CHAPTER 6

TEMPERATURE DEPENDENCE OF THE THERMODYNAMICAL PROPERTIES OF MOLTEN ALLOYS

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6.4 References
6.1 Introduction

What happens when the temperature is raised?
First, the liquid becomes more disordered and the stabilizing effect of the Madelung energy on the less metallic state decreases. Second, due to the increasing randomness of the potential, the band broaden [Anderson (1958)]. Both effects tend to increase $N(E_F)$ and the system becomes more metallic. A common and very striking feature is that the corresponding electronic properties like conductivity, thermopower, knight shift etc. exhibit a strong temperature dependence in such a way that metallic behaviour is recovered at high temperature [Holzhey et al (1984)], of course it is plausible that any structure in the electronic density of states of the alloy which may correspond to the observed anomalies should be washed out by increasing thermal disorder. Copestake et al (1983) have plotted the ordering potential $W(r)$ of Li$_4$Pb extracted from neutron diffraction data for several temperatures. They found that $W(r)$ decays fairly smoothly but not strongly temperature dependent. Copestake et al (1983) have also found that in order to explain the observed temperature dependence of $S_{cc}(q)$, it is necessary to assume that the charge transfer between the species decreases with increasing temperature. One possible explanation for LiPb type alloys may be as following. The strength of the chemical short-range order
is determined by the "ordering potential" -

\[ \mathcal{V}(r) = \Delta Q^2 e^2 \exp(-\lambda r)/r \]

divided by \( k_B T \) \((r<d)\). If the temperature is raised, \( \mathcal{V}(r)/k_B T \) and hence the chemical ordering becomes smaller. This leads to a decrease of the charge transfer \( Q \) and an increase of the screening parameter \( \lambda \) which, in turn leads to a further decrease of \( \mathcal{V}(r)/k_B T \) and so on. It is believed that such a feedback could be the reason for the strong temperature variation of the structural and electronic properties observed in alloys with partly ionic bonding type.

Let us now turn to the temperature dependence of the structure factors. The MSA and HNC results for \( S_{cc}(q) \) [Copestake et al (1983)] in the hard core model for different temperatures show that the main peak in \( S_{cc}(q) \) is reduced in a fashion which is consistent with experimental results. A decrease of charge transfer with increasing temperature would mean that the alloy becomes less 'ionic' at high temperatures. Evidence for this being the case comes from the measurements of electrical conductivity which increases very rapidly with increasing temperature.

Ruppersberg and Schirmacher (1984) have plotted \( \Delta H_{\text{ord}} \) (equation A7 of their paper) for liquid \( \text{Li}_4\text{Pb} \).
calculated at different temperatures from diffraction data. The slope of the linear regression in figure [Figure 2. Ruppersberg and Schirmacher (1984)] corresponds to an 'excess' specific heat of ordering $\Delta C_p^{\text{ord}}$ of 30 JK$^{-1}$ mol$^{-1}$ which is quite large but not unusual. This shows the strong temperature dependence of ordering potential with temperature. However for Li$_7$Ag$_3$ the value of $\Delta H^{\text{ord}}$ varies only slightly with temperature.

6.2 Effect of Temperature on the Volume of Mixing and Entropy of Mixing of Binary Alloys

The hard sphere system is a recent technique to understand the thermodynamic properties of liquid metal alloys [Umar et al 1976; Young 1977; Hafner 1977; Singh and Choudhary (1981)]. On the basis of structure factor evidence, most liquid metals behave quite like hard spheres. However, the anomaly exists in structure factor calculations exhibiting a low-lying shoulder on the first peak of the structure factor for liquids like Bi and Sn. Further, effective interatomic repulsions are softer particularly for alkali metals (Young 1977; McLaughlin and Young 1982). But the really interesting problem is the change in hard sphere parameters, mainly the change in volume for alloys having large size effects. So far, this theory has been applied to study the thermodynamic properties of simple alloys (non-compound forming).
systems. However, Hoshino and Young (1980) developed a theory for compound forming binary solutions in which the formation of molecules has been assumed. Recently, a semiempirical model for the concentration dependent volume of mixing was proposed to calculate the entropy of mixing of simple liquid mixtures (Chapter 3, Sec. 3.4) and of compound-forming alloys (Chapter 4). Here we investigate the effect of temperature on the compound formation of an alloy system. NaHg and NaGa are the two common examples of compound forming alloys. The properties of liquid NaHg alloys have been widely studied [Antoine (1967); Iverson and Recht (1967); Bartlett et al (1970); Faber (1972); Neale et al (1981); Ishiguro et al (1982); Tamaki et al (1982); Itami et al (1982)] and show the existence of NaHg\textsubscript{2} composition. The study on NaGa is very limited. Recent EMF measurements (Tamaki and Cusack (1979) predict the compound formation in NaGa liquid solution.

In order to observe the effect of temperature on the entropy of mixing, it is important to know the exact parameters to be used in the calculations. This is done by calculating the hard sphere parameters at different temperatures by using the experimental value of the entropy at those temperatures and the coefficient of thermal expansion. The estimated parameters are shown in Table 6.1.
TABLE 6.1: Input Parameters

<table>
<thead>
<tr>
<th>Alloy</th>
<th>T(K)</th>
<th>( \eta_1 )</th>
<th>( \eta_2 )</th>
<th>( \Omega_1 )</th>
<th>( \Omega_2 )</th>
<th>Expt. value of ( \Delta S^M ) at equiatomic concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHg</td>
<td>673</td>
<td>0.337</td>
<td>0.394</td>
<td>304.453</td>
<td>157.800</td>
<td>-0.4595</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>0.319</td>
<td>0.377</td>
<td>310.126</td>
<td>159.987</td>
<td></td>
</tr>
<tr>
<td>NaGa</td>
<td>843</td>
<td>0.298</td>
<td>0.379</td>
<td>316.426</td>
<td>139.599</td>
<td>-0.1957</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>0.286</td>
<td>0.370</td>
<td>321.385</td>
<td>140.554</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.266</td>
<td>0.356</td>
<td>330.087</td>
<td>142.229</td>
<td></td>
</tr>
</tbody>
</table>

The computed values of the entropy of mixing, for NaHg and NaGa at different temperatures are displayed in Figures 6.1(a,b) respectively. We find a close agreement with the experimental values of NaHg (Hultgren et al 1973) and a reasonable agreement with the experimental values of NaGa (Tamaki and Cusack 1979). The entropy of mixing curves plotted for ideal volume \( (\Delta \Omega = 0) \) of NaHg and NaGa solutions do not show the compound formation as also evident by the negative values of \( \Delta \eta \) throughout. It shows that the consideration of ideal volume in thermodynamic calculations is completely unjustified. It is also seen that the entropy of mixing has a strong temperature dependence and tends to be more positive with increase of temperature. This feature may be related to the compound forming effect and the possibility of compound formation may decrease with increasing temperature. Comparing the temperature effect on the two alloys NaGa and NaHg, it
Figure 6.1 (a) Concentration dependence of the entropy of mixing at different temperatures along with various contributions for the NaHg system at 673 K (-----) and 750 K (------) (x) experimental values [Hultgren et al. (1973a)] at 673 K. Calculations for ideal volume ($\Delta S_{\Omega = 0}$); (- - - - - - - -) for NaHg at 673 K.
Figure 6.1 (b) Concentration dependence of the entropy of mixing at different temperatures for the NaGa system. At 843 K (-----) at 900 K (--....--) at 1000 K (-.-.-.-), other contributions are not shown. (x) experimental values [Tamaki and Cusack (1979)] at 843 K. Calculations for ideal volume ($\Delta \Omega_0 = 0$); (-Δ-Δ-) for NaGa at 843 K.
is more dominant in the NaHg alloy. As one element (Na) is common to both alloys, it may be concluded that the large value of thermal expansion for Hg than for Ga causes a larger shifting in the entropy of mixing curve. Figure 6.1a for NaHg clearly shows that the dominant contribution to this shifting comes from the $\Delta S_1$ term. It is further noted that the temperature variation of $\Delta S^M$ on the Hg or Ga rich side is larger than that on the Na side as is also observed by EMF measurements [Ishiguro et al (1982)]. This fact suggests that there is an anomaly in the specific heat of an alloy and Kopp's law breaks down in alloys. Maximum change is observed at the compound forming composition. Similar features are also observed in the NaHg system by finding $C_p = T(\frac{\partial S}{\partial T})_P$ (section 6.3.3). Although we have no idea of the reason for this discrepancy at present it is worthwhile to consider that the anomaly is related to the gradual change in the structure with temperature (Takeda et al 1982). The explanation may be sought in terms of partial dissociation of compound formation with increasing temperature i.e. it may form the metallic cluster surrounded by similar and dissimilar media.

Figure (6.2 a,b) show that the change in packing fraction from ideality [$\Delta\eta = \eta - (C_1 \eta_1 + C_2 \eta_2)$] on alloying at different concentrations resulted in a decrease in $\Delta\eta$ with increasing temperature particularly at the compound-
Figure 6.2  (a & b) Concentration dependence of $\Delta \eta$ of liquid alloys of interest (a) NaHg system
(b) NaGa system. The notations are same as in figure 6.1.
Figure 6.3 (a & b) Concentration dependence of the fractional change in volume ($\Delta \Omega / \Omega$)
(a) NaHg system (b) NaGa system. The details are as in figure 6.1.
forming composition, showing a decrease in the possibility of compound formation with increasing temperature. The shifting of the volume of mixing curve upward i.e., increase in effective volume (Figures 6.3a,b) with increasing temperature also permit similar conclusions to those drawn from Figure (6.2). However, the composition of the compound forming mixture does not change with temperature.

The present work reflects the success of the hard sphere theory to describe the temperature effects in compound forming alloys and concludes that the possibility of formation of molecules/cluster decreases with increasing temperature, the reason for the decrease in compound formation is not well understood yet. However, the compound formation is very sensitive to temperature resulting in narrowing of the ordered region with increase of temperature as also reported by Franz et al (1982) for NaSb and CsSb alloys using the Green function technique.

6.3 Specific Heat of Binary Liquid Alloys
6.3.1 Introduction

The specific heat of liquid metals is well understood by using hard sphere system [Khanna (1983)] and Percus Yevick phonon theory [Ohkosi et al (1982)] but specific heat of binary liquid alloys is still a subject of interest and needs attention. So far, the ideal behaviour of specific
heat of an alloy is attributed, i.e. it varies linearly between the pure component values [Kopp's law]. Recent experiments performed by Neale et al (1981), Ishiguro et al (1982) and Matsunaga et al (1983) show serious departures from the Kopp's law even at small concentrations. As far as we know, there is no theory that describes the specific heat of the binary alloys accurately in hard sphere system. Thus, it is of the current interest to examine how far the alloy confirms the Kopp's law over the whole concentration range. In the present investigation a semiempirical model based on the hard sphere system is developed to describe the specific heat of an alloy system.

6.3.2 Formulation

Let us consider a binary solution with components of atomic concentrations $C_1$ and $C_2$ comprising $C_1N$ hard spheres with diameter $\sigma_1$ each and $C_2N$ with diameter $\sigma_2$ each. Following Visser et al (1980) and Yokoyama et al (1977) the entropy of the binary mixture of hard spheres can be written as

$$S_{hs} = S_{gas} + S_\eta + S_\sigma$$  \hspace{1cm} (6.1)

The various terms for the entropy appearing on the right side of equation (6.1) are already explained in section (3.2).
The specific heat at constant pressure \( C_p = T \left( \frac{\partial S}{\partial T} \right)_p \) is described by:

\[
C_p = T \left( \frac{\partial S_{\text{gas}}}{\partial T} \right)_p + T \left( \frac{\partial S_1}{\partial T} \right)_p + T \left( \frac{\partial S_C}{\partial T} \right)_p + T \left( \frac{\partial S_{\text{r}}}{\partial T} \right)_p \tag{6.2}
\]

We now examine the various terms of equation (6.2) one by one.

The first term is given by

\[
\frac{S_{\text{gas}}}{N k_B} = 2.5 + \ln \left[ \Omega (m_1 m_2 k_B T / 2\pi h^2)^{3/2} \right] \tag{6.3}
\]

\[
\frac{1}{N k_B} \left( \frac{\partial S_{\text{gas}}}{\partial T} \right)_p = \frac{3}{2T} + \frac{1}{\Omega} \left( \frac{d\Omega}{dT} \right)_p \]

\[
= \frac{3}{2T} + \alpha_T \tag{6.4}
\]

\( \alpha_T \) represents the coefficient of thermal expansion of the alloy system, which in turn, can be calculated by the linear variation of the coefficients of thermal expansion \( \alpha_1 \) and \( \alpha_2 \) of two elements comprising an alloy.

\[
\alpha_T = C_1 \alpha_1 + C_2 \alpha_2 \tag{6.5}
\]

The actual feature [Figure 7, Neale et al (1982)] exhibited by coefficient of thermal expansion of an alloy is different from equation (6.5) that is used due to lack of experimental data. However, that too hardly affects the
results [Neale and Cusack (1982)].

The second term of equation (6.1), the total packing fraction term, is given by

\[
\frac{S_\eta}{N K_B} = -(\xi - 1)(\xi + 3) \text{ with } \xi = \frac{1}{(1-\eta)}
\]  

(6.6)

It follows that

\[
\frac{1}{N K_B} \left( \frac{\partial S_\eta}{\partial T} \right) = -2\left(\frac{1-\eta}{1-\eta}\right)^3 \left( \frac{d\eta}{dT} \right)
\]

(6.7)

where \( \eta \) is the packing fraction of the alloy system and can be written as

\[
\eta = \frac{\pi}{6V} (C_1 \sigma_1^3 + C_2 \sigma_2^3) = \frac{1}{V} (\eta_1 \Omega_1 + \eta_2 \Omega_2)
\]

(6.8)

the atomic volume \( \Omega \) of the binary solution, different from ideal volume, is determined by the procedure described in the section (3.4). Using this procedure, we obtain the packing fractions over the whole composition range. The value of \( \frac{d\eta}{dT} \) can be computed by using an empirical relation [Khanna (1981), (1983)]

\[
\eta = 0.56 - \alpha \frac{T}{T_m}
\]

(6.9)

where \( \alpha \) is an adjustable parameter to fit the packing fraction of an alloy at its melting temperature. The
validity of equation (6.9) has also been tested for liquid metals by comparing the packing fraction at different temperatures with those obtained by fitting the entropy at different temperatures. [Khanna and Shanker (1985)].

From equation (6.9) it follows that

\[
\frac{1}{Nk_B} \frac{\partial S}{\partial T} p = \frac{2(2 - \eta)}{(1 - \eta)^3} \frac{\alpha}{T_m}
\]  

(6.10)

Third term, the ideal entropy of mixing term is concentration dependent term and is given by

\[
\frac{S_C}{NK_B} = -C_1 \ln C_1 - C_2 \ln C_2
\]  

(6.11)

hence

\[
\frac{1}{Nk_B} \frac{\partial S_C}{\partial T} p = -(1 + \ln C_1) \frac{\partial}{\partial T} \left( \frac{\Omega_2}{\Omega_1 + \Omega_2} \right) - (1 + \ln C_2) \frac{\partial}{\partial T} \left( \frac{1}{\Omega_1 + \Omega_2} \right)
\]

since

\[
\frac{\partial}{\partial T} \left( \frac{\Omega_1}{\Omega_1 + \Omega_2} \right) = \frac{\alpha_1 \Omega_1}{\Omega_1 + \Omega_2} - \Omega_1 \left( \frac{\alpha_1 \Omega_1 + \alpha_2 \Omega_2}{(\Omega_1 + \Omega_2)^2} \right)
\]

hence

\[
\frac{1}{Nk_B} \frac{\partial S_C}{\partial T} p = \frac{\alpha_1 \Omega_1 + \alpha_2 \Omega_2}{(\Omega_1 + \Omega_2)^2} \left( \Omega_1 \ln C_2 + \Omega_2 \ln C_1 \right)
\]

\[
- \frac{\alpha_1 \Omega_1 \ln C_2 + \alpha_2 \Omega_2 \ln C_1}{(\Omega_1 + \Omega_2)}
\]  

(6.12)

Fourth term, the mismatch term between the hard spheres due to different diameters \( \sigma_1 \) and \( \sigma_2 \) is considered as...
[Hoshino (1980)]

\[
\frac{S\sigma}{NK_B} \propto C_1C_2 (\sigma_1 - \sigma_2)^2 \quad (6.13)
\]

Hence

\[
\frac{1}{NK_B} \left( \frac{\partial S\sigma}{\partial T} \right)_p = \frac{2S\sigma}{(\sigma_1 - \sigma_2)} \left[ \frac{d\sigma_1}{dT} - \frac{d\sigma_2}{dT} \right]_p \quad (6.14)
\]

Now, by using the relation \( \eta_i = \pi \sigma_i^3 / 6 \Omega_i \), we find that

\[
\frac{d\sigma_i}{dT}_p = \frac{1}{3} \sigma_i \left[ \frac{1}{\eta_i} \left( \frac{d\eta_i}{dT} \right)_p - \frac{1}{\Omega_i} \left( \frac{d\Omega_i}{dT} \right)_p \right]
\]

\[
= \frac{1}{3} \sigma_i \left[ -\frac{1}{\eta_i} \frac{\alpha_i}{T_m} + \alpha_{T,i} \right] \quad (6.15)
\]

Thus the deviation from its ideal behaviour can be obtained as

\[
\frac{\Delta C_p}{NK_B} = C_{p,\text{alloy}} - C_{p,\text{ideal}} \quad (6.16)
\]

with

\[
C_{p,\text{ideal}} = C_1 \cdot C_{p,1} + C_2 \cdot C_{p,2}
\]

\( C_{p,1} \) and \( C_{p,2} \) represent the specific heats of the individual components of an alloy system.
6.3.3 Calculation of Sp-heat of Binary Liquid Alloys

The specific heat defined by equation (6.2) may now be used to apply for certain alloy solutions. We intend to examine the Kopp's law for a wider class of homovalent and heterovalent alloys, NaHg, MgZn, CdSn and LiPb to ensure the valid application for our model. The specific heat calculation requires the effective packing fraction on mixing as input information that depends upon the effective volume on mixing [equation (6.8)]. Therefore, we evaluate the volume of mixing across the whole composition range by fitting the entropy of mixing to its experimental value at equiatomic concentration. In the present work the same approach is followed and requires no repetition. However, the parameters used in the calculations are displayed in Table (6.2) that are obtained by fitting the entropy of the constituent elements (Hultgren et al 1973) for LiPb and NaHg while for CdSn and MgZn are taken from elsewhere [Singh and Choudhary (1981)].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temp (K)</th>
<th>Ω₁ (a.u.)</th>
<th>Ω₂ (a.u.)</th>
<th>η₁</th>
<th>η₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiPb</td>
<td>800</td>
<td>151.38</td>
<td>218.05</td>
<td>.449</td>
<td>.334</td>
</tr>
<tr>
<td>NaHg</td>
<td>673</td>
<td>304.45</td>
<td>157.80</td>
<td>.310</td>
<td>.370</td>
</tr>
<tr>
<td>CdSn</td>
<td>773</td>
<td>158.80</td>
<td>198.236</td>
<td>.447</td>
<td>.462</td>
</tr>
<tr>
<td>MgZn</td>
<td>923</td>
<td>171.49</td>
<td>111.59</td>
<td>.483</td>
<td>.489</td>
</tr>
</tbody>
</table>
As shown in Fig. (6.4) a large deviation from the law of
additivity of the specific heats of the components (Kopp's
law) has been found. The general feature exhibited by $\Delta C_p$
curves is the maximum value around equiatomic concentration.
In fact, the packing fraction and the atomic volume of
an alloy are the most influential in determining the change
of $C_p$ on mixing and the discussions on $\Delta C_p$ are mostly
centred around the relative role of packing fractions of
the components and the packing fraction of the mixture.
Thus we can say that excess volume indirectly, plays an
important role in the variation of $C_p$ from its ideal
behaviour as we are aware of its importance in the determi-
nation of other thermodynamical properties [Harder et al
(1980); Bhatia and Singh (1980); Elwenspock (1983),
Hultgren et al (1973)]. All the values of $\Delta C_p$ are negative
and increase with increasing atomic volume difference between
components. Figure (6.4) gives a comparison of $\Delta C_p$ with
experimental values [Hultgren et al (1973)] for CdSn. The
experimental informations regarding $\Delta C_p$ for liquid alloys
are very meagre. In comparison with solid alloys that
is available for MgZn [Hultgren et al 1973], we may
infer that the violation of Kopp's law is more dominant in
liquid alloys. Further, the plots of $\Delta C_p$ with respect to
concentration are asymmetric about the mean concentration
value ($C_1 = C_2 = 0.5$). This phenomenon is seen to be
associated with the volumes of the constituent elements; in
Figure 6.4 Concentration dependence of $\Delta C_p$ for four liquid binary alloys; LiPb (800 K); NaHg (673 K); CdSn (773 K) and MgZn (923 K). Crosses (x) represent the experimental values for CdSn alloy [Hultgren et al (1973)].
the present cases as $Q_1/Q_2 > 1$, the maximum occurs at $c_1 < 0.5$ and vice versa. Similar trend is observed in the shifting of $\Delta \eta (\Delta \eta = \eta - \eta_{\text{ideal}})$. Figure (6.4) also gives that the magnitude of $\Delta C_p$ increases with increasing difference between atomic volumes. The maximum observed around $\text{NaHg}_2$ and $\text{Li}_4\text{Pb}$ is a special feature. It reveals that the excess specific heat ($\Delta C_p$) is closely associated with the structural change and the departure from the law of additivity may be related with the gradual change in the structure with temperature. The similar features have been observed while investigating the effect of temperature on the entropy of mixing [section (6.2)].

Figure [6.5 (a to d)] depicts the composition dependence of all the four terms contributing to specific heat for $\text{LiPb, NaHg, MgZn and CdSn alloys}$. The contribution of the $T(\frac{\partial S}{\partial T})_p$ and $T(\frac{\partial C}{\partial T})_p$ to specific heat is very small while the influence of $T(\frac{\partial \eta}{\partial T})_p$ is dominant and is mainly responsible for the nonlinearity of $C_p$. 
Figure: 6.5 (a to d) Concentration dependence of various contributions to specific heat for four liquid binary alloys.

Crosses (x-x) $T (\partial S_{\text{gas}} / \partial T)$: Open circles (o-o-o) $T (\partial S_{\eta} / \partial T)$: Squares (□—□—□) $T (\partial S_{\phi} / \partial T)$ and triangles (Δ—Δ—Δ) $T (\partial S_{c} / \partial T)$.

LiPb

NaHg
Figure: 6.5 (c)
6.4 References


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Umar I.H., Yokoyama I. and Young W.H., Phil. Mag. 34, 535 (1976).