

LATENT HEAT AND ELECTRODE POTENTIAL

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In 1869, François Marie Raoult (1830-1901) briefly described the influence of temperature and of the state of the metallic electrodes on the electromotive force (emf) of a voltaic cell (1). In the copper-zinc Daniell cell he had found that sheet, electrodeposited, and other types of copper, combined with various types of zinc, produced essentially the same emf. Here the electrodes were solid; Raoult decided to investigate what happens when a metal electrode passes from the solid to the liquid state, or the reverse.

He chose bismuth as an example. The metal, cast in a small crucible and immersed in concentrated H_3PO_4 , was made into a cell with copper in CuSO_4 solution. The two half-cells were electrically joined by an inverted U-tube filled with H_3PO_4 . This liquid was chosen so that the bismuth half-cell could be heated to 300°C . The cell emf fell slowly and the bismuth was attacked, as evidenced by evolution of hydrogen. After several hours, the emf stabilized and was unaffected by stirring the melt with the thermometer. The bismuth half-cell was then allowed to cool and the temperature was observed frequently; the onset of solidification was checked by probing with a fine glass tip. The temperature of the copper half-cell remained unchanged throughout the experiment. Raoult found that, as the bismuth cooled from 280° to 250°C , the emf underwent the slight and irregular change from 23.3 to 23.1 (emf of Daniell cell = 100). He reported a sharp change of liquid bismuth to solid at 264°C . (The mp. of the pure metal is 271.3°C , so possibly supercooling occurred.) He stated that *there is no abrupt change of this force at the moment where the bismuth changes state*. No details were

given of experiments with tin and with lead, but the results were similar.

Raoult pointed out that, if convertible into electricity, the latent heat of fusion of bismuth should produce an emf change of 5.5 (Daniell). This number is 25 times larger than the observed total change, including passage through solidification. Thus the emf of a cell does not depend upon the state of aggregation of the metallic electrodes, but on chemical effects.

In 1875, Emil le Coq de Boisbaudran (1838-1912) discovered gallium, which melts at 29.78°C and can remain supercooled extensively. Jules Antoine Regnault (1820-1895) used these properties to see whether an electrical response could be obtained, at uniform temperature, from a cell with electrodes of the same metal, but in differing states (2). The 4 mm^2 electrodes, solid and liquid respectively, of the then very rare gallium, were placed on a layer of $\text{Ga}_2(\text{SO}_4)_3$ solution. When connected to a galvanometer, deflections of more than 40° were reported, thus indicating a flow of current and hence

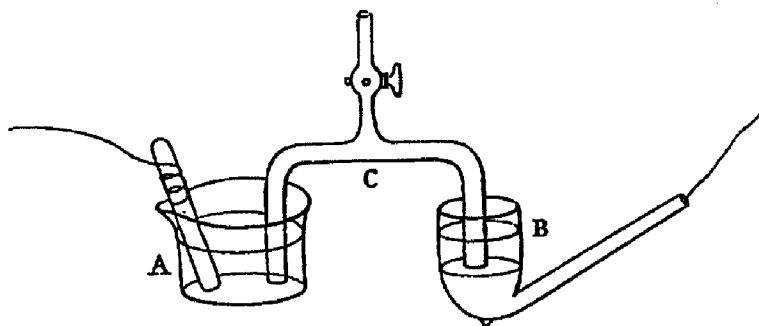


Figure 1. Gore's fusible alloy cell

a difference in the potentials of the electrodes. Regnault noted that the solid electrode was the positive pole, analogous to the copper electrode in a Daniell cell. Raoult's paper was not mentioned; Regnault was probably unaware that his evidence was contrary to Raoult's conclusions.

George Gore (1826-1908), Director of the Institute of Scientific Research in Birmingham, England, knew of Regnault's findings but made no mention of Raoult. Gore continued the liquid-solid studies with alloys of low melting point (3). His apparatus is shown in Fig. 1. The electrode in glass cup A was a bar of the chosen alloy, which was immersed in the electrolyte solution. A portion of this alloy was melted in the bowl of the clay tobacco pipe B and allowed to travel well into the stem. This was to avoid thermoelectric junction effects. After the alloy had solidified and cooled, electrolyte solution was added to B. Some of this solution was drawn up into the siphon tube, thus providing electrical continuity.

Connections to the 100-W galvanometer were made by iron wires. The electrolyte solutions were (a) 1% HCl;

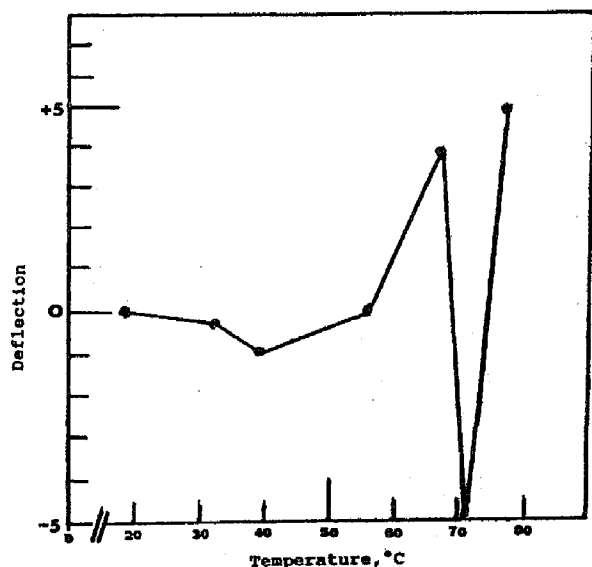


Figure 2. Galvanometer response to the fusion of a cadmium amalgam

(b) 1% NaCl and (c) nearly saturated NaCl solution. Solution (a) at 16° C was used with the alloy: Bi 70 parts, Pb 40, Sn 20, Cd 15; mp @ 66° C. A small flame was applied to bowl B until the alloy melted and the solution above it nearly boiled. Up to the mp the alloy in B gradually became electrically positive to that in A. The galvanometer reading increased suddenly from 20°

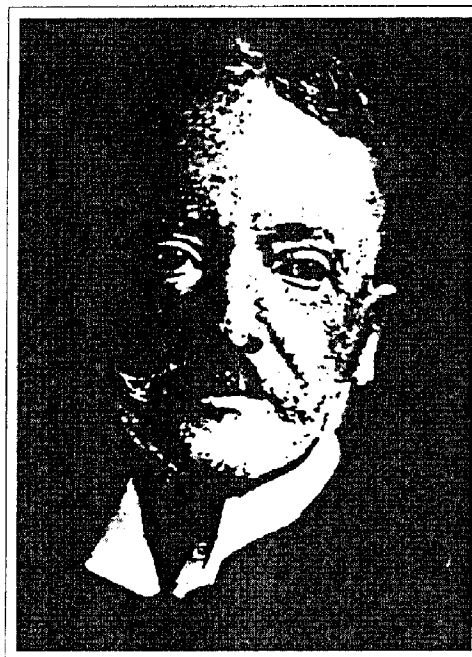


Figure 3. William Lash Miller

to 60°, at a point apparently coincident with the melting in B. An experiment with solution (b) gave similar results. The same kind of behavior was shown by an alloy of mp 107° C, used with solution (c).

Subsequent experiments were made with various amalgams. The sudden increase in deflection was small, probably because the amalgam melted gradually. Most successful was the amalgam: Cd 1 part, Hg 4 parts, which was more solid at 16° C than the others. This amalgam was used with solution (b). Fig. 2, sketched from Gore's diagram, shows the galvanometer response as the temperature rose. A deflection maximum just before the complete liquefaction of the amalgam was followed by a sudden depression, with reversal of sign. Then the deflection swung back as shown. Gore attributed the depression to a sudden act of chemical union of the ingredients of the amalgam.

William Lash Miller (Fig. 3) re-examined the problem of emf shift when a metal electrode melts or freezes in Ostwald's laboratory in Leipzig (4). Miller (1866-1940) graduated from the University of Toronto in 1887 and obtained his Ph.D. in organic chemistry from the University of Munich in 1890 but on the basis of research carried out under the direction of A. W. Hofmann. Miller, who moved to Leipzig from Munich, later became one of Canada's greatest chemists.

Miller's cell, shown in Fig. 4, was based on a large test tube. The fusible electrode, which had been melted into the funnel of the J-tube, and the adjacent second

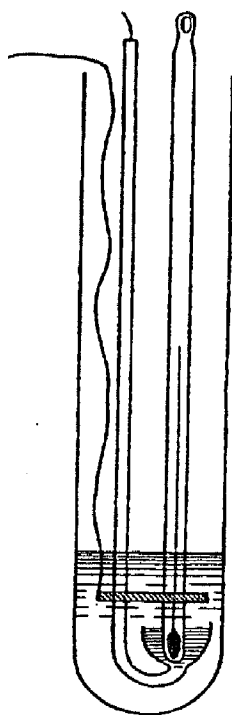


Figure 4. Lash Miller's fusible metal cell

electrode were connected by platinum wires to the potentiometer circuit. Heating or cooling was controlled at approximately $1^\circ\text{C}/\text{min}$. Unless the amount of fusible metal was kept small, the thermometer reading showed an arrest, followed by sudden rise or fall. This caused nonuniformity of temperature within the cell.

Carefully purified lead was used for one electrode; for the other, silver coated with AgCl . A mixture of ZnCl_2 and KCl , which melted at approximately 255°C , was used as a fused-salt electrolyte. Fig. 5, constructed from Lash Miller's data, shows the change, in potentiometer units, as the temperature of the lead decreases.

The total emf change was only 20 mV, with a brief rise of 1-2 mV at the solidification point, 316.5°C as read on the thermometer. With tin as the fusible electrode the electrolyte was an approximately equimolar mixture of KNO_3 , NaNO_3 and $\text{Ca}(\text{NO}_3)_2$, melting at approximately 185°C . In cooling from 268° to 200°C , there was no potentiometric indication of change of state at 225°C , the thermometric solidification point of tin.

Gore (3) had noted that the response at the mp of an amalgam diminished when the amalgam had been remelted several times. From his experiments with these substances, Lash Miller made a similar observation. He concluded that the processes that occur in the melting of amalgams and other alloys were complicated. He finally examined the cell 10% Cd amalgam— Ag/AgCl , 5% NaCl solution, over the temperature range 90° to 45°C . The emf fluctuated irregularly between 650 and 660 mV and underwent no special change at the transition point.

The expectation of a potential difference (pd) at the mp between a solid electrode and its liquid form may have arisen from an extrapolation of a theory proposed by William Thomson (1824-1907), later Lord Kelvin, in 1851 (5). He suggested that the electrical energy ob-

tainable from a cell should be equivalent to the heat of reaction of the chemical processes involved. He found that this was true for the Daniell cell. That Thomson's theory includes all kinds of thermal effects within the cell may have become a common supposition. However, the investigations of Ferdinand Braun (1850-1918) showed that Thomson's theory was valid only when the temperature coefficient, dE/dT , of the emf, E , of the cell was negligible (6). This was the case with the Daniell cell. The theoretical developments by Josiah Willard Gibbs (1839-1903) and Hermann Helmholtz (1821-1894) led to the conclusion that E differed from the value calculated from the chemical heat of the cell reaction by the quantity $T(dE/dT)$, where T is the absolute temperature.

Miller, aware of these developments, also applied a "thought experiment" to the solid-liquid problem. Consider a cell at the melting point X of the electrodes, both of metal M . However, one electrode is liquid, the other, solid. If the cell has an emf, internal electrolysis will occur when the electrodes are connected together. Then, for example, M will dissolve from the liquid electrode and deposition will occur on the solid electrode.

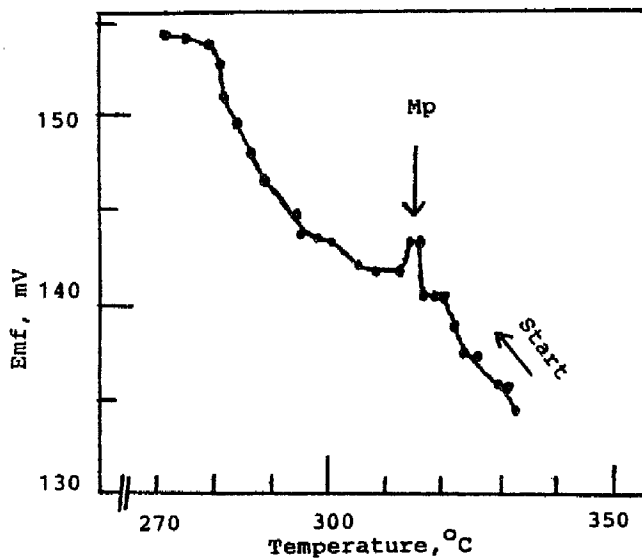


Figure 5. Response of $\text{Pb—Ag}/\text{AgCl}$ cell (from ref. 4)

Now the deposit can be melted without change of temperature and taken back to the liquid electrode, so that electrolysis can continue indefinitely. Further, suppose that the electrodes are connected to a small motor; then we will have perpetual motion. If a short wire resistor replaces the motor, the temperature of the wire will be-

come greater than X. Such results are contrary both to experience and to the principles of thermodynamics.

Theory (7) and experiment indicate that at the mp of M, the liquid and solid forms of M must have the same potential. Although this potential, or the emf, E, of a cell of which M forms one electrode, may change with change of temperature, the E-T curve should be smooth, *i.e.*, should show no irregularity as the temperature rises or falls through the mp of M. However, the small "kink," sometimes observed in the curve, seems to be real. Ostwald suggested that the observed effect is due to a change in the *temperature coefficient*, dE/dT , as change of state occurs (8). This change, F, depends upon the latent heat of fusion L and the absolute temperature, T (9). For lead, $L = 1224/2 \text{ cal eqvt}^{-1}$, or $5121/2 \text{ J eqvt}^{-1}$, and $T = 601^\circ \text{ K}$. Hence $F = (2561 \times 1000) / (96485 \times 601) \approx 4.4 \times 10^{-2} \text{ mV K}^{-1}$. The apparent slope in the 290° to 330° C range in Fig. 5 is approximately 0.25 mV / deg. , so that F is about 18% of this.

Because the change in temperature coefficient is brief when melting or freezing is sharp, the change could be difficult to detect. Raoult and Miller made use of "opposition" or "compensation" potentiometry which, involving instrument adjustment throughout measurements, does not provide continuous indication.

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2. J. Regnaud, "Influence de l'état physique du gallium sur son rôle électrochimique". *Compt. Rend.*, **1878**, 86, 1457-1458.
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5. W. Thomson, "On the mechanical theory of electrolytes," *Philos. Mag.*, **1851**, 4, 429-444.
6. F. Braun, "Ueber galvanische Elemente, welche angeblich nur aus Grundstoffen bestehen, und den electromotorischen Nutzeffect chemischer Prozesse," *Ann. Phys. Chem.*, **1882**, 17, 593-642.
7. Since liquid and solid are in equilibrium at the melting point, DG, the free energy of fusion per equivalent, and the corresponding potential E must both be zero ($DG = -FE$, where F is the Faraday constant).
8. W. Ostwald, *Chemische Energie*, Engelmann, Leipzig, 2nd ed., 1893, 869.
9. This change, $F = DS/F = L/FT$, where F is the change in dE/dT due to fusion; DS and L are, respectively, the entropy and latent heat of fusion per equivalent.

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