Prediction of Activities of Oxygen in Dilute Quaternary Solutions Using Binary Data

K. T. JACOB AND C. B. ALCOCK

Equations are developed for predicting the activity coefficients of oxygen dissolved in ternary liquid alloys. These are extensions of earlier treatments, and are based on a model in which each oxygen atom is assumed to make four bonds with neighboring metal atoms. It is also postulated that the strong oxygen-metal bonds distort the electronic configuration around the metal atoms bonded to oxygen, and that the quantitative reduction of the strength of bonds made by these atoms with all of the adjacent metal atoms is equivalent to a factor of approximately two. The predictions of the quasichemical equation which is derived agree satisfactorily with the partial molar free energies of oxygen in Ag-Cu-Sn solutions at 1200°C reported in literature. An extension of this treatment to multicomponent solutions is also indicated.

$\mathbf{K}$NOWLEDGE of the activity coefficients of oxygen in quaternary and multicomponent solutions are of interest in the control and design of extractive processes. In spite of the research efforts of the last 30 years, there is only one reported investigation[1] of the activities of oxygen in a ternary metallic solvent which covers the whole range of a ternary composition triangle. This lack of information and the tedious experimentation required to generate such data encourages the development of a solution model which will enable the prediction of the properties of oxygen with useful accuracy in various complex solutions from binary data.

The thermodynamic properties of a ternary regular solution may be expressed in three different ways:

i) Meijering[2] has shown that

$$\Delta G^E_{(A+B+C)} = \Delta H_{(A+B+C)} = N_A N_B \beta_{AB} + N_A N_C \beta_{AC} + N_B N_C \beta_{BC}$$

where

$$\beta_{AB} = -ZN' \left[E_{AB} - \left(\frac{E_{AA} + E_{BB}}{2} \right) \right] \text{ and so forth } [1]$$

and

$$
\begin{aligned}
\Delta \mu^E_{A(A+B+C)} &= \Delta H_{A(A+B+C)} \\
&= \beta_{AB} N_B (N_B + N_C) + \beta_{AC} N_C (N_B + N_C) \\
&\quad - N_B N_C \beta_{BC} \quad [2]
\end{aligned}
$$

ii) The value of $\Delta G^E_{(A+B+C)}$ may also be expressed in terms of binary values of ΔG^E along composition paths where N_A and N_B/N_C are constant,[3] as shown in Fig. 1.

$$
\begin{aligned}
\frac{\Delta G^E_{(A+B+C)}}{RT} &= \left[\frac{N_B}{(1-N_A)} \frac{\Delta G^E_{(A+B)}}{RT} + \frac{N_C}{(1-N_A)} \right. \\
&\quad \left. \times \frac{\Delta G^E_{(A+C)}}{RT} \right]_{N_A} + (1-N_A)^2 \\
&\quad \times \left[\frac{\Delta G^E_{(B+C)}}{RT} \right]_{N_B/N_C} \quad [3]
\end{aligned}
$$

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It follows that

$$
\begin{aligned}
\Delta \mu^E_{A(A+B+C)} &= \left[\frac{N_B}{1-N_A} \Delta \mu^E_{A(A+B)} \right. \\
&\quad \left. + \frac{N_C}{1-N_A} \Delta \mu^E_{A(A+C)} \right]_{N_A} \\
&\quad - (1-N_A)^2 [\Delta G^E_{(B+C)}]_{N_B}/N_C \quad [4]
\end{aligned}
$$

iii) The third alternate expression[3] in terms of binary values of ΔG^E along composition paths with constant N_A/N_B, N_B/N_C and N_A/N_C, shown in Fig. 2, is:

$$
\begin{aligned}
\frac{\Delta G^E_{(A+B+C)}}{RT} &= (1-N_C)^2 \left(\frac{\Delta G^E_{(A+B)}}{RT} \right)_{N_A/N_B} \\
&\quad + (1-N_A)^2 \left(\frac{\Delta G^E_{(B+C)}}{RT} \right)_{N_B/N_C} \\
&\quad + (1-N_B)^2 \left(\frac{\Delta G^E_{(A+C)}}{RT} \right)_{N_A/N_C} \quad [5]
\end{aligned}
$$

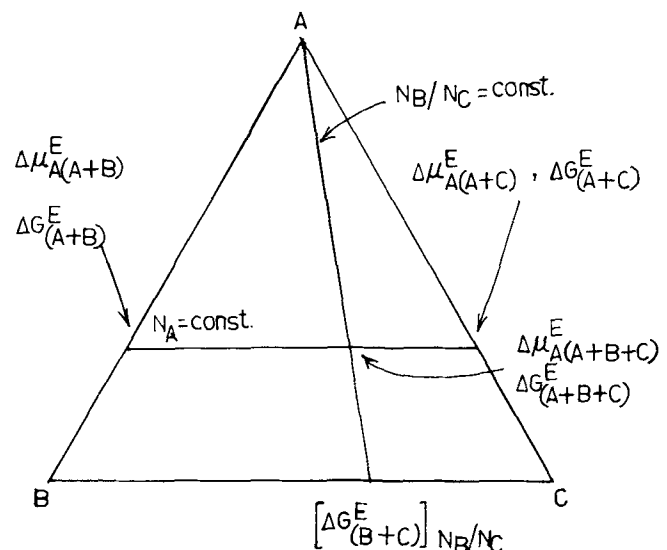The partial molar properties are given by expressions of the type

Fig. 1—Location of binary data points used in Eqs. [3] and [4].

$$\Delta \mu_{B(A+B+C)}^{E} = [(1 - N_C)\Delta \mu_{B(A+B)}^{E}$$
$$+ N_C(1 - N_C)\Delta G_{(A+B)}^{E}]N_A/N_B$$
$$+ [(1 - N_A)\Delta \mu_{B(B+C)}^{E}$$
$$+ N_A(1 - N_A)\Delta G_{(B+C)}^{E}]N_B/N_C$$
$$- (1 - N_B)^2[\Delta G_{(A+C)}^{E}]N_A/N_C \qquad [6]$$

Olson and Toop[3] have shown that the excess free energy of nonregular liquid solutions formed by three metallic constituents may be obtained in an empirical manner from the data on the three binaries involved, even though the binaries do not conform to a simple regular behavior. The second and third treatments shown above are more useful for the empirical calculation of binary excess free energies for nonregular systems, because the experimental binary ΔG^E values may be used directly in these expressions rather than averaged values for the constants β_{AB}, and so forth, in Eqs. [1] and [2]. However, the second method of representation has been shown[3] to give different results for the excess ternary free energy surface of a nonregular solution, depending on the choice of component subscripts. Eqs. [5] and [6] are therefore most suitable for calculating $\Delta G_{(A+B+C)}^{E}$ and the activity coefficients of A, B, and C in a ternary solution, formed by three metallic constituents.

Based on a regular solution model, the partial molar free energy of solution of oxygen dissolved in a ternary alloy may be expressed by the relation

$$\Delta \mu_{O(A+B+C)} = N_A \Delta \mu_{O(A)} + N_B \Delta \mu_{O(B)} + N_C \Delta \mu_{O(C)}$$
$$- \Delta G_{(A+B+C)}^{E} \qquad [7]$$

Judging from the results which are obtained when applying the regular solution equation to oxygen dissolved in binary alloys, this simple expression is not expected to predict activity coefficients of oxygen with sufficient accuracy. Equations that have been found[4,5] to give a good fit to experimental data on oxygen in solution in binary alloys are based on a model in which each oxygen atom is assumed to make four bonds with
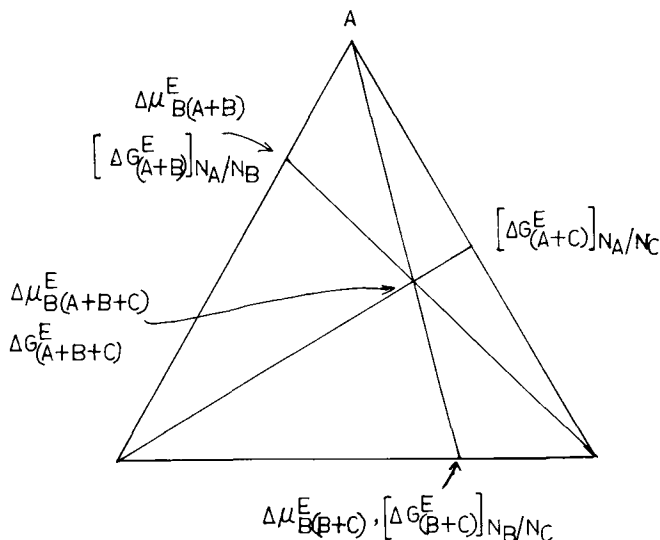

Fig. 2—Location of binary data points used in Eqs. [5] and [6].

metal atoms around it. These strong metal-oxygen bonds are assumed to distort the metal-metal bonds made by metal atoms which are bonded to oxygen, and the effect is the same as a reduction in these bond energies or bond numbers by a factor of two. Information now available on the activity of oxygen in binary alloys can be satisfactorily predicted when the reduction in metal-metal bond energies are considered to be independent of the strength of metal-oxygen bonds. This treatment will now be extended to quaternary solutions.

Analysis of the geometry of liquids in terms of the random closed packed hard sphere model by Bernal and coworkers[6] indicate that 73 pct of the holes in the liquid are tetrahedral and 20 pct are half-octahedral. While their conclusions are not directly applicable to typical ternary metallic solutions, a bond number of four for oxygen is in reasonable agreement, if oxygen atoms are assumed to occupy the interstitial positions in the alloy.

DERIVATION OF EQUATIONS

In the general case, let each oxygen atom make X bonds with metal atoms. The fractional decrease $(1 - \alpha)$ in the energies of metal-metal bonds made by metal atoms bonded to oxygen can be quantitatively treated by defining α as

$$\alpha = \frac{ZE - ZE^x}{ZE} = \frac{ZE - Z^x E}{ZE}$$

where Z is the number of metal-metal bonds made by each atom in the absence of oxygen, and Z^x is the number of such bonds made by metal atoms that are bonded to oxygen. Since the chemical bond models treat a product of bond energy and bond number, a decrease in the energy of Z bonds from E to E^x can be written in an equivalent way as a decrease in the number of bonds from Z to Z^x, each bond being associated with an energy E.

The oxygen atom is introduced into the metal after a hole has been made by removing a metal atom to the surface. Then each oxygen atom forms X bonds with metal atoms around it. The remaining bonds which are broken in creating the hole and in forming X metal-oxygen bonds are remade, so that all metal atoms not bonded to oxygen make Z bonds, and those bonded to oxygen make Z^x bonds. Then,

$$\Delta H_{O(A)} = N'\left[\frac{1}{2}D_{O_2} + E_{AA}\left(\frac{Z - Z^x}{Z}\right)X - XE_{OA}\right] \qquad [8]$$

and so forth, where N' is Avogadro's number, D is the dissociation energy, and E_{AA} and so forth are the energies of pairwise interaction.

If there are large differences in the energies of A-O, B-O, and C-O bonds (i.e., $E_{OC} \gg E_{OB} \gg E_{OA}$), then there would be preferential clustering of B and C atoms around oxygen atoms. When the A, B, and C atoms have attained the equilibrium distribution around each oxygen atom, corresponding to a minimum in the free energy of mixing of the quaternary solution, the free energy changes associated with exchange reactions

$$A\text{-O} + B\text{-}Av \rightarrow B\text{-O} + A\text{-}Av \qquad [9]$$

$$A\text{-O} + C\text{-}Av \rightarrow C\text{-O} + A\text{-}Av \qquad [10]$$
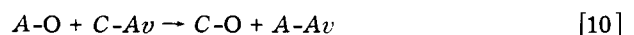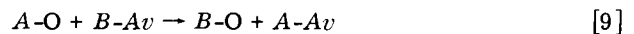
must be zero. In other words, when the equilibrium configuration is attained, there is no driving force for changing an A-O bond to a B-O bond by the exchange of an A atom in the first coordination shell of an oxygen atom with a B atom in the volume of the melt. The energy change accompanying reaction [9] is:

$$\Delta E = N'[E_{OA} + (Z - Z^x)(N_B E_{BB} + N_A E_{AB}$$
$$+ N_C E_{BC}) - E_{OB} - (Z - Z^x)(N_A E_{AA} + N_B E_{AB}$$
$$+ N_C E_{AC})] \qquad [11]$$

Combining Eqs. [8] and [11],

$$\Delta E = \frac{-\Delta H_{O(A)} + \Delta H_{O(B)}}{X} + N'(Z - Z^x)(N_B E_{BB}$$
$$+ N_A E_{AB} + N_C E_{BC}) + N' \frac{(Z - Z^x)}{2} E_{AA}$$
$$- N'(Z - Z^x)(N_A E_{AA} + N_B E_{AB} + N_C E_{AC})$$
$$- N' \frac{(Z - Z^x)}{2} E_{BB}$$

$$\Delta E = \frac{-\Delta H_{O(A)} + \Delta H_{O(B)}}{X} + E_{AB} N'(Z - Z^x)$$
$$\times [N_A - N_B] - N'(Z - Z^x)(N_A - N_B)$$
$$\times \left(\frac{E_{AA} + E_{BB}}{2}\right) + E_{BC} N'(Z - Z^x) N_C$$
$$- N'(Z - Z^x) N_C \left(\frac{E_{BB} + E_{CC}}{2}\right)$$
$$- E_{AC} N'(Z - Z^x) N_C +$$
$$N'(Z - Z^x) N_C \times \left(\frac{E_{AA} + E_{CC}}{2}\right)$$

$$\Delta E = \frac{-\Delta H_{O(A)} + \Delta H_{O(B)}}{X} +$$
$$(N_A - N_B) N'(Z - Z^x) \times \left[E_{AB} - \frac{E_{AA} + E_{BB}}{2}\right] +$$
$$N_C N'(Z - Z^x) \times \left[E_{BC} - \frac{E_{BB} + E_{CC}}{2}\right] -$$
$$N_C N'(Z - Z^x) \times \left[E_{AC} - \frac{E_{AA} + E_{CC}}{2}\right]$$

Noting that from Eq. [2],

$$\Delta H_{A(A+B+C)} - \Delta H_{B(A+B+C)} = \beta_{AB}(N_B - N_A) - \beta_{BC} N_C$$
$$+ \beta_{AC} N_C$$

the enthalpy of the exchange reaction may be written as

$$\Delta H \approx \Delta E = \frac{-\Delta H_{O(A)} + \Delta H_{O(B)}}{X} +$$
$$\frac{(Z - Z^x)}{Z} \times (\Delta H_{A(A+B+C)} - \Delta H_{B(A+B+C)}) \qquad [12]$$

Following the method used in the earlier paper[5] the entropy change associated with the exchange reaction can be expressed by:

$$\Delta S = \frac{-\Delta S^E_{O(A)} + \Delta S^E_{O(B)}}{X} + \frac{\Delta S^E_{A(A+B+C)} - \Delta S^E_{B(A+B+C)}}{Z}$$
$$+ R \ln \frac{N^o_A}{N^o_B} + R \ln \frac{N_B}{N_A} \qquad [13]$$

where N^o_A and N^o_B are the fractions of A and B atoms in the metal atoms bonded to oxygen. By combining Eqs. [12] and [13] and equating the free energy change

of the exchange reaction to zero, it is found that

$$\frac{N^o_B}{N^o_A} = \frac{N_B}{N_A}\left(\frac{\gamma_{O(A)}}{\gamma_{O(B)}}\right)^{1/X}\left(\frac{\gamma_{B(A+B+C)}}{\gamma_{A(A+B+C)}}\right)^\alpha \qquad [14]$$

Similarly by equating the free energy change for the exchange reaction [10] to zero, one obtains:

$$\frac{N^o_C}{N^o_A} = \frac{N_C}{N_A}\left(\frac{\gamma_{O(A)}}{\gamma_{O(C)}}\right)^{1/X}\left(\frac{\gamma_{C(A+B+C)}}{\gamma_{A(A+B+C)}}\right)^\alpha \qquad [15]$$

By rearranging Eqs. [14] and [15] and remembering that

$$N^o_A + N^o_B + N^o_C = 1$$

the following equations are obtained:

$$N^o_A = \frac{N_A}{N_A + K_1 N_B + K_2 N_C} \qquad [16]$$

$$N^o_B = \frac{K_1 N_B}{N_A + K_1 N_B + K_2 N_C} \qquad [17]$$

$$N^o_C = \frac{K_2 N_C}{N_A + K_1 N_B + K_2 N_C} \qquad [18]$$

where

$$K_1 = \left(\frac{\gamma_{O(A)}}{\gamma_{O(B)}}\right)^{1/X}\left(\frac{\gamma_{B(A+B+C)}}{\gamma_{A(A+B+C)}}\right)^\alpha$$

and

$$K_2 = \left(\frac{\gamma_{O(A)}}{\gamma_{O(B)}}\right)^{1/X}\left(\frac{\gamma_{C(A+B+C)}}{\gamma_{A(A+B+C)}}\right)^\alpha$$

Having thus calculated the number of O-A, O-B, and O-C bonds in solution, the partial heat of solution of oxygen in $A + B + C$ solution can be calculated by summing up the energies of bonds made and broken in introducing an oxygen atom into the ternary alloy, using a procedure similar to that employed in evaluating the energy change associated with the exchange reactions [9] and [10].

$$\Delta H_{O(A+B+C)} = N^o_A[\Delta H_{O(A)} - X\alpha \, \Delta H_{A(A+B+C)}]$$
$$+ N^o_B[\Delta H_{O(B)} - X\alpha \, \Delta H_{B(A+B+C)}]$$
$$+ N^o_C[\Delta H_{O(C)} - X\alpha \, \Delta H_{C(A+B+C)}] \qquad [19]$$

The expression for the partial molar entropy of oxygen in the ternary alloy would contain terms representing the vibrational and configurational contributions due to clustering around the oxygen atom. Following the procedure outlined in the earlier paper[5]

$$\Delta S_{O(A+B+C)} = (N^o_A \Delta S_{O(A)} + N^o_B \Delta S_{O(B)} + N^o_C \Delta S_{O(C)})$$
$$- XR\left(N^o_A \ln \frac{N^o_A}{N_A} + N^o_B \ln \frac{N^o_B}{N_B}\right.$$
$$+ N_C \ln \frac{N^o_C}{N_C}\right) - X\alpha(N^o_A \Delta S^E_{A(A+B+C)}$$
$$+ N^o_B \Delta S^E_{B(A+B+C)} + N^o_C \Delta S^E_{C(A+B+C)})[20]$$

The terms in the first bracket represent the sum of ideal and excess vibrational contributions; the terms in second and third brackets denote configurational excess entropy contributions. By combining Eqs. [19] and [20], the partial molar free energy of solution of oxygen is obtained as:

$$\Delta \mu_{O(A+B+C)} = N^o_A(\Delta \mu_{O(A)} - X\alpha \, \Delta \mu^E_{A(A+B+C)})$$
$$+ N^o_B(\Delta \mu_{O(B)} - X\alpha \, \Delta \mu^E_{B(A+B+C)})$$

$$+ N^\circ_C(\Delta\mu_{O(C)} - X\alpha \Delta\mu^E_{C(A+B+C)})$$

$$+ XRT\left(N^\circ_A \ln \frac{N^\circ_A}{N_A} + N^\circ_B \ln \frac{N^\circ_B}{N_B}\right.$$

$$\left. + N^\circ_C \ln \frac{N^\circ_C}{N_C}\right) \qquad [21]$$

By expressing the partial molar free energies in Eq. [21] in terms of activity coefficients and simplifying the resulting expressions, it can be shown that:

$$N_A\left(\frac{\gamma^\alpha_{A(A+B+C)}}{\gamma^{1/X}_{O(A)}}\right) + N_B\left(\frac{\gamma^\alpha_{B(A+B+C)}}{\gamma^{1/X}_{O(B)}}\right) + N_C\left(\frac{\gamma^\alpha_{C(A+B+C)}}{\gamma^{1/X}_{O(C)}}\right)$$

$$= \left(\frac{1}{\gamma^{1/X}_{O(A+B+C)}}\right) \qquad [22]$$

DISCUSSION

Block and Stuve[1] have measured the partial molar free energy of solution of oxygen at one atom percent concentration in Ag-Cu-Sn alloys at 1200°C, over the whole range of the composition triangle. Their results for the free energy of solution of oxygen in pure silver and copper are in good agreement with other published data;[7,4] their value for oxygen in pure tin is approximately 4 kj more negative than those calculated from the results of Alcock and Belford,[8] Carbo,[9] and Fisher and Ackermann.[10] The results of Block and Stuve for

the free energy of solution of oxygen in binary Cu-Sn and Ag-Cu alloys are in reasonable agreement with those obtained by other investigators.[11,12] In view of this, their results for the solutions of oxygen in the ternary alloys may be considered to be sufficiently reliable to test the equations which were derived above. Since the partial molar free energy surface of oxygen at 1200°C varies sharply from -6900 joules in pure silver to -75,975 joules in pure copper and -147,350 joules in pure tin across the ternary triangle, the Ag-Cu-Sn-O system provides a critical test for the theoretical model.

It has been shown in an earlier paper[5] that the activity coefficients of oxygen in a number of binary alloys can be predicted using a model in which each oxygen is assumed to make four bonds, and the fractional decrease (α) in energies of bonds between metal atoms bonded to oxygen was assumed to be equal to 0.5. Eq. [22] then reduces to:

$$\left(\frac{1}{\gamma^{1/4}_{O(A+B+C)}}\right) = N_A\left(\frac{\gamma^{1/2}_{A(A+B+C)}}{\gamma^{1/4}_{O(A)}}\right) + N_B\left(\frac{\gamma^{1/2}_{B(A+B+C)}}{\gamma^{1/4}_{O(B)}}\right)$$

$$+ N_C\left(\frac{\gamma^{1/2}_{C(A+B+C)}}{\gamma^{1/4}_{O(C)}}\right) \qquad [23]$$

Using the binary data on Cu-Ag and Cu-Sn alloys obtained from the supplements to the compilation of

Table I. Comparison of Calculated and Predicted Values for the Chemical Potential of Oxygen in Ag + Cu + Sn Alloys at 1200°C (Joules per Mole)

| N_{Ag}	N_{Cu}	N_{Sn}	Properties of Ag + Cu + Sn Solution Calculated Using Eqs. [5] and [6]				$-\Delta\mu_{O(Ag+Cu+Sn)}$ Measured Values	$-\Delta\mu_{O(Ag+Cu+Sn)}$ Proposed Model; Eq. [23]	$-\Delta\mu_{O(Ag+Cu+Sn)}$ Regular Solution Model; Eq. [7]
			$\Delta\mu^E_{Ag}$	$\Delta\mu^E_{Cu}$	$\Delta\mu^E_{Sn}$	ΔG^E			
0.8	0.1	0.1	469	7,761	-8,464	301	58,746	56,260	28,226
0.7	0.1	0.2	456	6,040	-7,769	-632	78,939	74,385	41,328
0.6	0.1	0.3	-1,072	4,173	-32,818	-1,209	97,584	94,478	54,786
0.5	0.1	0.4	-1,452	1,758	-2,177	-1,410	110,016	107,078	68,621
0.4	0.1	0.5	-1,498	-883	-1,687	-1,528	118,769	116,370	82,539
0.3	0.1	0.6	-1,486	-3,596	-1,147	-1,490	126,945	124,742	96,638
0.2	0.1	0.7	-1,461	-6,304	-7,535	-1,423	133,236	132,277	109,853
0.1	0.1	0.8	-1,365	-9,017	-159	-1,168	138,540	139,100	124,755
0.7	0.2	0.1	1,214	4,734	-10,021	963	64,150	60.571	35,780
0.6	0.2	0.2	1,222	2,524	-8,204	-398	80,748	80,915	48,461
0.5	0.2	0.3	84	645	-3,993	-1,025	99,920	97,115	61,869
0.4	0.2	0.4	167	-1,498	-2,980	-1,423	111,356	107.036	75,507
0.3	0.2	0.5	502	-3,759	-2,152	-1,674	120,285	116,956	89,291
0.2	0.2	0.6	829	-5,994	-1,574	-1,976	127,485	125,287	103,026
0.1	0.2	0.7	1,298	-8,422	-854	-2,152	134,161	132,989	116,886
0.6	0.3	0.1	2,365	2,327	-12,181	900	69,140	64,130	42,622
0.5	0.3	0.2	2,344	12	-8,405	-1,561	82,389	80,162	54,196
0.4	0.3	0.3	2,038	-2,206	-4,479	-1,189	101,247	96,362	68,604
0.3	0.3	0.4	2,537	-4,253	-3,223	-1,804	111,624	107,873	82,025
0.2	0.3	0.5	3,186	-6,208	-2,189	-2,319	121,423	117,836	95,545
0.1	0.3	0.6	3,751	-8,355	-1,256	-3,257	129,481	126,082	108,643
0.5	0.4	0.1	3,893	791	-15,061	758	72,765	66,432	49,378
0.4	0.4	0.2	3,776	-1,812	-7,468	-707	85,022	83,092	61,949
0.3	0.4	0.3	4,500	-4,370	-4,906	-1,871	102,390	97,576	74,820
0.2	0.4	0.4	5,634	-6,438	-3,039	-2,662	113,382	109,129	88,065
0.1	0.4	0.5	6,341	-8,338	-1,716	-3,558	123,625	119,092	105,391
0.4	0.5	0.1	5,789	-297	-17,045	460	75,444	69,069	55,979
0.3	0.5	0.2	6,019	-5,643	-8,660	-958	87,425	82,644	68,596
0.2	0.5	0.3	7,489	-5,793	-4,998	-2,897	104,244	98,287	80,693
0.1	0.5	0.4	8,904	-7,869	-2,830	-4,173	114,864	110,175	93,452
0.3	0.6	0.1	7,727	-624	-22,818	-335	79,325	71,204	62,082
0.2	0.6	0.2	9,117	-4,295	-9,837	-2,721	89,618	84,850	73,732
0.1	0.6	0.3	12,512	-6,597	-4,785	-4,139	103,628	99,794	86,349
0.2	0.7	0.1	10,013	-1,486	-22,843	-1,323	81,681	73,799	67,993
0.1	0.7	0.2	12,704	-4,701	-11,214	-4,261	90,179	85,436	79,090
0.1	0.8	0.1	12,093	-1,482	-26,049	-2,578	81,627	75,515	73,636
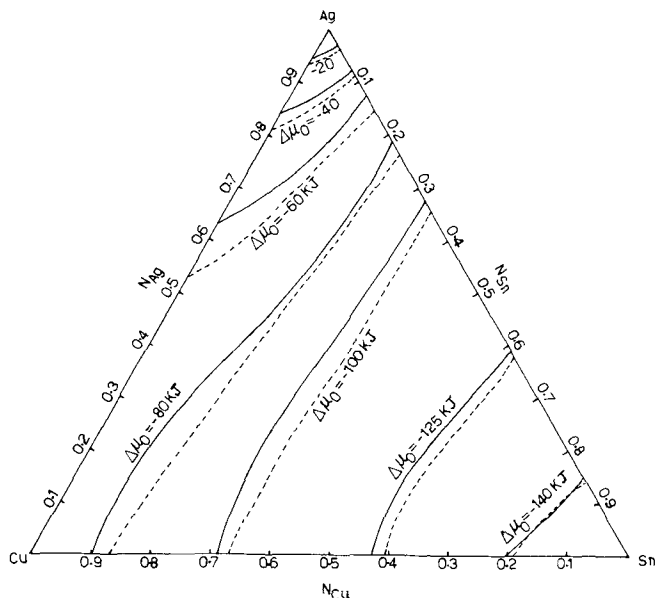
Fig. 3—The partial molar free energy surface of oxygen (at 1 at. pct) in Ag + Cu + Sn alloys at 1200°C. —— Measured iso-activity coefficient lines; --- values predicted by Eq. [23].

Hultgren et al.[13] and the data recommended by Castanet et al.[14] for Ag-Sn alloys, the integral excess free energy and the activity coefficients of Ag, Cu, and Sn in ternary Ag-Cu-Sn alloys may be calculated at different compositions from Eqs. [5] and [6]. The partial excess free energies obtained are tabulated in Table I. Using these values, the activity coefficient or the partial molar free energy of oxygen in Ag-Cu-Sn alloys can be calculated using Eq. [23]. The calculated values are compared with the measured ones in Table I and Fig. 3. It is seen that at all compositions in the ternary triangle, the predicted values agree within 6 kj with those measured by Block and Stuve. This agreement is considered to be satisfactory in view of the assumptions used in deriving the equations and the uncertainty limits on the binary data used in the calculation. A serious drawback of the proposed theoretical treatment may appear to arise from the neglect of electronic effects accompanying alloy formation. However, since the partial molar free energy surface of oxygen changes by several kilojoules across this ternary system, errors from the neglect of the electronic contribution (probably only about 4 to 8 kJ in binary alloys) may be neglected. Eq. [23] may also be expected to predict satisfactorily the activity coefficients of sulfur in dilute solution in metallic alloys. Unfortunately, no data are available for the activity of sulfur in quaternary systems, for which all the binary data are also known. When other interstitial solutes like carbon, hydrogen, or nitrogen are dissolved in alloys, the reduction in metal-metal bond energies would be less significant, since the energies of the bonds made by these interstitial solutes with metal atoms are considerably weaker than in the case of oxygen and sulfur.

When the activity coefficients of oxygen in pure A, B, and C do not differ significantly, the number of A, B, and C atoms bonded to oxygen would be proportional to their atom fractions. It therefore follows that $N_A = N_A^o$, $N_B = N_B^o$, and so forth, and if $x = 4$ and $\alpha = \frac{1}{2}$, Eq. [21] simplifies to:

$$\Delta\mu_{O(A+B+C)} = N_A\,\Delta\mu_{O(A)} + N_B\,\Delta\mu_{O(B)} + N_C\,\Delta\mu_{O(C)}$$
$$- 2\,\Delta G^E_{(A+B+C)} \qquad [24]$$

This equation may be expected to predict activity coefficients of oxygen in liquid Cu + Ni + Co alloys with useful accuracy, since the activity coefficients of oxygen in the three pure metals differ by factors less than 10.

Comparison of Eq. [23] with that for oxygen in a binary $A + B$ alloy[5] suggests that the activity coefficient of oxygen or sulfur dissolved in a multicomponent metallic solution $(A + B + C \ldots + Y)$ may be calculated from binary data from the relation,

$$\left(\frac{1}{\gamma^{1/4}_{O(A+B+C\ldots+Y)}}\right) = N_A\left(\frac{\gamma^{1/2}_{A(A+B\ldots+Y)}}{\gamma^{1/4}_{O(A)}}\right)$$
$$+ N_B\left(\frac{\gamma^{1/2}_{B(A+B\ldots+Y)}}{\gamma^{1/4}_{O(B)}}\right)$$
$$+ \ldots + N_Y\left(\frac{\gamma^{1/2}_{Y(A+B\ldots+Y)}}{\gamma^{1/4}_{O(C)}}\right) \qquad [25]$$

The predicted activity coefficient of oxygen can be combined with the standard free energy of formation of the stable oxide in equilibrium with the multicomponent alloy phase to obtain quantitative information on deoxidation equilibria or oxygen solubility.

APPENDIX

The notation and units which have been used in this paper follow the recommendations of IUPAC. The following table shows how the thermodynamic property symbols are to be read:

$\Delta\mu_{O(A)}$ $\Delta\mu_{A(A+B)}$ $\Delta\mu^E_{C(A+B+C)}$ and so forth
Partial and excess partial free energies (chemical potentials)

$\Delta H_{B(A+B)}$ $\Delta H_{O(A+B+C)}$ and so forth
Partial heats of solution

$\Delta S_{C(A+B+C)}$ $\Delta S^E_{A(A+B)}$ and so forth
Partial and excess partial entropies

$\Delta G_{(A+B)}$ $\Delta H_{(A+B+C)}$ $\Delta S^E_{(A+B)}$ and so forth
Integral properties

The unit of energy is the joule.

One cal (thermal) is equivalent to 4.184 joule.

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