| Ideal gases |

low density gases :
- microscopic billiard / pool : elastic shocks between atoms (molecules)
- no intermolecular forces (well separated atoms)

• energy (internal energy) : kinetic energy of atoms / molecules
  of gas

  $\Rightarrow$ any change in energy results in a Temp change

(exp) • exp. observation : $P \cdot V = $ constant , for a given T

Boyle-
Ramiott

(RBoyle, 17th Century) $\overset{\text{volume}}{\uparrow}$
  pressure

  exp. observation : $P \cdot V = $ const $\cdot T$ (const is > 0)

(exp) $\begin{pmatrix} J. \text{ Charles} & 18^{th}-19^{th} \\ J. \text{ Gay-Lussa} & \text{Cent} \end{pmatrix}$ $\overset{\text{temperature}}{\uparrow}$

Gay-
Lussac

• const = ... ?   take 2 containers P, V, T P, V, T $\dfrac{p \cdot V}{T} = const$
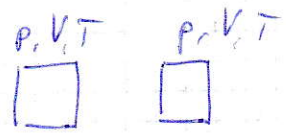
  $\rightarrow$ merge as one $\dfrac{p \cdot 2V}{T} = const'$
     system

  hence : const $\propto$ nb of gas molecules (const' = 2·const)
                      (amount of gas)

  and, def :   const = $k_B N$
                        $\nearrow$ nb molecules
               $\overset{\nwarrow}{R}$ other constant ...(!)

  and $\underline{p \cdot V = N \cdot k_B \cdot T}$

         $k_B = 1.38 \cdot 10^{-23} \cdot J/k$, Boltzmann constant
                                        (value found exp.)

         $N = n \cdot N_A$

         $N_A = 6.022 \cdot 10^{-23} \, mol^{-1}$, Avogadro number
         n : nb of moles (mol)

  def: 1 mol of a substance contains N_A elements
                                              (atoms or
        (measure of the amount of a gas, here)   molecule)
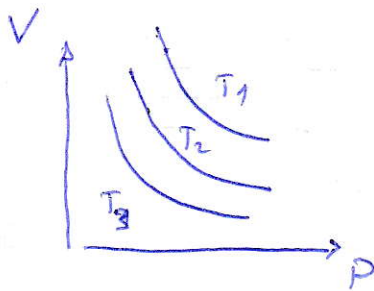
thus

         $P \cdot V = N \cdot k_B \cdot T = n \cdot N_A \cdot k_B \cdot T$

ideal gas $\left\| \; P \cdot V = n \cdot R \cdot T \right.$, $R = N_A \cdot k_B = 8.314 \, \dfrac{J}{mol \cdot K}$
law
(slide) univ. gas constant   note $[P \cdot V] = \dfrac{N}{m^2} \cdot m^3 = N \cdot m = J$ universal gas constant
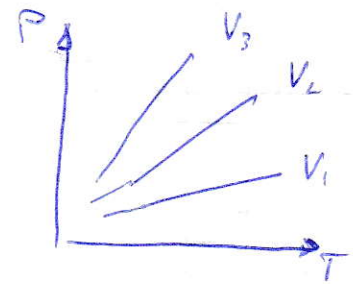   energy / work

a)

schematic
behavior $PV = n \cdot R \cdot T$, take $n = const$ (e.g. 1 mol)

$T_1 > T_2 > T_3$

isotherms
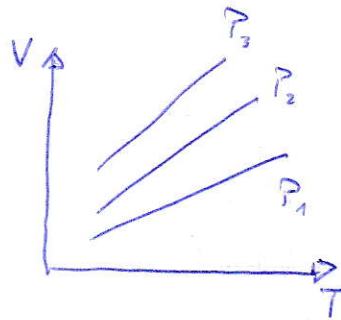
$P_1 > P_2 > P_3$

isobars

$V_1 > V_2 > V_3$

isochores

b) $PV = n \cdot RT$,   take $n = 1$, N_A molecules

$$V = \frac{R \cdot T}{P} \simeq 22.7\, l = 2.27 \cdot 10^{-2}\, m^3$$

exp show
molvolumen

at standard pressure
& temperature   (STP)

$P = 100\, kPa$

$T = 273.15\, K$

$R = 8.314\, \dfrac{J}{mol\, k}$

$PV = n \cdot R \cdot T$

- relation between P, V and T for an ideal gas ,   state equation
  (gas law)
- correction required when gas density increases

-

exp Boyle Mariott :   P V = const

work really ?

exp Gay Lussac : $\dfrac{P}{T}$ = const   for V = const

Measure P for various T   · R.T   { write values
for fixed volume of gas V   · boiling water   { + plot
        (He)   · 0°C

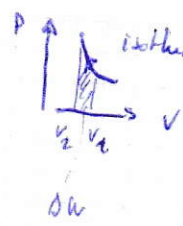   · N_2 liquid 77k

examples of expansion of gas (ideal) from V_1 to V_2 at $T = \text{const}$

work:
$$\Delta W = \int_{V_1}^{V_2} P \cdot dV = \int_{V_1}^{V_2} n \cdot R \cdot T \cdot \frac{dV}{V} = n \cdot R \cdot T \cdot (\ln V_2 - \ln V_1)$$
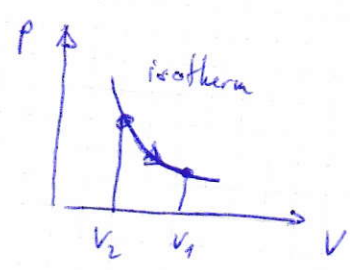
isotherm ($T = \text{const}$)

$PV = nRT$

$P = \frac{nRT}{V}$

nb of moles

$$\boxed{\Delta W = nRT \ln \frac{V_2}{V_1}} \qquad (1)$$

b) energy required to fill a nitrogen (N_2) gas bottle from ambient pressure (1 bar) to 200 bar (in the bottle)

$P_1 = 1 \text{ bar}$ $\qquad P_2 = 200 \text{ bar}$

$V_1, T_1 = 300 k$ $\qquad V_2 = 50 \ell$

$\qquad\qquad\qquad T_2 = 300 k$

$\qquad\qquad\qquad = T_1 = T$

isotherm

isotherm: $P_1 V_1 = P_2 V_2$, so $V_1 = \dfrac{P_2 V_2}{P_1}$

ideal gas: $P_2 V_2 = n R T$, and $n = \dfrac{P_2 V_2}{R T}$

from eq (1) above:

$$\Delta W = n \cdot R \cdot T \cdot \ln \frac{V_2}{V_1} = \frac{P_2 V_2}{R T} \cdot R T \cdot \ln \frac{V_2}{\frac{P_2 V_2}{P_1}}$$

$$= P_2 \cdot V_2 \cdot \ln \frac{P_1}{P_2} \quad ; \quad \text{indep. of } T$$

$$\boxed{\Delta W = 2 \cdot 10^7 \frac{N}{m^2} \cdot 5 \cdot 10^{-2} m^3 \cdot \ln \left(\frac{1 \text{ bar}}{200 \text{ bar}} \right) = -5.3 \cdot 10^6 \text{ J}}$$

$1 \text{ bar} = 10^5 \text{ Pa}$

$\qquad = 10^5 \frac{N}{m^2}$

$\longrightarrow$ energy required: $5.3 \cdot 10^6 \text{ J}$

$\qquad\qquad\qquad (\simeq 1.47 \text{ kWh})$

$1 \ell = 10^{-3} m^3$

fridge ~ 200 kWh / year

computer ~ 0.1 kWh

kinetic gas theory

- thermodynamics : macroscopic description, state variables P, V, T

- statistical mechanics : takes into account microscopic phenomena by acknowledging/assuming a description at the atomic/molecular scale (constituents of matter)

  → kinetic theory provides a link between average microscopic quantities and macroscopic variables

 NB: talk about molecules as gas constituents even if considering monoatomic gases

- assumptions :   Consider gas (air) in a container (this room):
  many (!) molecules moving fast (how fast…? ↓ later)

  — neglect effects of gravity : no preferred direction, no preferred position

  NB: density shall increase at bottom of container due to gravity of gas

    (on earth : density at 5.5 km altitude ~ $\frac{1}{2}$ density at surface, negligible effects for ~~surface~~ "small" containers)

  — neglect intermolecular interactions (dilute gas, ideal)
  — intermolecule distance large compar. to molecule size
  — elastic collisions between molecules (and with wall of container) no effect on total momentum (conserved), → can be neglected

pressure exerted by ~~a~~ gas on a container wall
↑
due to collisions of molecules with container wall

Volume V, N gas molecule
mass m, speed v

→ force on wall ▱ ?

wall area A
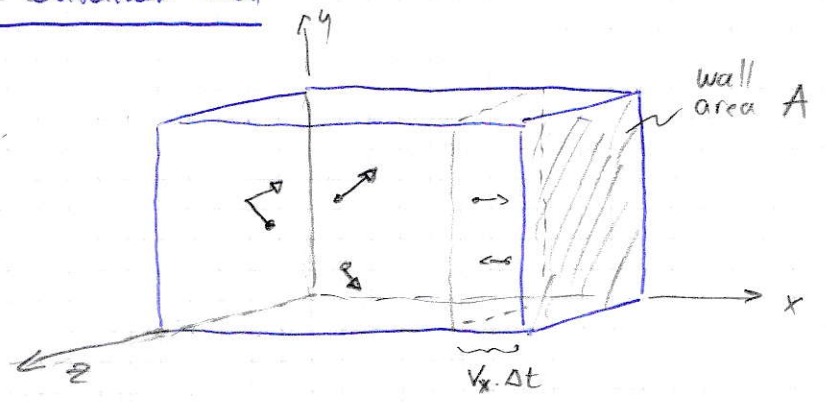
nb. molecules hitting the wall $= \frac{1}{2} \cdot \frac{N}{V} \cdot |V_x| \cdot \Delta t \cdot A$
along x axis
time Δt 50% molec.   nb. molec.   volume with molecules "within reach", i.e. at
              moving right   per unit volume   distance $\leq |V_x| \Delta t$

• momentum of molecule before hitting the wall : $+ m \cdot v_x$ (elastic choc)

"   "   "   "   _after_   "   - $: - m \cdot v_x$

⟶ total change in momentum $|\Delta \vec{p}|$ during time interval Δt : $2m \cdot |v_x|$ per molecule

hence $|\Delta \vec{p}| = 2 \cdot m \cdot |v_x| \cdot \frac{1}{2} \frac{N}{V} |v_x| \cdot \Delta t \cdot A$

$= \frac{N}{V} m \cdot v_x^2 \cdot A \cdot \Delta t$

force on wall $F = |\Delta \vec{p}| / \Delta t = F$

pressure $P = \dfrac{\text{force}}{\text{area}} = \dfrac{F}{A} = \dfrac{1}{A} \cdot \dfrac{|\Delta \vec{p}|}{\Delta t} = \dfrac{N}{V} \cdot m \cdot v_x^2$

8.12 or $\parallel P \cdot V = N \cdot m \cdot v_x^2$
⊥

All molecules do not necessarily have the same speed : replace v_x^2 by its average value $(v_x^2)_{avg}$

and $\parallel P \cdot V = \left(\frac{1}{2} m v_x^2 \right)_{avg} \cdot 2 \cdot N$ N: nb of molecules in container with volume V

$\underbrace{\qquad}$
avg kinetic energy allocated with motion along axis X.

$\underline{\text{Gas law}}$ $P \cdot V = n R \cdot T = N \cdot k_B \cdot T$ Avogadro nb
(ideal gas) $N = n \cdot N_A$
thus   nb moles
$\left(\frac{1}{2} m v_x^2 \right)_{avg} = \frac{1}{2} k_B \cdot T$ $k_B = 1.38 \cdot 10^{-23}$ J/k

Considering all 3 possible directions x, y, z : $(v_x^2)_{avg} = (v_y^2)_{avg} = (v_z^2)_{avg}$

and $(v^2)_{avg} = \sum_i (v_i^2)_{avg} = 3 (v_x^2)_{avg}$

we thus have

molecular
interpretation $\parallel k_{trans, avg} = \left(\frac{1}{2} m v^2 \right)_{avg} = \frac{3}{2} k_B \cdot T$ temperature T is thus a measure of the avg translational kinetic energy of molecule
of temperature

average translational kinetic energy of a molecule
for an ideal gas ↑

(also rotational or vibrational kinetic energy but not relevant for pressure calculation)

slide Hauseophrope
Loch in Metalplate

for N molecules, $\left\|\; U_{tran} = N\cdot\left(\frac{1}{2}mv_x^2\right)_{avg} = \frac{3}{2}N\cdot k_B T = \frac{3}{2}n\,R\cdot T \;\right\|$
or n moles of
gas $(N = n\cdot N_A)$

$$N = n\cdot N_A$$

energy : $\frac{3}{2}k_B T$ per molecule , $N_A\cdot k_B = R$

$\frac{3}{2}R\cdot T$ per mole

speed of molecules ... ?

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

$$(v^2)_{avg} = \frac{3\cdot k_B\cdot T}{m} = \frac{3\cdot N_A\cdot k_B\cdot T}{N_A\, m} = \frac{3\,R\cdot T}{\Pi} \qquad \Pi: \text{molar mass}$$
$$\Pi = m\cdot N_A$$

$$\left\|\; v_{rms} = \sqrt{(v^2)_{avg}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3\,R\,T}{\Pi}} \;\right\|$$

↑
root mean square

NB: similar to sound speed in air ... !

$$v_{sound} = \sqrt{\frac{\gamma\cdot R\,T}{\Pi}} \qquad , \qquad \gamma \simeq 1.4 \text{ for air}$$

sound wave = pressure disturbance/variation propagated by collision between
air molecules

examples   Oxygen O_2 : $\Pi_{O_2} = 32\,g/mol$ $\qquad v_{rms} \simeq 484\ m/s$, $T = 300K$
Hydrogen H_2 : $\Pi_{H_2} = 2\,g/mol$ $\qquad v_{rms} \simeq 1934\ m/s$, "

~~speed of sound in air~~ ~~$v = 343\,m/s$~~ ~~mix O_2 and N_2~~
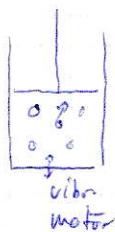
gas model   − increase motor speed,
momentum ↗ and pressure ↗
(speed)

vibr
motor

− note : larger atoms, slower : $\left(k_B T: \text{kinetic energy}\right)$

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

↑
effect
of mass

Equipartition theorem

just seen

$$\left(\frac{1}{2} m v_x^2\right)_{avg} = \frac{1}{2} k_B T \qquad \text{per molecule}$$

avg kinetic energy associated with translational motion

per direction (1D)

$\left(\text{MMMMMM} = \frac{1}{2} R \cdot T \; ; \; \text{per mole} = N_A \text{ molecules}\right)$

collision between molecule in gas redistribute energy quickly if energy is added
(e.g. shock with moving piston for a few molecule)

→ gas reaches equilibrium quickly, energy equally partitioned among translational kinetic energies (x, y, z directions)

(follows from classical statistical mechanics)

equipartition theorem $\|$ for substance in equilibrium, $\frac{1}{2} k_B T$ corresponds to the avg energy per molecule associated with each degree of freedom

deg. of freedom : each component of position and momentum (incl angular) ~~such~~ that appears ( )² in energy.
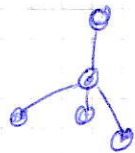
practically : kinetic energy of translation, rotation, vibration
~~(pot energy of vibration)~~
pot energy of vibration

e.g.
(ignore vibration)   ⓐ—ⓑ   3 translation   linear molecule
                               2 rotation $O_2, H_2 \cdots$ %

3 trans   non-linear
3. rot. CH_4

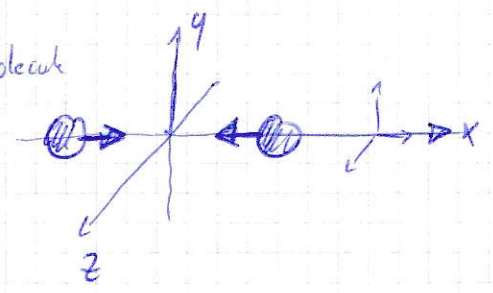(slide) Vibration CO_2

2) table degree of freedom

o N atoms in molecule : 3N deg. free.

o comment p.10' : pot + kin for vibrations

vibrational modes contribute kin energy + pot energy:

e.g. diatomic molecule

- 3 translations (V_x, V_y, V_z)

$$\sum_i \frac{1}{2} m v_i^2 \quad , \quad i = \{x, y, z\}$$

- 2 rotations

$$\sum_i \frac{1}{2} I_i \omega_i^2 \quad , \quad i = \{x, y\}$$

1 vibration: $V_x^{vibr.} \rightarrow \frac{1}{2} m (V_x^{vibr})^2 = E_{kin}$

elastic modulus $\rightarrow E_{pot} = \frac{1}{2} k \cdot (x - x_0)^2$

k

(spring constant)

↑ rest position (no vibration)