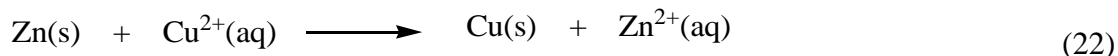


Electrochemical Cells

Electrochemical cells are devices that can make chemical energy available in the very convenient form of electrical energy. They are also useful and flexible devices for studying the thermodynamics of ionic solutions.

If a zinc plate is placed into a solution of copper sulphate (in a cell that looks like the Daniell cell, the simplest example of the Voltaic Cell (Figure 7)), the chemical reaction shown below will occur spontaneously.



But when done this way, virtually no work can be obtained from the system, and the chemical energy is dissipated as heat. This is because the other half-cell where copper strip is immersed in ZnSO_4 is non-spontaneous. However, if the reaction is carried out exactly as depicted in Figure 7, in which the two solutions, $\text{CuSO}_4(\text{aq})$ and $\text{ZnSO}_4(\text{aq})$, separated by a porous barrier contained respectively copper metal and zinc metal plates, the reaction (Eq. 22) will occur spontaneously involving both half-cells, and with a flow of positive charges (current) which can be made to do work (for example, driving an electric motor).

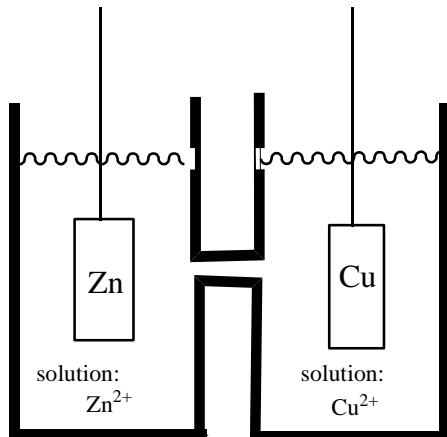


Figure 7: The Daniell cell. The solutions are separated by a barrier, such as a glass frit that permits the passage of electrical current but inhibits the convective mixing of the solutions.

For the correct operation of the Daniell cell, the copper plate in the CuSO_4 solution is the site of the reduction:



and the zinc plate in the ZnSO_4 solution is oxidized:



This cell was the first practical source of electrical power invented. It was invented in 1836 by J.F Daniell in the days when copper and zinc were cheap and electricity could not be obtained by plugging into a socket. It was widely used then, and one important application was as a power source for the electrical telegraph invented by S.F.B. Morse in 1844.

Electrochemical cells and batteries are still very important sources of electrical power in applications where portability is critical, but the major interest in this course will be their use for studying the thermodynamics of chemical reactions.

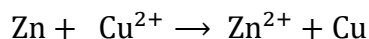
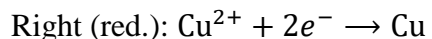
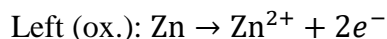
Cell notation

Cell notation is presented formally by listing its phases, electrode to electrode. Vertical bar (|) to indicate a phase separation; if a single phase contains several components, they will be separated by commas (excluding solvents). The salt-bridge is represented by two parallel lines. The Daniell cell for example can be notated as:



The phase boundary between the two solutions is called a **liquid junction**; such junctions raise complications when discussing cell thermodynamics.

The reaction at the left electrode is always written as an **oxidation**, while that at the right electrode is written as a **reduction**:



Measurement of electrode potentials

It is useful to think of an electrode as having an electrical potential of its own; although these single-electrode potentials cannot be measured. But in principle, the potentials of all possible unknown single-electrodes can be measured *versus* another single electrode that is chosen as a standard, and from which the relative electrode potentials of the unknown single-electrodes can be obtained. The convention is that the emf of the cell is equal to the potential of the right electrode *minus* that of the left electrode (both being “reduction” potentials).

$$E_{\text{emf}} = E_{\text{Right}} - E_{\text{Left}} = E_{\text{R}} - E_{\text{L}} \quad (26)$$

Equation 26 refers only to electrode processes; a cell such equation 25 (Daniell cell), has a potential due to the liquid junction (E_{J}), so its emf must be written as:

$$E_{\text{emf}} = E_{\text{Cu}^{2+}|\text{Cu}} - E_{\text{Zn}^{2+}|\text{Zn}} + E_{\text{J}} \quad (27)$$

When using cells to study the thermodynamics of ionic reactions, it is the electrode potential that is of primary interest.

While it is possible to minimize the junction potential in such cells by using salt bridges, it is preferable to deal with cells without a liquid junction; then the thermodynamic results would be exact and accurate.

The conventions “right” and “left” are pure formalities that depend on how we choose to write the cell notation. If the Daniell cell (Eq. 25) is written as $\text{Cu(s)} | \text{CuSO}_4(\text{aq}) || \text{ZnSO}_4(\text{aq}) | \text{Zn(s)}$; the cell reaction would be reversed: $\text{Zn}^{2+} + \text{Cu} \rightarrow \text{Zn} + \text{Cu}^{2+}$ and the calculated emf would have the opposite sign (it would in fact be negative because the Daniell cell, Eq. 25 has a positive emf).

Determination of Unknown emf

The method of measuring cell emfs is illustrated in Figure 8. A standard cell is connected to the circuit as shown in figure 8A in a way that no current flows through the galvanometer G from the source emf. This is achieved by varying the variable resistor. A value of resistance, R_{std} is recorded when the current in the galvanometer is zero. The current i that flows through the ammeter connected in series with the source emf is also noted. The standard cell is removed and the cell whose emf is to be determined is connected in the same manner. This is shown in figure 8B. The resistance R_{Ukn} when the galvanometer reads zero is recorded together with the value of the current i flowing through the circuit as given by the ammeter. The unknown emf is then calculated as follows:

If the current that flows in the circuit in each case is i , $E_{\text{Ukn}} = E_{\text{std}} i R_{\text{Ukn}} / i R_{\text{std}}$

$$\text{where } E_{\text{std}} = i \times R_{\text{std}}. \text{ Thus, } E_{\text{Ukn}} = \frac{R_{\text{Ukn}}}{R_{\text{std}}} \cdot E_{\text{std}} \quad (28)$$

If the cell reaction that produces the current i in the cell of interest involves transfer of n moles of electrons, the electrical work done by the system is given by:

$$w = -nFE_{\text{Ukn}} = \Delta G_{\text{rxn}} \quad (29)$$

Generally, the maximum work done by any electrochemical process at constant (T, P) is given by:

$$\Delta G_{\text{rxn}} = -nFE \quad (30)$$

where F is the Faraday constant and n is the number of moles of electrons transferred.

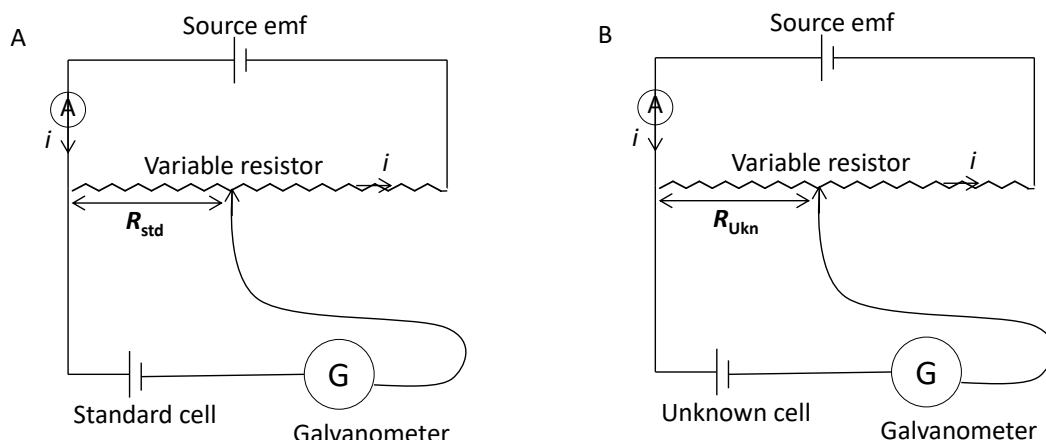


Figure 8: Determination of an unknown emf.

Types of electrodes

(i) *The SHE*: The $H^+ | H_2$ couple is the basis of the primary standard around which the whole edifice of electrode potentials rests. This $H^+ | H_2$ is called the **standard hydrogen electrode (SHE)** under standard conditions. SHE is the reference electrode used to establish standard state potentials of other half-reactions. It consists of a Pt electrode immersed in a solution of hydrogen ion whose activity is 1.00 and temperature is 298 K. Hydrogen gas at standard pressure is in equilibrium with the aqueous solution of hydrogen ion to give E^0 value of 0 at all temperatures. Note that all other standard electrode potentials are temperature dependent.

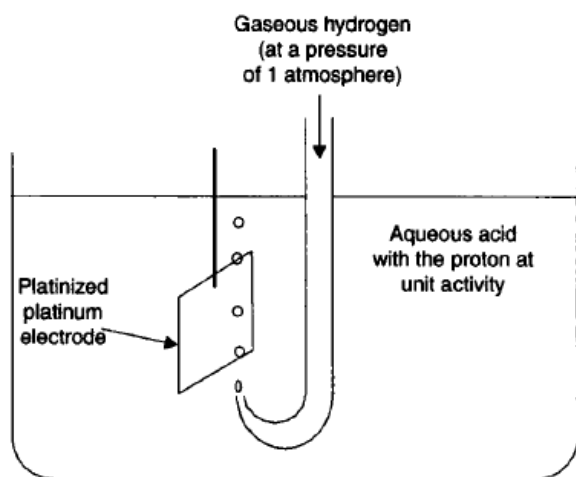
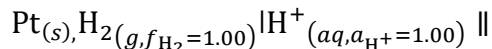


Figure 9: The schematic representation of the primary reference, the SHE

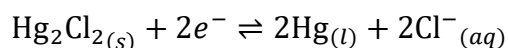
The short-hand notation for the standard hydrogen electrode is



and the standard state potential for the reaction

$\text{H}^+_{(aq)} + e^- \rightleftharpoons \frac{1}{2} \text{H}_{2(g)}$ is 0.00 V at all temperature by definition. Despite its importance as the fundamental reference electrode against which we measure all other potentials, the SHE is rarely used because it is difficult to prepare and not convenient to use.

(ii) *Calomel electrodes*: A calomel reference electrode is based on the following redox couple between Hg_2Cl_2 and Hg (not that the use of this is now mostly discouraged for toxicity reason).



for which the potential is:

$$E = E^o_{\text{Hg}_2\text{Cl}_2/\text{Hg}} - \frac{0.05916}{2} \log(a_{\text{Cl}^-})^2 = +0.2682 \text{ V} - \frac{0.05916}{2} \log(a_{\text{Cl}^-})^2 \quad (31)$$

The potential of a Calomel electrode, therefore depends on the activity of Cl^- in equilibrium with Hg and Hg_2Cl_2 .

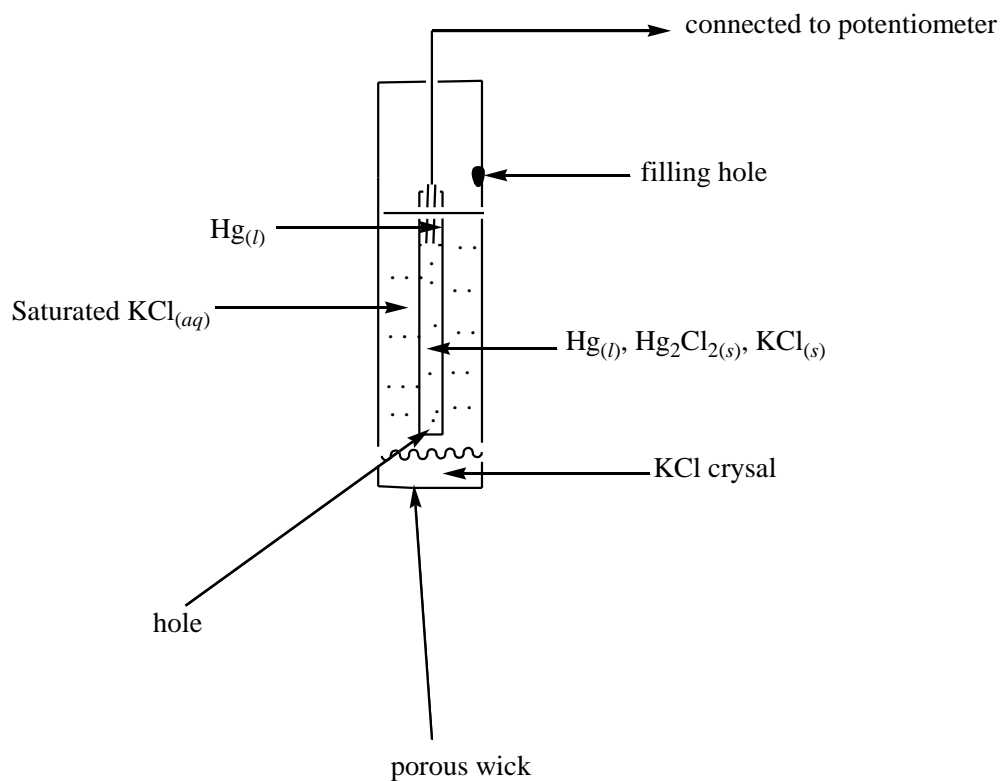
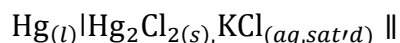
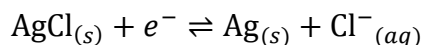


Figure 10: Schematic diagram showing saturated Calomel electrode (SCE)

As shown above in Fig. 10, the concentration of Cl^- in SCE is determined by the solubility of KCl. The electrode consists of inner tube packed with a paste of Hg, Hg_2Cl_2 and KCl, and situated within a second tube that contains a saturated solution of KCl. A small hole connects the two tubes and a porous wick serves as a salt bridge to the solution in which the SCE is immersed. A stopper in the outer tube provides an opening for addition of saturated KCl. The concentration of Cl^- is fixed by the solubility of KCl, hence the electrode potential of SCE, even if some of the inner solution of KCl is lost to evaporation. The only factor that affects SCE potential is temperature. At higher temperatures, the solubility of KCl increases and the electrode's potential decreases. For example, potential of SCE is +0.2444 V at 25°C and +0.2376 V at 35°C.. The potential of a Calomel electrode that contains an unsaturated solution of KCl is less dependent on the temperature. The short hand notation for this cell is:



(iii) *Silver/Silver chloride electrodes*: This is based on the reduction of AgCl to Ag.



As in the case of the Calomel electrode, the activity of Cl^- determines the potential of the Ag|AgCl electrode; thus,

$$E = E_{\text{AgCl/Ag}}^{\circ} - 0.05916 \log a_{\text{Cl}^-} = +0.2223 \text{ V} - 0.05916 \log a_{\text{Cl}^-} \quad (32)$$

With saturated solution of KCl, the electrode's potential is +0.197 V at 25°C. Another common Ag|AgCl electrode uses a solution of 3.5 M KCl and has a potential of +0.205 V at 25°C. A typical Ag|AgCl electrode is shown in Figure 16 below. It consists of a silver wire, the end of which is coated with a thin film of AgCl, immersed in a solution that contains the desired concentration of KCl. A porous plug serves as the cell salt bridge. The electrode's short hand notation: $\text{Ag}_{(s)}|\text{AgCl}_{(s)}, \text{KCl}_{(aq, a_{\text{Cl}^-}=x)} \parallel$

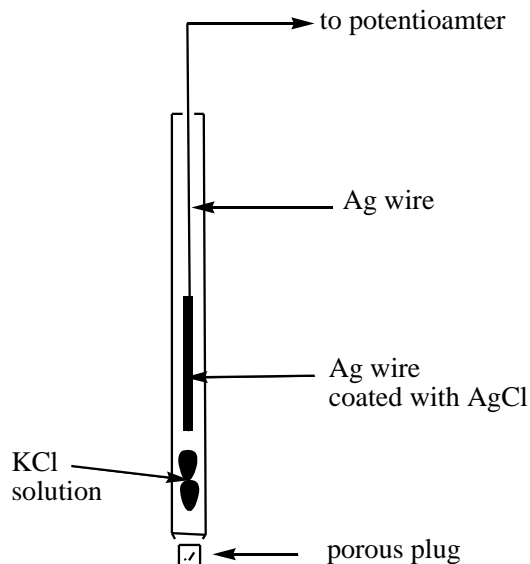
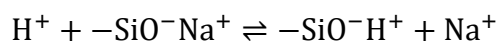


Figure 11: Schematic diagram showing a Ag/AgCl electrode

(iv) *Glass Ion-Selective Electrodes*: The first glass electrodes were manufactured using Corning 015, a glass with a composition that is approximately 22% Na_2O , 6% CaO , and 72% SiO_2 . The outer part which is approximately 10 nm of the membrane's surface becomes hydrated when the electrode is immersed in an aqueous solution for several hours, resulting in the formation of negatively charged sites, $-\text{SiO}^-$. Sodium ions Na^+ , serve as counter ions. Because H^+ binds more strongly to $-\text{SiO}^-$ than does Na^+ , they displace the sodium ions.



Thus, explaining the membrane's selectivity for H^+ . The transport of charge across the membrane is carried by the Na^+ ions. The potential of a glass electrode using Corning 015 obeys the equation:

$$E_{\text{cell}} = K + 0.05916 \log a_{\text{H}^+} \quad (33)$$

Over a pH range of approximately 0.5 – 9.0

At more pH levels, the glass membrane is more responsive to other cations, such as Na^+ and K^+ than H^+ . Replacing Na_2O and CaO with Li_2O and BaO extends the useful pH range of glass membrane electrodes to pH levels greater than 12. Due to the fact that Corning 015 glass membrane responds to ions other than H^+ , there has been development of glass membranes with

a greater selectivity for other cations. Other glass ion-selective electrodes have been developed for the analysis of Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ , Ag^+ and Tl^+ .

Additional materials

You may wish to view the following videos to enhance your understanding in electrochemistry.

Video links: <https://www.youtube.com/watch?v=evhh9CuCPOM>

<https://www.youtube.com/watch?v=Vod6c2iQw8I>