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A THERMODYNAMIC TREATMENT OF THE ELECTROMOTIVE FORCE OF FUSION

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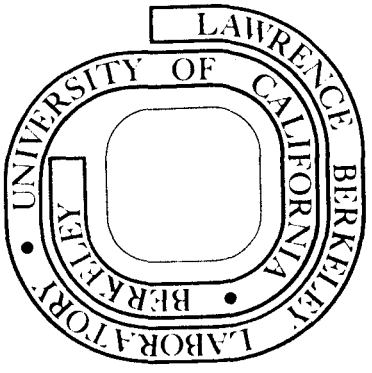

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LBL-4448

A THERMODYNAMIC TREATMENT OF THE ELECTROMOTIVE FORCE OF FUSION*

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In an earlier letter[1] an electromotive force, (EMF), of fusion was explained as arising from a difference in chemical potentials or Fermi brim energy levels for the electrons between the molten liquid and the forming crystal or surface. It will be shown that this explanation is in accord with both a thermodynamic treatment of the phenomena and an explanation in terms of the Fermi electron distribution.

The Fermi factor, f(E), is defined as:[2]

$$f(E) = \frac{N(E)\,dE}{S(E)\,dE} = \frac{1}{e^{(E - E_0)/kT} + 1} \qquad (1)$$

where N(E)dE is the number of electrons per unit volume with total energy between E and E + dE, S(E)dE is the number of quantum states per unit volume with total energy between E and E + dE, k is the Boltzman constant and T is the temperature in °Kelvin, E_0 is the Fermi brim energy or the Fermi level and is given with reservations related to the mass of the electron as[2]

$$E_0 = \frac{h^2}{8m}\left(\frac{3N}{\pi}\right)^{2/3} \text{ electron volts} \qquad (2)$$

where h is Plancks constant, m is the electron mass, and N is the number of conduction electrons per unit volume. E_0 is given as equal to the electrochemical potential,[2] and it is also equal to the chemical potential, μ_e, or the escaping tendency for electrons. A plot of f(E) versus E is shown in Fig. 1. It is clear from Fig. 1 and Eq. (2) that

$$dE_0/dT = 0 \qquad (3)$$

and thus

$$d\mu_e/dT = 0 \quad . \tag{4}$$

The difference of chemical potential of electrons between two conductors connected to points at differing chemical potentials[3(p.463)] is

$$\mathcal{F}\varepsilon = -\Delta u_e \tag{5}$$

where ε is the electomotive force and $\mathcal{F}$ is the Faraday equivalent. It follows that

$$d\varepsilon/dT = 0$$

which reduces the Gibbs-Helmholtz relationship[3(p.165)]

$$\varepsilon + \frac{\Delta H}{n\mathcal{F}} = T\frac{d\varepsilon}{dT} \tag{7}$$

where ΔH is the change in enthalpy and n is the number of equivalents passing for the change ΔH or $\Delta\mu_e$ in a closed system, to

$$\varepsilon = -\frac{\Delta H}{n\mathcal{F}} \tag{8}$$

This is in agreement with Gibbs' definition of the chemical potential[3(p.203)]

$$dE = TdS - PdV + \sum_i \mu_i dn_i \tag{9}$$

for constant entropy and volume, where E is the internal energy, P is the pressure, V is the volume, and n_i is the number of moles of component i; or[4(p.92)]

$$dF = -SdT + VdP + \sum_i (\partial F/\partial n_i)_{T,P,n_j} dn_i \quad , \tag{10}$$

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where F is the Gibbs free energy (now usually given as G), and $(\partial F/\partial n_i)_{T,P,n_j}$ is equal to the chemical potential, μ_i, and the subscripts correspond to constant temperature, constant pressure, and constant number of moles of the other components, j, in the system. Also[3(p.203)]

$$dH = TdS + VdP + \sum_i \mu_i dn_i \tag{11}$$

Therefore, from Eqs. (9, 10) and (11),

$$\mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} = \left(\frac{\partial E}{\partial n_i}\right)_{S,V,n_j} \tag{12}$$

Also, from a treatment of surface effects[3(p.482)] Eq. (10) may be written

$$dF = -SdT + VdP + \sigma dA_s + \sum_i \mu_i dn_i \tag{13}$$

where σ is the surface tension and A_s is the area, and thus

$$\mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,P,A_s,n_j} \tag{14}$$

where the restriction of constant surface area during electron transfer is met for any shape or surface if the electron moves rapidly enough, or along a short enough path.

The reported experiments are in agreement with Eqs. (3, 4, 5) and (6) with respect to observed constant EMF values and variations in temperature.[1] The observed EMF's correspond closely to reported heat of fusion values, thus supporting Eq. (8), with additional support coming from Eq. (12),

where the chemical potential is defined in terms of the variation of enthalpy with number of electrons at constant entropy, pressure, and other species, and with no restriction on temperature.

The observation of a continuous surface EMF[1] of the same magnitude as the EMF of fusion is in agreement with Eqs. (5), (12) and (14) and indicates that new surface area was being continuously generated at the surface contact electrode. This suggests a convecting system. The equality of EMF of fusion and surface tension or contact EMF is not surprising if one imagines the two situations in terms of a compensation effect, where the equality of the Fermi contact surface brim energies is realized by a flow of electrons and establishment of an electrostatic potential difference so that the values of E_0 and μ_e become equal across all contacts at equilibrium. The value of μ_e on the crystal side of the contact is then by definition equal to μ_e on the atmosphere side of the surface and equal to μ_e in the liquid. The electrostatic neutrality of the crystal behind the contact is equivalent to the electrostatic neutrality above the liquid surface. The ability of the molten liquid to establish an electrostatic potential difference is the same whether it is with respect to a crystal of the same material and environment or a surface-atmosphere or vacuum layer interface. This indicates that molten liquid surfaces should give x-ray diffraction patterns equivalent to comparable crystal surfaces at the same temperature. This agrees with diffraction experiments on mercury liquid and crystals.[4(p.416)]

The process of reversible crystal formation or melting is a constant temperature one and therefore no heat may flow and $\Delta S = 0$. The charge which flows due to the electromotive force of fusion as new surface is formed or as an old surface melts can be used for an amount of work

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$n_e\mathcal{F}\varepsilon$. If a proper low resistance path is not provided, no work is done and the energy difference will dissipate as i^2R heat, where i is the current and R is the resistance, as electrostatic neutrality is reestablished. In this case $\Delta F = 0$, and

$$\Delta H = T\Delta S \tag{15}$$

rather than

$$\Delta H = -n_e\mathcal{F}\varepsilon \quad . \tag{16}$$

In conclusion, it is emphasized that the chemical potential is equal to a change in free or Gibbs energy with respect to a change in the number of moles of component, i, at constant temperature and pressure, and this is also equal to the change in enthalpy or internal energy with respect to a change in the number of moles of component, i, holding other variables constant in accord with Eq. (12). A measurement of any one of the equalities in Eq. (12) is a determination of the rest, including the change in work content with respect to the number of moles of component i at constant T, V, and n_j.[5]

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2. Robert L. Sproull, Modern Physics, The Quantum Physics of Atoms, Solids, and Nuclei, Second Edition (John Wiley & Sons, Inc., New York-London-Sydney, 1967).

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5. The condition of constant gravitational potential is also assumed for Eqs. (10), (12), and (14).

FIGURE CAPTION

Fig. 1. The Fermi factor as a function of E and T.

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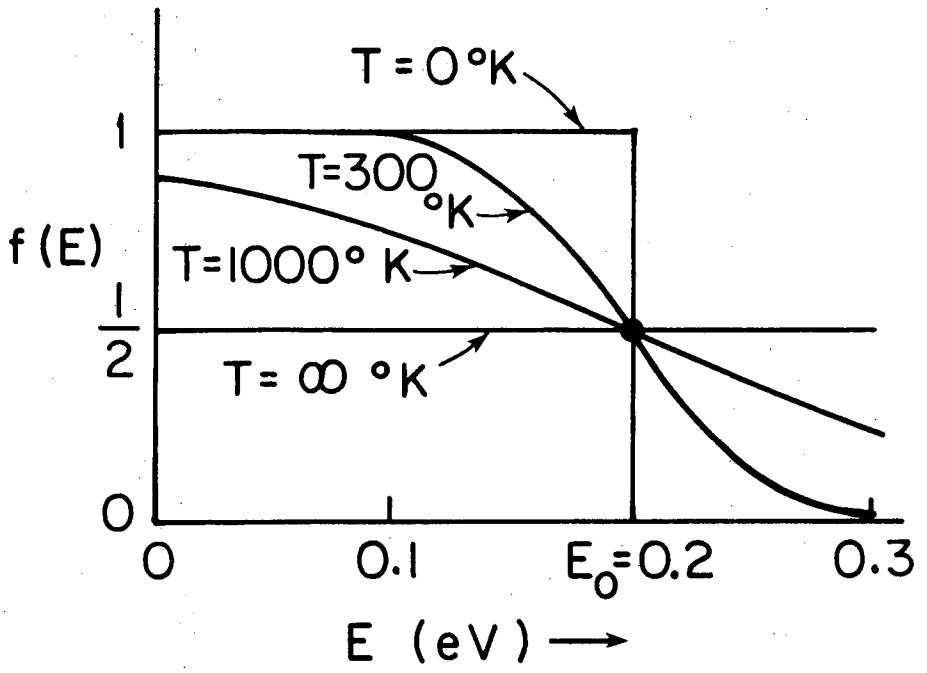

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Fig. 1

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