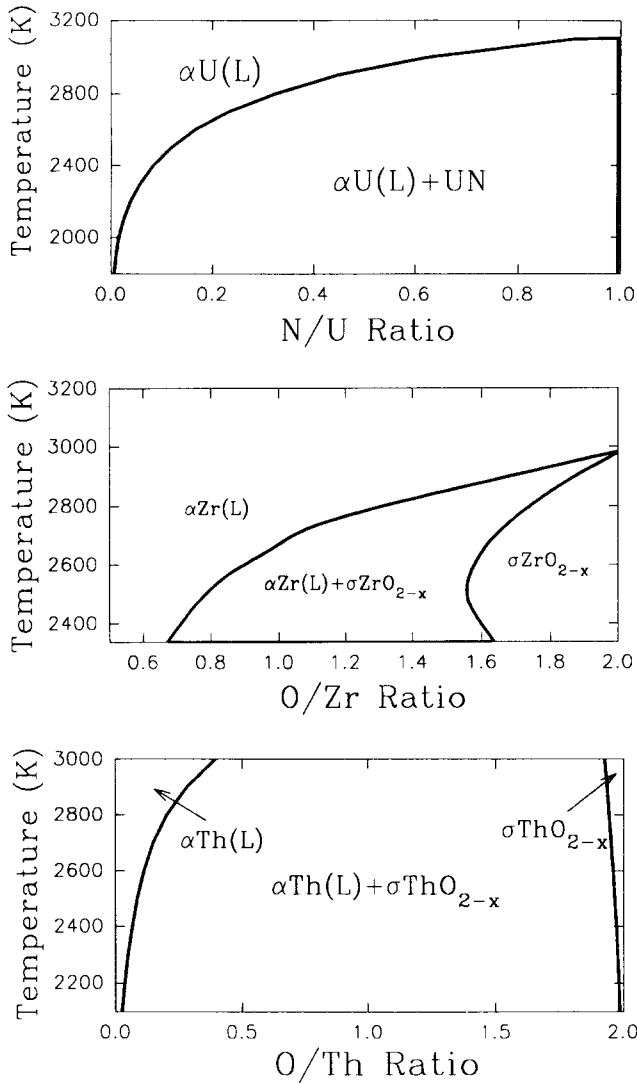


Fig. 1. Partial phase diagrams of the U(L)–N, Zr(L)–O, and Th(L)–O systems.

( $\Delta G_f^0(\text{UN})$ ) is approximated by the linear relation  $\Delta G_f^0(\text{UN}) = \Delta H_f^0(\text{UN}) - T\Delta S_f^0(\text{UN})$ . Reported values of  $\Delta H_f^0(\text{UN})$  (at 298 K) include  $-276$  [25],  $-287$  [26],  $-289$  [27],  $-295$  [21], and  $-311$  [28]  $\text{kJ mole}^{-1}$ . The value of  $\Delta S_f^0(\text{UN})$  proposed by Inouye and Leitnaker [27] has been disputed by Tagawa [21] who gives a value of  $-83.5 \text{ J mole}^{-1} \text{ K}^{-1}$ . According to the phase diagram of Fig. 1, the extremely narrow hypostoichiometric region suggests that  $\Delta G_f^0(\text{UN}_{C_{\text{upb}}}) \approx \Delta G_f^0(\text{UN})$ , or  $C_{\text{upb}} = 1$ . The terminal solubility  $C_s$  (listed in Table 1) is also provided by Tagawa [21]. It has been found that  $p^\alpha$  (derived using Eq. (6)) is very sensitive to the value of  $\Delta H_f^0(\text{UN})$  chosen. This sensitivity is demonstrated in Fig. 2 by the continuity check of Eq. (7), in which each of the calculated  $p^\alpha(C_s)$  values is compared with those of Eq. (9). Fig. 2 shows that unacceptable values of  $p^\alpha$  results from a small change of  $0.4 \text{ kJ mole}^{-1}$  of  $\Delta H_f^0(\text{UN})$ . It is obvious that the solid line derived from using  $\Delta H_f^0(\text{UN}) = -292.3 \text{ kJ mole}^{-1}$  yields the best fit:

$$\ln p_{\text{U-N}}^\alpha = 11.54 + 2 \ln \frac{C}{1-C} - \frac{29.23 \times 10^4}{RT} \quad (10)$$

The value of  $\Delta H_f^0(\text{UN})$  suggested ( $-292.3 \text{ kJ mole}^{-1}$ ) is very close to that proposed by Tagawa [21] in this temperature region.  $b = 0$  is assumed in the derivation of Eq. (10). Satisfactory results cannot be obtained if  $b \neq 0$  is assumed (i.e. the  $p^\alpha$  value obtained does not satisfy the continuity check of Eq. (7)). Eq. (10) is considered very reliable since it also obeys the enthalpy constraint of Eq. (8). The following Gibbs energy of solution can be determined by substituting  $p^{2\theta}$  from Eq. (9) and  $f(C_s) = C_s/(1-C_s)$  into Eq. (2):

$$RT \ln \gamma_N^0 = -121.7 + 0.037T \text{ kJ mole}^{-1} \quad (10a)$$

Table 1

Composition–temperature relationships at the phase boundaries  $C_s$  and  $C_{\text{upb}}$  (shown in Fig. 1)

(i) U(L)–N

$$\log \left( \frac{C_s}{1+C_s} \right) = 2.4143 - \frac{8480}{T}$$

$$C_{\text{upb}} = 1$$

(ii) Zr(L)–O

$$C_s = 30.35 - 28.32 \times 10^{-2}T + 88.6 \times 10^{-7}T^2 - 8.55 \times 10^{-10}T^3$$

$$C_{\text{upb}} = 19.56 - 15.97 \times 10^{-3}T + 337.8 \times 10^{-8}T^2$$

(iii) Th(L)–O

$$C_s = 271.9 - 46.91 \times 10^{-3}T + 30.29 \times 10^{-6}T^2 - 86.93 \times 10^{-10}T^3 + 938.7 \times 10^{-15}T^4$$

$$\log(2 - C_{\text{upb}}) = 0.506 - \frac{4934}{T}$$

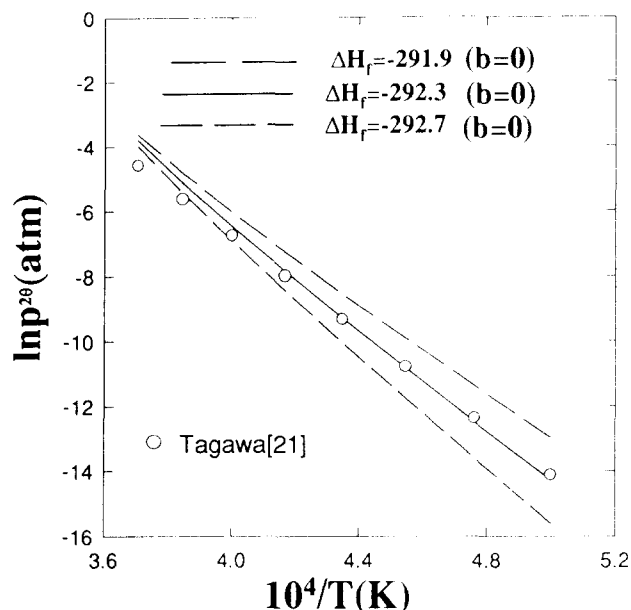


Fig. 2. Comparison of three sets of  $p^{2\theta}$  obtained from Eq. (6) (assuming  $b = 0$ ) and the measured values (symbols) [21] for the U(L)-N system. The solid line is obtained by assuming  $\Delta H_f = -292.3$  kJ mole<sup>-1</sup>, the long-dash line from  $\Delta H_f = -291.9$  kJ mole<sup>-1</sup>, and the short-dash line from  $\Delta H_f = -292.7$  kJ mole<sup>-1</sup>.

The Gibbs energy of solution from Eq. (10a) is more positive than that suggested by Chang et al. [1]. However, the latter was obtained based on the assumption that UN exists over a range of extensive homogeneity (such as  $\text{UO}_{2+x}$ ). According to the phase diagram from Tagawa [21], this assumption is not true.

## 2.2. Zr(L)-O

Oxygen dissolution in liquid zirconium was investigated by Wang and Olander [18]. Slight deviations from the classical Sievert's law was demonstrated. The  $p$ - $C$ - $T$  relationship in the liquid Zr region proposed by Wang and Olander [18] can be modified by Eq. (6) to account for this non-ideality.  $\Delta G_f^0(\text{ZrO}_{C_{\text{upb}}})$  (2338 K <  $T$  < 2800 K) and  $p^{2\theta}$  (2338 K <  $T$  < 2600 K) used in Eq. (6) are obtained from Ackermann et al. [29]:

$$\Delta G_f^0(\text{ZrO}_{C_{\text{upb}}}) = -5018.4 + 34.04 \times 10^{-1} T - 64.68 \times 10^{-1} T^2 \text{ kJ mole}^{-1} \quad (11a)$$

$$\ln p^{2\theta} = 16.3 - \frac{12.46 \times 10^4}{T} \quad (11b)$$

Substituting  $\Delta G_f^0(\text{ZrO}_{C_{\text{upb}}})$  and  $p^{2\theta}$  from Eqs. (11a) and (11b) and the corresponding values of  $C_{\text{sat}}$  and  $C_{\text{upb}}$  from Table 1 into Eq. (6) with  $m = 2$  results in two sets of  $p^\alpha$ . Each set of  $p^\alpha$  obtained is extrapolated to the terminal solubility  $C_s$  and is shown in Fig. 3. It is

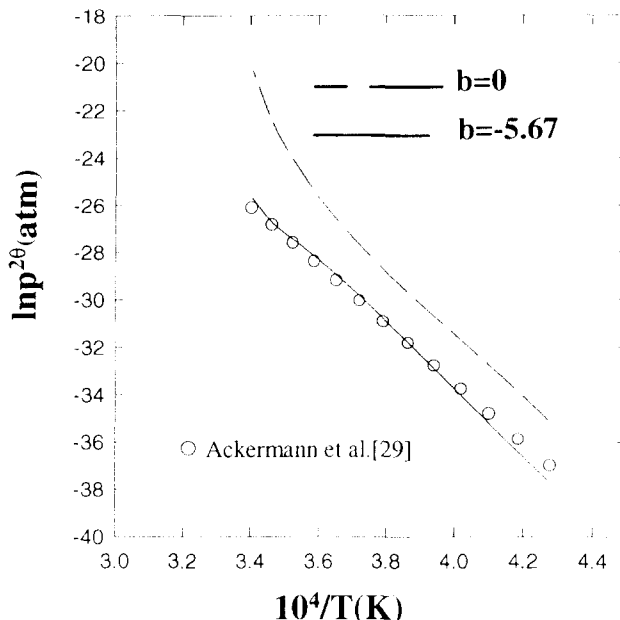


Fig. 3. Comparison of the two sets of extrapolated  $p^{2\theta}$  were obtained from Eq. (6) ( $b = 0$  and  $b = -5.67$ ) and the measured values from Ackermann et al. [29] for the Zr(L)-O system.

obvious that the one with  $b = -5.67$  best fits the measured  $p^{2\theta}$ , which yields

$$\ln p_{\text{Zr-O}}^\alpha = 31.14 - 5.67C + 2 \ln \frac{C}{2-C} - \frac{14.89 \times 10^4}{T} \quad (12)$$

Eq. (12) is further evaluated with Eq. (8). It has been found that the relative partial molal enthalpy obtained from Eq. (12) is more negative than that of Eq. (11b), which violates the enthalpy constraint. The discrepancy may be the result of the errors accumulated from all the other measured values including  $\Delta G_f^0(\text{ZrO}_{C_{\text{upb}}})$ ,  $C_s$ ,  $C_{\text{upb}}$ , and used in Eq. (6).

## 2.3. Th(L)-O

The Th(L)-O system has been reviewed extensively by Belle and Berman [30]. The phase diagram of the Th-O system is taken from Benz [23] except for the upper phase boundary of the two-phase  $\alpha\text{Th(L)}/\sigma\text{ThO}_C$  region. The  $C_{\text{upb}}$  value proposed by Benz [23] has been disputed by Ackermann and Tetenbaum [24] who suggested higher values.  $C_s$  and  $C_{\text{upb}}$  are listed in Table 1.

The equilibrium oxygen pressure has been studied in the hypostoichiometric thoria region by Ackermann and Tetenbaum [24]. Their data can be fit satisfactorily to the following  $p$ - $C$ - $T$  relationship:

$$\ln p_{\text{Th-O}} = -104.11 - 38.42 \times 10^{-1} C + 33.76 C^2 + 2 \ln \frac{C}{2-C} - \frac{19.82 \times 10^4}{T} \quad (13)$$

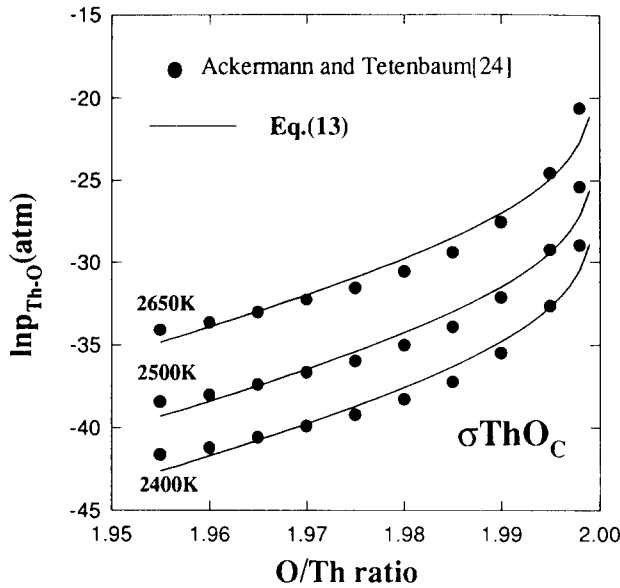


Fig. 4. Comparison between the best fit from Eq. (13) and the data of Ackermann and Tetenbaum [24].

The parabolic polynomial in Eq. (13) is required to fit the data shown as symbols in Fig. 4. A similar fitting technique has been successfully applied to the Zr–H [6] and the Ti–H [10] systems.  $\Delta G_f^0(\text{ThO}_{C_{\text{upb}}})$  can be calculated using the integral constraint of Eq. (5), which yields

$$\Delta G_f^0(\text{ThO}_{C_{\text{upb}}}) = \Delta G_f^0(\text{ThO}_2) - \frac{RT}{2} \int_{C_{\text{upb}}}^2 \ln p_{\text{Th-O}} dC' \quad (14)$$

Substituting  $p_{\text{Th-O}}$  from Eq. (13) and the corresponding  $C_{\text{upb}}$  from Table 1 into Eq. (5), we obtain

$$\Delta G_f^0(\text{ThO}_{C_{\text{upb}}}) = -1259.2 + 0.2T \text{ kJ mole}^{-1} \quad (15a)$$

The  $\Delta G_f^0(\text{ThO}_{C_{\text{upb}}})$  value obtained from Eq. (15a) is very close to that reported by Ackermann and Tetenbaum [24]. The equilibrium partial pressure at the univariant  $\alpha\text{Th(L)}/\sigma\text{ThO}_C$  two-phase region is obtained from Ackermann and Tetenbaum [24]

$$\ln p^{2\theta} = 21.17 - \frac{14.58 \times 10^4}{T} \quad (15b)$$

Substituting Eqs. (15a) and (15b) and the corresponding  $C_s$  and  $C_{\text{upb}}$  functions from Table 1 into Eq. (6) yields two sets of  $p^\alpha$  (with  $b=0$  and  $b \neq 0$ ). However, no resulting  $p^\alpha$  values fulfil the continuity check of Eq. (7). Higher-order polynomials in  $g(C)$  have also been attempted without success. This suggests that the databases used in Eq. (6) for the Th(L)–O system are not consistent. This inconsistency is investigated further as follows. It can be shown that  $\Delta G_f^0(\text{ThO}_{C_{\text{upb}}})$  from Eq. (15a) is almost equal to  $(C_{\text{upb}}/$

$2)RT \ln p^{2\theta}$  (from Eq. (15b)). However, according to Eq. (6) this can only be thermodynamically true if  $C_s$  is negligibly small, which contradicts the data of Benz [23]. The discrepancy between the database of Ackermann and Tetenbaum [24] and that of Benz [23] can be resolved using Eq. (5) and assuming  $f(C) = C$ , which yields

$$\ln p^{2\theta} = \frac{2}{C_{\text{upb}}} \left( \frac{\Delta G_f^0(\text{ThO}_{C_{\text{upb}}})}{RT} + \frac{C_s}{2} \right) \quad (16)$$

The assumption of  $f(C) = C$  has been applied to the Zr–O [18], U–O [18], and Zr–N [17] systems. This is equivalent to setting  $b=0$  and assuming a large value of  $m$  in the modified Sievert's law of Eq. (2). The equilibrium oxygen pressure over the  $\alpha\text{Th(L)}/\sigma\text{ThO}_C$  two-phase region calculated from Eq. (16) yields

$$\ln p^{2\theta} = 22.27 - \frac{14.8 \times 10^4}{T} \quad (17)$$

Equation (17) differs only slightly from Eq. (15b). The Gibbs energy of solution of oxygen dissolution in liquid thorium can be calculated by substituting Eq. (17) and  $C_s$  from Table 1 into Eq. (2). This yields

$$RT \ln \gamma_O^0 = -448.4 + 0.046T \text{ kJ mole}^{-1} \quad (17a)$$

No data from the literature are available for the heat of solution of oxygen dissolution in liquid thorium. The enthalpy of solution obtained from Eq. (17a) is considered reasonable because it is close to the heat of solution of the analogous systems, e.g. oxygen in liquid zirconium and in liquid uranium [18].

### 3. Conclusions

A modified form of Sievert's law, together with the thermodynamic constraints of Eqs. (6)–(8), has been applied to estimate the  $p$ – $C$ – $T$  relationships of gas (oxygen and nitrogen) dissolution in liquid metal (uranium, zirconium, and thorium).

Nitrogen dissolution in liquid uranium is found to follow the classical Sievert's law and the corresponding value of the Gibbs energy of solution has also been shown to be more accurate than that proposed by Chang et al. [1]. The integral Gibbs enthalpy of formation of UN obtained is very close to that reported by Tagawa [21].

The derived  $p$ – $C$ – $T$  relationship for oxygen over liquid zirconium has been shown to fulfill the integral constraints of Eqs. (6) and (7). However, according to the enthalpy constraint of Eq. (8), the enthalpy, as derived, appears to be overestimated. This suggests that further investigation of this system is required.

In the Th(L)–O system, the thermodynamic quantities measured by Ackermann and Tetenbaum [24]

have been shown to be inconsistent with the terminal solubility reported by Benz [23]. The equilibrium oxygen pressure at the two-phase  $\alpha\text{Th(L)}/\sigma\text{ThO}_C$  is reassessed using the thermodynamic constraint of Eq. (6) and the assumption that the oxygen dissolution in liquid thorium follows the modified form of Sievert's law. The Gibbs energy of solution of oxygen in liquid thorium is also determined.

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