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# THERMODYNAMIC PROPERTIES OF LIQUID METAL SOLUTIONS IN THE SODIUM-MERCURY SYSTEM AT 200° C

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# THERMODYNAMIC PROPERTIES OF LIQUID METAL SOLUTIONS IN THE SODIUM-MERCURY SYSTEM AT 200° C

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## SUMMARY

Measurements were made of the electromotive force of sodium - sodium amalgam cells. The amalgam composition ranged from 0.01 to 0.15 atomic fraction of sodium. Values were obtained at $150^{\circ}$, $200^{\circ}$, and $250^{\circ}$ C. The activity of sodium in the amalgam $a_{Na}$ was obtained from the relation $n\mathscr{F}\epsilon = -RT \ln a_{Na}$, where $n$ is the number of electrons in the stoichiometric relation, $\mathscr{F}$ is a constant (Faraday), 23 066 calories per volt, $\epsilon$ is the electromotive force in volts, $R$ is the gas constant in calories per degree, and $T$ is the temperature in $^{\circ}$K.

Partial free energy $\Delta\bar{F}_{Na}$, partial entropy $\Delta\bar{S}_{Na}$, and partial heat $\Delta\bar{H}_{Na}$ of mixing of sodium in sodium amalgam were calculated from the following equations:

$$\Delta\bar{F}_{Na} = -23\,066\,\epsilon = RT \ln a_{Na}, \text{ cal/g-atom}$$

$$\Delta\bar{S}_{Na} = 23\,066 \frac{d\epsilon}{dT}, \text{ cal/(g-atom)(deg)}$$

$$\Delta\bar{H}_{Na} = \Delta\bar{F}_{Na} + T\,\Delta\bar{S}_{Na} = 23\,066 \left[T \frac{d\epsilon}{dT} - \epsilon\right], \text{ cal/g-atom}$$

The partial excess free energy of sodium $\Delta\bar{F}^{e}_{Na}$ and excess entropy $\Delta\bar{S}^{e}_{Na}$ were obtained from the following equations:

$$\Delta\bar{F}^{e}_{Na} = RT \ln \gamma_{Na} \text{ cal/g-atom}$$

$$\Delta\bar{S}^{e}_{Na} = \Delta\bar{S}_{Na} + R \ln X_{Na} \text{ cal/(g-atom)(deg)}$$

where $\gamma$ is the activity coefficient and $X_{Na}$ is the atomic fraction of sodium.

The thermodynamic data for the other solution component, mercury, were also obtained. Integral values were obtained by graphical integration or by calculation from the partial values. The activity of sodium exhibited large negative deviations from ideality, while the activity of mercury followed closely Raoult's law in dilute sodium solutions. The formation of sodium-mercury alloys was accompanied by an exothermic heat effect. The free energies of mixing were large, while the entropy terms were small.

# INTRODUCTION

The small amount of thermodynamic data in the literature for liquid sodium-mercury systems has been derived primarily from electromotive-force and vapor-pressure measurements. Hauffe (ref. 1) measured the electromotive force of sodium - sodium amalgam cells of the type sodium/sodium ion in glass/sodium amalgam. The measurements were made at 299° and 375° C and covered the composition range of $X_{Na}$ from 0.41 to 0.91, where $X_{Na}$ is the atomic fraction of sodium in the amalgam. Bent and Hildebrand (ref. 2) measured the pressure of mercury vapor over amalgams in the range of $X_{Na}$ from 0.04 to 0.49 at 335° and 375° C.

The partial and integral values of the thermodynamic functions have been derived by Kubaschewski and Catterall (ref. 3) and by Hultgren and associates (ref. 4). The partial values are those for the process in which one component is dissolved in an infinite amount of alloy. The integral values are those that are involved in the formation of an alloy from its constituent elements. The partial free energy of sodium in amalgams $\Delta\overline{F}_{Na}$ (liquid) at 375° C has been derived from the results of reference 1; and the partial free energy of mercury in amalgams $\Delta\overline{F}_{Hg}$ (liquid) at 375° C has been derived from the results in reference 2.

Integral heats of mixing at 110° C were obtained calorimetrically (ref. 5) for the composition range of $X_{Na}$ from 0.04 to 0.14. Values for partial molar heats of mixing $\Delta\overline{H}_{Na}$ (liquid) for $X_{Na} > 0.4$ were derived from the electromotive-force results of reference 1. Values of $\Delta\overline{H}_{Na}$ (liquid) for $X_{Na} < 0.06$ have been derived from the electromotive force results at 25° C of Shibata (ref. 6).

There have been no electromotive-force measurements made on dilute amalgams ($X_{Na} < 0.4$) at other than room temperature. Other electromotive-force studies at (or near) room temperature are reported in references 7 to 9. In the present investigation, measurements were made of the electromotive force of sodium - sodium amalgam cells for $X_{Na}$ from 0.01 to 0.15 with glass as the electrolyte at 150°, 200°, and 250° C.

The thermodynamic properties of the liquid alloys were calculated from the values and temperature coefficients of electromotive force for the concentration cells sodium/sodium ion in glass/sodium amalgam. The state of each pure component at the given temperature was taken as the standard state. The activity of sodium $a_{Na}$ was calculated from the relation

$$n\mathcal{F}\epsilon = -RT \ln a_{Na}$$

or

$$\log a_{Na} = \frac{-5040\ \epsilon}{T}$$

where $\epsilon$ is the electromotive force and $T$ is the absolute temperature. The partial values of free energy, entropy, and heat of mixing for sodium were calculated from the following equations, respectively:

$$\begin{aligned}\Delta\bar{F}_{Na} &= -23\ 066\ \epsilon \\ &= RT \ln a_{Na} \\ &= 4.575\ T \log a_{Na}\ \text{cal/g-atom}\end{aligned}$$

$$\Delta\bar{S}_{Na} = 23\ 066 \frac{d\epsilon}{dT}\ \text{cal/(g-atom)(deg)}$$

$$\begin{aligned}\Delta\bar{H}_{Na} &= \Delta\bar{F}_{Na} + T\ \Delta\bar{S}_{Na} \\ &= 23\ 066 \left(T \frac{d\epsilon}{dT} - \epsilon\right)\ \text{cal/g-atom}\end{aligned}$$

The integral values for the heat of mixing $\Delta H$ were obtained by graphical integration from the equation

$$\Delta H = X_{Hg} \int_0^x \Delta\bar{H}_{Na}\ dx$$

where

$$x = \frac{X_{Na}}{X_{Hg}}$$

as given in reference 10. The integral values for the other functions, entropy and free energy, were obtained from the equation

$$\Delta G = X_{Na}\ \Delta\bar{G}_{Na} + X_{Hg}\ \Delta\bar{G}_{Hg}$$

where $\Delta G$ is any integral function of state and $\Delta\bar{G}$ is any partial function of state.

To calculate the thermodynamic data for the other solution component (mercury), the activity coefficient of mercury was obtained by graphical integration of the Gibbs-Duhem equation

$$\log \gamma_{Hg} = - \int_0^{X_{Na}} \frac{X_{Na}}{X_{Hg}} \, d \log \gamma_{Na}$$

where $\gamma$ is the activity coefficient, equal to the ratio of activity to atomic fraction. The partial values of mercury were obtained from the activity coefficients or the integral values.

Values of the excess thermodynamic properties were also calculated. Excess thermodynamic properties are equal to the difference between the total and ideal property changes. Thus, in general,

$$\Delta G = \Delta G^{i} + \Delta G^{e}$$

where $\Delta G$ is the value of the thermodynamic function for the solution, $\Delta G^{i}$ is the value which the function $\Delta G$ would have if the solution were ideal, and $\Delta G^{e}$ is the difference between the two.

The partial excess free energy of sodium $\Delta \overline{F}^{e}_{Na}$ and excess entropy $\Delta \overline{S}^{e}_{Na}$ were obtained from the following equations:

$$\begin{aligned} \Delta \overline{F}^{e}_{Na} &= \Delta \overline{F}_{Na} - RT \ln X_{Na} \\ &= RT \ln \gamma_{Na} \\ &= 4.575 \ T \log \gamma_{Na} \ \text{cal/g-atom} \end{aligned}$$

$$\begin{aligned} \Delta \overline{S}^{e}_{Na} &= \Delta \overline{S}_{Na} + R \ln X_{Na} \\ &= \Delta \overline{S}_{Na} + 4.575 \log X_{Na} \ \text{cal/(g-atom)(deg)} \end{aligned}$$

## SYMBOLS

| | |
|---|---|
| a | activity |
| $\Delta F$ | integral free energy of mixing |
| $\Delta \overline{F}$ | partial free energy of mixing |
| $\mathcal{F}$ | Faraday constant, 23 066 cal/V |
| $\Delta G$ | integral function of state |

| | |
|---|---|
| $\Delta\bar{G}$ | partial function of state |
| $\Delta H$ | heat of mixing |
| $\Delta\bar{H}$ | partial heat of mixing |
| $n$ | number of electrons in stoichiometric reaction |
| $R$ | gas constant, cal/deg |
| $\Delta S$ | integral entropy of mixing |
| $\Delta\bar{S}$ | partial entropy of mixing |
| $T$ | temperature, $^{\circ}K$ |
| $X$ | atomic fraction |
| $x$ | ratio of atomic fractions |
| $\gamma$ | activity coefficient |
| $\epsilon$ | electromotive force, V |
| Subscripts: | |
| Hg | mercury |
| Na | sodium |
| Superscripts: | |
| e | excess |
| i | ideal |

## EXPERIMENTAL PROCEDURE

The design of the measurement cell and the method of investigation were mainly the same as described in earlier investigations (refs. 11 and 12). The cell consisted of two borosilicate glass tubes, one placed inside the other. The inner tube was 300 millimeters long and 11 millimeters in diameter; the outer tube was 70 millimeters long and 22 millimeters in diameter. The inner tube, which served as the electrolyte, was thinned to about 1/2 millimeter at the closed end. Pure sodium was placed in the outer tube and a sodium alloy of known composition in the inner tube. These two tubes were placed inside a third tube (280 mm long and 28 mm in diam) which had a side arm that served to connect the cell to a supply of argon. Pure iron wires passing through rubber stoppers served as leads. The cell was placed in an electric furnace that consisted of a copper tube wound with nichrome wire. The temperature was controlled to within $\pm 1^{\circ}$ C by a temperature indicator controller and was measured with an iron-constantan thermocouple connected to a volt potentiometer. The potentiometer, with an electrometer as an impedance-matching amplifier, was used to measure the electromotive force.

The experiments were conducted in a dry box in an atmosphere of purified argon. Sodium of at least 99.9 percent purity was used; the mercury was triple distilled. The alloys were prepared in the inner tube by mixing weighed amounts of sodium and mercury. For each sample, an electromotive-force reading was obtained at the three temperatures, with the temperature held constant at least 20 minutes before the reading was taken. The electromotive-force values used in the calculations were average values taken from at least three measurements and did not differ by more than ±0.3 percent.

## RESULTS AND DISCUSSION

Values of the electromotive force of the sodium - sodium amalgam cell are given in table I. Also included in the table are values assumed for the temperature coefficient of the electromotive force at 200° C; the values were obtained by using the change in electromotive force over the 100° range:

$$\frac{\epsilon_{250^\circ} - \epsilon_{150^\circ}}{100^\circ}$$

The calculated thermodynamic data for the liquid sodium-mercury alloys at 200° C are given in table II and figure 1. Included in the figure are the curves for the composition range above 0.15 atomic fraction of sodium. These curves were obtained by using the values at 375° C given in reference 4.

The partial and integral free energies of mixing at 200° C are plotted in figure 1(a); the excess free energy values are shown in figure 1(b); the values for sodium are quite large. The partial and integral molar entropies of mixing are plotted in figure 1(c). In the most dilute solutions studied in this investigation, the partial entropy for sodium and the integral entropies are positive but become negative at higher sodium concentrations. The excess values are shown in figure 1(d). The partial excess values for sodium and the integral excess values are negative throughout the range. The partial and integral heats of mixing are shown in figure 1(e). In figure 2, activities are plotted as a function of the atomic fraction of sodium. Figure 2(a) shows the activities over the whole composition range. These curves were obtained by using the values given in reference 4 for sodium and mercury at 375° C. The dashed lines show the activities expected if the solution were ideal and followed Raoult's law. Figures 2(b) and (c) show the calculated activities of sodium and mercury, respectively, at 200° C, obtained from this study. The activities are, in all instances, less than they would be if Raoult's law were obeyed. However, in

## TABLE I. - VALUES AND TEMPERATURE COEFFICIENTS OF ELECTROMOTIVE FORCE

| Atomic fraction of sodium, $X_{Na}$ | Electromotive force, V |  |  | Temperature coefficient at 200° C, $\frac{d\epsilon}{dt} = \frac{\epsilon_{250^{o}} - \epsilon_{150^{o}}}{100^{o}}$, V/deg |
|---|---|---|---|---|
|  | Temperature, °C |  |  |  |
|  | 150 | 200 | 250 |  |
| 0.010 | 0.8764 | 0.8827 | 0.8897 | 0.00013 |
| .020 | .8422 | .8434 | .8474 | .00005 |
| .050 | .7797 | .7773 | .7768 | - .00003 |
| .100 | .7137 | .7034 | .6940 | - .00020 |
| .150 | .6183 | .6078 | .6000 | - .00018 |

## TABLE II. - THERMODYNAMIC DATA FOR LIQUID SODIUM-MERCURY ALLOYS AT 200° C

| Atomic fraction of sodium, $X_{Na}$ | 0.010 | 0.020 | 0.050 | 0.100 | 0.150 |
|---|---|---|---|---|---|
| Free energy: |  |  |  |  |  |
| Partial of sodium, $\Delta\overline{F}_{Na}$ | -20360 | -19450 | -17930 | -16230 | -14020 |
| Partial of mercury, $\Delta\overline{F}_{Hg}$ | -10 | -23 | -76 | -210 | -530 |
| Integral, $\Delta F$ | -210 | -410 | -970 | -1800 | -2500 |
| Excess free energy: |  |  |  |  |  |
| Partial of sodium, $\Delta\overline{F}^{e}_{Na}$ | -16030 | -15780 | -15110 | -14060 | -12240 |
| Partial of mercury, $\Delta\overline{F}^{e}_{Hg}$ | -1.0 | -3.9 | -28 | -110 | -380 |
| Integral, $\Delta F^{e}$ | -160 | -320 | -780 | -1500 | -2200 |
| Activity: |  |  |  |  |  |
| Sodium, $a_{Na}$ | $0.393\times10^{-9}$ | $0.103\times10^{-8}$ | $0.522\times10^{-8}$ | $0.320\times10^{-7}$ | $0.334\times10^{-6}$ |
| Mercury, $a_{Hg}$ | 0.989 | 0.976 | 0.922 | 0.797 | 0.569 |
| Activity Coefficient: |  |  |  |  |  |
| Sodium, $\gamma_{Na}$ | $0.393\times10^{-7}$ | $0.516\times10^{-7}$ | $0.104\times10^{-6}$ | $0.320\times10^{-6}$ | $0.223\times10^{-5}$ |
| Mercury, $\gamma_{Hg}$ | 0.999 | 0.996 | 0.971 | 0.885 | 0.669 |
| Heat: |  |  |  |  |  |
| Partial of sodium, $\Delta\overline{H}_{Na}$ | -18900 | -18900 | -18300 | -18400 | -16000 |
| Partial of mercury, $\Delta\overline{H}_{Hg}$ | -0.6 | -0.9 | -28 | -24 | -350 |
| Integral, $\Delta H$ | -190 | -380 | -940 | -1900 | -2700 |
| Entropy: |  |  |  |  |  |
| Partial of sodium, $\Delta\overline{S}_{Na}$ | 3.1 | 1.2 | -0.7 | -4.5 | -4.2 |
| Partial of mercury, $\Delta\overline{S}_{Hg}$ | 0.0 | 0.0 | 0.1 | 0.4 | 0.4 |
| Integral, $\Delta S$ | 0.1 | 0.1 | 0.1 | -0.1 | -0.3 |
| Excess entropy: |  |  |  |  |  |
| Partial of sodium, $\Delta\overline{S}^{e}_{Na}$ | -6.1 | -6.6 | -6.6 | -9.1 | -8.0 |
| Partial of mercury, $\Delta\overline{S}^{e}_{Hg}$ | 0.0 | 0.0 | 0.0 | 0.2 | 0.1 |
| Integral, $\Delta S^{e}$ | -0.1 | -0.1 | -0.3 | -0.7 | -1.2 |

the region rich in mercury, the departure of the activity of mercury from the law becomes small.

The behavior of sodium-mercury alloys may be attributed to the existence of structural groups of metallic compounds in the liquid phase (ref. 2). The phase diagram (ref. 4) indicates that one compound, $NaHg_2$, has a congruent melting point ($354^o$ C) and six compounds have incongruent melting points. Measurements have been made of the viscosity of sodium amalgams over the whole concentration range from $360^o$ to $400^o$ C (ref. 13). A marked maximum was obtained in the viscosity-concentration isotherm in the concentration region of the most stable compound, $NaHg_2$.

Previous measurements at room temperature have shown that, even in dilute solutions (0.1 atomic fraction of sodium), very substantial deviations from the laws of ideal dilute solutions occur. The results obtained in this study show this to be true over the range considered. The heats of mixing are large. Included in figure 1(e) are values of the integral heats of mixing obtained by Kawakami (ref. 5) by direct calorimetric determinations at $110^o$ C. These values are in good agreement with the ones obtained in the present study. The free energies of mixing are also large, while the entropy term $T\Delta S$ is small. Furthermore, $\Delta H$ and $\Delta F^e$ differ from each other in all compositions, by 30 calories per gram-atom at $X_{Na} = 0.01$ to 440 calories per gram-atom at $X_{Na} = 0.15$. For a "regular" solution, $\Delta H$ should equal $\Delta F^e$; therefore the solution cannot be classified as "regular" (ref. 14).

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 27, 1967,
120-34-01-11-22.

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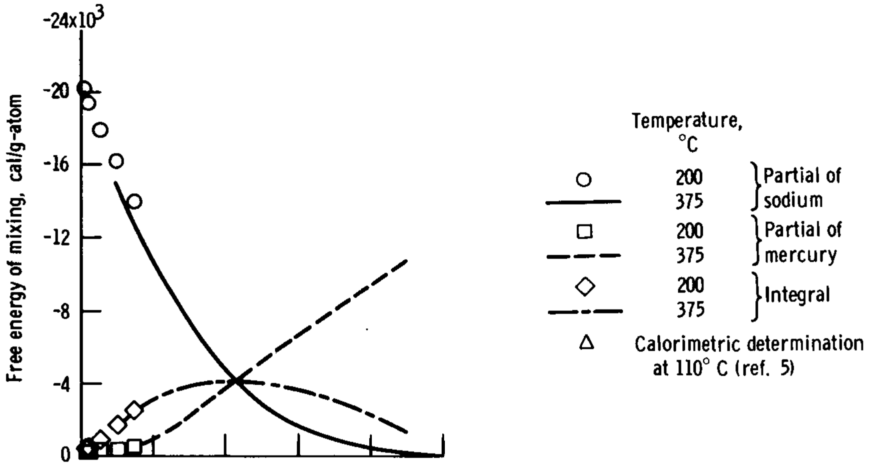
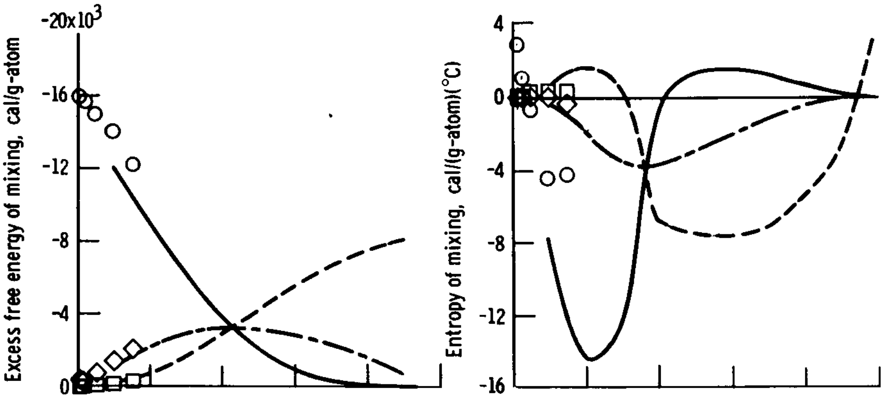
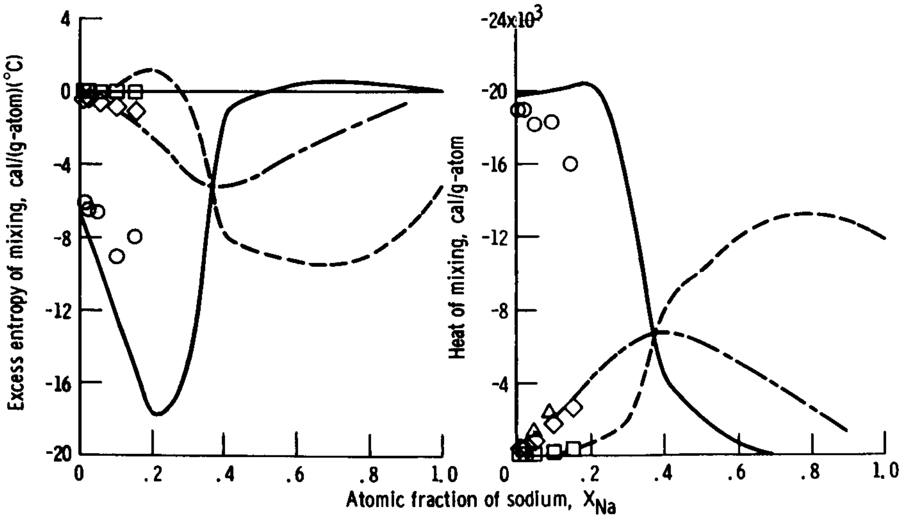


(a) Free energy of mixing.



(b) Excess free energy of mixing.

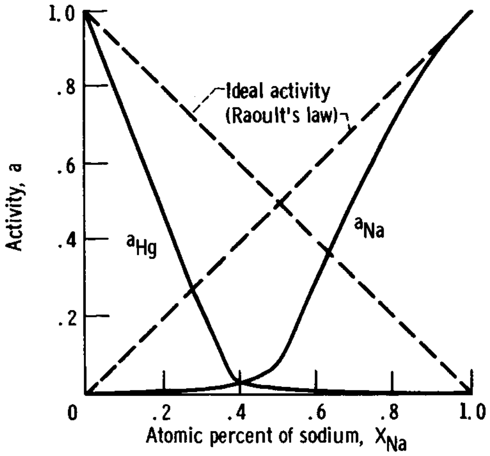
(c) Entropy of mixing.



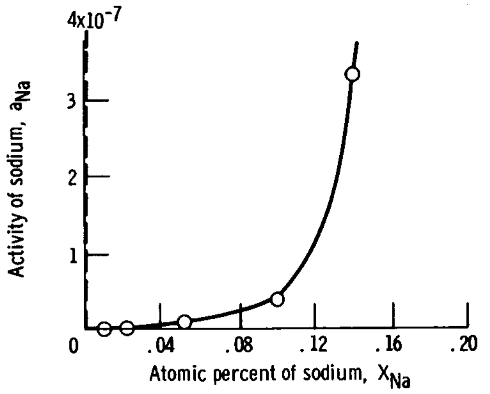
(d) Excess entropy of mixing.

(e) Heat of mixing.

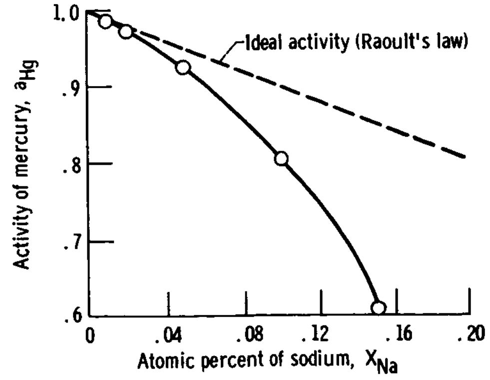
Figure 1. - Thermodynamic data for liquid sodium-mercury alloys.



(a) Activity of sodium and mercury at 375° C (ref. 4).



(b) Activity of sodium ($a_{Na}$) at 200° C.



(c) Activity of mercury ($a_{Hg}$) at 200° C.

Figure 2. - Activities of sodium and mercury in liquid sodium-mercury alloys.

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