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## Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information: <http://www.informaworld.com/smpp/title~content=t713646857>

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To cite this Article Cusack, N. E. and Cusack, S. A.(1976) 'Possible errors in thermoelectric power measurements in liquid alloys due to thermal diffusion', Physics and Chemistry of Liquids, 5: 2,  $109 - 112$ 

To link to this Article: DOI: 10.1080/00319107608084111 URL: <http://dx.doi.org/10.1080/00319107608084111>

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*Phys. Chem. Liq.,* 1976, **Vol.** *5,* pp. 109-112 *0* Gordon and Breach Science Publishers, Ltd., 1976. Printed in Dordrecht, Holland

# **Possible Errors in Thermoelectric Power Measurements in Liquid Alloys due to Thermal Diffusion**

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*(Received August 29. 1975)* 

The temperature gradient necessary for thermoelectric measurements must promote the separation of constituents of a binary alloy by thermal diffusion. **This** can lead to systematic error in the inferred absolute thermoelectric power but after a brief and simple discussion it is concluded that this **is** serious only in special combinations of circumstances.

There have been a number of measurements of the thermoelectric power of liquid binary metallic or semiconducting systems and they are of considerable interest. Such measurements necessarily involve a temperature gradient in the sample and thermal diffusion must occur. Thedifference between the junction temperatures,  $T_0$  and  $T_L$ , can be large with one junction temperature fixed ("large  $\Delta T$  method"<sup>1-4</sup>) in which case the Seebeck voltage  $E(T_0, T_1)$  is measured and later differentiated to give the thermoelectric power, S. Alternatively if  $(T_L - T_0)$  is kept less than or equal to about 12 °C then  $E/(T_L - T_0)$  is an approximation to the thermoelectric power ("small  $\Delta T$  method" e.g. references<sup>3,5-8</sup>).

It is clear that, if in the "small  $\Delta T$  method," a few values of  $(T_L - T_0)$  are used and the thermoelectric power extrapolated to  $(T_L - T_0) \rightarrow 0$ , the error in *S* will vanish in the limit. Consequently this method is definitely to be preferred when thermal diffusion may occur. However there are some experimental situations in which the "large  $\Delta T$  method" would be technically desirable and the following simple discussion offers some reassurance



FIGURE **<sup>1</sup>**

that even in this case thermal diffusion will be a danger only in special cases.

Consider a linear sample of binary alloy as in Figure 1. The temperature  $T_0$  is fixed.  $x_1(z)$  is the mole fraction of component 1 at position z. The thermoelectric power at z is  $S(x_1, T)$ .

The error introduced into the Seebeck voltage by thermal diffusion is

$$
\Delta E(T_0, T_L) = \int_{T_0}^{T_L} \{ S(x_1, T) - S(\bar{x}_1, T) \} dT \tag{1}
$$

where  $\bar{x}_1$  is the nominal concentration determined by sample preparation. The corresponding error in the observed thermoelectric power when the sample is one limb of a thermocouple is

$$
\Delta S(T_L) = \left(\frac{\partial \Delta E}{\partial T_L}\right)_{T_0} = S(x_1(L), T_L) - S(\bar{x}_1, T_L) + \int_{T_0}^{T_L} \frac{\partial S}{\partial T_L}(x_1, T) dT.
$$
 (2)

This error depends on the difference  $(x_1(L) - \overline{x}_1)$  and may be estimated with the help of the steady state equation: $9$ 

$$
\ln\left(\frac{x_1}{x_2}\right)T_L\left(\frac{x_2}{x_1}\right)T_0 = \alpha \ln T_L/T_0 \tag{3}
$$

where  $x_2 = 1 - x_1$  and  $\alpha$  is a property of the system. The mean concentration along the sample is not necessarily equal to  $\bar{x}_1$ , e.g. if there are significant number density changes from 0 to L, and it will depend on the temperature gradient. However there will be many cases in which the mean concentration will differ little from  $\bar{x}_1$  and, since the temperature distribution is to a considerable' extent experimentally disposable, we will assume it linear for simplicity. Then from Equation **(3),** 

$$
(T_{L} - T_{0})\overline{x}_{1} = \int_{T_{0}}^{T_{L}} x_{1}(T) dT = \int_{T_{0}}^{T_{L}} \frac{T^{a}}{A + T^{a}} dT.
$$
 (4a)

where

$$
A = T_0^{\alpha} (1 - x_1(0)) / x_1(0) \tag{4b}
$$

Equation 4(a) gives A for specified values of  $T_0$ ,  $T_L$ ,  $\overline{x}_1$  and  $\alpha$ .  $\alpha$  must be a function of both temperature and composition and some values of it for metallic alloys with  $\bar{x}_1 = 0.5$  lie between 0.1 and 4.1.<sup>10</sup>

The simplest useful assumption concerning  $S(x_1, t)$  is

$$
S(x_1, T) = S(\bar{x}_1, T_0) + a(T - T_0) + b(x_1 - \bar{x}_1) + c(T - T_0)(x_1 - \bar{x}_1).
$$
 (5)

The linear temperature variation is quite a good approximation for metals and the linear composition variation should be reasonable unless the component separation is very great.

From Equations *(5)* and (2), after simple manipulation,

$$
\Delta S(T_L) = c(x_1(L) - \overline{x}_1)(T_L - K \int_{T_0}^{T_L} \frac{T^{\alpha+1}}{(A + T^{\alpha})^2} dT)
$$
(6a)

where

$$
K^{-1} = \int_{T_0}^{T_L} \frac{T^{\alpha}}{(A + T^{\alpha})^2} dT.
$$
 (6b)

The value of A allows us to calculate  $x_1(0)$  from Equation (4b),  $x_1(L)$  from Equation **(3)** and K from Equation (6b).

A measure of c is the amount by which  $\partial S/\partial T$  differs between one liquid conductor and another. With simple metals, this might be  $5 \times 10^{-3} \mu$ VK<sup>-2 11</sup>. It would be much greater if Hg were involved because  $(\partial S/\partial T)_{Hg} = -23 \times$  $10^{-3}\mu$ VK<sup>-2</sup> - an order of magnitude larger than with other simple metals. With some liquid semiconductors c could be still greater, e.g.  $c \sim 0.9$  in  $Ga-Te.$ <sup>7</sup>

Using  $T_0 = 773$ K,  $T_L = 1073$ K,  $c = 10^{-2} \mu$ VK<sup>-2</sup>, the calculations show (Table I) that although very significant segregation of components could occur thesystematicerrorin Sisnotveryserious compared withthenumerous other errors likely to be present. Since  $\alpha$  will not usually be known for a particular experiment, corrections will not be calculable and Table Isimply illustrates the possibilities. In Winter and Drickamer,<sup>10</sup> 12 hours is referred to **as** "ample" time for the steady state to settle down. No doubt this time will vary from apparatus to apparatus. Workers who measure thermoelectric power sometimes regard the steady state **as** a sign that their alloy **has** *homogenised* but it may in fact have *separated.* Nevertheless it appears from Table

#### TABLE I



In each block the figures are  $\mathbf{x}_1(0)$ ,  $\mathbf{x}_1(L)$ ,  $\Delta S(T_L) \mu \mathbf{V} \mathbf{K}^{-1}$ 

 $\Delta S(T_L)$  is proportional to c and in some systems c  $\Delta S(1_L)$  is proportional to c and in some system<br>might be 10 to 100 times greater than the value<br> $\mu$ VK<sup>-2</sup> used in the table.

**I** that the "large **AT** method" **is** safe in this respect other than in unfortunate combinations of circumstances which might include  $(i)$  Hg as one constituent, (ii) large values of  $T_L$ , (iii) strong quadratic dependence of *S* on  $x_1$  which certainly occurs in some systems  $4,7,8$  and which, in the case that  $S(\bar{x}_1)$  is near **a** maximum in *S* (probably a composition of great interest), would make *<sup>S</sup>* too low at allpoints of the specimen, (iv) concentrated alloys, (v) large values of  $(\partial^2S/\partial x)\partial T$  especially if occurring at a composition where *S* is changing sign in which case the error in S might falsify the composition for which  $S = 0$ .

#### **Acknowledgement**

**SAC** wishes **to** acknowledge the award of a Postgraduate Research Studentship by the Science Research Council.

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