Lecture 5: Equilibrium electrochemistry. Molecular motion and conductivity. 04-10-2010

- Lecture plan:
 - equilibrium electrochemistry
 - representing redox reactions in terms of half-reactions
 - electrochemical cells
 - the Nernst equation
 - standard potentials and electrode calibration
 - transport properties
 - transport properties of gases
 - mobilities of ions
 - problems

Equilibrium electrochemistry

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

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

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

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

$$Ox + \nu e^- \rightarrow Red$$





Equilibrium electrochemistry

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

Cathode
$$Ox_1 + \nu e^- \rightarrow Red_1$$

Anode
$$\operatorname{Red}_2 \to \operatorname{Ox}_2 + \nu e^-$$

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



Electrochemical cells



Notation:





Electrode

Electrode



Types of half-cells



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



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



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

Standard efm can be found from the offset



Electrochemical series

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

$$\operatorname{Red}_1, \operatorname{Ox}_1 \| \operatorname{Red}_2, \operatorname{Ox}_2$$

$$E^{\theta} = E_2^{\theta} - E_1^{\theta}$$

Red₁ 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 ^o /V		
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.61		
$Cu^{2+}(aq) + 2 e^{-} \rightarrow Cu(s)$	+0.34		
$\mathrm{H}^{+}(\mathrm{aq}) + \mathrm{e}^{-} \rightarrow \frac{1}{2}\mathrm{H}_{2}(\mathrm{g})$	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*.

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

* 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:

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

 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)

 $PbO_{2} + 4H^{+}(aq) + SO_{4}^{2-}(aq) + 2e^{-} \rightarrow PbSO_{4}(s) + 2H_{2}O \qquad E^{\theta} = 1.685$ $Pb(s) + SO_{4}^{2-}(aq) \rightarrow PbSO_{4}(s) + 2e^{-} \qquad E^{\theta} = -0.356$

- 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:

 $Zn(s) + 2OH^{-}(aq) \rightarrow ZnO(s) + H_2O + 2e^{-}$ $E^{\theta} = 1.1$ $2MnO_2(s) + H_2O + 2e^{-} \rightarrow Mn_2O_3(s) + 2OH^{-}(aq)$ $E^{\theta} = -0.76$



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



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

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

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

Molecular motion

The Aim:

 Describe the migration of properties through the matter using simple random motion picture

Within this lecture:

- Transport properties of a substance: ability of transferring matter, energy or other property from one place to another
- Basis for description of the main transport properties:
 - **Diffusion**: migration of matter down a concentration gradient
 - Thermal conduction: migration of energy down a temperature gradient
 - Electric conduction: migration of charge along electric potential
 - Viscosity: migration of linear momentum down a velocity gradient

- Rate of migration of a property is measured by its *flux J* (quantity of property passing through a unit area per unit time), e.g. matter flux , energy flux
- Flux of property is usually proportional to the first derivative of some other related property (from experimental observation), e.g. matter flux~*dN/dz* (*N* - number density of particles), energy flux ~*dT/dz*



- Viscosity of fluids (arises due to transfer of momentum)

 $J(x-component of momentum) = -\eta \frac{dv_x}{dz}$ coefficient of viscosity

A The second sec

- Transport properties of gases can be fairly accurately predicted with the kinetic theory gases.
- Kinetic model assumes that the only contribution to gas energy is a kinetic energy
- Three main assumptions:
 - Gas consist of molecules of mass **m**
 - Size of molecules is negligible (d << distances)</p>
 - Molecules interact through elastic collisions (e.g. kinetic energy is conserved at every collision)

• Application of kinetic theory of gases

Property	Transported quantity	Simple kinetic theory	Units
Diffusion	Matter	$D = \frac{1}{3}\lambda \bar{c}$	$m^2 s^{-1}$
Thermal conductivity	Energy	$\kappa = \frac{1}{3} \lambda \bar{c} C_{V,m}[A]$	J $K^{-1} m^{-1} s^{-1}$
		$=\frac{\bar{c}C_{V,m}}{3\sqrt{2}\sigma N_{A}}$	
Viscosity	Linear momentum	$\eta = \frac{1}{3} \lambda \bar{c} m \mathcal{N}$	${\rm kg}~{\rm m}^{-1}~{\rm s}^{-1}$
		$=\frac{m\bar{c}}{3\sqrt{2}\sigma}$	

where
$$\lambda$$
 is a mean free path and $\overline{c} = \int_{0}^{\infty} v f(v) dv = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}$ is a mean velocity

- The diffusion coefficient: $D = \frac{1}{3}\lambda \overline{c}$
 - 1. Mean free path is decreasing when pressure increases, so D decreases with increasing pressure
 - 2. Mean velocity increasing with T, so does the D.
 - 3. Mean free path increases when the collision cross section decreases, so D is larger for small molecules
- The thermal conductivity: $\kappa = \frac{1}{3} \lambda \overline{c} C_{v,m}[A]$
 - 1. Mean free path is decreasing when pressure increases, and therefore inversely proportional to the concentration, so κ is independent on pressure
 - 2. Thermal conductivity is greater for gases with high heat capacity.

• The viscosity:
$$\eta = \frac{1}{3} M \lambda \overline{c}[A]$$

- 1. The viscosity is independent on pressure
- 2. Because $\overline{c} \propto T^{\frac{1}{2}}$, $\eta \propto T^{\frac{1}{2}}$ the viscosity of gas is increasing with T

Molecular motion in liquids

- Experimentally measured in inelastic neutron scattering, as a relaxation time in e.g. NMR and through viscosity
- Activation origin for viscosity in liquids (i.e. a molecule needs to escape from its neighbors).

Thus, it should be inversely proportional to the probability of escape:

$$\eta \propto \exp(E_A/RT)$$

Viscosity drops sharply with temperature



Conductivity of electrolyte solution



Conductivity of electrolyte solution

- Strong electrolytes
 - fully ionized in the solution
 - Kohlrausch's law

$$\Lambda_{m} = \Lambda_{m}^{0} - Kc^{1/2}$$
Limiting molar conductivity

 Law of the independent migration of ions: limiting molar conductivity can be expressed as a sum of ions contribution

$$\Lambda_m^0 = \nu_+ \lambda_+ + \nu_- \lambda_-$$

i.e. ions migrate independently in the zero concentration limit

	$\lambda/(\mathrm{mS}\mathrm{m}^2\mathrm{mol}^{-1})$		$\lambda/(\mathrm{mS}\mathrm{m}^2\mathrm{mol}^{-1})$
H^+	34.96	OH-	19.91
Na ⁺	5.01	Cl ⁻	7.63
K^+	7.35	Br ⁻	7.81
Zn ²⁺	10.56	SO_{4}^{2-}	16.00

For example, limiting molar conductivity of $BaCl_2$ in water will be: 12.73+2*7.63=27.98 mS m² mol⁻¹.

Conductivity of electrolyte solution

• Weak electrolytes: not fully ionized in the solution

$$HA(aq) + H_2O \longrightarrow H_3O^+(aq) + A^-(aq) \qquad K_a = \frac{a_{H_3O^+}a_{A^-}}{a_{HA}}$$

If we define degree of deprotonation:

$$\begin{bmatrix} H_{3}O^{+} \end{bmatrix} = \alpha c \quad \begin{bmatrix} A^{-} \end{bmatrix} = \alpha c \quad \begin{bmatrix} HA \end{bmatrix} = (1 - \alpha)c_{1/\Lambda_{m}}$$

$$K_{a} = \frac{\alpha^{2}c}{1 - \alpha} \quad \alpha = \frac{K_{a}}{2c} \left(\left(1 + \frac{4c}{K_{a}} \right)^{1/2} - 1 \right)$$

$$\Lambda_{m} = \alpha \Lambda_{m}^{0}$$
Ostwald's dilution law
$$\frac{1}{\alpha} = 1 + \frac{\alpha c}{K_{a}} \qquad \frac{1}{\Lambda_{m}} = \frac{1}{\Lambda_{m}^{0}} + \frac{c\Lambda_{m}}{K_{a} \left(\Lambda_{m}^{0} \right)^{2}}$$

$$L_{a} = 1 + \frac{\alpha c}{K_{a}} \qquad \frac{1}{\Lambda_{m}} = \frac{1}{\Lambda_{m}^{0}} + \frac{c\Lambda_{m}}{K_{a} \left(\Lambda_{m}^{0} \right)^{2}}$$

• We need to know how ions move to understand e.g. Kohlrausch law

Let's consider uniform electric field between the electrodes in solution:



Example: Cs⁺ ion: z=1, r=170pm, η =1*10⁻³ kg m⁻¹ s⁻¹. Than μ =5*10⁻⁸ m²/Vs, i.e. with 1V applied across 1cm the drift speed is 5um/s.

• Mobility and conductivity

$$\lambda = z\mu F, \qquad F = N_A e \qquad \text{Faraday constant}$$
Let's consider a fully dissociated electrolyte:

$$J(ions) = \frac{s\Delta tA \cdot vcN_A}{A\Delta t} = svcN_A$$

$$J(charge) = zes vcN_A = zsvcF = z\mu EvcF$$

$$I = J \cdot A = z\mu EvcFA = z\mu vcFA \frac{\Delta \phi}{l}$$

$$I = \frac{\Delta \phi}{R} = G\Delta \phi = \kappa A \frac{\Delta \phi}{l} \qquad \Longrightarrow \qquad \mathbf{K} = z\mu vcF$$

 $s_{\Delta t}$

 $s_{+}\Delta t$

• In solution

$$\Lambda_m^0 = (z_+ \mu_+ \nu_+ + z_- \mu_- \nu_-) F$$

Example: if μ =5*10⁻⁸ m²/Vs and z=1, Λ =10mS m² mol⁻¹.

• Transport numbers – fraction of total current carried by ions of specific type

$$t_{\pm} = \frac{I_{\pm}}{I}, \qquad t = t_{+} + t_{-}$$

• Limiting transport numbers – defined in the limit of zero concentration of electrolyte solution

$$t_{\pm}^{0} = \frac{z_{\pm}\mu_{\pm}\nu_{\pm}}{z_{+}\mu_{+}\nu_{+} + z_{-}\mu_{-}\nu_{-}}$$

as $z_{+}\nu_{+} = z_{-}\nu_{-} \implies t_{\pm}^{0} = \frac{\mu_{\pm}}{\mu_{+} + \mu_{-}}$
or, using $\lambda = z\mu F \implies t_{\pm}^{0} = \frac{\nu_{\pm}\lambda_{\pm}}{\nu_{+}\lambda_{+} + \nu_{-}\lambda_{-}} = \frac{\nu_{\pm}\lambda_{\pm}}{\Lambda_{m}^{0}}$

as we can measure transport number of individual ions, the ionic conductivity and ionic mobility can be determined as well

• mobility of ions is not directly correlated with their size



conduction mechanism for hydrogen



Moving boundary technique



Conductivities and ion-ion interactions

 Λ_m° //(S cm² mol⁻¹)

- Reduction of ion mobility due to retardation of ionic atmosphere is called relaxation effect
- Enhanced viscous drag due to ionic atmosphere moving in opposite direction is called electrophoretic effect

Those two effect taken into account lead to $c^{\frac{1}{2}}$ dependence in Kolrausch law



Ion channels and Ion pumps

- passive ion transport: ions transport down the concentration and membrane potential gradient
- active transport: driven by an exergonic process
- transport mechanisms:
 - by carrier molecule
 - through a channel former
- Channel formers:
 - ion channels: highly selective proteins that can open and close in response to some stimuli (e.g. potential built-up or effector molecule)
 - ion pumps: proteins actively transporting particular ions



Integral

protein

Bilayer

Interior

Ion channels and Ion pumps

- K⁺ ion channel:
 - 1. K⁺ ion stripped of the hydration shell
 - 2. gripped by carbonyl group in the selectivity filter region
 - 3. K⁺ ion is driven out by electrostatic interaction with the next ion
- H⁺-ATPase ion pump that couples proton flow to synthesis of ATP





Class problems:

- Atkins 6.21(a) Devise cells in which the following are the reactions and calculate the standard emf in each case:
 (a) Zn(s) + CuSO₄(aq) → ZnSO₄(aq) + Cu(s)
 (b) 2 AgCl(s) + H₂(g) → 2 HCl(aq) + 2 Ag(s)
 (c) 2 H₂(g) + O₂(g) → 2 H₂O(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,0.050mol/kg)||Cd(NO₃)₂(aq, 0.010mol/kg) |Cd at 25°C.
- Atkins 20.24a The mobility of Rb⁺ ion in aqueous solution is 7.92x10⁻⁸ m²/sV at 25°C. Potential difference between two electrodes 8mm apart is 35V. Calculate the drift speed of Rb ions.
- Atkins 20.25a The limiting molar conductivities of KCI, KNO₃, and AgNO₃ are 14.99 mS m² mol⁻¹, 14.50 mS m² mol⁻¹, and 13.34 mS m² mol⁻¹, respectively (all at 25°C). What is the limiting molar conductivity of AgCI at this temperature?