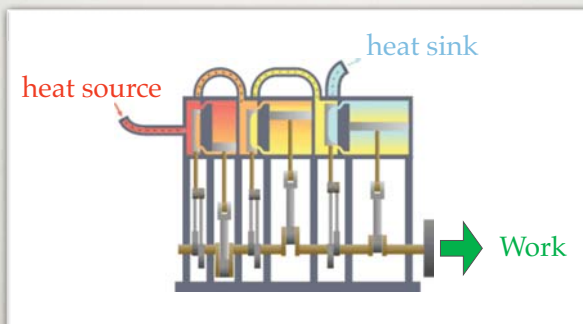# Thermodynamics

Miklós Kellermayer

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.

What is thermodynamics?

Definition: branch of physics studying the effects of changes in temperature, pressure and volume (energy changes).

Therme (Gr) heat, *dynamis* (Gr) power.

Thermodynamics

"Classical thermodynamics… is the only physical theory of universal content concerning which I am convinced that, within the framework of applicability of its basic contents, will never be overthrown."

-Albert Einstein

- Its importance stems from its generality.

- It reveals the driving forces behind natural phenomena.

- Due to its generalizations, it has abstract, complex and difficult-to-understand concepts.

"Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time your are so used to it, it doesn't bother you any more."

-Arnold Sommerfeld

SHORT HISTORY OF THERMODYNAMICS

Otto von Guericke (1650) first vacuum pump.

Robert Boyle (1660) Boyle's law: $pV=constant$.

Joseph Louis Gay-Lussac (1802) universal gas law: $pV=nRT$.

Sadi Carnot (1824) father of thermodynamics. Concept of "work".

William Thomson (Lord Kelvin) (1849) name of "thermodynamics".

Rudolf Clausius (1850) concepts of enthalpy, entropy.

James Clerk Maxwell (1871) statistical thermodynamics, concept of equilibrium.

Ludwig Boltzmann (1875) statistical interpretation of entropy ($S=k\ln W$).

Willard Gibbs (1876) concept of free energy (useful work).

Lars Onsager (1929) irreversible thermodynamics, Onsager's linear relationship.

Christopher Jarzynski (1997) Jarzynski's equality. Free-energy change can be calculated from average irreversible work: $e^{-\Delta G/k_B T} = \left\langle e^{-W/k_B T} \right\rangle$

THERMODYNAMIC SYSTEM

Economic system

Social system

Financial system

Chromatin

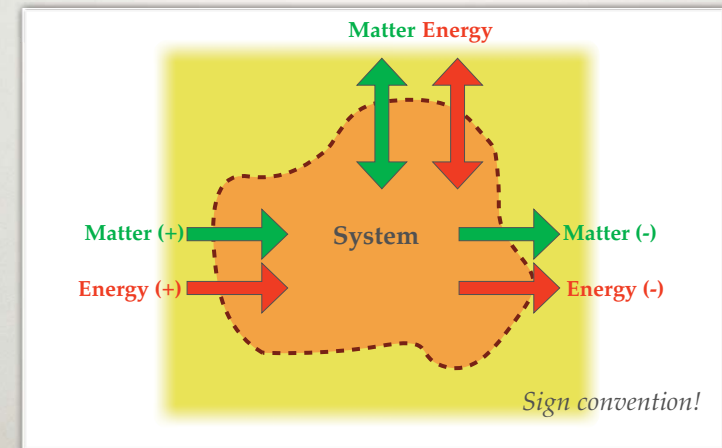
ABSTRACTION OF THE THERMODYNAMIC SYSTEM

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

Surroundings (environment)

System

Boundary
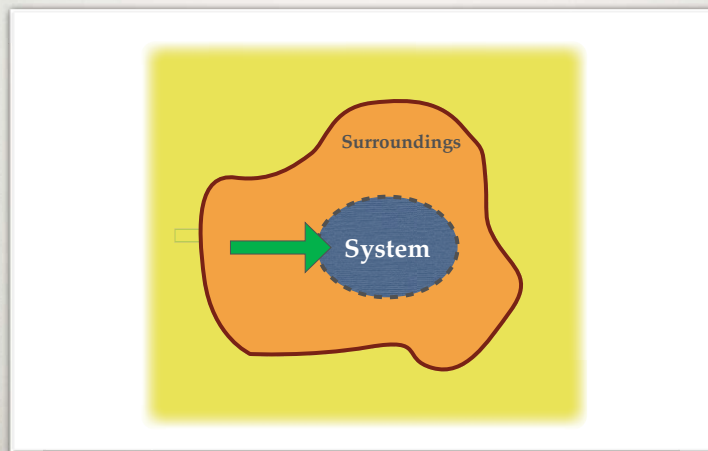(connects the system and the surroundings)
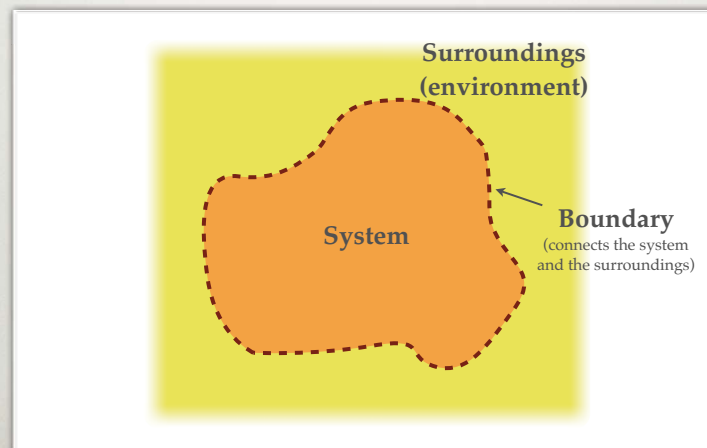
THE THERMODYNAMIC SYSTEM INTERACTS WITH THE SURROUNDINGS

Exchange of matter and energy may occur across the boundary.

Matter Energy

Matter (+)   System   Matter (-)

Energy (+)   Energy (-)
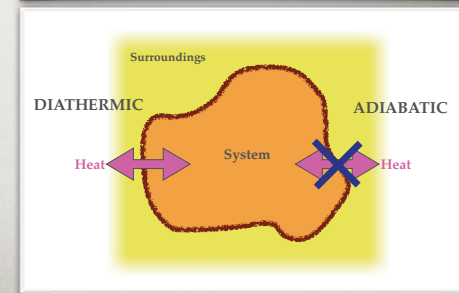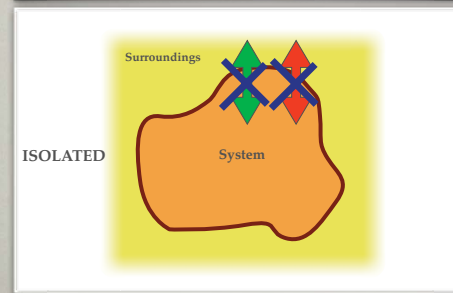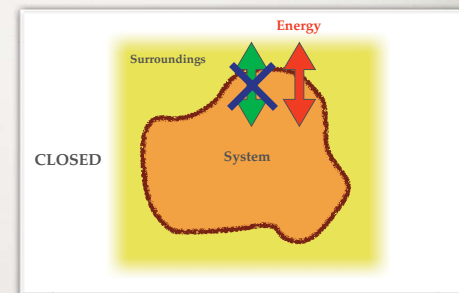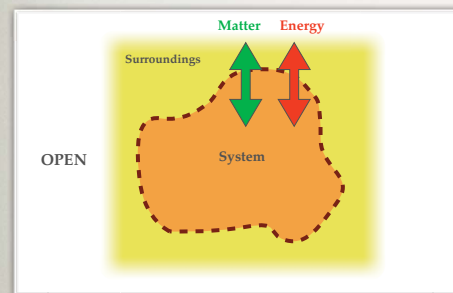
Sign convention!

The thermodynamic system interacts with the surroundings

Defining the thermodynamic system has consequences for processes.

Surroundings

System
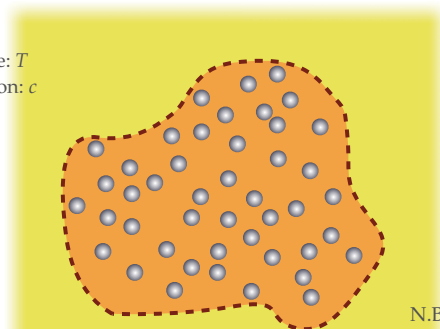

Types of thermodynamic systems

Matter   Energy

OPEN   Surroundings   System

CLOSED   Energy   Surroundings   System

ISOLATED   Surroundings   System

DIATHERMIC   Surroundings   System   ADIABATIC   Heat   Heat

Characterization of the thermodynamic system

Macroscopic characterization: state variables - explicitly determine the *state* of the system.

Pressure: p
Volume: V
Temperature: T
Concentration: c

N.B.: universal gas law
$pV=nRT$

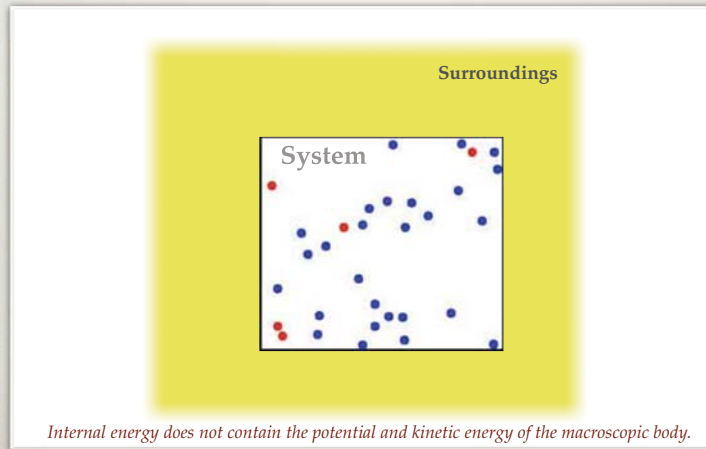# Characterization of the thermodynamic system

Macroscopic characterization: extensive and intensive variables
Extensive variables: their value is proportional to the size of the system
Intensive variables: their value is independent of the size of the system

Extensive variable	Intensive variable	Product: energy change
Volume (V)	Pressure (p)	Volumetric work ($p\Delta V$)
Matter (n)	Chemical potential (μ)	Work of material transport ($\mu\Delta n$)
Charge (Q)	Electric potential (ϕ)	Electric work ($\phi\Delta Q$)
Entropy (disorder, S)	Temperature (T)	Heat ($T\Delta S$)

CHARACTERIZATION OF THE THERMODYNAMIC SYSTEM

Microscopic characterization: internal energy (E)

$$E = E_{el} + E_{vib} + E_{rot} + E_{other}$$

Surroundings

System

Internal energy does not contain the potential and kinetic energy of the macroscopic body.

INTERNAL ENERGY (E) IS "STATE FUNCTION"

*State functions*: single-value functions of the state variables (independent variables) of the system.
Change in the state functions depend only on the initial and final states of the system; it is independent of the path.

"A" state

ΔE
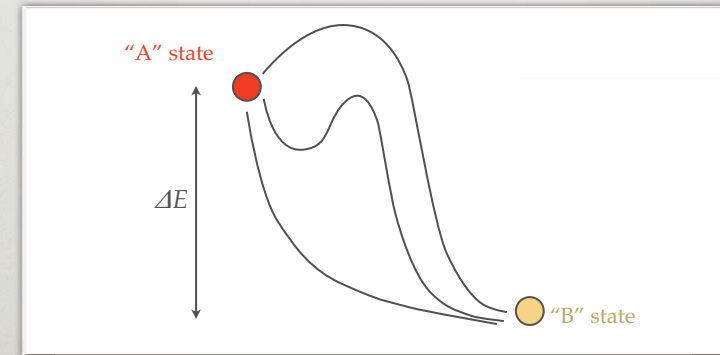
"B" state

Other state functions: enthalpy (H), Helmholtz free energy (F), Gibbs free energy (G), entropy (S)
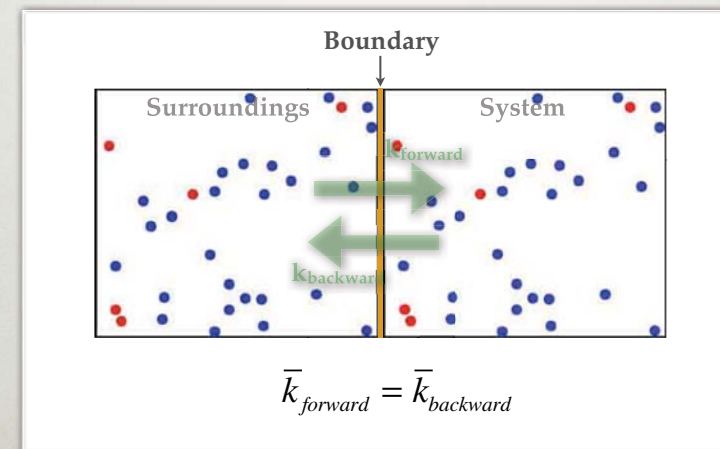

EQUILIBRIUM

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

p_k, μ_k, ϕ_k, T_k

p_r, μ_r, ϕ_r, T_r

$p_k, \mu_k, \phi_k, T_k = p_r, \mu_r, \phi_r, T_r$
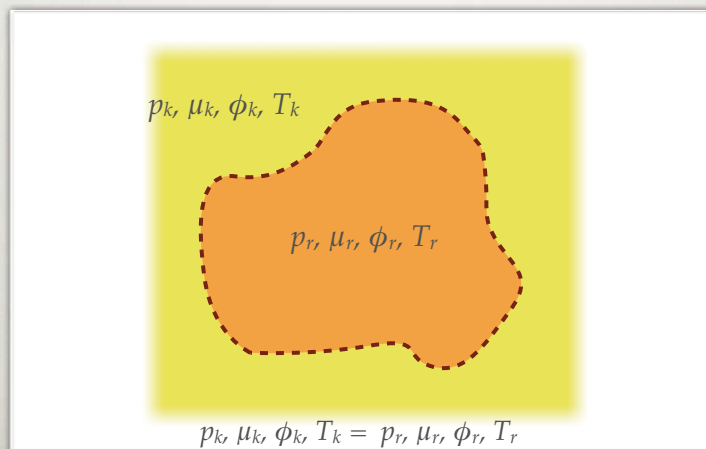
EQUILIBRIUM

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

Boundary

Surroundings   System

k$_{forward}$

k$_{backward}$

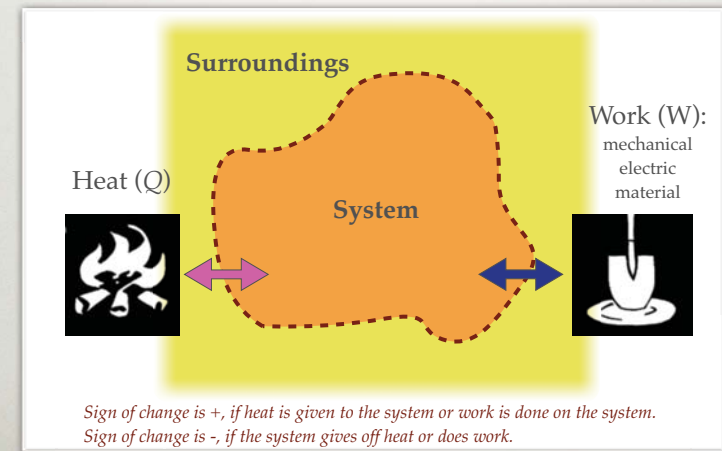$$\bar{k}_{forward} = \bar{k}_{backward}$$

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 equel (there are no thermodynamic currents).

$A = B$

C

p_1, μ_1, ϕ_1, T_1

p_2, μ_2, ϕ_2, T_2

p_3, μ_3, ϕ_3, T_3
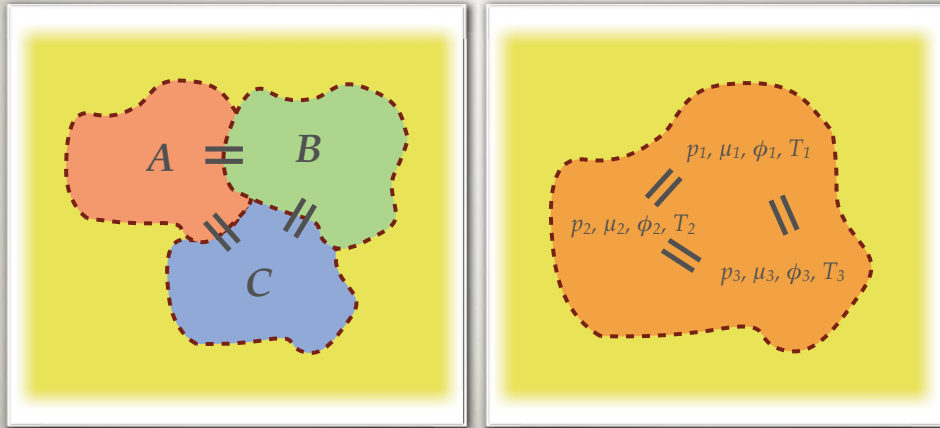
Change

Thermodynamics is interested in the changes within the system.
Changes may be evoked by: heating, work.
Result: internal energy of the system changes.

Surroundings

Heat (Q)

System

Work (W):
mechanical
electric
material

Sign of change is +, if heat is given to the system or work is done on the system.
Sign of change is -, if the system gives off heat or does work.

Equilibrium change

Definitions:
- Reversible change (reversibly driven proceess).
- Series of reversible (equilibrium, infinitesimal) steps; the sysem is in equilibrium during each step of the process.
- "Infinitely slow", "quasi-static" process.
- There are no permanent (compensating) energy changes in the surroundings (work done by the system and surroundings are equal).

Characteristics: Work done by the system is maximal.

Surroundings

System
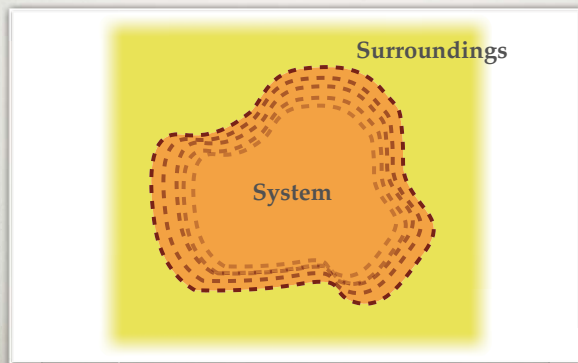
Thermodynamic processes

- ***Isobaric:*** at constant pressure.
- ***Isochoric (isometric, isovolumetric):*** at constant volume.
- ***Isothermic:*** at constant temperature.
- *Adiabatic:* no heat exchange.
- *Isentropic:* at constant entropy.
- *Isenthalpic:* at constant enthalpy.
- *"Steady state":* at constant internal energy.

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 stats 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:
$$W_Q = \varphi\Delta Q$$

Material transport:
$$W_n = \mu\Delta n$$

Generalized:
$$W^i = y^i_{int}\Delta x^i_{ext}$$

Izochoric process ($\Delta V = 0$):
$$\Delta E = Q_V$$
Change in internal energy is caused only by the heat exchange.

Izobaric process (p=constant):
$$\Delta E = Q_p + W_V = Q_p - p\Delta V$$

Enthalpy

- "Heat content" (H)
- Total heat absorbed by the system at constant pressure.
- Thermodynamic state function, by the help of which the useful work done at constant pressure may be calculated.
- *enthalpein* (Gr) to heat

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

Internal energy change of the system during isobaric process.

Enthalpy:
$$H = E + pV$$

E, p, V: equilibrium internal energy, pressure and volume.

Enthalpy change:
$$\Delta H = \Delta E + p\Delta V$$

Isobaric process:
$$\Delta H = Q_p$$

If there are no other energy changes beside volumetric work.
Q_p = Reaction heat at constant pressure.

Isochoric process (V=constant):
$$\Delta E = Q_V$$

Volumetric work = 0.
Q_V = Reaction heat at onstant volume.

Standard state: 25 ˚C, 1 atm. Standard enthalpy of compounds ($\Delta H°$): reaction heat of 1 mole of compound measured in standard state, at constant pressure.

Second law of thermodynamics

- "Law of entropy."
- Heat flows spotaneously 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 characterizd by entropy maximum.
- Spontaneous processes proceed towards the most probably 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.

Entropy

- *Entropy (S):* unavailability of the system to do useful work. State function (units: J/K).
- Measure of "unusable" energy.
- Measure of thermodynamic probability.
- Measure of disorder.
- *entrepein* (Gr) to turn around.

Phenomenologic description:

Energy change during thermodynamic processes (interactions):
$$\Delta E = \sum_i y^i_{int}\Delta x^i_{ext}$$

Product of intensive variables (y) and extensive variable-changes (Δx).

Energy change during thermal processes (thermal ineractions):
$$Q_E = T\Delta S$$

Intensive variable: temperature (T)
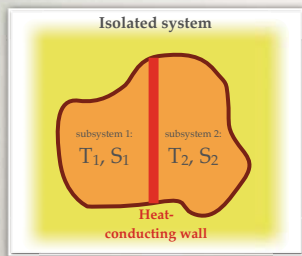Extensive variable: entropy change (ΔS)

Entropy change:
$$\Delta S = \frac{\Delta Q}{T}$$

Measure of heat exchanged during reversible (equlibrium) isothermal process.

ENTROPY

- In isolated system, during temperature equilibration entropy always increases.

Isolated system

subsystem 1: T_1, S_1 subsystem 2: T_2, S_2

Heat-conducting wall

$\Delta E = \Delta(E_1 + E_2) = \Delta E_1 + \Delta E_2 = 0$ — In an isolated system internal energy is constant ($\Delta E = 0$).

$\Delta E_1 = T_1 \Delta S_1 \qquad \Delta E_2 = T_2 \Delta S_2$ — Energy changes during thermal interaction.

$\Delta S = \Delta S_1 + \Delta S_2$ — Entropy is an extensive variable.
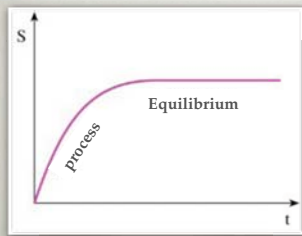
$\Delta S = \dfrac{\Delta E_1}{T_1} + \dfrac{\Delta E_2}{T_2} = \Delta E_1\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

S / process / Equilibrium / t

$T_1 > T_2 \;$ or $\; T_1 < T_2 : \Delta S > 0$ — If the initial temperatures are different, entropy increases.

$T_1 = T_2 \; : \; \Delta S = 0$ — If the initial temperatures are equal, entropy does not change.

STATISTICAL INTERPRETATION OF ENTROPY

- *Macrostate:* state of the system defined by state variables (e.g., *p, V, T*).
- *Microstate:* internal structre of the system (position, velocity of every particle)
- In the *most probable macrostate* the number of microstates is the greatest.
- Number of microstates describing a given macrostate: *thermodynamic probability* (Ω).

subsystem 1: subsystem 2: / transmissible wall
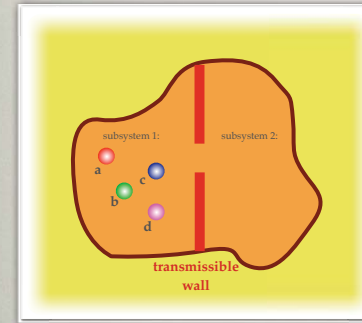
Macrostate	number of particles in subsystem 1	structure of subsystem 1	Number of microstates (Ω)
A	4	abcd	1
B	3	abc,abd,acd,bcd	4
C	2	ab, ac, ad, bc, bd, cd	6
D	1	a, b, c, d	4
E	0	-	1

Entropy: $\quad S = k_B \ln \Omega \quad$ k_B = Boltzmann's constant (1,38 x 10^{-23} J/K)

ENTROPY IS THE MEASURE OF DISORDER
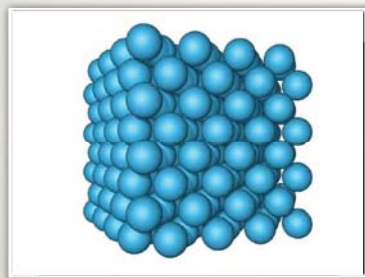
Ordered crystal: Low entropy
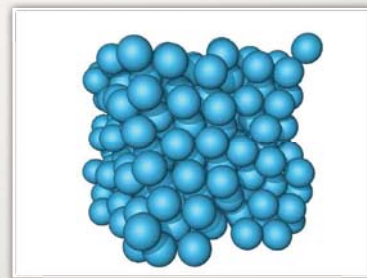
Disordered liquid: High entropy

THIRD LAW OF THERMODYNAMICS

- Nernst's law.
- The entropy of mon-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 ony 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

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{sur}$$

$$\Delta S_{sur} = -\frac{\Delta H_{sys}}{T}$$

$$\Delta S_{tot} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T}$$

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

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

$$H = G + TS$$

$$\text{Enthalpy} = \frac{\text{useful}}{\text{work}} + \frac{\text{unusable energy}}{\text{change}}$$

During spontanous 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.
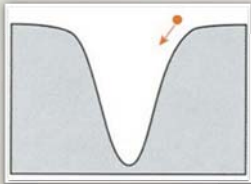- State function

$$F = E - TS$$

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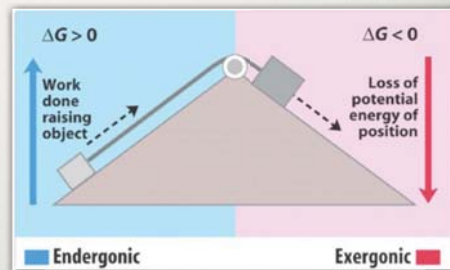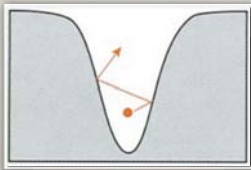T: absolute temperature
S: entropy

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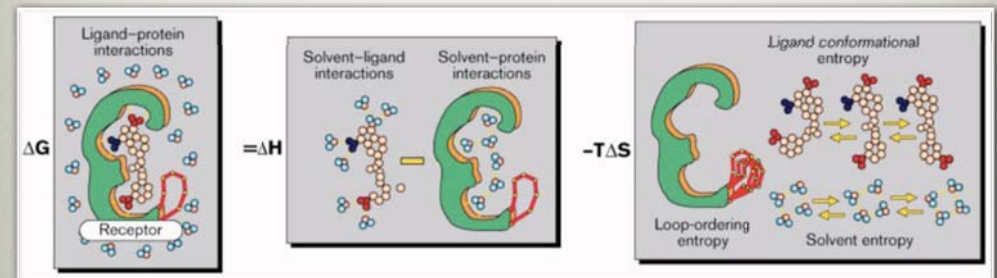
Gibbs free-energy change associated with receptor-ligand interaction binding

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 ith component (mol)
μ_i = free energy of one mol of the ith component (**chemical potential**)

$$\mu_i^0$$

standard chemical potential of the ith component:
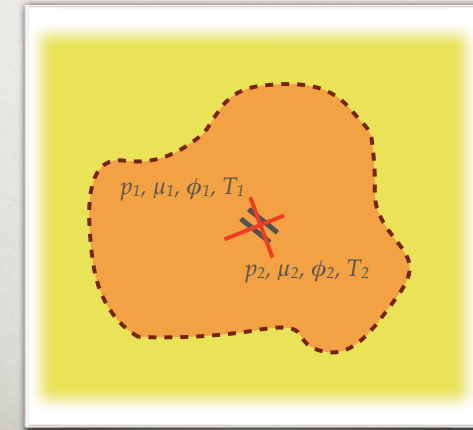molar free energy at standard conditions
(25 ˚C, 1 atm, 1 mol/l)

Meaning: free-energy change asociated with the addition/removal of 1 mol of the ith component into/from the system.

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

c_i = concentration of the ith 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.

p_1, μ_1, ϕ_1, T_1

p_2, μ_2, ϕ_2, T_2

THERMODYNAMIC CURRENTS

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

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

---

HEAT FLOW

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

T_1

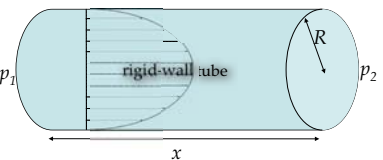heat-conducting material

R

T_2

x

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
λ = 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)	$J_V = -\dfrac{R^2}{8\eta}\dfrac{\Delta p}{\Delta x}$	Hagen-Poiseuille

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

$$A = R^2\pi$$

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

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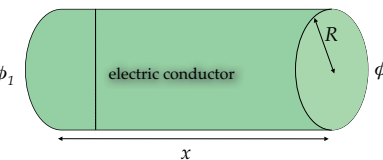A = cross-sectional area of tube
J_V = flow intensity

Electric Current

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

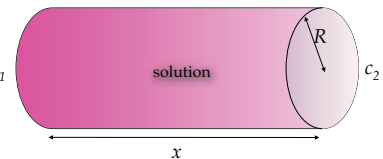$$\frac{q}{tA} = J_Q = -\frac{1}{\rho}\frac{\Delta\varphi}{\Delta x}$$

q = electric charge
t = time
R = tube radius
ϕ = electric potential
x = length of conductor
($\Delta\phi/\Delta x$ = potential gradient (voltage), maintained by ϕ_1-ϕ_2)
A = cross-sectional area of tube
J_Q = electric current

Material Transport (Diffusion)

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

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

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

Thermodynamic Currents

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

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

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) $J = \dfrac{\Delta x_{ext}}{A\Delta t}$ | $=$ | Coefficient of conductance (thermodynamic coefficient, L) | $\times$ | Change in intensive variable ("gradient", thermodynamic force, X) $X = -\dfrac{\Delta y_{int}}{\Delta x}$ |

A thermodynamic current may be evoked by several different intensive variables. E.g., thermodiffusion (material transport evoked by temperature gradient).
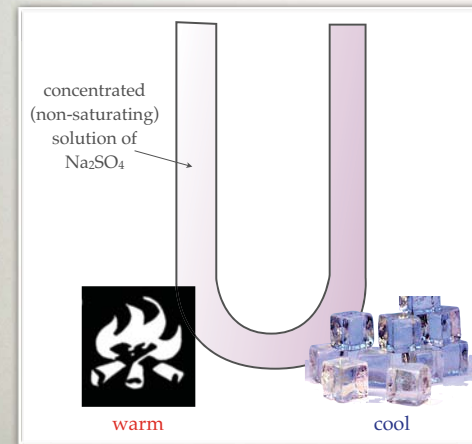
$$J_1 = L_{11}X_1 + L_{12}X_2 \qquad J_2 = L_{21}X_1 + L_{22}X_2$$

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)
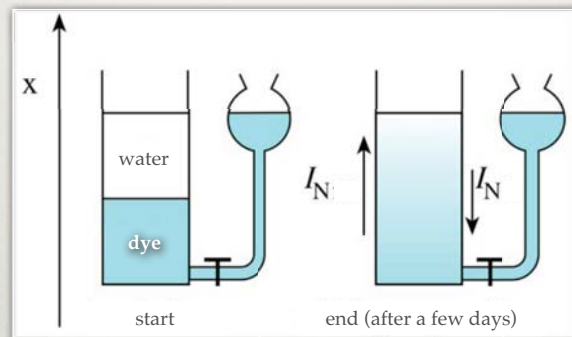- Charles Soret (1879)

concentrated (non-saturating) solution of Na_2SO_4

warm   cool

Two types of currents:

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

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

DIFFUSION

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

water

dye

I_N

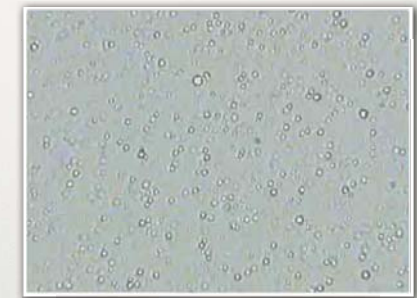start   end (after a few days)

$$x^2 = 2Dt$$

x = displacement of boundary
t = time
D = constant ("diffusion coefficient")

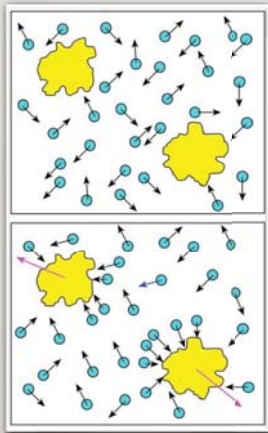# Microscopic manifestation of diffusion: Brownian movement
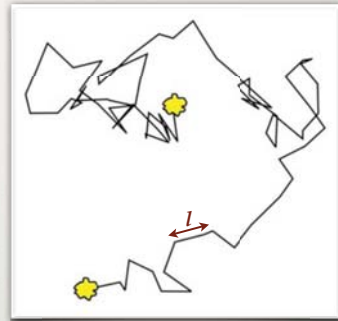

Robert Brown (1773-1858)

Fat droplets suspended in milk (droplet sizes 0.5 - 3 μm)

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 eviking 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:
$$D = \frac{1}{3}vl$$

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 (m^2/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
η = viscosity
r = radius of particle

DIFFUSION

- *Fick's Second Law:* instantaneous material flow density depends on the temporal change in evoking concentration gradient.
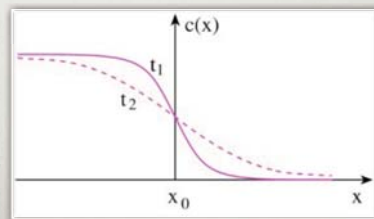
Material flow intensity:
$$-\frac{\Delta J_n}{\Delta x} = \frac{\Delta c}{\Delta t}$$

J_n = Flow intensity
x = distance
t = time

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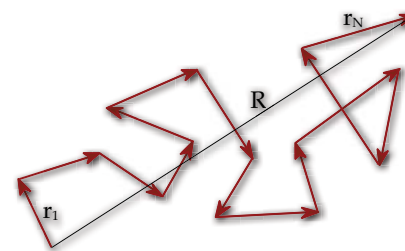$$D\frac{\Delta\left(\frac{\Delta c}{\Delta x}\right)}{\Delta x} = \frac{\Delta c}{\Delta t}$$

D = diffusion coefficient

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

RELATIONSHIP BETWEEN RANDOM WALK AND DIFFUSION

Brown-movement - "random walk"

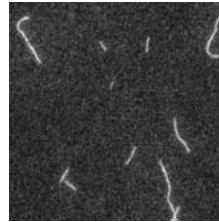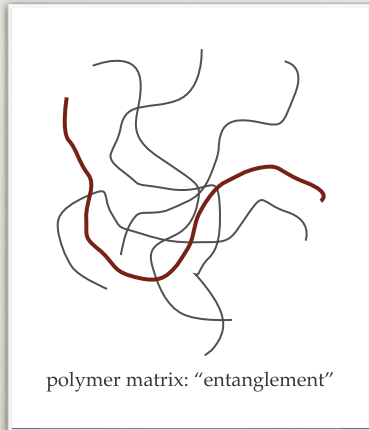**"Square-root law":**

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

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: $v = \dfrac{l}{\tau}$

Full walk time: $t = N\tau$

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

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

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 (π) = equilibrium hydrostatic pressure between each side of the semipermeable membrane (dP).
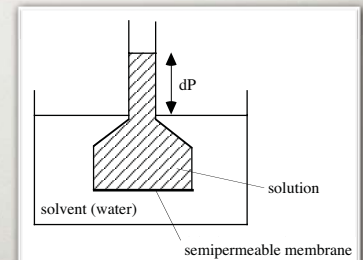
Semipermeable membranes:
-frog membrane
-copper-ferrocyanide gel (precipitated on the pores of clay cylinder):
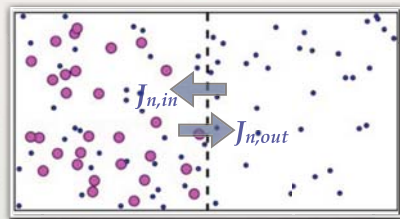
$$2\ CuSO_4 + K_4Fe(CN)_6 \longrightarrow Cu_2Fe(CN)_6 + 2\ K_2SO_4$$
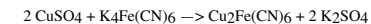
-cellulose membrane, dialysis bag

Biomedical importance: biological membranes, compartment surfaces.

dP

solution

solvent (water)

semipermeable membrane

A SPECIAL CASE OF DIFFUSION: OSMOSIS

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

$J_{n,in}$

$J_{n,out}$

$J_{n,in}$ 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 consant (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^3) sucrose soution?

π = 8.3 (J/mol.K) x 293 (K) x 0.1 (mol/dm^3) = 243 kPa ~ 2.4 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: $\mu_s = \mu_s^0 + RT \ln \chi_s$

μ_s^0= standard chemical potential of solvent
X_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^3/mol; for water: 18)

IMPORTANCE OF OSMOSIS

Properties of the semipermeable membrane: **reflexion coefficient** (σ)

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)
    π_1 = initial osmotic pressure
    π_2 = final osmotic pressure (after equilibration)

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