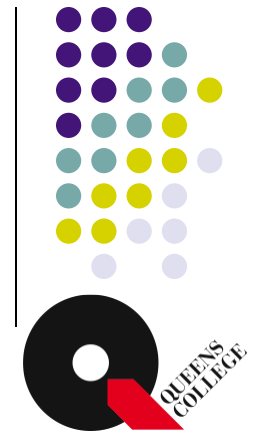# Chap. 7. <u>Chemical equilibrium</u>

Reaction Gibbs energy: $\quad \Delta_r G = \left(\dfrac{\partial G}{\partial \xi} \right)_{p,T}$

ξ: extent of reaction

(i) Unimolecular reaction, A ⟷ B

$$d\xi = -dn_A = dn_B$$

$$dG = \mu_A dn_A + \mu_B dn_B = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A)d\xi$$

$$\Delta_r G = \mu_B - \mu_A$$

(ii) General reaction, $\quad 0 = \sum_J \nu_J J$

Negative stoichiometry for reactant, and positive stoichiometry for product

$$dn_J = \nu_J d\xi \quad \textbf{and} \quad dG = \sum_J \mu_J dn_J = \sum_J \mu_J \nu_J d\xi$$

$$\Delta_r G = \left(\dfrac{\partial G}{\partial \xi} \right)_{p,T} = \sum_J \nu_J \mu_J$$

$\Delta_r G > 0$: **Endergonic reaction** $\Rightarrow$ $d\xi < 0$ **is spontaneous**

$\Delta_r G < 0$: **Exergonic reaction** $\Rightarrow$ $d\xi > 0$ **is spontaneous**
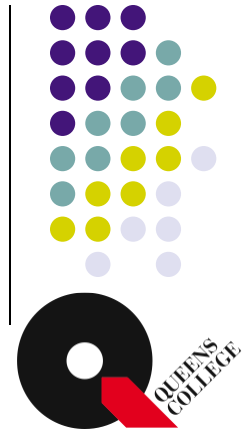
$\Delta_r G = 0$: **Equilibrium** $\Rightarrow$ $d\xi = 0$

$$\Delta_r G = \sum_J \nu_J \mu_J = \sum_J \nu_J \mu_J^{\ominus} + RT \sum_J \nu_J \ln a_J$$

$$= \Delta_r G^{\ominus} + RT \ln Q$$

Standard reaction Gibbs energy: $\quad \Delta_r G^{\ominus} = \sum_J \nu_J \mu_J^{\ominus}$

Reaction Quotient: $\quad Q = \prod_J a_J^{\nu_J}$

Equilibrium constant: $K = Q$ at equilibrium

$$RT \ln K = -\Delta_r G^{\ominus} \qquad K > 1 \text{ if } \Delta_r G^{\ominus} < 0$$

independent of ⬏
pressure

$$K < 1 \text{ if } \Delta_r G^{\ominus} > 0$$

$$\left(\frac{\partial K}{\partial p}\right)_T = 0$$

The extent of reaction can still depend on pressure.

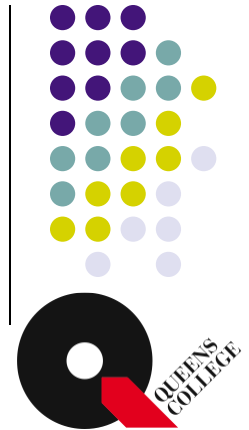**Example:** $A \leftrightarrow 2B$, **initially n mole of A**

αn **mole of A turns into** $2\alpha n$ **mole of B**

$$x_A = \frac{1-\alpha}{1+\alpha} \quad \textbf{and} \quad x_B = \frac{2\alpha}{1+\alpha}$$

$$K = \frac{p_B^2}{p_A p^\ominus} \quad \textbf{, where} \quad p_A = \frac{1-\alpha}{1+\alpha}p \quad \textbf{and} \quad p_B = \frac{2\alpha}{1+\alpha}p$$

$$\longrightarrow \quad K = \frac{p_B^2}{p_A p^\ominus} = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2 p^2}{\left(\frac{1-\alpha}{1+\alpha}\right)pp^\ominus} = \frac{4\alpha^2}{(1-\alpha^2)}\frac{p}{p^\ominus}$$

$$\longrightarrow \quad \alpha = \left(\frac{1}{1+4p/Kp^\ominus}\right)^{1/2} \quad \textbf{increase of pressure reduces } \alpha$$

van't Hoff equation

$$\ln K = -\frac{\Delta_r G^{\ominus}}{RT}$$

$$\longrightarrow \quad \frac{d}{dT}\ln K = -\frac{1}{R}\frac{d}{dT}\left(\frac{\Delta_r G^{\ominus}}{T}\right) = \frac{1}{R}\frac{\Delta_r H^{\ominus}}{T^2}$$
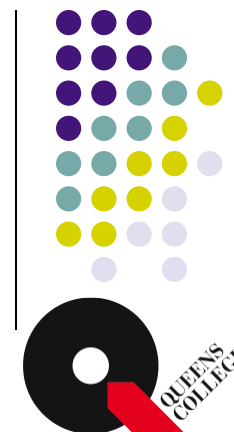
$$\longrightarrow \quad -T^2\frac{d}{dT}\ln K = \frac{d\ln K}{d(1/T)} = -\frac{\Delta_r H^{\ominus}}{R}$$

Exothermic reaction: $\quad \Delta_r H^{\ominus} < 0 \rightarrow \dfrac{d}{dT}\ln K < 0$

Endothermic reaction: $\quad \Delta_r H^{\ominus} > 0 \rightarrow \dfrac{d}{dT}\ln K > 0$

Temperature dependence of equilibrium constant

$$\ln K_2 - \ln K_1 = -\frac{1}{R}\int_{1/T_1}^{1/T_2} \Delta_r H^{\ominus} d\left(\frac{1}{T}\right) \approx -\frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
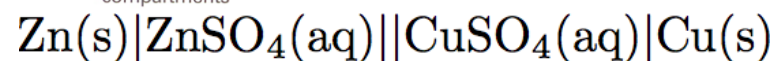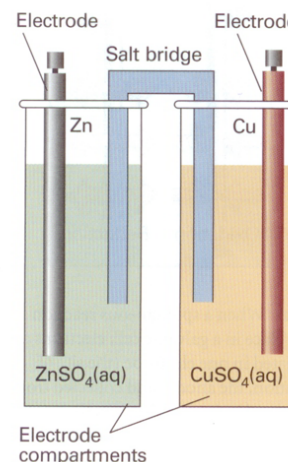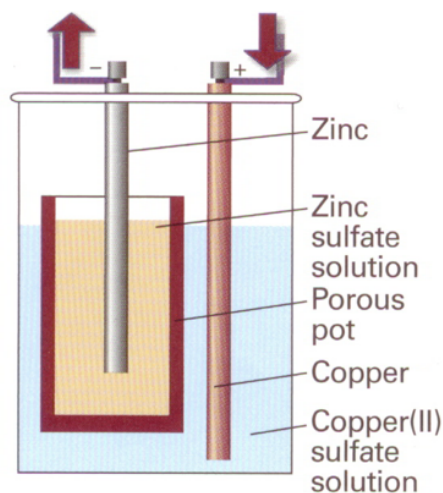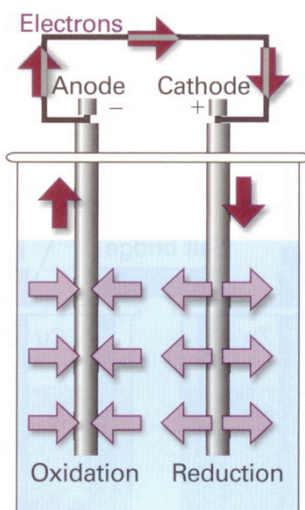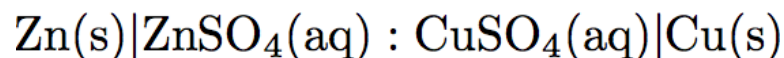
Equilibrium electrochemistry

Electrochemical cell - <u>two electrodes</u> and <u>electrolyte</u>

metallic conductors ⬆   ⬆ ionic conductor
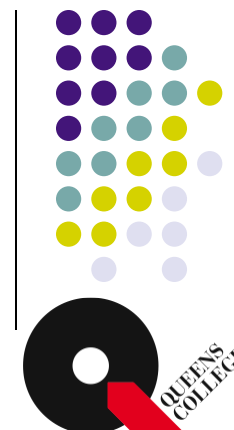
Electrode compartment - an electrode and its electrolyte

$$Zn(s)|ZnSO_4(aq) : CuSO_4(aq)|Cu(s)$$

$$Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$$

Salt bridge - joins two separate electrode compartments, a tube containing concentrated electrolyte solution (KCl in agar jelly)

Galvanic cell - chemical reaction ⟶ Electricity

Electrolytic cell - Electricity ⟶ non-spontaneous chemical reaction

Electrolyte concentration cell - electrode compartments are identical except for the concentrations of electrolytes

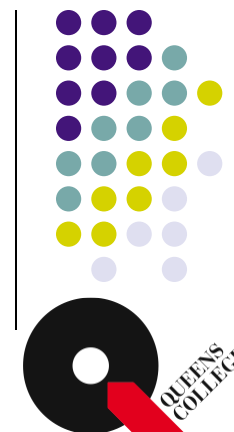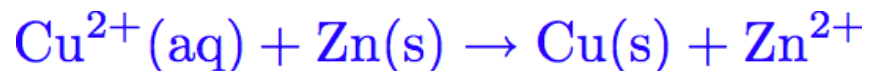**Electrode concentration cell** - electrodes have different concentrations

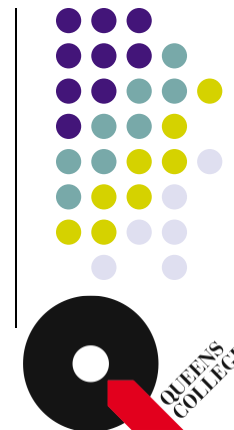**Reduction half reaction:** $\text{Ox} + \nu e^- \rightarrow \text{Red}$

Cell reaction: right-hand electrode is cathode

Example: $\text{Zn(s)}|\text{ZnSO}_4(\text{aq})||\text{CuSO}_4(\text{aq})|\text{Cu(s)}$

Right-hand electrode: $\text{Cu}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cu(s)}$

Left-hand electrode: $\text{Zn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Zn(s)}$

$$\text{Cu}^{2+}(\text{aq}) + \text{Zn(s)} \rightarrow \text{Cu(s)} + \text{Zn}^{2+}$$

Electromotive force

Cell potential established by a cell reaction in a reversible situation with exactly opposing potential.

$$dw_e = dG = \Delta_r G d\xi \quad \Longleftrightarrow \quad dw_e = -\nu F E d\xi$$

$$\nu F E = -\Delta_r G$$

Electric potential applied to the system
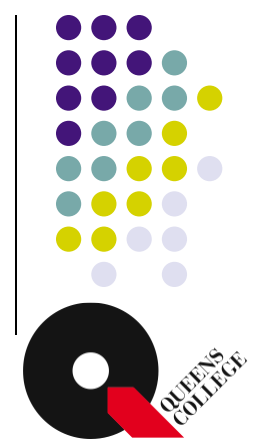
$-dw_e$: Maximum non-expansion work system can do

Nernst equation

$$E = -\frac{\Delta_r G}{\nu F} = -\frac{\Delta G^{\ominus}}{\nu F} - \frac{RT}{\nu F} \ln Q = E^{\ominus} - \frac{RT}{\nu F} \ln Q$$
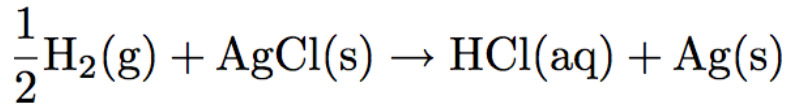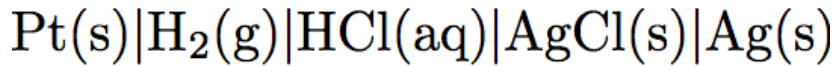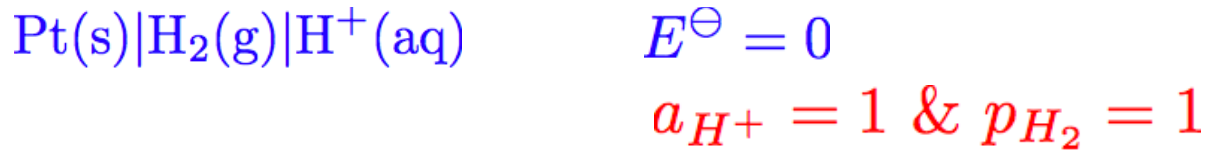
At equilibrium, $\qquad E^{\ominus} - \frac{RT}{\nu F} \ln K = 0$

$$\longrightarrow \qquad \ln K = \frac{\nu F E^{\ominus}}{RT}$$

Equilibrium constant can be calculated from the measurement of standard emf.

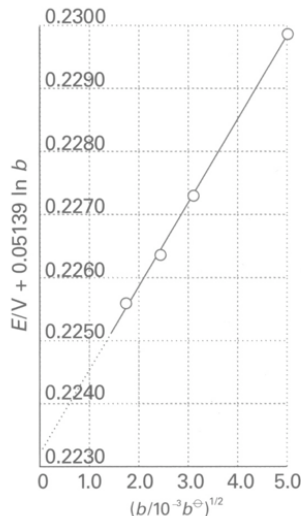# Standard hydrogen electrode (SHE): used as left hand electrode

$$\text{Pt(s)}|\text{H}_2(\text{g})|\text{H}^+(\text{aq}) \qquad E^\ominus = 0$$

$$a_{H+} = 1 \ \& \ p_{H_2} = 1$$

$$\text{Pt(s)}|\text{H}_2(\text{g})|\text{HCl(aq)}|\text{AgCl(s)}|\text{Ag(s)}$$

$$\frac{1}{2}\text{H}_2(\text{g}) + \text{AgCl(s)} \rightarrow \text{HCl(aq)} + \text{Ag(s)}$$

$$E = E^\ominus(AgCl/Ag, Cl^-) - \frac{RT}{F}\ln\frac{a_H^+ a_{Cl^-}}{a_{H_2}^{1/2}} = E^\ominus - \frac{RT}{F}\ln(a_{H+}a_{Cl-})$$

↳ **assumed to be 1.**

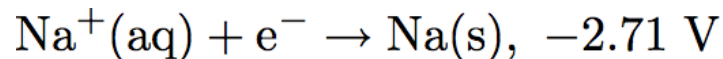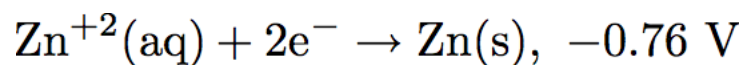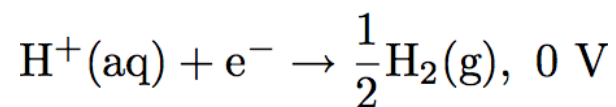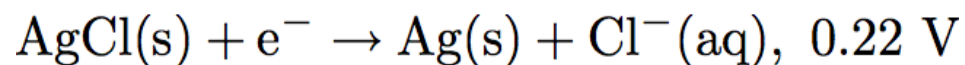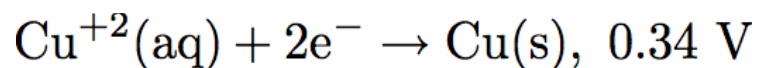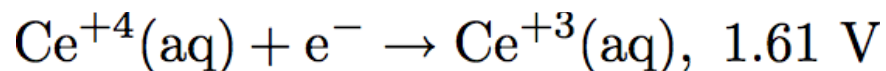$$= E^\ominus - \frac{RT}{F}\ln b^2 - \frac{RT}{F}\ln\gamma_\pm^2$$

↳**in the unit of molality**

$$E + \frac{2RT}{F}\ln b = E^\ominus + Cb^{1/2}$$

Extrapolation for the determination of standard emf.

Examples of half reactions

$$Ce^{+4}(aq) + e^- \rightarrow Ce^{+3}(aq), \; 1.61 \text{ V}$$

$$Cu^{+2}(aq) + 2e^- \rightarrow Cu(s), \; 0.34 \text{ V}$$

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq), \; 0.22 \text{ V}$$

$$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g), \; 0 \text{ V}$$

$$Zn^{+2}(aq) + 2e^- \rightarrow Zn(s), \; -0.76 \text{ V}$$

$$Na^+(aq) + e^- \rightarrow Na(s), \; -2.71 \text{ V}$$

Electrochemical Series

least strongly reducing   most strongly reducing
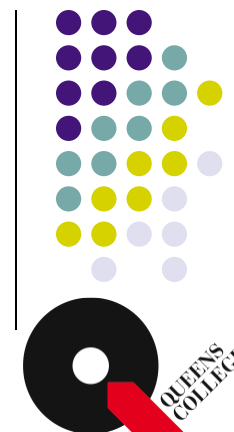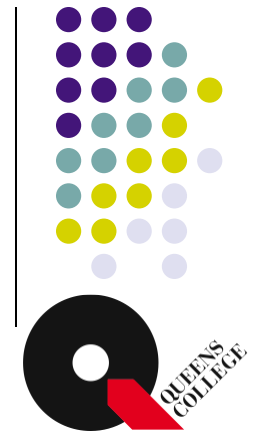
Au Pt Ag Hg Cu H Pb Sn Ni Fe Zn Cr Al Mg Na Ca K

favoring reduced form   favoring oxidized form

Determination of activity coefficients

Concetration dependence of emf gives information on activity coefficients

Example)   **From** $E = E^{\ominus} - \dfrac{2RT}{F} \ln b - \dfrac{2RT}{F} \ln \gamma_{\pm}$

$\ln \gamma_{\pm} = F \dfrac{E^{\ominus} - E}{2RT} - \ln b$

Relation of standard emf with thermodynamic functions

$$\Delta_r G^{\ominus} = -\nu F E^{\ominus}$$

$$\frac{dE^{\ominus}}{dT} = -\frac{1}{\nu F}\frac{d}{dT}\Delta_r G^{\ominus} = -\frac{1}{\nu F}\left(\frac{\partial \Delta_r G^{\ominus}}{\partial T}\right)_{p^{\ominus}} = \frac{\Delta_r S^{\ominus}}{\nu F}$$

$$\Delta_r H^{\ominus} = \Delta_r G^{\ominus} + T\Delta_r S^{\ominus} = -\nu F E^{\ominus} + T\nu F \frac{dE^{\ominus}}{dT} = -\nu F \left(E^{\ominus} - T\frac{dE^{\ominus}}{dT}\right)$$