Lecture 4: Equilibrium

28-09-2010

- Lecture plan:
  - equilibrium
    - equilibrium and Gibbs free energy
    - description of equilibrium
    - response of equilibrium to conditions (P, T, pH)
  - equilibrium electrochemistry
    - representing redox reactions in terms of half-reactions
    - electrochemical cells
    - the Nernst equation
    - standard potentials and electrode calibration
  - problems

EQUILIBRIUM

Chemical Equilibrium

$$A + B \rightleftarrows C + D$$

- Chemical reaction tend to move towards a dynamic equilibrium in which both reactants and products are present but have no tendency to undergo net change

<u>The question</u>: How to predict the composition of mixture at various condition

The Gibbs energy minimum

- Spontaneous change at const P and T happens towards lower values of the Gibbs energy
- Let's consider reaction

$$A \rightleftarrows B$$

extent of the reaction

If some amount $d\xi$ of A changed into B: $dn_A = -d\xi$

$$dn_B = +d\xi$$

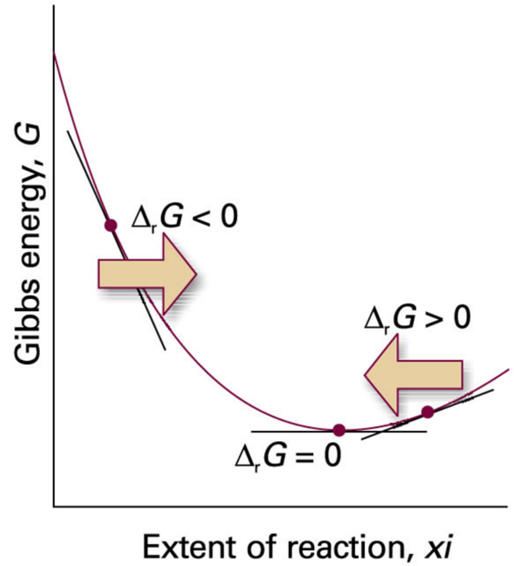
Reaction Gibbs energy (definition): $\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T}$

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

$$\boxed{\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \mu_B - \mu_A}$$

Difference between chemical potentials of the products and the reactants at the composition fo the reaction mixture

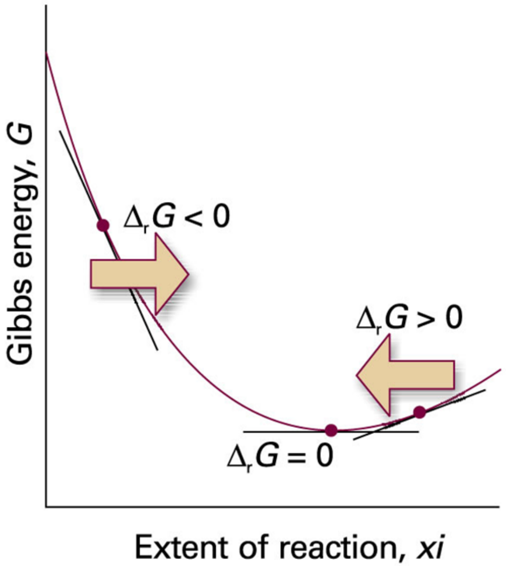
At equilibrium $\Delta_r G = 0$

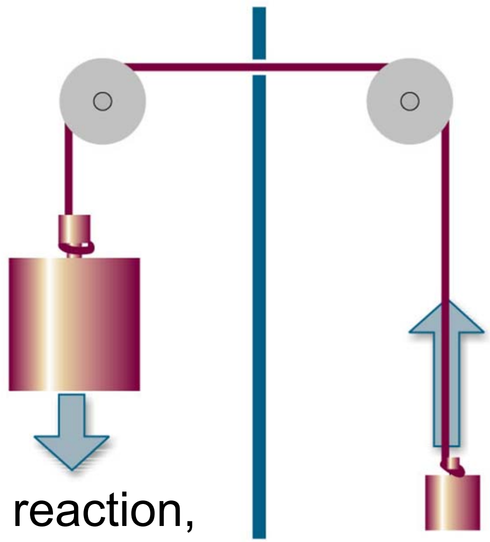


The Gibbs energy minimum

- Spontaneity reaction at const P, T

$\Delta_r G < 0$	Forward reaction is spontaneous, reaction ***exergonic*** (work-producing)
$\Delta_r G = 0$	Reaction at equilibrium
$\Delta_r G > 0$	Reverse reaction is spontaneous, reaction ***endergonic*** i.e. required work to go in forward reaction





Exergonic reaction,
e.g. glucose oxidation

Endergonic reaction,
e.g. protein synthesis

The description of equilibrium

dimensionless: $\frac{p_A}{p^\ominus}$

- Perfect gas equilibrium

$$\Delta_r G = \mu_B - \mu_A = (\mu_B{}^\ominus + RT \ln p_B) - (\mu_A{}^\ominus + RT \ln p_A) =$$

$$= \Delta_r G^\ominus + RT \ln \frac{p_B}{p_A}$$

Q – reaction quotient

K- equilibrium constant

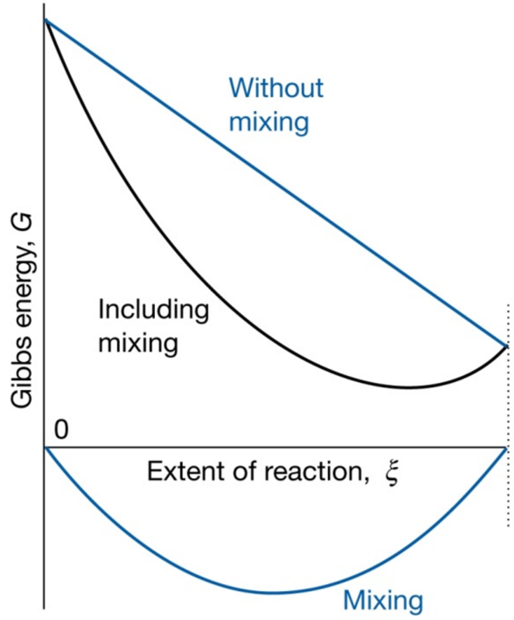
At equilibrium:

$$\Delta_r G = 0 = \Delta_r G^\ominus + RT \ln \frac{p_B}{p_A}$$

$$RT \ln K = -\Delta_r G^\ominus$$

Why reaction doesn't go till the end:

$$\Delta_{mix} G = nRT(x_A \ln x_A + x_B \ln x_B)$$



The description of equilibrium

- General case of a reaction $2A + B \longrightarrow 3C + D$

$$0 = 3C + D - 2A - B$$

standard Gibbs free energies of formation

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

$$\Delta_r G^{\theta} = \sum_{\text{products}} \nu \Delta_f G^{\theta} - \sum_{\text{reactants}} \nu \Delta_f G^{\theta}$$

$$Q = \frac{\text{activities of products}}{\text{activities of reactants}} \qquad Q = \prod_j a_j^{\nu_j}$$

For example, for the reaction above: $Q = \dfrac{a_C^{\ 3} a_D}{a_A^{\ 2} a_B}$

The description of equilibrium

At equilibrium:

$$K = \left(\prod_j a_j^{\nu_j} \right)_{equilibrium}$$

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

Example: Find degree of dissociation of water vapour at 2300K and 1 bar if standard Gibbs energy for decomposition is 118 kJ/mol

$$H_2O(g) \rightleftarrows H_2(g) + \frac{1}{2} O_2(g)$$

$$\ln K = -\frac{\Delta G^{\theta}}{RT} = \frac{118 * 10^3}{8.3 * 2300} \qquad K = 2.08 * 10^3$$

$$K = \frac{p_{H_2} p_{O_2}^{1/2}}{p_{H_2O}} = \frac{\alpha^{3/2} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}} \Rightarrow \alpha = 0.0205$$

The description of equilibrium

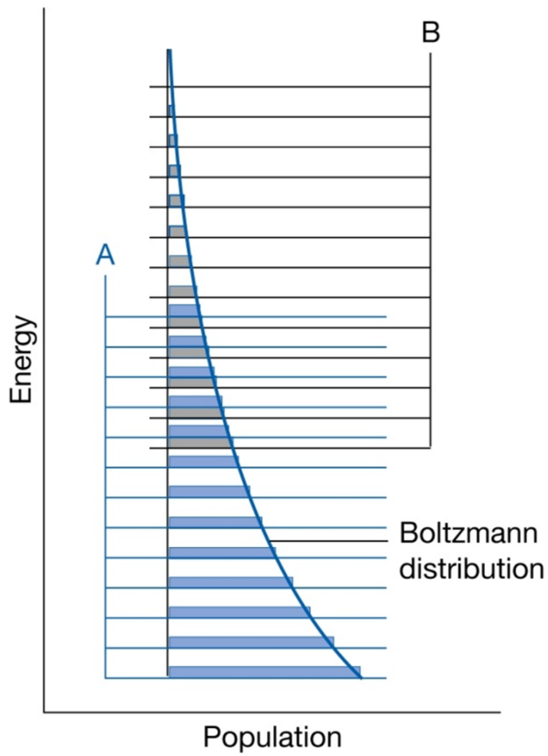
$$RT \ln K = -\Delta_r G^{\ominus} \qquad K = e^{-\Delta_r G^{\ominus}/RT} = e^{-\Delta_r H^{\ominus}/RT} e^{\Delta_r S^{\ominus}/R}$$

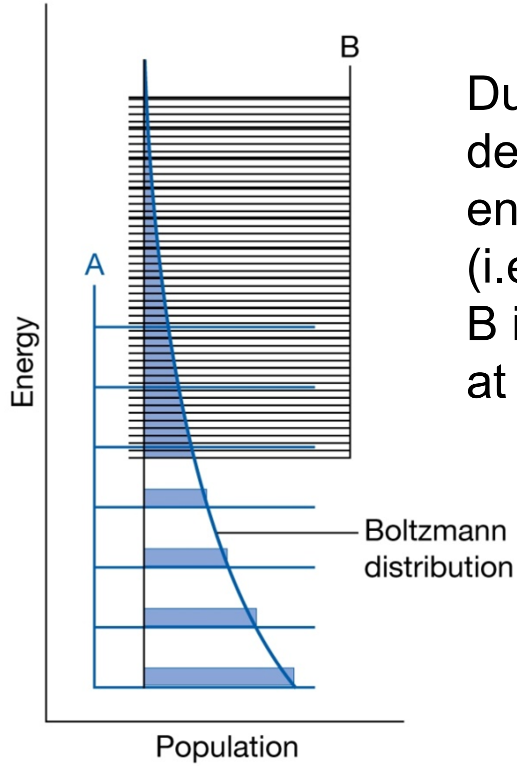
Increase with reaction entropy

decrease with reaction enthalpy

Boltzmann distribution interpretation:

$$p_i = N \frac{e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$$





Due to higher density of energy levels (i.e. higher S), B is dominant at equilibrium

The description of equilibrium

- Relation between equilibrium constants

$$K = \frac{a_C a_D}{a_A a_B} = \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \times \frac{b_C b_D}{b_A b_B} = K_\gamma K_b$$

At low concentration: $K \approx K_b$

- Using biological standard state

If a biological reaction involves H+ ions, we have to take into account that standard biological condition is at $pH = -\log a_{H^+} = 7$

$$NADH(aq) + H^+(aq) \longrightarrow NAD^+(aq) + H_2(g)$$

$$\Delta_r G^{\oplus} = \Delta_r G^{\theta} + 7\ln 10 \times RT =$$

$$= -21.8kJ/mol + 16.1 \times 8.3 \times 10^{-3} kJ/K\,mol \times 310K = 19.7kJ/mol$$

The response of equilibria to the conditions

- Equilibria will respond to temperature, pressure and concentration changes

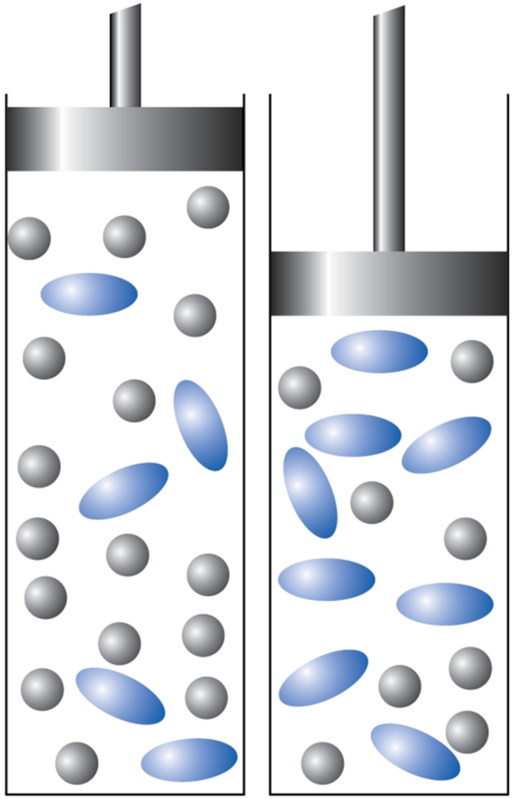
$$RT \ln K = -\Delta_r G^{\theta}$$

Pressure dependence:

Depends on standard $\Delta_r G^{\theta}$
(standard pressure)

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

$$A(g) \rightleftharpoons 2B(g) \qquad K = \frac{p_B{}^2}{p_A p^{\theta}}$$



(a) (b)

• Pressure increase by injecting inert gas: no change as partial pressures of reactants and products stay the same .
• Pressure increase by compression: system will adjust partial pressures so the constant stays the same.

The response of equilibria to the conditions

- Le Chatelier principle:
  A system at equilibrium, when subjected to disturbance responds in a way that tends to minimize the effect of disturbance

Extent of dissociation, **α**:

$$A(g) \rightleftharpoons 2B(g) \qquad K = \frac{p_B^{\,2}}{p_A p^{\ominus}}$$

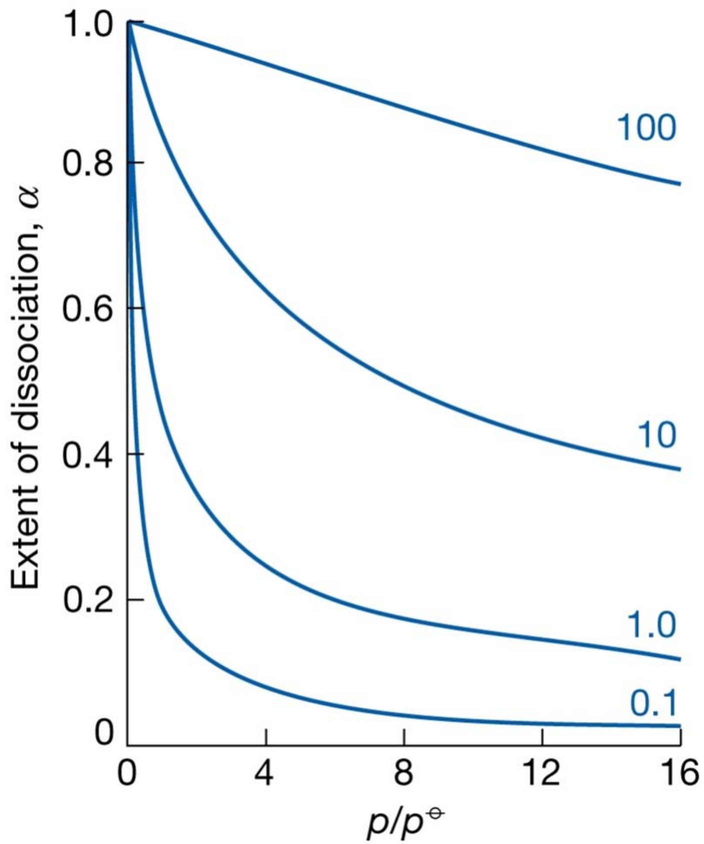
$$(1-\alpha)n \qquad\qquad 2\alpha n$$

Mole fractions at equilibrium:

$$\kappa_A = \frac{(1-\alpha)n}{(1-\alpha)n + 2\alpha n} = \frac{1-\alpha}{1+\alpha} \qquad \kappa_B = \frac{2\alpha}{1+\alpha}$$

$$K = \frac{p_B^{\,2}}{p_A} = \frac{\kappa_B^{\,2} p^2}{\kappa_A p} = \frac{4\alpha^2 p}{1-\alpha^2}$$

$$\alpha = \left(\frac{1}{1 + 4p/Kp^{\ominus}}\right)^{1/2}$$



The response of equilibria to the conditions

- Temperature response

Equilibrium will shift in endothermic direction if temperature is increased and in exothermic direction if temperature is lowered.

Van't Hoff equation:

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

Gibbs-Helmholtz equation

$$\frac{d\ln K}{dT} = -\frac{1}{R}\frac{d(\Delta_r G^{\theta}/T)}{dT} \qquad \frac{d(\Delta_r G^{\theta}/T)}{dT} = -\frac{\Delta_r H^{\theta}}{T^2}$$

$$\boxed{\frac{d\ln K}{dT} = \frac{\Delta_r H^{\theta}}{RT^2} \qquad \frac{d\ln K}{d(1/T)} = -\frac{\Delta_r H^{\theta}}{R}}$$

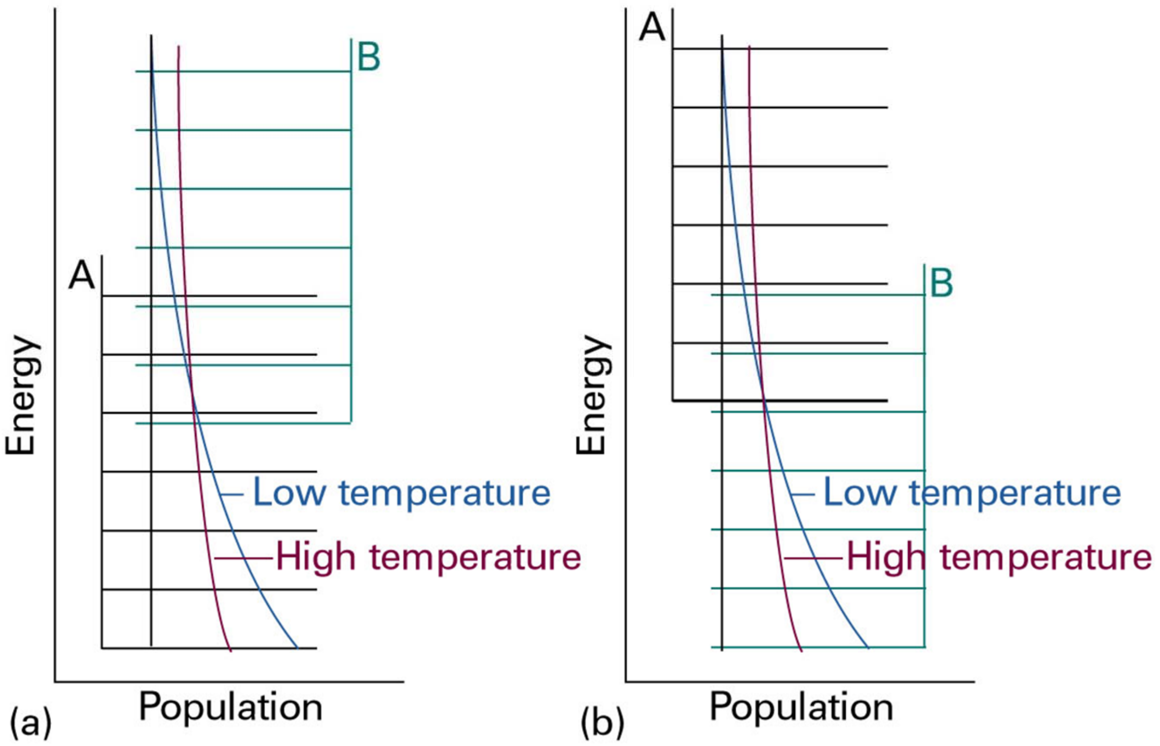
i.e. for exothermic reaction:

$$\Delta_r H^{\theta} < 0 \qquad \frac{d\ln K}{dT} < 0$$

So, we can predict the equilibrium constant at another temperature: $\ln K_2 - \ln K_1 = -\frac{\Delta_r H^{\theta}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

The response of equilibria to the conditions

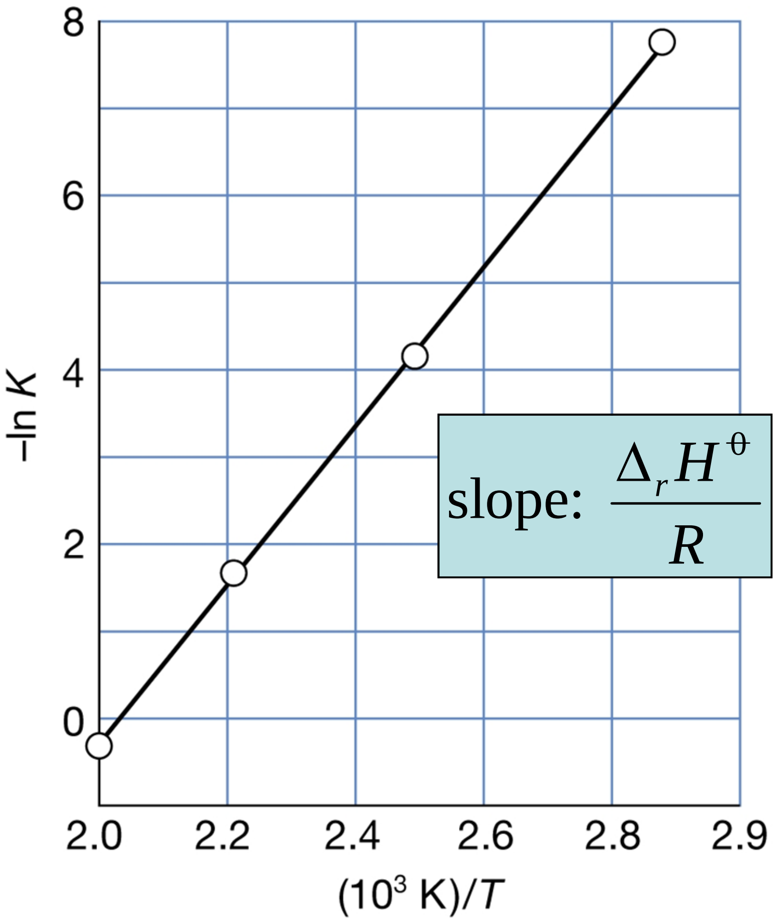
- Boltzmann distribution interpretation



The response of equilibria to the conditions

- Noncalorimetric measuring reaction enthalpy

$$\frac{d\ln K}{d(1/T)} = \frac{\Delta_r H^{\theta}}{R}$$



The response of equilibria to the conditions

- Value of K at different temperatures

$$\frac{d\ln K}{d(1/T)} = \frac{\Delta_r H^{\theta}}{R}$$

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

Equilibria and pH

- Dissociation of water (autoprotolysis)

$$2H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$$

$$K_w = \frac{a_{H_3O^+} a_{OH^-}}{a_{H_2O}{}^2} = a_{H_3O^+} a_{OH^-} = 10^{-14} \; at \, 298K$$

Ionic dissociation constant of water

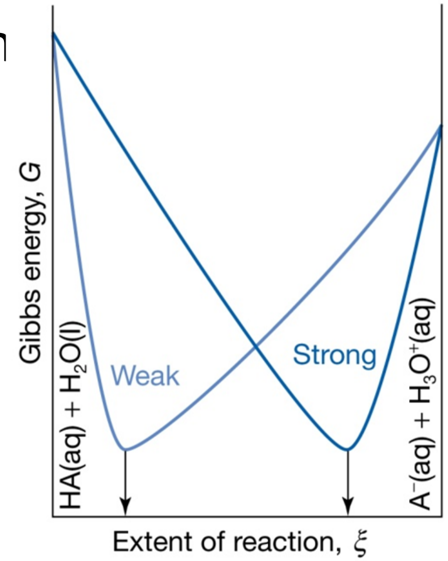
For pure water: $a_{H_3O^+} = a_{OH^-} = 10^{-7}$

$$pH = -\log a_{H_3O^+}$$

at low concentration equal to molarity

The response of equilibria to pH

- Arrhenius acid: increases concentration of H_3O^+ in solution
  Arrhenius base: increases concentration of OH^- in solution



Can be done via donation of OH^- or removing of H^+.

$$NaOH(aq) \rightleftharpoons Na^+(aq) + OH^-(aq)$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Acidity constant, K_a:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad K_a = \frac{a_{H_3O^+} a_{A^-}}{a_{HA}} \qquad pK_a = -\log K_a$$

Conjugate base

Basicity constant, K_b:

Conjugate acid

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq) \qquad K_b = \frac{a_{HB^+} a_{OH^-}}{a_B} \qquad pK_b = -\log K_b$$

Example: dissociation of formic acid

- Example: pK of formic acid is 3.77 at 298K. What is pH of 0.01M solution? What would happen if it were strong acid?

$$HCOOH + H_2O(l) \rightleftarrows HCOO^- + H_3O^+$$

$$K_a = \frac{\left[H_3O^+\right]\left[HCOO^-\right]}{\left[HCOOH\right]} = 1.695\times10^{-4} \Rightarrow x^2 + 1.695\times10^{-4}x - 1.695\times10^{-6} = 0 \xrightarrow{x_{\pm} = \frac{-b\pm\sqrt{b^2-4ac}}{2a}} x = 1.22\times10^{-3}$$

Answer: $[H_3O^+] = 1.22\times10^{-3}$

$$pH = 2.91$$

- What would be dissociation degree at pH=4 and pH=10?

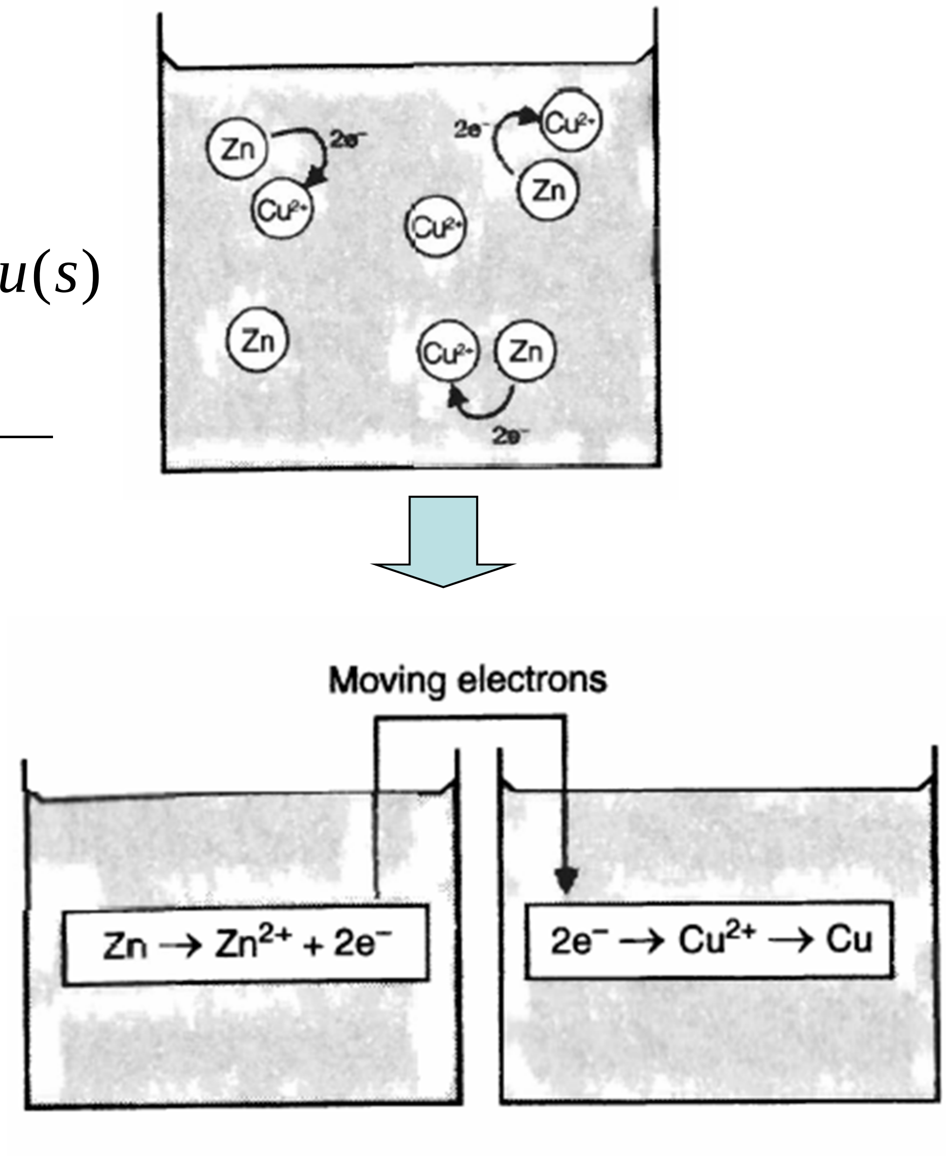
Equilibrium electrochemistry

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

$$+\quad \begin{array}{l} Zn(s) \longrightarrow Zn^{2+}(aq) + 2e \\ Cu^{+2}(aq) + 2e \longrightarrow Cu(s) \end{array}$$

- Any redox reaction can be expressed as difference of two half-reactions, which are conceptual reactions showing gain of electrons

$$\mathrm{Ox} + \nu e^{-} \rightarrow \mathrm{Red}$$

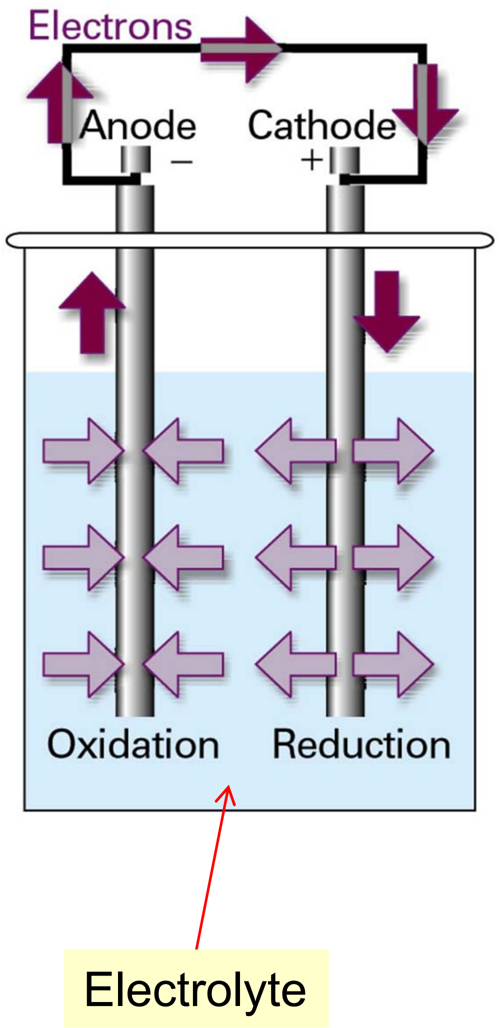


Equilibrium electrochemistry

- Two half-reactions will run in the opposite directions in two half cells

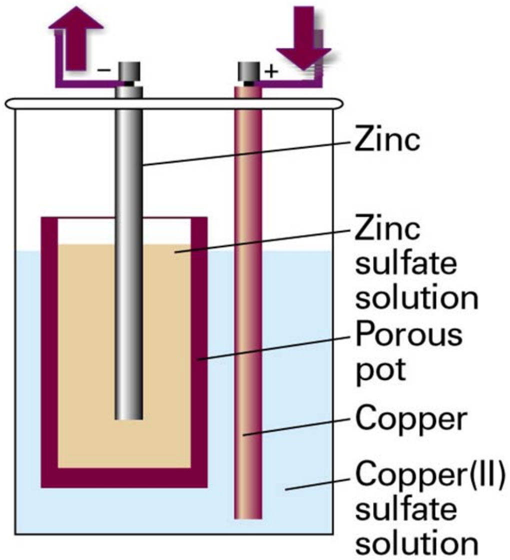
Cathode $\mathrm{Ox}_1 + \nu e^- \rightarrow \mathrm{Red}_1$

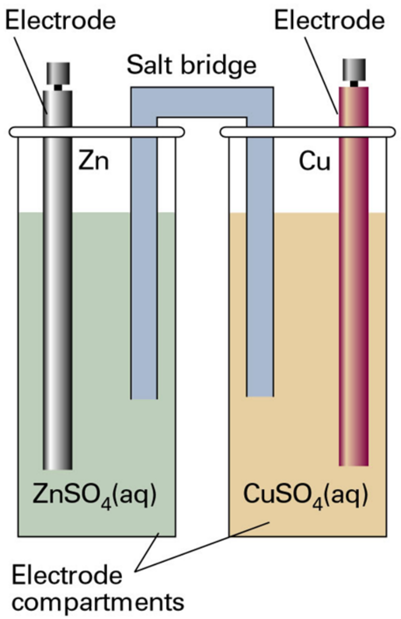
Anode $\mathrm{Red}_2 \rightarrow \mathrm{Ox}_2 + \nu e^-$



The electrode where oxidation occurs is called **anode**, the electrode where reduction occurs is called **cathode**.

Electrochemical cells





Notation:

$$Zn(s)\,|\,ZnSO_4(aq)\,\vdots\,CuSO_4(aq)\,|\,Cu(s)$$

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

Phase boundary

Liquid junction

Liquid junction potential assumed eliminated

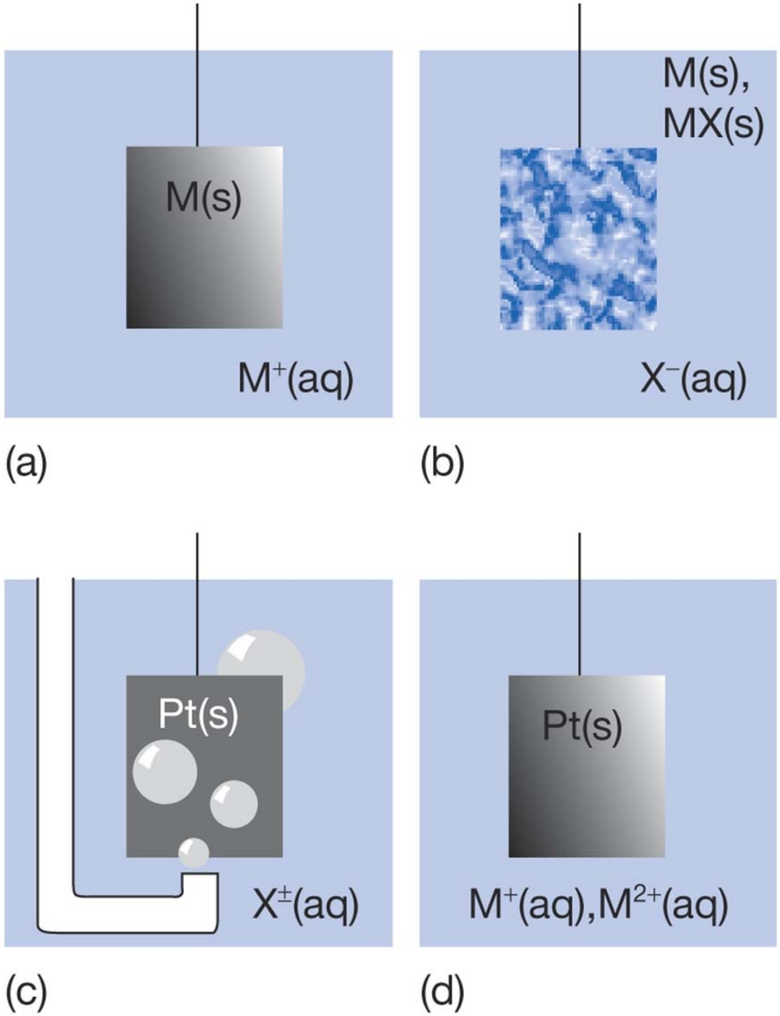
Types of half-cells

- Metal in a solution of it's ions

$$Zn^{2+} + 2e^{-} \rightarrow Zn$$

- Metal in contact with its insoluble salt

$$AgCl(s) + e^{-} \rightarrow Ag(s) + Cl^{-}$$



- Gas in contact with a solution of it's ions

$$2H^{+} + 2e^{-} \rightarrow H_2$$

- Two different oxidation states of the same species

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$$

The Nernst equation

- A cell where overall cell reaction hasn't reached chemical equilibrium can do electrical work as the reaction drives electrons through an external circuit

$$w_{e,\max} = \Delta_r G$$

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

Faraday constant $F = eN_A$

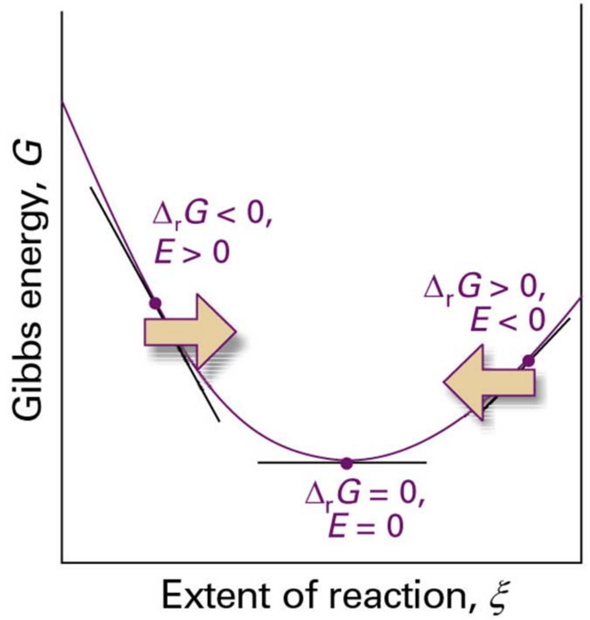
Cell **emf**:

$$E = -\frac{\Delta_r G}{\nu F}$$

$$\boxed{E = -\frac{\Delta_r G^{\ominus}}{\nu F} - \frac{RT}{\nu F}\ln Q = E^{\ominus} - \frac{RT}{\nu F}\ln Q}$$

- As there is no potential difference at equilibrium:

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



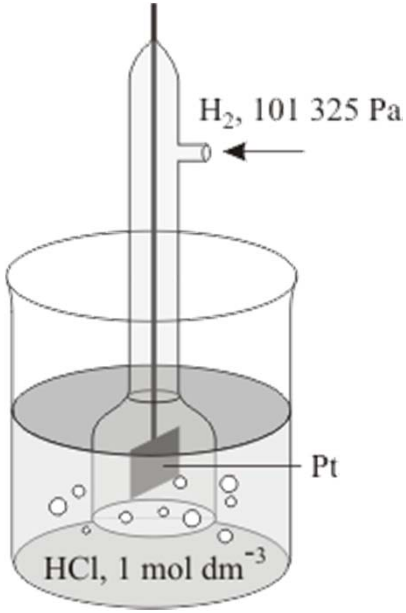
Standard potentials and SHE

- Although it's not possible to measure potentials of electrodes separately, we can define a particular electrode as having **zero potential at all temperatures**.

  Standard Hydrogen Electrode (SHE) at a_{H+}=1 (pH=0) and p=1bar

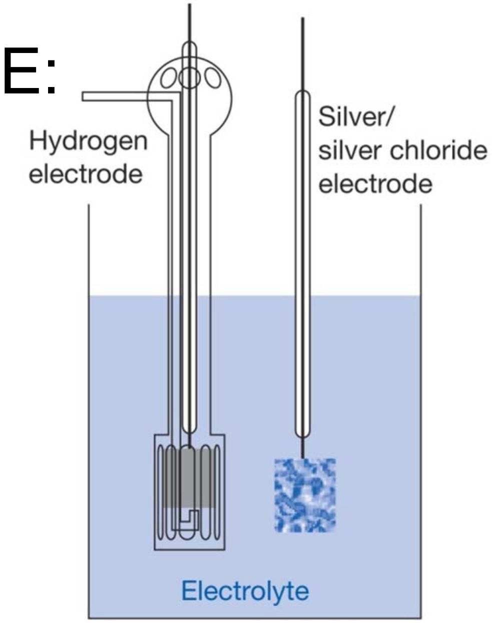
$$Pt(s)|H_2(g)|H^+(aq) \qquad E^{\theta}=0$$

$$2H^+ + 2e^- \rightleftharpoons H_2$$



Standard potentials and SHE

- All other electrodes can be calibrated using SHE:
  ("Harned cell" – calibration of Ag/AgCl electrode)

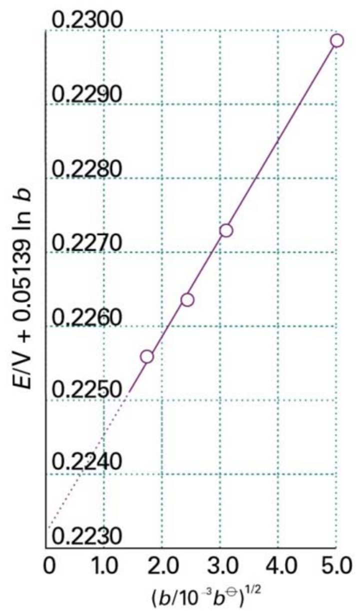


$$Pt(s)\,|\,H_2(g)\,|\,H^+(aq)\,|\,HCl(aq)\,|\,AgCl(s)\,|\,Ag(s)$$

$$\frac{1}{2}H_2(g) + AgCl(s) \rightarrow HCl(aq) + Ag(s)$$

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

$$E = E^{\theta} - \frac{RT}{F}\ln a_{H^+}a_{Cl^-} = E^{\theta} - \frac{RT}{F}\ln b^2 - \frac{RT}{F}\ln \gamma_{\pm}{}^2$$



For experimental calibration: $E + \frac{2RT}{F}\ln b = E^{\theta} + Cb^{½}$

Standard efm can be found from the offset

Electrochemical series

- Cell emfs are convenient source for data on equilibrium constants, Gibbs energies etc.

$$\mathrm{Red_1,Ox_1 \| Red_2,Ox_2} \qquad E^{\theta} = E_2^{\theta} - E_1^{\theta}$$

Red_1 has thermodynamic tendency to reduce Ox_2 if: $E_2^{\theta} > E_1^{\theta}$

low reduces high

Synoptic Table 7.2* Standard potentials at 298 K

Couple	$E^{\ominus}/V$
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.61
$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$	+0.34
$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$	0
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$	−0.76
$Na^+(aq) + e^- \rightarrow Na(s)$	−2.71

* More values are given in the *Data section*.

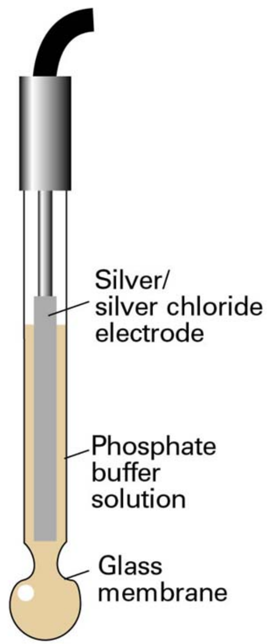
Table 7.3 The electrochemical series of the metals*

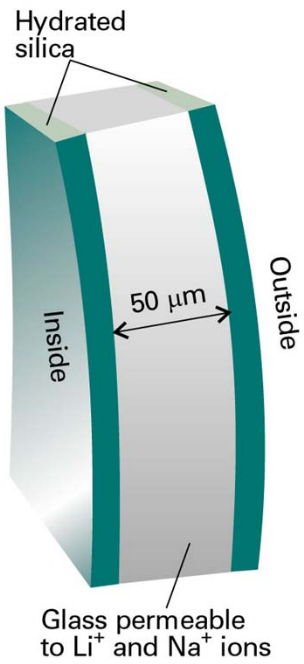
Least strongly reducing
Gold
Platinum
Silver
Mercury
Copper
(Hydrogen)
Lead
Tin
Nickel
Iron
Zinc
Chromium
Aluminium
Magnesium
Sodium
Calcium
Potassium
Most strongly reducing

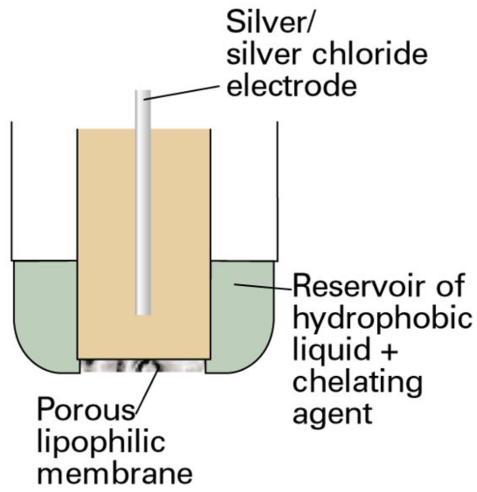
* The complete series can be inferred from Table 7.2.

Species selective electrodes

- Ion-selective electrode is an electrode that generates a potential in response to the presence of a solution of specific ions







Determination of thermodynamic functions by emf

- By measuring emf Gibbs energy can be determined:

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

- The temperature coefficient of standard emf gives standard entropy of the reaction:

doesn't depend on pressure

$$\frac{dE^\theta}{dT} = \frac{\Delta_r S^\theta}{\nu F}$$

- and therefore provides non-calorimetric way to measure enthalpy

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

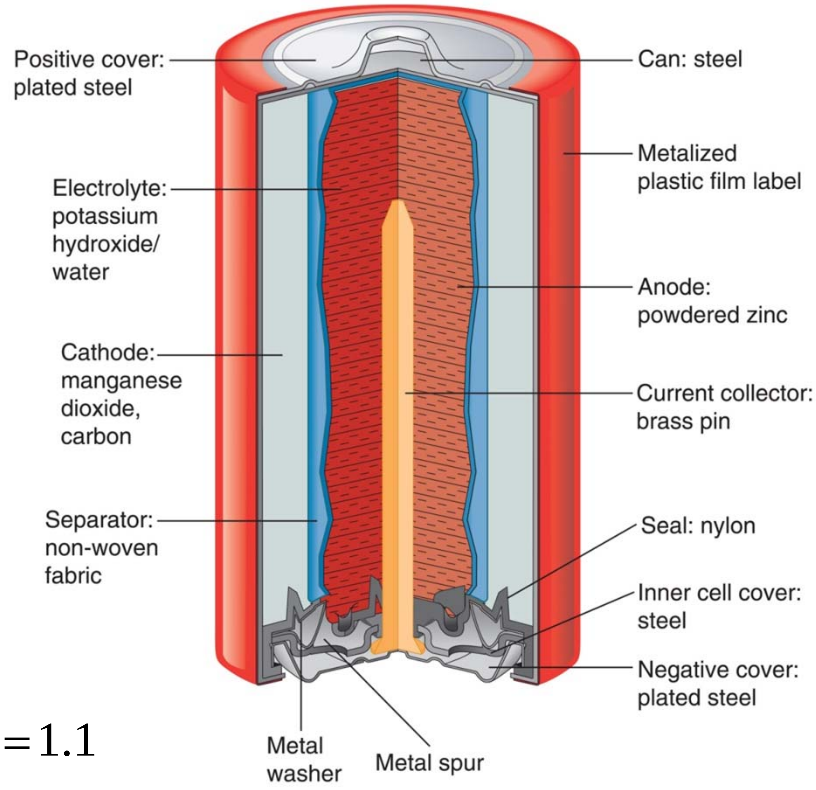
Application: Batteries

- Lead-acid rechargeable battery (inv. 1859)

$$PbO_2 + 4H^+(aq) + SO_4^{\;2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O \qquad E^\theta = 1.685$$

$$Pb(s) + SO_4^{\;2-}(aq) \rightarrow PbSO_4(s) + 2e^- \qquad E^\theta = -0.356$$

- During the charging, the reactions are reversed
- Life time is limited due to mechanical stress due to formation and dissolution of solid material



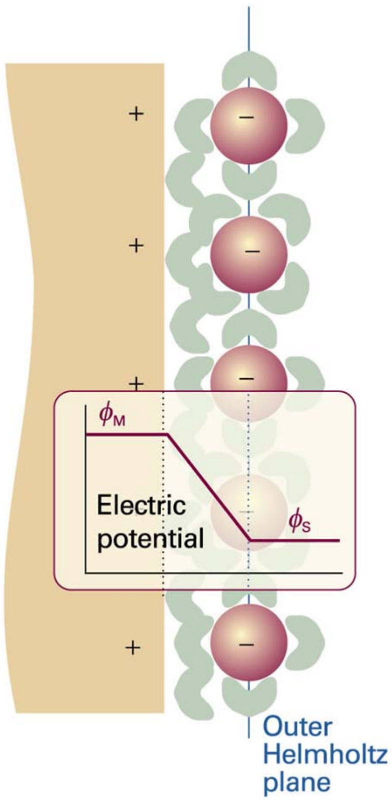
- Alkaline cell:

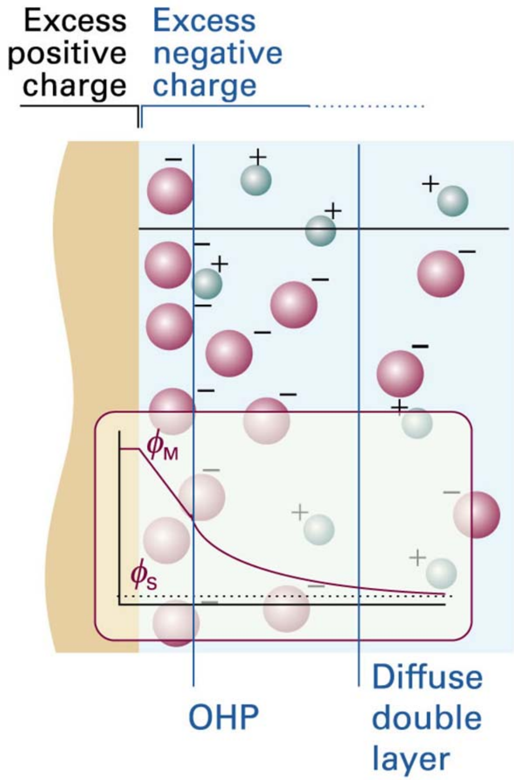
$$Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O + 2e^- \qquad E^\theta = 1.1$$

$$2MnO_2(s) + H_2O + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq) \qquad E^\theta = -0.76$$

Structure of metal-electrolyte interface

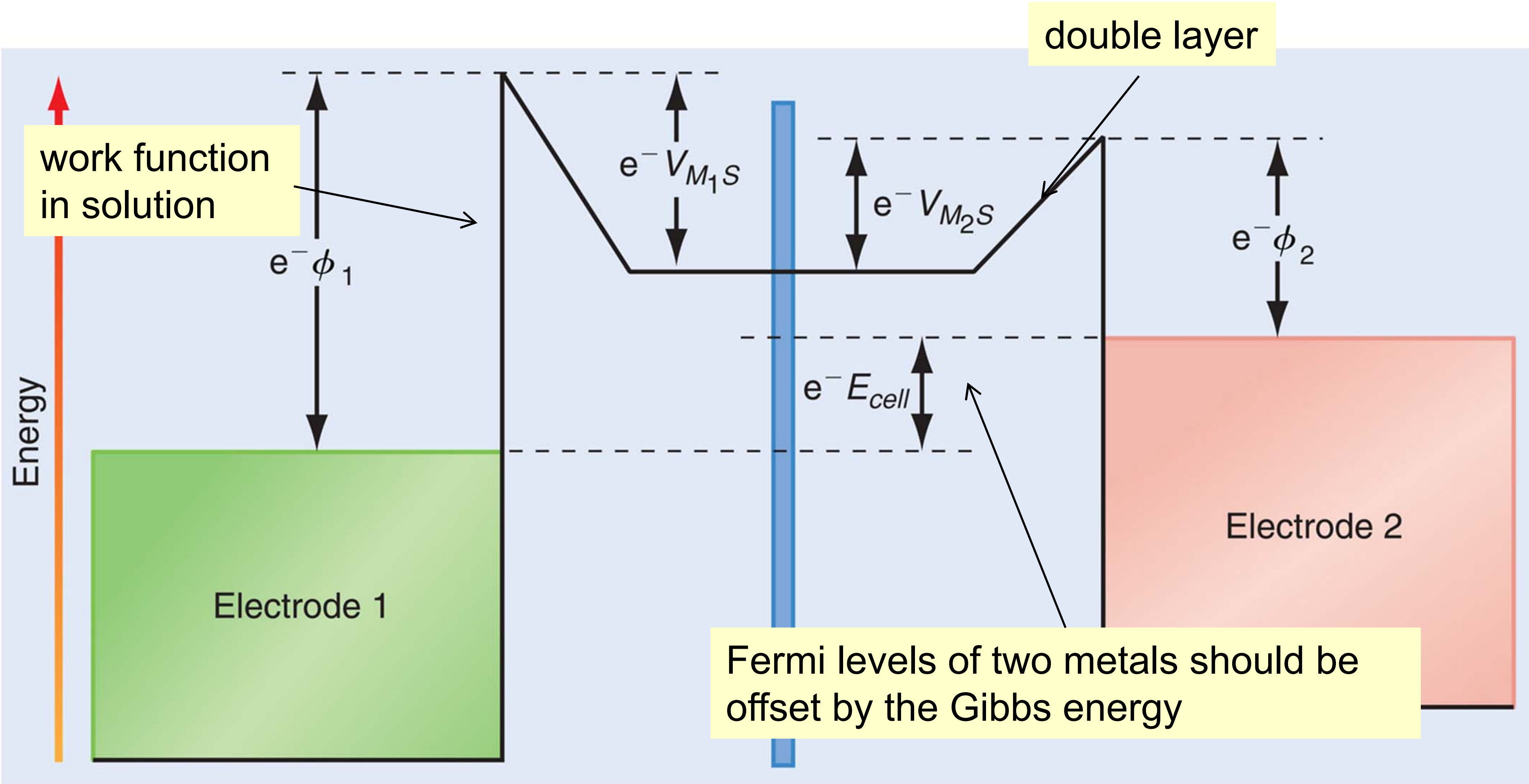
- Formation of electrical double layer due to specifically and non-specifically adsorbed ions





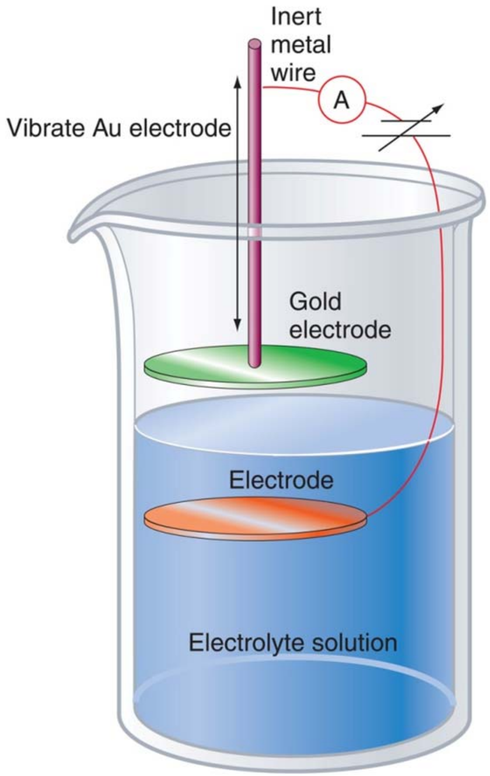
Measuring absolute half-cell potential

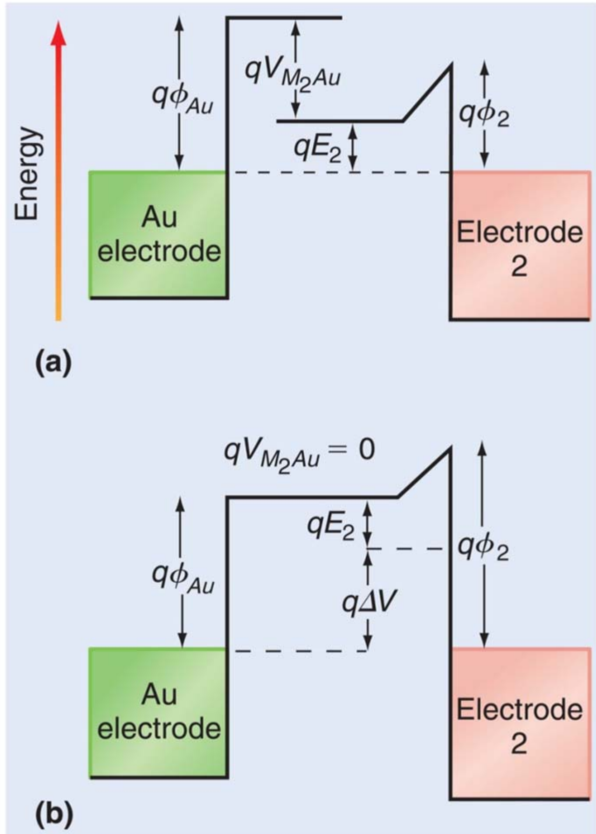
- The energy diagram of the cell:



Measuring absolute half-cell potential

- Gomer and Tryson experiment (J.Chem.Phys 66(1977), 4413): variable DC voltage is applied to the gold-electrode capacitor with a vibrating plate, AC voltage is measured





$V_{dc}=0$

$V_{dc}=V_{m2Au}$

- Absolute half cell potential for gold air electrode can be measured

$$E_{Au} = V_{M\,2\,Au} - \phi_{Au}$$

- Absolute SHE potential $E^{\theta}_{SHE} = -4.73V$

Class problems:

- **Atkins 6.8b**: In the gas phase reaction A+B=C+2D it was found that when 2mol A, 1mol B and 3 mol D were mixed and allowed to come to equilibrium at 25C, the mixture contained 0.79mol of C at 1 bar. Calculate mol fraction of every species at equilibrium, K_x, K and $\Delta_r G^0$.

- **Atkins 6.21(a)** Devise cells in which the following are the reactions and calculate the standard emf in each case:
  (a) $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$
  (b) $2\ AgCl(s) + H_2(g) \rightarrow 2\ HCl(aq) + 2\ Ag(s)$
  (c) $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

- **Atkins 6.22(a)** Use the Debye-Huckel limiting law and the Nernst equation to estimate the potential of the cell

  $Ag|AgBr(s)|KBr(aq, 0.050 mol/kg)||Cd(NO_3)_2(aq, 0.010 mol/kg)|Cd$

  at 25°C.