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SOLUBILITY AND ACTIVITY OF OXYGEN IN LIQUID INDIUM AND COPPER–INDIUM ALLOYS

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Summary

The solubility of oxygen in liquid indium in the temperature range 650 - 820 °C and in liquid copper–indium alloys at 1100 °C in equilibrium with indium sesquioxide has been measured by a phase equilibration technique. The solubility of oxygen in pure indium is given by the relation

$$\log(\text{at.\% O}) = -4726/T + 3.73 \ (\pm 0.08)$$

Using the recently measured values for the standard free energy of formation of In_2O_3 and assuming that oxygen obeys Sievert's law up to saturation, the standard free energy of solution of molecular oxygen in liquid indium is calculated as

$$\tfrac{1}{2}O_2 \rightarrow O_{In}$$
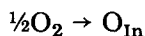
$$\Delta G^\circ = -51\ 440 + 8.07 \ T \ (\pm 500) \ \text{cal}$$

where the standard state for dissolved oxygen is an infinitely dilute solution in which activity is equal to atomic per cent. The effect of indium additions on the activity coefficient of oxygen dissolved in liquid copper was measured by a solid oxide galvanic cell. The interaction parameter ϵ_O^{In} is given by

$$\epsilon_O^{In} = \left(\frac{d\ln\gamma_O}{dX_{In}}\right)_{X_{In}\to 0} = -7.0 \ (\pm 1)$$

The experimentally determined variation of the activity coefficient of oxygen in dilute solution in Cu–In alloys is in fair agreement with that predicted by a quasichemical model in which each oxygen atom is assumed to be interstitially coordinated to four metal atoms and the nearest neighbour metal atoms are assumed to lose approximately half their metallic cohesive energies.

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Introduction

In an attempt to enlarge our present knowledge of the thermodynamic behaviour of oxygen dissolved in liquid metals, the saturation solubility and activity of oxygen in liquid indium and copper–indium alloys have been measured. Previous studies [1, 2] on oxygen dissolved in liquid alloys of copper with elements of Group IVA such as Ge and Sn showed a rapid change in the value of the activity coefficient of oxygen at the composition of the binary alloy which corresponds to the minimum in the heat of mixing. Owing to the very low solubility of oxygen in Cu–Ga liquid alloys in the composition range 5 - 30 at.% gallium [3], the nature of variations of the activity coefficient in this composition range could not be determined experimentally. Since indium belongs to the same group of the periodic table as gallium (IIIA), and indium sesquioxide is less stable than the corresponding oxide of gallium so that the solubility of oxygen in Cu–In alloys may be higher than in Cu–Ga alloys of the same composition, the Cu–In system was chosen as a typical Group IB–Group IIIA alloy for the study of the behaviour of dissolved oxygen.

The solubility of oxygen in liquid indium has not previously been measured. The oxygen potential corresponding to a mixture of liquid indium and indium sesquioxide has been measured by Schaefer [4], Chatterji and Vest [5], Katayama *et al.* [6], Jacob [7] and Kang [8] using solid oxide galvanic cells up to a temperature of 1000 °C. Klinedinst and Stevenson [9] have suggested that indium sesquioxide is unstable in the presence of indium and may decompose above 813 °C according to the reaction

$$\text{In}_2\text{O}_3(\text{s}) + 4 \text{ In(l)} \rightarrow 3 \text{ In}_2\text{O (s)} \tag{1}$$
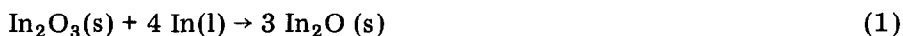
This finding is not supported by other investigators and the change in the slope of the e.m.f. *versus* temperature plots of Klinedinst and Stevenson [9] may be caused by the presence of impurities in indium or by interaction of the oxide with container materials. However, mass spectrometric studies [10, 11] have shown that In_2O molecules are present in the gas phase in equilibrium with a mixture of indium and indium sesquioxide.

A conventional two-phase equilibration technique was used in this study to measure the saturation solubility of oxygen in liquid indium and copper–indium alloys and the effect of indium on the activity of oxygen in liquid copper was determined by e.m.f. measurements on a solid oxide galvanic cell.

Experimental methods

Materials

The indium metal used in this study was 99.999% pure and was obtained from Cerac Inc.; indium sesquioxide and copper obtained from Alfa Inorganics were 99.99% pure. The argon gas used as the atmosphere

during e.m.f. measurements was supplied by Matheson of Canada. Fully stabilized CaO–ZrO$_2$ solid electrolyte tubes were obtained from Zircoa, and chromium cermet Metamic 612 was made by Morgan Refractories.

Apparatus and procedure
Oxygen solubility measurements

The conventional two-phase equilibration technique used for determining the saturation solubility of oxygen in liquid indium and copper–indium alloys has been described previously [1]. A mixture of indium metal (or alloy) and indium sesquioxide was placed in a closed-end silica tube which was then sealed under vacuum. After equilibrating the metal and oxide in the silica capsule at the desired temperature for 24 h the capsule was quenched in liquid nitrogen. Examination of the capsule at the end of the experiment indicated that there had been no significant reaction between silica and indium or its oxides.

E.m.f. measurements

The oxygen–indium interaction in liquid copper at 1100 °C was investigated by an e.m.f. technique which has been described in detail in earlier papers [2, 12] on Cu + Sn + O and Cu + Pb + O systems. The oxygen potential of an unsaturated liquid Cu + O solution was measured with the solid oxide galvanic cell

$$\text{Pt, Ni + NiO} \mid \text{CaO–ZrO}_2 \mid \text{Cu + O, cermet, Pt} \tag{2}$$

The Cu + O solution was held in a high purity alumina crucible under a stream of prepurified argon gas in a vertical reaction tube at 1100 °C. The conducting lead of chromium cermet about 35 mm long was held in an alumina tube which also fitted over the platinum wire tightly wound around one end of the cermet. The junction between the cermet and the platinum wire was at almost the same temperature (± 1.5 °C) as the liquid copper, so that the thermoelectric contribution to the cell e.m.f. was negligible. The oxygen content of copper in the cell was adjusted by adding copper oxide to the melt, the oxygen concentration being determined by the analysis of suction samples. Weighed samples of oxygen-free indium were dropped into the Cu + O solution in the cell. The oxygen-free samples were prepared by reducing metallic indium with dry hydrogen for 24 h. After each addition an approximately constant e.m.f. (± 2.5 mV) was recorded after 10 - 25 min. A sample of the melt corresponding to this e.m.f. was drawn into a silica sampling tube for analysis. The indium content of the alloy was calculated from a mass balance. After several indium additions and the measurement of e.m.f. and oxygen content after each addition, a pellet of In$_2$O$_3$(s) was dropped into the melt to saturate the alloy with oxygen. The constant e.m.f. obtained after adding In$_2$O$_3$ was also recorded.
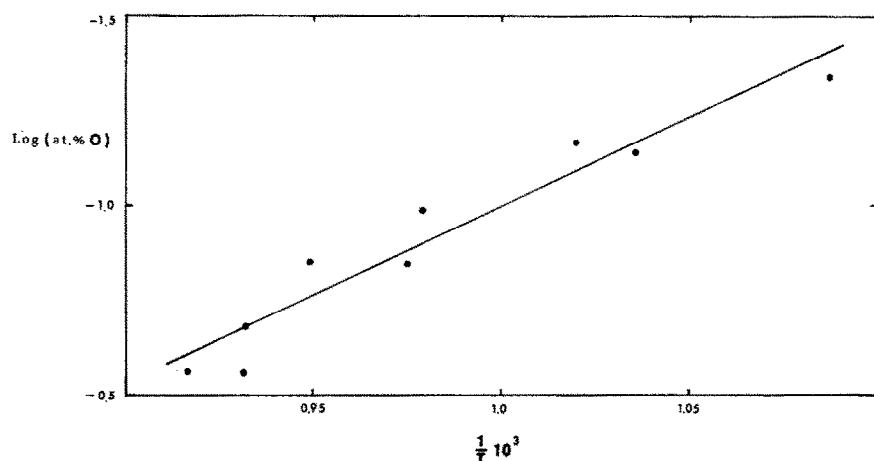
Fig. 1. Temperature dependence of the solubility of oxygen in liquid indium.

TABLE 1

The solubility of oxygen in
pure liquid indium

T (°C)	Oxygen (at.%)
819	0.2726
800	0.2749
800	0.2109
781	0.1365
753	0.1422
748	0.1017
708	0.0680
693	0.0717
647	0.0450

Analysis

The oxygen analysis of the metal and alloy samples equilibrated with In_2O_3 was carried out using the Leco RO-16 Oxygen Analyser as described in an earlier paper [3].

Results

The saturation solubility of oxygen in liquid indium obtained by analysis of the metal or alloy after isothermal equilibration with its oxide is plotted as a function of the reciprocal of absolute temperature in Fig. 1. The analytical results for oxygen are also summarized in Table 1 with the corresponding temperatures of equilibration. The least mean square regression analysis of the results suggests the following equation for oxygen solubility:

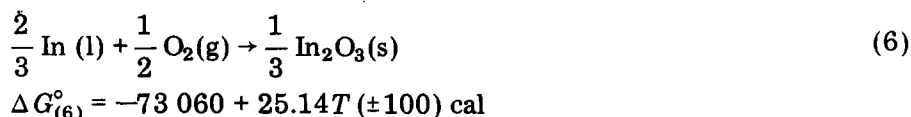$$\log(\text{at.\% O}) = -4726/T + 3.73 \ (\pm 0.08) \tag{3}$$

The solution of In_2O_3 in liquid indium may be represented by the reaction

$$\frac{1}{3} In_2O_3(s) \rightarrow \frac{2}{3} In\ (l) + O_{In} \tag{4}$$

where the standard state for oxygen is an infinitely dilute solution in liquid indium in which its activity is equal to its atomic per cent. The standard free energy change for reaction (4) is calculated from the relation

$$\Delta G^{\circ}_{(4)} = -RT \ln K = -RT \ln \frac{(\text{at.\% O})\ a_{In}^{2/3}}{a_{In_2O_3}^{1/3}}$$

$$= 21\ 622 - 17.07\,T \ (\pm 450)\ \text{cal} \tag{5}$$

Since the solubility of oxygen in liquid indium is less than 1 at.% over the temperature range used in this study and the liquid metal was in equilibrium with solid indium sesquioxide, the activities of In and In_2O_3 have been assumed to be equal to unity. When eqn. (5) is combined with the standard free energy of formation of In_2O_3 [6] given by

$$\frac{2}{3} In\ (l) + \frac{1}{2} O_2(g) \rightarrow \frac{1}{3} In_2O_3(s) \tag{6}$$

$$\Delta G^{\circ}_{(6)} = -73\ 060 + 25.14\,T \ (\pm 100)\ \text{cal}$$

and assuming that Sievert's law is obeyed by oxygen dissolved in indium, the standard free energy change for the solution of molecular oxygen in liquid indium is obtained:

$$\frac{1}{2} O_2 \rightarrow O_{In} \tag{7}$$

$$\Delta G^{\circ}_{(7)} = -51\ 440 + 8.07\,T \ (\pm 500)\ \text{cal}$$
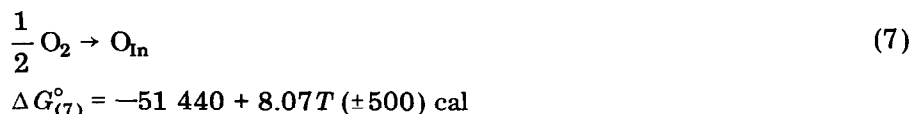
The variation of the saturation solubility of oxygen in liquid copper–indium alloys at 1100 °C with the alloy composition is shown in Table 2. Since there was no measurable weight change of the alloy beads during the experiment, the alloy composition was calculated from the initial weight of the component metals used to form the alloy. Phase relations in the system

TABLE 2

The solubility of oxygen in liquid indium–copper alloys at 1100 °C

X_{In}	Oxygen (at.%)
0.17	0.0425
0.44	0.2461
0.64	0.6901
0.81	1.2603

TABLE 3

Effect of indium on the activity coefficient $\gamma_{O(Cu)}$ of oxygen in copper at 1100 °C

| System	E.m.f. (mV)		Oxygen (at.%) (analysed)	X_{In} (calculated)	$\log \gamma_{O(Cu)}^{In}$
	E	E'			
Cu + O	78.3		0.1016	—	—
Cu + O + In		68.0	0.0876	0.004	−0.01125
Cu + O + In		18.6	0.0427	0.018	−0.06198
Cu + O + In		12.3	0.0388	0.021	−0.06665
Cu + O + In		− 6.8	0.0301	0.029	−0.09666
Cu + O + In + In$_2$O$_3$		− 6.5	—	0.029	—
Cu + O	173.0		0.5111	—	—
Cu + O + In		40.6	0.0610	0.014	−0.04919
Cu + O + In		− 5.7	0.0309	0.029	−0.09385
Cu + O + In		−26.7	0.0235	0.045	−0.12919
Cu + O + In		−49.5	0.0188	0.065	−0.19972
Cu + O + In + In$_2$O$_3$		−46.3	—	0.065	—

In$_2$O$_3$–Cu$_2$O–CuO have not been investigated. If ternary oxide phases are unstable and Cu$_2$O and In$_2$O$_3$ do not have significant mutual solubility in the liquid or solid state, it can be shown from thermodynamic data on binary oxides that the displacement reaction

$$In_2O_3(s) + Cu (l) \rightarrow 3Cu_2O (s) + 2 In (l) \qquad (8)$$
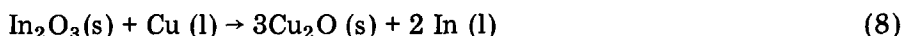
would occur at 1100 °C only when $a_{In} \leqslant 3 \times 10^{-11}$ or $X_{In} \leqslant 3 \times 10^{-10}$. From the oxygen solubility data the activity coefficient of oxygen in copper–indium alloys, relative to that in pure indium, can be calculated from the relation

$$\gamma_{O(Cu+In)} = \frac{K^{1/3}}{a_{In}^{2/3}} \frac{1}{\text{at.\% O}} \qquad (9)$$

where K is the equilibrium constant for the reaction
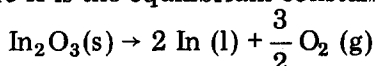
$$In_2O_3(s) \rightarrow 2 In (l) + \frac{3}{2} O_2 (g)$$

The effect of indium additions on the activity coefficient of oxygen dissolved in liquid copper at 1100 °C can be calculated from the e.m.f. measurements and oxygen analyses of samples of Cu + O and Cu + In + O solutions taken during the e.m.f. measurements. The experimental results are summarized in Table 3. The effect of indium on oxygen activity is related to the change in e.m.f. and oxygen concentration:

$$\log \gamma_O^{In} = \frac{2F(E' - E)}{4.575T} - \log \frac{X_{O(Cu+In)}}{X_{O(Cu)}} \qquad (10)$$

where γ_O^{In} denotes the effect of indium on the activity coefficient of oxygen, E' and E are the e.m.f.s of cell (2) in volts with and without the addition of indium, respectively, and $X_{O(Cu)}$ and $X_{O(Cu+In)}$ are the mole fractions of oxy-
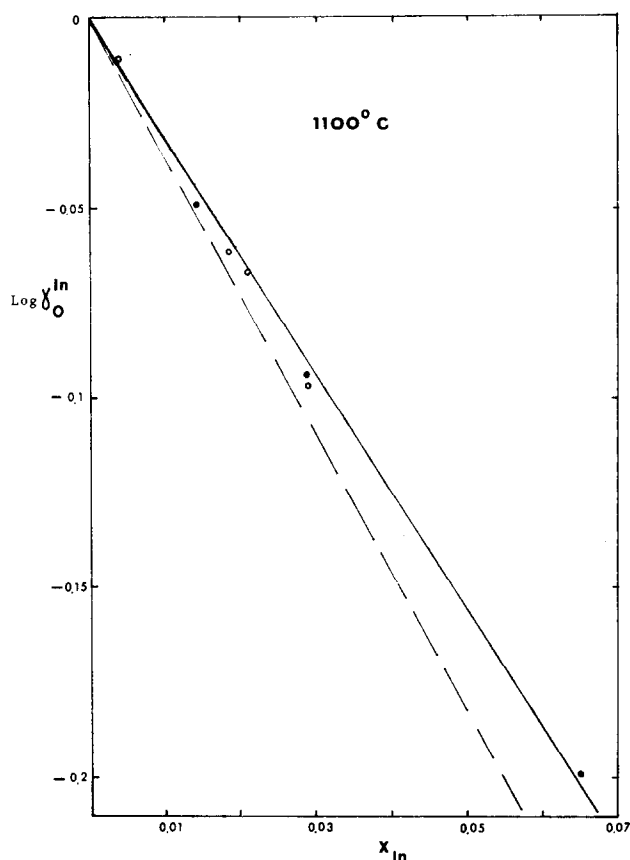
Fig. 2. The effect of indium at low concentrations on the activity coefficient of oxygen in Cu + In alloys at 1100 °C as determined by e.m.f. measurements: ○ first run, ● second run; the broken line corresponds to the linear change of the logarithm of the activity coefficient.

gen in liquid copper and alloy, respectively. As the oxygen concentration of the melt was less than 0.52 at.%, the variation of the activity coefficient of oxygen with its concentration may be neglected. Detailed studies on oxygen dissolved in copper [12] suggest that the deviation from Sievert's law at the oxygen concentration employed in the e.m.f. measurements is less than 5%. The effect of indium on the activity coefficient of oxygen dissolved in liquid copper is shown in Fig. 2. It is seen that the results obtained from the two separate experiments are in good agreement. The Wagner interaction parameter at 1100 °C is

$$\epsilon_O^{In} = \left(\frac{d\ln\gamma_O}{dX_{In}}\right)_{X_{In} \to 0} = -7.0 \ (\pm 1) \tag{11}$$

An inspection of Table 3 reveals that after each addition of indium there was a significant loss of oxygen, which may be attributed to the formation
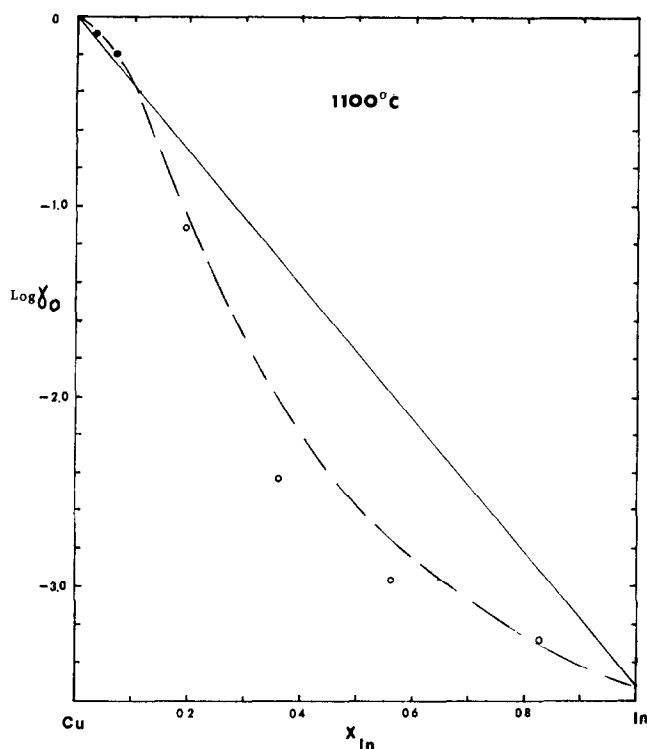
Fig. 3. The composition dependence of the activity coefficient of oxygen in liquid copper–indium alloys at 1100 °C relative to that of oxygen in pure copper: ○ experimental results obtained by equilibration technique; ● results obtained from e.m.f. measurements for $X_{In} = 0.03$ and $X_{In} = 0.065$; ———— quasichemical model of Jacob and Alcock [14], $n = 4$, $\alpha = 1/2$.

of In_2O_3(s) or In_2O (g). From thermodynamic data on In_2O (g) [10, 11] it can be shown that the partial pressure of In_2O over the Cu + In + O solutions under these experimental conditions varies between 3×10^{-6} and 3×10^{-4} atm. These low values for the partial pressure of the In_2O species and the fact that the e.m.f. did not change significantly when In_2O_3 was added to the Cu + In + O solution at the end of each run, suggest that In_2O_3 was precipitated from the solution after each addition of indium. Since the oxygen concentration in the solution is insignificant in comparison with the indium concentration, the change in indium concentration owing to the precipitation of In_2O_3 from the solution is negligible.

At 1100 °C the activity coefficient of oxygen at infinite dilution in liquid indium relative to that in pure copper [12] is 4.24×10^{-4}. The activity coefficient of oxygen in liquid copper–indium alloys obtained from the solubility and e.m.f. measurements is shown as a function of alloy composition in Fig. 3.

From the e.m.f. of the cell after addition of In_2O_3 to Cu + In + O solution, the activity of indium in oxygen-saturated alloys can be derived:
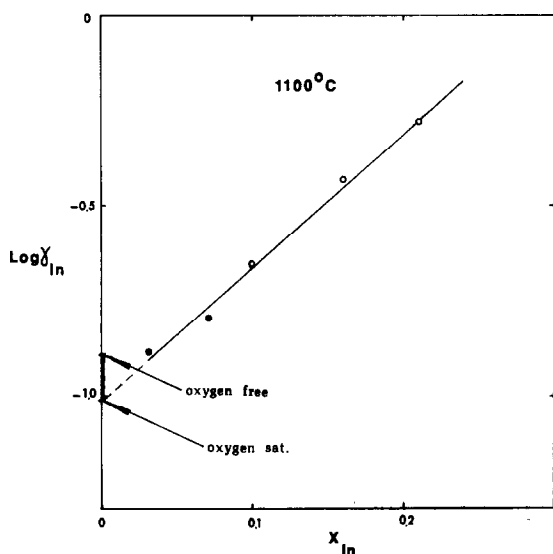
Fig. 4. The variation of the activity coefficient of indium in oxygen-saturated Cu + In + O solutions at 1100 °C: ● results of this study, ○ results obtained by Kang [8]; the effect of dissolved oxygen on the activity coefficient of indium at infinite dilution as evaluated in the appendix is also shown.

$$RT \ln a_{In} = -\frac{3}{4}(2\Delta G^{\circ}_{NiO} + 4FE) + \frac{3}{2}\Delta G^{\circ}_{(6)} \tag{12}$$

where ΔG°_{NiO} is the standard free energy of formation of NiO ($-55\,965 + 20.29T$ cal) [13], $F = 23\,063$ cal V^{-1} mol^{-1}, E is the e.m.f. in volts and $\Delta G^{\circ}_{(6)}$ is the standard free energy change for reaction (6). In Fig. 4 the logarithm of the activity coefficient of indium is plotted as a function of indium concentration in oxygen-saturated copper—indium alloy at 1100 °C. The results obtained by Kang [8] at higher concentrations are in good agreement with the results of this study. Since the experimental results can be represented by a straight line, the activity coefficient of indium at infinite dilution in oxygen-saturated copper can be obtained by linear extrapolation; the value of the activity coefficient so obtained is 0.098. Owing to the strong interaction between dissolved oxygen atoms and indium and copper atoms, the activity coefficients of the metallic components would be lower at oxygen saturation than in oxygen-free binary alloy. In the appendix, analytical equations are developed for calculating the effect of dissolved oxygen on the activity coefficients of indium and copper. It is shown that the value of the activity coefficient of indium at infinite dilution at 1100 °C in oxygen-free copper is 0.126, 28% higher than in oxygen-saturated copper. Similar effects of dissolved non-metals have not been quantitatively assessed in any previous study using the e.m.f. method on the thermodynamic properties of alloys.
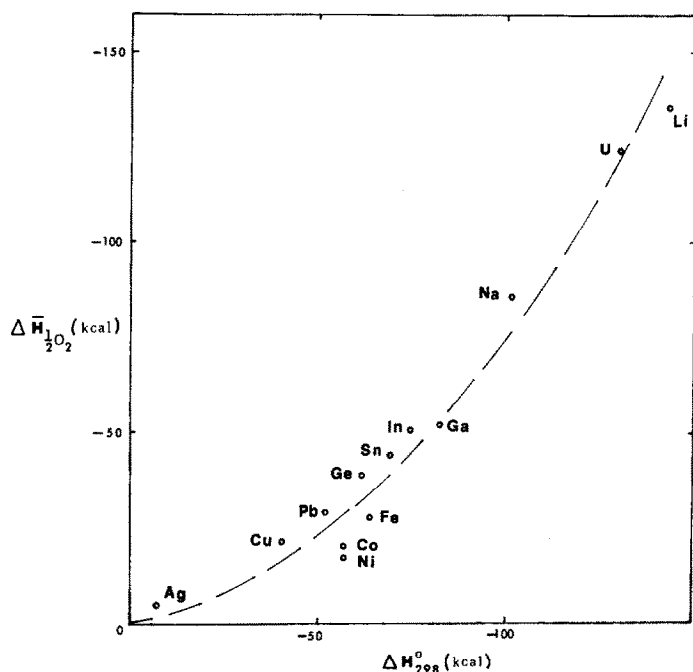
Fig. 5. Heat of solution of oxygen in liquid metals as a function of the standard heat of formation of their oxides per g atom of oxygen.

Discussion

The experimental values for the activity coefficient of oxygen in liquid copper–indium alloys at 1100 °C are compared in Fig. 3 with those calculated from a quasichemical model suggested by Jacob and Alcock [14]. According to this model the activity coefficient of oxygen in the ternary solution can be predicted from binary data by the equation

$$\frac{1}{\gamma_{O(Cu+In)}^{1/n}} = X_{In}\left(\frac{\gamma_{In(Cu+In)}^{\alpha}}{\gamma_{O(In)}^{1/n}}\right) + X_{Cu}\left(\frac{\gamma_{Cu(Cu+In)}^{\alpha}}{\gamma_{O(Cu)}^{1/n}}\right) \tag{13}$$

where $\gamma_{O(In)}$, $\gamma_{O(Cu)}$ and $\gamma_{O(Cu+In)}$ are the activity coefficients of oxygen at infinite dilution in liquid indium, copper and copper–indium alloys, respectively, $\gamma_{In(Cu+In)}$ and $\gamma_{Cu(Cu+In)}$ are the activity coefficients of indium and copper in the Cu + In binary system and X_{In} and X_{Cu} are the mole fractions of indium and copper in the alloy.

It has been shown [14] that for a large number of systems the experimental data can be reconciled with the model values $n = 4$ and $\alpha = 1/2$. The results of this study indicate a rapid change in the values of the activity coefficient of oxygen at $X_{In} = 0.25$. The X-ray diffraction investigations of Isherwood and Orton [15] on liquid copper–indium alloys suggest closer packing of atoms at 25.5 at.% indium than in the pure metals, a feature also

found in Group IB–Group IVA alloy systems such as Cu–Sn and Cu–Ge. There is strong evidence that cluster formation in the liquid alloy affects the thermodynamic properties of dissolved oxygen and often causes a minimum in the oxygen saturation solubility at the composition of the liquid alloy which corresponds to cluster formation or to the minimum value of the heat of mixing.

It has been suggested by Gellings *et al.* [16, 17] that oxygen may enter the liquid metal as negative ions, by acquiring electrons from the conduction band of the metal. For liquid Tl + Te solutions Cutler [18] has recently discussed the implication of the "molecular" structure of the liquid for the change in the electronic structure. As the concentration of "molecules" increases in the liquid, transition from states associated with pure metal to those associated with an admixture of metal and molecules will decrease the number of states. A similar process may explain the drop in the oxygen solubility when more clusters are formed in the solution and fewer electrons are available to form oxygen ions. However, detailed numerical calculations based on this model cannot be undertaken in the present state of knowledge. One may therefore focus on empirical trends, which are useful for the prediction of the behaviour of oxygen in liquid metals. Richardson [19] suggested a correlation between the heat of solution of oxygen and the heat of formation of the corresponding oxide per gram atom of oxygen. Available information on partial heats of solution of oxygen in metals is compared with the heat of formation of the oxides in Fig. 5. A parabolic correlation between these parameters is apparent, especially in the case of metals with full d shells. This correlation, with another correlation between partial heat and entropy of solution of oxygen in liquid metals suggested previously [1, 3] and the quasi-chemical model [14] discussed above, can be used for approximate prediction of the thermodynamic properties of oxygen in metals and alloys.

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Appendix

Estimation of the effect of dissolved oxygen on the activity coefficients of Cu and In in oxygen-saturated Cu + In + O solutions

It is generally accepted that oxygen occupies interstitial positions in metals and alloys [14, A1]. The composition of oxygen may therefore be represented by the ratio of interstitial to substitutional atoms:

$$y_O = \frac{\eta_O}{\eta_{Cu} + \eta_{In}} \tag{A1}$$

where η_i is the number of moles of component i. For convenience the concentrations of Cu and In can be represented by their atomic ratios:

$$y_{Cu} = \frac{\eta_{Cu}}{\eta_{Cu} + \eta_{In}} \tag{A2}$$

$$y_{In} = \frac{\eta_{In}}{\eta_{Cu} + \eta_{In}} \tag{A3}$$

It follows by definition that $y_{Cu} = 1 - y_{In}$. The main advantage of these composition variables is that y_O is independent of y_{Cu} and y_{In} along paths of constant η_{Cu}/η_{In} or y_{Cu}. This analytical advantage is exploited in the following derivation.

By dividing each term in the general Gibbs–Duhem equation

$$\Sigma \eta_i \mathrm{dln}\gamma_i = 0 \tag{A4}$$

by $\eta_{Cu} + \eta_{In}$ one obtains

$$\Sigma y_i \mathrm{dln}\gamma_i = 0 \tag{A5}$$

Further, by dividing eqn. (A5) by $\mathrm{d}y_O$ and $\mathrm{d}y_{In}$, one obtains the following equations:

$$y_O \frac{\mathrm{dln}\gamma_O}{\mathrm{d}y_O} + y_{In} \frac{\mathrm{dln}\gamma_{In}}{\mathrm{d}y_O} + (1 - y_{In}) \frac{\mathrm{dln}\gamma_{Cu}}{\mathrm{d}y_O} = 0 \tag{A6}$$

$$y_O \frac{d\ln\gamma_O}{dy_{In}} + y_{In} \frac{d\ln\gamma_{In}}{dy_{In}} + (1 - y_{In}) \frac{d\ln\gamma_{Cu}}{dy_{In}} = 0 \tag{A7}$$

Differentiation of eqns. (A6) and (A7) with respect to y_{In} and y_O, respectively and subtraction of the resulting equations gives the relation

$$\frac{d\ln\gamma_O dy_O}{dy_{In}} = d\ln\gamma_{In} - d\ln\gamma_{Cu} \tag{A8}$$

Equation (A8) may be integrated between $y_O = 0$ and $y_O = y_O^*$, where * represents the oxygen-saturated composition:

$$\left(\frac{d\ln\gamma_O}{dy_{In}} \right)_{\substack{y_O=0 \\ y_{In}=k}} y_O^* + \frac{1}{2} \left(\frac{d\ln\gamma_O}{dy_O} \right)_{y_{In}=k} y_O^{*2} = \ln\left(\frac{\gamma_{In,y_O=y_O^*}}{\gamma_{In,y_O=0}} \right)_{y_{In}=k} -$$

$$- \ln\left(\frac{\gamma_{Cu,y_O=y_O^*}}{\gamma_{Cu,y_O=0}} \right)_{y_{In}=k} \tag{A9}$$

The second term on the left-hand side contains the first order self-interaction parameter for oxygen,

$$\epsilon_O^O = \left(\frac{d\ln\gamma_O}{dy_O} \right)_{y_O \to 0}$$

In the integration of eqn. (A8), it has been assumed that any deviation from Sievert's law for oxygen dissolved in alloys can be represented by this first order interaction parameter. Available data on oxygen activity in metals and alloys support this assumption [12].

In the limit when y_{In} approaches zero, eqn. (A9) reduces to

$$\epsilon_O^{In} y_{O(Cu)}^* + \frac{1}{2} \epsilon_{O(Cu)}^O y_{O(Cu)}^{*2} = \ln\left(\frac{\gamma_{In,y_O=y_O^*}}{\gamma_{In,y_O=0}} \right)_{y_{In} \to 0} \tag{A10}$$

where $y_{O(Cu)}^*$ is the saturation solubility of oxygen in liquid copper, which has a value of 0.036 at 1100 °C, $\epsilon_{O(Cu)}^O$ is the self-interaction parameter of oxygen in pure copper which has a value of -10 (± 1) at 1100 °C [12] and

$$\epsilon_O^{In} = \left(\frac{d\ln\gamma_O}{dy_O} \right)_{y_{In}, y_O \to 0}$$

Therefore

$$\ln\left(\frac{\gamma_{In,y_O=y_O^*}}{\gamma_{In,y_O=0}} \right)_{x_{In} \to 0} = -0.255 \tag{A11}$$

Reference to the Appendix

A1 C. Wagner, Acta Metall., 21 (1973) 1297.