

DIFFUSIVITY, ACTIVITY AND SOLUBILITY OF OXYGEN IN LIQUID BISMUTH

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ABSTRACT

The standard free energy of formation of Bi_2O_3 was measured by means of the solid oxide galvanic cell, yielding

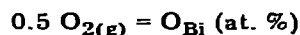
$$\Delta G_T^0 = -605\,283 + 314.42 T \text{ J mol}^{-1} \quad T < 997 \text{ K}$$

$$\Delta G_T^0 = -561\,271 + 270.30 T \text{ J mol}^{-1} \quad T > 997 \text{ K}$$

The diffusivity and activity coefficient of oxygen in liquid bismuth for an unsaturated Bi–O liquid solution were determined from coulometric titration experiments, which were performed in the temperature range 951–1100 K. The diffusivity is

$$D_{\text{O}}^{\text{Bi}} = (1.08 \times 10^{-2}) \exp(-11\,789/RT) \text{ cm}^2 \text{ sec}^{-1}$$

while the standard free energy of dissolution of oxygen in liquid bismuth, calculated for the reaction



is

$$\Delta G_{\text{O}(\text{Bi})}^0 = -95\,503 + 9.68 T \text{ J g-atom O}$$

Finally, the saturation solubility was calculated and the respective equations took the forms

$$\log(\text{at. \% O}) = -(5543/T) + 4.96 \quad T < 997 \text{ K}$$

$$\log(\text{at. \% O}) = -(4778/T) + 4.19 \quad T > 997 \text{ K}$$

INTRODUCTION

Solid oxide galvanic cells are a powerful tool for gathering experimental data on the behaviour of oxygen in liquid metals. Due to the importance of knowledge of the thermodynamic properties of oxygen in pyrometallurgical processes, a number of metals and alloys have been investigated by means of this method. Surprisingly, the bismuth–oxygen system has so far drawn little attention. As part of a larger programme concerned with investigations of liquid, dilute metal–nonmetal systems, it was decided to determine the diffusivity of oxygen and its thermodynamic properties in liquid bismuth.

Bi-O SATURATED SOLUTION

In the case of a saturated solution, bismuth oxide remains in equilibrium with liquid bismuth and the conditions of equilibrium are determined by the value of $\Delta G_{f, \text{Bi}_2\text{O}_3}^0$. Solid bismuth oxide undergoes the $\alpha \rightarrow \delta$ transition at 990 K [1], and melts at 1090 K. Thermodynamic properties of Bi_2O_3 were determined electrochemically by Chatterji and Smith [2], Rao and Tare [3] and Mehrotra et al. [4].

The cell used in this study was as follows



and the free energy of formation of Bi_2O_3 was obtained from the equation

$$\Delta G_{f, \text{Bi}_2\text{O}_3}^0 = 6EF + 1.5 \Delta G_{f, \text{NiO}}^0 \quad (1)$$

Materials

Nickel and nickel oxide (Fisher Co.) were 99.9% pure while bismuth and bismuth oxide (Cerac, Inc.) were 99.999 and 99.999% pure, respectively. CZS tubes, closed at one end, were supplied by the Yamari Trading Co., Japan.

Experimental

Cell (I) was arranged in the following way. An electrolyte tube was attached to a tight-fitting alumina tube by means of alumina cement. The alumina tube was suspended on an upper brass head which closed the tube of a resistant furnace. The metal-metal oxide mixture for the electrode under investigation was prepared by mixing Bi and Bi_2O_3 powders and then packing the mixture into the bottom of the electrolyte tube. A tungsten leading wire was inserted into the electrolyte tube inside the alumina shield. A solid electrolyte tube was inserted into an alumina crucible filled with Ni + NiO sintered powder. The cell was kept in the constant-temperature zone of the furnace under a stream of purified argon. After constant temperature had been reached, the system attained equilibrium after about 2 h. The EMF was then recorded by means of a digital V 534 voltmeter (Elwro, Poland) and the temperature was changed.

Results

EMF values produced by cell (I) after the necessary thermo-EMF Pt-W corrections are shown in Fig. 1. Combining eqn. (2), the value of $\Delta G_{f, \text{NiO}}^0$ determined by Charette and Flengas [5], and equations calculated for EMF values by the least-squares method, one obtains

$$\Delta G_{f, \alpha\text{-Bi}_2\text{O}_3}^0 = -605\,283 + 314.42 T \text{ J mol}^{-1} \quad T < 997 \text{ K} \quad (2)$$

$$\Delta G_{f, \delta\text{-Bi}_2\text{O}_3}^0 = -561\,271 + 270.30 T \text{ J mol}^{-1} \quad T > 997 \text{ K} \quad (3)$$

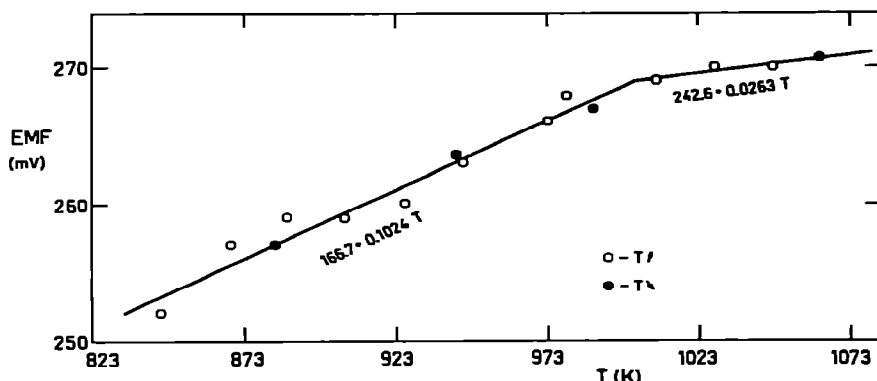
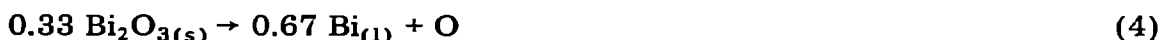


Fig. 1. The plot of EMF vs. temperature produced by cell (I).

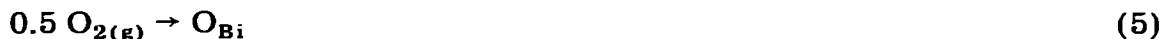
The characteristic temperature of the $\alpha \rightarrow \delta$ transition found from the condition $\Delta G_{f,\alpha\text{-Bi}_2\text{O}_3}^0 = \Delta G_{f,\delta\text{-Bi}_2\text{O}_3}^0$ is 997 K (724°C), compared to the values found by Mehrotra et al. [4] and Rao and Tare [3] of 991 and 978 K, respectively. The heat of the $\alpha\text{-Bi}_2\text{O}_3 \rightarrow \delta\text{-Bi}_2\text{O}_3$ transition is found to be 44 kJ mol⁻¹, which is in very good agreement with that determined by Mehrotra et al. (43.4 kJ mol⁻¹), and slightly lower than the value found by Rao and Tare (57 kJ mol⁻¹).

Bi-O DILUTE SOLUTION

The only available study to date was made by Griffith and Mallett [6], who determined the solubility limit of oxygen in liquid bismuth in the temperature range 400–750°C. From the solubility data, the change in standard free energy for the reaction



was calculated. However, after combining eqn. (4) with the standard free-energy data for solid Bi₂O₃, unexpectedly high values of $\Delta \bar{H}_0$ and $\Delta \bar{S}_0^{x_s}$ for the dissolution reaction



were obtained [7].

In this study, the method of a solid-state coulometric titration was used to determine $\Delta G_{\text{O}(\text{Bi})}^0$ for reaction (5).

Theoretical

The principle of coulometric titration for oxygen solubility measurements in liquid lead and tin was employed by Alcock and Belford [8]. Gerlach et al. [9] determined the miscibility gap between liquid copper and copper(I) oxide in this way. Rapp and co-workers [10,11] used this method for investigations of the diffusivity and solubility of oxygen in liquid copper, silver and tin. Recently, a number of measurements were made by Otsuka

and Kozuka [12–15], and Charlé and Osterwald [16] investigated the Pb–O system. In this work, the approach of Rapp and co-workers was applied.

At equilibrium, when the concentration $C_{O(1)}$ is attained throughout the metal, the measured EMF of the cell



corresponds to $p_{\text{O}_2(1)}$ via the equation

$$E_1 = (RF/4F) \ln(p_{\text{O}_2,\text{air}}/p_{\text{O}_2(1)}) \quad (6)$$

During the potentiostatic experiment, the equilibrium voltage suddenly jumps to $E_{2(\text{appl})}$, so that concentration $C_{O(2)}$ is established instantaneously at the metal–solid electrolyte interface. The diffusion of oxygen atoms can then be followed by recording the current through the external circuit as a function of time. The diffusion of oxygen in the liquid metal electrode for a cylindrical electrolyte tube is described by Fick's second law for cylindrical coordinates

$$\partial C_{\text{O}}/\partial t = (1/r)[rD_{\text{O}}(\partial C_{\text{O}}/\partial r)] \quad (7)$$

where C_{O} represents concentration of oxygen in the metal in mol cm^{-3} , D_{O} is a diffusion coefficient for oxygen in the metal in $\text{cm}^2 \text{sec}^{-1}$, t is the time in sec, and r is the radius in cm. The solution to eqn. (7) was given by Crank [17], and, after the necessary differentiation and rearrangements, Rapp and co-workers [10,11] arrived at the conclusion

$$I_{\text{ion}} = 8\pi hFD_{\text{O}}[C_{\text{O}(1)} - C_{\text{O}(2)}] \exp(-2.405^2D_{\text{O}}t/a^2) \quad (8)$$

where a is the inner diameter of the electrolyte tube, h is the height of the liquid metal column, and the constant 2.405 is the first root of the Bessel function of zeroth order.

The logarithm of eqn. (8) may be written in the form

$$\ln I_{\text{ion}} = \ln B - At \quad (9)$$

and an experimental curve of $\ln I_{\text{ion}}$ vs. t should be linear. From constants A and B , the diffusion coefficient D_{O} and the difference in oxygen concentration expressed in at.%

$$X_{\text{O}(1)} - X_{\text{O}(2)} = [C_{\text{O}(1)} - C_{\text{O}(2)}] V_{\text{Bi}} \times 100 \quad (10)$$

(where V_{Bi} is the molar volume of Bi) can be obtained. When, after a sufficiently long period, a steady-state is attained ($I_{\text{ion}} = 0$), an oxygen pressure corresponding to a new equilibrium concentration $C_{\text{O}(2)}$ is determined by the relation

$$E_2(I_{\text{ion}} = 0) = (RT/4F) \ln(p_{\text{O}_2,\text{air}}/p_{\text{O}_2(2)}) \quad (11)$$

Assuming Sievert's law to be valid for oxygen concentrations as high as the saturation limit, one can express an activity coefficient for oxygen in liquid bismuth as

$$\gamma_{\text{O}(\text{Bi})} = \Delta p_{\text{O}_2}^{1/2}/\Delta X_{\text{O}} = (p_{\text{O}_2(1)}^{1/2} - p_{\text{O}_2(2)}^{1/2})/(X_{\text{O}(1)} - X_{\text{O}(2)}) \quad (12)$$

and, immediately, the standard free energy for reaction (5) can be calculated

$$\Delta G_{\text{O}(\text{Bi})}^0 = RT \ln \gamma_{\text{O}(\text{Bi})} \quad (13)$$

Experimental

An electrochemical cell arrangement represented schematically by eqn. (II) is shown in Fig. 2. The CSZ solid electrolyte tube was placed in a resistant furnace in such a manner that the cell was entirely within a constant-temperature zone. The furnace tube was flushed with air from outside, while a glass-head, made of pyrex, closed the solid electrolyte tube and enabled circulation of purified argon within the tube. The electrical circuit consisted of two parts working independently due to two tungsten wires being in contact with molten metal. Circuit (I) was devoted to EMF measurements at equilibrium, while circuit (II) enabled adjustment of the applied potential, E_{appl} , and current recording. The EMF and E_{appl} were measured by means of a digital V 534 voltmeter (Elwro, Poland), E_{appl} was adjusted by a ZT9803M potentiostat (Unitra, Poland), and the current was recorded using a Varg recorder (CSRS).

Argon gas was purified by passing over copper filings at 450°C to keep the partial pressure of oxygen in the gas phase close to that corresponding to the Bi-Bi₂O₃ equilibrium.

After the required temperature was reached, the cell was left for several hours to attain equilibrium. The equilibrium EMF, E_1 , was then measured by

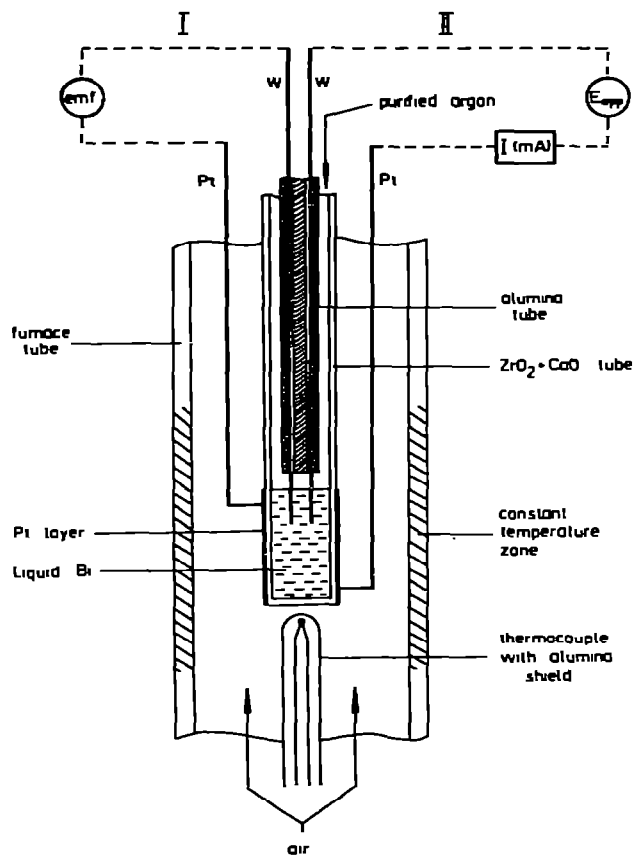


Fig. 2. Diagram of the electrochemical cell for coulometric titration experiments.

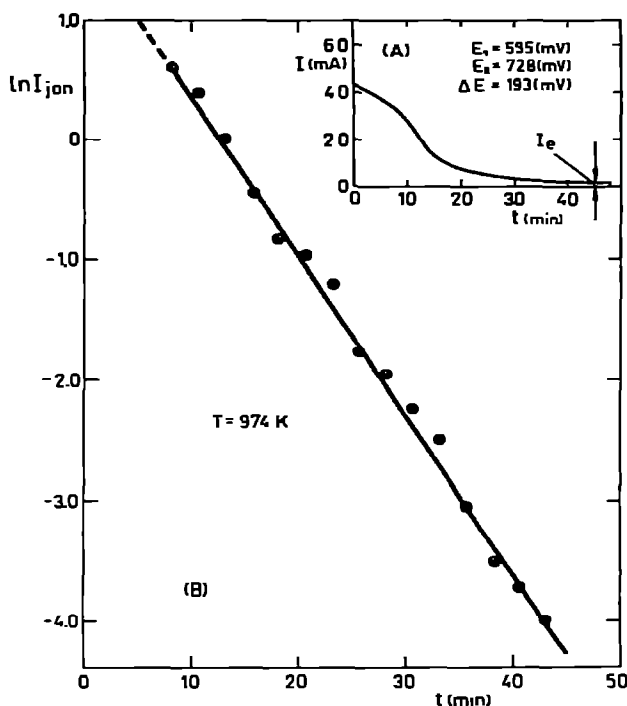


Fig. 3. (A) Cell current as a function of time in the potentiostatic experiment, and (B) a plot of $\ln I_{ion}$ vs. time.

circuit (I). The value was usually close to that corresponding to a saturated solution. Next, the potential difference ΔE was applied to the cell by circuit (II). This potential difference was always equal to 200 mV. Only pump-out experiments were made since these excluded the possibility of producing the overpotential mentioned by Otsuka and Kozuka [20]. The current flow in circuit (II) was then recorded until steady state was attained. However, when steady state was attained, the current did not vanish, because of the electronic current I_e passing through the electrolyte. In order to obtain the value of the ionic current I_{ion} , the measured current I must be corrected due to the existence of I_e . The value of I_e can be obtained from the experimental I vs. t curve. Finally, the value of the EMF at steady state, E_2 , was measured by circuit (I). It was observed that the EMF dropped by a few millivolts after the circuits were changed.

Results

A typical I vs. t curve obtained during the experiments as well as a $\ln I_{ion}$ vs. t plot are shown in Fig. 3. Values obtained for times shorter than 5 min were discarded and not taken into account during calculations. Equations of type (9), obtained by the least-squares method, as well as EMF values and tube parameters are summarized in Table 1. Calculated values of $\ln D_O^{Bi}$ are shown in Fig. 4, and the least-squares method yields the equation, which can be expressed in the form

$$D_O^{Bi} = (1.07 \times 10^{-2}) \exp(-11766/RT) \text{ cm}^2 \text{ sec}^{-1} \quad (14)$$

TABLE 1

Experimental results of coulometric titration measurements carried out on Bi-O dilute solutions

T (K)	$\ln I_{\text{ion}} = \ln B - At$		E_1 (mV)	E_2 (mV)	a (cm)	h (cm)
	A	$\ln B$				
951	0.23057	-0.34997	659	894	0.20	2.27
974	0.13304	1.71238	535	728	0.24	1.56
1009	0.15258	2.44862	510	712	0.24	1.56
1025	0.18386	1.82218	591	788	0.25	1.30
1055	0.20596	0.88446	622	810	0.25	1.30
1082	0.23458	1.14731	548	742	0.24	1.54
1096	0.30733	2.67796	564	756	0.24	1.54
1100	0.36431	3.02906	508	710	0.24	1.54

Finally, the values of $\Delta G_{\text{O(Bi)}}^0$ shown in Fig. 5 gave the equation

$$\Delta G_{\text{O(Bi)}}^0 = -120\,982 + 12.38 T \text{ J g-atom O} \quad (15)$$

where the standard state for dissolved oxygen is an infinitely dilute solution in which activity is equal to atomic %. The above method of interpretation does not allow a very precise determination of $\Delta G_{\text{O(Bi)}}^0$. Therefore, it was decided to repeat the experiments after the addition of a coulomb meter (Radelkis, Hungary) to circuit (II), which enabled measurements of the quantity of electricity passed due to I_{ion} . From the expression

$$X_1 - X_2 = 100 \times (M/W) \times (Q_{\text{ion}}/2F) \quad (16)$$

where X_1 and X_2 are oxygen concentrations in liquid metal (at.%), M is the atomic weight of liquid metal, W is the weight of liquid metal, and Q_{ion} is the quantity of electricity due to I_{ion} , and the difference in E

$$E_2 - E_1 = \Delta E = (RT/2F) \ln(X_1/X_2) \quad (17)$$

The concentration of oxygen in the liquid metal can be calculated exactly.

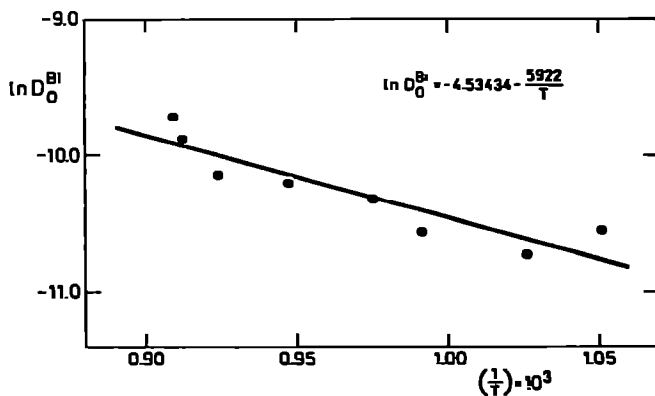


Fig. 4. The diffusion coefficient of oxygen in liquid bismuth as a function of temperature.

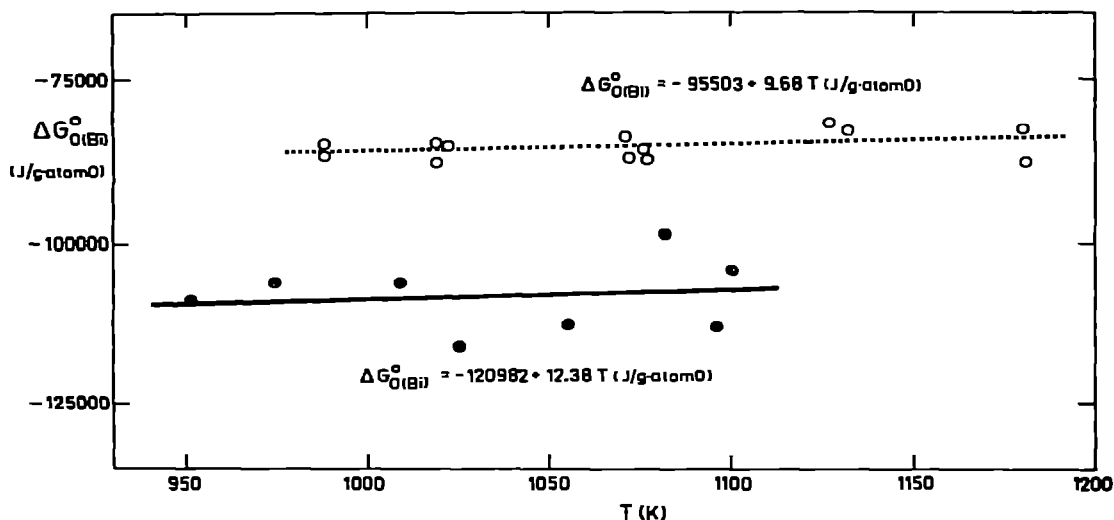


Fig. 5. The free energy of dissolution of oxygen in liquid bismuth: ●, first experiment; ○, second experiment.

Results of additional runs are shown in Table 2, while $\Delta G_{O(Bi)}^{\circ}$, calculated by the least squares method, is equal to

$$\Delta G_{O(Bi)}^{\circ} = -95\,503 + 9.68 T \text{ J g-atom O} \quad (18)$$

which is shown in Fig. 5.

TABLE 2

Results of coulometric titration experiments (second experiment)

T (K)	Q_{ion} (mC)	E_1 (V)	E_2 (V)	X_1	X_2	$\Delta G_{O(Bi)}^{\circ}$ * (J/g-atom O)
988	129	0.625	0.795	0.0057	0.0001	-84680
988	128	0.635	0.805	0.0056	0.0001	-86511
1019	110	0.653	0.833	0.0049	0.0001	-87630
1019	21	0.709	0.881	0.0009	0.00002	-84374
1022	77	0.656	0.859	0.0034	0.00004	-85028
1071	570	0.568	0.759	0.0251	0.0004	-83892
1072	102	0.663	0.853	0.0045	0.0001	-86871
1076	470	0.587	0.744	0.0211	0.0007	-85845
1077	413	0.600	0.789	0.0182	0.0003	-87051
1127	214	0.611	0.819	0.0094	0.0001	-81441
1132	234	0.614	0.814	0.0103	0.0002	-82916
1180	252	0.616	0.809	0.0112	0.0003	-82556
1181	140	0.671	0.846	0.0063	0.0002	-87487

* $\Delta G_{O(Bi)}^{\circ} = RT \ln p_{O_2}^{1/2}(1)/X_1$.

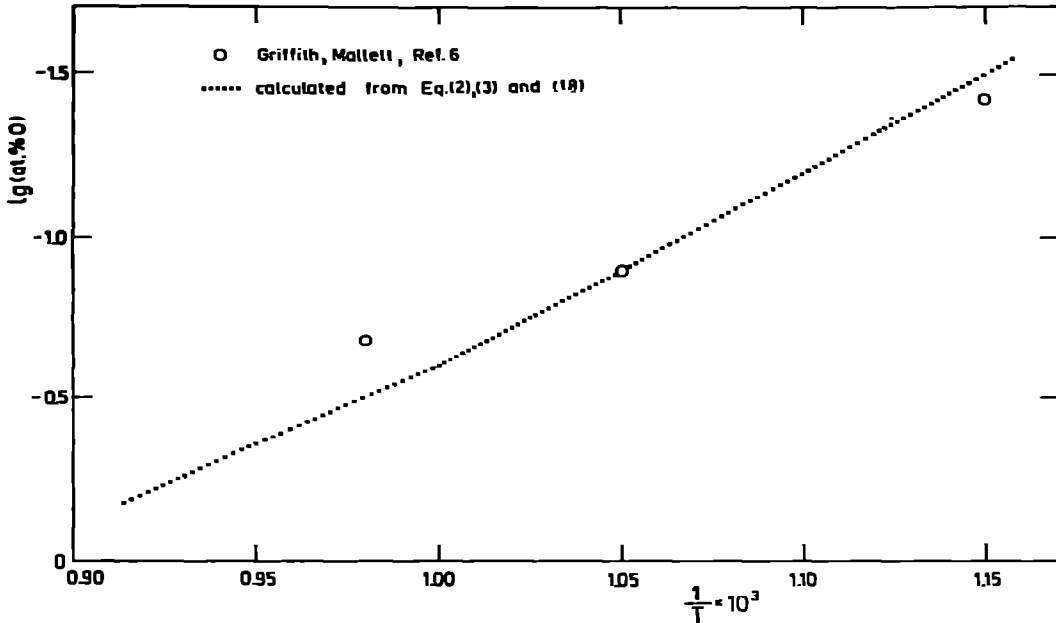


Fig. 6. The saturation solubility of oxygen in liquid bismuth.

SOLUBILITY OF OXYGEN IN LIQUID BISMUTH

From eqn. (18) and the free energy of formation of bismuth oxide, one may calculate the solubility of oxygen in liquid bismuth, providing Henry's law can be applied up to the saturation limit. The respective equations are

$$\log(\text{at.\% O}) = -(5543/T) + 4.96 \text{ for } T < 997 \text{ K} \quad (19)$$

$$\log(\text{at.\% O}) = -(4778/T) + 4.19 \text{ for } T > 997 \text{ K} \quad (20)$$

and the results of calculations are shown and compared with solubilities reported by Griffith and Mallet [6] in Fig. 6.

DISCUSSION

The coulometric titration method appears to be superior to any other experimental technique as far as investigations of the solubility and thermodynamic properties of oxygen in liquid metals are concerned. It enabled the link between diffusion and thermodynamics, either in pure metals or in their alloys, [18,19] to be followed, making it possible to determine the influence of alloy elements on transport properties. However, some experimental problems still exist in avoiding additional oxygen exchange with the gas phase in the cell. Moreover, in practice there exists a minimum oxygen level, below which oxygen cannot be eliminated from the melt. This phenomenon affects the values of X_1 calculated from eqns. (16) and (17) but during the experiments it was found that the limiting value mentioned above is of the order of X_2 from Table 2, i.e. it differs by two orders of magnitude from X_1 .

Thus, the error made in $\Delta G_{\text{O(Bi)}}^0$ due to the oxygen background calculated from X_1 and $p_{\text{O}_2(1)}$ does not seem to be significant. The difference between the values of $\Delta G_{\text{O(Bi)}}^0$ calculated from the first and second experiments may not have been exclusively caused by the method of interpretation and experimental approach. It is possible that it reflects the hidden influence caused by the deviation from Henry's law. In fact, Boureau and Kleppa [21] found that partial functions of hydrogen in solid palladium are subject to sharp changes in the range of very dilute solutions. Therefore, it would be interesting to follow the variation of $\Delta \bar{H}_0$ with oxygen concentration in liquid metals using calorimetric measurements.

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