Kinetic theory of gases (also developed by James Maxwell)

By mid 1800 people knew from experiments on gas

Boyle's law (T = temperature, P = pressure, V = volume) ($T=$ const. $P_1V_1 = P_2V_2$)

Charles' law ($P=$ const. $V \propto T$)

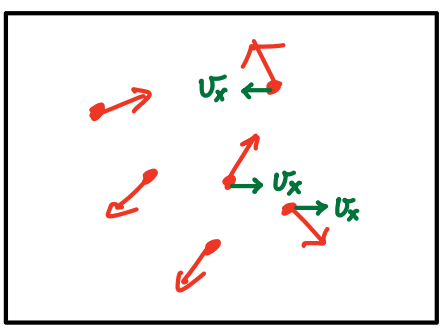
Gay-Lussac's law ($V=$ const. $P \propto T$)

Avogadro's law ($P, T=$ const. $V \propto N$, N = molecule #)

$\Rightarrow PV = NK_BT$ or $P = nK_BT$ (K_B = Boltzmann const., n = density $= N/V$)

ideal gas law

Microscopic model:



Assume N molecules in a box of volume $V = L^3$.

velocity of the molecules is v.

Total energy of the system is

$$U = N\frac{m}{2}\langle v^2\rangle = N\frac{m}{2}(\langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle)$$
$$= \frac{3}{2}Nm\langle v_x^2\rangle$$
$$\equiv N\varepsilon_K$$

(ε_K = mean kinetic energy per molecule.)

Pressure on the wall = Force/area

$$P = \frac{F}{A} = \frac{\langle \Delta p/\Delta t\rangle}{L^2} = \frac{1}{L^2}N\left\langle \frac{2mv_x}{2L/v_x}\right\rangle = \frac{N}{L^3}m\langle v_x^2\rangle = \frac{N}{V}\frac{m}{3}v^2 = \frac{2}{3}n\varepsilon_K$$

Compare with $P = nK_BT \Rightarrow \varepsilon_K = \frac{3}{2}KT$ or $\frac{m}{2}\langle v_x^2\rangle = \frac{m}{2}\langle v_y^2\rangle = \frac{m}{2}\langle v_z^2\rangle = \frac{1}{2}K_BT$

$$\Rightarrow U = N\gamma KT$$

Equipartition theorem: In equilibrium, each degree of freedom has a mean energy $\frac{1}{2}K_BT$.

Atomic gas: $E_k = \frac{3}{2}kT$ (translational energy) $\Rightarrow$ rms velocity $\sqrt{\langle v^2\rangle} = \sqrt{\frac{3kT}{m}}$

molecular gas: $E_k = \frac{3}{2}kT + kT$ + ~~vibrational~~ + ~~electronic~~ + ~~nuclear~~ ...

at room temperature. ↖ rotational energy

$$\Rightarrow U = N\gamma kT \qquad \gamma = \frac{3}{2}\ (\text{atoms}),\ \frac{5}{2}\ (\text{regular molecules})$$

What's the probability distribution $P(v_x, v_y, v_z)$. $\int P(\vec{v})\, d^3v = 1$?

Statistical mechanics: probability $P(E)$ of a particle with energy E is

$$P(E) = \frac{1}{Z} e^{-E/kT},$$ where Z is the normalization const $\sum_E \frac{1}{Z} e^{-E/kT} = 1 \Rightarrow Z = \sum_E e^{-E/kT}$.

Maxwell's approach: Probability $P(v_x, v_y, v_z)$ should be independent in all directions

$$P(v) = p(v_x)p(v_y)p(v_z) \qquad v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

$$\partial_{v_x} P(v) = P'(v)\frac{dv}{dv_x} = P'(v)\frac{v_x}{v} = p'(v_x)p(v_y)p(v_z)$$

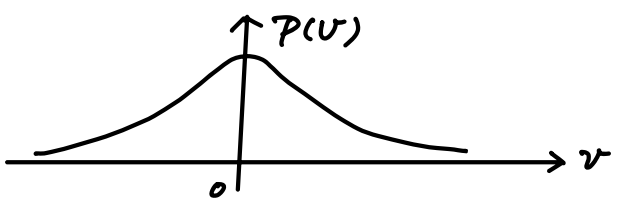
$$\Rightarrow \frac{P'}{vP} = \frac{p'}{v_x p} = \text{const} \Rightarrow \frac{dP}{P} = c\,v\,dv \qquad \frac{dp}{p} = c\,v_x\,dv_x$$

$$\Rightarrow P(v) = C_1 e^{-cv^2},\ p(v_x) = C_2 e^{-cv_x^2}$$

$$\Rightarrow P(v) = C_1 e^{-\beta v^2} = C_1 e^{-\beta v_x^2} e^{-\beta v_y^2} e^{-\beta v_z^2}$$

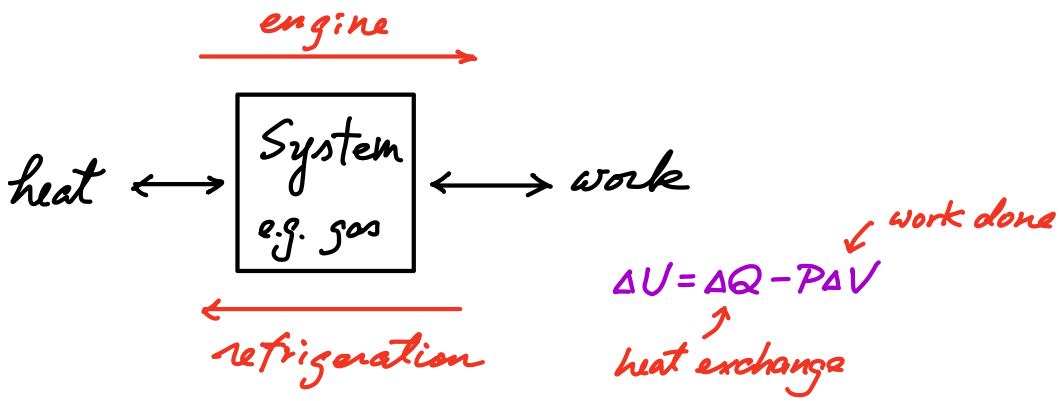
Using $\int P(v)\,dv = 1$ and $\langle \frac{1}{2}mv^2 \rangle = \frac{3}{2}kT$. we get

$$p(v_x, v_y, v_z) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\beta \frac{m}{2}(v_x^2 + v_y^2 + v_z^2)},\ \beta = 1/kT$$

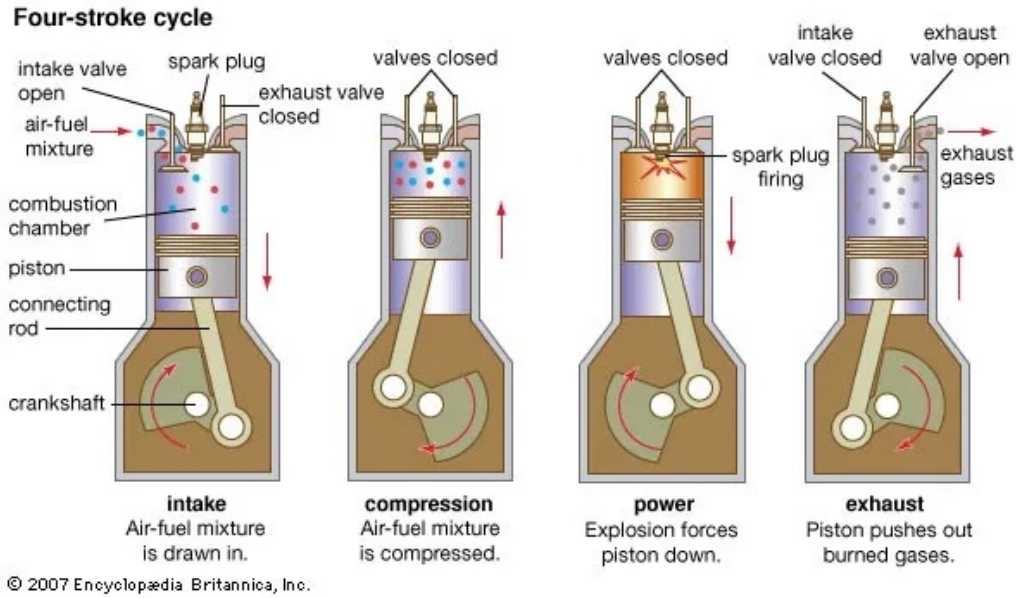


Heat engine

Thermodynamics was developed to understand and improve heat engine: Internal combustion engine (ICE), refrigeration.



We will use engine to illustrate how engine does work.

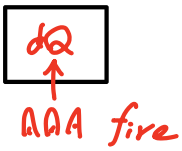


Intake stroke
→ combustion stroke
→ Ignition stroke
→ Power stroke
→ exhaust stroke

Engine absorbs heat and converts it into work.

Thermodynamical processes:

1. Isochoric process ($V=$ const)



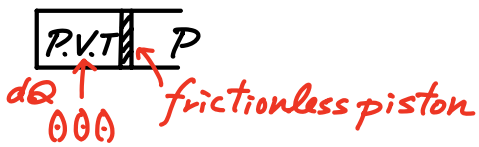
heat transfer → $dQ = C_V M dT$ ← temperature increase

isochoric specific heat, mass

$$dQ = dU = d[N\gamma kT] \Rightarrow C_V = \frac{1}{M}\frac{dU}{dT} = \frac{\gamma k}{m}$$

molecular mass

2. Isobaric process ($P=$ const.)

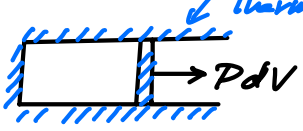


$$dU = dQ - F dx = dQ - P dV$$

isobaric specific heat $C_p \equiv \frac{1}{M}\frac{dQ}{dT} = \frac{1}{M}\left(\frac{dU}{dT} + P\frac{dV}{dT}\right)$ ← $PV=NkT$ $\Rightarrow \left.\frac{dV}{dT}\right|_{P=C} = \frac{Nk}{P}$

$$= \frac{N}{M}\gamma k + \frac{N}{M}k = \frac{N}{M}(\gamma+1)k = \frac{\gamma+1}{\gamma}C_V$$

3. Adiabatic process (no heat exchange, isolated system)



$$dU = -pdV = \gamma NK dT$$
$$= \gamma NK\, d(PV)$$

$$\Rightarrow PdV + \gamma P dV + \gamma V dp = 0$$
$$\Rightarrow (\gamma+1)pdV + \gamma V dp = 0$$

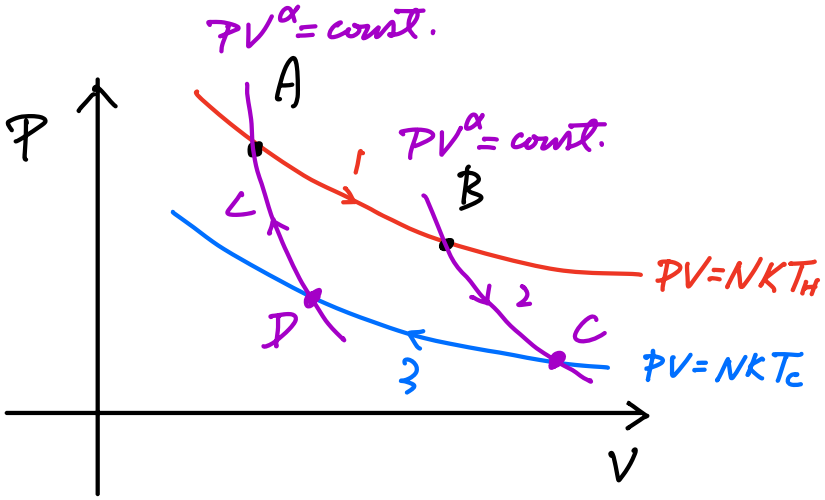
$$\Rightarrow (\gamma+1)\frac{dV}{V} + \gamma\frac{dP}{P} = 0 \Rightarrow PV^{\frac{\gamma+1}{\gamma}} = \text{const.}$$

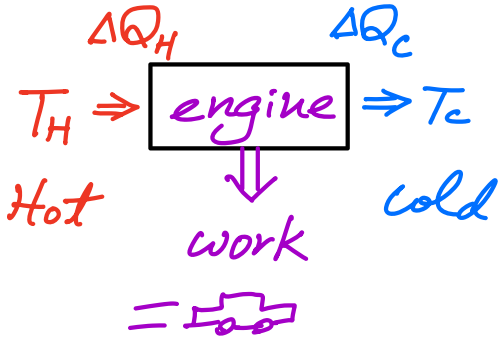
4. Isothermal process ($T=$ const.) $\Rightarrow PV = C.\ U = C.$

$$\Rightarrow dU = dQ - PdV = 0 \Rightarrow dQ = PdV$$

Carnot Cycle: The most efficient process we know for a heat engine.

System absorbs heat from T_H, does work, and cools down by T_C.





step 1: isothermal expansion ($T = T_H$, $V_A \to V_B$)

$$\Delta U = \Delta Q - P\Delta V = 0. \quad \Delta Q = P\Delta V = \int_A^B P\,dV$$

Absorb energy from heat source and do work by expanding

step 2: adiabatic expansion ($T_H \to T_C$, $\Delta Q = 0$)

Cool down the system and do some more work.

step 3: isothermal contraction ($T = T_H$, $V_C \to V_D$)

Contract and dump excess heat to cold reservior.

step 4: adiabatic contraction ($T_C \to T_H$, $\Delta Q = 0$)

More contraction and heat system back to T_H

Energy absorbed from the hot source @ T_H

$$\Delta Q = P\Delta V = \int_A^B P\,dV = \int_A^B \frac{NKT_H}{V}\,dV = NKT_H \ln\frac{V_B}{V_A}$$

Energy released into the cold source @ T_C

$$\Delta Q = P\Delta V = \int_C^D P\,dV = \int_C^D \frac{NKT_C}{V}\,dV = NKT_C \ln\frac{V_D}{V_C}$$

During steps 2 and 4, no heat exchange we only need to evaluate work $\int P\,dV$

Step 2 Work done $= \int_B^C P\,dV = P_B V_B^{\alpha} \int_B V^{-\alpha}\,dV = P_B V_B^{\alpha} \frac{1}{-\alpha+1}\left(V_C^{-\alpha+1} - V_B^{-\alpha+1}\right)$

Step 4 Work done $= P_A V_A^{\alpha} \frac{1}{-\alpha+1}\left(V_A^{-\alpha+1} - V_D^{-\alpha+1}\right)$

$P_A V_A = P_B V_B = NKT_H$

Total work done by the system:

$$\text{ABCD area} = \int_A^B + \int_B^C + \int_C^D + \int_D^A P\,dV$$

$$= NK\left(T_H \ln\frac{V_B}{V_A} + T_C \ln\frac{V_D}{V_C}\right) + NKT_H \frac{1}{1-\alpha}\left[\left(\frac{V_B}{V_C}\right)^{\alpha-1} - 1 + 1 - \left(\frac{V_A}{V_D}\right)^{\alpha-1}\right]$$

Step 1: $P_A V_A = P_B V_B$ Step 2: $P_B V_B^{\alpha} = P_C V_C^{\alpha}$ $\Longrightarrow$ $\frac{V_B^{\alpha}}{V_C^{\alpha}} = \frac{P_C}{P_B} = \frac{P_D}{P_A}\frac{V_D}{V_C}\frac{V_B}{V_A} = \frac{V_A^{\alpha} V_D V_B}{V_D^{\alpha} V_A V_C}$

Step 3: $P_C V_C = P_D V_D$ Step 4: $P_D V_D^{\alpha} = P_A V_A^{\alpha}$ $\Rightarrow$ $V_A/V_D = V_B/V_C$

Step 2 & 4 do zero network : $\int_B^C + \int_D^A P\,dV = 0$.

$\Rightarrow$ ABCD area $= NK(T_H - T_C)\ln\frac{V_B}{V_A}$

$$\text{Carnot cycle efficiency} = \frac{\text{work}}{\text{energy needed}} = \frac{NK(T_H - T_C)\ln\frac{V_B}{V_A}}{NKT_H \ln\frac{V_B}{V_A}} = 1 - \frac{T_C}{T_H}$$