Overview of electrochemistry

	Equilibrium electrochemistry (no current flows)	Dynamic electrochemistry (current does flow)
Homogeneous	Thermodynamics of electrolyte solutions: • electrolytic dissociation • thermodynamics and activities of ions	Conductance of electrolytes: • electrolytic conduction • mobilities of ions • Kohlrausch laws
Heterogeneous	Thermodynamics of electrodes and Galvanic cells: • electrochemical cells • cell and electrode potential • types of electrodes	Kinetics of electrode reactions: • exchange current • overpotential • Tafel equation • Butler-Volmer equation • electrolysis • batteries

HOMOGENOUS DYNAMIC ELECTROCHEMISTRY

Simultaneous or coupled **transport phenomena**

I. Conductivity of electrolytes (κ, Λ_m, Λ_m^o)
   - law of the independent migration of ions: $\Lambda_m = \nu_+\lambda_+ + \nu_-\lambda_-$

II. Strong electrolytes:
   - Kohlrausch law: $\Lambda_m = \Lambda_m^o - Kc^{1/2}$

III. Weak electrolytes: ($\alpha < 1$, $\alpha = \Lambda_m/\Lambda_m^o$)
   - Ostwald's dilution law

IV. Mobilities of ions

V. Ion transport number

VI. Consequences of ion-ion interactions

I. Conductivity of electrolytes

- Ionic conductivity: Ohm's law is valid: $I = U / R_{el}$
- Conductance G is the reciprocal of R_{el}: $G = 1/R_{el}$
- as T increases, so does G (opposite to metals).
- Solution: κ conductivity: $\kappa = Gl/A = GC$ (l: length of cell, A: surface, C: cell constant)
- Concentration is important, molar conductivity is used: $\Lambda_m = \kappa / c$
- The limiting value of Λ_m at infinite dilution is Λ_m^o (limiting molar conductivity).

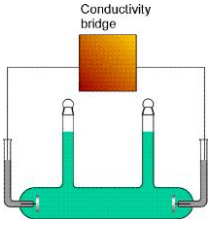
I. Conductivity of electrolytes

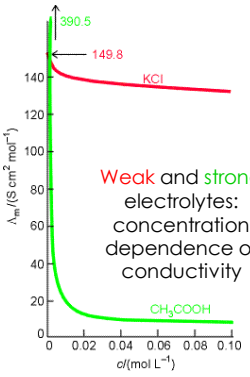
- The limiting value of Λ_m at infinite dilution is Λ_m^o (limiting molar conductivity).
- The conductivity of the electrolyte is obtained by adding the conductivities of ions: **law of the independent migration of ions**:

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

  - λ_+ and λ_-: limiting molar conductivities of (individual) cations and anions
  - ν_+ and ν_-: stoichiometric number of the cation and anion

Cell: measuring the conductivity of electrolytes



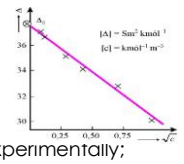


Weak and strong electrolytes: concentration dependence of conductivity

II. Strong electrolytes

- Concept (definition): in a solution of a strong electrolyte, dissociation is practically complete independently of the concentration, so $\alpha = 1$.
- Degree of dissociation (α): the ratio of dissociated molecules.
- Conductivity of electrolytes, **Kohlrausch law**:

$$\Lambda_m = \Lambda_m^0 - Kc^{1/2}$$



  - K: a constant to be determined experimentally; depends primarily on the type of the electrolyte and not on its identity

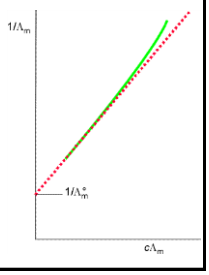
III. Weak electrolytes

- The degree of dissociation is reflected by the ratio of Λ_m and limiting Λ_m°: $\alpha = \frac{\Lambda_m}{\Lambda_m^0}$
- Acid dissociation constant:

$$K_a = \frac{c\alpha^2}{1-\alpha}$$

- Ostwald's dilution law:

$$\frac{1}{\Lambda_m} = \frac{1}{K_a\left(\Lambda_m^0\right)^2} \cdot c\Lambda_m + \frac{1}{\Lambda_m^0}$$



IV. Mobilities of ions

- drift speed(*s*)
- mobilities of ions (*u*)
- frictional coefficient(*f*)
- Connection between mobility (*u*) and conductivity (λ)
- transport numbers (t_+ and t_-)
- determination methods for transport numbers

IV. Mobilities of ions

- Molecular view: ions with radius a_{hydr} are accelerated in a medium of viscosity η by an electric force of F_{el}, but this is balanced by a counter-force of friction F_{fric} (Stokes law).

$$F_{el} = ze\varepsilon \qquad F_{fric} = fs = 6\pi\eta a_{hydr} s$$

- A stationary state is established with constant drift speed: $s = \frac{ze\varepsilon}{f} = u\varepsilon$
- The drift speed of the ion is the product of electric field ε and ion mobility u. The value of u: $u = \frac{ze}{f} = \frac{ze}{6\pi\eta a_{hydr}}$

IV. Mobilities of ions

Molar conductivities of a few ions at 298 K

Cation	Λ^∞/(S cm² mol⁻¹)	Anion	Λ^∞/(S cm² mol⁻¹)
H^+	349.8	OH^-	198.3
Li^+	38.7	F^-	55.4
Na^+	50.1	Cl^-	76.3
K^+	73.5	Br^-	78.1
Be^{+2}	90.0	I^-	76.8
Mg^{2+}	106.2	NO_3^-	71.5
Ca^{2+}	119.0	SO_4^{2-}	160.0
Ba^{2+}	127.2	CH_3COO^-	40.9
Al^{3+}	183.0	$C_6H_5CO^-$	32.4
Cu^{2+}	107.2	HCO_3^-	44.5
Ag^+	61.9	CO_3^{2-}	138.6
Zn^{2+}	105.6	$Fe(CN)_6^{3-}$	302.7
Ce^{3+}	209.4	$Fe(CN)_6^{4-}$	442.0

$$u = \frac{ze}{f} = \frac{ze}{6\pi\eta a_{hydr}}$$

IV. Mobilities of ions

- Connection between (ion) mobility and (molar) conductivity: it is understandable that the greater the mobility, the greater the conductivity:

$$\lambda = zuF$$

- So, for an infinitely dilute solution:

$$\Lambda_m^0 = \left(z_+u_+\nu_+ + z_-u_-\nu_-\right)F$$

- for a symmetrical electrolyte:

$$\Lambda_m^0 = z\left(u_+ + u_-\right)F$$

V. Ion transport number

- **Ion transport number**: the fraction of current transported by the ion: $t_\pm = \frac{I_\pm}{I}$
- Obviously: $t_+ + t_- = 1$
- The transport number of an infinitely dilute solution is obtained experimentally, with extrapolation.
- On the other hand, it can also be calculated from the ion mobilities: $t_\pm^0 = \frac{u_\pm}{u_+ + u_-}$
- Determination methods for transport numbers:
  - moving boundary method,
  - Hittorf's method (measuring concentration change in electrode compartments),
  - comparison of cell potentials with and without liquid junction.

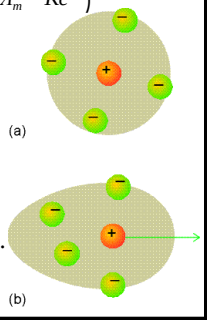
VI. Ion-ion interaction

- (see: Kohlrausch law: $\Lambda_m = \Lambda_m^0 - Kc^{1/2}$)

$$K = A + B\Lambda_m^0$$

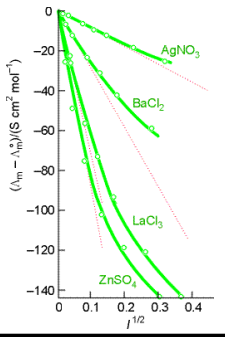
$$A = \frac{z^2 eF^2}{3\pi\eta}\left(\frac{2}{\varepsilon RT}\right)^{1/2}$$

$$B = \frac{qz^2 eF}{24\pi\varepsilon RT}\left(\frac{2}{\varepsilon RT}\right)^{1/2}$$

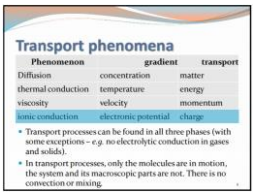


- Notice the effect of ε and η.

VI. Debye–Hückel–Onsager theory



- The use of the Debye–Hückel theory for ionic conduction.



Transport phenomena

Phenomenon	gradient	transport
Diffusion	concentration	matter
thermal conduction	temperature	energy
viscosity	velocity	momentum
ionic conduction	electronic potential	charge

- Transport processes can be found in all three phases (with some exceptions – *e.g.* no electrolytic conduction in gases and solids).
- In transport processes, only the molecules are in motion, the system and its macroscopic parts are not. There is no convection or mixing.

How the molar conductivity changes with changing ionic strength – Calculated curves and measured data: