



**SEMMELWEIS
UNIVERSITY**



**PÁZMÁNY PÉTER
CATHOLIC UNIVERSITY**



Development of Complex Curricula for Molecular Bionics and Infobionics Programs within a consortial* framework**

Consortium leader

PÁZMÁNY PÉTER CATHOLIC UNIVERSITY

Consortium members

SEMMELWEIS UNIVERSITY, DIALOG CAMPUS PUBLISHER

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**Molekuláris bionika és Infobionika Szakok tananyagának komplex fejlesztése konzorciumi keretben

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WORLD OF MOLECULES

(Molekulák világa)

SOLUTIONS, MIXTURES

(Oldatok, elegyek)

KRISTÓF IVÁN



Previously – States of matter

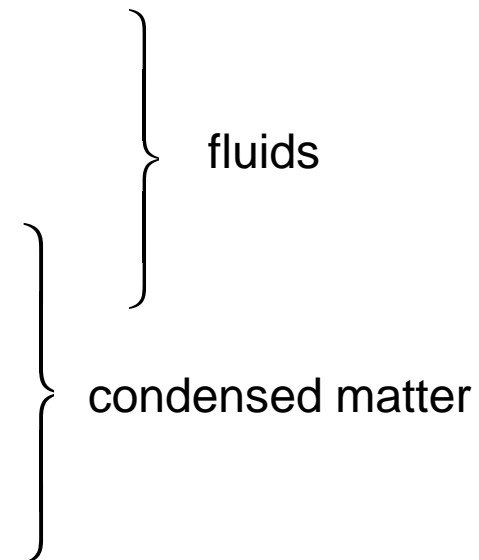
1. States of matter
2. Gas state
3. Gas laws
4. Liquid state
5. Properties of liquids, surface forces
6. Solid state
7. Crystal lattices
8. Plasma state





Previously - States of matter

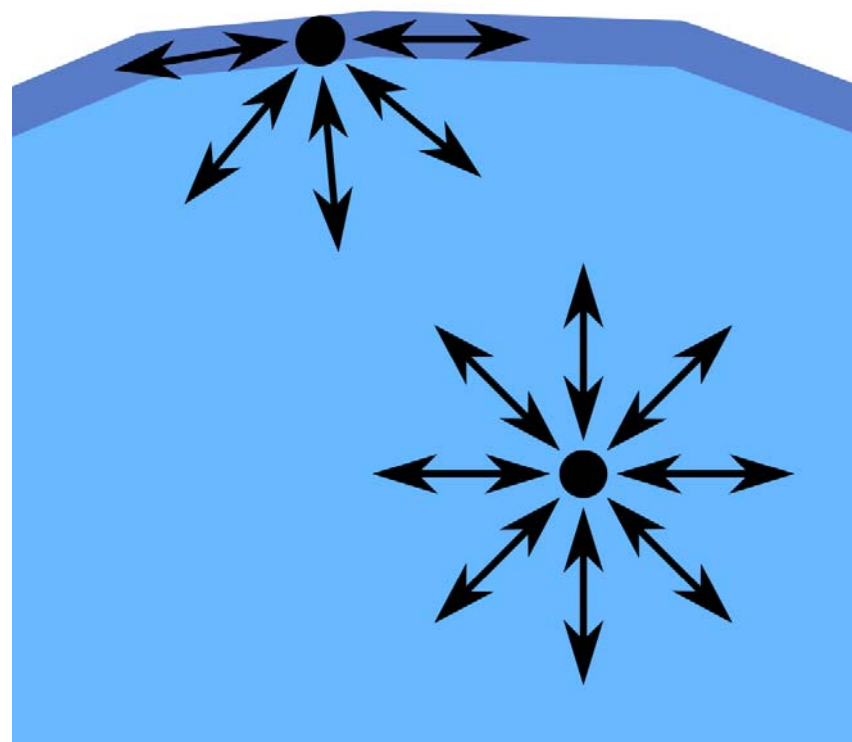
- **gas**: compressible fluid, with far away molecules
- **liquid**: incompressible fluid, mobile structure
- **solid**: closely packed molecules, immobile structures
- **plasma**: highly ionized gas state, usually at high temperatures
- ...



Previously - Surface tension

- the amount of attractive interactions are maximum in the bulk of a liquid
- the internal pressure forces the liquid to contract the surface to a minimum

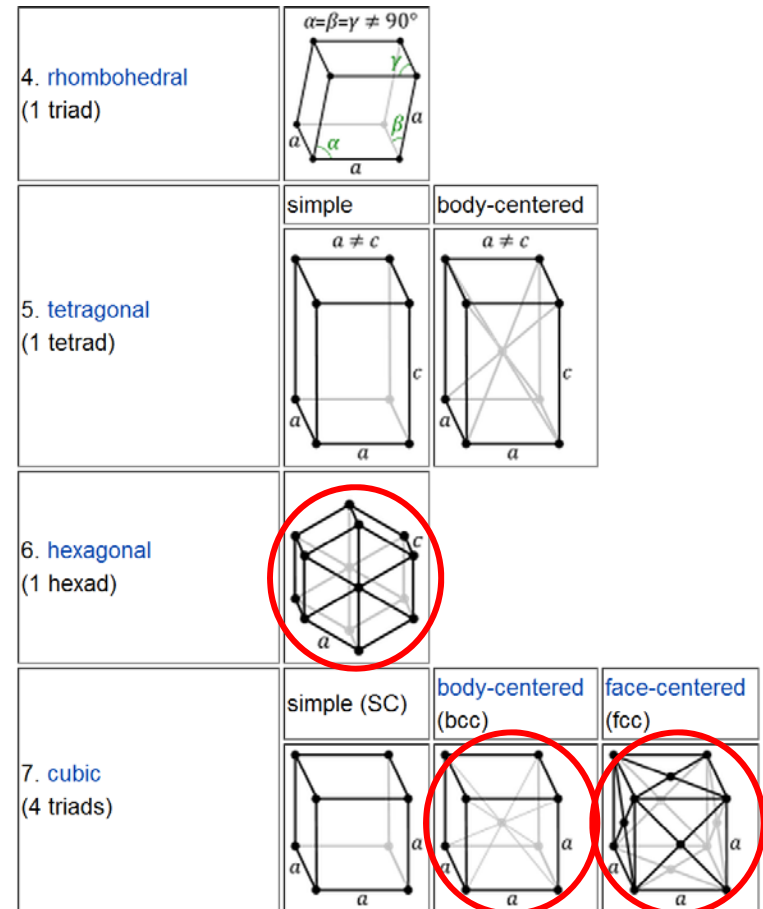
surface tension: amount of work required to create new area on the surface of a liquid ($\text{J/m}^2 = \text{N/m}$)



<http://en.wikipedia.org/wiki/File:Wassermolek%C3%BCleInTr%C3%B6pfchen.svg>

Bravais lattice system – in 3 dimensions

- all of the naturally occurring crystals can be classified into one of these lattice systems
- the most common lattices (c.f. red circles)
 - hexagonal (e.g. graphite)
 - bcc (metals)
 - fcc (NaCl salt crystals)



http://en.wikipedia.org/wiki/Crystal_structure



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1. mixtures
2. miscibility
3. solubility
4. azeotropes, eutectic systems
5. colligative properties
 - lowering of vapor pressure
 - freezing point depression, boiling point elevation
 - osmosis pressure





Mixtures

multicomponent solutions

- mixtures – created by mixing of two or more chemical substances
- no chemical reaction between the components
- chemically heterogenous systems
- solution: liquid state mixture
- usually one of the components is in excess, this is called solvent
- characteristic descriptors:
 - concentration, mole-, volume- or mass fraction



Solutions

real solutions

- contains molecules, unchanged, non dissociated

electrolyte solutions

- contains ions from the dissolved compound, smaller parts of the original molecule

• colloid solutions

- 5 nm to 500 nm sized particles dispersed, not molecules

- particles can be from different phase





Properties of mixtures

Rules for solutions

- usually, properties of a solution comes additively from the properties of the composing materials

in case of 2 components: $A = A_1x_1 + A_2x_2$, $x_2 = 1 - x_1$

in case of many components: $A = \sum_i A_i x_i$

A - a certain property of the mixture

- e.g. chemical potential

$$\mu_i = \mu_i^0 + RT \ln c_i$$

$$\mu = \mu_1x_1 + \mu_2x_2 = \sum_i \mu_i x_i$$

standard chemical potential of component i





Chemical potential

- denoted by μ
- in equilibrium, chemical potential tend to equilibrate in the system (like temperature)
- if two different systems are mixed the chemical potential difference will be the driving force for the changes (e.g. dissolving salt in water)
- in case of gas mixtures we can write

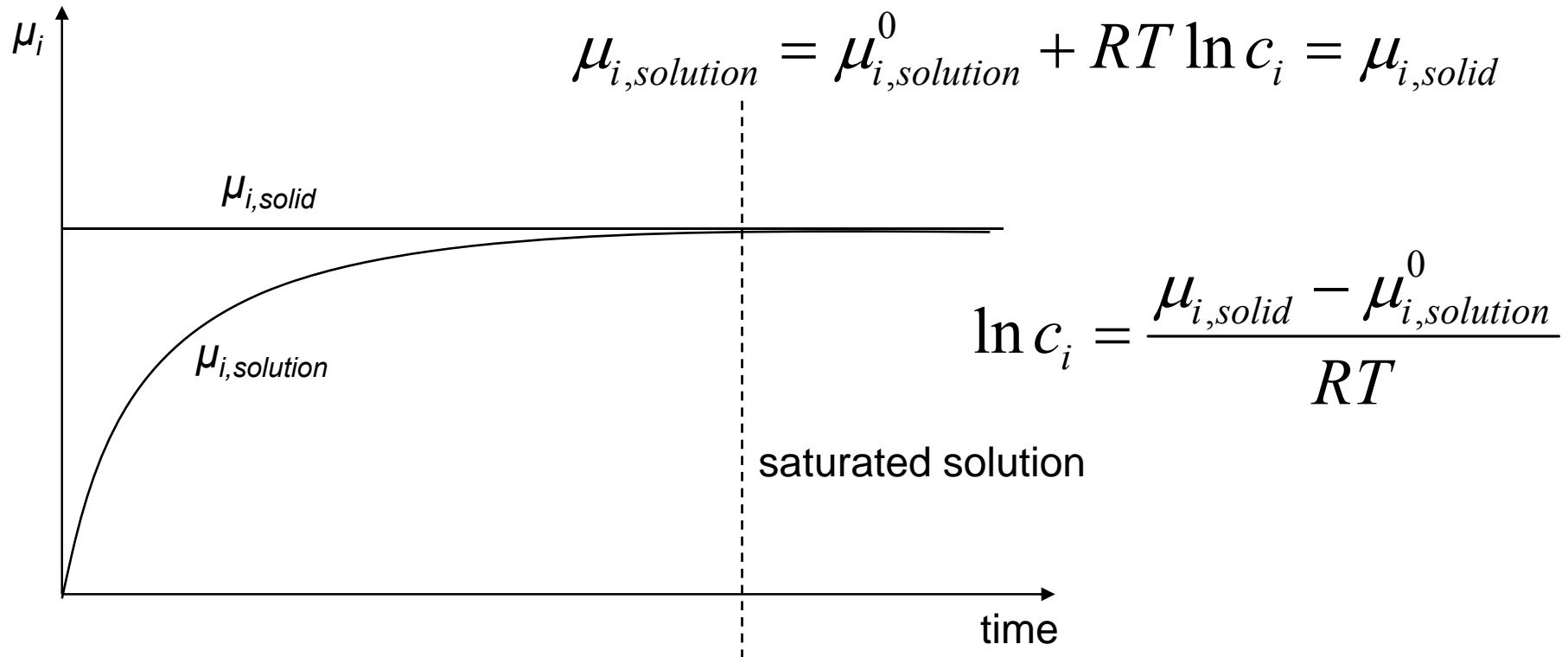
$$\mu_i = \mu_i^0 + RT \ln \frac{p_i}{p_0} = \mu_i^0 + RT \ln x_i$$

partial pressure of component i mole fraction of component i



Chemical potential – equilibration

dissolving salt in water: the chemical potential of the solution will be equal to the solid

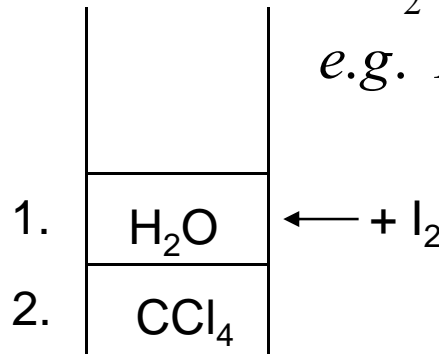


Solutions

- dissolving salt in two immiscible solvents
- partition coefficient can determine the ratio of dissolution in each solvent
- also, the chemical potential of the salt will equilibrate in the two solvents (e.g. 1 and 2):

$$\mu_1^0 + RT \ln c_1 = \mu_2^0 + RT \ln c_2 \Rightarrow \ln \frac{c_1}{c_2} = \frac{\mu_1^0 - \mu_2^0}{RT}$$

- dissolving iodine in H₂O and CCl₄



e.g. $K = 9 = \frac{c_2}{c_1}$ (in equilibrium)

$$c_2' = 0.9 \cdot c_2^0$$

$$c_1' = 0.1 \cdot c_1^0$$

- CCl₄ will contain 90%



Gas laws for mixtures – ideal gases

partial pressure : p_i

- the pressure of the i -th component if that would occupy the whole volume

Dalton's law (1801)

- the pressure of the gas mixture is the sum of the partial pressures
- can be derived from the ideal gas law:

$$\sum_i p_i = p$$

$$pV = nRT$$

$$pV = \sum_i n_i RT$$

$$p_i V = n_i RT$$

$$\left. \begin{array}{l} pV = \sum_i n_i RT \\ p_i V = n_i RT \end{array} \right\} \frac{p_i}{p} = \frac{n_i}{\sum_i n_i} = x_i \Rightarrow \underline{\underline{p_i = x_i \cdot p}}$$





Gas laws for mixtures – ideal gases

Amagat's law (1880) – law of partial volumes

- partial volume: V_i
- the volume of the gas mixture is the sum of the partial volumes

$$V_i = V \cdot x_i$$

$$V = \sum_i V_i$$

Raoult's law (1882)

- liquid-gas equilibrium of two or more components
- assuming ideal gas and ideal solution
- vapor pressure: is the pressure of a gas in equilibrium with its liquid state. (p^0)



Gas laws for mixtures – ideal gases

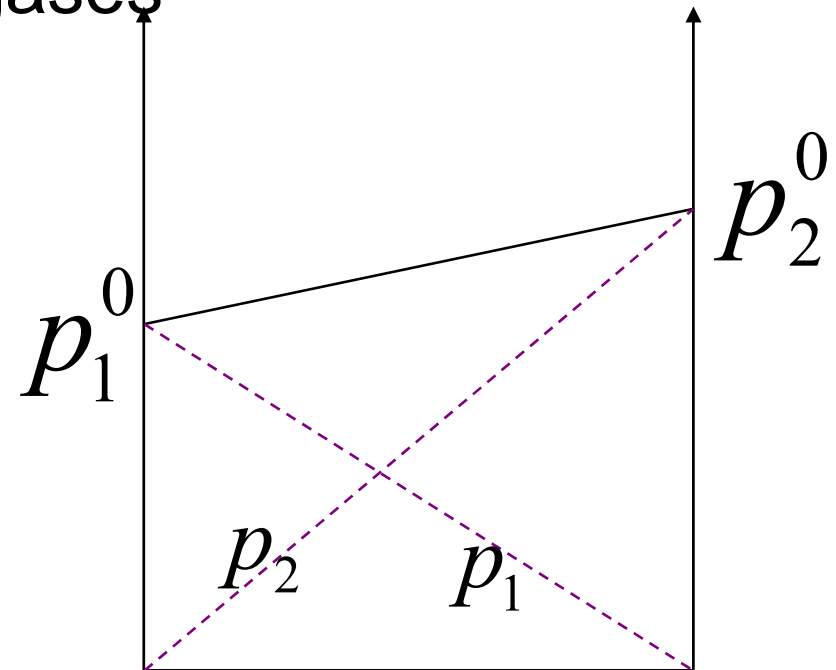
Raoult's law (1882)

- the vapor pressure of a liquid mixture is dependent on its composition (x_i) and vapor pressure (p_i^0) of each chemical components.

$$p = p_1 + p_2 = p_1^0 \cdot x_1 + p_2^0 \cdot x_2$$

$$p_i = p_i^0 \cdot x_i$$

more volatile component: the one with the higher vapor pressure (here: material 2)



$$x_1 = 1$$

$$x_2 = 0$$

$$x_1 = 0$$

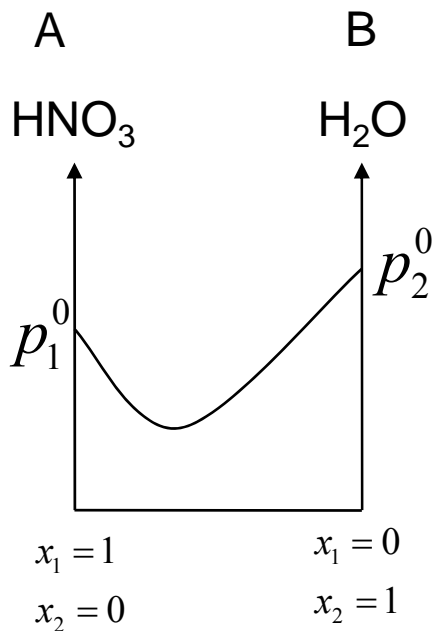
$$x_2 = 1$$

Gas mixtures – real gases

cohesive forces increase



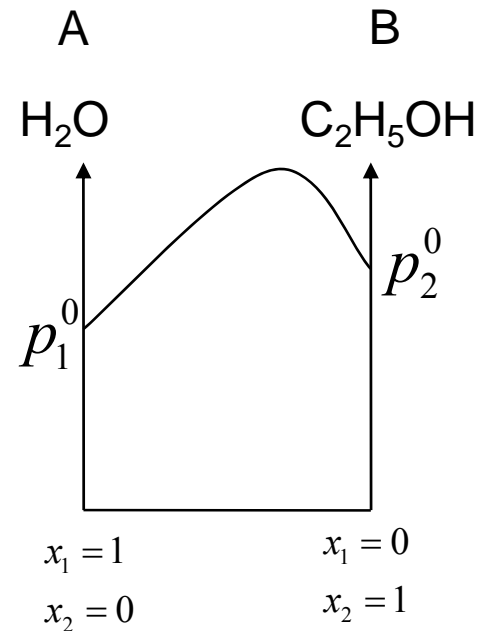
vapor pressure decreases



cohesive forces decrease



vapor pressure increases





Two component systems

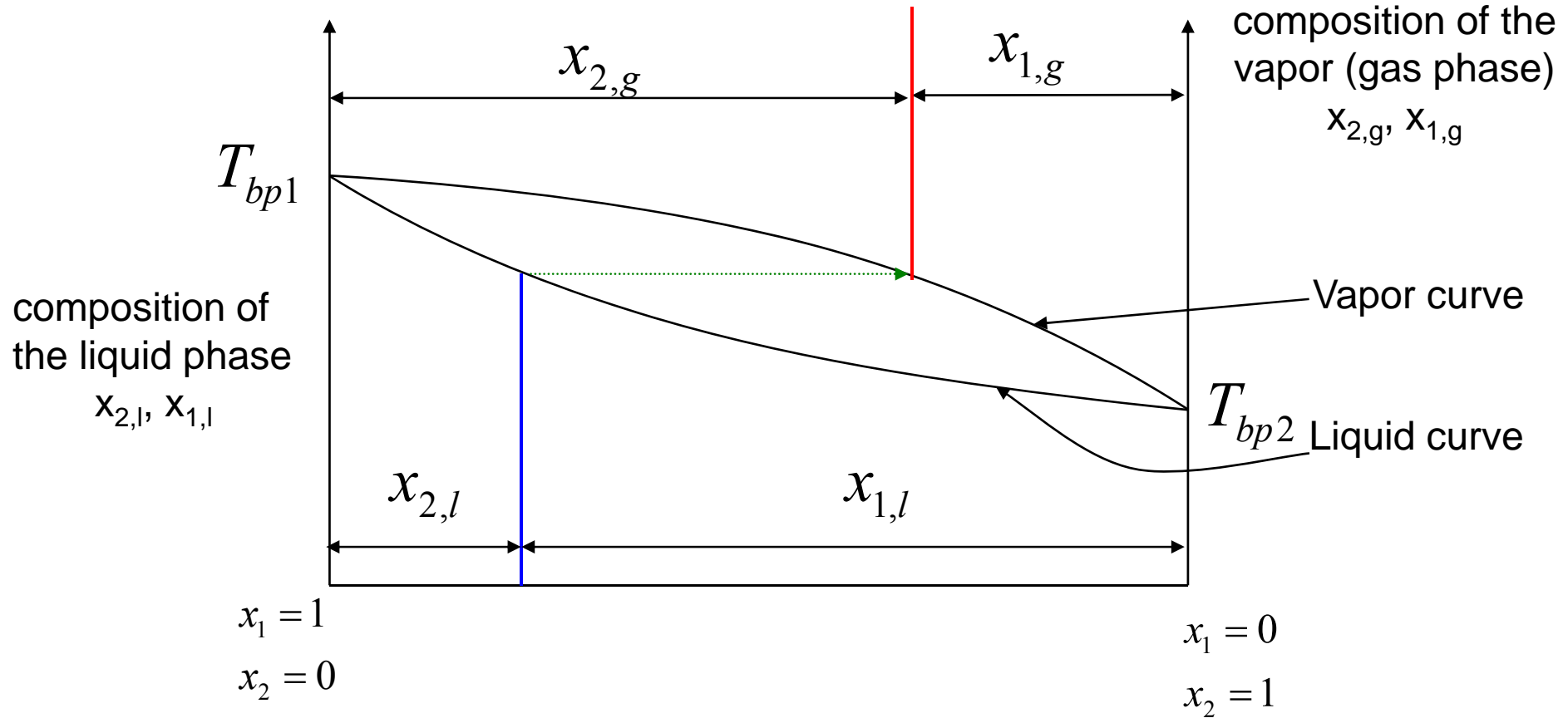
Liquid – vapor equilibrium

- pressure is held constant
- temperature and composition dependent
- in case of two compounds with different vapor pressure, the composition of the liquid phase and the gas phase in equilibrium will be different
- in general, the mole fraction of the volatile component will increase in the gas/vapor phase
- usually described by composition vs. temperature diagrams





Two component systems - liquid – vapor equilibrium





Two component systems

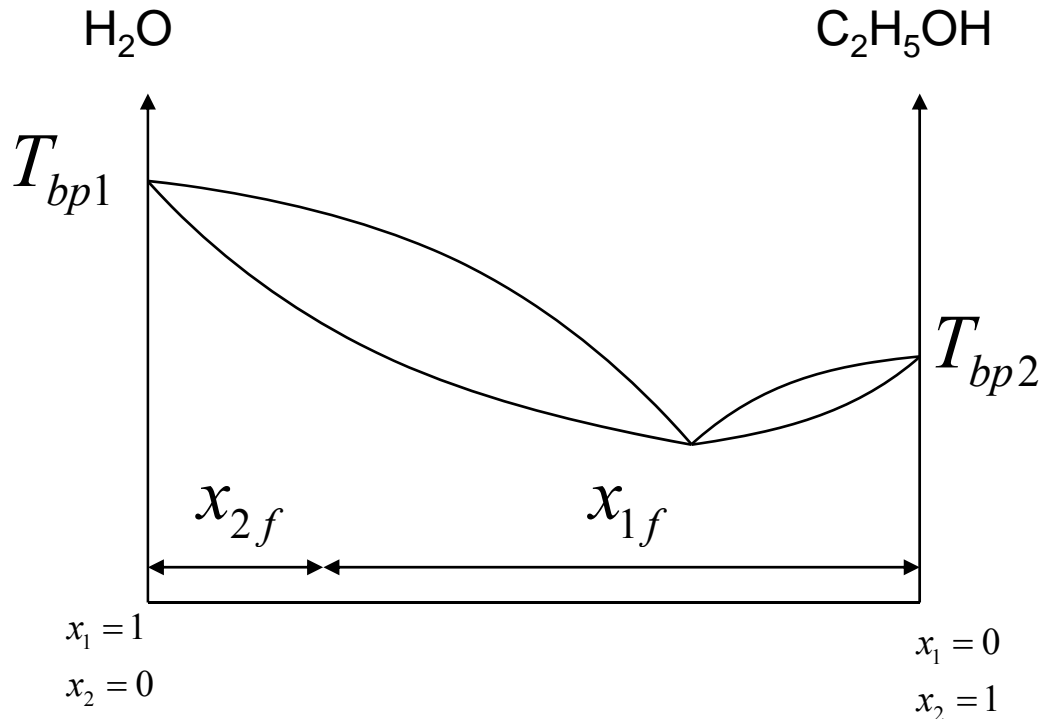
Liquid – vapor equilibrium

- the diagram shows the equilibrium of the liquid and the vapor phase (in a closed system)
- in real life situations (e.g. distillation) the system is not closed, the gas phase is being removed constantly
- removing the gas phase, which is enriched in the volatile component, the composition of the liquid phase is changing:
the mole fraction of the volatile component decreases
- this results in a change of boiling point (i.e. increase), and a change of gas phase composition (less volatile component than previously)
- the following processes are based on this equilibrium:
 - distillation, fractional distillation, continuous distillation, rectification (successive distillations)

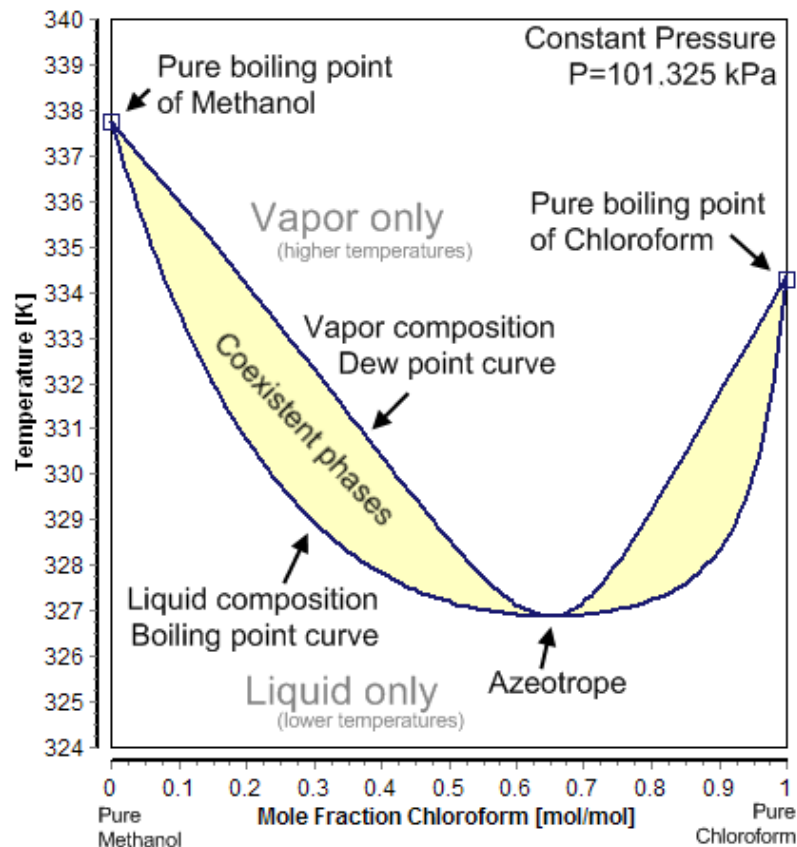


Two component systems - Liquid – vapor equilibrium

- the binary azeotrope composition behaves as a separate compound
- e.g.: water + ethanol at 96 m/m% ethanol composition: positive or minimum azeotropes



Liquid – vapor equilibrium: positive azeotropes

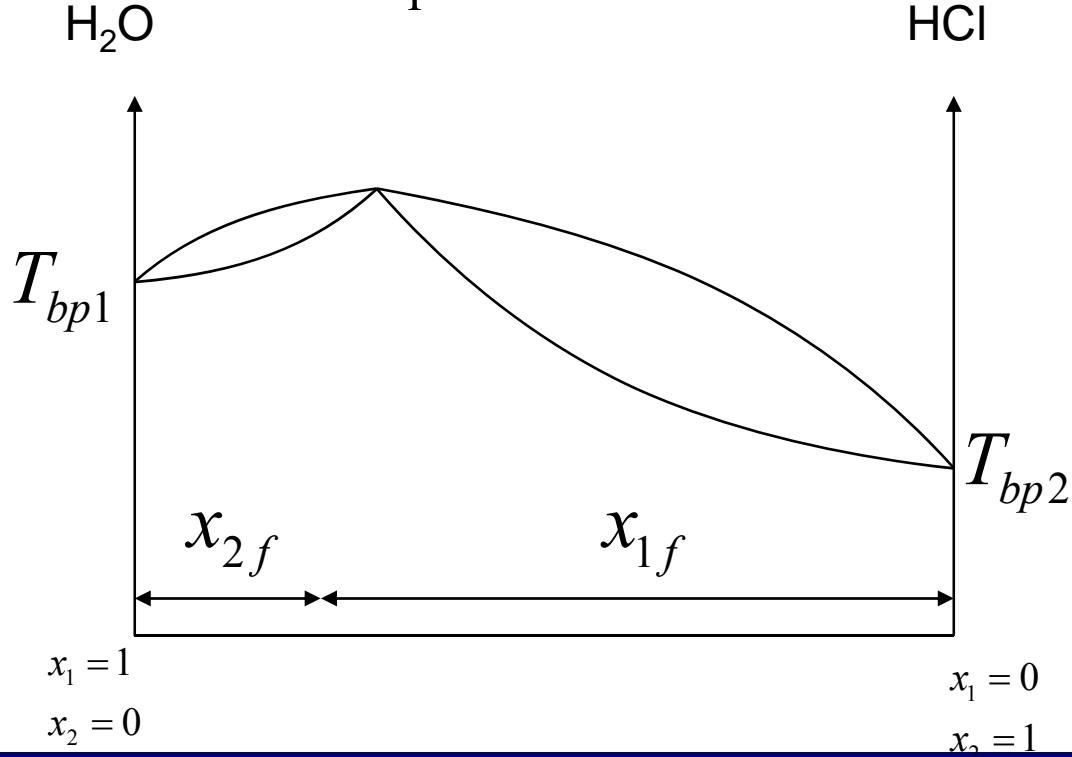


T-x diagram of a minimum azeotrope chloroform and methanol

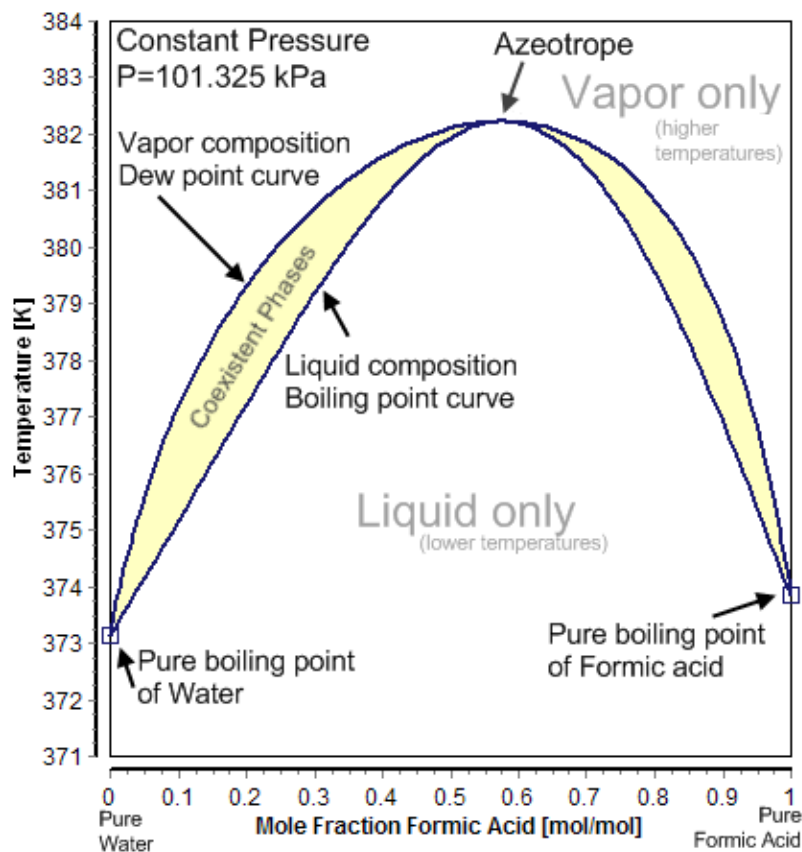
http://en.wikipedia.org/wiki/File:Positive_Azeotrope.png

Two component systems - Liquid – vapor equilibrium

- the azeotrope comp. has higher boiling point than any of the constituents
- e.g.: water + hydrochloric acid at 20 m/m% hydrochloric acid composition: negative or maximum azeotropes



Liquid – vapor equilibrium: negative azeotropes

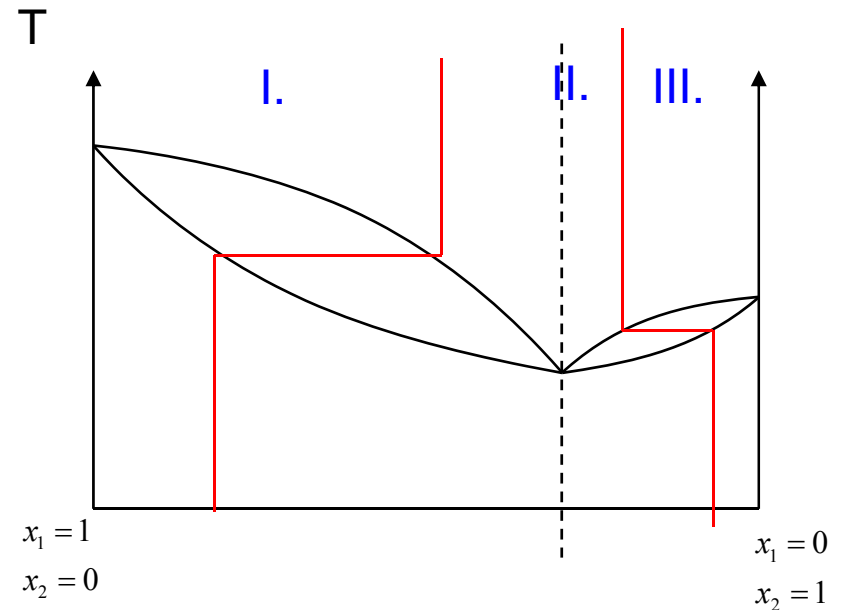


T-x diagram of a maximum azeotrope water and formic acid

http://en.wikipedia.org/wiki/File:Negative_Azeotrope.png

Two component systems - Liquid – vapor equilibrium

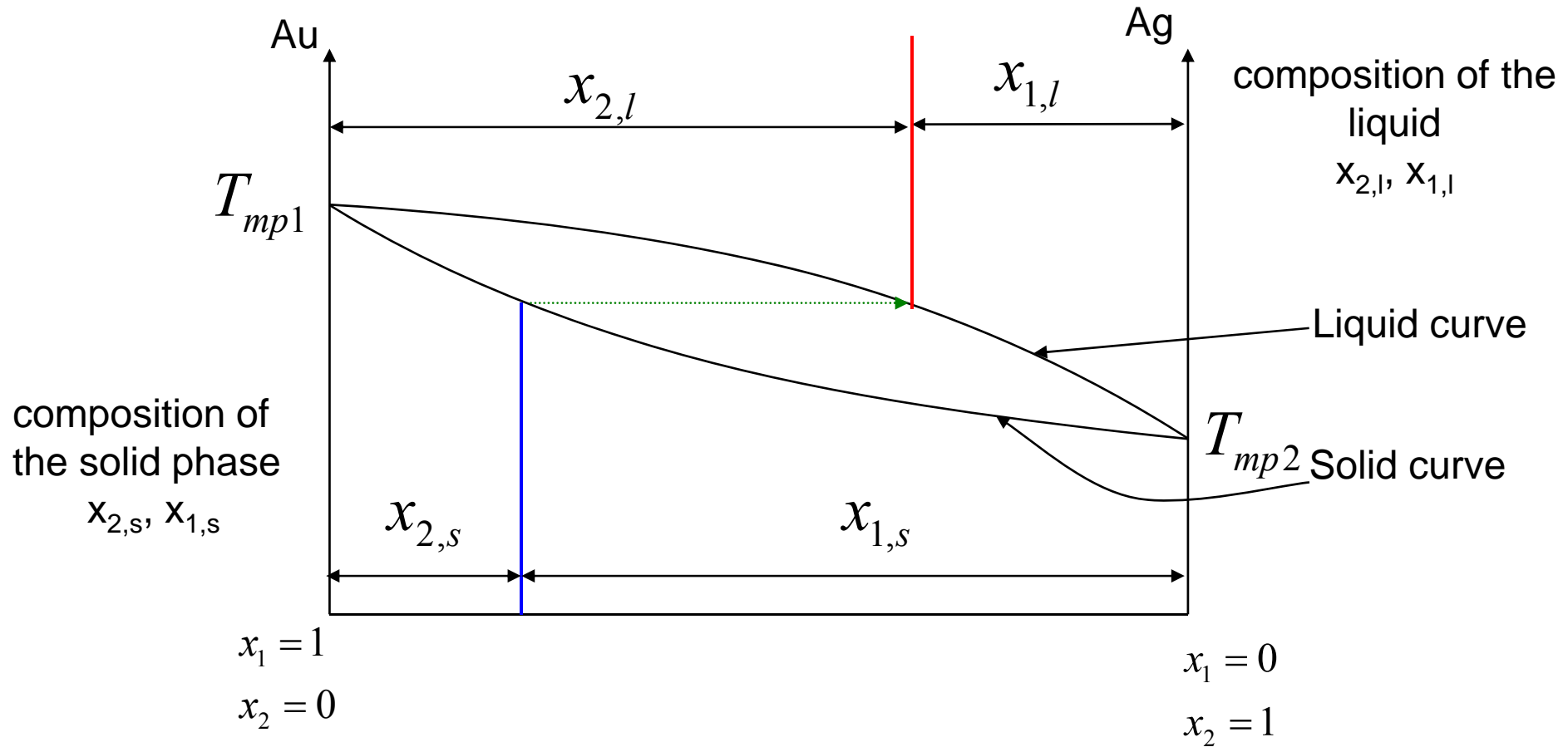
- the azeotrope behaves as a pure substance
- I. $x_{2f} < x_{2g}$, i.e. the more volatile component is enriched in the vapor
- II. $x_{2f} = x_{2g}$, i.e. the composition remains the same entering the vapor phase
- III. $x_{2f} > x_{2g}$, i.e. the less volatile component is enriched in the vapor



basically, the diagram can be separated into two simple diagrams

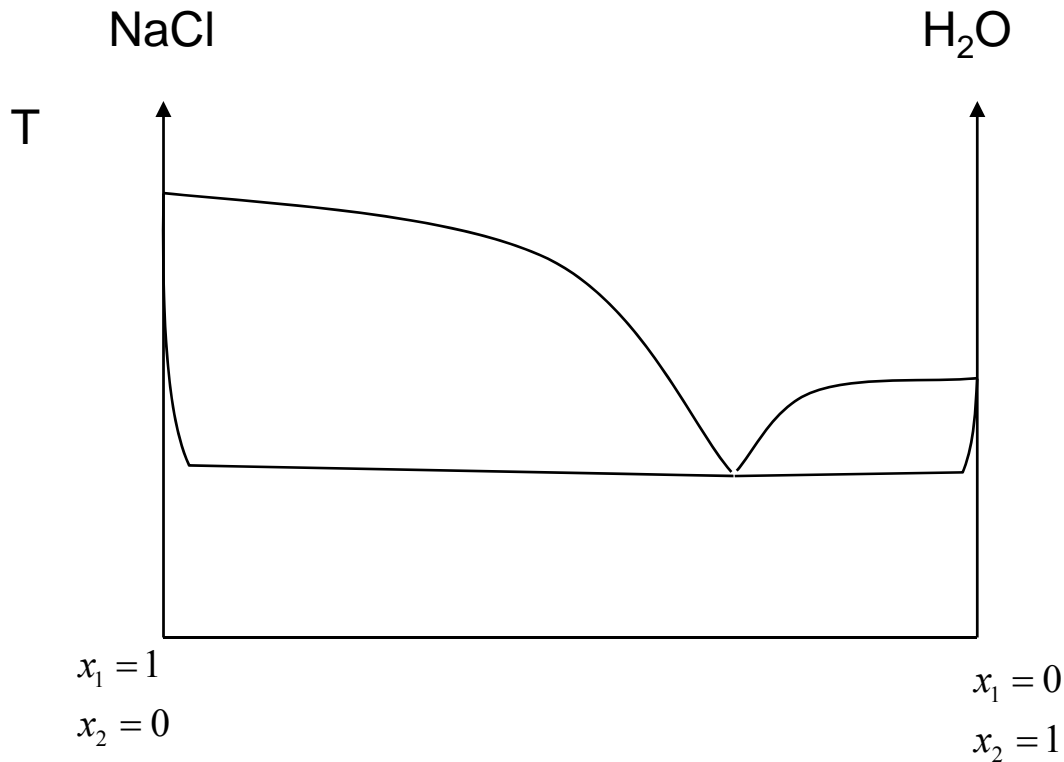


Two component systems – liquid – solid equilibrium



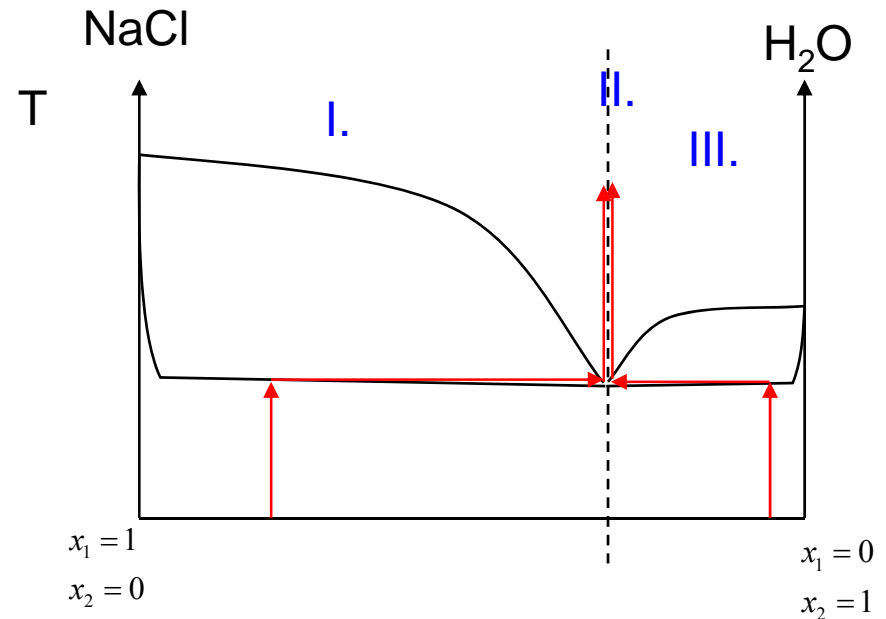
Two component systems - Liquid – solid equilibrium

- eutectic systems (most composite systems have as eutectics)
- melting a composition usually results in eutectic composition in the liquid phase



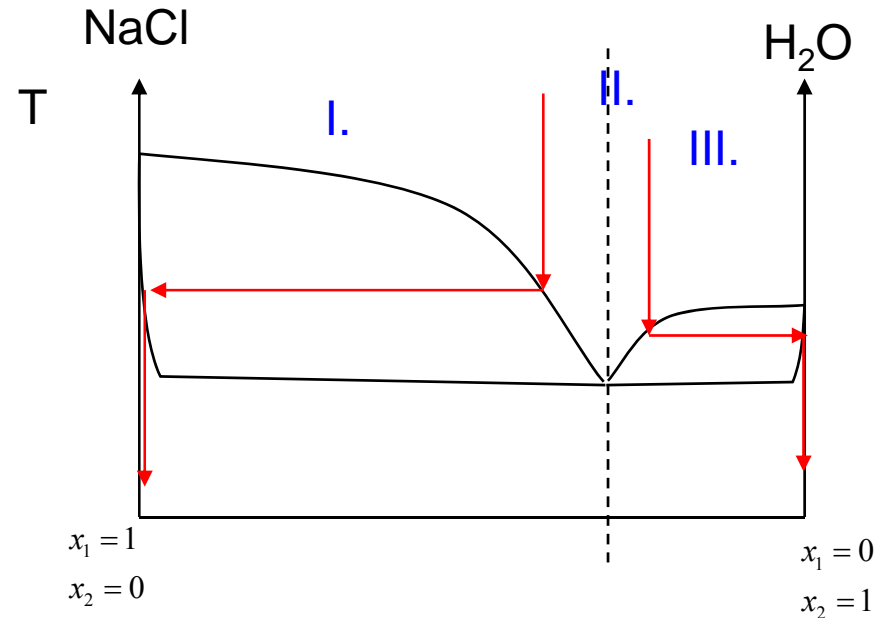
Two component systems - Liquid – solid equilibrium

- heating eutectic systems
- **I.** region: first eutectic composition, later mixture
- **II.** region: only eutectic composition
- **III.** region: first eutectic composition, later mixture
- upon melting any composition the melted solution will have a concentration near the eutectic



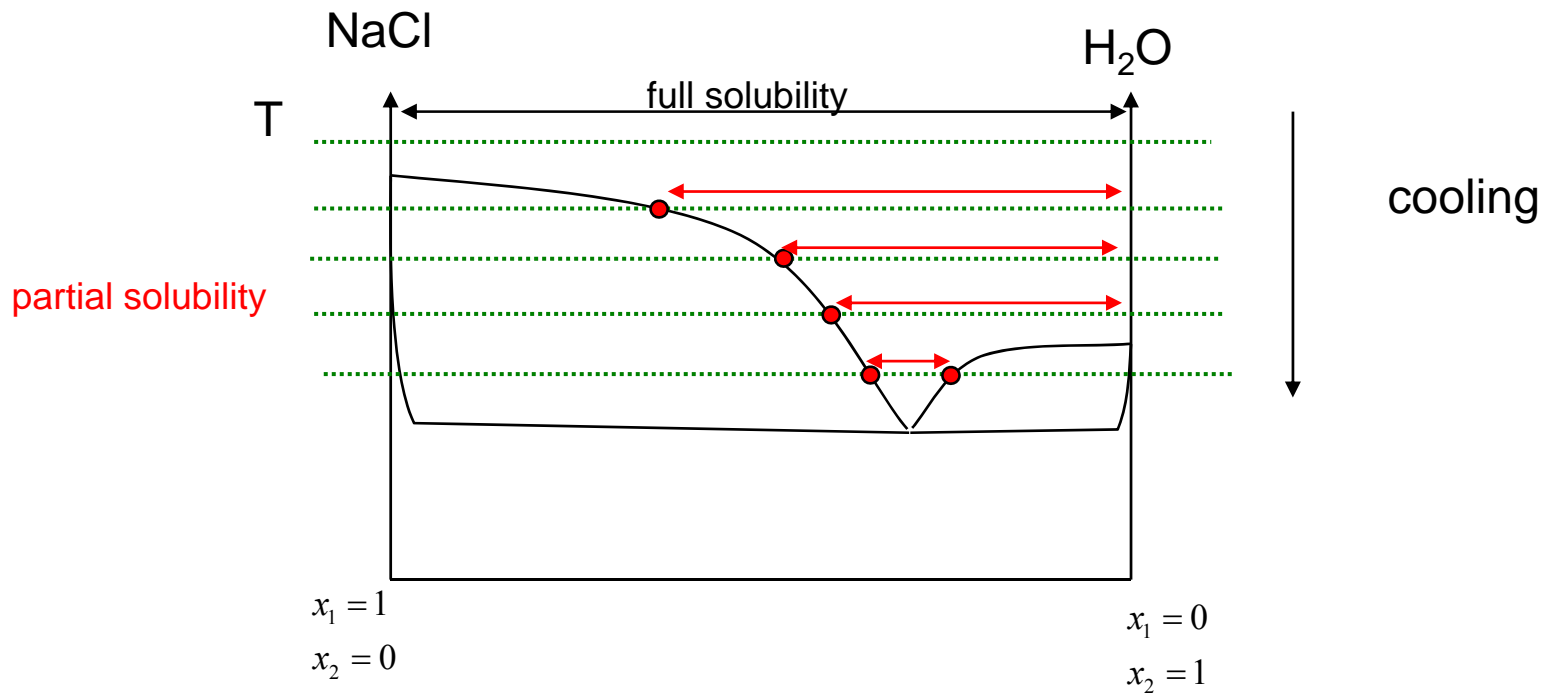
Two component systems - Liquid – solid equilibrium

- freezing an eutectic systems
 - compositions
 - I. region: first pure compound #1, later mixture
 - II. region: only eutectic composition
 - III. region: first pure compound #2, later mixture
-
- freezing a mixture usually results in one of the pure compounds to appear in the solid phase



Two component systems - Liquid – solid equilibrium

- eutectic systems
- the change of solubility at different temperatures
- solubility limit (saturated solutions...)





Two component systems – dilute solutions

Properties of dilute aqueous solutions

- colligative properties
 - these properties depend only on the solvent and the concentration of solute (not the chemical property of the solute)
 - depression of vapor pressure
 - boiling point elevation
 - freezing point depression
 - osmotic pressures





Two component systems – dilute solutions

Depression of vapor pressure

Raoult's law

$$p = p_1^0 \cdot x_1 + p_2^0 \cdot x_2, \quad x_2 \ll x_1, \quad p_2^0 \ll p_1^0$$

$$p = p_1^0 (1 - x_2)$$

$$x_2 = \frac{\Delta p}{p_1^0} = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1}$$

can be used to determine molar mass

$$M_2 = \frac{g_2}{g_1} M_1 \frac{p_1^0}{\Delta p}$$

where g_2 is the mass of the solute





Two component systems – dilute solutions

Boiling point elevation

Freezing point depression

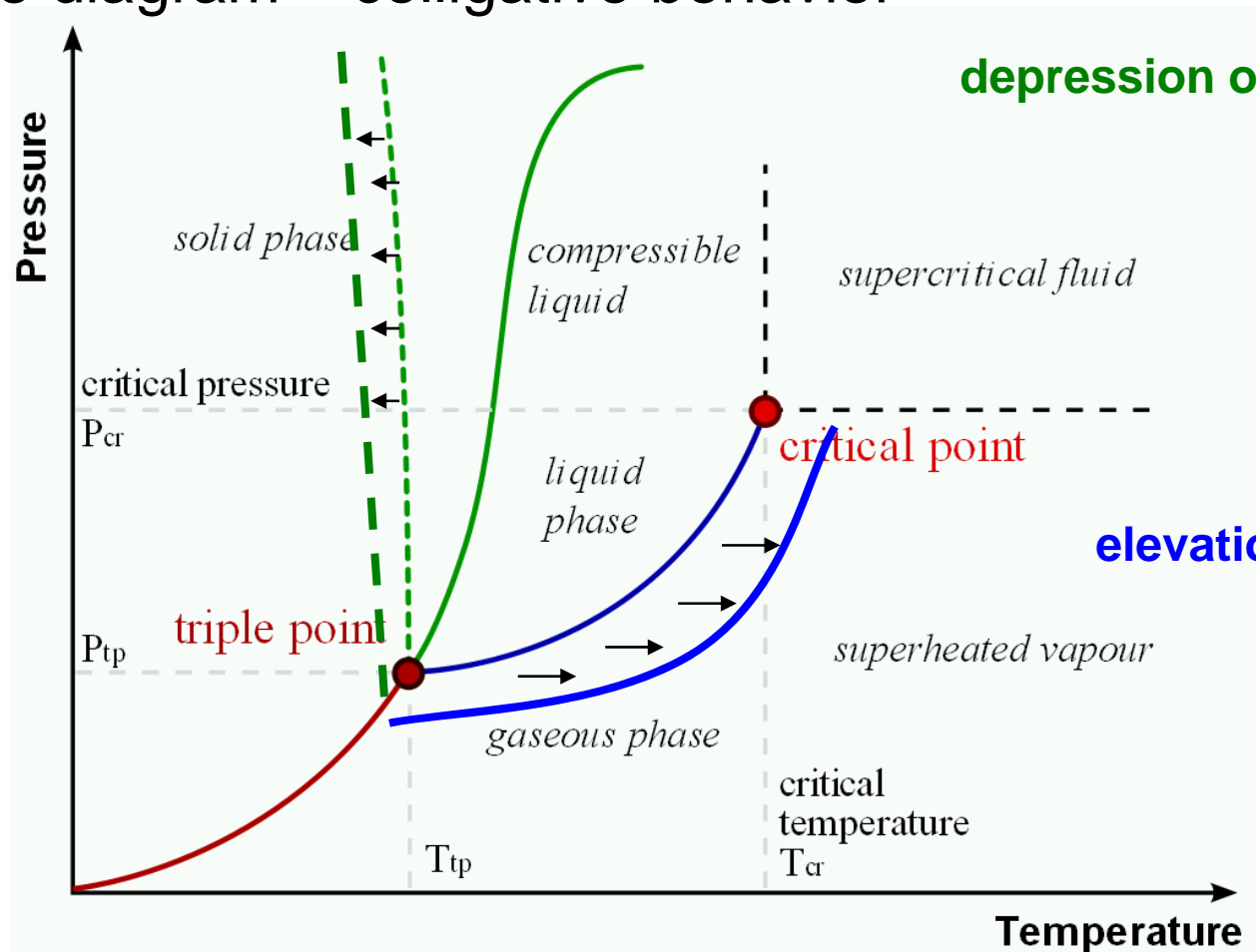
$$\Delta T = \Delta T_M \cdot c_R \longleftarrow \text{Raoult concentration}$$

- requires dilute solution ($c_R < 1$)
- total dissolution is necessary
- absence of chemical reactions
- in case of freezing, only the solvent becomes solid (cf. previously – eutectic systems)





Phase diagram – colligative behavior



<http://en.wikipedia.org/wiki/File:Phase-diag2.svg>



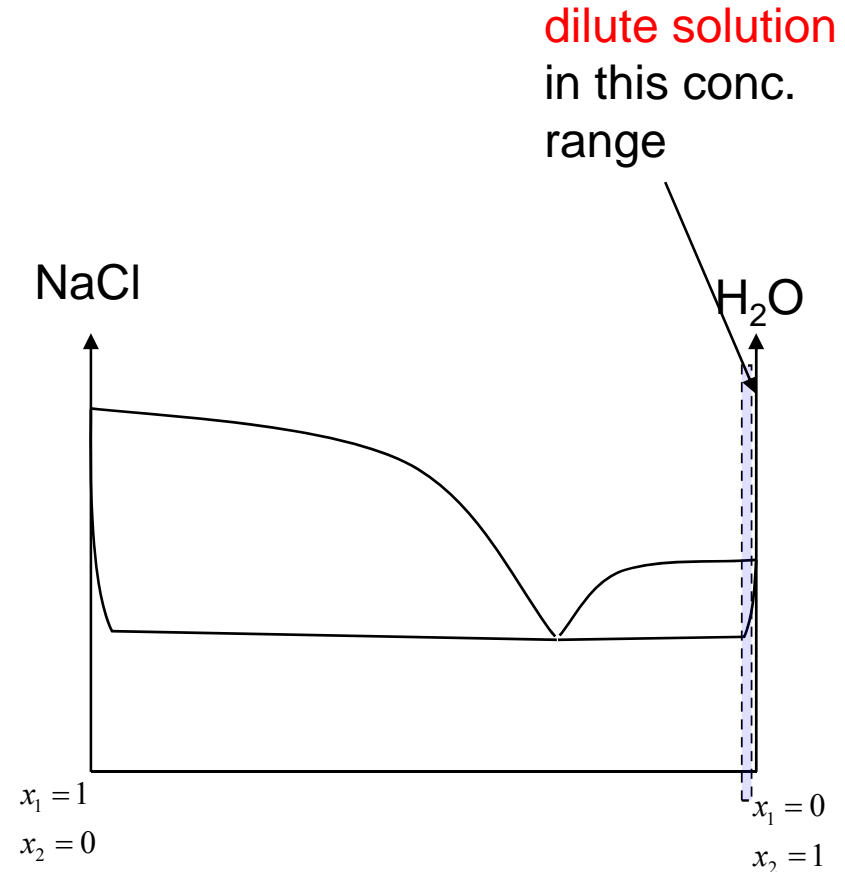
Two component systems – dilute solutions

Boiling point elevation

Freezing point depression

application of these properties

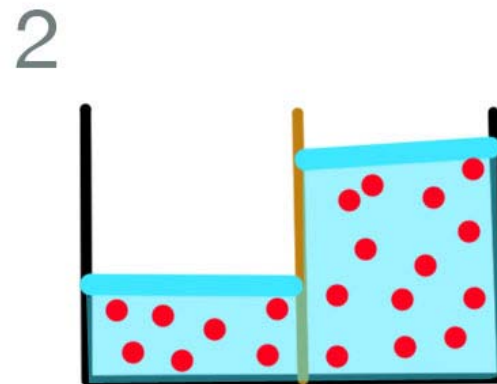
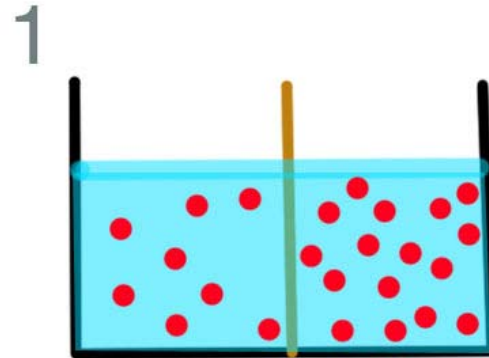
- salting icy roads (basically decreases the melting point of the mixture)
- winter engine coolants, or windshield cleaners
- heat transfer medium in radiators



Two component systems – dilute solutions

Osmotic pressure

- two different concentration compartments are separated by a semipermeable membrane
- chemical potential difference arises, drives the system to the equilibrium
- the solvent is diluting the more concentrated side
- hydrostatic *pressure* difference



<http://commons.wikimedia.org/wiki/File:Osmose2tolk.jpg>



Two component systems – dilute solutions

Osmotic pressure

- Pfeffer's law (at constant temperature)

$$\pi \cdot \varphi = \text{constant} \quad \frac{1}{c_m} = \varphi \quad \text{amount of dilution}$$

- van't Hoff's law (temperature dependence)

$$\pi = \pi_0 (1 - \alpha \cdot T)$$

- combined: Pfeffer - van't Hoff's law

$$\frac{\pi_0 \varphi_0}{T_0} = \frac{\pi \cdot \varphi}{T}, \quad \pi \cdot \varphi = R \cdot T, \quad \pi_0 = c \cdot R \cdot T_0,$$

$$\pi_0 = 2,27 \text{ MPa}$$





Two component systems – dilute solutions

Osmotic pressure

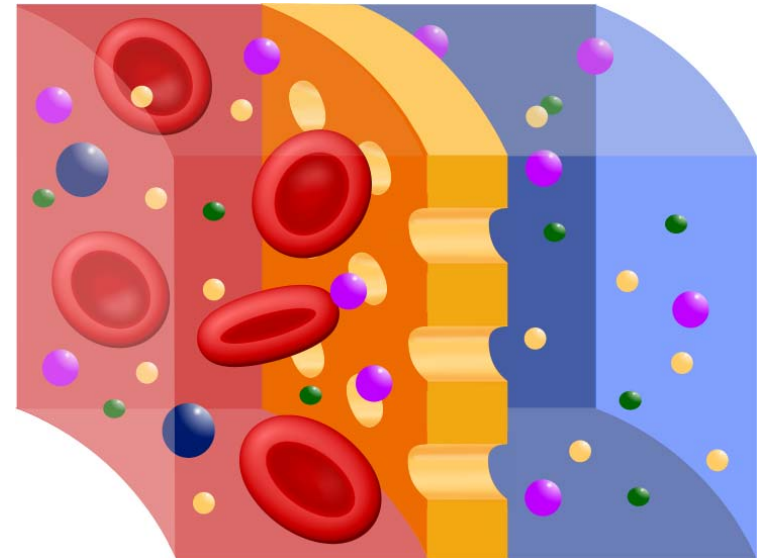
- applications
 - useful for molar mass determination
 - due to huge effects the molar weight of polimers can be measured
 - e.g. 1 M (mol/dm³) → $\pi = 2,27$ MPa !
 - e.g. 10⁻³ M anyagnál → $\pi = 2,27$ kPa
- cons
 - ideal semipermeable membrane is non-existent
 - reaching the equilibrium is a slow process



Two component systems – dilute solutions

Osmotic pressure

- in living organisms the balance of the osmotic pressure is critical
- i.e. keeping the important molecules inside the cell
- the following effects can be observed with different solutions
 - hypertonic: the solution is concentrated, causes the cells to shrink
 - hypotonic: the solution is dilute, causes the cells to swell
 - isotonic: equal concentration (in osmotic sense) no cell deformation

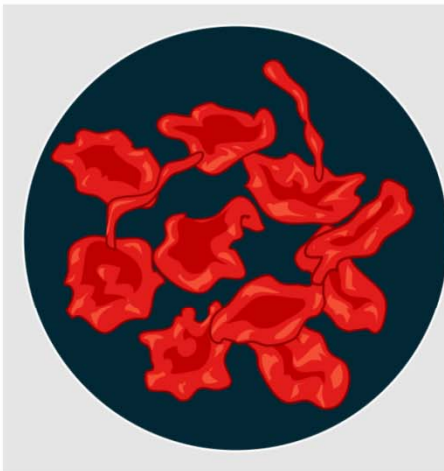


http://commons.wikimedia.org/wiki/File:Semipermeable_membrane.png

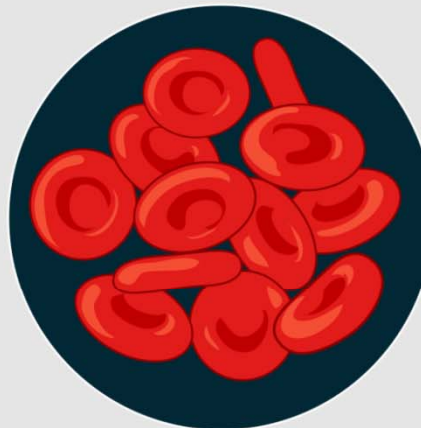


Osmotic pressure

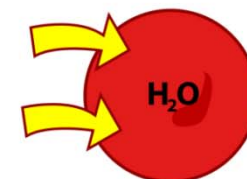
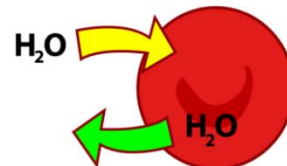
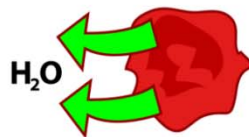
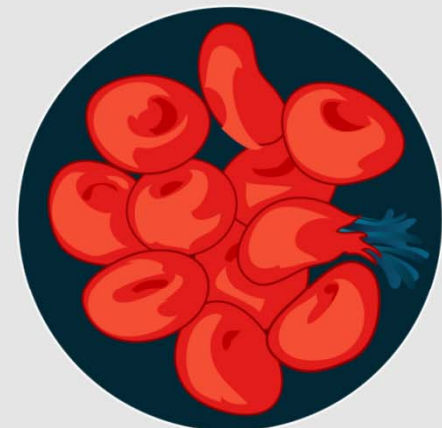
Hypertonic



Isotonic



Hypotonic



http://commons.wikimedia.org/wiki/File:Osmotic_pressure_on_blood_cells_diagram.svg



Next – Thermodynamics

1. Laws of thermodynamics
2. Chemical thermodynamics
3. Extensive and intensive quantities
4. Heat
5. Entropy
6. Enthalpy
7. Gibbs free energy
8. Equilibrium

