Vapor Pressure of Zinc in Tin-Zinc Binary Liquid Alloy

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For the development of the theory of metallic solution, systematic studies on thermodynamics of multi-component systems are required as well as those on electric and magnetic properties. Vapor pressure measurements directly provide the activity or the partial molar free energy of mixing of vaporizing components, though their temperature coefficients or heat terms are not so reliable as those determined by the calorimetric method. In the present work the applicability of Knudsen's effusion method was examined for the measurement of low vapor pressure of liquid alloy. This method is convenient for a measurement of this kind because small quantities of samples are enough to determine the vapor pressures. Also the concentration change of alloys with measuring time does not bring big error on account of low values of vapor pressure. In Knudsen's method, two conditions must be fulfilled. Firstly, vaporization velocity from alloy surface is so great that the vapor phase in the crucible may be maintained at equilibrium pressure. Secondly, diffusion through bulk phase of the alloy to surface is so rapid as to compensate for the decrease in the concentration of the vaporizing component. In relation to the above conditions, the effect of an oxide film and diffusivity in alloy phase as compared with the vaporization velocity must be taken into consideration. In order to make these points clear the vapor pressure of zinc in tin-zinc liquid alloy was measured. Further, thermodynamic excess functions of this system were discussed.

Experimental

Experimental Method.—In the effusion method vapor pressure is calculated from effusion velocity by an equation

$$P=\sqrt{\frac{2\pi RT}{M}}\cdot\frac{1}{KA}\cdot\frac{G}{\tau}\left(1+\frac{KA}{\alpha B}\right) \qquad (1)$$

where A is the geometric area of the effusion orifice and KA is the effective area. K is the Clausing factor, a correction for the inevitable thickness of the orifice. α is the accomodation coefficient and B is the effective vaporization area in the crucible. $KA/\alpha B$ is a correction term for deviation of pressure in the crucible from saturation. G is the weight (in grams) of effused molecule within time interval τ (sec.). M is the molecular weight of the effusing molecule. Other symbols mean ordinary quantities. In the temperature interval of this experiment, vapor pressure of tin may be neglected and besides zinc vapor is taken as monatomic, so M in this case becomes the atomic weight of zinc. As K cannot be precisely determined by experiment, the effective area KA has been determined by combining the effusion velocity of solid zinc and its vapor pressure, presented by Barrow¹⁾. The correction term $KA/\alpha B$ is negligible compared with unity, provided that α is not very small. As will be shown later, this correction was proved not necessary.

Apparatus. — The apparatus, which had been previously used in the authors' laboratory²⁾, was modified in the reading of thermobalance. The latter is shown in Fig. 1. The beam A is of aluminum and hung with a phosphorus bronze ribbon C from a frame of brass B, which is held in a brass vessel with a brass ring H. The effusion crucible is hung from D with a platinum wire. E is a dust core of 3 mm. in diameter and 1 cm. in length, and is used to convert the inclination of the balance into a change of electric current by means of a linear differential transformer. F is a counter weight of soft iron which can be shifted at a proper position along the beam by a magnet from the outside of the glass tube. A crucible of pyrex glass is 1 cm. in diameter and 1 cm. in height including its lid. An effusion orifice is bored at the center of the lid which is ground with the crucible. The orifice is ground as thin as possible (0.1 mm.) from both the up and down sides of the lid. The furnace consists of a porcelain tube wound by a nichrome resistance wire. The temperature was manually controlled at a constancy of ±1°C during each measurement (20 min. to 2 hr.). Temperature was measured by a platinum vs. platinum-rhodium thermocouple, the end of which was nearly in contact with the crucible through a quartz tube. The thermocouple was calibrated at the melting points of zinc, tin, bismuth, lead and antimony.

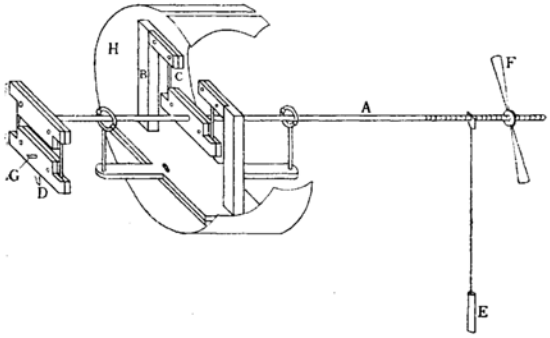

Fig. 1. Schematic diagram of the thermobalance.

Procedure.—About one gram of metal or alloy sample is placed in the crucible, which is hung from the thermobalance by a platinum wire of 0.2 mm. in diameter, then the counter weight is properly adjusted. Sensitivity of the balance is determined at each run by loading riders of known weight on G in Fig. 1 (about 0.1 mg./μA). Then a rider of the right weight is again loaded on the same position in order that the balance may be settled through the measuring time within the inclination range where the sensitivity has been measured. After that the system is evacuated to a pressure of 10^{-5} mmHg and the furnace is heated up to the desired temperature and the rate of weight loss is measured by way of the current in the transformer circuit.

Sample.—Purities of metals used are 99.9% (zinc), chemical pure (tin), 99.9% (bismuth), and 99.999% (indium). Zinc ribbon was used for the measurement in pure solid state. Alloys were prepared in the following way; pure metals of desired amount were sealed in a small pyrex tube in vacuo and kept at about 450°C for ten hr., followed by quenching.

Experimental Error.—As the sources of error of this measurement, temperature, area of the orifice, sensitivity of the balance and rate of change of current should be taken into account. Relative errors of these contents are 0.08, 2.7, 1.5 and 1% respectively. Then the fractional average deviation may amount to 3.2%. Next, the error of activity, calculated from the vapor pressure of pure liquid and alloys, amounts to 4%. The decrease in concentration of zinc with vaporization affects the activity coefficient by decreases of 6 and 3% at mole fractions of 0.05 and 0.1, respectively.

Measurement of Liquid Alloy.—The applicability of Knudsen's effusion method to alloy of liquid state was examined in the following points.

(A) Saturation of Vapor Phase.—In order to make certain that the vapor phase was saturated, vaporization velocity was measured, when the lid of the crucible was removed and the vapor freely escaped from the surface (nearly Langmuir-like). This velocity was about 1×10^{-2} mg./sec., while the ordinary effusion velocity was at most 6×10^{-4} mg./sec. Then, one can assume that zinc vapor is saturated in the crucible even in the case of liquid

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1) R. F. Barrow et al., *Trans. Faraday Soc.*, **51**, 1354 (1955).

2) Z. Shibata and K. Niwa, *J. Fac. Sci. Hokkaido Imp. Univ.* Ser. III, Vol. II, 183 (1938).

solution, where a thin film of zinc oxide may cover and disturb vaporization, or may reduce the accommodation coefficient.

(B) Concentration Difference between the Surface and the Bulk Phase of Liquid Alloy.—The surface concentration of zinc decreases with its vaporization, while the concentration recovers by diffusion through the bulk phase. The following calculation has been made for the sake of estimation of this concentration gradient in the steady state. Assuming (a) that there exists a linear concentration gradient between the surface and a position, $\varDelta L$ cm. distant under the surface, and (b) that there is no convection in the bulk phase, flow of zinc to the surface is given by

$$J(\text{g./sec.}) = -BD\varDelta C/\varDelta L$$

where B is the surface area and D, the diffusion coefficient of zinc in the solution and C, the concentration in g. per cc. This flow should be equal to effusion velocity at the steady state. The latter being at most 6×10^{-7} g./sec. at a vapor pressure of 10^{-2} mmHg, $\varDelta C/\varDelta L$ becomes 0.15, if B is 0.42 cm^2 and D is 10^{-5} cm^2/sec. Then $\varDelta C$ becomes 0.0045 g./cc., when $\varDelta L$ is 0.3 cm., the same length as the depth of the solution. This value of $\varDelta C$ corresponds to about 0.01 mol. fraction. At the practical condition the supplement of zinc would be faster, as there may occur convection and the concentration gradient is not linear.

(C) Concentration Change due to Vaporization.—In one run 1 to 2 mg. of zinc effuses out. This affects the concentration by 0.003 at 0.05 and 0.0015 at 0.1 respectively in mole fraction. Then this effect is not so severe except in a composition of high dilution, where the effusion time of one run is desirable to be short.

Results and Discussion

Vapor Pressure of Pure Zinc.—For the purpose of determining the effective area of the effusion orifice, effusion velocity was measured with pure solid zinc. An example of the results is shown in Table I. By means of the least square method, these values are expressed as a linear function of $1/T$ by

TABLE I. EFFUSION VELOCITY OF SOLID PURE ZINC

T, °K	$P\times KA$* mmHg×cm^2	T, °K	$P\times KA$ mmHg×cm^2
613	4.663×10^{-6}	646	17.15×10^{-6}
621	6.678 ″	649	18.58 ″
625	9.575 ″	658	25.88 ″
635	11.71 ″	661	34.46 ″
636	12.27 ″		

* The geometrical area A is 7.566×10^{-3} cm^2.

$$\log P\times(KA) = -6716/T + 5.649 \tag{2}$$

The vapor pressure of solid zinc has been investigated by many workers. The most reliable value, which Barrow and his coworkers derived[1], is

$$\log P = 9.8253 - 0.1923\log T - 0.2623\times10^{-3}\,T - 6862.5/T \tag{3}$$

Comparing Eq. 2 with Eq. 3, the effective area KA of the orifice is calculated as 0.5735 mm^2. The geometrical area (A) was 0.7566 by microscopic measurement. The ratio of these figures leads to 0.758 as the Clausing factor, which corresponds to 0.099 mm. of thickness of the orifice. Substituting the effective area in Eq. 2, it can be rewritten as

$$\log P = -6716/T + 8.891 \tag{4}$$

The vapor pressure of liquid zinc can be calculated from Eq. 4 and the free energy change of solidification of zinc[3] as a function of temperature. Thus the vapor pressure at 625°K is 1.603×10^{-2} mmHg, which is used as the reference in derivation of activity of zinc in alloys.

Vapor Pressure of Zinc in Liquid Alloy.—At the range of high content of zinc, zinc separates as solid matter over the temperature range where vapor pressure is appropriate in magnitude for the effusion method. The present measurement has covered up to 0.4 of mole fraction of zinc. Measured values are summarized in Table II, and plotted against reciprocal temperature in Fig. 2. The activity of zinc at 625°K, calculated from the above-mentioned values and 1.603×10^{-2} mmHg of

TABLE II. VAPOR PRESSURE OF ZINC IN LIQUID TIN-ZINC SYSTEM

X_{Zn}	T, °K	P_{Zn} mmHg $\times10^3$	X_{Zn}	T, °K	P_{Zn} mmHg $\times10^3$
0.027	645	2.99		659	18.1
	650	3.50		671	25.4
	660	4.31		686	40.5
	665	5.67	$\log P = -5976/T + 7.312$		
	675	6.09	0.252	615	6.08
	681	8.43		625	8.62
	685	8.90		636	11.9
$\log P = -5206/T + 5.546$				650	20.1
0.104	645	7.44	$\log P = -5822/T + 7.249$		
	655	10.1	0.364	597	4.11
	665	12.2		604	5.57
	670	15.0		606	5.74
	688	25.9		613	6.77
$\log P = -5432/T + 6.286$				621	9.15
0.150	616	4.34		625	12.2
	621	4.78		627	11.5
	626	5.83		635	13.9
	640	8.77		651	26.6
	640	9.95		659	34.8
	650	12.8	$\log P = -5769/T + 7.273$		
	652	13.5			

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[3] J. Lumsden, "Thermodynamics of Alloys", Institute of Metals, London (1952), p. 140.

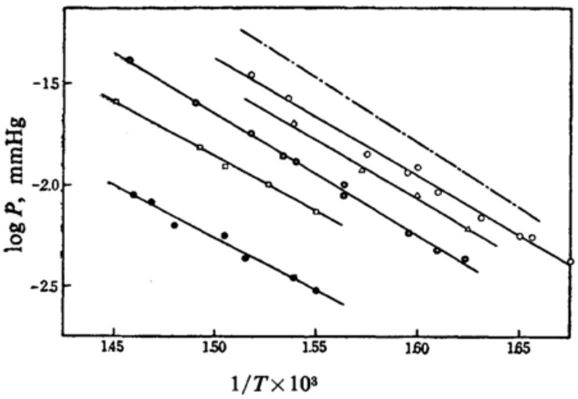

Fig. 2. Relation between logarithm of vapor pressure and reciprocal temperature.

---- liquid pure zinc ◎ $X_{Zn}=0.150$
○ $X_{Zn}=0.027$ □ 〃 0.252
△ 〃 0.104 ● 〃 0.364

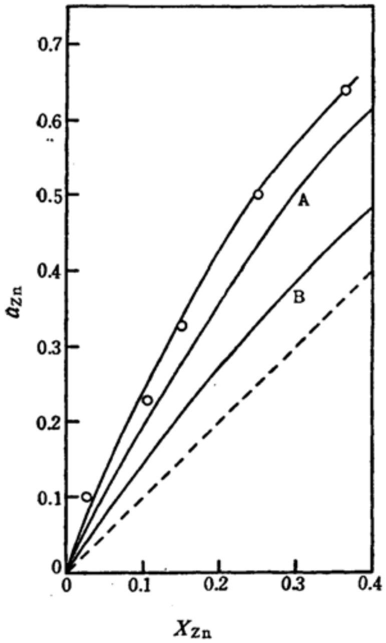

Fig. 3. Activity of zinc: open circle, present work at 625°K, line A, Taylor's value at 650°C, and line B, Jellinek's value at 700°C.

pure liquid zinc, is shown in Fig. 3. On this system Taylor[4] determined activity by e. m. f. method at 400 to 600°C, and Burmeister and Jellinek[5] measured vapor pressure of zinc by the transpiration method at a temperature range of 684 to 785°C. Their results are also shown in Fig. 3.

The thermodynamic property of alloys can be appropriately given in terms of excess function, where solutions are classified as ideal,

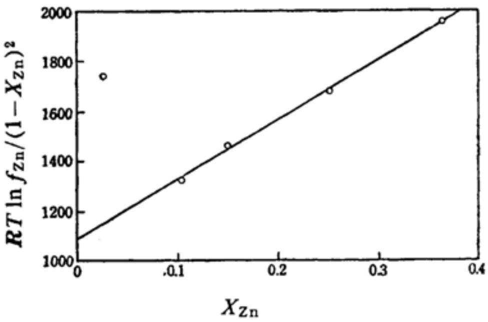

Fig. 4. Relation between $RT\ln f_{Zn}/(1-X_{Zn})^2$ and X_{Zn}.

regular or sub-regular ones. Wittig and his coworkers[6] have found that the heat of solution of this system behaves as a sub-regular solution as far as enthalpy is concerned. In Fig. 4 $RT\ln f_{Zn}/(1-X_{Zn})^2$ is plotted against concentration of zinc. All points are on a straight line

$$\frac{RT\ln f_{Zn}}{(1-X_{Zn})^2}=2370\,X_{Zn}+1090 \tag{5}$$

One point at $X=0.027$ deviates from this line, probably because of the uncertainty of concentration. It would be worth while to find what these figures mean when this system is regarded as a sub-regular solution. By definition[7] excess free energy of solution is related to concentration by

$$\frac{G^e}{X_{Zn}X_{Sn}}=A^0+(X_{Sn}-X_{Zn})A^1 \tag{6}$$

where A^0 and A^1 are constants. From this equation one can derive a formula for the excess chemical potential, defined as a difference between partial molar free energy of solution and ideal partial molar free energy of solution,

$$\mu^e{}_{Zn}/X^2{}_{Sn}=RT\ln f_{Zn}\times1/X^2{}_{Sn}=A^0 \\ +(1-4X_{Zn})A^1 \tag{7}$$

Comparing Eq. 7 with Eq. 5, values of As are given,

$$A^0=1680 \quad\text{and}\quad A^1=-590$$

Taylor's data at equal range of concentration lead to $A^0=1660$ and $A^1=-430$. Accounting for the temperature dependence of these quantities, two sets of data are in good agreement within experimental error.

This sub-regular behavior has not yet been completely interpreted. In the case of molecular liquid solutions, Hildebrand[8] succeeded in explaining energetic asymmetry by using

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[4] N. W. Taylor, *J. Am. Chem. Soc.*, **45**, 2865 (1923).

[5] E. Burmeister and K. Jellinek, *Z. phys. Chem.*, **A165**, 121 (1933).

[6] F. E. Wittig, *Z. Electrochem.*, **63**, 327 (1959).

[7] H. Hardy, *Acta Met.*, **1**, 202 (1952).

[8] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes", Reinhold, New York (1952), p. 109.

volume fraction in place of mole fraction. In the present case this correction is not enough. Kleppa[9] and Wittig[6] pointed out the correlation of the energetic asymmetry with valence electron concentration from the experimental data of many alloy systems. Recently some investigators[10] paid attention to the cohesive energy of metals in light of metallic characteristics and considered what happened on mixing. Shimoji[11] discussed the excess energy of binary alloys by using the cellular approximation for metals and explained energetic asymmetry on mixing, not by the simple volume effect, but by the changes of the energy due to the boundary correction, Fermi energy, interelectronic energy, closed shell repulsive energy, polarization energy etc. It is interesting to compare the calculation with the present data. In the moderately dilute range, integral heats of mixing can be expanded in a power series of the mole fraction of the solute,

$$\Delta H^{M}=P_1x_2+P_2x_2{}^2+\cdots\cdots \tag{8}$$

According to Shimoji the ratio $-P_2/P_1$ is 0.4 in the zinc dilute portion of tin-zinc system. From Eq. 8 one obtains the relative partial molar enthalpy as

$$\overline{\Delta H}_2=P_1+2P_2x_2+\cdots\cdots \tag{9}$$

The corresponding equation can be derived from the present data by the following equation, provided that the partial molar excess entropy is known,

$$\overline{\Delta H}_{\mathrm{Zn}}=\mu^{e}{}_{\mathrm{Zn}}+T\overline{\Delta S}^{e}{}_{\mathrm{Zn}} \tag{10}$$

Assuming that the excess entropy is mainly due to volume difference, partial molar excess entropy of solution of zinc can be calculated by free volume model[8]:

$$\overline{\Delta S}^{e}{}_{\mathrm{Zn}}=-\boldsymbol{R}\left[\ln\varphi_{\mathrm{Zn}}+\varphi\left(1-\frac{V_{\mathrm{Zn}}}{V_{\mathrm{Sn}}}\right)-\ln X_{\mathrm{Zn}}\right] \tag{11}$$

where φ is the volume fraction and V is the molar volume. Replacing φ by the mole fraction and molar volumes, one obtains

$$\overline{\Delta S}^{e}{}_{\mathrm{Zn}}=1.05-1.31\,X_{\mathrm{Zn}}+\cdots\cdots \tag{12}$$

where 16.9 and 9.9 is used as molar volumes of tin and zinc. On the other hand, Eq. 5 is rewritten as

$$\mu^{e}{}_{\mathrm{Zn}}=1090+190X_{\mathrm{Zn}}+\cdots\cdots \tag{13}$$

From Eqs. 12 and 13 the partial molar enthalpy of zinc at 625°K is

$$\overline{\Delta H}_{\mathrm{Zn}}=1750-630X_{\mathrm{Zn}}+\cdots\cdots \tag{14}$$

giving 1750 and -315 cal./mol. for P_1 and P_2 respectively. Then the present value 0.18 for $-P_2/P_1$ seems to agree with 0.4 (Shimoji's value) in deviation from $P_2/P_1=-1$ (regular solution). The experimental results about ternary solutions will be reported in the next paper.

Summary

The vapor pressure of zinc in liquid tin-zinc alloys has been measured by Knudsen's effusion method. Application of this method to liquid alloys has been found to be successful. Observed activity coefficients of zinc are discussed in relation to theoretical calculations. The deviation from the regular solution model has been interpreted in terms of the cellular approximation as well as the volume difference effect.

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[9] O. J. Kleppa, *Acta Met.*, **6**, 225 (1958).

[10] J. Friedel, *Phil. Mag.*, **43**, 153 (1952); J. H. O. Varley, ibid., **45**, 887 (1954).

[11] M. Shimoji, *J. Phys. Soc. Japan*, **14**, 1525 (1959).