Introduction to Physics I

Laws of thermodynamics & thermal properties of matter

heat machines

phase transitions and phase diagrams

diffusion

osmosis

L26, 21.12.2016

reversible heat-work transformation
Carnot cycle

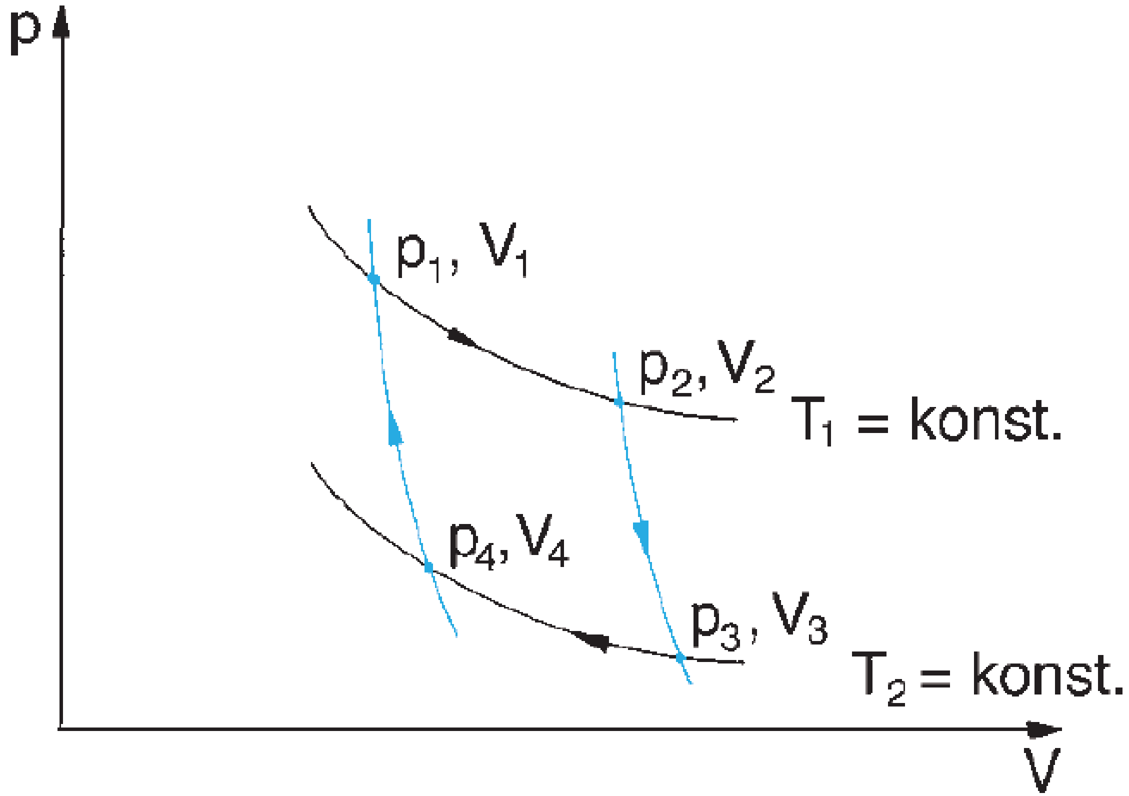
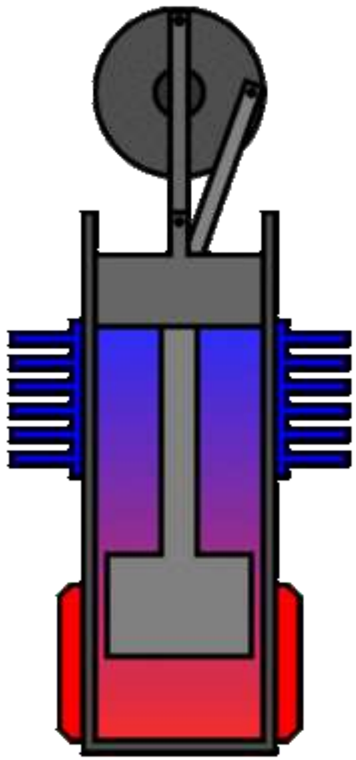
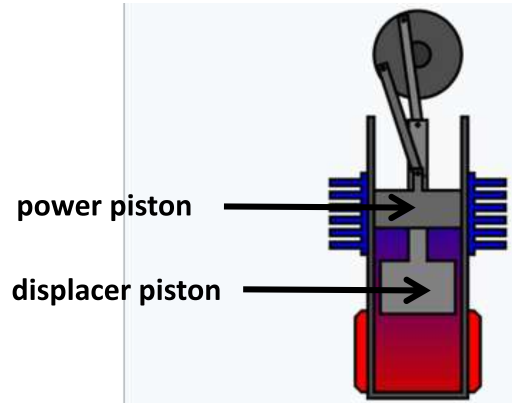


Abb. 12.1 *p-V*-Diagramm des Carnot'schen Kreisprozesses.

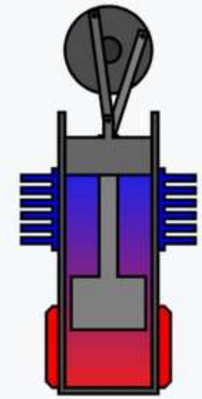
Trautwein

Stirling engine

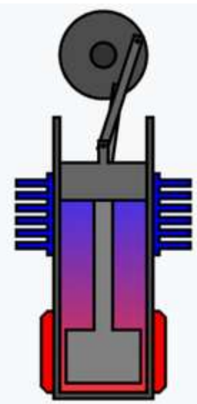




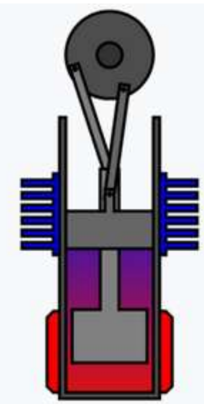
1. Power piston (dark grey) has compressed the gas, the displacer piston (light grey) has moved so that most of the gas is adjacent to the hot heat exchanger.



2. The heated gas increases in pressure and pushes the power piston to the farthest limit of the **power stroke**.



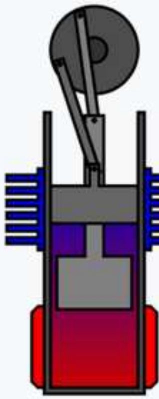
3. The displacer piston now moves, shunting the gas to the cold end of the cylinder.



4. The cooled gas is now compressed by the flywheel momentum. This takes less energy, since its pressure drops when it is cooled.

wiki

Stirling engine



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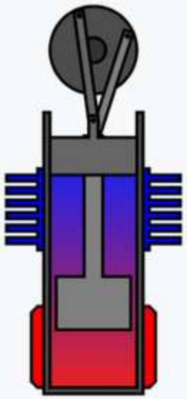

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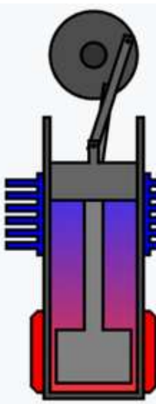

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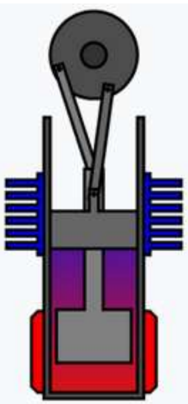

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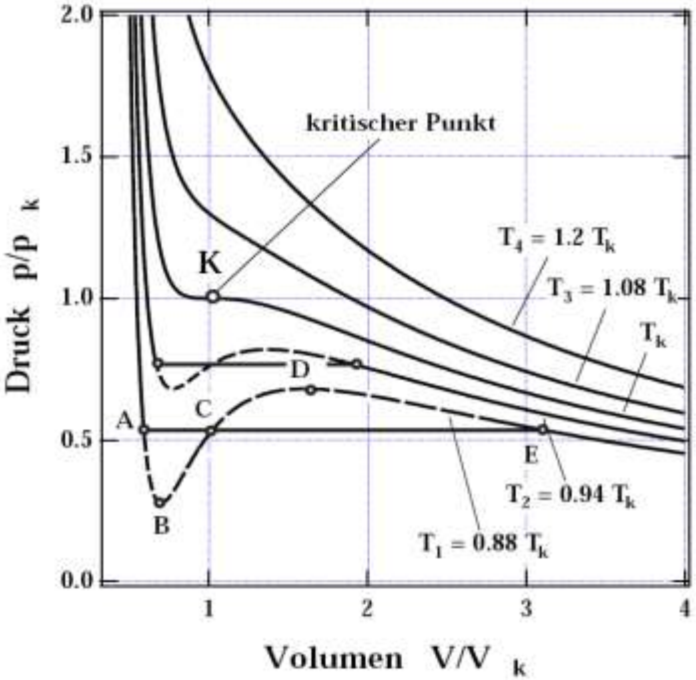
wiki

real gas law: van der Waals



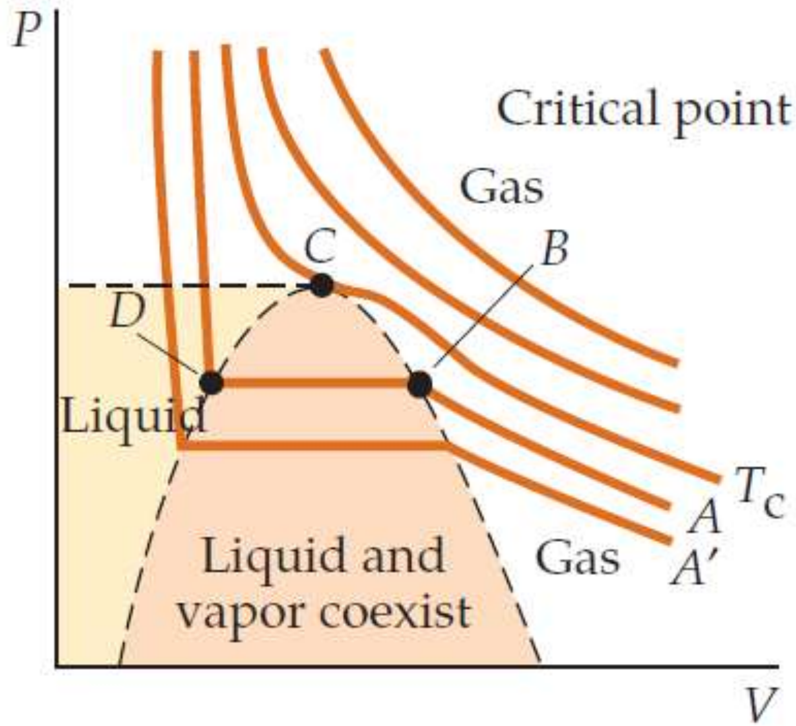
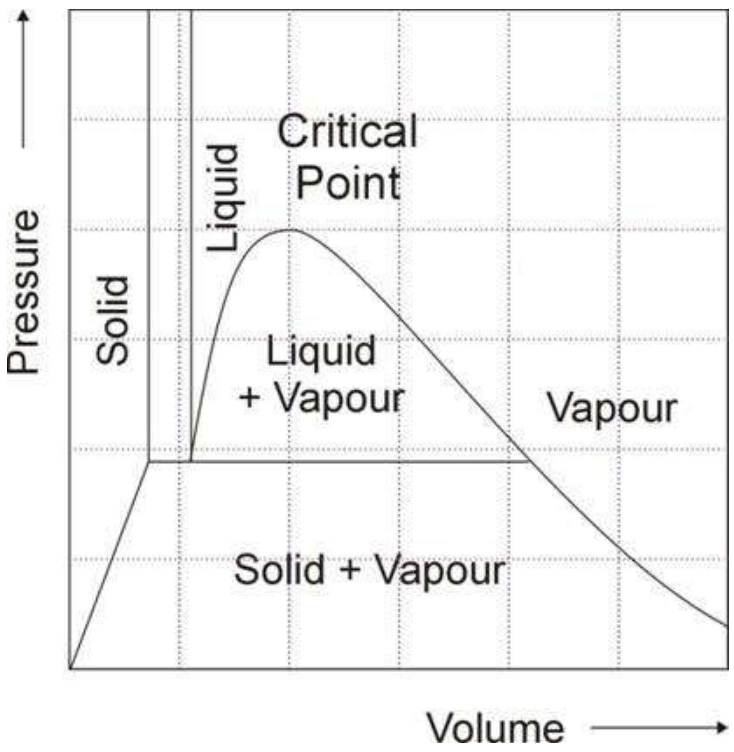


FIGURE 20-5 Isotherms on the *PV* diagram for a substance. For temperatures above the critical temperature T_c, the substance remains a gas at all pressures. Except for the region where the liquid and vapor coexist, these curves are described quite well by the van der Waals equation. The pressure for the horizontal portions of the curves in the shaded region is the vapor pressure which is the pressure at which the vapor and liquid are in equilibrium. In the region shaded yellow, to the left of the region shaded pink, the substance is a liquid and is nearly incompressible.

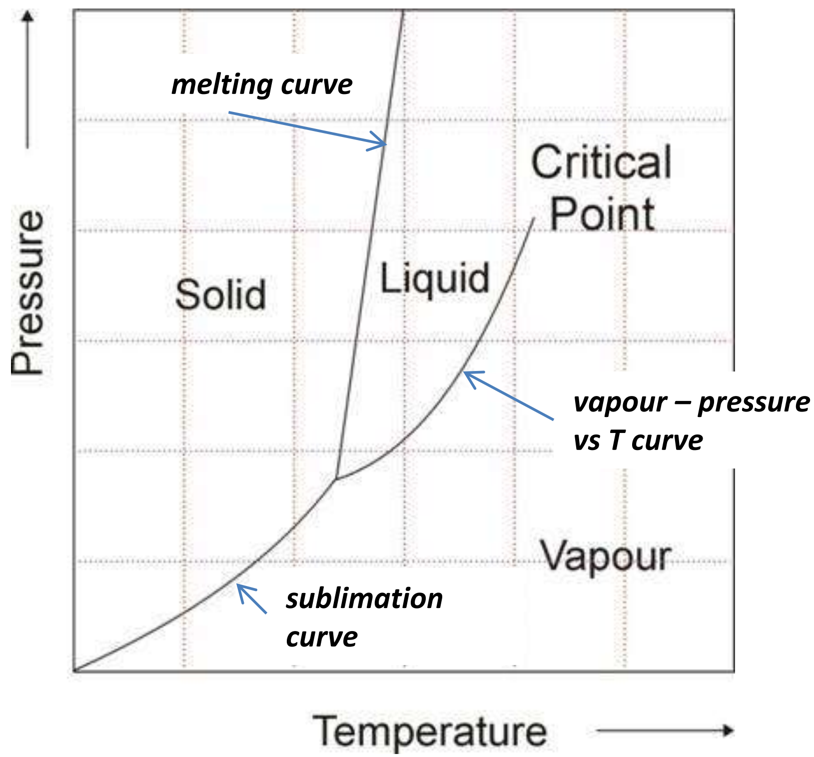
..pler

PV & PT phase diagrams

extended PV diagram

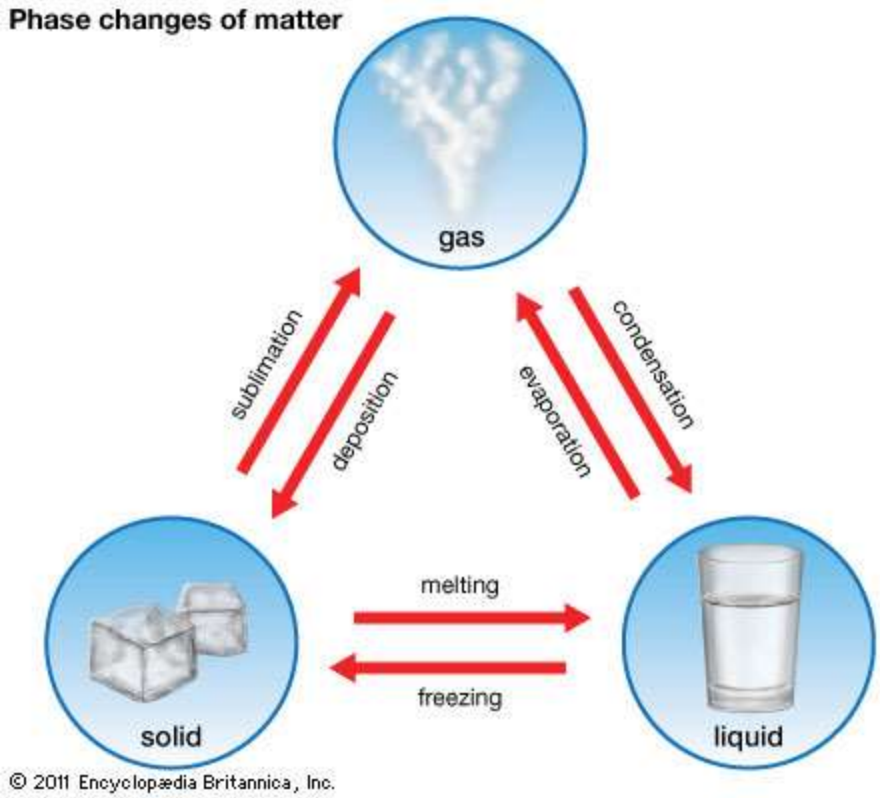


PT diagram

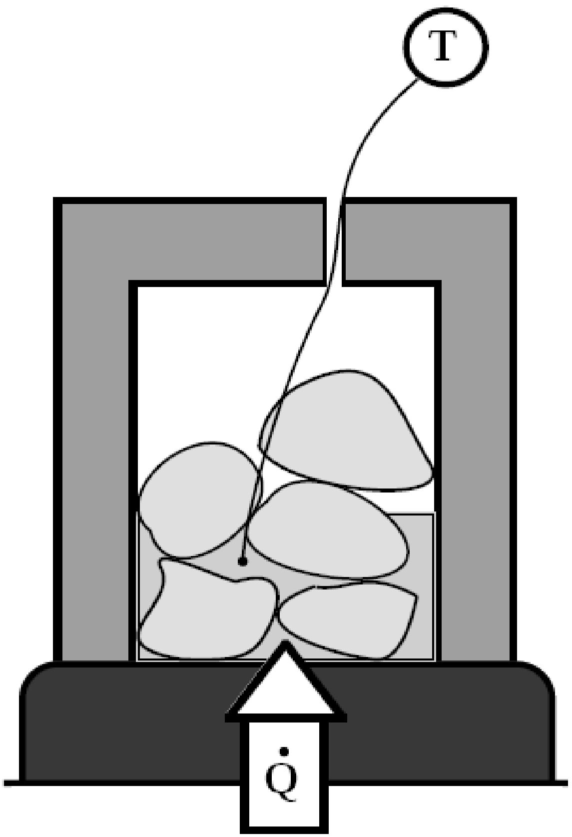


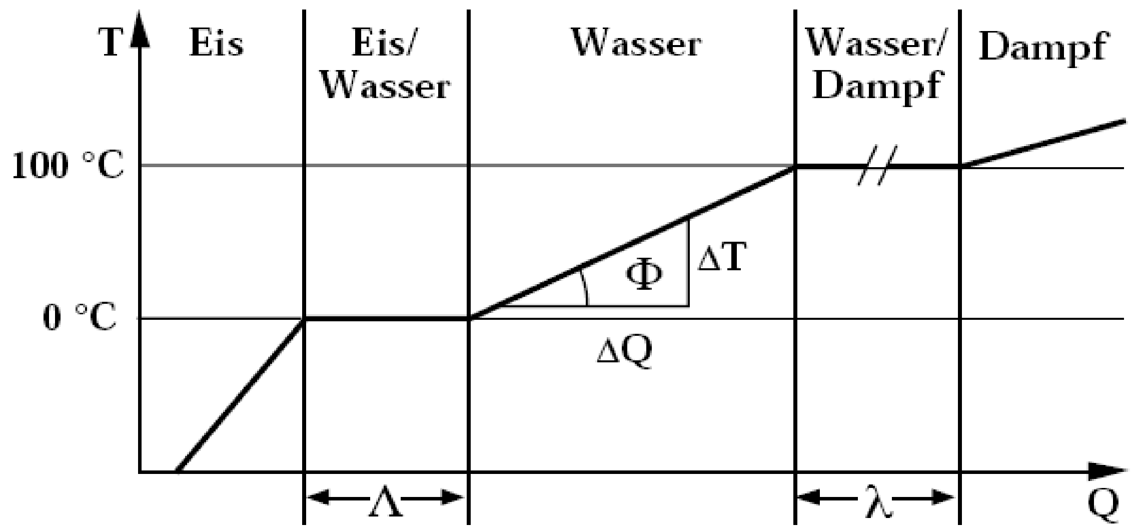
Uni Bristol

phase transitions



phase transition and latent heat





$$\frac{\Delta T}{\Delta Q} = \frac{1}{c_p} \qquad \Phi \sim \frac{1}{c_p}$$

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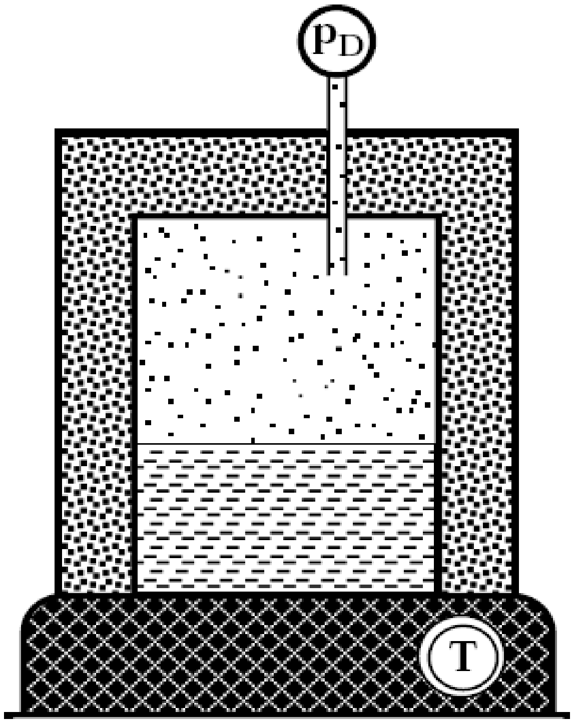
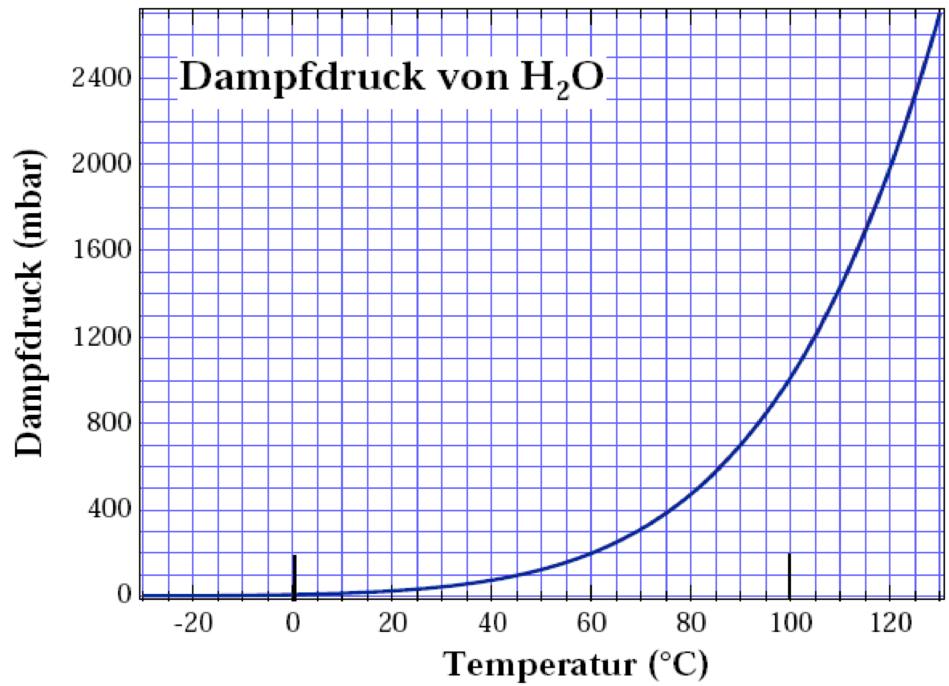
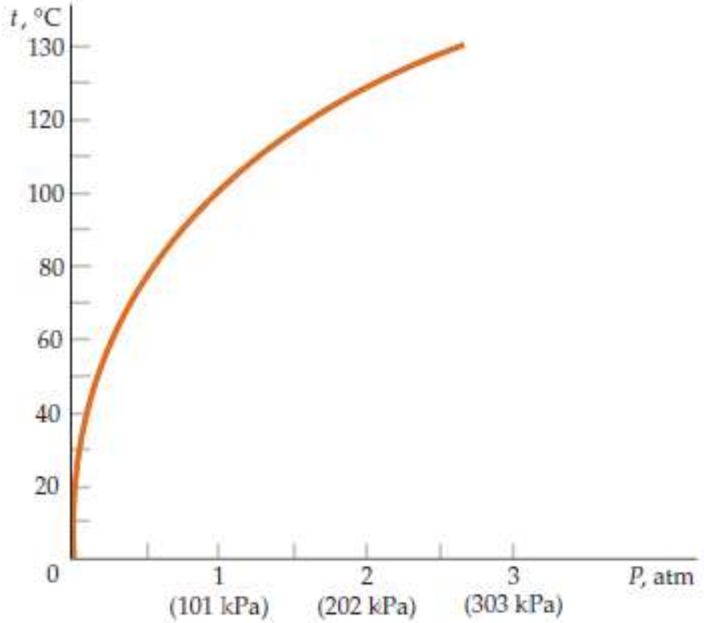
vapor pressure

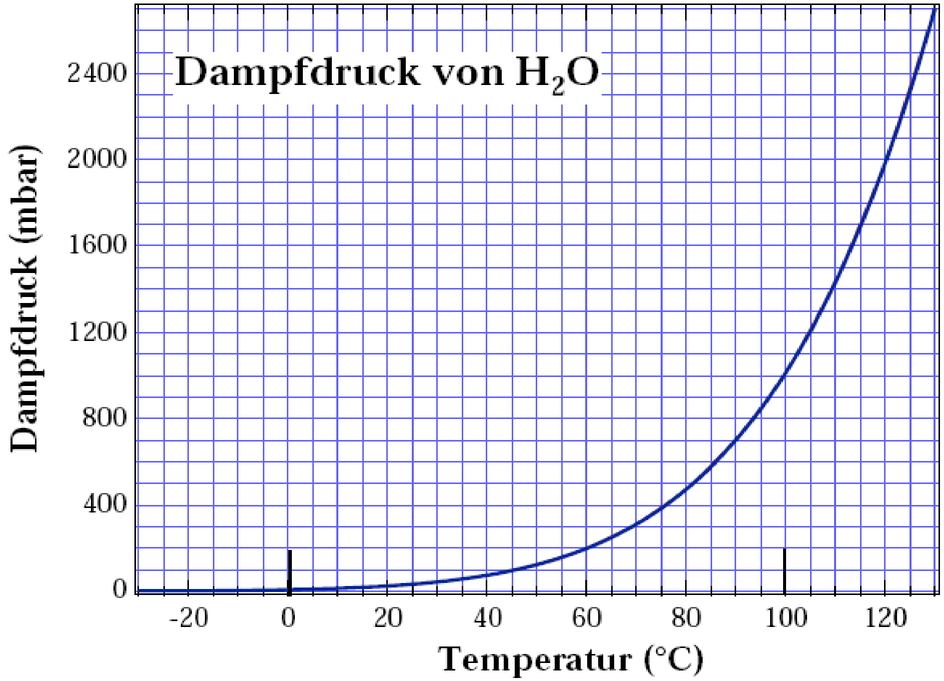




vapor pressure

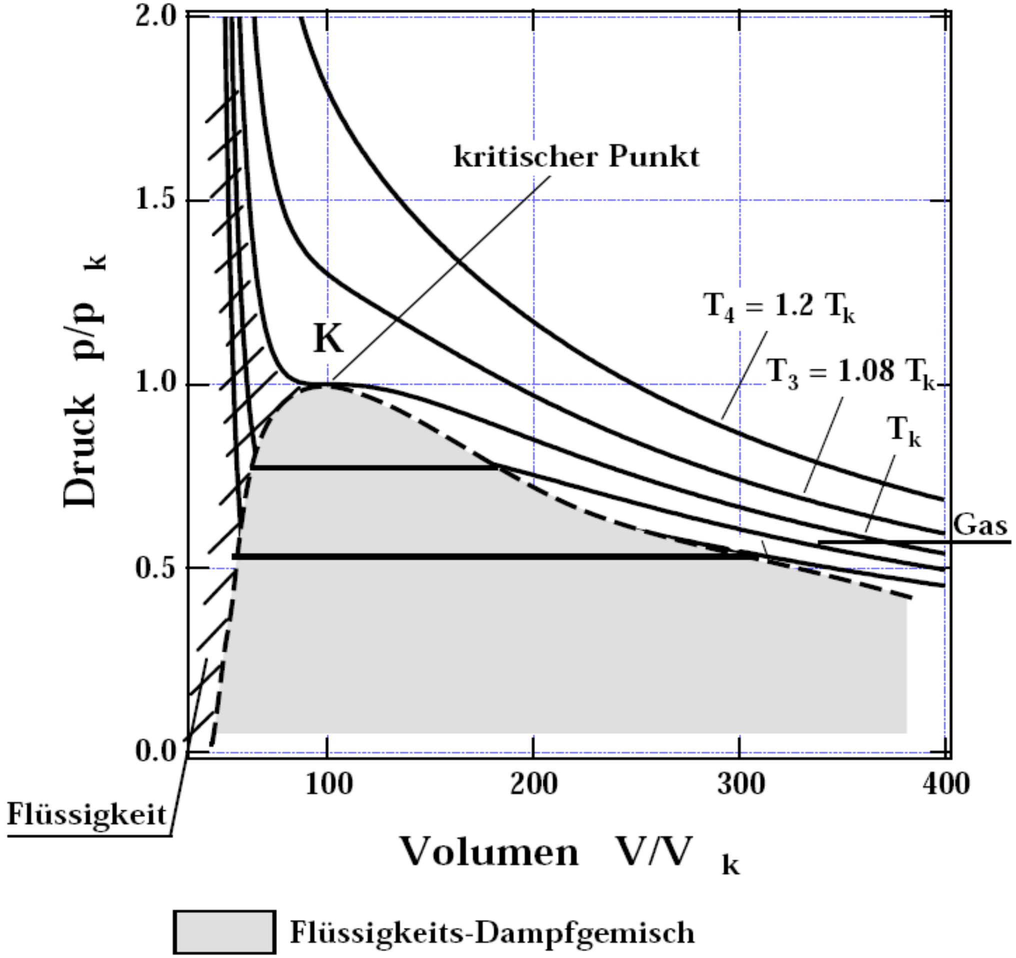
Boiling point of water vs pressure





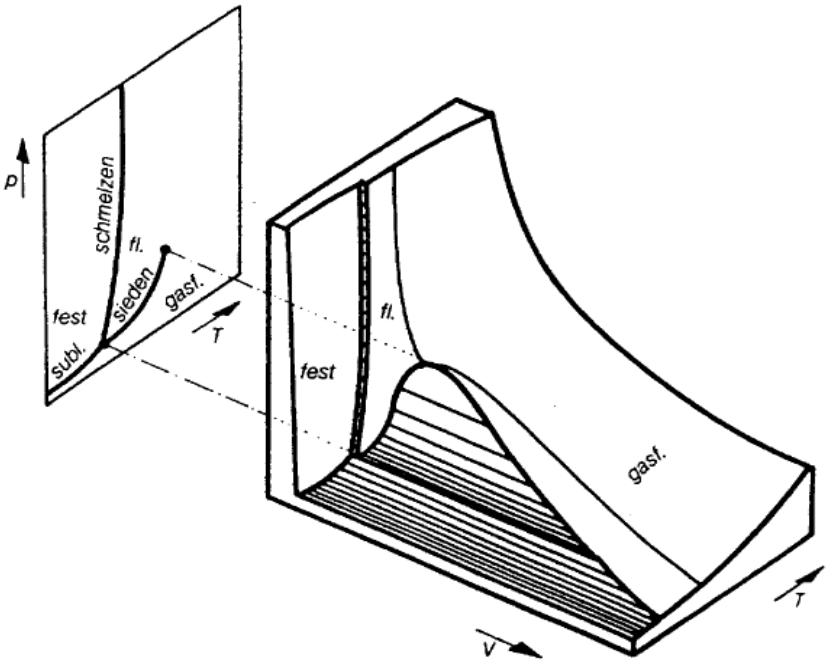
Tipler

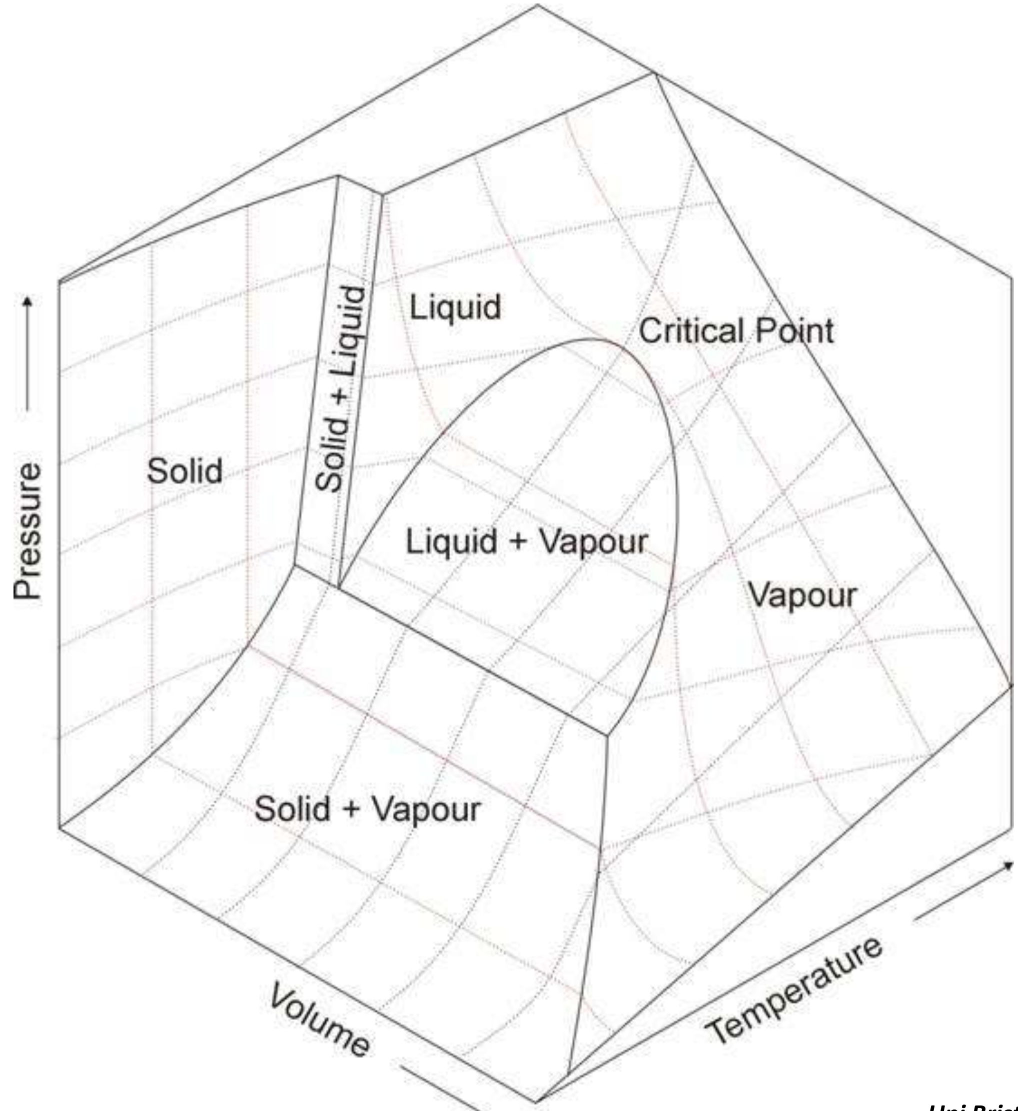
PV diagram



2.0
1.5
1.0
0.5
0.0
Druck p/p k
kritischer Punkt
K
T4 = 1.2 Tk
T3 = 1.08 Tk
Tk
Gas
100
200
300
400
Flüssigkeit
Volumen V/V k
Flüssigkeits-Dampfgemisch

PVT phase diagram





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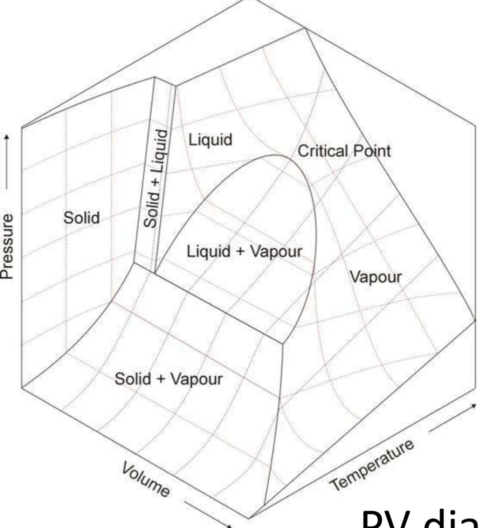
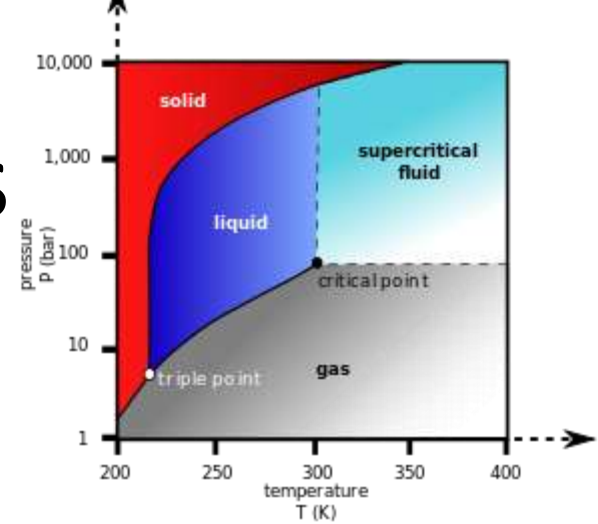
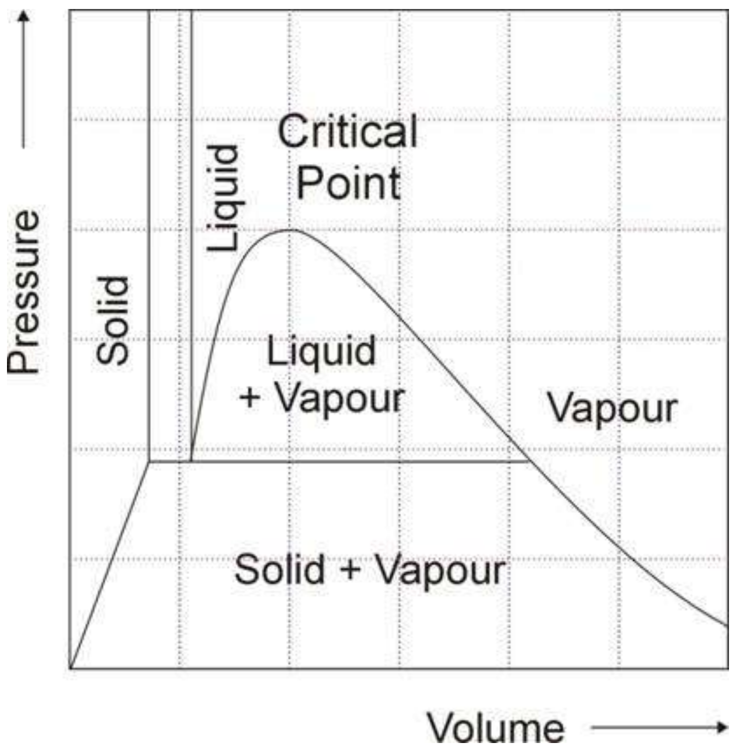
phase diagrams

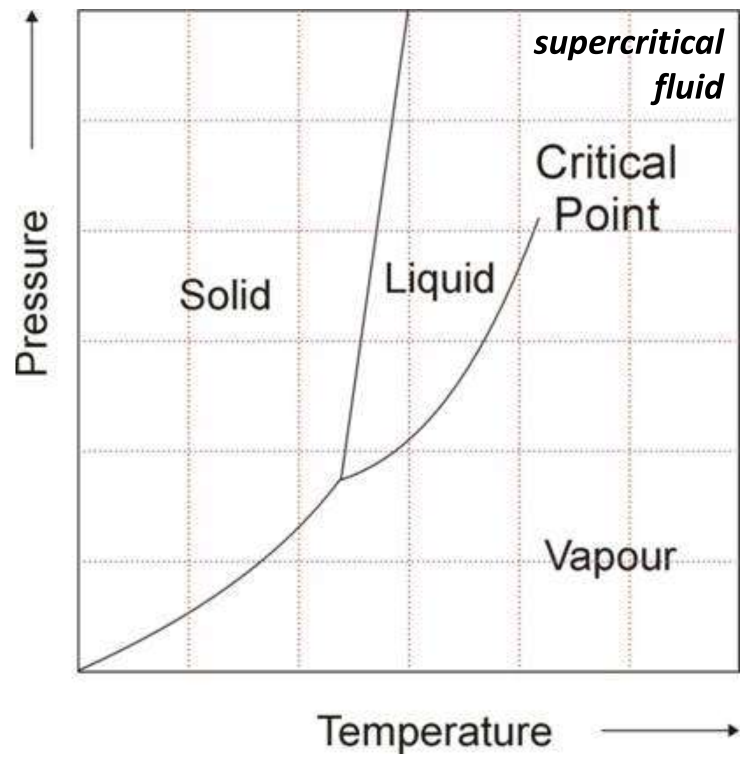




PV diagram

PT diagram





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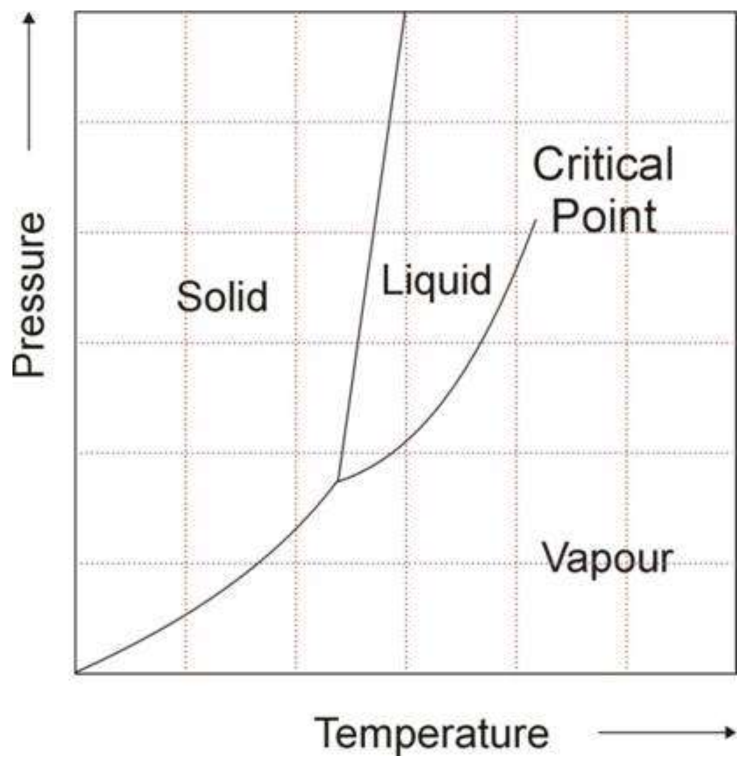
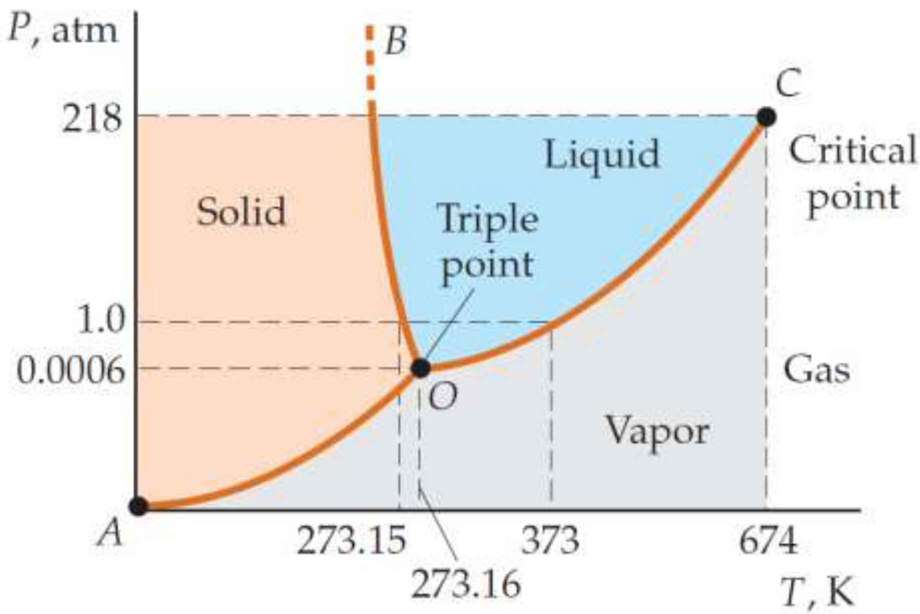
PT phase diagrams

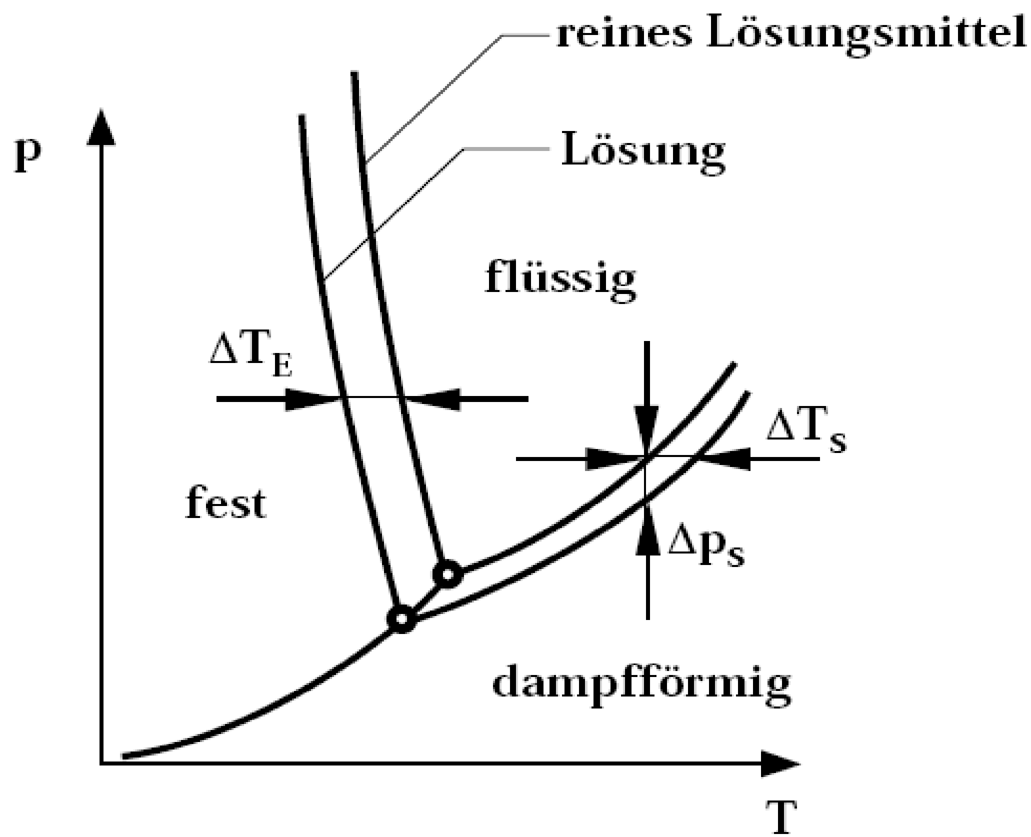


water

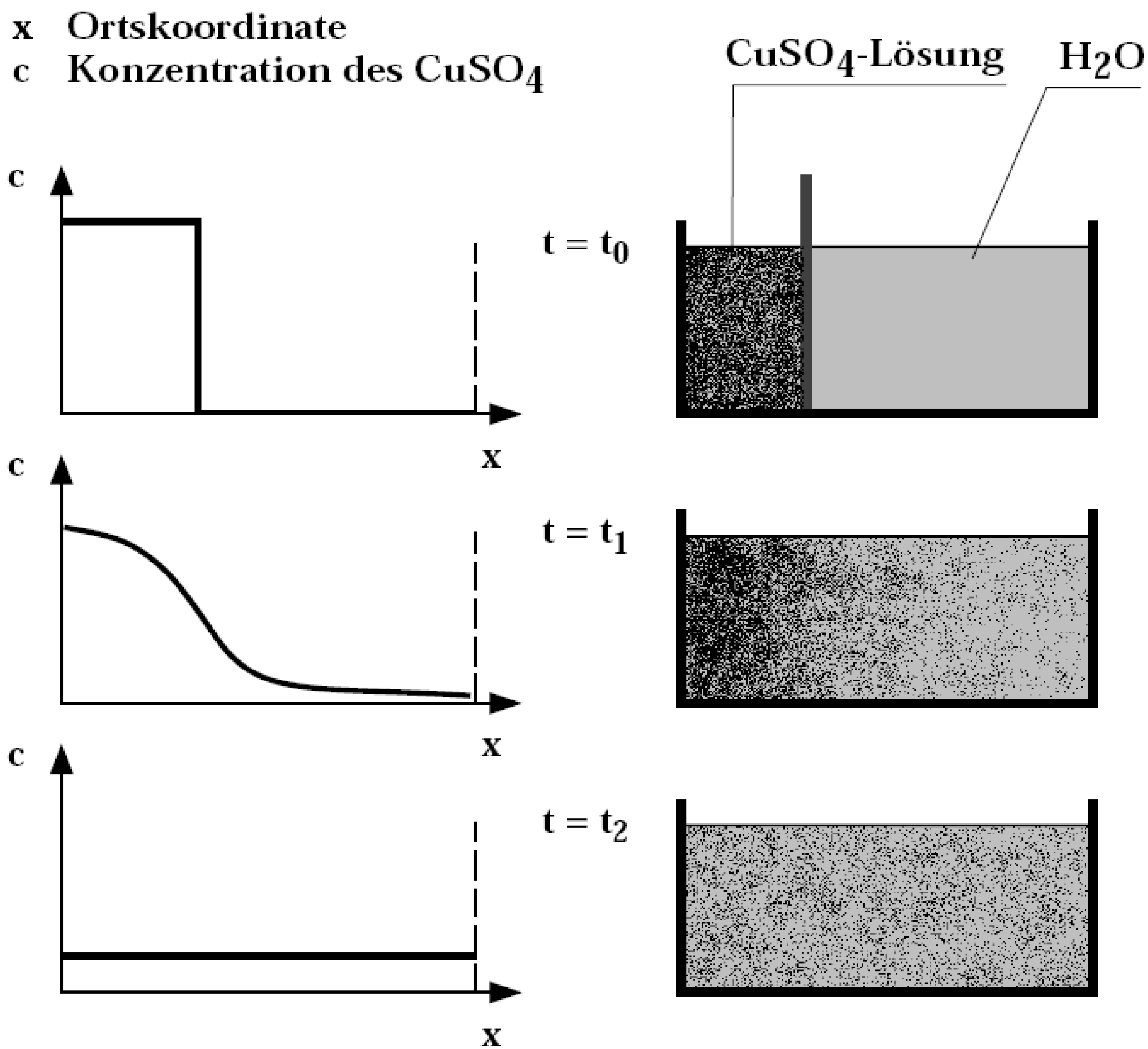


NB: The pressure and temperature scales are not linear but are compressed to show the points of interest.

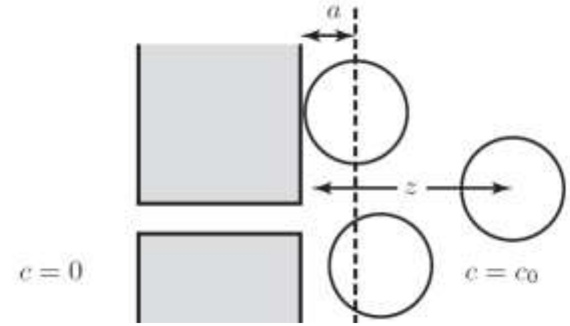
phase diagram: mixing substances

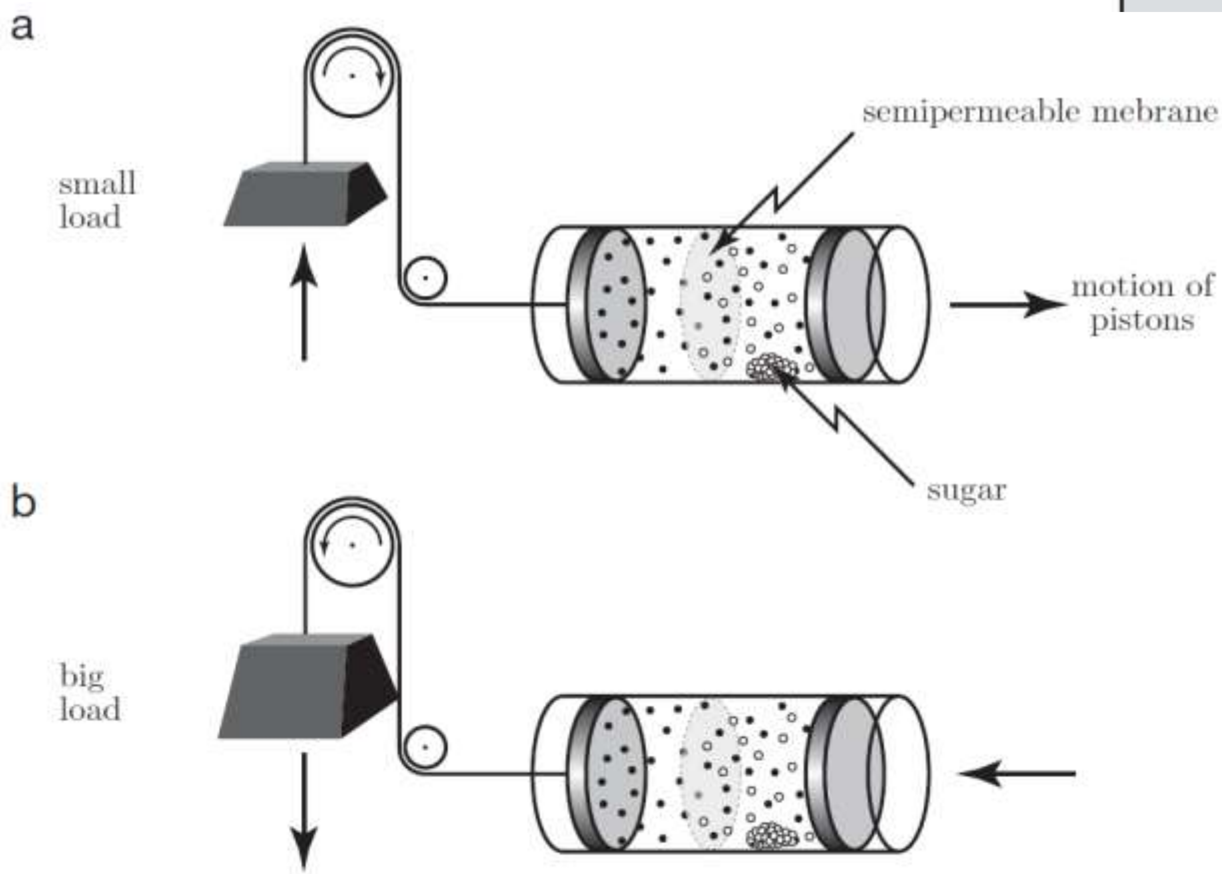


diffusion


x Ortskoordinate
c Konzentration des $CuSO_4$
$CuSO_4$-Lösung
H_2O
c
x
$t = t_0$
c
x
$t = t_1$
c
x
$t = t_2$

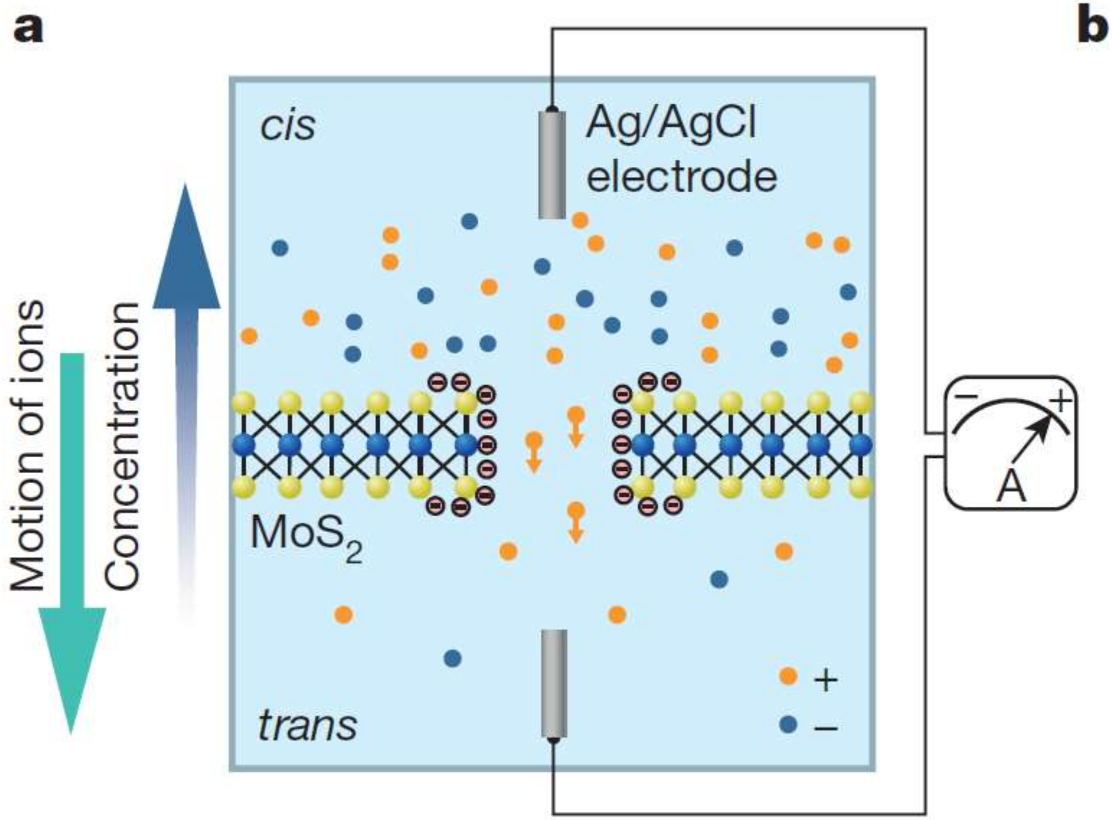
osmosis





Biological physics, P. Nelson

osmosis: electrical power generation

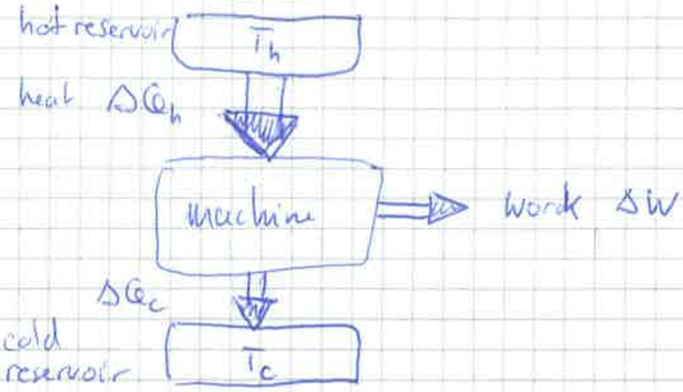


Radenovic et al., Nature (2016)

Merry Christmas
and
a happy new year!

Does hot water freeze faster than cold..?
Does cold water heat up faster than warm ..?
see Physics World, December 2017

heat machine : reversible process converting heat into work



reversible process

$\Delta S = 0$

$\Delta U = \Delta Q_{in} + \Delta W_{on} = 0$

heat absorbed — work done on system

$\Delta Q - \Delta W = 0$

$\Delta Q = \Delta Q_h - \Delta Q_c$

work done by system, that can be used to do mechanical work

and (1) $\Delta Q_h - \Delta Q_c = \Delta W$

entropy: $\Delta S = 0 = \Delta S_h + \Delta S_c$ total entropy change

$$-\frac{\Delta Q_h}{T_h} + \frac{\Delta Q_c}{T_c} = 0$$

and

$$(2) \quad \frac{\Delta Q_c}{\Delta Q_h} = \frac{T_c}{T_h}$$

- efficiency of machine $\eta = \frac{\Delta W}{\Delta Q_h} \underset{(1)}{=} 1 - \frac{\Delta Q_c}{\Delta Q_h} \underset{(2)}{=} 1 - \frac{T_c}{T_h}$

$$\| \quad \eta = 1 - \frac{T_c}{T_h} \quad \text{Carnot's efficiency}$$

- for an irreversible process :

$$\Delta S_{total} > 0$$

following the argument above ;

$$-\frac{\Delta Q_h}{T_h} + \frac{\Delta Q_c}{T_c} > 0 \quad \text{and} \quad \frac{\Delta Q_c}{\Delta Q_h} > \frac{T_c}{T_h}$$

for $\eta := 1 - \frac{\Delta Q_c}{\Delta Q_h}$

we get $\| \quad \eta < 1 - \frac{T_c}{T_h}$ real efficiency of a thermal machine

exp : steam machine
stirling engine %

- steam machine : James Watt

regulator balls : adjust steam admission (decrease) to decrease rotation speed

- stirling engine

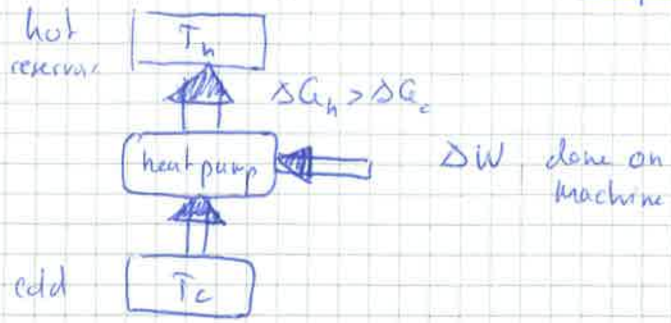
(slide)

low power - to - weigth ratio, but quiet, efficient

1) leybold version, 1 cylinder

2) stirling engine as cooling machine

heat machine using work (inverted)
for instance heat pump



$\Delta W = \Delta Q_h - \Delta Q_c$
as seen before

reversible system: $\Delta S = 0 = \Delta S_h + \Delta S_c$

hence $$\frac{\Delta Q_h}{T_h} - \frac{\Delta Q_c}{T_c} = 0 \ , \quad \frac{\Delta Q_c}{\Delta Q_h} = \frac{T_c}{T_h}$$

efficiency of the heat pump: $$\eta_{hp} = \frac{\Delta Q_h}{\Delta W} = \frac{\Delta Q_h}{\Delta Q_h - \Delta Q_c}$$ (we inject work ΔW and receive heat ΔQ_h)

$$\frac{1}{\eta_{hp}} = \frac{\Delta Q_h - \Delta Q_c}{\Delta Q_h} = 1 - \frac{\Delta Q_c}{\Delta Q_h} = 1 - \frac{T_c}{T_h} = \frac{T_h - T_c}{T_h}$$

$$\| \ \eta_{hp} = \frac{T_h}{T_h - T_c}$$

irreversible heat pump

$$\eta_{hp} < \frac{T_h}{T_h - T_c}$$

phase transitions (change of physical state)

reminder: Van der Waals gas law: $\left(p + a \cdot \frac{n^2}{V^2}\right) \cdot (V - n \cdot b) = n \cdot RT$

(a term: correction to pressure due to intermol. interactions; b term: volume of molecul. correction)

(ideal: $P \cdot V = n \cdot R \cdot T$)

→ gas becomes liquid.

(slides) vdw + PV, PT diagrams

after transitions:

- solid ↔ liquid — melting / freezing
- solid ↔ gas — sublimation / deposition
  - examples: frost (water vapor to ice), snow in clouds
  - graphene from CH_4 (chem. vap dep)
- liquid ↔ gas — evaporation / condensation (boiling)

(slide)

plasma

example: 1kg ice warming, constant ΔT/second, P = const (1 atm)

draw it % (slide) - drawing + latent heat: graph T vs Q (heat provided to system)

remember $\Delta Q = C_p \cdot \Delta T$

hence $\frac{\Delta T}{\Delta Q} = \frac{1}{C_p} = \varphi$ (slope in graph) — C_p: heat capacity at const. pressure

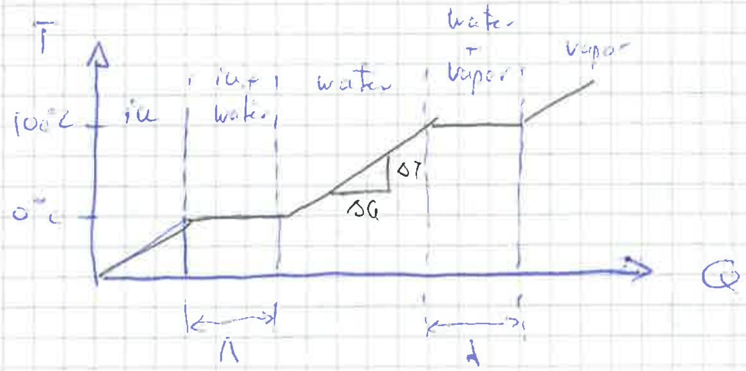
Λ: heat of fusion

λ: heat of vaporization

def: latent heat: energy absorbed or released by a substance during a phase transition occuring without changing its temperature

→ a characteristic of the material (property)

→ a measure of the interatomic / intermolecular forces



slope: $\frac{\Delta T}{\Delta Q} = 4$

seen: $\Delta Q = C_p \Delta T$ $\qquad P = \text{const}$

$$\Rightarrow \frac{\Delta T}{\Delta Q} = \frac{1}{C_p}$$

for water molecules: ice: $\Lambda \cong 3.35 \cdot 10^5$ J/kg
heat of fusion
water: $\lambda \cong 2.25 \cdot 10^6$ J/kg, note $\lambda > \Lambda$

$$C_p^{ice} \left(= \frac{\Delta G}{\Delta T}\right) \cong 2.1 \cdot 10^3 \text{ J/kg K}$$
$$C_p^{water} \cong 4.2 \cdot 10^3 \text{ J/kg K}$$

exp: evaporation of diethyl ether $(C_2H_5)_2O$ 

boiling point ~308 K = 34.6 °C; note T↘, heat taken from environment

- Vapor pressure: pressure at which a liquid is in thermodynamic equilibrium with its vapor (if p↗ further, condensation)

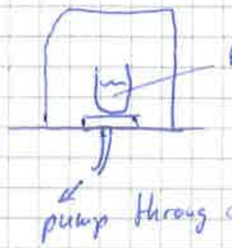
(slide)

per unit time, the nb of molecules evaporating and condensing is ~~constant~~ the same

exp: a) pressure cooker: p↗
~~water~~ water + water vapour in thermod. equilibr.

b) boiling at room temperature: water

P↘, water starts boiling / evaporating



c) drop of water of hot plate (Leidenfrost effect)

motion of droplet

note: drop evaporates only slowly
⇒ vapour acts as thermal insulator (lower thermal conductivity)

d) dip finger quickly in N_2: finger insulated by vapor layer
!

phase diagrams

(slides)

- PV phase diagram : gas, liquid, mixture liquid + gas
- PVT phase diagram
- PV and PT phase diagrams (projection)
  - note : supercritical fluid : substance above critical point (P_c, T_c)
- PT diagrams compared : case of water

  note, for water, volume increases upon freezing
  (Δ bottle in freezer)

note : bei mixing substances, the phase diagrams can be shifted

(slide) - shift of P(T) curve upon addition of a second substance

Diffusion: transport process by which a concentrated substance spreads out over a wider extent (lower concentration)
microscopically, diffusion is linked to the brownian motion of the mobile constituents of a substance (molecules)

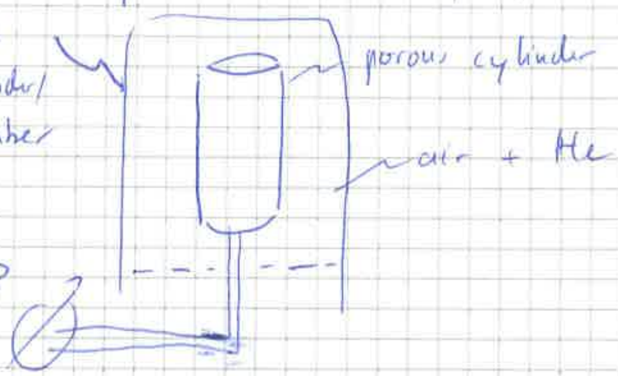
example:
- mixing of gases (after opening valve)

- diffusion of dopants in crystals
- mixing of two liquids

note: irreversible process $-\Delta S > 0$ (entropy)

slide: $CuSO_4$ solution diffuses in H_2O

exp: He diffusion through clay cylinder (ceramic)



ask: effect of porous cylinder?

1) add He into chamber
   - He diffuses through porous cylinder faster than air molecules can get out, $P \nearrow$ in cylinder

2) remove glass cylinder: He diffuses out faster than air can get back in, $P \searrow$ in cylinder

remember: $v_{rms} = \sqrt{\frac{3RT}{M}}$ — M: molar mass $[M] = kg/mol$

↑ root mean square velocity of molecules in gas

↳ $v_{rms}^{He} > v_{rms}^{N_2}$! $v_{rms} \propto \sqrt{T}$, $\propto \frac{1}{\sqrt{M}}$

diffusion depends on:
- substances
- concentration gradient
- temperature T

from: $v_{rms} = \sqrt{\langle v^2 \rangle_{avg}}$

$\left(\frac{1}{2} m v^2\right)_{avg} = \frac{3}{2} k_B T$

diffusion law (in one dimension)

$$\frac{dn}{dt} = -D \cdot \frac{dc}{dx}$$

n: molar flux $[n] = \frac{mol}{m^2 \cdot s}$

D: diffusion constant $[D] = m^2/s$

$x = \sqrt{D \cdot t}$

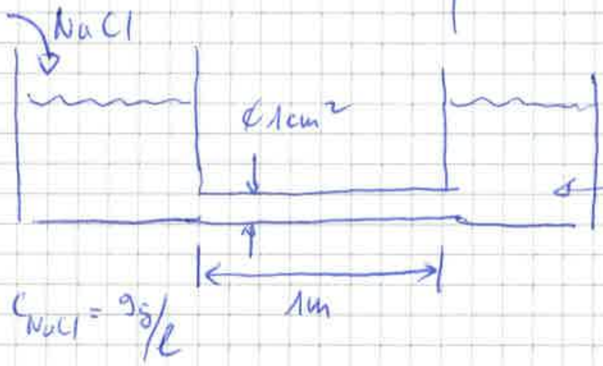
c: concentration of substance $[c] = \frac{mol}{m^3}$

~~A: cross section [A] = m²~~

D depend on temperature and diffusion medium.

example: compare values.

diffusion of	in	D [m²/s]
H_2	air (0°C)	$6.3 \cdot 10^{-5}$
H_2O vapor	"	$2.4 \cdot 10^{-5}$
sugar	water (12°C)	$3.0 \cdot 10^{-10}$



2 water reservoirs

NaCl after 1h?
(no salt at beginning)

$$\Delta M = \Delta t \cdot D \cdot \text{Area} \cdot \frac{dc_{kg}}{dx} \quad , \quad \frac{dc_{kg}}{dx} = \frac{9g/l}{1m} = \frac{9kg}{m^3} \cdot \frac{1}{m}$$

M: mass

$\frac{dc_{kg}}{dx}$: concentration in $\frac{kg}{m^3}$

$$\Delta M = \underbrace{3600}_{1\,\text{hour}} \cdot D \cdot 10^{-4} \cdot 9 \simeq 3.6 \cdot 10^{-9}\ kg = 3.6\ \mu g$$

micrograms!

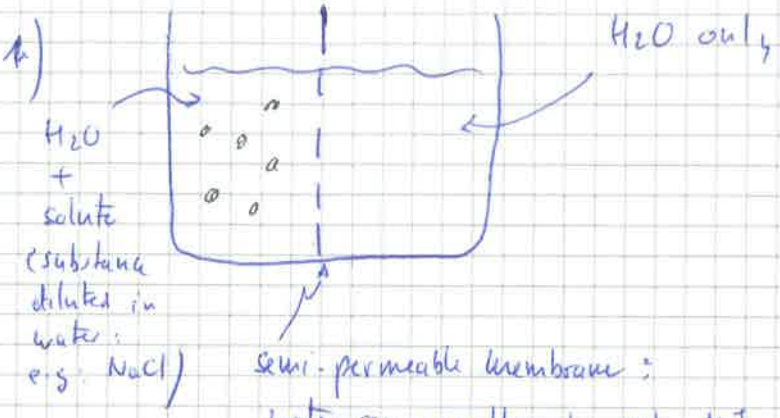
not very efficient mixing

$D \simeq 1.1 \cdot 10^{-9}\ m^2/s$

(NaCl in water, T = 15°C)

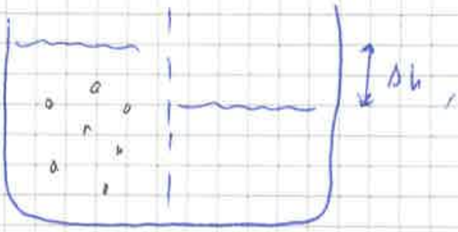
Osmosis : diffusion of a liquid through a semi-permeable membrane

1)



semi-permeable membrane: water can pass through, not Na^+ or Cl^- ions

2) system tries to equilibrate: diffusion of water to ...



$\Delta P = P_2 - P_1 = \rho\, g \cdot \Delta h$
$= P_{osmotic}$
osmotic pressure

phenomenological observations

a) Δp is independent of the substance type
b) Δp is related to the molar concentration (mol/m³) of the solute and to temperature
c) the solute cannot diffuse: hydration → (Na^+) ← water molecule

van't Hoff:

$$P_{osm} = \frac{n}{V} \cdot R \cdot T$$

, $\frac{n}{V}$: molar concentration of the solute

(ok for small $\frac{n}{V}$)

note: cell membranes are semi-permeable membranes!

(slide) - osmotic machine (P. Nelson)

osmosis / reverse osmosis

Where does the energy come from? (entropic force!)

- ~~heat taken from environment~~
- rectification of brownian motion:
  larger particles (solute) bouncing back pull
  fluid through membrane
- "price" to pay for rectification (not full conversion to work from thermal source):
  piston moves and V ↗ on solute side, losing order on
  solute side (ΔS!)

· reverse osmosis (ultrafiltration) → water purification %

· use membrane for selective ion diffusion:

(slides) - ion-selective membrane & power generation
draw it! → cf video

life / living organisms create order (assemble molecules, ... life)

by transforming / transducing energy.

a) 

b) plants

light, H_2O, CO_2 => waste heat, O_2

=> sugar, fat, plant tissue...

c) animals

sugar, fat, O_2 => waste heat, CO_2, H_2O

=> animal tissue, music, ... etc... ☺

Philip Nelson: biological physics