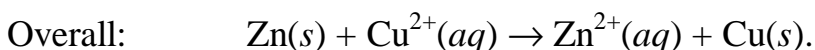
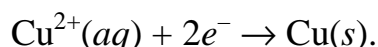
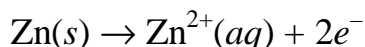


CHAPTER 8 LECTURE NOTES

8.1. The Daniel Cell

See Fig. 8.1, 8.2

- A Zn electrode dipping in $\text{Zn}^{2+}(aq)$ solution, connected to a Cu electrode dipping in $\text{Cu}^{2+}(aq)$ solution.
- The two electrodes are connected by an electrical conductor, which permits the flow of electrons from one electrode to the other.
- The two solutions are connected by a porous partition or a “salt bridge,” which permits the flow of ions.
- The electrode processes consist of **oxidation** (loss of electrons) at one electrode and **reduction** (gain of electrons) at the other:



- The force that drives this reaction is, of course, the decrease in free energy, ΔG . This force is manifested in the form of the **electromotive force** (emf) or cell voltage, denoted as E , which can be measured using a Wheatstone bridge, under conditions in which no current is drawn from the cell.
- If the concentrations of the ions are maintained at 1 mol kg^{-1} (or 1 m), the cell is called the **standard Daniel cell** and the cell emf is called the **standard cell emf**, denoted as E° .
- The fact that the spontaneous cell reaction leads to the oxidation of $\text{Zn}(s)$ to $\text{Zn}^{2+}(aq)$ and the reduction of $\text{Cu}^{2+}(aq)$ to $\text{Cu}(s)$ indicates that the tendency for $\text{Cu}^{2+}(aq)$ ions to accept electrons (to get reduced) is greater than that for $\text{Zn}^{2+}(aq)$ ions. In the terminology of electrochemistry, we say that $\text{Cu}^{2+}(aq)$ has a greater **reduction potential** than $\text{Zn}^{2+}(aq)$.

Conventions and notations:

There are a few conventions and notations used for short-hand representation of electrochemical cells.

An electrochemical cell is viewed as the combination of two “half-cells.” Each half-cell consists of an electrode, which may participate in the cell reaction, and chemicals in contact with that electrode.

Vertical lines are used to indicate important phase boundaries across which half-cell reactions take place. Often, the electrolyte concentration is also shown.

Examples:

Cu electrode dipping in $\text{Cu}^{2+}(aq)$: $\text{Cu}(s)|\text{Cu}^{2+}(c)$

Zn electrode dipping in $\text{Zn}^{2+}(aq)$: $\text{Zn}(s)|\text{Zn}^{2+}(c)$

When two half-cells are combined to make an electrochemical cell, the half-cell in which oxidation takes place is written on the left-hand side and the half-cell in which reduction takes place is written on the right.

The electrodes are written on the “outside” with the electrolytes in-between.

A double vertical line is drawn between the two electrolytes to indicate a physical separation, either by a porous membrane or a salt-bridge.

Example: The standard Daniel cell:



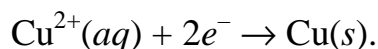
The electrode at which oxidation takes place is called the **anode**. The electrode at which reduction takes place is called the **cathode**.

In electrochemical cells, the anode is negatively charged because electrons are given to the electrode by the species undergoing oxidation. The cathode is positively charged because electrons are removed from it by the species undergoing reduction.

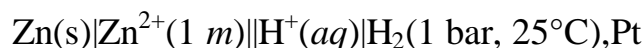
So, when an electrochemical cell is written as indicated above, the electron-flow in the external circuit is from the electrode on the left to the electrode on the right.

8.2. Standard Electrode Potentials

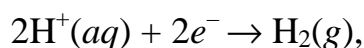
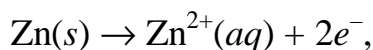
- The difference in the reduction potentials of the two electrodes chosen to make up the cell determines the total cell emf.
- A scale of reduction potentials is needed to quantitatively assign the reduction potentials of various electrodes used to make up electrochemical cells.
- Since there is no way to measure the reduction potential of a single electrode, the hydrogen electrode (see Fig. 8.3) is chosen as the ultimate standard. The Hydrogen electrode operating at 25°C and 1 bar pressure is assigned a reduction potential of 0.0 V. If we were to construct a cell using a Cu(s)|Cu²⁺(1 m) electrode and the standard hydrogen electrode [Pt, H₂(1 bar, 25°C)|H⁺(1 m)], the electrode reactions would be



- The measured emf of such a cell would be 0.3419 V. Therefore, we say that the standard reduction potential of the Cu(s)|Cu²⁺(1 m) electrode is +0.3419 V.
- The fact that Cu²⁺ ions undergo spontaneous reduction indicates that the tendency for Cu²⁺(aq) ions to accept electrons (to get reduced) is greater than that for H⁺ ions.
- In contrast, in the cell



the cell reactions will be

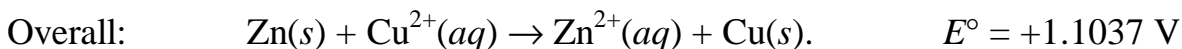


and the measured cell emf will be -0.7618 V. In this case, it is clear that the tendency for H⁺ ions to accept electrons is greater than for the Zn²⁺(aq) ions.

- Therefore, the reactions and electrode potentials in the cell



will be

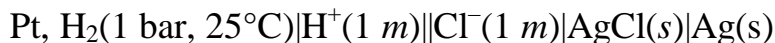


Other Standard Electrodes

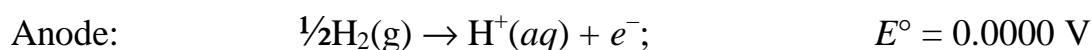
A hydrogen electrode is difficult to set up and is not portable. Therefore, other standard electrodes have been adopted.

The Ag|AgCl(s)|Cl⁻(1 *m*) electrode:

This electrode consists of a silver wire in contact with solid AgCl which, in turn, is in contact with 1 *m* KCl solution. The reduction potential of this electrode is measured by constructing the cell



in which the following reactions take place:



The Standard Calomel electrode:

The half-cell is Hg(*l*)|Hg₂Cl₂(s)|Cl⁻(1 *m*). Calomel is the common name for the mercury (II) chloride used in this electrode. The electrode develops a half-cell reduction potential of 0.3337 V.

If saturated potassium chloride solution used (rather than 1 *m*), the half-cell potential is 0.2412 V, and the electrode is called the saturated calomel electrode.

Another very common reference electrode is the glass electrode, which is essentially a thin-walled glass bulb filled with 0.1 *m* HCl, in contact with a AgCl(s)|Ag electrode. The glass membrane is permeable to H⁺ ions and, therefore, the glass electrode is commonly used for pH determinations.

Problems: 8.1–8.3, 8.5–8.7, 8.9

8.3. The Thermodynamics of Electrochemical Cells

The relationship between the standard cell emf E° and the standard Gibbs free energy ΔG° is

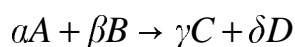
$$\Delta G^\circ = -nFE^\circ, \quad (8.2)$$

where the superscript on G and E denotes the standard concentrations (strictly speaking, activities) of the electrolytes in the cell.

Under non-standard concentrations, we use the relationship

$$\Delta G = \Delta G^\circ + RT \ln Q,$$

where Q is the reaction quotient for the cell reaction (see Eq. 4.28 on p. 159). So, for a cell reaction



in which n electrons are involved, we write

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta} \right),$$

or, in terms of cell emf's,

$$-nFE = -nFE^\circ + RT \ln \left(\frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta} \right).$$

This is easily simplified to give

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta} \right). \quad (8.13)$$

This is called the Nernst equation, and is one of the most important equations in electrochemistry. The Nernst equation is the basis for many practical applications of electrochemical principles.

Problems: Example 8.4, 8.12–8.16, 8.19, 8.20, 8.38*, 8.40* (note error in question)

Temperature Coefficients of Cell EMF's

The temperature coefficient of an electrochemical cell is the rate of change of cell emf with temperature, denoted as $(\partial E/\partial T)$. From Chapter 3,

$$dG = -SdT - VdP.$$

Therefore,

$$S = -\left(\frac{\partial G}{\partial T}\right). \quad (8.21)$$

Therefore,

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right). \quad (8.22)$$

Substituting for ΔG from Eq. (8.3), we get

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right). \quad (8.23)$$

Also, since $\Delta H = \Delta G + T\Delta S$, we get

$$\Delta H = -nF\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right]. \quad (8.25)$$

Therefore, determining the temperature coefficient of an electrochemical cell allows us to calculate the three main thermodynamic state functions for the cell reaction.

Problems: Example 8.7, 8.32–8.35

READING ASSIGNMENT: Sections 8.4 and 8.5