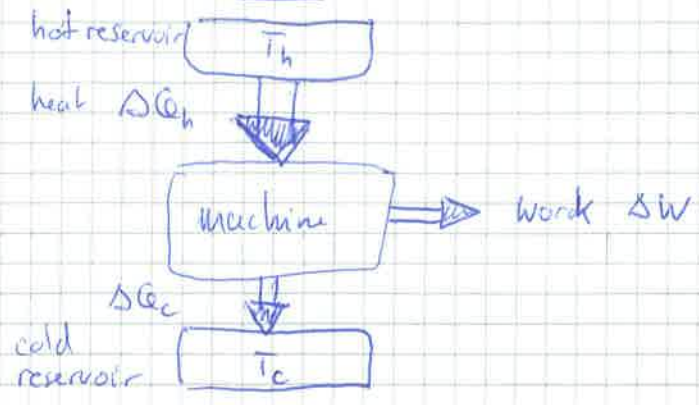


heat machine: reversible process converting heat into work



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

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

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

$\eta = 1 - \frac{T_c}{T_h}$ 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 $\eta < 1 - \frac{T_c}{T_h}$

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

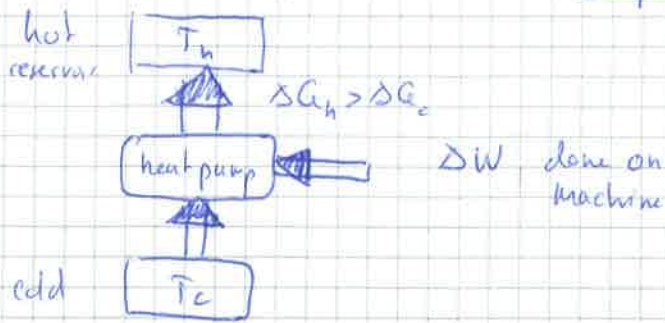
slide

1) Leybold version, 1 cylinder

2) Stirling engine as cooling
machine

heat machine using work (inverted)
 for instance heat pump

L25 ✓



$$\Delta W = \Delta Q_h - \Delta Q_c$$

as seen before

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

hence

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

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

$$= \frac{\Delta Q_h}{\Delta Q_h - \Delta Q_c}$$

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

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

irreversible heat pump

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

phase transitions (change of physical state)

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

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

↑
correction to pressure due to intermolecular interactions
↑
volume of individual correction

→ gas becomes liquid.

slides

vdw + PV, PT diagrams

after transitions:

- solid ↔ liquid
- solid ↔ gas

melting / freezing

sublimation / deposition

examples: • frost (water vapor to ice)
• snow in clouds

slide

• graphene from CH₄ (chem. imp. dep.)

plasma

- liquid ↔ gas

evaporation / condensation (boiling)

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

draw it of

slide

- drawing + latent heat: graph T vs Q

↑
heat provided to system

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

hence $\frac{\Delta T}{\Delta Q} = \frac{1}{C_p} = \phi$ C_p : heat capacity at const. pressure
↑
slope in graph

Λ: heat of fusion

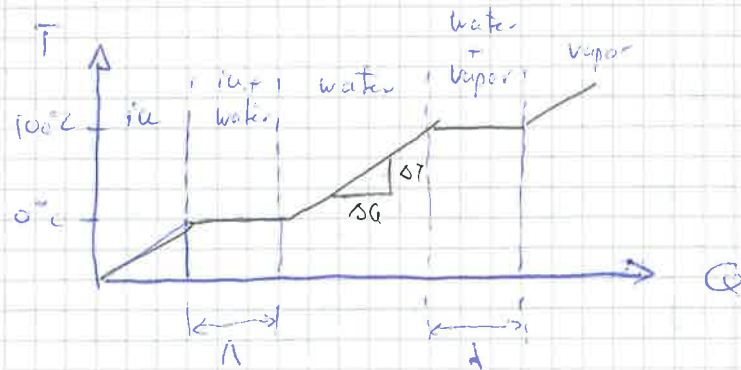
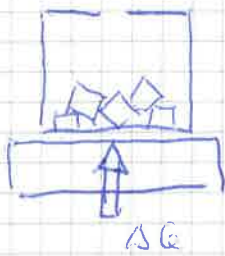
Δ: heat of vaporization

def:

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

→ a characteristic of the material (property)

→ a measure of the interatomic / intermolecular forces



$$\text{slope} = \frac{\Delta T}{\Delta Q} = 1$$

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


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

for water molecules: ice : $\Lambda \approx 3.35 \cdot 10^5 \text{ J/kg}$

heat of fusion

water : $\lambda \approx 2.25 \cdot 10^6 \text{ J/kg}$, note $\lambda > \Lambda$

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

exp : evaporation of diethyl ether (C2H5)₂ 

boiling point $\sim 308 \text{ K} = 34.6 \text{ }^\circ\text{C}$; note $T \downarrow$, heat taken from environment

o Vapor pressure : pressure at which a liquid is in thermodynamic equilibrium with its vapor

slide

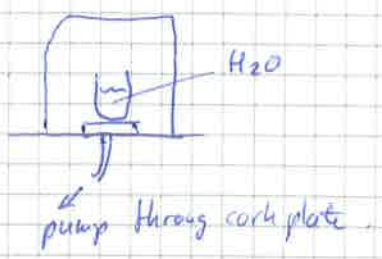
(i) $P \uparrow$ further, condensation)

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

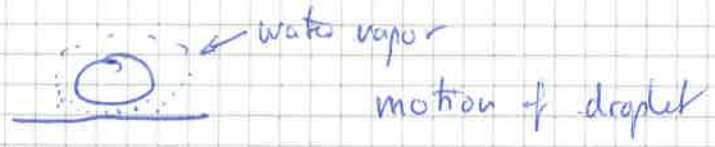
exp : a) pressure cooker : $P \uparrow$
water + water vapor in thermod. equilbr.

b) boiling at room temperature : water

$P \downarrow$, water starts boiling / evaporating



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



note : drop evaporates only slowly
 \Rightarrow vapor acts as thermal insulator (lower thermal conductivity)

d) dip finger quickly in N2 : finger insulated by vapor layer
!

phase diagrams

(slide)

- PV phase diagram: gas, liquid, mixtures liquid + gas
- PVT phase diagram
- PV and PT phase diagrams (projection)
 - note: supercritical fluid: substance above critical point (Pcrit)
- PT diagrams compared. case of water
 - note, for water, volume increases upon freezing
(N bottle in freezer)

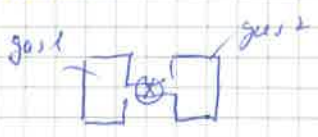
note: bei mixing substances, the phase diagrams can be shifted

(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 ~~area~~ 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 valves)
 - diffusion of dopants in crystals
 - mixing of two liquids

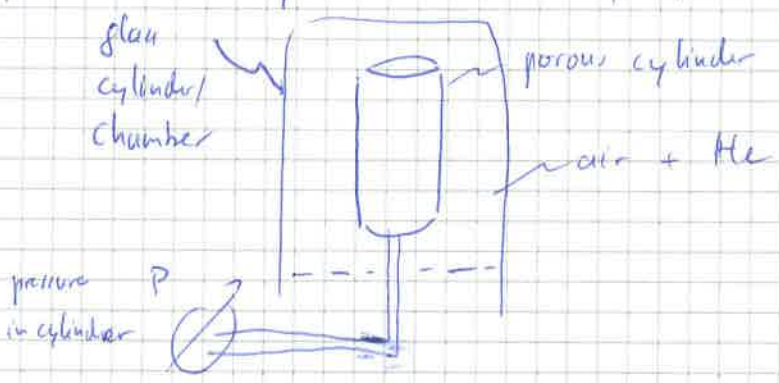


note: irreversible process
 $-\Delta S > 0$
 (entropy)

slide

CaSO_4 solution diffusion in H_2O

exp: He diffusion through clay cylinder (ceramic)



note: effect of porous cylinder?

- 1) add He into chamber
 - He diffuses through porous cylinder faster than air molecules can get out, $P \uparrow$ in cylinder
- 2) remove glass cylinder: He diffuses out faster than air can get back in, $P \downarrow$ in cylinder

remember:

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

root mean square velocity of molecules in gas

n : molar mass [M] = kg/mol

$$v_{rms}^{\text{He}} > v_{rms}^{\text{N}_2} \quad \left| \quad v_{rms} \propto \sqrt{\frac{1}{M}} \right.$$

diffusion depends on:

- substances
- concentration gradient
- temperature T

from:

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

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

diffusion law (in one dimension)

L26/5

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

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

D : diffusion coefficient $[D] = \frac{\text{m}^2}{\text{s}}$
 $x = \sqrt{D \cdot t}$

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

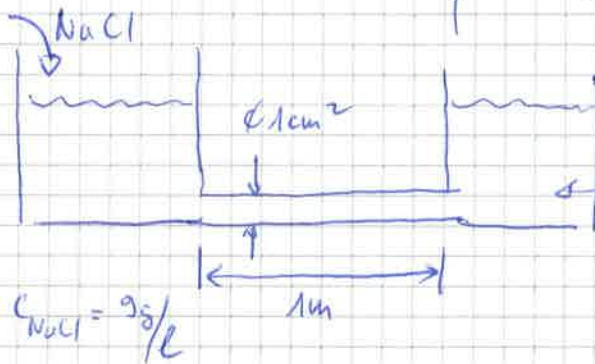
~~A : cross section $[A] = \text{m}^2$~~

D depends on temperature and diffusion medium

example:

(compare values)

diffusion of	in	D [m^2/s]
H_2	air (0°C)	$6.3 \cdot 10^{-5}$
H_2O vapor	"	$2.4 \cdot 10^{-5}$
sugar	water (20°C)	$3.0 \cdot 10^{-10}$



2 water reservoirs
 NaCl after 1h?
 (no salt at beginning)

$$\Delta M = \Delta t \cdot D \cdot \text{Area} \cdot \frac{dc_{\text{NaCl}}}{dx}$$

↑
 wall area

↑
 concentration in $\frac{\text{kg}}{\text{m}^3}$

$$\frac{dc_{\text{NaCl}}}{dx} = \frac{9 \text{ g/l}}{1 \text{ m}} = \frac{9 \text{ kg}}{\text{m}^3} \cdot \frac{1}{\text{m}}$$

$$\Delta M = 3600 \cdot D \cdot 10^{-4} \cdot 9 \approx 3.6 \cdot 10^{-9} \text{ kg} = 3.6 \mu\text{g}$$

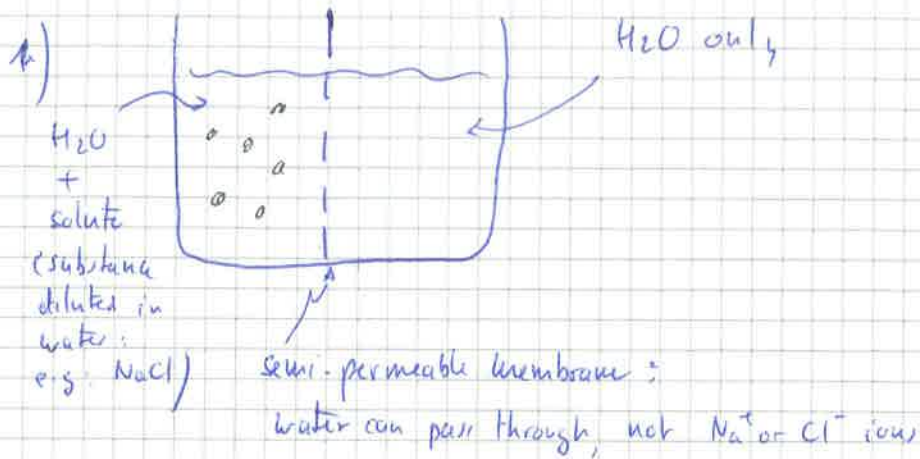
↑
 1 hour

$$D \approx 1.1 \cdot 10^{-9} \frac{\text{m}^2}{\text{s}}$$

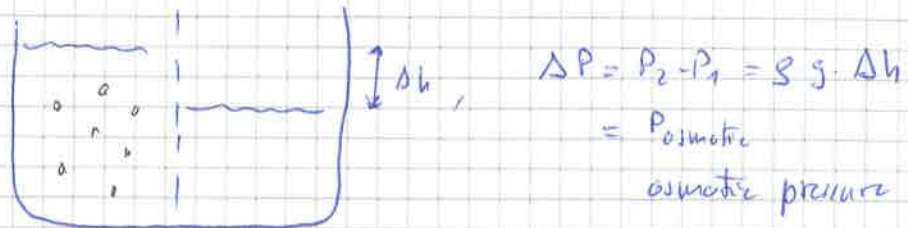
↑
 (NaCl in water, $T = 15^\circ\text{C}$)

micrograms!
 not very efficient mixing

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



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



phenomenological observations:

- Δp is independent of the substance type
- Δp is related to the molar concentration (mol/m^3) of the solute and to temperature
- the solute cannot diffuse: hydration \rightarrow water molecules

van't Hoff:

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

$\frac{n}{V}$: 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 $V \uparrow$ on solute side, losing order on solute side ($\Delta S!$)

reverse osmosis (ultrafiltration) → water purification %

• use membrane for selective ion diffusion:

slides - ion-selective membrane & power generation draw it! - of video

life / living organisms create order (assemble molecules, ... like) by transforming/transducing energy.



b) plants



c) animals

