Thermodynamics for ideal gases

Main parameters : state variables
$P, V, T, S, \ldots \Delta E_{int}$
plus
W, Q (depend on the process detail)
$W = \int_{V_1}^{V_2} P\,dV$

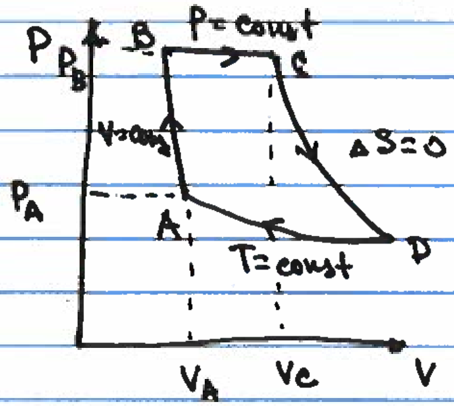
Two main equations: $PV = nRT$ ideal gas law
$Q = W + \Delta E_{int}$ 1^{st} law of TD

$\Delta E_{int} = \frac{3}{2} nRT$ monoatomic gas
$\frac{5}{2} nRT$ (or $\frac{7}{2} nRT$) diatomic gas, will be specified

If $V = const$ $Q = \Delta E_{int} = n C_V \Delta T$
$C_V = 3/2\, R$ (monoatomic gas)
$C_V = 5/2\, R$ (diatomic gas, usually)
$C_P = R + C_V$ always, $\gamma = C_P/C_V$

Adiabatic process $PV^{\gamma} = const$
or $TV^{\gamma-1} = const$

Sample cycle



Ideal gas law

$P_A V_A = nRT_A$

$P_B V_A = nRT_B$

$P_B V_C = nRT_C$

$P_D V_D = nRT_A$

Assume diatomic gas

$C_V = 5/2 \quad C_p = 7/2 \quad \gamma = 7/5$

AB: Isochoric ~~compression~~ heating

$W = 0$

$Q = \Delta E_{int} = \frac{5}{2} nR(T_B - T_A) = \frac{5}{2}(P_B - P_A)V_A$

BC: isobaric expansion

$W = P_B(V_C - V_A)$

$\Delta E_{int} = \frac{5}{2} nR(T_C - T_B) = \frac{5}{2} P_B(V_C - V_B)$

$Q = W + \Delta E_{int} = \frac{7}{2} P_B(V_C - V_B)$

DA: isothermal compression

$\Delta E_{int} = 0$

$$W = \int_{V_D}^{V_A} P\,dV = \int_{V_D}^{V_A} \frac{nRT_A}{V} dV = nRT_A \ln\frac{V_A}{V_D} < 0$$

or $W = -nRT_A \ln\frac{V_D}{V_A}$

CD: adiabatic expansion $\quad P_C V_C^{\gamma} = P_D V_D^{\gamma}$

$Q = 0$

$\Delta E_{int} = \frac{5}{2} nR(T_D - T_C) = \frac{5}{2}(P_D V_D - P_C V_C) < 0$

$$W = \int_{V_C}^{V_D} \frac{P_C V_C^{\gamma}}{V^{\gamma}} dV = -\frac{1}{\gamma - 1} P_C V_C^{\gamma}\left(\frac{1}{V_D^{\gamma-1}} - \frac{1}{V_C^{\gamma-1}}\right) =$$

$$= \frac{-1}{\gamma-1}\left[\frac{P_C V_C^{\gamma}}{V_D^{\gamma-1}}\,\frac{P_D V_D}{P_D V_D} - P_C V_C\right] = \frac{1}{\gamma-1}(P_C V_C - P_D V_D) = -\Delta E_{int}$$

Efficiency of a heat engine

$$e = \frac{W}{Q_H}$$

W - total work done by the gas during the cycle

$$W = \underset{>0}{W_{AB}} + \underset{>0}{W_{CD}} + \underset{<0}{W_{AD}}$$

Q_H - total heat added to the system

$$Q_H = Q_{AB} + Q_{BC} \qquad [Q_c = Q_{DA}]$$

To compare with Carnot cycle efficiency

- hottest $T_{hot} \to T_C$
- lowest $T_{cold} \to T_A$

$$e_{carnot} = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{T_A}{T_C}$$

Heat pump $COP = \frac{|Q_H|}{|W|}$ Runs on reversed cycle.

Refrigirator $COP = \frac{Q_c}{|W|}$

Entropy change : $\Delta S = \int \frac{dQ}{T}$

$$\Delta S_{AB} = \int_A^B \frac{nC_v dT}{T} = nC_v \ln T_B/T_A$$

$$\Delta S_{BC} = \int_B^C \frac{nC_p dT}{T} = nC_p \ln T_C/T_B$$

$$\Delta S_{CD} = 0$$

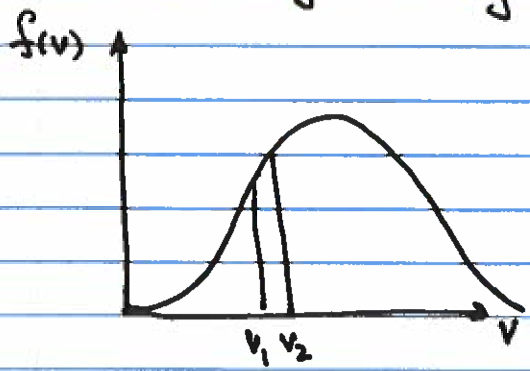
$$\Delta S_{DA} = \frac{Q}{T_A} = \frac{W_{DA}}{T_A} = -nR \ln V_D/V_A$$

Microscopic ~~(thgn~~ kinetic theory of gasses

$$\Delta E_{int} = \frac{3}{2} k_B \cdot N \cdot T = N \cdot \left\langle \frac{mv^2}{2} \right\rangle$$ monoatomic gas

Maxwell's velocity distribution

Probability density $f(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_BT}$



Probability of finding atoms $v_1 < v < v_2$

$$P = \int_{v_1}^{v_2} f(v)\,dv$$

Average velocity

$$\langle v \rangle = \int_0^{\infty} v f(v)\,dv = \sqrt{\frac{8k_BT}{\pi m}}$$

Root-mean square velocity

$$v_{RMS} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_BT}{m}}$$

Solids / liquids

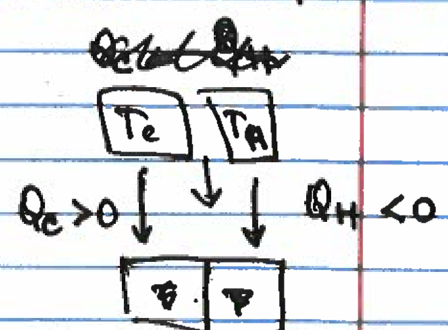
$Q = m \cdot C \cdot \Delta T$

Phase transition $Q = Lm$

Two substances of different temperature brought to contact

$$Q_{cold} = Q_{hot}$$

energy flows from hot to cold



same temperature