## Physics and Chemistry of Liquids

## Possible errors in thermoelectric power measurements in liquid alloys due to thermal diffusion

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

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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. The difference between the junction temperatures, $T_0$ and $T_L$, can be large with one junction temperature fixed ("large $\Delta T$ method"[1–4]) in which case the Seebeck voltage $E(T_0, T_L)$ 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 $12\,^\circ$C then $E/(T_L - T_0)$ is an approximation to the thermoelectric power ("small $\Delta T$ method" e.g. references[3,5–8]).

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 $(T_L - T_0) \to 0$, 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
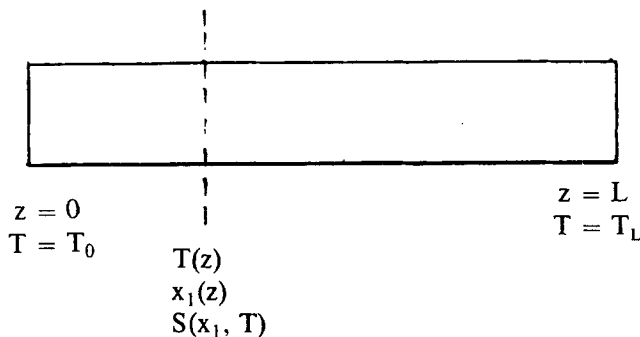
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FIGURE 1.

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

$$\Delta S(T_L) \equiv \left(\frac{\partial \Delta E}{\partial T_L}\right)_{T_0} = S(x_1(L), T_L) - S(\bar{x}_1, T_L) +$$

$$\int_{T_0}^{T_L} \frac{\partial S}{\partial T_L} (x_1, T) dT. \tag{2}$$

This error depends on the difference $(x_1(L) - \bar{x}_1)$ 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),

$$(T_L - T_0)\bar{x}_1 = \int_{T_0}^{T_L} x_1(T)\,dT = \int_{T_0}^{T_L} \frac{T^\alpha}{A + T^\alpha}\,dT. \tag{4a}$$

where

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

Equation 4(a) gives A for specified values of $T_0$, $T_L$, $\bar{x}_1$ 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.[10]

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

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

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,

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

where

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

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 $5 \times 10^{-3}\mu VK^{-2}$[11]. It would be much greater if Hg were involved because $(\partial S/\partial T)_{Hg} = -23 \times 10^{-3}\mu VK^{-2}$ – 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.[7]

Using $T_0 = 773$ K, $T_L = 1073$ K, $c = 10^{-2}\mu VK^{-2}$, the calculations show (Table I) that although very significant segregation of components could occur the systematic error in S is not very serious compared with the numerous other errors likely to be present. Since $\alpha$ will not usually be known for a particular experiment, corrections will not be calculable and Table I simply illustrates the possibilities. In Winter and Drickamer,[10] 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

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TABLE I

In each block the figures are $x_1(0)$, $x_1(L)$,
$\Delta S(T_L)\ \mu VK^{-1}$

| $\dfrac{\alpha}{\overline{x}_1}$ | 0.5 | 1.0 | 4.0 |
|---|---|---|---|
| 0.1 | 0.092 | 0.085 | 0.050 |
|  | 0.107 | 0.114 | 0.163 |
|  | 0.01 | 0.02 | 0.08 |
| 0.5 | 0.478 | 0.457 | 0.334 |
|  | 0.519 | 0.539 | 0.650 |
|  | 0.03 | 0.06 | 0.22 |

$\Delta S(T_L)$ is proportional to c and in some systems c might be 10 to 100 times greater than the value $10^{-2}$ $\mu VK^{-2}$ used in the table.

I that the "large $\Delta T$ 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 $S(\overline{x}_1)$ is near a maximum in S (probably a composition of great interest), would make S too low at *all* points of the specimen, (iv) concentrated alloys, (v) large values of $(\partial^2 S/\partial x)\partial T$ especially if occurring at a composition where S is changing sign in which case the error in S might falsify the composition for which $S = 0$.

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