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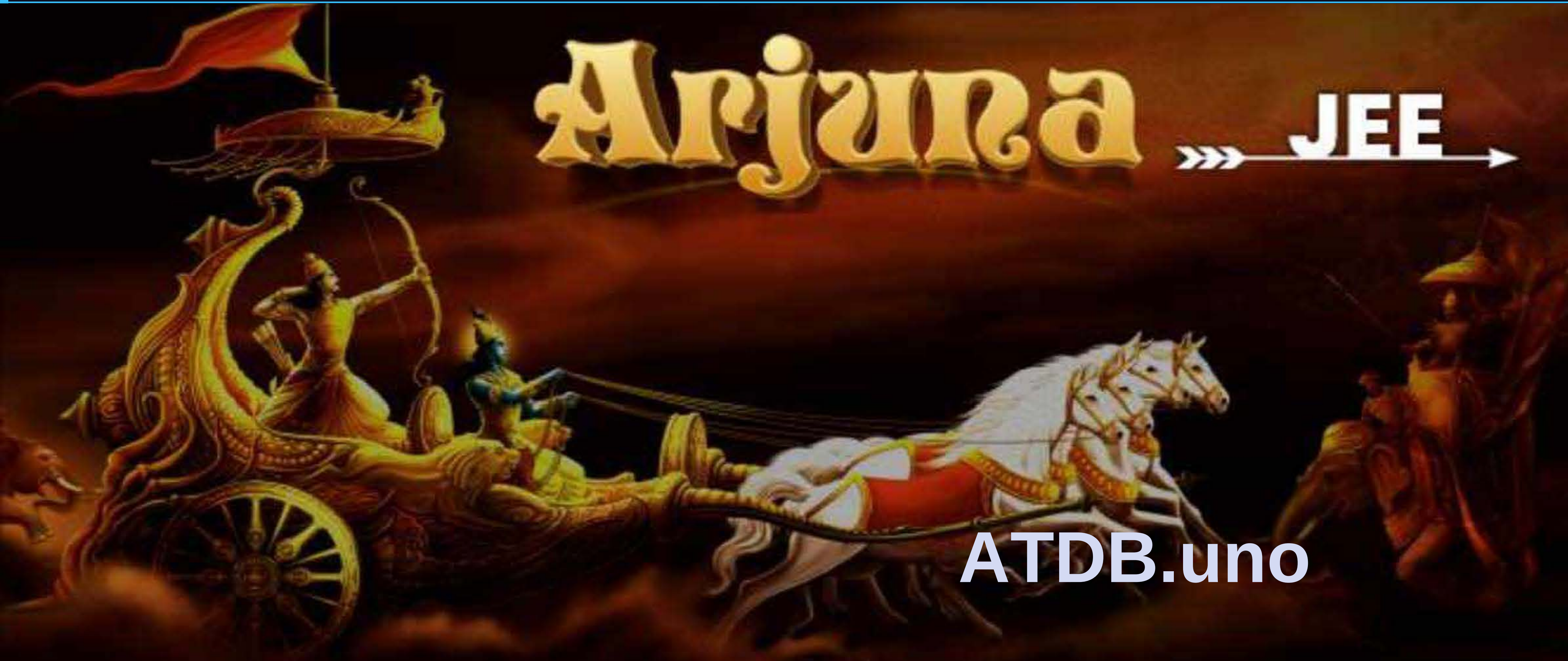

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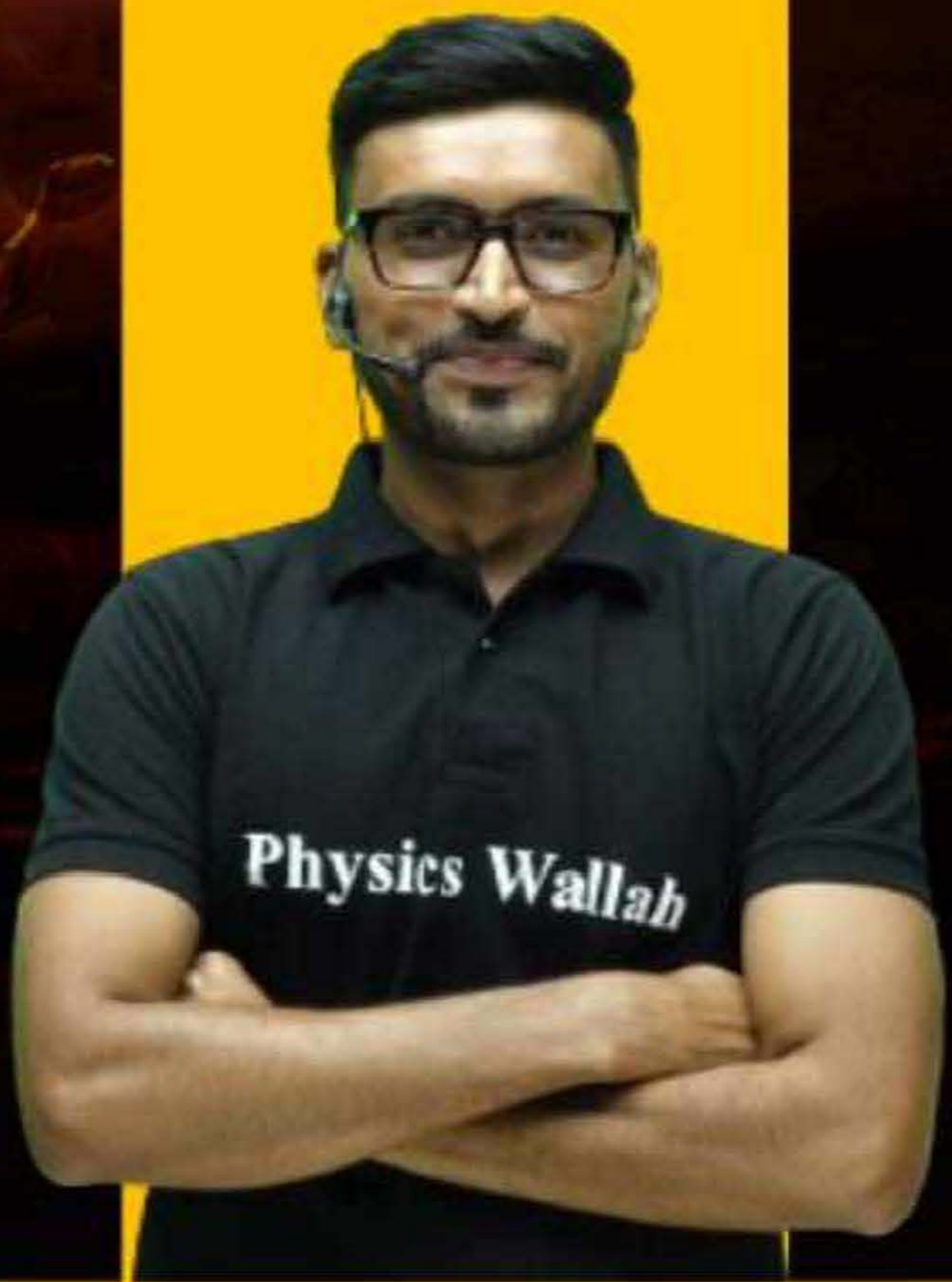
- ☐ Subject - Chemistry
- ☐ Chapter – Thermodynamics



One shot

By- Rahul Dudi Sir

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Today's Targets

Chapter

1. Introduction and Thermodynamic Terms
2. Thermodynamic Properties and FLOT
3. Thermochemistry
4. Entropy and 2nd law of Thermodynamics

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Introduction

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Introduction

Thermo + dynamics

- Thermodynamics is a branch of science dealing with the study of different forms of energy and their interconversions.

- **In chemistry using the thermodynamics**

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1. We can predict the feasibility of a reaction.
2. If reaction does take place, what are the energy changes involved during the reaction.
3. If a chemical equilibrium is going to be attained than what will be the equilibrium concentrations of different reactants and products.

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Introduction

Limitations of Thermodynamics:

- It is applicable to macroscopic systems consisting matter in bulk and not to microscopic systems of individual atoms and molecules.

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- It does not tell anything about the rate of physical change or a chemical reaction.

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Thermodynamic Terms

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The System and the Surroundings

- A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings.
- The universe = The system + The surroundings
- The wall that separates the system from the surroundings is called boundary.

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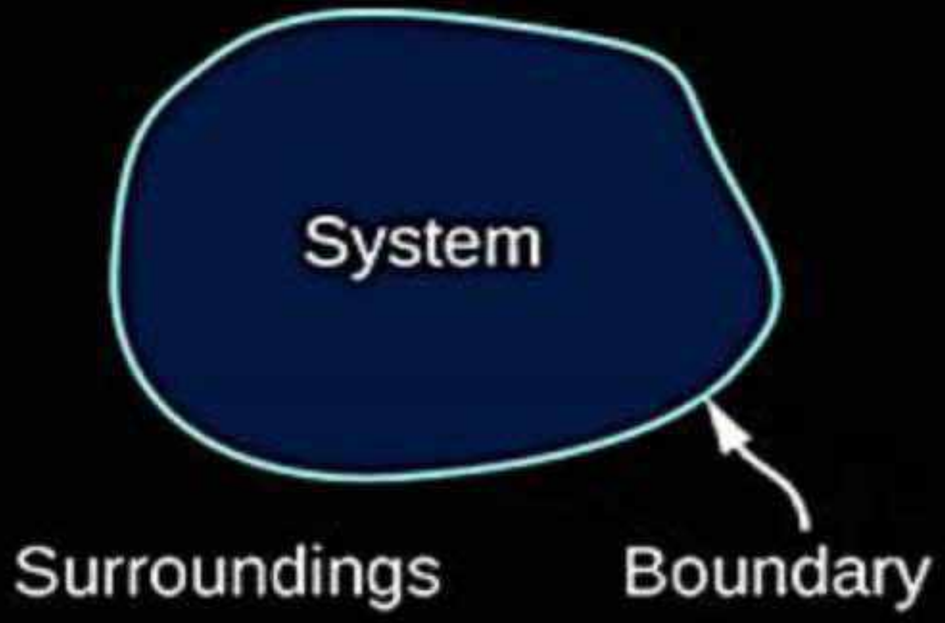

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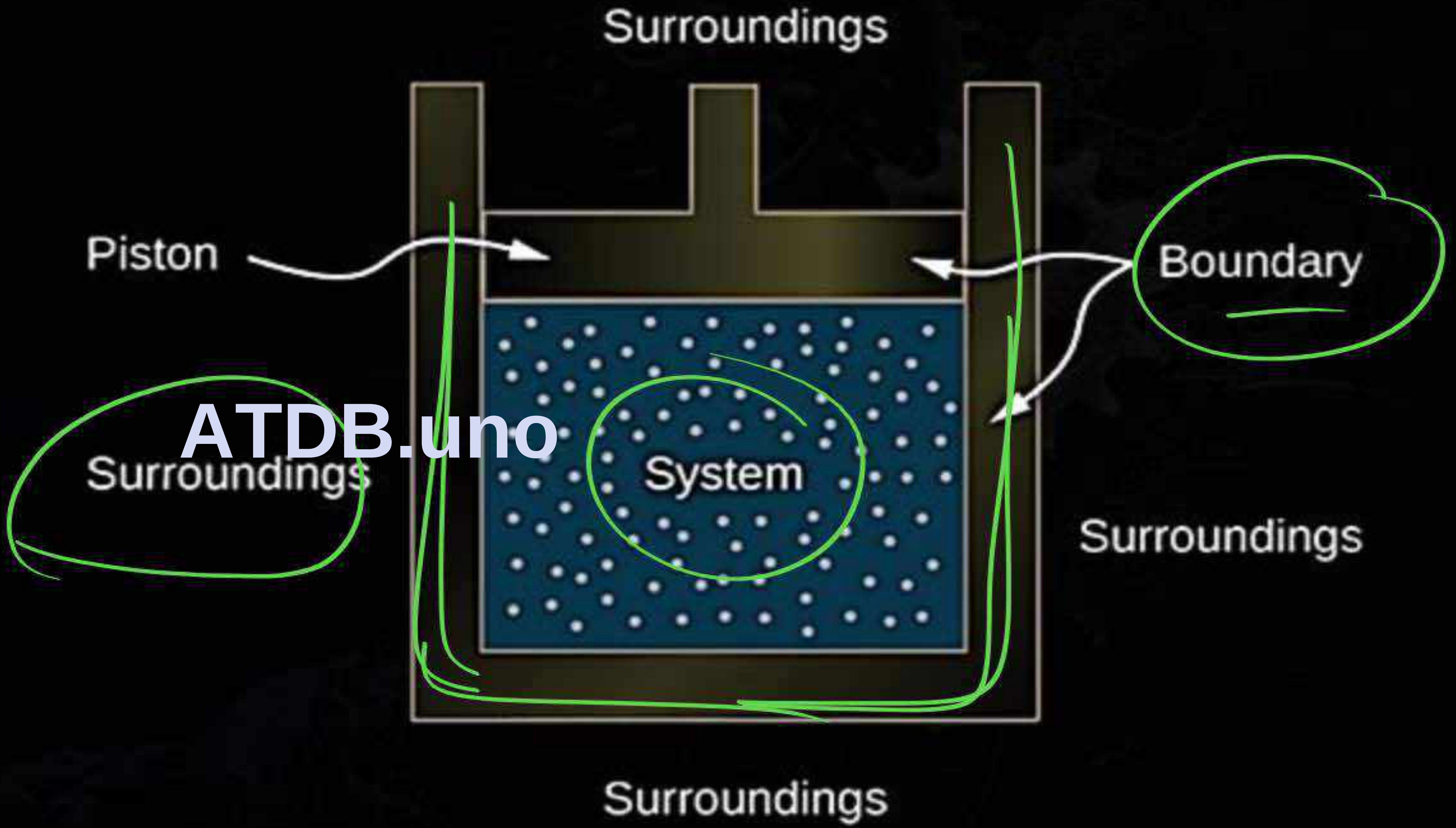

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Types of system

1. Open System

- In an open system, there is exchange of energy and matter between system and surroundings.
- The presence of reactants in an open beaker is an example of an open system.
- Here the boundary is an imaginary surface enclosing the beaker and reactants.

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Open system

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Types of system

2. Closed System

- In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings.
- The presence of reactants in a closed vessel made of conducting material e.g., copper or steel is an example of a closed system.

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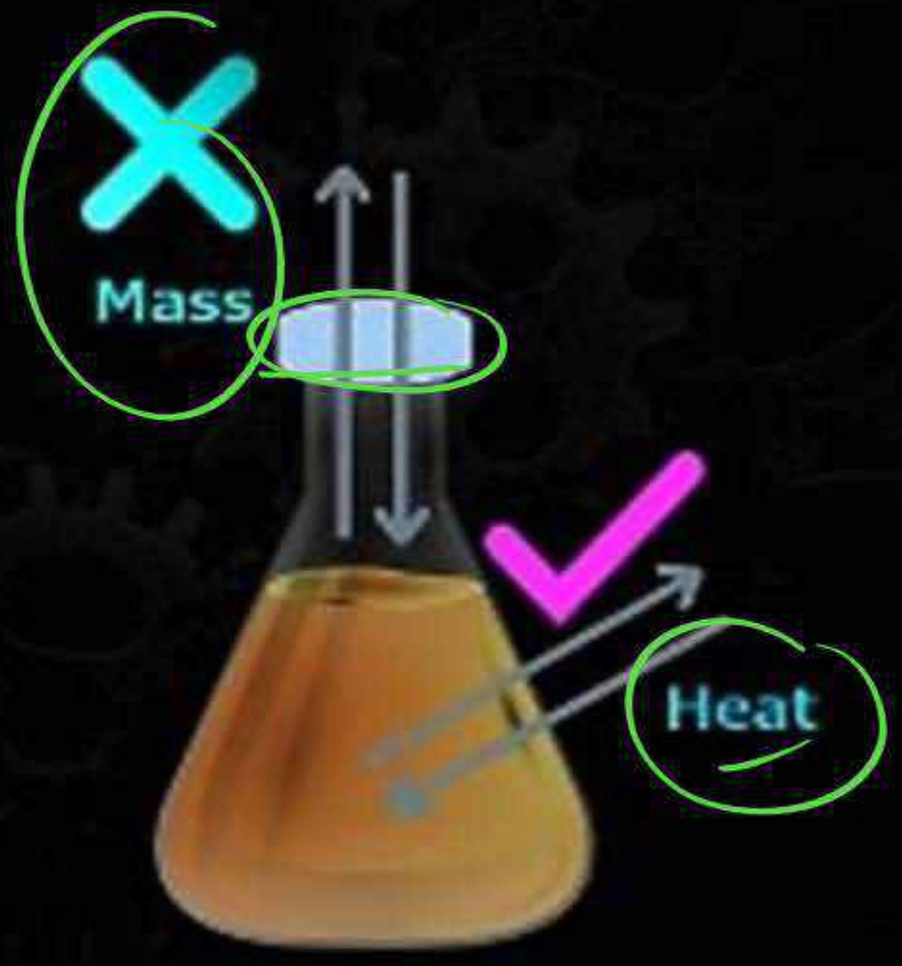

Closed system

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Types of system

3. Isolated System

- In an isolated system, there is no exchange of energy or matter between the system and the surroundings.

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- The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

Isolated system

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State of a system

- State is the condition of a system as specified by it's physical properties.
- Macroscopic properties such as pressure, temperature, volume, amount, etc. which determine the state of a system are referred to as state variables .

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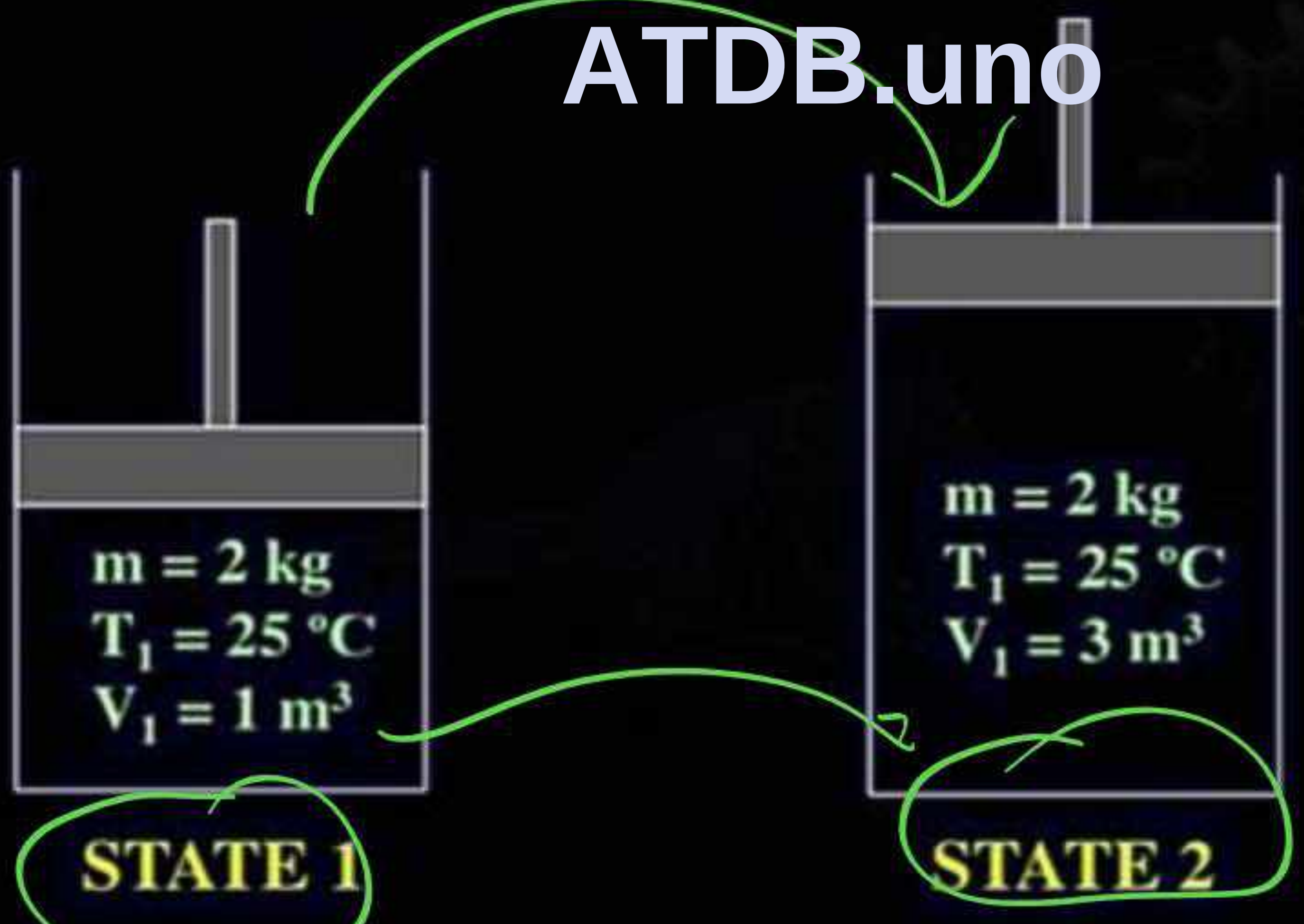
$PV = nRT$

④ X

③ ✓

P, V, T. → State functions



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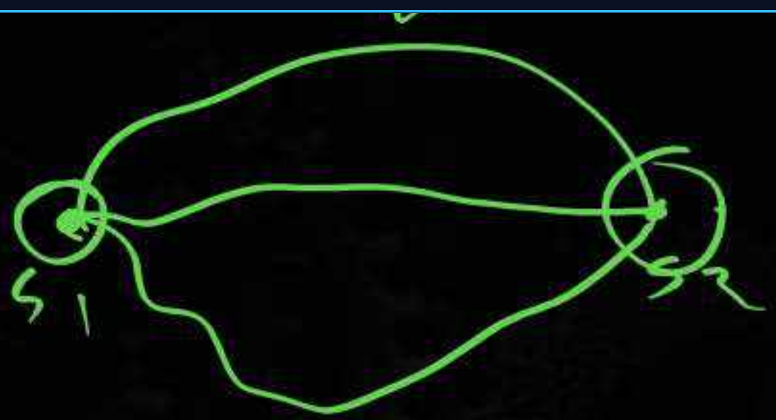
State and Path Function



State Functions:

- Variables like p, V, T are called state variables or state functions because their values depend only on the state of the system and not on how it is reached.

Ex :→ P, V, T, Internal energy (U), Enthalpy (H), Entropy (S), Gibb's energy (G) etc.

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Path Functions:

Ex :→ Heat (q), work (ω).

- Those physical quantities which depends on the path followed, are called as path functions.

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Extensive and Intensive Properties

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Extensive Property

- An extensive property is a property whose value depends on the quantity or size of matter present in the system.
- For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties.

(U) (H)

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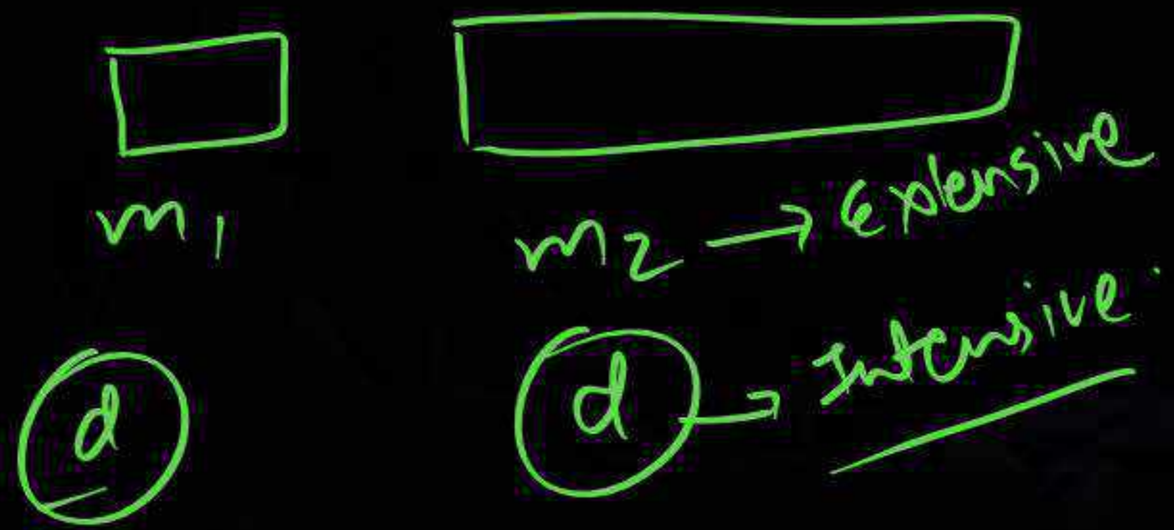

Entropy (S), Gibb's energy (G),

Resistance (R) etc.

moles

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Intensive Property

- Those properties which do not depend on the quantity or size of matter present are known as intensive properties.
- For example temperature, density, pressure etc. are intensive properties

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↳ Viscosity, surface tension, E°_{cell}, pH, Concentration, molar volume,

P = 1 atm

$\frac{20}{4} = 5m^3$ 25°c	$\frac{20}{4} = 5m^3$ 25°c
$\frac{20}{4} = 5m^3$ 25°c	$5 m^3$ 25°c

→ P = 1 atm.

→ T = 25°c.

→ V = 20 m³.

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Note

① X and Y → Intensive Properties

$$\left.X+Y,\ XY,\ \frac{X}{Y},\ \frac{\partial X}{\partial Y}\right] \rightarrow \text{Intensive.}$$

② X and Y → Extensive Properties.

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X+Y → extensive.

$$\left.\frac{X}{Y},\ \frac{\partial X}{\partial Y}\right] \rightarrow \text{Intensive.}$$

$$\underset{\substack{\downarrow \\ \text{Intensive.}}}{\text{density}} = \frac{\text{Mass} \rightarrow \text{Ext.}}{\text{Vol.} \rightarrow \text{Ext.}}$$

$$\underset{\substack{\downarrow \\ \text{Int}}}{\text{Conc.}} \Rightarrow \frac{\text{moles} \rightarrow \text{Ex.}}{\text{volume} \rightarrow \text{Ex.}}$$

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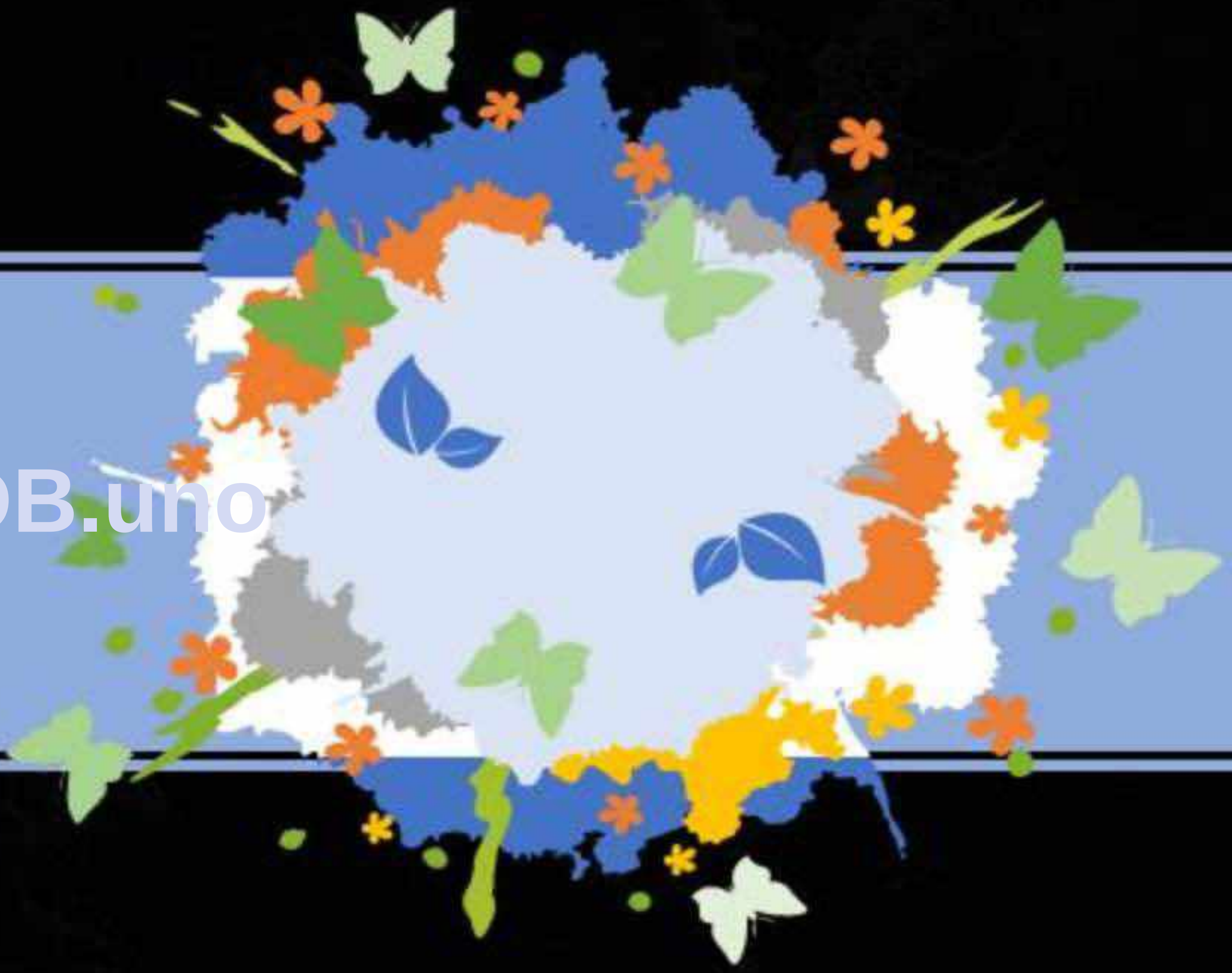
Thermodynamic Process



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Thermodynamic Process

- The sequential steps followed to change the state of a system, is called as a process.

State-1. → State-2.

Steps.

Process.

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- * Isothermal.
- * Isobaric
- * Isochoric
- * Adiabatic
- * Cyclic
- * Reversible and Irreversible

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Thermodynamic Process

1. Isothermal Process:

- The process in which temperature is kept constant for the entire process is known as isothermal process.

T = Constant.

$dT = 0 \;] \Rightarrow \underline{\Delta T = 0}$.

Boyle's Law :->

$\boxed{P \propto \frac{1}{V}}$

$\boxed{P_1V_1 = P_2V_2}$

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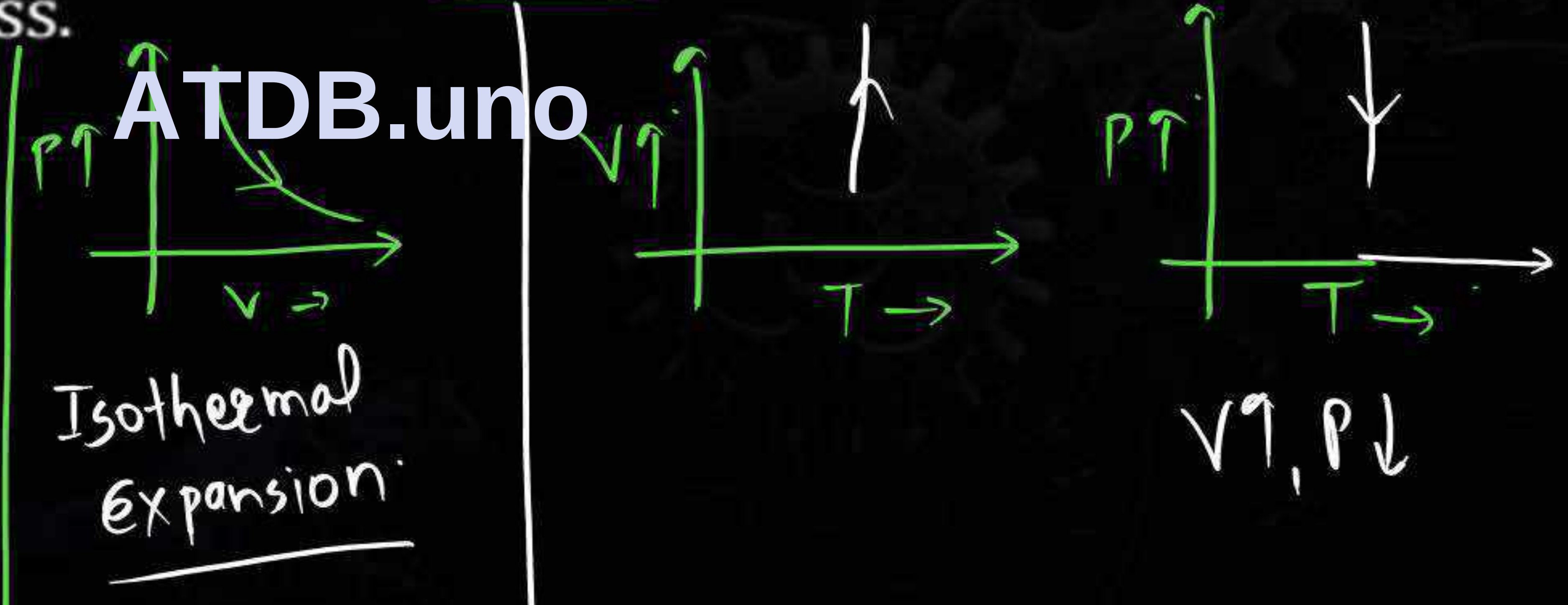

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Thermodynamic Process

2. Isobaric Process:

- ➢ The process in which pressure is kept constant for the entire process, is known as isobaric process.

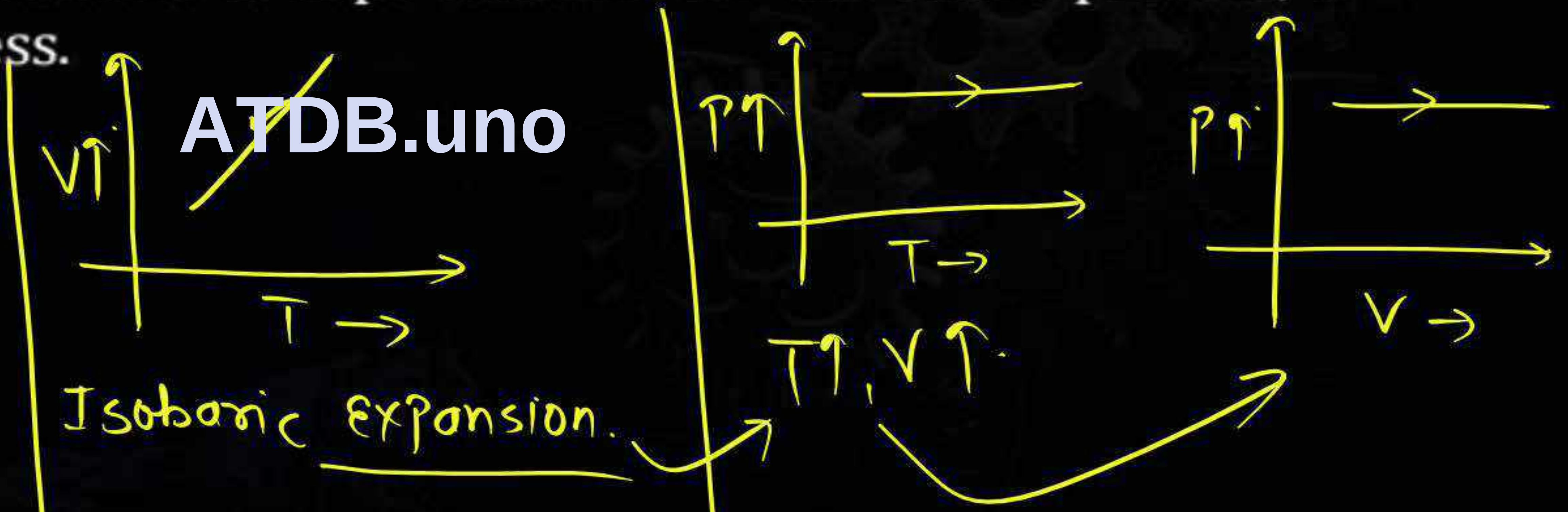
P = Constant.

$dP = 0 \Rightarrow \Delta P = 0$

Charle's law :→

$V \propto T(K)$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$



Isobaric expansion.

T↑, V↑.

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Thermodynamic Process

3. Isochoric Process:

- The process in which volume is kept constant for the entire process, is known as isochoric process.

V = Constant.

$dV = 0 \Rightarrow \Delta V = 0$

$\boxed{P \propto T(K)}$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

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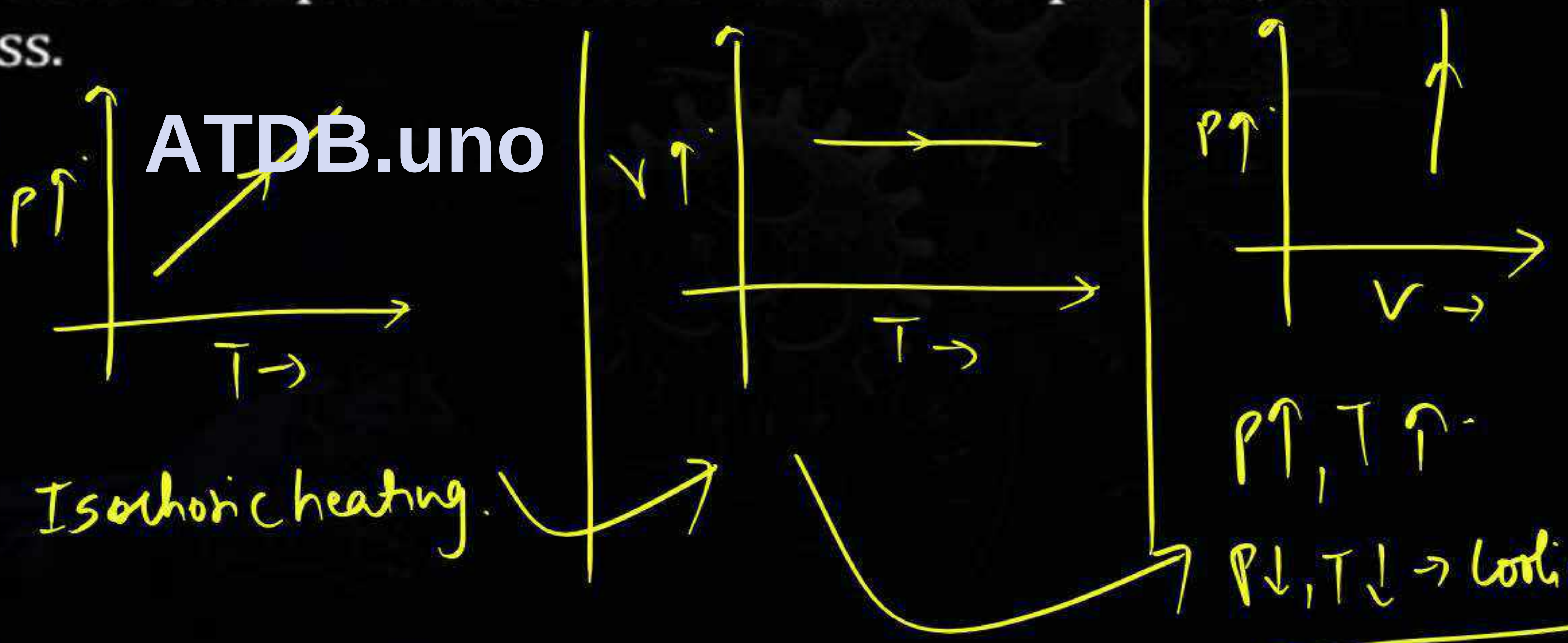

Isochoric heating.

P↑, T↑.

P↓, T↓ → Cooling.

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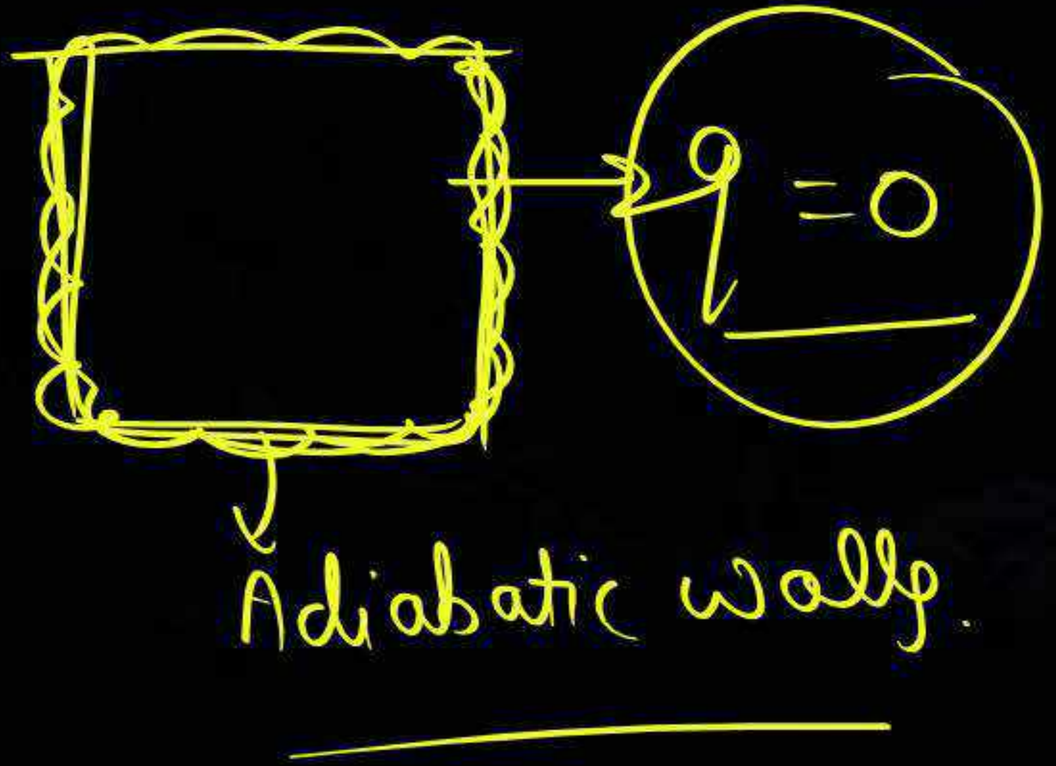
Thermodynamic Process

4. Adiabatic Process:

- The process in which heat exchange across the walls is not possible , is known as adiabatic process.



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

γ → Poisson's Ratio

$\gamma > 1$

$PV = \text{Constant} \rightarrow \text{Isothermal}$

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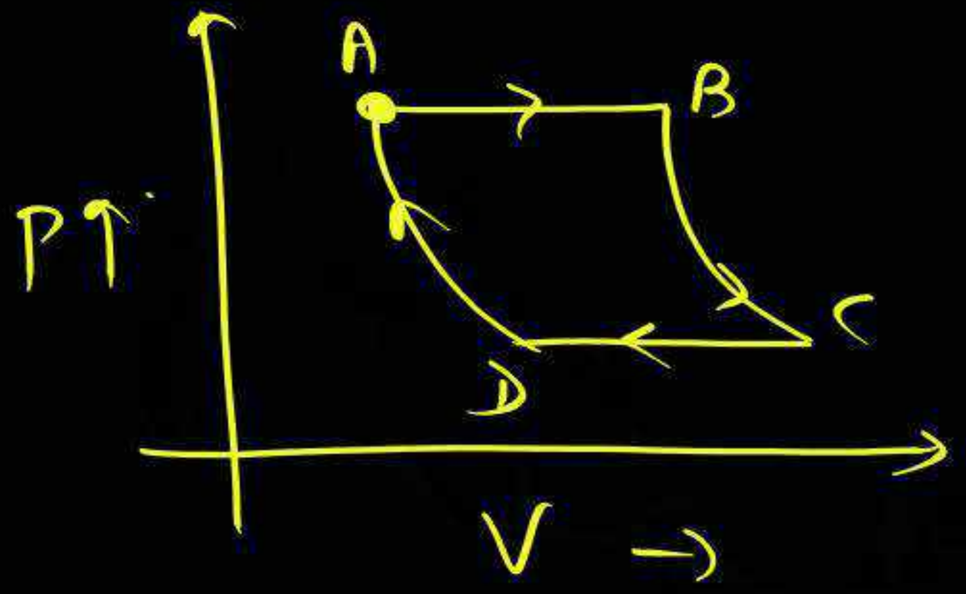
Thermodynamic Process

Cyclic Process:

- The process in which initial and final states are same, is called as cyclic process.



Change in state function = 0.

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$\Delta H = H_2 - H_1$

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Reversible and Irreversible Process

Reversible Process	Irreversible Process
1. It takes place in infinite number of infinitesimally small steps and it would take *infinite time* to occur	1. It takes place *infinite time*.
2. It is *imaginary* as it assumes the presence of frictionless and weightless piston.	2. It is *real* and can be performed actually.
3. It is in equilibrium state at *all stages* of the operation.	3. It is in equilibrium state only at the *initial and final stages* of the operation.
4. All changes are *reversed* when the process is carried out in reversible direction.	4. After this type of process has occurred all changes *do not return* to the initial state by themselves.
5. It is extremely slow.	5. It proceeds at *measureable speed*.

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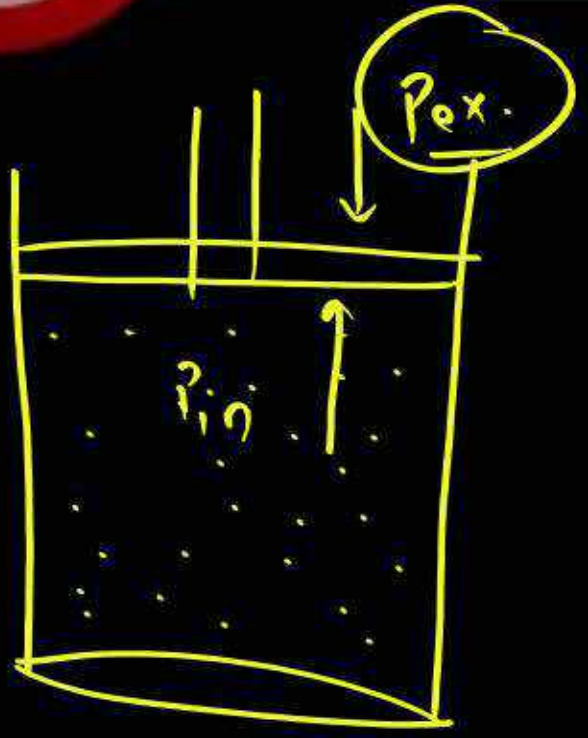
Reversible and Irreversible Process

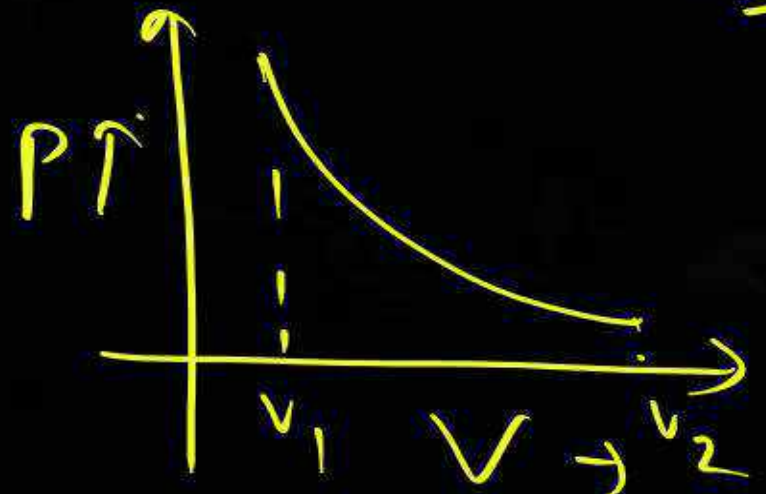


Reversible.

$P_{ex} = P_{in} \pm \underbrace{dP}$ → driving force.

dP → negligible ≃ 0.

$P_{ex} \simeq P_{in}$
(P_{gas}).



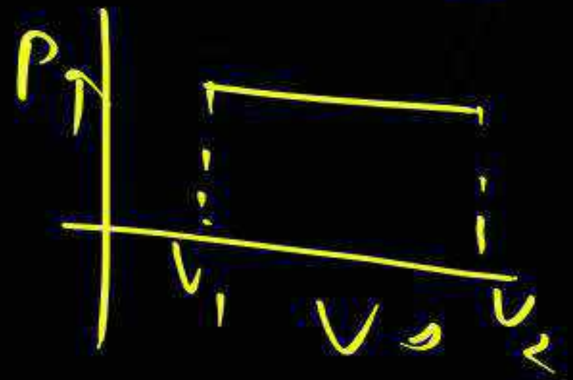
Irreversible :→ ✓

$P_{ex} = P_{in} \pm \Delta P$

$\Delta P \neq 0$.

$P_{ex} \neq P_{in}$

→ At Constant Pressure



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Thermodynamic Equilibrium

- A system in which the macroscopic properties do not undergo any change with time is called thermodynamic equilibrium.

- It is of three types:

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Thermodynamic Equilibrium

1. Thermal equilibrium:

- If there is no flow of heat from one portion of the system to another, the system is said to be in thermal equilibrium.

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Thermodynamic Equilibrium

2. Mechanical equilibrium:

$P = \text{Constant}$

- If no mechanical work is done by one part of the system on another part of the system, it is said to be in mechanical equilibrium. Such a condition exists when pressure remains constant.

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Thermodynamic Equilibrium

3. Chemical equilibrium: ✓

- In chemical equilibrium the composition of different phases remains same and chemical composition of the system remains constant and there is no chemical reaction taking place.

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$$\left. A + B \rightleftharpoons C + D \right]$$

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Work

$W = mgh.$

$$\boxed{W = qV}$$

* (P-V) work done.

$$W = \int f \cdot ds$$

$$P = f/A \Rightarrow f = P.A.$$

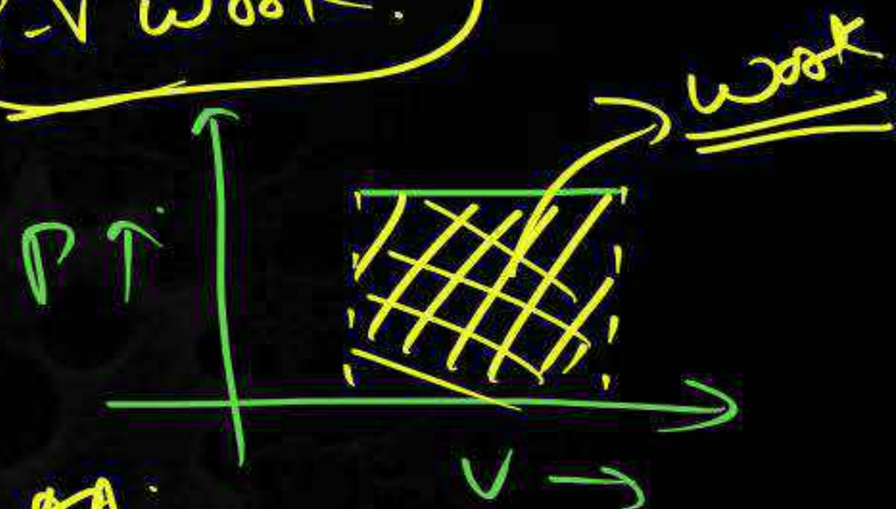
$$W = \int P.(A.ds)$$

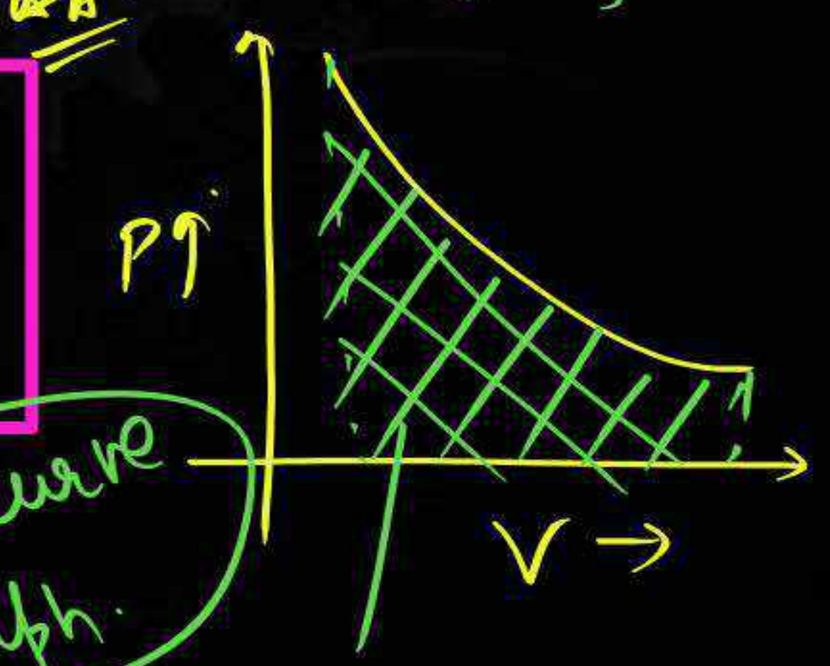
$$W = \int P.dV \rightarrow \text{P-V work.}$$

Chemistry →

$$\boxed{W = -\int P_{ex} \cdot dV.}$$

Area under the curve of (P-V) Graph.





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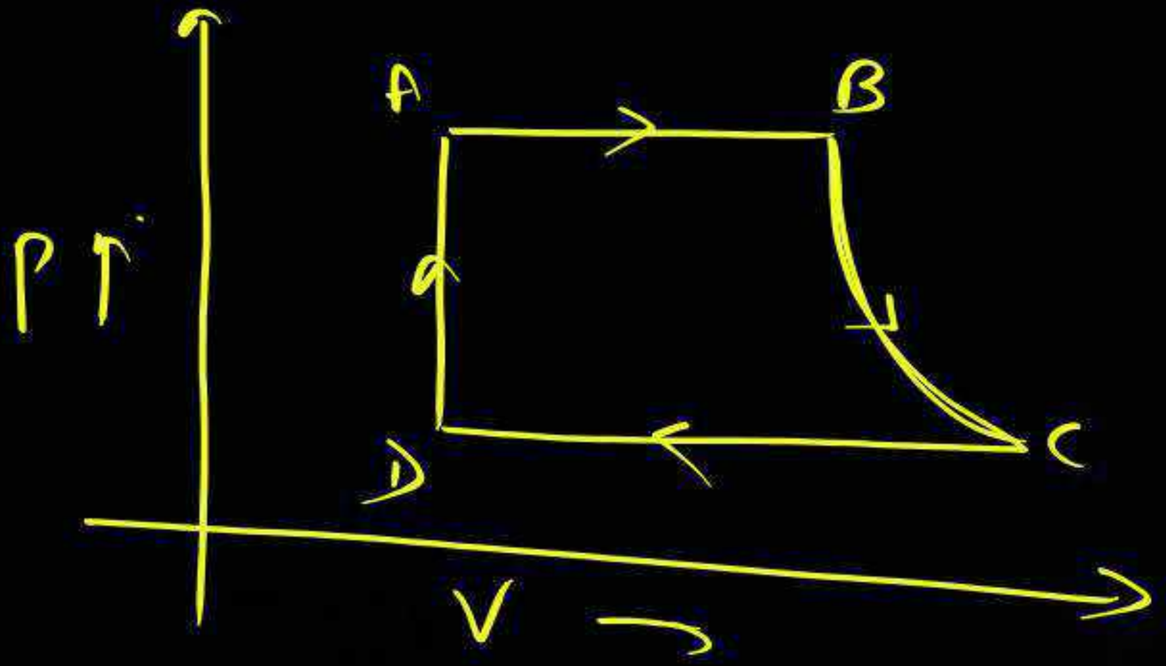
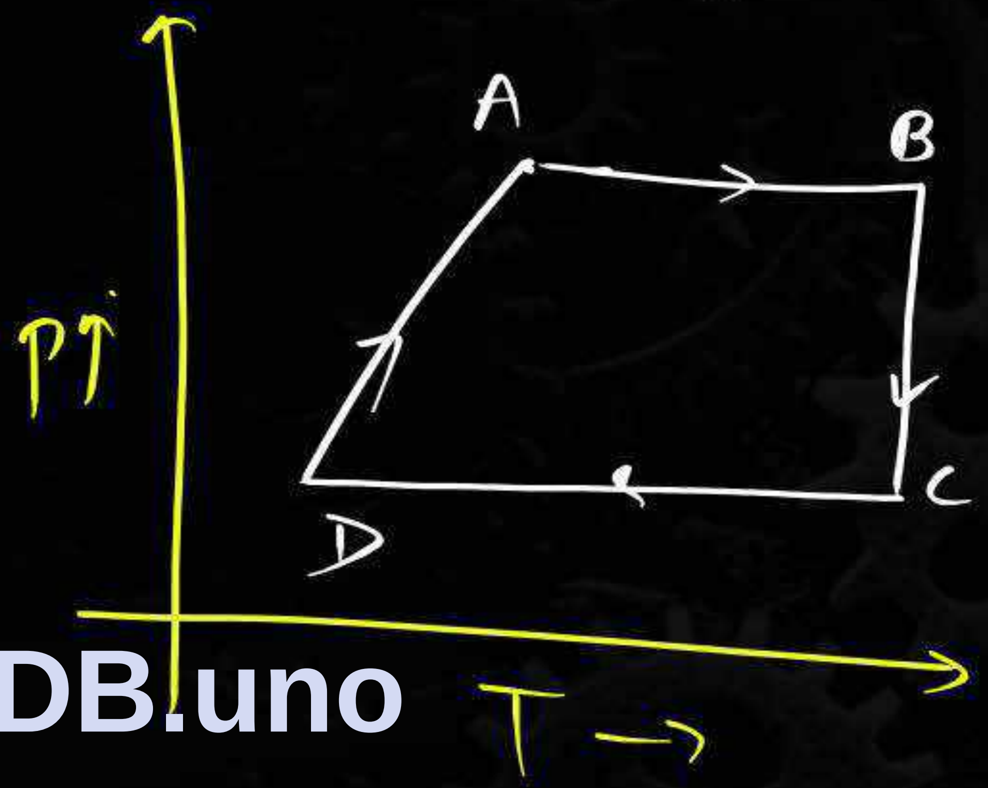
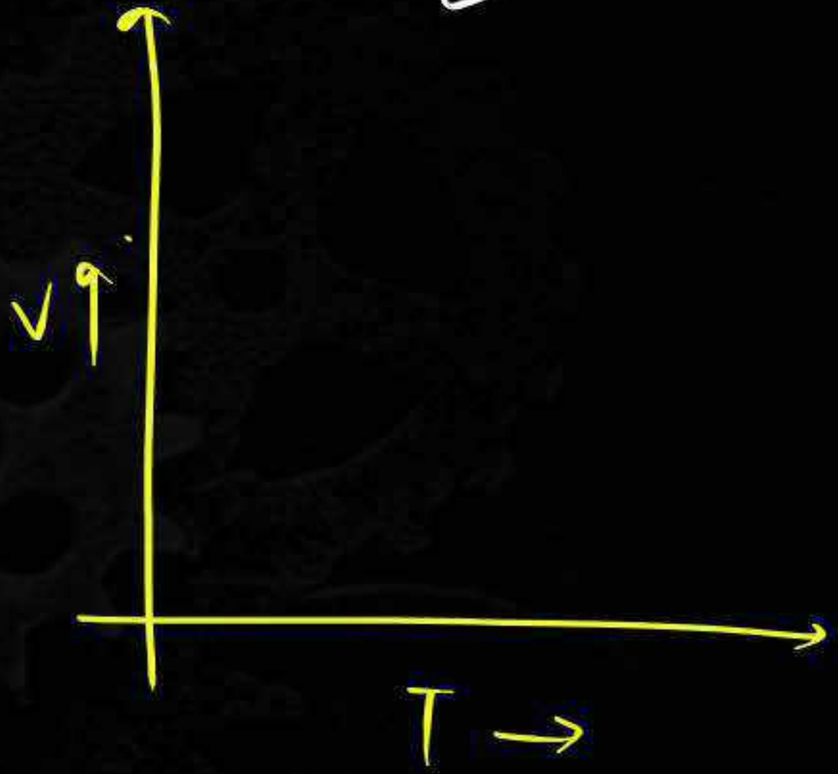
* Conversion of Graph :→







$AB \Rightarrow \underline{P = k}, V\uparrow \underline{T}\uparrow \; (V \propto T).$

$BC \Rightarrow \underline{T} = k, \underline{P}\downarrow V\uparrow \; (P \propto 1/V)$

$CD \Rightarrow P = k, V\downarrow, \underline{T\downarrow} \; (V \propto T)$

$DA \Rightarrow V = k, \boxed{P \propto T} \; P\uparrow, T\uparrow.$

Hw

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Question

Which of the following is/are extensive properties?

- A Entropy ✓
- B Density ✗
- C Enthalpy ✓
- D Boiling point ✗

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Question

Which of the following is/are state function?

A Enthalpy ✓

B Heat ✗

C Entropy ✓

D Gibb's free energy(G) ✓

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Question

Which of the following statements is false? (2001, 1M)

[✓ A] Work is a state function

B Temperature is a state function

C Change in the state is completely defined when the initial and final states are specified

D Work appears at the boundary of the system

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Question

In thermodynamics, a process is called reversible when (2001, 1M)

A Surroundings and system change into each other

B There is no boundary between system and surroundings

[✓ C] The surroundings are always in equilibrium with the system

D The system changes into the surroundings spontaneously

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Internal Energy [$\underline{U}$ or E]

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Internal Energy

- It is the sum of all different types of energies associated with all the particles present in the system.

$U = K.E + P.E + V.E. + E.E. + \ldots\ldots$

→ State function ($\Delta U = U_2 - U_1$)

→ Extensive Property.

Gravational Energy ✗ .

$$\boxed{\Delta U = n\underline{C_v}(\Delta T)}$$

→ molar heat Capaci

if $\Delta T = 0, \Delta U = 0$

- Its absolute value cannot be determined but experimentally change in internal energy (Δ) can be determined.

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Internal Energy

➢ A change in internal energy may be brought about when :

i. heat passes into or out of the system,
ii. work is done on or by the system,
iii. matter enters or leaves the system.

[Extensive Property]

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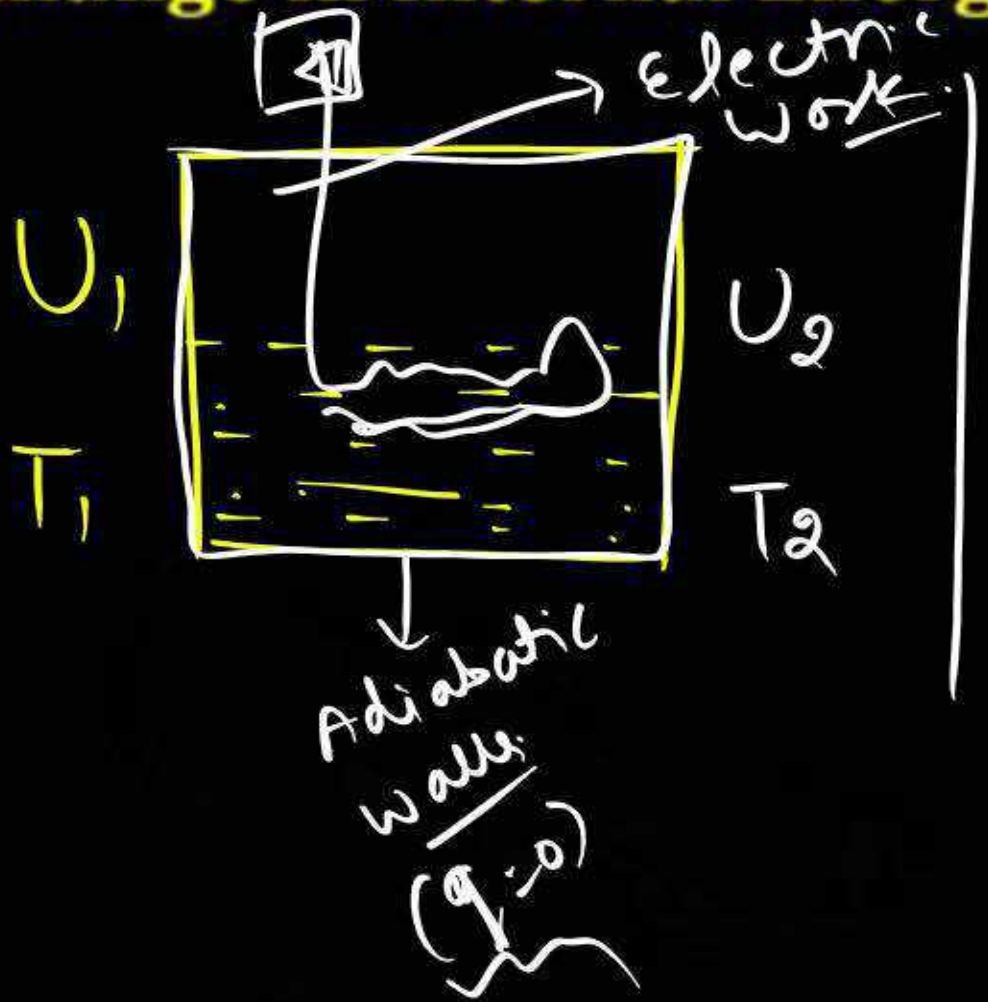
Internal Energy

Change in Internal Energy by Doing Work:



$$\Delta U = U_2 - U_1$$

$$\Delta U = (W)_{adiabatic}$$

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Sign convention :-

work done by the system ⇒ $W = -ve$

work done on the system ⇒ $W = +ve$

* Compression. $P_{ex} > P_{in}$

⇒ $W = +ve$.

* Expansion $[P_{in} > P_{ex}]$

⇒ $W = -ve$.

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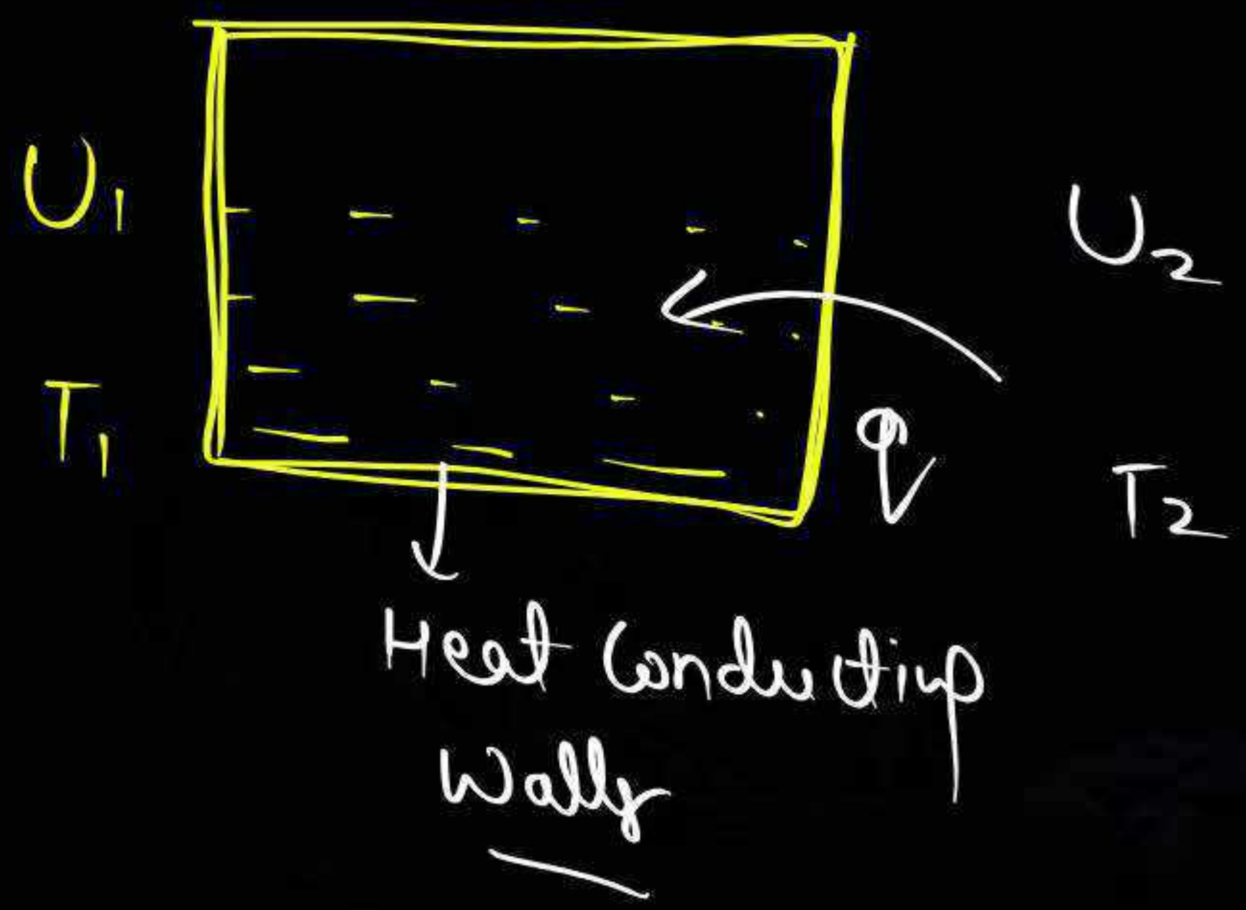
Internal Energy

Change in Internal Energy by Heat:



$$\Delta U = U_2 - U_1$$

$$\boxed{\Delta U = q} \star$$

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sign convention

Heat absorbed ⇒ $q = +ve$.

Heat released ⇒ $q = -ve$.

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General Case:

- When change in internal energy is because of both heat and work:

$$\boxed{\Delta U = q + w} \rightarrow$$ 1st law of thermodynamics.

↓

law of energy conservation.

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*

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Question

If 5J are taken away by heat from the system, and the system does 5J of work, what is the change in internal energy of the system?

[✓ A] −10 J

B 0 J

C 10 J

D 25 J

$q = -5J$

$w = -5J.$

$\Delta U = q + w$

$\Rightarrow -5 + (-5)$

$\boxed{\Delta U \Rightarrow -10J.}$

$\Delta U = \boxed{U_2} - U_1$

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Question

160 J of work is done on the system and at the same time 100 J of heat is given out. What is the change in the internal energy?

Ans :-

$w = +160\text{ J}$

$q = -100\text{ J}$

$\Delta U = q + w$

$\Rightarrow (-100) + 160$

$\underline{\Delta U \Rightarrow 60\text{ J}}$

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Question

If change in internal energy –80 J. The work done by system is +40 J. Calculate the heat change.

hw

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Question

If the external pressure is more than the internal pressure then what will be the sign convention for the work done on a cylinder fitted with a frictionless and weightless piston containing one mole of an ideal gas?

$P_{ex} > P_{in}$

↓

Compression

↓

work done on the system

↓

$w = +ve$

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Question

During compression of a spring the work done is 10 kJ and 2 kJ escaped to the surroundings as heat. The change in internal energy, ΔU (in kJ) is

(2019 Main, 9 April II)

Ans :-

$w = +10 \text{ kJ}$

$q = -2 \text{ kJ}.$

$\Delta U = 10 - 2$

$\Rightarrow 8 \text{ kJ}.$ Ans

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Question

Among the following the set of parameters that represents path functions, is

(1) $q + W \rightarrow \Delta U$ ✗ (2) q ✓

(3) W ✓ (4) $H - TS \rightarrow G$ (2019 Main, 9 April I)

- A (1) and (4)
- B (1), (2) and (3)
- C (2), (3) and (4)
- D (2) and (3) ✓

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Question

ΔU is equal to

(2017 Main)

A isochoric work

B isobaric work

[✓ C adiabatic work]

D isothermal work

$\Delta U = W_{ad}$.

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Question

A piston filled with 0.04 mole of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and W for the process will be (R = 8.314 J/mol K, ln 7.5 = 2.01)

(2013 Main)

[✓ (A) q = +208 J, W = – 208 J]

(B) q = –208 J, W = – 208 J

(C) q = –208 J, W = + 208 J

(D) q = +208 J, W = + 208 J

$q = +208\ J.$

$T = \text{Constant},\ \Delta T = 0$

$\underset{0}{\underset{\downarrow}{\Delta U}}$ [illegible] $\underset{0}{\underset{\downarrow}{\Delta T}}$

$\boxed{\Delta U = 0}$

$* \quad \underset{0}{\underset{\downarrow}{\Delta U}} = q + w$

$w = -q.$

$\boxed{w = -208\ J}$

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Thermodynamic Definition of Ideal Gas

- If for a gas the internal energy is directly proportional to its absolute temperature, the gas is termed as an ideal gas.

$$\left.\left[\frac{\partial U}{\partial P}\right]_T = 0 \qquad \left[\frac{\partial U}{\partial V}\right]_T = 0 \right\} \rightarrow \boxed{\text{Ideal Gas}}$$

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Degree of Freedom (f).

- The total number of modes on which a molecule of an ideal gas can exchange energy during collisions, is known as its degree of freedom.

→ Translational $[f_T)$
→ Rotational $[f_R]$
→ vibrational $[f_V]$ → only at very high temp.

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* Translational D.o.f. = 3 [All the Gases].

* Rotational D.o.f.

↳ 0 [for monoatomic Gas]. ↗ O=C=O.

↳ 2 [for Diatomic or linear polyatomic Gas.]

↳ 3 [for polyatomic non-linear gas].

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* for <u>monoatomic Gas.</u>

$f = 3$

* for <u>Diatomic Gas.</u>

$f = 3+2 = \boxed{5}$

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* for <u>Polyatomic Gas</u> :→

(a) <u>Linear</u> ⇒ $f = 3+2 = \boxed{5}$

(b) Non-Linear ⇒ $f = 3+3 = \boxed{6}$

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Law of Equipartition of Energy

Boltzman's Constant

- Energy equal to ½ KT is associated with each degree of freedom per ideal gas molecule.

$$U/\text{molecule} = f\left[\frac{1}{2}KT\right]$$

$$U/\text{mole} = f\left\{\frac{1}{2}\times\left[\underbrace{K\times N_A}\right]T\right\}$$

$$U/\text{mole} = f\left[\frac{1}{2}\times R\times T\right]$$

for n-moles :→

$$U = \frac{1}{2}\times n\times f\times R\times T$$

$$\boxed{\Delta U = \frac{nfR}{2}(\Delta T)}$$

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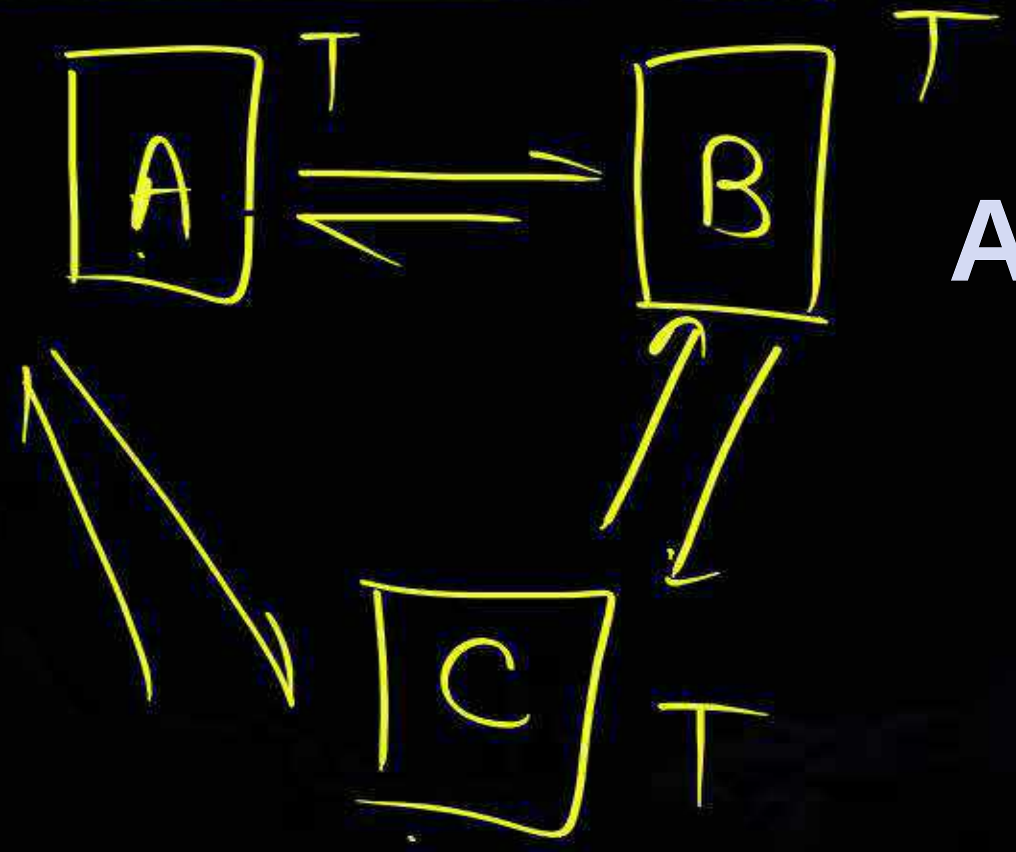
Zeroth Law of Thermodynamics

- If A and B are in thermal eq. , B and C are also in thermal eq. then A and C will assentially be in thermal eq.



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Heat Capacity [C]

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Heat Capacity

- Heat capacity or thermal capacity is a physical property of matter, defined as **the amount of heat to be supplied to an object to produce a unit change in its temperature.**

$$q \propto \Delta T$$

$$\boxed{q = \underset{\downarrow}{C}(\Delta T)}$$

Heat Capacity.

$$\boxed{C = \frac{q}{\Delta T}}$$

$J\,K^{-1}$ or $J\,{}^{\circ}C^{-1}$

$\Delta T = 1$, $C = q$

C: Temp. dependent.

$$C = aT^2 + bT + c$$

$$q = \int_{T_1}^{T_2} C\,dT$$

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Heat Capacity

Specific Heat Capacity: (s)

- The specific heat capacity is defined as **the quantity of heat (J) absorbed per unit mass (kg) of the material when its temperature increases 1 K (or 1°C),**

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$$\boxed{S = \frac{q}{m(\Delta T)}}$$

J Kg^{-1} K^{-1}

$m=1,\ \Delta T = 1.$

$q = s$

$$\boxed{q = ms(\Delta T).}$$

$$q = \int_{T_1}^{T_2} ms \cdot dT$$

temp. dependent.

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Heat Capacity

Molar Heat Capacity: $[C_m]$.

- The molar heat capacity is the amount of energy required to raise the temperature of one mole of a substance by one degree.

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$$\boxed{C_m = \frac{q}{n(\Delta T)}}$$

$\mathrm{J\,mol^{-1}\,K^{-1}}$.

$$\boxed{q = n C_m (\Delta T)}$$

$$q = \int_{T_1}^{T_2} n C_m \, dT$$

$$\boxed{C_p - C_v = R}$$

R → gas constant.

C_p → molar heat capacity at constant P.

C_v → molar heat capacity at const. volume

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Heat Capacity

Question : The amount of heat required to raise the temperature of 3 g Al from 25ºC to 30ºC is 4.5 KJ. Find molar and specific heat capacity of Al.

Ans:→ $m = 3g$.

$M_w = 27$

$n = \frac{w}{M_w} = \frac{3}{27} = 1/9$

$T_1 = 25°c,\ T_2 = 30°c$

$\boxed{\Delta T = 5}$

$q = 4.5\times10^3$ J.

$S = \frac{q}{m(\Delta T)} = \frac{4.5\times10^3}{3\times5}$

$C_m = \frac{q}{n(\Delta T)} = \frac{4.5\times10^3}{1/9\times5}$

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Calculation of Work

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Work

❖ In Isochoric Process:

V = constant, dV = 0.

$$W = -\int P_{ex} \cdot dV$$

$$\boxed{W = 0}$$

1st law of thermo.

$$\Delta U = q + \underset{0}{\underset{\downarrow}{w}}$$

$$\boxed{\Delta U = q_v = nC_v(\Delta T)}$$

$$\Delta U = \frac{f}{2} nR(\Delta T)$$

$$C_v = \frac{f}{2} R$$

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Work

❖ **In Isobaric Process:**

$P = \text{Constant}, \; dP = 0$

$$W = -\int_{V_1}^{V_2} P_{ex} \cdot dV$$

$$\boxed{W = -P_{ex}\left[V_2 - V_1 \right]} \checkmark$$

for Reversible Process, $P_{ex} = P_{gas}$

$$W_{rev.} = -P_{gas}\left[V_2 - V_1 \right)$$

$$W_{rev.} = -\left[P_{gas} \cdot V_2 - P_{gas} V_1 \right]$$

$PV = nRT$

$$W_{rev.} = -\left[nRT_2 - nRT_1 \right)$$

$$\boxed{W_{rev.} = nR\left(T_1 - T_2 \right)}$$

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Question

Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal gas? (Assume non-expansion work is zero) **(2019 Main, 8 April 1)**

- **A** Cyclic process : $q = -W$ ✓
- **B** Adiabatic process : $\Delta U = -W$ ✓
- **C** Isochoric process : $\Delta U = q$ ✓
- **D** Isothermal process : $q = -W$ ✓

(a) $\Delta U = 0$

$\Delta U = q + w$

$q = -w$

(b) $q = 0$

$\Delta U = q + w$

$\Delta U = w$

(c) $V = K,\ w = 0$

$\Delta U = q + w$

$\Delta U = q$

(d) $\Delta T = 0,\ \Delta U = 0$

$\Delta U = q + w$

$q = -w$

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Work

❖ In Isothermal Reversible Process:

$$W_{rev.} = -\int P_{ex} \cdot dV$$

$$P_{ex} \simeq P_{in} \simeq P_{gas}.$$

$$W_{rev.} = -\int P_{gas} \cdot dV$$

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$$W_{rev.} = -\int \frac{nRT}{V} \cdot dV$$

$$W_{rev.} = -nRT \int_{V_1}^{V_2} \frac{1}{V} \cdot dV$$

$$\int \frac{1}{x} \cdot dx = \ln(x)$$

$$W_{rev.} = -nRT \left[\ln V\right]_{V_1}^{V_2}$$

$$W_{rev} = -nRT\left[\ln V_2 - \ln V_1\right]$$

$$\log m - \log n = \log \frac{m}{n}$$

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Work

❖ In Isothermal Reversible Process:

$$W_{rev.} = -nRT\ln\left(\frac{V_2}{V_1}\right)$$

$8.314\,J\,K^{-1}\,mol^{-1}.$

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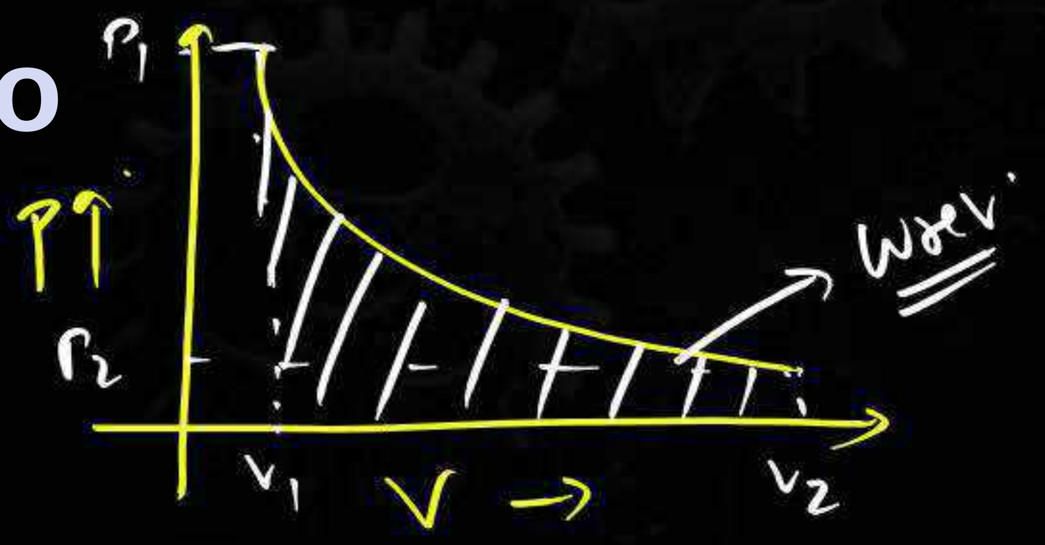
$$\boxed{W_{rev.} = -2.303\,nR\underset{\text{in kelvin.}}{T}\log_{10}\left(\frac{V_2}{V_1}\right)}\ J.$$

$T = \text{Constant},\ P \propto 1/V$

$$P_1V_1 = P_2V_2$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\boxed{W_{rev.} = -2.303\,nRT\log_{10}\left(\frac{P_1}{P_2}\right)}$$



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Work

At constant external pressure.

In Isothermal Irreversible Process: **

$$\boxed{W_{irr.} = -P_{ex}(V_2 - V_1)}$$

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$\boxed{W_{irr.} = -P_{ex}\left[\frac{nRT}{P_2} - \frac{nRT}{P_1}\right]}$$

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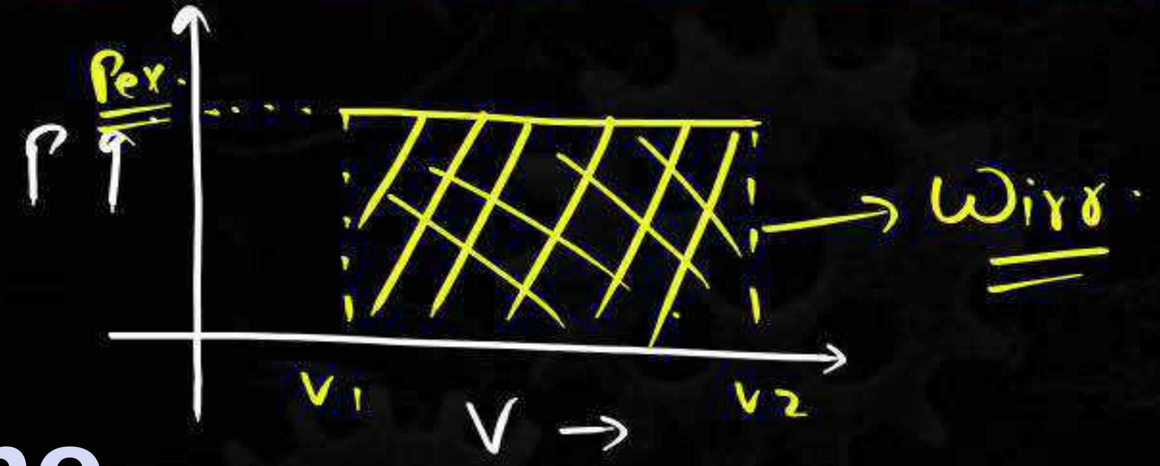

* Compression → $P_1 P_2$ में से जो ज्यादा → P_{ex}.

* Expansion → ______ जो कम → P_{ex}.

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Work

❖ In Isothermal Irreversible Process:

$W_{irr.} = -P_{ex}(V_2 - V_1)$

Compression, $V_2 < V_1$

$W = +ve$ (work done on the system)

Expansion, $V_2 > V_1$

$W = -ve.$ [work done by the system].

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Comparison of Work Done

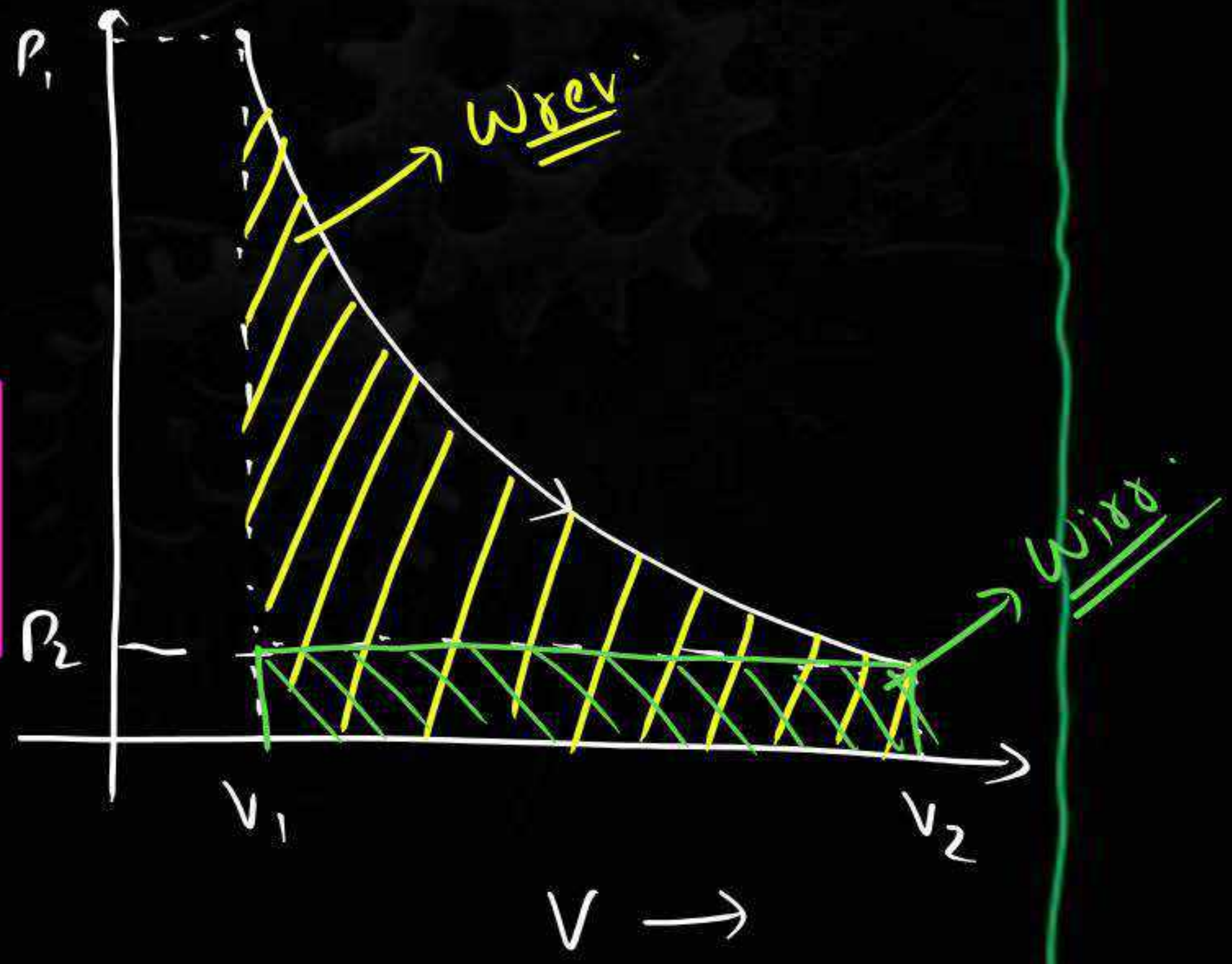
❖ In Isothermal Expansion:

$$W_{rev.} = -\int P_{ex} \cdot dV$$

$$W_{irr.} = -P_{ex}(V_2 - V_1)$$

$$= -P_2(V_2 - V_1)$$

$$\boxed{|W_{rev}| > |W_{irr}|}$$



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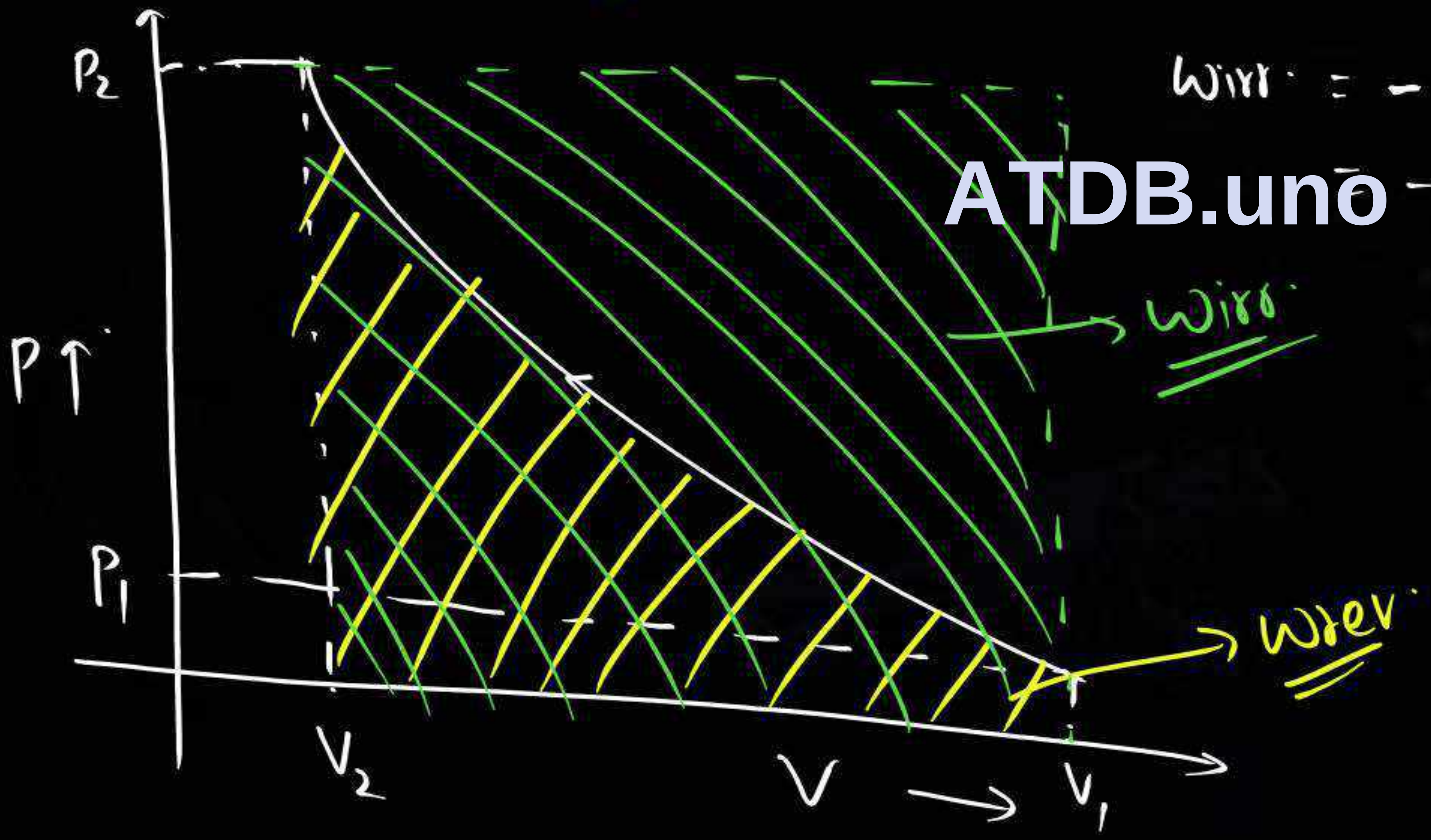
Comparison of Work Done

❖ In Isothermal Compression:



$$W_{rev.} = -\int P_{ex} \cdot dV$$

$$W_{irr.} = -P_{ex}(V_2 - V_1)$$

$$= -P_2(V_2 - V_1)$$

$$\boxed{W_{irr.} > W_{rev.}}$$

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Question

Calculate the amount of work done when 1 mol of an ideal gas is allowed to expand from 1 L to 5 L against a constant external pressure of 1 atm at 300 K.

irr. Process

Ans :->

$n = 1$

$V_1 = 1V$

$V_2 = 5L$

$W_{irr.} = -P_{ex}(V_2 - V_1)$

$= -1(5-1)$

$\Rightarrow -4$ atm-L

1 atm L $\Rightarrow$ 101.3 J.

$W_{irr.} = -4(101.3)$ J.

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Question

One mole of oxygen is allowed to expand isothermally and reversibly from 5 m^3 to 10 m^3 at 300 K. Calculate the work done in expansion of the gas.

<u>Ans</u> :→ $n = 1$.

$V_1 = 5$

$V_2 = 10$

$T = 300K$

$$W_{rev.} = -2.303\, nRT \log_{10}\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow -2.303 \times 1 \times 8.314 \times 300 \log\left(\frac{10}{5}\right) \ J.$$

$\rightarrow \log_{10} 2 \Rightarrow 0.3010$

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Question

The work done on the system when one mole of an ideal gas at 500 K is compressed isothermally and reversibly to $\frac{1}{10}$ th of its original volume (R = 2 cal)

A 500 kcal

B 15.1 kcal

C 25.03 kcal

[✓ D] 2.303 kcal

$T = 500\,K$

$V_2 = \frac{V_1}{10}$

$R \to 2\ cal\ K^{-1}\ mol^{-1}$

$W_{rev.} = -2.303\, nRT \log\left[\frac{V_2}{V_1}\right]$

$= -2.303 \times 1 \times 2 \times 500 \log\left(\frac{V_1}{10 \times \cancel{V_1}}\right)$

$\Rightarrow -2.303 \times 1000 \log\left(\frac{1}{10}\right) \to \log 1 - \log 10 \to 0 - 1$

$\Rightarrow 2.303 \times 1000$ cal

$\Rightarrow 2.303$ K·cal

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Work Done in Free Expansion

- Expansion of a gas in vacuum, is known as free expansion.

$P_{ex} = 0$

$w = -\int P_{ex} \cdot dv$

$\boxed{w = 0}$

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Work Done in Free Expansion

Isothermal Free Expansion:

$\Delta T = 0$

$\Delta U = nC_v\Delta T$

$\Delta U = 0$

$P_{ex} = 0$

$w = 0$

FLOT:→ $\underset{\substack{\downarrow \\ 0}}{\Delta U} = q + w$

$$\boxed{q = -w}$$

$$\boxed{q = 0}$$

~~$q = 2.303\, nRT \log\left(\frac{V_2}{V_1}\right)$~~

~~OR~~

~~$q = 2.303\, nRT \log\left(\frac{P_1}{P_2}\right)$~~

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Work Done in Free Expansion

Adiabatic Free Expansion:

$P_{ex} = 0 \Rightarrow w = 0$

$q = 0$

$\Delta U = q + w$

$\boxed{\Delta U = 0}$

$nC_v(\Delta T) = 0$

$\boxed{\Delta T = 0}$

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Question

Two litres of an ideal gas at a pressure of 10 atm expands isothermally into a vacuum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion ?

Ans :-> $P_{ex} = 0,\ w = 0.$

$\Delta T = 0,\ \Delta U = 0.$

$\underline{\Delta U} = q + \underline{w}$

$$\boxed{q = 0}$$

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Question

A gas is provided with 300 Joule heat at STP, so that its volume increases from 2 litre to 3 liter at 1 atm. Calculate the change in its internal internal energy.

Ans:→ $q = +300J$

$V_1 = 2L$

$V_2 = 3L$

$\Delta U = ?$

$\Delta U = \underline{q} + \boxed{\underline{w}}$

$w = -P_{ex}(V_2 - V_1)$ $\boxed{\underline{J}}$

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Question

ΔU is equal to

[✓ A] Adiabatic work

B Isothermal work

C Isochoric work

D Isobaric work.

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Question

When 5 moles of He gas expand isothermally and reversibly at 300 K from 10 litre to 20 litre, the magnitude of the maximum work obtained is______J. [Nearest integer] **(JEE Main 2022 (June) Shift -2)**

[Given: R = 8.3 J K^{-1} mol^{-1} and log 2 = 0.3010]

Ans :→ $n = 5$

$T = 300\ K$

$V_1 = 10\ L$

$V_2 = 20\ L$

$$W_{rev} = -2.303\, nRT \log\left(\frac{V_2}{V_1}\right)$$

$$= -2.303 \times 5 \times 8.314 \times 300 \log 2$$

→ 0.3010

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Ans. [8360]

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Question

4.0 L of an ideal gas is allowed to expand isothermally into vacuum until the total volume is 20 L. The amount of heat absorbed in this expansion is____________ L atm. (JEE Main 2022 (June) Shift -1)

HW

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Ans. [0]

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Question

An ideal gas is allowed to expand from 1 L to 10 L against a constant external pressure of 1 bar. The work done in kJ is (2019 Main, 12 April 1)

A – 9.0

B + 10.0

HW

C – 0.9

D – 2.0

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Question

An ideal gas undergoes isothermal compression from 5 m^3 to 1 m^3 against a constant external pressure of 4 Nm^{-2}. Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is 24 J $mol^{-1}K^{-1}$, the temperature of Al increases by (2019 Main, 10 Jan II)

(A) $\frac{3}{2}$ K

(B) 1 K

(C) 2 K

(D) $\frac{2}{3}$ K ✓

$V_1 = 5 m^3$

$V_2 = 1 m^3$

$P_{ext} = 4 N/m^2$

$\Delta U = 0$

$\boxed{q = -w}$

$W_{irr.} = -P_{ex}(V_2 - V_1)$

$W_{irr} = -4(4) = +16 J$

$\boxed{q = -16 J}$

$n = 1$

$C_m = 24 J mol^{-1} K^{-1}$

$\Delta T = ?$

$q = n C_m (\Delta T)$

$16 = 1 \times 24 (\Delta T)$

$\Delta T = \frac{16}{24} \Rightarrow 2/3$

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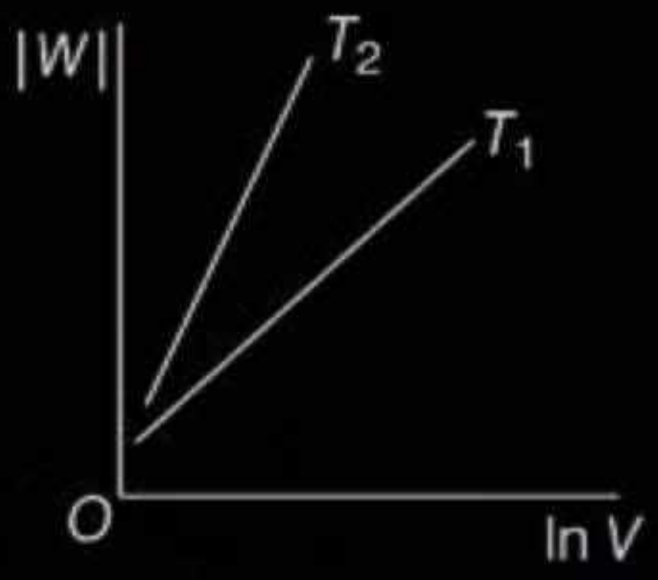
Question

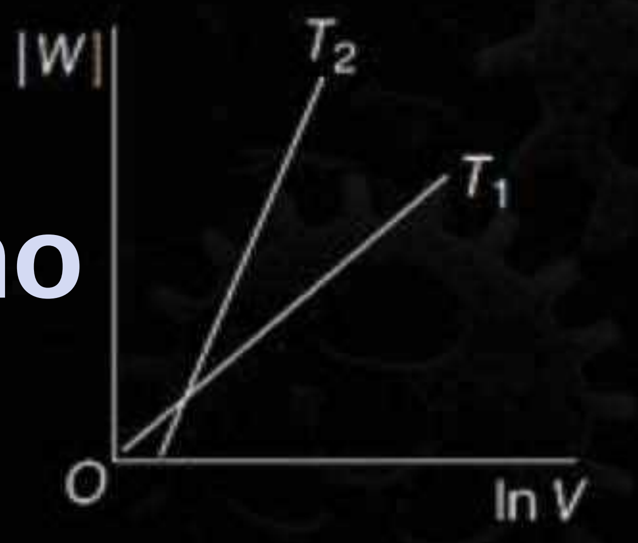
Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperatures T_1 and T_2 ($T_1 < T_2$). The correct graphical depiction of the dependence of work done (W) on the final volume (V) is (2019 Main, 9 Jan 1)

HW

A



B



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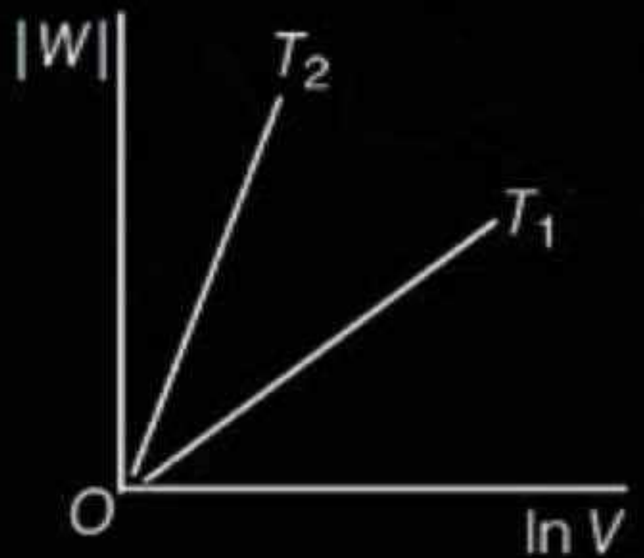
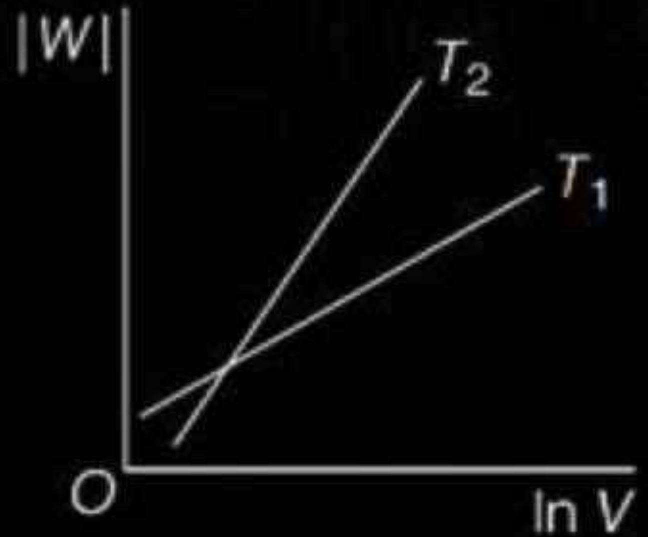
C



D



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Poisson's Ratio (γ)

- It gives the idea about the atomicity of a gas.

$$\boxed{\gamma = \frac{C_p}{C_v}}$$

$$C_p - C_v = R$$

$$C_p = R + C_v \Rightarrow R + \frac{f}{2}R$$

- $C_v = f/2R$

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Poisson's Ratio

① for monoatomic gas :->

$f = 3$

$C_V = \frac{3}{2}R$, $C_P = \frac{5}{2}R$

$\gamma = \frac{C_P}{C_V} = \frac{5}{3}$

$\boxed{\gamma = 1.66}$ **

② for Diatomic gas :-> and linear polyatomic Gas

$f = 5$

$C_V = \frac{5}{2}R$, $C_P = \frac{7}{2}R$

$\gamma = \frac{C_P}{C_V} = \frac{7}{5}$

$\boxed{\gamma = 1.4}$ **

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Poisson's Ratio

③ for Non-linear polyatomic Gas :->

$f = 6$

$C_v = 3R, \quad C_p = 4R$

$\gamma = \frac{C_p}{C_v} = 4/3$

$\boxed{\gamma = 1.33}$ **

$\underline{\gamma > 1}$ **

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Work Done in Adiabatic Reversible Process

$$\underline{q = 0}$$

$$dU = dq + dw$$

$$dw = dU$$

$$dw = nC_v dT$$

$$\boxed{w = nC_v[T_2 - T_1]}$$

$$C_v = \frac{R}{\gamma - 1}$$

$$\boxed{w = \frac{nR}{\gamma - 1}[T_2 - T_1]}$$

$$\underline{W_{r}} = nC_v(T_2 - T_1) = \frac{nR}{\gamma - 1}[T_2 - T_1]$$

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Work Done in Adiabatic Reversible Process

for Reversible adiabatic Process :→

$$\boxed{\begin{array}{c} PV^{\gamma} = K \\ TV^{\gamma-1} = K \\ P^{1-\gamma}T^{\gamma} = K \end{array}}$$

$[P_1V_1^{\gamma} = P_2V_2^{\gamma})$

$[T_1V_1^{\gamma-1} = \underline{T_2}V_2^{\gamma-1}]$

$[P_1^{1-\gamma}T_1^{\gamma} = P_2^{1-\gamma}T_2^{\gamma}]$.

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Work Done in Adiabatic Irreversible Process

$$W_{irr.} = -P_{ex}[V_2 - V_1]$$

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$\boxed{W_{irr.} = -\underline{P_{ex}}\left[\frac{nRT_2'}{P_2} - \frac{nRT_1}{P_1}\right]}$$

$$nC_v(T_2' - T_1) = -P_{ex}\left[\frac{nRT_2'}{P_2} - \frac{nRT_1}{P_1}\right]$$

$$W_{irr} = \underline{nC_v(T_2' - T_1)}$$

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Note

→ work done by the system.

For Adiabatic Expansion (Both reversible and irreversible)

W < 0

$nC_v(T_2 - T_1) < 0$

$(T_2 - T_1) < 0$

$\boxed{T_2 < T_1}$

temp. decreases

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Note

For Adiabatic Compression (Both reversible and irreversible)

Temp increases **

W > 0

$$nC_v(T_2 - T_1) > 0$$

$$(T_2 - T_1) > 0$$

$$\boxed{T_2 > T_1}^{*}$$

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Question

A monoatomic gas undergoes adiabatic process. Its volume and temperature are related as TV^P = constant. The value of p will be

- A 133
- B 1.67
- [✓ C] 0.67
- D 0.33

$\gamma = 1.6.$

$TV^P = \text{Constant}.$

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

$P = \gamma - 1$

$= 1.67 - 1$

$\boxed{P = 0.67}$

Ans. 0.67

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Question

An ideal gas with pressure P, volume V and temperature T is expanded isothermally to a volume 2V and final pressure P_1. If the same gas is expanded adiabatically to a volume 2V, the final pressure is P_2. The ratio of specific heat for the gas is 1.67. Calculate the value of ratio $\frac{P_2}{P_1}$.

(γ)

Ans :→ Isothermal.

$P_1V_1 = P_2V_2$

$PV = P_1(2V)$

$P_1 = P/2$

Adiabatic.

$PV^{\gamma} =$ [illegible]

$P_1V_1^{\gamma} = P_2V_2^{\gamma}$

$PV^{\gamma} = P_2[2V]^{\gamma}$

$P_2 = \frac{P}{2^{\gamma}}$

$$\frac{P_2}{P_1} = \frac{\cancel{P}}{2^{\gamma} \times \cancel{P}} \times 2 \Rightarrow \frac{2}{2^{\gamma}}$$

$$\Rightarrow 2^{1-\gamma}$$

$$\Rightarrow 2^{1-1.67}$$

$$\Rightarrow 2^{-0.67} \Rightarrow \boxed{\frac{1}{2^{0.67}}}$$

Ans.

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Question

Two moles of an ideal monoatomic gases are allowed to expand adiabatically and reversibly from 300 K and 200 K. The work done in the system is (C_V – 12.5 J/K/mole).

- **A** –12.5 kJ
- **B** –2.5 kJ
- **C** –625 kJ
- **D** 500 kJ

$n = 2$

$T_1 = 300$

$T_2 = 200\,K$

$C_V = \underline{12.5}$.

$W_{rev.} = nC_V(T_2 - T_1)$.

Ans

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Ans. –12.5 kJ

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Question

One mole of ideal gas is allowed to expand reversibly and adiabatically from a temperature of 27°C. If the work done during the process is 3 kJ. The final temperature will be equal to ($C_V = 20\ JK^{-1}$)

(A) 150 K

(B) 100 K

(C) 26.85 K

(D) 295 K

$n = 1$

$T_1 = 27^\circ C = 300\ K.$

$W = -3\ KJ \Rightarrow -3000\ J$

$T_2 = ?$

$C_V = 20.$

$W = nC_V(T_2 - T_1)$

$-300\cancel{0} = 1 \times 2\cancel{0}[T_2 - 300]$

$-150 = T_2 - 300$

$\boxed{T_2 = 150\ K}$

Ans. A

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Question

5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K. If $C_V = 28\ JK^{-1}\ mol^{-1}$, calculate AU and ΔpV for this process. ($R = 8.0\ JK^{-1}\ mol^{-1}$).

(2019 Main, 8 April II)

A $\Delta U = 2.8$ kJ; $\Delta(pV) = 0.8$ kJ

B $\Delta U = 14$ J; $\Delta(pV) = 0.8$ J

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C $\Delta U = 14$ kJ; $\Delta(pV) = 4$ kJ

HW

D $\Delta U = 14$ kJ; $A(pV) = 18$ kJ

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Question

One mole of monoatomic ideal gas expands adiabatically at initial temperature T against a constant external pressure of 1 atm from 1 to 2 L. Find out the final temperature

($R = 0.0821$ L atm K^{-1} mol^{-1}). (2005, 1M)

A) T

B) $\frac{T}{(2)^{5/3-1}}$

C) $T - \frac{2}{3 \times 0.082}$

D) $T + \frac{2}{3 \times 0.082}$

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HW

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Enthalpy (H)

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Enthalpy (H).

→ Extensive Property.

→ State function.

$\boxed{\Delta H = q_p}$ → Heat absorbed or released by the system at Constant Pressure.

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$\boxed{\Delta H = n\underline{C_p}(\Delta T)}$

↓

Molar heat capacity at constant P.

$\underline{q_p} = \underline{\Delta H}$.

$\underline{q_v} = \underline{\Delta U}$

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Enthalpy

$$\boxed{\Delta H = \Delta U + P(\Delta V)}$$

$$PV = nRT$$

$$P\Delta V = \Delta n_g RT$$

$$\boxed{\Delta H = \Delta U + \Delta n_g RT}$$

$$q_p = q_v + \Delta n_g RT$$

$$\Delta n_g = \begin{bmatrix} \text{No. of gases moles} \\ \text{of Products} \end{bmatrix} - \begin{bmatrix} \text{No. of gaseous moles} \\ \text{of Reactants} \end{bmatrix}$$

Ex:- $PCl_{5(g)} \rightarrow PCl_{3(g)} + Cl_{2(g)}$ $\quad \Delta n_g = 1$

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$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

$\Delta n_g = 1 - 0 \Rightarrow 1$

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Question

If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1 bar and 100°C is 41 kJ mol^{-1}. Calculate the internal energy change, when

(i) 1 mol of water is vaporised at 1 bar pressure and 100°C.

Ans :> $\Delta H = 41 \times 10^3$ J/mol. | $T = 100^\circ C = 373\ K$)

$H_2O(l) \longrightarrow H_2O(g)$ $[\Delta n_g = 1 - 0 = 1]$

$\Delta U = ?$

$\Delta H = \Delta U + \Delta n_g RT$

$41 \times 10^3 = \Delta U + 1 \times 8.314 \times 373$

$\Delta U = ?$

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Question

For the combustion reaction at 298 K

$$2Ag(s) + O_2(g) \rightarrow 2Ag_2O(s)$$

Which of the following relation will be true?

A $\Delta H = \Delta E$

B $\Delta H > \Delta E$

[✓ C $\Delta H < \Delta E$]

D ΔH and ΔE bear no relationship with each other

$\Delta n_g = 1 - 1 \Rightarrow -1.$

$\Delta H = \Delta U + \Delta n_g RT$

$\underline{\Delta H} = \Delta U - RT$

$\boxed{\underline{\Delta U} > \Delta H}$

Ans. C

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Question

For the reaction,
$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4\cancel{H_2}O(l)$ at constant temperature, $\Delta H - \Delta E$ is

$\Delta H - \Delta U = ?$

A −RT

B RT

[✓ C] −3RT

D +3RT

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta H - \Delta U = \Delta n_g RT$$

$$\Delta n_g = 3 - 6 \Rightarrow -3$$

$$\Delta H - \Delta U = -3RT$$

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Question

One mole of carbon undergoes incomplete combustion to produce carbon monoxide. Calculate $(\Delta H - \Delta U)$ for the formation of CO at 298 K. Given $R = 8.314\ JK^{-1}\ mol^{-1}$.

Ans :⇒ $C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}$

$\Delta n_g = 1 - \frac{1}{2} = 0.5$

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$\Delta H - \Delta U = \Delta n_g RT$

$\Rightarrow 0.5 \times 8.314 \times 298$

Ans

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Question

A fish swimming in water body when taken out from the water body is covered with a film of water of weight 36 g. When it is subjected to cooking at 100°C, then the internal energy for vaporization in kJ mol^{-1} is ________. [nearest integer]

[Assume steam to be an ideal gas. Given $A_{vap}H^{\ominus}$ for water at 373 K and 1 bar is 41.1 kJ mol^{-1}; R = 8.31 JK^{-1} mol^{-1}] (JEE Main 2022 (June) Shift -2)

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HW

Ans. [38]

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Question

The difference between ΔH and ΔU ($\Delta H - AU$), when the combustion of one mole of heptane (l) is carried out at a temperature T, is equal to

(2019 Main, 10 April II)

A $-4\ RT$

B $3\ RT$

C $4\ RT$

D $-3\ RT$

HW

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Question

For silver, $C_p(JK^{-1}\ mol^{-1}) = 23 + 0.01\ T$. If the temperature (T) of 3 moles of silver is raised from 300 K to 1000 K at 1 atm pressure, the value of AH will be close to (2019 Main, 8 April 1)

A 62 kJ

B 16 kJ

C 21 kJ

D 13 kJ

HW

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Question

The combustion of benzene (l) gives $CO_2(g)$ and $H_2O(l)$. Given that heat of combustion of benzene at constant volume is -3263.9 kJ mol^{-1} at 25°C; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be ($R = 8.314$ $JK^{-1}mol^{-1}$) (2018 Main)

- **A** 4152.6
- **B** –452.46
- **C** 3260
- **D** –3267.6

$$C_6H_{6(l)} + \frac{15}{2}O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)}$$

$$T = 25^\circ C = 298\ K$$

$$\Delta n_g = 6 - \frac{15}{2} = \frac{12-15}{2} = -3/2.$$

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$$q_v = \Delta U = -3263.9 \times 10^3\ J.$$

$$q_P = \Delta H = ?.$$

$$\Delta H = \Delta U + \Delta n_g RT$$

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Measurement Of ΔU and ΔH: CALORIMETRY

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- Practical measurement of heat change in a chemical or physical change , is known as calorimetry.
- Measurements are done in an apparatus called calorimeter.
- Measurements can be made under two conditions :

  (a) At constant volume ✓ $q_v = \Delta U$
  (b) At constant Pressure ✓ $\rightarrow$ $q_p = \Delta H$

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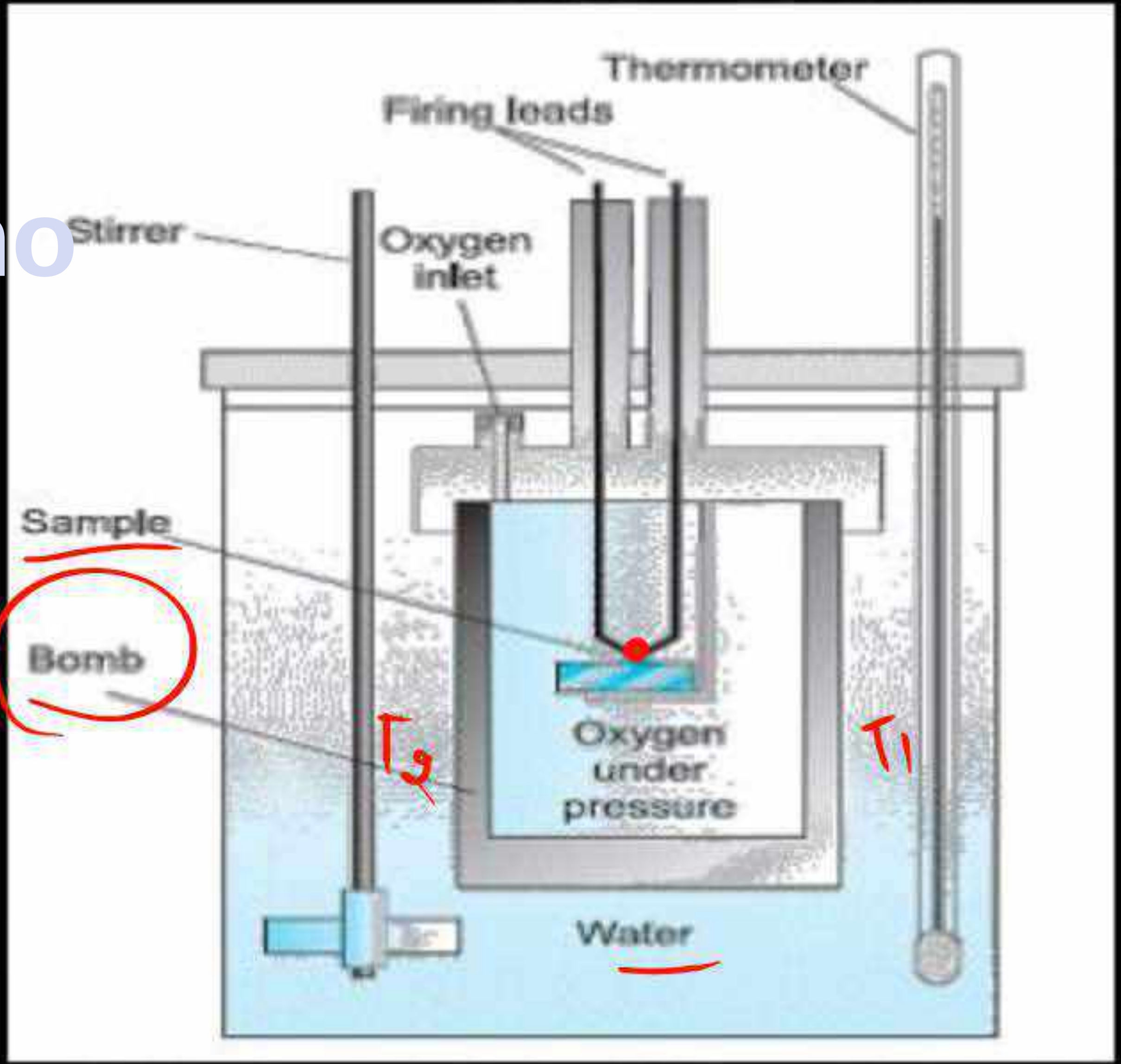
Measurement of ΔU

$q_{comb} = -[q_{water} + q_{bomb}]$

- For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter. → Constant volume calorimeter.



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Change in temp (ΔT) = $T_2 - T_1$

$q_{comb} = -[q(bomb)]$

$q_v = q_{comb} = -[C_{bomb}\Delta T]$

$$\boxed{\Delta U = -[C_{bomb}\Delta T]}$$

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Measurement of ΔH

$$\boxed{\Delta H = q_p}$$

$$= nC_p(\Delta T).$$

$\downarrow$

Heat capacity at Constant Pressure.

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Question

1g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation

$C\,(graphite) + O_2\,(g) \rightarrow CO_2\,(g)$ $\Delta n_g = 1 - 1 \Rightarrow 0$

During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm? $\Delta H = ?$

Ans:→ $\Delta T = 299 - 298 \Rightarrow 1$

$C = 20.7 \times 10^3\ J/K$

$\Delta U = -C(\Delta T)$

$\Delta U = -20.7 \times 10^3\ J$

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta H = \Delta U$ Ans

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Question

For complete combustion of methanol (JEE Main 2022 (June) Shift -1)

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$\Delta n_g = 1 - 3/2 \Rightarrow -0.5$

the amount of heat produced as measured by bomb calorimeter is 726 kJ mol^{-1} at 27°C. The enthalpy of combustion for the reaction is $-x$ kJ mol^{-1}, where x is ________. (Nearest integer)

(Given: $R = 8.3\ JK^{-1}\ mol^{-1}$)

$\Delta H = ?$

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Ans :→ $\Delta U = -726 \times 10^3\ J$

$T = 300\ K$

$\Delta H = \Delta U + \Delta n_g RT$

Ans. [727]

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Enthalpy of Rx^n or heat of Rx^n.

Enthalpy Change of a Reaction ($\Delta_r H$)

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Enthalpy of Reaction

- The enthalpy change accompanying a reaction is called the reaction enthalpy.
- The enthalpy change of a chemical reaction, is given by the symbol $\Delta_r H$

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$A \longrightarrow B$, $\Delta H = ?$

$\Delta_r H = (H)_B - (H)_A$

$\Delta H = +ve$ [Endothermic Rx^n]
(Heat absorbing Rx^n)

$\Delta H = -ve$ [Exothermic Rx^n]
(Heat releasing Rx^n)

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Enthalpy of Reaction

$\Delta_r H$ = (sum of enthalpies of products) – (sum of enthalpies of reactants)

$$\Delta_r H = \sum b_i (H)_{\text{Products}} - \sum a_i (H)_{\text{Reactants}}.$$

a_i and b_i are the stoichiometric coefficient of R. and P resp.

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Ex :→ $CH_4(g) + 2O_2(g) \longrightarrow 1\,CO_2(g) + 2H_2O(l)$, $\Delta_r H = ?$

$$\Delta_r H = \left[1\times H(CO_2,g) + 2\times H(H_2O,l)\right] - \left[1\times H(CH_4,g) + 2\times H(O_2,g)\right]$$

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Thermochemical Equation

- A balanced chemical equation together with the value of its $\Delta_r H$ is called a thermochemical equation.

- We specify the physical state (along with allotropic state) of the substance in an equation.

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$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \ , \ \Delta H = -x \ kJ/mol.$$

Balanced chemical eq.

$$\underset{(graphite,s)}{C} + \underset{(g)}{O_2} \longrightarrow CO_2(g) \ , \ \Delta H = -y \ kJ/mol$$

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Thermochemical Equation

Note: $A_{(g)} + B_{(g)} \longrightarrow C_{(g)}$, $\Delta H = x$ KJ/mol.

* $C_{(g)} \longrightarrow A_{(g)} + B_{(g)}$, $\Delta H = -x$ KJ/mol.

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* $2A_{(g)} + 2B_{(g)} \longrightarrow 2C_{(g)}$, $\Delta H = 2x$ KJ/mol

$\frac{1}{2}A_{(g)} + \frac{1}{2}B_{(g)} \longrightarrow \frac{1}{2}C_{(g)}$, $\Delta H = x/2$ KJ/mol.

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Hess's Law

" If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature."

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Hess's Law

$$\begin{tikzcd}
A \arrow[r, "\Delta H"] \arrow[d, "\Delta H_1"] & D \\
B \arrow[r, "\Delta H_2"] & C \arrow[u, "\Delta H_3"]
\end{tikzcd}$$

$$\boxed{\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3}$$

$A \rightarrow \cancel{B}, \quad \Delta H_1$

$\cancel{B} \rightarrow \cancel{C}, \quad \Delta H_2$

$\cancel{C} \rightarrow D, \quad \Delta H_3$

$A \rightarrow D, \quad \Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H$

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Ex :> $C(s) + \frac{1}{2}O_2(g) \longrightarrow \cancel{CO}(g), \; \Delta H = x \text{ kJ/mol.}$

$\cancel{CO}(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g), \; \Delta H = y \text{ kJ/mol.}$

$C(s) + O_2(g) \longrightarrow CO_2(g), \; \Delta H = ? \;\; x + y$ Ans

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Standard Enthalpy of Reaction

The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.

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The standard state of a substance at a specified temperature is its pure form at 1 bar.

$H_2(g)$
$O_2(g)$
$Br_2(l)$
$I_2(s)$
$N_2(g)$

$Na(s)$
$Al(s)$
$C(graphite, s)$

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Enthalpy changes during phase transformations

1. Molar Enthalpy of Fusion: [$s \rightarrow L$]

$H_2O(s) \longrightarrow H_2O(l)$

$\Delta_r H^0 = \Delta_{fus} H^0 (H_2O, s)$.

The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion, $\Delta_{fus}H^0$

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Enthalpy changes during phase transformations

2. Molar Enthalpy of Vaporisation: [L → G]

Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1bar) is called its standard enthalpy of vaporization or molar enthalpy of vaporization, $\Delta_{vap}H^{o}$.

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$$H_2O(l) \longrightarrow H_2O(g), \quad \Delta_r H^{\circ} = \Delta_{vap}H^{\circ}_{(H_2O, l)}.$$

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Enthalpy changes during phase transformations

3. Molar Enthalpy of Sublimation:

Standard enthalpy of sublimation, $\Delta_{sub}H^o$ is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1bar).

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solid $\longrightarrow$ Gas. , $\Delta_r H^\circ = \underline{\Delta_{sub} H^\circ}$

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NOTE - The magnitude of the enthalpy change depends on the strength of the intermolecular interactions in the substance undergoing the phase transformations.

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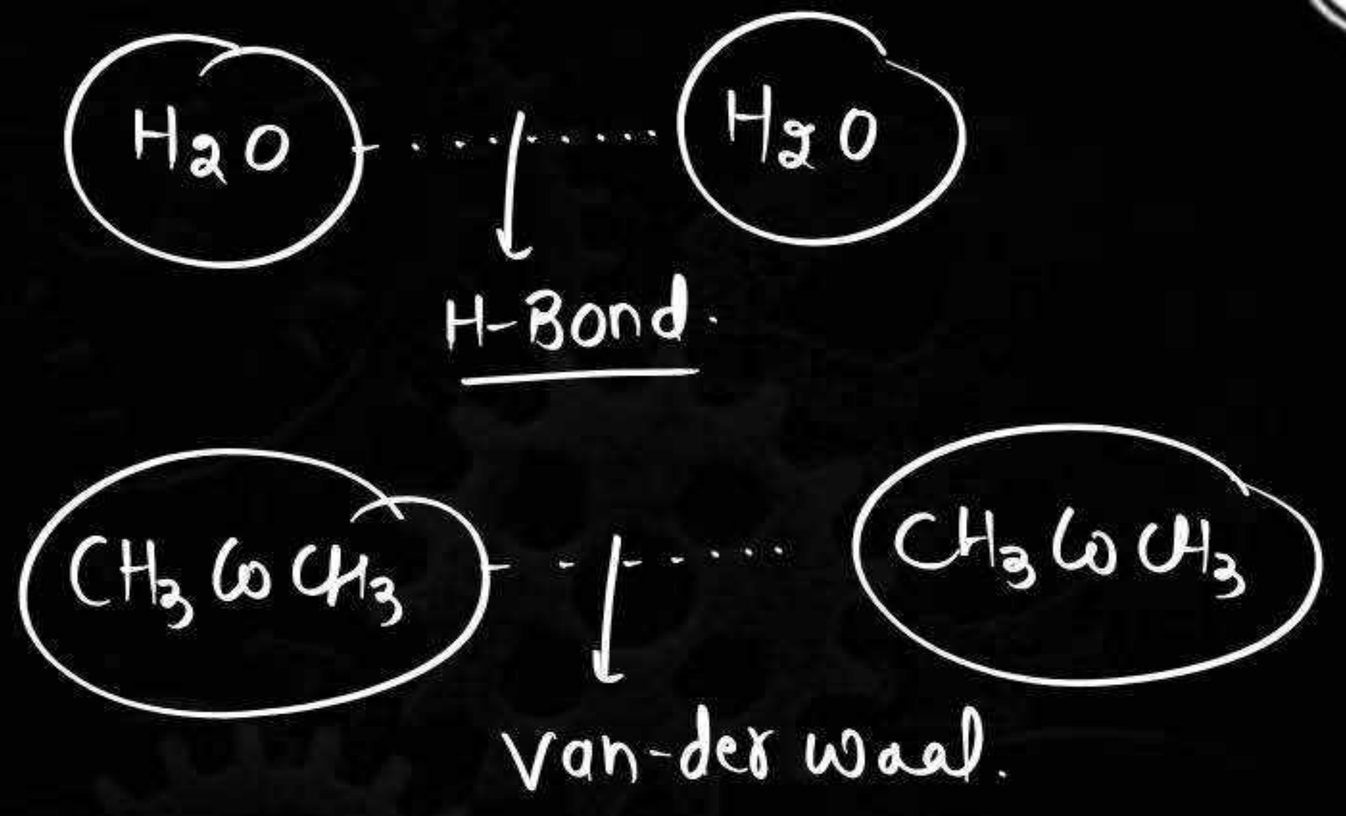

Strength → H-Bond > van-der waal.

$$* \quad \Delta_{vap}H^{0}_{(H_2O)} > \Delta_{vap}H^{0}_{(Acetone)}$$

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Question

A swimmer coming out from a pool is covered with a film of water weighing about 18 g. Calculate the internal energy of vaporisation at 100°C.

$\Delta_{vap}H^0$ for water at 373K = 40.66 kJ mol^{-1}

Ans :-> $w_{H_2O} = 1g.$ | $T = 100^\circ C = 373K.$

$n_{H_2O} = 1 mol$

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$H_2O(l) \longrightarrow H_2O(g)$, $\Delta vapH^0 = 40.66 \times 10^3$ J/mol

$\to \Delta n_g = 1$

$\Delta U = ?$

$$\underline{\Delta H} = \underset{?}{\underline{\Delta U}} + \underline{\Delta n_g} \underset{8.314}{R} \overset{}{T} \to 373.$$

$\underline{\Delta U = ?}$

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Question

90 g of water spilled out from a vessel in the room on the floor. Assuming that water vapour behaving as an ideal gas, calculate the internal energy change when the spilled water undergoes complete evaporation at 100ºC. (Given the molar enthalpy of vaporization of water at 1 bar and 373 K = 41 kJ mol^{-1})

$\Delta H = 5 \times 41$ kJ.

Ans :- $n_{H_2O} = 5$ mol.

HW

$H_2O(l) \rightarrow H_2O(g)$.

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Standard Enthalpy of Formation

$[\underline{\Delta_f H^\circ}]$

defn

The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation.

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Standard Enthalpy of Formation

Ex. $H_{2(g)} + \frac{1}{\ }O_{2(g)} \longrightarrow H_2O(l)$, $\Delta_r H^\circ = \Delta_f H^\circ(H_2O, l)$.

$C_{(graphite,s)} + O_{2(g)} \longrightarrow CO_2(g)$, $\Delta_r H^\circ = \Delta_f H^\circ(CO_2, g)$.

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$2C_{(graphite,s)} + 3H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow C_2H_5OH(l)$, $\Delta_r H^\circ = \Delta_f H^\circ(C_2H_5OH, l)$

$\frac{1}{2}H_{2(g)} + \frac{1}{2}Br_{2(l)} \longrightarrow HBr_{(g)}$, $\Delta_r H^\circ = \Delta_f H^\circ(HBr, g)$.

$CaO_{(s)} + CO_{2(g)} \longrightarrow CaCO_{3(s)}$ ✗

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Standard Enthalpy of Formation

①

Note:

$$\boxed{\underbrace{\Delta_r H^\circ}_{\text{Standard enthalpy of Rx}^n} = \sum b_i \, \Delta_f H^\circ_{(\text{Products})} - \sum a_i \, \Delta_f H^\circ_{(\text{Reactants})}}$$

$a_i, b_i \rightarrow$ stoichiometric coeff.

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② $\Delta_f H^\circ$ of Elements in their standard state is taken zero.

$$\Delta_f H^\circ(H_2, g) = 0$$

$$\underline{\Delta_f H^\circ(N_2, g) = 0.}$$

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Question

Enthalpies of formation of CO(g), CO_2 (g), N_2O(g) and N_2O_4 (g) are –110, –393, 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction:

$$N_2O_{4(g)} + 3CO_{(g)} \rightarrow N_2O_{(g)} + 3CO_{2(g)}$$

Ans :→ $\Delta_r H^0 = \left[1\times \Delta_f H^0(N_2O,g) + 3\times \Delta_f H^0(CO_2,g)\right] - \left[1\times \Delta_f H^0(N_2O_4,g) + 3\times \Delta_f H^0(CO,g)\right]$

$\Delta_r H^0 = ?$ (Ans).

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Question

Calculate the enthalpy change where the standard heat of formation for gaseous NH_3 is –11.02 kcal/mol at 298 K. The reaction given is

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$$

Ans :→

$$\Delta_r H^0 = \left[\Delta_f H^0(NH_3)\right] - \left[\frac{1}{2} \times \Delta_f H^0(N_2, g) + \frac{3}{2} \cdot \Delta_f H^0(H_2, g)\right]$$

$$= -11.02 - \left[\frac{1}{2} \times 0 + \frac{3}{2} \times 0\right]$$

$$\boxed{\Delta_r H^0 = -11.02 \text{ K cal/mol}}$$

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Question

The standard heats of formation of at 298 K for $CCl_4(g)$, $H_2O(g)$, $CO_2(g)$ and $HCl(g)$ are –25.5, –57.8, –94.1 and –22.1 kcal mol^{-1} respectively. Calculate $\Delta_r H^\ominus$ for the reaction

$$CCl_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4HCl(g)$$

HW

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Question

The values of heat of formation of SO_2 and SO_3 are –398.2 kJ and –198.2 kJ. The heat of this reaction will be

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$

(A) –200 kJ

HW

(B) –356.2 kJ

(C) +200 kJ

(D) –396.2 kJ

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Ans. C

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Standard Enthalpy of Combustion ($\Delta_c H^0$).

Standard enthalpy of combustion is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the reactants and products being in their standard states at the specified temperature.

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$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)\ ,\ \underbrace{\Delta_r H^0 = \Delta_c H^0_{(CH_4,g)}}$$

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Standard Enthalpy of Combustion

$\Delta_c H^0 (C_6H_{12}O_6) = -\underline{300}$ KJ/mol.

1 mol Glucose → 300 KJ

180 g. Glucose → 300 KJ.

1 g. Glucose → $\frac{300}{180}$ KJ → Calorific value.

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Calorific Value – It may be defined as the heat produced when 1 gram of the substance is completely burnt in excess of oxygen.

$$* \quad \Delta_r H^0 = \sum a_i (\Delta_c H^0)_{Reactants} - \sum b_i \Delta_c H^0 (Products).$$

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Question

Enthalpy of combustion of carbon to CO_2 is -393.5 kJ mol^{-1}. Calculate the heat released upon formation of $\underline{35.2 \text{ g of } CO_2}$ from carbon and dioxygen gas.

Ans :→ $C_{(s)} + O_{2(g)} \longrightarrow \underset{(1 mol).}{CO_{2(g)}}$, $\Delta H = -393 \cdot KJ/mol$.

$1 mol\ CO_2 \longrightarrow 393.5 KJ/mol.$

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$\therefore 44g.\ CO_2 \longrightarrow 393.5\ KJ.$

$\therefore \underbrace{35.2g.\ CO_2} \longrightarrow \left[\frac{393.5}{44} \times 35.2\right] KJ.$

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Question

If 150 kJ of energy is needed for muscular work to walk a distance of one km, then how much of glucose one has to consume to walk a distance of 5 km. Provided only 30% energy is available for muscular work. The enthalpy of combustion of glucose is 3000 kJ mol^{-1}.

Ans :⇒ ∵ 1 km → 150 KJ.

∴ 5 km → 150×5 → $\boxed{750\ KJ}$

1 mol Glucose → 3000 KJ

180 g. Glucose → 3000 KJ.

Total Energy available → $30\cancel{00} \times \frac{30}{1\cancel{00}} \Rightarrow 900$ KJ.

∵ 900 KJ Energy → 180 g. Glucose

∴ 750 KJ Energy → $\frac{18\cancel{0}}{9\cancel{00}} \times 750$

5

→ $\boxed{150\ g}$ Glucose.

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Question

An athlete is given 180 g of glucose ($C_6H_{12}O_6$). He utilizes 50% of the energy due to internal combustion in the body. In order to avoid storage of energy in the body, calculate the mass of water he would need to perspire. Given enthalpy of combustion of glucose is -2800 kJ mol^{-1} and enthalpy of evaporation of water is 44 kJ mol^{-1}.

HW

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Ans. 572.73 g

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Question

A gobar gas plant produces methane and supplies to the families. If a family requires 15,000 kJ of energy per day, how many days will the quota of 10 kg will last? ($\Delta_C H$ of $CH_4 = -1665$ kJ mol^{-1}).

Hw

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Ans. 69.37

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Question

The Enthalpies of combustion of carbon and carbon monoxide are –390 kJ and –278 kJ respectively. The enthalpy of formation of carbon monoxide is

(A) 669 kJ

(B) 112 kJ

[✓ (C) –112 kJ]

(D) –668 kJ

$\boxed{C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}, \; \Delta_r H = ?}$ ✓

✓ $C_{(s)} + O_{2(g)} \longrightarrow \cancel{CO_2}_{(g)}, \; \Delta H_1 = -390\ kJ.$

$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}, \; \Delta H_2 = -278\ kJ.$

$\cancel{CO_2}_{(g)} \longrightarrow CO_{(g)} + \frac{1}{2}O_{2(g)}, \; \Delta H_2 = +278\ kJ.$

$+$

$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}, \; \Delta H = \underbrace{-390+278}.$

Ans. C

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Question

At 25°C and 1 atm pressure, the enthalpy of combustion of benzene (l) and acetylene (g) are –3268 kJ mol^{-1} and –1300 kJ mol^{-1}, respectively. The change in enthalpy for the reaction $\boxed{3C_2H_2(g) \rightarrow C_6H_6(l), \text{ is}}$, $\Delta H = ?$

(JEE Main 2022 (June) Shift -2)

A +324 kJ mol^{-1}

B +632 kJ mol^{-1}

C –632 kJ mol^{-1}

D –732 kJ mol^{-1}

$$\Delta_r H^\circ = \sum a_i (H_c)_R - \sum b_i (H_c)_P .$$

$$\Delta_r H^\circ = 3 \times \Delta_c H^\circ (C_2H_2, g) - 1 \times \Delta_c H^\circ (C_6H_6, l).$$

$$= 3 \times (-1300) - [-3268].$$

$$\Delta_r H^\circ = \boxed{\text{Ans}}$$

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Question

For combustion of one mole of magnesium in an open container at 300 K and 1 bar pressure, $\Delta_C H^\ominus = -601.70$ kJ mol^{-1}, the magnitude of change in internal energy for the reaction is ________ kJ. (Nearest integer)

(JEE Main 2022 (June) Shift -2)

(Given: $R = 8.3\ \text{J K}^{-1}\text{mol}^{-1}$)

H/W

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Ans. [600]

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Question

The heat of combustion of enthanol into carbon dioxids and water is –327 kcal at constant pressure. The heat evolved (in cal) at constant volume and 27°C (if all gases behave ideally) is ($R = 2\ \text{cal mol}^{-1}\text{K}^{-1}$)________. (JEE Main 2020 (Sep.) Shift -2)

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HW

Ans. [–326400]

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Question

The standard heat of formation ($\Delta_f H_{298}^0$) of ethane (in kJ/mol), if the heat of combustion of ethane, hydrogen and graphite are –1560, –393.5 and –286 kJ/mol, respectively is______________. (JEE Main 2020 (Jan.) Shift -2)

HW

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Ans. [–192.5]

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Standard Enthalpy of Atomization $(\Delta_a H^{\circ})$.

It may be defined as the enthalpy change during the conversion of 1 mol of molecule or element into gaseous atoms.

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$H_2(g) \longrightarrow 2H(g)$, $\Delta_r H^{\circ} = \Delta_a H^{\circ}(H_2, g)$

$N_2(g) \longrightarrow 2N(g)$, $\Delta_r H^{\circ} = \Delta_a H^{\circ}(N_2, g)$

$CH_4(g) \longrightarrow C(g) + 4H(g)$, $\Delta_r H^{\circ} = \Delta_a H^{\circ}(CH_4, g)$

$Na(s) \longrightarrow Na(g)$, $\Delta_r H^{\circ} = \Delta_a H^{\circ}(Na, s) = \Delta_{sub} H^{\circ}(Na, s)$.

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Bond Enthalpy

$\boxed{\Delta H = +ve} \rightarrow$ Endothermic

It may be defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in the gaseous phase.

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$$H_2(g) \longrightarrow 2H(g), \quad \Delta_r H^\circ = \Delta_{H-H} H^\circ$$

$$O_2(g) \longrightarrow 2O(g), \quad \Delta_r H^\circ = \Delta_{O=O} H^\circ$$

$$N_2(g) \longrightarrow 2N(g), \quad \Delta_r H^\circ = \Delta_{N\equiv N} H^\circ$$

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Bond Enthalpy

For Diatomic Molecules it is equal to the enthalpy of atomization.

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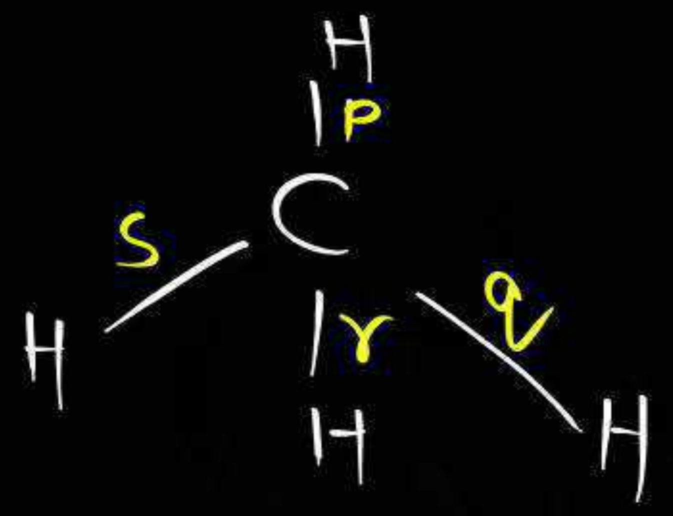
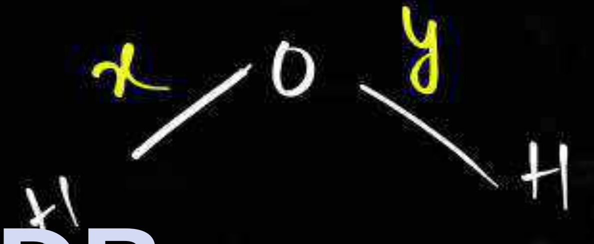
Bond Enthalpy

For Polyatomic molecules **mean or average** bond enthalpy is used.

CH_4.



Mean or Average Bond Enthalpy $= \frac{p+q+r+s}{4}$



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Avg. Bond enthalpy $= \frac{x+y}{2}$

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

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

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

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

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Bond Enthalpy

Note:

[illegible]

$$\Delta_r H^{\circ} = \sum a_i \, \Delta_{bond} H_{(Reactants)} - \sum b_i \, \Delta_{bond} H_{(Products)}$$

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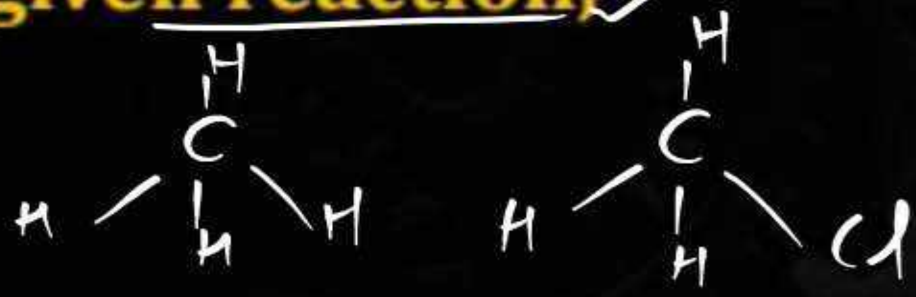
Question

Determine the enthalpy change for the given reaction,

$\underline{CH_4}(g) + \underline{Cl_2(g)} \rightarrow \underline{CH_3Cl}(g) + HCl(g)$



Bond energies are given as follows:

C – H = 412 kJ mol^{-1}

C – Cl = 338 kJ mol^{-1}

Cl – Cl = 242 kJ mol^{-1}

H – Cl = 431 kJ mol^{-1}

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Ans :⇒ $$\Delta_r H^0 = \left[\underline{4 \times \Delta_{C-H}H^0 + \Delta_{Cl-Cl}H^0}\right] - \left[3 \times \underline{\Delta_{C-H}H^0 + 1 \times \Delta_{C-Cl}H^0 + 1 \times \Delta_{H-Cl}H^0}\right]$$

$$= \left[(4 \times 412) + 242\right] - \left[3 \times 412 + 338 + 431\right]$$

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Question

Calculate the heat of combustion of ethene

$[CH_2 = CH_2(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)]$, $\Delta_r H^\circ = ?$

The bond energy data are given below

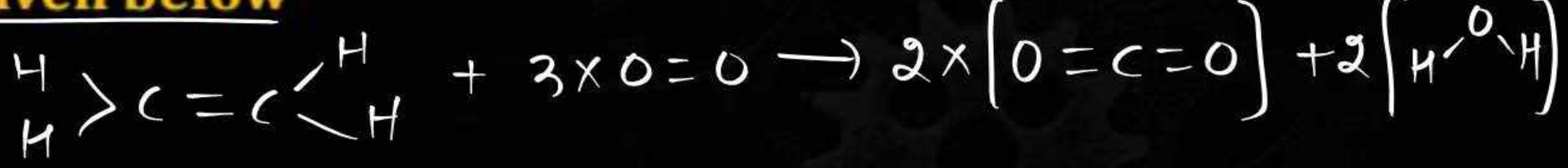
$C = C = 619$ kJ mol^{-1}

$C - H = 414$ kJ mol^{-1}

$O = O = 499$ kJ mol^{-1}

$C = O = 724$ kJ mol^{-1}

$O - H = 460$ kJ mol^{-1}



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Ans:→ $\Delta_r H^\circ = [4 \times \Delta_{C-H}H^\circ + 1 \times \Delta_{C=C}H^\circ + 3 \times \Delta_{O=O}H^\circ] - [4 \times \Delta_{C=O}H^\circ + 4 \times \Delta_{H-O}H^\circ]$

Ans

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Question

If enthalpy of atomisation for $Br_2(l)$ is x kJ/mol and bond enthalpy for Br_2 is y kJ/mol, the relation between them: (JEE Main 2020 (Jan.) Shift -1)

- **A** is $x = y$
- **B** does not exist
- **C** is $x > y$
- **D** is $x < y$

Hw

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Ans. [C]

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Enthalpy of Solution ($\Delta_{sol}H^0$)

Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent.

The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.

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$KCl_{(s)} + \underbrace{5H_2O_{(l)}} \rightarrow KCl\cdot 5H_2O_{(s)}$

$KCl_{(s)} + \underbrace{10H_2O_{(l)}} \rightarrow KCl\cdot 10H_2O_{(s)}$

$KCl_{(s)} + aq. \longrightarrow KCl_{(aq.)}$

$CuSO_{4(s)} + aq. \rightarrow \underline{CuSO_{4(aq.)}}$ ✓

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Enthalpy of Solution ($\Delta_{sol}H^0$)

Ionic solid.

$$\begin{tikzcd}
\begin{array}{c} KCl_{(s)} \\ (\text{Lattice}) \end{array} \arrow[rr, "\Delta_{sol.}H"] \arrow[dr, "\Delta_{lattice}H^0"'] & & \begin{array}{c} KCl_{(aq.)} \\ {[K^+_{(aq.)} + Cl^-_{(aq.)}]} \end{array} \\
& K^+_{(g)} + Cl^-_{(g)} \arrow[ur, "\Delta Hyd.H^0"'] &
\end{tikzcd}$$

$$\boxed{\Delta_{sol}H = \Delta H_{Lattice} + \Delta H_{Hyd.}}$$

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Lattice Enthalpy

The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

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$$NaCl(s) \longrightarrow \underbrace{Na^{+}(g) + Cl^{-}(g)}, \quad \Delta_r H^{\circ} = \Delta_L H^{\circ}(NaCl, s).$$

$$\underline{KCl(s) \longrightarrow K^{+}(g) + Cl^{-}(g)}$$

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ENTHALPY OF NEUTRALIZATION

- The amount of heat released when one gram equivalent of an acid is neutralized by one gram equivalent of a base.

Or

- The amount of heat released in formation of one mole of water when an acid is neutralized by a base.

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A↑

- For SA + SB this heat of neutralization is always equal to –13.7 kcal/~~mole~~ eq. or –57.1 kJ/~~mol~~. eq.

for any other combination of acid and base this heat is less than –13.7 kcal/mole or –57.1 kJ/mole.

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ENTHALPY OF NEUTRALIZATION

HCl (SA) [1 gram eq.] + $NaOH$ (SB) [1 gram eq.] $\longrightarrow NaCl + H_2O$, $\Delta_{neut.}H^0 = -13.7\ Kcal/eq.$

$$H^+ + \cancel{Cl^-} + \cancel{Na^+} + OH^- \longrightarrow \cancel{Na^+} + \cancel{Cl^-} + H_2O$$

$$\boxed{\underset{\sim}{H^+} + \underset{\sim}{OH^-} \longrightarrow H_2O,\ \Delta H = -13.7\ Kcal.}$$

$$\boxed{\text{Gram eq.} = \text{moles} \times \text{n-factor}}$$

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* $H_2SO_4 + NaOH \longrightarrow Na_2SO_4 + H_2O$, $\Delta_r H^0 = ?$

H_2SO_4 (1mol)	$NaOH$ (2mol)
n-factor = 2.	n-factor = 1.
Gram Eq. ⇒ 1×2 ⇒ 2	Gram eq. ⇒ 2×1

$2 \times (-13.7\ Kcal).$

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* $H_2SO_4 + NaOH \longrightarrow Na_2SO_4 + H_2O$. , $\Delta_r H = ?$

1 mol   1 mol.

−13.7 Kcal.

Eq. → 2.   Eq. → 1.

L.R. → NaOH.

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* $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$, $\Delta_r H^\circ = -13.2$ Kcal.

(WA)   (SB)

Enthalpy of Ionisation

[Diff. ⇒ 13.7 − 13.2 ⇒ 0.5 kcal.]

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Question

ΔH_f^o of water is -285.8 kJ mol^{-1}. If enthalpy of neutralization of monoacid strong base is -57.3 kJ mol^{-1}, ΔH_f^o of OH^- ion will be

$[\Delta_f H^o(H^+) = 0]$

[✓ A] -228.5 kJ mol^{-1}

B 228.5 kJ mol^{-1}

C 114.25 kJ mol^{-1}

D -114.25 kJ mol^{-1}

$$H^+ + OH^- \longrightarrow H_2O \ , \ \Delta H = -57.2 \text{ KJ.}$$

$$\Delta_r H^o = [\Delta_f H^o(H_2O)] - [\Delta_f H^o(H^+) + \Delta_f H^o(OH^-)]$$

$$-57.2 = -285.8 - [0 + x]$$

$$x = -285.8 + 57.2$$

Ans. A

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Question

WA (NaOH)

The Enthalpy of neutralization of acetic acid and sodium hydroxide is –55.4 kJ. What is the enthalpy of ionization of acetic acid?

$= 57.2 - 55.4$

$= \boxed{+1.9}$

- A –5.54 kJ
- B +5.54 kJ
- [✓ C +1.9 kJ]
- D –1.9 kJ

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Ans. C

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Question

Heat of neutralization is least when

A NaOH is neutralized by CH_3COOH

B NaOH is neutralized by HCl

[✓ C] NH_4OH is neutralized by CH_3COOH

D NH_4OH is neutralized by HNO_3

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Ans. C

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ENTHALPY OF Transition.

- Enthalpy of transition is the enthalpy change when one mole of one allotropic form changes to another.
- For example:

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$$C(\text{graphite}) \rightarrow C(\text{diamond}) \qquad \Delta H_{trs}^{0} = 1.90 \text{ kJ mol}^{-1}$$

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HEAT OF HYDROGENATION OR ENTHALPY OF HYDROGENATION

- It is the enthalpy change when one mole of unsaturated compound is converted to saturated compound.
- It is always exothermic.

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$$CH_2=CH_2 + H_2 \longrightarrow CH_3-CH_3$$

(Unsaturated) (Saturated).

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Variation of enthalpy with temperature (Kirchhoff's Equation)

$$\Delta C_p = \frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1}$$

$$\Delta C_v = \frac{\Delta U_{T_2} - \Delta U_{T_1}}{T_2 - T_1}$$

$\Delta C_p = (C_p)_{\text{Products}} - (C_p)_{\text{Reactants}}$

$\Delta C_v = (C_v)_{\text{Products}} - (C_v)_{\text{Reactants}}$.

ΔH_{T_1} → Enthalpy change at T_1

ΔH_{T_2} → ______ at T_2.

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SPONTANEITY

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Spontaneous Process

An irreversible process which has a natural tendency to occur on its own or after the proper initiation under the given set of conditions and can be reversed by some external agency only, is known as spontaneous process.

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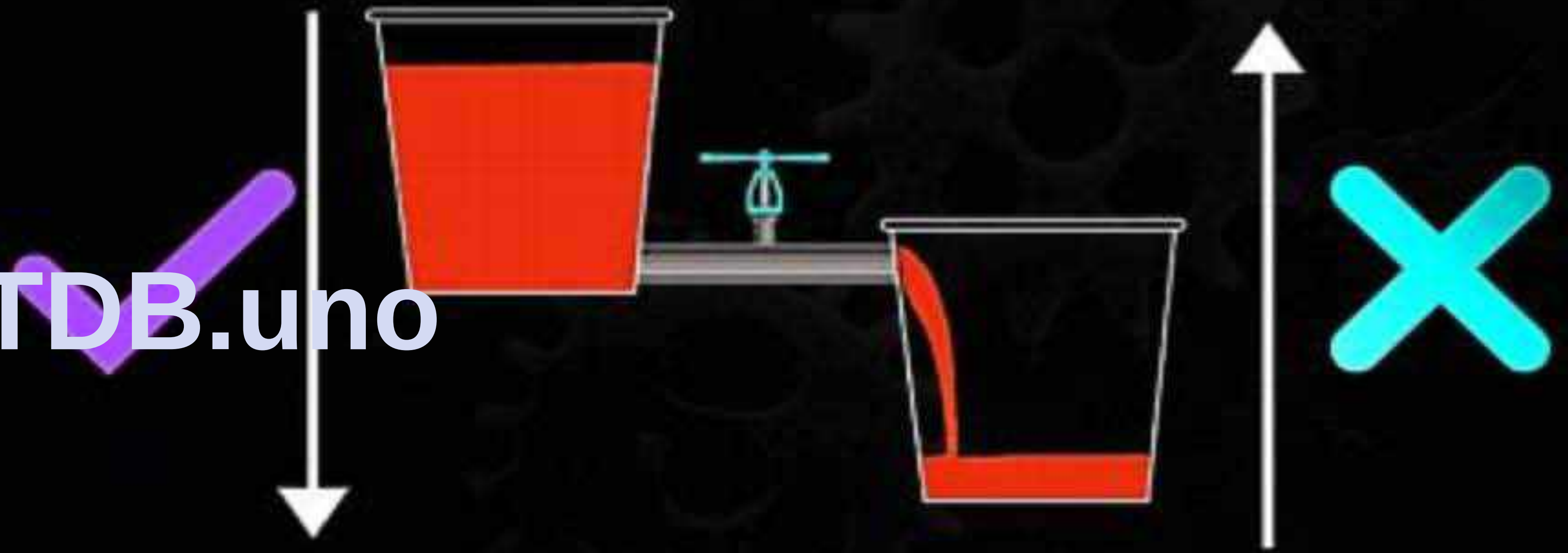

Water flows spontaneously from higher level to lower level

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Is decrease in enthalpy a criterion for spontaneity ????

$\Delta H = -ve.$

$\rightarrow \Delta H = +ve.$

$H_2O(s) \longrightarrow H_2O(l)$, $T = 25^\circ C.$ ✓

$H_2O(l) \longrightarrow H_2O(s)$, $\Delta H = -ve.$

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Entropy and spontaneity

[S].

Entropy is a thermodynamic function which is used to measure the extent of disorder or randomness.

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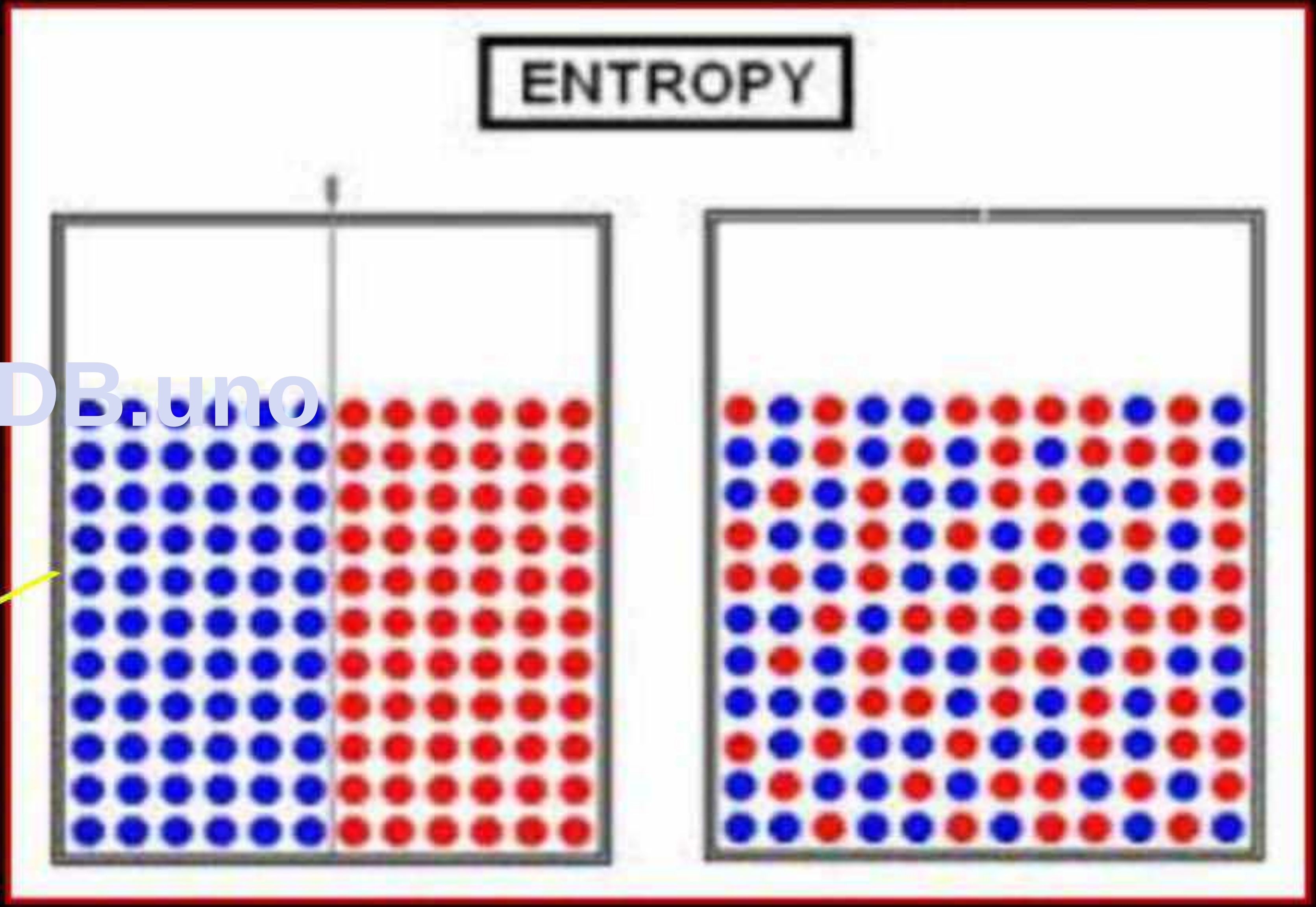

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Entropy and spontaneity

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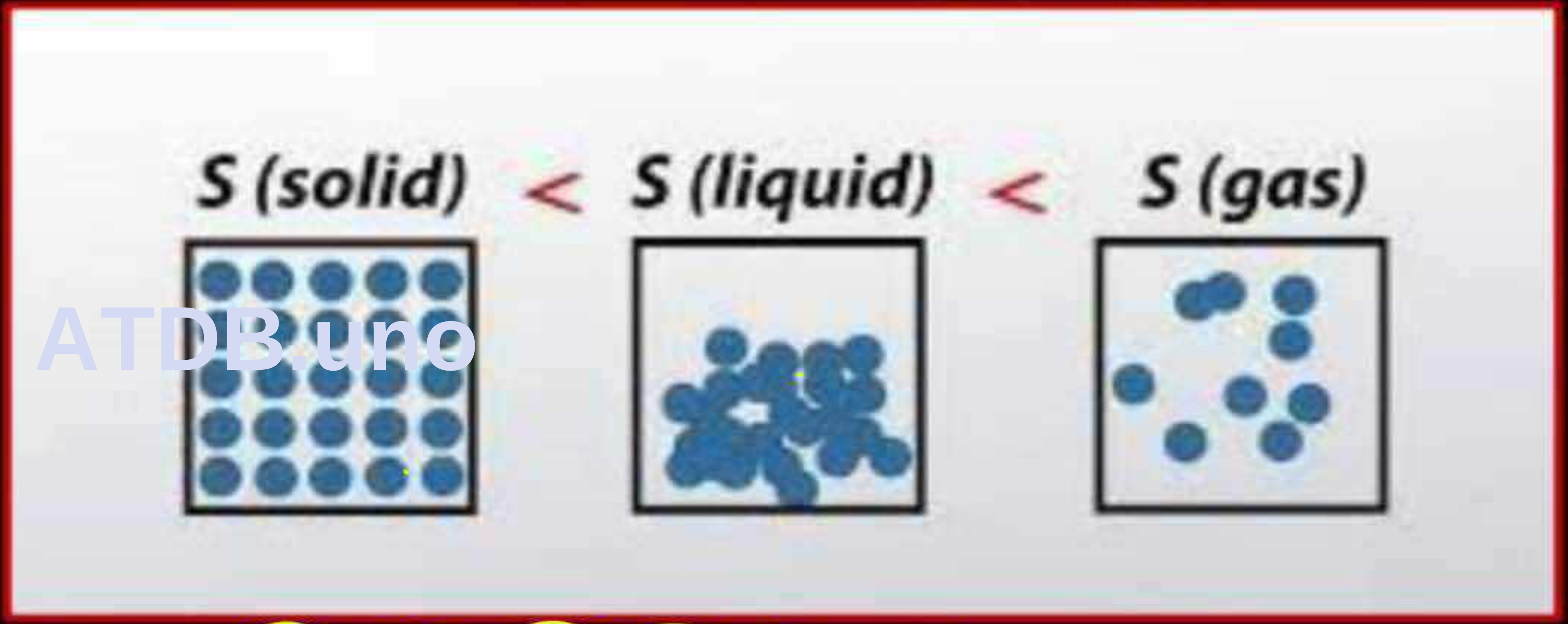

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Temp ↑, entropy ↑

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Entropy and spontaneity

Entropy ∝ Temp.

- Heat added to a system at lower temperature causes greater randomness than when the same quantity of heat is added to it at higher temperature. This suggests that the entropy change is inversely proportional to the temperature.

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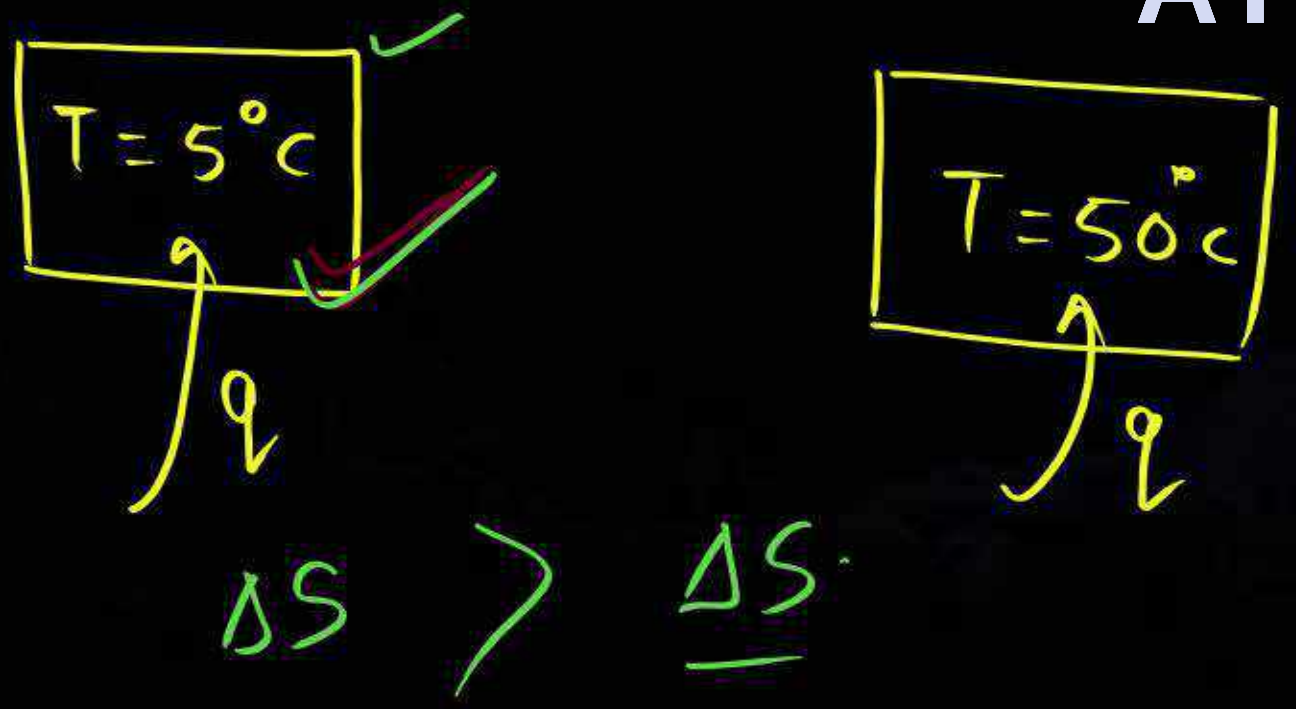
$$\boxed{\text{Entropy Change } (\Delta S) \propto \frac{1}{\text{Temp.}}}$$



$\Delta S > \Delta S$

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Question

The true statement amongst the following is:

(JEE Main 2020 (Jan.) Shift -2)

(A) Both ΔS and S are functions of temperature.

(B) Both S and ΔS are not functions of temperature.

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(C) S is not a function of temperature but ΔS is a fuction of temperature.

(D) S is a function of temperature but ΔS is not a function of temperature.

Ans. [A]

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Entropy and spontaneity

$\Delta S \propto \frac{1}{T}.$

$$\boxed{\Delta S_{sys.} = \frac{q_{rev,\,sys.}}{T}}$$

$*\ \Delta S_{Total} = \Delta S_{system} + \Delta S_{surr.}$

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$\overbrace{N_2(g) + 3H_2(g)}^{4\,mol.} \longrightarrow \overbrace{2NH_3(g)}^{2\,mol}, \ \Delta S = \underline{-ve.}$

$\underset{(1\,mol)}{PCl_5(g)} \rightarrow \underbrace{PCl_3(g) + Cl_2(g)}_{(2\,mol)}, \ \underline{\Delta S = +ve}$

$*$ Dissolution of NaCl, $\Delta S = +ve$

$*\ H_2(g) \longrightarrow 2H(g), \ \underline{\Delta S = +ve.}$

$\underline{CaCO_3(s)} \rightarrow CaO(s) + CO_2(g)$

$\underline{\Delta S = +ve.}$

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2^{nd} Law of Thermodynamics

For any isolated system, entropy of the universe always increases.

$\Delta S_{Total} > 0$, → spontaneous Process.

$\Delta S_{Total} < 0$, → non-spontaneous Process

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$\Delta S_{Total} = 0$. (Eq.)

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Entropy change in Various Thermodynamic Process

1. Reversible Isothermal Process:

$$\Delta U = 0$$

$$q = -w = -\left[-2.303\, nRT \log \frac{V_2}{V_1}\right]$$

$$q = 2.303\, nRT \log\left(\frac{V_2}{V_1}\right)$$

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$$\boxed{\begin{aligned} \Delta S &= \frac{q}{T} \\ \Delta S &= 2.303\, nR \log_{10}\left(\frac{V_2}{V_1}\right) \\ &\text{or} \\ &= 2.303\, nR \log_{10}\left(\frac{P_1}{P_2}\right) \end{aligned}}$$

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Entropy change in Various Thermodynamic Process

2. Reversible Adiabatic Process:

$q = 0$

$\Delta S_{rev.} = \frac{q}{T}$

$\boxed{\Delta S = 0}$

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Entropy change in Various Thermodynamic Process

3. Reversible Isobaric Process:

$$dq = nC_p\,dT$$

$$ds = \frac{dq}{T} = \frac{nC_p\,dT}{T}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_p\,dT}{T}$$

$$\Delta S = nC_p\left[\ln T\right]_{T_1}^{T_2}$$

$$\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right)$$

$$\boxed{\Delta S = 2.303\, n\underbrace{C_p}_{\text{molar Heat capacity at Constant Pressure}} \log_{10}\left(\frac{T_2}{T_1}\right)}$$

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Entropy change in Various Thermodynamic Process

4. Reversible Isochoric Process:

$\partial q = nC_v dT.$

$$\boxed{\Delta S = 2.303\, n \underbrace{C_v}_{\downarrow} \log_{10}\left(\frac{T_2}{T_1}\right)}$$

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Molar heat capacity at Constant volume.

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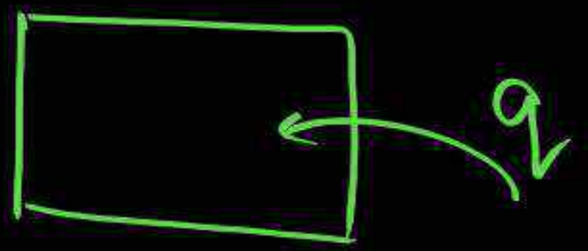
Entropy change in reversible Process

For an isothermal reversible process, a system absorbs heat (q) from surroundings at temperature T.



$\Delta S_{sys.} = \frac{q}{T}$

$\Delta S_{surr.} = -\frac{q}{T}$

$\Delta S_{Total} = \Delta S_{sys.} + \Delta S_{surr.}$

$\boxed{\Delta S_{Total} = 0}$

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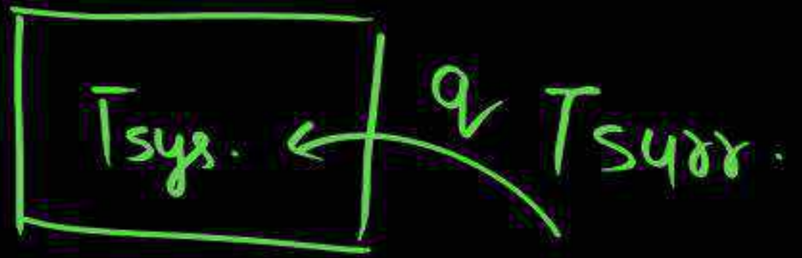
Entropy change in Irreversible Process

Let heat (q) flows from surroundings at temperature T_{surr} to a system at temperature T_{sys}



$$\boxed{T_{surr.} > T_{sys.}}$$ *

$$\Delta S_{sys.} = \frac{q}{T_{sys.}}$$

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$$\Delta S_{surr.} = \frac{-q}{T_{surr.}}$$

$$\Delta S_{Total} = \frac{q}{T_{sys.}} + \left[-\frac{q}{T_{surr}}\right]$$

$$\boxed{\Delta S_{Total} \neq 0}$$ *

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Molar Entropy change in a reaction

$(\Delta_r S^\circ)$.

$R \longrightarrow P$.

$\Delta_r S = (S)_P - (S)_R$.

$$\boxed{\Delta_r S^\circ = \sum b_i (S^\circ)_{\text{Products}} - \sum a_i (S^\circ)_{\text{Reactants}}}$$

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Question

Predict in which of the following, entropy increases/decreases:

(i) A liquid crystallizes into a solid. , $\Delta S = -ve$.

(ii) Temperature of a crystalline solid is raised from 0 K to 115 K. , $\Delta S = +ve$.

Ans :> $L \longrightarrow S$

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Question

During which of the following processes, does entropy decrease?

(1) Freezing of water to ice at 0°C → ΔS = -ve.

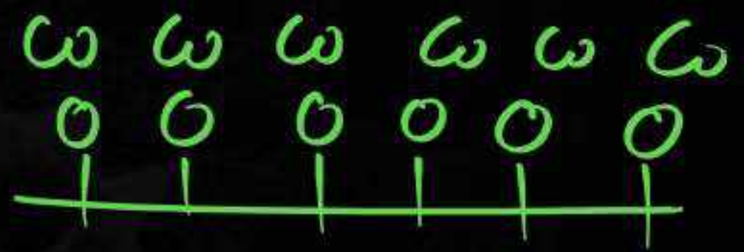
(2) Freezing of water to ice at –10°C ΔS = -ve.

(3) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ → ΔS = -ve.

(4) Adsorption of CO(g) on lead surface ΔS = -ve

(5) Dissolution of NaCl in water

(JEE Main 2021 (March) Shift -2)



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[✓ A] 1, 2, 3, and 4 only

B 2 and 3 only

C 1 and 5 only

D 1, 3 and 5 only

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Question

The process with negative entropy change is (2019 Main, 10 Jan II)

A synthesis of ammonia from N_2 and H_2

B dissociation of $CaSO_4(s)$ to $CaO(s)$ and $SO_3(g)$

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C dissolution of iodine in water

D sublimation of dry ice

HW

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Question

$\Delta S \rightarrow$ State function.

The direct conversion of A to B is difficult, hence it is carried out by the following shown path

$$\begin{tikzcd}
C \arrow[r, "30"] & D \arrow[d, "-20"] \\
A \arrow[u, "50"] \arrow[r] & B
\end{tikzcd}$$

$\Delta S_{A \to B} = 50 + 30 - 20 \Rightarrow 60.$

Given that $\Delta S_{(A \to C)} = 50$ eu

$\Delta S_{(C \to D)} = 30$ eu

$\Delta S_{(B \to D)} = 20$ eu where, eu is entropy unit

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Then, $\Delta S_{(A \to B)}$ is (2006, 3M)

(A) + 100 eu

[✓ (B) + 60 eu]

(C) – 100 eu

(D) – 60 eu

Ans. [B]

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Entropy change in Phase Transformation

Molar Entropy of Fusion:

$S \rightarrow L \ , \ \Delta S = (S)_L - (S)_S \ .$

$$\Delta S_{fus.} = \frac{q_{fus.}}{T_f}$$

$$\boxed{\Delta S_{fus.} = \frac{\Delta H_{fus.}}{T_f .}} \longrightarrow \text{Ethalpy of fusion.}$$

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Entropy change in Phase Transformation

Molar Entropy of Vaporisation: $L \rightarrow G.$

$$\Delta S = (S)_G - (S)_L.$$

$$\Delta S^{\circ}_{vap.} = \frac{q_{vap.}}{T_b}$$

$T_b \rightarrow$ B.P.

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$$\boxed{\Delta S^{\circ}_{vap.} = \frac{\Delta_{vap}H^{\circ}}{T_b}}$$

$\Delta_{vap}H^{\circ} \rightarrow$ Enthalpy of vaporisation.

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Entropy change in Phase Transformation

Molar Entropy of Sublimation: $S \longrightarrow G$

$$\Delta S = (S)_G - (S)_S$$

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$$\Delta S_{sub.} = \frac{q_{sub.}}{T_{sub.}}$$

$$\boxed{\Delta S^{0}_{sub.} = \frac{\Delta_{sub} H^{0}}{T_{sub.}}} \longrightarrow \text{Enthalpy of sublimation.}$$

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Question

What is entropy change for the conversion of one gram of ice to water at 273 K and 1 atm pressure? Given that enthalpy of ~~vaporisation~~ fus. is 6 KJ/mol.

Ans :→ S → L

$T_f = 273 \text{ K}$

$\Delta H_{vap.} = 6 \text{ KJ/mol}$

$\because$ 1 mol $\longrightarrow$ 6 KJ.

$\because$ 18 g. $\longrightarrow$ 6 KJ.

$\therefore$ 1 g. $\longrightarrow \frac{6}{18} \Rightarrow \frac{1}{3}$ KJ.

$$\Delta S_{fus.} = \frac{\Delta H_{fus.}}{T_f}$$

$$= \frac{1/3}{273} \times 1000$$

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Gibbs energy and spontaneity

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$\underline{[G]}$.

$\underline{\underline{\Delta G}}$

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Gibbs energy and spontaneity

- Neither decrease in enthalpy nor increase in entropy alone can determine the direction of spontaneous change for these systems. For this purpose, we define a new thermodynamic function the Gibbs energy or Gibbs function

$$\boxed{\underbrace{\Delta G}_{\text{Gibb's Energy change.}} = \underbrace{\Delta H}_{\text{Enthalpy change}} - T\underbrace{\Delta S}_{\text{Entropy change.}}}$$

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Gibbs energy and spontaneity

$\Delta G = -ve$ [Spontaneous Process]

$\Delta G = +ve$ [Non- ________]

$\Delta G = 0$ [Process at Eq.]

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	ΔH	ΔS	ΔG
(i)	+ve	−ve	+ve [Non-spontaneous Process at all temp.]
(ii)	−ve	+ve	−ve [spontaneous ______]
(iii)	+ve	+ve	Process is spontaneous at high temp.
(iv)	−ve	−ve	______ at low temp.

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Question

For the reaction at 298 K, $2A + B \rightarrow C$, $\Delta H = 400$ kJ mol^{-1} and $\Delta S = 0.2$ kJ K^{-1} mol^{-1}. At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range?

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Hw

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Gibbs energy and spontaneity

Note:

- ΔG is the net energy available to do useful work and is thus a measure of the ‘free energy’. For this reason, it is also known as the free energy of the reaction.

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$\Delta G = -[W_{useful}]$

Gibb's free energy change.

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Gibbs energy and spontaneity

$$\boxed{\underline{\Delta G} = \underline{\Delta G^0} + 2.303RT\log_{10} Q}$$

→ Reaction Quotient.

ΔG → Gibb's energy change.

ΔG^0 → standard Gibb's Energy change

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* At eq. $\underline{\Delta G = 0}$, $Q = K_{eq}$ → Eq. Constant.

$$\boxed{\Delta G^0 = -2.303RT\log K_{eq}}$$

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Standard Free energy of formation ($\Delta_f G^\circ$).

- The standard Gibbs free energy of formation (G_f°) of a compound is **the change of Gibbs free energy that accompanies the formation of 1 mole of a substance in its standard state from its constituent elements in their standard states.**

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$$\boxed{\Delta_r G^\circ = \sum b_i (\Delta_f G^\circ)_{Products} - \sum a_i (\Delta_f G^\circ)_{Reactants}.}$$

Standard Gibb's free Energy of Rx^n.

$\Delta_f G^0$ of elements in their standard State is taken as zero.

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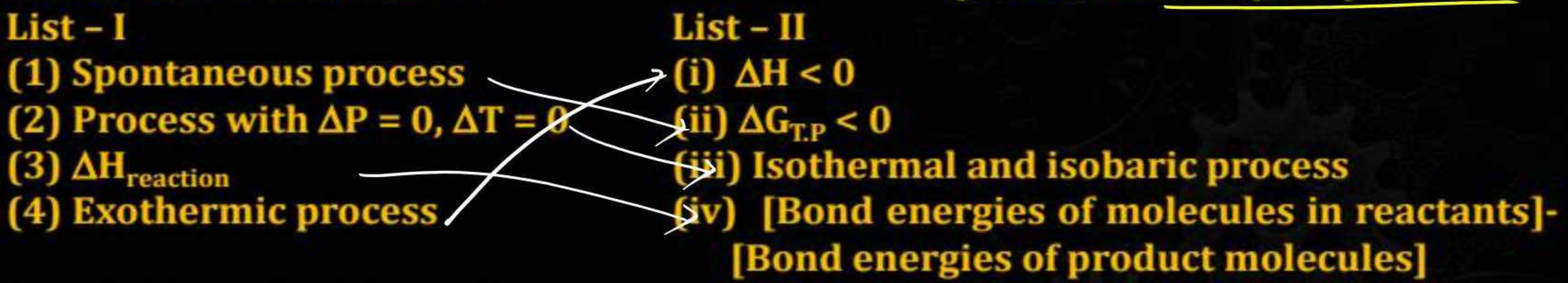
Question

Match List – I with List – II (JEE Main 2022 (June) Shift -1)



List – I	List – II
(1) Spontaneous process	(i) $\Delta H < 0$
(2) Process with $\Delta P = 0, \Delta T = 0$	(ii) $\Delta G_{T.P} < 0$
(3) $\Delta H_{reaction}$	(iii) Isothermal and isobaric process
(4) Exothermic process	(iv) [Bond energies of molecules in reactants]-[Bond energies of product molecules]

Choose the correct answer from the options given below:

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(A) (1) – (iii), (2) – (ii), (3) – (iv), (4) – (i) ✗

[✓ (C)] (1) – (ii), (2) – (iii), (3) – (iv), (4) – (i) ✓

(B) (1) – (ii), (2) – (iii), (3) – (i), (4) – (iv)

(D) (1) – (ii), (2) – (i), (3) – (iii), (4) – (iv) ✗

Ans. [[redacted]]

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Question

Assuming ideal behaviour, the magnitude of log K for the following reaction at 25°C is $x \times 10^{-1}$. The value of x is______.(Integer answer)

$$3HC \equiv CH_{(g)} \rightleftharpoons C_6H_{6(\ell)}$$

[Given: $\Delta_f G^o (HC \equiv CH) = -2.04 \times 10^5$ J mol^{-1}; $\Delta_f G^o (C_6H_6) = -1.24 \times 10^5$ J mol^{-1} R = 8.314 J K^{-1} mol^{-1}]

(JEE Main 2021 (Feb.) Shift -2)

Ans :⇒ $\Delta G^0 = -2.303\, RT \log_{10} K$ [T = 298 K]

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$\Delta_r G^0 = [\Delta_f G^0 (C_6H_6)] - [3 \times \Delta_f G^0 (C_2H_2)]$

$\Delta_r G^0 = (-1.24 \times 10^5) - [3 \times (-2.04 \times 10^5)]$

Ans. [855]

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Question

For a chemical reaction $A + B \rightleftharpoons C + D$ ($\Delta_r H^\ominus = 80$ kJ mol^{-1}) the entropy change $\Delta_r S^\ominus$ depends on the temperature T (in K) as $\Delta_r S^\ominus = 2T$ (J K^{-1}mol^{-1}). Minimum temperature at which it will become spontaneous is ______ K.

(JEE Main 2021 (Feb) Shift -1)

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Ans. [200]

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Question

For a dimerization reaction, $2A(g) \rightarrow A_2(g)$, at $\underline{298\ K}$, $\underline{\underline{\Delta U^\ominus}} = -20$ kJ mol^{-1}, $\underline{\Delta S^\ominus = -30}$ J K^{-1}mol^{-1}, then the $\Delta G^\ominus$ will be ________ J.

(JEE Main 2020 (Sep.) Shift -2)

$\Delta n_g = 1 - 2 \Rightarrow -1$

Ans :→ $\underline{\Delta G} = \underline{\Delta H} - T\,\underline{\underline{\Delta S}}\,.$

$\Delta H = \Delta U + \Delta n_g RT$

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Ans. [–13538]

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Question

A process will be spontaneous at all temperature if

(2019 Main, 10 April 1)

A $\Delta H > 0$ and $\Delta S < 0$

[✓ B] $\Delta H < 0$ and $\Delta S > 0$

C $\Delta H < 0$ and $\Delta S < 0$

D $\Delta H > 0$ and $\Delta S > 0$

$\Delta G = \underline{\Delta H} - T\underline{\Delta S}$.

$\Delta G = -ve$.

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Question

The reaction, $MgO(s) + C(s) \rightarrow Mg(s) + CO(g)$, for which $\Delta_r H^o = +\ 491.1$ kJ mol^{-1} and $\Delta_r S^o = 198.0$ JK^{-1} mol^{-1}, is not feasible at 298 K. Temperature above which reaction will be feasible is

- **A** 2040.5 K
- **B** 1890.0 K
- **C** 2380.5 K
- **D** 2480.3 K

Hw

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Ans. [D]

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Question

The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by, $\Delta_r G^o = A - BT$ Where A and B are non-zero constants. Which of the following is true about this reaction?

(2019 Main, 11 Jan II)

A Endothermic if, $A < 0$ and $B > 0$

B Exothermic if, $B < 0$

C Exothermic if, $A > 0$ and $B < 0$

[✓ D] Endothermic if, $A > 0$

$$\Delta G = A - BT$$

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

$$A = \Delta H$$

$$\downarrow \qquad \downarrow$$

$$+ve \qquad +ve$$

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Ans. [D]

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Question

A process has $\Delta H = 200\ \text{J mol}^{-1}$ and $\Delta S = 40\ \text{JK}^{-1}\ \text{mol}^{-1}$. Out of the values given below, choose the minimum temperature above which the process will be spontaneous (2019 Main, 10 Jan 1)

- **A** 20K
- **B** 4K
- **C** 5K
- **D** 12 K

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HW

Ans. [C]

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Question

For the process $H_2O(l)$ (1 bar, 373 K) → $H_2O(g)$ (1 bar, 373 K), the correct set of thermodynamic parameters is (2007, 3M)

- **A** $\Delta G = 0, \Delta S = +\text{ve}$
- **B** $\Delta G = 0, \Delta S = -\text{ve}$
- **C** $\Delta G = +\text{ve}, \Delta S = 0$
- **D** $\Delta G = -\text{ve}, \Delta S = +\text{ve}$

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Ans. [A]

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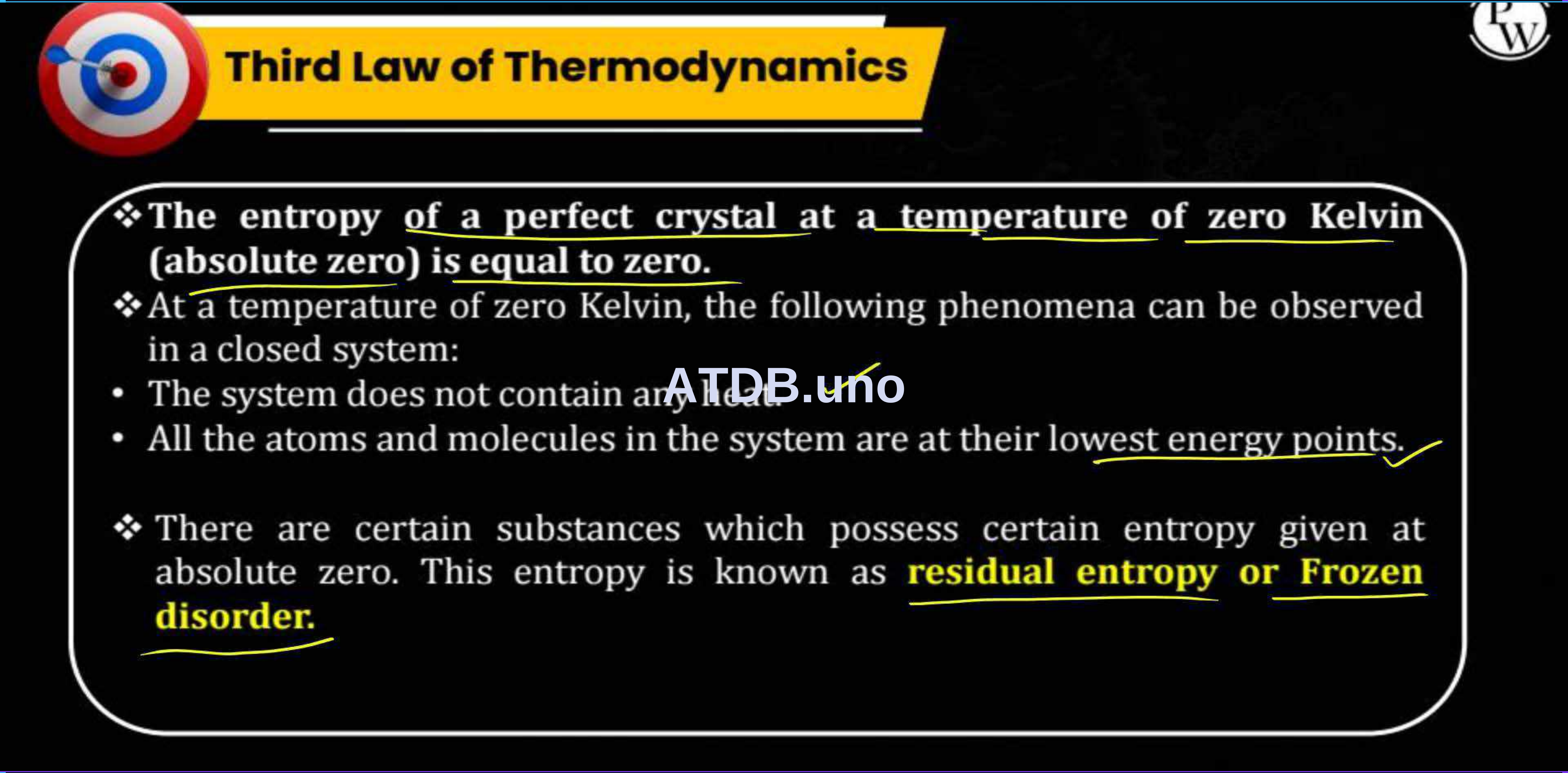

Third Law of Thermodynamics

- ❖ **The entropy of a perfect crystal at a temperature of zero Kelvin (absolute zero) is equal to zero.**
- ❖ At a temperature of zero Kelvin, the following phenomena can be observed in a closed system:
  - The system does not contain any heat.
  - All the atoms and molecules in the system are at their lowest energy points.
- ❖ There are certain substances which possess certain entropy given at absolute zero. This entropy is known as **residual entropy or Frozen disorder.**

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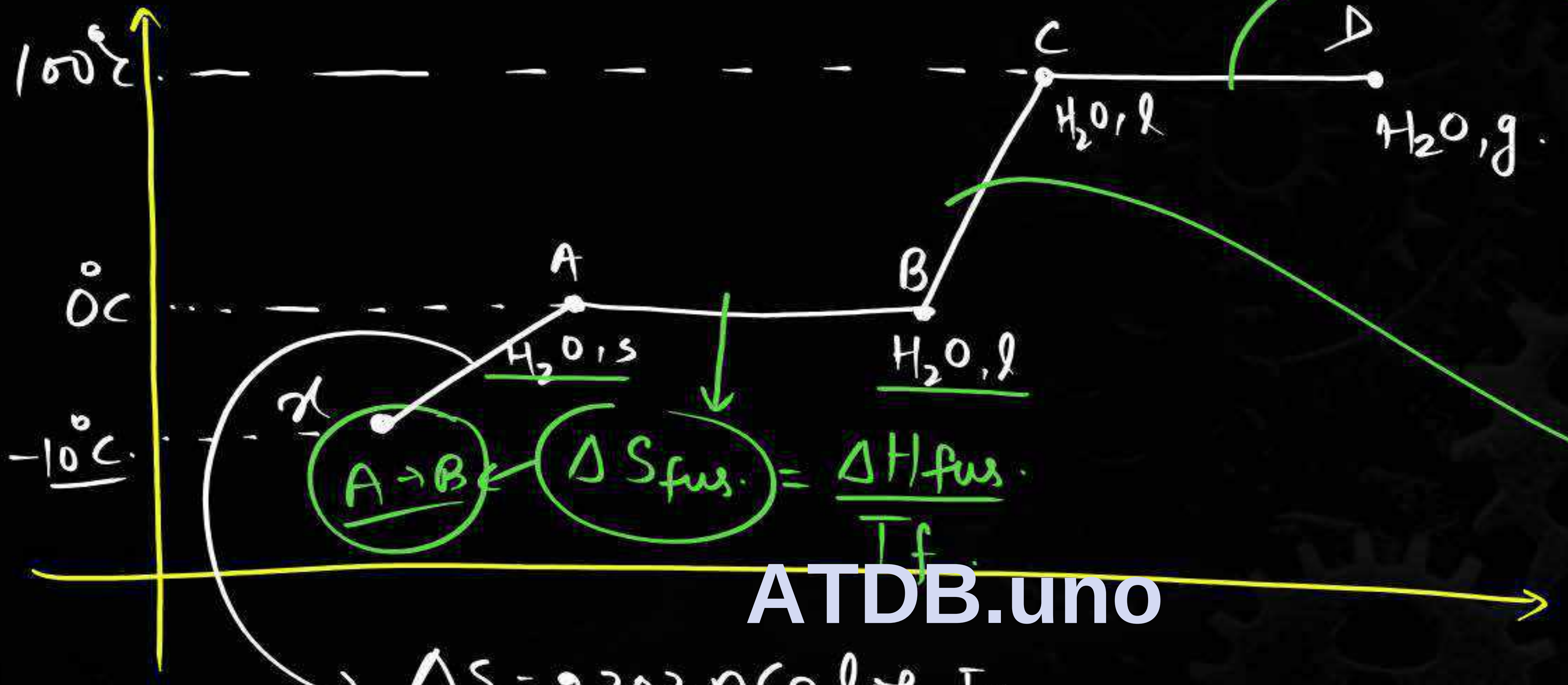

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_f}$$

$$\Delta S = 2.303\, nC_p \log \frac{T_2}{T_1}$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$$

$$dq = nC_p\, dT$$

$$ds = \int \frac{dq}{T}$$

$$\Delta S = 2.303\, nC_p \log \frac{T_2}{T_1}$$

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