Lecture 5: Equilibrium Electrochemistry

17-11-2009

- Lecture plan:
  - – representing redox reactions in terms of half-reactions
  - – electrochemical cells
  - – the Nernst equation
  - – standard potentials and electrode calibration
  - – problems

Equilibrium electrochemistry

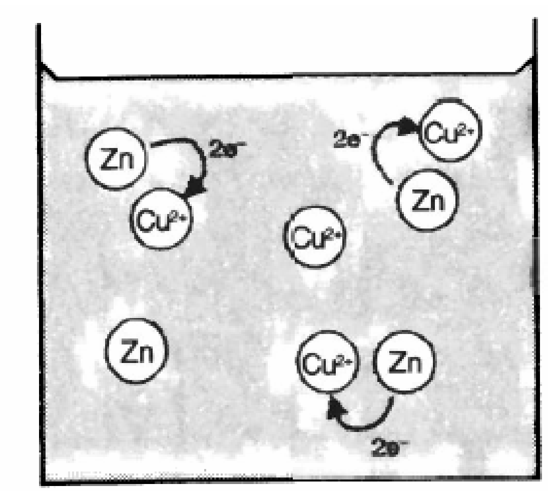
$$Zn(s) + Cu^{2+}(aq) \rightleftarrows Zn^{2+}(aq) + Cu(s)$$

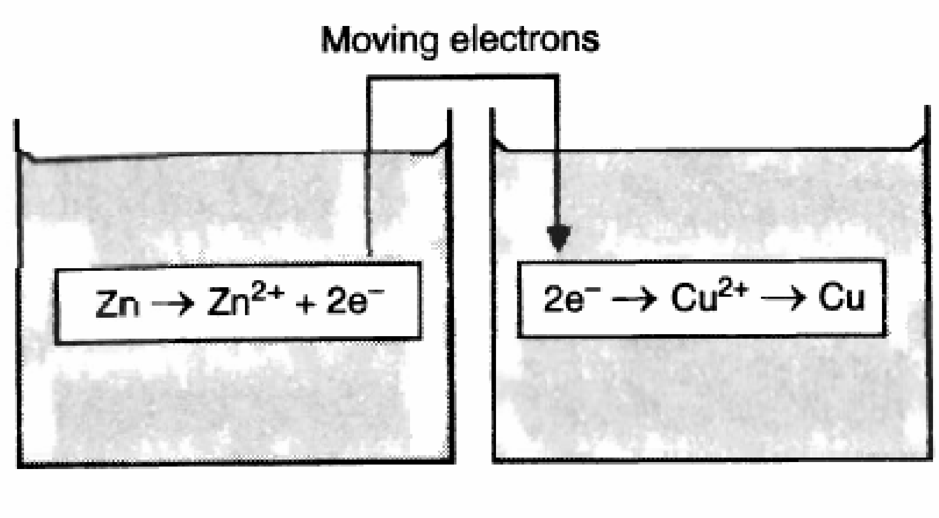
$$Zn(s) \rightleftarrows Zn^{2+}(aq) + 2e$$

$$Cu^{2+}(aq) + 2e \rightleftarrows Cu(s)$$

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

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





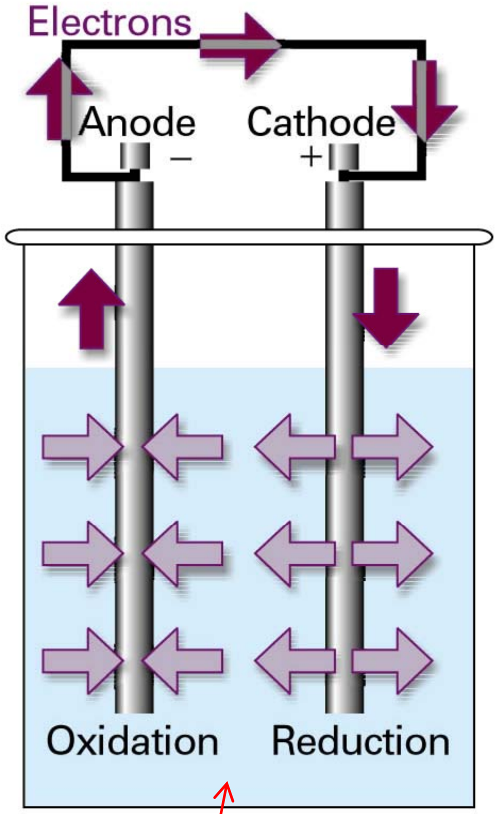
Equilibrium electrochemistry

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

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

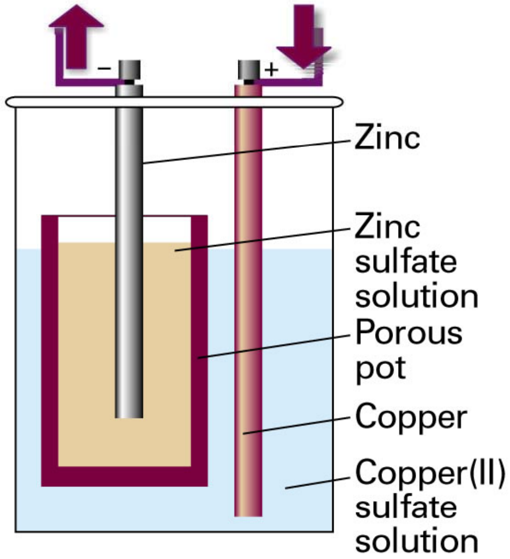
Anode $\mathrm{Red}_2 \rightarrow \mathrm{Ox}_2 + \nu e^-$

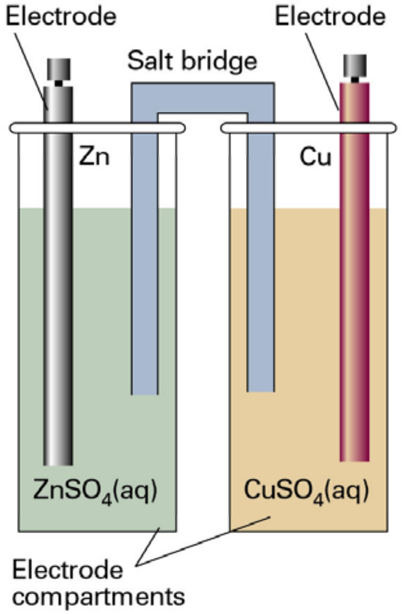
The electrode where oxidation occurs is called **anode**, the electrode where reduction occurs is called **cathode**.



Electrolyte

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

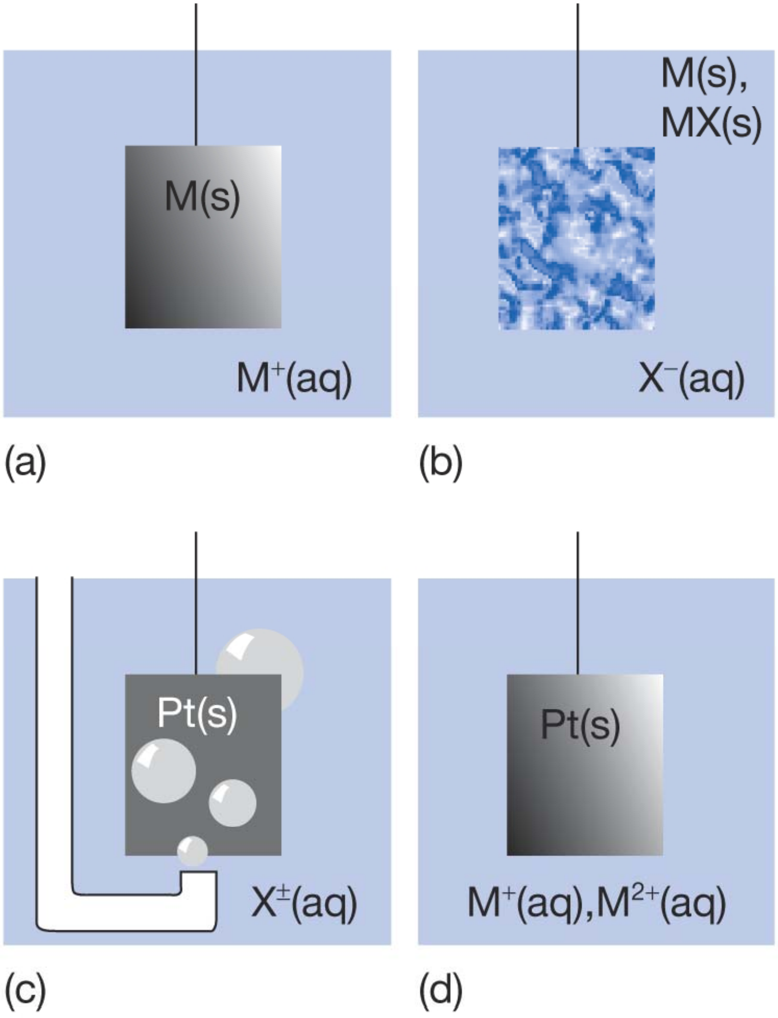
Liquid junction

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

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

$$-\nu FE = \Delta_r G$$

Faraday constant $F = eN_A$

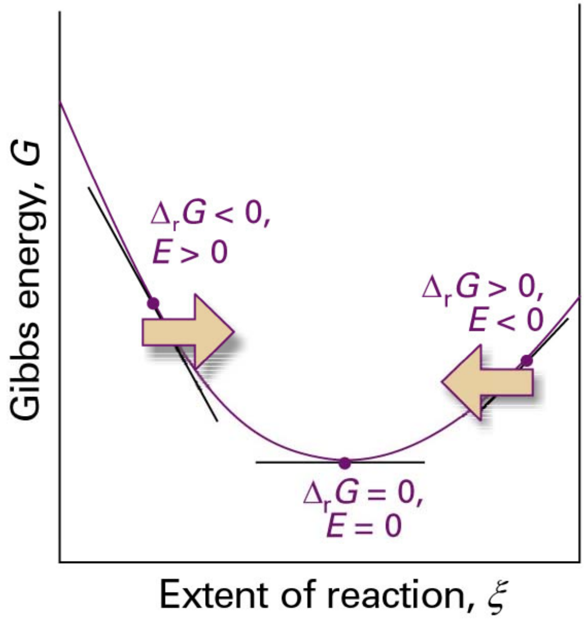
Cell **emf**:

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

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

- As there is no potential difference at equilibrium:

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



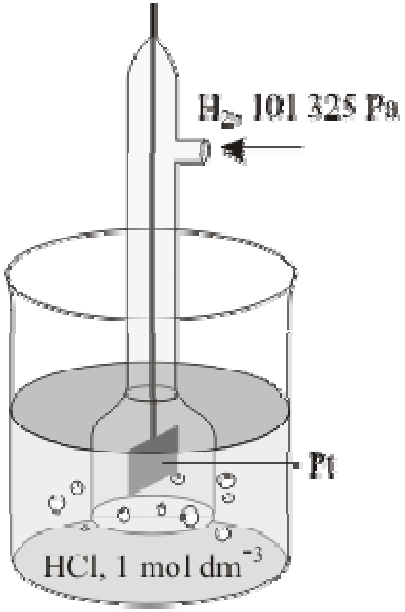
Standard potentials and SHE

- 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

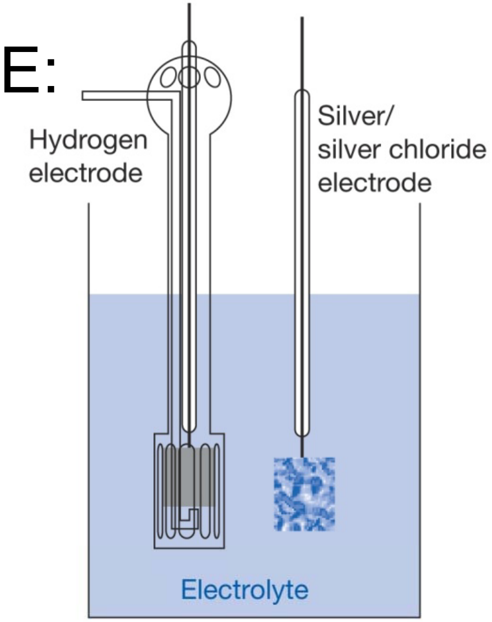
$$Pt(s)\,|\,H_2(g)\,|\,H^+(aq) \qquad E^\theta = 0$$

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



Standard potentials and SHE

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

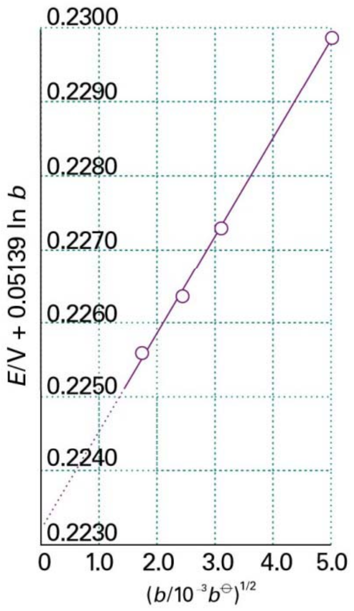


$$Pt(s)|H_2(g)|H^+(aq)|HCl(aq)|AgCl(s)|Ag(s)$$

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

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

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



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

Standard efm can be found from the offset

Adding electrochemical reaction (Hess law)

- Hess law
  “Standard enthalpy of an overall chemical reaction is the sum of the standard enthalpies of the individual reactions it can be divided into”
  is applicable to the thermodynamic functions (ΔG, ΔH etc.)

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E^{\theta} = +0.340 \qquad \Delta_r G^{\theta} = -2*0.340/F$$

$$Cu^{+}(aq) + e^- \rightarrow Cu(s) \qquad E^{\theta} = +0.522 \qquad \Delta_r G^{\theta} = -1*0.522/F$$

$$Cu^{2+}(aq) + e^- \rightarrow Cu^{+}(aq) \qquad E^{\theta} = +0.158 \qquad \Delta_r G^{\theta} = -(2*0.340 - 0.522)/F$$

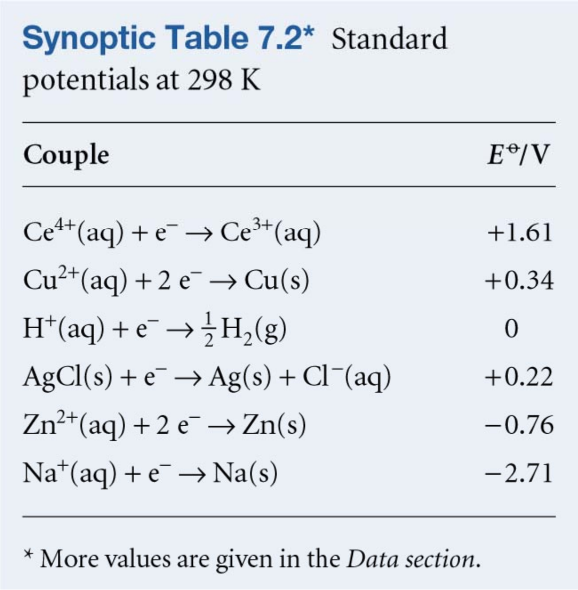
Electrochemical series

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

$$\mathrm{Red}_1,\mathrm{Ox}_1\|\mathrm{Red}_2,\mathrm{Ox}_2 \qquad E^\ominus = E_2^\ominus - E_1^\ominus$$

Red_1 has thermodynamic tendency to reduce Ox_2 if: $E_2^\ominus > E_1^\ominus$

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*.

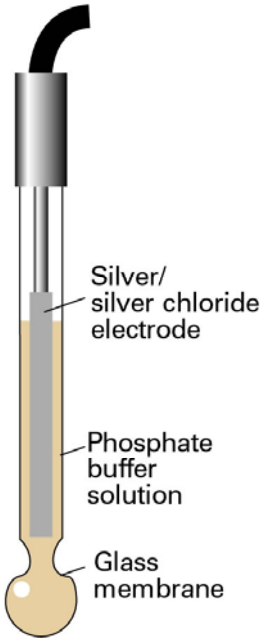
Table 7.3 The electrochemical series of the metals*

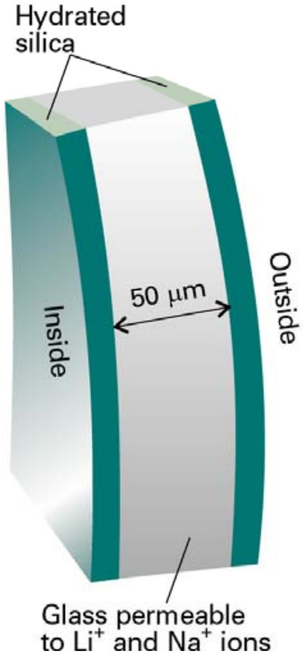
Least strongly reducing
Gold
Platinum
Silver
Mercury
Copper
(Hydrogen)
Lead
Tin
Nickel
Iron
Zinc
Chromium
Aluminium
Magnesium
Sodium
Calcium
Potassium
Most strongly reducing

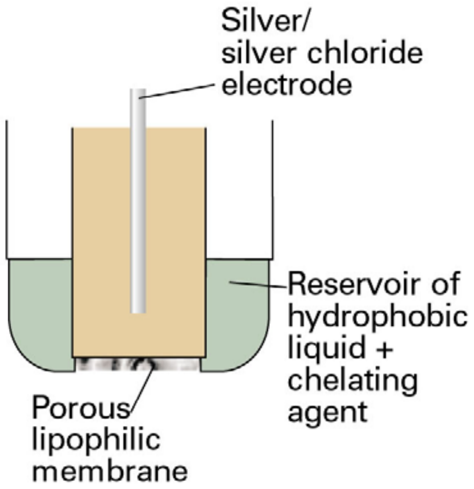
* The complete series can be inferred from Table 7.2.

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)

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

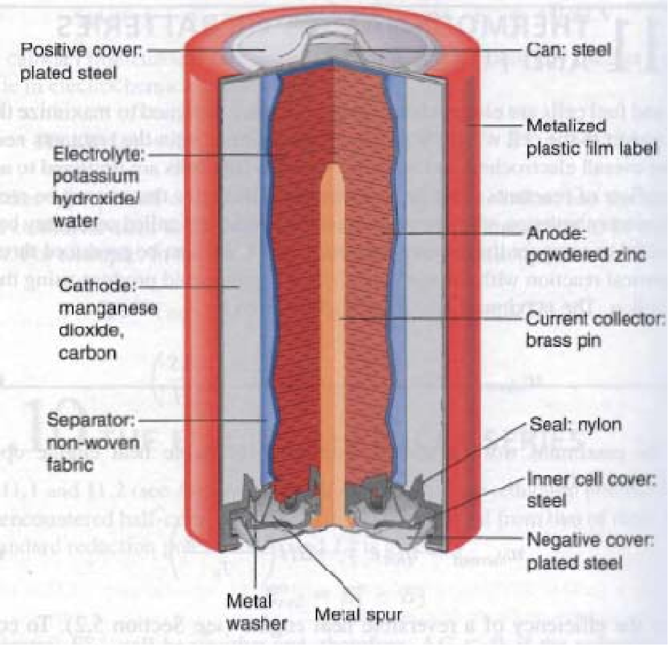
$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^- \qquad E^\theta = -0.356$$

- 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:

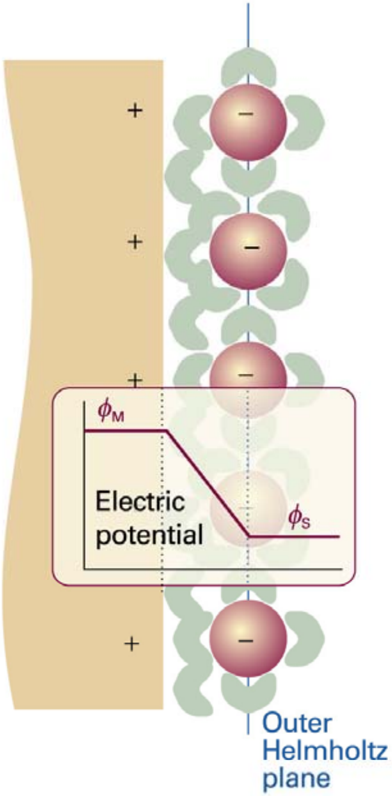
$$Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O + 2e^- \qquad E^\theta = 1.1$$

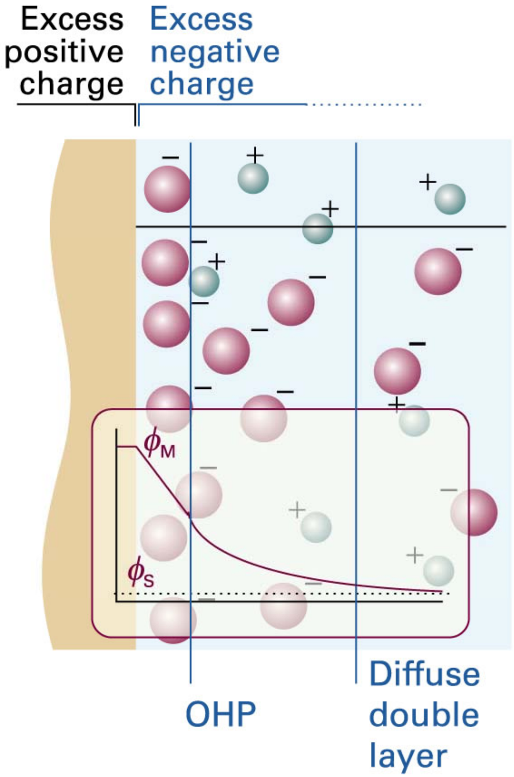
$$2MnO_2(s) + H_2O + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq) \qquad E^\theta = -0.76$$



Structure of metal-electrolyte interface

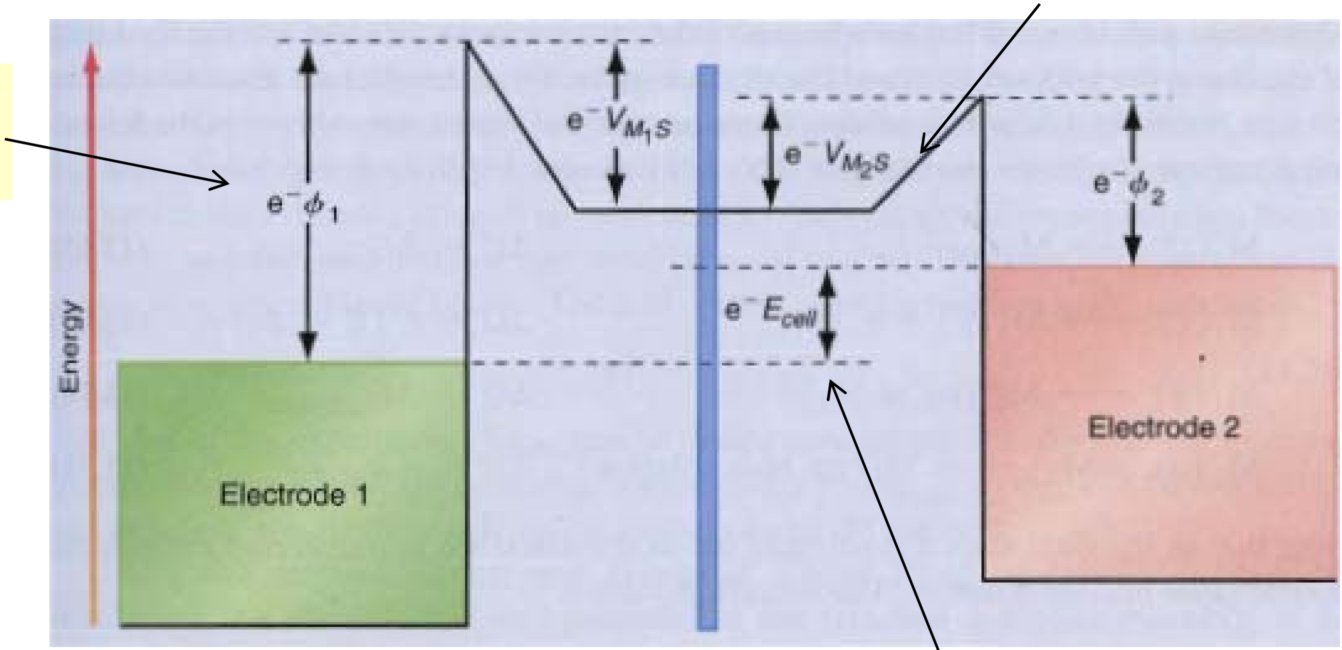
- Formation of electrical double layer due to specifically and non-specifically adsorbed ions





Measuring absolute half-cell potential

- The energy diagram of the cell:



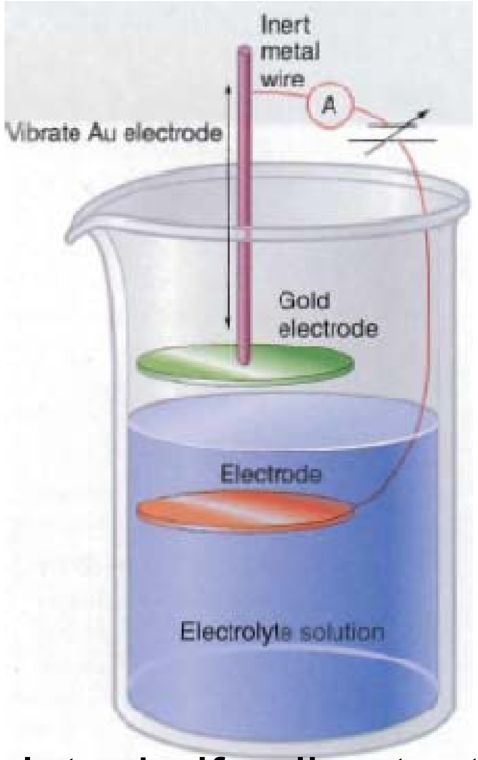
work function in solution

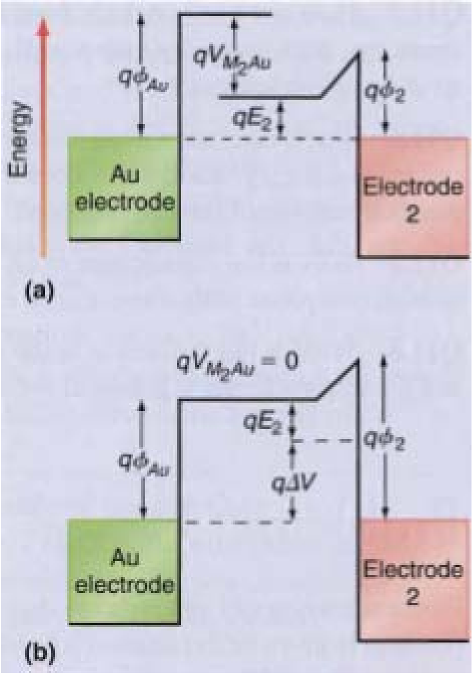
double layer

Fermi levels of two metals should be offset by the Gibbs energy

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

$$E_{Au} = V_{M2Au} - \phi_{Au}$$

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

New problems

- **Atkins 7.15(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 7.16(a)** Use the Debye-Huckel limiting law and the Nernst equation to estimate the potential of the cell

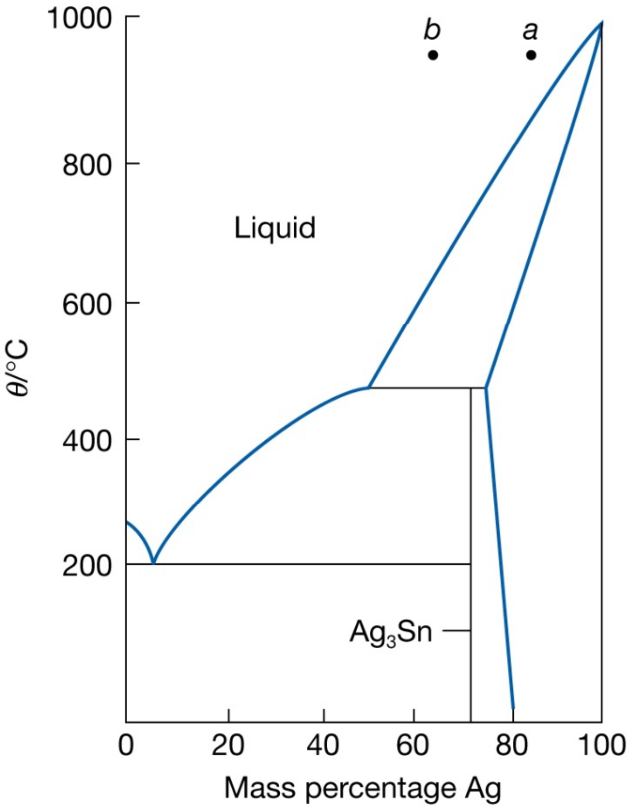
  $Ag|AgBr(s)|KBr(aq, 0.050 mol/kg)||Cd(NO_3)_2(aq, 0.010 mol/kg)|Cd$

  at 25°C.

- **Atkins 7.18(a)** The emf of the cell Ag|AgI(s)|AgI(aq)|Ag is +0.9509 V at 25°C. Calculate (a) the solubility product of AgI and (b) its solubility.

Last lecture problems

- Atkins 6.9b: sketch the phase diagram of the system NH_3/N_2H_4 given that the two substances do not form a compound and NH_3 freezes at -78C, N_2H_4 freezes at +2C, eutectic formed with mole fraction of N_2H_4 0.07 and melts at -80C.
- Atkins 6.10b Describe the diagram and what is observed when a and b are cooled down



Assignment V

- **P7.16.** Consider the cell
  $Zn(s)|ZnCl_2(aq, 0.005\ mol/kg)|Hg_2Cl_2(s)|Hg(l)$
  for which the reaction is
  $$Hg_2Cl_2(s) + Zn(s) \rightarrow 2Hg(l) + 2Cl^-(aq) + Zn^{2+}(aq)$$
- Given that $E^{\theta}(Zn^{2+}, Zn) = -0.7628;\ E^{\theta}(Hg_2Cl_2, Hg) = +0.2676$
- and the measured emf E=+1.2272
  a) write the Nernst equation for the cell
  b) determine the standard emf
  c) find $\Delta_r G$, $\Delta_r G^{\theta}$ and K for the cell reaction
  d) the mean ionic activity and activity coefficient for $ZnCl_2$ from the measured cell potential
  e) the mean ionic activity and activity coefficient for $ZnCl_2$ from the Debye-Huckel limiting law
  f) given the emf temperature coefficient $-4.52 \cdot 10^{-4}$ V/K calculate ΔS, ΔH.