

Module 5 : Electrochemistry

Lecture 22 : Free energy and EMF

Objectives

After studying this Lecture you will be able to

- Distinguish between electrolytic cells and galvanic cells.
- Write the cell representation for electrochemical reactions.
- Derive the Nernst equation.
- Use the Nernst equation for calculating the electromotive force (emf) of a cell for any combination of activities of solution species.
- Evaluate $\Delta_r G$, $\Delta_r H$ and $\Delta_r S$ from dE/dT .

22.1 Introduction

Both electrolytic cells and galvanic cells provide wonderful examples of conversion of one form of energy into another. In an electrolytic cell, a current is passed through a fluid medium (solutions, molten salts) causing migration of ions towards electrodes and the charge deposition by the ions at the electrodes. For example, if a current is passed through a solution of sodium chloride, the following reactions occur at the cathode and anode.

Cathode: $\text{Na}^+ + e \rightarrow \text{Na}$, reduction; The cathode is connected to the – ve terminal of the battery or cell that is causing electrolysis.

Anode: $\text{Cl}^- \rightarrow \frac{1}{2} \text{Cl}_2 + e$, oxidation; The anode is connected to the + ve terminal of the cell or battery (see Fig 22.1).

The complete reaction may be written as

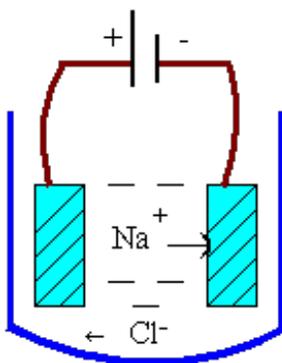
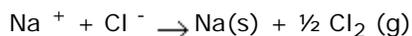


Figure 22.1: An electrolytic cell showing the migration of cations and anions.

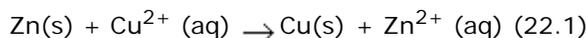
In a galvanic cell on the other hand, the two electrodes are present in differing chemical environments with different chemical potentials / free energies. We have already seen in the earlier chapter that a decrease in the Gibbs free energy is equal to the maximum non pressure volume work obtainable from the system.

$$\Delta_r G^0 = - n F \mathcal{E}^0$$

The net free energy difference between the electrodes forces the current to flow in the external circuit (wires connecting the electrodes). At the electrode (anode) with the greater reduction potential, reduction (gain of electrons) occurs. At the electrode which has a lower reduction potential (cathode), oxidation (loss of electrons) occurs and the electrons move from anode to cathode in the external circuit.

22.2 Galvanic cells or Electrochemical cells

Consider a redox reaction between Zn(s) and copper ions shown below



Counterions are of course present in the solution but are not shown because they do not participate in the reaction. The above reaction is spontaneous. If pieces of Zn metal are added to a CuSO₄ solution, Cu(s) starts depositing on the Zn pieces. To get useful electrical work from such a process, it is best to place the Cu and Zn rods (electrodes) in separate compartments as indicated below.

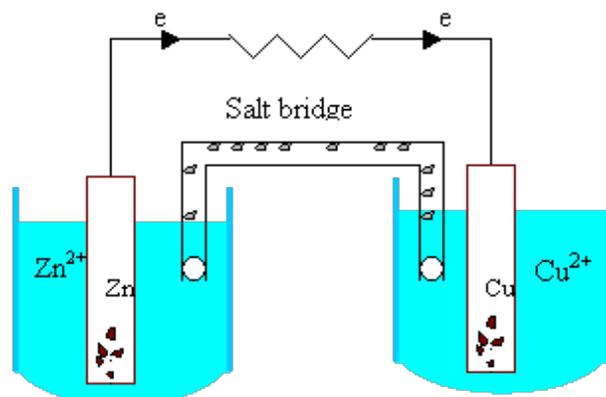


Fig 21.1 A schematic view of a Daniell cell.

The left compartment consists of a zinc rod dipped in a solution containing Zn²⁺ ions (such as zinc sulphate) and the right compartment consists of a copper rod dipped in a solution containing Cu²⁺ ions (e.g., CuSO₄ solution). The external circuit is completed by a wire of known resistance (for producing heat, light or other forms of work). The contact between the solutions is provided by a salt bridge containing saturated KCl or NH₄NO₃ solution along with gelatin or agar for confining the electrolyte in the tube. The salt bridge prevents mixing of the electrolytes, allows the flow of ions and reduces polarization near the electrodes. Electrons flow from the Zn electrode to the Cu electrode in the external circuit, or the positive charge flows from the Cu electrode to the Zn electrode. If this cell were to operate as a battery, the Cu electrode would be the positive terminal of the battery.

For the reaction (22.1), $\Delta_r G^\circ = -212.9 \text{ kJ / mol}$ and this energy is made available as the electrical energy in the external circuit.

22.3 Cell Representation and sign convention

The above Daniell cell may be conveniently represented in a compact form as



Here, the vertical line denotes a boundary separating two phases. The double vertical lines indicate a salt bridge. On either side of the salt bridge are two half cells, or electrodes. On the left hand side (L), oxidation (O) occurs. This electrode is referred to as the anode (A) and it is the negative (N) terminal. A simple way to remember this arrangement is to remember the word "LOAN" (left, oxidation, anode, negative). Automatically this implies that at the other electrode on the right (R), reduction (R) occurs; the electrode is called the cathode (C) and it is the positive terminal (P), (RRCP).

The reactions at the anode and the cathode are respectively,



The emf (electromotive force) of this cell is 1.103V. The potential (emf) of a single electrode or a half cell can not be measured; we always need to electrodes to obtain an emf.

Instead of listing the potentials of all "pairs" of cells, it is far more convenient to take any one half cell as the standard and list all the other electrode potentials (actually reduction potentials, as recommended by the international Union of Pure and Applied Chemists, IUPAC) with reference to this standard. This reference electrode is taken as the standard hydrogen electrode (SHE) whose emf is assigned a reference value of 0 V



Table 22.1 lists the standard electrode potentials of a number of half cells. In the standard electrodes, species in all forms (solids, liquids or gases) are present with unit activities, i.e., in their standard states. It is to be noted that emf is an intensive property and that the half cell $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 (\text{g})$ will have the same emf as eq (22.3) but the free energy change for this reaction will be twice the value for eq. (22.3), because $\Delta_r G^\circ = -nF E^\circ$ and $\Delta_r G^\circ$ is an extensive property depending on the number of moles of electrons transferred.

Table 22.1 Standard electrode potentials at 298.15 K

Electrode	Half Cell Reaction	E°
$\text{Li}^+ \text{Li}$	$\text{Li}^+ + \text{e}^- = \text{Li}$	-3.045
$\text{Mg}^{2+} \text{Mg}$	$\text{Mg}^{2+} + 2\text{e}^- = \text{Mg}$	-2.37
$\text{Zn}^{2+} \text{Zn}$	$\text{Zn}^{2+} + 2\text{e}^- = \text{Zn}$	-0.763
$\text{Fe}^{2+} \text{Fe}$	$\text{Fe}^{2+} + 2\text{e}^- = \text{Fe}$	-0.440
$\text{Cd}^{2+} \text{Cd}$	$\text{Cd}^{2+} + 2\text{e}^- = \text{Cd}$	-0.403
$\text{Ni}^{2+} \text{Ni}$	$\text{Ni}^{2+} + 2\text{e}^- = \text{Ni}$	-0.250
$\text{H}^+ \text{H}_2 \text{Pt}$	$2\text{H}^+ + 2\text{e}^- = \text{H}_2$	0.000
$\text{Br}^- \text{AgBr} (\text{s}) \text{Ag}$	$\text{AgBr} + \text{e}^- = \text{Ag} + \text{Br}^-$	0.09
$\text{Cu}^{2+}, \text{Cu}^+ \text{Pt}$	$\text{Cu}^{2+} + \text{e}^- = \text{Cu}^+$	0.153
$\text{Cl}^- \text{AgCl} (\text{s}) \text{Ag}$	$\text{AgCl} + \text{e}^- = \text{Ag} + \text{Cl}^-$	0.2224
$\text{Cl}^- \text{Hg}_2\text{Cl}_2 (\text{s}) \text{Hg}$	$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- = 2\text{Hg} + 2\text{Cl}^-$	0.268
$\text{Cu}^{2+} \text{Cu}$	$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$	0.337
$\text{OH}^- \text{O}_2 \text{Pt}$	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-$	0.401

Cu ⁺ Cu	Cu ⁺ + e = Cu	0.521
Fe ³⁺ , Fe ²⁺ Pt	Fe ³⁺ + e = Fe ²⁺	0.771
Ag ⁺ Ag	Ag ⁺ + e = Ag	0.79991
Br ⁻ Br ₂ (l) Pt	Br ₂ (l) + 2e = 2Br ⁻	1.0652
Cl ⁻ Cl ₂ (g) Pt	Cl ₂ (g) + 2e = 2Cl ⁻	1.3595
F ⁻ F ₂ (g) Pt	F ₂ (g) + 2e = 2F ⁻	2.87

22.4 The Nernst Equation

In the previous chapter, we have seen that for a reaction such as



which is at any stage of completion, the free energy change is given by

$$\Delta G = \Delta G^\circ + RT \ln [C]^c [D]^d / [A]^a [B]^b \quad (22.5)$$

where the bracketed quantities [A], [B], [C] and [D] refer to the actual activities (or concentrations in ideal solutions, pressures or fugacities (divided by p°) for gases) of these species in the reaction mixture. The quotient on the right hand side is denoted by Q and if the reaction has reached equilibrium, it becomes equal to K, the equilibrium constant. Using the relation between the change in free energy and emf, i.e., $\Delta G = -nF$ and $\Delta G^\circ = -nF^\circ$,

$$E = E^\circ - (RT/nF) \ln Q \quad (22.6)$$

And at equilibrium, $\Delta G = 0$, $E = 0$ and

$$E^\circ = (RT / nF) \ln K \quad (22.7)$$

$$\text{Or } K = \exp [n F E^\circ / RT] \quad (22.8)$$

The equation (22.6) / (22.7) is referred to as the Nernst equation. This is the fundamental equation of equilibrium electrochemistry. Using this equation, the cell potential at any stage of the reaction can be calculated. At 298K and 1 atm (101.3 kPa) pressure, $RT / F = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 298 \text{ K} / (96500 \text{ C/mol}) = 0.02569 \text{ V}$ and the Nernst equation becomes

$$E = E^\circ - (0.02569 / n) \ln Q \text{ or} \quad (22.9)$$

$$E = E^\circ - (0.05916 / n) \log_{10} Q \quad (22.10)$$

The above equations are convenient forms of the Nernst equation for calculations done at a room temperature of 25°C.

Example 22.1

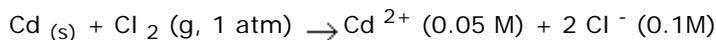
For the galvanic cell

$\text{Cd} \mid \text{Cd}^{2+} (0.05 \text{ M}) \parallel \text{Cl}^- (0.10 \text{ M}) \mid \text{Cl}_2 (1 \text{ atm}) \mid \text{Pt}$,

$E^\circ = 1.76 \text{ V}$. Calculate a) the standard electrode potential of the cadmium electrode, b) the equilibrium constant for the cell reaction and c) the emf at 25°C .

Solution:

The cell reaction is



a) The value of E° for the cell is 1.76 V . The standard electrode potential for the $\text{Cl}_2 \mid \text{Cl}^- \mid \text{Pt}$ cell is 1.3595 V . Therefore the electrode (reduction) potential for the $\text{Cd}^{2+} \mid \text{Cd}$ cell is: $1.76 \text{ V} = E^\circ = E^\circ_{\text{Cl}^- / \text{Cl}_2} - E^\circ_{\text{Cd}^{2+} / \text{Cd}}$

$$E^\circ_{\text{Cd}^{2+} / \text{Cd}} = 1.3595 - 1.76 = -0.4005 \text{ V}$$

b) The equilibrium constant for the reaction ($n = 2$) is

$$K = \exp [2 \times 96500 \times 1.76 / 8.314 \times 298] = \exp(137.1) = 3.49 \times 10^{59}$$

c) The reaction quotient for the reaction is

$$Q = [\text{Cd}^{2+}] / [\text{Cd (s)}] \times [\text{Cl}^-]^2 / \text{Cl}_2(\text{g})$$

Both the denominators Cd(s) and $\text{Cl}_2(\text{g})$ at 1 atm pressure are in their standard states.

$$\therefore Q = 0.05 \times (0.1)^2 = 0.0005$$

$$\begin{aligned} E &= E^\circ - (0.02569 / n) \ln Q \\ &= 1.76 - 0.012845 \times (-76) \\ &= 1.858 \text{ V} \end{aligned}$$

22.5 Temperature Dependence of emf

We have already commented that equilibrium electrochemistry allows us to estimate thermodynamic properties such as $\Delta_r G^\circ$ very accurately. The same quantities can be obtained from "thermal" measurements such as the free energies and enthalpies of formation and standard entropies of substances wherein an error of about 0.5 % can not be ruled out. But emfs can be measured to an accuracy of better than 0.0001V.

The temperature dependence of emf can be measured by keeping the galvanic cells in suitable thermostats, allowing for proper equilibration, and then measuring the cell potentials in suitable ranges of temperature.

The rate of change of emf E with temperature T , dE / dT is related to dG / dT as follows

$$\frac{d(\Delta_r G)}{dT} = -nF \left(\frac{dE}{dT} \right) \quad (22.11)$$

But since $d(\Delta_r G) / dT = -\Delta_r S$ (See problem 21.7, Chapter 21), we have

$$\Delta_r S = nF \left(\frac{dE}{dT} \right) \quad (22.12)$$

and knowing $\Delta_r S$ and $\Delta_r G$, $\Delta_r H$ can be calculated through

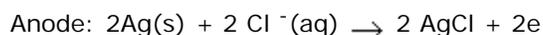
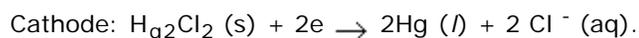
$$\Delta_r H = \Delta_r G + (22.13) T \Delta_r S$$

Example

The E° s for the following cell at 298 K and 308 K are 0.058V and 0.0614 V respectively. What is the cell reaction? Calculate $\Delta_r G^\circ$, $\Delta_r S^\circ$ and $\Delta_r H^\circ$ at 298 K. The cell is: $\text{Ag (s)} \mid \text{AgCl (s)} \mid \text{KCl (1M)} \mid \text{Hg}_2\text{Cl}_2 \text{ (s)} \mid \text{Hg (l)}$

Solution

The reactions at the cathode (right electrode) and anode (left electrode) are respectively.



Adding these two, we get the cell reaction, $2\text{Ag(s)} + \text{Hg}_2\text{Cl}_2 \rightleftharpoons 2\text{AgCl} + \text{Hg (l)}$

$$\Delta_r G^\circ = -n F E^\circ = -2 \times 96500 \times 0.058 = -11.194 \text{ kJ for the reaction given above.}$$

To obtain $\Delta_r S^\circ$, we need dE / dT at 298 K.

The correct way of obtaining dE / dT at a temperature T_0 is to obtain the values of E at several values of T around T_0 and plot E vs T and obtain the tangent to the curve at $T = T_0$. It is not practical to have thermostats at every 1 degree (Celsius) or 0.1 degree interval. Since the emf generally does not vary by more than 0.001 V for a change in temperature of one degree, we may take dE / dT to be $\Delta E / \Delta T = (0.0614 - 0.058) / 10 = 3.4 \times 10^{-4} \text{ V / K}$ at all temperatures in the range from 298 K to 308 K.

$$\begin{aligned} \Delta_r S^\circ &= n F d E^\circ / dT = 2 \times 96500 \times 3.4 \times 10^{-4} \\ &= 57.9 \text{ VC / K} = 57.9 \text{ J / K} \end{aligned}$$

$$\text{Finally } \Delta_r H^\circ = \Delta_r G^\circ + T \Delta_r S^\circ$$

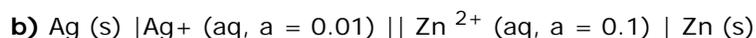
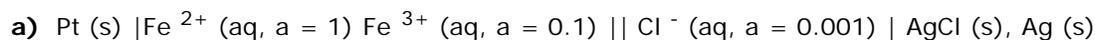
$$= -11,194 + 278 \times 57.9$$

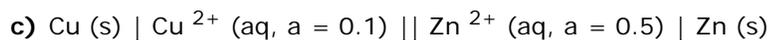
$$= 6060 \text{ J}$$

The values of $\Delta_r G^\circ$, $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are for the cell reaction as written above wherein two moles of electrons are transferred ($n = 2$) and therefore, the phrase per mole is excluded in the units.

22.6 Problems

22.1) For the following cells, write the cell reaction. Find the cell potential and find the equilibrium constants.





Comments:

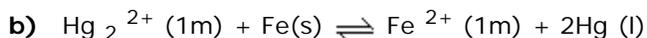
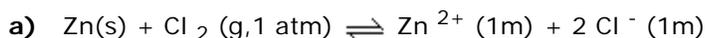
If the cell potential is negative, it implies that the reaction is not spontaneous. In such a case, exchange the electrodes such that the electrode with a greater reduction potential is to the right and complete the calculation.

In ionic solutions, the activity of cations a_+ and anions a_- can not be separately determined. What is determined is the mean activity a_{\pm} . For simplicity this has been written as a in the above problem. Use a as given above to calculate the emfs. If one molecule of an electrolyte dissociates into ν_+ positive ions and ν_- negative ions, then $n_+ = n \nu_+$ and $n_- = n \nu_-$ where n = no of moles of electrolyte in solution. The mean ionic activity a_{\pm} is defined as

$$a_{\pm}^{\nu} = a_+^{\nu_+} a_-^{\nu_-} \text{ where } \nu = \nu_+ + \nu_- = \text{no of ions produced per molecule of the electrolyte.}$$

For a 1:1 electrolyte such as NaCl, $a_{\pm} = \sqrt{a_+ a_-}$. For a 2:1 electrolyte such as MgCl_2 , $a_{\pm} = [a_+ a_-^2]^{1/3}$

22.2) For the following reactions, write down an appropriate galvanic cell, identify the electrode reaction, show the direction of flow of electrons in the external circuit and find the value of E° for the cell

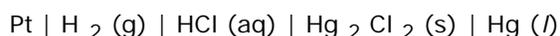


When temperature is not explicitly specified, use 298 K (We have generally not distinguished between 298 K and 298.15K. In accurate calculations, we need to use 298.15 K).

22.3)

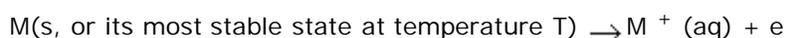
A cell consists of $\text{Ag(s)} \mid \text{Ag}^+$ and $\text{Cu (s)} \mid \text{Cu}^{2+}$ electrodes. If the concentrations of $\text{Ag}^+ (\text{aq})$ and $\text{Cu}^{2+} (\text{aq})$ are $2 \times 10^{-6} \text{ M}$ and $3 \times 10^{-3} \text{ M}$ respectively, what is the emf of the cell at 298 K?

22.4) The standard cell potential E° for the following cell was found to be 0.2684 V at 298 K and 0.2669 V at 303K.



Write the cell reaction, calculate $\Delta_r G^\circ$ at 298 K and also $\Delta_r S^\circ$ and $\Delta_r H^\circ$ for the reaction at 298 K and 303 K.

22.5) The standard Gibbs free energy for the formation of ions $\Delta_f G_{M^+}^\circ$ is defined as the free energy change for the process



For the reaction $\frac{1}{2} \text{H}_2 (\text{g}) \rightarrow \text{H}^+ (\text{aq}) + e$, $\Delta_f G_{\text{H}^+}^\circ$ is taken as zero. Combining the SHE with a) $\text{Ag} \mid \text{Ag}^+$ electrode and b) $\text{Na} \mid \text{Na}^+$ electrodes, find $\Delta_f G_{M^+}^\circ$ for Ag^+ and Na^+ ions from their respective cell potentials w.r.t. the SHE.

22.6) Devise suitable cells in which the following reactions can be carried out:

- a) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{HCl}(\text{aq})$
- b) $\text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s}) \rightleftharpoons 2 \text{Cu}^+(\text{aq})$
- c) $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$
- d) $\text{Na}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NaOH}(\text{aq}) + 1/2 \text{H}_2(\text{g})$

If some of the cell potentials are not found in this web course, please consult any of the reference textbooks mentioned in the Overview given at the beginning of the course.

22.7) Calculate the equilibrium constants for the reactions in problem (22.6).

22.8) For the reaction given below (at 298 K).

$\text{K}_2\text{CrO}_4(\text{aq}) + 2\text{Ag}(\text{s}) + \text{FeCl}_3(\text{aq}) \rightleftharpoons \text{Ag}_2\text{CrO}_4(\text{s}) + 2\text{FeCl}_2(\text{aq}) + 2\text{KCl}(\text{aq})$, $\Delta_r G^\circ = -62.5 \text{ kJ}$.
What is the standard cell potential? What is the standard electrode potential for the silver/silver chromate electrode?

22.9) Oxidation numbers are associated with atoms in their compounds. These are useful in keeping track of oxidation states of atoms during redox reactions. The oxidation numbers of atoms in their pure states (e.g., $\text{Ag}(\text{s})$, $\text{O}_2(\text{g})$ or $\text{Hg}(\text{l})$) are taken to be zero. In H_2O , the oxidation number of H is +1 and O is -2. The oxidation number of O is -2 in its compounds (except in peroxides wherein its oxidation number is -1). The oxidation numbers do not represent the charge on the atom in a molecule. Find the oxidation numbers of N in NO , N_2O , NO_2 , N_2O_4 and N_2O_5 .

22.10) The Temperature dependence of E° for the following cell $\text{Pt} | \text{H}_2 | \text{HBr}(\text{aq}) | \text{AgBr}(\text{s}) | \text{Ag}(\text{s})$ is given (in volts) by $E^\circ = 0.07131 - 4.99 \times 10^{-4} (T/\text{K} - 298) - 3.95 \times 10^{-6} [T/\text{K} - 298]^2$ where T is in Kelvin. Find $\Delta_r G^\circ$, dE°/dT , $\Delta_r S^\circ$ and $\Delta_r H^\circ$ at 298 K.

Recap

In this Lecture you have learnt the following

Summary

In this chapter, we began by distinguishing between electrolytic cells and galvanic cells. In a galvanic cell, chemical energy is converted to electrical energy and the voltage or the emf of the cell is given by $\Delta_r G = -nF E$. The negative sign signifies that a decrease in the free energy of the chemical (cell) system and this corresponds to positive emf available to do work on the surroundings.

The cell representation and the convention used in writing the electrode on the right side, where reduction is occurring in the electrode written on the right hand side was outlined. The standard (reduction) potentials were arranged in an "electrochemical" series, using which the cell potentials of any cell can be easily calculated. The Nernst equation enables one to calculate the emf of a cell for any given activities (concentrations) of ions in solution.

The last section dealt with calculating $\Delta_r S$ and $\Delta_r H$ for reactions, if in addition to E (which gives $\Delta_r G$), the temperature dependence of E, dE/dT can be measured experimentally. This option provides a very accurate method for determining $\Delta_r G$, $\Delta_r H$ and $\Delta_r S$ for "electrochemical" reactions.