



Arjuna

JEE

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- ❑ Subject – Chemistry
- ❑ Chapter – Thermodynamics

One shot

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Today's Targets

Chapter



Introduction and Thermodynamic Terms

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Thermodynamic Properties and FLO T



Thermochemistry



Entropy and 2nd law of Thermodynamics

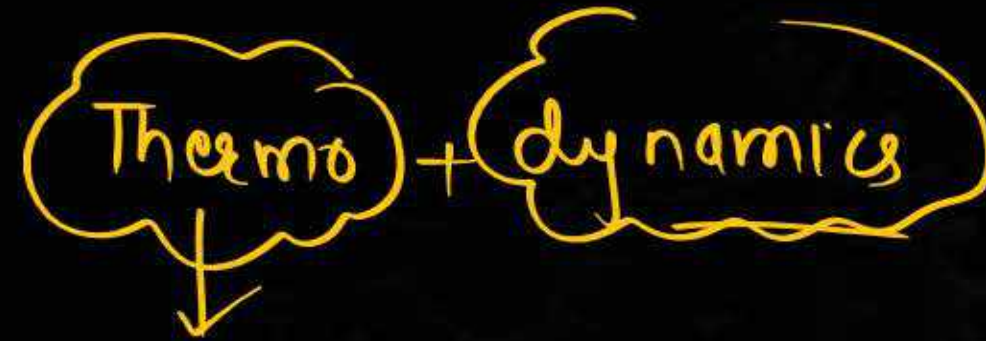




Introduction



Introduction



➤ 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.



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.



ATDB.uno Thermodynamic Terms

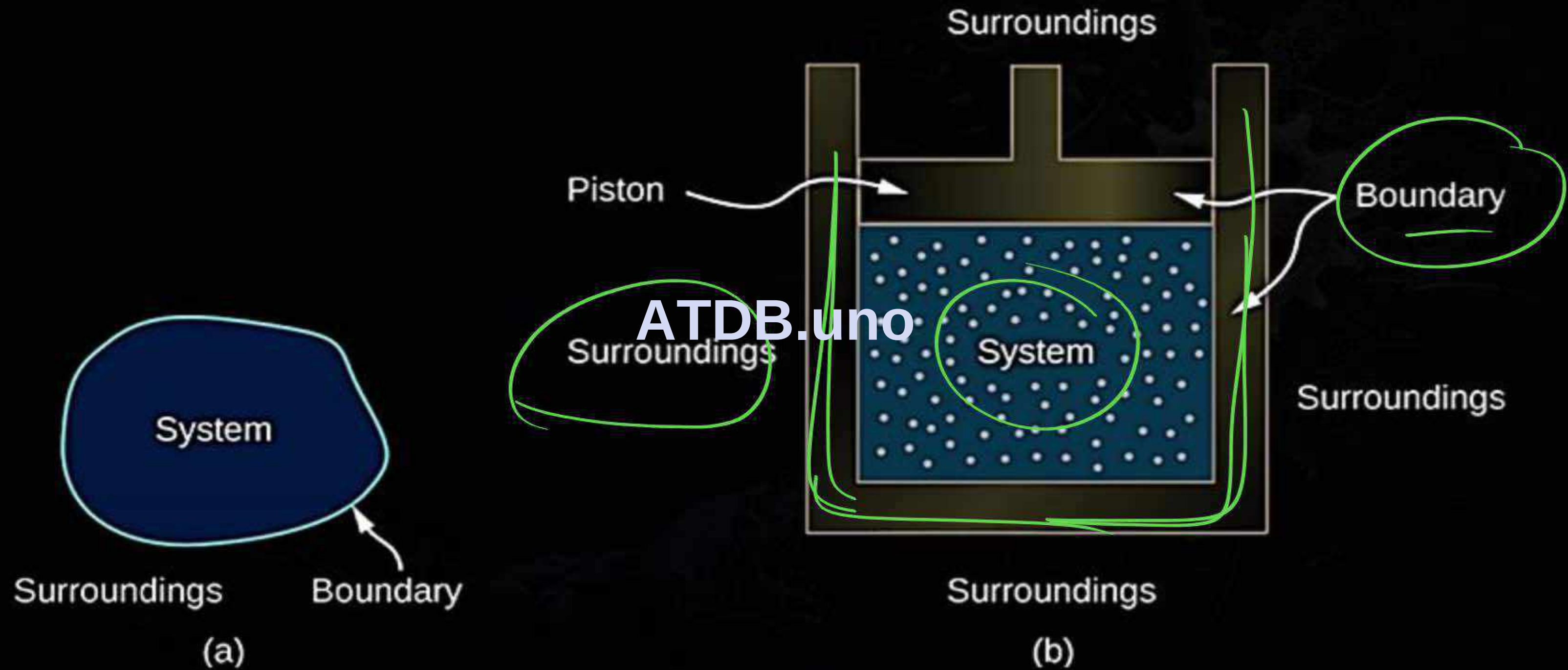


The System and the Surroundings



- 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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Types of system



1. Open System

- In an open system, there is exchange of energy and matter between system and surroundings.

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- 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.



Open system

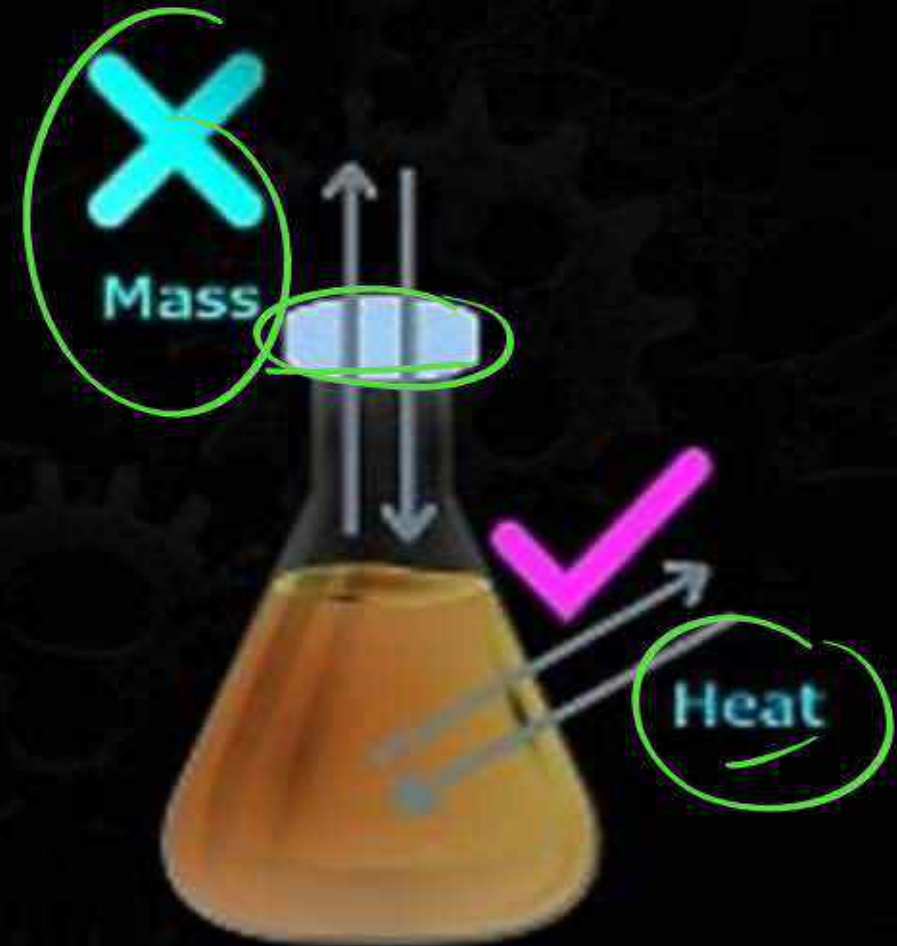


Types of system



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.



Closed system



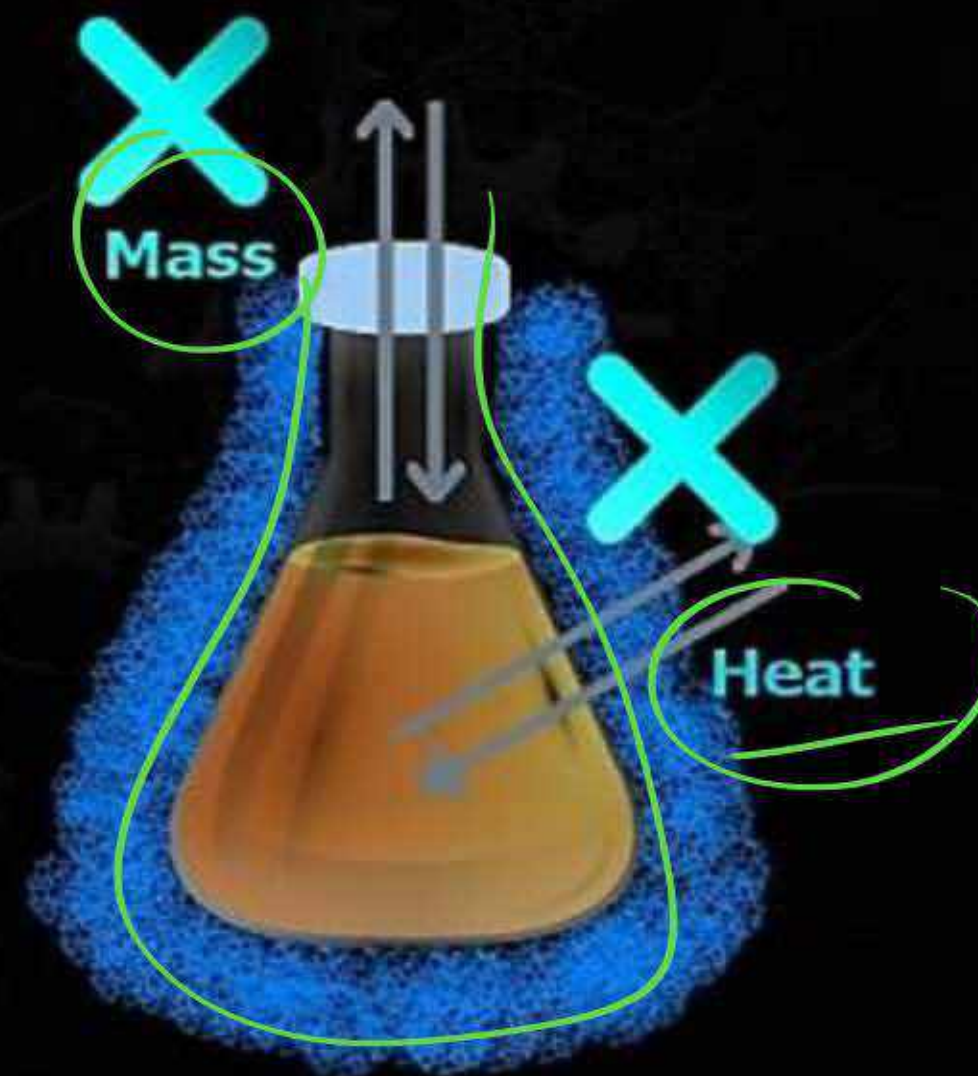
Types of system



3. Isolated System

- In an isolated system, there is no exchange of energy or matter between the system and the surroundings.
- The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

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Isolated system



State of a system



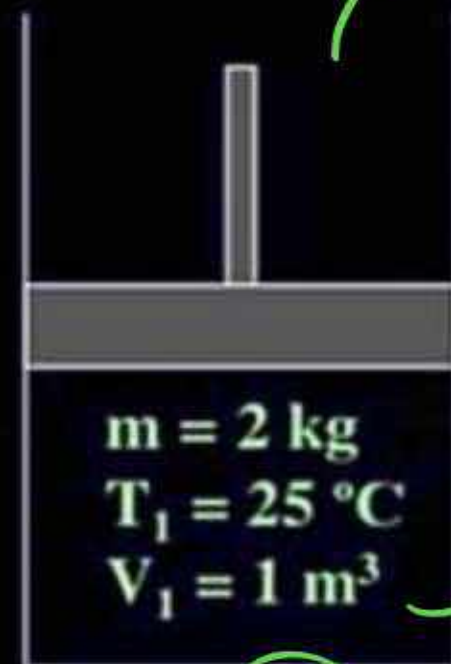
- ❖ State is the condition of a system as specified by it's physical properties.
- ❖ Macroscopic properties such as pressure, temperature, volume, amount, etc. which determine the state of a system are referred to as state variables.

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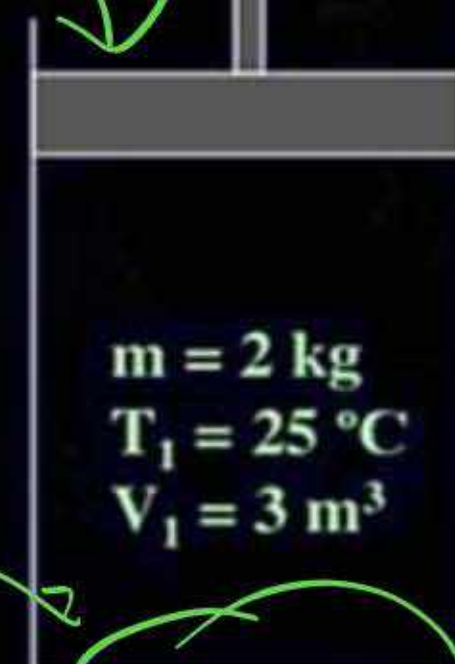
$$PV = nRT$$

(4) X

(3) ✓



STATE 1

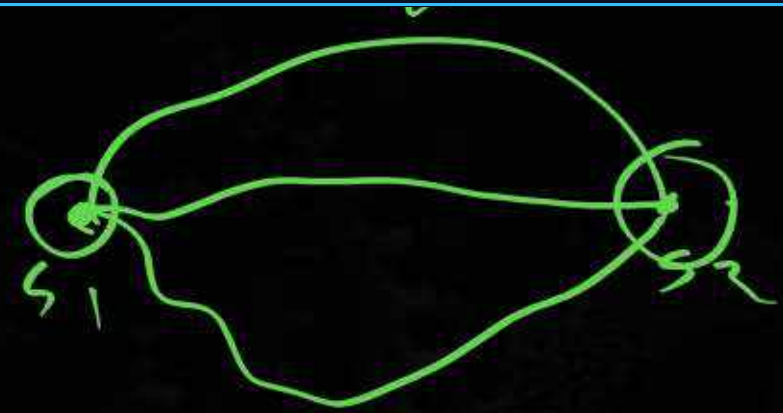


STATE 2

P, V, T
State functions



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.

Path Functions:

Ex :- Heat (q), work (w).

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



Extensive and Intensive Properties

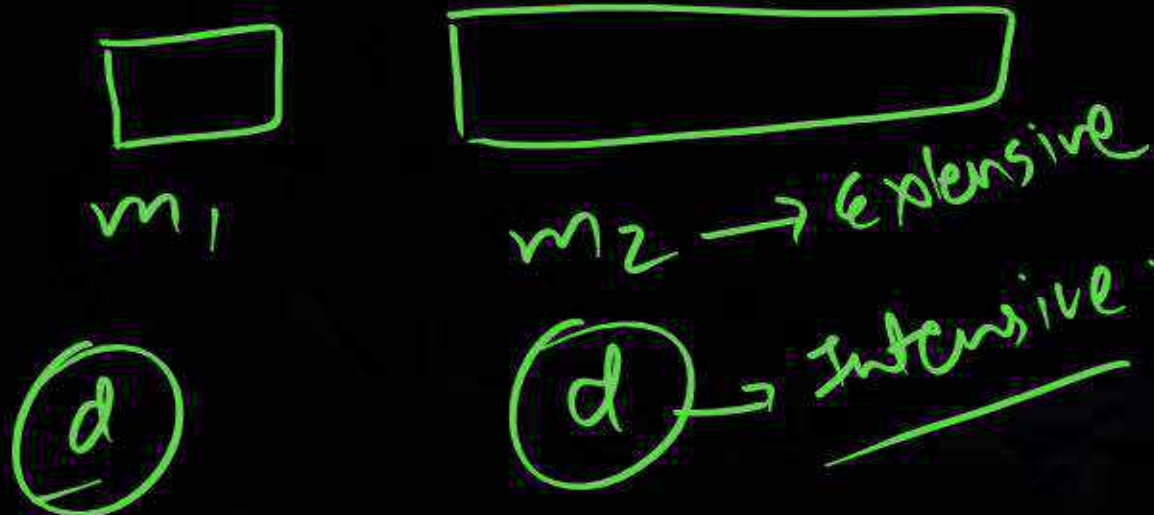


Extensive Property



- 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.

ATDB.uno (H)



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

Resistance (R) etc.

moles



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, free, pH, concentration,
molar volume,

$P = 1 \text{ atm}$

$\frac{20}{4} = 5 \text{ m}^3$ 25°C	$\frac{20}{4} = 5 \text{ m}^3$ 25°C	$\rightarrow P = 1 \text{ atm.}$
$\frac{20}{4} = 5 \text{ m}^3$ 25°C	5 m^3 25°C	$\rightarrow T = 25^\circ\text{C.}$
		$\rightarrow V = 20 \text{ m}^3.$

✓ ✓



Note

① x and $y \rightarrow$ Intensive Properties

$$x+y, xy, \frac{x}{y}, \frac{\partial x}{\partial y} \rightarrow \text{Intensive}$$

② x and $y \rightarrow$ Extensive Properties.

$$x+y \rightarrow \text{extensive}$$

$$\frac{x}{y}, \frac{\partial x}{\partial y} \rightarrow \text{Intensive}$$

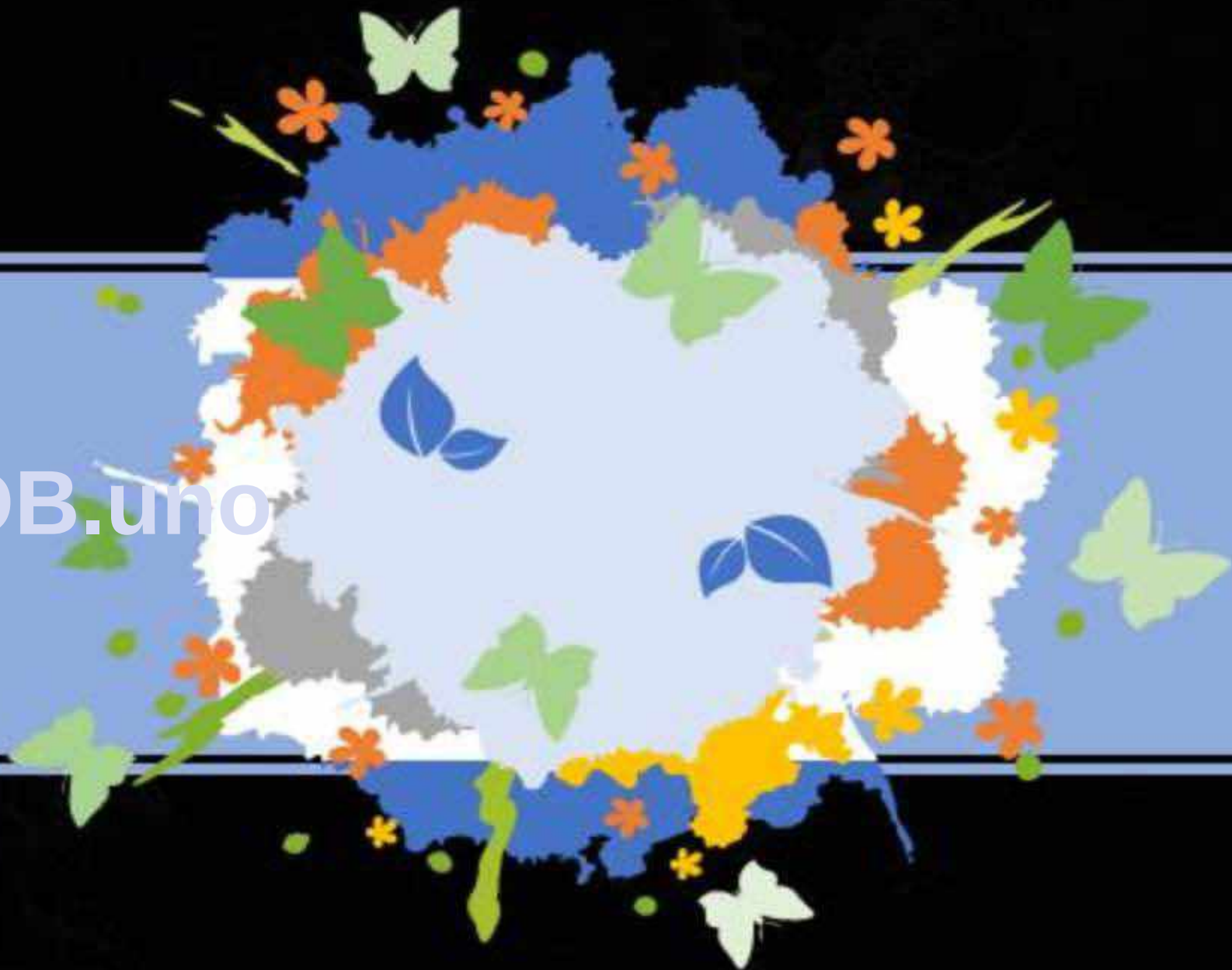
$$\begin{array}{l} \text{density} = \frac{\text{Mass} \rightarrow \text{Ext.}}{\text{Vol.} \rightarrow \text{Ext.}} \\ \downarrow \\ \text{Intensive} \end{array}$$

$$\begin{array}{l} \text{Conc.} \Rightarrow \frac{\text{moles} \rightarrow \text{Ext.}}{\text{volume} \rightarrow \text{Ext.}} \\ \downarrow \\ \text{Int} \end{array}$$



Thermodynamic Process

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Thermodynamic Process



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



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



Thermodynamic Process



1. Isothermal Process:

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

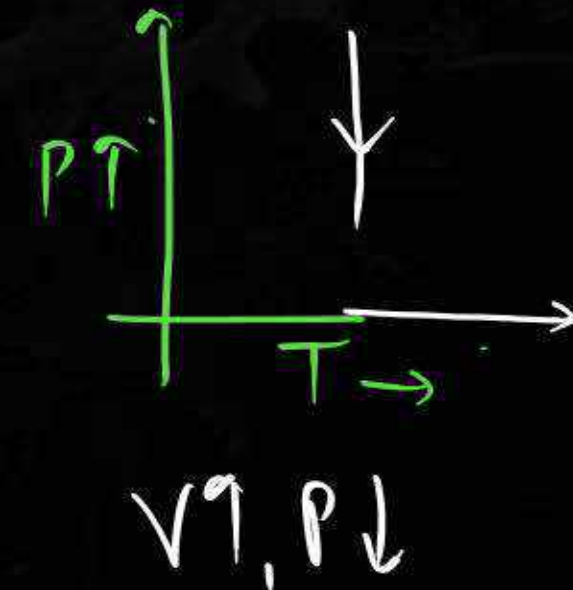
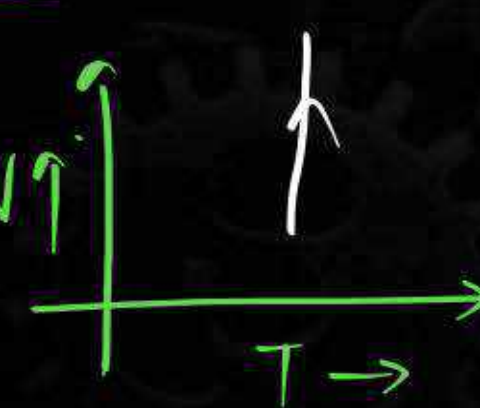
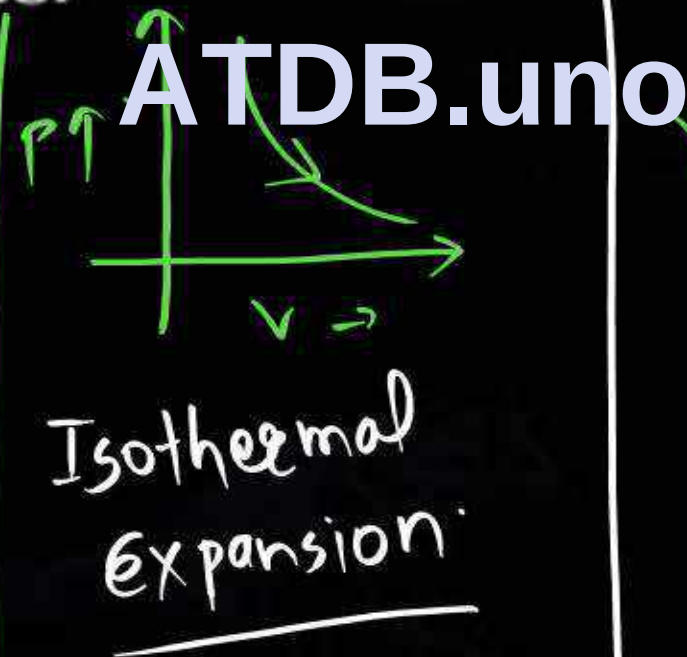
$$T = \text{Constant}$$

$$dT = 0 \Rightarrow \underline{\Delta T = 0}$$

Boyle's Law $\Rightarrow$

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

$$P_1 V_1 = P_2 V_2$$





Thermodynamic Process



2. Isobaric Process:

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

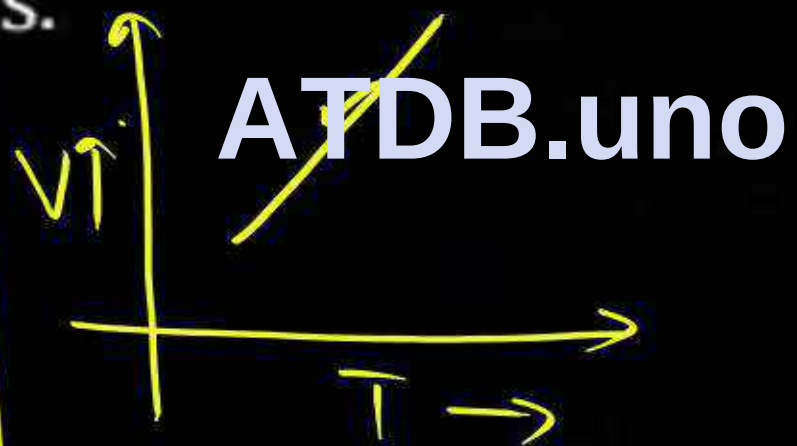
$$P = \text{Constant}$$

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

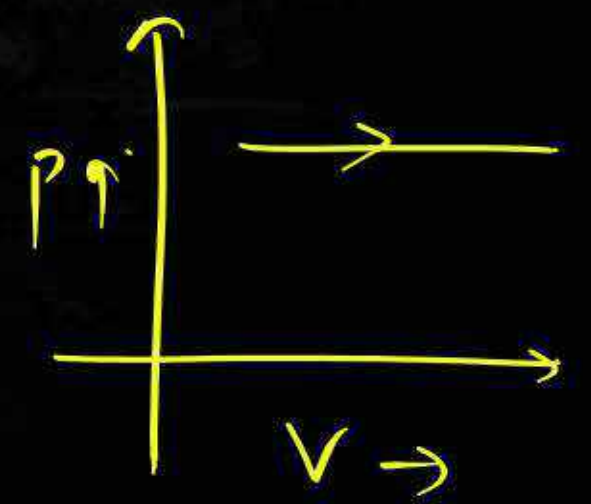
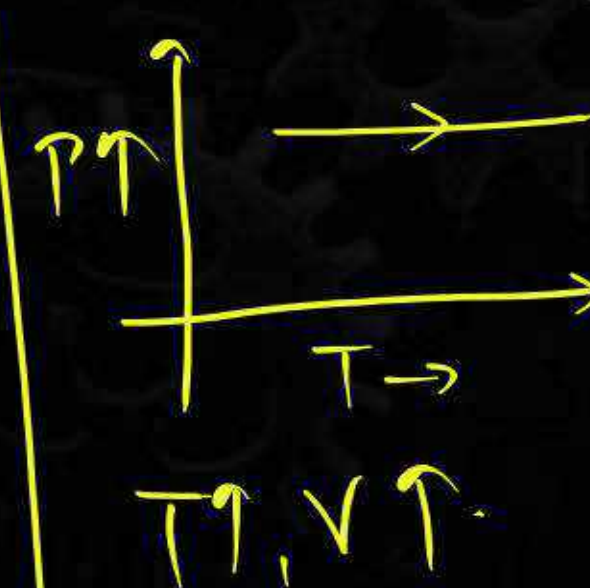
Charles's law $\Rightarrow$

$$V \propto T(K)$$

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



Isobaric Expansion.





Thermodynamic Process



3. Isochoric Process:

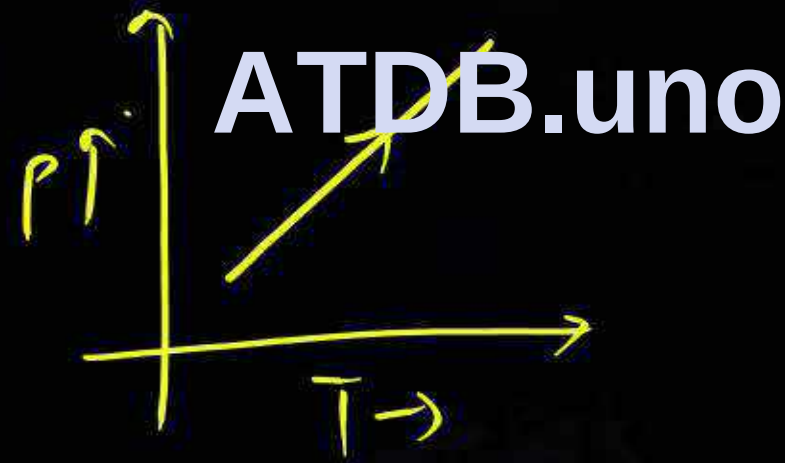
- The process in which volume is kept constant for the entire process, is known as isochoric process.

$$V = \text{Constant}$$

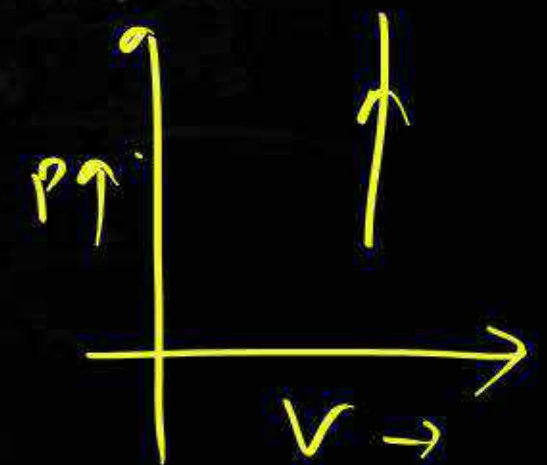
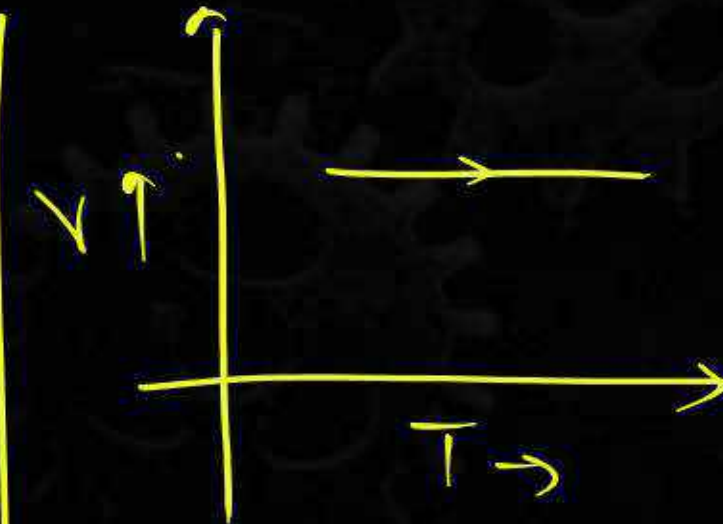
$$dv = 0 \Rightarrow \Delta V = 0$$

$$P \propto T(K)$$

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



Isochoric heating.



$P \uparrow, T \uparrow$

$P \downarrow, T \downarrow \rightarrow \text{cooling}$

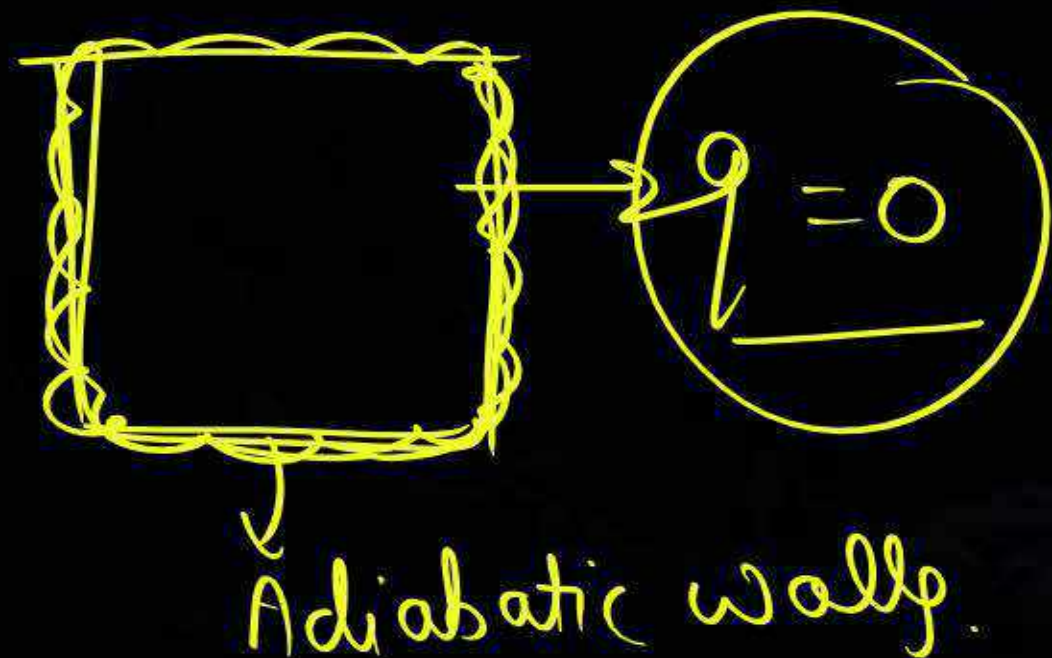


Thermodynamic Process



4. Adiabatic Process:

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



Adiabatic wall.

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

$$\gamma > 1$$

Poisson's Ratio.

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

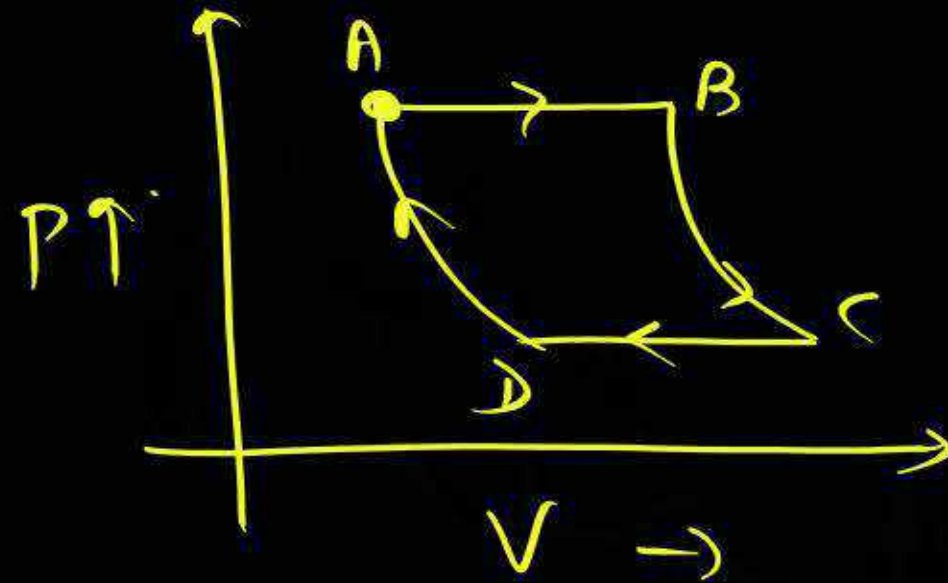


Thermodynamic Process



Cyclic Process:

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



Change in state function = 0.

$$\Delta H = H_2 - H_1$$



Reversible and Irreversible Process



Reversible Process

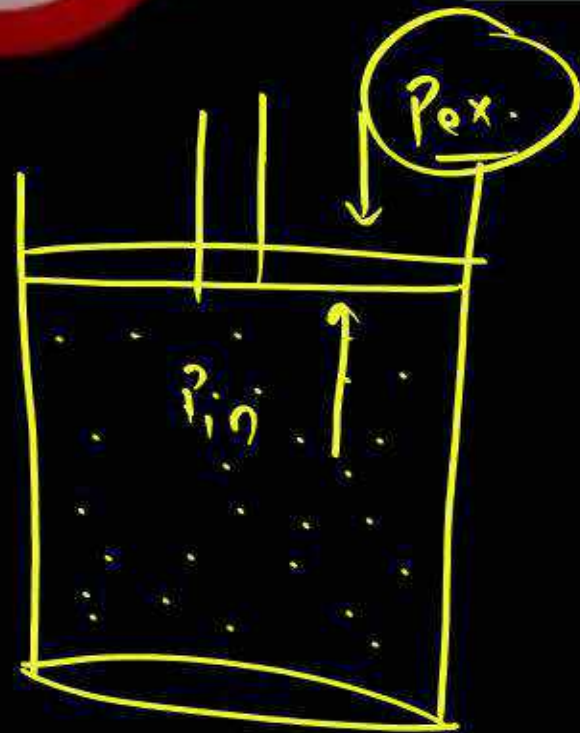
1. It takes place in infinite number of infinitesimally small steps and it would take *infinite time* to occur
2. It is *imaginary* as it assumes the presence of frictionless and weightless piston.
3. It is in equilibrium state at *all stages* of the operation.
4. All changes are *reversed* when the process is carried out in reversible direction.
5. It is extremely slow.

Irreversible Process

1. It takes place *infinite time*.
2. It is *real* and can be performed actually.
3. It is in equilibrium state only at the *initial and final stages* of the operation.
4. After this type of process has occurred all changes *do not return* to the initial state by themselves.
5. It proceeds at *measureable speed*.



Reversible and Irreversible Process



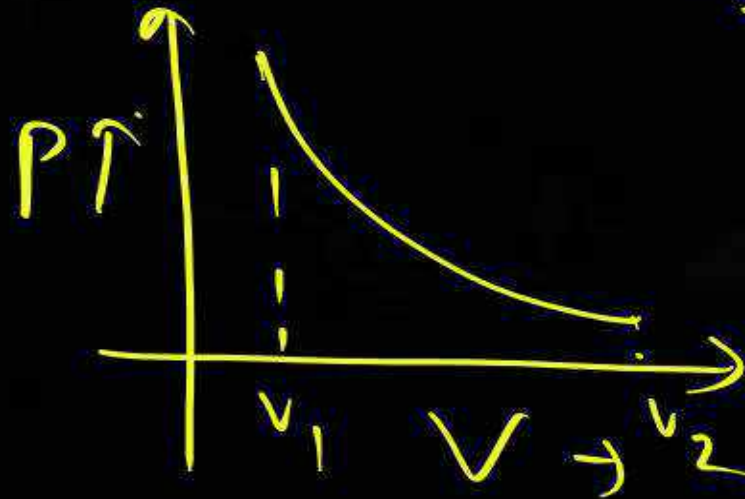
Reversible.

$$P_{ex} = P_{in} \pm dp$$

driving force

negligible ≈ 0

$$P_{ex} \approx P_{in} \quad (P_{gas})$$



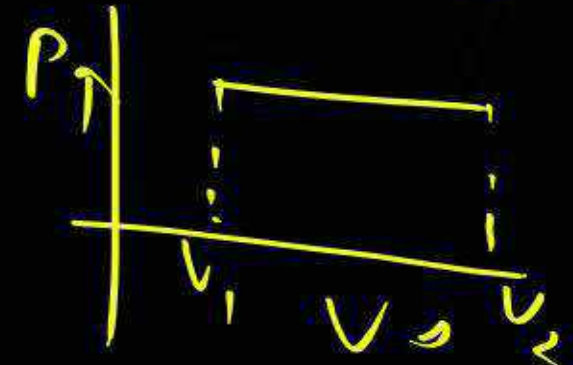
Irreversible :>

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

$$\Delta P \neq 0$$

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

At Constant Pressure





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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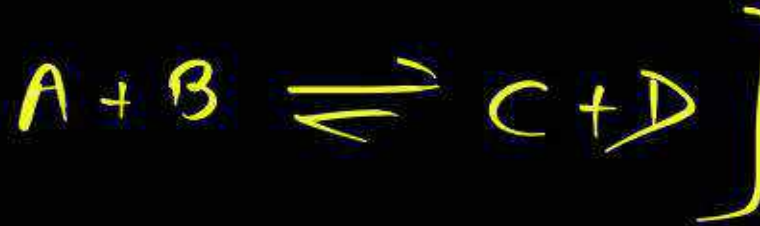
Thermodynamic Equilibrium



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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Work

$$W = mgh.$$

$$W = qV$$

* (P-V) work done.

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

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

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

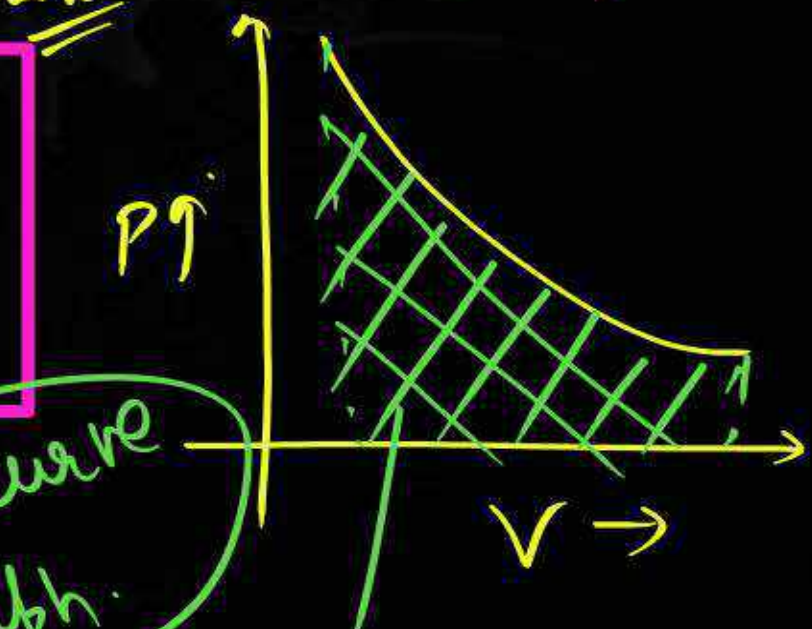
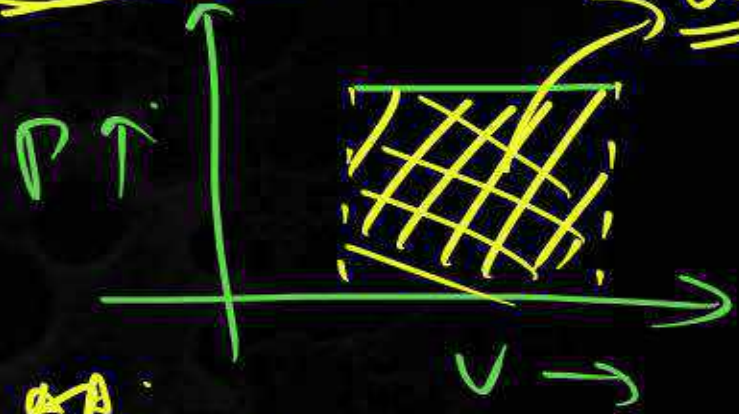
$$W = \int P \cdot dv$$

P-V work.

Chemistry $\rightarrow$

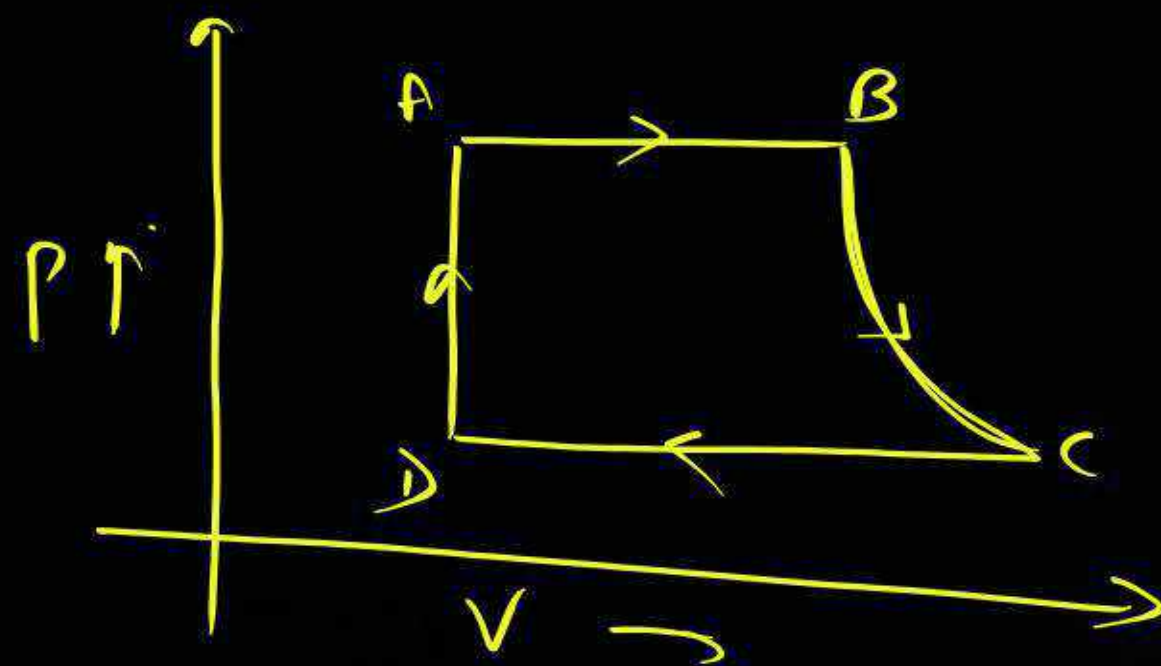
$$W = - \int P_{\text{ox}} \cdot dv$$

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

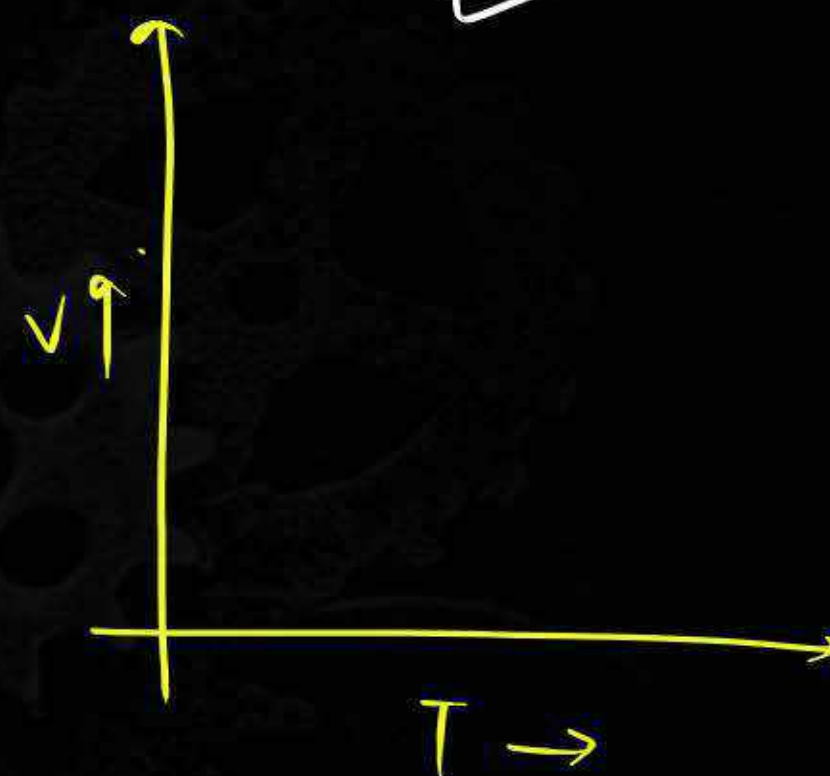
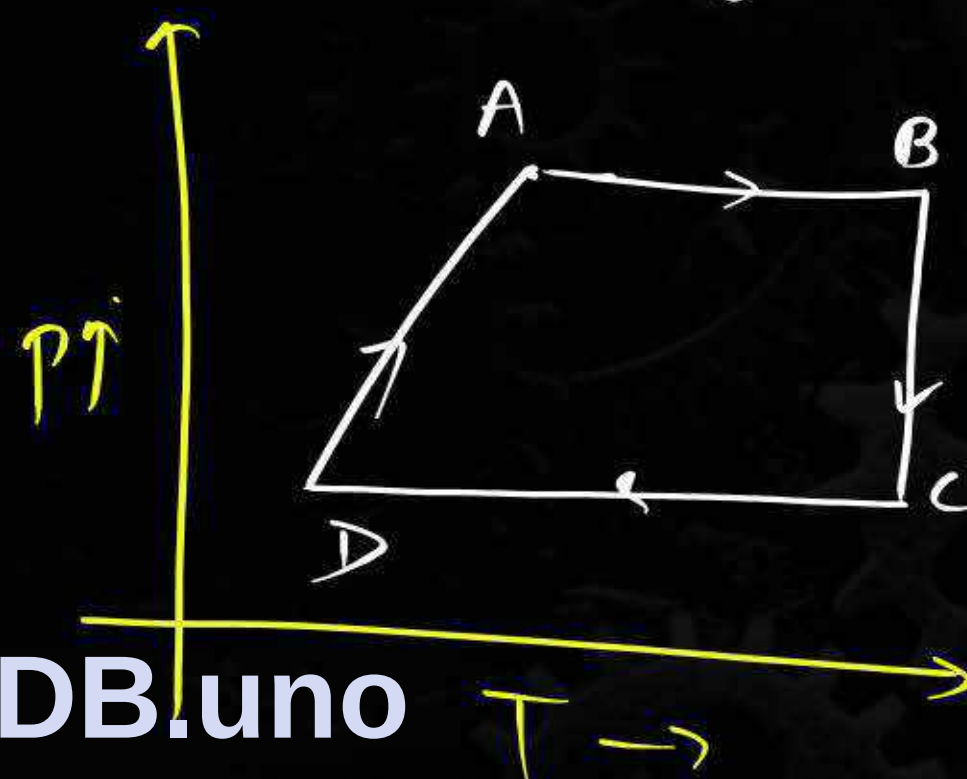


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* Conversion of Graph :-



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

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

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

$$DA \Rightarrow \underline{V=K}, \textcircled{P \propto T}, P \uparrow, T \uparrow$$

How

Question



Which of the following is/are extensive properties?



Entropy ✓



Density ✗



Enthalpy ✓



Boiling point ✗

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Question



Which of the following is/are state function?



Enthalpy ✓



Heat ✗



Entropy ✓



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 $\left[\underline{U} \text{ or } E \right]$



Internal Energy



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

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

Gravational Energy X

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

→ Extensive Property.

$$\Delta U = n C_v (\Delta T)$$

if $\Delta T = 0, \Delta U = 0$ ^{molar heat capacity}

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



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]

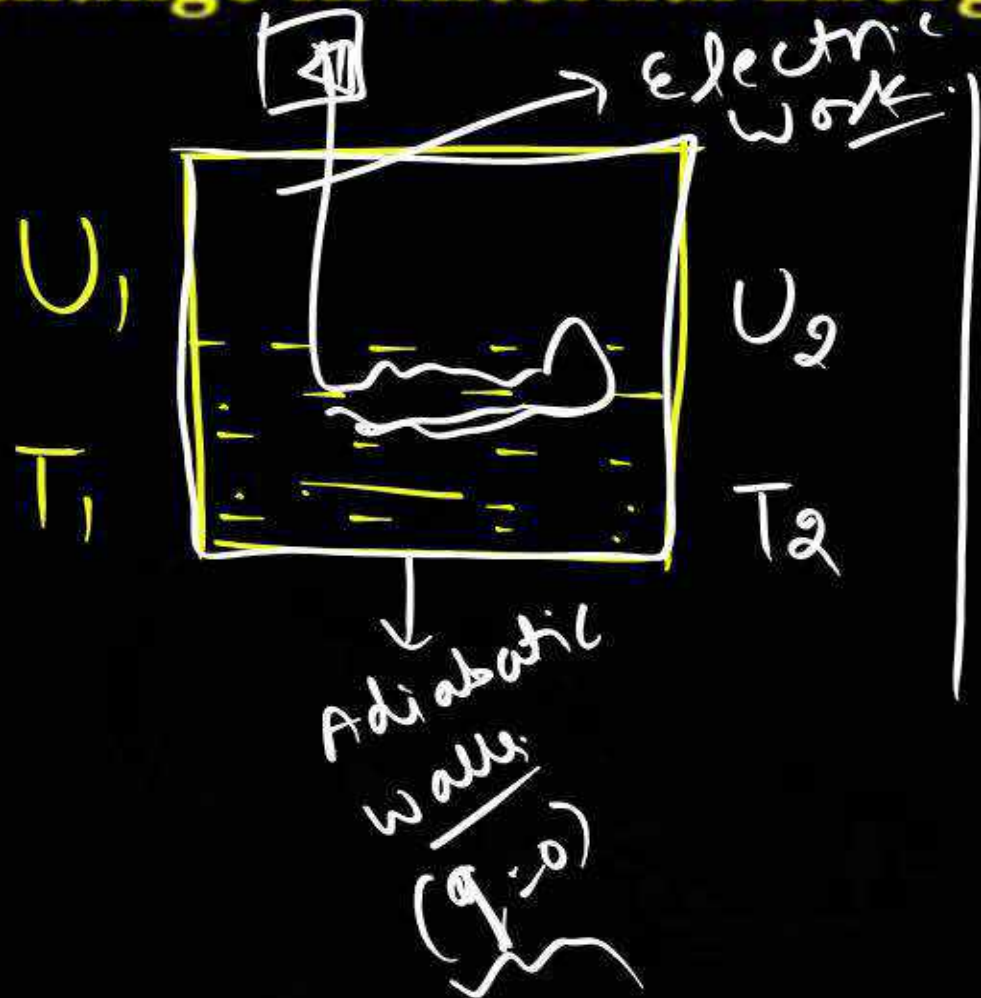
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Internal Energy



Change in Internal Energy by Doing Work:



$$\Delta U = U_2 - U_1$$

$$\Delta U = W_{\text{adiabatic}}$$

Sign Convention :-

Work done by the system $\Rightarrow W = -ve$

Work done on the system $\Rightarrow W = +ve$

* Compression. $P_{\text{ex}} > P_{\text{in}}$
 $\Rightarrow W = +ve$

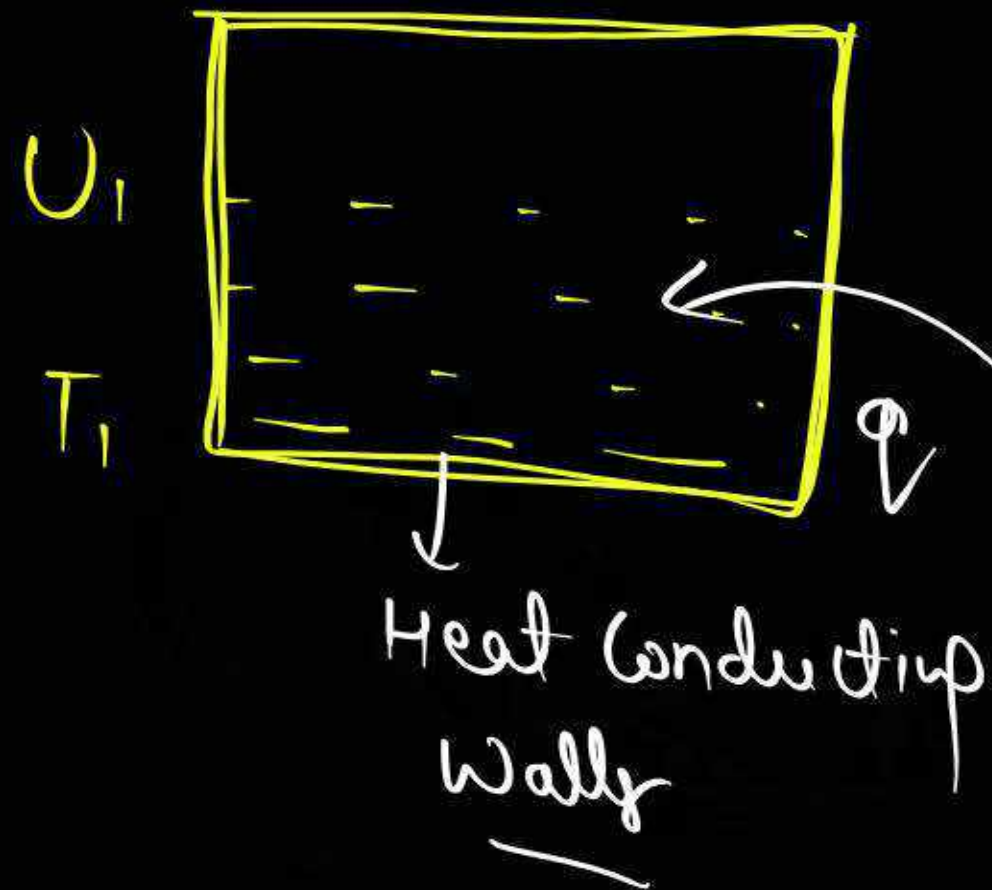
* Expansion [$P_{\text{in}} > P_{\text{ex}}$]
 $\Rightarrow W = -ve$



Internal Energy



Change in Internal Energy by Heat:



$$\Delta U = U_2 - U_1$$

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sign convention

Heat absorbed $\Rightarrow q = +ve$

Heat released $\Rightarrow q = -ve$



General Case:

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

$$\Delta U = q + w$$

→ 1st law of thermodynamics.



Law of energy conservation.



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

$$q = -5\text{ J}$$
$$w = -5\text{ J.}$$

$$\Delta U = q + w$$

$$\Rightarrow -5 + (-5)$$

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

$$\Delta U = (U_2 - U_1)$$

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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.

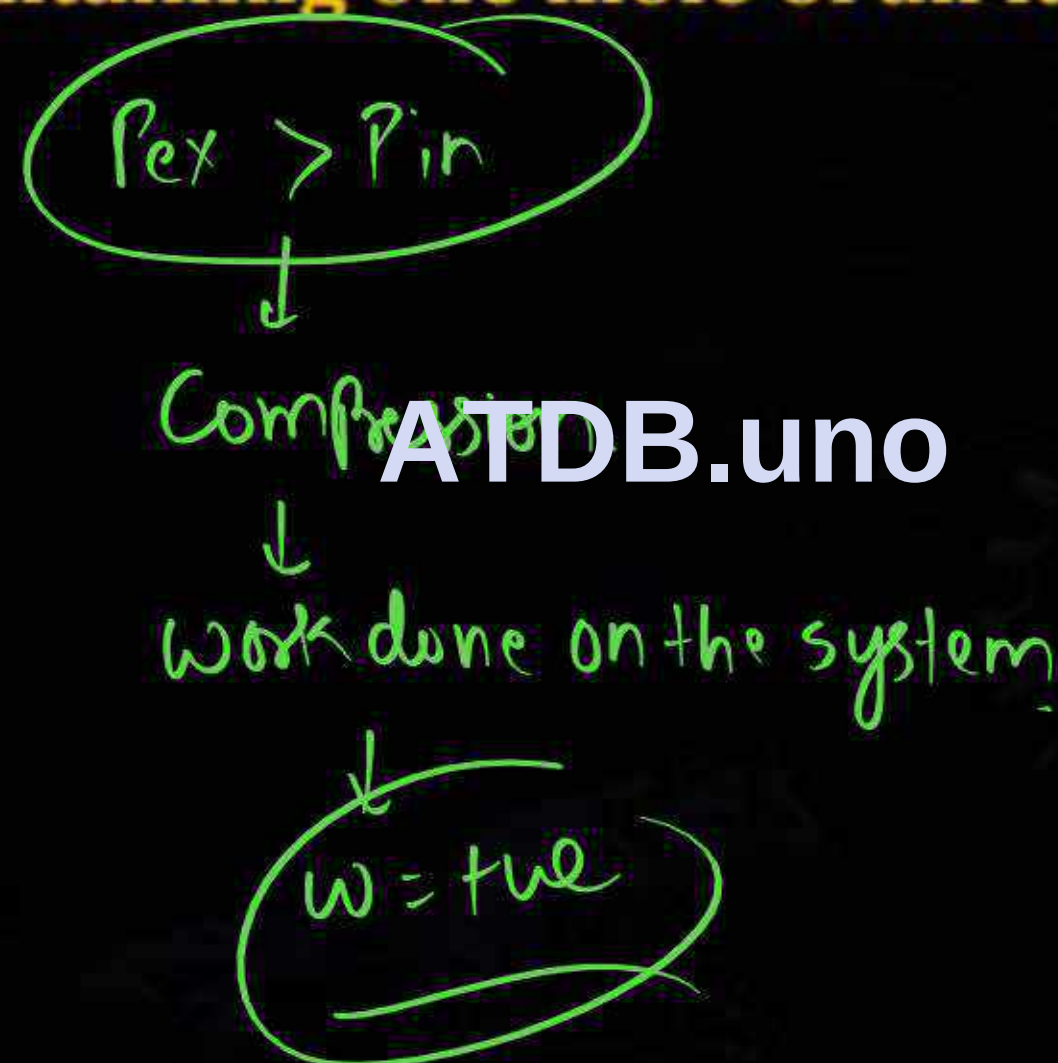


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Question



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?



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 :->

$$W = +10 \text{ kJ}$$

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

$$\Delta U = 10 - 2$$

$$\Rightarrow \underline{8 \text{ kJ}}$$

Ans

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Question



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

(1) $q + W$ $\rightarrow \Delta U$ ~~X~~
(3) W ✓

(2) q ✓
(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

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$\Delta U = W_{ad}$

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 ($R = 8.314 \text{ J/mol K}$, $\ln 7.5 = 2.01$)

(2013 Main)

☒ **A** $q = +208 \text{ J}, W = -208 \text{ J}$

☐ **B** $q = -208 \text{ J}, W = -208 \text{ J}$

☐ **C** $q = -208 \text{ J}, W = +208 \text{ J}$

☐ **D** $q = +208 \text{ J}, W = +208 \text{ J}$

$$q = +208 \text{ J}$$

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

$$\Delta U = 0$$

$$\Delta U = 0$$

$$\Delta U = q + w$$

$$w = -q$$

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



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.

$$\left[\frac{\partial U}{\partial P} \right]_T = 0$$

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$$\left[\frac{\partial U}{\partial V} \right]_T = 0$$

Ideal Gas



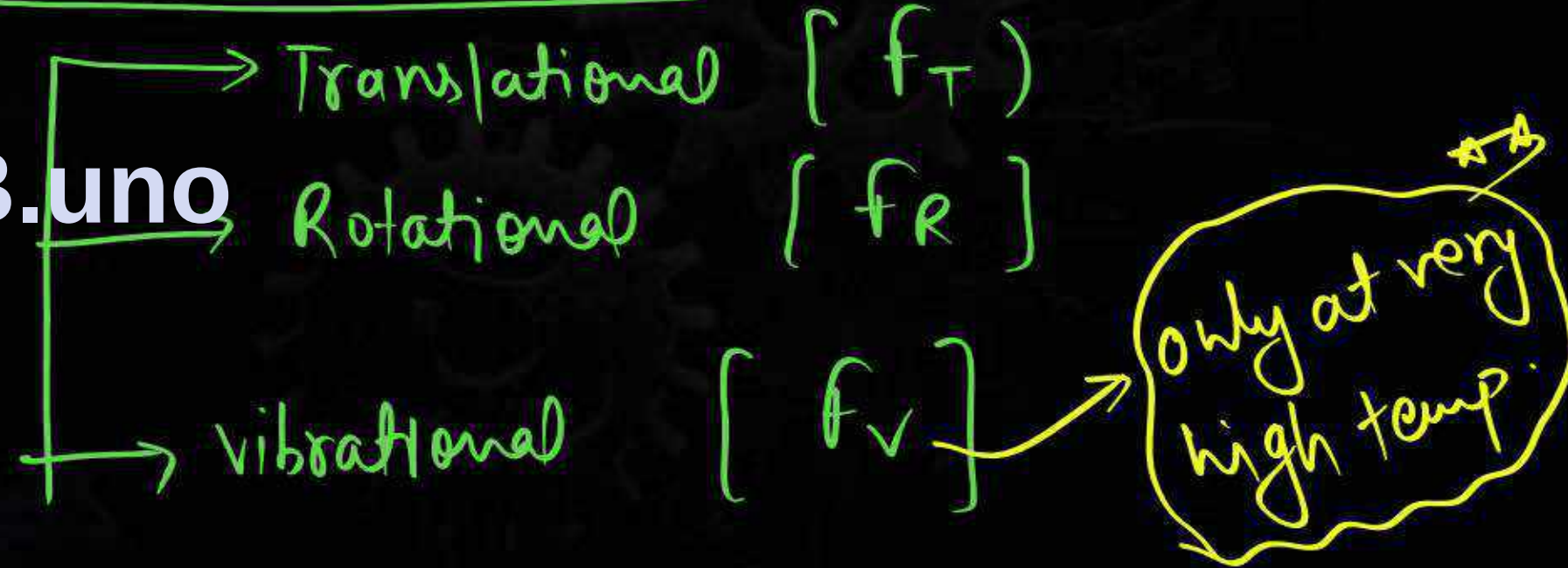
Degree of Freedom

(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.

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

* Rotational D.o.f.

↳ 0 [for monoatomic Gas].

↳ 2 [for Diatomic or linear polyatomic Gas].

↳ 3 [for polyatomic non-linear gas].



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* for monoatomic Gas.

$$f = 3$$

* for Diatomic Gas.

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

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* for Polyatomic Gas:->

$$(a) \text{ Linear } \Rightarrow f = 3 + 2 = \underline{\underline{5}}$$

$$(b) \text{ Non-Linear } \Rightarrow f = 3 + 3 = \underline{\underline{6}}$$



Law of Equipartition of Energy



- Energy equal to $\frac{1}{2} KT$ is associated with each degree of freedom per ideal gas molecule.

→ Boltzmann's Constant

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

for n-moles. $\therefore \rightarrow$

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

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

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

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

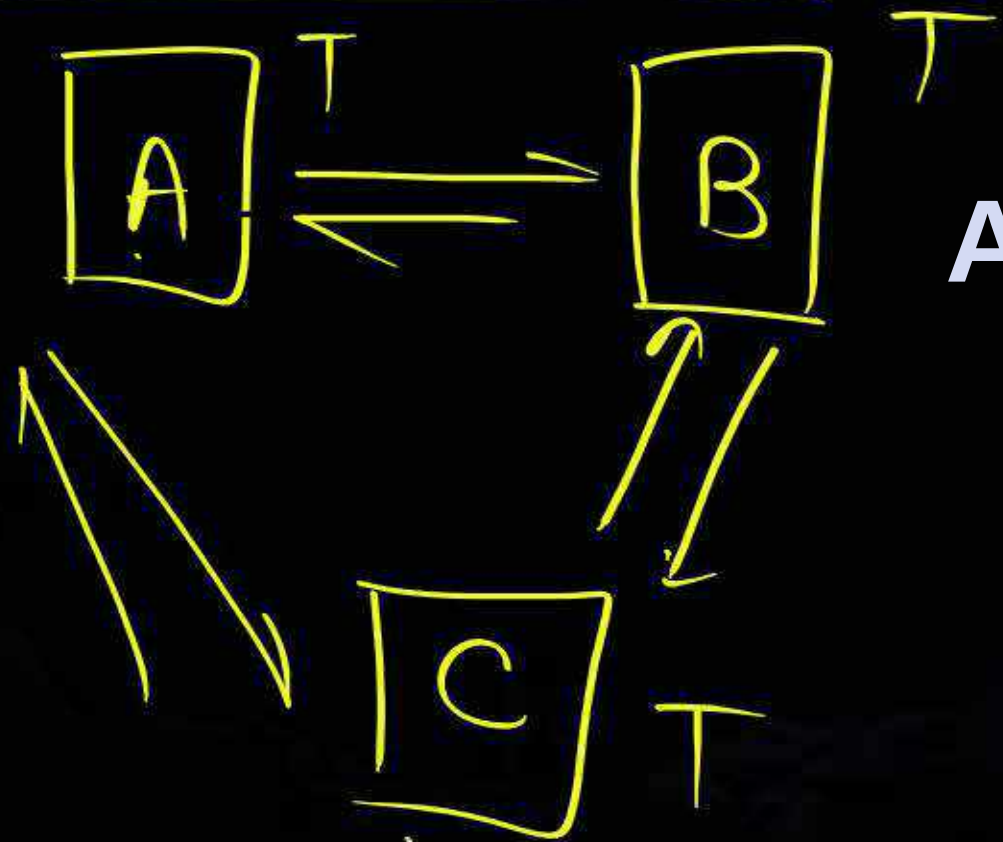
KA



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 $[c]$



Heat Capacity

$$\boxed{\frac{q}{m}}$$

- 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.

$$q \propto \Delta T$$

$$q = C(\Delta T)$$

Heat Capacity.

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

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

$$\Delta T = 1, \quad \underline{C = q}$$

C :- Temp. dependent.

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

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



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),**

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

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

$$q = S$$

$$\text{J kg}^{-1} \text{K}^{-1}$$

$$q = ms(\Delta T)$$

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

↓
temp. dependent.



Heat Capacity



Molar Heat Capacity: $\left[\underline{C_m} \right]$

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

$$C_m = \frac{q}{n(\Delta T)} \quad \text{J mol}^{-1} \text{K}^{-1}$$

$$q = n C_m (\Delta T)$$

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

$$C_p - C_v = R$$

molar heat capacity
at constant P.

molar
heat
capacity
at const.
volume

gas constant



Heat Capacity



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

Ans: $\rightarrow m = 3 \text{ g}$
 $M_w = 27$
 $n = \frac{m}{M_w} = \frac{3}{27} = \frac{1}{9}$
 $T_1 = 25^\circ\text{C}, T_2 = 30^\circ\text{C}$
 $\Delta T = 5$
 $q = 4.5 \times 10^3 \text{ J}$

$S = \frac{q}{m(\Delta T)} = \frac{4.5 \times 10^3}{3 \times 5}$
 $C_m = \frac{q}{n(\Delta T)} = \frac{4.5 \times 10^3}{\frac{1}{9} \times 5}$



Calculation of Work



Work



❖ In Isochoric Process:

$$V = \text{Constant}, dV = 0.$$

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

$$\boxed{W = 0}$$

1st law of thermo.

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

$$\Delta U = q_v = n C_v (\Delta T)$$

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

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



Work



❖ In Isobaric Process:

$$P = \text{constant}, dp = 0$$

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

$$W = - P_{\text{ex}} [V_2 - V_1] \checkmark \checkmark$$

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

$$W_{\text{rev.}} = - P_{\text{gas}} [V_2 - V_1]$$

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$$W_{\text{rev.}} = - [P_{\text{gas}} V_2 - P_{\text{gas}} V_1]$$

$$PV = nRT$$

$$W_{\text{rev.}} = - [nRT_2 - nRT_1]$$

$$W_{\text{rev.}} = nR [T_1 - T_2] \text{ KJ}$$

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) $V = K, w = 0$
 $\Delta U = q + \underline{w}$
 $\Delta U = q$

(d) $\Delta T = 0, \Delta U = 0$
 $\Delta U = q + w$
 $q = -w$



Work

Imp. ^{KA}



❖ In Isothermal Reversible Process:

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

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

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

$$PV = nRT$$

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

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

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

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

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

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

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



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

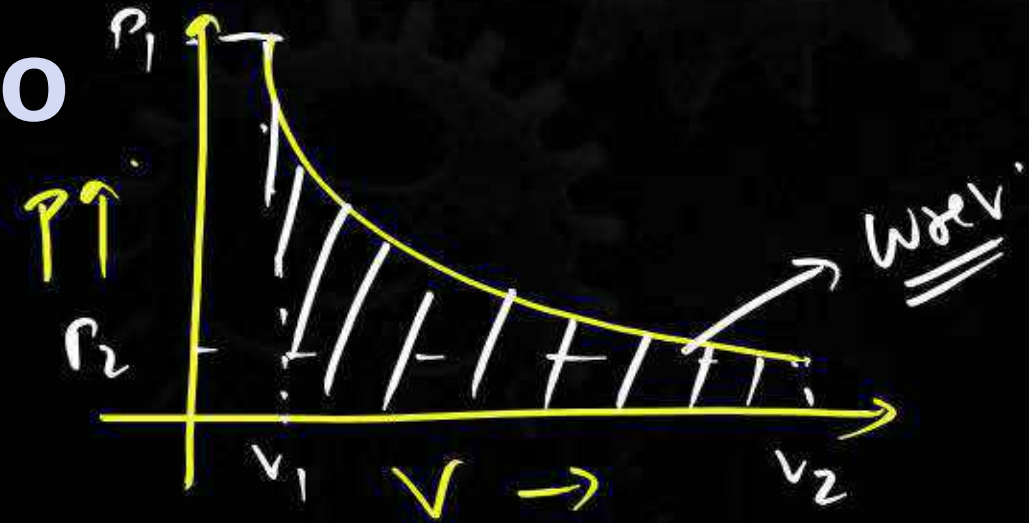
in kelvin.

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

$$P_1 V_1 = P_2 V_2$$

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

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





Work



❖ In Isothermal Irreversible Process:

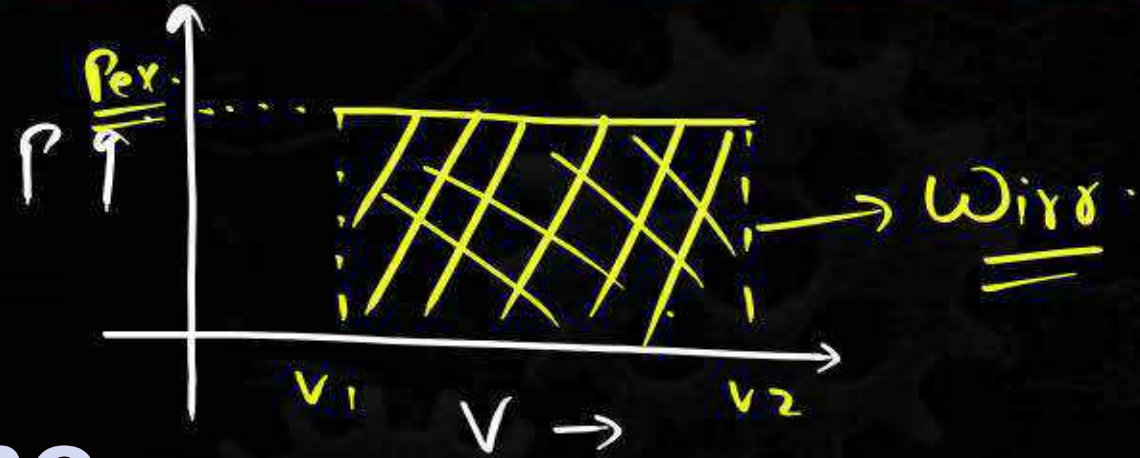
$$W_{irr.} = -P_{ex} (V_2 - V_1)$$

$$PV = nRT$$

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

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

At constant external pressure.



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

* Expansion → ————— जो कम → P_{ex} .



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]



Comparison of Work Done



❖ In Isothermal Expansion:

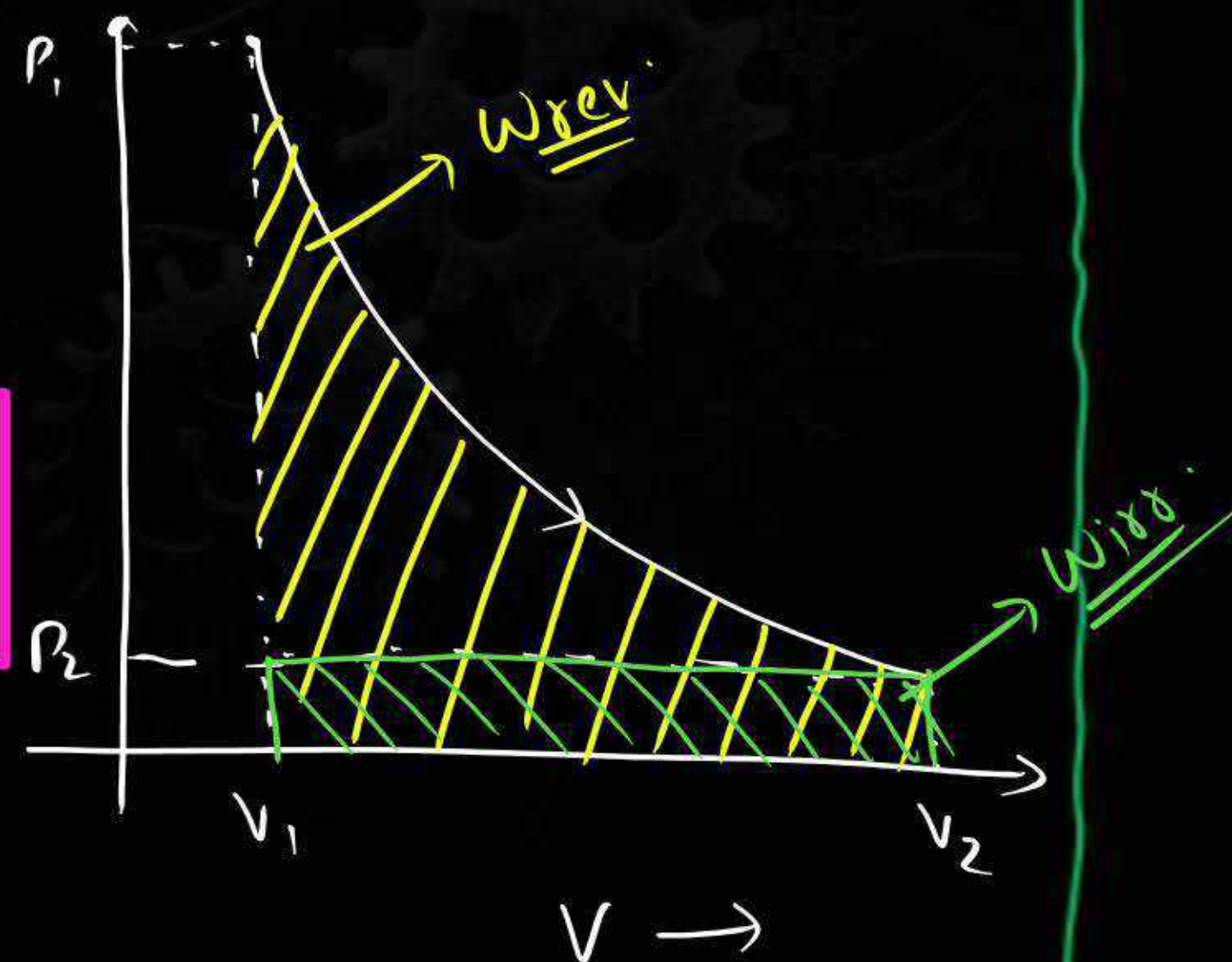
$$W_{rev} = - \int P_{ex} \cdot dV$$

$$W_{irr} = - P_{ex} (V_2 - V_1) \\ = - P_2 (V_2 - V_1)$$

AA

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

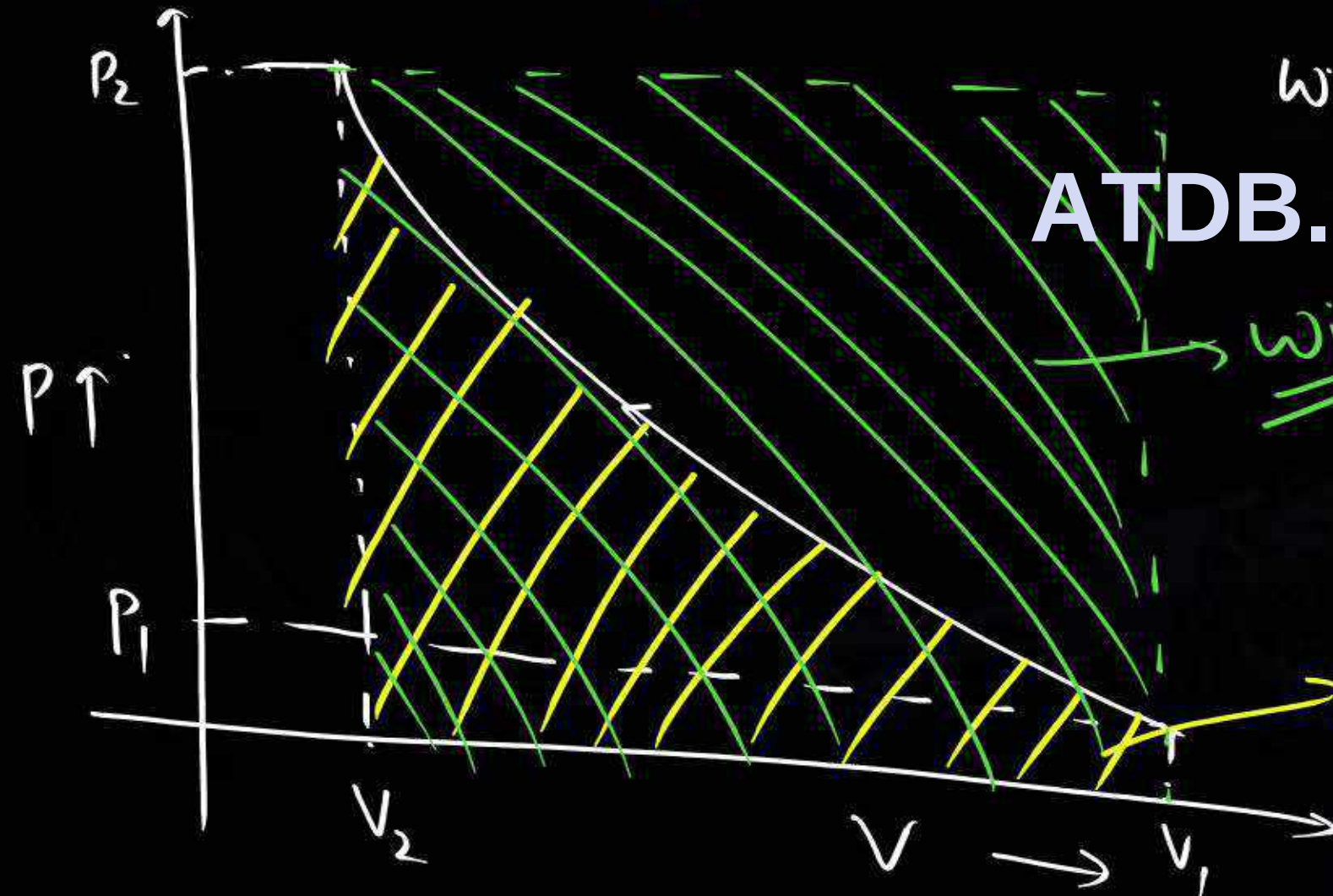




Comparison of Work Done



❖ In Isothermal Compression:



$$W_{rev} = - \int P_{ex} \cdot dV$$
$$W_{irr} = - P_{ex} (V_2 - V_1)$$
$$ATDB.uno - P_2 (V_2 - V_1)$$

W_{irr}

W_{rev}

$$W_{irr} > W_{rev}$$

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: $\rightarrow$

$$n = 1$$

$$V_1 = 1 \text{ L}$$

$$V_2 = 5 \text{ L}$$

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

$$= -1 (5 - 1)$$

$$\Rightarrow -4 \text{ atm-L}$$

$$1 \text{ atm-L} \Rightarrow 101.3 \text{ J}$$

$$-4 (101.3) \text{ J}$$

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.

Ans :- $n = 1$
 $V_1 = 5$
 $V_2 = 10$
 $T = 300 \text{ K}$

$$W_{\text{rev}} = -2.303 nRT \log_{10} \left(\frac{V_2}{V_1} \right)$$
$$\Rightarrow -2.303 \times 1 \times 8.314 \times 300 \log \left(\frac{10}{5} \right) \text{ J}$$

$\log_{10} 2 \Rightarrow 0.3010$

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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 ($R = 2 \text{ cal}$)

-  **A** 500 kcal
-  **B** 15.1 kcal
-  **C** 25.03 kcal
-  **D** 2.303 kcal

$$T = 500 \text{ K}$$

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

$$W_{\text{rev.}} = - 2.303 n R T \log \left(\frac{V_2}{V_1} \right)$$

$\rightarrow 2 \text{ cal K}^{-1} \text{ mol}^{-1}$

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

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

$$\Rightarrow 2.303 \times 1000 \text{ cal}$$

$$\Rightarrow 2.303 \text{ K} \cdot \text{cal}$$



Work Done in Free Expansion



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

$$P_{\text{ex}} = 0$$

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

$$W = 0$$

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Work Done in Free Expansion



Isothermal Free Expansion:

$$\Delta T = 0$$

$$\Delta U = n C_V \Delta T$$

$$\Delta U = 0$$

$$P_{\text{ex}} = 0$$

$$W = 0$$

$$\text{FLOT} \rightarrow \Delta U = q + w$$

$$\downarrow$$

$$0$$

$$q = -w$$

$$q = 0$$

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$$q = 2.303 n R T \log \left(\frac{V_2}{V_1} \right)$$

OR

$$q = 2.303 n R T \log \left(\frac{P_1}{P_2} \right)$$



Work Done in Free Expansion



Adiabatic Free Expansion:

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

$$q = 0$$

$$\Delta U = q + w$$

$$\boxed{\Delta U = 0}$$

$$nC_V(\Delta T) = 0$$

$$\boxed{\Delta T = 0}$$

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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 : $\rightarrow P_{\text{ex}} = 0, w = 0$

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

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

$$\boxed{q = 0}$$

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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 $\Rightarrow q = +300 \text{ J}$

$$V_1 = 2 \text{ L}$$

$$V_2 = 3 \text{ L}$$

$$\Delta U = ?$$

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

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

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Question



ΔU is equal to

 **A** Adiabatic work

The diagram for option A shows a circle with a dashed outer boundary and a solid inner boundary. Arrows on the dashed boundary point outwards, and arrows on the solid boundary point inwards. A green checkmark is drawn over the letter 'A'.

 **B** Isothermal work

The diagram for option B shows a circle with a dashed outer boundary and a solid inner boundary. Arrows on the dashed boundary point outwards, and arrows on the solid boundary point inwards.

 **C** Isochoric work

The diagram for option C shows a circle with a dashed outer boundary and a solid inner boundary. Arrows on the dashed boundary point outwards, and arrows on the solid boundary point inwards.

 **D** Isobaric work.

The diagram for option D shows a circle with a dashed outer boundary and a solid inner boundary. Arrows on the dashed boundary point outwards, and arrows on the solid boundary point inwards.

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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: $R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\log 2 = 0.3010$]

Ans : $\rightarrow n = 5$

$T = 300 \text{ K}$

$V_1 = 10 \text{ L}$

$V_2 = 20 \text{ L}$

$$W_{\text{rev}} = -2.303 n R T \log \left(\frac{V_2}{V_1} \right)$$

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

$\rightarrow 0.3010$

Ans. [8360]

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]

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** $+ 10.0$

H/w

 **C** $- 0.9$

 **D** $- 2.0$

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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 $24 \text{ J mol}^{-1}\text{K}^{-1}$, the temperature of Al increases by (2019 Main, 10 Jan II)



A $\frac{3}{2} \text{ K}$

$V_1 = 5 \text{ m}^3$
 $V_2 = 1 \text{ m}^3$
 $P_{\text{ext}} = 4 \text{ N/m}^2$

$\Delta U = 0$
 $q = -w$

$w_{\text{irr.}} = -P_{\text{ex}}(V_2 - V_1)$
 $w_{\text{irr}} = -4(4) = +16 \text{ J}$
 $q = -16 \text{ J}$



B 1 K

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C 2 K

$w_{\text{irr.}} = -P_{\text{ex}}(V_2 - V_1)$
 $w_{\text{irr}} = -4(4) = +16 \text{ J}$
 $q = -16 \text{ J}$



D $\frac{2}{3} \text{ K}$

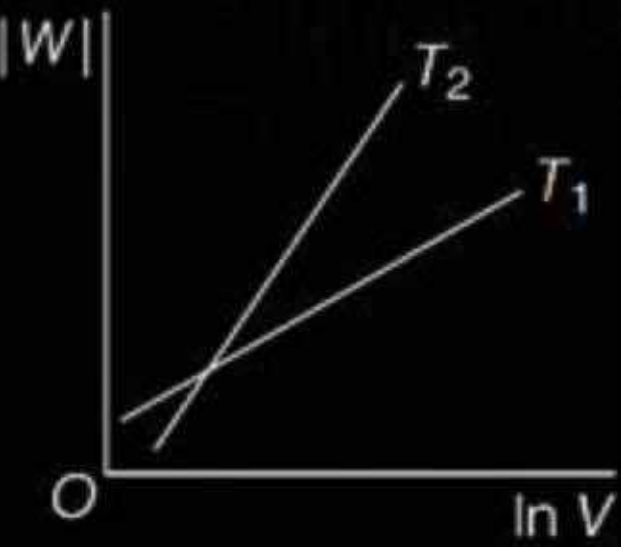
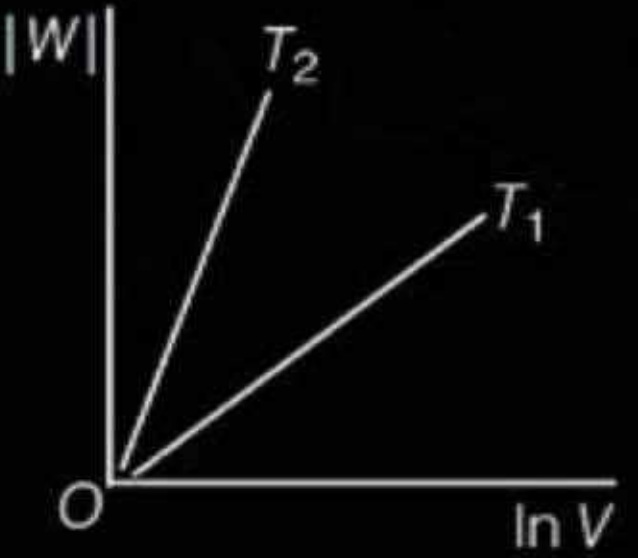
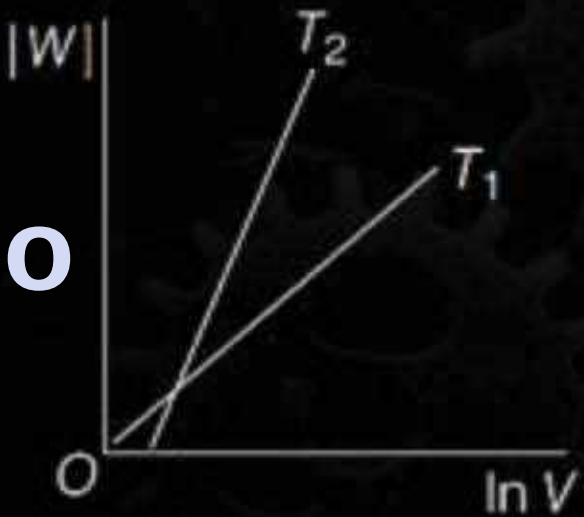
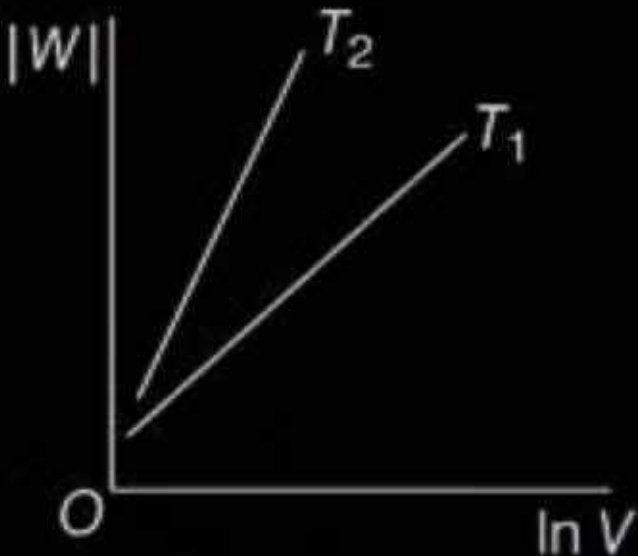
$$\Delta T = \frac{16}{24} \Rightarrow \frac{2}{3}$$

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





Poisson's Ratio

(γ)



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

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

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$$C_p - C_v = R$$

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

- $C_v = f/2R$



Poisson's Ratio



① for monoatomic gas $\rightarrow$

$$f = 3$$

$$C_v = \frac{3}{2}R, \quad C_p = \frac{5}{2}R$$

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3}$$

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

② for diatomic gas $\rightarrow$ and linear polyatomic gas

$$f = 5$$

$$C_v = \frac{5}{2}R, \quad C_p = \frac{7}{2}R$$

$$\gamma = \frac{C_p}{C_v} = \frac{7}{5}$$

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



Poisson's Ratio



③ for non-linear polyatomic Gas :->

$$f = 6$$

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

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

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

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$$\gamma > 1$$



Work Done in Adiabatic Reversible Process



$$\underline{q = 0}$$

$$dU = dq + dw$$

$$dw = dU$$

$$dw = nC_v dT$$

$$w = nC_v [T_2 - T_1]$$

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

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

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



Work Done in Adiabatic Reversible Process



for Reversible adiabatic process: >

$$PV^\gamma = K$$

$$TV^{\gamma-1} = K$$

$$P^{1-\gamma} T^\gamma = K$$

$$[P_1 V_1^\gamma = P_2 V_2^\gamma]$$

$$[T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}]$$

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

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Work Done in Adiabatic Irreversible Process



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

$$PV = nRT$$

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

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

$$W_{irr} = \underbrace{n(V(T_2' - T_1))}_{\text{work done}}$$

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



Note



work done by the system.

For Adiabatic Expansion (Both reversible and irreversible)

$$\underline{W < 0}$$

$$n C_v (T_2 - T_1) < 0$$

$$(T_2 - T_1) < 0$$

$$\boxed{T_2 < T_1}$$

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temp. decreases



Note



For Adiabatic Compression (Both reversible and irreversible)

$$\underline{W > 0}$$

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

$$(T_2 - T_1) > 0$$

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

Temp increases **
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Question



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

A 133

B 1.67

C 0.67

D 0.33

$$\gamma = 1.67$$

$$TV^p = \text{constant}$$

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

$$p = \gamma - 1$$

$$= 1.67 - 1$$

$$p = 0.67$$

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Ans. 0.67

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 $\frac{P_2}{P_1}$.

Ans: $\rightarrow$ Isothermal.

$$P_1 V_1 = P_2 V_2$$

$$P V = P_1 (2V)$$

$$P_1 = \frac{P}{2}$$

(r)

Adiabatic.

$$P V^r =$$

$$P_1 V_1^r = P_2 V_2^r$$

$$P V^r = P_2 [2V]^r$$

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

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

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

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

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

Ans.

$$\frac{1}{2^{0.67}}$$

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 ($C_v = 12.5 \text{ J/K/mole}$).

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

$n = 2$
 $T_1 = 300$

$T_2 = 200 \text{ K}$

$C_v = 12.5$

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

Ans

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Ans. -12.5 kJ

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 ($C_v = 20 \text{ JK}^{-1}$)



150 K

$$n = 1$$

$$T_1 = 27^\circ\text{C} = 300 \text{ K}$$

$$W = -3 \text{ kJ} \Rightarrow -3000 \text{ J}$$

$$T_2 = ?$$

$$C_v = 20$$

$$W = nC_v(T_2 - T_1)$$

$$-3000 = 1 \times 20 [T_2 - 300]$$

$$-150 = T_2 - 300$$

$$T_2 = 150 \text{ K}$$



100 K



26.85 K



295 K

Ans. A

Question



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

(2019 Main, 8 April II)

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

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

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

D $\Delta U = 14 \text{ kJ}; \Delta(pV) = 18 \text{ kJ}$

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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)



T



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



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



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

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Hw



Enthalpy (H)



Enthalpy

(H)



→ Extensive Property.

→ State function.

$$\Delta H = q_p$$

→ Heat absorbed or released by the system at constant Pressure.

$$\Delta H = n \underset{\substack{| \\ \text{molar heat capacity at constant } p.}}{C_p} (\Delta T)$$

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

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



Enthalpy



$$\Delta H = \Delta U + P(\Delta V)$$

$$PV = nRT$$

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

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

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

$$\Delta n_g = \left[\begin{array}{c} \text{No. of gases moles} \\ \text{of Products} \end{array} \right] - \left[\begin{array}{c} \text{No. of gaseous moles} \\ \text{of Reactants} \end{array} \right]$$



$$\Delta n_g = 1 - 0 \Rightarrow \underline{1}$$

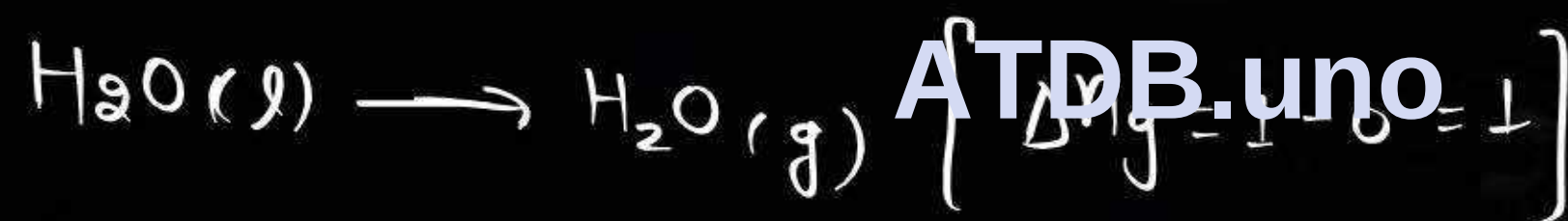
Question



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 :- $\Delta H = 41 \times 10^3 \text{ J/mol.} \quad \left| \quad T = 100^\circ\text{C} = 373 \text{ K} \right|$



$\Delta U = ?$

$\Delta H = \Delta U + \Delta n_g R T$

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

$\Delta U = ?$

Question



For the combustion reaction at 298 K



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

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

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

$\Delta H = \Delta U - RT$

$\Delta U > \Delta H$

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Ans. C

Question



For the reaction,

$\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$ at constant temperature, $\Delta H - \Delta E$ is

$$\Delta H - \Delta U = ?$$

A $-RT$

B RT

C $-3RT$

D $+3RT$

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

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

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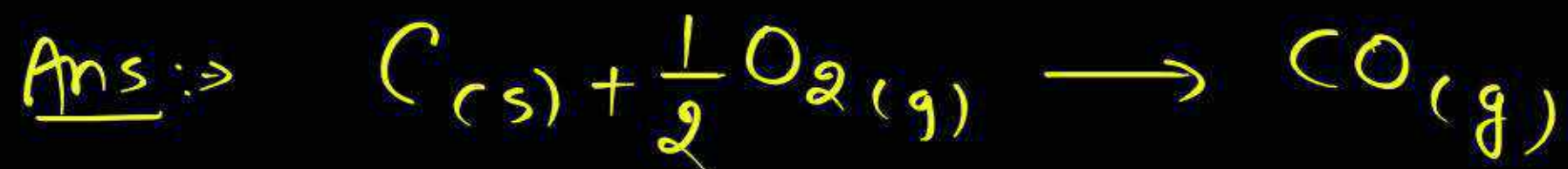
$$\Delta n_g = 3 - 6 = -3$$

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

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 $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$.



$$\Delta n_g = 1 - \frac{1}{2} = 0.5 \quad \text{ATDB.uno}$$

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

$$\Rightarrow 0.5 \times 8.314 \times 298$$

Ans

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 $A_{\text{vap}}H^\ominus$ for water at 373 K and 1 bar is 41.1 kJ mol⁻¹; $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$] (JEE Main 2022 (June) Shift -2)

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Ans. [38]

Question



The difference between ΔH and ΔU ($\Delta H - \Delta U$), 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, $C_p(\text{JK}^{-1} \text{mol}^{-1}) = 23 + 0.01 T$. If the temperature (T) of 3 moles of silver is raised from 300 K to 1000 K at 1 atm pressure, the value of ΔH 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 $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$. Given that heat of combustion of benzene at constant volume is $-3263.9 \text{ kJ mol}^{-1}$ at 25°C ; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be ($R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$) (2018 Main)

A 4152.6

B -452.46

C 3260

D -3267.6



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

$$q_v = \Delta U = -3263.9 \times 10^3 \text{ J}$$

$$q_p = \Delta H = ?$$

$$\Delta H = \Delta U + \Delta n_g R T$$

$$T = 25^\circ\text{C}$$
$$= 298 \text{ K}$$



Measurement Of ATDB.uno: CALORIMETRY



➤ 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 ✓

(b) At constant Pressure

$$q_v = \Delta U$$

$$q_p = \Delta H$$



Measurement of ΔU

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

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

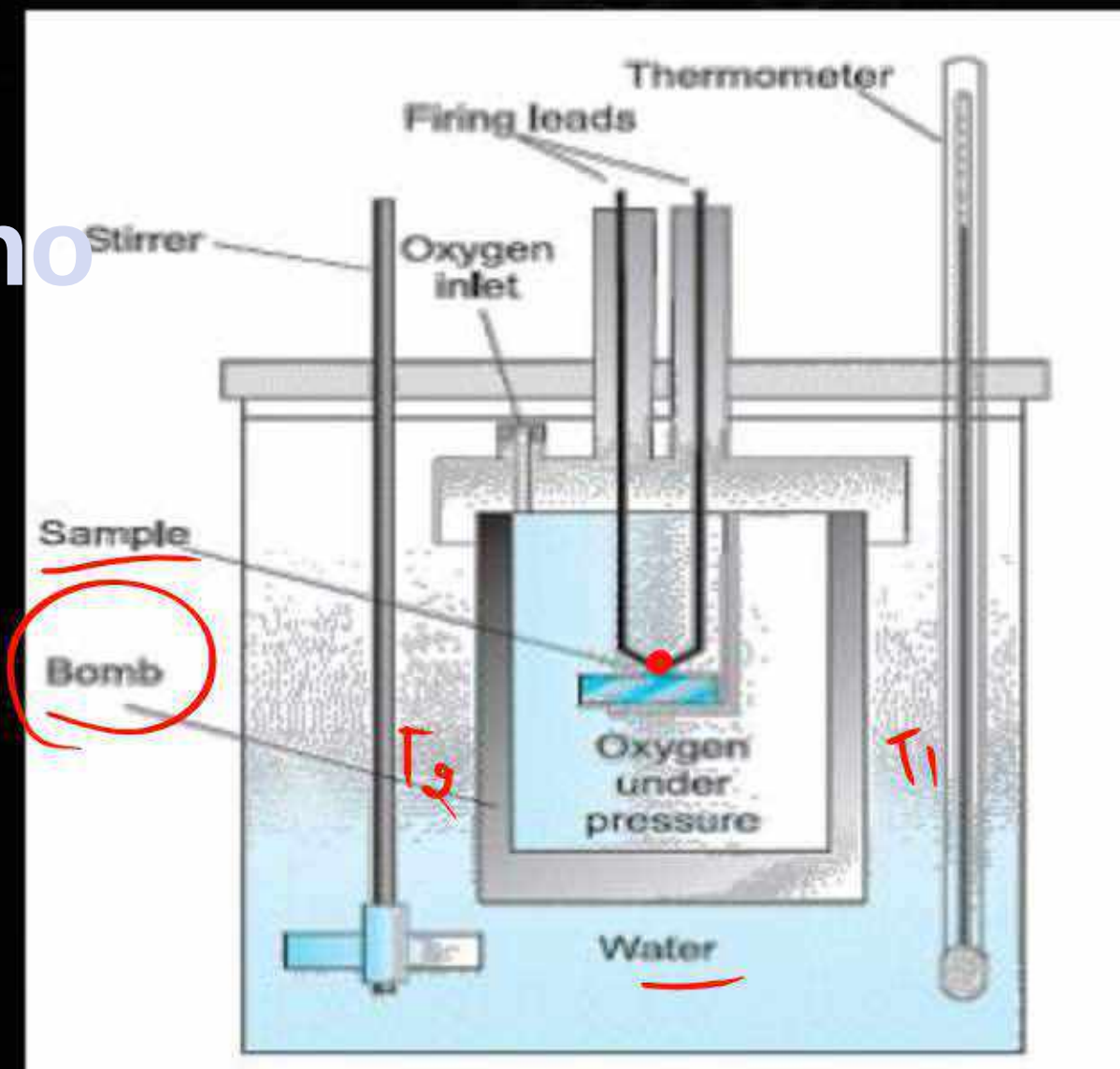
Constant volume calorimeter.

$$\text{Change in temp } (\Delta T) = T_2 - T_1$$

$$q_{\text{comb}} = -[q_{\text{bomb}}]$$

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

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





Measurement of ΔH



$$\Delta H = q_p$$

$$= n C_p (\Delta T)$$

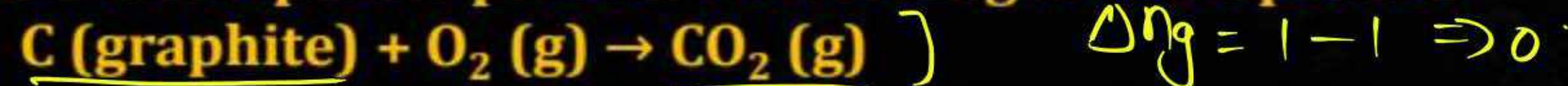
Heat Capacity at Constant Pressure.

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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



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

Ans:→

$$\Delta T = 299 - 298 \Rightarrow 1$$

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

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

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

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$$\Delta H = \Delta U + \Delta n_g R T$$

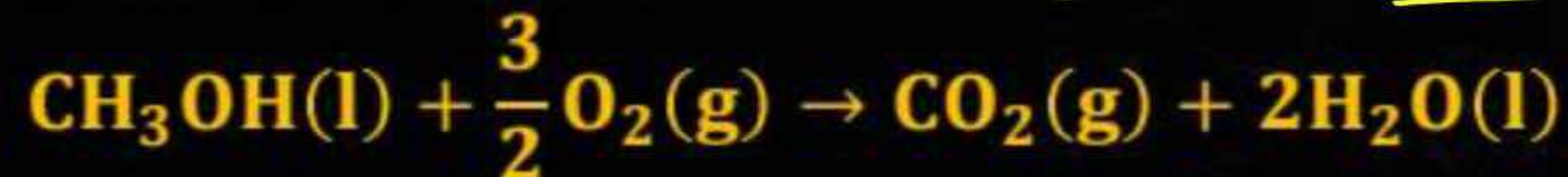
$$\Delta H = \Delta U \quad (\text{Ans})$$

Question



For complete combustion of methanol

(JEE Main 2022 (June) Shift -1)



$$\Delta n_g = 1 - \frac{3}{2} \Rightarrow -\underline{\underline{0.5}}$$

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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$$\underline{\text{Ans}} \Rightarrow \Delta U = -726 \times 10^3 \text{ J}$$

$$\underline{T = 300 \text{ K}}$$

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

Ans. [727]



enthalpy of $R_x^\wedge$ or heat of $R_x^\wedge$

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



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 $\Delta_r H$



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

✓ → $\Delta H = +ve$ [Endothermic Rxn]
(Heat absorbing Rxn)

$\Delta H = -ve$ [Exothermic Rxn]
(Heat releasing Rxn)



Enthalpy of Reaction



$$\Delta_r H = (\text{sum of enthalpies of products}) - (\text{sum of enthalpies of reactants})$$

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

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



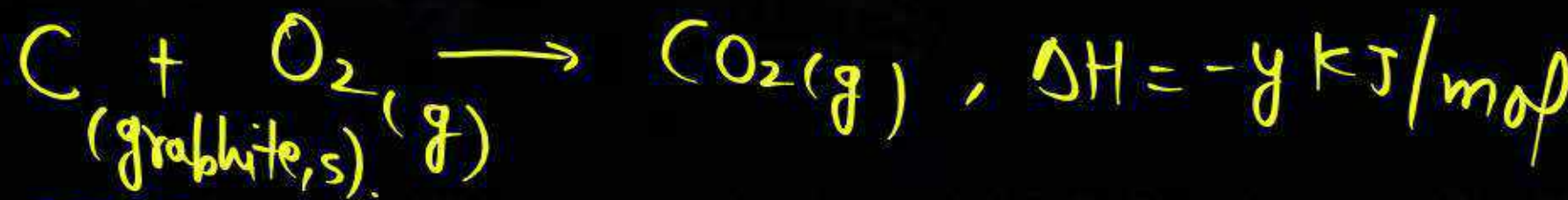
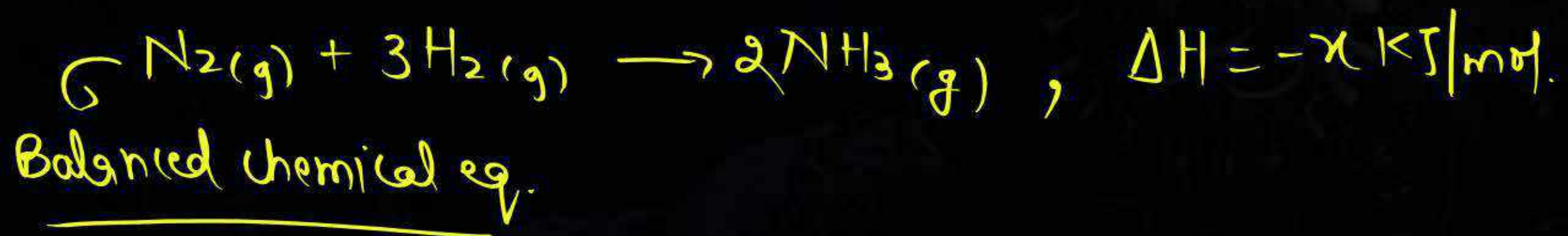
$$\Delta_r H = [1 \times H(\text{CO}_2, \text{g}) + 2 \times H(\text{H}_2\text{O}, \text{l})] - [1 \times H(\text{CH}_4, \text{g}) + 2 \times H(\text{O}_2, \text{g})]$$



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.





Thermochemical Equation



Note:



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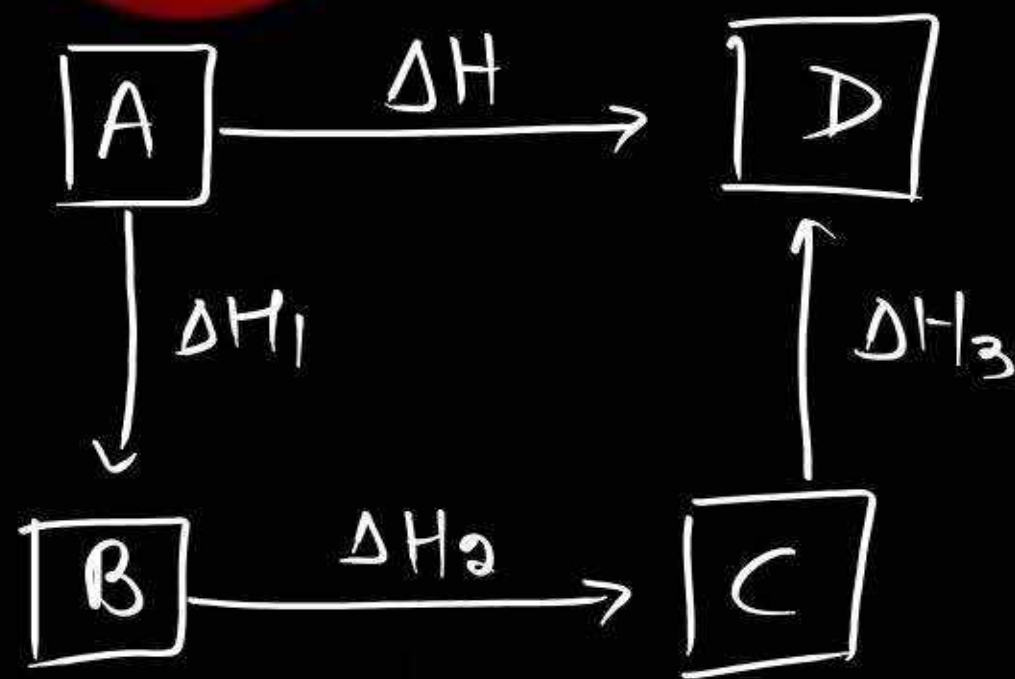
Hess's Law



“ 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.”



Hess's Law



$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$



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Ans

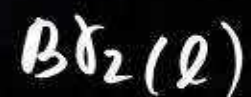
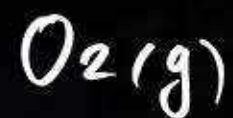
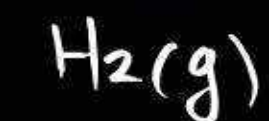


Standard Enthalpy of Reaction



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.



Enthalpy changes during phase transformations



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



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

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,

$$\Delta_{\text{fus}} H^\circ$$

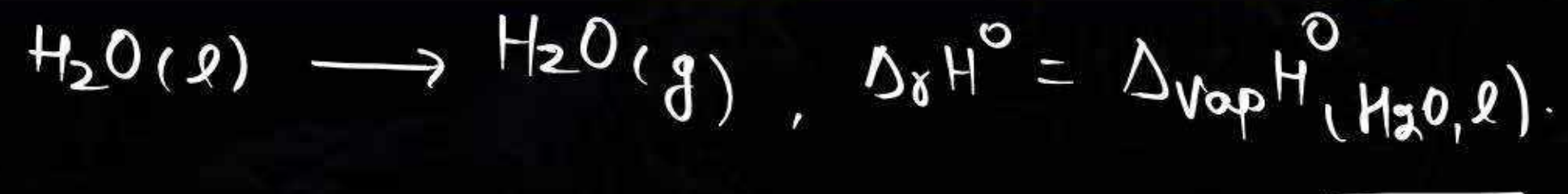


Enthalpy changes during phase transformations



2. Molar Enthalpy of Vaporisation: $[L \rightarrow G]$

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





Enthalpy changes during phase transformations



3. Molar Enthalpy of Sublimation:

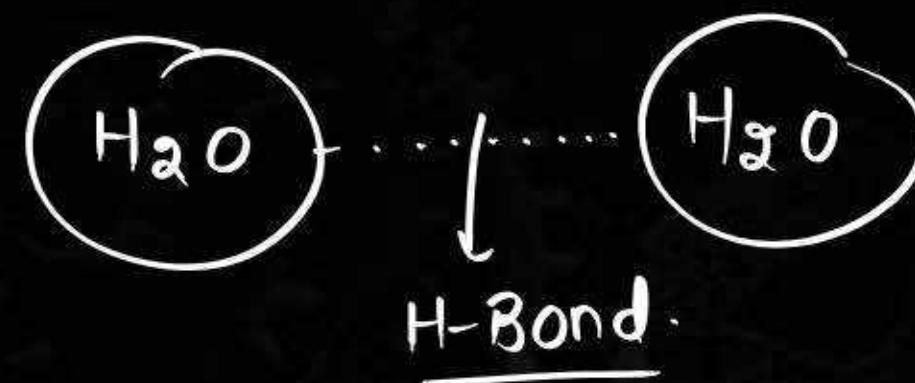
Standard enthalpy of sublimation, $\Delta_{\text{sub}}H^\circ$ is the change in enthalpy when one mole of a solid substance sublimates at a constant temperature and under standard pressure (1bar).





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 $\rightarrow$ H-Bond $>$ van-der waal.

$$* \Delta_{\text{vap}} H^{\circ}(\text{H}_2\text{O}) > \Delta_{\text{vap}} H^{\circ}(\text{Acetone})$$

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.

$\Delta_{\text{vap}} H^\circ$ for water at 373K = 40.66 kJ mol⁻¹

Ans $\Rightarrow$ $w_{\text{H}_2\text{O}} = 18 \text{ g}$ | $T = 100^\circ\text{C} = 373 \text{ K}$
 $n_{\text{H}_2\text{O}} = 1 \text{ mol}$

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$$\Delta H = \Delta U + \Delta n_g \frac{RT}{T}$$

$\Delta U = ?$ 8.314×373

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 100°C. (Given the molar enthalpy of vaporization of water at 1 bar and 373 K = 41 kJ mol⁻¹)

$$\Delta H = 5 \times 41 \text{ kJ}$$

Ans: $n_{\text{H}_2\text{O}} = 5 \text{ mol}$



(11w)



def.

Standard Enthalpy of Formation

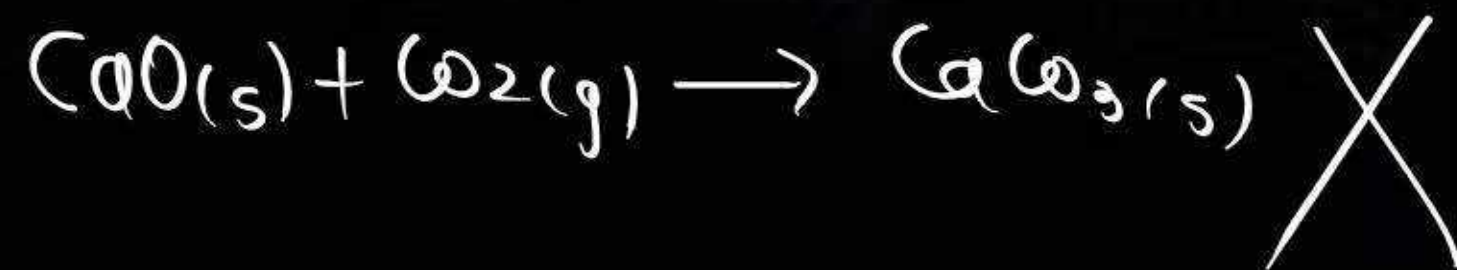
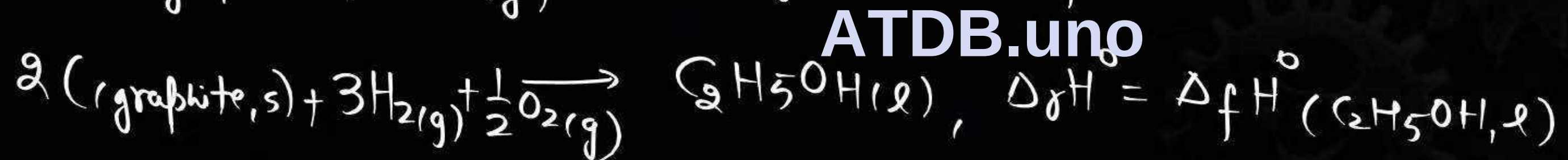
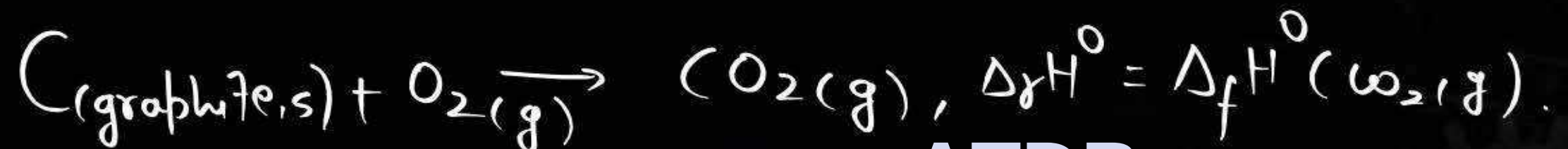


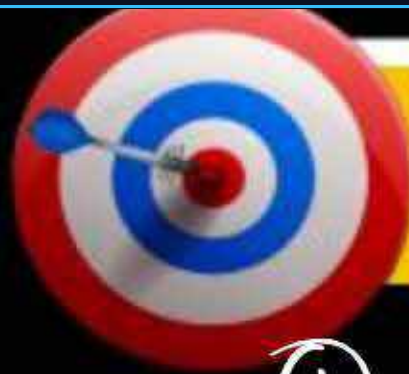
The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called
Standard Molar Enthalpy of Formation.

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Standard Enthalpy of Formation





Standard Enthalpy of Formation

①

Note:

$$\Delta_r H^\circ = \sum b_i \Delta_f H^\circ(\text{Products}) - \sum a_i \Delta_f H^\circ(\text{Reactants})$$

Standard enthalpy
of Rxn

a_i stoichiometric coeff.

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

$$\Delta_f H^\circ(\text{H}_2, \text{g}) = 0$$

$$\underline{\Delta_f H^\circ(\text{N}_2, \text{g}) = 0.}$$

Question



Enthalpies of formation of CO(g) , $\text{CO}_2\text{(g)}$, $\text{N}_2\text{O(g)}$ and $\text{N}_2\text{O}_4\text{(g)}$ are -110 , -393 , 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction:



Ans $\Rightarrow \Delta_r H^\circ = \left[1 \times \Delta_f H^\circ(\text{N}_2\text{O}, \text{g}) + 3 \times \Delta_f H^\circ(\text{CO}_2, \text{g}) \right] - \left[1 \times \Delta_f H^\circ(\text{N}_2\text{O}_4, \text{g}) + 3 \times \Delta_f H^\circ(\text{CO}, \text{g}) \right]$

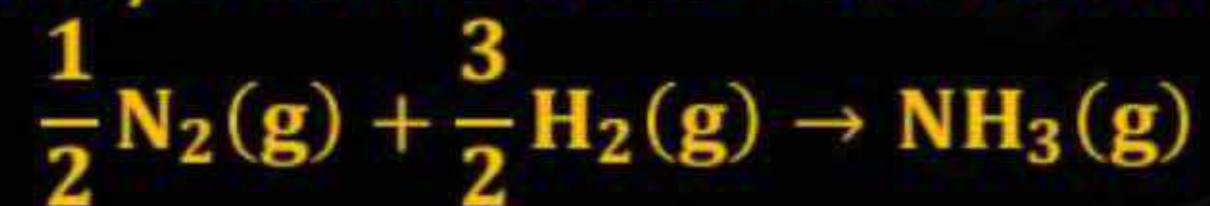
$\Delta_r H^\circ = ?$
(Ans)

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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



Ans $\Rightarrow$

$$\Delta_r H^\circ = \left[\Delta_f H^\circ(\text{NH}_3) \right] - \left[\frac{1}{2} \times \Delta_f H^\circ(\text{N}_2(\text{g})) + \frac{3}{2} \times \Delta_f H^\circ(\text{H}_2(\text{g})) \right]$$

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

$$\Delta_r H^\circ = -11.02 \text{ kcal/mol}$$

Question



The standard heats of formation of at 298 K for $\text{CCl}_4(\text{g})$, $\text{H}_2\text{O}(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{HCl}(\text{g})$ are -25.5 , -57.8 , -94.1 and $-22.1 \text{ kcal mol}^{-1}$ respectively. Calculate $\Delta_r H^\ominus$ for the reaction

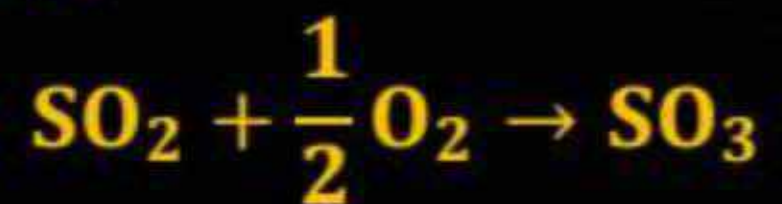


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Question



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



-200 kJ



-356.2 kJ



$+200 \text{ kJ}$



-396.2 kJ



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Ans. C



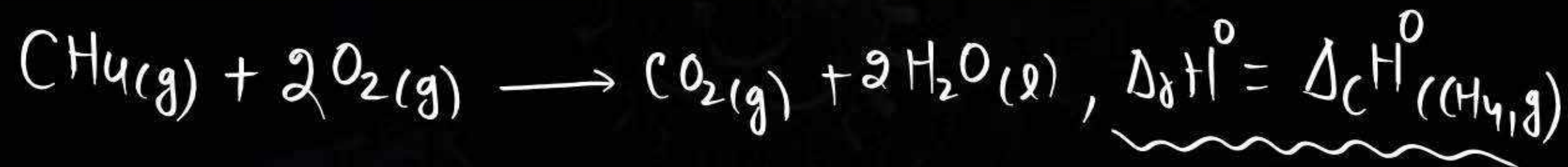
Standard Enthalpy of Combustion

$(\Delta_c H^\circ)$



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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Standard Enthalpy of Combustion

$$\Delta_c H^\circ (\text{C}_6\text{H}_{12}\text{O}_6) = -300 \text{ kJ/mol.}$$

$$1 \text{ mol glucose} \rightarrow 300 \text{ kJ}$$

$$180 \text{ g. glucose} \rightarrow 300 \text{ kJ.}$$

$$1 \text{ g. Glucose} \rightarrow \frac{300}{180} \text{ kJ}$$

Calorific value.

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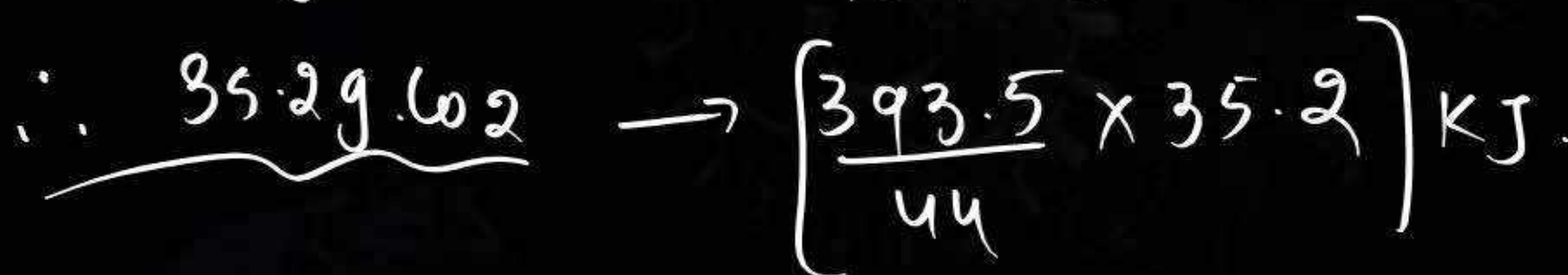
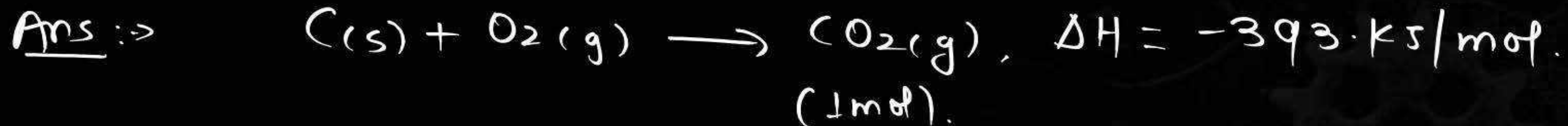
Calorific Value – It may be defined as the heat produced when 1 gram of the substance is completely burnt in excess of oxygen.

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

Question



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



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 $\Rightarrow \therefore 1 \text{ km} \rightarrow 150 \text{ KJ}$.

$\therefore 5 \text{ km} \rightarrow 150 \times 5 \rightarrow 750 \text{ KJ}$

1 mol Glucose $\rightarrow 3000 \text{ KJ}$

180g. Glucose $\rightarrow 3000 \text{ KJ}$.

Total energy available $\rightarrow 3000 \times \frac{30}{100} \Rightarrow 900 \text{ KJ}$.

$\therefore 900 \text{ KJ Energy} \rightarrow 180 \text{ g. Glucose}$

$\therefore 750 \text{ KJ Energy} \rightarrow \frac{180}{900} \times 750$

$\frac{5}{5} \rightarrow 150 \text{ g}$
Glucose.

Question



An athlete is given 180 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$). 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 $-2800 \text{ kJ mol}^{-1}$ and enthalpy of evaporation of water is 44 kJ mol^{-1} .



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Ans. 572.73 g

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 $\text{CH}_4 = -1665 \text{ kJ mol}^{-1}$).

Hw

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Ans. 69.37

Question



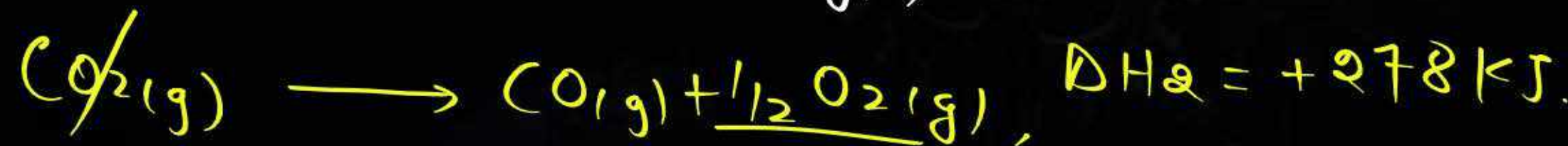
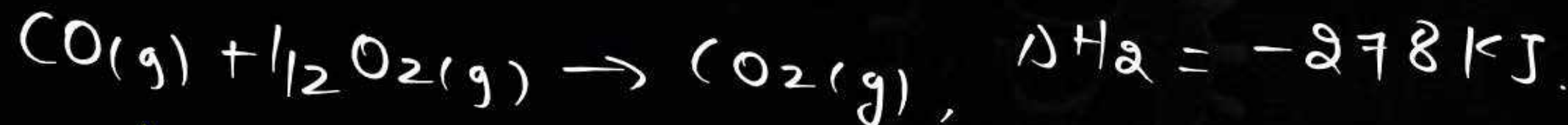
The Enthalpies of combustion of carbon and carbon monoxide are -390 kJ and -278 kJ respectively. The enthalpy of formation of carbon monoxide is

A 669 kJ

B 112 kJ

C -112 kJ

D -668 kJ



Ans. C

Question



At 25°C and 1 atm pressure, the enthalpy of combustion of benzene (l) and acetylene (g) are $-3268 \text{ kJ mol}^{-1}$ and $-1300 \text{ kJ mol}^{-1}$, respectively. The change in enthalpy for the reaction $3\text{C}_2\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{l})$, is $\Delta H = ?$

(JEE Main 2022 (June) Shift -2)

A $+324 \text{ kJ mol}^{-1}$

B $+632 \text{ kJ mol}^{-1}$

C -632 kJ mol^{-1}

D -732 kJ mol^{-1}

$$\Delta_r H^\circ = \sum a_i (H_c)_p - \sum b_i (H_c)_r$$

$$\Delta_r H^\circ = 3 \times \Delta_c H^\circ (\text{C}_2\text{H}_2, \text{g}) - 1 \times \Delta_c H^\circ (\text{C}_6\text{H}_6, \text{l})$$
$$= 3 \times (-1300) - [-3268]$$

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

Question



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

(JEE Main 2022 (June) Shift -2)

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

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Ans. [600]

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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Ans. $[-326400]$

Question



The standard heat of formation ($\Delta_f H_{298}^\circ$) 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)

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Ans. $[-192.5]$

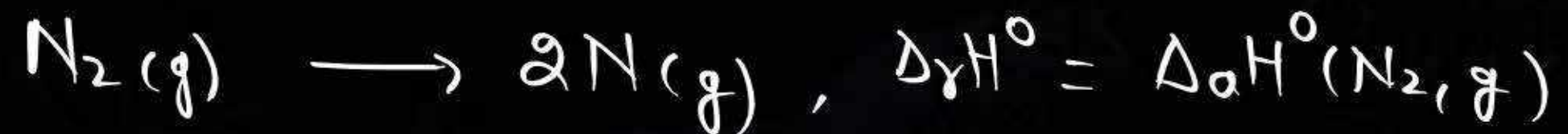


Standard Enthalpy of Atomization

($\Delta_a H^\circ$).



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





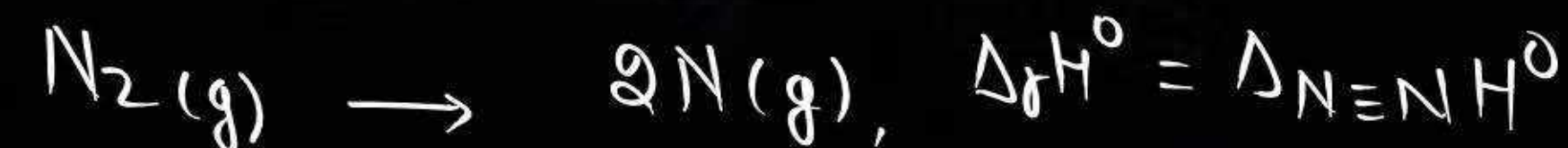
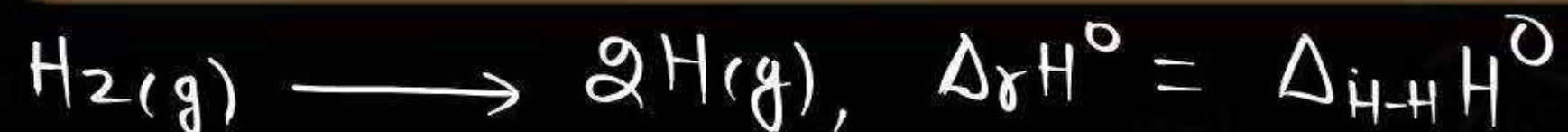
Bond Enthalpy



$\Delta H = +ve$ $\rightarrow$ 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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Bond Enthalpy



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

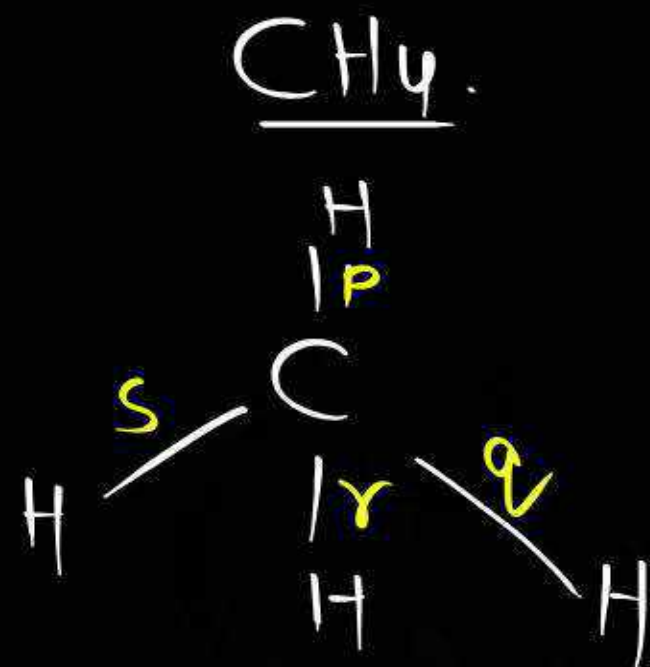
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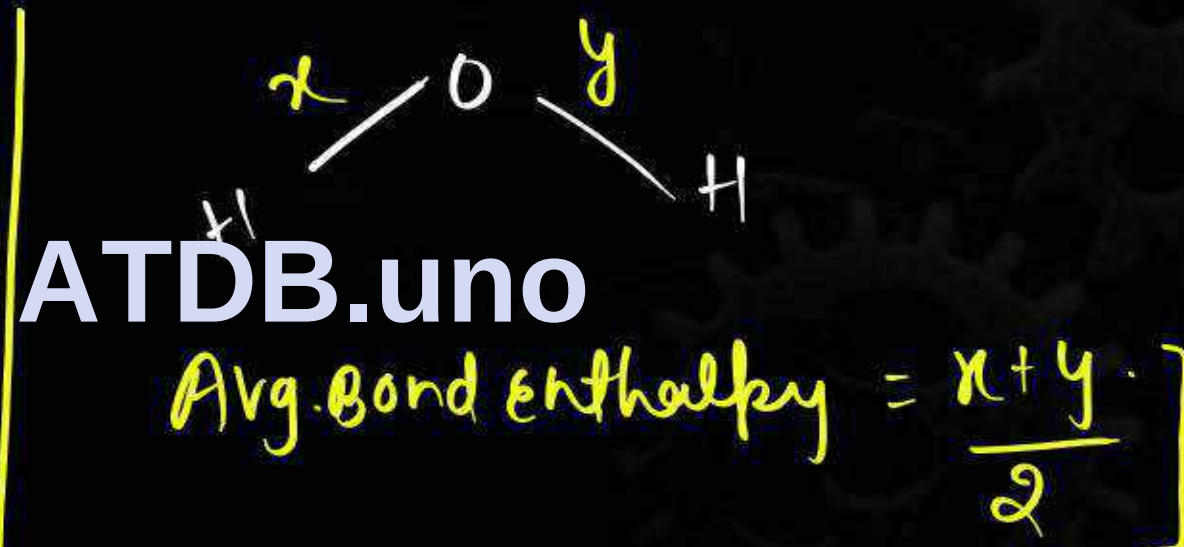
Bond Enthalpy



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



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





Bond Enthalpy



Note:

or

$$\Delta_r H^\circ = \sum q_i \Delta_{\text{bond}} H (\text{Reactants}) - \sum b_i \Delta_{\text{bond}} H (\text{Products})$$

Question



Determine the enthalpy change for the given reaction, ✓



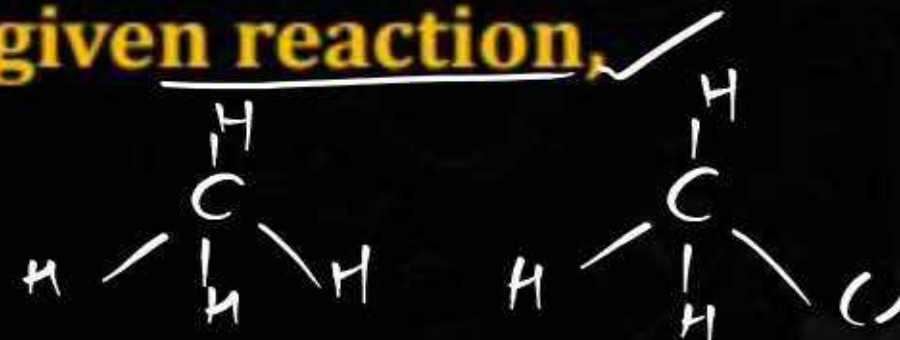
Bond energies are given as follows:

$$\text{C} - \text{H} = 412 \text{ kJ mol}^{-1}$$

$$\text{C} - \text{Cl} = 338 \text{ kJ mol}^{-1}$$

$$\text{Cl} - \text{Cl} = 242 \text{ kJ mol}^{-1}$$

$$\text{H} - \text{Cl} = 431 \text{ kJ mol}^{-1}$$



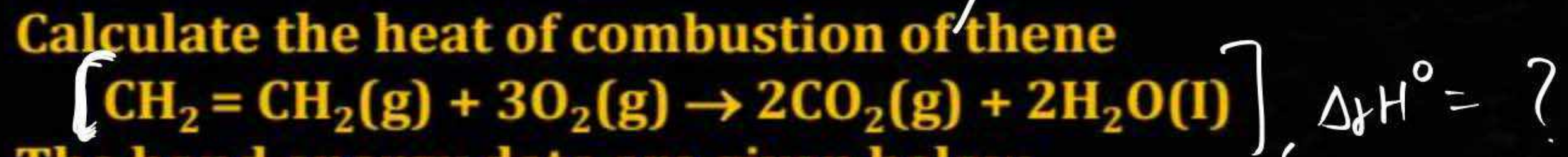
Ans: $\Delta_r H^\circ = \left[4 \times \Delta_{\text{C-H}}^\circ + \Delta_{\text{Cl-Cl}}^\circ \right] - \left[3 \times \Delta_{\text{C-H}}^\circ + 1 \times \Delta_{\text{C-Cl}}^\circ + 1 \times \Delta_{\text{H-Cl}}^\circ \right]$

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

Question



Calculate the heat of combustion of **ethene**



The bond energy data are given below

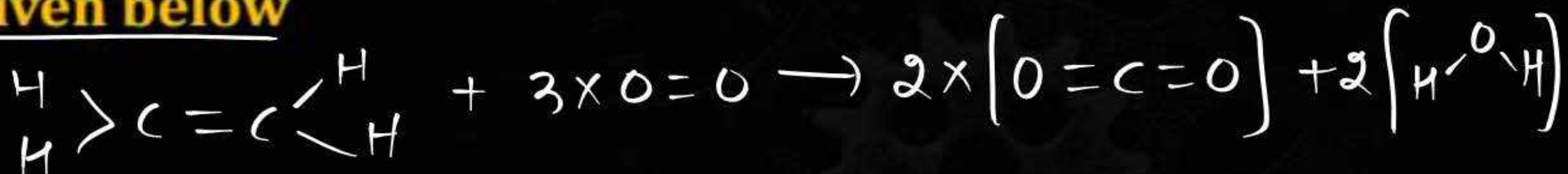
$$\text{C} = \text{C} = 619 \text{ kJ mol}^{-1}$$

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

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

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

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



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

Ans ✓

Question



If enthalpy of atomisation for $\text{Br}_2(\text{l})$ 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 $x < y$

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Ans. [C]

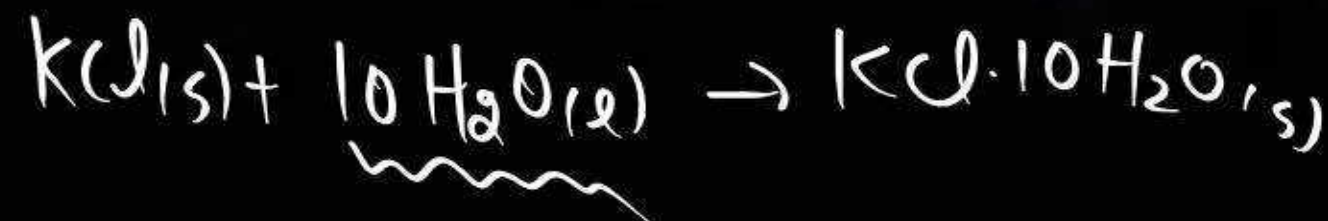
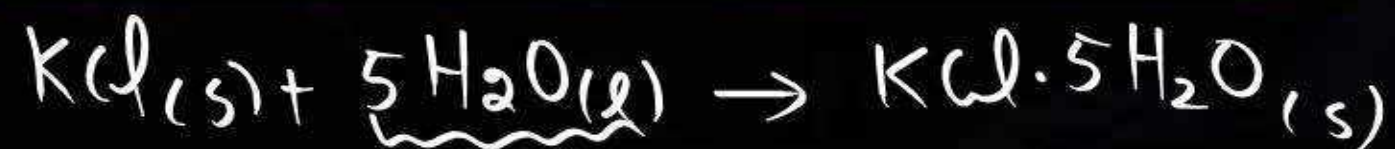


Enthalpy of Solution ($\Delta_{\text{sol}}H^0$)



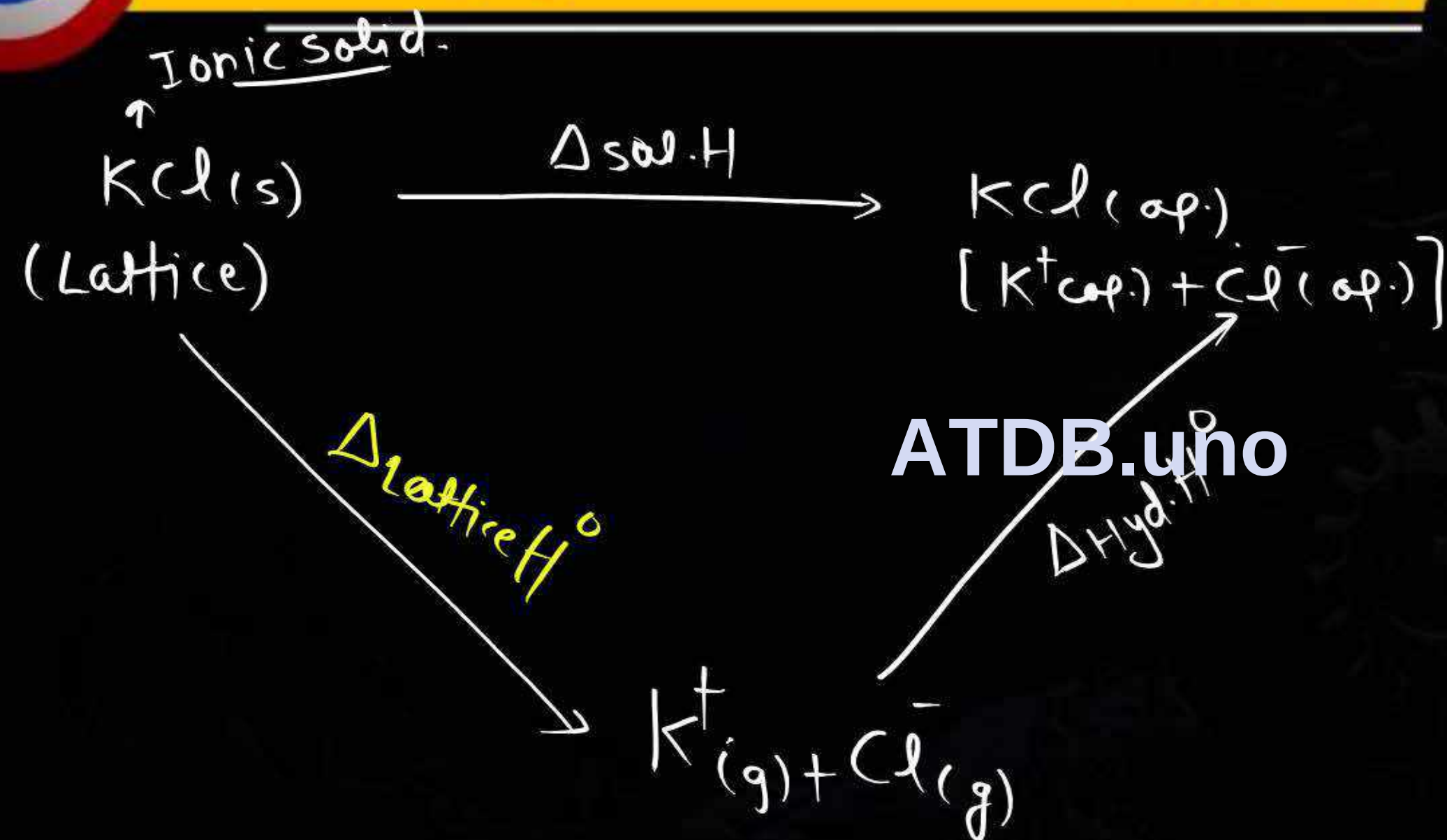
Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent.

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.





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



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

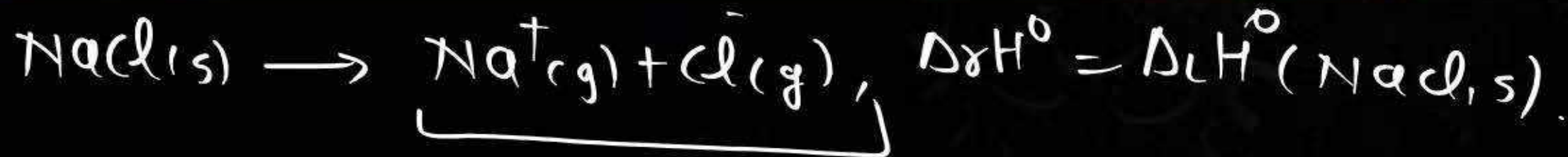


Lattice Enthalpy



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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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

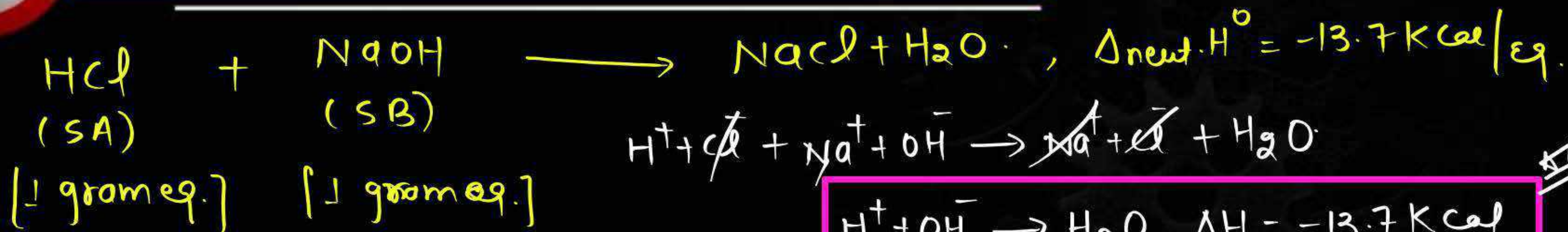
- The amount of heat released in formation of one mole of water when an acid is neutralized by a base.

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

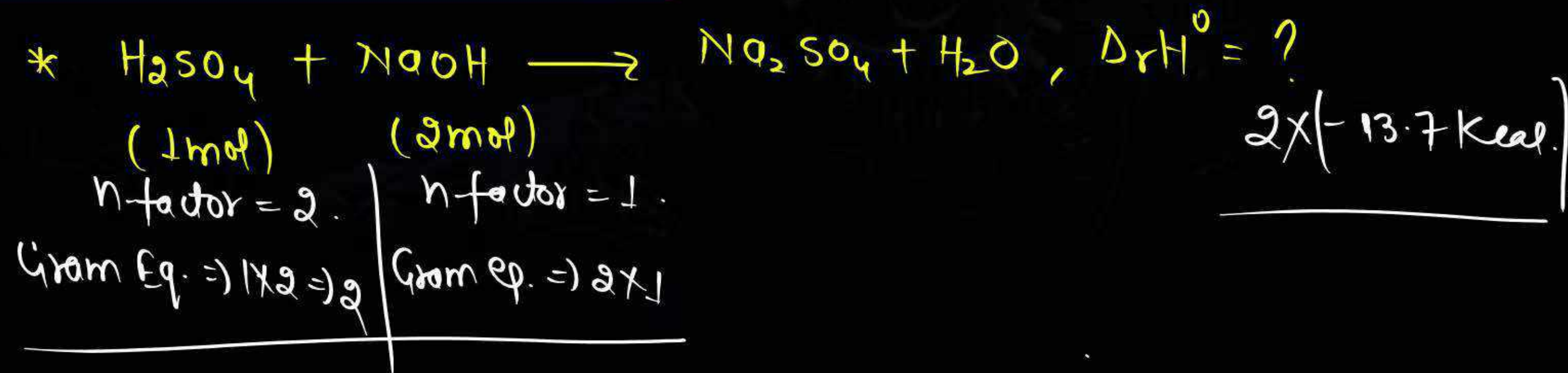
for any other combination of acid and base this heat is less than -13.7 kcal/mole or -57.1 kJ/mole .

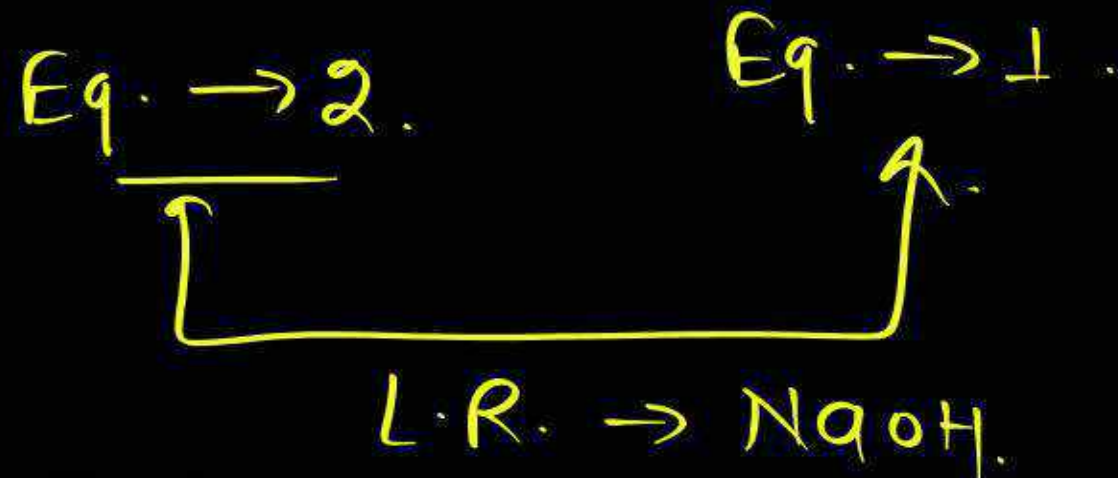


ENTHALPY OF NEUTRALIZATION



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





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Enthalpy of Ionisation

Diff. $\Rightarrow 13.7 - 13.2 \Rightarrow \underline{0.5 \text{ Kcal.}}$

Question



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

$$[\Delta_f H^\circ(\text{H}^+) = 0] \text{ is given.}$$

☒ **A** $-228.5 \text{ kJ mol}^{-1}$

☐ **B** $228.5 \text{ kJ mol}^{-1}$

☐ **C** $114.25 \text{ kJ mol}^{-1}$

☐ **D** $-114.25 \text{ kJ mol}^{-1}$



$$\Delta_r H^\circ = [\Delta_f H^\circ(\text{H}_2\text{O})] - [\Delta_f H^\circ(\text{H}^+) + \Delta_f H^\circ(\text{OH}^-)]$$

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

$$x = -285.8 + 57.2$$

Ans. A

Question



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

A -5.54 kJ

B $+5.54$ kJ

C $+1.9$ kJ

D -1.9 kJ

$$\begin{aligned} &= 57.2 - 55.4 \\ &= +1.9 \end{aligned}$$

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Ans. C

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



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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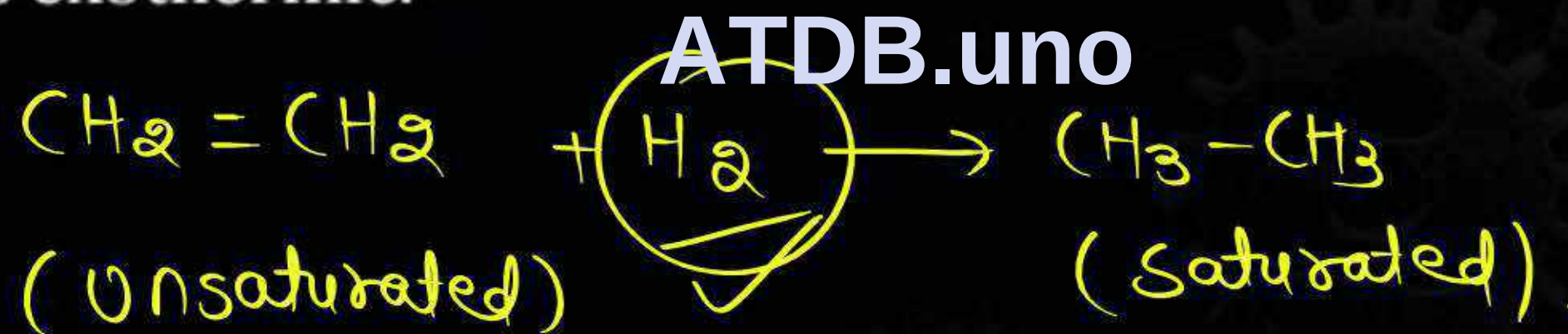
$$\Delta H_{\text{trs}}^0 = 1.90 \text{ kJ mol}^{-1}$$



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.





Variation of enthalpy with temperature (Kirchhoff's Equation)

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

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

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

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

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$\Delta H_{T_1} \rightarrow$ Enthalpy change at T_1

$\Delta H_{T_2} \rightarrow$ _____ at T_2 .



SPONTANEITY

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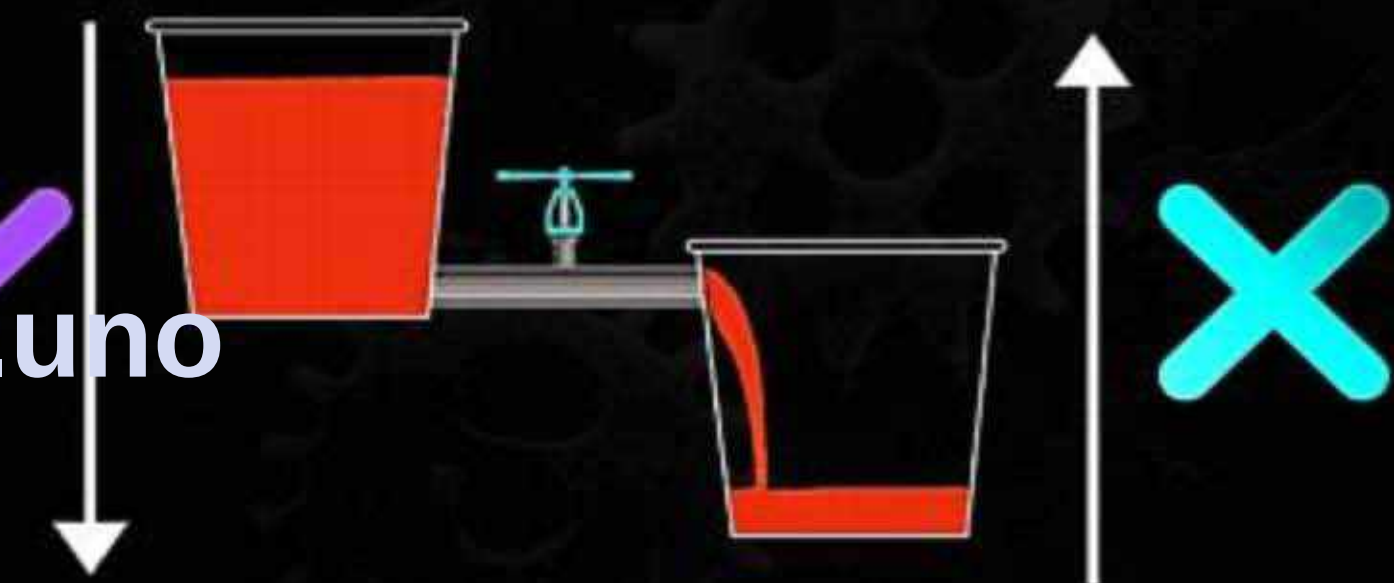


Spontaneous Process



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



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

$$\Delta H = -ve.$$

$$\rightarrow \Delta H = +ve.$$



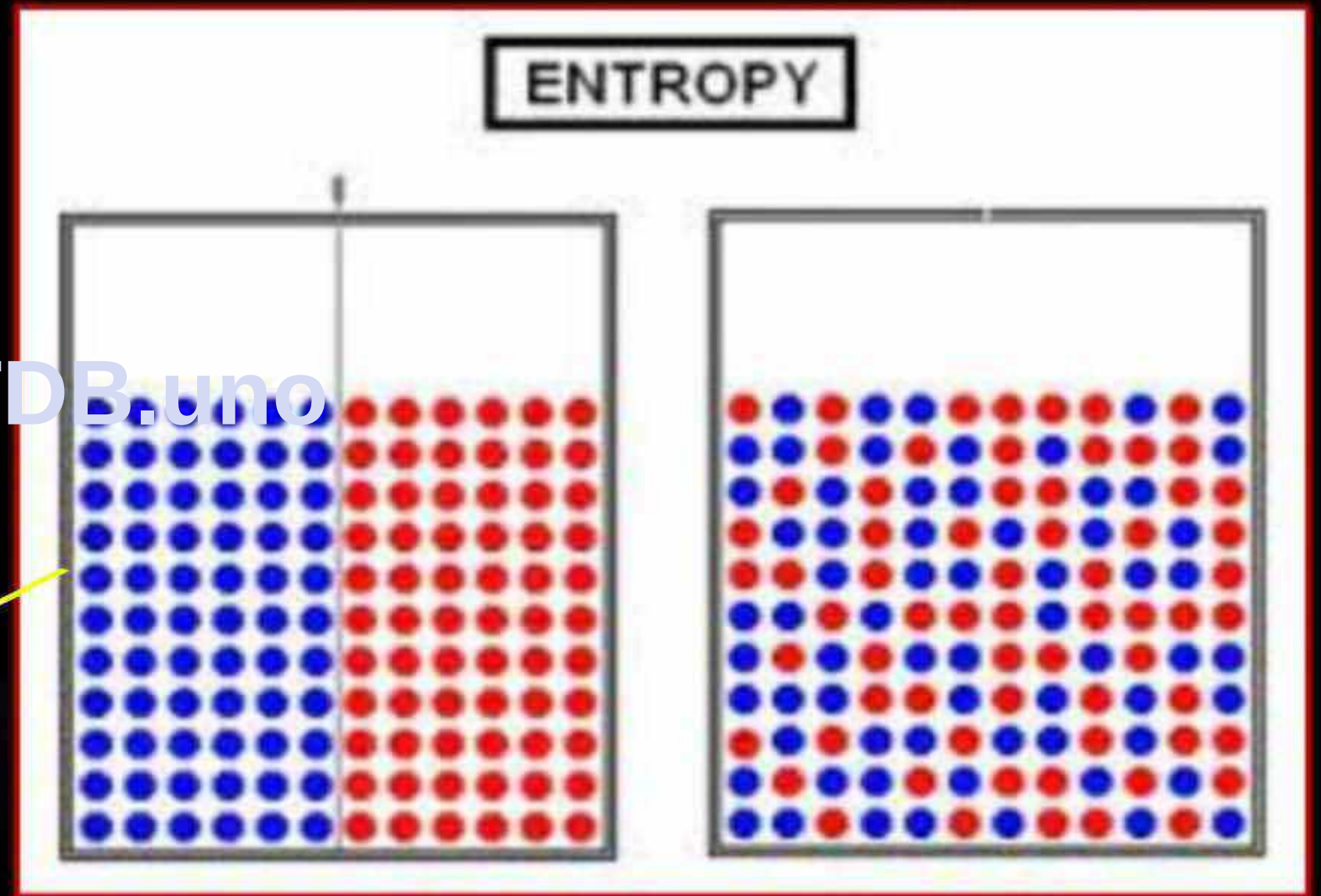


Entropy and spontaneity

[S]

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

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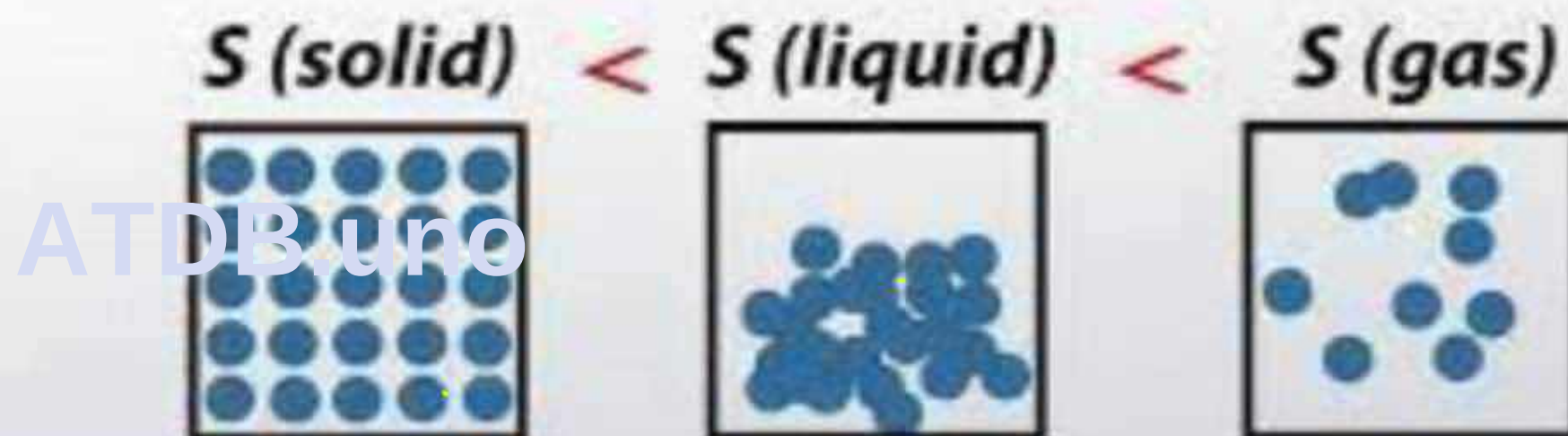




Entropy and spontaneity



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



Temp $\uparrow$, Entropy $\uparrow$ ^{AA}



Entropy and spontaneity



$$\text{Entropy} \propto \text{Temp.}$$

- ❖ 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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$$\text{Entropy change } (\Delta S) \propto \frac{1}{\text{Temp.}}$$

$$T = 5^{\circ}\text{C}$$

q

$$T = 50^{\circ}\text{C}$$

q

$$\Delta S > \underline{\Delta S}$$

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.
- 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.

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Ans. [A]



Entropy and spontaneity

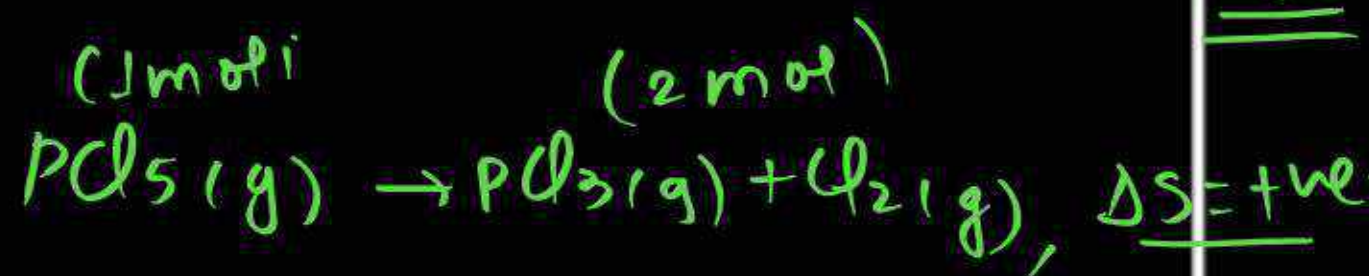
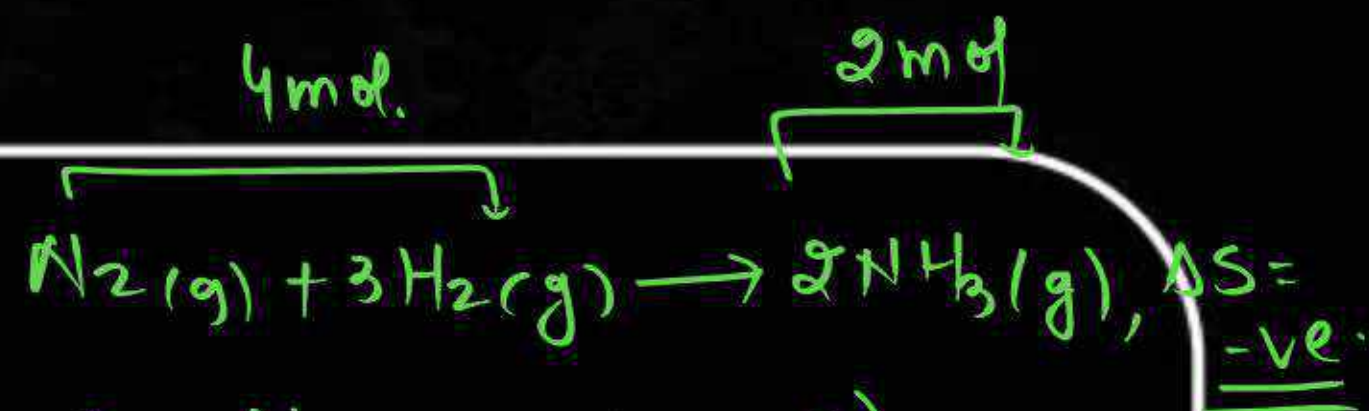


$$\Delta S \propto \frac{1}{T}$$

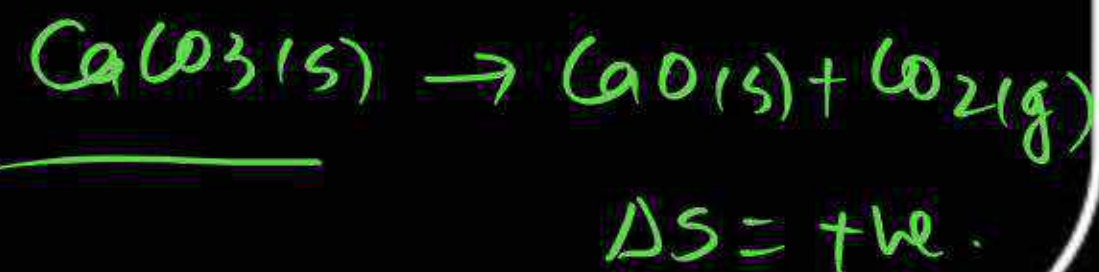
$$\Delta S_{\text{sys}} = \frac{q_{\text{rev, sys}}}{T}$$

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



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





2nd Law of Thermodynamics



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

$\Delta S_{\text{Total}} > 0$, $\rightarrow$ Spontaneous Process.

$\Delta S_{\text{Total}} < 0$, $\rightarrow$ Non-Spontaneous Process

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

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Entropy change in Various Thermodynamic Process



1. Reversible Isothermal Process:

$$\Delta U = 0$$

$$q = -w = - \left[-2.303 n R T \log \frac{V_2}{V_1} \right]$$

$$q = 2.303 n R T \log \left[\frac{V_2}{V_1} \right]$$

$$\Delta S = \frac{q}{T}$$

$$\Delta S = 2.303 n R \log_{10} \left(\frac{V_2}{V_1} \right)$$

or

$$= 2.303 n R \log_{10} \left(\frac{P_1}{P_2} \right)$$



Entropy change in Various Thermodynamic Process



2. Reversible Adiabatic Process:

$$q = 0$$

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

$$\Delta S = 0$$

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Entropy change in Various Thermodynamic Process



3. Reversible Isobaric Process:

$$dq = nC_p dT$$

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

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

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

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

$$\Delta S = 2.303 n C_p \log_{10} \left(\frac{T_2}{T_1} \right)$$

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molar Heat Capacity at Constant Pressure



Entropy change in Various Thermodynamic Process



4. Reversible Isochoric Process:

$$\underline{dq = n C_v dT.}$$

$$\Delta S = 2.303 n C_v \log_{10} \left(\frac{T_2}{T_1} \right)$$

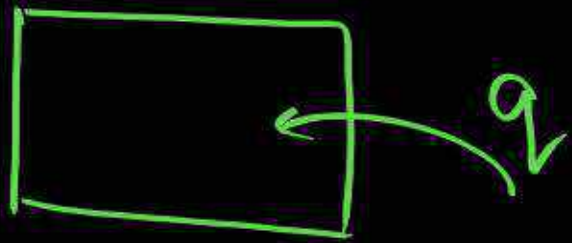
↓
Molar heat capacity at constant
volume.



Entropy change in reversible Process



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



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

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

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

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



Entropy change in Irreversible Process

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



$$T_{\text{surr.}} > T_{\text{sys.}}$$

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

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

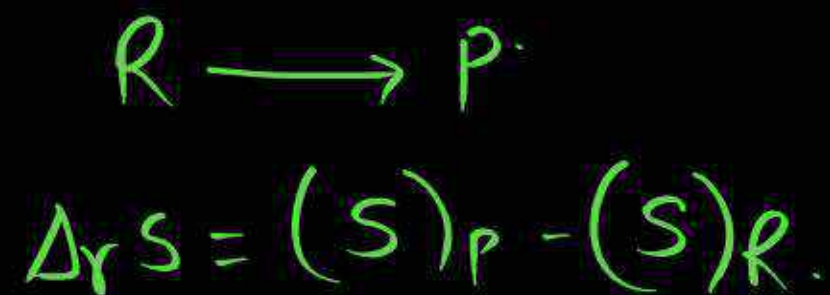
$$\Delta S_{\text{total}} = \frac{q}{T_{\text{sys.}}} + \left[-\frac{q}{T_{\text{surr}}} \right]$$

$$\Delta S_{\text{Total}} \neq 0$$



Molar Entropy change in a reaction

($\Delta_r S^\circ$).



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

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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: $L \rightarrow S$

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Question



During which of the following processes, does entropy decrease?

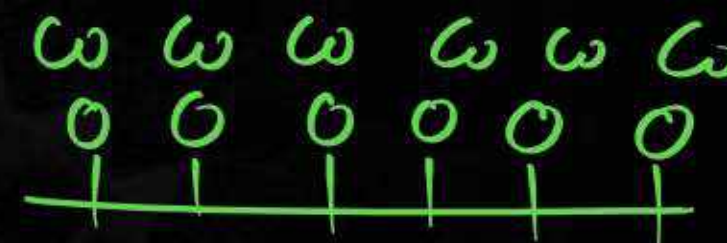
(1) Freezing of water to ice at 0°C } $\Delta S = -ve$

(2) Freezing of water to ice at -10°C } $\Delta S = -ve$

(3) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ } $\Delta S = -ve$

(4) Adsorption of CO(g) on lead surface } $\Delta S = -ve$

(5) Dissolution of NaCl in water } - (JEE Main 2021 (March) Shift -2)



☒ **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 $\text{CaSO}_4(\text{s})$ to $\text{CaO}(\text{s})$ and $\text{SO}_3(\text{g})$
-  **C** dissolution of iodine in water
-  **D** sublimation of dry ice

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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



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

Given that $\Delta S_{(A \rightarrow C)} = 50$ eu
 $\Delta S_{(C \rightarrow D)} = 30$ eu
 $\Delta S_{(B \rightarrow D)} = 20$ eu where, eu is entropy unit

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

 + 100 eu

 - 100 eu

 + 60 eu

 - 60 eu

Ans. [B]



Entropy change in Phase Transformation



Molar Entropy of Fusion:

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

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

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

→ Enthalpy of fusion.



Entropy change in Phase Transformation



Molar Entropy of Vaporisation:



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

$$\Delta S_{\text{vap}}^0 = \frac{q_{\text{vap}}}{T_b}$$

$T_b \rightarrow \text{B.P.}$

$$\Delta S_{\text{vap}}^0 = \frac{\Delta_{\text{vap}} H^0}{T_b}$$

$\rightarrow$ Enthalpy of vaporisation.



Entropy change in Phase Transformation



Molar Entropy of Sublimation:



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

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

$$\Delta S_{\text{sub.}}^{\circ} = \frac{\Delta_{\text{sub}} H^{\circ}}{T_{\text{sub.}}} \rightarrow \text{enthalpy of sublimation.}$$

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~~ is 6 KJ/mol.

Ans : $\rightarrow$



$$T_f = 273 \text{ K}$$

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

$$\therefore 1 \text{ mol} \rightarrow 6 \text{ KJ}$$

$$\therefore 18 \text{ g} \rightarrow 6 \text{ KJ}$$

$$\therefore 1 \text{ g} \rightarrow \frac{6}{18} = \frac{1}{3} \text{ KJ}$$

Ans.

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

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



Gibbs energy and spontaneity





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

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

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Gibb's energy change.

Enthalpy change

Entropy change.



Gibbs energy and spontaneity



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

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

$\Delta G = 0$ [Process at Equilibrium]

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

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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.

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

Gibb's free
energy change.



Gibbs energy and spontaneity



$$\Delta G = \Delta G^0 + 2.303 RT \log_{10} Q \rightarrow \text{Reaction Quotient}$$

Gibb's energy
Change.

Standard Gibb's
Energy change

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

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



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**.

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

Standard Gibbs free
Energy of Rxⁿ.

$\Delta_f G^\circ$ of elements in their standard state is taken as zero.

Question

PW

Match List – I with List – II

(JEE Main 2022 (June) Shift -1)

- List – I

(1) Spontaneous process

(2) Process with $\Delta P = 0, \Delta T = 0$

(3) $\Delta H_{\text{reaction}}$

(4) Exothermic process
- List – II

(i) $\Delta H < 0$

(ii) $\Delta G_{T,P} < 0$

(iii) Isothermal and isobaric process

(iv) [Bond energies of molecules in reactants]-
[Bond energies of product molecules]

Choose the correct answer from the options given below:

- 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. [C]

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)



[Given: $\Delta_f G^\circ (\text{HC} \equiv \text{CH}) = -2.04 \times 10^5 \text{ J mol}^{-1}$; $\Delta_f G^\circ (\text{C}_6\text{H}_6) = -1.24 \times 10^5 \text{ J mol}^{-1}$ $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]
(JEE Main 2021 (Feb.) Shift -2)

Ans $\Rightarrow \underline{\Delta G^\circ} = -2.303 RT \log_{10} K \quad [T = 298 \text{ K}]$

$$\Delta_r G^\circ = \left[\Delta_f G^\circ (\text{C}_6\text{H}_6) \right] - \left[3 \times \Delta_f G^\circ (\text{C}_2\text{H}_2) \right]$$

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

Ans. [855]

Question



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

(JEE Main 2021 (Feb) Shift -1)



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Ans. [200]

Question



For a dimerization reaction, $2A(g) \rightarrow A_2(g)$, $\Delta n_g = 1 - 2 \Rightarrow -1$
at 298 K, $\Delta U^\ominus = -20 \text{ kJ mol}^{-1}$, $\Delta S^\ominus = -30 \text{ J K}^{-1}\text{mol}^{-1}$, then the $\Delta G^\ominus$ will be
_____.
(JEE Main 2020 (Sep.) Shift -2)

Ans: $\Rightarrow$

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

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

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Ans. [-13538]

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 $\Delta S > 0$

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

$$\Delta G = -w_e.$$

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Question



The reaction, $\text{MgO(s)} + \text{C(s)} \rightarrow \text{Mg(s)} + \text{CO(g)}$, for which $\Delta_r H^\circ = + 491.1 \text{ kJ mol}^{-1}$ and $\Delta_r S^\circ = 198.0 \text{ JK}^{-1} \text{ mol}^{-1}$, 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



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Ans. [D]

Question



The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by, $\Delta_r G^\circ = A - BT$ 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, $A > 0$

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

$$\begin{array}{cc} \textcircled{A} = \Delta H & \\ \downarrow & \\ +ve & \textcircled{+ve} \end{array}$$

Ans. [D]

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]

Question



For the process $\text{H}_2\text{O}(l)$ (1 bar, 373 K) $\rightarrow$ $\text{H}_2\text{O}(g)$ (1 bar, 373 K), the correct set of thermodynamic parameters is (2007, 3M)

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

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1465

Ans. [A]



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.

