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The Absolute Thermoelectric Power of Some Dilute Liquid Sodium Alloys

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Abstract-The absolute thermoelectric powers of liquid **sodium** and of dilute liquid alloys of sodium with silver, **cadmium,** indium and tin have been measured within the temperature range 100-460°C. The thermopower of liquid sodium is decreased by the addition of cadmium, indium or tin, with cadmium having the smallest and indium the greatest effect, whereas it is increased slightly on the addition of 1 at. $\%$ of silver. Values of the dimensionless thermopower parameter, ξ , derived from the experimental data, are compared with those predicted by the **Faber-ziman** theory; the agreement **is** quite good for Na-Ag and Na-Cd but less satisfactory for Na-In and Na-Sn. The discrepancies are discussed in terms of the assumptions involved in the calculations, namely the use of only one structure factor and local dielectric screening of the ionic pseudopotentials.

1. Introduction

Absolute thermoelectric power is a property which is intimately related to electrical conductivity and any theory which attempts to explain the resistance characteristics of a metal or alloy should also be able to account for its thermoelectric properties. The theory proposed by Ziman and his co-workers,l.z baaed on the Born approximation and on **a** model of nearly *free* conduction electrons, hss been remarkably successful in predicting the electronic transport properties, including the thermopower, of many pure molten metals. Initially, the agreement with experiment was generally qualitative but subsequent improvements in pseudopotential^{3,4} and phaseshift⁵ data and the establishment of more reliable absolute thermopower data for counter-electrode materials, such **as** copper,6 have resulted in much closer agreement between predicted and observed thermopowers, particularly for the molten alkali metals.^{7,8,9}

 \ddagger Work performed under the auspices of the U.S. Atomic Energy Commission. §Now at the Department of Metallurgy, The University, Nottingham, England.

The theory was subsequently extended to the electronic properties of binary molten alloys1° and detailed calculations have given good agreement with experimental resistivity data^{11,12,13,25} for a wide range of alloys. The thermopower of liquid alloys has hitherto received relatively little theoretical attention, partly became of a paucity of useful and reliable experimental data and partly because its evaluation is critically dependent on precise structure and pseudopotential data. Howe and Enderby¹⁴ successfully applied the theory to predict the thermoelectric behavior of a simple substitutional system, Ag-Au. However, much of the systematic experimental work that has been done has dealt with mercury-based alloys^{15,16,17} but these are not easily amenable to theoretical interpretation since the thermoelectric behavior of pure liquid mercury is itself not understood.

The purpose of the present work was to investigate the thermoelectric properties of a series of dilute liquid sodium-based alloys and to compare the data with those predicted by the Faber-Ziman theory. **Sodium** was chosen **aa** a solvent because it is a simple monovalent metal whose structure is relatively well established and because theory and experiment show particularly good agreement for the thermopower and resistivity of this pure metal.^{7,8} The work was restricted to dilute solutions, as a first step, partly to avoid the uncertainties which, at the present level of our understanding, are associated with the determination of the three partial structure factors which characterize the structure of an alloy and partly for technical reasons.

2. Experimental

There are in principle two methods of obtaining the thermoelectric power of a circuit made up of two different metals. The first is to keep one junction at a constant temperature and to measure the Seebeck potential E as the temperature T of the other junction is varied; the thermopower is then simply dE/dT . The other method is to vary the temperature of both junctions and to keep a small difference *AT* between them. The thermopower for the mean temperature of the couple is then *AE/AT* where ΔE is the small Seebeck emf. This latter technique was employed for the present work since it **was** considered to be mora convenient for measurements at elevated temperatures and to be sufficiently precise, in view of the numerous sources of error which can be anticipated when studying molten alkali metals.

The experimental set-up and technique were dictated to a large extent by the high reactivity of the liquid sodium. The cell, shown schematically in Fig. 1, waa constructed of stainless steel and consisted of two sections,

Fig. 1. Diagram of apparatus.

the inner of which could be raised and lowered relative to the other, without atmospheric contamination, by means of a vacuum-tight coupling seal. Sealed to the inner section, with epoxy-resin, waa a high density alumina tube of $\frac{1}{2}$ " O.D. and 18" long which, when in the lowered position, dipped **into** the liquid sodium alloy contained in **a** high-density alumina crucible. Containment of the liquid specimen in a crucible facilitated its removal for chemical analysis after completion of the measurements. Also *paasing* through and sealed to the **inner** section were two insulated copper leads for the auxiliary heater, not shown in the diagram, **and** two **4"** O.D. thin walled closed-end stainless steel tubes, one centrally located and passing **into** the alumina tube and the other, about 9" longer and located radially,

reaching almost to the bottom of the crucible when in the lowered position. These tubes acted **as** thermocouple sheaths and intermediate metal since neither the couples nor the copper reference electrodes could be brought **into** direct contact with molten sodium ; they were coated with "Glyptal" electrical insulating enamel where they pawed **into** and out of the chamber.

Three ports were provided, one each to the inner and outer sections, respectively, for atmosphere control and the other to facilitate alloying additions ; all ports could be connected either to **a** high vacuum system or to a purified helium supply, the total and differential pressures being monitored by means of gages. When the alumina tube was in the lowered position, the liquid could be raiaed inside it and thus complete the thermoelectric circuit. Heating was provided by **a** large clam-shell furnace; transient temperature variations and temperature gradients within the cell were greatly minimized by surrounding the cell with a large cylindrical copper block.

The thermocouples were constructed from 0.01" diam. chromel and alumel wire and threaded through $\frac{1}{16}$ " O.D. four bore insulation. High purity copper, **in'** the form of **0.01"** diam. wire, was chosen **as** the counterelectrode metal since its absolute thermopower is better known than any other at elevated temperatures⁶ and also it is thermoelectrically reproducible.

 $\text{For } 300^{\circ} < T < 1300^{\circ} \text{K}$

$$
Q_{\text{Cu}} = 0.05 + (5.45 \times 10^{-3})T \pm 0.15
$$
 μ V °K⁻¹.

The copper was threaded through the insulation with the couple and spot welded to the couple junction bead. Each thermocouple/copper junction was then spot-welded to the inside bottom of the respective thermocouple tube, this arrangement insuring **god** thermal and electrical contact with the stainleea steel and hence with the liquid metal. Each tube was assumed to be isothermal **across** its bottom so, by the law of intermediate metals, the stainless steel had no effect on the copper/liquid metal circuit.

The chromel/alumel couple material **was** calibrated beforehand ; and this calibration was used for estimating the overall liquid temperature. However, since the temperature difference between the two junctions was to be small, it was essential to have **a** very accurate knowledge of the difference, if any, between the calibrations of the two couples **after** they had been spot welded in place, this difference arising from inhomogeneities within the materials and from different amounts of strain which they may have sustained during their construction and installation.

The thermopower of the liquid/copper couple is given by

$$
Q_{\text{Liq}} - Q_{\text{Cu}} = \Delta E / \Delta T \tag{1}
$$

where Q_{Liq} and Q_{Cu} are the absolute thermoelectric power of the liquid and copper respectively.

Let us assume that the calibrations of the two couples differ by AT_{corr} when the real temperature difference is ΔT and the observed temperature difference is AT_{obs}

$$
\varDelta T = \varDelta T_{\text{obs}} \pm \varDelta T_{\text{corr}}.
$$

Before each measurement, the auxiliary heater was adjusted so that the outputs of the two chromel/alumel couples were exactly equal, then the emf of the liquid/copper couple, ΔE_{corr} , corresponding to the real temperature difference, was noted

$$
\Delta T_{\rm corr} = \frac{\Delta E_{\rm corr}}{Q_{\rm Liq} - Q_{\rm Cu}}
$$

Substituting and rearranging terms we find

$$
(Q_{\text{Liq}} - Q_{\text{Cu}}) \Delta T_{\text{obs}} \pm \Delta E_{\text{corr}} = \Delta E
$$

$$
Q_{\text{Liq}} = \frac{\Delta E + \Delta E_{\text{corr}}}{\Delta T_{\text{obs}}} + Q_{\text{Cu}}.
$$
 (2)

Hence the chromel/alumel couples were, in effect, calibrated in situ before each thermopower measurement. AT_{corr} was obtained at a temperature of $\Delta T/2$ below the mean temperature but any error due to this was considered to be negligible.) AT_{corr} was generally between 0.5 and 1.5"C depending on the temperature. The Seebeck emf's which were normally of the order 100 to $250 \mu V$, were measured with an accuracy of 0.3μ V by a standard potentiometric method.

The sodium was supplied by MSA Research in a 10 Ib drum containing an internal Zr hot trap and was specified $99.9(8)\%$ pure, the principal impurities *being* the other alkali metals. The solute metals, Ag, *Cd,* In and Sb were purchased from American Smelting and Refining *Co.* and **Sn** from Johneon Matthey and *Co.* ; all were **specified** 99.999% +pure. **Sodium** transfers were performed in an inert gas/vacuum *dry* box to **minimize** oxidation and all measurements were made below **460°C** *in* order **to** pre-

clude intergranular attack of the alumina by the molten sodium and to keep the evaporation of the sodium at **an** acceptable level. Chemical analyses were performed for sodium and solute metal at the completion of each run.

3. Results

The system and technique were first tested with pure liquid **sodium** at temperatures ranging between **100"** and **460°C** ; the absolute thermoelectric power of several different sodium samples is plotted in Fig. 2 together with

Fig. 2. The absolute thermoelectric power of pure liquid sodium. Published data are included for comparison [Bradley (Ref. 26), Kendall (Ref. 8), Bonilla *et al.* **(Ref. 18), Bidwell (Ref. 27)J.**

other published data. The present results which show a **scatter** of less than $\pm 0.2 \mu V^{\circ} C^{-1}$ are in good agreement with the more recent and reliable of the literature data namely those of Kendall⁸ and Bonilla *et al.*¹⁸ Since these published data were obtained by the constant cold-junction temperature method, this close agreement was taken to be sufficient confirmation of the

precision of the present technique. The thermopower at the melting point is $7.8 \,\mu\text{V}^{\,\circ}\text{C}^{-1}$ compared with the value of $8.0 \,\mu\text{V}^{\,\circ}\text{C}^{-1}$ observed by Kendall and by Bonilla et al. It then increases linearly with temperature between the melting point and about **300°C** but shows **a** slightly greater temperature dependence than was observed by Kendall ; above **300°C** the temperature dependence shows a slight curvature which is also suggested by the results **of** Kendall when copper counter-electrodes were used (it is interesting to note that the electrical resistivity of pure sodium also shows a marked deviation from linearity above **300°C).19**

Four binary sodium based alloy systems were studied, the solutea *being* Ag, *Cd,* In and Sn. Since the maximum working temperature was limited to about **460°C,** the concentration range that could be studied was determined in each case by the liquidus of the alloy system-up to about 5 at. % being permissible **for** Na-Cd and Na-In but Na-Ag being limited to about 1 at. %. The absolute thermoelectric powers of one Na-Ag, three Na-Cd, two Na-In and three Na-Sn alloys are plotted as a function of temperature in Figs. **3,4,5** and **6,** respectively. No published data could be found in the literature **for** any of these systems, **for** comparison. Within the experimental scatter which was less than $\pm 0.2 \mu V^{\circ}C^{-1}$ the thermopower was, in all cases, a linear function of temperature. Equations of the form $Q = B + AT$ were fitted to the data by the method of least squares and the derived constants *A* and *B* for the alloys studied are given in Table **1.** The estimated overall error in the data is $\pm 3\%$.

Alloy Na-1.0 at. $\%$ Ag	A $-2.32(6) \times 10^{-2} \mu V$ °C ⁻²	B $-5.79~\mu\mathrm{V}~^{\circ}\mathrm{C}^{-1}$
-2.37 at. % Cd	$-2.14(8) \times 10^{-2}$	$-5.56(5)$
-5.87 at. % Cd	-2.10×10^{-2}	$-5.37(2)$
-1.37 at. % In	$-2.15(4) \times 10^{-2}$	$-4.75(4)$
-3.92 at. $\%$ In	$-1.73(2) \times 10^{-2}$	$-4.60(1)$
-1.0 at. $\%$ Sn	$-2.05(6) \times 10^{-2}$	$-5.46(4)$
-2.0 at. % Sn	$-2.02(4) \times 10^{-2}$	$-5.14(2)$
-3.99 at. % Sn	$-1.85(5) \times 10^{-2}$	$-5.34(1)$

TABLE 1 Values of the constants A and B for equations $Q = B + AT$ fitted to **the thermopower** data **for** the sodium based **alloys**

Fig. 3. Absolute thermopower of liquid sodium **containing 1 8t.** *yo* **silver.**

Fig. 4. Absolute thermopower of some liquid sodium-cadmium alloys.

Fig. 5. Absolute thermopower of some liquid sodium-indium alloys.

Fig. 6. Absolute thermopower of some liquid sodium-tin **alloys. A2 P.C.L.**

200 **H. A. DAVIES**

It can be seen that the addition of cadmium, tin or indium lowers the absolute thermopower of molten sodium, whilst, over the temperature range covered, silver increases it. It is noteworthy that the thermopower of alloys containing silver, cadmium and tin extrapolate approximately to the value for pure sodium at its melting point. **This** may be purely fortuitous and a consequence of the small change in thermopower on alloying

Fig. 7. Absolute thermopower-compoaition isotherms at **325°C** for **dilute** sodium-based **liquid alloys.**

since the alloys containing indium, which show the greatest change, do not extrapolate to this value. Absolute thermopower/concentration isotherms at **326°C** for the four systems are plotted in Fig. **7.** (The temperature 325°C was chosen because, except for **lOO"C,** this is the **only** temperature for which experimentally derived structure data are available for liquid sodium.) The thermopower change for **a** given solute concentration does not increase in strict order with increasing valence of the solute **as** is the case for resistivity,'B indium having a **greater** effect than, tin over most of the concentration range studied.

4. *Theory* **and** Discussion

The absolute thermoelectric power *Q* of a metal or alloy can be expressed by :

$$
Q = \frac{-\pi^2 k^2 T}{3 \mid e \mid E_{\mathbf{F}} \cdot \xi} \tag{3}
$$

where E_F is the Fermi energy, T is the absolute temperature, k is Boltzmann)s constant, e is the charge per electron and ξ is a dimensionless thermopower parameter given theoretically by :

$$
\xi = -E_{\mathbf{F}} \left[\frac{d \ln \rho(E)}{dE} \right]_{E=E_{\mathbf{F}}} \tag{4}
$$

 $p(E)$ is the electrical resistivity which the metal or alloy would have if its Fermi surface were at energy E .

According to the Faber-Ziman theory,¹⁰ the resistivity of a molten binary alloy of metallic species **1** and 2 **can** be expressed on a free electron model **as** :

 $\rho = \rho_a + \rho_b$

where

$$
\rho_a = (3\pi V/\hbar e^2 v_F^2) \left[(c_1 - c_1^2) \langle u_1(x)^2 \rangle + (c_2 - c_2^2) \langle u_2(x)^2 \rangle - 2c_1 c_2 \langle u_1(x) u_2(x) \rangle \right]
$$

\n
$$
\rho_b = (3\pi V/\hbar e^2 v_F^2) \left[c_1^2 \langle a_{11}(x) u_1(x)^2 \rangle + c_2^2 \langle a_{22}(x) u_2(x)^2 \rangle + 2c_1 c_2 \langle a_{12}(x) u_1(x) u_2(x) \rangle \right]
$$
 (5)

 x is the scattering wave vector, K , expressed in units of twice the Fermi wave vector of the conduction electrons $k_{\mathbf{F}}$, c_1 and c_2 are the atom fractions of the two components; $u_1(x)$ and $u_2(x)$ are the effective atomic pseudopotentials appropriate to the electron screening of the alloy; $a_{11}(x)$, $a_{22}(x)$, and $a_{12}(x)$ are the three partial structure factors representing the Fourier transforms of the pair correlation functions for **1-1,** *2-2* and **1-2** pairs, respectively; the $\langle \ \rangle$ brackets represent the integral

$$
4\int_0^1 f(x)x^3\,dx
$$

*⁸⁰*that the scattering is integrated over all values of K up to the **back** scattering limit, v_F is the Fermi velocity of the conduction electrons and V is the average volume per atom. fi and **e** have their usual meaning.

If we restrict the analysis to very dilute solutions (of the order of **1 at.** % solute or less), it can be **assumed** that interactions between solute-atoms

are negligible so that $a_{22}(x)$ will approximate to unity over the whole range of x $(=K/2k_F)$. Density measurements on liquid Na-Cd²⁰ and Na-Sn²¹ alloys have shown that the molar volume remains approximately unchanged up to about 1 at. % solute although at greater solute concentrations a great deal of contraction occurs. There is a measurable, although small, excess volume of mixing associated with a Na $-$ 1 at. $\%$ In alloy²¹ but for the purposes of the present analysis we shall assume that it, and any that may be associated with the Na -1 at. $\%$ Ag alloy, are negligible. On this basis we can make the reasonable approximation that the structure of liquid sodium is not significantly altered by the addition of up *to* I-at. *yo* of these solutes so that, if thc solute is randomly distributed, the cross partial structure factor $a_{Na-2}(x)$ will approximate to that of the pure sodium, $a_{\text{Na}}(x)$.

The resistivity of a dilute liquid sodium alloy can then be approximated $by:$

$$
\rho = (3\pi V/\hbar e^2 v_F^2) \left[(1 - 2c) \langle a_{\text{Na}}(x) u_{\text{Na}}(x)^2 \rangle + c \langle u_{\text{Na}}(x)^2 \rangle \right. \\ \left. + c \langle u_2(x)^2 \rangle + 2c \langle a_{\text{Na}}(x) u_{\text{Na}}(x) u_2(x) \rangle - 2c \langle u_{\text{Na}}(x) u_2(x) \rangle \right] \\ = (3\pi V/\hbar e^2 v_F^2) \langle \text{Alloy} \rangle \tag{6}
$$

For **a** strictly free-electron case and where the pseudopotentials have local screening so that they are functions **only** of the momentum transfer and not also of the **total** electron momentum,2 application of Eq. **(4)** to (6) gives the thermopower of a dilute sodium alloy **as** :

$$
\xi = 3 - \frac{2[(1 - 2c)(a_{\text{Ns}}(2k_{\text{F}})u_{\text{Ns}}(2k_{\text{F}})^{2}) + c(u_{\text{Ns}}(2k_{\text{F}})^{2} + u_{2}(2k_{\text{F}})^{2})}{\langle \text{Alloy} \rangle} + \frac{2c(a_{\text{Ns}}(2k_{\text{F}}) - 1)(u_{\text{Ns}}(2k_{\text{F}})u_{2}(2k_{\text{F}}))}{\langle \text{Alloy} \rangle}
$$
(7)

For pure sodium, this expression reduces to simply **:z**

$$
\xi = 3 - \frac{2[a_{\mathrm{Na}}(2k_{\mathrm{F}}) u_{\mathrm{Na}}(2k_{\mathrm{F}})^2]}{\langle a_{\mathrm{Na}}(x) u_{\mathrm{Na}}(x)^2 \rangle} \tag{8}
$$

Ashcroft4 has proposed a simplified form for the pseudopotential which is applicable to the treatment of electronic properties involving $x \leq 2$ and which **is** simpler **to** evaluate numerically than the detailed scrccned model potential of Heine and Abarenkov,³ especially for the solute ions in these sodium alloys where the electron screening is drastically different from those in their pure states. This potential gave good agreement between theory and experiment for the resistivities of **a** wide range of alloy systems.12 For alloys comprised of ions with tightly-bound cores, the Ashcroft potential is given by

is comprised of ions with tightly-bound cores, the
given by

$$
V_i(x) = -\frac{\lambda^2 \cos sx}{x^2 + \lambda^2 f(x)} \frac{z_i}{z^*} \frac{2(a_0 k_F)^2}{3}
$$
(9)

where $\lambda^2 = (\pi a_0 k_F)^{-1}$, a_0 being the Bohr radius; z_i is the charge on the ion, z^* is the average electron density for the alloy; $f(x)$ is the Lindhard dielectric function;²² and $s = 2k_F R_{\text{core}}$ where R_{core} represents an effective core **radius** outside of which the electron interaction is Coulomb-like and inside of which it is very weak and negligible. *Reore* for each of the elements involved in the present work was established by fitting the potential to the observed resistivity of the respective pure molten metal at its melting point.

Theoretical values of ξ were calculated for the four alloys from Eq. (7) and *using* this form of the potential. The neutron diffraction data of Gingrich and Heaton at $325^{\circ}C^{23}$ were used for the structure factor of liquid sodium. At low angles, below $\sin \theta / \lambda \sim 0.06$, the scattering data were not considered to be very precise so low-angle values of $a_{\text{Na}}(x)$ were obtained by extrapolation of the higher-angle data to the compressibility value of $a(0) = 0.043$.

The calculated ξ for the four alloys and corresponding experimental values, derived from the experimental **Q** assuming free-electron values of *EF* with effective mass unity, are given in Table **2** along with their respective atomic volumes and *Reore.* Included also are the predicted values of resistivity for the four alloys (Eq. **(6))** and corresponding experimental data. **l9**

The quantitative agreement between predicted and observed values of *5* is, superficially, fairly good but closer examination will show that, **since** $\xi = 3 - 2q$, the agreement is rather poor when we compare values of *q*. This is particularly true for pure liquid sodium where the value of *q* using the Ashcroft potential is 0.004 compared with the "experimental" value of 0.15. For this metal, the pseudopotential changes its sign very near to $2k_{\text{F}}$ and hence a small absolute error in the potential would result in a very large relative error around $2k_F$ and this would consequently have a much more pronounced effect on the numerator of q than on its denominator. Also, it can be seen in Eq. **(7) for** the thermopower of the alloys that an error in $u_{\text{Na}}(2k_F)$ will not only cause a systematic error (from one alloy to another) associated with the first two terms of the numerator but also a

non-systematic error associated with the "cross" term involving $u_{\text{Na}}(2k_{\text{F}}) u_{2}(2k_{\text{F}})$. The absence of qualitative agreement between theory and experiment for the relative effects of the various solutes could therefore be accounted for, in part at least, by the failures of the Ashcroft potential **as** applied to the thermopower of pure sodium.

It has been shown5.6 that the Heine-Abarenkov model potential yields a value of thermopower for pure liquid Na at its melting point in much better agreement with experiment than is obtained here. We, therefore, recalculated ξ for pure Na at 325°C using the Heine-Animalu²⁴ (H-A) potential data, corrected for volume change between 0 and 602°K then, by substituting the H-A value of $u_{\text{Na}}(2k_F)$ for the Ashcroft value in Eq. (7), recalculated the quantities q and ξ for the four alloys. These recalculated values are now in much better agreement with the experimental values. For pure sodium, the theoretical *q,* 0.16, is in excellent agreement with the value 0.15 derived from the experimental data. That Ag and *Cd* have a similar effect on *q* is successfully predicted although the order is reversed. The predicted resistivity increment for 1 at. $\%$ Ag and *Cd* are in satisfactory agreement with the corresponding observed values but that predicted for 1 at. $\%$ Sn is greater than the experimental value by **a** factor of almost 3. Such a large discrepancy cannot be readily explained but an error in the predicted resistivity would almost certainly lead to an erroneoua value for the predicted thermopower. Although no experimental data are available, the predicted resistivity increment for $Na-1\%$ In would also seem to be somewhat high. The apparently satisfactory agreement between theory and experiment for the thermopower parameters of the indium and tin alloys should, therefore, be viewed with caution. For $Na-1\%$ In, an additional source of error could be that a small but significant negative exccss volume of mixing (-3.5%) occurs (in contrast to the almost ideal behavior of $Na-1\%$ *Cd and* Na-1% Sn) so that the validity of the assumption that $a_{11}(x) = a_{12}(x)$ is open to doubt.

However, the most serious source of error in the calculation of the theoretical thermopowers probably arises from the assumption, particularly for the solutes, that the ionic pseudopotentials have local screening, i.e., they are independent of the electron energies. Bradley *et aL2* first drew attention to the possible importance of non-local screening ; its effect on the thermopower expression is to add another term so that $\xi = 3 - 2q - r/2$. Young et al.⁹ and Ashcroft²² have subsequently elaborated on its quanti-

solute THERMOELECTRIC POW

205

tative effect for pure alkali metals but the potential data for pure polyvalent metals would not, at present, seem to be sufficiently precise and detailed to justify extension of the treatment to these alloys.

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