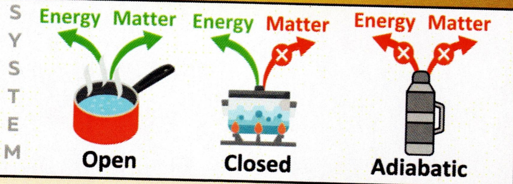
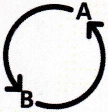
THERMO DYNAMICS



- **Diathermal Boundary** :Heat Flow Possible
- **Adiabatic Boundary** : NO Heat Flow Possible
- **Rigid Boundary** : Volume Change not possible
- **Permeable Boundary** : Mass Flow Possible

Types of Processes

Isothermal	$\Delta T=0$	**Isochoric**	$\Delta V=0$
Isobaric	$\Delta P=0$	**Adiabatic**	$q=0$
Cyclic Process	Same Initial and Final State		



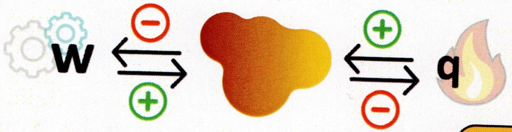
Cyclic

- **State Function** Only Depends on Initial and Final State; ΔU, ΔH, ΔA, ΔG, P, V, T; These are 0 for Cyclic process
- **Path Function** Depends on Path followed from state A to B; e.g. q ,w, C ; Non-Zero for Cyclic Process

Extensive Properties	Intensive Properties
Mass/Amount dependent	Mass/Amount Independent
Internal Energy (U), Enthalpy (H), Gibbs Free Energy(G) , Mass (m), Entropy (S), Volume (V).	Temperature (T), Boiling & Melting Point, Specific & Molar Heat Capacity, Refractive Index, Density
Additive in Nature	Non-Additive in Nature

- Ratio of two Extensive Properties is Intensive in nature, eg : Mass/Volume = Density (Intensive)
- If Extensive property is defined per unit (mass, mole), it becomes intensive, Molar Volume (V/n)

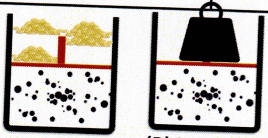
Term	Definition
Internal Energy (ΔU)	Sum of All the Energies in a system Absolute Value cannot be calculated
Heat (q)	Energy exchange due to Temp. difference
Work (w)	Energy exchange due to displacement



Some Important Formulas from 1st Law

P-V Work	$-P_{ext}\,\Delta V$
1st Law of Thermo	$\Delta U = q + w$
1st Law targets energy conservation (not for open system)	
Enthalpy Change	$\Delta H = \Delta U + P\Delta V$
Heat at constant V	$\Delta U = q_v$
Heat at constant P	$\Delta H = q_p$
Exothermic Process	$\Delta H < 0 ; \Delta H_r > \Delta H_p$
Endothermic Process	$\Delta H > 0 ; \Delta H_r < \Delta H_p$
Relation Between ΔH and ΔU for Ideal Gas	$\Delta H = \Delta U + \Delta n_g RT$

Reversible Process	Irreversible Process
Slow process carried out in infinite steps	Instant Process which can also be called Natural process.

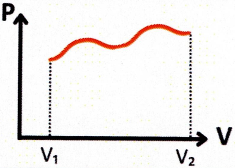


(A) Reversible

(B) Irreversible
Constant Ext. pressure

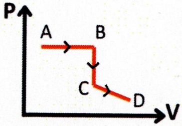
- Infinite steps to remove grains of sand in A
- Instant Removal of weight in B

Work under P-V Diagram



$$dw = -P_{ext}.\,dV$$

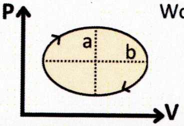
$$w = -\int_{V_1}^{V_2} P_{ext}.\,dV$$



$$w_{net} = w_{AB} + w_{BC} + w_{CD}$$

BC is iso-choric process

$$w_{BC} = 0$$



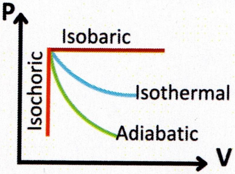
Work done is area enclosed in cycle

$$w = \pi.\,a.\,b$$

Clockwise = **+ve** work done

Anti-Clockwise = **-ve** work done

PV diagram for different processes and work done



- Isothermal work > Adiabatic work
- Reversible work > Irreversible work
- **Maximum work :** Reversible isothermal process.

Heat Capacity (C)	
Amount of Heat required to increase the temperature by 1° (J/K)	$C = \frac{+q}{\Delta T}$
Molar Heat Capacity (C_m) Heat Capacity per mole (J/mol.K)	$C_m = \frac{+q}{n\Delta T}$
Molar Heat Capacity (C_m) Heat Capacity per gram (J/gm.K)	$C_s = \frac{+q}{m\Delta T}$

C at constant volume	C at constant pressure
$q_p = C_p . dT = dH$	$q_v = C_v . dT = dU$

- C = Path function ; Cp and Cv = State functions.
- Heat capacity is an extensive property. Cm and Cs are intensive properties.
- For any substance, $C_{pm} - C_{vm} = R$ and $C_p/C_v = \gamma$
- For solids and liquids, $C_{pm} \approx C_{vm}$
- Heat capacity increases with increase in temperature due to increase in vibrational degree of freedom.
- C (isothermal) = ∞ > C_p > C_v > C (Adiabatic) = 0

FUN FACT

Balloon with gas bursts in seconds

Balloon with water doesn't bursts.

Due to Cv of water

Degrees of Freedom

Atomicity	Monoatomic	Di/Linear	Non-Linear
Translational	3	3	3
Rotational	1	2	3
Vibrational	$3N - f_{trans} - f_{rot}$		

Vibrational DOF's only contribute at High Temperature

Other Important formulas related to DOF

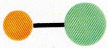
$C_v = f.R/2$	$\gamma = 1 + 2/f$

In Adiabatic Process, q=0

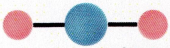
Gas	f	C_v	C_p	γ
Mono	3	3R/2	5R/2	5/3
Di/Linear	5	5R/2	7R/2	7/5
Non-Linear	6	3R	4R	4/3

With increase in γ, Atomicity decreases

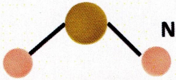
Mono



Diatomic



Linear - Tri/Poly



Non-Linear : Tri/Poly

Calculated U,H,q,w for the two main processes

Isothermal Process

ΔU	$= 0$	ΔH	$= 0$	q	$= -w$

Irreversible work

$$w = -P_{ext}\Delta V = -P_{ext}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$$

Reversible work

$$ww = 2.303nRT\log\frac{V_2}{V_1} = 2.303nRT\log\frac{P_1}{P_2}$$

Adiabatic Process

ΔU	$= nC_v\,\Delta T$	ΔH	$= nC_p\,\Delta T$	q	$= 0$

Irreversible work

$$w = \frac{nR\Delta T}{\gamma - 1}$$

Find Final Temperature using

$$nC_{v,m}\Delta T = -P_{ext}(V_2 - V_1)$$

Reversible work

$$w = \frac{nR\Delta T}{\gamma - 1}$$

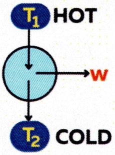
Find Final Variables using

$$TV^{\gamma-1} = \text{Constant}$$

$$PV^{\gamma} = \text{Constant}$$

$$T^{\gamma}P^{1-\gamma} = \text{Constant}$$

Carnot Cycle



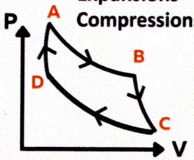
Heat Engine - Thermal Efficiency

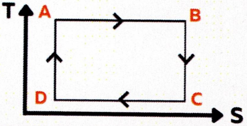
$$\eta = \frac{\text{Work done}}{\text{Total amount of heat absorved}}$$

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

Expansions AB : Isothermal; BC : Adiabatic

Compressions CD : Isothermal; DA : Adiabatic

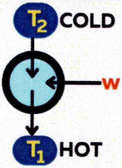




Refrigerator

$$\beta = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

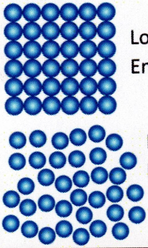
$$\beta = \frac{1 - \eta}{\eta}$$



- A state function is obtained from the derivation of Carnot cycle. i.e. **Entropy** $dS = \frac{dq_{rev}}{T}$

ENTROPY (S)

- Degree of Randomness.
- S (Gas) > S (Liquid) > S (Solids)
- Entropy is 0 in cyclic process (State function).
- It is an Extensive property
- Units are J/K.



Low Entropy

High Entropy

Entropy in an Isolated system

- **dS > 0** (Irreversible Process, Spontaneous)
- **dS = 0** (Reversible Process, at Equilibrium)
- **dS < 0** (Impossible process or NON-Spontaneous)

Second Law of Thermodynamics

- Entropy of universe is always increasing.
- $\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} = 0$ (Reversible process)
- $\Delta S_{universe} > 0$ (Irreversible process)

Other Important Points

- Higher Atomicity, Higher Entropy. $S(NH_3) > S(H_2)$.
- For same atomicity, Higher size, Higher Entropy.
- Entropy increases on mixing of gases.
- Allotropic forms with ordered arrangements have lower entropy. S (Diamond) < S (Graphite)

General Formulas for Entropy

$$\Delta S = nC_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$$

In Iso-choric process, 2nd Term becomes 0

$$\Delta S = nC_p \ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$$

In Iso-baric process, 2nd Term becomes 0

In Iso-thermal process, 1st Term becomes 0

In **Reversible Adiabatic** process, q=0. Thus, $\Delta S = 0$

Entropy during phase change

$$dS = \frac{dQ_p}{T} = \frac{dH}{T} = \frac{mL}{T}$$

At Constant T & P or During a Phase Change

L = Latent heat

Fusion $S \rightleftharpoons L$	**Vaporisation $L \rightleftharpoons G$**	**Sublimation $S \rightleftharpoons G$**

Gibbs Free energy (G) $(-\Delta G = w_{useful})$

- It is a state function, an Extensive Property and Used to calculate Spontaneity.
- Spontaneity means that the reaction can be carried out on it's own (it is feasible). All Natural processes are spontaneous.
- $\Delta G = \Delta H - T\Delta S$ and Spontaneity will be achieved at all temperatures when $\Delta H < 0$ and $\Delta S > 0$.

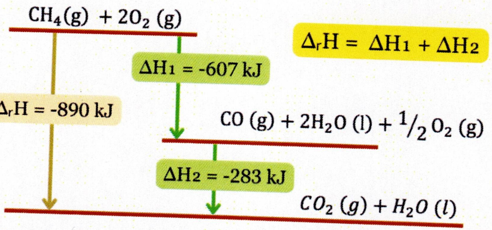
Enthalpy of a Reaction ($\Delta_r H$)

The heat exchanged during complete course of reaction at constant pressure.

Exothermic : Negative $\Delta_r H$	Endothermic : Positive $\Delta_r H$

Hess's law of constant summation

At Constant T & P, the total enthalpy change for the reaction is the sum of all changes. (Single or Multistep)



Different Types of Enthalpy

1. Enthalpy of Phase Transition
2. Enthalpy of Formation
3. Enthalpy of Combustion
4. Lattice Enthalpy
5. Hydration Enthalpy
6. Enthalpy of Solution
7. Enthalpy of Neutralisation
8. Enthalpy of Atomisation and Bond Enthalpy

Enthalpy of Phase Transition ($\Delta H_{transition}$)

The ΔH of reaction when 1 mole of a substance in one physical state converts to another physical state.	
Fusion, Melting, Vaporisation **(+ve)**	Freezing **(-ve)**

Enthalpy of Formation ($\Delta_f H$)

- The ΔH of reaction when 1 mole of a substance is **produced from** its constituent elements which are present in their **free state**.
- ($\Delta_f H$) for free state elements is considered as **Zero**.
- Some elements in their free state are
  - $F_2(g)$; $Cl_2(g)$; $Br_2(l)$; $I_2(s)$; $P_4(s)$; $H_2(g)$; $O_2(g)$; $S_8(s)$; C (s, Graphite) ; Metal - M(s) ; Hg (l).
- For any Reaction,

$$\Delta_r H = \sum V_P \, \Delta_f H_P - \sum V_R \, \Delta_f H_R$$

Enthalpy of Combustion ($\Delta_C H$)

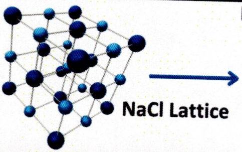
ΔH of the reaction in which one mole substance is burnt in the excess of O_2 (air). Always **(-ve ΔH).**

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

Lattice Enthalpy

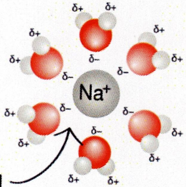
Energy to convert 1 mole of Ionic Solid into gaseous ions

Energy Required to Break.
Thus **+ve ΔH**



Hydration Enthalpy

Energy produced when 1 mole of the gaseous ions is mixed with H_2O (water) to produce hydrated ions.



This Stabilises Ions. Thus, **-ve ΔH**

e.g. $CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O(l)$

Enthalpy of Solution (ΔH_{sol})

1 mole substance (s/l/g) converts to aqueous substance
e.g. Glucose dissolved in water to form a solution.

Enthalpy of neutralisation

- One gram equivalent of the acid is completely neutralised by a base in dilute solution.
- SA & SB releases -57.1 kJ/mol at 298 K.
- SA-WB, WA-SB, WA-WB < -57.1 kJ/mol

Enthalpy of Atomisation

1 mole gas molecules converts to free ions in gas phase.

e.g. $CH_4(g) \rightarrow C(g) + 4H(g)$; $H_2(g) \rightarrow 2H\ (g)$

Bond Enthalpy

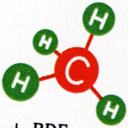
Average Enthalpies when 1 mole of compound is converted into atoms. Eg.

$CH_4(g) \rightarrow CH_3(g) + H(g)$ BDE$_1$

$CH_3(g) \rightarrow CH_2(g) + H(g)$ BDE$_2$

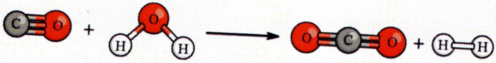
$CH_2(g) \rightarrow CH(g) + H(g)$ BDE$_3$

$CH(g) \rightarrow C(g) + H(g)$ BDE$_4$



$$\text{Bond Energy} = \frac{BDE_1 + BDE_2 + BDE_3 + BDE_4}{4}$$

- For Any Reaction, $\Delta_r H = (B.E)_R - (B.E)_P$



Kirchoff's Equation

Enthalpy of a reaction's variation with temperature changes.

$$\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}$$

$$\Delta C_p = \Delta C_p\ (prod.) - \Delta C_p\ (reac.)$$

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \, .dT$$