# ON SOME SPECIAL BEHAVIOR OF THE THERMODYNAMIC FUNCTIONS FOR THE BINARY METALLIC SOLUTIONS

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In the previous paper, the authors have presented some experimental data on the thermodynamic properties of the binary systems Cd-Sn,[1] Zn-Cd[2] and Zn-Sn,[2] as the partial report of the investigation of the ternary liquid solution Zn-Cd-Sn.

The purpose of the present work is to study the general behavior of the thermodynamic functions for the binary solutions on the basis of these experimental data reported.

## 1. On the behavior of the entropy

The entropies of mixing in each one of the binary liquid systems, having no intermetallic compounds in the solid state, are shown as a function of $\ln N$ in Fig. 1-*a* and 1-*b* graphically.

This type of the plot used by Chipman[3] was used as a convenient method for representation of the deviation from the ideal relation and the characteristics with regard to the entropy curves.

From these representations, it is found that the relations for the system Zn-Sn are nearly linear, that is to say,

$$\Delta\bar{S}_{Zn} = -D \ln N_{Zn}, \tag{1}$$

where $D$ is constant, and the similar relations for the system Cd-Sn have a slight curvature. It is of particular interest to note that the deviation from the ideal relation for the system Zn-Sn is sufficiently the same order in magnitude as the one for the system Zn-Bi[4] and also the system Cd-Sn behaves the same as the system Cd-Bi[5] with relation to this representation. For lead alloys, in which the one system has intermediate phase in the solid state but the other system has not it, it is found that from the experimental results by Chipman and Elliott[6] for the ternary system Cd-Pb-Sn, the system Pb-Sn shows so small negative deviation that the behavior of the system may be considered approximately ideal within experimental and computational uncertainties, and also the relation for the system Pb-Bi obtained from the experimental values by Strickler and Seltz[7] is nearly ideal.

In Fig. 1-*c*, the curves for the systems which exhibit intermetallic compound formation in the solid state have somewhat complex forms. The partial molal entropy $\Delta\bar{S}_{Bi}$ in the system Au-Bi[8] shows a slight difference from $\Delta\bar{S}_{Sn}$ in the system Au-Sn,[9] but, with relation to the deviation from the ideal relation, these two values are considered approximately to be equal.

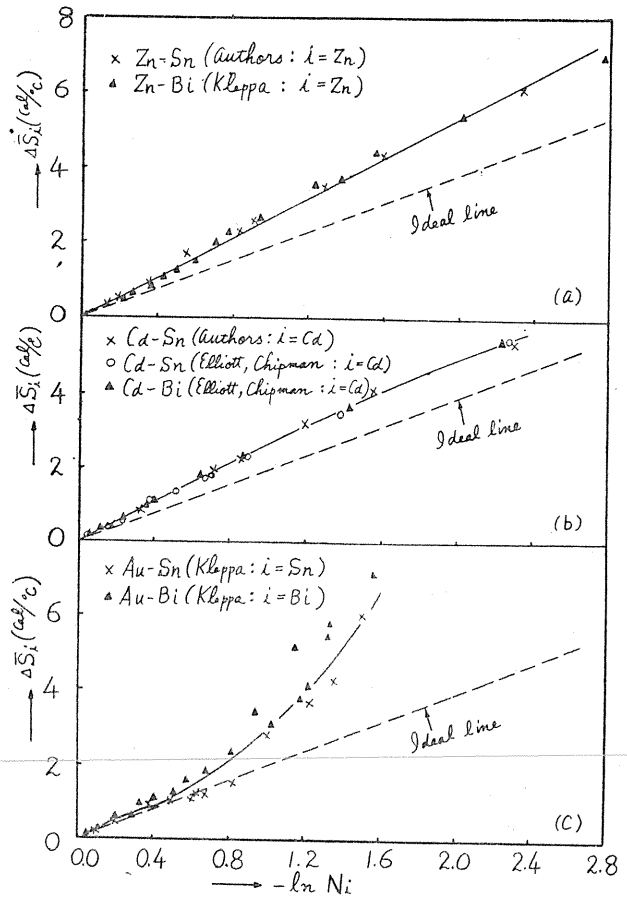


FIG. 1. The relations between $\Delta\bar{S}_i$ and $-\ln N_i$.

From the considerations for the Zn-, Cd-, Pb-systems, and Au-systems, it can be safely concluded that Bi and Sn behave equivalently with respect to the entropy for binary solutions. However, this characteristic of the components Sn and Bi is not seen for the partial molal heat contents of those components.

Of course, there is a clear need for more extensive measurements regarding to the systems containing those components.

In addition, it is desirable to call attention to the fact that the system Bi-Sn[10] is the ideal solution, in which there is no heat of mixing and no excess entropy.

### 2. On the behavior of the free energy

A regular solution is defined as one which possesses the ideal entropy of mixing due to maximum randomness. The activity coefficient of the binary regular solution is expressed in the following equation which is derived from statistical mechanics,

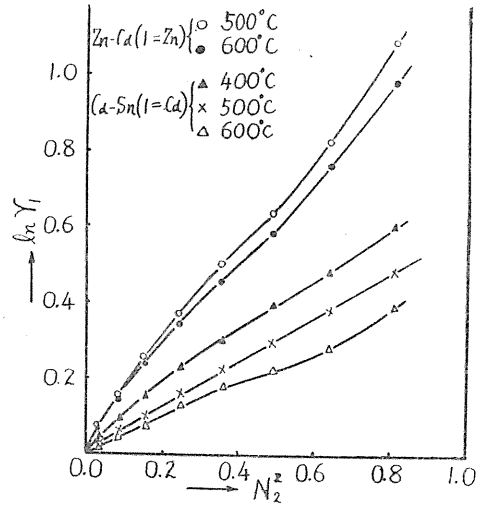


FIG. 2. The relation between $\ln r_1$ and $N_2^2$ (by authors).

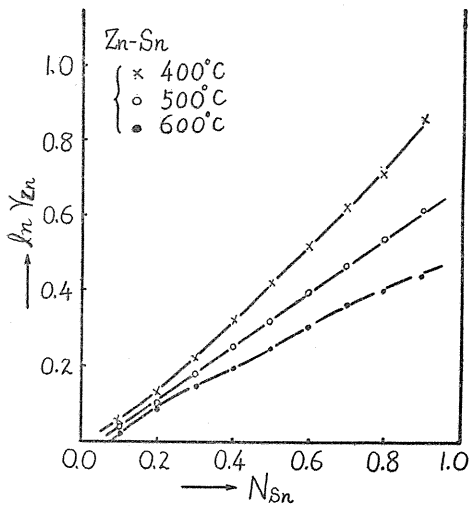


FIG. 3. The relation between $\ln r_{Zn}$ and $N_{Sn}$ (by authors).

$$RT \ln \frac{a_1}{N_1} = RT \ln r_1 = BN_2^2, \tag{2}$$

where the constant $B$ is independent of the concentration.

The logarithm of the activity coefficient $r_1$ is plotted against the square of the mole fraction $N_2$ in Fig. 2.

In the system Zn-Cd, the plot is approximately linear, establishing the fact that this system is nearly one of the regular solution and its linearity does not vary with temperature.

On the other hand, it is interesting that a plot of $\ln r_{Cd}$ against $N_{Sn}^2$ in the system Cd-Sn is linear at 500° C just as in the regular solution, but there is a departure from linearity as temperature varies far from 500° C.

The system Zn-Sn is similar in the relation between the activity coefficient and the mole fraction to the system Cd-Sn and has the following linear relation at 500° C:

$$RT \ln \frac{a_{Zn}}{N_{Zn}} = RT \ln r_{Zn} = AN_{Sn} + C, \tag{3}$$

where $A$ and $C$ are constants.

However, from Fig. 3, we see in some detail that the relation between $\ln r_{Zn}$ and $N_{Sn}$ deviates from linearity more or less as the temperature departs from 500° C.

### 3. Entropy from the solubility curve of phase diagram

It may be useful to illustrate the application of above relations by considering some special systems. We accordingly discuss two such examples. For the systems Zn-Sn[11] and Cd-Sn,[12] in which the solid solubility of either metal in the other is

very small, it is possible to determine the activity in the liquid solutions from the liquidus curves.

The methods adopted are based on the following well-known principle; if the liquid and solid phases are in equilibrium, the activities of each component are equal in both the phases. For these calculations, the free energies of fusion of the two components are needed.

According to reference,[13] heat of fusion of zinc is found to be 1,595 cal. and that of cadmium is 1,460 cal.. Combining with the heat capacity data recommended by Kelley,[14] the free energies of fusion are given by

$$\mathrm{Zn(S)} = \mathrm{Zn(l)} \qquad F = 490 - 2.34\,T\ln T + 1.075 \times 10^{-3}\,T^2 + 13.860\,T \tag{4}$$

$$\mathrm{Cd(S)} = \mathrm{Cd(l)} \qquad F = 903 - 1.67\,T\ln T + 1.233 \times 10^{-3}\,T^2 + 8.415\,T \tag{5}$$

From equations (4) and (5), the activity of the pure solid relative to the pure liquid taken as the standard state, is calculated.

In order to determine the thermodynamic quantities from the phase diagrams, we have to make one assumption regarding to the dependence of these quantities on concentrations.

It is found that the excess partial molal entropy of zinc in the system Zn-Sn changes with concentration in accordance with the equation $\Delta\bar{S}^E_{Zn} = -D' \ln N_{Zn}$, where $D'$ is constant. In the system Cd-Sn, this relation holds under limiting conditions of the solution containing Cd more than 0.4 mole fraction.

Extrapolating an excess partial molal free energy of component $i$ for solution of the fixed composition from the corresponding temperature on the liquidus to 500° C (773° K) by assuming that the partial molal entropy is independent of the temperature, we obtain

$$\Delta F^E_{i(773)} = RT_{773} \ln r_{i(773)} = RT \ln r_i + D' \ln N_i (773 - T). \tag{6}$$

For the system Zn-Sn up to 0.9 mol fraction zinc, the activity coefficient of zinc is expressed as follows:

$$RT_{773} \ln r_{Zn} = 1119\,N_{Sn} - 55. \tag{7}$$

Calculating the mean value of $D'$ for several points on the liquidus from equations (6) and (7), we obtain

$$\Delta\bar{S}^E_{Zn} = -0.964 \ln N_{Zn}. \tag{8}$$

For the system Cd-Sn, as an average value for $B$ in the equation (2) from the experimental values at 500° C, we can take the value 986. Therefore, calculating the mean value of $D'$ from equations (2) and (6), we obtain

$$\Delta\bar{S}^E_{Cd} = -0.602 \ln N_{Cd}. \tag{9}$$

The results of these calculations are shown in Fig. 4 and 5 for the partial molal entropy and in Table 1 for the activity at 500° C, and are compared with those of the observation. From these representations, it will be noted that the good agreement is obtained.

The small discrepancy between the calculation and the observation in the case

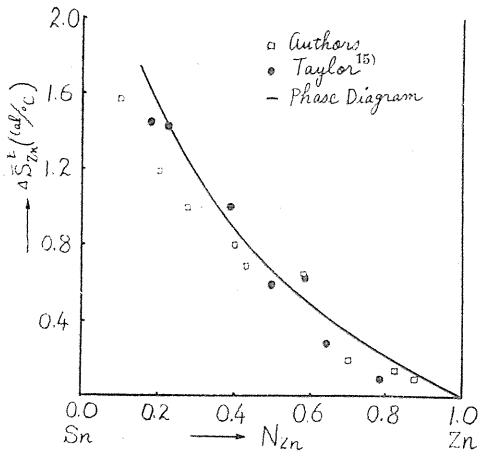


FIG. 4. Comparison between observed and calculated values for the excess molal entropy of zinc.

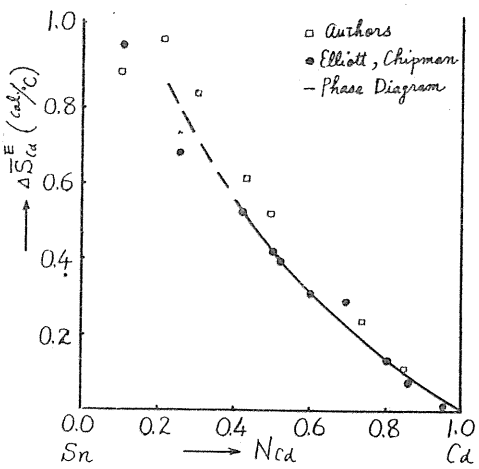


FIG. 5. Comparison between observed and calculated values for the excess molal entropy of cadmium.

Table 1. The solubilities and calculated results for the systems Zn-Sn and Cd-Sn

| Zn-Sn system | | | | | |
|---|---|---|---|---|---|
| $N_{Zn}$ On liquidus | $T$ (° K) On liquidus | $a_{Zn}$ On liquidus | $\Delta\bar{F}^E_{Zn}$ (cal.) On liquidus | $a_{Zn}$ at 500° C (calc.) | $a_{Zn}$ at 500° C (exp.) |
| 0.9 | 662 | 0.949 | 70 | 0.935 | 0.939 |
| 0.8 | 648 | 0.921 | 181 | 0.884 | 0.892 |
| 0.7 | 634 | 0.898 | 313 | 0.832 | 0.843 |
| 0.6 | 623 | 0.881 | 475 | 0.779 | 0.775 |
| 0.5 | 610 | 0.851 | 644 | 0.708 | 0.692 |
| 0.4 | 585 | 0.807 | 816 | 0.611 | 0.596 |
| 0.3 | 552 | 0.751 | 1,006 | 0.489 | 0.483 |
| Cd-Sn system | | | | | |
| $N_{Cd}$ On liquidus | $T$ (° K) On liquidus | $a_{Cd}$ On liquidus | $\Delta\bar{F}^E_{Cd}$ (cal.) On liquidus | $a_{Cd}$ at 500° C (calc.) | $a_{Cd}$ at 500° C (exp.) |
| 0.9 | 556 | 0.919 | 23 | 0.905 | 0.913 |
| 0.8 | 529 | 0.860 | 75 | 0.822 | 0.824 |
| 0.7 | 509 | 0.816 | 155 | 0.746 | 0.746 |
| 0.6 | 491 | 0.774 | 248 | 0.666 | 0.665 |
| 0.5 | 473 | 0.732 | 358 | 0.582 | 0.587 |
| 0.4 | 458 | 0.697 | 505 | 0.496 | 0.501 |

of the two systems will be of no significance when we understand some uncertainties in the accepted phase diagram for those systems and in the assumption that the entropy is independent of temperature. The excellent agreement obtained in this comparison must be considered as substantial evidence for the validity of the assumptions on which the comparison is built.

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