

THERMODYNAMICS

&

no. of molecules

K.T.G

Thermal eq^b: when all macroscopic prop (P, V, T, m, n) are const wrt time.
- insulated with surrounding.

ZEROth LAW
A & C in thermal eqⁿ (T_A = T_C)
A & B in " then B & C in "

INTERNAL ENERGY of system
U = P.E of molecule + KE of molecule
due to intermolecular force of attractⁿ motion of molecule

> It does not depend on overall KE of system eg:

Ideal gas:
No intermol attractⁿ ⇒ PE = 0
∴ Total energy = Int. energy = KE of gas molecule

DEGREE OF FREEDOM (f)
no. of independent terms in expression for K.E.
Monoatomic 3 (translatory)
Diatomic 5 (+2 rotatⁿ)
Polyatomic 6 (+3 rotatⁿ)
↳ except linear (C=0): 5
> +2 in vibratⁿ (high temp)

Law of equipartitⁿ of energy
energy for each degree of freedom in thermal eqⁿ is $\frac{1}{2} k_B T$ for a molecule.

K.E of 1 molecule = $f \times \frac{1}{2} k_B T$
 $k_B = \frac{R}{N_A} = \text{Boltzmann's const} = 1.38 \times 10^{-23} \text{ J/K}$

KE of 1 mole = $\frac{f}{2} RT$
KE of n mole = $n \frac{f}{2} RT$

> T in Kelvin > T.E of Ideal gas = U = KE + int. erg

Specific Heat & Molar specific heat
 $c = \frac{Q}{m \Delta T}$ $C = \frac{Q}{n \Delta T}$

$C = M c$ → SHC
C_v & C_p
↓ const. P (isobaric)
Molar SHC at const volume (Isochoric)

C_v & C_p in terms of f
 $C_v = \frac{f}{2} R$ $C_p = (\frac{f}{2} + 1) R = (\frac{f+2}{2}) R$
Molar SHC at const P
 $C_p - C_v = R$ → for any gas

Molar SHC of mixture
 $C_{mix} = \frac{n_1 C_1 + n_2 C_2}{n_1 + n_2}$
C_p/C_v (γ)
 $\frac{f}{2} = \frac{1}{\gamma - 1}$
 $\frac{C_p}{C_v} = \gamma$ $\gamma = 1 + \frac{2}{f} = \frac{f+2}{f}$
γ_{mono} > γ_{dia} > γ_{tri}
1.67 1.4 1.3
 $\gamma_{mix} = \frac{n_1 C_{p1} + n_2 C_{p2}}{n_2 C_{v2} + n_1 C_{v1}}$

WORK (W) (sign opp. in chem)
 $W = \int_{V_i}^{V_f} P dV$
ΔV = +ve / gas expand / ⇒ W = +ve
Work is done by gas

Work is done on the gas ⇒ W = -ve
> 101.5 x atm l = J / $\frac{N}{m^2} \frac{m^3}{m^3}$
↳ It is path dependent
P. not state function
∴ W_I > W_{II} > W_{III} (area)
↳ Work done in cyclic process

C.W W = +ve
A.C.W W = -ve

INTERNAL ENERGY (ΔU)
For ideal gas ΔU = ΔK.E
 $\Delta U = \frac{n f R \Delta T}{2} = \frac{n R \Delta T}{\gamma - 1}$
• state function
• path independent ΔU = n C_v ΔT
• ΔU closed cycle = 0
 $\Delta U = \frac{f}{2} \Delta(PV)$
• ΔU only depend on ΔT. • same in all process

HEAT (ΔQ)
 $Q = n C \Delta T$ at const V, Q = n C_v ΔT
const P, Q = n C_p ΔT
Q = m c ΔT
• It is path dependent
↳ Heat given to system, Q = +ve
Heat given by system / release Q = -ve

Ist LAW OF THERMODYNAMICS.
- law of conservatⁿ of energy
 $\Delta Q = \Delta U + W$ → Put with sign.

feel: Heat give ⇒ w done by gas + inc in int. erg.

TYPES OF PROCESSES
ISOBARIC PROCESS P = const.
① charle's law V ∝ T - sim kelvin
② Graphs:

③ Molar SHC = C_p = $(\frac{f}{2} + 1) R = \frac{\gamma}{\gamma - 1} R$
④ ΔQ = n C_p ΔT
⑤ ΔU = n C_v ΔT = $n \frac{f}{2} R \Delta T = \frac{n R \Delta T}{\gamma - 1}$
⑥ W = P ΔV = n R ΔT
⑦ W : ΔQ : ΔU = 1 : $\frac{f}{2} + 1$: $\frac{f}{2}$
1 : C_p : C_v = 1 : $\frac{\gamma}{\gamma - 1}$: $\frac{1}{\gamma - 1}$

ISOCORIC PROCESS V = const
① P ∝ T
② Graph

③ Molar SHC = C_v = $\frac{f}{2} R = \frac{R}{\gamma - 1}$
④ ΔQ = n C_v ΔT
⑤ ΔU = n C_v ΔT (same)
⑥ W = 0

ISOTHERMAL PROCESS T = const
very slowly ⇒ Perfectly conducting boundaries.
① Boyle's law P ∝ 1/V
② Graphs:

③ Molar SHC C = ∞ = $\frac{Q}{n \Delta T}$ ΔT → 0 C → ∞
④ ΔU = 0
⑤ W = nRT ln $\frac{V_f}{V_i} = \frac{nRT}{P_i V_i} \ln \frac{P_i}{P_f} = \frac{P_i V_i}{\gamma - 1} \ln \frac{P_i}{P_f}$
⑥ ΔQ = W

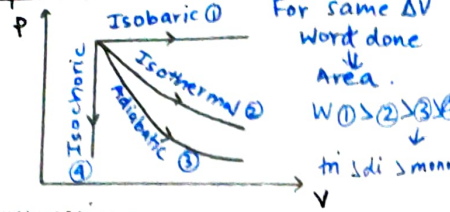
ADIABATIC PROCESS ΔQ = 0
very rapidly/fast ⇒ perfectly insulating.
① PV^γ = const
TV^{γ-1} = const
T^γ P^{1-γ} = const
② Graph:

③ Molar SHC, C = 0 = $\frac{\Delta Q}{m \Delta T}$
④ ΔU = n C_v ΔT
⑤ W = -ΔU

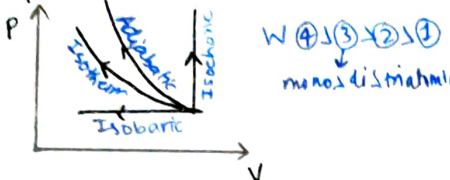
γ_{mono} > γ_{dia} > γ_{tri}

Comparison of diff process

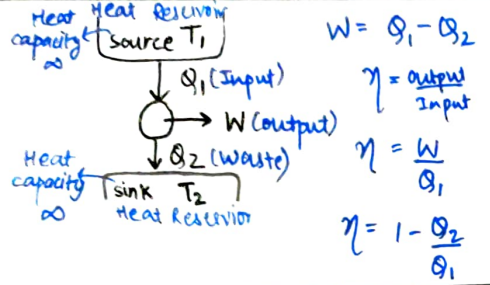
Expansion:



Compression:



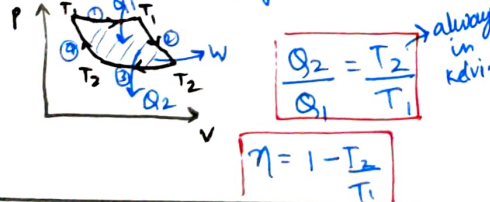
HEAT ENGINE



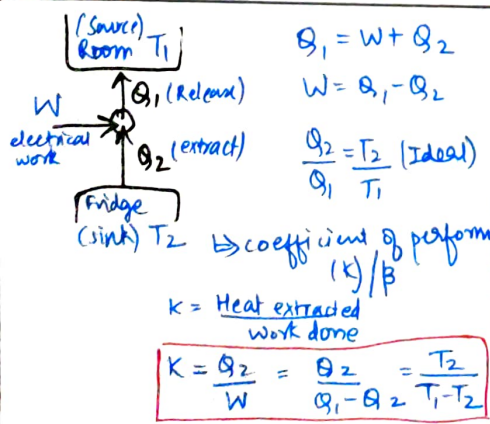
Carnot's Heat Engine

$\eta \rightarrow$ Max for Carnot's heat engine
 No heat engine operating b/w same temp. can have efficiency more than Carnot
 \rightarrow Ideal heat engine.

- 1 Isothermal expansion
 > Heat is given to system Q_1
- 2 Adiabatic expansion
- 3 Isothermal compression
 > Heat is released by system Q_2
- 4 Adiabatic compression.



REFRIGERATOR

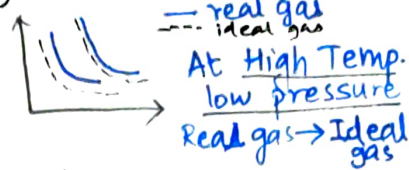


2nd law of thermo:

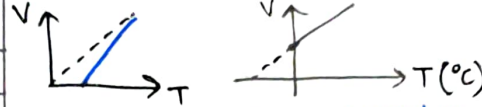
\rightarrow Kelvin plank: All heat cannot be converted to work
 \rightarrow Clausius: no process is possible whose sole result is heat transfer from cold to hot.

IDEAL GAS LAW

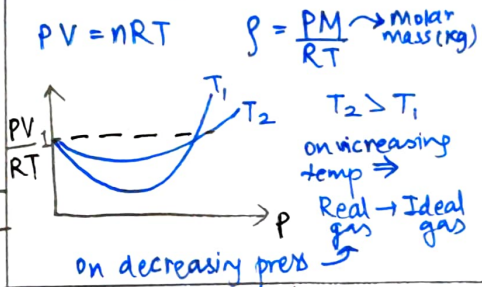
Boyle's law: Isothermal



Charles's law: Isobaric



Avagadro equal volume \Rightarrow equal no. of molecule (at const P, T)



Kinetic theory of gas:

- random motion
- identical gas molecule
- elastic collision
- $P \propto$ No. of collision per unit area
- $K.E \propto T$ (only)
- $V_{\text{gas molecule}} = 0$
- No intermolecular force.

$PV = \frac{Nm}{3} V_{\text{rms}}^2$ (N \rightarrow no. of molecule, m \rightarrow mass of each molecule)

$KE = \frac{3PV}{2} = \frac{3RT}{2}$

$KE = \frac{f}{2} k_B T$ (for one molecule)

V_{rms} (Root mean sq. velocity)

$V_{\text{rms}} = \sqrt{\frac{v_1^2 + v_2^2}{n}}$

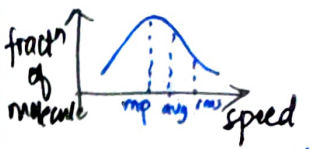
$V_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_B T}{m}}$ (Molar mass (kg), m \rightarrow molecule mass)

$V_{\text{rms}} = \sqrt{\frac{3P}{\rho}}$ (in Pa, ρ \rightarrow kg/m³, less preferred)

• If pressure is inc. at const Temp $\Rightarrow V_d \downarrow \Rightarrow \rho \uparrow \therefore$ No effect on V_{rms} .
 So use 1st formula to compare.

$V_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}}$ $V_{\text{most probable}} = \sqrt{\frac{2RT}{M}}$

Maxwell's speed distribution law:



$V_{\text{rms}} \downarrow V_{\text{avg}} \downarrow V_{\text{mp}}$
 $R \quad A \quad M$
 $\sqrt{3} : \sqrt{2.5} : \sqrt{2}$

Mean free path:
 distance b/w two successive collision.

$\lambda_m = \frac{1}{\sqrt{2} n \pi d^2} = \frac{RT}{\sqrt{2} n d^2 P N_A}$

(no. of molecule per unit volume, diameter of molecule)