THERMODYNAMIC PROPERTIES OF BINARY ALLOYS EXHIBITING MISCIBILITY IN SOLID AND LIQUID PHASES

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INTRODUCTION

Most of the methods (Chipman, 1948) used for determining activities in solutions can also be used for determining the same in the alloys. The more significant methods are those involving measurement of vapour pressures of alloys and E.M.F.'s of suitable cells. Due to comparatively high vapour pressure of mercury the first method is specially well adopted to the study of amalgams. Other methods which are not so general are also often employed. Thus the activity of the volatile component when the second is non-volatile may be determined from the boiling point of the solution. The distribution method makes use of the fact that when a solute is distributed between two immiscible solvents, the state of equilibrium at constant temperature is characterised by a constant ratio of the activity in one phase to that in the other. Activity can also be determined from studies of chemical equilibrium.

Phase equilibrium data can be used for obtaining similar thermodynamic information (Rastogi and Rama Varma, 1956, 1957, 1958). Seltz has described a method for computing ideal solidus and liquidus curves for binary alloys exhibiting complete miscibility in solid and liquid phases (Seltz, 1934). This procedure was later on extended to regular solutions (Scatchard and Hamer, 1935). For such alloys Wagner has derived formulae to calculate excess integral molar-free energies of the solid and the liquid phase from phase diagrams (Wagner, 1954). In spite of the value of phase diagrams, no efforts have been made to deduce thermodynamic properties for mixtures which are non-ideal and non-regular, including unsymmetrical regular mixtures.

In the present paper thermodynamic properties of nickel-manganese alloys are determined from phase diagram. The system is unsymmetrical
regular, \textit{i.e.}, the activity coefficients are unsymmetrical function of mole-fractions.

\textbf{Equations for the Slopes of Solidus and Liquidus Curves}

It has been observed that in a large number of cases the excess thermodynamic functions can be expressed as power series in \((x_2 - x_1)\), (Scatchard, Ticknor, Goates and McCartney, 1952; Scatchard and Westlund, 1953) where \(x_1\) and \(x_2\) are the mole-fraction of component 1 and 2. Thus the heat of mixing is often given by an expression of the form

\[
H^E = x_1 x_2 \left[ A + B (x_2 - x_1) + C (x_2 - x_1)^2 + \ldots \right]
\]  

where \(A\), \(B\), and \(C\) are constants. This is so even in the case of metallic systems such as cadmium-magnesium alloys. By using the recent data (Trumbore, Wallace and Craig, 1952) we find that the excess chemical potentials (in cal./gm.-atom.) of the two components in the cadmium-magnesium alloys at 270\(^\circ\)C are approximately given by the following equations

\[
\begin{align*}
\mu_1^E &= x_2^2 \left[ -4501 + 77\cdot8 (1 - 4x_1) + 1053 (1 - 2x_1) (1 - 6x_1) \right] \\
\mu_2^E &= x_1^2 \left[ -4501 + 77\cdot8 (3 - 4x_1) + 1053 (1 - 2x_1) (5 - 6x_1) \right]
\end{align*}
\]  

The heat of mixing (in cal./gm.-atom) of the solid alloy at 270\(^\circ\)C is given by the equation

\[
H^E = x_1 x_2 \left[ -7752 - 2278 (x_2 - x_1) + 3930 (x_2 - x_1)^2 \right]
\]  

The constants \(A\), \(B\), \(C\), etc., in equation (1) may depend upon temperature. In view of the uncertainties in the observed solid-liquid equilibrium data, it is rather difficult to determine their temperature dependence. Accordingly we shall assume in the present paper that these constants are independent of temperature. This has been found to be the case for Cd-Mg alloy and also for certain liquid alloys such as Bi-Pb, Cd-Pb and Pb-Sn.

The equations for slopes are easily derived if we simply assume that the activity coefficients are given by

\[
\begin{align*}
RTlny_1 &= x_2^2 \left[ A + B (1 - 4x_1) + C (1 - 2x_1) (1 - 6x_1) \right] \\
RTlny_2 &= x_1^2 \left[ A + B (3 - 4x_1) + C (1 - 2x_1) (5 - 6x_1) \right]
\end{align*}
\]  

where the Gibbs-Duhem equation is satisfied automatically. For a system consisting of two components involving solid-liquid equilibrium, the change in temperature is related to the change in composition according to following equation (Rastogi, 1955):
\[-\{x_1^s (s_1^l - s_1^s) + x_2^s (s_2^l - s_2^s)\} \, dT\]
\[= - \left\{ x_1^s \left( \frac{\partial \mu_1^s}{\partial x_1^s} \right)_{T, P} + x_2^s \left( \frac{\partial \mu_2^s}{\partial x_2^s} \right)_{T, P} \right\} \, dx_1^l \]  
(5)
and
\[-\{x_1^l (s_1^l - s_1^s) + x_2^l (s_2^l - s_2^s)\} \, dT\]
\[= \left\{ x_1^l \left( \frac{\partial \mu_1^l}{\partial x_1^l} \right)_{T, P} + x_2^l \left( \frac{\partial \mu_2^l}{\partial x_2^l} \right)_{T, P} \right\} \, dx_1^s \]  
(6)
where the superscripts \(s\) and \(l\) refer to the solid and liquid phase respectively and the subscripts 1 and 2 refer to the respective components. \(s\) represents the partial molar entropy and \(\mu\) is the chemical potential which is given by
\[\mu_i = \mu_i^0 (T, P) + RT \ln x_{wi} \quad (i = 1, 2) \]  
(7)
Using equations (4) and (7), equations (5) and (6) yield for unsymmetrical regular mixtures
\[\frac{dx_1^l}{dT} = \frac{x_1^s \triangle h_1^0 + x_2^s \triangle h_2^0 - x_1^s x_2^s [x_2^s M^s + x_1^s N^s] + x_1^s (x_2^l)^2 M^l + x_2^s (x_1^l)^2 N^l}{RT^2 \left( \frac{x_1^l}{x_1^s} - \frac{x_2^s}{x_2^l} \right) - 2T \left( x_1^s x_2^l - x_2^s x_1^l \right) P^l} \]  
(8)
and
\[\frac{dx_1^s}{dT} = \frac{x_1^l \triangle h_1^0 + x_2^l \triangle h_2^0 + x_1^l x_2^l [x_1^l M^l + x_1^s N^l] - x_1^l (x_2^s)^2 M^s - x_2^l (x_1^s)^2 N^s}{RT^2 \left( \frac{x_2^l}{x_2^s} - \frac{x_1^s}{x_1^l} \right) - 2T \left( x_2^s x_1^l - x_1^s x_2^l \right) P^s} \]  
(9)
where \(\triangle h^0\) is the heat of fusion and
\[M = A + B (1 - 4x_1) + C (1 - 2x_1) (1 - 6x_1)\]
\[N = A + B (3 - 4x_1) + C (1 - 2x_1) (5 - 6x_1)\]
\[P = A + 3B (1 - 2x_1) + C (5 - 24x_1 + 24x_1^2)\]
with the proper suffixes.

Selzt's procedure can be very conveniently used for testing the ideality of a system or predicting the ideal phase boundaries but sometimes it is not able to give us any idea of the magnitude of the deviations from ideality. By comparing the experimental slopes of the phase boundaries with those calculated by the equations (Rastogi, 1955)
\[\frac{dx_1^l}{dT} = \frac{x_1^s \triangle h_1^0 + x_2^s \triangle h_2^0}{RT^2 \left( \frac{x_1^l}{x_1^s} - \frac{x_2^s}{x_2^l} \right)} ; \]
\[\frac{dx_1^s}{dT} = \frac{x_1^l \triangle h_1^0 + x_2^l \triangle h_2^0}{RT^2 \left( \frac{x_2^l}{x_2^s} - \frac{x_1^s}{x_1^l} \right)} \]  
(10)
which hold for ideal solutions, it is possible to get an idea of these magnitudes. Thus, copper-nickel alloy which has frequently been cited as an example of ideal solid solutions (Prigogine and Defay, 1954) is found to be markedly non-ideal (Rama Varma, 1957).

From the usual methods of thermodynamics (Prigogine and Defay, 1954) we have,

\[-\ln \frac{x_i^{L} \gamma_i^{L}}{x_i^{S} \gamma_i^{S}} = \frac{\Delta f h_i^0}{R} \left(\frac{1}{T} - \frac{1}{T_i^0}\right) + \Delta f C_{p,i}^0 \left(\ln \frac{T_i^0}{T} + 1 - \frac{T_i^0}{T}\right)\]  

(i = 1, 2)  

(11)

where \(\Delta f C_{p,i}^0\) represents the difference in specific heats of the solid and the liquid phases of the pure component 'i'; \(T_i^0\) is the melting point of the pure component 'i'. From the above equation, the ratio of activity coefficients corresponding to different compositions of the phases at the solidus or liquidus temperature can be calculated. It is not possible to determine the excess thermodynamic properties unless the dependence of the activity coefficients on temperature and composition is known.

For non-ideal mixtures but conforming to unsymmetrical regular behaviour it is possible to evaluate the constants A, B and C by using equations (11). The values of the slopes can be calculated by using these constants and can be compared against the experimental values. This can afford to serve as a method for checking the internal consistency of the data. Once these constants are known, all the excess thermodynamic properties can be computed.

In this paper we shall examine the phase equilibrium data for nickel-manganese alloys in order to compute heat of mixing for solid as well as liquid alloys.

**ANALYSIS OF PHASE DIAGRAMS OF NICKEL-MANGANESE ALLOYS**

For this system which shows a minimum, recently reliable data has been obtained by Hume-Rothery and Coles (Hume-Rothery and Coles, 1951). Equations (11) when applied to the data give the following values (in cal./gm.-atom) for the constants:

\[A^s = -14500; \quad B^s = -3200; \quad C^s = -1300.\]
\[A^l = -1500; \quad B^l = -4300; \quad C^l = -300.\]

Using these constants the slopes can be calculated which can be compared with the observed values. This is done in Table I.

For the sake of mere comparison, ideal slopes are also given.
Table I

Nickel-manganese alloys

\[ \Delta h_f^0 = 3560 \text{ cal./gm.-atom}; \quad \Delta h_f^0 = 4302 \text{ cal./gm.-atom} \]

<table>
<thead>
<tr>
<th>Temp. K.</th>
<th>( x_1 )</th>
<th>( x_2 )</th>
<th>( \frac{dx_1}{dT} \times 10^4 )</th>
<th>( \frac{dx_2}{dT} \times 10^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1673</td>
<td>0.055</td>
<td>0.076</td>
<td>-10.0</td>
<td>-10.0</td>
</tr>
<tr>
<td>1623</td>
<td>0.102</td>
<td>0.132</td>
<td>-10.0</td>
<td>-10.0</td>
</tr>
<tr>
<td>1573</td>
<td>0.152</td>
<td>0.188</td>
<td>-10.0</td>
<td>-10.0</td>
</tr>
<tr>
<td>1523</td>
<td>0.203</td>
<td>0.242</td>
<td>-10.5</td>
<td>-11.0</td>
</tr>
<tr>
<td>1473</td>
<td>0.256</td>
<td>0.300</td>
<td>-11.0</td>
<td>-10.5</td>
</tr>
<tr>
<td>1423</td>
<td>0.317</td>
<td>0.358</td>
<td>-13.0</td>
<td>-13.0</td>
</tr>
<tr>
<td>1373</td>
<td>0.386</td>
<td>0.422</td>
<td>-14.5</td>
<td>-18.0</td>
</tr>
<tr>
<td>1323</td>
<td>0.468</td>
<td>0.505</td>
<td>-20.0</td>
<td>-24.0</td>
</tr>
<tr>
<td>1273</td>
<td>0.765</td>
<td>0.728</td>
<td>+22.0</td>
<td>+22.0</td>
</tr>
<tr>
<td>1323</td>
<td>0.856</td>
<td>0.806</td>
<td>+16.0</td>
<td>+13.0</td>
</tr>
<tr>
<td>1473</td>
<td>0.928</td>
<td>0.882</td>
<td>+11.0</td>
<td>+9.0</td>
</tr>
<tr>
<td>1473</td>
<td>0.976</td>
<td>0.955</td>
<td>+4.0</td>
<td>+8.0</td>
</tr>
</tbody>
</table>

The constants A, B, etc., can depend upon temperature. However, for the sake of simplicity it is assumed that these are independent of temperature in the temperature range considered. This in effect means that the excess heat capacity of the alloys is zero. This result also follows from the empirically observed rule of Kopp and Neumann according to which the specific heats of alloys are linear combination of the specific heats of the constituent metals. The relation is found to hold in alloys to within 5 or 10%. Deviations from this law are expected to occur at low temperatures. In the above
calculation it was not possible to take into account the temperature dependence of heats of fusion owing to the lack of heat capacity data for the two phases.

As there is a maximum possible error of ±2% in reading the mole-fraction from the graphs it can be shown that there is maximum possible error of ±10% in the computed value of the constants and a maximum possible error of ±20% in the calculated values of the slopes. Hence the agreement between the calculated and observed values of the slopes should be considered as quite good if the percentage difference between them is within this amount. Table I clearly shows that barring the region near the melting point where the slightest error in the phase boundary is material, the agreement is satisfactory and points out the internal consistency of the data.

The heat of mixing can be readily calculated and is given in Table II.

**TABLE II**

<table>
<thead>
<tr>
<th>Solid phase</th>
<th>Liquid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_i^s$</td>
<td>$H^s$</td>
</tr>
<tr>
<td></td>
<td>(cal./gm.-atom)</td>
</tr>
<tr>
<td>0.1</td>
<td>-1600.0</td>
</tr>
<tr>
<td>0.2</td>
<td>-2700.0</td>
</tr>
<tr>
<td>0.5</td>
<td>-3600.0</td>
</tr>
<tr>
<td>0.8</td>
<td>-2100.0</td>
</tr>
<tr>
<td>0.9</td>
<td>-1150.0</td>
</tr>
</tbody>
</table>

**DISCUSSION**

From Table II, it is clear that the heat of mixing in the two phases for similar composition is the same. Similar behaviour is observed in mixtures of diphenylacetylene and trans-stilbene (Rastogi and Nigam, 1958). In the present case the entropy of mixing would be ideal since the constants A, B and C are independent of temperature. Thus the distribution of nickel atoms in manganese or manganese atoms in nickel would
be perfectly random in both the phases. When an alloy is formed between two metals, the heat of formation will depend on:

(i) The redistribution of valence electrons and the energy changes associated with it.

(ii) The size of the constituent atoms and the resulting strain energy.

(iii) The change in the interaction between the underlying filled shells of the electrons in the ion.

(iv) Brillouin zone effect.

Recently Varley has used a model for calculating heats of formation of concentrated solid solution which is hybrid between the quantum-mechanical approach of Sommerfeld and the wave-mechanical Cellular method of Weigner and Seitz (Varley, 1954). The theoretical treatment shows that the contribution of the first factor to heat of mixing is always negative or zero. The effect of second factor is always positive or zero. The influence of other factors on heat of mixing is not significant.

In the present case the heat of mixing is found to be negative in both the phases which suggests that in nickel-manganese alloys, only the first factor predominates. The influence of the redistribution of valence electrons is likely to be the same in both the phases and hence the heat of mixing has got the same magnitude.

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**Summary**

Excess thermodynamic functions are computed from phase diagram of nickel-manganese alloys exhibiting complete miscibility in solid and liquid phases. A method is outlined for testing the internal consistency of the data. Heat of mixing of solid and liquid alloys is found to be similar. It is concluded that the redistribution of valence electrons in the alloy is responsible for negative heat of mixing.

**References**


Binary Alloys Exhibiting Miscibility in Solid and Liquid Phases


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