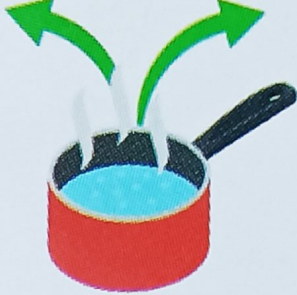


THERMODYNAMICS

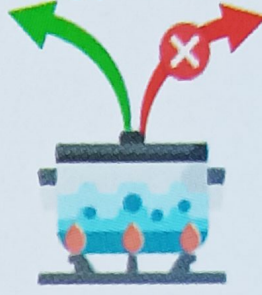
S
Y
S
T
E
M

Energy Matter



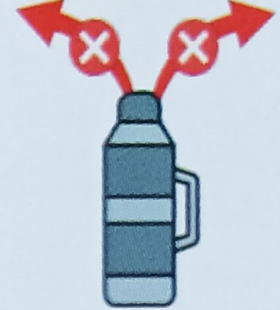
Open

Energy Matter



Closed

Energy Matter

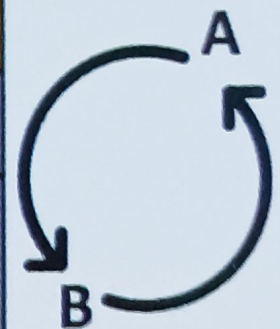


Adiabatic

BOUNDARY	Discription
DITHERMAL	Heat Flow Possible
Adiabatic	NO Heat Flow Possible
RIGID	Volume Change not possible
PERMEABLE	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		

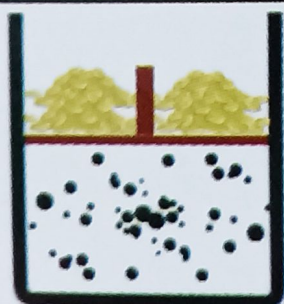


State Functions	Path Function
Only Depends on Initial and Final State	Depends on Path followed from state A to B
$\Delta U, \Delta H, \Delta A, \Delta G, P, V, T$	q (Heat) and w (Work), C
$\Delta f = 0$ for Cyclic process	Non-Zero for Cyclic Process
Extensive Properties	Intensive Properties
Mass/Amount 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
<ul style="list-style-type: none"> 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, e.g. Molar Volume (V/n) 	



Some Important Formulas from 1st Law

P-V Work	$-P_{\text{ext}} \Delta V$
1 st Law of Thermo	$\Delta U = q + w$
1 st 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



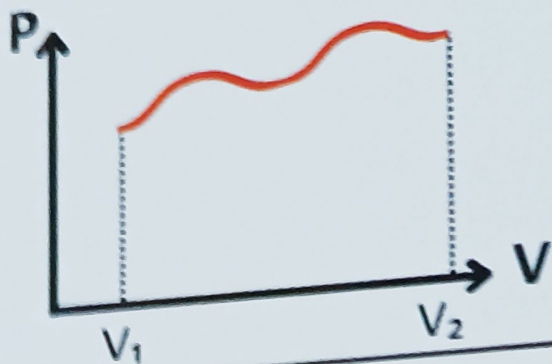
(B) Irreversible

Constant Ext. pressure

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

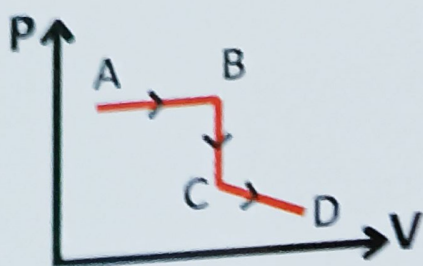
Only Depend on State

Work under P-V Diagram



$$dw = -P_{ext} \cdot dV$$

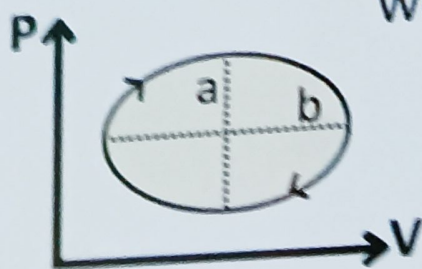
$$w = - \int_{V_1}^{V_2} P_{ext} \cdot dV$$



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

BC is iso-choric process

$$W_{BC} = 0$$



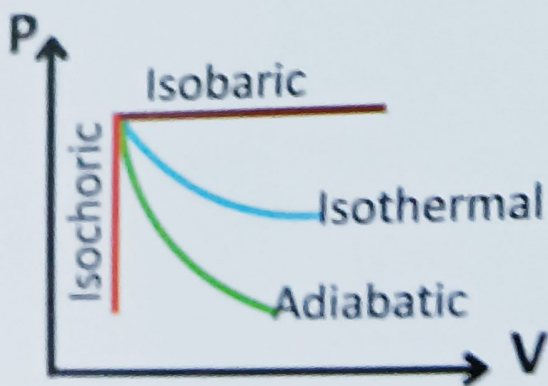
Work done is area enclosed in cycle

$$w = \pi \cdot a \cdot b$$

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
$q_p = C_p \cdot dT = dH$	$q_v = C_v \cdot dT = dU$
<ul style="list-style-type: none"> • C = Path function ; C_p and C_v = State functions. • Heat capacity is an extensive property. C_m and C_s 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) = $\infty > C_p > C_v > C$ (Adiabatic) = 0 	



Balloon with gas bursts in seconds

FUN FACT

Balloon with water doesn't burst.



Due to C_v of water

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

Isothermal Process

ΔU	$= 0$	ΔH	$= 0$	q	$= -w$
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Irreversible work

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

Reversible work

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

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

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

Reversible work

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

Find Final Variables using

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

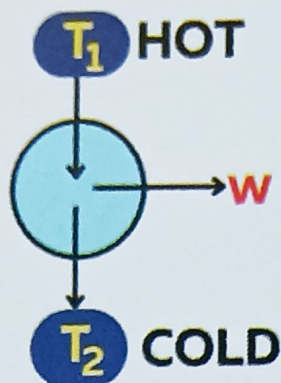
$$PV^{\gamma} = \text{Constant}$$

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



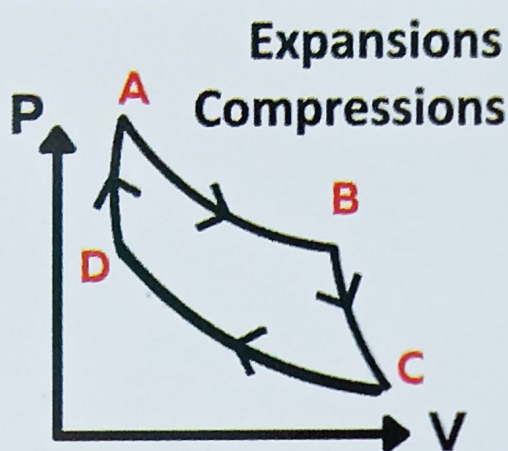
Carnot Cycle

Heat Engine - Thermal Efficiency

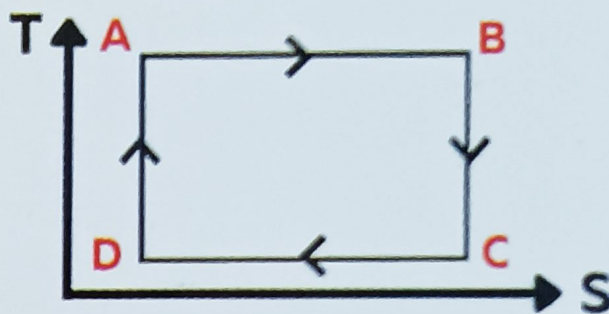


$$\eta = \frac{\text{Work done}}{\text{Total amount of heat absorbed}}$$

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



Expansions AB : Isothermal; BC : Adiabatic
Compressions CD : Isothermal; DA : Adiabatic

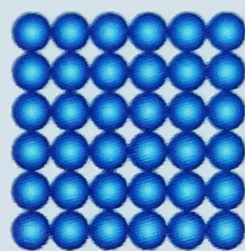


A state function is obtained from the derivation of Carnot cycle. i.e. **Entropy**

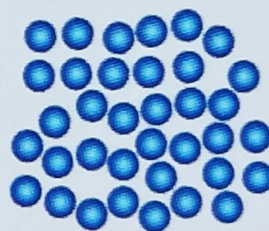
$$dS = \frac{dq_{rev}}{T}$$

ENTROPY (S)

- Degree of Randomness.
- $S (\text{Gas}) > S (\text{Liquid}) > S (\text{Solids})$
- 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.
- $\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$ (Reversible process)
- $\Delta S_{\text{universe}} > 0$ (Irreversible process)

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

General Formulas for Entropy

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
L = Latent heat

Fusion $S \rightleftharpoons L$

Vaporisation $L \rightleftharpoons G$

Sublimation $S \rightleftharpoons G$

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Gibbs Free energy (G)

- The decrease in Gibbs free energy is equal to the maximum useful work.
- $(-\Delta G = W_{\text{useful}})$
- It is a state function, Used to calculate Spontaneity.
- Extensive Property
- Used to calculate Spontaneity.

Gibbs Helmholtz Equation & Spontaneity

$$\Delta G = \Delta H - T\Delta S$$

Spontaneity means that the reaction can be carried out on it's own (it is feasible). All Natural processes are spontaneous.

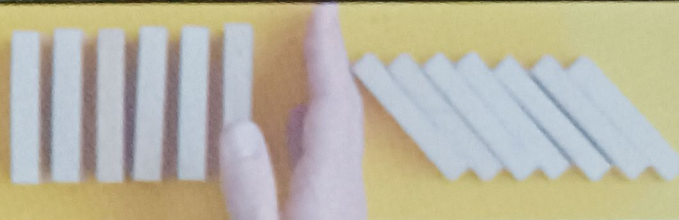
$$\Delta S > 0$$

$$\Delta S < 0$$

$$\Delta H < 0$$

$$\Delta H > 0$$

Spont. at all T	Spont. at High T
Spont. at Low T	Non Spont.



THERMOCHEMISTRY

(NEXT FACE)

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Enthalpy of a Reaction ($\Delta_r H$)

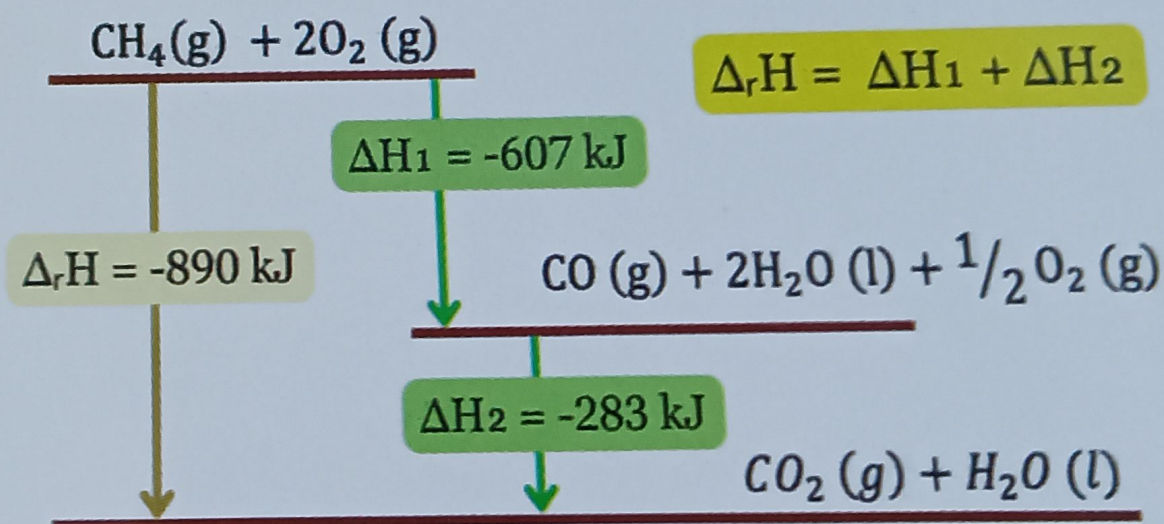
The heat exchanged during complete course of reaction at constant pressure.

Exothermic : Negative $\Delta_r H$

Endothermic : Positive $\Delta_r H$

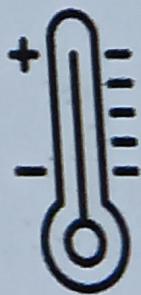
Hess's law of constant summation

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



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

Different Types of Enthalpy



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

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 ($\Delta_f H$)

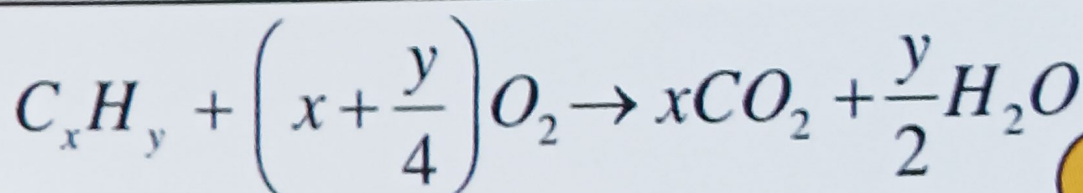
- The ΔH of reaction when 1 mole of a substance is **produced from** its constituent elements which are present in their **free state**.
- ($\Delta_f H$) for free state elements is considered as **Zero**.
- Some elements in their free state are
 - $F_2(g)$; $Cl_2(g)$; $Br_2(l)$; $I_2(s)$; $P_4(s)$; $H_2(g)$;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



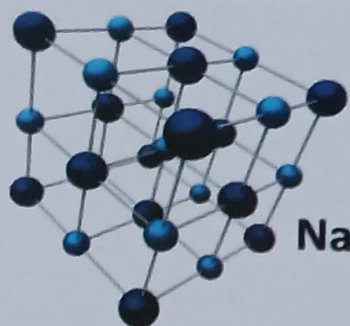
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Enthalpy of a Reaction ($\Delta_r H$)

The heat exchanged during complete course of reaction at

Lattice Enthalpy

Energy to convert 1 mole of Ionic Solid into gaseous ions



NaCl Lattice

Energy Required to Break.

Thus +ve ΔH



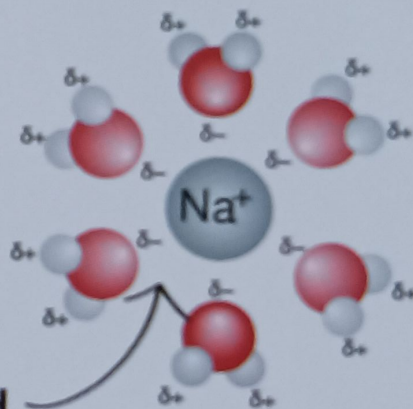
Na⁺



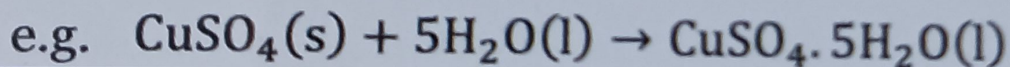
Cl⁻

Hydration Enthalpy

Energy produced when 1 mole of the gaseous ions is mixed with H₂O (water) to produce hydrated ions.



This Stabilises Ions. Thus, -ve ΔH



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

