Activities of Oxygen in Liquid Ag–Bi and Ag–Tl Alloys

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The activity coefficients of oxygen, γ_{O} , in liquid Ag–Bi and Ag–Tl alloys at 1273 K have been measured over the entire composition range utilizing a modified coulometric titration method with the electrochemical cell: O in liquid Ag–Bi or Ag–Tl alloys/ $\text{ZrO}_2(+\text{CaO})/\text{Air}$, Pt. The measured $\ln \gamma_{\text{O}}$ values for both systems, plotted in terms of alloy composition, lie on upwardly concave curves. The data were found to be somewhat larger than those calculated from Jacob and Alcock's quasi-chemical equation. This trend appears to be in line with the observation for the Ag–Pb–O system.

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I. Introduction

There seem to be several keys to understand the thermodynamic behavior of oxygen dissolved in liquid binary alloys. A highly effective approach is to measure the activity coefficients of oxygen, γ_{O} , over the entire composition range of various binary alloys and to evaluate the shape of the $\ln \gamma_{\text{O}}$ vs alloy composition curves. Two important contributions, coming from the thermodynamic properties of the respective binary systems, have been visualized through this approach^{(1)–(4)}. The data on the partial entropy and enthalpy of dissolution of oxygen should also provide a detailed information on the mechanism of oxygen dissolution⁽⁵⁾⁽⁶⁾. However, the measurements may be difficult to make accurately in some systems. Several solution models have been proposed on the basis of the available data on the compositional variation of $\ln \gamma_{\text{O}}$ ^{(1)(2)(7)–(11)}. Therefore, another possible approach is to compare the measured γ_{O} values with the calculated values and find out correlations among them. The quasi-chemical equation derived by Jacob and Alcock⁽¹⁾ appears to be most useful for this research program, because it has no adjustable parameter if one uses a single set of values for the parameters of n and α . It has been reported that, in many binary alloys, the measured γ_{O}

values exhibit much or less a negative deviation from the calculated values^{(4)(6)(12)–(23)}. An exception hitherto known is the Ag–Pb–O system, in which the data exhibited a positive deviation. In view of the fact that the oxygen behavior in liquid silver appeared to differ from that in the other elements of group Ib to VIb⁽²⁴⁾, the positive deviation of γ_{O} may be characteristic of the systems including silver. In order to verify this speculation, it was carried out in the present study to measure the activity coefficients, γ_{O} , of oxygen dissolved in liquid Ag–Bi and Ag–Tl binary alloys at 1273 K, utilizing a modified coulometric titration method.

II. Experimental

The modified coulometric titration method proposed by Otsuka and Kozuka^{(25)–(27)} has been successfully applied to the measurements of γ_{O} in various liquid metals and alloys. This technique was successful even for melts with rather high vapor pressures, due to the geometrical design of the emf cell⁽⁶⁾⁽¹³⁾⁽¹⁴⁾⁽¹⁷⁾⁽²⁷⁾. Since the details of the experimental set-up and procedures were given elsewhere^{(15)(26)–(28)}, only a brief description is given here. The schematic diagram of the following electrochemical cell, constructed in this study, is similar to that shown in Fig. 1 in ref. (13):

O in liquid Ag–Bi or Ag–Tl alloys/ $\text{ZrO}_2(+\text{CaO})/\text{Air}$, Pt. cell(I)
A $\text{ZrO}_2(+5 \text{ mass \% CaO})$ solid electrolyte tube closed at one end was supplied by Nippon

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Kagaku Togyo Co., Ltd. in the form of 8 mm o.d., 5 mm i.d., and 300 mm length. Silver, bismuth and thallium used in this study were of 99.999, 99.999 and 99.99 mass % purities, respectively. These metals, weighed with a precision of 0.1 mg, were loaded in the electrolyte tube in quantity corresponding to about 62 mm length in the liquid state. Iridium wires (0.5 mm), spot-welded to Kanthal wires were used as lead wires for the liquid alloys. These junctions were placed in a uniform temperature zone so that the measured emf's could be corrected for the thermoelectric emf between Kanthal and platinum wires, i.e., 12.8 mV at 1273 K. All emf's presented in this paper are corrected values. Nomenclatures used here are the same as in previous papers⁽⁶⁾⁽¹³⁾⁻⁽²⁰⁾⁽²⁶⁾⁻⁽²⁸⁾.

While the emf of cell(I) was monitored for 0.6 or more ks, the liquid alloy in the electrolyte tube was stirred intermittently by moving an alumina rod up and down, (see Fig. 1 in ref. (13)). After a rather stable emf was achieved and the equilibrium of oxygen between the electrolyte and melt was confirmed⁽²⁹⁾, the alumina rod was pulled from the melt. The initial open-circuit emf, $E_1(r)$, of cell(I) was recorded, and then a voltage was applied between wires ①' and ②' by use of a potentiostat (Hokuto-Denko HA-101) so that the emf between wires ① and ② had a preselected value, $E_2(m)$. In the range of very low initial oxygen concentration in the melt, $E_1(m)$ was established in terms of $E_1(r)$ in a manner described previously⁽²⁶⁾⁽²⁸⁾⁽²⁹⁾. A condition, $\Delta E = E_2 - E_1 = 200$ mV, was adopted. Upon initiation of the potentiostatic pump-out operation, the current smoothly decreased with time and reached a nearly constant value, I_∞ , in 1.2 or more ks. After evaluating the ionic current, I_{ion} , by subtracting the nearly constant current from the measured current at earlier times, the apparent initial oxygen concentration, $C_1(\text{app.})$ in mol % for $E_1(r)$ or $E_1(m)$ was calculated from the quantity of electrical charge due to I_{ion} , according to⁽¹⁵⁾⁽²⁸⁾,

$C_1(\text{app.})$

$$= 100y \left\{ (y+1) + (y-1) \exp \left(\frac{-2\Delta EF}{RT} \right) \right\}^{-1}, \quad (1)$$

where $y = (Q_{ion}/2F) \times \{(W_A/M_A) + (W_B/M_B)\}^{-1}$ with Q_{ion} (coulomb), the quantity of electrical charge due to I_{ion} , F the Faraday constant, R the gas constant, T the experimental temperature in K, ΔE the difference between the initial and final emf's, and M_A , W_A , M_B , W_B the molar mass and the mass of solvent elements A and B, respectively.

When the logarithm of $C_1(\text{app.})$ for liquid Ag-Bi or Ag-Tl alloys was plotted against the initial emf, $E_1(r)$ or $E_1(m)$, the trend of $C_1(\text{app.})$, observed in the range of very low initial oxygen concentration, was in good agreement with previous ones⁽¹³⁾⁻⁽²⁰⁾⁽²⁶⁾⁻⁽²⁸⁾. The initial oxygen concentration in the liquid alloys, C_1 in mol % for relatively low values of $E_1(r)$, was evaluated from the $C_1(\text{app.})$ value according to the same analytical procedures as in previous papers⁽¹⁵⁾⁽²⁶⁾⁻⁽²⁸⁾.

III. Experimental Results

In the pump-out experiments with liquid Ag-Bi alloys, typical decay curves of electric current with time are shown in Fig. 1 for various initial emf's. Similar decay curves were also

Fig. 1 Change in electric current with time for experiments with liquid Ag-Bi alloy of $N_{Bi} = 0.50$, at 1273 K and $\Delta E = 200$ mV.

Table 1 Experimental values for various liquid Ag-Bi alloys with previous results for Ag⁽²⁸⁾ and Bi⁽³¹⁾.

N_{Bi} Int. time ΔE , mV $\frac{W_{\text{Ag}}}{W_{\text{Bi}}}$	E_1 , mV	C_1 (app.), 10^{-3} mol%	$10^{-3} C_1$, mol%	$-\Delta G^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$ [$\ln \gamma_{\text{O}}$]
0.00 ⁽²⁸⁾				7.84 [3.86]
	283.4(r)	16.30	15.98	19.17
0.10	310.1(r)	10.38	10.03	19.39
(1.2 ks)	312.1(r)	9.76	9.41	19.10
200 mV	317.7(r)	8.80	8.44	19.03
9.1575 g	339.7(r)	6.15	5.76	19.23
1.9715 g	350.9(r)	5.02	4.61	19.03
	700.4(m)	1.52		19.16 Ave.
	900.6(m)	3.22		[2.80] Ave.
	308.8(r)	33.28	32.8	31.68
0.20	316.6(r)	29.13	28.6	31.73
(1.2 ks)	321.5(r)	26.84	26.3	31.79
200 mV	328.2(r)	23.66	23.1	31.71
7.1993 g	333.0(r)	22.06	21.5	31.88
3.4891 g	899.9(m)	4.72		31.76 Ave.
	1099.7(m)	10.01		[1.60] Ave.
	353.8(r)	71.98	71.9	48.67
0.35	360.8(r)	63.06	63.0	48.62
(1.2 ks)	367.8(r)	55.39	55.3	48.59
200 mV	371.8(r)	51.60	51.5	48.61
5.2085 g	377.0(r)	46.90	46.8	48.60
5.4343 g	385.8(r)	39.80	39.7	48.56
	392.5(r)	35.30	35.2	48.58
	900.7(m)	4.01		48.60 Ave.
	1100.1(m)	17.55		[0.01] Ave.
	395.8(r)	109.57	108.9	61.17
	401.0(r)	100.44	99.8	61.25
	403.4(r)	96.42	95.7	61.27
0.50	404.6(r)	94.19	93.5	61.25
(1.2 ks)	409.3(r)	86.64	85.9	61.26
200 mV	415.2(r)	77.11	76.4	61.16
3.6051 g	425.1(r)	64.84	64.1	61.21
6.9853 g	432.9(r)	56.39	55.6	61.21
	448.2(r)	42.93	42.1	61.22
	456.0(r)	37.38	36.5	61.21
	900.1(m)	5.25		61.22 Ave.
	1099.8(m)	11.94		[−1.18] Ave.
	445.0(r)	107.26	106.8	70.46
	451.8(r)	94.45	94.0	70.42
0.65	461.1(r)	79.97	79.5	70.44
(1.2 ks)	472.1(r)	64.48	63.9	70.25
200 mV	475.8(r)	60.98	60.4	70.37
2.3143 g	486.1(r)	50.32	49.7	70.29
8.3278 g	491.9(r)	45.18	44.6	70.26
	497.3(r)	41.29	40.7	70.34
	900.0(m)	4.86		70.35 Ave.
	1100.4(m)	13.54		[−2.04] Ave.

Table 1 Continuous

N_{Bi} Int. time ΔE , mV $\frac{W_{\text{Ag}}}{W_{\text{Bi}}}$	E_1 , mV	C_1 (app.), 10^{-3} mol%	C_1 , 10^{-3} mol%	$-\Delta G^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$ [$\ln \gamma_\text{O}$]
	484.9(r)	101.77	100.6	77.52
	490.3(r)	92.19	91.0	77.50
0.80	494.9(r)	84.82	83.6	77.49
(1.2 ks)	502.9(r)	73.44	72.2	77.48
200 mV	509.3(r)	65.52	64.3	77.49
1.2113 g	516.9(r)	57.42	56.1	77.52
9.4408 g	523.6(r)	50.73	49.4	77.46
	900.3(m)	6.51		77.49 Ave.
	1099.8(m)	15.90		[−2.78]Ave.
1.00 ⁽³¹⁾				84.12
				[−3.34]

(r) and (m) indicate $E(r)$ and $E(m)$, respectively.

Table 2 Experimental values for various liquid Ag–Tl alloys with previous results for Ag⁽²⁸⁾ and Tl⁽²⁴⁾⁽²⁷⁾

N_{Tl} Int. time ΔE , mV $\frac{W_{\text{Ag}}}{W_{\text{Tl}}}$	E_1 , mV	C_1 (app.), 10^{-3} mol%	C_1 , 10^{-3} mol%	$-\Delta G^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$ [$\ln \gamma_\text{O}$]
0.00 ⁽²⁸⁾				7.84
				[3.86]
	257.7(r)	35.26	34.60	22.38
0.10	270.4(r)	27.61	26.92	22.18
(1.2 ks)	273.7(r)	26.25	25.56	22.27
200 mV	287.7(r)	20.79	20.07	22.41
9.2794 g	301.9(r)	16.25	15.49	22.41
1.9529 g	642.9(m)	2.28		22.33 Ave.
	843.1(m)	4.35		[2.50]Ave.
	294.0(r)	57.00	56.1	34.50
0.20	307.0(r)	45.15	44.2	34.49
(1.2 ks)	332.6(r)	28.35	27.4	34.37
200 mV	366.6(r)	15.65	14.55	34.23
7.4495 g	378.3(r)	12.94	11.80	34.27
3.5290 g	663.7(m)	2.78		34.37 Ave.
	862.4(m)	5.18		[1.36]Ave.
	343.6(r)	100.63	100.3	50.22
	349.5(r)	89.97	89.6	50.17
0.35	362.5(r)	72.10	71.7	50.32
(1.2 ks)	369.9(r)	61.91	61.5	50.12
200 mV	403.8(r)	33.63	33.1	50.11
5.5218 g	423.3(r)	23.84	23.3	50.15
5.6339 g	444.2(r)	16.55	15.97	50.19
	750.0(m)	2.16		50.18 Ave.
	1003.9(m)	6.42		[−0.14]Ave.

Table 2 Continuous

N_{Tl} Int. time ΔE , mV W_{As} W_{Tl}	E_1 , mV	C_1 (app.), 10^{-3} mol%	C_1 , 10^{-3} mol%	$-\Delta G^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$ [$\ln \gamma_{\text{O}}$]
	393.7(<i>r</i>)	124.88	123.7	62.11
0.50	412.6(<i>r</i>)	89.01	87.8	62.13
(1.2 ks)	419.9(<i>r</i>)	78.10	76.9	62.14
200 mV	438.9(<i>r</i>)	56.89	55.6	62.37
3.8725 g	473.4(<i>r</i>)	31.26	29.8	62.43
7.3373 g	799.7(<i>m</i>)	4.15		62.24 Ave.
	999.8(<i>m</i>)	7.85		[−1.27]Ave.
	436.6(<i>r</i>)	139.84	139.0	71.62
	446.8(<i>r</i>)	115.38	114.5	71.54
0.65	459.1(<i>r</i>)	92.51	91.6	71.55
(1.2 ks)	461.0(<i>r</i>)	89.55	88.7	71.58
200 mV	474.2(<i>r</i>)	71.61	70.7	71.72
2.5145 g	481.2(<i>r</i>)	63.31	62.4	71.75
8.8490 g	492.0(<i>r</i>)	52.06	51.1	71.72
	812.8(<i>m</i>)	3.20		71.64 Ave.
	985.0(<i>m</i>)	5.99		[−2.16]Ave.
	470.2(<i>r</i>)	161.51	160.5	79.63
	483.7(<i>r</i>)	125.84	124.7	79.56
0.80	495.2(<i>r</i>)	102.16	101.0	79.55
(1.2 ks)	505.7(<i>r</i>)	85.06	83.9	79.61
200 mV	522.8(<i>r</i>)	63.13	61.9	79.70
1.3539 g	538.0(<i>r</i>)	48.30	46.9	79.69
10.2607 g	551.3(<i>r</i>)	37.98	36.6	79.63
	869.9(<i>m</i>)	5.00		79.62 Ave.
	1069.7(<i>m</i>)	10.94		[−2.92]Ave.
1.00 ⁽²⁴⁾⁽²⁷⁾				88.07
				[−3.72]

obtained in the experiments with liquid Ag–Tl alloys. The nearly constant current at 1.2 ks was subtracted from the measured current to evaluate the ionic current at earlier times. Evaluated values of C_1 are summarized in Tables 1 and 2, together with the corresponding values of C_1 (app.). The initial oxygen concentration in various liquid Ag–Bi and Ag–Tl alloys at 1273 K are shown in Figs. 2 and 3 as a function of initial emf, $E_1(r)$, corresponding to the initial equilibrium partial pressure of oxygen, P_{O_2} in Pa, above the melts exerted by the dissolved oxygen in the melts. As seen from Figs. 2 and 3, the oxygen dissolved in liquid Ag–Bi and Ag–Tl alloys obeys Henry's law indicated by each dashed line.

The activity of oxygen in liquid Ag–Bi and Ag–Tl alloys, a_{O} , with respect to the standard

state of oxygen gas at one atmospheric pressure is related to the activity coefficient of oxygen, γ_{O} , the initial oxygen concentration and the initial emf, $E_1(r)$, by the following equation⁽¹⁵⁾⁽³⁰⁾,

$$a_{\text{O}} = (P_{\text{O}_2}/P_{\text{O}_2}^*)^{1/2} = \gamma_{\text{O}} N_1 = \gamma_{\text{O}} C_1/100 \\ = \sqrt{0.21} \exp\left(\frac{-2E_1(r)F}{RT}\right), \quad (2)$$

where $P_{\text{O}_2}^* = 101325$ Pa and N_1 is the initial oxygen concentration in the melts in mole fraction. Further, the standard Gibbs energy of dissolution of oxygen in the liquid Ag–Bi or Ag–Tl alloys, ΔG° for $1/2\text{O}_2(101325 \text{ Pa}) \rightarrow \text{O}(1 \text{ mol}\%)$, the reference state for dissolved oxygen being an infinitely dilute solution, is related to the activity coefficient of oxygen according to

Fig. 2 Initial oxygen concentrations in various liquid Ag-Bi alloys plotted versus initial emf, $E_1(r)$, corresponding to the initial equilibrium partial pressure of oxygen, P_{O_2} , above the melts exerted by the dissolved oxygen in the melts.

Fig. 3 Initial oxygen concentrations in various liquid Ag-Tl alloys plotted versus initial emf, $E_1(r)$, corresponding to the initial equilibrium partial pressure of oxygen, P_{O_2} , above the melts exerted by the dissolved oxygen in the melts.

$$\Delta G^\circ = RT \ln (\gamma_O/100). \quad (3)$$

The average value of γ_O for each alloy composition is presented in Tables 1 and 2 together with the corresponding value of ΔG° .

Figures 4 and 5 show the variation of $\ln \gamma_O$ at 1273 K as a function of mole fraction of bismuth, N_{Bi} , and thallium, N_{Tl} . The γ_O values for pure silver, bismuth and thallium, presented in

Fig. 4 Variation of $\ln \gamma_O$ with mole fraction of bismuth in liquid Ag-Bi alloys at 1273 K. —○☆—; experimental values of the authors, ---; from Jacob and Alcock's⁽¹⁾eq. (4) with $Z=8$, $n=4$, $\alpha=1/2$, -.-.-; from Wagner's equation⁽²⁾ using the relationship (5). 15 kJ indicates the corresponding width on ΔG° scale.

this paper, were taken from previous reports of Otsuka and co-workers⁽²⁴⁾⁽²⁷⁾⁽²⁸⁾⁽³¹⁾. As can be seen from Tables 1 and 2, the present results are highly consistent and reproducible. The scatter (within $\pm 180 \text{ J} \cdot \text{mol}^{-1}$ in ΔG°) is completely covered by the data circle in Figs. 4 and 5.

IV. Discussion

As described earlier, the main objective of this study is to compare the measured γ_O values with those calculated from Jacob and Alcock's equation with $Z=8$, $n=4$ and $\alpha=0.5$). Their equation obtained by a quasi-chemical treatment is

$$\frac{1}{\gamma_{O(A+B)}^{1/n}} = N_A \frac{\gamma_{A(A+B)}^\alpha}{\gamma_{O(A)}^{1/n}} + N_B \frac{\gamma_{B(A+B)}^\alpha}{\gamma_{O(B)}^{1/n}}, \quad (4)$$

where $\gamma_{O(A+B)}$, $\gamma_{O(A)}$ and $\gamma_{O(B)}$ are the activity coefficients of the infinitely dilute solution of oxygen in A-B alloys, pure A and B, respectively, and $\gamma_{A(A+B)}$ and $\gamma_{B(A+B)}$ the activity

Fig. 5 Variation of $\ln \gamma_{\text{O}}$ with mole fraction of thallium in liquid Ag-Tl alloys at 1273 K. —○☆—; experimental values of the authors, —; from Jacob and Alcock's⁽¹⁾ eq(4), with $Z=8$, $n=4$, $\alpha=1/2$, ---; from Wagner's equation⁽²⁾ using the relationship (5). $\uparrow$ 5 kJ indicates the corresponding width on ΔG° scale.

coefficients of solvent elements A and B. The calculated γ_{O} values are indicated by dot-dashed lines in Figs. 4 and 5. The binary data on Ag-Bi and Ag-Tl alloys, used for the calculation, were taken from the compilation of Hultgren *et al.*⁽³²⁾. As can be seen from Figs. 4 and 5, the calculated $\ln \gamma_{\text{O}}$ values lie on upwardly concave curves, just as the measured values do. However, the data themselves are apparently larger than the calculated values in both Ag-Bi-O and Ag-Tl-O systems. The quasi-chemical equation derived by Jacob and Alcock has been tested for a number of systems. A negative deviation of the data from the calculated values has been observed in the following many systems: Cu-Ag-O⁽¹²⁾, Cu-Bi-O⁽¹³⁾, Cu-Fe-O⁽¹⁾, Cu-Ge-O⁽¹⁷⁾, Cu-In-O⁽¹⁸⁾, Cu-Ni-O⁽¹²⁾, Cu-Sb-O⁽¹⁷⁾, Cu-Sn-O⁽¹⁸⁾, Cu-Tl-O⁽¹⁴⁾, Bi-In-O⁽²²⁾, Bi-Pb-O⁽¹⁹⁾, Bi-Sb-O⁽¹⁹⁾, Bi-Tl-O⁽¹⁵⁾, In-Sb-O⁽¹⁶⁾, In-Sn-O⁽²³⁾, Pb-Sb-O⁽²⁰⁾, Sb-Sn-O⁽²³⁾ and Tl-Te-O⁽⁶⁾. Only an exception was the Ag-Pb-O system⁽²¹⁾⁽²³⁾, in

which the data exhibited a positive deviation from the calculated values. Therefore, such an observation appears to be very important that the thermodynamic behavior of oxygen dissolved in liquid Ag-Bi and Ag-Tl alloys is quite similar to that in Ag-Pb alloys.

Otsuka and Kozuka⁽²⁴⁾ measured the entropy, ΔS_{O} , and enthalpy, ΔH_{O} , of oxygen dissolution into various liquid elements of group Ib to VIb. The ΔH_{O} , plotted in terms of the standard enthalpy of formation of the respective oxide at 298 K per mole of oxygen, lay on a straight line. The experimental point for silver, however, deviated positively from this line. It was also reported that the ΔS_{O} value for liquid elements of a particular group was decreased along a rough curve with increasing strength of the metal-oxygen bond. The curve was shifted gradually toward higher values of entropy, as the group of the element was changed from VIb to VIII. However, the measured ΔS_{O} value for silver also did not follow this correlation. These results implied the characteristic nature of chemical bonds of silver with oxygen⁽³³⁾. The experimental results on the compositional variation of γ_{O} in liquid Ag-Bi, Ag-Tl and Ag-Pb alloys appear to be in line with the previous observation for pure silver.

The present authors measured the γ_{O} values for various binary alloys including copper and recognized the trend that the negative deviation of the data from the calculated values was increased with change in the group of the alloying elements from IIIb to Vb⁽³⁴⁾. When a similar examination is applied to the results for Ag-Bi-O, Ag-Tl-O and Ag-Pb-O systems, one may perceive the trend that the positive deviation of the data from the calculated values is decreased with change in the group of the alloying element from IIIb to VIb. This trend observed for the binary alloys including silver appears to be identical with that for the alloys including copper, and therefore, to be an essential property of oxygen dissolution into liquid alloys. An inflection point around $N_{\text{Bi}}=0.15$ in the $\ln \gamma_{\text{O}}$ vs alloy composition curve may be observed in Fig. 4 for the Ag-Bi-O system. This is attributable to the fact that the mixing enthalpy of Ag-Bi alloys exhibits a positive maximum around $N_{\text{Bi}}=0.75$.

In accordance with a series of our investigations^{(6)(13)–(23)}, the present results are compared in Figs. 4 and 5 with the values calculated from the theoretical equation of Wagner⁽²⁾. One adjustable energy parameter, h , involved in his equation was predicted by the following relationship⁽¹⁵⁾⁽¹⁶⁾,

$$h = \frac{2\varepsilon}{Z^2} + 0.09 \left\{ \varepsilon \left(\frac{V_b}{V_a} \right)^2 \right\} + 0.04 |\Delta G^\circ(A) - \Delta G^\circ(B)|, \quad (5)$$

which was originally proposed by Chiang and Chang⁽³⁾. V_a and V_b are the metallic valences of the solvent elements A and B, which are always selected to make $(V_b/V_a) \leq 1$. $\Delta G^\circ(A)$ and $\Delta G^\circ(B)$ are the standard Gibbs energies of solution of oxygen for solvent metals, A and B, respectively, and Z is the coordination number of the dissolved oxygen, ($Z=6$). In this calculation, the values of 5.56, 3.56 and 1.56 were used as the metallic valences of Ag, Tl and Bi, which were taken from Pauling⁽³⁵⁾. The regular solution parameters, ε , were estimated to be $+6.85 \text{ kJ} \cdot \text{mol}^{-1}$ for Ag–Bi alloys and $+9.99 \text{ kJ} \cdot \text{mol}^{-1}$ for Ag–Tl alloys. The equation, $\varepsilon = \Delta H_{\text{max or min}} / (0.5 \times 0.5)$ was used, in which $\Delta H_{\text{max or min}}$ was the maximum or minimum value of the mixing enthalpy for A–B melts. The values of h at 1273 K, evaluated from eq. (5), were $+3.48 \text{ kJ} \cdot \text{mol}^{-1}$ for the Ag–Bi–O system and $+4.13 \text{ kJ} \cdot \text{mol}^{-1}$ for the Ag–Tl–O system. Chang and Chiang⁽³⁾ expected that Wagner's equation, used together with the relationship (5), could give a satisfactory representation of the data on the compositional variation of γ_O in liquid binary alloys, when the solution behavior of alloys was not far from regular. However, in the Ag–Bi–O and Ag–Tl–O systems, as shown in Figs. 4 and 5, the agreement between the calculated and measured γ_O values appeared not to be within useful accuracy. When the parameter of h was properly selected, a better representation of the data could be obtained in these systems, as expected. Recently, Blander and co-workers⁽⁷⁾ proposed a more generalized equation for γ_O in liquid binary alloys, using a statistical mechanical approach. Compared to the equation derived by Jacob and Alcock⁽¹⁾, Blander *et al.*'s expression also contains an adjustable parameter,

h_b , even if one uses a single set of values for the parameters of Z and t . The calculated values from their equation will be discussed elsewhere⁽²³⁾.

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