TRANSPORT OF IONS IN SOLUTION

- Conductivity of electrolyte solutions
- Strong and weak electrolyte
- Ion Mobility
  - Ion mobility and conductivity,
  - Transport number
- Diffusion

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Conductivity of Electrolyte Solution

- Ions in solution can be set in motion by applying a potential difference between two electrodes.
- The conductance \((G)\) of a solution is defined as the inverse of the resistance \((R)\):
  \[
  G = \frac{1}{R}, \quad \text{in units of } \Omega^{-1}
  \]
- For parallel plate electrodes with area \(A\), it follows:
  \[
  G = \frac{\kappa A}{L}
  \]
  Where,
  \(\kappa\): the conductivity,
  \(L\): the distance separating the plates

Units:
- \(G \rightarrow S\) (siemens)
- \(R \rightarrow \Omega\)
- \(\kappa \rightarrow S\ m^{-1}\)
The conductivity of a solution depends on the number of ions present. Consequently, the molar conductivity $\Lambda_m$ is used

$$\Lambda_m = \frac{K}{C}$$

- $C$ is molar concentration of electrolyte and unit of $\Lambda_m$ is $S \text{ m}^2 \text{ mol}^{-1}$

In real solutions, $\Lambda_m$ depends on the concentration of the electrolyte. This could be due to:
- Ion-ion interactions $\Rightarrow \gamma_{\pm} \neq 1$
- The concentration dependence of conductance indicates that there are 2 classes of electrolyte
  - **Strong electrolyte**: molar conductivity depends slightly on the molar concentration
  - **Weak electrolyte**: molar concentration falls sharply as the concentration increases
Conductivity of Electrolyte Solution

In real solutions, $\Lambda_m$ depends on the concentration of the electrolyte. This could be due to:

1. Ion-ion interactions $\rightarrow \gamma_\pm \neq 1$

2. Incomplete dissociation of electrolyte

   - strong electrolyte, weak dependence of $\Lambda_m$ on $C$
   - weak electrolyte, strong dependence of $\Lambda_m$ on $C$
Strong Electrolyte

- Fully ionized in solution
- Kohlrausch’s law
  \[ \Lambda_m = \Lambda^0_m - KC^{1/2} \]
  - \( \Lambda^0_m \) is the limiting molar conductivity
  - \( K \) is a constant which typically depends on the stoichiometry of the electrolyte
- \( C^{1/2} \) arises from ion-ion interactions as estimated by the Debye-Hückel theory.
Strong Electrolyte

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

\[ \Lambda_0^m = \nu_+ \lambda_+ + \nu_- \lambda_- \]

- ions migrate independently in the zero concentration limit

<table>
<thead>
<tr>
<th></th>
<th>( \lambda/(\text{mS m}^2 \text{ mol}^{-1}) )</th>
<th>( \lambda/(\text{mS m}^2 \text{ mol}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>34.96</td>
<td>OH(^-)</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>5.01</td>
<td>Cl(^-)</td>
</tr>
<tr>
<td>K(^+)</td>
<td>7.35</td>
<td>Br(^-)</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>10.56</td>
<td>SO(_4^{2-})</td>
</tr>
</tbody>
</table>

For example, limiting molar conductivity of BaCl\(_2\) in water will be: 12.73+2*7.63=27.98 mS m\(^2\) mol\(^{-1}\).
Weak Electrolyte

- Not fully ionized in solution

\[ \text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \]

\[ (1 - \alpha) c \rightleftharpoons \alpha c \]

\[ K_a = \frac{\alpha^2 c}{1 - \alpha}, \quad \frac{1}{\alpha} = 1 + \frac{\alpha c}{K_a} \]

\[ \alpha^2 c = K_a - K_a \alpha \]

\[ c \alpha^2 + K_a \alpha - K_a = 0 \]

\[ \alpha = \frac{-K_a \pm \sqrt{K_a^2 + 4K_a c}}{2c} \]

\[ \alpha = \frac{-K_a}{2c} \pm \frac{K_a}{2c} \left(1 + \frac{4c}{K_a}\right)^{1/2} \]

\[ \alpha = \frac{K_a}{2c} \left[\left(1 + \frac{4c}{K_a}\right)^{1/2} - 1\right] \]

\[ \alpha \] is degree of ionisation
**Weak Electrolyte**

- The molar Conductivity (at higher concentrations) can be expressed as:
  \[ \Lambda_m = \alpha \Lambda^0_m \]

- At infinite dilution, the weak acid is fully dissociated (\(\alpha = 100\%\))

- It can be proven by the Ostwald dilution law which allows estimating limiting molar conductance:
  \[
  \frac{1}{\Lambda_m} = \frac{1}{\Lambda^0_m} + \frac{c \Lambda_m}{K_a (\Lambda^0_m)^2}
  \]

\[
\Lambda_m = \alpha \Lambda^0_m
\]

\[
\frac{1}{\Lambda_m} = \frac{1}{\alpha \Lambda^0_m}
\]

\[
\frac{1}{\Lambda_m} = \frac{1}{\Lambda^0_m} x \frac{1}{\alpha}
\]

\[
\frac{1}{\Lambda_m} = \frac{1}{\Lambda^0_m} x \left(1 + \frac{\alpha c}{K_a}\right)
\]

\[
\frac{1}{\Lambda_m} = \frac{1}{\Lambda^0_m} + \frac{c}{K_a \Lambda^0_m} x \frac{\Lambda_m}{\Lambda^0_m}
\]
Weak Electrolyte

- The limiting molar conductance:

\[
\frac{1}{\Lambda_m} = \frac{1}{\Lambda^0_m} + \frac{c\Lambda_m}{K_a (\Lambda^0_m)^2}
\]

Graph to determine the limiting value of the molar conductivity of a solution by extrapolation to zero concentration
The Mobility of Ions

- Ion movement in solution is random. However, a migrating flow can be onset upon applying an electric field, 

\[ E = \frac{\Delta \phi}{L} \quad F = zeE = \frac{ze\Delta \phi}{L} \]

- \( \Delta \phi \) is the potential difference between 2 electrodes separated by a distance \( L \)
- \( F \) accelerates cations to the negatively charged electrode and anions in the opposite direction. Through this motion, ions experience a frictional force in the opposite direction. Taking the expression derived by Stoke relating friction and the viscosity of the solvent (\( \eta \)), it follows:

\[ F_{fric} = 6\pi\eta rs, \ (for \ ions \ with \ raidus \ r \ and \ velocity \ v) \]
The Mobility of Ions

- When the accelerating and retarding forces balance each other, $s$ is defined by:

$$s = \frac{zeE}{6\pi \eta r} = \mu E,$$

where $\mu = \frac{ze}{6\pi \eta r}$

- $u$ is mobility of ions, and $r$ is hydrodynamic radius, that might be different from the ionic radius, small ions are more solvated than the bulk ones.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$u$ (10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H+</td>
<td>36.23</td>
</tr>
<tr>
<td>Na+</td>
<td>5.19</td>
</tr>
<tr>
<td>K+</td>
<td>7.62</td>
</tr>
<tr>
<td>Li+</td>
<td>4.01</td>
</tr>
<tr>
<td>Zn^{2+}</td>
<td>5.47</td>
</tr>
<tr>
<td>OH^-</td>
<td>20.64</td>
</tr>
<tr>
<td>Cl^-</td>
<td>7.91</td>
</tr>
<tr>
<td>Br^-</td>
<td>8.09</td>
</tr>
<tr>
<td>SO_4^{2-}</td>
<td>8.29</td>
</tr>
</tbody>
</table>

Mobility in water at 298 K.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\eta$ (10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.601</td>
</tr>
<tr>
<td>Mercury</td>
<td>1.55</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.224</td>
</tr>
<tr>
<td>Water</td>
<td>0.891</td>
</tr>
</tbody>
</table>

Viscosity of liquids at 298 K.
Finally, it can be shown that:

\[ \lambda = z \mu F, \text{ where } F = N_A e \]

Fully dissociated electrolyte:

\[
J(\text{ions}) = \frac{s \Delta t A \cdot \nu c N_A}{A \Delta t} = s \nu c N_A
\]

\[
J(\text{charge}) = z e r v c N_A = z r v c F = z \mu E v c F
\]

\[
I = J \cdot A = z \mu E v c F A = z \nu v c F A \frac{\Delta \phi}{L}
\]

\[
I = \frac{\Delta \phi}{R} = G \Delta \phi = \kappa \frac{\Delta \phi}{L}
\]

\[ \kappa = z \mu \nu v c F \]
In solution:

\[ \lambda = z \mu F \]

\[ \Lambda^0_m = (z_+ \mu_+ v_+ + z_- \mu_- v_-) F \]

Example:
1. if \( \mu = 5 \times 10^{-8} \text{ m}^2/\text{Vs} \) and \( z = 1 \), \( \Lambda = 10 \text{mS m}^2 \text{ mol}^{-1} \).
2. From the mobility of Cl\(^-\) in aqueous solution, calculate the molar ionic conductivity.

\[ \lambda = z \mu F \]

\[ \lambda = 7.91 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{V}^{-1} \times 96485 \text{ Cmol}^{-1} = 7.63 \times 10^{-3} \text{ sm}^2 \text{ mol}^{-1} \]
The Mobility of Ions and Conductivity

- Taking a conductimetre cell with electrodes separated by 1 cm and an applied voltage of 1 V, calculate the drift speed in water at 298 K.

  \[
  r_{\text{Cs}} = 170 \text{ pm} \\
  \pi_{\text{H}_2\text{O}} = 0.891 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}
  \]

\[
\mu = \frac{z e}{6 \pi \eta r} = \frac{1.602 \times 10^{-19} \text{ C}}{6 \times 3.1416 \times 0.891 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1} \times 170 \times 10^{-12} \text{ m}}
\]

\[
\mu \approx 5 \times 10^{-8} \text{ m}^2 \text{V}^{-1} \text{ s}^{-1}
\]

\[
E = \frac{\Delta \phi}{L} = \frac{1 \text{ V}}{0.01 \text{ m}} = 100 \text{ V m}^{-1}
\]

\[
s = \mu E = 5 \times 10^{-8} \text{ m}^2 \text{V}^{-1} \text{ s}^{-1} \times 100 \text{ V m}^{-1} = 5 \times 10^{-6} \text{ m s}^{-1}
\]

- It will take a Cs\(^+\) ion 2000 s to go from one electrode to another.
- For H\(^+\) ion, \(\mu_{H^+} = 36.23 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}\), it will take 276 s.
Transport Numbers

- **Transport numbers** – fraction of total current carried by ions of specific type
  \[ t_\pm = \frac{I_\pm}{I}, \quad t = t_+ + t_- \]

- **Limiting transport numbers** – defined in the limit of zero concentration of electrolyte solution
  \[ t_\pm^0 = \frac{Z_\pm \mu_\pm v_\pm}{Z_+ \mu_+ v_+ + Z_- \mu_- v_-} \]

  as \( z_+ v_+ = z_- v_- \) \( \Rightarrow \)
  \[ t_\pm^0 = \frac{\mu_\pm}{\mu_+ + \mu_-} \]

  or, using \( \lambda = z\mu F \) \( \Rightarrow \)
  \[ t_\pm^0 = \frac{v_\pm \lambda_\pm}{v_+ \lambda_+ + v_- \lambda_-} = \frac{v_\pm \lambda_\pm}{\Lambda_m^0} \]

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

If the chemical potential depends on position, the maximum nonexpansion work

\[ dw = d\mu = \left(\frac{\partial \mu}{\partial x}\right)_{p,T} \, dx \]

Comparing with \[ dw = -F dx \]

\[ F = -\left(\frac{\partial \mu}{\partial x}\right)_{p,T} \]

\[ w = \Delta \mu \]

\[ \mu \]

\[ \mu + \Delta \mu \]

→ **Thermodynamic force**
• **Thermodynamic force**

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\( w = \Delta \mu \)

\( \mu + \Delta \mu \)

---

**Thermodynamic force**
• Thermodynamic force of concentration gradient

\[ \mu = \mu_0 + RT \ln a \]

\[ F = -RT \left( \frac{\partial \ln a}{\partial x} \right)_{p,T} \quad \text{For ideal solution} \]

\[ F = -\frac{RT}{c} \left( \frac{\partial c}{\partial x} \right)_{p,T} \]

Fick’s law of diffusion:

Particles flux: \[ J \sim \text{drift velocity} \sim F \sim \frac{\partial c}{\partial x} \]
The Einstein relation

\[ J = -D \frac{\partial c}{\partial x} \]
\[ J = \frac{s\Delta Atc}{A\Delta t} = sc \]
\[ sc = -D \frac{\partial c}{\partial x} \]
\[ s = -\frac{D}{c} \frac{\partial c}{\partial x} = \frac{DF}{RT} \]

We know drift speed vs force relation for ion mobility, so we can deduce diffusion constant

\[ s = \mu E = \frac{DzeN_A E}{RT} \]
\[ D = \frac{\mu RT}{zF} \]

For example: for \( \mu = 5 \times 10^{-8} \ m^2 / sV \) we find \( D = 1 \times 10^{-9} \ m^2 / s \)
**Diffusion**

- The Nernst-Einstein equation
  
  Molar conductivity of ions in the solution
  
  \[ \lambda = z \mu F = \frac{z^2 DF^2}{RT} \]

  \[ \Lambda_m = (v_+ z^2 D_+ + v_\text{ } z^2 D_-) \frac{F^2}{RT} \]

- The Stokes-Einstein equation

  \[ \mu E = \frac{ezE}{f} \]

  Frictional force

  \[ D = \frac{\mu RT}{zF} \]

  \[ D = \frac{zeRT}{fzF} = \frac{zekN_A T}{fzeN_A} = \frac{kT}{f} \]

  Using Stokes’s law

  \[ D = \frac{kT}{6\pi \eta a} \]

  No charge involved -> applicable to all molecules
**Diffusion**

- How concentration distribution evolves with time due to diffusion

\[
\frac{\partial c}{\partial t} = \frac{JAdt}{Aldt} - \frac{J'Adt}{Aldt} = \frac{J - J'}{l}
\]

\[
J - J' = -D \frac{\partial c}{\partial x} + D \frac{\partial c'}{\partial x} = -D \frac{\partial c}{\partial x} + D \frac{\partial}{\partial x} \left( c + \left( \frac{\partial c}{\partial x} \right) l \right) = Dl \frac{\partial^2 c}{\partial x^2}
\]

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}
\]

Diffusion with convection

\[
\frac{\partial c}{\partial t} = \frac{JAdt}{Aldt} - \frac{J'Adt}{Aldt} = \frac{J - J'}{l}
\]

\[
J - J' = cv - c'v = \left( c - \left( c + \left( \frac{\partial c}{\partial x} \right) l \right) \right) \nu = \nu l \frac{\partial c}{\partial x}
\]

\[
\frac{\partial c}{\partial t} = v \frac{\partial c}{\partial x} \quad \text{due to convection only}
\]

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x}
\]
Solution of Diffusion Equation

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \]

- 2nd order differential equation: two boundary condition are required for spatial dependence and single for time dependence

Example 1:

one surface of a container \((x=0)\) is coated with \(N_0\) molecules at time \(t=0\)

\[ c(x, t) = \frac{n_0}{A(\pi D t)^{1/2}} e^{-x^2/4Dt} \]

Example 2:

dissolution infinitely small solid containing \(N_0\) molecules at time \(t=0\) in 3D solvent

\[ c(r, t) = \frac{n_0}{8(\pi D t)^{3/2}} e^{-r^2/4Dt} \]
• Probability to find a particle at a given slab of thickness $dx$ is proportional to the concentration there: $p(x) = c(x)AN_A dx / N_0$

• The mean distance traveled by the particles:

$$\langle x \rangle = \int_0^\infty \frac{c(x)AN_A dx}{N_0} = \frac{1}{(\pi Dt)^{1/2}} \int_0^\infty xe^{-x^2/4Dt} dx = 2 \left( \frac{Dt}{\pi} \right)^{1/2}$$

$$\langle x^2 \rangle^{1/2} = (2Dt)^{1/2}$$

Diffusion in unstirred solution, $D=5 \times 10^{-10}$ m$^2$/S
Random Walk

- Apparently diffusion can be modeled as a random walk, where particle is jumping distance $\lambda$ in a time $\tau$. Direction of the jump is chosen randomly.

- One dimensional walk:

$$p = \left(\frac{2\tau}{\pi t}\right)^{1/2} e^{-\frac{x^2\tau}{2t\lambda^2}}$$

Comparing with the solution of diffusion equation

$$D = \frac{\lambda^2}{2\tau}$$

Einstein-Smoluchowski equation

Connection between microscopic and macroscopic parameters.
Problems

• **Atkins 21.24a** What fraction of the total current is carried by Li+ ions when current flows through an aqueous solution of LBr at 25° C.

• **Atkins 21.25a** The limiting molar conductivities of KCl, KNO₃, and AgNO₃ are 14.99 mS m⁻² mol⁻¹, 14.50 mS m⁻² mol⁻¹, and 13.34 mS m⁻² mol⁻¹, respectively (all at 25° C). What is the limiting molar conductivity of AgCl at this temperature?

• **Atkins P24.36.** The diffusion coefficient of particular RNA molecule is 1.0x10⁻¹¹ m²/s. Estimate time required for a molecule to diffuse 1 um from nucleus to the cell wall
Summary

- **Migration**: Transport of ions induced by an electric field. The concentration dependence of the molar conductivity strongly differs for strong and weak electrolytes.

- **Diffusion**: Mass transport generated by a gradient of concentration.

\[
\Lambda^0_m = (z_+ v_+ D_+ + z_- v_- D_-) \frac{F^2}{RT}
\]

\[
\Lambda_m = \Lambda^0_m - KC^{1/2}
\]

\[
D = \frac{\mu RT}{zF}
\]

\[
D = \frac{k_B T}{6\pi\eta r}
\]
Thank You