

# Lecture 6

Molecular motion  
and  
Transport properties

# 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

# Transport properties of a perfect gas

- 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  $\sim dN/dz$  ( $N$  - number density of particles) , energy flux  $\sim dT/dz$

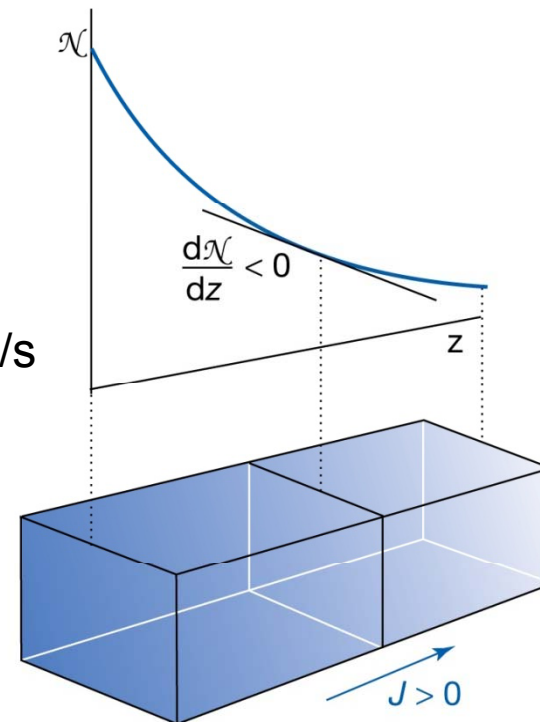
Fick's first law of diffusion:

$$J(\text{matter}) = -D \frac{dn}{dz}$$

Diffusion coefficient,  $\text{m}^2/\text{s}$

$$J(\text{energy}) = -\kappa \frac{dT}{dz}$$

Coefficient of thermal conductivity

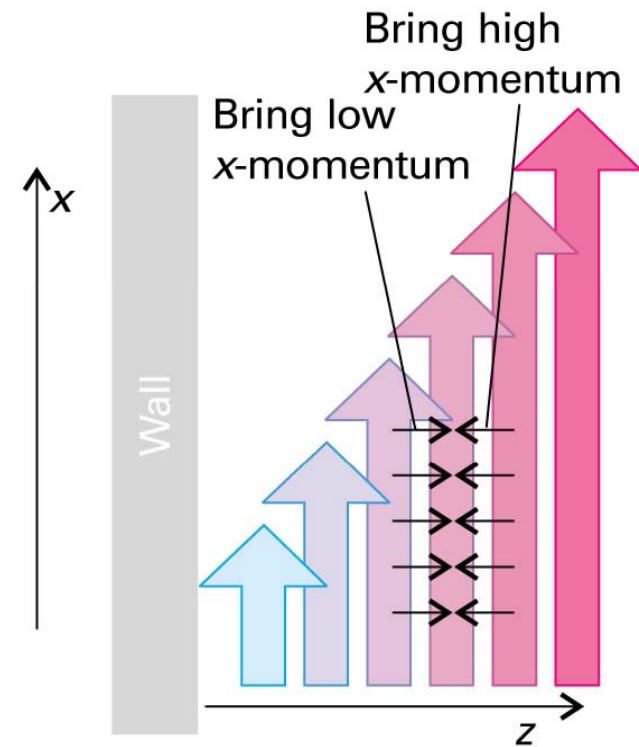


# Transport properties of a perfect gas

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

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

↑  
coefficient of viscosity



# Transport properties of a perfect gas

- 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 ( $d \ll$  distances)
  - Molecules interact through elastic collisions (e.g. kinetic energy is conserved at every collision)

# Transport properties of a perfect gas

- Application of kinetic theory of gases

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

where  $\lambda$  is a mean free path and  $\bar{c} = \int_0^{\infty} vf(v)dv = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}$  is a mean velocity

# Transport properties of a perfect gas

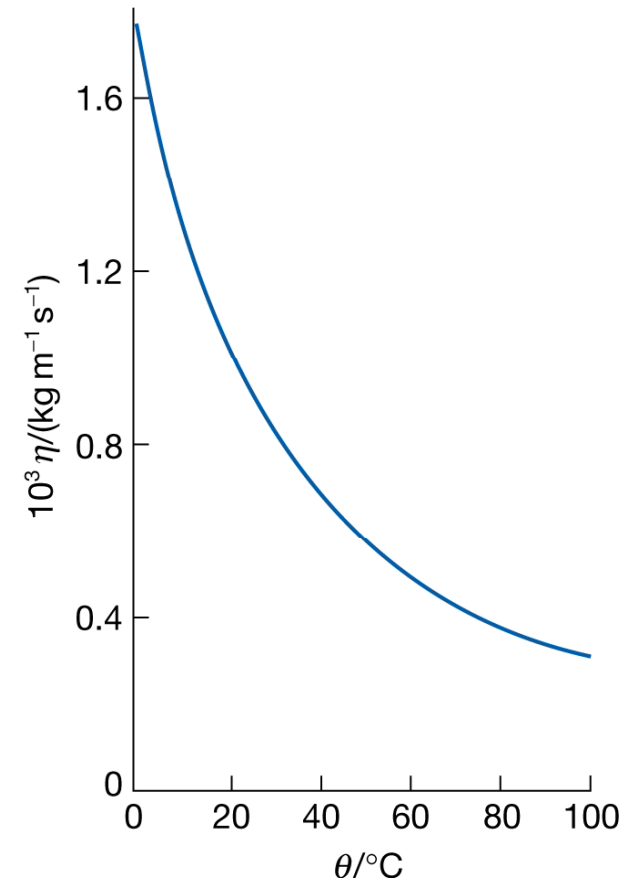
- The diffusion coefficient:  $D = \frac{1}{3} \lambda \bar{c}$ 
  1. Mean free path is decreasing when pressure increases, so D decreases with increasing pressure
  2. Mean velocity increasing with T, so does the D.
  3. Mean free path increases when the collision cross section decreases, so D is larger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

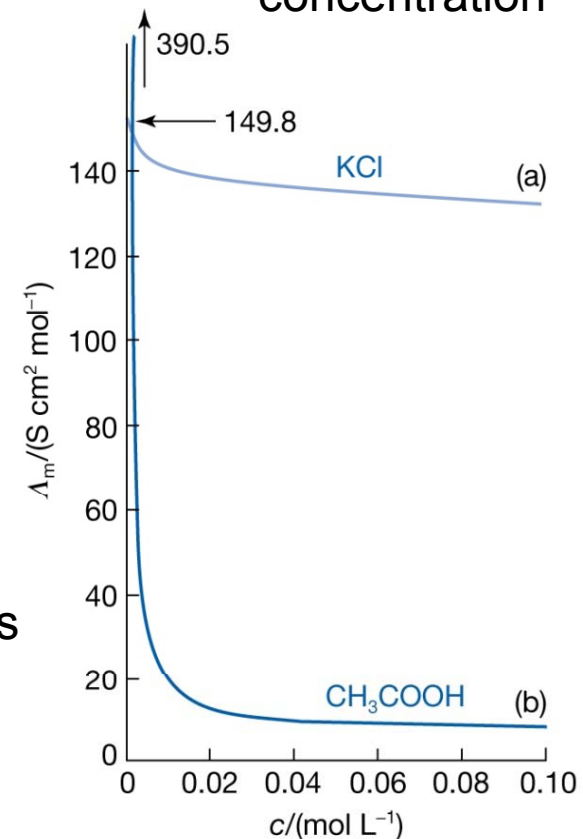
Conductance, [S]:  $G = \frac{\overset{\text{conductivity}}{\kappa} A}{l}$

Conductivity depends on a number of ions present:  $\Lambda_m = \frac{\kappa}{c}$

Molar conductivity, typically 10mS m<sup>2</sup>/mol

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

- 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

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

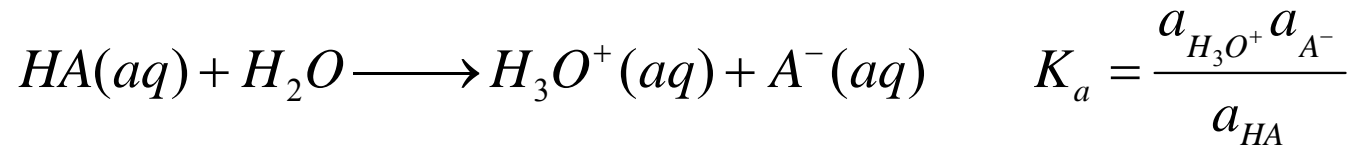
i.e. ions migrate independently in the zero concentration limit

	$\lambda / (\text{mS m}^2 \text{ mol}^{-1})$		$\lambda / (\text{mS m}^2 \text{ mol}^{-1})$
H <sup>+</sup>	34.96	OH <sup>-</sup>	19.91
Na <sup>+</sup>	5.01	Cl <sup>-</sup>	7.63
K <sup>+</sup>	7.35	Br <sup>-</sup>	7.81
Zn <sup>2+</sup>	10.56	SO <sub>4</sub> <sup>2-</sup>	16.00

For example, limiting molar conductivity of BaCl<sub>2</sub> in water will be: 12.73+2\*7.63=27.98 mS m<sup>2</sup> mol<sup>-1</sup>.

# Conductivity of electrolyte solution

- Weak electrolytes: not fully ionized in the solution



If we define degree of deprotonation:

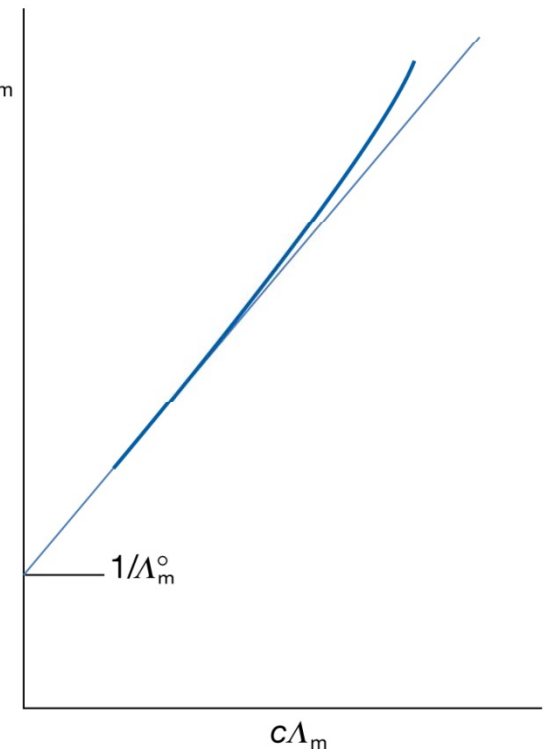
$$[H_3O^+] = \alpha c \quad [A^-] = \alpha c \quad [HA] = (1 - \alpha)c$$

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

$$\Lambda_m = \alpha \Lambda_m^0$$

Ostwald's dilution law

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



# Mobilities of ions

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

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

$$E = \frac{\Delta\phi}{l}$$
$$F = zeE = \frac{ze\Delta\phi}{l}$$
$$F_{fric} = 6\pi\eta rs \quad (\text{for ion with radius } r \text{ and velocity } v)$$
$$s = \frac{zeE}{6\pi\eta r}$$

$$s = \mu E$$

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

hydrodynamic radius, might be different from the ionic radius, small ions are more solvated than the bulk ones

Example: Cs<sup>+</sup> ion: z=1, r=170pm, η=1\*10<sup>-3</sup> kg m<sup>-1</sup> s<sup>-1</sup>. Then μ=5\*10<sup>-8</sup> m<sup>2</sup>/Vs, i.e. with 1V applied across 1cm the drift speed is 5μm/s.

# Mobilities of ions

- Mobility and conductivity

$$\lambda = z\mu F, \quad F = N_A e \quad \text{Faraday constant}$$

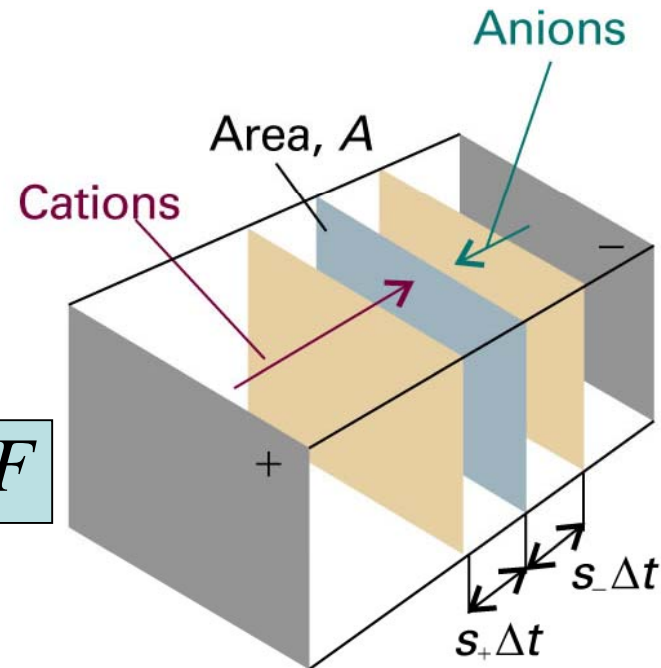
Let's consider a fully dissociated electrolyte:

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

$$J(\text{charge}) = z e s\nu c N_A = z s\nu c F = z\mu E \nu c F$$

$$I = J \cdot A = z\mu E \nu c F A = z\mu \nu c F A \frac{\Delta\phi}{l}$$

$$I = \frac{\Delta\phi}{R} = G\Delta\phi = \kappa A \frac{\Delta\phi}{l} \quad \Rightarrow \quad \boxed{\kappa = z\mu \nu c F}$$



- In solution

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

Example: if  $\mu = 5 \cdot 10^{-8} \text{ m}^2/\text{Vs}$  and  $z=1$ ,  $\Lambda = 10 \text{ mS m}^2 \text{ mol}^{-1}$ .

# Mobilities of ions

- **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

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

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

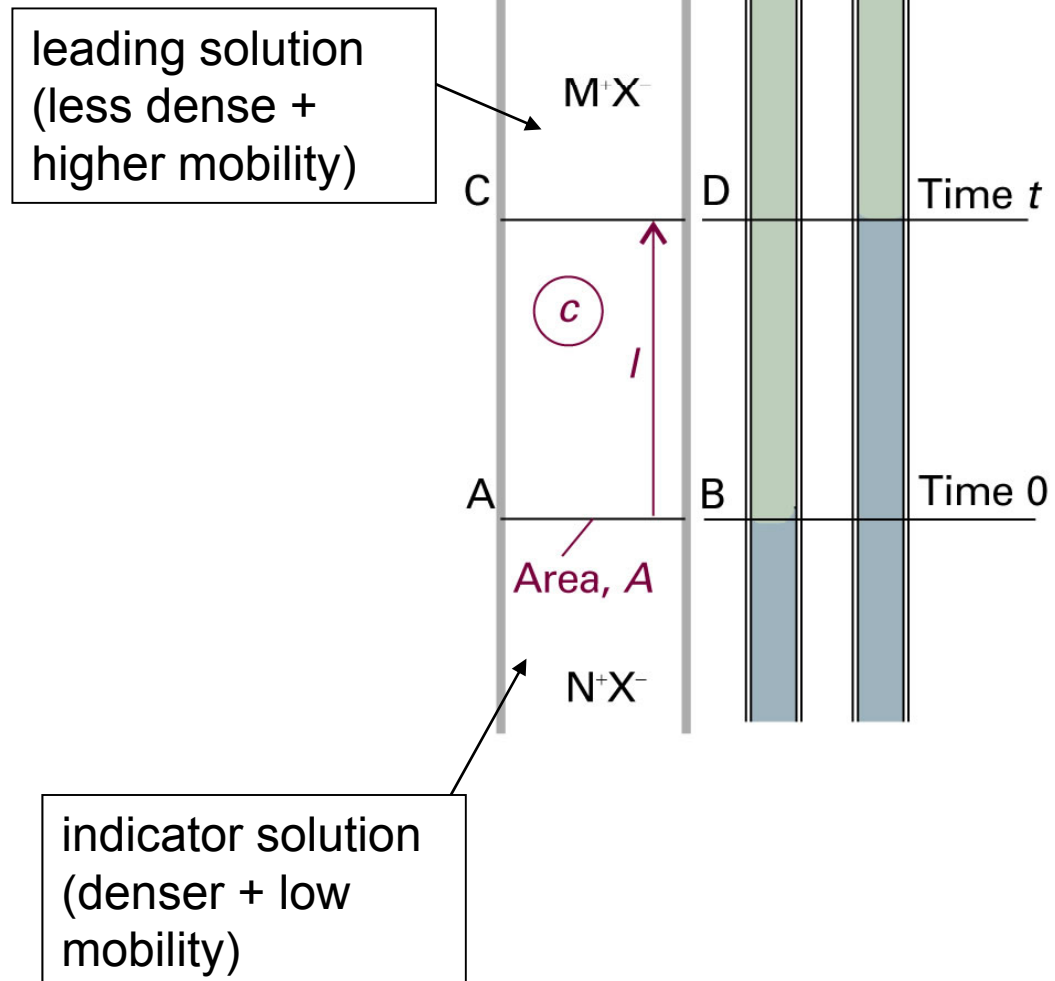
$$\text{or, using } \lambda = z\mu F \Rightarrow t_{\pm}^0 = \frac{\nu_{\pm} \lambda_{\pm}}{\nu_{+} \lambda_{+} + \nu_{-} \lambda_{-}} = \frac{\nu_{\pm} \lambda_{\pm}}{\Lambda_m^0}$$

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

# Moving boundary technique

- Measuring transport numbers
  - Moving boundary technique

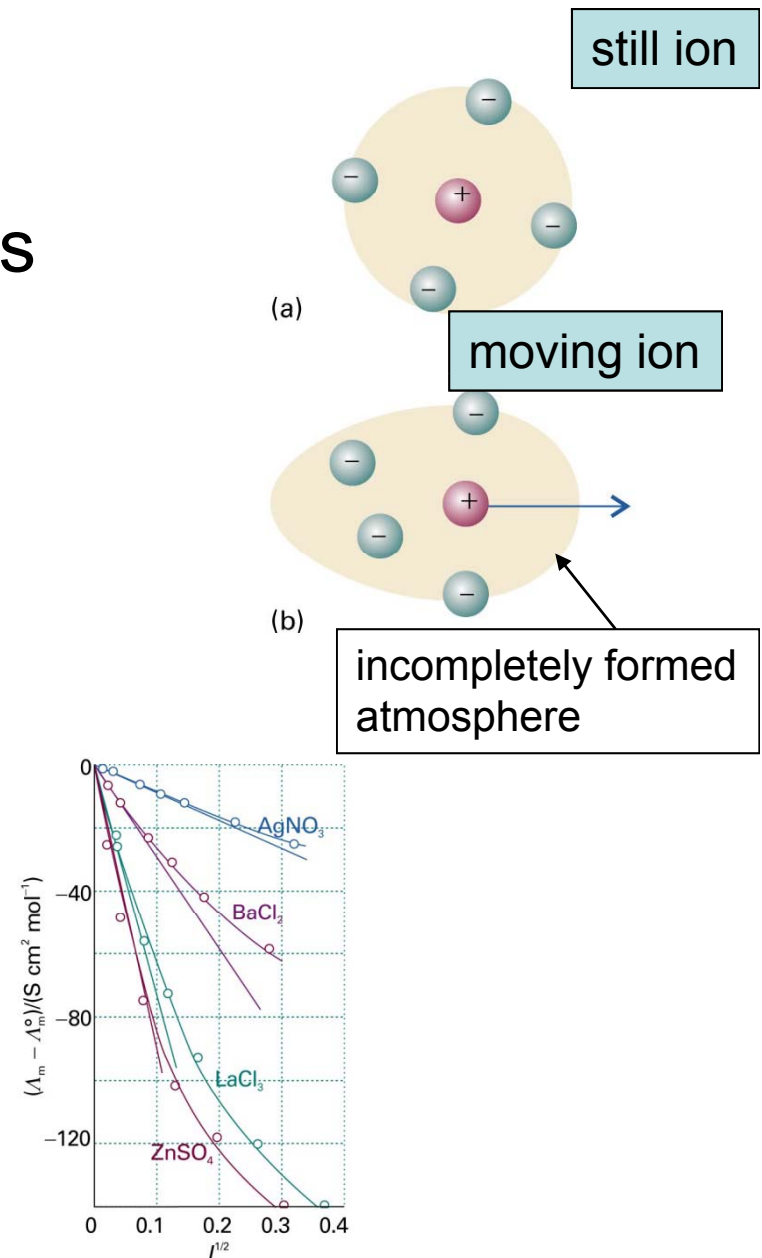
$$t_+ = \frac{z_+ c l A F}{I \Delta t}$$



# Conductivities and ion-ion interactions

- 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**

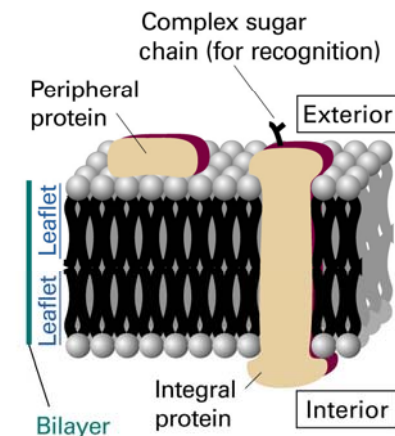
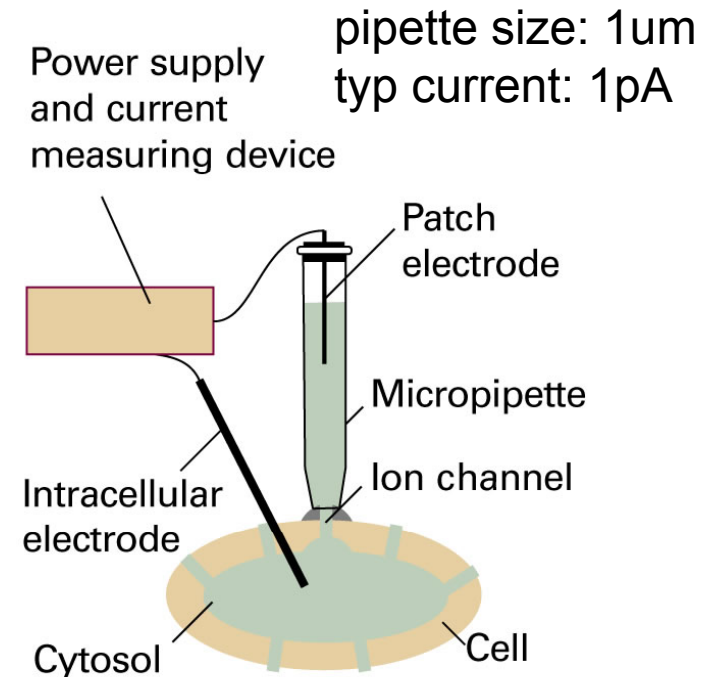
Those two effects taken into account lead to  $c^{1/2}$  dependence in Kohlrausch law





# Ion channels and Ion pumps

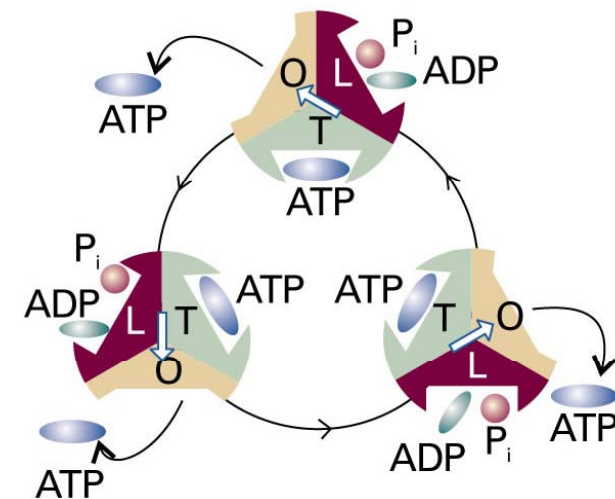
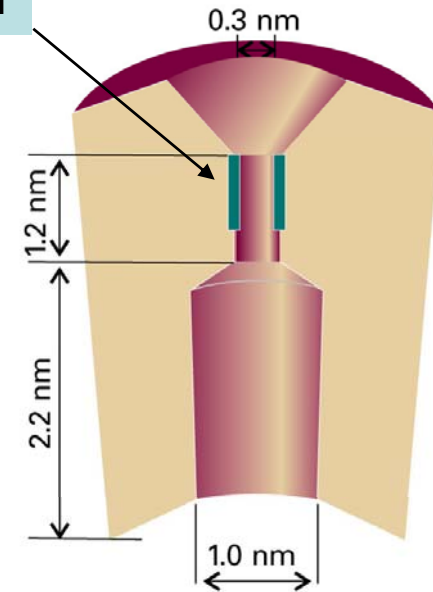
- passive ion transport: ions transport down the concentration and membrane potential gradient
- active transport: driven by an exergonic process
- transport mechanisms:
  - by carrier molecule
  - through a channel former
- Channel formers:
  - ion channels: highly selective proteins that can open and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



# 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

selectivity filter

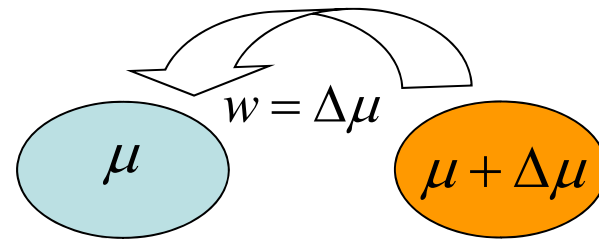


# Diffusion

- **Thermodynamic force**

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

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



Comparing with  $dw = -Fdx$

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

# Diffusion

- Thermodynamic force of concentration gradient

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

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

Fick's law of diffusion:

$$\text{Particles flux: } J \sim \text{drift velocity} \sim F \sim \frac{\partial c}{\partial x}$$

# Diffusion

- The Einstein relation

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

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

$$s = \mu E = \frac{D z e N_A E}{RT} \quad \Longrightarrow \quad \boxed{D = \frac{\mu RT}{zF}}$$

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

# Diffusion

- The Nernst-Einstein equation

Molar conductivity of ions in the solution

$$\lambda = z\mu F = \frac{z^2 DF^2}{RT}$$

$$\Lambda_m = (v_+ z_+^2 D_+ + v_- z_-^2 D_-) \frac{F^2}{RT}$$

- The Stokes-Einstein equation

$$\begin{array}{l}
 \mu E = \frac{ezE}{f} \\
 \text{Frictional force} \rightarrow f \\
 D = \frac{\mu RT}{zF}
 \end{array}
 \rightarrow
 D = \frac{zeRT}{fzF} = \frac{zekN_A T}{fzeN_A} = \frac{kT}{f}$$

Using Stokes's law

$$D = \frac{kT}{6\pi\eta a}$$

No charge involved -> applicable to all molecules

# Diffusion equation

- 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

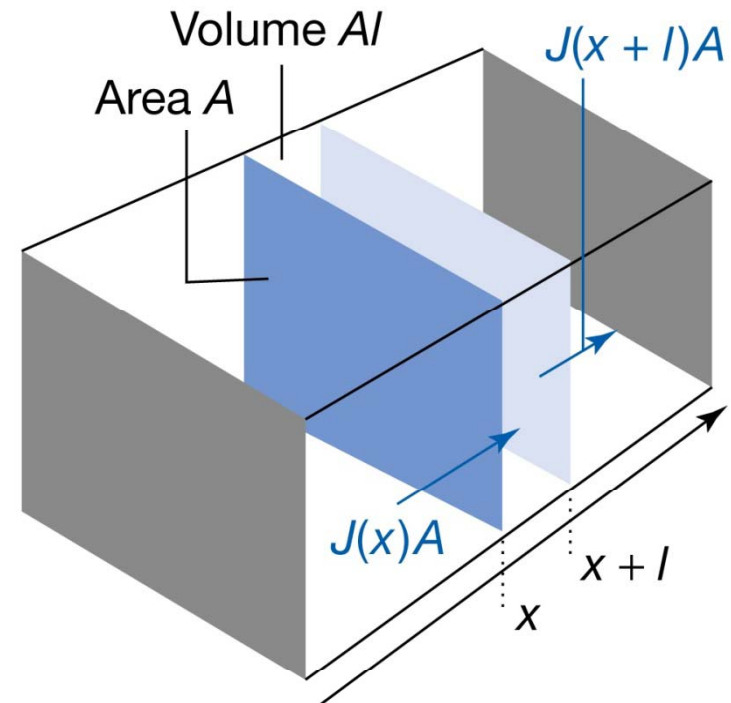
$$\frac{\partial c}{\partial t} = \frac{JAdt}{Aldt} - \frac{J'Adt}{Aldt} = \frac{J - J'}{l}$$

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

$$\frac{\partial c}{\partial t} = v \frac{\partial c}{\partial x}$$

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

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

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

Example 1:

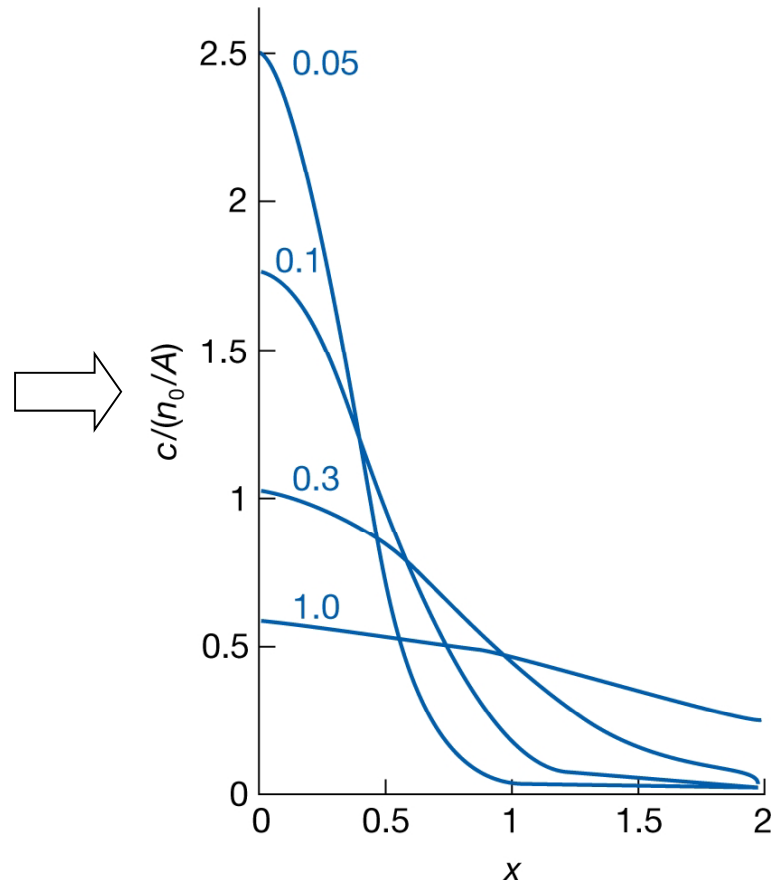
one surface of a container ( $x=0$ ) is coated with  $N_0$  molecules at time  $t=0$

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

Example 2:

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

$$c(r, t) = \frac{n_0}{8(\pi Dt)^{3/2}} e^{-r^2/4Dt}$$





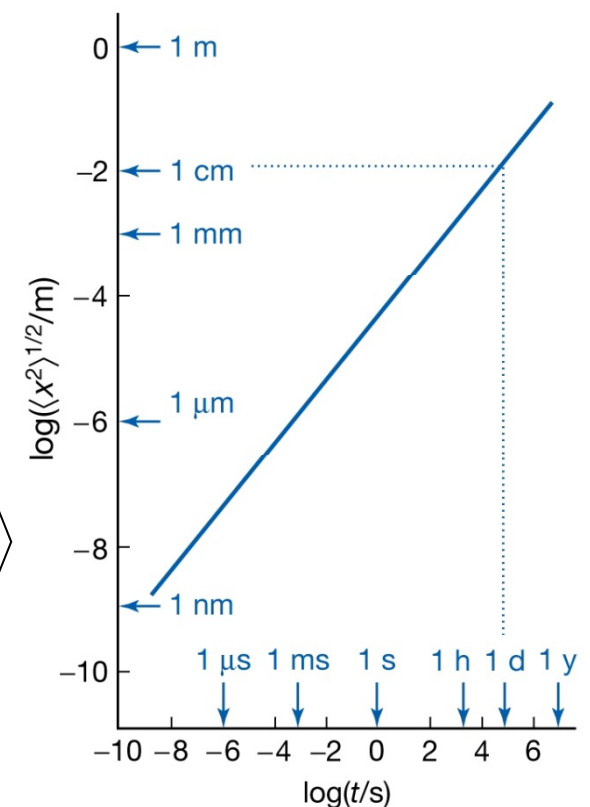
# Diffusion probabilities

- 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,  $D=5 \times 10^{-10} \text{ m}^2/\text{S}$



# 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:

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

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  $\text{Li}^+$  ions when current flows through an aqueous solution of  $\text{LiBr}$  at  $25^\circ\text{C}$ .
- **Atkins 21.25a** The limiting molar conductivities of  $\text{KCl}$ ,  $\text{KNO}_3$ , and  $\text{AgNO}_3$  are  $14.99 \text{ mS m}^2 \text{ mol}^{-1}$ ,  $14.50 \text{ mS m}^2 \text{ mol}^{-1}$ , and  $13.34 \text{ mS m}^2 \text{ mol}^{-1}$ , respectively (all at  $25^\circ\text{C}$ ). What is the limiting molar conductivity of  $\text{AgCl}$  at this temperature?
- **Atkins P24.36.** The diffusion coefficient of particular RNA molecule is  $1.0 \times 10^{-11} \text{ m}^2/\text{s}$ . Estimate time required for a molecule to diffuse  $1 \text{ }\mu\text{m}$  from nucleus to the cell wall

# Assignment VI

- **P21.8** Conductivities are often measured by comparing the resistance of a cell filled with some standard solutions. The conductivity of water is 76 mS/m at 25°C and 0.1M KCl(aq) is 1.1639 S/m. A cell has resistance of 33.21 Ohm when filled with 0.1M KCl(aq) and 300.0 Ohm when filled with 0.1M CH<sub>3</sub>COOH. What is the molar conductivity of the acetic acid at that concentration and temperature
- **P21.16** Estimate the diffusion coefficient and the effective hydrodynamic radii of the alkali metal cations at 25°C. Estimate the approximate number of water molecules dragged along by the cations. Take ionic radii from the Table 20.3