

## Transfer of charge in liquid alloys

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MS received 18 July 1987; revised 25 November 1987

**Abstract.** Hard sphere diameters of liquid alkali metal alloys (Na-Cs and K-Rb) are calculated at 373 K ensuring the minimum Helmholtz free energy of the system. These diameters are then used to fix the packing density of the alloy. On alloying, the hard sphere diameters of Na in Na-Cs and K in K-Rb alloys expand whereas those of Cs and Rb contract.

**Keywords.** Partial densities; hard sphere diameters; packing density.

**PACS No.** 61-25

### 1. Introduction

Recently, much attention has been focussed on charge transfer in solid and liquid alloys (Bennett and Willens 1974; Hoshino *et al* 1981). In this paper we consider the charge transfer in those simple liquid alloys which are characterized by the following features: (a) the amount of charge transfer is small (b) the difference between the electronegativities of the constituent metals is small (c) the volume change on alloying is small and (d) the hard sphere model is applicable.

In the widely used metallic model, a metallic system is a system of positive ions plus another system of valence electrons. In a metallic alloy of two components with small difference of electronegativity it is more favourable for the valence electrons to be associated with more electronegative ions and hence to be partially localized on these ions. This is often called the 'partial localization model'. Therefore, some fraction of the valence-electron charge is transferred to the more electronegative ions. Correspondingly, valence-electron charge on the lesser electronegative ion is reduced. As the electronegativities of component metals of the binary alloy differ by a small amount, the amount of charge transfer is small. Consequently, change of volume on alloying is small. The hard-sphere diameter is intensely related to the electron distribution around ions. Our estimation of charge transfer is based on the idea that a relation exists between the charge transfer and the change in hard-sphere diameters of both constituent metals on alloying.

We discuss the charge transfer in liquid Na-Cs and K-Rb alloys because the structure factors for constituent metals in both the alloys obey the hard sphere model as is well known in the case of liquid metals and alloys (see, for example, the review article by Young 1977).

## 2. Formulation

Charge transfer from an ion  $B$  to an ion  $A$  in an  $A - B$  alloy distributes itself around the ion  $A$ , which results in decrease in hard sphere diameter of  $B$  ion and the increase in that of the  $A$ -ion. It may be qualitatively a good idea to assume that the charge transferred to an ion is distributed homogeneously. Then, we have the following relation in the case of a small charge transfer (Tamaki 1987)

$$4\pi(D_A/2)^2\Delta D_A = \Delta Z_A(4/3\pi r_A^3), \quad (1)$$

or

$$\Delta D_A/D_A = 4/3(r_A^3/D_A^3)\Delta Z_A. \quad (2)$$

Similarly

$$\Delta D_B/D_B = 4/3(r_B^3/D_B^3)\Delta Z_B, \quad (3)$$

where  $r_A$  and  $r_B$  are the Wigner-Seitz radii and  $\Delta Z_A$  and  $\Delta Z_B$  are the amounts of charges transferred to  $A$  and transferred from  $B$  respectively.  $\Delta D_A$  and  $\Delta D_B$  are the variations of the hard sphere diameters of  $A$  and  $B$  respectively.

Following the optimization of the Helmholtz free energy  $F$ , on alloying as obtained by Singh and Singh (1985), the total volume of the alloy is written as

$$V = x_A \cdot V_A + x_B \cdot V_B, \quad (4)$$

where  $x_A$  and  $x_B$  are the concentration fractions of constituents  $A$  and  $B$ . Then the atomic volume of the alloy is given as

$$\Omega = V/N, \quad (5)$$

where  $N$  is the Avogadro's number. Concentrations of the individual constituents in the alloy are given as (Gallego and Alonso 1984)

$$C_A = x_A \cdot V_A/V, \quad (6a)$$

and

$$C_B = x_B \cdot V_B/V, \quad (6b)$$

where  $C_A + C_B = 1$  and  $V_A$  and  $V_B$  are the volumes of  $x_A$  and  $x_B$  fractions of the constituents respectively. The packing fraction of the alloy is given (Singh and Singh 1985) in terms of the partial densities and hard sphere diameters of the individual constituents of the alloys as

$$\eta = \pi/6(N_A D_A^3 + N_B D_B^3), \quad (7)$$

where

$$N_A = C_A/\Omega \quad (8a)$$

and

$$N_B = C_B/\Omega \quad (8b)$$

are the partial densities and  $D_A$  and  $D_B$  are the hard sphere diameters.

### 3. Results and discussion

For the present calculations the concentration dependence of  $\eta$  for Na-Cs and K-Rb alloys is obtained from Singh and Singh (1985). Maximum variation in  $\eta$  with respect to concentration was observed in the case of Na-Cs alloy. The slope in K-Rb is minimum with

$$(\partial\eta/\partial C)_{\text{K-Rb}} < (\partial\eta/\partial C)_{\text{Na-Cs}}.$$

As mentioned earlier, the heavier elements contract while the lighter ones expand because of charge transfer from one ion to another. This behaviour dominates in Na-Cs as compared to K-Rb alloy. However, the ratio of  $D_A$  and  $D_B$  remains almost constant throughout the range of composition. For actual calculations the values of these ratios in the two alloys have been taken from Hafner (1977).

Thus, having fixed the  $\eta$  and  $(D_A/D_B)$  for an alloy for the whole range of composition, hard sphere diameters  $D_A$  and  $D_B$  are calculated in Na-Cs and K-Rb alloys. Tables 1 and 2 show calculated values of the hard sphere diameters in the case of the two alloys for all the concentrations ranging from 0 to 1. As shown in table 1,  $\Delta D_{\text{Na}}$  increases and  $\Delta D_{\text{Cs}}$  decreases as concentration of Cs increases. Similarly,  $\Delta D_{\text{K}}$  increases and  $\Delta D_{\text{Rb}}$  decreases with the increase of Rb content in the K-Rb alloy. Thus, the change in the effective hard sphere diameter on alloying indicates that  $\Delta D_{\text{Na}} > 0$  and  $\Delta D_{\text{Cs}} < 0$  in Na-Cs alloy and  $\Delta D_{\text{K}} > 0$  and  $\Delta D_{\text{Rb}} < 0$  in K-Rb alloy. For comparison, we show the composition dependence of  $(\Delta D/D_0)_{\text{Na}}$  and  $(\Delta D/D_0)_{\text{Cs}}$  in figure 1 and  $(\Delta D/D_0)_{\text{K}}$  and  $(\Delta D/D_0)_{\text{Rb}}$  in figure 2 respectively. Results of the values  $(\Delta D/D_0)$ , estimated from the experimental structure data, are not available in Na-Cs and K-Rb alloys as far as we are aware and hence could not be given in support of the calculated results.

As discussed by Tamaki *et al* (1981), there is no unique definition of charge transfer and a convenient definition might start from the net charge within the Wigner-Seitz (WS) cell of the metal in the pure state. The expressions for charge transfers are given as

$$\Delta Z_A = (Z_A x_A a_{AA}(0) + Z_B x_B a_{AB}(0)) + (Z_A x_A + Z_B x_B)(V_A - V)/V \quad (9)$$

and

$$\Delta Z_B = (Z_B x_B a_{BB}(0) + Z_A x_A a_{AB}(0)) + (Z_A x_A + Z_B x_B)(V_B - V)/V, \quad (10)$$

where  $a_{ij}(0)$ ; ( $i, j = A, B$ ) are the partial structure factors in long-wavelength limit,  $x_A$  and  $x_B$  are the concentration fractions of constituents  $A$  and  $B$ ,  $V_A$  and  $V_B$  are the molar volumes of metals  $A$  and  $B$ .

These formulae are basic expressions for the relation between charge transfer in liquid alloys and their structure. From the charge neutrality of the alloy one gets,

$$0 = Z_A x_A^2 a_{AA}(0) + (Z_A + Z_B) x_A x_B a_{AB}(0) + Z_B x_B^2 a_{BB}(0). \quad (11)$$

Equation (11) gives a validity condition for equations (9) and (10) to exist.

For large charge transfer in a binary liquid alloy, the change of volume on mixing is large and then one has to modify the preceding arguments, introducing the partial

**Table 1.** Effective hard sphere diameters of Na<sub>x</sub>Cs<sub>1-x</sub> alloy at 373 K at different composition.

$x_{\text{Na}}$	$D_{\text{Na}} (\text{\AA})$	$D_{\text{Cs}} (\text{\AA})$
0.0	—	4.688
0.1	3.684	4.605
0.2	3.610	4.513
0.3	3.536	4.420
0.4	3.462	4.327
0.5	3.388	4.235
0.6	3.311	4.139
0.7	3.240	4.050
0.8	3.179	3.974
0.9	3.137	3.921
1.0	3.135	—

**Table 2.** Effective hard sphere diameters of K<sub>x</sub>Rb<sub>1-x</sub> alloy at 373 K at different composition.

$x_{\text{K}}$	$D_{\text{K}} (\text{\AA})$	$D_{\text{Rb}} (\text{\AA})$
0.0	—	4.261
0.1	4.069	4.239
0.2	4.054	4.223
0.3	4.037	4.205
0.4	4.022	4.190
0.5	4.008	4.175
0.6	3.995	4.161
0.7	3.978	4.144
0.8	3.962	4.127
0.9	3.950	4.114
1.0	3.935	—

molar volumes  $\bar{V}_A$  and  $\bar{V}_B$  instead of  $V_A$  and  $V_B$  as follows:

$$\bar{V}_A = (\partial V / \partial x_A)_{pTN}, \quad \bar{V}_B = (\partial V / \partial x_B)_{pTN}.$$

If the volume change of  $A - B$  alloys is given by the form  $x_A x_B \Omega$ , then the partial molar volumes of the  $A$  and  $B$  atoms are expressed as

$$\bar{V}_A = V_A + x_B^2 \Omega, \quad \bar{V}_B = V_B + x_A^2 \Omega. \quad (12)$$

In the case of strongly compound-forming liquid alloys, where large volume contractions were often found, the partial structure factor of unlike atoms in the long wavelength limit is expressed in the form (McAlister and Turner 1972):

$$a_{AB}(0) = 1 + \phi \quad (13)$$

where

$$\phi = (Nk_B T / V) \chi_T.$$

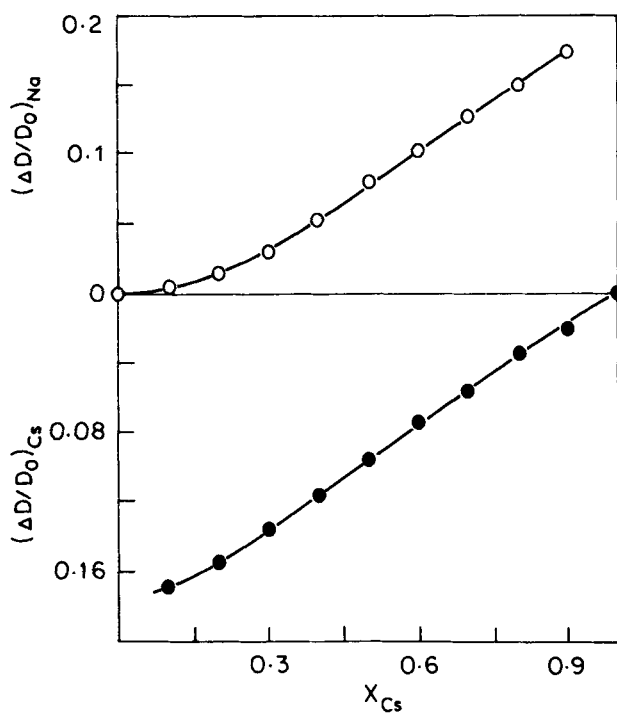


Figure 1. Composition dependence of the change in the hard-sphere diameters for Na-Cs alloy.

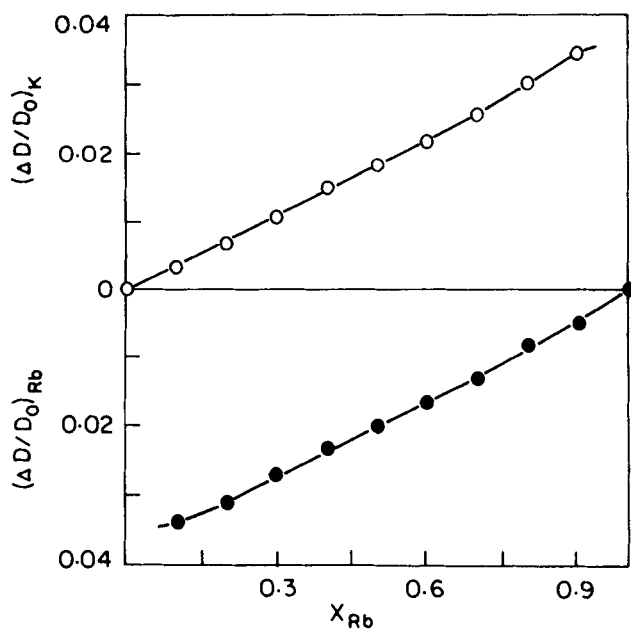


Figure 2. Composition dependence of the change in the hard-sphere diameters for K-Rb alloy.

Since the  $\phi$  value is negligible as compared with unity, we have the following expression for charge transfer:

$$\Delta Z_A = Z_A x_A (a_{AA}(0) - 1) + (Z_A x_A + Z_B x_B) (\bar{V}_A) / (V) \quad (14a)$$

and

$$\Delta Z_B = Z_B x_B (a_{BB}(0) - 1) + (Z_A x_A + Z_B x_B) (\bar{V}_B) / (V). \quad (14b)$$

We examine the validity of (14a) and (14b) using a rewritten form of (11) as follows:

$$O = Z_A x_A^2 a_{AA}(0) + (Z_A + Z_B) x_A x_B + Z_B x_B^2 a_{BB}(0). \quad (15)$$

However, the procedure of averaging out the electron distribution outside the WS cell may not be a good approximation in these compound-forming alloys, and cases which satisfy equation (15) may be rare. In these alloys the tendency between the unlike atoms is strong and the first principle statistical mechanical or pseudopotential type calculations of their physical properties are difficult. Bhatia and Singh (1980) examined the variation of volume of mixing with concentration for compound-forming systems using the idea of chemical complexes. They have given the numerical results for LiPb and NaPb alloys. Tamaki (1987) has also discussed in detail the charge transfer in liquid Na-Pb alloy. He has concluded that a large charge transfer from the Pb to a Na atom appears at the composition of Na<sub>4</sub>Pb.

### Acknowledgements

One of us (AP) is thankful to Ms Lavina Nagar for constant encouragement and help. Financial support from UGC, New Delhi is gratefully acknowledged.

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