# Study of electric potentials across a moving solid-liquid interface

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**Abstract.** The electric potential across a melting sample of pure lead was measured as a function of time. A difference of the order of a few hundred microvolts was seen between the measured values of the potential and those calculated using the temperature gradients and the thermopowers of the solid and the liquid phases. This difference persists as long as the solid-liquid interface moves and is attributed to the Galvani potential present at the solid-liquid interface. It is suggested that such measurements can be used to obtain the value of the Fermi energy for liquids.

**Keywords.** Solid-liquid interface; Galvani potential; Fermi energy; lead; thermopower.

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## 1. Introduction

Consider two dissimilar metals which are characterized by Fermi energies $E_{F1}$ and $E_{F2}$ and work functions $\phi_1$ and $\phi_2$ such that $\phi_1 > \phi_2$ and the Fermi energy $E_{F2}$ is at a level higher than $E_{F1}$. If these metals are brought into contact with each other at one end, electrons will flow from the metal 2 to metal 1. Metal 2 will get positively charged such that metal 2 is at a potential $V_c$ with respect to metal 1 given by

$$V_c = (\phi_1 - \phi_2)/e,$$

(1)

where $e$ is the charge on the electron. $V_c$ is called the contact potential difference. The difference in Fermi energies between the two metals can also be expressed in terms of the so-called Galvani potential, $V_g$, given by

$$V_g = (E_{F1} - E_{F2})/e.$$

(2)

It may be noted that a contact potential results due to the difference in the work functions while the Galvani potential is due to Fermi level differences. This aspect is highlighted in figure 1 and further discussed by Van der Ziel (1968).

It is generally believed that $V_c$ is measurable directly while $V_g$ is perceived only by
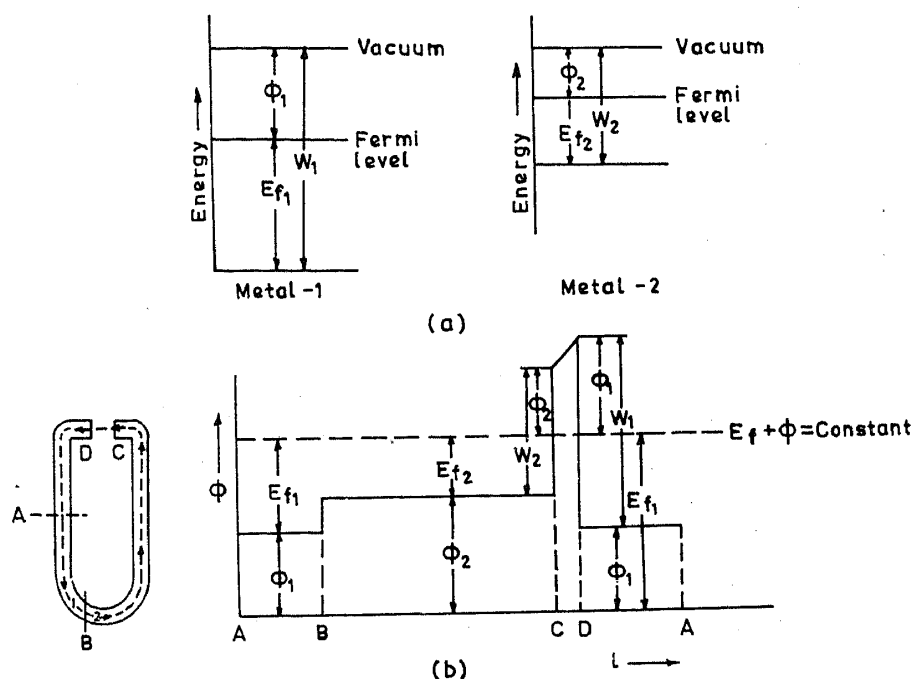
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**Figure 1.** Schematic representation of Fermi energy levels ($E_{F1}$ and $E_{F2}$) and work functions ($\phi_1$ and $\phi_2$) for two metals 1 and 2 when they are (a) separate and (b) in contact with the electron moving around from A. Note the existence of Galvani potential at B and contact potential between D and C.

its temperature dependence which manifests itself as the contact component of the thermoelectric e.m.f. (Van der Ziel 1968).

The Fermi levels of metal in the solid and liquid states are expected to be different. Since most metals expand on fusion, one anticipates a lower Fermi level in the liquid state. By virtue of the Fermi level difference, a Galvani potential arises at a solid-liquid interface. Whenever a solid phase is brought into physical contact with its own liquid, an instantaneous electron flow will ensue from the solid to the liquid and establishes the Galvani potential. When the solid-liquid interface moves i.e. whenever the solid melts or the liquid freezes at the interface it is accompanied by an electron flow in an appropriate direction. The latter type of electron flow affords a method of measuring the Galvani potential by monitoring the potential across a solid-liquid interface in continuous motion. The present report is in continuation of our earlier efforts at measuring the potential across a solid-liquid interface through the design of appropriate cells (Gupta *et al* 1987; Bhuniya 1989).

## 2. Experimental procedure

A cell was fabricated for the purpose of detecting the interface voltage. As shown in figure 2 the cell consists of two electrodes for measuring the potential and two thermocouples for measuring the temperature. The choice of the electrodes was limited by the following criteria:

(a) The material should not interact either chemically or by way of dissolution in the sample: Perusal of literature, especially phase diagrams, shows that most electrode
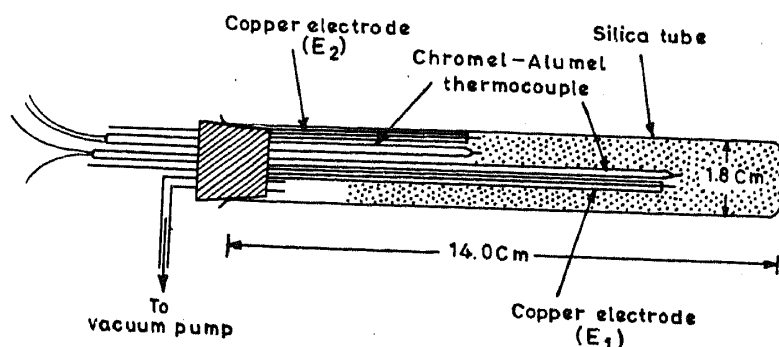
**Figure 2.** Schematic drawing of the solidification cell. The dotted portion represents the sample.

materials form monotectics/eutectics with lead. Only copper dissolves to a negligible extent at the temperatures of our interest. In a few cases, no phase diagram information was available thus preventing the selection of such materials.

(b) The thermopower of the electrode material should be smaller than or comparable to that of the sample for greater accuracy. Otherwise, the small interface potentials tend to get lost in the associated experimental errors. From this point of view as well, copper is the most suitable electrode for lead.

The two copper electrodes of circular cross-section with a diameter of 0·8 mm were held at a vertical separation of 5 cm in a silica tube of length 14 cm and internal dia of 1·8 cm (figure 2). These were sheathed in glass tube (with only the tip being exposed) and held in place with the aid of a rubber stopper. Two sheathed and fine chromel-alumel thermocouples were located very close to the two electrodes to monitor the temperatures.

The tube was initially filled with metal to be studied and heated until a pool of liquid metal is formed. The rubber stopper was then positioned and sealed. The output from the thermocouples was monitored using a digital microvoltmeter (model DMV₋ 001). The output from the electrodes was amplified using a d.c. amplifier fabricated and calibrated by us and fed to a Perkin–Elmer 56 chart recorder. A typical experiment using this cell consisted of inserting the bottom end of the assembly vertically into a pre-heated resistance furnace which was maintained at a temperature above the melting point of metal to be studied. Initially the portion below electrode $E_1$ melts (see figure 2) and a solid-liquid interface is formed. It then progressively moves towards $E_2$ during which time the temperatures and the voltage between $E_1$ and $E_2$ are monitored.

## 3. Results

Figure 3 shows the output across the electrodes $E_1$ and $E_2$ (figure 2) and the temperature profiles of these electrodes during the melting of pure lead. It may be noted that the temperature in the region near $E_1$ rises linearly and attains the melting temperature $(T_m)$ of lead (600·5 K). Temperature of electrode $E_2$ lags behind and attains 600·5 K after a lapse of about 360 seconds. This is the time it takes for the interface to move from electrode $E_1$ to electrode $E_2$. The potential recorded between $E_1$ and $E_2$ rises linearly, stabilizes prior to $E_1$ attaining $T_m$ of lead, shows precursor
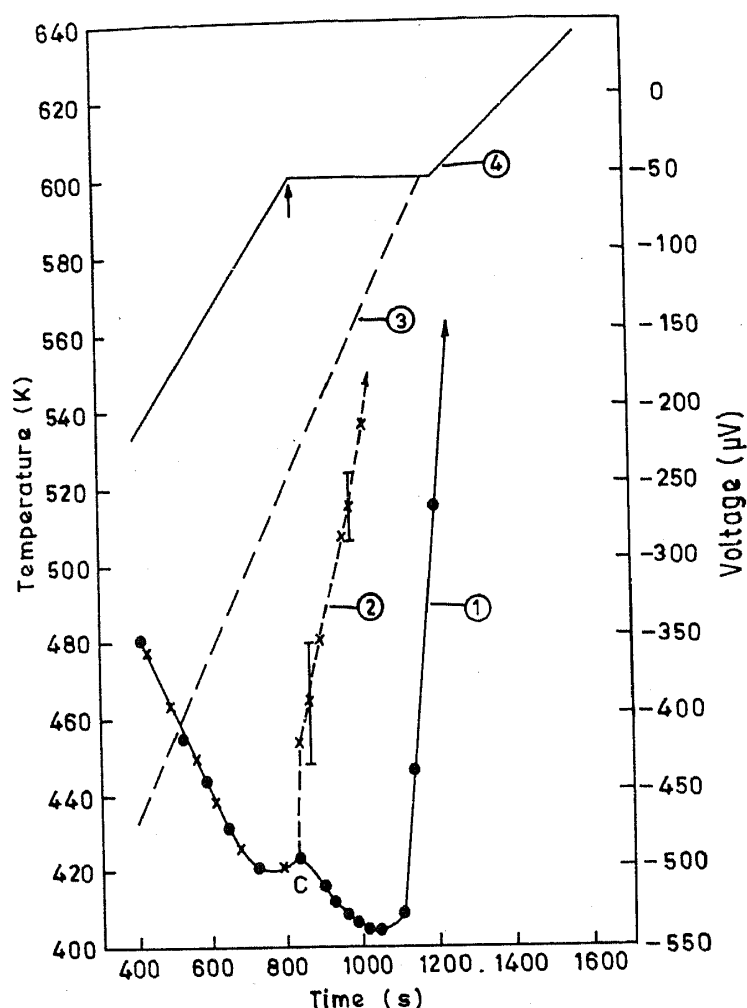
**Figure 3.** Observed voltage (curve 1) across the electrodes $E_1$ and $E_2$ (figure 2) plotted as a function of time. The calculated thermo e.m.f. is shown by curve 2 while the temperatures near the electrodes $E_1$ and $E_2$ are shown by curves 3 and 4 respectively.

effects (point C in figure 3) and then rises almost linearly until $E_2$ attains $T_m$ after which it drops suddenly (see curve 3 in figure 3).

The thermopower of the solid phase with respect to the pure copper electrode could be readily evaluated from the portions of e.m.f. plot prior to melting. The value obtained by us for solid lead near $T_m$ is $-5\cdot39\pm0\cdot83$ $\mu VK^{-1}$ and compares very favourably with the value of $-5\cdot50$ $\mu VK^{-1}$ reported earlier (Verhoeven and Gibson 1969; Blatt *et al* 1976). The thermopower of the liquid phase could not be determined with the same accuracy due to the very small gradients in the liquid phase. We, therefore, use the value of $-7\cdot0$ $\mu VK^{-1}$ reported by them.

## 4. Discussion

What potential differences are expected between electrodes $E_1$ and $E_2$? In a cell of the type described above, the solid and/or liquid phases are maintained in a temperature gradient before, during and after melting. The observed gradients (as evaluated from the temperature near $E_1$ and $E_2$) are greater in the initial solid phase

than in the final liquid phase. These gradients lead to thermoelectric e.m.f.s. When the region between $E_1$ and $E_2$ is a single phase, the thermo e.m.f. is given by the product of thermopower $S$ and the temperature difference between $E_1$ and $E_2$. The expected thermo e.m.f. was calculated from the following expression due to Verhoeven and Gibson (1969).

$$V = (S_p - S_l)\delta f G_l + (S_p - S_s)(1 - f)G_s\delta, \tag{3}$$

where $f$ is the fraction of the length between the probes which is the liquid. $S_p$, $S_l$ and $S_s$ are the absolute thermoelectric powers of the probe, liquid and solid respectively, $\delta$ is the separation between probes and $G_s$ and $G_l$ are the values of thermal gradient in solid and liquid respectively. It can be shown that equation (3) reduces to

$$V = (S_p - S_l)(T_2 - T_m) + (S_p - S_s)(T_m - T_1), \tag{4}$$

where $T_m$ is the melting temperature of the metal and $T_1$ and $T_2$ are the temperatures at $E_1$ and $E_2$ respectively. One normally expects the output between $E_1$ and $E_2$ to be entirely due to the thermo e.m.f.s.

In figure 3 is also shown the thermo e.m.f. calculated from equation (4). While the general trend of the plot is reproduced, there are significant and inexplicable differences between the observed e.m.f. and the expected e.m.f. when the region between $E_1$ and $E_2$ is partially liquid and partly solid. Attempts at compensating for the difference by altering the thermopowers of the liquid and solid phases lead to unreasonable values for these parameters. In an earlier study on the freezing of an aqueous solution Zhekhamukov and Kambiev (1985) attributed potentials of the order of 100 $\mu$V, observed during the movement of the solid-liquid interface to change separation at the interface. In the present case where we are dealing with a highly conducting material such processes of charge separation are unlikely and an alternate explanation is required.

We propose that the discrepancy is due to the existence of a Galvani potential. It is well known that the Galvani potential at a single interface cannot be measured since any such attempt will introduce additional interfaces between the probes and the phases concerned (Bockris and Reddy 1973). However, in the present set of experiments, such additional interfaces are present both when the interfaces are stationary and when they are mobile. Any contributions from these interfaces are eliminated when we take the differences between the observed and calculated potentials since the thermopowers used in the calculation also refer to the same electrodes. From our observations it can be said that subtracting the thermo e.m.f. due to gradients is equivalent to subtracting the effects at a stationary interface in the present experiments. Since the equilization of Fermi levels is being slowed down to match the rate of movement of the interface, it is likely that the Galvani potential at the interface is being sensed in the present experiments. This conclusion is in agreement with Sommerfeld's arguments (Sommerfeld 1964) that the electric field present in a conductor carrying a current $I$ and placed in a thermal gradient is given by,

$$E = (1/\sigma)I - S \, \mathrm{grad} \, T - \mathrm{grad} \, (\mu/e), \tag{5}$$

where $\sigma$ is the electrical conductivity and $\mu$ is the chemical potential per electron. Even in the absence of temperature gradients and electric current a potential given

by $\Delta\mu/e$ can arise due to a finite difference ($\Delta\mu$) in chemical potential of the two phases at a moving interface. In metals, in the absence of any external fields, ($\Delta\mu/e$) can be equated to the Galvani potential ($\Delta E_f/e$). The interface temperature $T_i$ deviates from $T_m$ when the interface moves and leads to the differences in chemical-potentials of electrons. The difference may be expected to be dependent on the rate of interface movement.

The Galvani potential can be expanded as a function of temperature with respect to its value at $T_m$ by the use of Taylor series. To a first approximation,

$$V_g(T) = \left(\frac{E_{F1} - E_{F2}}{e}\right)_{T_m} + \left[\frac{\partial}{\partial T}\left(\frac{E_{F1} - E_{F2}}{e}\right)\right]_{T_m} (T_m - T_i). \tag{6}$$

The second term on the right hand side of the above expression is the contact component of the thermo e.m.f. (Yepifanov and Moma 1984). One can now express the total observed output ($V_{obs}$) from the electrodes $E_1$ and $E_2$ as

$$V_{obs} = V_1 + V_2, \tag{7}$$

where $V_1$ is the component arising from the Galvani potential $V_g$ and is given by equation (2) for $T = T_m$ i.e. the first term of equation (6). $V_2$ is the contribution for thermoelectric e.m.f. from all causes including the second term on the right hand side of (6). The difference, $V_{obs} - V_2$, must then correspond to $V_g$ at $T_m$. If so the observed discrepancy of about 100–400 $\mu$V implies a Fermi level difference of 0·1 MeV between the solid and liquid states of lead. $T_i$ will be a function of the rate of interface movement. $V_2$ will therefore be a function of the rate at which the interface moves. On the basis of the above arguments, the discrepancy between observed and calculated e.m.f.s should be a constant for a constant rate of interface movement. However, the difference changes from 100 $\mu$V at the beginning of melting to 400 $\mu$V at the end. This would imply a progressively increasing rate of melting. Such an increase may be expected following improvement in heat transfer from the furnace to the sample in the presence of a liquid phase.

The present analysis indicates the possibility of estimating the Fermi level difference between the solid and liquid phases of a pure metal and consequently the Fermi level in the liquid state. The present experimental set-up permitted only the use of low melting metals. Suitable modifications of the system and careful selection of electrodes should enable us to extend the study to other high melting metals. In the case of alloys, the situation will be further modified by the rejection of solute at the solid-liquid interface. Study of such situations will help in understanding the role of the observed potential in controlling the microstructure through feedback and superimposition of appropriate external potentials.

## 5. Conclusions

The present investigation shows that the electric potential measured across suitably located electrodes in a cell in which solidification takes place cannot be accounted for in terms of thermoelectric phenomena. The difference between the observed potential and that expected from temperature gradients and thermoelectric power of

the solid and liquid phases is of the order of few hundred microvolts in case of pure lead. The discrepancy is attributed to the contribution due to a Galvani potential across the moving solid-liquid interface. This potential is found to be dependent on the rate of solidification.

## Acknowledgements

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