Measurement of Vapor Pressure of Phosphorus over Sn–P Alloys by Dew Point Method

By Minoru Arita* and Kunio Kamo**

The dew points of phosphorus vapor over Sn–P alloys containing 45 mol% P or less have been determined at temperatures ranging from 703 to 973 K. The dew consisting of metastable liquid phosphorus, rather than stable red phosphorus, was utilized. The vapor pressures of P$_2$ and P$_4$ were determined from the dew points. Thermodynamic activities and enthalpies of P and Sn were calculated from the vapor pressures. The liquidus line was determined from the temperature and composition dependence of the vapor pressure over coexisting liquid and Sn$_4$P$_3$.

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I. Introduction

Bronze is a copper alloy of very old history. It always contains tin as an alloying element, and phosphorus is often added to strengthen it, presumably by precipitation of fine tin phosphide particles. Vivian(1) determined the liquidus boundaries in the Sn–P system by means of thermal, microscopic and residue analytical investigations. Apparently, no other thermodynamic studies have been reported.

In the present study, therefore, we have determined the vapor pressure of phosphorus over liquid Sn–P alloys and solid Sn$_4$P$_3$ compound by the dew-point technique, in order to determine thermodynamic functions and to reconfirm the phase boundaries. Thermal analyses have also been made for the cross check of the boundary compositions.

II. Experimental

1. Materials

Starting materials used in this work are tin shots of 99.999 mass% purity (major impurities: 1 mass ppm Pb and 1 mass ppm Cu) and red phosphorus powder of 99.999% purity (2 ppm Mg, 3 ppm Fe, 3 ppm Si and 1 ppm Ca; trace As, Al, Cu and Pb; no others detected). All the above figures were given by the suppliers of these materials. Sn shots were washed with dilute hydrochloric acid solution and then with distilled water, and after washed supersonically with ethanol, they were dried in vacuum. The red phosphorus powder was kept in a vacuum decicator when not in use.

About 3 g of an alloy were prepared by weighing the starting materials with an accuracy of 0.05 mg, drying the mixture in vacuum of $10^{-5}$ Pa at 373 K for 1.8 ks, vacuum sealing in a quartz capsule, melting for homogenization at 893 K for 24 h (86.4 ks) and cooling in furnace. The quartz capsule was kept vacuum sealed till it was broken immediately before the pressure measurement of the alloy in it.

2. Experimental procedure

After the quartz capsule was broken, the quartz crucible containing the Sn–P alloy was weighed and then inserted into another quartz tube of 11.5 mm I.D., which was sealed under a pressure of $10^{-5}$ Pa with the shape shown in Fig. 1. The tube was then placed in a double furnace composed of two separated furnaces. Figure 1 also shows an example of the temperature distribution within the furnace and location of the quartz tube when the dew point is being measured. The lower temperature furnace is equipped with two heaters, an
inner one (longer) and an outer one (shorter), with the latter located near the dew end, so that the dew (or inner wall) end may be at the lowest temperature and yet the slope of the temperature drop may be relatively small. In Fig. 1, the contact position of the two furnaces is indicated by a vertical broken line.

After setting the tube in the furnace, the lower T furnace was firstly heated to a prescribed sample temperature, and afterwards the higher T furnace was heated to the same temperature. In this way, a loss of P as Sn4P3 due to too much evaporation and condensation was avoided. Appearance of phosphorus dew on the inner wall surface at the tube end was observed with a telescope of ten times magnification. The dew temperature was measured with a calibrated (by standard mercury thermometers) CA thermocouple of 0.3 mm diameter at the outer surface of the tube end wall. The alloy was held at a constant temperature within ±0.2 K, and its temperature was measured with a CA thermocouple calibrated with a standard Pt/Pt-Rh thermocouple.

For the observation purpose, light from a 40 W bulb was introduced through a transparent quartz bar into the left (or sample) end of the sample tube so that the dew end might be bright enough to see drops of dew forming on the inner surface. The dew temperature was determined as a mean of two measurements, one made while cooling the dew end wall at the rate of around 5 × 10⁻³ K/s and the other made while heating it at the rate of around 10⁻² K/s. The end wall temperature was monitored with a digital voltmeter having a hold switch, which was pushed on at the time the dew appeared or dissapeared.

3. Principle of pressure determination

From the measured dew temperature, the vapor pressure over an Sn–P alloy may be determined in the following way.

In the experimental conditions in the present work, the vapor pressure of monomer P is negligibly small in comparison with those of dimer P₂ and tetramer P₄(2). Therefore, on the end wall with precipitation of phosphorus dew at the temperature Tₐ, the total pressure may be expressed by

\[ P(T_d) = f_2(T_d) + f_4(T_d), \] (1)

where \( f_i \) is the fugacity of vapor species \( P_i \). For \( f_i < 10^5 \) Pa, the partial pressure of species \( i \) is essentially the same as \( f_i \), thereby eq. (1) being valid. For the thermodynamic equilibrium \( 2P_2 = P_4 \) in the vapor phase, we have the following equilibrium constant.

\[ K_p(T) = \frac{f_4}{(f_2)^2}. \] (2)

Combining eqs. (1) and (2) leads to

\[ P(T_d) = f_4(T_d) + \left[ \frac{f_4(T_d)}{K_p(T_d)} \right]^{1/2}. \] (3)

Accordingly, when the vapor pressure over the dew is known, the total pressure may be calculated according to eq. (3).

Since the mechanical equilibrium or the constant total pressure within the sample tube is a reasonable and common assumption, the total pressure over the Sn–P sample is given by

\[ P(T_s) = f_2(T_s) + f_4(T_s) = P(T_d), \] (4)

where \( T_s \) is the sample temperature.

A combination of eqs. (2), (3) and (4) yields

\[ f_4(T_s) = \frac{1}{\sqrt{K_p(T_s)}} + 4P_s(T_d) \right\end{array} \right. - \frac{1}{\sqrt{K_p(T_s)}} \right\end{array} / 4, \] (5)

where the value of \( K_p \) should be taken at \( T_s \). The last equation yields the vapor pressure of species \( P_4 \) over the Sn–P alloy.

4. Thermal analysis of liquidus temperature

About 6 g of an alloy sample with the P
## Table 1 Measured dew points and calculated fugacities of P₄ and P₂ vapors.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$W_{Sn}$ g</th>
<th>$X_{P^a}$</th>
<th>$T_{a}$ K</th>
<th>$T_{d}$ K</th>
<th>$p_1$</th>
<th>$f_2$</th>
<th>$f_4$</th>
<th>$X_{P^b}$</th>
<th>$\ln \gamma_p$</th>
<th>(1-$X_p$)²</th>
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<td>18</td>
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<td>0.0400</td>
<td>723.15</td>
<td>351.22</td>
<td>1.682E-3</td>
<td>1.9E-6</td>
<td>1.680E-3</td>
<td>0.0398</td>
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<tr>
<td>26</td>
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<td>0.0500</td>
<td>743.15</td>
<td>347.72</td>
<td>1.395E-3</td>
<td>3.0E-6</td>
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<td>0.0600</td>
<td>703.15</td>
<td>344.34</td>
<td>1.160E-3</td>
<td>9.6E-6</td>
<td>1.159E-3</td>
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<td>0.1300</td>
<td>803.15</td>
<td>454.83</td>
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<td>0.4000</td>
<td>773.15</td>
<td>442.41</td>
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<td>1.0E-4</td>
<td>1.092E-1</td>
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<td>4.4E-4</td>
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<td>1.0E-3</td>
<td>1.348E-1</td>
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<tr>
<td>973.15</td>
<td>-</td>
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<td>2.3E-3</td>
<td>1.427E-1</td>
<td>0.1217</td>
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</tr>
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</table>

*Original mole fraction.

Two immiscible liquids.

Mole fraction under the experimental conditions.

Bourdon spoon gauge.

mole fraction ranging from 0.02 to 0.35 were vacuum sealed in a quartz capsule of 9 mm I.D. and 40 mm length under a $10^{-5}$ Pa pressure. The bottom of the capsule had a hollow cavity of 3 mm diameter and 5 mm depth, in which a calibrated CA thermocouple of 0.3 mm diameter was inserted for the measurement of solidifying temperature.

### III. Results

1. **Confirmation of thermodynamic equilibration**

Before every dew point was taken as an equilibrium value, its time variation had been examined. Typical examples are shown in Fig. 2. When the dew point was constant for a duration equal to or longer than that of the initial fluctuation stage, it was determined as the equilibrium value. Generally, about 10 h (36 ks) were sufficient for reaching the equilibrium, except that more than 40 h (144 ks) were needed for $X_{p}^{0}=0.04$.

In Table 1, measured values of the dew point, along with the measurement conditions, and tabulated.

2. **Dew point and vapor pressure of phosphorus**

Two measurements of the dew point (on cooling and heating) agreed within 0.5 K. From the measured (or averaged) dew point, the fugacity of the P$_4$ vapor at the dew point was calculated according to the following equation.

$$\log \left( \frac{f_4}{101.3 \text{kPa}} \right) = 16.192 + 1.7079 \times 10^{-4} T - 3374.9 / T - 3.6993 \log T,$$

(6)

which has been obtained from the total pressure measurement of the predominating vapor P$_4$ over liquid P by a spoon gauge$^{(3)}$. Arita and Watanabe$^{(3)}$ also have evaluated the $K_p$ value in the following form.

$$\log \left( \frac{K_p}{(101.3 \text{kPa})^{-1}} \right) = -8.069 + 1.627 \times 10^{-4} T + 11990 / T,$$

(7)

which was obtained from the total pressure measurement of the gas phase consisting of P$_2$ and P$_4$ vapors. Upon substituting eqs. (6) and (7) for eqs. (3), (4) and (5), the values of the total pressure and the fugacities of P$_2$ and P$_4$ at the sample temperature were obtained, and they are listed in Table 1.

The composition of the Sn–P alloy is considered to vary with the vapor pressure, because the number of moles of phosphorus in the gas phase is not negligible but comparable with that in the alloy phase. A correction of the composition, therefore, was made as follows. First, the temperature profile in the quartz tube was simplified so that it consisted of two zones, one at the level of the sample temperature and the other at the level of the dew point, as was given as broken lines in Fig. 1. The two zones had an equal length, and each had a gas volume $V=(7.5 \pm 0.25) \times 10^{-6} \text{m}^3$. Since the vapor pressure of P$_2$ at $T_d$ is negligible in comparison with that of P$_4$, the number of moles of P in the vapor phase was evaluated from the following equation according to the ideal gas law.

![Fig. 2 Variation of the dew temperature with time.](image-url)
where \( f_i(T_j) \) denotes the fugacity of vapor \( i \) at temperature \( T_j \) and \( R \) is the gas constant. With the use of eq. (8), the number of moles of \( P \) in the alloy phase was given by

\[
n_P(\text{alloy}) = n_P^0 - n_P(\text{vap.}), \tag{9}
\]

where \( n_P^0 \) is the original value calculated from the final weight of \( P \) in the alloy before the dew point measurement. The vapor pressure of Sn was negligibly small in the present experimental conditions, and hence, the mole fraction of \( P \) was given as \( X_P = n_P(\text{alloy})/(n_P(\text{alloy}) + n_Sn^0) \). These values of \( X_P \) are listed in Table 1. The accuracy of the \( X_P \) determination depends on the deviation of the assumed temperature profile from the actual one, as shown in Fig. 1. The uncertainty \( \delta X_P \), thus, may be considered to be smaller than 3% of \( X_P \).

The thermodynamic activity of \( P \) is defined in the present paper as

\[
a_P = (f_P/f_P^0)^{1/4}. \tag{10}
\]

In this definition the standard state for the phosphorus activity is pure liquid phosphorus. The activity coefficient \( \gamma_P = a_P/X_P \) was calculated from eq. (10), and the values of \( \ln \gamma_P/(1-X_P)^2 \) are tabulated in Table 1.

Figure 3 shows the temperature dependence of \( f_P \). Except for one data point of Run No. 24, below certain temperatures depending on the composition, all the points fall on a steep line.

### 3. Thermal analysis

Figure 4 shows cooling curves for chemical analysis of two alloys (\( X_P 0.02, 0.35 \)). All the alloys investigated showed supercooling, after which a length of horizontal line, or a constant temperature, followed. Therefore, a backward extrapolation of the line to the primary cooling curve gives the same temperature as that for the horizontal line. Accordingly, the latter temperature was determined as the liquidus point. Measured values of the liquidus point are listed in Table 2.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>( X_P )</th>
<th>Solidifying at 1st</th>
<th>Solidifying at 2nd</th>
<th>Average K</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.02</td>
<td>658.6 K</td>
<td>660.8 K</td>
<td>659.7</td>
</tr>
<tr>
<td>14</td>
<td>0.10</td>
<td>769.5</td>
<td>771.9</td>
<td>770.7</td>
</tr>
<tr>
<td>12</td>
<td>0.15</td>
<td>800.9</td>
<td>796.1</td>
<td>798.5</td>
</tr>
<tr>
<td>11</td>
<td>0.25</td>
<td>820.2</td>
<td>817.8</td>
<td>819.0</td>
</tr>
<tr>
<td>16</td>
<td>0.35</td>
<td>829.4</td>
<td>832.2</td>
<td>830.8</td>
</tr>
</tbody>
</table>
4. Pressure measurement with a quartz spoon gauge

In order to confirm that the present measurement of dew points is correct, the total pressure over an Sn–P alloy was measured with a Bourdon spoon gauge made of quartz. Details of the technique are given elsewhere. The results are shown in Table 1 and in Fig. 3 as well. The sample for the spoon gauge contained 12.17 to 12.32 mol% P, and that for the dew point technique contained 12.50 to 12.58 mol% P (Run No. 20). As seen in Fig. 3, the two are in excellent agreement.

IV. Activities of P and Sn and Molar Free Energy

The activity of P for temperatures not shown in Table 1 was calculated with the aid of eq. (10) using the smoothed curve of $\log f_P$ vs $1/T$ in Fig. 3. The calculated values at temperatures between 723 and 873 K are plotted in Fig. 5, where the dependence of $\ln \gamma_P/(1-X_P)^2$ on the composition is shown. The dependence may be considered to be essentially convex upward, represented by straight lines in Fig. 5. The initial up-hill slope has been obtained from the heat of mixing data, shown later in Fig. 8, by using the Gibbs-Helmholtz relation, $\Delta H_f = R \ln \gamma_P / T^2$ and by assuming the constancy of $(\ln \gamma_P)/(1-X_P)^2$ at 773 K. The down-hill curve for $X_P>0.32$ has been drawn so that the $\Delta G$ curve, shown later in Fig. 7, may have a common tangent contacting at $X_P=0.32$ and 0.46 (the phase boundaries for $L_1/L_1+L_2$ and $L_1+L_2/L_2$, respectively, given later in Fig. 9).

From the smoothed curves in Fig. 5, the activity of P was calculated, and it is plotted in Fig. 6. The activity coefficient of Sn with pure liquid Sn taken as the standard state was calculated according to the following Gibbs-Duhem integration.

$$\ln \gamma_{Sn} = -(X_P \ln \gamma_P)/(1-X_P)$$

$$+ \int_0^{X_P} dX_P (\ln \gamma_P)/(1-X_P)^2. \quad (11)$$

From the last equation the Sn activity was obtained, and it is shown in Fig. 6. For compositions up to $X_P=0.16$, there is very little difference between $T=723$ and 873 K.

The molar free energy of formation or mixing was calculated according to

$$\Delta G = RT[X_P \ln \alpha_P + X_{Sn} \ln \alpha_{Sn}], \quad (12)$$

where the values of the activities were taken from the curves in Fig. 6. Thus calculated values at 873 K (solid curve) and 773 K (broken curve) are shown in Fig. 7, where tie lines are drawn between two equilibrated phases (liquid with $X_P=0.101$ and Sn$_4$P$_3$ at 773 K; liquid with $X_P=0.32$ and liquid with $X_P=0.46$ at 873 K). The $\Delta G$ values of Sn$_4$P$_3$ equilibrated with the corresponding liquid phase were calculated...
from the boundary values of $a_p$ and $a_{Sn}$ marked with triangles, rhombs and cubes in Fig. 6, and they are listed in Table 3.

V. Enthalpy of Formation

For $X_p < 0.25$, the partial molar enthalpy of formation (or mixing) of phosphorus was calculated in accordance with $\Delta H_p = (R/4) \frac{d}{dT} \ln \left( \frac{f_4}{f_3} \right)$, using the smoothed iso-compositional lines in Fig. 3. For the liquid phase with $X_p > 0.25$, it was calculated as $R \ln \gamma_p \frac{d}{dT}$ with the aid of Fig. 5. These calculated values are shown in the form of $\Delta H_p/(1-X_p)^2$ in Fig. 8.

The molar enthalpy of formation was calculated from the following Gibbs-Duhem-like integration.

$$
\Delta H = (1-X_p) \int_0^{X_p} dX_p \Delta H_p/(1-X_p)^2,
$$

(13)

where the integrand is given as a broken and a solid curve (drawn through data points in the least-square sense) in Fig. 3. The values of $\Delta H$ are plotted also in Fig. 8.

In the phase diagram (Fig. 9) the phase next to the liquid is $Sn_4P_3$, which is solid. Therefore, the steep line shown in Fig. 3 corresponds to the two phase (liquid + $Sn_4P_3$) equilibrium. From the slope of this line, $\Delta H_p$ of this $Sn_4P_3$ phase was calculated to be $-66.6 \pm 0.2$ kJ/mol P. This value is listed in Table 3, and the value divided by $(1-3/7)^2$ is shown in Fig. 8. The above error (0.2 kJ/mol P) is associated with 7 data point for $X_p < 0.30$. The $\Delta H$ value shown in Table 3 was obtained from the Gibbs-Helmholtz equation, $\Delta H = \partial (\Delta G/T) / \partial T^{-1}$, and it is also shown in Fig. 8.

<table>
<thead>
<tr>
<th>$T$</th>
<th>$\Delta G$</th>
<th>$\Delta H$</th>
<th>$\Delta H_p$</th>
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<tr>
<td>K</td>
<td>kJ/mol (Sn+P)</td>
<td>kJ/mol (Sn+P)</td>
<td>kJ/mol P</td>
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<td>715–823</td>
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</table>

$^a$From $a_{Sn}$ and $a_p$ in Fig. 6.

$^b$$\Delta H = \partial (\Delta G/T) / \partial T^{-1}$.

$^c$$\Delta H_p = (R/4) \partial \ln f_4/f_3 / \partial T^{-1}$ in Fig. 3.
The liquidus curve for the $L_1/\text{Sn}_4\text{P}_3$ phase boundary is drawn through the thermo-analytical and other data points in Fig. 9. The other points were obtained as intersections of the $L_1/\text{Sn}_4\text{P}_3$ line and each of the smoothed iso-compositional lines shown in Fig. 3. The peritectic point for $L_1+L_2/\text{Sn}_4\text{P}_3$ was determined to be 832 K, from the thermal analysis for $X_p=0.35$ in Table 2 as well as the topmost intersection for $L_1$, $L_2$ and $\text{Sn}_4\text{P}_3$ in Fig. 3. In Fig. 3, the iso-compositional lines for $X_p^0=0.400$($X_p=0.325$ to 0.341) and $X_p^0=0.450$($X_p=0.368$ to 0.377) coincide with each other, and hence, two liquid phases are considered to coexist on this line. The left end of the peritectic line is temporarily determined to be located at $X_p=0.322$ in consistant agreement with the $f_4$ data points for the $L_1$ phase shown in Table 1 and Fig. 3. The $L_1/L_1+L_2$ boundary is also drawn without contradiction to the data points for $X_p^0=0.400$.

Fig. 9 Phase boundaries, $L_1/L_1+\text{Sn}_4\text{P}_3$ and $L_1/L_1+L_2$, and peritectic temperature for $L_1+L_2/\text{Sn}_4\text{P}_3$.

VI. Sn–P Phase Diagram

The liquidus curve for the $L_1/\text{Sn}_4\text{P}_3$ phase boundary is drawn through the thermo-analytical and other data points in Fig. 9. The other points were obtained as intersections of the $L_1/\text{Sn}_4\text{P}_3$ line and each of the smoothed iso-compositional lines shown in Fig. 3. The peritectic point for $L_1+L_2/\text{Sn}_4\text{P}_3$ was determined to be 832 K, from the thermal analysis for $X_p=0.35$ in Table 2 as well as the topmost intersection for $L_1$, $L_2$ and $\text{Sn}_4\text{P}_3$ in Fig. 3. In Fig. 3, the iso-compositional lines for $X_p^0=0.400$($X_p=0.325$ to 0.341) and $X_p^0=0.450$($X_p=0.368$ to 0.377) coincide with each other, and hence, two liquid phases are considered to coexist on this line. The left end of the peritectic line is temporarily determined to be located at $X_p=0.322$ in consistant agreement with the $f_4$ data points for the $L_1$ phase shown in Table 1 and Fig. 3. The $L_1/L_1+L_2$ boundary is also drawn without contradiction to the data points for $X_p^0=0.400$.

VII. Discussion

The error in the determination of $f_4$ at the temperature $T_s$ comes from uncertainties in the measurements of 1) $T_d$ and 2) $T_s$, and in the calculation of 3) $X_p$. With the aid of eq. (3), differentiation of eq. (5) gives

$$\delta \ln f_4(T_s) = \left( \delta \ln K_p + \left( \delta \ln P_t \right) 4K_p P_t / \sqrt{1 + 4K_p P_t} - 1 \right) / \sqrt{1 + 4K_p P_t},$$

(14)

where $P_t=f_4$ at the temperature $T_d$. The uncertainties $\delta T_d$ and $\delta T_s$ enter eq. (14) through eqs. (6) and (7). The third contribution of $\delta X_p$ may be expressed in the following form, with the aid of eq. (10) and upon noting $a_p=\gamma_p X_p$.

$$\delta \ln f_4(T_s) = 4(1 + X_p) \partial \ln \gamma_p / \partial X_p \delta \ln X_p,$$

(15)

where the partial derivative may be obtained from Fig. 5. As has been given earlier in this report, the uncertainties $\delta T_d$ and $\delta T_s$ are $\pm 0.5$ and $\pm 0.2$ K, respectively, and $\delta X_p/X_p < 0.03$. Upon noting the dependence of the total error on independent errors: $|\delta| = [\Sigma(\delta_i)^2]^{1/2}$, the combination of eqs. (14) and (15), including the measurement errors: $|\delta \ln K_p| = 0.07$ and $|\delta \ln f_4(T_d)| = 0.08^{3}$, leads to $|\delta \ln f_4(T_s)| \approx 0.22$.

One of the most important points in the dew-point measurement is to know the species and physico-chemical state of the dew. In the present work two kinds of substances were observed to condense on the inside wall: one was a congregation of red particles, apparently red phosphorus; the other was transparent liquid wet and wide spread over the inside wall, apparently liquid phosphorus. The data given in this report are those for liquid phosphorus. At higher temperatures, i.e. larger vapor pressures, red phosphorus was observed to condense as dew. Though red P is the stable condensed phase, liquid P firstly formed probably as an intermediate metastable phase. At temperatures above a certain point, the latter is considered to be unstable rather than metastable. For some samples the dew point of red phosphorus was measured, though not
very accurate because of the relative invisibility of scattering red P particles of very small size. The fugacity \( f_4 \) calculated from these results, however, fell more or less on the extrapolated line from the liquid P values.

Another point of importance is to determine if the measured dew temperature is true or false. In other words, the phosphorus vapor might be supercooled, thereby the measurement being false. In this study, however, all the two measurements both on heating and cooling agreed within 0.5 K, and hence, no supercooling or superheating is considered to have occurred. Therefore, it may be concluded that the present measurement gave true dew points.

In Fig. 3 the steep line for the two phase (liquid/Sn\(_4\)P\(_3\)) equilibrium has been drawn through the data points for \( X_P < 0.3 \) and not through those for \( X_P > 0.32 \). This is because, when lowering the temperature in the \( L_1 + L_2 \) field for \( X_P > 0.32 \), not only Sn\(_4\)P\(_3\) but also Sn\(_3\)P\(_4\) should have formed according to the phase diagram shown in Fig. 9, thereby raising the vapor pressure. In Fig. 3, one data point for \( X_P = 0.45 \) at 771 K is much higher than the others at this temperature. According to the phase diagram in Fig. 9, this point corresponds to the two phase (Sn\(_4\)P\(_3\)/Sn\(_3\)P\(_4\)) equilibrium. The broken lines in Fig. 3 are drawn in qualitative agreement with the phase diagram.

The liquidus data points by the dew point technique as well as the thermal analysis shown in Fig. 9 are in excellent agreement with those in Ref. (1), except for the lefthand boundary of the two phase (\( L_1 + L_2 \)) field. A careful review of the thermal analyses in Ref. (1) revealed that the \( L_1 / L_1 + L_2 \) boundary might best be fitted around \( X_P = 0.3 \) rather than \( X_P = 0.23 \), in good agreement with the present determination.

In Fig. 7, the \( \Delta G \) curve for 873 K has a common tangent contacting at \( X_P = 0.32 \) and 0.46, in good agreement with the phase diagram in Fig. 9. This is because the curve of \( (\ln \gamma_P)/(1-X_P)^2 \), on which the calculation of \( \Delta G \) is based, for \( X_P > 0.32 \) has been drawn so that the \( \Delta G \) curve may have such a common tangent. In Fig. 7, at 773 K a tangential line is drawn on the \( \Delta G \) curve of the liquid phase, passing through the point for Sn\(_4\)P\(_3\). The contact point at \( X_P = 0.101 \) reasonably coincides with the phase diagram in Fig. 9, because the \( \Delta G \) value of Sn\(_4\)P\(_3\) was calculated from the activities of the liquid phase at \( X_P = 0.101 \).

The activity curves in Fig. 6 are not smooth but sharply inflected. This is because they were calculated in accordance with the smooth broken curve of \( (\ln \gamma_P)/(1-X_P)^2 \) in Fig. 5. It may be considered that the function curve should be rounder and so is the activity curve in Fig. 6. In the present work, the P activity is defined by eq. (10), while other definitions such as \( a_P = (f_2/f_0)^{1/2} \) and \( f_1/f_2 \) should give the same value. This is obvious, upon noting that the equilibria \( 2P_2(g) = P_4(g) \) and \( 4P(g) = P_4(g) \) give the constants \( K_{24} = f_4/(f_2)^2 \) and \( K_{14} = f_2/(f_1)^4 \), respectively.

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