

# THERMODYNAMICS, IRREVERSIBLE THERMODYNAMICS

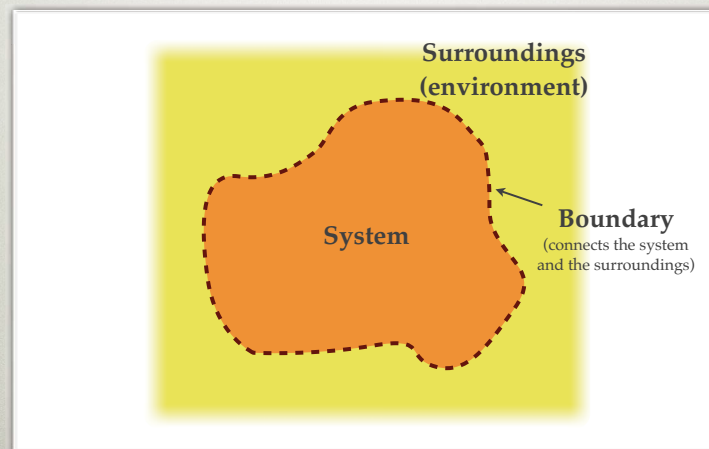
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## OUTLINE

- Thermodynamic system.
- Characterization of the system. Thermodynamic variables.
- Microscopic structure of the system - internal energy.
- Equilibrium, reversibility.
- Zeroth Law of thermodynamics.
- Change, reversible change, thermodynamic processes.
- First Law of thermodynamics. Change in internal energy. Energy is conserved!
- Enthalpy.
- Second Law of thermodynamics.
- Direction of spontaneous processes. Entropy. Statistical interpretation. Thermodynamic probability. Phenomenological interpretation of entropy.
- Third Law of thermodynamics.
- **Helmholtz- and Gibbs-free energy. Significance of free energy and entropy.**
- **Chemical potential.**
- **Irreversible thermodynamics, transport phenomena.**
- **Diffusion, Brown-movement.**
- **Osmosis.**

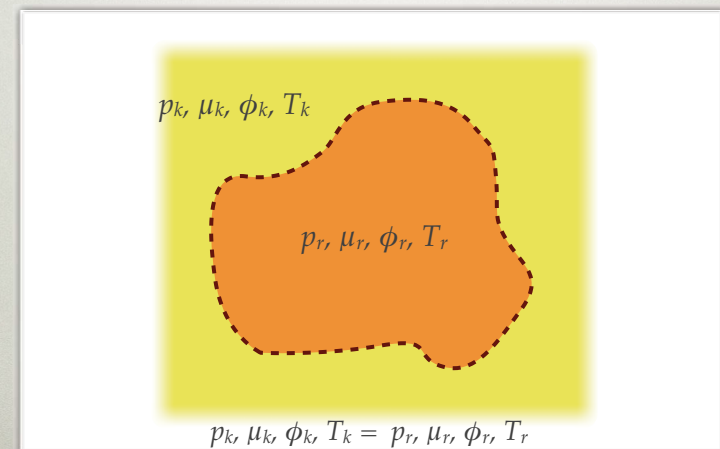
## THE THERMODYNAMIC SYSTEM

*Definition:* the thermodynamic system is the part of nature under investigation.



## EQUILIBRIUM

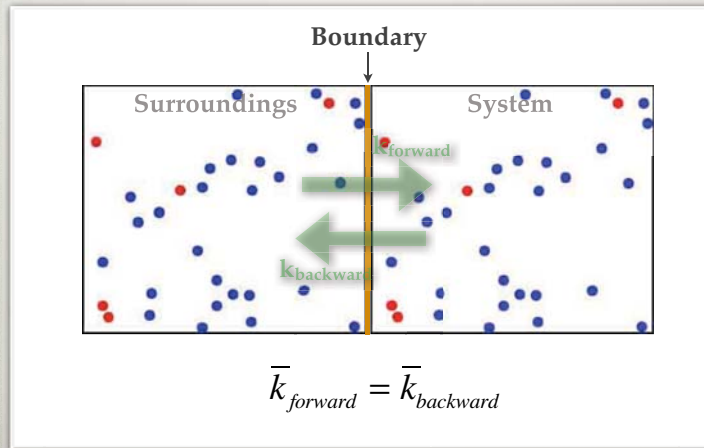
*Macroscopic description:* intensive variables are identical (between the system and surroundings, or between different parts of the system)





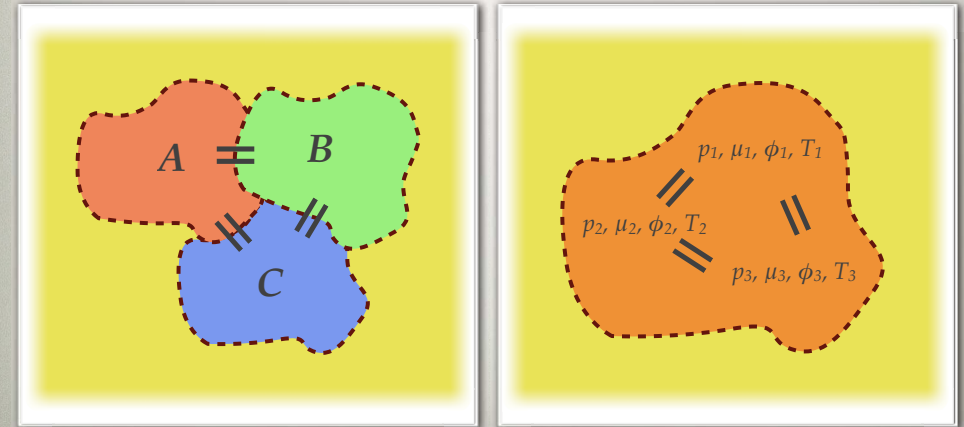
# EQUILIBRIUM

*Microscopic description:* average rates of forward and reverse reactions are equal.



# ZEROth LAW OF THERMODYNAMICS

- If two systems (A and B) are independently in equilibrium with a third one (C), then they are in equilibrium with each other as well.
- Between different points of a system in equilibrium, the intensive variables are equal (there are no thermodynamic currents).



# FIRST LAW OF THERMODYNAMICS

- Law of conservation of energy.
- Energy may be converted into different forms, but the total energy of the system remains constant.
- The change in the internal energy of the system is the sum of the supplied heat ( $Q_E$ ) and the work ( $W$ ) done on the system.

$$E_2 - E_1 = \Delta E$$

Difference between the internal energies of the initial and final states of the system.

$$\Delta E = Q_E + W$$

Work parts: Volumetric work

$$W_V = -p\Delta V$$

Negative, because in the case of work done on the system  $V_2 - V_1 < 0$ .

Electric work:

$$W_Q = \phi\Delta Q$$

Material transport: Generalized:

$$W_n = \mu\Delta n$$

$$W^i = y_{int}^i \Delta x_{ext}^i$$

Isochoric process ( $\Delta V=0$ ):

$$\Delta E = Q_V$$

Change in internal energy is caused only by the heat exchange.

Izobaric process ( $p=\text{constant}$ ):

$$\Delta E = Q_p + W_V = Q_p - p\Delta V$$

# SECOND LAW OF THERMODYNAMICS

- "Law of entropy."
- Heat flows spontaneously from regions of high to low temperature.
- In an isolated system only such processes occur spontaneously which tend to equilibrate the respective intensive variables.
- During spontaneous processes entropy increases. Thermodynamic equilibrium is characterized by entropy maximum.
- Spontaneous processes proceed towards the most probable state (irreversible).
- Statistical law.



The fallen and broken flower pot does not spontaneously return to its original place.



The essentially endless heat content of oceans cannot be used to spontaneously produce useful work.



# THIRD LAW OF THERMODYNAMICS

- Nernst's law.
- The entropy of mono-component, crystallizing material at 0 K temperature is 0.

At 0 K thermal motions halt,  
there are no thermal crystal faults.

$$\Omega = 1$$

Number of microstates is 1.

Because of mono-component system,  
only one type of molecular  
arrangement is possible.

$$S = k_B \ln 1 = 0$$

# GIBBS FREE ENERGY

- Gibbs free energy (G), Gibbs potential.
- Useful work extractable from isothermic, isobaric (not isolated) system.
- State function

Entropy is an extensive  
variable.

$S_{tot}$  = total entropy (entropy  
of the universe)  
 $S_{sys}$  = system entropy  
 $S_{sur}$  = entropy of  
surroundings

$$\begin{aligned}\Delta S_{tot} &= \Delta S_{sys} + \Delta S_{sur} \\ \Delta S_{sur} &= -\frac{\Delta H_{sys}}{T} \\ \Delta S_{tot} &= \Delta S_{sys} - \frac{\Delta H_{sys}}{T} \\ -T\Delta S_{tot} &= \Delta H_{sys} - T\Delta S_{sys}\end{aligned}$$

$$\Delta G = \Delta H_{sys} - T\Delta S_{sys}$$

$$H = G + TS$$

Enthalpy = useful work + unusable energy change

During spontaneous processes the  
entropy of the universe increases  
( $\Delta S_{tot} > 0$ ):

$$\Delta S_{sys} > \frac{\Delta H_{sys}}{T}$$

During spontaneous processes,  
Gibbs free energy decreases  
( $\Delta G < 0$ ):

$$\Delta G = \Delta H_{sys} - T\Delta S_{sys} < 0$$

# HELMHOLTZ FREE ENERGY

- Helmholtz free energy (F)
- Useful work extractable from isothermic, isochoric (constant volume) (not isolated) system.
- State function

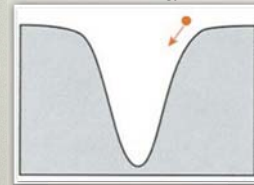
$$F = E - TS$$

F : Helmholtz free energy  
E: internal energy  
T: absolute temperature  
S: entropy

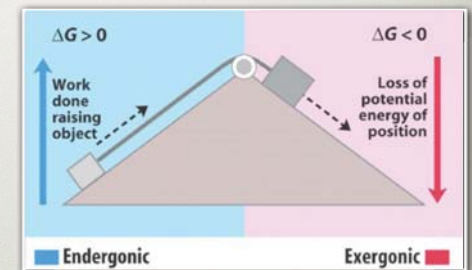
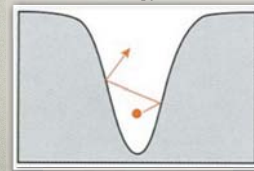
# SIGNIFICANCE OF ENTROPY AND GIBBS FREE ENERGY

- Spontaneous processes are those, during which Gibbs free energy decreases ( $\Delta G < 0$ ) and the entropy of the universe increases ( $S_{tot} > 0$ ).

Decrease in free energy: stabilizes



Increase in entropy: randomizes

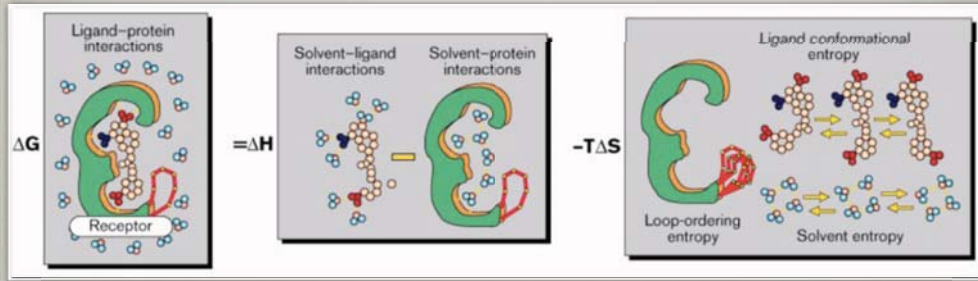


- Useful work is done by exergonic processes.
- Endergonic processes can be driven by coupling to exergonic processes.
- Entropy can be decreased locally.
- Life consumes entropy (its entropy is decreased at the expense of increasing total entropy).



# SIGNIFICANCE OF ENTROPY AND GIBBS FREE ENERGY

- Enthalpic component: molecular interactions (covalent, van der Waals, electrostatic, hydrogen bond)
- Entropic component: internal structural disorder (arrangement of solvent molecules and counter-ions, degrees of freedom, rotational and translational arrangements)



Gibbs free-energy change associated with receptor-ligand interaction binding

Enthalpic component: changes in molecular interactions

Entropic component: conformational changes

# CHEMICAL POTENTIAL

- Relevant biomedical thermodynamic systems are usually mixtures of chemicals.
- Chemical potential characterizes the thermodynamics of mixtures.
- Mixtures contain many components in different concentrations.

Gibbs free energy of a mixture: sum of free energies of components

$$G = \sum_{i=1}^k n_i \mu_i$$

$k$  = number of components  
 $n_i$  = amount of  $i^{\text{th}}$  component (mol)  
 $\mu_i$  = free energy of one mol of the  $i^{\text{th}}$  component (**chemical potential**)

$$\mu_i^0$$

**standard chemical potential** of the  $i^{\text{th}}$  component:  
 molar free energy at standard conditions  
 (25 °C, 1 atm, 1 mol/l)

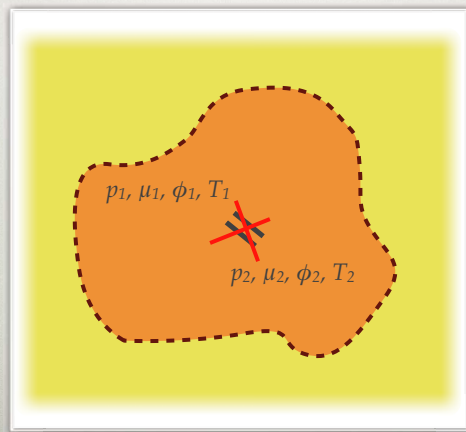
*Meaning: free-energy change associated with the addition/removal of 1 mol of the  $i^{\text{th}}$  component into/from the system.*

$$\mu_i = \mu_i^0 + RT \ln \frac{c_i}{c_i^0}$$

$c_i$  = concentration of the  $i^{\text{th}}$  component (mol/l)  
 $c_i^0$  = 1 mol/l

# IRREVERSIBLE THERMODYNAMICS

- Natural processes are rarely reversible.
- If there are inequalities in the intensive variables at different locations within the system, thermodynamic currents arise.
- Thermodynamic currents aim at the restoration of equilibrium.



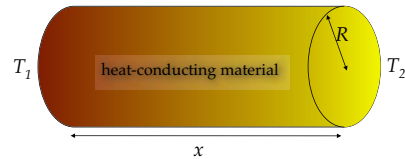
# THERMODYNAMIC CURRENTS

- Natural processes are rarely reversible.
- If there are inequalities in the intensive variables at different locations within the system, thermodynamic currents arise.
- Thermodynamic currents aim at the restoration of equilibrium.

Thermodynamic current	Relevant intensive variable (its difference maintains current)	Current density	Physical law
Heat flow	Temperature ( $T$ )	$J_E = -\lambda \frac{\Delta T}{\Delta x}$	Fourier
Volumetric flow	Pressure ( $p$ )	$J_V = -\frac{R^2}{8\eta} \frac{\Delta p}{\Delta x}$	Hagen-Poiseuille
Electric current	Electric potential ( $\phi$ )	$J_Q = -\frac{1}{\rho} \frac{\Delta \phi}{\Delta x}$	Ohm
Material transport (diffusion)	Chemical potential ( $\mu$ )	$J_n = -D \frac{\Delta c}{\Delta x}$	Fick

# HEAT FLOW

Thermodynamic current	Relevant intensive variable (its difference maintains current)	Current density	Physical law
Heat flow	Temperature ( $T$ )	$J_E = -\lambda \frac{\Delta T}{\Delta x}$	Fourier



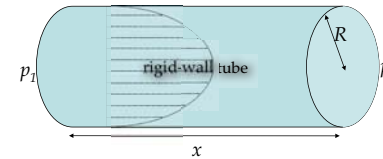
$Q$  = heat  
 $t$  = time  
 $R$  = tube radius  
 $x$  = length  
 $(\Delta T/\Delta x)$  = temperature gradient, maintained by  $T_1-T_2$   
 $A$  = cross-sectional area of tube  
 $J_E$  = heat current density  
 $\lambda$  = coefficient of heat conductance

$$\frac{Q}{At} = J_E = -\lambda \frac{\Delta T}{\Delta x}$$

$$A = R^2 \pi$$

# VOLUME FLOW

Thermodynamic current	Relevant intensive variable (its difference maintains current)	Current density	Physical law
Volumetric flow	Pressure ( $p$ )	$J_V = -\frac{R^2}{8\eta} \frac{\Delta p}{\Delta x}$	Hagen-Poiseuille



$V$  = volume  
 $t$  = time  
 $R$  = tube radius  
 $\eta$  = viscosity  
 $p$  = pressure  
 $x$  = tube length  
 $(\Delta p/\Delta x)$  = pressure gradient, maintained by  $p_1-p_2$   
 $A$  = cross-sectional area of tube  
 $J_V$  = flow intensity

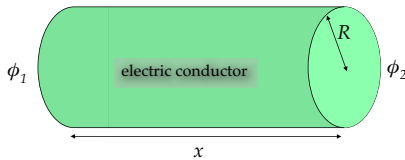
$$\frac{V}{t} = \frac{R^4 \pi}{8\eta} \frac{\Delta p}{\Delta x}$$

$$A = R^2 \pi$$

$$J_V = \frac{V}{tA} = \frac{R^2}{8\eta} \frac{\Delta p}{\Delta x}$$

# ELECTRIC CURRENT

Thermodynamic current	Relevant intensive variable (its difference maintains current)	Current density	Physical law
Electric current	Electric potential ( $\phi$ )	$J_Q = -\frac{1}{\rho} \frac{\Delta \phi}{\Delta x}$	Ohm

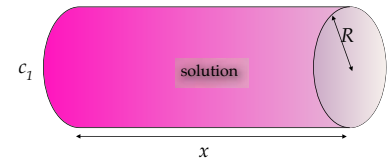


$q$  = electric charge  
 $t$  = time  
 $R$  = tube radius  
 $\phi$  = electric potential  
 $x$  = length of conductor  
 $(\Delta \phi/\Delta x)$  = potential gradient (voltage), maintained by  $\phi_1-\phi_2$   
 $A$  = cross-sectional area of tube  
 $J_Q$  = electric current

$$\frac{q}{tA} = J_Q = -\frac{1}{\rho} \frac{\Delta \phi}{\Delta x}$$

# MATERIAL TRANSPORT (DIFFUSION)

Thermodynamic current	Relevant intensive variable (its difference maintains current)	Current density	Physical law
Material transport (diffusion)	Chemical potential ( $\mu$ )	$J_n = -D \frac{\Delta c}{\Delta x}$	Fick



$m$  = amount of material transported  
 $t$  = time  
 $R$  = tube radius  
 $x$  = length  
 $(\Delta c/\Delta x)$  = concentration gradient, maintained by  $c_1-c_2$   
 $A$  = cross-sectional area of tube  
 $J_n$  = heat current density  
 $D$  = diffusion coefficient

$$\frac{m}{tA} = J_n = -D \frac{\Delta c}{\Delta x}$$



# THERMODYNAMIC CURRENTS

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# ONSAGER'S LINEAR FUNCTION

- Lars Onsager (1903-1976), Nobel prize (1968)
- General relationship between transport processes.

$$J = LX$$

Flow intensity of transported extensive variable (thermodynamic current,  $J$ )  
 $J = \frac{\Delta x_{ext}}{A \Delta t}$

=

Coefficient of conductance (thermodynamic coefficient,  $L$ )

x

Change in intensive variable ("gradient", thermodynamic force,  $X$ )  
 $X = -\frac{\Delta y_{int}}{\Delta x}$

A thermodynamic current may be evoked by several different intensive variables.  
 E.g., thermodiffusion (material transport evoked by temperature gradient).

$$J_1 = L_{11}X_1 + L_{12}X_2$$

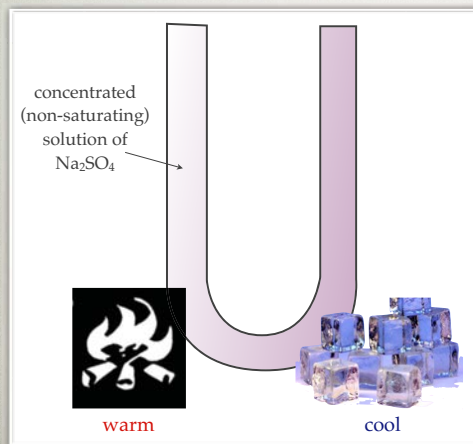
$$J_2 = L_{21}X_1 + L_{22}X_2$$

$L_{11}, L_{22}$  = "linear" coefficients of conductance

$L_{12}, L_{21}$  = "cross" coefficients of conductance

# THERMODIFFUSION

- Ludwig-Soret effect
- Carl Friedrich Wilhelm Ludwig (1856)
- Charles Soret (1879)



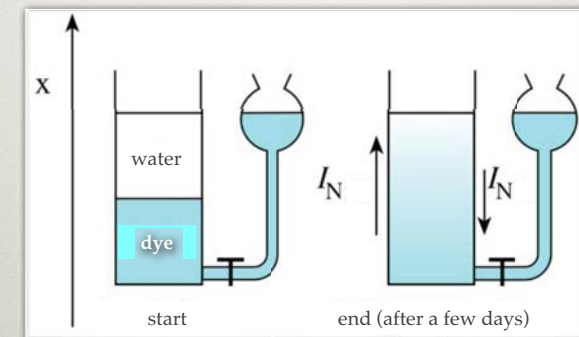
Two types of currents:

material flow  $J_V = -L_T \frac{\Delta T}{\Delta x}$

heat flow flow  $J_E = -\lambda \frac{\Delta T}{\Delta x}$

# DIFFUSION

- Spontaneous mixing, distribution, concentration-equilibration driven by the thermal motion of particles.



$$x^2 = 2Dt$$

$x$  = displacement of boundary

$t$  = time

$D$  = constant ("diffusion coefficient")



# Microscopic manifestation of diffusion: Brownian movement

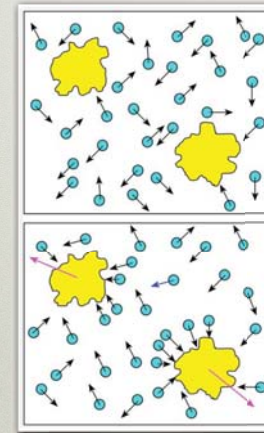


Robert Brown  
(1773-1858)

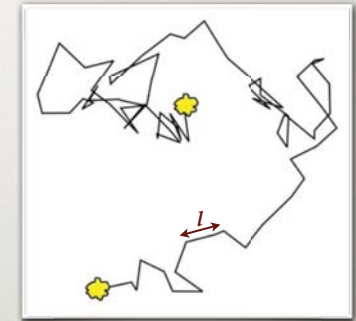


Fat droplets suspended in milk (droplet sizes 0.5 - 3  $\mu\text{m}$ )

# Brownian movement



Movement of microscopic particle is the result of random collisions with molecules.



$l$  = mean free path (average distance between consecutive collisions)  
 $v$  = average velocity of thermally propelled particle

# DIFFUSION

- *Fick's First law*: material flow density is the product of the evoking concentration gradient and the diffusion coefficient

Material transport:  $J_n = -D \frac{\Delta c}{\Delta x}$

$J_n$  = material flow  
 $\Delta c / \Delta x$  = drop in concentration ("gradient")  
 $D$  = constant ("diffusion coefficient")

Diffusion coefficient:  $D = \frac{1}{3} v l$

$v$  = average velocity of thermally propelled particle  
 $l$  = mean free path (average distance between consecutive collisions)  
 $D$  = amount of material transported through unit area per unit time ( $\text{m}^2/\text{s}$ ) (at unitary concentration drop).



Brown-movement

Diffusion coefficient for spherical particle:  $D = \frac{k_B T}{6 \pi \eta r}$

*Einstein-Stokes formula:*  
 $k_B$  = Boltzmann's constant  
 $T$  = absolute temperature  
 $\eta$  = viscosity  
 $r$  = radius of particle

# DIFFUSION

- *Fick's Second Law*: instantaneous material flow density depends on the temporal change in evoking concentration gradient.

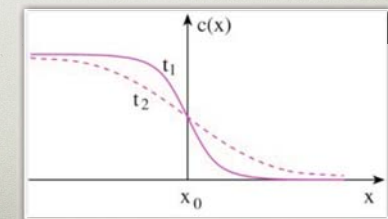
Material flow intensity:  $-\frac{\Delta J_n}{\Delta x} = \frac{\Delta c}{\Delta t}$

$J_n$  = Flow intensity  
 $x$  = distance  
 $t$  = time

Diffusion coefficient:  $D \frac{\Delta \left( \frac{\Delta c}{\Delta x} \right)}{\Delta x} = \frac{\Delta c}{\Delta t}$

$D$  = diffusion coefficient

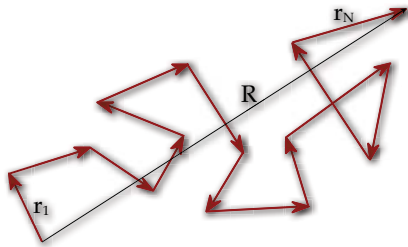
Concentration gradient decreases with time (boundary becomes "smeared")





# RELATIONSHIP BETWEEN RANDOM WALK AND DIFFUSION

## Brown-movement - "random walk"



## "Square-root law":

$$\langle R^2 \rangle = Nl^2 = Ll$$

$R$  = displacement  
 $N$  = number of unit vectors (steps)  
 $l = |\vec{r}_i|$  = mean free path  
 $r_i$  = unit step  
 $Nl = L$  = total distance

Mean particle velocity:  $v = \frac{l}{\tau}$

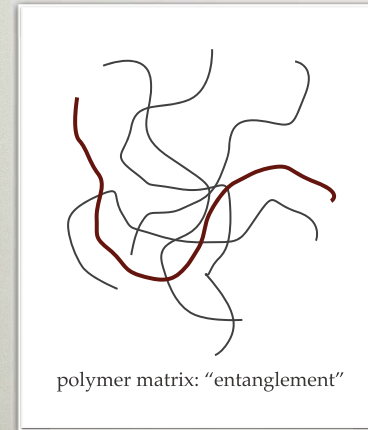
Full walk time:  $t = N\tau$

Diffusion coefficient:  $D = \frac{1}{3}vl$

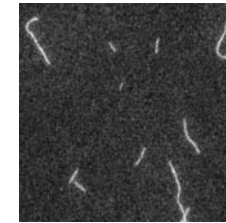
$$\langle R \rangle = \sqrt{Nl^2} = \sqrt{\frac{t}{\tau}l^2} = \sqrt{tvl} = \sqrt{3Dt}$$

# A SPECIAL CASE OF DIFFUSION: REPTATION

- *Reptation*: "snake-like" diffusion within polymer network (*Reptilia*)



polymer matrix: "entanglement"



Actin filaments in methyl-cellulose matrix.  
 "unidirectional diffusion"

# A SPECIAL CASE OF DIFFUSION: OSMOSIS

*Osmosis* ~ osmos (Gr) thrust, push

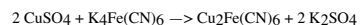
**History:** -Nollet (1748): pig bladder containing alcohol swells in water  
 -Dutrochet (1830): first osmometer  
 -van't Hoff: gas-law mechanism of osmosis  
 -Arrhenius and Findlay: vapor-pressure mechanism of osmosis

**Osmosis:** diffusion-driven process between two compartments separated by semipermeable membrane (solvent diffusion).

**Osmotic pressure ( $\pi$ )** = equilibrium hydrostatic pressure between each side of the semipermeable membrane (dP).

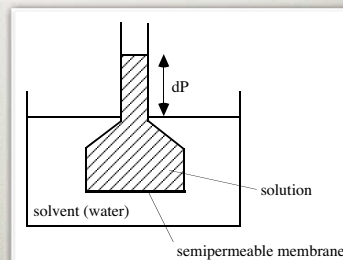
Semipermeable membranes:  
 -frog membrane

-copper-ferrocyanide gel (precipitated on the pores of clay cylinder):



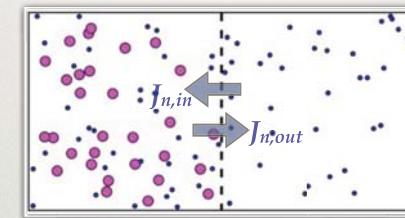
-cellulose membrane, dialysis bag

Biomedical importance: biological membranes, compartment surfaces.



# A SPECIAL CASE OF DIFFUSION: OSMOSIS

- *Osmosis*: one-directional solvent transport by diffusion.



$J_{n,in}$  driving force: solvent concentration difference

$J_{n,out}$  driving force: pressure difference

Osmotic equilibrium:  $J_{n,in} = J_{n,out}$

*van't Hoff's Law:*

$c$  = concentration of solute

$R$  = universal gas constant

$T$  = absolute temperature

Osmotic pressure:  $p_{osmosis} = cRT$

Importance of osmosis: cell swelling, edema, hemodialysis.



# MECHANISMS OF OSMOSIS I.

## van't Hoff's gas-law mechanism

Universal gas law:  $pV = RT$

$$p = \frac{1}{V}RT$$

Osmotic pressure:  $p_{osm} = \pi = cRT$

$p$  = pressure  
 $V$  = volume  
 $R$  = gas constant (8,3 J/mol.K)  
 $T$  = absolute temperature  
 $c$  = molar concentration of solute

### Problem:

What is the osmotic pressure of a 0.1 M (0.1 mol/dm<sup>3</sup>) sucrose solution?

$$\pi = 8.3 \text{ (J/mol.K)} \times 293 \text{ (K)} \times 0.1 \text{ (mol/dm}^3\text{)} = 243 \text{ kPa} \sim 2.4 \text{ atm.}$$

Note: the formula applies to dilute solutions.

# MECHANISMS OF OSMOSIS II.

## Corrected van't Hoff's law

$$\pi = fnRTc$$

$n$  = number of ions produced during complete dissociation

$f$  = osmotic coefficient:

$$f = \frac{\pi_{measured}}{\pi_{calculated}} = \frac{\pi_{measured}}{nRTc}$$

## Arrhenius-Findlay's vapor pressure mechanism

Changes in the chemical potential of the solvent due to the solute (chemical activity of the solvent becomes reduced upon the addition of the solute).

Chemical potential of solvent:  $\mu_s = \mu_s^0 + RT \ln \chi_s$

$\mu_s^0$  = standard chemical potential of solvent  
 $\chi_s$  = mole fraction of solvent

Mole fraction of solvent:  $\frac{n_0}{n_0 + n_1}$

$n_0$  = number of moles of solvent  
 $n_1$  = number of moles of solute

Raoult's law:  $\frac{p_1}{p_0} = \frac{n_0}{n_0 + n_1}$

$p_0$  = vapor pressure of pure water  
 $p_1$  = vapor pressure of solution water

Arrhenius-Findlay law:  $\pi = \frac{RT}{v} \ln \frac{p_0}{p_1}$

$v$  = molar volume of solvent (cm<sup>3</sup>/mol; for water: 18)

# IMPORTANCE OF OSMOSIS

Properties of the semipermeable membrane: *reflexion coefficient* ( $\sigma$ )

For a perfect semipermeable membrane:

$$\Delta P = \Delta \pi \quad \text{and} \quad \sigma = \frac{\Delta P}{\Delta \pi} = 1$$

In reality:

$$\Delta P < \Delta \pi \quad \text{and} \quad \sigma = \frac{\Delta P}{\Delta \pi} < 1$$

$$0 < \sigma < 1$$

### Osmotic work:

$$-L = nRT \ln \frac{c_1}{c_2} = nRT \ln \frac{\pi_1}{\pi_2}$$

$R$  = gas constant

$n$  = total number of moles of solute

$c_1$  = initial molarity of solution

$c_2$  = final molarity of solution (after equilibration)

$\pi_1$  = initial osmotic pressure

$\pi_2$  = final osmotic pressure (after equilibration)

**Equivalent osmotic pressure** (osmotic concentration): concentration of non-electrolyte solution in equilibrium with a heterogeneous solution system.

Units: mmol/kg = mOsmol/kg = mOsm

Osmolarity of blood plasma ~ 300 mOsm.

**Oncotic pressure:** colloid osmotic pressure. Osmotic pressure of a solution of colloidal macromolecules.

