Syllabus

1. Introduction

2. Fluids

1. General Characteristics
2. Dispersions
3. Thermodynamics
4. Transport Phenomena
5. **Solutions**
6. Surface Tension
7. Electrical Properties
8. Optical Properties
9. Biological Fluids

Physics of Microfluidic Systems

1. Navier-Stokes Equation
2. Laminar and Turbulent Flow
3. Fluid Dynamics
4. Fluid Networks
5. Transport of Heat
6. Interfacial Surface Tension
7. Electrokinetics

2.5 Solutions

- Outstanding relevance for **chemistry** and **biology**
  - Natural carrier medium
- Often liquid („solvent“) and substance added („solute“)
- Concentrations expressed in quotients between
  - Weight
  - Volume
  - Moles of solute and solvent
- Notation for molar concentration c
  - E.g., for molecule CH_3COOH: $[CH_3COOH]$
- n-molar solution
  - Solution containing n moles of solute per liter

2.5. Solutions

2.5.1. Solvation

2.5.2. Mass Action Law

2.5.3. Electrolytes

2.5.4. Buffers

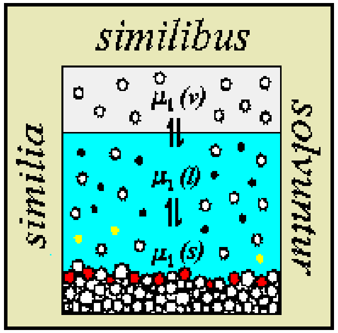
2.5.5. Limit of Solubility

2.5.6. Colligative Properties

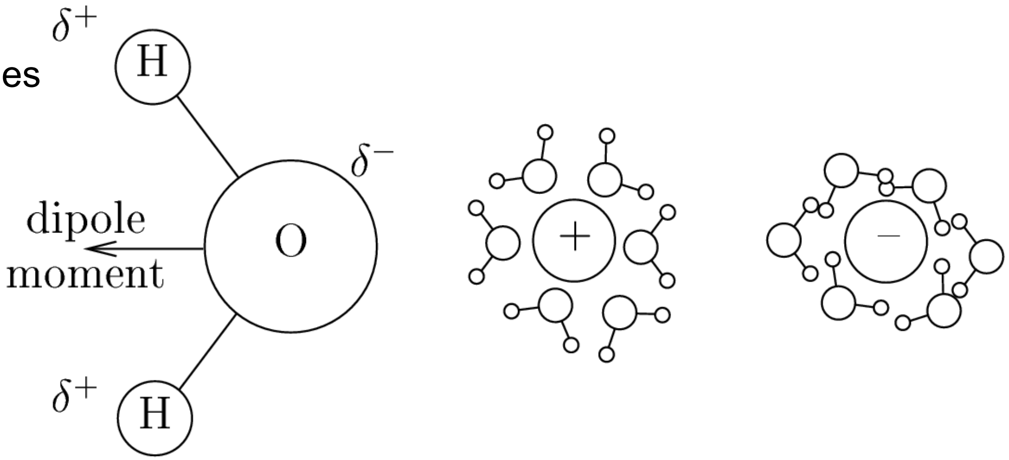
2.5.1. Solvation

- Intermolecular forces

$\Rightarrow$ **„like dissolves like“**



- Electric polarization of molecules
  - Example: water with dipole moment of $6.2 \cdot 10^{-30}$ C m
- Intramolecular bonds influence mutual polarization
- „Hydrogen bonding“
  - Mediated by hydrogen atoms (electro-positive)
  - Hydrogen ends attach to electronegative atoms forming complexes
  - „Association“
    - Between identical molecule types
  - „Solvation“
    - Between different molecule types



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2.5.2. Mass Action Law

- **Dynamic equilibrium**
    - **Reversible** chemical reaction
    - Equal reaction rates $dn\,/\,dt$ in forward and reverse direction
    - Stationary concentrations

$$\boxed{v\mathrm{V} w\mathrm{W} + \ldots \rightleftharpoons x\mathrm{X} + y\mathrm{Y} + \ldots}$$

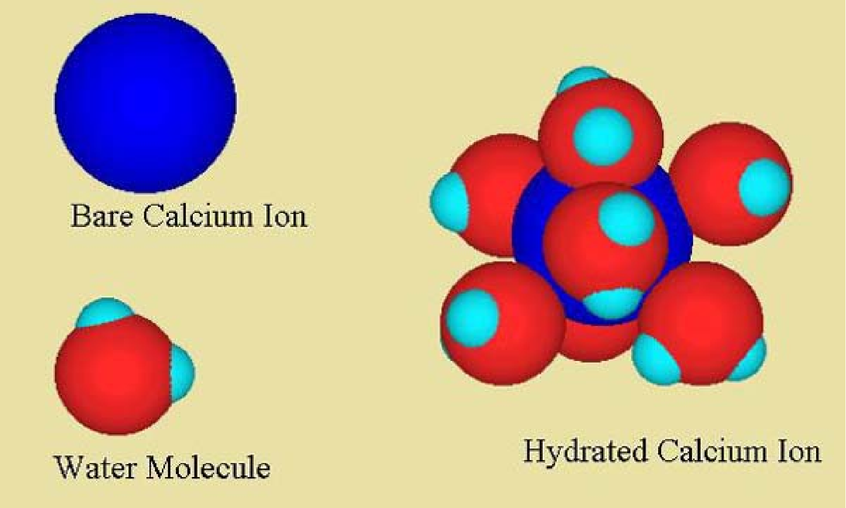
- Heterogeneous equilibrium between multiple phases
- **Le Chatelier**
    - Change in condition counteracted by shift in dynamic equilibrium
- Mass action law

$$\boxed{k_c = \frac{c^x(\mathrm{X})c^y(\mathrm{Y})}{c^v(\mathrm{V})c^w(\mathrm{W})}}$$

- Constant of equilibrium k_c
- Cato Guldberg and Peter Waage (1864)

2.5. Solutions

2.5.3. Electrolytes



- Free charge carriers
  - **Ions**

- Aqueous solutions of acids, bases, or salts, certain pure liquids and molten salts...
  - Acid: “proton-donator”
  - Base: ”proton acceptor”
- All inorganic acids, bases, and salts
- **Strong electrolytes**
  - E.g., NaOH (sodium hydroxide, also known as lye and caustic soda)
  - Complete dissociation when brought into solution or fused

2.5.3. Electrolytes

- **Weak electrolytes**
  - Partially remain in their molecular form
  - Mass action law for monovalent electrolytes like KCl (potassium chloride)

$$\kappa_c = \frac{[\mathrm{K}^+][\mathrm{Cl}^-]}{[\mathrm{KCl}]}$$

- Dilution law of Ostwald
  - Degree of dissociation a_c

$$\boxed{\alpha_c = \frac{\kappa_c}{2c}\left(\sqrt{1+\frac{4c}{\kappa_c}}-1\right)}$$

  - c: concentration of [KCl] and $[\mathrm{K}^+] = [\mathrm{Cl}^-]$
  - For strong electrolyte $a_c = 1$

2.5.3 Dissociation of Water and pH-Value

- Water
  - Weak electrolyte
  - Dissociation
  - More accurately
  - Mass action law

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$\boxed{2H_2O \rightleftharpoons H_3O^+ + OH^-}$$

$$\kappa_c = \frac{[H^+][OH^-]}{[H_2O]}$$

- **Ionic product**
  - Nearly constant H_2O concentration in diluted solutions

$$\boxed{\kappa_{\text{water}} = 1.0 \times 10^{-14} = [H^+][OH^-].}$$

- Pure water
  - Neutral solution at 25°C, $[H^+] = [OH^-] = 10^{-7}$ mol l^{-1}

$\Rightarrow a_c \ll 1$

2.5.3 Dissociation of Water and pH-Value

- **pH-value**

$$\boxed{\mathrm{pH} = -\log \frac{[\mathrm{H}^+]}{\mathrm{mol\,l^{-1}}} = \log \frac{\mathrm{mol\,l^{-1}}}{[\mathrm{H}^+]}}$$

  - ➢ $[\mathrm{H}^+] = 10^{-\mathrm{pH}}$

- Complementary **pOH-value**

$$\boxed{\mathrm{pH} + \mathrm{pOH} = 14}$$

  - ➢ Follows from ionic product

2.5.3 Activity

optional

- For given solution

$$\boxed{a = f_a c}$$

  - Debye-Hückel theory of solutions
  - (Coulomb) interactions between solute molecules
  - Motion of ions not independent
  - „Effective concentration“ with empirical factor f_a
  - f_a unity for non-electrolytes and smaller for electrolytes

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2.5.4. Buffers

- **Stabilization** of certain **pH-value**
  - Tolerating addition of small amounts of acids or bases
  - Composition of
    - Weak acid or base
    - In combination with salt of weak electrolyte
- Ethanoic acid and sodium acetate in identical concentrations

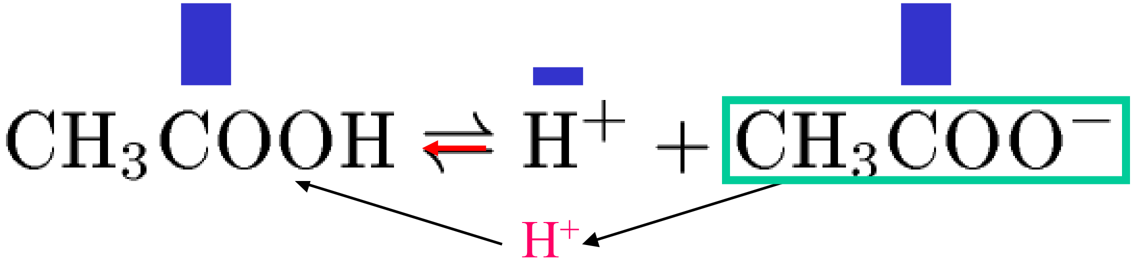
$$\boxed{\mathrm{CH_3COOH} \rightleftharpoons \mathrm{H^+} + \mathrm{CH_3COO^-}}$$

- Mass action law and known $\kappa_c = 1.8 \times 10^{-5}$

$$\boxed{[\mathrm{H^+}] = \kappa_c \frac{[\mathrm{CH_3COOH}]}{[\mathrm{CH_3COO^-}]}}$$

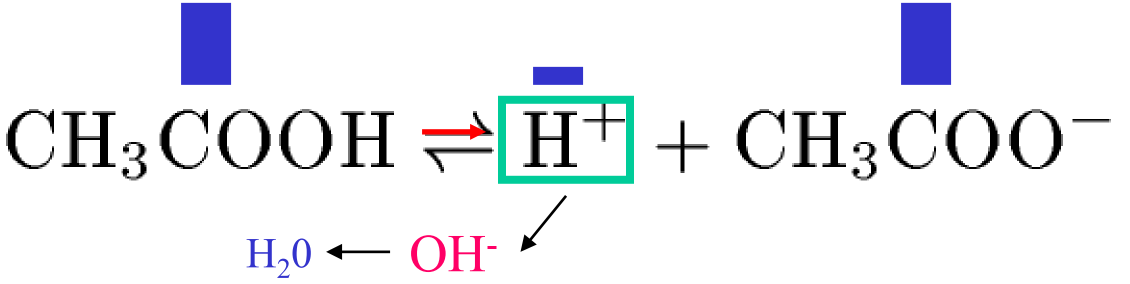
  - pH-value stabilized in vicinity of 4.7
    - $[\mathrm{CH_3COOH}]$ and $[\mathrm{CH_3COO^-}]$ exceed $[\mathrm{H^+}]$ by factor of 50,000

2.5.4. Buffers



$$CH_3COOH \rightleftharpoons H^+ + \boxed{CH_3COO^-}$$

- Addition of small amount of hydronium ions [H^+]
  - Quickly neutralized by large reservoir of acetate ions
  - Relative change in [CH_3COO^-] supplied by buffer negligible



$$CH_3COOH \rightleftharpoons \boxed{H^+} + CH_3COO^-$$

- Analogous: Small increase in number of hydroxide ions [OH^-]
  - Compensated by H^+ ions
  - H^+ ions quickly substituted by dissociation of salt from buffer

2.5.4. Buffers

optional

- **pK-value** of weak electrolyte

$$\boxed{\mathrm{pK} = -\log \kappa_c}$$

- Henderson-Hasselbalch equation

$$\boxed{\mathrm{pH} = \mathrm{pK} + \log \frac{[\mathrm{salt}]}{[\mathrm{acid}]}}$$

- Properly working buffer
  - Ratio between molecular form and ionic partner between 0.1 and 10
  - pH-range [pK - 1; pK + 1]

- Example: Ethanoic buffer with pK-value of 4.7
  - pH-values between 3.7 and 5.7

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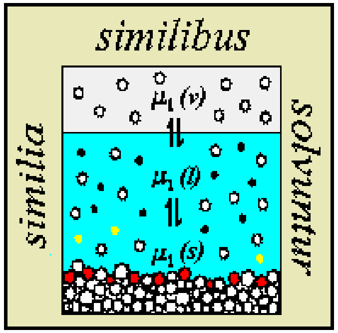
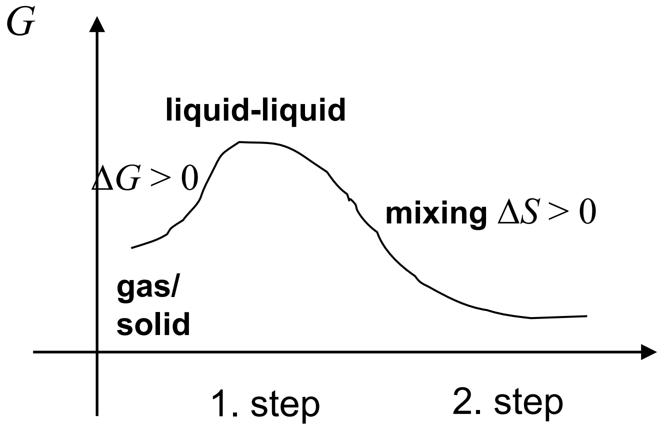


2.5.5. Limit of Solubility

- Dissolution of substances within one another
- Beyond limit of solubility, further addition leaves concentration in solution unchanged
- Thermodynamic analysis
  - Spontaneous process governed by $\Delta G < 0$
  - Two steps for phase transition
    - „preparation“
    - „liquid-liquid“ mixing
  - Preparative step accompanied by $\Delta G > 0$ for solids and gases
    - Counteracting mixing of phases
    - Second step must imply larger $\Delta G < 0$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$



2.5.5. Limit of Solubility - Gases

- Process of dissolution
  1. Constant-temperature condensation of pure gas to liquid ($\Delta G > 0$)
  2. Constant-temperature mixing of that liquid with solvent ($\Delta S > 0$)
- Henry's Law
  - Molar concentration c_{gas} of gas dissolved in liquid
  - Partial pressure p_{gas}
  - Valid: vapor pressure of gas $\gg$ vapor pressure of solvent

$$\boxed{c_{\mathrm{gas}} = k_{\mathrm{H}} p_{\mathrm{gas}}}$$

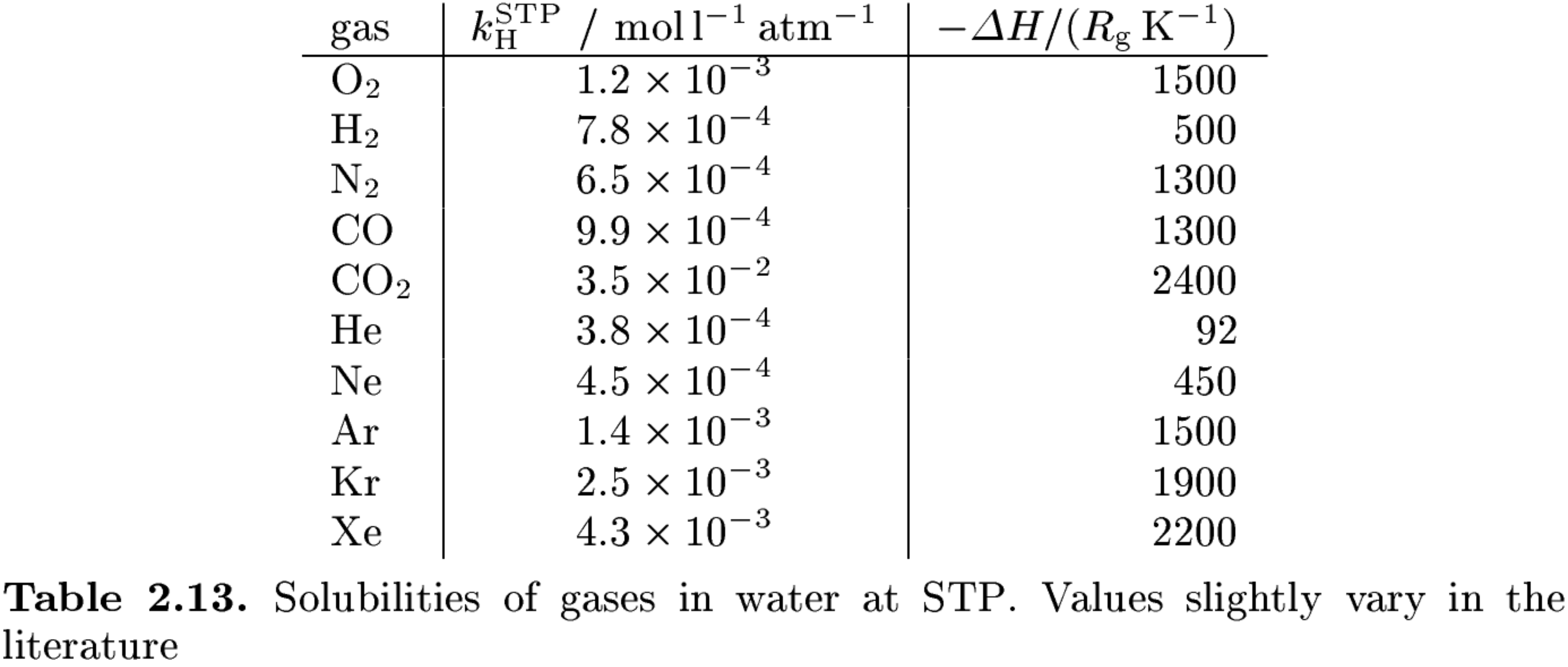
- Henry's Law constant k_{H}

$$\boxed{k_{\mathrm{H}}(T) = k_{\mathrm{H}}^{\mathrm{STP}} \exp\left[-\frac{\Delta H}{R_{\mathrm{g}}}\left(\frac{1}{T} - \frac{1}{298.15\,\mathrm{K}}\right)\right]}$$

- Solubility
  - Decreases with T
  - Increases with partial pressure of gas p_{gas}

$$T\uparrow \;\Rightarrow\; k_{\mathrm{H}}(T)\downarrow$$

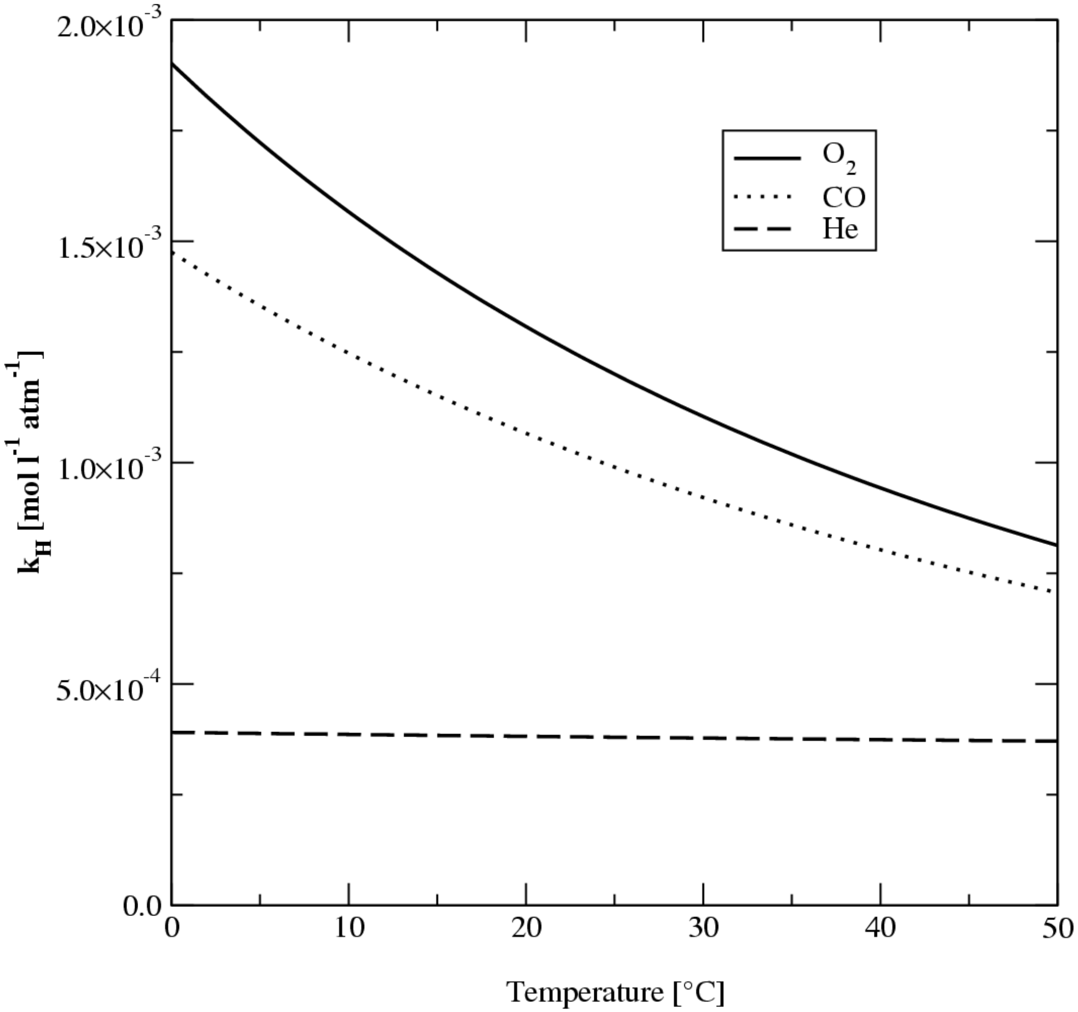
2.5.5. Limit of Solubility - Gases



gas	k_H^{STP} / $\mathrm{mol\,l^{-1}\,atm^{-1}}$	$-\Delta H/(R_g\,\mathrm{K}^{-1})$
O_2	1.2×10^{-3}	1500
H_2	7.8×10^{-4}	500
N_2	6.5×10^{-4}	1300
CO	9.9×10^{-4}	1300
CO_2	3.5×10^{-2}	2400
He	3.8×10^{-4}	92
Ne	4.5×10^{-4}	450
Ar	1.4×10^{-3}	1500
Kr	2.5×10^{-3}	1900
Xe	4.3×10^{-3}	2200

Table 2.13. Solubilities of gases in water at STP. Values slightly vary in the literature

2.5.5. Limit of Solubility - Gases



$T \uparrow \mapsto k_H \downarrow$

Fig. 2.17. Solubility of gases as a function of the temperature

2.5.5. Limit of Solubility - Solids

optional

- Dissolution
  1. Pure solid melted at constant T to pure liquid ($\Delta G > 0$)
  2. Dissolution at constant T ($\Delta S > 0$)
- Gibbs energy barrier depends on melting temperature
  - Barrier high if $T\,(\text{solution}) \ll T\,(\text{melt})$
  - Principle of Le Chatelier
- Dynamic equilibrium
  - Reached after sufficient amount of time
  - Rate of precipitation coincides with rate of dissolution
  - Example: AgCl
- Mass action law

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}$$

$$K' = \frac{[\mathrm{Ag^+}][\mathrm{Cl^-}]}{[\mathrm{AgCl}]}$$

- **Product of solubility**
  - Concentration in solid phase constant

$$\boxed{K_{\mathrm{sol}} = [\mathrm{Ag^+}][\mathrm{Cl^-}]}$$

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2.5.6. Colligative Properties

$$pV = Nk_BT$$

- Osmotic pressure
  - Dissolved molecules
  - Liquid in contact with semipermeable membrane
  - Solute like gas in free space discarding solvent
  - Law of van‘t Hoff

$$\boxed{p_{\text{osmotic}} = \frac{\boxed{N}k_BT}{V}}$$

  - Number of solved molecules N
  - „**Isotonic**“ or „**isomotic**“ solutions
    - Same osmotic pressure

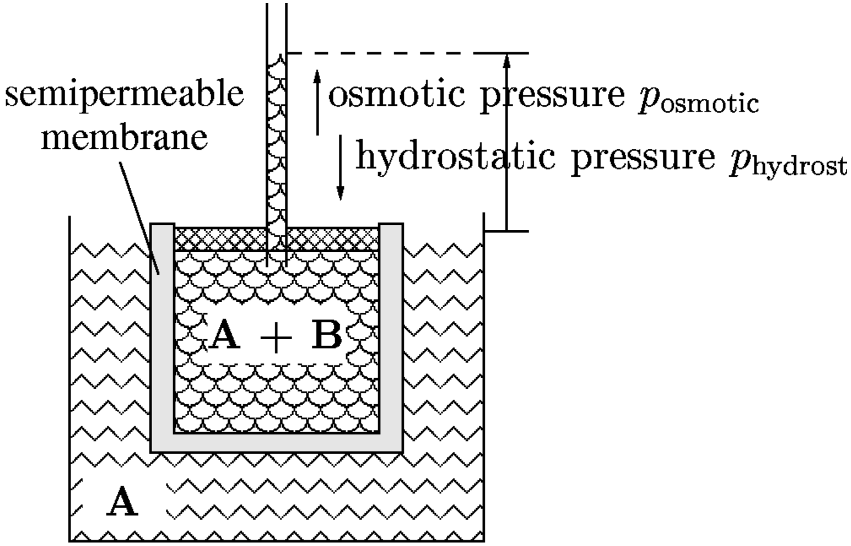


Fig. 2.18. Pfeffer cell. The semipermeable membrane lets A pass in either direction while constituent B is kept in the inner vessel. The osmotic pressure p_{osmotic} is equivalent to the hydrostatic pressure in the column

2.5.6. Colligative Properties

optional

- Vapor pressure of mixtures
  - Total vapor pressure p_{vap}
  - Sum of partial (vapor) pressures (fugacities) $p_{\text{vap}}(i)$

$$\boxed{p_{\text{vap}}(i) = y_i p_{\text{vap}}}$$

  - Constituents i, each possessing mole fraction y_i and $\Sigma y_i = 1$
- Relation between p_{vap} and mole fractions in liquid phase x_i

$$\boxed{p_{\text{vap}}(i) = \gamma_i x_i p^0_{\text{vap}}(i)}$$

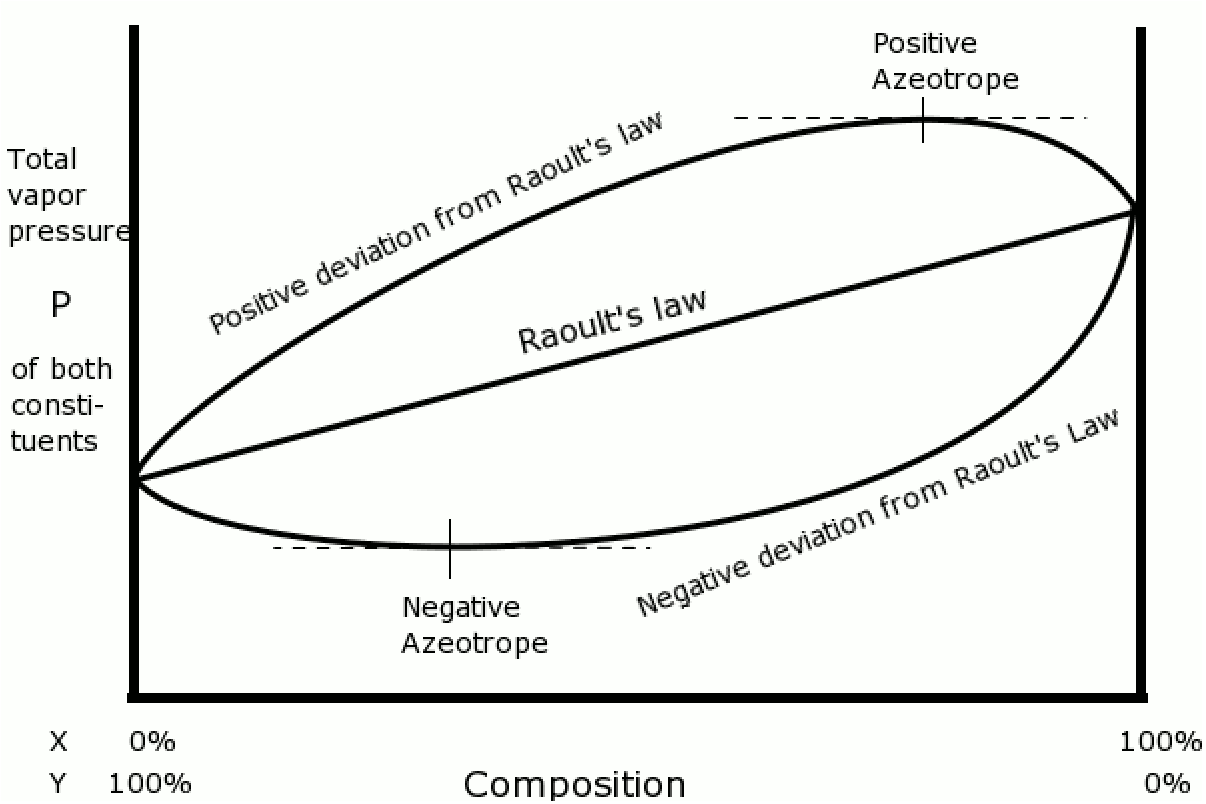
  - Activity coefficients x_i
  - Mole fractions in liquid phase γ_i (see above)
  - Vapor pressure of pure liquid p^0_{vap}
- Raoult's law

$$p_{\text{vap}} = x_1 [p^0_{\text{vap}}(1) - p^0_{\text{vap}}(2)] + p^0_{\text{vap}}(2)$$

  - For ideal binary solution (uncommon) with $\gamma_i = 1$

2.5.6. Colligative Properties

optional



- Deviation of Raoult’s (idealized) linear relationship

2.5.6 Change in Boiling and Freezing Point

solvent	$T_{\mathrm{boil}}/^{\circ}\mathrm{C}$	$\mathcal{T}_{\mathrm{boil}}/\mathrm{K\,kg\,mol^{-1}}$	$T_{\mathrm{freeze}}/^{\circ}\mathrm{C}$	$\mathcal{T}_{\mathrm{freeze}}/\mathrm{K\,kg\,mol^{-1}}$
water	100.0	0.514	0.0	-1.86
benzol	80.1	2.53	5.5	-5.12
ethanol	78.4	1.21	-114.6	-1.99

Table 0.1. The coefficients $\mathcal{T}_{\mathrm{boil}}$ and $\mathcal{T}_{\mathrm{freeze}}$ describe the change in the boiling point T_{boil} and the freezing point T_{freeze} of a given (dilute) solution as a function of the molality c_m

- Presence of solute
  - Boiling / melting point depend on **type** and **concentration** of solute c_m
- Dilute solutions
  - Linear approximation
  - Weak dependence on solute
  - Rise in boiling point

$$\boxed{\Delta T = \mathcal{T}_{\mathrm{boil}} c_m}$$

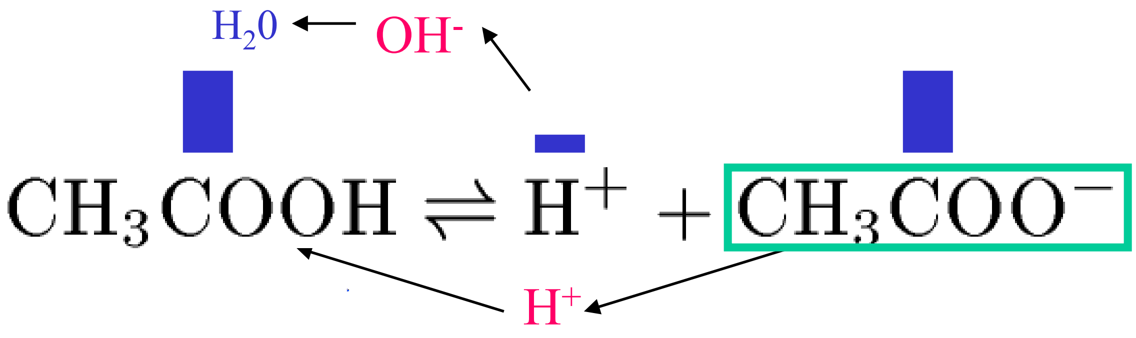
  - Decrease in freezing point

$$\boxed{\Delta T = \mathcal{T}_{\mathrm{freeze}} c_m}$$

Summary

$$\boxed{\mathrm{pH} = -\log \frac{[\mathrm{H}^+]}{\mathrm{mol\,l}^{-1}} = \log \frac{\mathrm{mol\,l}^{-1}}{[\mathrm{H}^+]}} \qquad \boxed{\mathrm{pH} + \mathrm{pOH} = 14}$$

Buffers:



$$\mathrm{CH_3COOH} \rightleftharpoons \mathrm{H}^+ + \boxed{\mathrm{CH_3COO}^-}$$

Solubility:

gases

$$\boxed{c_{\mathrm{gas}} = k_{\mathrm{H}} p_{\mathrm{gas}}}$$

solids

$$\boxed{K_{\mathrm{sol}} = [\mathrm{Ag}^+][\mathrm{Cl}^-]}$$

Vapor pressure:

$$\boxed{p_{\mathrm{vap}}(i) = y_i p_{\mathrm{vap}}}$$

Shift in phase transition of liquid:

$$\boxed{\Delta T = T_{\mathrm{boil}} c_m} \qquad \boxed{\Delta T = T_{\mathrm{freeze}} c_m}$$