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:

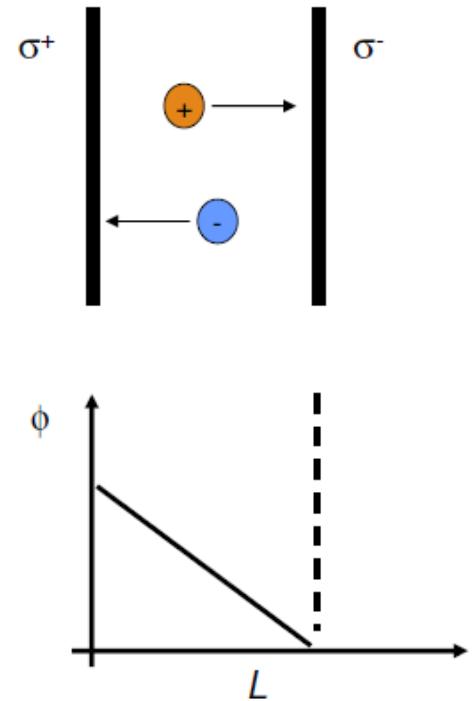$$G = \frac{\kappa A}{L}$$

  Where,

  K: the conductivity,
  L : *the distance separating the plates*

  Units:

  $G \rightarrow S$ *(siemens)*
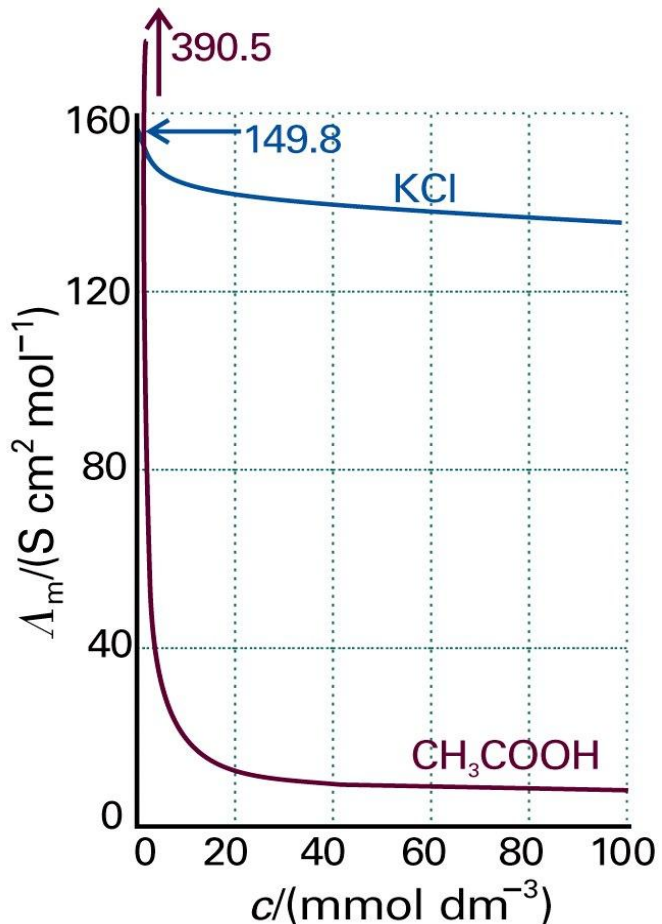 $R \rightarrow \Omega$
  $\kappa \rightarrow S\ m^{-1}$

Conductivity of Electrolyte Solution

- The conductivity of a solution depends on the number of ions present. Consequently, the molar conductivity Λ_m is used

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

✓ *C is molar concentration of electrolyte and unit of Λ_m is $S\ m^2\ mol^{-1}$*

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

- Ion-ion interactions → $\gamma_\pm \neq 1$
- 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, Λ_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 Λ_m on C

weak electrolyte,
strong dependence of Λ_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
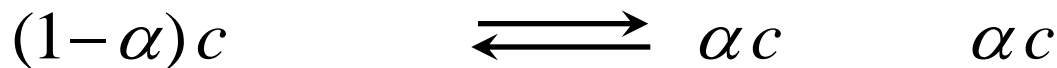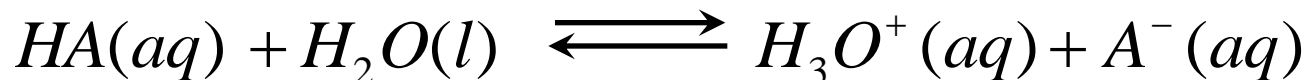
$$\Lambda^0{}_m = \nu_+ \lambda_+ + \nu_- \lambda_-$$

✓ *ions migrate independently in the zero concentration limi*

	$\lambda/(\mathrm{mS\ m^2\ mol^{-1}})$		$\lambda/(\mathrm{mS\ m^2\ mol^{-1}})$
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 m^2 mol^{-1}.

Weak Electrolyte

- Not fully ionized in solution

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$(1-\alpha)c \rightleftharpoons \alpha c \qquad \alpha c$$

$$K_a = \frac{\alpha^2 c}{1-\alpha}, \qquad \frac{1}{\alpha} = 1 + \frac{\alpha c}{K_a} \qquad \alpha \text{ is degree of ionisation}$$

$$\alpha^2 c = K_a - K_a \alpha$$

$$c\alpha^2 + K_a \alpha - K_a = 0$$

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

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

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

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

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:

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

$$\Lambda_m = \alpha \Lambda^0{}_m$$

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

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

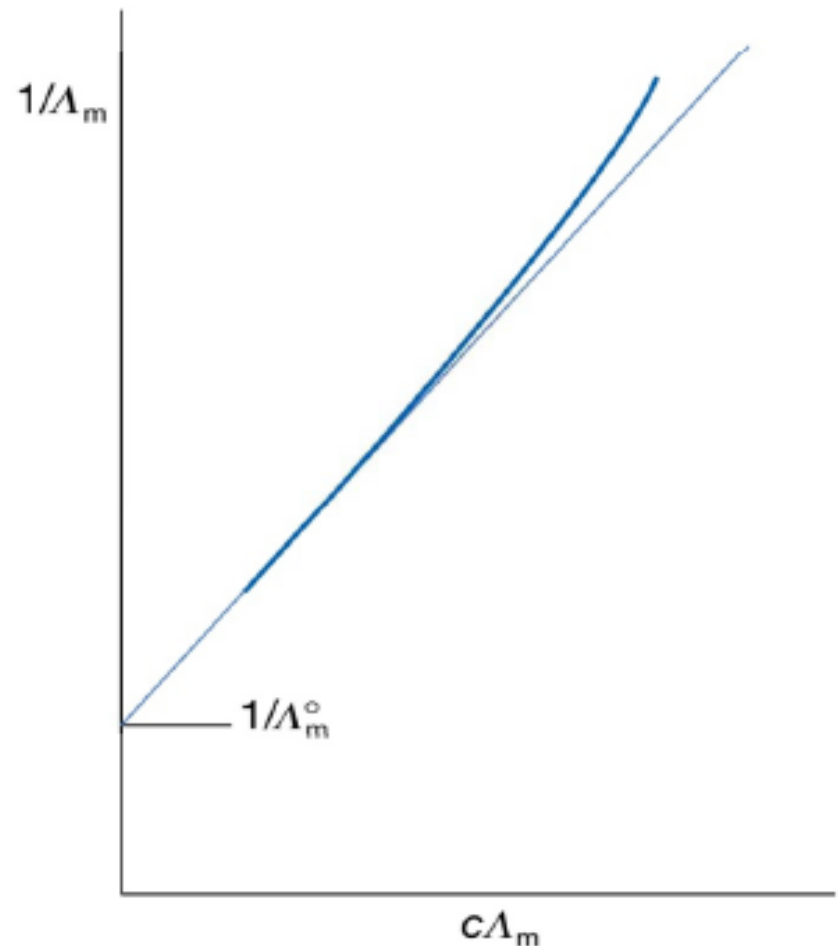$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda^0{}_m} x \left(1 + \frac{\alpha c}{K_a}\right)$$

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda^0{}_m} + \frac{c}{K_a \Lambda^0{}_m} x \frac{\Lambda_m}{\Lambda^0{}_m}$$

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,

$$E = \frac{\Delta\phi}{L} \qquad F = zeE = \frac{ze\Delta\phi}{L}$$

- $\Delta\phi$ 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 (η), it follows:

$$F_{fric} = 6\pi\eta rs, \quad (for\ ions\ with\ raidus\ r\ and\ velocity\ v)$$

The Mobility of Ions

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

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

	u (10^{-8} m^2 s^{-1} V^{-1})
H$^+$	36.23
Na$^+$	5.19
K$^+$	7.62
Li$^+$	4.01
Zn^{2+}	5.47
OH$^-$	20.64
Cl$^-$	7.91
Br$^-$	8.09
SO$_4^{2-}$	8.29

- *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.*

	η (10^{-3} kg m^{-1} s^{-1})
Benzene	0.601
Mercury	1.55
Pentane	0.224
Water	0.891

Mobility in water at 298 K.

Viscosity of liquids at 298 K

The Mobility of Ions and Conductivity

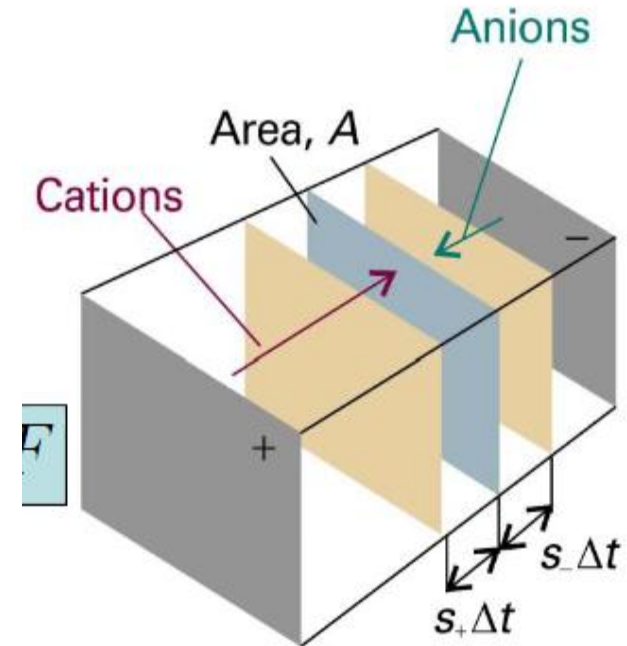- Finally, it can be shown that:

$$\lambda = z\mu F, \ where \ F = N_A e$$

- Fully dissociated electrolyte:

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

$$J(ch\arg e) = zervcN_A = zrvcF = z\mu EvcF$$

$$I = J.A = z\mu EvcFA = z\mu vcFA\frac{\Delta\phi}{L}$$

$$I = \frac{\Delta\phi}{R} = G\Delta\phi = \kappa\frac{\Delta\phi}{L} \implies \kappa = z\mu vcF$$

Anions

Area, A

Cations

$s_-\Delta t$

$s_+\Delta t$

The Mobility of Ions and Conductivity

- In solution:

$$\lambda = z\mu F$$

$$\Lambda^0{}_m = (z_+ \mu_+ v_+ + z_- \mu_- v_-) F$$

Example:

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

$$\lambda = z\mu F$$

$\lambda = 7.91 \times 10^{-8}$ m^2 s^{-1}V^{-1} x 96485 Cmol^{-1} = 7.63×10^{-3} sm^2 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_{Cs} = 170 pm

  π_{H_2O} = 0.891x10^{-3} kg m^{-1} s^{-1}

$$\mu = \frac{ze}{6\pi\eta r} = \frac{1.602 x 10^{-19}\ C}{6\,x\,3.1416\,x\,0.891\,x\,10^{-3}\ kgm^{-1}s^{-1}\ x\,170\,x\,10^{-12}\ m}$$

$$\mu \approx 5\,x\,10^{-8}\ m^2 V^{-1} s^{-1}$$

$$E = \frac{\Delta\phi}{L} = \frac{1V}{0.01\,m} = 100 V m^{-1}$$

$$s = \mu E = 5\,x\,10^{-8}\ m^2 V^{-1} s^{-1}\ x\ 100 V m^{-1} = 5\,x\,10^{-6}\ ms^{-1}$$

- It will take a Cs$^+$ ion 2000 s to go from one electrode to another.
- For H$^+$ ion, $\mu_{H}{}^+ = 36.23\ x10^{-8}\ m^2\ s^{-1}\ V^{-1}$, it will take 276 s.

Transport Numbers

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

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

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

or, using $\lambda = z\mu F$ $\Rightarrow$ $t_{\pm}^0 = \frac{\nu_{\pm}\lambda_{\pm}}{\nu_+\lambda_+ + \nu_-\lambda_-} = \frac{\nu_{\pm}\lambda_{\pm}}{\Lambda_m^0}$

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

Diffusion

- ## Thermodynamic force

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

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

$$w = \Delta\mu$$

$$\mu \qquad \mu + \Delta\mu$$

Comparing with $\quad dw = -Fdx$

$$F = -\left(\frac{\partial\mu}{\partial x}\right)_{p,T} \quad \longleftarrow \quad \textbf{\textit{Thermodynamic force}}$$

Diffusion

- ## Thermodynamic force

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

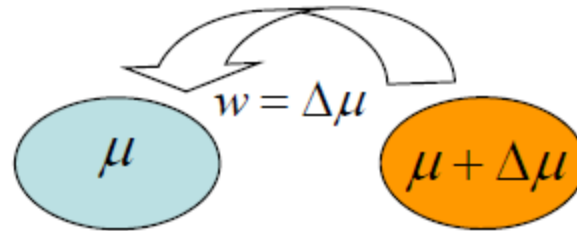$$dw = d\mu = \left(\frac{\partial \mu}{\partial x}\right)_{p,T} dx$$

$w = \Delta\mu$

μ

$\mu + \Delta\mu$
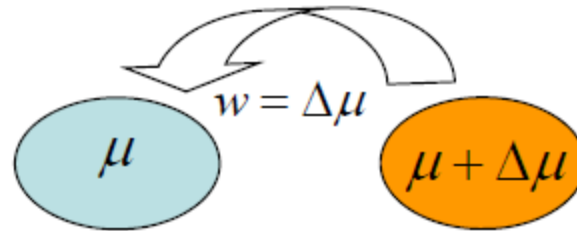
Comparing with $\quad dw = -Fdx$

$$F = -\left(\frac{\partial \mu}{\partial x}\right)_{p,T} \quad \longleftarrow \quad \textbf{Thermodynamic force}$$

Diffusion

- Thermodynamic force of concentration gradient

$$\mu = \mu_0 + RT \ln a$$

For ideal solution

$$F = -RT \left(\frac{\partial \ln a}{\partial x} \right)_{p,T} \qquad \Longrightarrow \qquad F = -\frac{RT}{c} \left(\frac{\partial c}{\partial x} \right)_{p,T}$$

Fick's law of diffusion:

Particles flux: $\quad J \sim drift\ velocity \sim F \sim \dfrac{\partial c}{\partial x}$

Diffusion

- The Einstein relation

$$J = -D \frac{\partial c}{\partial x} \qquad J = \frac{s \Delta A t c}{A \Delta t} = sc$$

$$sc = -D \frac{\partial c}{\partial x}$$

$$s = -\frac{D}{c} \frac{\partial c}{\partial x} = \frac{DF}{RT}$$

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

$$s = \mu E = \frac{Dze N_A E}{RT} \qquad \Longrightarrow \qquad \boxed{D = \frac{\mu RT}{zF}}$$

For example: for $\mu = 5 \cdot 10^{-8} \ m^2 / sV$ we find $D = 1 \cdot 10^{-9} \ m^2 / s$

Diffusion

- ## The Nernst-Einstein equation

  Molar conductivity of ions in the solution $\quad \lambda = z\mu F = \dfrac{z^2 D F^2}{RT}$

  $$\Lambda_m = (\nu_+ z^2_+ D_+ + \nu_- z^2_- D_-)\dfrac{F^2}{RT}$$

- ## The Stokes-Einstein equation

  $\mu E = \dfrac{ezE}{f}$

  Frictional force $\longrightarrow f$

  $D = \dfrac{\mu RT}{zF}$

  $D = \dfrac{zeRT}{fzF} = \dfrac{zekN_A T}{fzeN_A} = \dfrac{kT}{f}$

  Using Stokes's law $\qquad D = \dfrac{kT}{6\pi\eta a}$ $\qquad$ No charge involved -> applicable to all molecules

Diffusion

- How concentration distribution evolves with time due to diffusion

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

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

$$\boxed{\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}}$$
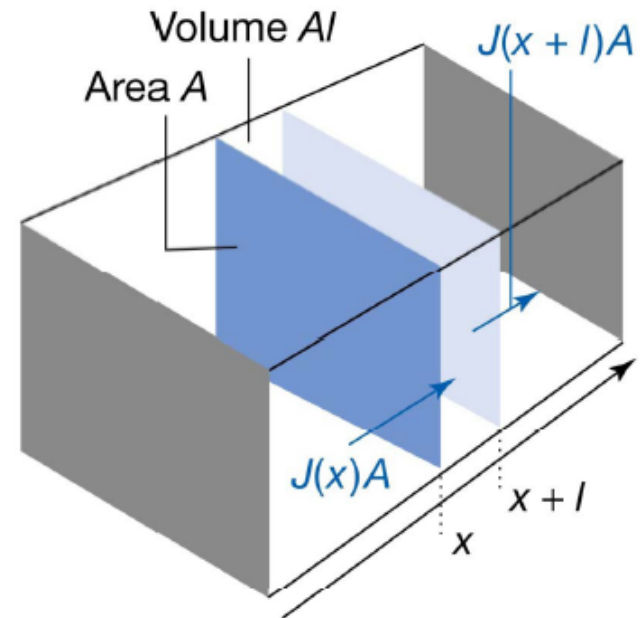
Diffusion with convection

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

$$J - J' = cv - c'v = \left(c - \left(c + \left(\frac{\partial c}{\partial x}\right)l\right)\right)v = vl\frac{\partial c}{\partial x}$$

$$\frac{\partial c}{\partial t} = v\frac{\partial c}{\partial x} \qquad \text{due to convection only}$$

$$\boxed{\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x}}$$

Volume Al

Area A

$J(x + l)A$

$J(x)A$

$x + l$

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
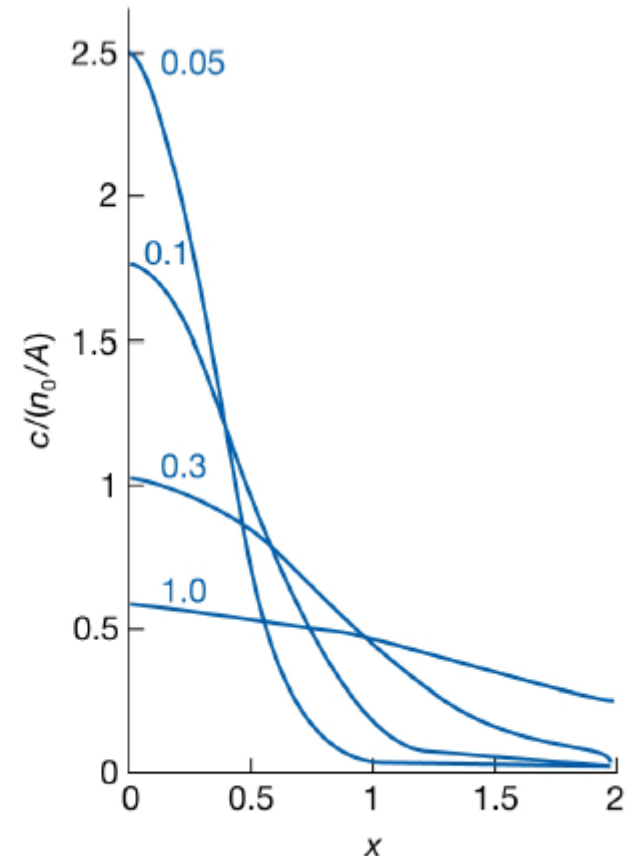
Example 1:
one surface of a container (x=0) is coated with N_0 molecules at time t=0

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

$\Longrightarrow$

Example 2:
dissolution infinitely small solid containing N_0 molecules at time t=0 in 3D solvent
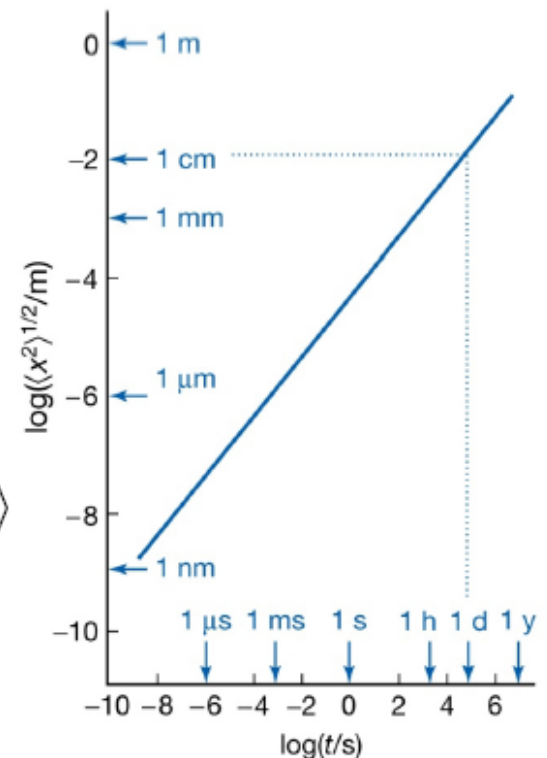
$$c(r,t) = \frac{n_0}{8(\pi Dt)^{3/2}} e^{-r^2/4Dt}$$

Diffusion Probablities

- 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:

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

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

Diffusion in unstirred solution, D=5x10^{-10} m^2/S $\Rightarrow$

Random Walk

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

- One dimensional walk:

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

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, KNO_3, and $AgNO_3$ 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 1.0×10^{-11} m^2/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