AP ELECTROCHEMISTRY

I. ELECTROLYSIS CALCULATIONS

Definition: A **COULOMB** (C) is the basic unit of electrical charge.

Experimentally, we find : 1 mol e^- has a charge of 96 500 C.

Definitions: | **1 Faraday** = 1 F = **96 500 C** = charge on 1 mol e^-

An **AMPERE** (A) is the rate of flow of electrical charge.

$$\textbf{1 ampere} = 1 \ \frac{\text{coulomb}}{\text{second}} \quad \text{or:} \quad 1 \ A = 1 \ \frac{C}{s}$$

EXAMPLE: What mass of Co(s) is produced by passing 25.0 A through a solution of $CoCl_2$ for 1.00×10^4 s?

$$\text{\# of C available} = 25.0 \ \frac{C}{s} \ \text{x} \ 1.00 \times 10^4 \ s = 2.50 \times 10^5 \ C$$

$$\text{\# of mol } e^- \text{ available} = 2.50 \times 10^5 \ C \ \text{x} \ \frac{1 \, \text{mol} \, e^-}{96\,500 \ C} = 2.59 \ \text{mol}$$

since: $Co^{2+} + 2 \ e^- \longrightarrow$ Co(s) , then

$$\text{moles Co(s) produced} = 2.59 \ \text{mol} \ e^- \ \text{x} \ \frac{1 \, \text{mol} \, Co}{2 \ \text{mol} \, e^-} = 1.30 \ \text{mol}$$

$$\text{mass Co(s) produced} = 1.30 \ \text{mol} \ \text{x} \ \frac{58.9 \, g}{\text{mol}} = \textbf{76.6 g}$$

or, in one collective conversion factor calculation:

$$\text{mass Co} = 1.00 \times 10^4 \ s \ \text{x} \ 25.0 \ \frac{C}{s} \ \text{x} \ \frac{1 \, \text{mol} \, e^-}{96\,500 \ C} \ \text{x} \ \frac{1 \, \text{mol} \, Co}{2 \ \text{mol} \, e^-} \ \text{x} \ \frac{58.9 \, g}{\text{mol}} = \textbf{76.6 g}$$

Note: The concentration of the solution is NOT relevant. As long as there are sufficient ions in the solution, the reaction proceeds as required.

The conversion factor approach can be translated into a generalized method.

EXAMPLE: How many seconds are required to plate out 90.0 g of Sn(s) by passing 40.0 A through Sn^{2+}(aq)?

$$90.0 \ g = T \ s \ \text{x} \ 40.0 \ \frac{C}{s} \ \text{x} \ \frac{1 \, \text{mol} \, e^-}{96\,500 \ C} \ \text{x} \ \frac{1 \, \text{mol} \, Sn}{2 \ \text{mol} \, e^-} \ \text{x} \ \frac{118.7 \, g}{\text{mol}}$$

Solving: T = **3.66×10^3 s**

EXAMPLE: How many amperes are required to produce 10.0 g of Cu(s) from a solution of $CuSO_4$(aq) in 800.0 s?

$$10.0 \ g = 800.0 \ s \ \text{x} \ Z \ \frac{C}{s} \ \text{x} \ \frac{1 \, \text{mol} \, e^-}{96\,500 \ C} \ \text{x} \ \frac{1 \, \text{mol} \, Cu}{2 \ \text{mol} \, e^-} \ \text{x} \ \frac{63.5 \, g}{\text{mol}}$$

Solving: Z = **38.0 A**

EXAMPLE: If 5.36 g of Sn(s) is produced by passing 1.74×10^4 C through a solution containing an ion of tin, what is the charge on the tin ions?

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$$5.36 \text{ g} = 1.74 \times 10^4 \text{ C} \times \frac{1 \text{ mol e}^-}{96\,500 \text{ C}} \times \frac{1 \text{ mol Sn}}{Z \text{ mol e}^-} \times \frac{118.7 \text{ g}}{\text{mol}}$$

Solving: $Z = 3.99 \approx 4$

Since there were 4 electrons involved then the ions were **Sn^{4+}**.

HINTS: If you are given the starting charge of an ion and can determine the number of electrons involved in a reaction, then the charge on the final ion can be determined. Also, use oxidation numbers to quickly determine the number of electrons involved in a reaction if you know the initial species and the final species involved.

EXERCISES:

1.   How many moles of Cu(s) are produced by passing a 2.50 A current through 1 M $CuSO_4$(aq) for 4.00×10^3 s?

2.   How many coulombs are required to produce 0.325 g of I_2 by electrolysis of an aqueous solution of KI?

3.   A 12.5 A current is passed through a 1 M solution of $Pb(NO_3)_2$ for 1.00 h using inert electrodes. How much will the mass of the cathode increase after 1.00 h? What mass of gaseous product is produced at the anode?

4.   What quantity of electricity (in coulombs) is required to produce 2.50 kg of Br_2 by electrolyzing a KBr solution?

5.   What mass of tin is plated out of a Sn^{2+} solution if we pass 3.00 A for 6.00 h?

6.   If a certain amount of electricity can deposit 75.0 g of Ag from a solution containing Ag^+ ions, what mass of copper can a similar amount of electricity deposit from a solution of $CuSO_4$?

7.   An electrolysis cell contains X^{3+} ions. When a 5.45 A current is passed through the cell for 2.16×10^3 s, 8.50 g of elemental X are formed. What is the molar mass of X and at which electrode does X appear?

8.   When 8.47×10^4 C of electricity are passed through a solution containing AsO_4^{3-} ions, a compound containing 32.9 g of arsenic is deposited at the anode. What is the charge on the arsenic in the compound that is deposited?

9.   When a hot solution of NaBr and NaOH is electrolyzed, the oxidation reaction

$$Br^- + 6 \text{ OH}^- \longrightarrow BrO_3^- + 3 \text{ H}_2\text{O} + 6 \text{ e}^-$$

occurs at the anode. How long must a current of 7.49 A be passed through the solution to produce 25.0 g of $NaBrO_3$?

10.   What is the charge (in coulombs) on a single electron?

11.   When $CoSO_4$(aq) is electrolyzed using inert electrodes, 112.0 mL of O_2(g) at STP are liberated at the anode.
(a) How many grams of cobalt are deposited at the cathode?
(b) If a 7.50 A current is used in the electrolysis, what time is required to deposit the cobalt?

12.   A 3.80 A current is passed through a solution of thallium ions for 975 s. If 2.62 g of Tl(s) is deposited at the cathode, what is the charge on the thallium ions?

13.   What current is required to produce 1.50 g of Re(s) by passing electricity through a solution of Re^{3+} for 125 s?

14.   What mass of Cd(s) is produced by passing 11.5 A through a solution of Cd^{2+} for 5.00 h?

15. How long must a current of 24.7 A be passed through a solution of HNO_3 to produce 100.0 g of $NO(g)$?

16. When 9.90 A are passed through a solution of ZO_3^- for 2.40 x 10^3 s, 1.75 g of elemental Z_2 are formed. What is the molar mass of Z_2? At which electrode does Z_2 appear?

17. A 5.00 A current is passed through $KNO_2(aq)$ for 1.25 x 10^3 s. If a gaseous oxide of nitrogen containing 0.452 g of nitrogen is produced at the cathode, what is the formula of the nitrogen oxide?

18. A 6.00 A current is passed through a solution containing green $[V(H_2O)_6]^{3+}$ ions for 60.0 s. If the blue ion, $[VO(H_2O)_5]^{X+}$, containing 0.190 g of vanadium is formed at the anode, what is the oxidation number of vanadium in the blue vanadium ions?

19. A 1.50 V silver oxide battery contains, among other things, 1.50 g of Ag_2O. A small electronic device which acts as an equivalent resistance of 6818 Ω, draws a steady current from the battery. The cathode reaction involves the reduction of silver oxide to silver metal. How long will the battery last?

II. THERMODYNAMICS AND THE NERNST EQUATION

A. INTRODUCTION

The difference in the Gibbs free energies between the reactants and products of an electrochemical cell determines the cell potential (also called the "emf" — electromotive force) according to the equation:

$$\Delta G = -n \bullet F \bullet E_{CELL}$$

where ΔG = the change in free energy for a reaction
             n   = the number of moles of electrons transferred during the reaction
             F   = the Faraday constant = the charge on 1 mol of electrons
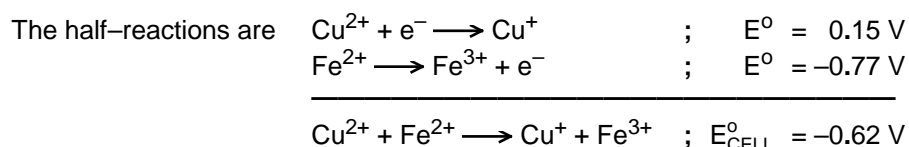   = 96 486 C/mol e^- = 96 500 C/mol e^- (approximately)

At standard state, the above equation becomes:

$$\boxed{\Delta G^o = -n \bullet F \bullet E_{CELL}^o}$$

Note: $\boxed{1 \text{ V} = 1 \dfrac{J}{C}}$

EXAMPLE: Calculate ΔG^o for the reaction $Cu^{2+} + Fe^{2+} \longrightarrow Cu^+ + Fe^{3+}$. Is this cell spontaneous?

The half–reactions are $Cu^{2+} + e^- \longrightarrow Cu^+$; E^o = 0.15 V
                                         $Fe^{2+} \longrightarrow Fe^{3+} + e^-$; E^o = –0.77 V
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                                         $Cu^{2+} + Fe^{2+} \longrightarrow Cu^+ + Fe^{3+}$; E_{CELL}^o = –0.62 V
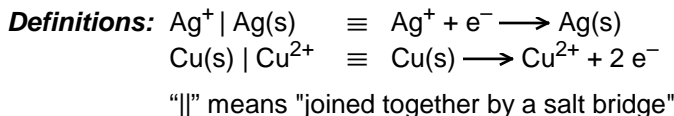
The negative value for E_{CELL}^o indicates the cell is not spontaneous.
Since 1 mol e^-/mol Cu^{2+} are transferred

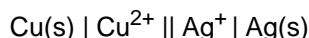$$\Delta G^o = - (1 \text{ mol } e^-) (96\ 500 \text{ C / mol } e^-) (-0.62 \text{ J/C}) = \textbf{6.0 x } 10^4 \textbf{ J} = \textbf{6.0 x } 10^1 \textbf{ kJ}$$

and the positive value of ΔG^o is another indication that the reaction is **not spontaneous**.

A DIGRESSION ON CELL NOTATION

Definitions: $Ag^+ | Ag(s) \equiv Ag^+ + e^- \longrightarrow Ag(s)$
$Cu(s) | Cu^{2+} \equiv Cu(s) \longrightarrow Cu^{2+} + 2\ e^-$

"||" means "joined together by a salt bridge"

The equation $2\ Ag^+ + Cu(s) \longrightarrow 2\ Ag(s) + Cu^{2+}$ can therefore be re–written as shown below.

$$Cu(s) | Cu^{2+} || Ag^+ | Ag(s)$$

Note that the OXIDATION half–cell is always written first, by convention.

B. CONCENTRATION CELLS

If two half–cells consisting of a strip of $Cu(s)$ in 1 M Cu^{2+} are connected together, the cell voltage is zero since both half–cells have the same tendency to reduce and/or oxidize.

Consider what happens if some water is poured into **one** of the half–cells until $[Cu^{2+}] = 0.1$ M.

Cell #1: $Cu^{2+}(1 \text{ M}) + 2\ e^- \longrightarrow Cu(s)$
Cell #2: $Cu^{2+}(0.1 \text{ M}) + 2\ e^- \longrightarrow Cu(s)$
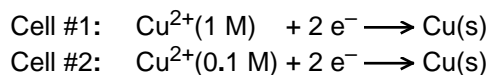
Cell #1 has a greater tendency to go forward and reduce than the 0.1 M half–cell, #2. Therefore, cell #1 undergoes reduction and cell #2 undergoes oxidation. Electrons flow from cell #2 to cell #1, simply by diluting cell #2! This electrochemical cell is called a **CONCENTRATION CELL**. The cell continues to operate until $[Cu^{2+}]$ in cell #1 has decreased and $[Cu^{2+}]$ in cell #2 has increased to the point where the $[Cu^{2+}]$ is again equal in both half–cells.

C. THE NERNST EQUATION

Recall that: $\Delta G = \Delta G^o + R \cdot T \cdot \ln Q$

But: $\Delta G = -n \cdot F \cdot E_{CELL}$ and $\Delta G^o = -n \cdot F \cdot E^o_{CELL}$

so that $-n \cdot F \cdot E_{CELL} = -n \cdot F \cdot E^o_{CELL} + R \cdot T \cdot \ln Q$

which is re–written as

$$\boxed{E_{CELL} = E^o_{CELL} - \frac{RT}{nF} \ln Q}$$ This is called the "Nernst equation"

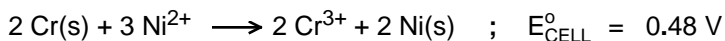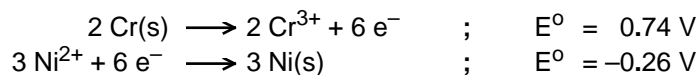For solutions at 25°C, the values of R, T and F can be combined to give

$$\boxed{E_{CELL} = E^o_{CELL} - \frac{0.0592}{n} \log Q}$$ Note that this expression uses "log"

The Nernst equation is used in the following situations.

1. Calculating the emf of electrochemical cells with non-standard concentrations.

EXAMPLE: What is the emf of Cr(s) | Cr^{3+}(0.200 M) || Ni^{2+}(2.00 M) | Ni(s) ?

The standard cell potential for 1 M solutions is

$$2\ Cr(s) \longrightarrow 2\ Cr^{3+} + 6\ e^- \quad ; \quad E^o = 0.74\ V$$
$$3\ Ni^{2+} + 6\ e^- \longrightarrow 3\ Ni(s) \quad ; \quad E^o = -0.26\ V$$
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$$2\ Cr(s) + 3\ Ni^{2+} \longrightarrow 2\ Cr^{3+} + 2\ Ni(s) \quad ; \quad E^o_{CELL} = 0.48\ V$$

and $Q = \dfrac{[Cr^{3+}]^2}{[Ni^{2+}]^3} = \dfrac{(0.200)^2}{(2.00)^3} = 0.00500$

Since 6 electrons are transferred, n = 6.

Hence $E_{CELL} = E^o_{CELL} - \dfrac{0.0592}{n} \log Q = 0.48 - \dfrac{0.0592}{6} \log(0.00500) = \mathbf{0.50\ V}$

2. Calculating the potential of half-cells at non-standard concentrations.

EXAMPLE: Calculate the value of E$_{CELL}$ for   Ni^{2+}(0.0500 M) + 2 e$^-$ $\longrightarrow$ Ni(s)

Here $Q = \dfrac{1}{[Ni^{2+}]} = \dfrac{1}{0.0500} = 20$ and   n = 2, so that

$$E_{CELL} = E^o_{CELL} - \dfrac{0.0592}{n} \log Q = -0.26 - \dfrac{0.0592}{2} \log(20) = \mathbf{-0.30\ V}$$

3. Determining the concentration of an ion in a cell or half-cell.

EXAMPLE: A cell consists of a silver electrode in a 1.0 M Ag$^+$ solution and a lead electrode in a solution having an unknown [Pb^{2+}]. If the cell has an emf of 1.04 V, what is the unknown [Pb^{2+}]?

The standard cell potential is

$$2\ Ag^+ + 2\ e^- \longrightarrow 2\ Ag(s) \quad ; \quad E^o = 0.80\ V$$
$$Pb(s) \longrightarrow Pb^{2+} + 2\ e^- \quad ; \quad E^o = 0.13\ V$$
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$$2\ Ag^+ + Pb(s) \longrightarrow 2\ Ag(s) + Pb^{2+} \quad ; \quad E^o_{CELL} = 0.93\ V$$
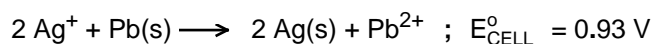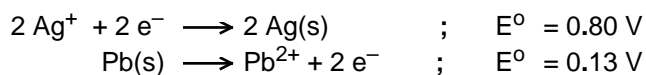
So that $E_{CELL} = E^o_{CELL} - \dfrac{0.0592}{n} \log Q$

becomes $1.04 = 0.93 - \dfrac{0.0592}{2} \log \dfrac{[Pb^{2+}]}{(1.0)^2}$

solving   [Pb^{2+}] = **1.9 x 10^{-4} M**
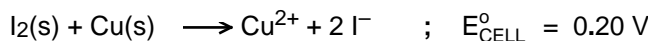
Note: only the concentrations of aqueous species are used to calculate Q.

4. Calculating the equilibrium constant, K_C, for an electrochemical reaction.

EXAMPLE: Calculate K_C for the reaction   I$_2$(s) + Cu(s) $\longrightarrow$ Cu^{2+} + 2 I$^-$

The standard cell potential is

$$I_2(s) + 2\ e^- \longrightarrow 2\ I^- \quad ; \quad E^o = 0.54\ V$$
$$Cu(s) \longrightarrow Cu^{2+} + 2\ e^- \quad ; \quad E^o = -0.34\ V$$
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$$I_2(s) + Cu(s) \longrightarrow Cu^{2+} + 2\ I^- \quad ; \quad E^o_{CELL} = 0.20\ V$$
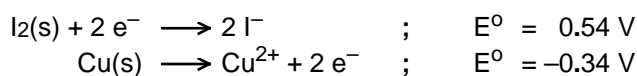
A cell at equilibrium has $E_{CELL} = 0$ and the Nernst equation becomes

$$E^o_{CELL} = \frac{0.0592}{n} \log K_C$$

and $\quad K_C = \text{antilog}\left(\frac{n}{0.0592}\ E^o_{CELL}\right) = \text{antilog}\left(\frac{2}{0.0592} \times 0.20\right) = \textbf{5.7 x 10}^\textbf{6}$

Note: Such large K_C values are usual for electrochemical reactions. This implies many electrochemical reactions commonly go virtually 100% to completion.

EXERCISES:

20. Calculate ΔG^o for the reaction $\quad 3\ Ag^+ + MnO_2 + 4\ OH^- \longrightarrow 3\ Ag + MnO_4^- + 2\ H_2O$.

21. Calculate the emf of the concentration cell $\quad Cu(s) \mid Cu^{2+}(0.010\ M) \parallel Cu^{2+}(1.0\ M) \mid Cu(s)$.

22. Calculate K_C for $\quad Sn^{4+} + H_2S \longrightarrow Sn^{2+} + S + 2\ H^+ \quad$ at 25°C.

23. Calculate ΔG^o for the reaction $\quad 3\ Mn^{2+} + 2\ Cr \longrightarrow 3\ Mn + 2\ Cr^{3+}$.

24. Given the half–cell $\quad \frac{1}{2}\ O_2(g) + 2\ H^+(aq) + 2\ e^- \longrightarrow H_2O(l) \ ; \ E^o = 1.229\ V$
     calculate the half–cell potential for $\ \frac{1}{2}\ O_2(aq) + 2\ H^+(1.00 \times 10^{-7}\ M) + 2\ e^- \longrightarrow H_2O(l)$.

25. Calculate the emf of the half–cell
     $$NO_3^-(aq) + 4\ H^+(1.00 \times 10^{-7}\ M) + 3\ e^- \longrightarrow NO(g) + 2\ H_2O(l).$$
     Would nitrate ion in a neutral solution be suitable as a spectator ion in all electrochemical cells?

26. What is K_C for $\quad PbO_2 + SO_4^{2-} + Ni^{2+} \longrightarrow PbSO_4 + NiO_2$, if $E^o_{CELL} = 0.013\ V$?

27. If $K_C = 6.88 \times 10^{87}$ for the reaction $\quad OsO_4 + 2\ Co + 4\ H^+ \longrightarrow OsO_2 + 2\ H_2O + 2\ Co^{2+}$
     what is E^o for $\ OsO_4 + 4\ H^+ + 4\ e^- \longrightarrow OsO_2 + 2\ H_2O$?   What is ΔG^o for the reaction?

28. Calculate ΔG^o and K_C at 25°C for $\quad H_2 + F_2 \longrightarrow 2\ HF$, proposed as a power source for satellite-based military lasers.

29. The $[Cl^-]$ in a solution is measured using an *ion selective electrode.* The ion selective electrode is made by depositing silver chloride over a thin silver wire and immersing the electrode in a chloride solution of unknown concentration. The half–reaction occurring in the resulting half–cell is
     $$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^- \ ; \ E^o = 0.2223\ V.$$
     The cell is completed by using a $Ag^+(1.000\ M) \mid Ag(s)$ half–cell having $E^o = 0.7996\ V$. What is the unknown $[Cl^-]$ if the value of E_{CELL} is 0.5604 V?

30. The cell $\quad Zn(s) \mid Zn^{2+} \parallel Fe^{3+} \mid Fe^{2+} \quad$ is made by connecting a zinc electrode immersed in 0.650 M $Zn^{2+}(aq)$ to a platinum wire placed in a solution made up of 0.125 M Fe^{3+} and an unknown concentration of Fe^{2+}. If ΔG for the reaction is –316 kJ, what is the $[Fe^{2+}]$?

31. If $E^o_{CELL} = 0.57\ V$ and $\Delta G^o = -2.20 \times 10^2\ kJ$ for $\quad Fe(s) \mid Fe^{2+}(1.0\ M) \parallel Ge^{Z+}(1.0\ M) \mid Ge(s)$, what is the charge on Ge^{Z+}?

32. Consider the electrochemical cell: $\quad Cu(s) \mid Cu^{2+}(1.000\ M) \parallel Ag^+(1.000\ M) \mid Ag(s)$.
     If each half–cell contains 1.000 L of solution and the cell produces a current of 1.25 A for 8.00 h, what is E_{CELL} after 8.00 h?

33. An electrochemical cell is made from a $Ag^+(aq) \mid Ag(s)$ half–cell ($E^o = 0.7996\ V$) and a

Cu^{2+}(aq) | Cu(s) half–cell (E^o = 0.3419 V). The silver half–cell contains 100.0 mL of 1.000 M Ag^+ and the copper half–cell contains 100.0 mL of 1.000 M Cu^{2+}. When 100.0 mL of 1.000 M $Na_2C_2O_4$ is added to the silver half–cell, a precipitate of $Ag_2C_2O_4$(s) forms and the cell potential drops to 0.1331 V.

(a) What is [Ag^+] in the cell after adding the $Na_2C_2O_4$?

(b) What is [$C_2O_4^{2-}$] after adding the $Na_2C_2O_4$?

(c) What is K_{SP} for $Ag_2C_2O_4$(s)?

34. An electrochemical cell is made by connecting the following two half–cells,

$$2 H^+(aq) + 2 e^- \longrightarrow H_2(g) \quad ; \quad E^o = 0.0000 \text{ V}$$
$$Zn^{2+}(aq) + 2 e^- \longrightarrow Zn(s) \quad ; \quad E^o = -0.7618 \text{ V},$$
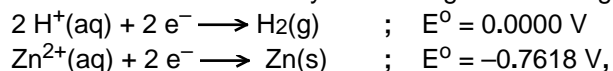
where [Zn^{2+}] = 1.00 M and the H_2(g) is at 1 atm. The hydrogen electrode is immersed in various concentrations of HCl(aq).

(a) Derive a relationship expressing the pH of HCl(aq) as a function of E_{CELL} and E^o_{CELL}.

(b) Calculate E_{CELL} for an HCl solution with a pH of 4.28.

(c) If a solution has E_{CELL} = 0.4172 V, what is the pH of the solution?