

Lecture General Chemistry Winter Term 2023/24

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- Website (Slides, Exercises):
- <http://www.chemie.uni-siegen.de/pc/lehre/nanoscitec/>

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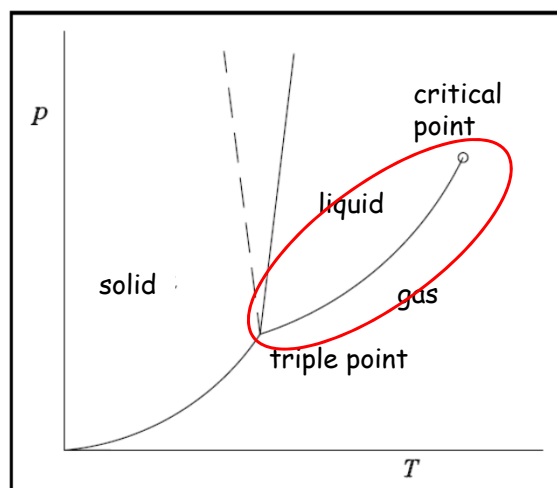
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vapour pressure of liquids

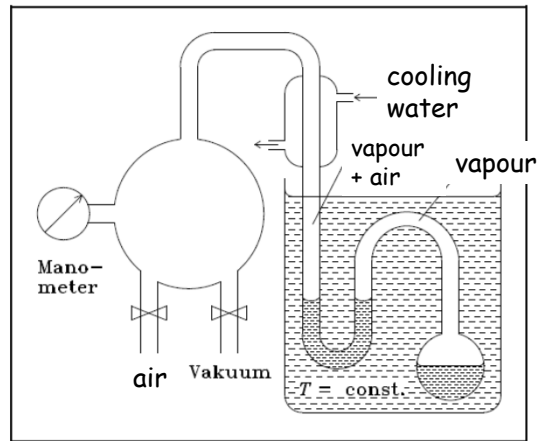


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measuring the vapour pressure

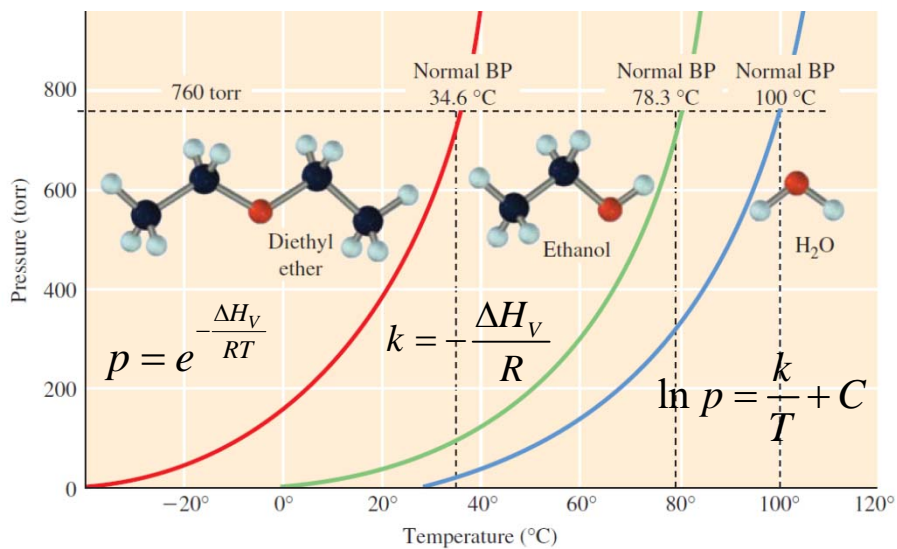


measuring device for vapour pressure

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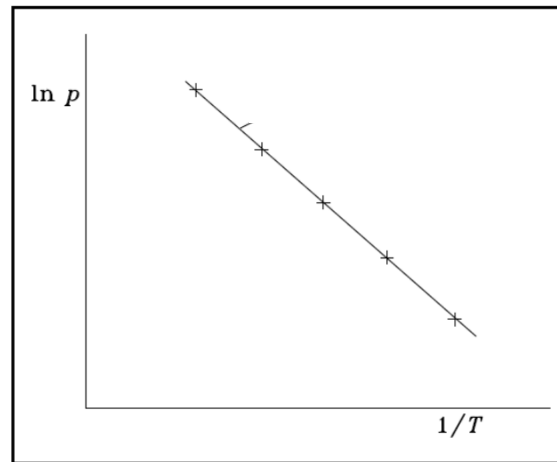
vapour pressure as $f(T)$ 

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making the vapour pressure curve linear



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$$\ln p = \frac{k}{T} + C \quad \text{elimination of integration constant:} \quad \ln p_0 = \frac{k}{T_s} + C$$

$$\ln \frac{p}{p_0} = k \left(\frac{1}{T} - \frac{1}{T_s} \right) \quad \text{Clausius-Clapeyron's law}$$

$$k = -\frac{\Delta H_v}{R}$$

important equation:

determine ΔH_v , if $p = f(T)$ is knowndetermine p for any T , if ΔH_v is known

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boiling point

(def. bp: vapour pressure = ambient pressure)

Substance	boiling point	
He	4K	Big differences!
H ₂ O	373K	
W	≈6000K	Reason: Forces between particles
		London, Dipol-Dipol, Coulomb, hydrogen bonds, metallic bond

another difference: molar mass

noble gas	He	Ne	Ar	Kr	Xe	Rn
T _s / K	4	27	87	120	166	208

Alkane	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	C ₆ H ₁₄
T _s / K	112	184	231	273	309	342

Why?

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$$E_{kin} = \frac{mv^2}{2} = \frac{3kT}{2} \quad \text{heavy particles are slower}$$

Intermolecular forces between heavy (big) particles are stronger
stronger forces: higher boiling point

relation between boiling point and boiling enthalpy?

Pictet-Trouton's rule $\frac{\Delta H_V}{T_S} \approx \text{const. } (= \Delta S_V)$

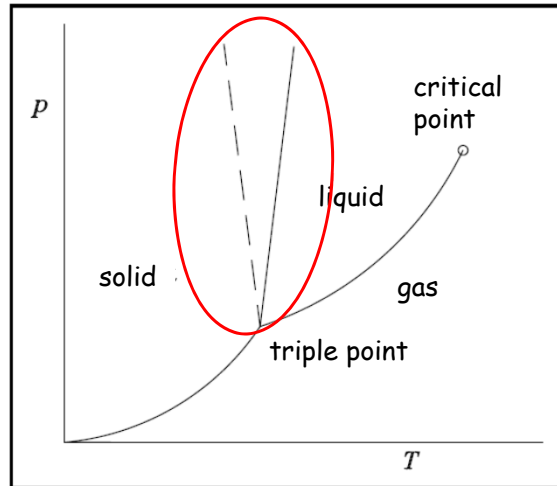
	Diethyl ether	Chloroform	Benzene	Water
T _s [K]	308	335	353	373
ΔH _v [kJ mol ⁻¹]	26,0	29,4	30,8	40,7
ΔH _v /T _s [J mol ⁻¹ K ⁻¹]	85	88	87	109

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Melting or Freezing point



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Melting or Freezing point

same here: strong forces -> high melting point

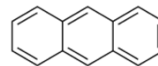
- **type of lattice**

• Molecular lattice	low
• Ionic lattice	medium
• 3-dim Molecular crystal	high

- molecular structure of particles
 - rigid- flexible
 - symmetric - unsymmetric

Benzene
5 °C

Toluene
-95 °C



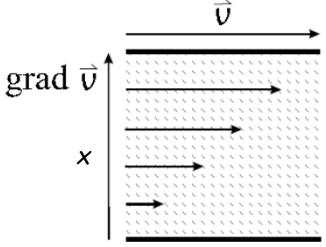
Anthracen
Smp: 217 °C
see Diesel:
C₁₄- Molecules
start to freeze
at 0 °C

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Viscosity



2 Planes, in between: liquid

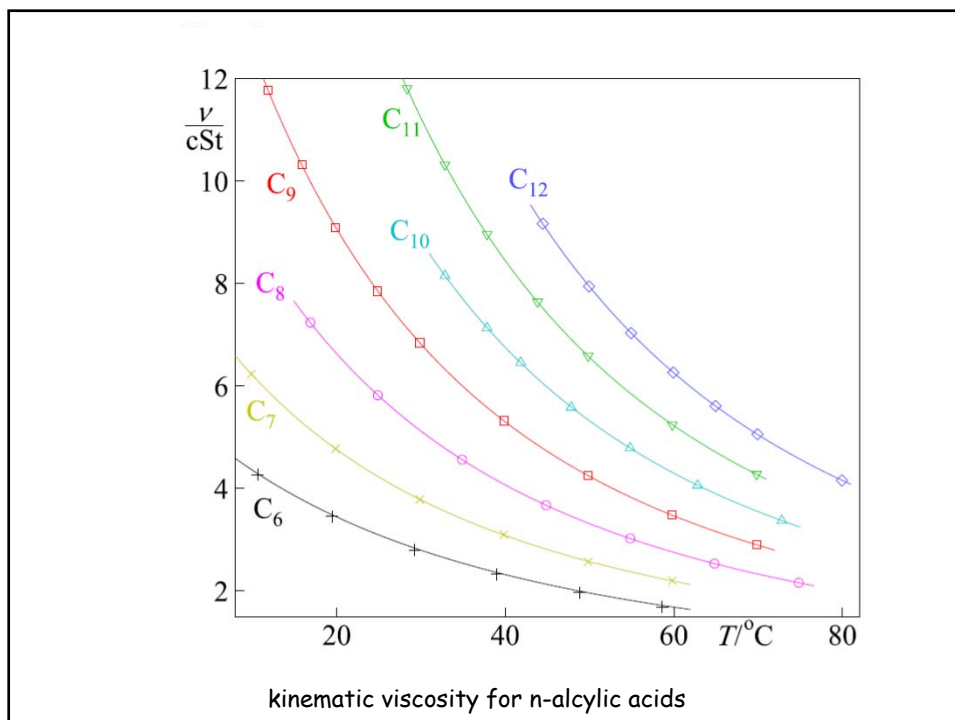
Force \propto area $\cdot \frac{dv}{dx}$

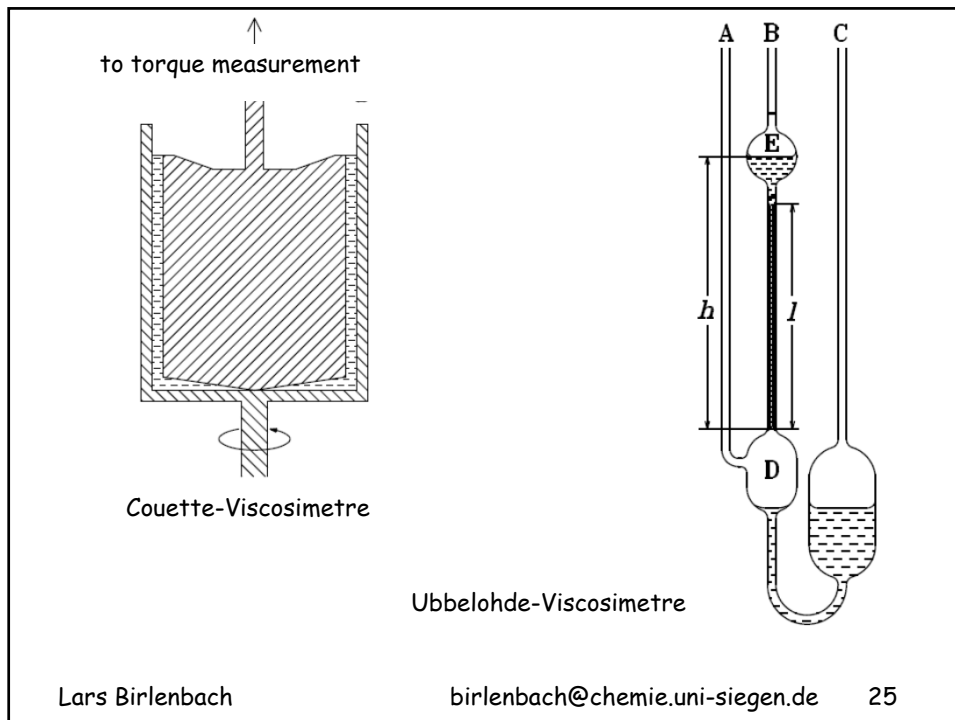
strong dependence on temperature!

Grease, motor oil, general: lubricants

Improvement of lubrication at high temperature via polymers that swell at high temperatures

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Solutions

- in solvent H_2O , there are soluble
 - solids: $NaCl$
 - liquids: $Ethanol$
 - gases: CO_2

more than one solute can be in the same solution

extreme differences of solubility in water

Examples: solubility in water

- **inorganic solids**
 - BaSO_4 0,002 g in 1 kg, 25 °C
 - NH_4NO_3 2100 g in 1 kg, 25 °C
- **organic solids**
 - urea 790 g per ℓ, 5 °C
 - 1200 g per ℓ, 25 °C
 - Paraffine --- (nothing)
- **organic liquids**
 - Methanol, Ethanol, Acetone: miscible
 - Octanol 0,3g per ℓ, 20 °C
- **gases**
 - Ammonia 702 ℓ per ℓ, 20 °C
 - Nitrogen 0,0162 ℓ per ℓ, 20 °C and 1,013 bar

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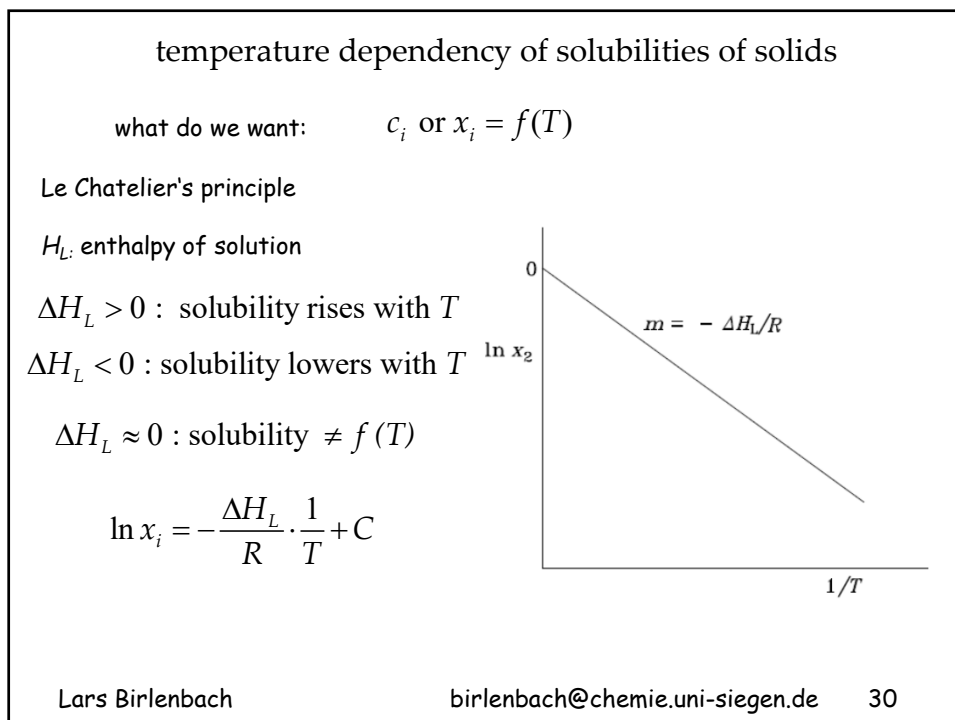
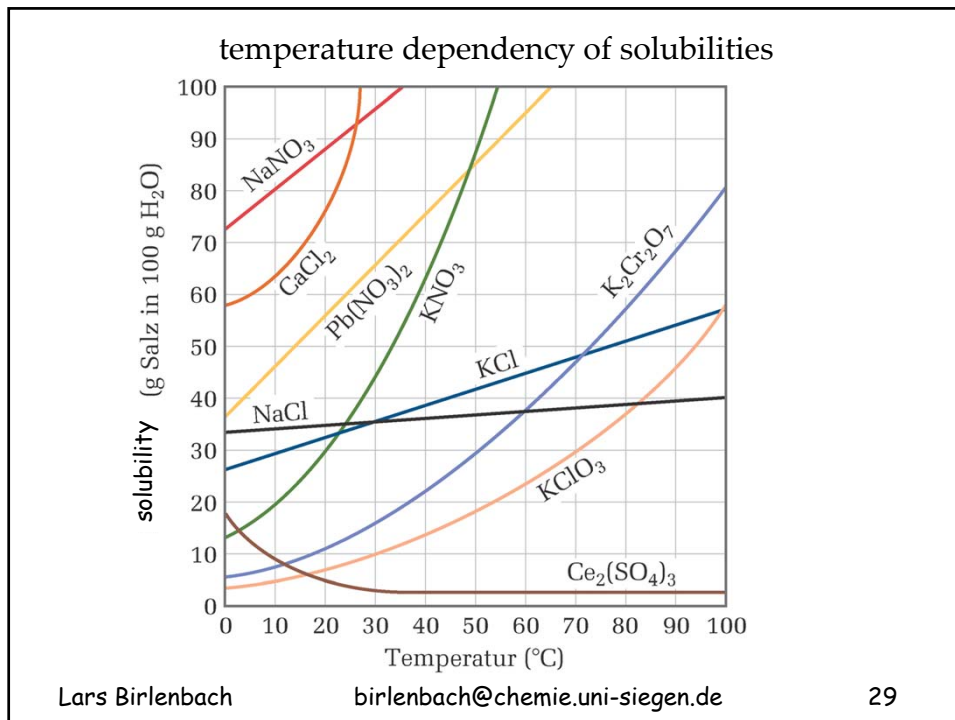
reasons for different solubilities?

forces between particles:
solvent, solute

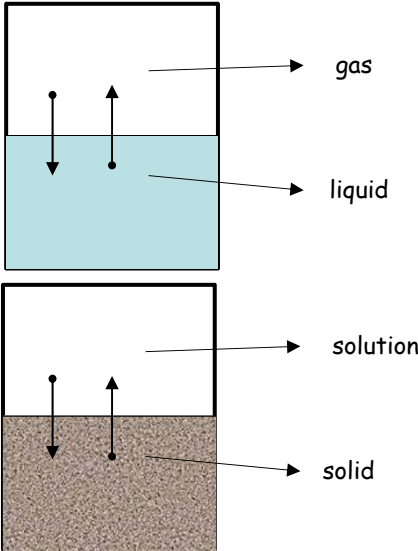
in water: polar Substances or Substances capable of hydrogen-bridging dissolve well. Hydration!

Similar compounds mix well,
dissimilar compounds do not.

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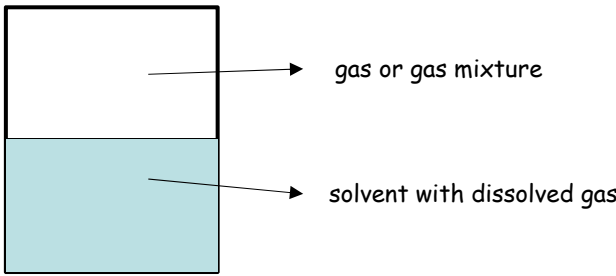
Analogy: dissolving -- evaporation



similar processes,
similar laws

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solubility of gases

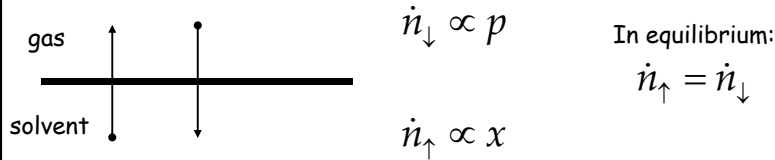


strong interactions between solvent and gas: good solubility
here: 702 l NH₃ in 1 l H₂O bei 20 °C
(that is: 29 mol in 55 mol)
„water absorbs ammonia“

not our topic here. We will describe poor solubility of gases.

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Microscopic view: solubility of gases in liquids



In equilibrium: $p \propto x$

$$p = kx \quad \text{Henry's Law}$$

$$p_i = k_i x_i \quad \text{Henry-Dalton's law for gas mixtures}$$

The indices i denominate different gases. Each gas obeys Henry's law as if no other gas were present. (only true for nonreactive gases)

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Example: solubility of N_2 and O_2 in water

at 20 °C and 1,013 bar

$$\text{O}_2 : x_{\text{O}_2} = 2,5 \cdot 10^{-5}$$

$$\text{N}_2 : x_{\text{N}_2} = 1,3 \cdot 10^{-5}$$

$$k_{\text{O}_2} : \frac{p_{\text{O}_2}}{x_{\text{O}_2}} = \frac{1,013 \text{ bar}}{2,5 \cdot 10^{-5}} = 4,1 \cdot 10^4 \text{ bar}$$

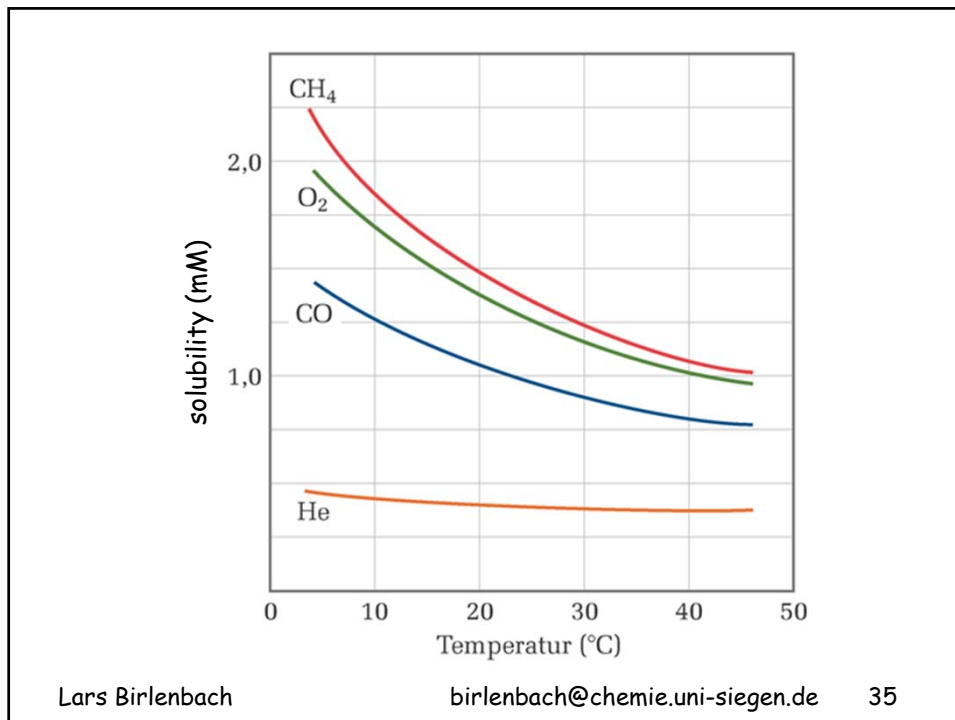
important in industry: washing (purifying) gases,
Technological use: gas scrubbing, eg removing
hydrogen sulfide from coke oven gas

coke from coal: CO , H_2 , CH_4 , H_2S form in the process
removing H_2S by weak aqueous base solution

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vapour pressure of solutions

Benzene_(g)

Benzene_(l) and Anthracene

→ gas phase (only benzene)

→ solution of Anthracene in Benzene

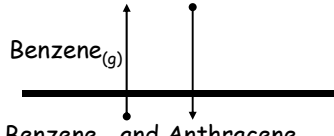
difference to former problem?

former problem: gas (some other compound)
above solvent with dissolved gas

now: solvent in the gas phase

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Microscopic view: vapour pressure of solutions



Benzene_(g)

Benzene_(l) and Anthracene

$\dot{n}_\downarrow \propto p$
 $\dot{n}_\uparrow \propto x_1$ Index 1: Benzol

In equilibrium:

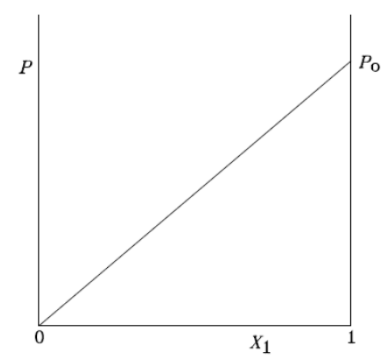
 $\dot{n}_\uparrow = \dot{n}_\downarrow$

In equilibrium: $p \propto x_1$

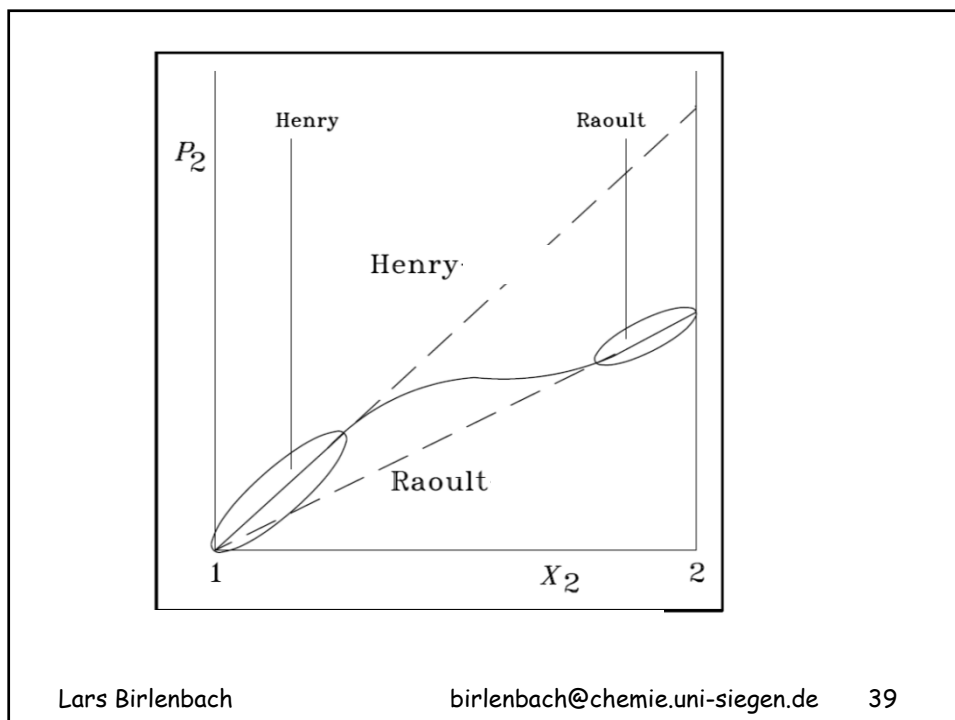
$$p = ax_1$$

Therefore: $a = p_0$
(p_0 : vapour pressure of pure benzene)

$p_1 = p_0 x_1$ **Raoult's Law**



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Properties of solutions

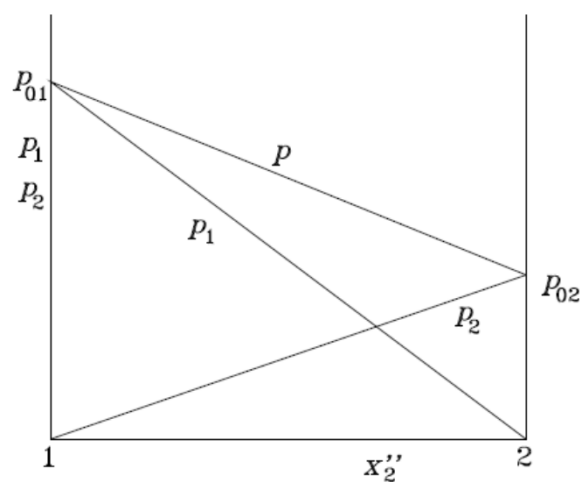
- Solubility of solids
- Solubility of gases
- Vapor pressure of solutions
- distillation
- boiling point elevation
- freezing point depression
- Stability condition of phases

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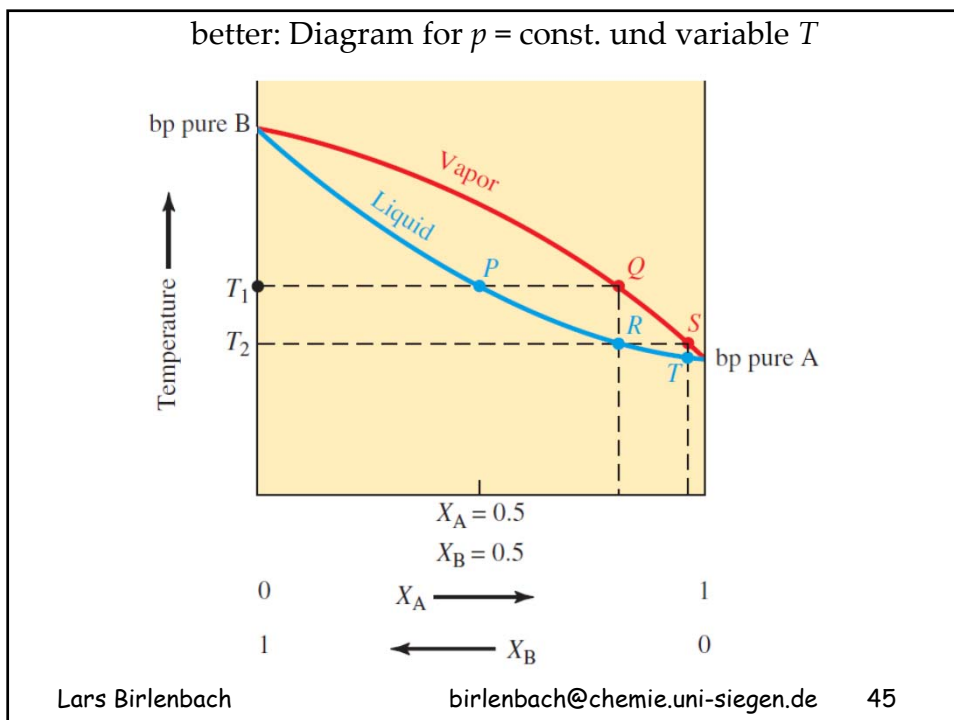
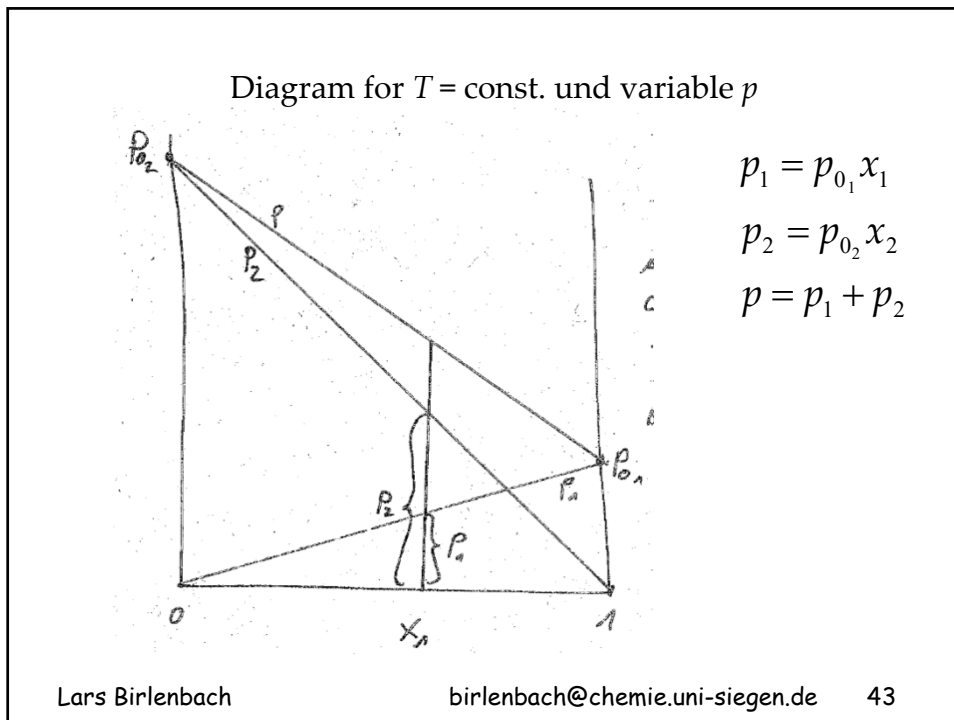
Diagram for Raoult for $T = \text{const.}$ and variable p

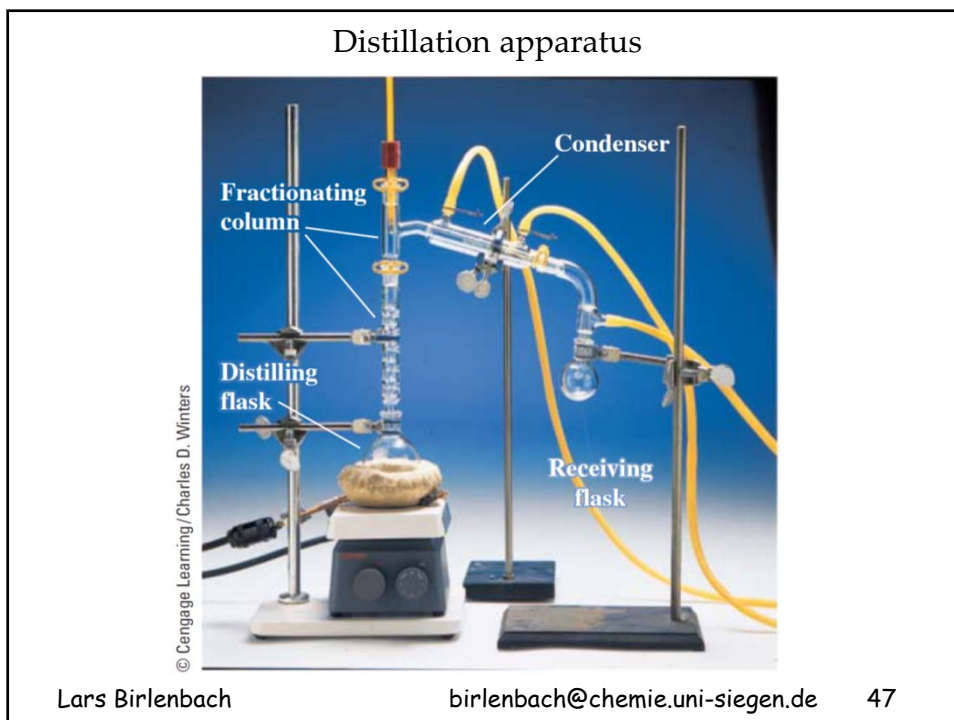
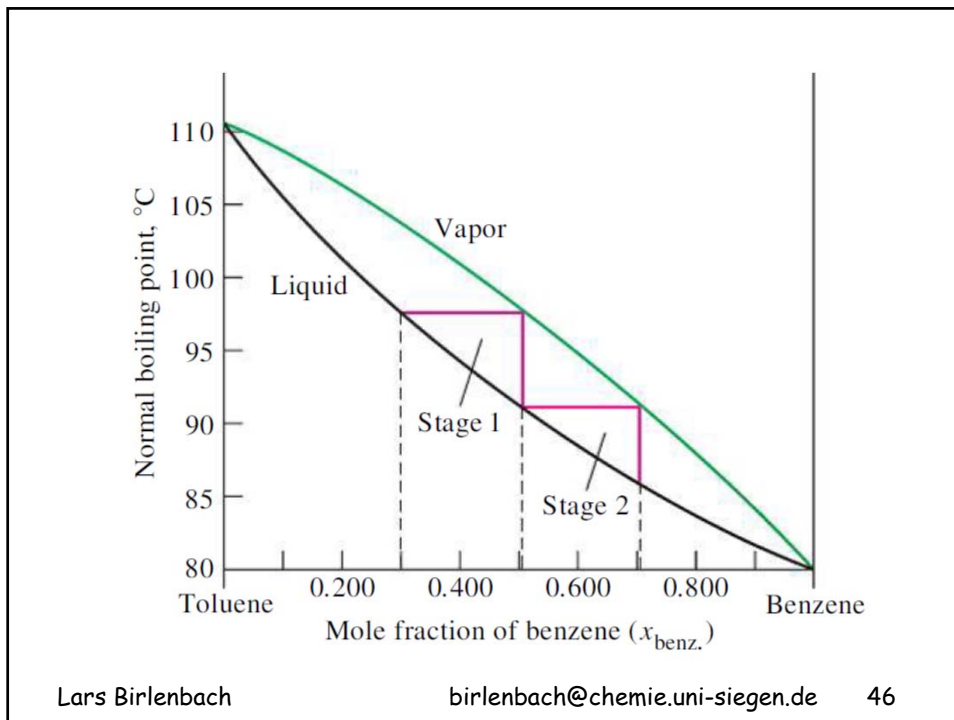


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Deviations from ideal behaviour

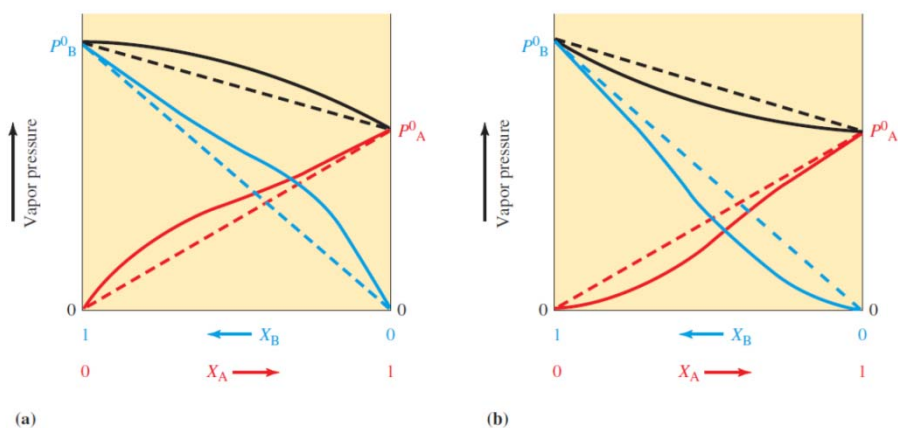


Figure 14-11 Deviations (solid lines) from Raoult's Law for two volatile components. Ideal behavior (Raoult's Law) is shown by the dashed lines. (a) Positive deviation. (b) Negative deviation.

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