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On the Heat of Mixing of Liquid Copper Alloys*

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Synopsis

The heat of mixing of liquid copper alloys is measured in terms of the temperature change of liquid alloys on mixing.

In the liquid Cu-Bi alloy, a heat absorption depending parabolically upon alloying composition is observed. In the liquid alloys of Cu-Sb, Cu-Ge, Cu-Sn and Cu-In, on the other hand, the heat of mixing curve shows a deep minimum of heat evolution in the range of 75% to 80% of Cu.

The results indicate that Cu and Bi atoms are randomly mixed in the Cu-Bi alloy, but in the other alloys such as Cu-Sn and Cu-In, not every constituent atom can always be randomly distributed. It may be expected from the above results and other physical properties that in these liquid alloys some atoms are randomly distributed, but others associate into clusters of small groups of atoms, which are like molecules of the type $A_mB_n$ bound by a sort of covalent bond and having a flexible structure different from a rigid molecule. These will be referred to as pseudo-molecules. The heat evolved on mixing may be mainly due to the formation of these pseudo-molecules.

Under the above assumption free energy of an assembly consisting of the pseudo-molecules and free atoms is calculated, and from the condition of the minimum free energy the distribution of the pseudo-molecules $n_R$ is determined as a function of alloy composition. The heat of mixing curves for the liquid Cu-Sn and Cu-In alloys calculated with the above $n_R$ functions are in good agreement with the observations. Considering the large difference between atomic volumes of Cu and Bi the heat of mixing of the liquid Cu-Bi alloy is estimated. The calculated results give a parabolic curve with a maximum at 40% Bi, which is in good agreement with the experiment.

I. Introduction

The regular arrangement of atoms in solid metals is generally considered to change into a random arrangement if the metals are melted. This assumption, however, does not always hold true. If metals with crystal structures of high symmetry, such as Na, Cu, Al, Pb, Fe or Mg of f.c.c., b.c.c. or h.c.p. structures, are melted, their structure factors resemble those of an assembly of hard spheres in random distribution, and, hence, in their liquid states the atoms can be considered to be in a random arrangement. On the other hand, if their temperatures are not so far from their melting points, metals in a liquid state, such as Hg, Sn, Bi or Sb, with complex crystal structures of low symmetry, have structure factors quite different from those in the case of a random arrangement of hard spheres. Therefore, all the atoms of such liquids can not be considered to be randomly arranged. To clarify these suppositions it is necessary to observe variations of structure

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factors and of other physical properties with respect to change in temperature.

In certain liquid alloys which have a solid solution structure or a simple eutectic structure in the solid state, all constituent atoms are considered to be randomly arranged, but in some liquid alloys which contain compounds of complex structures in solid state, their atomic distributions are supposed to be different from a random arrangement as seen from their structure factors.

Liquid copper alloys such as Cu-Bi, Cu-In, Cu-Sn, Cu-Ge and Cu-Sb, are known to a simple eutectic structure or to contain electron compounds of complex crystal structures in their respective solid state. Neutron scattering, magnetic susceptibility, electric resistivity and heat of mixing of these liquid alloys have been measured in order to investigate the quantitative aspects of difference in atomic arrangement. This paper gives the observed results and the thermodynamical analysis of heat of mixing for the above liquid alloys.

II. Method of measuring heat of mixing and experimental results

Heat of absorption or of evolution can be estimated from the temperature variations in a liquid alloy on mixing liquid metals A with B. Figure 1 shows the main part of the calorimeter consisting of a graphite container with two cylindrical chambers 13 mm in diameter, which hold two silica crucibles 10 mm in diameter and 17 mm in length containing the liquid metals A and B, respectively. Above the silica crucibles are placed two graphite cells, each containing the liquid metal A. These cells have a bottom plate which simultaneously drop the liquid metal into the silica crucibles through its hole upon rotation around its axis. Consequently the liquid metal A is added to the liquid metal A in one of the silica crucibles, whereas it is mixed with the liquid metal B in the other. Before mixing,
Fig. 2. Cooling curve and temperature change of liquid metal with respect to time after mixing at $t=0$.

the upper and the lower crucibles are kept at the same temperature in an atmosphere of argon. On mixing, the temperature of the alloyed liquid changes suddenly, and then approaches exponentially with time $t$ towards the temperature before mixing by heat conduction through the legs of the silica crucibles. The temperature change on mixing is determined by extrapolation of the cooling curve to $t=0$, as shown in Fig. 2. The heat of mixing is estimated from the amount of temperature change at $t=0$.

The experimental results on the heat of mixing of liquid alloys In-Sn, In-Bi and Bi-Pb measured by means of the above method are in good agreement with the results obtained by the adiabatic method of Kleppa and Wittig$^{(1)}$.

Figures 3 through 7 show the composition dependencies of the heat of mixing for liquid copper alloys obtained by the cooling method described above. Figure 3 shows that the heat absorbed has a parabolic dependence upon composition in alloying liquid Cu with liquid Bi. No compound is formed in the case of the heat absorption on mixing. As will be shown in our next report$^{(2)}$, the magnetic

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susceptibility of the Cu-Bi liquid alloy has nearly a linear dependence upon composition in good agreement with that calculated under the assumption of random distribution of Cu\(^{+1}\) and Bi\(^{+5}\) ions in a dense gas atmosphere of conduction electrons. In the Cu-Bi liquid alloy, therefore, Cu and Bi atoms are considered as randomly mixed. On the other hand a considerable amount of heat is evolved on mixing in the liquid alloys of Cu-In, Cu-Sn, Cu-Ge and Cu-Sb systems, as seen in Figs. 4, 5, 6 and 7. These alloys exhibit a sharp maximum in heat evolved on mixing with respect to the change in alloy composition. Each curve in these figures is greatly different from the parabolic dependence in the case of Cu-Bi alloy. Accordingly, in these liquid alloys all mixed atoms are not considered to lie in random arrangement. Some of them are distributed randomly while others associate into small groups bound by a sort of covalent bond. The composition of these atomic groups is considered to be nearly the same as that corresponding to the peak in the heat of evolution described above. If these atomic groups are formed, a large diamagnetic susceptibility is expected to be present. Measured magnetic susceptibility for these liquid alloys shows a large diamagnetic peak at a composition corresponding to the maximum in the heat of evolution as shown in the following paper\(^6\).

Bound atoms in the atomic group are also affected closely by surrounding
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Fig. 5. Heat of mixing curve for liquid Cu-Sn alloy at 1090°C.

Fig. 6. Heat of mixing curve for liquid Cu-Ge alloy at 1090°C.

Fig. 7. Heat of mixing curve for liquid Cu-Sb alloy at 1080°C.
free atoms which are randomly distributed. Some of these groups dissociate into free atoms and sometimes groups are formed from free atoms at high temperatures (about 1000°C). Therefore, it is considered that associated atomic groups and free atoms are statistically in a state of dissociative equilibrium and, hence, the lifetimes of atomic groups are not of appreciable duration, and decrease with increasing temperature. The diamagnetic peak in the susceptibility curve decreases with increasing temperature. Thus the associated atomic group is not so large but rather is similar to a molecule of the composition $A_mB$. Examples of this type of the atomic group are the molecules $Cu_4In$ in the Cu-In liquid alloy and $Cu_4Sn$ in the Cu-Sn liquid alloy. Since the magnitude of the peak of heat evolution in the heat of mixing curve is of an order of several Kilo-joule/mole, the number of electrons contributing to the bonding of a molecule is considered as less than the saturation value necessary for the complete covalent bonding of the molecule described above. The molecule under consideration, therefore, is likely to have a flexible structure in which the interatomic distance between unlike atoms is kept nearly constant, but the bonding angle is variable over a wide range. Such a molecule is referred as a pseudo-molecule\(^{(3)}\) since it differs from a real molecule of rigid structure. Therefore, the heat evolved on mixing a liquid copper with a liquid metal such as tin, indium, germanium or antimony is attributed mainly to the formation of these pseudo-molecules.

In this study the free energy of a liquid alloy is calculated under the above mentioned model of pseudo-molecule and the heat of mixing for liquid Cu-In, Cu-Sn and Cu-Sb alloys is estimated from the calculation of the distribution of pseudo-molecules\(^{(3)}\).

### III. Partition function and distribution of pseudo-molecules

If a liquid alloy consisting of $N_A$ atoms of element A and $N_B$ atoms of element B contains $n_R$ pseudo-molecules of the $A_mB$ type and $n_A$ and $n_B$ free atoms at a given temperatures $T$, we have the following relations between $n_A$, $n_B$ and $n_R$.

$$n_A + mn_R = N_A, \quad n_B + n_R = N_B, \quad N_A + N_B = N \quad (1)$$

If the volume of the liquid alloy under consideration is assumed to be nearly constant independent of any configuration of $N$ atoms of A and B and, therefore, the specific volume of atoms A and B being nearly equal, one may estimate the probability of the formation of $n_R$ molecules on mixing $N_A$ and $N_B$ atoms of A and B, respectively, at temperature $T$. After $(\ell-1)$ molecules have been formed, the number of possible ways in which a $l$th B atom may occupy an available position in the remaining volume are $N - (m+1)(\ell-1)$. The chance of the B atom to associate with an atom A is given by $Z_1\left[1 - \frac{(m+1)(\ell-1)}{N}\right]$, where $Z_1$ is the number

of available positions adjacent to the B atom, and therefore the chance that
combines with a second atom A is written as \( Z_2 \left[ 1 - \frac{(m+1)(l-1)}{N} \right] \). \( Z_2(n) \) is the
remaining number of position which are expected to be occupied on the reaction
sphere of the B atom after the first A atom has taken its position. Thus,
the chance of the \( l \)th molecule being formed is given by

\[
\nu_l = \frac{1}{\sigma} \left\{ N - (m+1)(l-1) \right\} Z_1 \left[ 1 - \frac{(m+1)(l-1)}{N} \right] Z_2 \left[ 1 - \frac{(m+1)(l-1)}{N} \right] \ldots
\]

\[
\ldots Z_m \left[ 1 - \frac{(m+1)(l-1)}{N} \right]
\]

\[
= \left( \frac{\rho}{\sigma} \right) N \left[ 1 - \frac{(m+1)(l-1)}{N} \right]^{m+1},
\]

where

\[
\rho = Z_1 Z_2 \ldots Z_m
\]

and \( \sigma \) is the symmetric number of a pseudo-molecule \( A_m B \). Accordingly the number
of ways for the formation of \( n_R \) molecules is given by

\[
\prod_{l=1}^{n_R} \nu_l = \prod_{l=1}^{n_R} \left( \frac{\rho}{\sigma} \right) N \left[ 1 - \frac{(m+1)(l-1)}{N} \right]^{m+1}.
\]

(2)

Since the remaining atoms \( n_A \) and \( n_B \) are randomly arranged at the \( n_A + n_B \) positions, we obtain the total number of ways of arranging \( n_R \) molecules, \( n_A \) and \( n_B \) atoms in the volume \( V \),

\[
g(n_A, n_B, n_R) = \frac{(n_A + n_B)!}{n_A! n_B!} \prod_{l=1}^{n_R} \left( \frac{\rho}{\sigma} \right) N \left[ 1 - \frac{(m+1)(l-1)}{N} \right]^{m+1}
\]

\[
= \left( \frac{\rho}{\sigma} \right)^{n_R} \frac{(n_A + n_B)!}{n_A! n_B!} \left( \frac{N}{n_R} \right)^{(m+1)n_R} \left( \frac{N}{m+1} \right)! \left( \frac{N}{m+1} - n_R \right)!
\]

(3)

The potential energy \( E \) of the alloy is given by the sum of the binding energy of
\( n_R \) pseudo-molecules, the interaction energies between the pseudo-molecules and
free atoms, and the mutual potential energy between the free atoms. The mixing
energy is defined as the difference \( dE \) between the potential energy of the liquid
alloy and that of pure liquid metals A and B before mixing.

Consider a particular pseudo-molecule consisting of \( m+1 \) atoms. Each of
these atoms contacts, on average, with \( Z \) neighbouring atoms, but some of them
are other elements in the same molecule. So a pseudo-molecule consisting of
(m+1) atoms contacts with Z atoms, in which atoms composing the same molecule are not included. A quantity \( q \) is related to \( m+1 \) by

\[
\frac{1}{2} Z (m+1-q) = m .
\]

(4)

Of the \( Zq \) neighbours of each molecule we assume that \( Zq_u \) comes from A atoms and \( Zq_v \) from B atoms. Then it follows:

\[
u + v = 1
\]

(5)

If we substitute

\[
N' = n_A + n_B + q n_R
\]

then the total number of pairs of atoms which make contact with each other is given by

\[
Q = \frac{1}{2} Z N'.
\]

Accordingly it can be considered that we have only \( N' \) atoms in spite of \( N \) total atoms and also that \( n_R \) pseudo-molecules are replaced by \( q n_R \) atoms with \( Z \) effective number of contacting atoms. Denoting the mutual interaction energy of a pair of contacting atoms by \( \varphi \) and atoms A and B which compose a pseudo-molecule by \( \Lambda' \) and \( \Lambda'' \) respectively, the potential energies of \( \Lambda A \) pairs and \( \Lambda B \) pairs which contribute to the configurational energy \( E \) of a liquid alloy are given by the terms

\[
n_A Z \frac{q n_R}{N'} \varphi_{AA'} = \frac{n_A n_R}{N'} qu \chi_{AA'}
\]

and

\[
n_A Z \frac{q n_R}{N'} \varphi_{AB'} = \frac{n_A n_R}{N'} qv \chi_{AB'}
\]

respectively, where

\[
Z \varphi_{AA'} = \chi_{AA'}, \quad Z \varphi_{AB'} = \chi_{AB'}.
\]

Thus, the heat of mixing \( \Delta E \) is given by the following equation;

\[
\Delta E = E - E_0
\]

\[
= n_R w_R + \frac{n_A n_R}{N'} (qu \chi_{AA'} + qv \chi_{AB'}) + \frac{n_B n_R}{N'} (qu \chi_{BA'} + qv \chi_{BB'})
\]

\[
+ \frac{n_R^2}{N'} \left( \frac{1}{2} q^2 u^2 \chi_{AA'} + \frac{1}{2} q^2 v^2 \chi_{BB'} + q^2 u v \chi_{A'B'} \right)
\]

\[
+ \frac{1}{2} \frac{n_A^2}{N'} \chi_{AA} + \frac{1}{2} \frac{n_B^2}{N'} \chi_{BB} + \frac{n_A n_B}{N'} \chi_{BA} - \frac{1}{2} \frac{N_A \chi_{AA}^2}{N'} - \frac{1}{2} \frac{N_B \chi_{BB}^2}{N'},
\]

(7)

where \( w_R \) denotes the binding energy of pseudo-molecule \( A_m B \). The potential
energies \( x_{AA} \) and \( x_{BB} \) can be assumed nearly equal to \( x_{AA}^2 \) and \( x_{BB}^2 \) which are the potential energies of the AA and BB pairs in the liquid states of A and B metals, respectively. Also the mutual interactions between pseudo-molecules are small compared to the other interactions described above. If, now, we introduce the abbreviations

\[
\begin{align*}
\omega_R &= \omega_R^0 - \frac{1}{2} (m \chi_{AA} + \chi_{BB}) \\
\omega_{AB} &= \chi_{AB} - \frac{1}{2} (\chi_{AA} + \chi_{BB}) \\
\omega_{AR} &= q \left[ (u \chi_{AA'} + v \chi_{AB'}) - \frac{1}{2} \chi_{AA} \right] \\
\omega_{BR} &= q \left[ (u \chi_{BA'} + v \chi_{BB'}) - \frac{1}{2} \chi_{BB} \right],
\end{align*}
\]

then \( \Delta E \) in eq. (7) is rewritten as

\[
\Delta E = n_R \omega_R + \frac{n_A n_B}{N'} \omega_{AB} + \frac{n_A n_R}{N'} \omega_{AR} + \frac{n_B n_R}{N'} \omega_{BR}.
\] (9)

According to eqs. (3) and (9) the excess free energy of the liquid alloy is expressed as

\[
F_C = -kT \log g(n_A, n_B, n_R) \exp \left( -\frac{\Delta E}{kT} \right)
\]

\[
- n_R \omega_R + \frac{n_A n_B}{N'} \omega_{AB} + \frac{n_A n_R}{N'} \omega_{AR} + \frac{n_B n_R}{N'} \omega_{BR}
\]

\[
+ kT \left[ n_R \left( m - \log \frac{p_A}{\sigma} \right) + n_R \log \frac{n_R}{N} \right. \\
+ n_A \log \frac{n_A}{N} + n_B \log \frac{n_B}{N} \right].
\] (10)

The most probable values of \( n_R \) at a given temperature are calculated from the condition that the free energy should be at a minimum with respect to \( n_A, n_B \) and \( n_R \),

\[
\frac{\partial F_C}{\partial n_A} \delta n_A + \frac{\partial F_C}{\partial n_B} \delta n_B + \frac{\partial F_C}{\partial n_R} \delta n_R = 0
\] (11)

with the following restriction conditions given from eq. (1),

\[
\begin{align*}
\delta n_A + m \delta n_R &= 0 \\
\delta n_B + \delta n_R &= 0.
\end{align*}
\] (12)
Solving eq. (11) under the condition of eq. (12), we obtain a relation for the dissociative equilibrium between pseudo-molecules and free atoms,

$$m \frac{\partial F_C}{\partial n_A} + \frac{\partial F_C}{\partial n_B} = \frac{\partial F_C}{\partial n_R}.$$  \hspace{1cm} (13)

And from eqs. (13) and (10) the following relations are derived,

$$kT \left[ \log \frac{\rho}{\sigma} - \log \frac{n_R}{N} + m \log \frac{N_A - mn_R}{N} + \log \frac{N_B - n_R}{N} \right]$$

$$= \left(1 - \frac{N}{N'}\right) w_R + \frac{N}{N'} \left[ \frac{1}{n_R} \left( \Delta E - \frac{N_A N_B}{N} w_{AB} \right) - \frac{n_R}{N} (w_{BR} - mw_{AB} + mw_{AR}) \right],$$  \hspace{1cm} (14)

where $\Delta E$ of eq. (9) can be rewritten as

$$\Delta E = \frac{N}{N'} \left[ \frac{N_A N_B}{N} w_{AB} + n_R \left( \frac{N'}{N} w_R + \frac{N_A}{N} (w_{AR} - w_{AB}) \right) \right.$$

$$\left. + \frac{N_B}{N} (w_{BR} - mw_{AB}) - \frac{n_R}{N} (w_{BR} - mw_{AB} + mw_{AR}) \right].$$  \hspace{1cm} (15)

and

$$\frac{N}{N'} = \frac{1}{1 - (m + 1 - q) \frac{n_R}{N}}.$$  \hspace{1cm} (16)

When the energy parameters $w_R$, $w_{AR}$, $w_{BR}$ and $w_{AB}$ are given numerically, we can determine the value of $n_R$ as a function of $N_A$ and $N_B$ from eq. (14) and using these values of $n_R$ the heat of mixing $\Delta E$ is calculated from eq. (15).

IV. Composition dependence of $n_R$ and calculation of heat of mixing

In this section, the composition dependences of $n_R$ in the liquid alloys of Cu-Sn and Cu-In are calculated and the heat of mixing of these alloys are evaluated from these values of $n_R$.

In the case of liquid alloys of the Cu-Sn system the observed value of heat of mixing shows a maximum of heat evolution at approximately 20%Sn, and a similar peak in diamagnetism is observed in the magnetic susceptibility of the same alloy. From these facts we can assume the existence of a pseudo-molecule of the type Cu$_2$Sn.

Next, numerical values of $w_R$, $w_{AB}$, $w_{AR}$ and $w_{BR}$ are determined by comparing $\Delta E$ of eq. (15) with the observed $\Delta E$.

(i) In the region of $N_A \gg N_B$, it can be considered that $n_R/N \ll 1$ and hence $N' = N$. Then, we have
\[ \Delta E = \frac{N A N B}{N} w_{AB} + n_R(w_R + w_{AR} - w_{AB}) - n_R \frac{N B}{N} (w_{AR} - w_{AB}), \] (16)

where in the region of \( N_B \approx 0 \), especially, we can take the approximation \( N_R = N_B \), then it follows:

\[ \frac{\Delta E}{N} = \frac{N B}{N} (w_R + w_{AR}). \]

\( w_R + w_{AR} \) can be determined from the tangent at \( N_B = 0 \) on the observed curve of heat of mixing and we have

\[ w_R + w_{AR} = -31.7 \text{ kJ/mol}. \]

(ii) In the region of \( N_A \approx 0 \), it can be considered that

\[ \frac{n_R}{N} \approx 0 \text{ and } \frac{N'}{N} = 1, \text{ and then} \]

\[ \frac{\Delta E}{N} = \frac{N A N B}{N^2} w_{AB} = \frac{N A (N - N_A)}{N^2} w_{AB} = \frac{N A}{N} w_{AB} \]

From the tangent at \( N_A = 0 \) on the observed \( \Delta E \) curve we have

\[ w_{AB} = 1.25 \text{ kJ/mol} \]

Further, in the concentration range of \( N_B \gg N_A \), eqs. (15) and (14) can be written as

\[ \left( \frac{\Delta E}{N} - \frac{N A N B}{N^2} w_{AB} \right) = \frac{n_r}{N} \left[ (w_R + w_{AR} - w_{AB}) \right. \]
\[ \left. + \frac{N B}{N} (w_{BR} - w_{AR} - 3w_{AB}) \right] \] (17)

and

\[ \left( \frac{\Delta E}{N} - \frac{N A N B}{N^3} w_{AB} \right) = kT \frac{n_r}{N} \left[ \log \frac{\rho}{\sigma} - \log \frac{n_R}{N} \right. \]
\[ \left. + 4 \log \frac{N_A - 4n_R}{N} + \log \frac{N_B - n_R}{N} \right]. \] (18)

The values of \( n_r \) in this range can be determined from eq. (18) in which \( \rho/\sigma = 15 \) and the observed values of \( \Delta E \) are substituted in place of \( \Delta E \). Thus, \( w_{BR} - w_{AR} \) is estimated from eq. (17) using the values determined by the above method. It follows:

\[ w_{BR} - w_{AR} = 21.90 \text{ kJ/mol}, \quad \left( \frac{\rho}{\sigma} = 15 \right). \]
\( w_{AR} \) or \( w_{BR} \) can not be determined from the above boundary conditions. Therefore, the value of \( w_{AR} \) is taken as 4 kJ/mol through the comparison of the calculated value of \( \Delta E \) derived from eqs. (14) and (15) at \( N_B/N=0.2 \) with the observed one.

For numerical calculation of eqs. (14) and (15), \( N' \) or \( q \) must be given.

We obtain \( m+1=q \) or \( N'=N \) by making \( Z \rightarrow \infty \) and if \( Z \approx 10 \), it follows:

\[
\frac{m+1}{q} \geq 1.
\]

However, values of \( \Delta E \) calculated for various \( q \) within the above range are not so different from each other due to the relationship \( n_B/N<1 \). Hence, for practical purposes it is assumed that \( N=N' \) through the whole range of concentration. Using the above value of \( w_{AR} \) we obtain the energy parameters for the liquid Cu-Sn alloy at 1090°C,

\[
\begin{align*}
  w_R &= -35.7 \text{ kJ/mol} \\
  w_{AB} &= 1.25 \quad " \\
  w_{AR} &= 4 \quad " \\
  w_{BR} &= 25.9 \quad " 
\end{align*}
\]

(19)

From eq. (14) the value of \( n_B/N \) for various concentrations can be obtained. Figure 8 shows \( n_B/N \) plotted against concentration for the liquid Cu-Sn alloy at 1090°C. As seen in Fig. 8 \( n_B/N \) increases rapidly to a maximum at \( N_B/N=0.2 \) and then decreases to nearly zero toward the range of \( N_A \ll N_B \) as \( N_B/N \) increases. We have

\[
\left( \frac{n_B}{N} \right)_{\text{max}} = 0.136 \quad \text{at} \quad \frac{N_B}{N} = 0.2.
\]

The heat of mixing \( \Delta E \) calculated using \( n_B/N \) of Fig. 8 and the energy values of eq. (19) is shown by open circles in Fig. 5 which are in good agreement with the experimental results over the whole range of concentration.

The pseudo-molecule of the liquid Cu-In alloy is considered to be of the type Cu\(_3\)In from the fact that the maximum in heat evolution or in the diamagnetic susceptibility is found in the neighbourhood of 25% In. The energy parameters can be determined by the same method as employed in the case of the liquid Cu-Sn alloy, thus we have

\[
\begin{align*}
  w_R &= -23 \text{ kJ/mol} \\
  w_{AB} &= 3 \quad " \\
  w_{AR} &= 3 \quad " \\
  w_{BR} &= 28 \quad " 
\end{align*}
\]

\( \left( \frac{\rho}{\sigma} = 15 \right) \).

(20)
The concentration dependence of \( n_R/N \) calculated using the energy values of eq. (20) from the eq. (14) is given in Fig. 9, in which the \( n_R/N \) curve has a maximum

\[
\left( \frac{n_R}{N} \right)_{\text{max}} = 0.172 \text{ at } 25\% \text{ In.}
\]

Using the \( n_R/N \) curve of Fig. 9 and the energy values of eq. (20), the heat of mixing \( \Delta E \) is evaluated from eq. (15) and found to be in good agreement with the observation as shown in Fig. 4.

The observed curve of \( \Delta E \), as seen in Fig. 4, has a peak of heat evolution in the vicinity of 25% In and also a small maximum of heat absorption in the range of high concentration of In. Such a maximum of heat absorption results from the relatively large positive value of \( w_{AB} = \kappa_{AB} - 1/2(\kappa_{AA} + \kappa_{BB}) \). If, in this alloy, \( n_R = 0 \) and, hence, all Cu and In atoms are randomly mixed, it follows from eq. (15)

\[
\Delta E = \frac{N_A N_B}{N} w_{AB},
\]

therefore, we have a parabolic dependence of heat absorption upon concentration.

As stated previously, in the case of the liquid Cu-Bi alloy a random mixing
of Cu and Bi atoms is expected. Therefore, the heat of mixing will be given by eq. (21). In the above theory it is assumed for simplicity that constituent atoms A and B of a liquid alloy are of nearly the same atomic volume. However, in the case of the Cu-Bi liquid alloy, there is a marked difference between the atomic volumes of Cu and Bi. On the other hand the measurement of heat of mixing is performed not under the condition of a constant volume but of a constant number of atoms. The molar volume of the alloy depends upon the concentration of Bi. Therefore, $N_A/N$ and $N_B/N$ in eq. (21) must be replaced by volume fractions of A and B atoms. Thus, we have, in place of eq. (21),

$$\frac{\Delta E}{N} = \frac{N_A v_A - N_B v_B}{(N_A v_A + N_B v_B)^2} \bar{w}_{AB}$$

$$= \frac{N_A N_B v_B}{v_A} \frac{v_B}{v_A} \bar{w}_{AB}.$$  

If we put

$$\frac{N_A}{N} = 1 - x, \quad \frac{N_B}{N} = x \quad \text{and} \quad \frac{v_B}{v_A} = C,$$

then it follows

$$\frac{\Delta E}{N} = \frac{C x(1-x)}{(1+(C-1)x)^2} \bar{w}_{AB},$$  \hspace{1cm} (22)

where C denotes the volume ratio of Bi and Cu atoms. The heat of mixing calculated from eq. (22) for $C=1.5$ and $\bar{w}_{AB}=22 \text{ kJ/mol}$ is shown by closed circles in Fig. 3. Then eq. (22) gives a parabolic curve with a maximum at nearly 40% Bi and it is in good agreement with observed results.

V. On the flexible structure of pseudo-molecules

It is assumed in the above discussions that a pseudo-molecule has a flexible structure different from the rigid structure of a real molecule. This model is supported by many experimental results. If a pseudo-molecule has a definite structure, and if the structure actors $a(K)$ of the liquid alloys are determined by neutron scattering or X-ray scattering, a subpeak in a range of $K$ smaller than the position of the first peak will be found due to mutual interference between these molecules. But such a subpeak has not yet been observed even for near the maximum concentration of pseudo-molecule. From our studies on magnetic susceptibility it is shown that the number of localized electrons contributing to bonding of a pseudo-molecule is much less than the saturation number. This fact gives a basis for the supposition of a flexible structure to a pseudo-molecule.
Due to the number of unsaturated bonding electrons a pseudo-molecule is positively charged. If it is not of the size of type $A_nB$ molecules, but forms a cluster which contains large numbers of positive ions, it may be very unstable because of its high concentration of positive charge, and therefore will decompose into a number of particles of a size similar to that of a molecule.

In the calculations of $n_R$ and of the heat of mixing, the parameter $\rho/\sigma$ is assumed to be about 15. $\sigma$ is the symmetric number of a pseudo-molecule and $\rho = Z_1 \cdots Z_m$ is the number of possible configurations of Cu atoms occupying available positions on the reaction sphere of a central atom in a pseudo-molecule. However a pseudo-molecule has a flexible structure and therefore $\rho$ and $\sigma$ respectively are mean values for various configurations of atoms in the pseudo-molecule. This value of $\rho/\sigma$ is determined so that the calculated values of the heat of mixing are in good agreement with observed results.

**Summary**

1. The heat of mixing of liquid copper alloys has been measured within an error of ±4%.

2. In the liquid Cu-Bi alloy heat of absorption depends parabolically upon alloying composition. In this case Cu and Bi atoms are regarded as randomly arranged.

3. On the other hand, in the case of the liquid copper alloys Cu-Sb, Cu-Ge, Cu-Sn, and Cu-In observed heat of mixing exhibits a deep valley in the heat of evolution in the ranges of 75% to 80% Cu. In these alloys, some atoms are randomly mixed but other atoms associate into small groups of atoms similar to the type $A_nB$ molecules and are bound by a sort of covalent bond. The number of electrons contributing to the bonding in this pseudo-molecule is less than the saturation number. The pseudo-molecule has a flexible structure different from the rigid structure of a real molecule. The heat evolved on mixing is mainly due to the formation of this pseudo-molecule.

4. The partition function has been calculated for an assembly of randomly distributed A and B atoms and pseudo-molecules of the type $A_nB$. The condition for the minimum free energy derived from the above partition function gives the distribution of pseudo-molecules $n_R$ as a function of composition. Using this distribution curves of $n_R$ the relationship between the heat of mixing and alloying composition has been calculated and found to be in good agreement with the observed.

5. The heat of mixing curve of the liquid Cu-Bi alloy has been calculated with consideration for the large difference in the atomic volume between Cu and Bi. It gives a parabolic curve with a maximum at 40% Bi which is in good agreement with the observation.