

Mass Transfer: Diffusion

Phase equilibrium

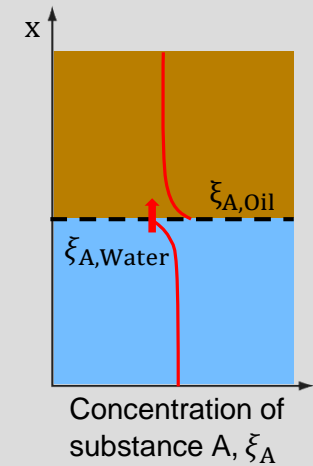
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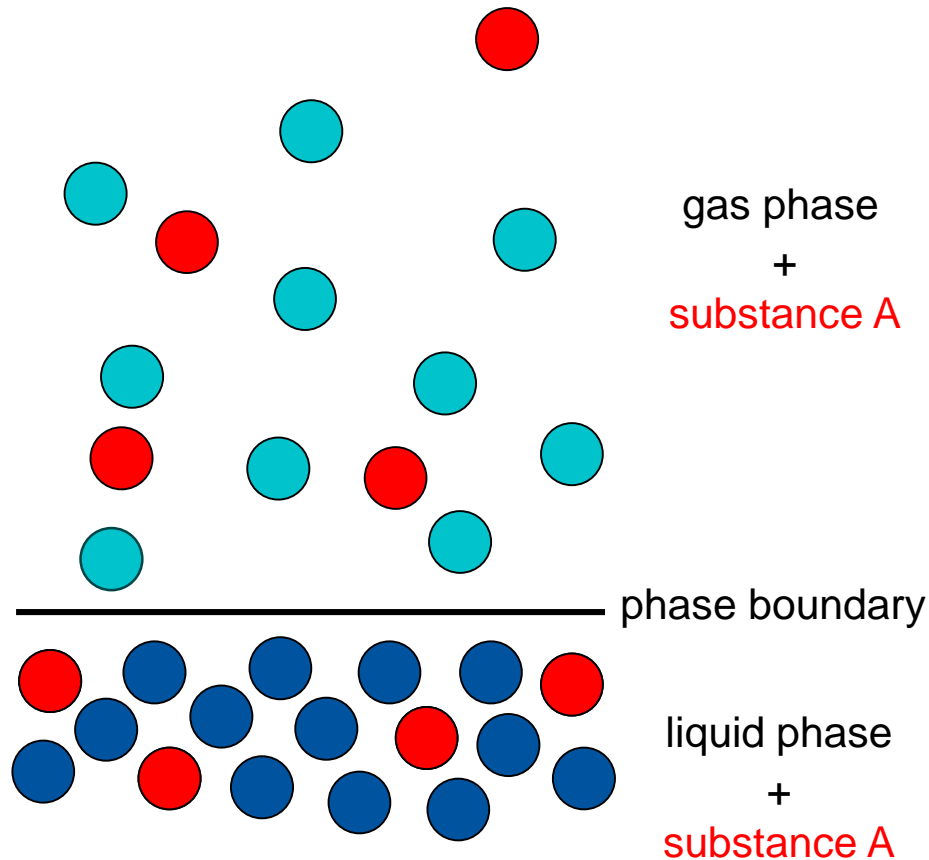
Learning goals

Phase equilibrium:

- ▶ How is the equilibrium between two phases, liquid/gas or liquid/liquid described?
- ▶ Consequences for the concentration course



Molecular view of phase equilibrium



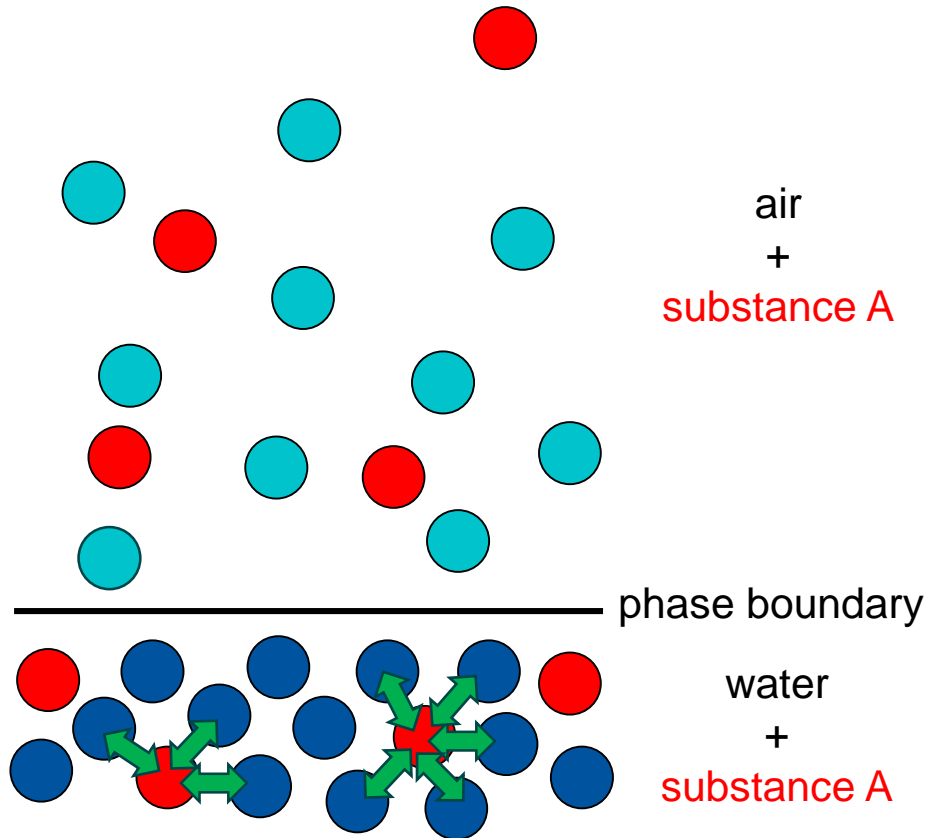
Problem definition:

- ▶ **Substance A** is in the gas phase and dissolved in an adjacent liquid phase
- ▶ The system is in equilibrium

Question:

- ▶ What is the concentration of **substance A** in the liquid or gas phase?

Phase equilibrium at liquid/gas interface: Henry coefficient



What happens in this situation?

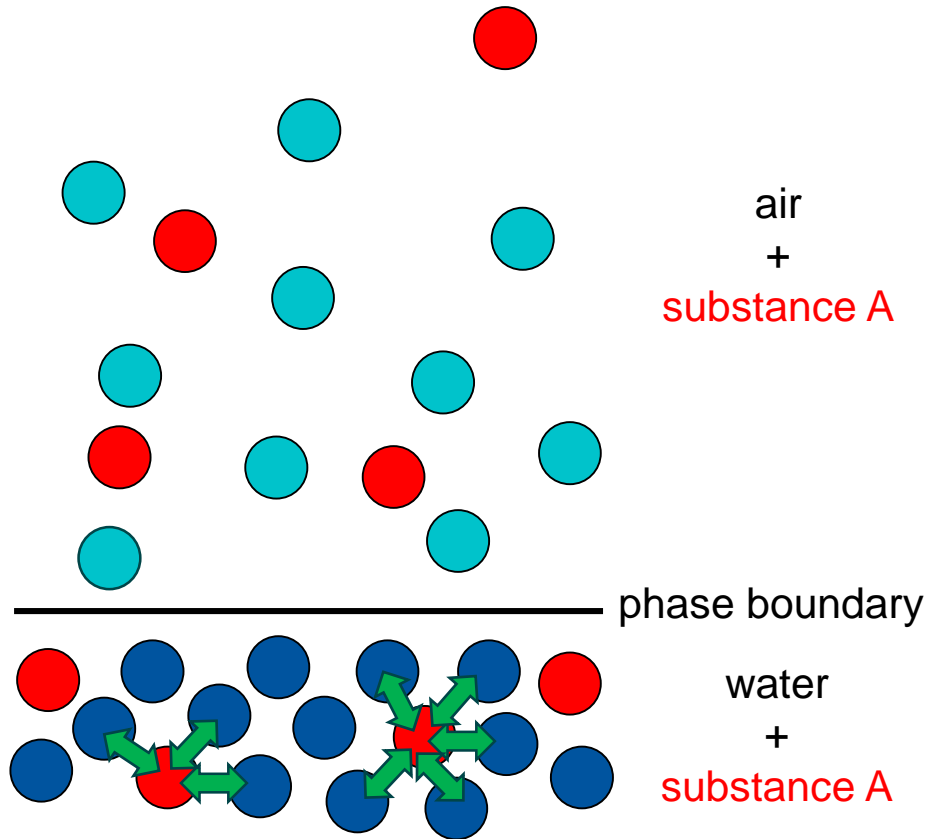
- ▶ The solubility of **A** in water depends strongly on intermolecular interactions in the liquid
→ some substances are highly soluble in water, others are not
- ▶ The distribution of **A** in the liquid and gas phases is described by the substance-dependent and temperature-dependent



Henry coefficient:

$$H_i^{cc} = \frac{C_{i,liq}}{C_{i,g}} \quad \text{with} \quad C_i = \frac{n_i}{V}$$

Phase equilibrium at liquid/gas interface: Henry coefficient



Relationship for mass fractions ξ_i :

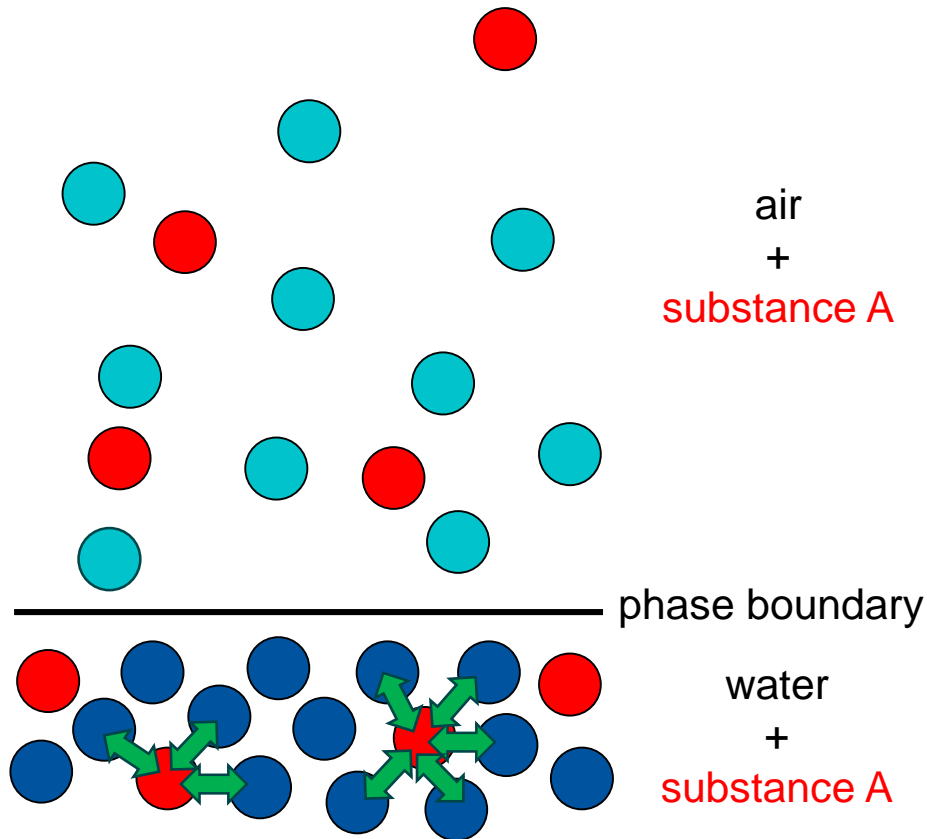
$$C_i = \frac{n_i}{V} = \frac{\frac{m_i}{M_i}}{\frac{m_{\text{tot}}}{\rho_{\text{tot}}}} = \xi_i \frac{\rho_{\text{tot}}}{M_i}$$

$$\Rightarrow H_i^{cc} = \frac{C_{i,\text{fl}}}{C_{i,\text{g}}} = \frac{\xi_{i,\text{liq}} \rho_{\text{tot,liq}}}{\xi_{i,\text{g}} M_i} \frac{M_i}{\rho_{\text{tot,g}}} = \frac{\xi_{i,\text{liq}} \rho_{\text{tot,liq}}}{\xi_{i,\text{g}} \rho_{\text{tot,g}}}$$

- Thus, the following applies to the mass concentrations in the phases at equilibrium:

$$\xi_{i,\text{liq}} = \xi_{i,\text{g}} H_i^{cc} \underbrace{\frac{\rho_{\text{tot,g}}}{\rho_{\text{tot,liq}}}}_{H^*}$$

Phase equilibrium at liquid/gas interface: Henry coefficient



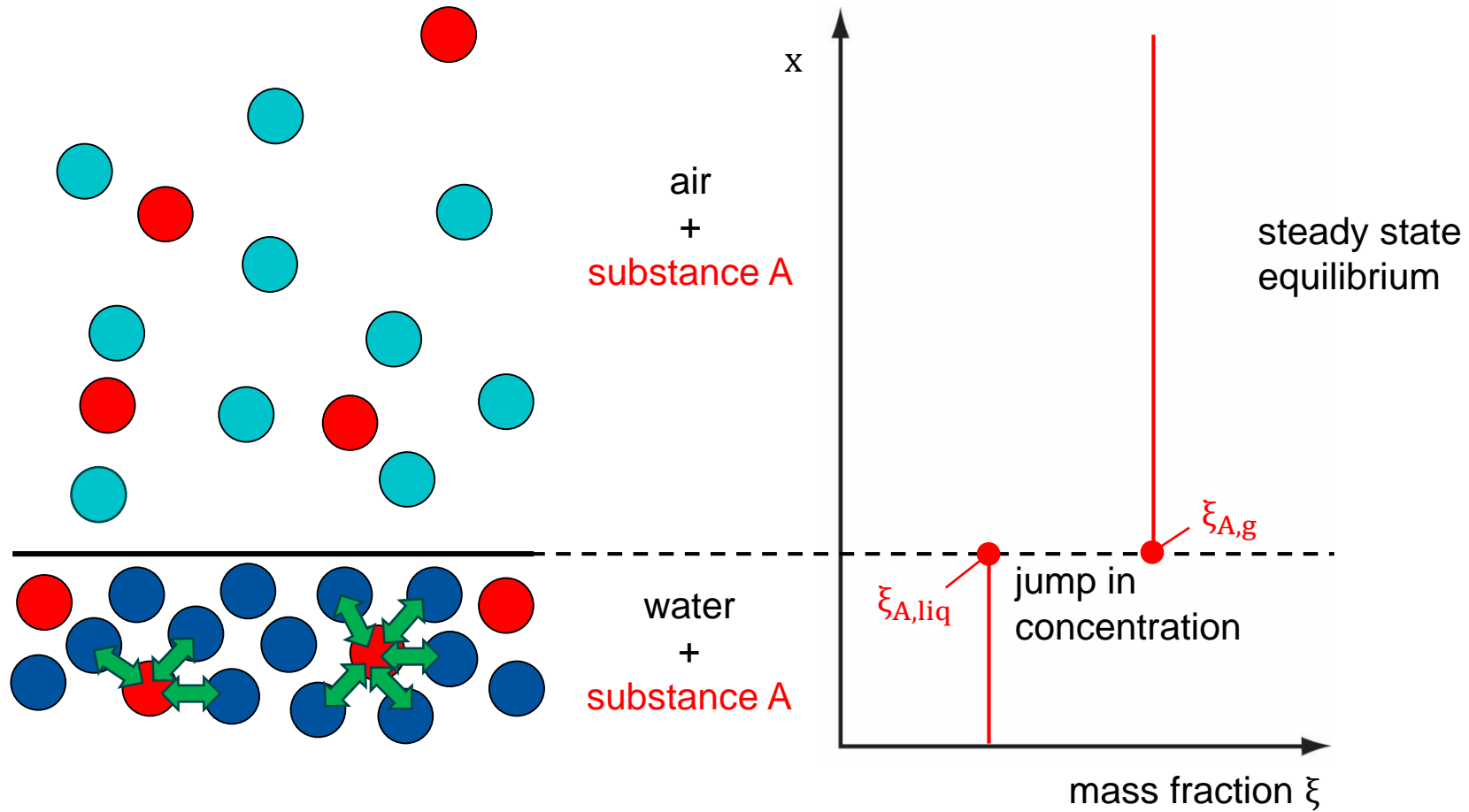
Relationship for mass fractions ξ_i :

$$\xi_{i,\text{liq}} = \xi_{i,\text{g}} \underbrace{H_i^{\text{cc}} \frac{\rho_{\text{tot,g}}}{\rho_{\text{tot,liq}}}}_{H^*}$$

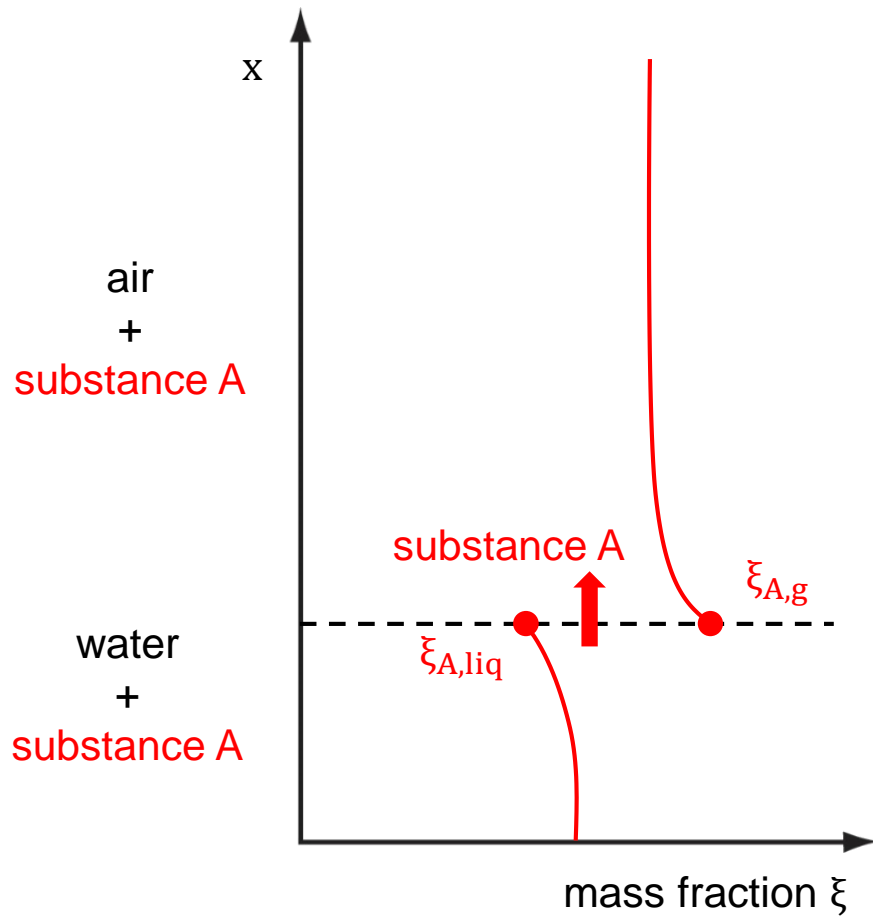
The mass concentrations at equilibrium depends on the:

- ▶ Density difference of the liquid and gas phases
- ▶ and the **Henry coefficients** (intermolecular interactions)

Concentration jump at the phase boundary



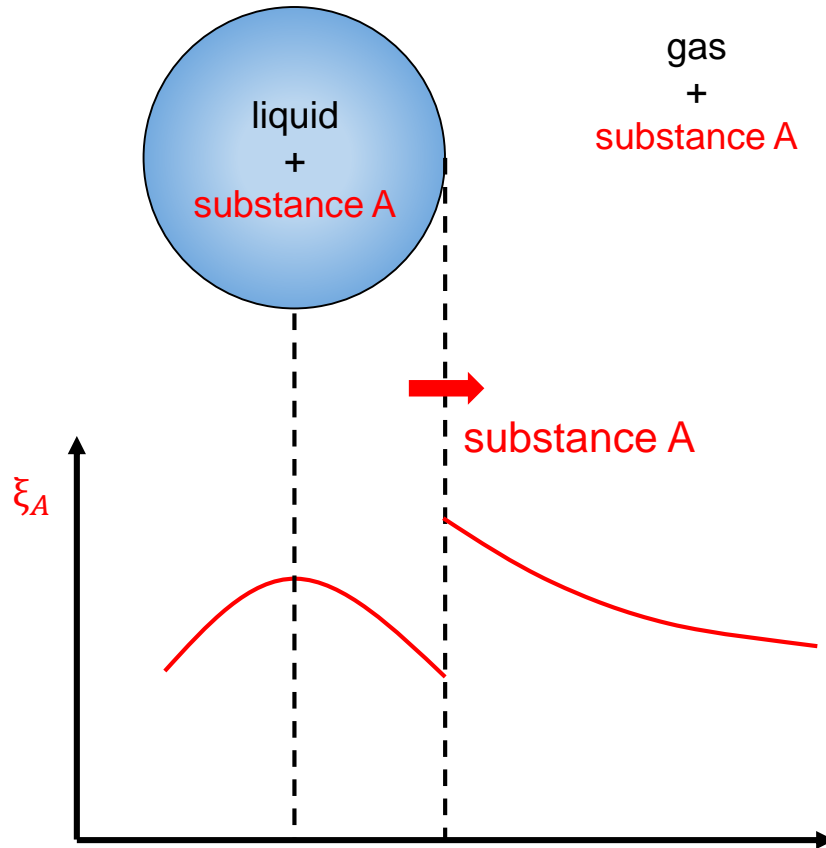
Concentration jump at the phase boundary



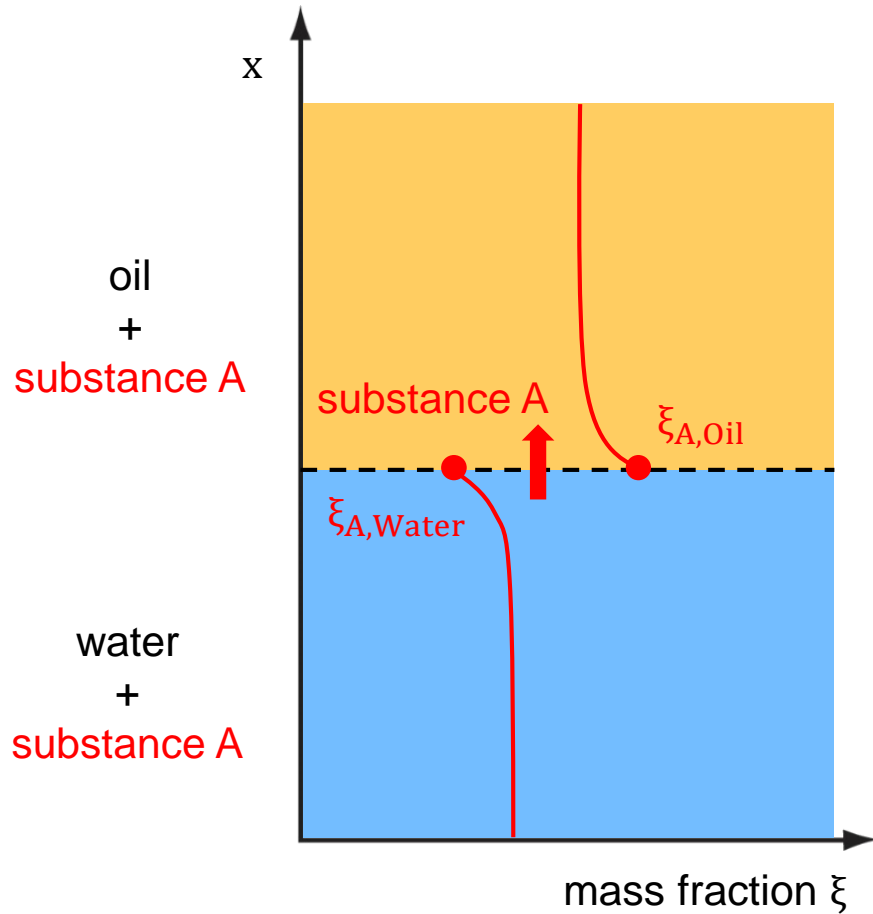
Transient case:

- ▶ The phase change occurs much faster than other transport processes
 - At the phase interface, the system is in the equilibrium given by the **Henry coefficient**
- ▶ In the case shown, the concentration of **A** in the water is higher than the equilibrium concentration
 - Mass transfer of A occurs from water towards air

Example: Transient mass transfer from a droplet into the surrounding gas atmosphere



Phase equilibrium at liquid/liquid interface: Nernst coefficient



Equilibrium at a phase interface between two liquids:

- Approach similar to liquid/gas phase interface:

$$\underbrace{K_N}_{\text{Nernst's distribution coefficient}} = \frac{\xi_{i,1}}{\xi_{i,2}}$$

- In the case shown, the concentration of A in the water is higher than the equilibrium concentration
→ Mass transfer of A takes place from water towards oil

Comprehension questions

Which quantities determine the ratio of the mass concentration at a phase interface between liquid and gas phase?

Why do the mass concentrations at the interface correspond to the equilibrium state even in the transient case?

SÄTTIGUNGSDRUCK (Das Gleichgewicht zwischen Temperatur und Druck)

