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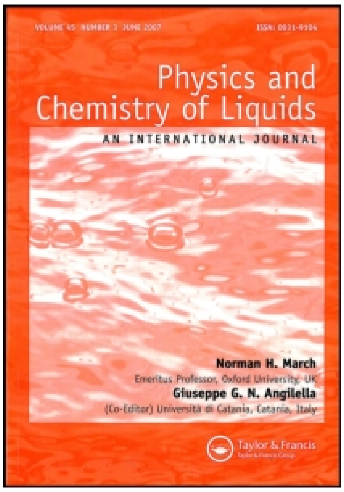

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TEMPERATURE DEPENDENCE OF THE EXCESS ENTROPY FOR LIQUID ALLOYS

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A simple approach has been used to calculate the excess entropy of mixing (ΔS^{xs}) of liquid Na-K and Na-Cs alloys as a function of concentration and temperature. The basic ingredients are the entropy of pure liquid metals and the observed volume of mixing. The temperature dependence ΔS^{xs} for Na-Cs is strikingly diffierent than Na-K· HΔS^{xs} for Na-Cs first increases with T and then starts decreasing whereas for Na-K it decreases continuously with increasing T above T_m.

The temperature dependence of the excess entropy of mixing (ΔS^{xs}) of liquid alloys is crucial to the understanding of structural behaviour in the undercooled ($T < T_m$, T_m melting temperatures) as well as in the high temperature region ($T > T_m$). ΔS^{xs} directly reflects the increased number of configurations on mixing. Due to extreme experimental conditions, a direct measurement in these regions is enormously difficult and, therefore, a theoretical analysis based on established models could be very useful. A good deal of work exists to investigate the concentration dependence of the properties of liquid alloys but very little is known on the temperature scale. Besides academic interest, such investigations are of considerable significance to understand the physical processes that are linked to the fabrication of alloys.

The hard sphere model which is extremely successful (for recent review see Young [1] to calculate the entropy of mixing of liquid alloys near the melting temperature has been used here to study the

T-dependence of ΔS^{xs} above T_m. Our approach is subject to the following conditions:

(i) The observed entropy and the observed specific volume of pure liquid metals at a given temperature are used to determine the hard sphere diameter of pure liquid.
(ii) On alloying, the total packing ($\eta = \pi\sigma^3/6\Omega$) is controlled by the effective hard sphere diameter $\sigma^3 (= C_1\sigma_1^3 + C_2\sigma_2^3)$ and the experimentally observed volume Ω for the alloy.
(iii) The temperature and the concentration dependence of the observed excess volume on mixing is then used to calculate the various contributions to the entropy of mixing.

The scheme is applied to determine the $\Delta S^{xs} - T$ course for Na-K and Na-Cs liquid alloys. Though Na-Cs, by virtue of its size effect, is characteristically different [2–4] than Na-K, the entropy of mixing of both alloys is very much closer to the ideal value. The measured excess volume [5, 6] for Na-K and Na-Cs are negative which are around -1.45% and -5.8% respectively near the melting temperature. It is well established [7] that the excess volume of the alloy plays a very important role in the calculation of entropy of mixing.

The microscopic properties like concentration fluctuations, $S_{cc}(o)$ indicate that both Na-K and Na-Cs are segregating systems where like atoms (i.e. Na-Na, K-K or Cs-Cs) prefer to pair as nearest neighbour. However, the C-dependence of $S_{cc}(o)$ of Na-Cs is quite different than Na-K. $S_{cc}(0) - C$ course of Na-K is like a regular alloy but $S_{cc}(0)$ of Na-Cs is quite assymetric and exhibit a strong peak $S_{cc}(0) \gg S_{cc}^{id}(0))$ around $C_{\mathrm{Na}} = .8$. $S_{cc}(o)$ of Na-Cs is found [4] to be very sensitive to T and changes considerably, in particular, in the concentration range $C_{\mathrm{Na}} = .5$ to $.9$. These authors observed that the composition of the alloy conforming to maximum segregation is also affected by T-the peak in $S_{cc}(o)$ at 383.13 K occurs at $C_{\mathrm{Na}} = .82$ and shifts to $C_{\mathrm{Na}} = .79$ at 473.13 K.

Herein, we present the results for ΔS^{xs} as a function of C and T. The inputs are the entropies of pure elements and the observed volume of mixing of the liquid alloys. The temperature dependence of ΔS^{xs} for Na-Cs reveals an interesting feature that, first it increases with temperature ($T_m < T \leqslant 600$ K) and then decreases with increasing temperature ($T \geqslant 600$ K). Contrary to this ΔS^{xs} for Na-K decreases continuously with temperature above T_m.

Consider an alloy consisting of hard sphere species of diameters σ_1 and σ_2. Mansoori *et al.* [8] analytically fitted the computer experiment result and showed that the entropy of a hard sphere mixture can be expressed as (also see Umar *et al.* [9]),

$$S = S_{\text{gas}} + S_c + S_\eta + S_\sigma . \tag{1}$$

With

$$S_{\text{gas}} = \frac{5}{2} K_B + K_B \ln \left\{ \Omega \left(\frac{m_1^{C_1} m_2^{C_2} K_B T}{2\pi \hbar^2} \right)^{3/2} \right\} \tag{2}$$

$$S_c = -K_B \sum_{i=1}^{2} C_i \ln C_i \tag{3}$$

$$S_\eta = -K_B \ln \alpha + 1.5 K_B (1 - \alpha^2) \tag{4}$$

$$S_\sigma = K_B \pi C_1 C_2 (\sigma_1 - \sigma_2)^2 \alpha^2 \left\{ \frac{\sigma_1 + \sigma_2}{2\Omega} - \frac{\pi (C_1 \sigma_1^4 + C_2 \sigma_2^4)}{24\Omega^2} \right\} \tag{5}$$

where

$$\alpha = (1 - \eta)^{-1} \quad \text{and} \quad \eta = \frac{\pi}{6\Omega} (C_1 \sigma_1^3 + C_2 \sigma_2^3) . \tag{6}$$

Here, the first two terms are ideal contributions. S_η represents the total packing while S_σ reflects the mismatch of the hard sphere diameters σ_1 and σ_2. m is the atomic mass, C is the concentration and Ω is the atomic volume.

In our approach σ_i is independent of C but depends on T, whereas Ω depends on both C and T. The T dependence of σ_i has been ascertained from the observed entropy of the pure elements. The entropy expressions for pure elements (i) is obtained using the above relations by setting either $C_1 = 0$ (i.e. $C_2 = 1$), or $C_2 = 0$ (i.e., $C_1 = 1$), in which case S_c an S_σ terms are identically zero leaving behind

$$S^i = S^i_{\text{gas}} + S^i_\eta \tag{7}$$

with

$$S^i_{\text{gas}} = \frac{5}{2}K_B + K_B \ln\left\{\Omega_i\left(\frac{m_1 K_B T}{2\pi h^2}\right)^{3/2}\right\} \tag{8}$$

$$S^i_\eta = K_B(1-\eta_i) + \frac{3}{2}K_B\{1-(1-\eta_i)^{-2}\} \tag{9}$$

$\eta_i = \pi\sigma_i^3/6\Omega_i$ is the packing fraction of the pure element i. It may be noted that the equation (9) is slightly different than the well known Carnahan-Starling [10] expression. The later can readily be procured from eq. (9) by expanding $\ln(1-\eta_i)$ and retaining the terms up to η^2. The observed entropy (Hultgren *et al.* [11]) and the observed volume [5, 6] of the pure elements are used in equation (7) to determine σ_1 and σ_2 as a function of T. These are then used in equations (2) to (6) to calculate the various contributions to the entropy of the alloy. The excess entropy of mixing becomes

$$\Delta S^{xs} = K_B \ln\left(\frac{\Omega}{\Omega_1^{C_1}\Omega_2^{C_2}}\right) + \Delta S_\eta + S_\sigma \tag{10}$$

with

$$\Delta S_\eta = S_\eta - C_1 S_\eta^{(1)} - C_2 S_\eta^{(2)}. \tag{11}$$

It should be emphasized that in equation (10) one should always consider the experimentally determined values of Ω which depends both on C and T. It can readily be seen that if the mixing is performed at constant volume (i.e., $\Omega = C_1\Omega_1 + C_2\Omega_2$, Ω_i is the specific volume of pure elements) then $\Delta S^{xs} > 0$. For many liquid alloys $\Delta S^{xs} < 0$ which can be achieved (see for example Umar *et al.* [7]) by incorporating the observed $\Delta\Omega$.

The calculated values of ΔS^{xs} as a function of T for different composition of Na-K and Na-Cs liquid alloys are plotted in Figures 1 and 2 respectively. The calculated values near T_m for Na-K at $C_{\text{Na}} = .5$ i.e., $\Delta S^x/R = +.04$ is in reasonable agreement with the observed value,

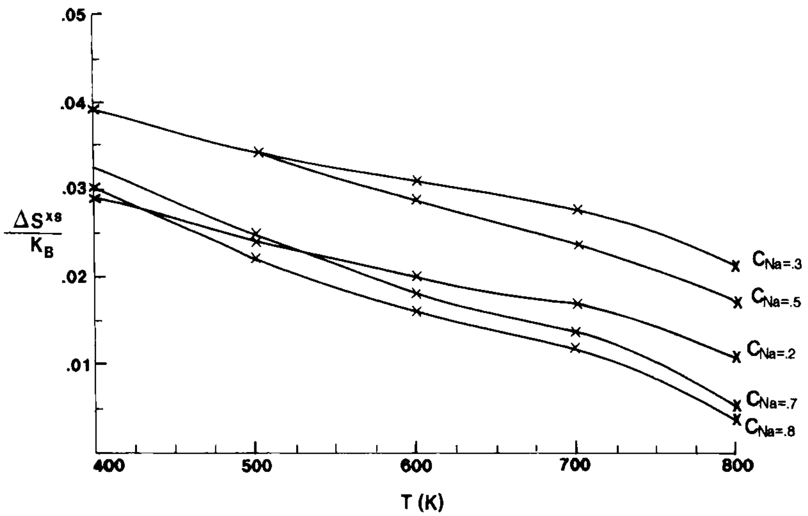

FIGURE 1 Temperature (T) dependence of the excess entropy, ΔS^{xs}, for Na-K liquid alloys at different concentration, C_{Na} = .2, .3, .5, .7 and .8.

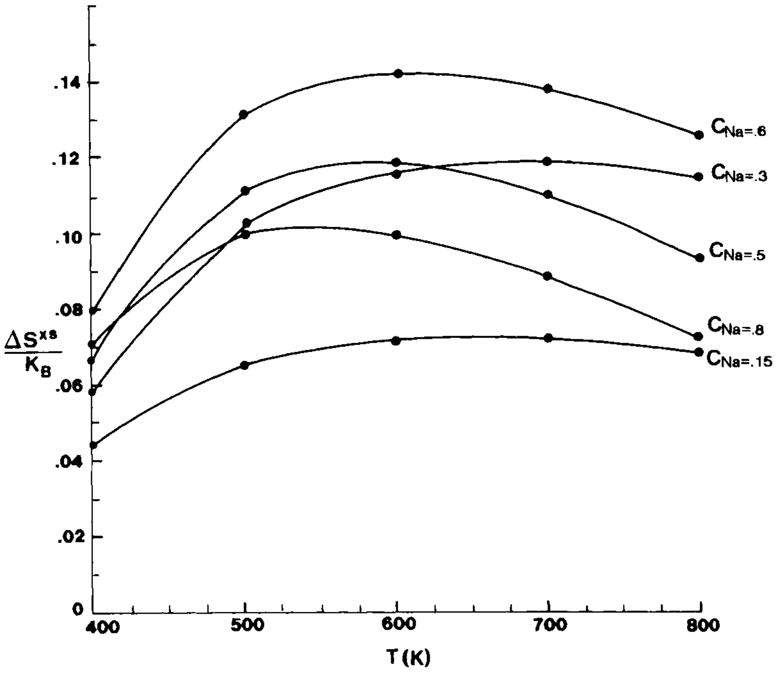

FIGURE 2 Temperature (T) dependence of the excess entropy, ΔS^{xs}, for Na-Cs liquid alloys at different concentrations, C_{Na} = .15, .3, .5, .6 and .8.

($\Delta S^{xs}/R = 0.05$) (source Faber [12]). Similarly, the calculated $\Delta S^{xs}/R = +0.06$ for Na-Cs at $C_{\text{Na}} = .5$ compared to experimental values of .019 [3].

The temperature dependence of ΔS^{xs} for Na-Cs liquid alloys is characteristically different than Na-K system. ΔS^{xs} for Na-K, at all concentrations, decreases with increasing temperature above T_m. But contrary to the expectations, ΔS^{xs} for Na-Cs first increases and then decreases with increasing temperature. Also the nature of variation of ΔS^{xs} is found to depend on the composition of the alloy. For smaller contents of Na (at $C_{\text{Na}} = 15\%$ and 30%) the reversal of trend in ΔS^{xs} is not as distinct as in other Na-rich ($C_{\text{Na}} = 50\%$, 60% and 80%) alloys of Na-Cs systems.

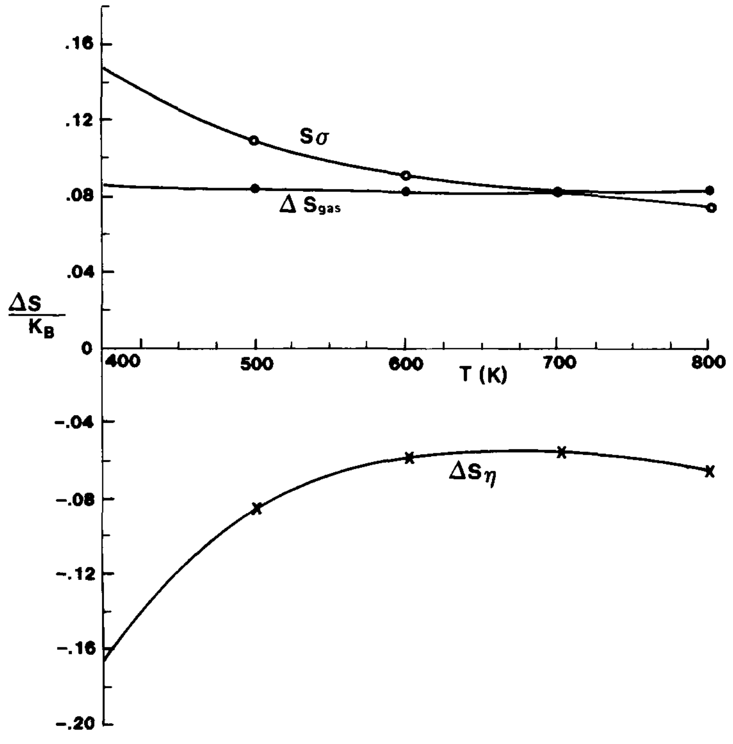

FIGURE 3 Temperature (T) dependence of the various contributions to the entropy of mixing (ΔS) of equiatomic Na-Cs liquid alloys; 0–0–0 (S_σ), 0–0–0 (ΔS_{gas}) and x-x-x (ΔS_η).

In order to understand the reversal of trend in $\Delta S^{xs} - T$ variation in Na-Cs, the various contributions to entropy for equiatomic composition are plotted in Figure 3. ΔS_{gas} and S_σ are positive, whereas ΔS_η are negative. ΔS_{gas} varies very little with temperature. Though S_σ continuously decreases with increasing temperature, the variation is more distinct near T_m than at higher temperature. The magnitude of $|\Delta S_\eta|$, however, first decreases and then starts increasing with rise in temperature. The analysis reveals that the reversal of trend in ΔS^{xs} explicitly arises due to ΔS_η. It has been emphasized by Singh and Singh [13] that near the melting temperature, $(\Delta S_{\mathrm{gas}} + S_\sigma)$ counter balances the ΔS_η and thereby implies almost ideal entropy of mixing for Na-Cs. At higher temperature, however, ΔS_{gas} being constant to T, it is a delicate balance of the packing term (ΔS_η) and the mismatch term (S_σ) which induces the characteristic behaviour of $\Delta S^{xs} - T$ variation.

It may be recalled that the present analysis is based on the fact that the core sizes of the pure elements do not change on alloying. The inclusion of the volume contraction allows the electronic readjustment to take place in the outer region of the shell which ultimately contribute to ΔS_η and S_σ. It could be of interest to examine the $\Delta S^{xs} - T$ variation based on electronic theory [9, 14] where ΔS^{xs} is found to be sensitive to both core-ion pseudopotential and the screening function. Such an approach within the framework of Gibbs-Bogoliubov variational technique also allows the change in the core sizes and hence in σ_i on mixing. We intend to pursue this point later in the forthcoming publication.

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