General and Inorganic Chemistry Department,
National Technical University “Kharkiv Polytechnic Institute”

Properties of solutions

Responsible Lecturer: **Andrey V. Kramarenko**
e-mail: `andrii.kramarenko@khpi.edu.ua`

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Part I

Introduction

1 Definitions

- *Solution* is a variable composition homogeneous system being in chemical equilibrium
- Classification
  - ✓ **State of aggregation**: gas, liquid, solid (amorphous, crystal)
  - ✓ **Degree of dispersion**:
    - ∗ mechanical mixtures ($> 10^{-7}$ m),
    - ∗ colloids ($10^{-7} - 10^{-9}$ m),
    - ∗ true solutions ($< 10^{-9}$ m)
- The mechanical mixtures and colloids have special names

Other comp.	Basic component gas	 liquid	 solid
gas	–	foam	porous systems
liquid	fog	emulsion	capillars
solid	smoke, *aerosol*	suspension	solid solution

- *Gel* is a 3D-structure formed by polymeric component with cavities in this structure filled with another component.
- *Sol* is dispersed system based on a liquid (lyosol) or gas (*aerosol*).

2 Describing solution composition

- *Solvent* and *solute* is a pure substances from which the solution is prepared
- *Solvent* is a component
  1. which determines the solution state of aggregation
  2. whose amount is greatest
- The ways of describing solution composition
  - ✓ Mole fraction $x_i = \frac{n_i}{\sum_j n_j}$ and $\sum_i x_i = 1$!
  - ✓ Mass fraction $\omega_i = \frac{m_i}{\sum_j m_j}$, $(\sum_i \omega_i = 1)$
  - ✓ Molarity $c_i = \frac{n_i}{V_{\text{solution}}}$, $\quad [c] = \text{mol/L} \equiv \text{M}$

  - ✓ Molality $\tilde{m} = b = \frac{n_i}{m_{\text{solvent}}}, \quad [\tilde{m}] = \text{mol/kg of solvent}$
  - ✓ *Equilibrium concentrations*: $c_{\text{eq}}(SO_4^{2-}) \equiv [SO_4^{2-}]$

- *Solubility, s* is a maximum concentration of solution
  - ✓ Solution having such a concentration is a **saturated** one
  - ✓ Unsaturated solutions have a concentration lower than s
  - ✓ Supersaturated solutions are always unstable so excess solute amount can release easily

Crystalline hydrates

- *Crystalline hydrates* is a crystals which content a certain amount of water
  - ✓ because solute "binds" the water
  - ✓ An examples: $CuSO_4 \cdot 5H_2O$, $Na_2SO_4 \cdot 10H_2O$
  - ✓ *Hygroscopicity* is an ability to absorb water vapour from the air

- A problem. In 100 g of water 40 g $CuSO_4 \cdot 5H_2O$ is dissoved. What is the $CuSO_4$ mass fraction $\omega(CuSO_4)$ in this solution?
  - ✓ $\omega(CuSO_4) = \dfrac{m(CuSO_4)}{m_{\text{soln}}}$, $m_{\text{soln}} = 100 + 40 = 140$ g
  - ✓ $\dfrac{m(CuSO_4)}{M(CuSO_4)} = \dfrac{m(CuSO_4 \cdot 5H_2O)}{M(CuSO_4 \cdot 5H_2O)} = n_{\text{hydrate}}$
  - ✓ $m(CuSO_4) = \dfrac{M(CuSO_4) \cdot m(CuSO_4 \cdot 5H_2O)}{M(CuSO_4 \cdot 5H_2O)} = \dfrac{159.5 \cdot 40}{249.5} \approx 26$ g
  - ✓ $\omega(CuSO_4) = \dfrac{26}{140} = 0.1857 \approx 19\%$

Part II

Ideal solutions properties

3 The concept of an ideal solution

- *Ideal solution* is a solution in which there is no specific chemical interaction between the components
  - ✓ particles are mixed homogeneously

  - ✓ very diluted solutions of one weak-polar substance in another one are very close to ideal

- Properties of ideal solution determines by its composition, not by nature of its components!

- Dependence of quantity P for ideal solution can be expressed as follows:

$$P_{\text{soln}} = x_1 \cdot P_1 + x_2 \cdot P_2 + \ldots + x_i \cdot P_i = \textstyle\sum_n x_n \cdot P_n$$

- For example, for the density ρ of two-component ideal solution:

$$\rho_{\text{soln}} = x_1 \cdot \rho_1 + x_2 \cdot \rho_2$$

4 Raoult's and Henry's laws

- The vapour pressure above the solution is determined by its composition

- Total vapour pressure above the solution: $p_{\text{tot}} = p_{\text{A}} + p_{\text{B}}$
  Notations: A is a solute; B is a solvent

- **Raoult's law** (1886): a vapour pressure of solvent above the solution is proportional to solvent mole fraction $p_{\text{B}} = p^{\circ}_{\text{B}} x_{\text{B}}$,
  where p°_{B} is vapour pressure above the pure solvent

- Another formulation: *relative decrease in vapor pressure of solvent* is equal to **mole fraction of solute**:

$$\frac{p^{\circ}_{\text{B}} - p_{\text{B}}}{p^{\circ}_{\text{B}}} = x_{\text{A}}$$

- The constrain is that solute A must be non-volatile, $p_{\text{A}} \approx 0$. The solution of sugar in water, for example.

- If solute A is volatile ($p_{\text{A}} \gg 0$) it is impossible to neglect its vapour pressure

- **Henry's law** (1803): $x_{\text{A}} = kp_{\text{A}}$ – gas solubility x_{A} is proportional to its partial pressure

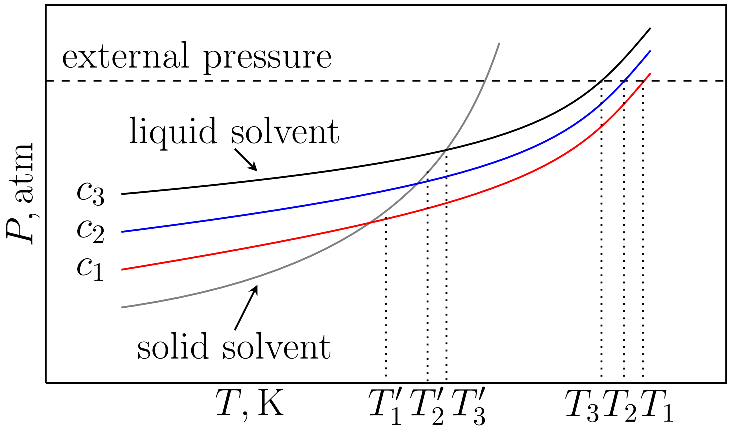
- As a consequence, abrupt pressure drop causes releasing of gas dissolved

- The ***Decompression sickness*** can be mentioned for example

- The increase in pressure always increases the solubility of gases in liquids (carbonated drinks)

- The vapour pressure lowering influent on boiling and freezing points of solution

- The solution boils when the vapour pressure is equal to atmospheric one
- The solution freezes when the vapour pressure due to the solid phase becomes equal to the vapour pressure due to the liquid phase
    - ✓ The vapour is present even due to the solid solvent so wet linen becomes dry even in the frost
    - ✓ normally, pure solvent crystallizes out of the solution
- It is known, that *the solution boils at higher temperature and crystallizes at lower temperature than the pure solvent.* Why?
- Vapor pressure above solutions ($c_3 < c_2 < c_1$):

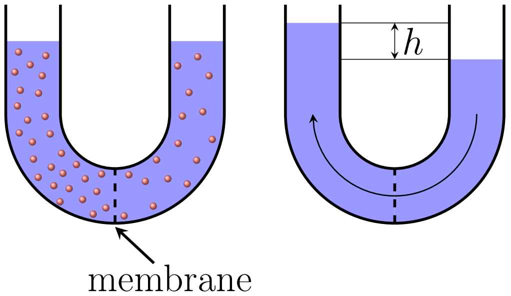


- It's obvious, that $T_3 < T_2 < T_1$, but $T'_3 > T'_2 > T'_1$!
- The change of temperature of freezeng and boiling points is used on analysis
    - ✓ *Ebullioscopy* is a technique of solution boiling point elevation ΔT_{boil} measurement;
    - ✓ *Cryoscopy* is a technique of solution freezing point depression ΔT_{freez} measurement;
- There is a simple relationship between ΔT and the composition of the solution
    - ✓ as it is mentioned above, molality b is quantity of solute in moles per 1 kg of solvent
    - ✓ $\Delta T_{\text{boil}} = K_{\text{E}} b$
    - ✓ $\Delta T_{\text{freez}} = K_{\text{C}} b$
    - ✓ K_{E}, K_{C} are the constants of solvent (reference data)
- Molar mass of solute A:

$$M(\text{A}) = Kb/\Delta T$$

5 Osmosis

- Osmosis is a phenomenon of spontaneous selective diffusion through semipermeable membrane



● is a solute, 🟦 is a solvent

- $p_{\text{exc}} = \rho g h$ is hydrostatic pressure
- $p_{\text{osm}} = cRT$ is van't Hoff equation
- Reversed osmosis is a forced transfer of solvent molecules under external pressure, may be used in water purification.