Lecture General Chemistry
Winter Term 2023/24

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

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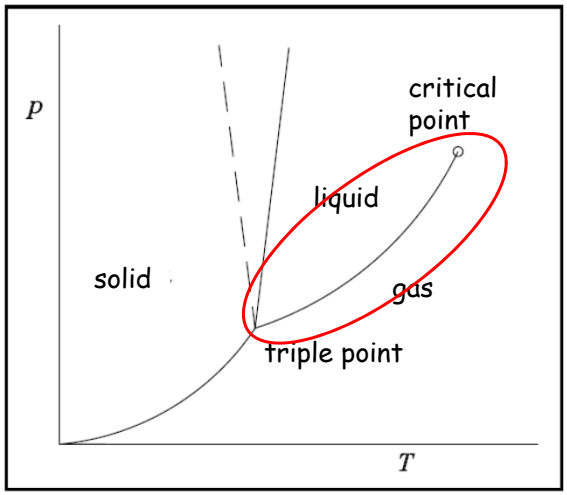
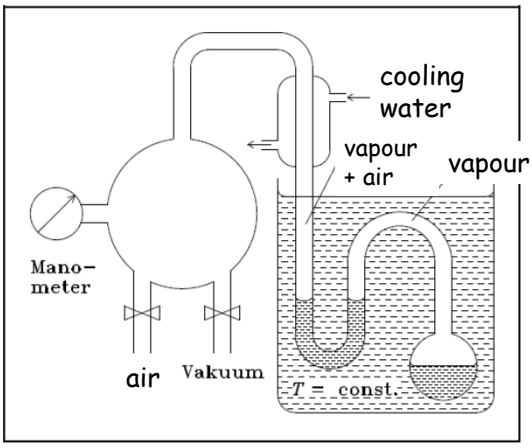
vapour pressure of liquids

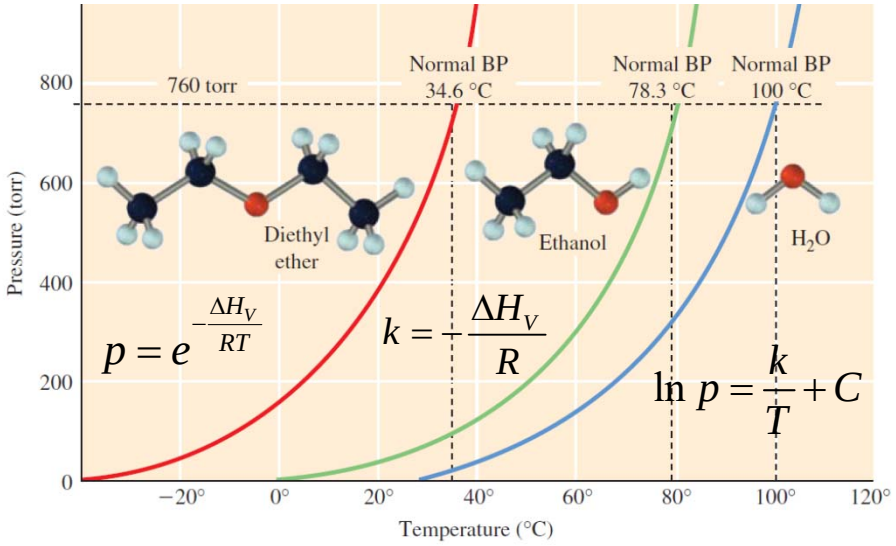


measuring the vapour pressure

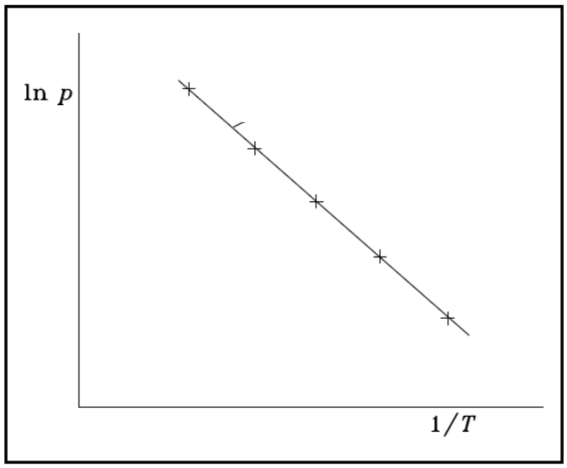


measuring device for vapour pressure

vapour pressure as f(T)



making the vapour pressure curve linear



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

$$\ln \frac{p}{p_0} = k\left(\frac{1}{T} - \frac{1}{T_S}\right)$$

Clausius-Clapeyron's law

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

important equation:
determine ΔH_V, if p = f (T) is known
determine p for any T, if ΔH_V is known

boiling point

(def. bp: vapour pressure = ambient pressure)

Substance	boiling point
He	4K
H_2O	373K
W	≈6000K

Big differences!

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_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}
T_S / K	112	184	231	273	309	342

Why?

$$E_{kin} = \frac{mv^2}{2} = \frac{3kT}{2}$$

heavy particles are slower

Intermolecular forces between heavy (big) particles are stronger

stronger forces: higher boiling point

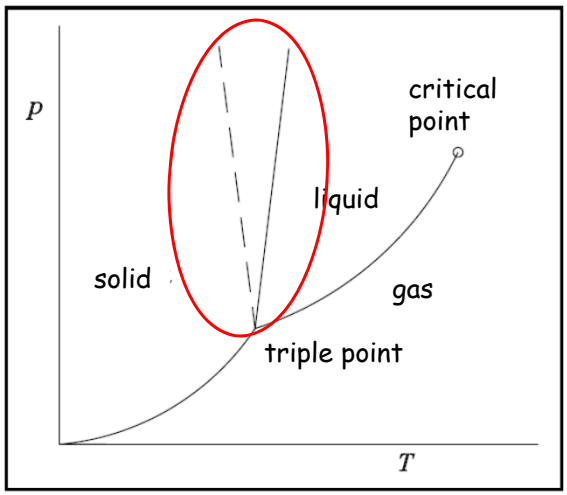
relation between boiling point and boiling enthalpy?

Pictet-Trouton's rule

$$\frac{\Delta H_V}{T_S} \approx \text{const.} \quad (= \Delta S_V)$$

	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
$\Delta H_V / T_S$ [J mol^{-1}K^{-1}]	85	88	87	109

Melting or Freezing point



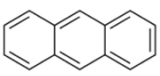
Melting or Freezing point

same here: strong forces -> high melting point

- type of lattice — Fp
  - Molecular lattice — low
  - Ionic lattice — medium
  - 3-dim Molecular crystal — high

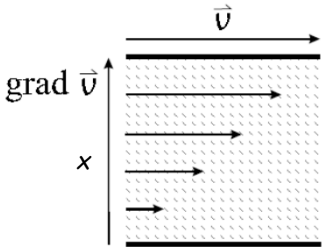
- molcular structur of particles
  - rigid- flexible
  - symmetric - unsymmetric

Benzene	Toluene
5 °C	-95 °C



Anthracen
Smp: 217 °C
see Diesel:
C_{14}- Molecules start to freeze at 0 °C

Viscosity



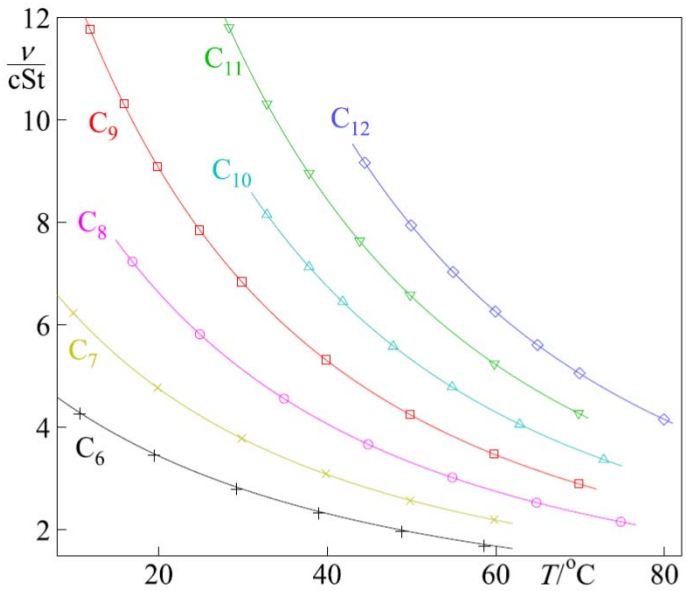
2 Planes, in between: liquid

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

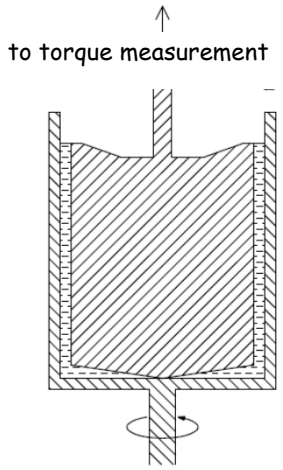
strong dependence on temperature!

Grease, motor oil, general: lubricants

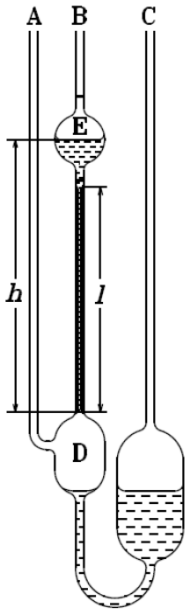
Improvement of lubrication at high temperatur via polymers that swell at high temperatures



kinematic viscosity for n-alcylic acids



Couette-Viscosimetre



Ubbelohde-Viscosimetre

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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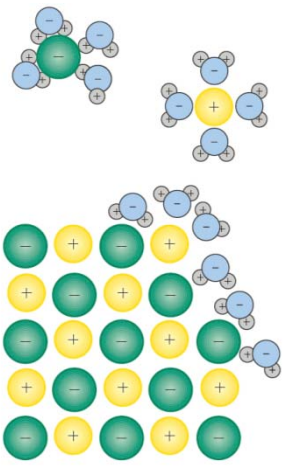
reasons for different solubilities?

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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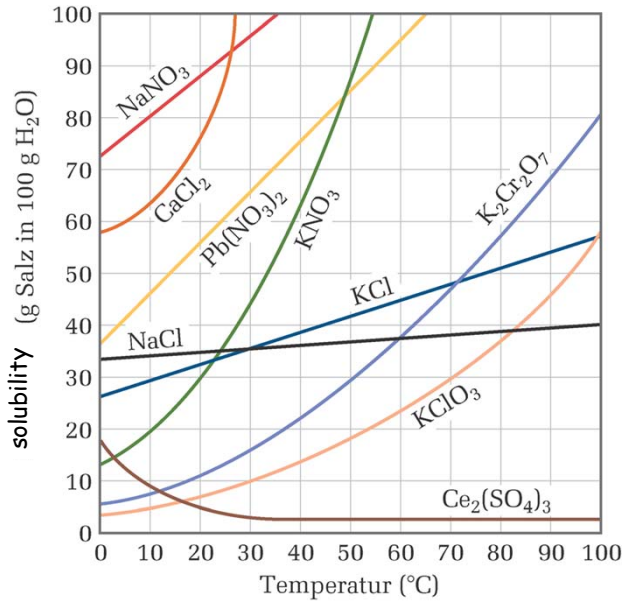
temperature dependency of solubilities



temperature dependency of solubilities of solids

what do we want: c_i or $x_i = f(T)$

Le Chatelier's principle

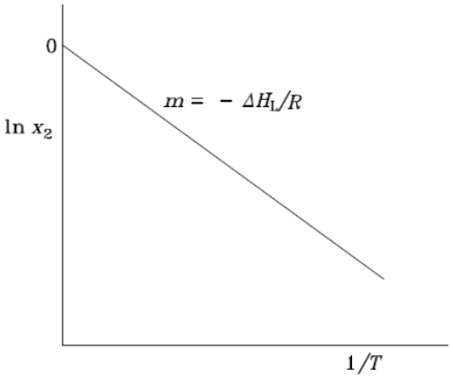
H_L: enthalpy of solution

$\Delta H_L > 0$: solubility rises with T

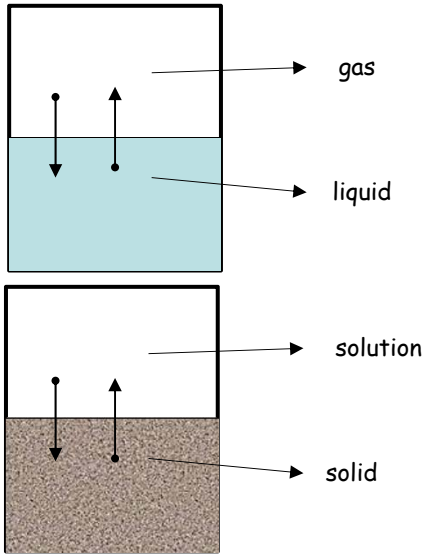
$\Delta H_L < 0$: solubility lowers with T

$\Delta H_L \approx 0$: solubility $\neq f(T)$

$$\ln x_i = -\frac{\Delta H_L}{R} \cdot \frac{1}{T} + C$$

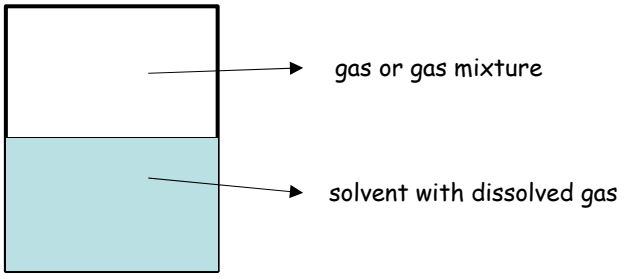


Analogy: dissolving -- evaporation



similar processes,
similar laws

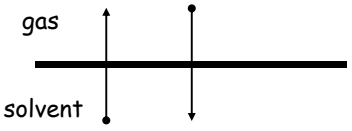
solubility of gases



strong interactions between solvent and gas: good solubility
here: 702 ℓ NH_3 in 1 ℓ H_2O bei 20 °C
(that is: 29 mol in 55 mol)
„water absorbs ammonia"

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

Microscopic view: solubility of gases in liquids



$\dot{n}_{\downarrow} \propto p$

$\dot{n}_{\uparrow} \propto x$

In equilibrium: $\dot{n}_{\uparrow} = \dot{n}_{\downarrow}$

In equilibrium: $p \propto x$

$p = kx$ Henry's Law

$p_i = k_i x_i$ 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)

Example: solubility of N_2 and O_2 in water

at 20 °C and 1,013 bar

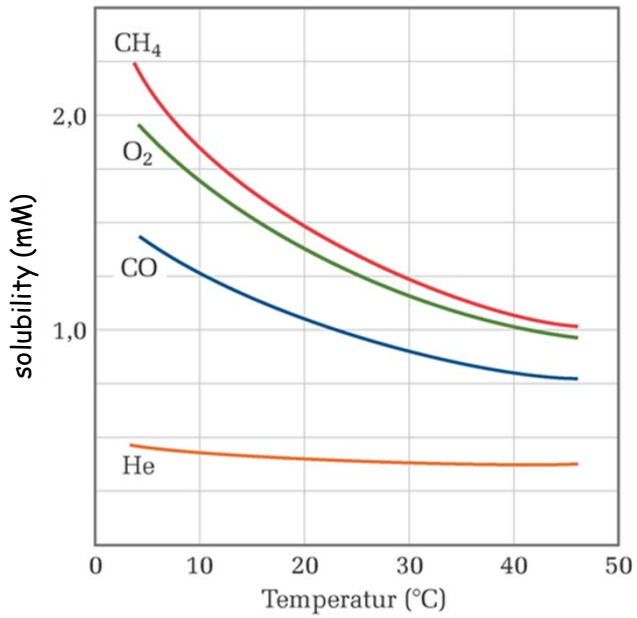
$O_2 : x_{O_2} = 2{,}5 \cdot 10^{-5}$

$N_2 : x_{N_2} = 1{,}3 \cdot 10^{-5}$

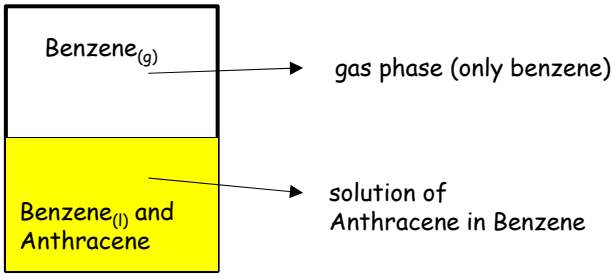
$k_{O_2} : \frac{p_{O_2}}{x_{O_2}} = \frac{1{,}013\,\text{bar}}{2{,}5 \cdot 10^{-5}} = 4{,}1 \cdot 10^{4}\,\text{bar}$

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 aquous base solution



vapour pressure of solutions

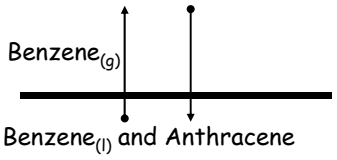


difference to former problem?

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

now: solvent in the gas phase

Microscopic view: vapour pressure of solutions



$\dot{n}_{\downarrow} \propto p$

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

In equilibrium:

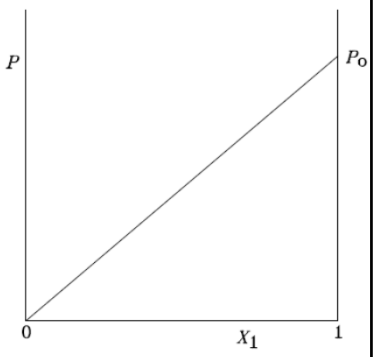
$\dot{n}_{\uparrow} = \dot{n}_{\downarrow}$

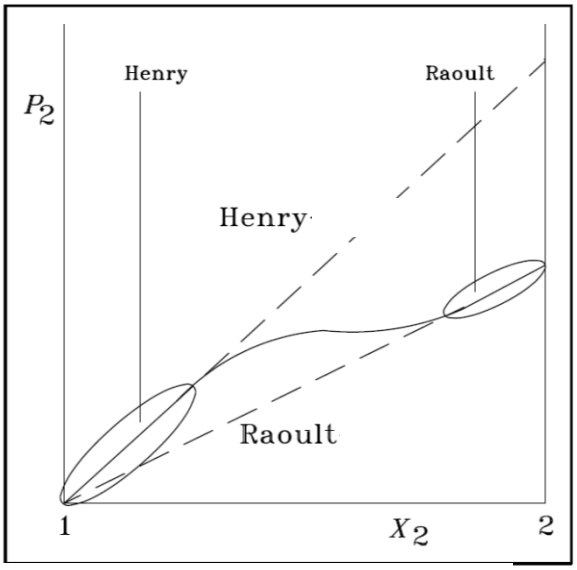
In equilibrium: $p \propto x_1$

$p = a x_1$

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

$p_1 = p_0 x_1$ Raoult's Law





Properties of solutions

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

Diagram for Raoult for T = const. and variable p

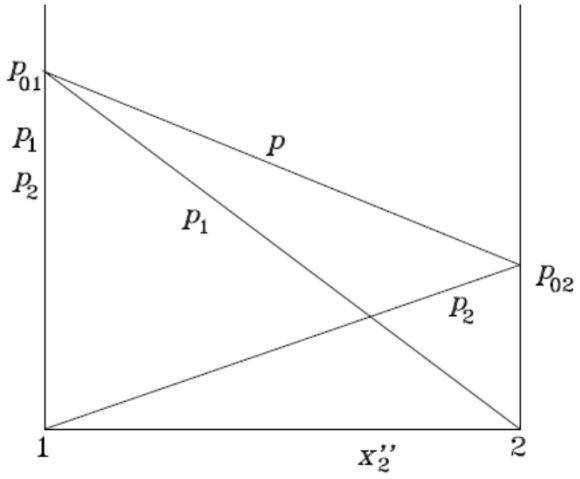
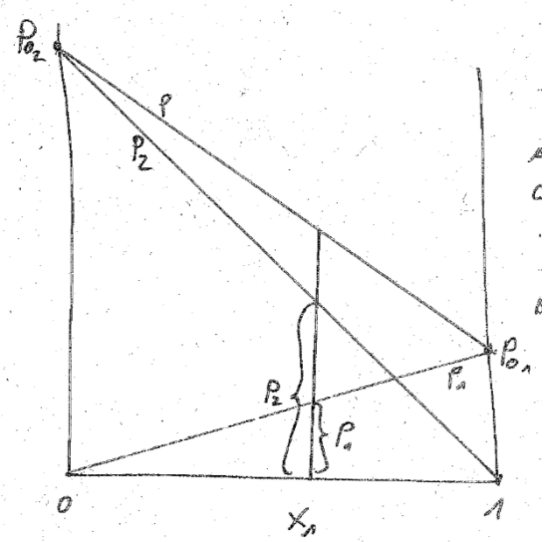


Diagram for T = const. und variable p

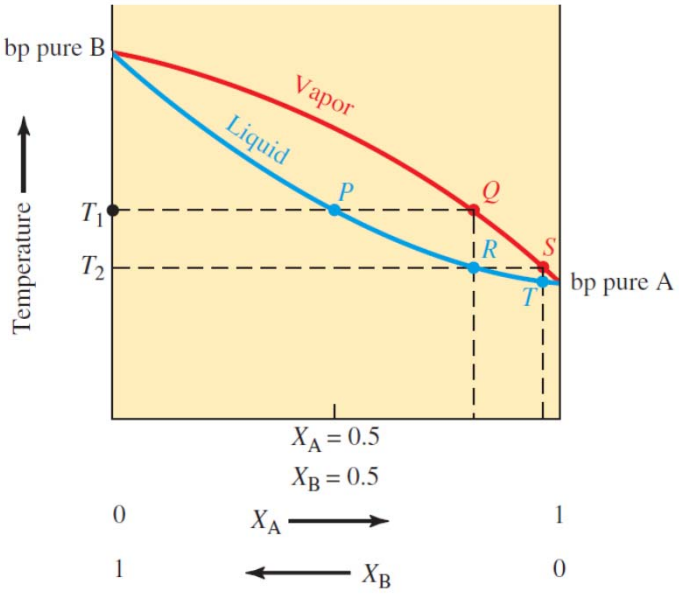


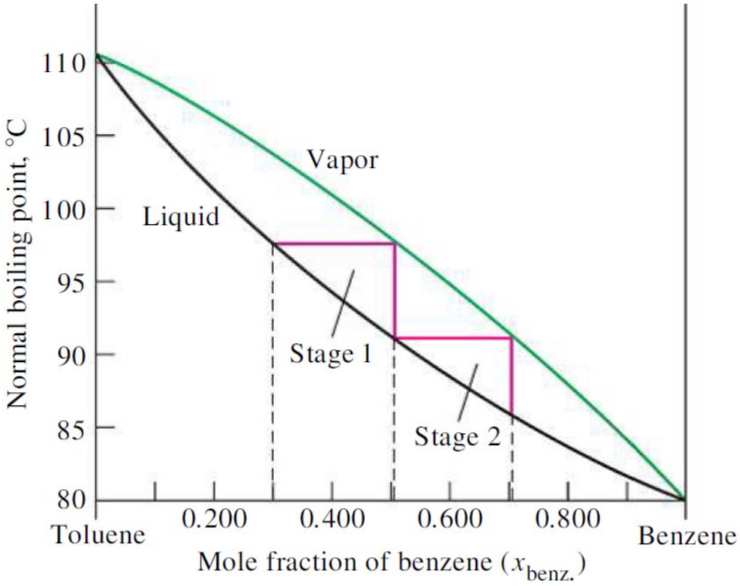
$$p_1 = p_{0_1} x_1$$

$$p_2 = p_{0_2} x_2$$

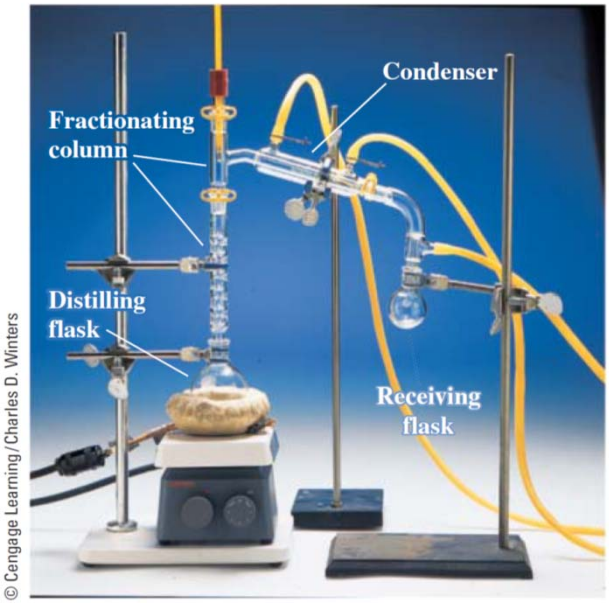
$$p = p_1 + p_2$$

better: Diagram for p = const. und variable T





Distillation apparatus



Deviations from ideal behaviour

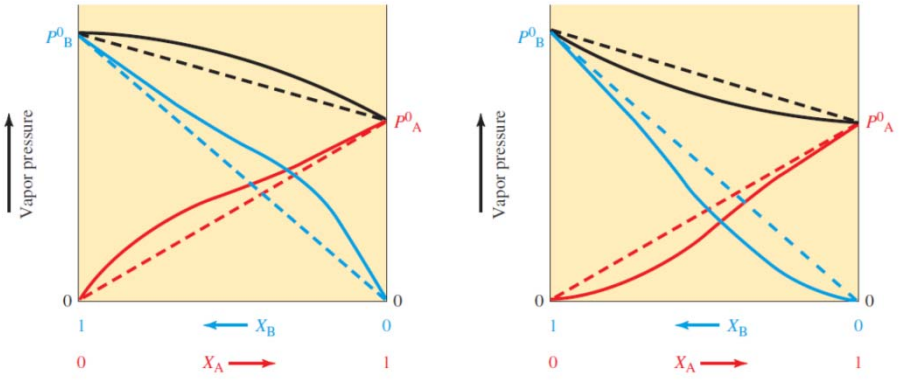
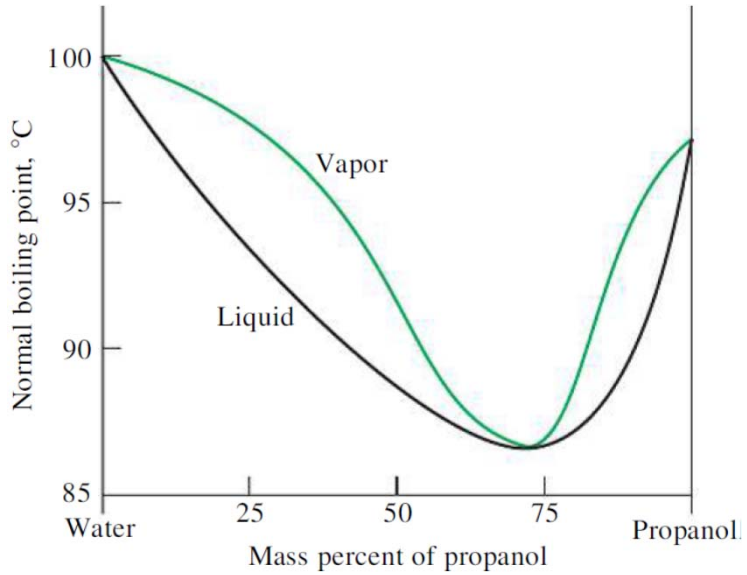


Figure 14-11 Deviations (*solid lines*) from Raoult's Law for two volatile components. Ideal behavior (Raoult's Law) is shown by the dashed lines. (a) Positive deviation. (b) Negative deviation.

Azeotropic mixtures