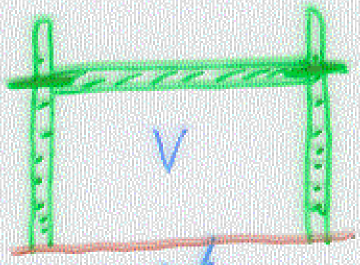
Ideal Gases: Specific Heats

① Heat n moles at constant vol:



From 1st law of TD : $Q = \Delta E_{int} + \cancel{W} = 0$

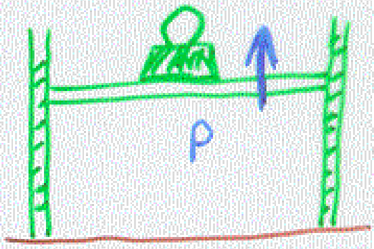
From kinetic theory : $\Delta E_{int} = \frac{3}{2} N k_B \Delta T = \frac{3}{2} n R \Delta T$ (monatomic)

$\therefore$ since no work done $Q = \underbrace{\frac{3}{2} n R}\, \Delta T$

Molar specific heat c_V defined as : $Q = n c_V \Delta T$

$\Rightarrow c_V = \frac{3}{2} R$ (ideal monatomic gas)

② Heat same gas at constant P :



piston moves up, V increases

Work done $W = P\Delta V = nR\Delta T$ (ideal gas law)

From 1st law of TD: $Q = \Delta E_{int} + W$

i.e. $Q = n c_V \Delta T + n R \Delta T$

Define molar specific heat at constant P, c_P as

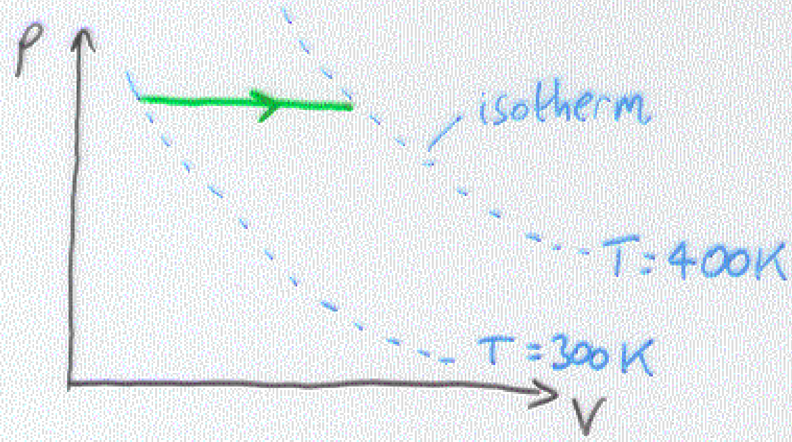
$$Q \equiv n c_P \Delta T$$

$$\Rightarrow n c_P \Delta T = n c_V \Delta T + n R \Delta T$$

OR $\boxed{c_P = c_V + R \quad [\mathrm{J\,mol^{-1}\,K^{-1}}]}$

i.e. $$\frac{\Delta Q}{n\Delta T} = \frac{\Delta E_{int}}{n\Delta T} + \frac{\text{Work}}{n\Delta T}$$

Using P-V diagrams



1. For ideal gas, $PV = nRT = Nk_BT$
at all points along path

2. If path crosses isotherms, $\Delta E_{int} \neq 0$
in fact: $\Delta E_{int} = \frac{3}{2} nR(T_f - T_i) = \frac{3}{2}(P_fV_f - P_iV_i)$
(monatomic gas)
For an isothermal change $\Delta E_{int} = 0$ (heat Q flows in/out to keep T constant)

3. Work done by gas = Area under curve
i.e. $W = \int_{V_i}^{V_f} P.dV$ >0 for left $\rightarrow$ right
<0 " right $\rightarrow$ left

4. Heat input $Q = \Delta E_{int} + W$
>0 heat flows in
<0 heat flows out
$=0$ adiabatic

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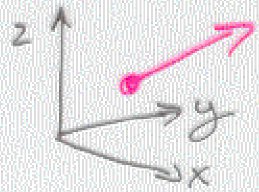
Equipartition of Energy (Maxwell)

For a general gas $\quad E_{int} = \frac{f}{2} nRT$

so $\quad C_V = \frac{f}{2} R$

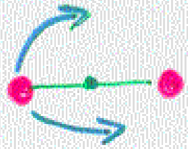
where f = no. of "degrees of freedom"

monatomic : $\quad f = 3$



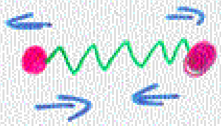
translation

diatomic : $\quad +2$



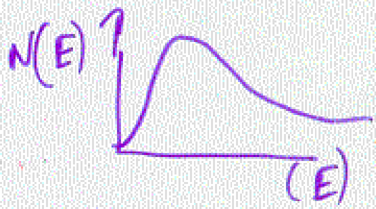
rotation

$+2$

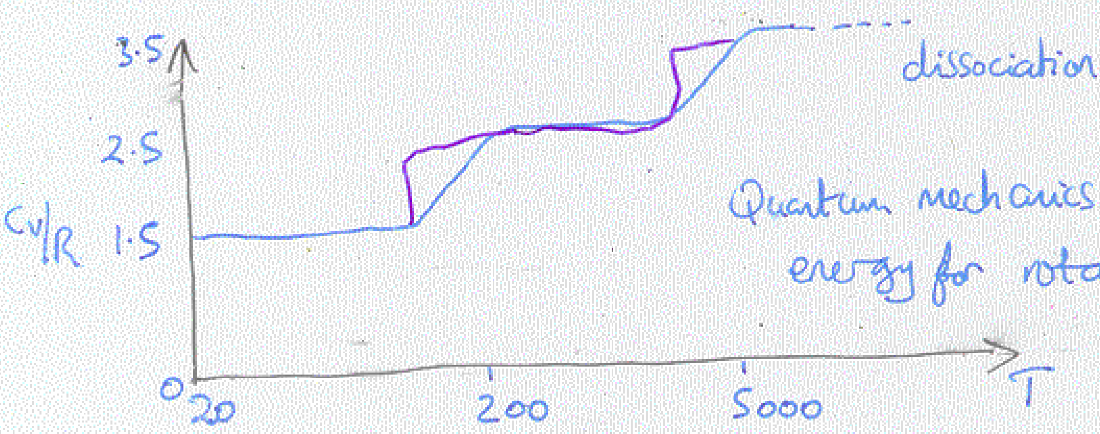


vibration

(p.e. and k.e.)



e.g. H_2 molecule (fig. 20.12)



Quantum mechanics ⇒ theshold energy for rotation, vibration

Adiabatic Transformations of Ideal Gas

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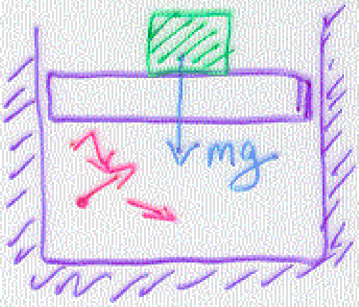
$Q = 0$: no heat exchange with outside

e.g.



Insulated container;

add / remove weight from piston

$\Rightarrow$ pressure, volume, temp change

Add weight $\Rightarrow$ piston drops $(V\downarrow)$ $\Rightarrow$ molecules rebound faster $(T\uparrow)$.

For small change in volume dV, temp. dT

Adiabatic $Q = dE_{int} + W = 0$

i.e. $dE_{int} = nc_v dT = -P.dV$ $(*)$

Use gas law $PV = nRT$ to eliminate P in $(*)$

$$\Rightarrow \quad nc_v dT = -n\frac{RT}{V}dV$$

$$\text{or} \quad \frac{dT}{T} = \left(\frac{R}{c_V}\right)\frac{dV}{V}$$

Integrate : $\ln T = \left(\frac{R}{c_V}\right)\ln V + \text{constant}$

Use $\underline{R = c_p - c_V}$ and define $\underline{\gamma = c_p/c_V}$

$\Rightarrow$ $\underline{TV^{\gamma-1} = \text{constant}}$ or $\underline{PV^{\gamma} = \text{constant}}$.

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Adiabatic Processes : Examples

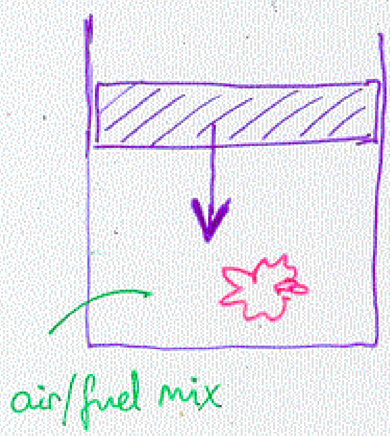
- Sound waves : compression / expansion too rapid for heat transfer

- Rapid decompression (spray can, fridge valve, airplane!)

As pressure released, gas cools rapidly when it expands into surroundings.

- Bicycle pump : each stroke compresses air volume → T rises. (After many strokes, pump heats up by conduction)

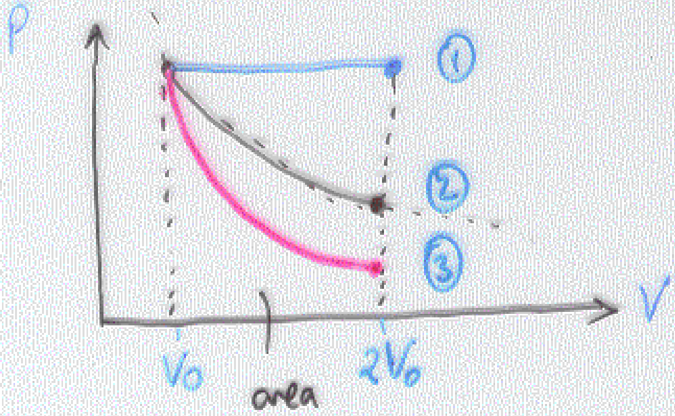
- Diesel engine :



Piston compresses fuel/air mixture. T rises above flashpoint for diesel fuel

(in gasoline engines → "detonation")

4 Ways to Double a Volume of Gas $V_0 \Rightarrow 2V_0$



Work = area

① Isobaric (constant P) : $W = \int P.dV = P_0(2V_0 - V_0) = \underline{P_0 V_0}$

② Isothermal : $W = \int P.dV$ where $P = \frac{nRT}{V}$

$$\Rightarrow W = nRT \ln\left(\frac{2V_0}{V_0}\right) = P_0 V_0 \ln 2 \approx \underline{0.7 P_0 V_0}$$

③ Adiabatic : $Q = 0 = \Delta E_{int} + W$

$W = \int P.dV$ where $P_0 V_0^{\gamma} = P V^{\gamma}$, i.e. $P = \frac{P_0 V_0^{\gamma}}{V^{\gamma}}$

$$\Rightarrow W = P_0 V_0^{\gamma} \int_{V_0}^{2V_0} \frac{dV}{V^{\gamma}} = \frac{P_0 V_0}{-\gamma+1}\left[\frac{1}{2^{\gamma-1}} - 1\right]$$

Using $\gamma = 5/3$ for monatomic gas $\Rightarrow W = \frac{3P_0V_0}{2}\left[1 - \frac{1}{2^{2/3}}\right]$

$$\approx \underline{0.4 P_0 V_0}$$

④ Free expansion : No work done $W = 0$

so $P_0 V_0 = P_f V_f = nRT$