The Equilibrium between the Sn-Pb Liquid Solution and the H_2-H_2O Gaseous Mixture

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The thermodynamic investigation of metallic solutions is very important in order to have a deep understanding of their structure1). In the tin-lead system the primary solid solutions have very limited solid solubilities in the respective solvents. The immiscibility of these primary solid solutions is found over a wide range of the concentration2). This fact may reflect the fact that the excess heat of the tin-lead liquid solution shows a positive value according to the simple model of solutions, for example, that of the regular solution3). Thermodynamic data on this binary system, all of which have been based on calorimetric measurements, enable one to confirm the above expectation. The excess heat of this system has been measured by Magnus and Mannheimer4), by Kawakami5), by von Samson-Himmelstjerva6), and by Kleppa7).

However, no direct measurement of the excess free energy of this system has so far been carried out. This may presumably be due to some experimental difficulties which accompany the direct methods of measuring the activity of this system such as those of electromotive force and of vapor pressure. The activities of the tin-lead system have been calculated by Elliott and Chipman8) from the experimental results on the tin-lead-cadmium system.

In this paper the activity of tin in the tin-lead liquid solution is obtained by measuring the equilibrium of the tin-lead system with the hydrogen-water vapor mixture.

The principle of this method is as follows:—

If the hydrogen-water vapor mixture is in equilibrium with liquid tin and its dioxide in accordance with Eq. I,

$$Sn(l) + 2H_2O(g) = SnO_2(s) + 2H_2(g) \qquad (I)$$

one can write, as the equilibrium constant K for reaction I,

$$K = (P_{H_2}/P_{H_2O})^2 \qquad (1)$$

where P_{H_2} and P_{H_2O} are the partial pressures of H_2 and H_2O respectively. On the other hand, a similar equation (II) can be given for the tin-lead liquid solution, if the oxide of tin is stable as compared with that of lead.

$$Sn(liq.\ soln.) + 2H_2O(g) = SnO_2(s) + 2H_2(g) \qquad (II)$$

Corresponding to Eq. 1, one has

$$K = (P_{H_2}'/P_{H_2O}')^2/a_{Sn} \qquad (2)$$

where a_{Sn} is the activity of tin relative to pure liquid tin, and the prime labeled for the pressures means the equilibrium partial pressure in the tin-lead system. From Eqs. 1 and 2 one obtains

$$a_{Sn} = (P_{H_2}'/P_{H_2O}')^2/(P_{H_2}/P_{H_2O})^2 \qquad (3)$$

Thus, in principle, the activity of tin in this system can be determined by measuring the partial pressures of hydrogen and water vapor in equilibrium with both pure tin and tin-lead.

Stability of Oxides

It is the fundamental condition for Eq. 3 that the oxide, SnO_2, is most stable among all oxides conceivable in the present system. In thermodynamic terms, an oxide should be stable in case the partial pressure of oxygen in equilibrium with the oxide is low. In other words the formation of a stable oxide is associated with a small amount of oxygen. In Table I the partial pressures of oxygen in equilibrium with several oxides are shown, which are calculated from the free energies of formation of respective oxides9) at 1000°K.

It is readily found that tin oxides are stable

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TABLE I. PRESSURES OF OXYGEN IN EQUILIBRIUM WITH TIN- AND LEAD-OXIDES AT 1000°K

Oxides		Pressures of oxygen $\log P_{O_2}$ (atm.)
SnO_2	(s)	−19.6
SnO	(s)	−19.0
SnO	(g)	− 7.1
PbO	(s)	−12.6
Pb_3O_4	(s)	− 8.9
PbO_2	(s)	− 4.5

compared with lead oxides. Although the value of SnO(s) is close to that for SnO_2(s), the solid SnO is found unstable as compared with SnO_2 in other studies⑩. Further, according to the electron diffraction study by Shimaoka and Yamai⑪, the oxide film formed on the surface of the tin-lead solution under the condition of temperatures higher than 470°C and of pressures below 1 atmosphere of air, shows complete patterns of the stannic oxide. After the present experiment has been finished, the samples should be examined by means of the X-ray or by the electron diffraction, but the amount of oxides formed by reaction II is too small to be determined in such a way. However, the fact of the stannic oxide being most stable may be assured by the other reasons already described above.

Experimental

The same apparatus, used in the measurement of equilibrium in GeO_2-H_2-Ge-H_2O system⑫, is employed with a modification of the sizes of both the furnace and the reaction tube.

Metallic solutions are prepared by fusing each mixture of pure metals (Kanto Kagaku, 1st grade) in a closed vessel under vacuum; their concentrations are confirmed by chemical analysis.

The boat of high alumina filled with 3∼4 g. of the powdered sample, which has been dispersed in alumina powder, is set in the reaction tube. After the tube has been evacuated to the pressure of 10^{-5} mmHg, water vapor saturated at 18 ± 0.01°C (15.45 mmHg), is introduced for oxidation, while hydrogen, generated by electrolysis of a potassium hydroxide solution, is introduced for reduction. The oxidation method is used for liquid metallic solutions, since there is no assurance of obtaining the required metallic solution from the reduced tin metal. The rate of gas flow is about 200 cc./min. The measurements have been carried out over the range of 700∼800°C.

The whole error in a_{Sn} may be about 3% which is due to the inaccuracies of the furnace temperature (±2°C) and of the temperature of water (±0.01°C), as well as of the reading of the cathetometer (pressure: ±0.01 mmHg), etc. As one of the other sources of error, the change of concentration in liquid solutions should be taken into account, since tin in the solution is oxidized during the reaction. However, the amount of this change estimated from the volume of the reaction system (about 850 ml.) is at most 10^{-5} mol., and small compared with the initial amount of tin in solutions (at least 10^{-3} mol.). Though the vapor pressure of lead is about 10^{-2} mmHg at 700∼800°C, the rate of vaporization is then at most 10^{-5} mol./hr. Thus, this effect may be negligible because of the short time taken for the present reaction (1∼5 hr.).

Results

Equilibrium in the Sn-H_2O-SnO_2-H_2 System: —The results for this system are shown in Table

TABLE II. EQUILIBRIUM IN Sn-H_2O-SnO_2-H_2

Temperature °C	Total pressure* mmHg	Equilibrium constant (*K*)	log *K*	Method
875	18.75	0.0456	−1.341	reduction
850	19.10	0.0558	−1.258	〃
825	19.45	0.0670	−1.174	〃
802	19.70	0.0757	−1.121	oxidation
800	19.80	0.0793	−1.101	reduction
777	20.20	0.0945	−1.024	〃
750	20.75	0.1177	−0.929	〃
750	20.80	0.1199	−0.921	oxidation
700	22.30	0.1994	−0.700	〃

* The pressure of water vapor is kept constant at 15.45 mmHg.

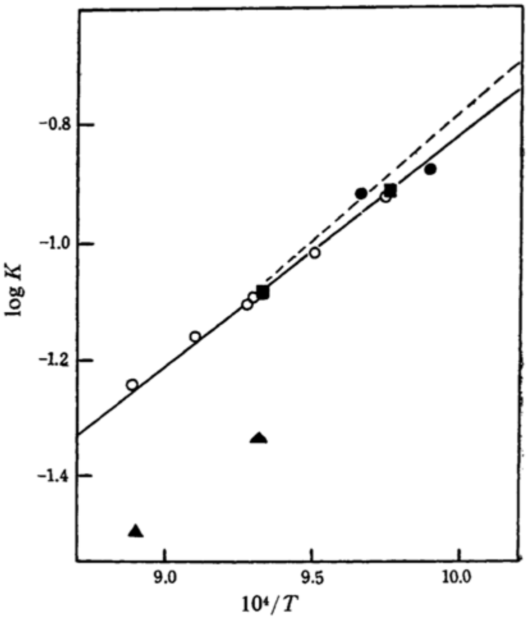

Fig. 1. Temperature dependence of equilibrium constant in the system
Sn(pure)-H_2O-SnO_2-H_2
○ Present work. ● Meyer and Scheffer. ■ Emmett and Shultz. ▲ Eastman and Robinson. --- Ishikawa and Ando.

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TABLE III. EQUILIBRIUM IN Sn(in soln.)-H_2O-SnO_2-H_2

Temperature °C	x_{Sn}	Total pressure mmHg	$(P_{H_2}/P_{H_2O})^2$	Activity of tin	$\overline{G}^e_{Sn}$
750	0.0521	17.30	0.0143	0.116	1630
〃	0.100	17.90	0.0251	0.204	1450
〃	0.151	18.35	0.0352	0.285	1290
〃	0.199	18.70	0.0442	0.358	1190
〃	0.301	19.20	0.0589	0.477	930
〃	0.403	19.55	0.0704	0.570	700
〃	0.501	19.80	0.0793	0.642	500
〃	0.711	20.25	0.0965	0.781	190
775	0.0521	17.10	0.0114	0.115	1650
〃	0.100	17.65	0.0203	0.205	1490
〃	0.151	18.00	0.0272	0.276	1260
〃	0.199	18.35	0.0352	0.356	1210
〃	0.301	18.75	0.0456	0.462	890
〃	0.403	19.10	0.0558	0.565	700
〃	0.501	19.30	0.0621	0.628	460
〃	0.711	19.74	0.0775	0.784	200
800	0.0521	16.90	0.0088	0.110	1600
〃	0.100	17.40	0.0159	0.199	1470
〃	0.151	17.75	0.0222	0.277	1290
〃	0.199	18.00	0.0272	0.341	1140
〃	0.301	18.45	0.0377	0.472	960
〃	0.403	18.70	0.0443	0.554	690
〃	0.501	18.90	0.0499	0.624	480
〃	0.711	19.30	0.0621	0.777	180

II. If the common logarithms of the equilibrium constant, K, thus obtained, are plotted against the reciprocal temperature, as shown in Fig. 1, they lie close about a straight line, which is expressed by Eq. 4. (This equation is established by means of the least square).

$$\log K = 4150/T - 4.965(\pm 0.05) \qquad (4)$$

This result is in good agreement with the data of other investigators[13-16]. For example, the following values are obtained by means of Eq. 4.

t, °C	K
750	0.1235
775	0.0988
800	0.0799

Equilibrium in Sn (in Soln.)—H_2O-SnO_2-H_2 System:—The equilibrium constant and the activity of tin, measured in this system, are indicated in Table III. The activity of tin, shows a positive deviation from Raoult's law, as is seen in Fig. 2. The partial excess free energy of tin, $\overline{G}^e_{Sn}$, is related to its activity by

$$\begin{aligned}\overline{G}^e_{Sn} &= \boldsymbol{R}T \ln a_{Sn}/x_{Sn} \\ &= \boldsymbol{R}T \ln f_{Sn} \qquad (5)\end{aligned}$$

where $\boldsymbol{R}$ is the gas constant, x_{Sn} is the atomic fraction of tin, and f_{Sn} is the actitvity coefficient. If the values of $\overline{G}^e_{Sn}/(1-x_{Sn})^2$ are plotted against x_{Sn}, they lie close about a straight line, shown in Fig. 3, which is expressed by Eq. 6 at 775°C.

$$\overline{G}^e_{Sn}/(1-x_{Sn})^2 = 2330 - 600(1-x_{Sn}) \quad (\pm 50\ \text{cal./mol.}) \qquad (6)$$

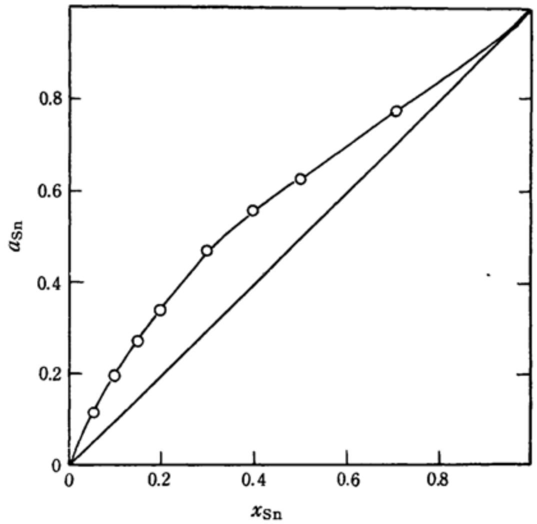

Fig. 2. Observed activity of tin in the tin-lead liquid solution at 800°C.

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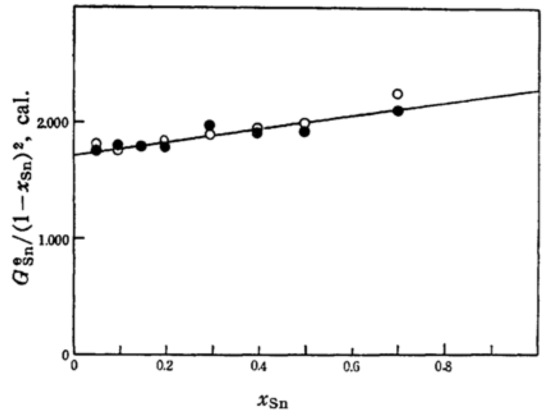

Fig. 3. Concentration dependence of partial molar excess free energy of tin in the tin-lead liquid solution. ○ Observed values at 750°C. ● Observed values at 800°C.

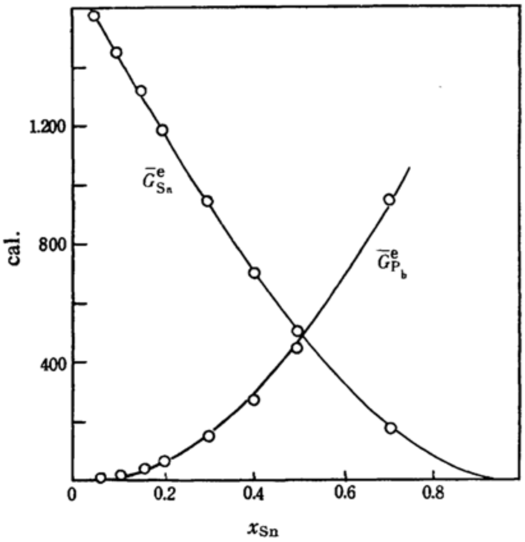

Fig. 4. Partial excess free energies in the tin-lead solution at 775°C.

Applying Gibbs-Duhem's relation to the above results, one obtains not only the partial molar excess free energy of lead, but also the (integral) excess free energy of the solutions, G^{e}_{m}, as are shown in Figs. 4 and 5 which are expressed respectively by Eqs. 7 and 8 at 775°C

$$\overline{G}^{e}_{Pb}=1430\ x_{Sn}{}^{2}+600\ x_{Sn}{}^{3} \tag{7}$$

$$G^{e}_{m}=x_{Sn}x_{Pb}(1730+300x_{Sn}) \tag{8}$$

Unfortunately, the temperature dependence of a_{Sn} could not be accurately obtained in this experiment owing to the limited range of temperatures (750∼800°C). This limitation is due to the fact that the vapor pressure of lead is very high at temperatures above 800°C, while the reaction rate for oxidation is very slow if the temperature is lower than 700°C.

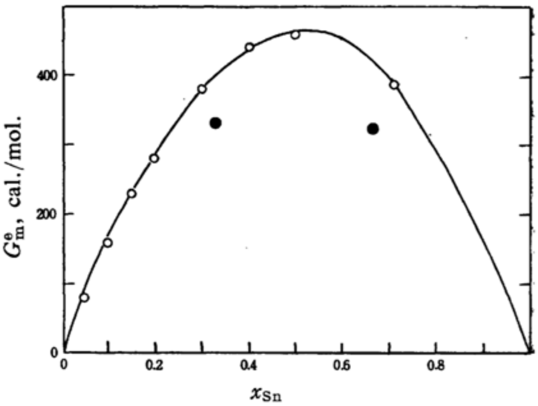

Fig. 5. Excess free energy in the tin-lead liquid solution at 775°C. ○ Observed values. ● Calculated from the data of Elliott and Chipman for the ternary system.

Discussion

So far as the excess free energy of the tin-lead system is concerned, there are no experimental data available except an indirect result calculated from those of the cadmium-tin-lead system obtained by Elliott and Chipman⁸⁾. They have given only two values of the excess entropy at about 500°C, which can be extrapolated to 775°C. The excess free energy, G^{e}_{m}, thus obtained is as follows.

x_{Sn}	0.333	0.667
G^{e}_{m}(cal.)	333	320

By a combination of these values with the present results, a comparison is made in Fig. 5. It is found that the results, obtained by Elliott and Chipman for only two concentrations, have a tendency to represent slightly small values compared with the present ones. However, the values of the heat of mixing calculated from those for the cadmium-tin-led system are 15∼20% smaller than those directly measured by Kleppa⁷⁾. Hence, if the excess free energy is calculated by combining Kleppa's values for the excess heat with those of Elliott and Chipman for the excess entropy, the agreement between the values thus obtained and those of the present study is quite reasonable. It should be noted that the excess entropy shows a slightly negative deviation from ideal mixing.

It is of interest to examine the excess function on liquid tin-lead solutions from simplified models of metallic solutions. According to Haissinsky¹⁷⁾, the electronegativity of tin is almost in agreement with that of lead. (Sn^{II}, 1.65; Pb^{II}, 1.6; Sn^{IV}, 1.8; Pb^{IV}, 1.8.) So the electrochemical effect due to transfer of electrons may be very small in the tin-lead system. For

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these cases, the theoretical calculation of excess functions can be simplified, as pointed out by Hildebrand and Scott[18].

$$H^e_m = [(L_A/V_A)^{\frac{1}{2}} - (L_B/V_B)^{\frac{1}{2}}]^2 \varphi_A \varphi_B V_S \qquad (9)$$

and

$$S^e_m = 0 \qquad (10)$$

L_A and L_B are the energies of vaporization of pure A and B respectively. V_A and V_B denote their volumes in pure states. V_S represents the volume of the solution. φ_A and φ_B are the volume fractions respectively.

As the interatomic potential in liquid metals cannot always be expressed by the well known 6–12 potentials or 6–∞ potentials, Shimoji[19] has proposed the following theoretical expression for the excess energy after taking into account the generalized potential.

$$H^e_m = [(L_A/V_A)^{\frac{1}{2}} - (L_B/V_B)^{\frac{1}{2}}]^2 \varphi_A \varphi_B V_S + \frac{nl}{8}\rho^2\left(1+\frac{\delta_v}{2}\right)\frac{L_{AA}}{V_A}\varphi_A \varphi_B V_S \qquad (11)$$

Here,

$$\rho = 2(r_B - r_A)/(r_B + r_A)$$

and

$$\delta_v = (L_B/V_B - L_A/V_A)/L_A/V_A \qquad (12)$$

r_i means the interatomic distance in the pure state of i. It is found that the parameter nl in Eq. 11 is about 10 or 20 in most liquid metals. If $nl = 72$, Eq. 12 corresponds to the one derived by Prigogine[20]. Of course Hildebrand's Eq. 9 can be obtained if the term due to the difference of atomic radii (size factor) is neglected in Eq. 11. Furthermore, the assumption of the geometric mean of energies between unlike atoms used in deriving Eq. 9 might be open to doubt because of metallic forces. If the arithmetic mean is used for the energies, H^e_m should be zero for Eq. 9, (or the first term of Eq. 11 should be zero.) It is noteworthy that Eq. 11 gives a positive excess energy even if the assumption of the arithmetic mean is used.

In Table IV the calculated values of the excess energy and the exsess entropy at $x_{Sn} = 0.5$ are compared with the observed ones. The most reasonable approach to the excess energy of an alloy is based on the collective electron theory of metals, such as the cellular approximation etc.[21,22] Unfortunately, no reliable values of the parameters adaptable for these theories have yet been determined either experimentally or theoretically in either the liquid tin or lead systems. However, according to Varley's calculation[21] based on the free electron approximation, the electrochemical factor is nearly zero in the lead-tin system. Then, the size factor indicating the positive excess energy plays an important role in liquid metals as well as in solid alloys. Rigorous estimation in the liquid state can not be achieved because of lack of knowledge concerning the parameters of pure metals, but the same conclusion may thus be obtained either from the theories of the pair bond interaction[18,19] or from those of the free electron approximation based upon the band model of metals.

TABLE IV. COMPARISON OF CALCULATED VALUES OF THE EXCESS FUNCTIONS IN TIN-LEAD LIQUID SOLUTIONS (cal./mol.)

	Hildebrand	Shimoji ($nl = 10$)	6–12 potential	Expl.
H^e_m	860(0*)	1050(200*)	2150(1300*)	330[7]
G^e_m	860	1000		460

H^e_m : The excess heat at $x_{Sn} = 0.5$
G^e_m : The excess free energy at $x_{Sn} = 0.5$ (at 800°C)
* : Values based upon the arithmetic mean rule.

Summary

Equilibrium in Sn (in liquid alloy)-H_2O-SnO_2-H_2 system has been determined from 750 to 800°C by measuring the ratio of pressures between H_2O and H_2 gas mixtures. From this the activity of tin liquid tin-lead solutions has been calculated, and the following equation has been derived at 775°C.

$$\overline{G}^e_{Sn} = 2330(1 - x_{Sn})^2 - 600(1 - x_{Sn})^3 \text{ cal./mol.}$$

The temperature dependence of $\overline{G}^e_{Sn}$ could not be determined. However, if this value is calculated by combining Kleppa's value for the excess heat, calorimetrically determined, with that of Elliott and Chipman for the excess entropy, the agreement between the value thus obtained and that of the present investigation is quite reasoable, taking into consideration the accuracies of these experiments. Theoretical considerations have been given for the excess functions of this system. It shonld be emphasized that the electrochemical effect of charge transfer is very small or may be regarded as zero in the lead-tin system and that the size factor is important.

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