

PREDICTION OF THERMODYNAMIC PROPERTIES OF OXYGEN IN LIQUID TRANSITION METALS

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ABSTRACT

Two correlations between the heat of solution of oxygen in liquid metals and the standard heats of formation of the respective oxides, and between the heat of solution and the excess entropy of solution are proposed in the form

$$\Delta \bar{S}_0^E = \left[-2.2 \times 10^{-5} (\Delta \bar{H}_0) - 4.141 \times 10^{-3} \right] (\Delta \bar{H}_0)^2 + 6.0$$

$$\Delta \bar{H}_0 = \left[1.6 \times 10^{-5} (\Delta H_{298}^o) - 5.252 \times 10^{-3} \right] (\Delta H_{298}^o)^2$$

The above equations enable prediction of the activity coefficient of oxygen in liquid transition metals for systems in which experimental data is not available

INTRODUCTION

Technological importance of interaction between gases and liquid metals and alloys resulted in the development of a number of theoretical models, which describe the thermodynamic behavior of non-metallic solutes such as O, S, N, etc. in the liquid phase [1–5]. All of them, however, share the same weakness; a knowledge of the thermodynamic properties of the solute in pure liquid metals is necessary to apply any of them.

Despite the fact that experimental evidence on the thermodynamic properties of oxygen in liquid metals has increased recently, there is still little known about oxygen behavior in liquid transition metals. In fact, only three systems were studied carefully, viz. Fe–O, Ni–O and Co–O. In this situation, one is forced to estimate the Gibbs free energy of the reaction of dissolution



for a number of metals, and an empirical correlation suggested between the heat of solution of oxygen, entropy of solution of oxygen and the standard heat of

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formation of the most stable oxide calculated per g-atom O can be very useful [6,7]. This correlation was supported by coulometric titration studies on Bi-O, Sb-O and In-O systems [8-10]. The trend was generally confirmed by Otsuka and Kozuka [11]. Moreover, Seetharaman and Staffansson [12] observed that the ratio of the experimental and theoretical interaction parameters, measured in liquid copper, seems to decrease as the *d*-shells of respective transition metals get filled up successively, which supports a previous suggestion about different oxygen behavior [6] in liquid transition metals.

Taking these facts into account, one can assume that within experimental uncertainties, there exist functions between $\Delta\bar{H}_0$ vs. $\Delta\bar{S}_0^E$ and $\Delta\bar{H}_0$ vs. ΔH_{298}° , which can be represented by mathematical formulae. If such an approach may reproduce existing data, there is strong evidence that it is possible to use this dependence for the prediction of oxygen thermodynamic properties in unknown systems.

CORRELATION BETWEEN $\Delta\bar{H}_0$ AND $\Delta\bar{S}_0^E$

Experimental information gathered to date encouraged a look for $\Delta\bar{H}_0$ vs. $\Delta\bar{S}_0^E$ dependence among data for metals with full *d*-shells. This plot shown in Fig. 1 looks, at first sight, like a parabolic-type curve, and one may seek the correlation between

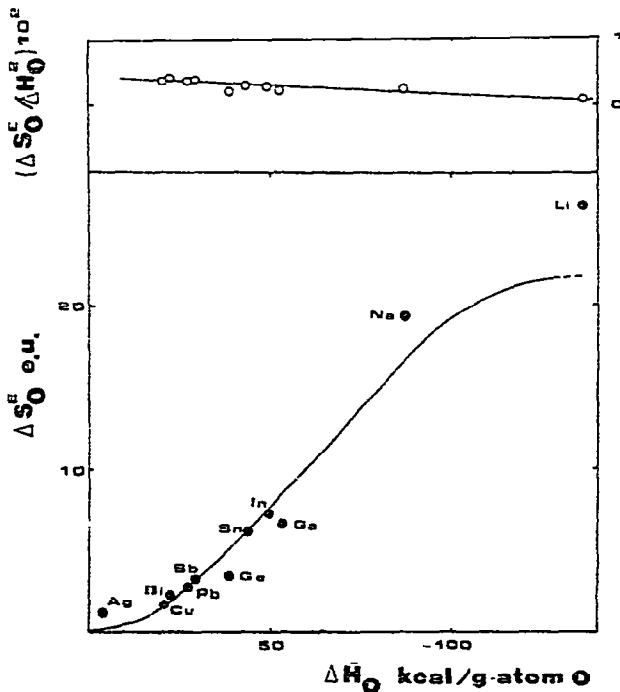


Fig. 1 Correlation between the partial excess entropy of solution $\Delta\bar{S}_0^E$ and the partial heat of solution $\Delta\bar{H}_0$ of oxygen in liquid metals with full *d*-shells

these two parameters using the relationship

$$\left[\Delta \bar{S}_0^E / (\Delta \bar{H}_0)^2 \right] = a + b(\Delta \bar{H}_0) \quad (2)$$

Indeed, a straight line was obtained for the plot described by eqn. (2) (Fig. 1) with the following parameters a and b

$$\left[\Delta \bar{S}_0^E / (\Delta \bar{H}_0)^2 \right] \times 10^2 = -0.0022 (\Delta \bar{H}_0) - 0.4141 \quad (3)$$

After rearrangement of eqn (3), one can arrive at the expression

$$\Delta \bar{S}_0^E = \left[-2.2 \times 10^{-5} (\Delta \bar{H}_0) - 4.141 \times 10^{-3} \right] (\Delta \bar{H}_0)^2 \quad (4)$$

where $\Delta \bar{S}_0^E$ is given in entropy units and $\Delta \bar{H}_0$ in kcal */g-atom. Equation (4) allows the calculation of the excess partial entropy of oxygen in liquid metals with a full d -shell. In the previous study [6] it was observed, that the partial excess entropy of oxygen in liquid transition metals with unfilled d -shells appears to be significantly different. Despite rather large uncertainties in the partial entropies of oxygen in these metals, it can be estimated that the shift toward higher entropy values is approximately equal to 6.0 entropy units, which may be connected with the change in bonding.

Indeed, if one assumes that oxygen enters the liquid as an interstitial ion with coordination number $Z = 4$, there are two possibilities of acquiring electrons in the case of transition metals (from s , p or d band) but only one in case of metals with full d -shell (from s , p band). The corresponding entropy change between these two states can be calculated

$$\Delta S_{\text{bond}} = Z k \ln[(2)^N] \approx 6.0 \text{ e.u.} \quad (5)$$

This kind of entropy change due to change in bonding states was first calculated by Van Vechten [13]. Therefore, it is suggested, that the partial excess entropy of oxygen in liquid transition metals can be estimated from

$$\Delta \bar{S}_0^E = \Delta \bar{S}_{0(4)}^E + 6.0 \text{ e.u.} \quad (6)$$

CORRELATION BETWEEN $\Delta \bar{H}_0$ AND ΔH_{298}°

At this stage, it is clear that as long as $\Delta \bar{H}_0$ is known, the partial excess entropy of oxygen can be estimated either from eqn. (4) or eqn.(6). Now, one can recall Richardson's suggestion [14] about the correlation between the heat of solution of oxygen $\Delta \bar{H}_0$ and the heat of formation of the corresponding oxide per gram atom of oxygen. It has been shown previously [7] that such a plot yields apparent parabolic dependence, especially, in the case of metals with a full d -shell, which is shown in

* As the correlations are based on the value of ΔH_{298}° , which in most thermochemical tables is given in kcal, 1 kcal = 4.184 kJ is used throughout the paper

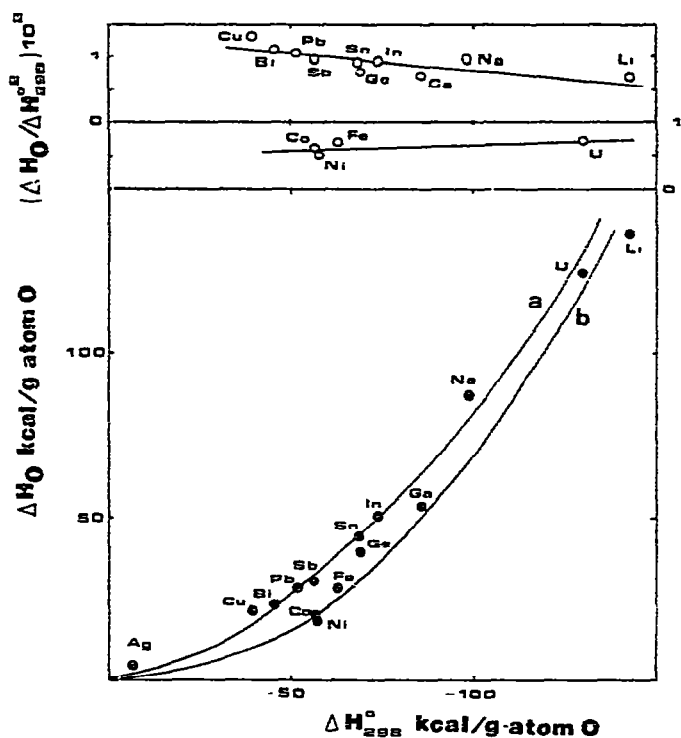


Fig 2 Correlation between the partial heat of solution $\Delta\bar{H}_0$ and the standard heat of formation of respective oxides ΔH_{298}° for metals with full d -shells (curve a) and unfilled d -shells (curve b)

Fig. 2. Again, it was assumed there is a shift between the correlation for transition metals and those with full d -shells. Experimental results were described using the equation

$$\left[\frac{\Delta\bar{H}_0}{(\Delta H_{298}^\circ)^2}\right] = a + b(\Delta H_{298}^\circ) \quad (7)$$

Consequently, the following formulae were obtained for metals with full d -shells

$$\left[\frac{\Delta\bar{H}_0}{(\Delta H_{298}^\circ)^2}\right] \times 10^2 = -0.0050 (\Delta H_{298}^\circ) - 1.2964 \quad (8)$$

for metals with unfilled d -shells

$$\left[\frac{\Delta\bar{H}_0}{(\Delta H_{298}^\circ)^2}\right] \times 10^2 = 0.0016 (\Delta H_{298}^\circ) - 0.5252 \quad (9)$$

where ΔH_{298}° is taken in kcal per g-atom O for the most stable oxide.

After necessary rearrangement of eqn. (9), the following expression is given in the case of transition metals.

$$\Delta\bar{H}_0 = [1.6 \times 10^{-5} (\Delta H_{298}^\circ) - 5.252 \times 10^{-3}] (\Delta H_{298}^\circ)^2 \quad (10)$$

Using the standard heat of formation values available in literature [15,16] the terms $\Delta\bar{H}_0$ and $\Delta\bar{S}_0^E$ were calculated respectively, and the corresponding equations for ΔG_0° of reaction (1) for a number of transition metals are given in Table 1.

TABLE I

Predicted equations for the Gibbs free energy of reaction (1)

System	$\Delta G_{O(1)}^{\circ} = \Delta \bar{H}_0 - T\Delta \bar{S}_0^{\circ}$ (cal/g-atom O) $= RT \ln \gamma_O$
Ti-O	-117,200 + 15.46 T
V-O	-73,500 + 7.64 T
Cr-O	-54,200 + 2.66 T
Mn-O	-56,900 + 3.36 T
Zr-O	-128,300 + 15.70 T
Nb-O	-64,000 + 5.19 T
Mo-O	-31,200 - 2.64 T
Tc-O	-16,300 - 5.0 T
Ru-O	-7,700 - 5.76 T
Rh-O	-4,800 - 5.90 T
Pd-O	-2,300 - 5.98 T
Hf-O	-139,700 + 14.84 T
Ta-O	-65,200 + 5.51 T
W-O	-32,200 - 2.44 T
Re-O	-16,200 - 5.01 T
Os-O	-7,200 - 5.79 T
Ir-O	-5,500 - 5.88 T
Pt-O	-500 - 6.0 T

VERIFICATION OF SUGGESTED ΔG° EQUATIONS

Generally, it is impossible to check the estimated equations given in Table I as there is virtually no data on the thermodynamic properties of oxygen in liquid transition metals over the range of dilute solutions. However, in the case of a few systems, the predicted formulae can be confirmed indirectly.

Cr-O system

Using the oxygen potentials calculated from phase equilibria in this system by Banik, et al. [17] as well as the reported Cr-Cr₂O₃ phase diagram, the Gibbs free energy of reaction (1) was calculated for three compositions. Comparison of these results with the predicted equation is shown in Fig. 3 (a) revealing fairly good agreement.

Ti-O system

By fitting available experimental data on the solubility of oxygen in liquid iron-titanium alloys, Liang [18] arrived at the most probable equation for the Gibbs free energy of the reaction of dissolution of oxygen in liquid titanium, which is shown in Fig. 3 (b) together with the predicted values.

Nb-O and Ta-O systems

Fromm and Gebhardt [19] reported Nb-O and Ta-O phase diagrams. As the thermodynamic properties of oxygen in solid Nb and Ta are known, it is possible to estimate the activity of oxygen in liquid niobium at 2188 K and 40.5 atom %O, and the activity of oxygen in liquid tantalum at 2153 K and 43 atom %O. Results are shown in Figs. 4 (a) and (b) together with predicted values. Fairly good agreement has been reached, and the revealed difference of the order of 3 kcal can be attributed to the deviations from Henry's law, which had to be assumed for calculations.

Mn-O system

The solubility of oxygen in liquid manganese was measured by Schenck et al. [20] by the equilibration of the liquid metal with a MnO crucible. Recalculated from their data $\Delta G_{0(\text{Mn})}^\circ$ values are shown in Fig. 5 (a) in comparison with the predicted equation. Again, within experimental scatter, a reasonable agreement was found. Moreover, if the predicted equation for ΔG_0° of reaction (1) is taken for the calculation of part of the Mn-MnO phase diagram, a more plausible liquidus line is obtained than that suggested by Schenck et al. [Fig. 5 (b)].

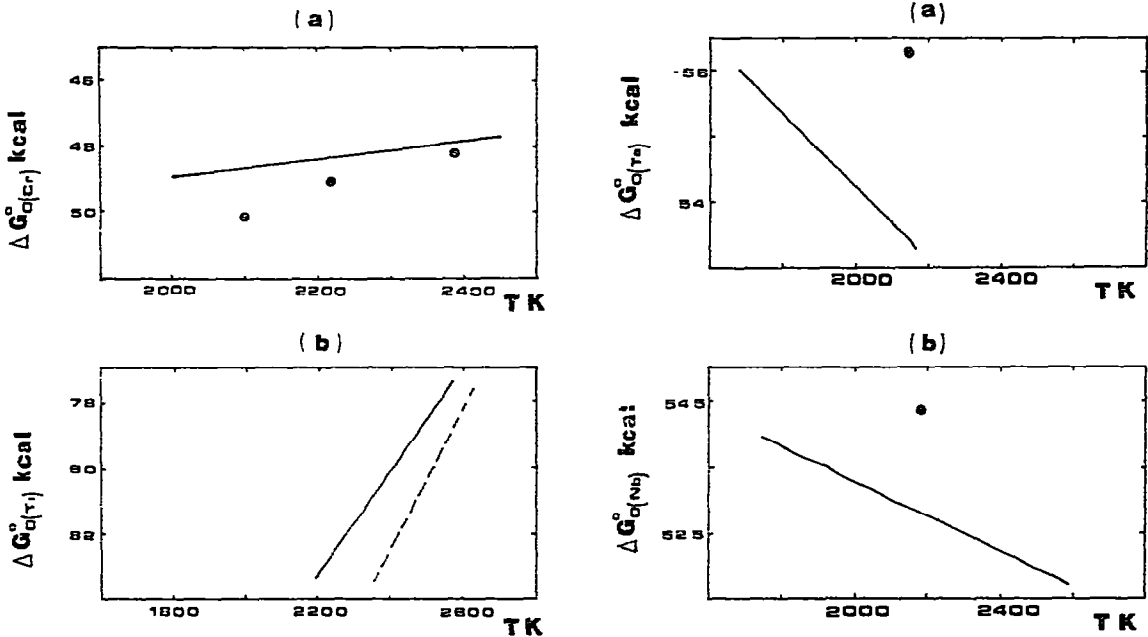


Fig 3 Gibbs free energy of reaction (1) for oxygen dissolution in liquid chromium (a) and liquid titanium (b) ●, calculated from the Cr-O phase diagram (ref 17), - - - - -, Liang (ref 18), ———, predicted (this study)

Fig 4 Gibbs free energy of reaction (1) for oxygen dissolution in liquid tantalum (a) and liquid niobium (b) ●, calculated from the phase diagram (ref 19), ———, predicted (this study).

V-O system

Using the predicted equation for $\Delta G_{O(V)}^{\circ}$, the solubility of oxygen in the liquid iron-vanadium alloys in equilibrium with different vanadium oxides was calculated

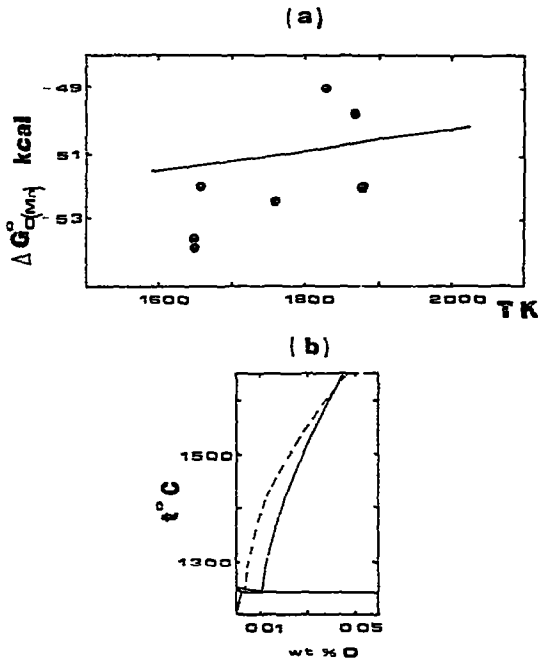


Fig 5. Gibbs free energy of reaction (1) for oxygen dissolution in liquid manganese (a) ●, Calculated from the solubility data (ref 20); ———, predicted (this study) Part of Mn-O phase diagram (b) ———, suggested by Schenck et al (ref 20), - - - - -, predicted (this study)

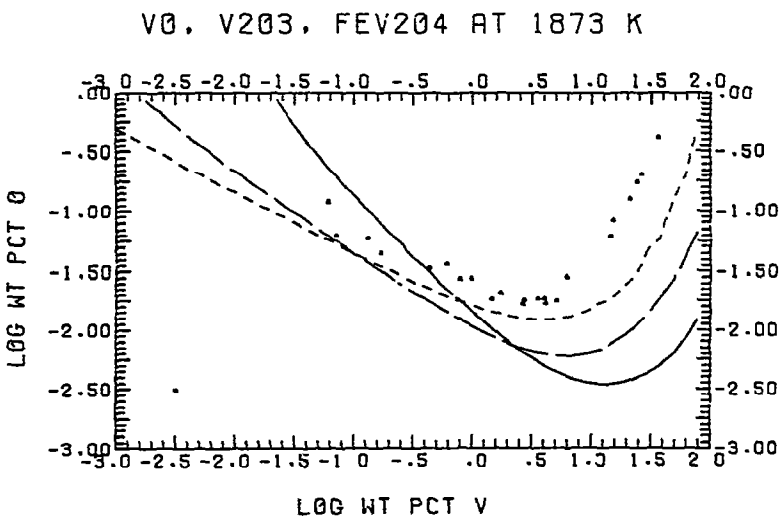


Fig 6 Oxygen solubility in the liquid iron-vanadium alloys ▲, experimental values (ref 21) Calculated with the aid of $\Delta G_{O(V)}^{\circ}$ equation from Table I for equilibrium with ———, $VO_{(s)}$, - - -, $V_2O_{3(s)}$, ·····, $FeV_2O_{4(s)}$

and compared with Fruehan's experimental data [21]. Results obtained at 1873 K are shown in Fig. 6.

Taking into account experimental difficulties on the one hand and assumptions made during calculations on the other, a reasonable agreement was reached. The calculated interaction parameter $\epsilon_0^V = -15.2$ corresponds reasonably well with the measured value $\epsilon_0^V = -29$, which was reported by Fruehan [21].

DISCUSSION

The Gibbs free energies of reaction (1) were calculated using ΔH_{298}° values taken from refs. 14 and 15. If the difference in ΔH_{298}° values from these two sources was larger than 2 kcal, the average value was taken. While correlations (4) and (8) were established, the silver-oxygen system was not taken into account. The small temperature range covered by the experiments as well as the small free energy value did not guarantee that the split into $\Delta \bar{H}_0$ and $\Delta \bar{S}_0^E$ terms was correct, even if the free energy itself was measured precisely. Application of the suggested equations to such different systems as Cr-O, Mn-O, Nb-O, Ta-O, Ti-O and V-O showed fairly good agreement in comparison with available data. Moreover, the number of ΔG_0° values for Cr-O, Mn-O, Mo-O, Nb-O, Ti-O and V-O systems at the constant temperature 1873 K was estimated by Chang and Hu [22]. Comparison revealed very good agreement in the case of Cr-O and Mo-O systems (about 1 kcal difference), while there are differences for other metals of as much as 17 kcal in the case of V-O solution. This is not surprising since the first two estimates were adjusted to measured interaction parameters, where the other values were obtained by the authors with the aid of the equation

$$RT \ln \left[\frac{\gamma_{O(A)}}{\gamma_{O(B)}} \right] = (\Delta H_{A,O} - \Delta H_{B,O}) \quad (12)$$

which is only an approximation and does not take the entropy effect into account. It is believed that the range of suggested correlation should not exceed the value of $\Delta \bar{H}_0$ for the Li-O system (or $\Delta H_{298}^\circ, \text{Li}_2\text{O}$). The function obtained does not represent a linear equation but the higher order dependence and calculations performed outside the range of values covered by experimental data are expected to be erroneous. Moreover, the value of $\Delta G_{O(L)}^\circ$ itself is not measured directly but calculated from the solubility of oxygen in liquid lithium.

It seems that still more experimental data on oxygen behavior in liquid metals is needed, especially for systems exhibiting higher affinity to oxygen. Such experimental evidence may help to prove the validity of suggested correlations or to bring about their change. A similar approach can be worked out for sulfur-metal systems. Because of the fact that sulfur behavior in liquid metals is much more difficult to investigate, the existence of this kind of dependence would be very useful for predictions in multicomponent systems.

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