Thermotransport Studies in Liquid Alkali Metal Alloys*

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Abstract

Thermotransport has been studied as a function of composition in the Na-K liquid alloy system. Thermotransport of trace concentration of Rb in K, Rb in Na and Na in Rb have also been investigated. A reversal in direction of specie migration occurred at an intermediate composition in the Na-K system. In K rich alloys Na for example migrated toward the hot end of the capillary whereas in Na rich alloys, Na migrated to the cold end. At some intermediate composition (between 64.6 at % Na and 76.6 at % Na) a crossover occurred and consequently no thermotransport occurred at that composition. This study compares with electromigration studies by other investigators which indicate that a sign reversal in direction of electromigration occurs in both the Na-K and Na-Rb systems.

Theoretical calculations of the heats of transport in the alloy systems studied yield quite good agreement with the observed sign of the heat of transport for most of the alloys investigated.

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Introduction

Recently thermotransport studies of gold, antimony and sulphur in liquid silver⁽¹⁾ and of silver in liquid gold⁽²⁾ were reported. Experimental values of Q_{exp}^* , the net heat of transport defined as

$$Q_{\text{exp}}^* = (Q_2^* - Q_1^* \frac{\bar{V}_2}{\bar{V}_1}) \quad (1)$$

were obtained. In equation (1), the subscripts 1 and 2 refer to solvent and solute respectively. The term $\bar{V}_i$ refers to the partial molal volume of component i . In references 1 and 2 classical theories of diffusion in liquid metals were found to be inadequate in interpreting the experimental results. An approach based on the sum of two contributions was developed. The two contributions are (i) an electronic contribution due to the charge difference between solute and the solvent and (ii) a contribution due to mass difference between two species in the alloy. The first contribution was calculated by extending Gerl's calculations⁽³⁾ for solids to liquids and the second was estimated by use of the theories of transport applicable to a dense gas⁽⁴⁾. This approach yielded numbers which compared reasonably well with experimental findings for silver base systems.

Some interesting work has been reported on electromigration in alkali metal alloys. In Na-K alloys for example a reversal in direction of migration of each species occurs at an alloy composition of about 39 - 40 at. % K^(5 - 7) and of 32.1 at. % K at 140°C.⁽⁸⁾ In Na-Rb this occurs at 30 at. % Rb⁽⁹⁾. Various theoretical attempts have been made to explain this behavior. The most successful is the phase shift approach used by

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Epstein et al⁽⁷⁾ which has been extended by Olson et al⁽¹⁰⁾ to various binary liquid alloys of Li, Na, K, Rb, Cu, Ag and Au. This approach predicts correctly the cross-over in electrotransport but fails to yield accurate values of composition at which this reversal should occur. For example in case of Na-K alloys, the cross-over is predicted to occur at about 62 at.%K whereas the experimental value is in the region of 40 at.% K.

Fundamentally both the processes of thermotransport and electrotransport may be considered to have the same origin⁽¹¹⁾ and correlation between them may be expected. Thus, corresponding to the cross-over phenomenon in electrotransport, a reversal in the direction of migration of each species could possibly occur in thermotransport in alkali metal alloys. This means that the species going to the hot end of the thermal-gradient at one extreme alloy composition, will go to the cold end at the other extreme alloy composition. This conclusion has an important consequence - namely: if reversal occurs, for each temperature gradient there will be a time invariant alloy composition.

In view of the above experiments, investigation of thermotransport in liquid alkali metal alloys was initiated. This paper reports some of the work done on Na-K, Na-Rb and K-Rb alloys together with the results of theoretical calculations by use of Bhat and Swalin's⁽¹⁾ approach.

Experimental

Na-K, Na-Rb and K-Rb alloys were investigated. Experimental procedure consisted of four major steps: (i) preparation of liquid alloys in fine bore capillaries; (ii) annealings in a given thermal gradient; (iii) sectioning of the capillaries and determination of the concentration in each section and (iv) determination of the heat

of transport from the concentration vs. temperature data. Full description of each of these steps is reported elsewhere⁽¹²⁾ and only a brief summary is described here.

Alloys of the desired composition were prepared in the laboratory. The radio-isotopes Na^{22} and Rb^{86} were obtained in the form of carrier free Na^{22}Cl and Rb^{86}Cl in solution respectively, whereas K^{42} was obtained by thermal neutron irradiation of pure potassium metal encapsulated in fused quartz tube.

Capillary tubes of 0.5 mm diameter precision bore were filled to a length of about 7 cm with alloys of the desired compositions and subsequently sealed. Samples were then placed in a temperature gradient in a vertical tube furnace, closed at one end. The furnace could be evacuated to a pressure of $< 1\mu$ of Hg to minimize air convection currents. The thermotransport samples were fastened to the end of a fused quartz tube closed at the bottom end which contained a chromel-alumel thermocouple. The thermocouple could be moved, along the axis of the furnace during the progress of the experiment. This enabled a temperature profile to be determined before, during or after the experimental anneal. The controlling thermocouples were placed outside the main tube on the windings.

Figure 1 shows a typical temperature profile of the furnace. The temperature difference was about 100°K over the 7 cm sample length. A sample was held in this gradient for several days in order to ensure achievement of the stationary state. After the diffusion treatment anneal, samples were sliced into 10 to 15 sections, dissolved in distilled water and analyzed.

The radioactive tracer concentration was determined in each section by use of a well-type scintillation counting set up. Gamma rays of energies 1.27, 1.52 and 1.08 Mev were monitored for Na^{22} , K^{42} and Rb^{86} respectively. A problem existed however with K^{42} since the short half life (12.4 hr.) precluded long annealing times. In order to employ long annealing times, an alternative method of analysis was employed. This technique was based on absorption spectroscopy and was satisfactory for alloys which contained appreciable concentrations of K. For dilute alloys, the presence of high concentrations of Na resulted in interference and thus the less desirable radioisotope technique was employed for Na-rich alloys.

Normally the experimental configuration was such that the high temperature was at the top, although several experiments were performed which had the gradient inverted.

Experimental Results

Table 1 shows the list of alloys studied.

Table 1

<u>Alloy</u>	<u>Composition wt %</u>
K - Na^{22}	< 0.01% Na in K
Rb - Na^{22}	< 0.01 % Na in Rb
Na - K^{42}	~ 0.5 % K in Na
Na - Rb^{86}	~ 0.5 % Rb in Na
K - Rb^{86}	~ 0.5 % Rb in K
Na - K	34% K, 66% Na (23.2 at. % K, 76.7 at. % Na)
Na - K	50% K, 50% Na (35.4 at. % K, 64.6 at. % Na)

For a two component system in a thermal gradient, one can derive the following expression for the stationary state. (1,2)

$$-\left(\frac{\partial \mu_1}{\partial z}\right)_T - \frac{Q_1^*}{T} \frac{dT}{dz} - \frac{\bar{V}_1}{\bar{V}_2} \left[-\left(\frac{\partial \mu_2}{\partial z}\right)_T - \frac{Q_2^*}{T} \cdot \frac{dT}{dz} \right] = 0 \quad (2)$$

where μ_i , Q_i^* and $\bar{V}_i$ are the chemical potential, the heat of transport and the partial molar volume of component i respectively. The symbol z represents distance.

From the relation $\mu_i = (\mu_{0i})_{T,P} + RT \ln a_i$, one obtains

$$\left(\frac{\partial \mu_1}{\partial z}\right)_T = RT \frac{d \ln a_1}{dz}, \quad \left(\frac{\partial \mu_2}{\partial z}\right)_T = RT \frac{d \ln a_2}{dz} \quad (3)$$

Combining equation (1), (2) and (3), one obtains

$$Q_{\text{exp}}^* = R \left(\frac{d \ln a_2}{d \left(\frac{1}{T} \right)} - \frac{d \ln a_1}{d \left(\frac{1}{T} \right)} \cdot \frac{\bar{V}_2}{\bar{V}_1} \right) \quad (4)$$

For very dilute solutions, $a_1 \simeq x_1 \simeq 1$ and

$$Q_{\text{exp}}^* = R \frac{d \ln x_2}{d \left(\frac{1}{T} \right)} \quad (5)$$

Thus equation (4) can be used for concentrated alloys, and equation (5) is applicable for very dilute alloys.

Figure 2 shows a typical plot of $\ln$ concentration vs. $1/T$ for very dilute alloys. Q_{exp}^* were obtained from the slopes of these plots which correspond to $\frac{Q_{\text{exp}}^*}{R}$ according to equation (5).

For concentrated sodium - potassium alloys, the mole fraction of each component in each section which we measured by absorption spectroscopy was converted to the activity of each component by use of the activity data measured by Cafasso, Khanna and Feder⁽¹³⁾.

The partial molar volume data of each component for this alloy system in different concentration and temperature is not available. As a first approximation, $\frac{\bar{V}_2}{\bar{V}_1}$ was assumed to be same as the ratio of molar volume of pure potassium and sodium, and to be independent of temperature. Then from equation (4),

$$Q_{\text{exp}}^* = R \frac{d \ln \frac{a_2}{a_1 \frac{\bar{V}_2}{\bar{V}_1}}}{d \left(\frac{1}{T} \right)} \quad (6)$$

Figure 3 shows a typical plot of $\ln \frac{a_2}{a_1 \frac{\bar{V}_2}{\bar{V}_1}}$ vs. $1/T$ for concentrated

sodium potassium alloys. The slopes of these plots yielded values of $\frac{Q_{\text{exp}}^*}{R}$

In Table 2 are listed the experimental values of Q_{exp}^* with their standard deviation for the alloy systems investigated.

Table 2

<u>System</u>	<u>Heat of transport, Q_{exp}^* (calories/mole)</u>
Trace conc. of Na^{22} in K	- 1080 $\pm$ 600
Trace conc. of K^{42} in Na	negative*
Trace conc. of Na^{22} in Rb	- 4570 $\pm$ 590
Trace conc. of Rb^{86} in Na	+ 1070 $\pm$ 670
Trace conc. of Rb^{86} in K	+ 1280 $\pm$ 540
23.3 at. % K - 76.7 at. % Na	- 8680 $\pm$ 1800
35.4 at. % K - 64.6 at. % Na	+ 1610 $\pm$ 390

* The K^{42} - Na thermotransport experiments were carried out only for a few days because of short half-life of K^{42} isotope. Thus accurate results could not be obtained and the purpose of these experiments was to obtain the migration direction of K in sodium.

Discussion

The investigation of thermotransport in liquid alkali metal alloys, namely Na-K, Na-Rb and K-Rb, at the extreme ends of phase diagram (where one of the element is present in tracer form) was carried out to determine the heat of transport values at these concentrations. These values will be then compared with the values calculated from the procedure of Bhat and Swalin.

Bhat and Swalin^(1,2) considered the heat of transport Q^* to consist of two terms:

$$Q_{\text{calc}}^* = Q_e^* + Q_i^* \quad (7)$$

where Q_e^* represents the extrinsic contribution which arises from (a) electrostatic fields created in a metal due to the presence of the temperature gradient and (b) interaction of the diffusing ion with charge carriers. Q_i^* represents the intrinsic contribution due to interaction among the ions themselves. Q_e^* was calculated by use of the method of Gerl⁽³⁾ and Q_i^* was estimated by use of Chapman's⁽²⁾⁽⁴⁾ expression for thermotransport in dense gases. These quantities are given by following expressions:

$$Q_e^* = \frac{K_e T}{\sqrt{2}} \left(\frac{m^*}{m} \right)^{1/2} E_F^{-1/2} A_Z(E_F) \left[1 + 2 \left(\frac{dA/A}{dE/E} \right)_{E_F} \right] \quad (8)$$

where K_e = electronic contribution to thermal conductivity of solvent
 m and m^* = rest mass and effective mass of electron respectively
 Z = effective charge on the diffusing ion
 A_Z = resistivity scattering cross-section of solute atoms for electrons
 E = Energy of electrons
 E_F = Fermi level

$$Q_i^* = RTK \left[\left(\frac{m_2 - m_1}{m_2 + m_1} \right) + 0.2 \left(\frac{s_2^2}{s_{21}^2} - 1 \right) X_2 - 0.2 \left(\frac{s_1^2}{s_{12}^2} - 1 \right) X_1 \right] \quad (9)$$

where K is a factor involving three integrals evaluated from the law of force between atoms. K has been evaluated from the results of isotope thermotransport experiments and lies in a rather narrow range for alkali metals. The terms m_1 and m_2 are the mass of solvent and solute atoms respectively and s_1 and s_2 are their equivalent

molecular diameters. The term s_{12} is given by $(s_1 + s_2) / 2$. For very dilute alloys ($X_2 \ll X_1 \simeq 1$), and thus

$$Q_i^* = RTK \left[\left(\frac{m_2 - m_1}{m_2 + m_1} \right) - 0.2 \left(\frac{s_1^2}{s_{12}^2} - 1 \right) \right] \quad (10)$$

From substitution of the appropriate quantities into equations (9) and (10) Q_e^* and Q_i^* may be calculated. Table 3 lists calculated values of Q_e^* , Q_i^* and Q_{calc}^* for Na²² in K, K⁴² in Na, Na²² in Rb, Rb⁸⁶ in Na, Rb⁸⁶ in K. Calculations for Ag¹¹⁰ in Au and Au¹⁹⁵ in Ag as reported in ref. 1 and 2 are shown for comparison. It is interesting to see that the overall agreement between calculated and experimental values is reasonably good. In all the alkali metal alloys which were investigated, the electronic contribution appears to be the controlling factor whereas in Ag-Au alloys on the other hand the mass contribution appears to dominate.

One of the purposes of these investigations was to find out if there is a reversal in migration direction of each species in binary alkali metal alloys when placed in a thermal gradient.

For this temperature gradient, in the Na-K alloy system, there is reversal in the direction of thermomigration of potassium somewhere in the concentration range 23.3 at. % K and 35.4 at. % K. K migrates toward the hot end on the Na rich side and to the cold end on the K rich side. This concentration range of the reversal is to be compared with the value of 32.1 at. % K at which a cross-over in direction of electromigration occurs. (8)

Table 3

Comparison between calculated and experimental results of Q^* for dilute alloys (cal/mol)

Alloys	Na - K		Na - Rb		K - Rb	Ag - Au	
	Na ²² in K	K ⁴² in Na	Na ²² in Rb	Rb ⁸⁶ in Na	Rb ⁸⁶ in K	Ag ¹¹⁰ in Au	Au ¹⁹⁵ in Ag
Temp. range employed (°K)	(423 - 523)	(423 - 523)	(373 - 473)	(373 - 473)	(323 - 423)	(1338 - 1438)	(1248 - 1348)
Q_e^*	- 950	- 1070	- 910	-2070	- 130	- 500	- 480
Q_i^*	- 870	+ 880	-1260	+1210	+ 640	-1860	+1770
Q_{calc}^*	-1820	- 190	-2170	- 860	+ 510	-2360	+1290
Q_{exp}^*	-1080	negative	-4570	+1070	+1280	-1230	+1690
Tracer goes to	Hot end	Hot end	Hot end	Cold end	Cold end	Hot end	Cold end

Q_e^* and Q_i^* are calculated at the midpoint temperature of temperature range employed for each system.

For the Na-Rb system, Bhat and Swalin's approach predicts a reversal in the direction of migration of each species at two extreme ends of composition. Experimental results at these two points of Na-Rb alloy are contrary to the calculation since Na migrates to the hot end in both cases, although study of intermediate compositions is necessary to confirm that a non-reversal exists. In the case of Ag-Au alloys, the direction of migration is correctly predicted by Bhat and Swalin's approach for both composition extremes.

One may compare these data with the results of electromigration studies of the same liquid alloys. Electromigration experiments indicate that a reversal occurs in direction of specie migration in both the Na-K and Na-Rb systems. These results are consistent with theoretical calculations⁽¹⁰⁾. Our thermomigration studies on the other hand show a reversal for only the Na-K system. Electromigration studies have not been performed for the Au-Ag system however, theoretical calculations of Olson et al⁽¹⁰⁾ indicate that no reversal is expected. Our earlier thermomigration studies for the Au-Ag system indicates that no reversal of sign of migration occurs at the composition extremities.

Summary

Thermotransport has been studied as a function of composition in the Na-K liquid alloys systems. Thermotransport of trace concentration of Rb in K, Rb in Na and Na in Rb was also investigated. A reversal in direction of specie migration occurred at an intermediate composition in the Na-K system. That is to say that in K rich alloys Na migrated to the hot end of the capillary whereas in Na rich alloys, Na

migrated to the cold end. At some intermediate composition (between 64.6 at.% Na and 76.6 at. % Na) a crossover occurred and no thermotransport occurred at that composition. Electromigration studies by other investigators indicate that a sign reversal occurs in both the Na-K and Na-Rb systems.

Theoretical calculations of the heats of transport in the alloy systems studied yield good agreement with the observed sign of the heat of transport for most of the alloys investigated.

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Fig. 1

A typical temperature profile of thermotransport apparatus.