PRACHAND NEET

ONE SHOT

Physical Chemistry

Thermodynamics

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Topics *to be covered*

1. Basic Terms
2. Laws of Thermodynamics
   - Zeroth
   - 1st
   - 2nd
   - 3rd
3. Entropy and Gibbs free energy
4. Thermochemistry

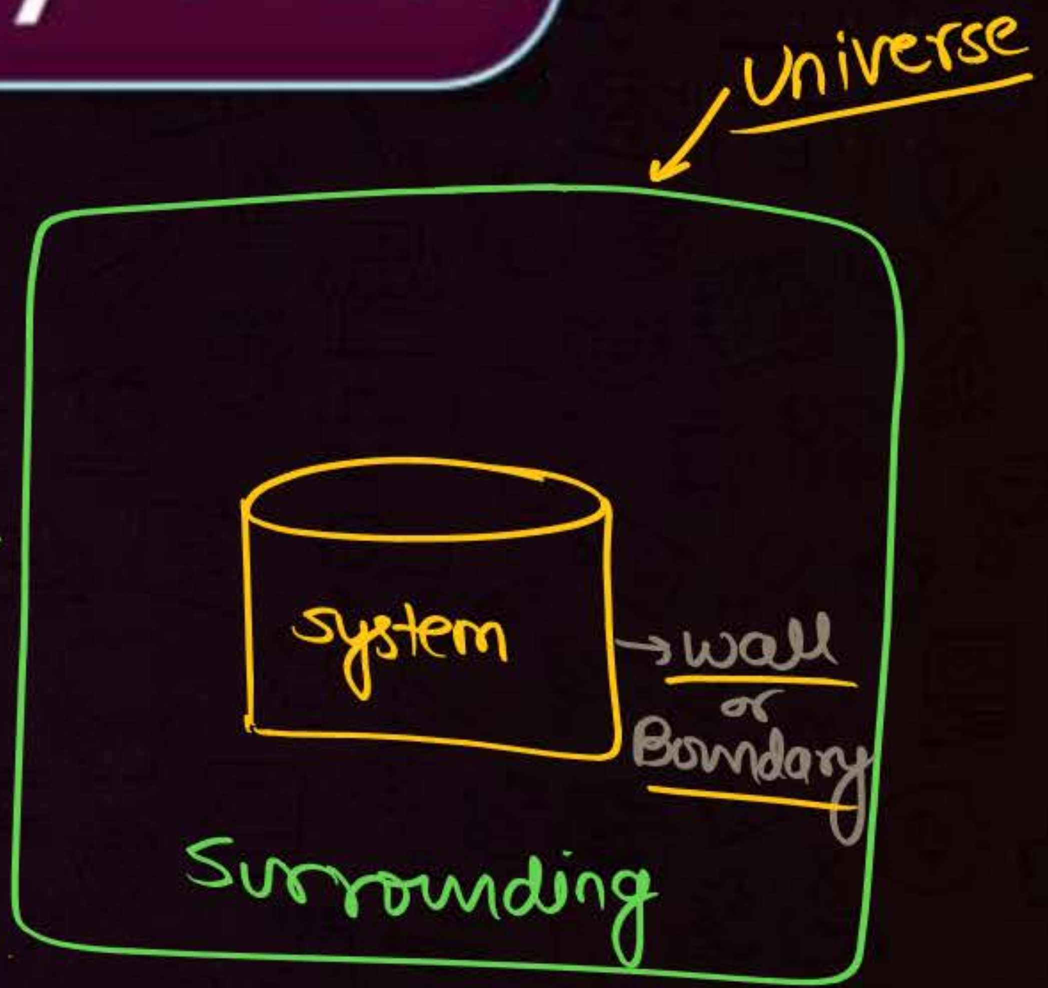
Introduction

Thermodynamics ⇒ Branch of physical chemistry which deals with energy and its changes in different type of processes and chemical reaction.

Energy
- → Work (W)
- → Heat (Q)
- → Internal energy (U/E)
- → Enthalpy
- → Entropy
- → Gibbs free energy

Min. 2Q in NEET 2025
- ↳ electrochemisty
- → equilibrium
- → chemical kinetics

Some Basic Terms in Thermodynamics



① **System** ⇒ observable part of universe.

② **Surrounding** ⇒ that part of universe which may be affected by change in system.

③ $\boxed{\text{Universe} = \text{System} + \text{Surrounding}}$

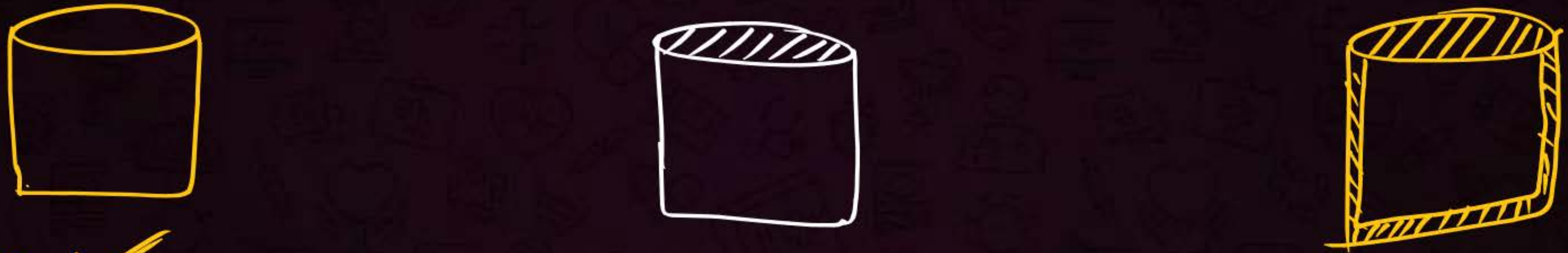
④ **Wall/Boundary** ⇒ separates system and surrounding.

- Fixed or Rigid wall
  - no movement
- Movable wall
  - movement is allowed.

Wall/Boundary

- Heat Conducting walls or Diathermic walls.
- Heat insulating walls or Adiabatic wall

Types of system



	open system	Closed system	Isolated system
mass exchange →	✓	×	×
Energy exchange →	✓	✓	×
Boundary →	open & heat Conducting.	closed but Heat Conducting	Closed and heat insulating walls.

System

- Homogeneous system ⇒ same phase/state of Reactant & product.

  $A(l) \rightleftharpoons B(l)$

- Hetrogeneous system ⇒ more than one phase of Reactant and product.

  $A(l) \rightleftharpoons C(g)$

Parameters of state of system

(P, V, T, n, Energy)

State variables/state function → $\Delta U, \Delta H, \Delta S, \Delta G$

(path independent) depends only on initial and final state of process.

Path variable/functions

depends on the path taken for Change from initial state to final state

Q (Heat)
W (work)

Some Basic Terms in Thermodynamics

Types of Boundaries

- A real boundary is also called a wall. The types of walls are as follows:

Rigid wall:
The wall (boundary) is immovable

Non-rigid wall:
The wall is movable

Adiabatic wall:
The heat can't be exchanged across the wall.

Diathermic wall:
The heat can be exchanged across the wall.

Example: Air in a flexible balloon (flexible boundary) while air in a room (fixed boundary).

- Boundaries can be adiabatic (non-conducting) or diathermic (conducting).

Some Basic Terms in Thermodynamics

Keep it in mind

	Open	Closed	Isolated
			
Matter exchange	✓	✗	✗
Energy exchange	✓	✓	✗

Some Basic Terms in Thermodynamics

Table: On the basis of composition, there are two types of system.

Homogeneous System	**Heterogeneous System**
A system is said to be homogeneous when it is completely uniform throughout. A homogeneous system is made of one phase only.	A system is said to be heterogeneous when it is not uniform throughout. It is made of two or more phase.
Examples: A pure solid, mixture of gases, true solution.	**Examples:** Colloidal solutions, suspensions (insoluble solid in contact with a liquid), a solid in contact with its liquid state (ice $\rightleftharpoons$ water).

QUESTION

What is thermodynamics?

[✓ A] Study of the relationship between heat and other forms of energy.

B Study of the conversion of chemical energy to other forms of energy.

C Study of the relationship between mechanical energy to other forms of energy.

D Study of the conversion of mechanical energy to other forms of energy.

QUESTION

Statement I : System is a part of universe. ✓✓
Statement II : System is a part of surrounding. ✗

- (A) Statement I and Statement II both are correct.
- (B) Statement I is correct but Statement II is incorrect. ✓✓
- (C) Statement I is incorrect but Statement II is correct.
- (D) Statement I and Statement II both are incorrect.

QUESTION

A system is said to be heterogeneous when it;

A is completely uniform throughout. ✗

B is consist of one phase only. ✗

[✓ **C** is not uniform throughout.]

D has uniform composition throughout. ✗

QUESTION

System that cannot exchange both energy and matter with the surroundings is called;

A open system.

B closed system.

[✓ **C** isolated system.]

D None of these.

QUESTION

Match List-I with List-II to find out the correct option.

List-I		List-II	
A.	Rigid wall	I.	Movable
B.	Isolated system	II.	Exchange of energy Only
C.	Open system	III.	No exchange of energy and matter
D.	Non-rigid wall	IV.	Immovable
E.	Closed system	V.	Exchange of both energy and matter

[✓ (A)] A-IV, B-III, C-V, D-I, E-II

(B) A-I, B-III, C-IV, D-V, E-II

(C) A-I, B-II, C-IV, D-V, E-III

(D) A-II, B-III, C-IV, D-I, E-V

QUESTION

An isolated system is that system in which;

A there is no exchange of energy with the surroundings.

B there is exchange of mass and energy with the surroundings.

[✓ C] there is no exchange of energy and mass with the surroundings.

D there is exchange of mass with the surroundings.

QUESTION

A system that can exchange only energy but cannot exchange matter with the surrounding is known as;

Ⓐ open system.

Ⓑ isolated system.

Ⓒ [✓ closed system.]

Ⓓ None of these

State of a System:

- The state of a system means the condition in which the system is present. It is defined by specifying some measurable properties of the system like pressure, volume, temperature, etc.

State Function

- The thermodynamic properties whose values depend on the state of the system. It is independent of the path adopted to attain a particular state.

Examples: Temperature (T), Pressure (P), Volume (V), Total internal energy (E or U), Enthalpy (H), Gibbs free energy (G), Entropy (S) are all state functions.

Path Function:

- The thermodynamic properties whose values depend on the path followed to reach the final state of the system are called path functions.

  Example: Heat and work.

QUESTION

In thermodynamics, a quantity whose value simply depends upon the initial and final state of the system is called;

- A thermodynamic quantity.
- [✓ B] state function.
- C adiabatic quantity.
- D path function.

QUESTION

A thermodynamic state function is;

- **A** one which obeys all the law of thermodynamics. ✗
- **B** a quantity which is used in measuring thermal changes. ✗
- **C** one which is used in thermochemistry. ✗
- [✓ **D** a quantity whose value depends only on the state of the system.] ✓✓

QUESTION

Which of the following is not a state function?

(A) Internal energy

(B) Free energy

[✓ (C) Work]

(D) Enthalpy

QUESTION

Which one of the following statements is false?

[✓ A] Work is a state function.

B Temperature is a state function.

C Change in the value of state function is completely defined when the initial and final states are specified.

D None of these.

QUESTION

Enthalpy is a;

[✓ A state function.]

B path function.

C Both (A) and (B).

D None of these.

Properties of System

(non-additive in nature) ← intensive Property

↓ independent of mass/matter of system.

extensive property ← additive in nature

↓ depends on mass/matter of system.

e.g → internal energy
- entropy
- enthalpy
- mass
- volume
- Gibbs free energy

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

→ Temperature

→ Density

→ refractive index

→ viscosity

→ Molar volume

$$\frac{\text{enthalpy}}{\text{mass}} = \text{specific enthalpy}$$

**

$$\Rightarrow \frac{\text{extensive}}{\text{extensive}} = \text{intensive property}$$

$$\Rightarrow \frac{\text{extensive}}{\text{mass}} = \text{intensive property}$$

Intensive Properties:

- Functions or properties that are not mass or size dependent on the system.
- These are not additive in nature.

(i) Temperature
(ii) Density
(iii) Specific heat
(v) Melting point
(iv) Surface tension
(vi) Boiling point

Extensive Properties:

- Functions or properties of the system that are dependent on mass or on size of the system. These are additive in nature.
  - (i) Mass
  - (ii) Volume
  - (iii) Internal energy
  - (iv) Entropy
  - (v) Enthalpy

QUESTION

Which of the following sets contains only extensive properties?

A Mole, volume, pressure

[✓ B H, U, V]

C T, P, V

D Density, entropy, heat capacity

QUESTION

Which among the following state functions is an extensive property of the system?

Ⓐ Temperature

Ⓑ [✓ Volume]

Ⓒ Refractive index

Ⓓ Viscosity

Thermodynamics

- Thermodynamics is derived from Greek words 'therme' and 'dynamis'. Its literal meaning is motion or flow (dynamics) of heat (thermos). However, the term is used in a more general way.

- Thermodynamics is a branch of science that deals with the quantitative relationship between heat and other forms of energies. When we confine our study to thermodynamics of chemical processes, it is referred to as chemical thermodynamics.

- Thermodynamics is not concerned with the total energy of the body but only with energy changes taking place during the transformation.

Applications of Thermodynamics:

- Feasibility of the reaction is to be predicted i.e. if two substances are mixed, then the reaction between them will take place or not.

- If a reaction does take place, then what are the energy changes involved during the reaction.

- If in a chemical reaction, equilibrium is going to get attained, then what will be the equilibrium concentrations of different reactants and products, can be calculated with thermodynamics.

Limitations of Thermodynamics:

- Laws of thermodynamics are applicable to that matter which are in bulk or on the system as a whole, these cannot be applied on individual particles.

- Using thermodynamics, we cannot calculate the time taken for completion of a reaction or for attainment of chemical equilibrium.

Heat (Q)

... it is a form of energy which flows from hot body to cold body without any external force.

sign-convention

Heat released / given out = (-ve)

Heat absorbed (given to) = +ve

- disordered form of energy.
- non-directional.
- path function.
- low quality of energy

Units of Heat/energy

- Joule (S.I unit)
- Calorie.
- l-atm

$1\ cal = 4.2\ J$

$1\ l\ atm = 101.3\ J \simeq 100\ J$

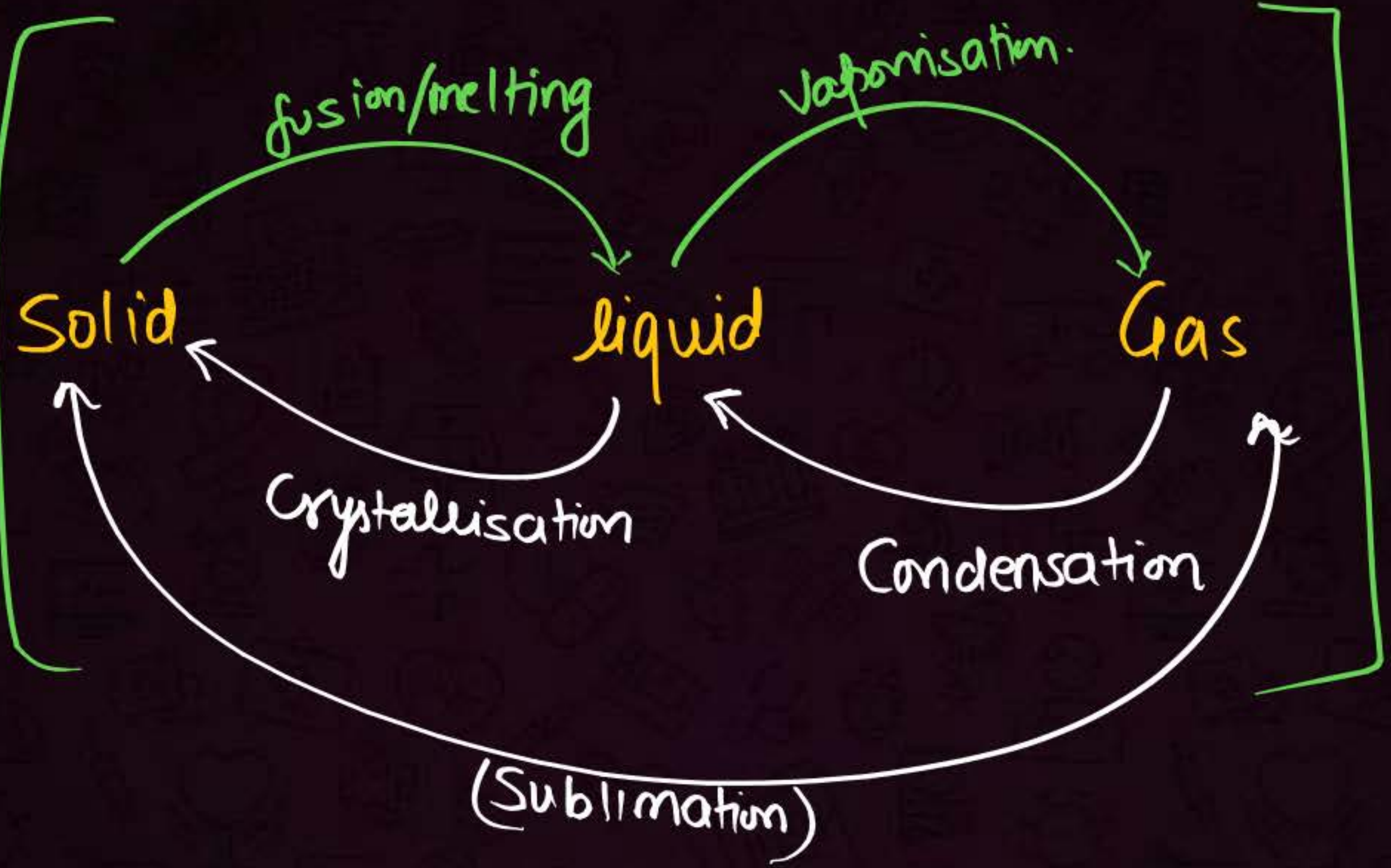
Heat

- Latent heat (Q_L) ⇒ heat given/required to change the state of system at constant Ⓣ & Ⓟ
- Sensible Heat (Q_S) ⇒ heat given/required to change the temp. of a system without changing its phase/state.

latent heat (Q_L)

phase change at constant Ⓣ & Ⓟ

L_{fus}
L_{vap} } endothermic



fusion/melting

vaporisation.

Solid

liquid

Gas

Crystallisation

Condensation

(Sublimation)

latent heat of fusion (L_{fus}) ⇒ heat required to change the state from solid to liquid.

at Melting/freezing point temp.

latent heat of vaporisation (L_{vap}) ⇒ heat required to change the state from liquid to gas.

at Boiling point temp.

$$Q_L = \underset{\text{mol}}{n}\ \underset{\text{J/mol}}{L} = \underset{\text{g}}{\boxed{m}}\ \underset{\text{J/g}}{L} = \underset{\text{kg}}{m}\ \underset{\text{J/kg}}{L}$$

$$n = \frac{w}{M} = \frac{V}{V_m} = \frac{n}{N_A}$$

Q Calculate heat change when

(a) A solid of 10 g is subjected to fusion at its M.pt ($L_{fusion} = 10$ kJ/kg)

(b) A liquid of 2 kg is subjected to vaporisation at its B.pt (L. Vap = 120 J/g)

Sol:

(a) $Q_L = mL_{fus}$

$$= \frac{1\cancel{0}}{10\cancel{0}\cancel{0}}\cancel{\text{kg}} \times 1\cancel{0}\,\frac{\text{kJ}}{\cancel{\text{kg}}} = 0.1 \text{ kJ}$$

$$\Rightarrow 100 \text{ J}$$

(b) $Q_L = mL_{vap}$

$= 2 \times 1000 \times 120$ J

$\Rightarrow 240000$ J $\Rightarrow 240$ kJ

Sensible Heat(Q_s) ⇒ heat to Change the temp.

$\underbrace{\text{Temp.} \uparrow}$ → Heat given ($Q = +ve$)

Temp ↓ → Heat released ($Q = -ve$)

$Q_s = C \, \boxed{\Delta T}$ → change in temp.

C → Heat capacity

Unit = J / K

$Q_s = m \, c \, \Delta T$

m → kg, g

c → specific heat Capacity

unit = J / k-kg or J / k-g

$C = m \, c$

C → Heat capacity

m → mass

c → specific heat capacity

C_p = Heat Capacity at constant Pressur

C_v = Heat Capacity at Constant volum

Heat Capacity(C) = Heat required to Change the temp. of a system by 1c / K.

Heat Capacity → extensive property.

Specific heat capacity (c) = Heat required to change the temp. of 1g / 1 kg of system by 1c / 1K.

Specific heat capacity → intensive Property

molar heat capacity (C_m) ⇒ Heat required to change the temp. of 1 mol of system by 1°C / 1K.

↳ unit ⇒ J/mol-K

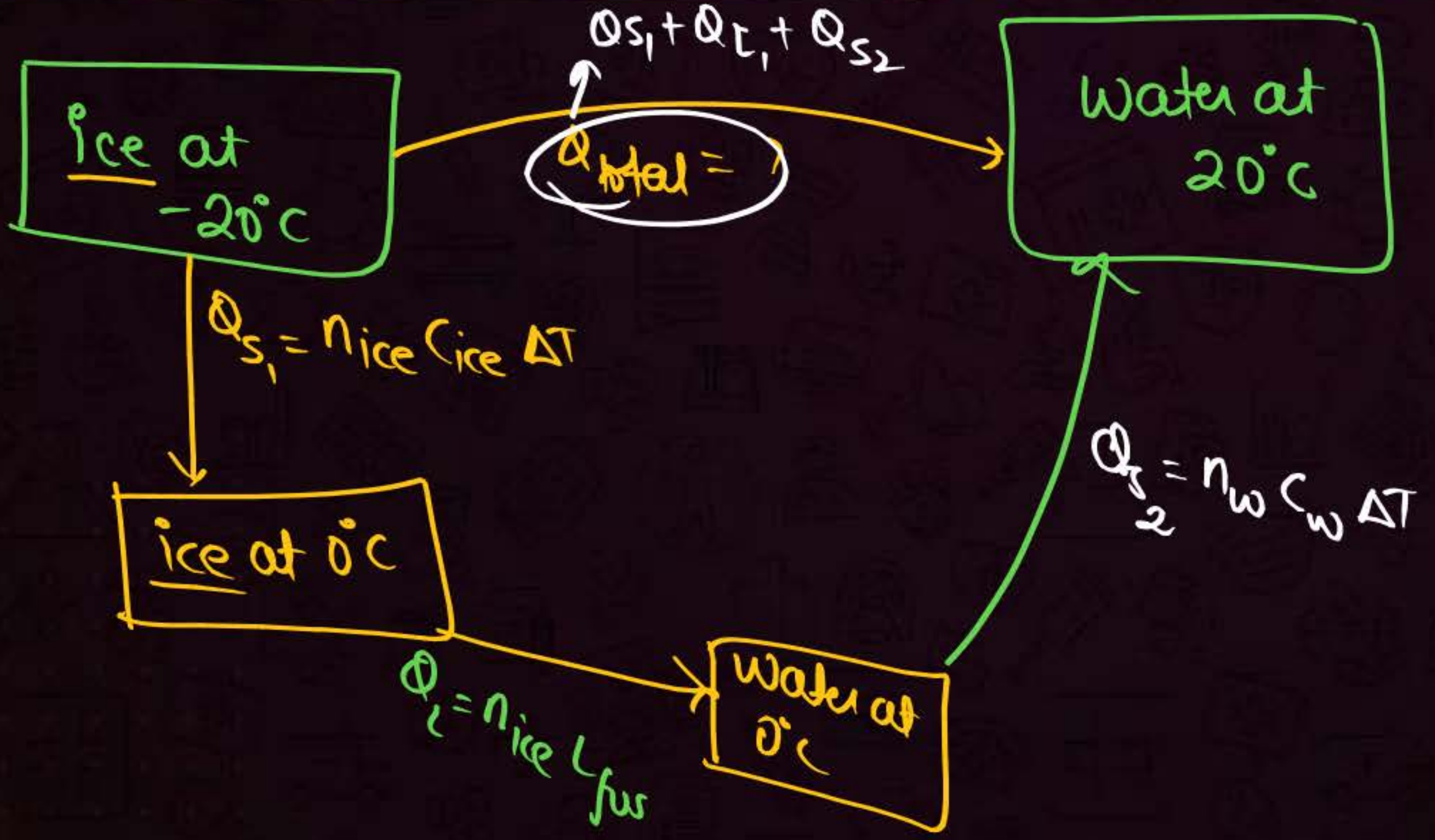
$$\boxed{Q_s = n C_m \Delta T}$$

$$Q_s = \underset{\text{J/K}}{\underset{\downarrow}{C}}\ \underset{\text{K}}{\underset{\downarrow}{\Delta T}}$$

$$Q_s = \underset{\text{kg}}{\underset{\downarrow}{m}}\ \underset{\text{J/K-kg}}{\underset{\downarrow}{s}}\ \underset{\text{K}}{\underset{\downarrow}{\Delta T}}$$

$$Q_s = \underset{\text{mol}}{\underset{\downarrow}{n}}\ \underset{\text{J/K-mol}}{\underset{\downarrow}{C_m}}\ \underset{\text{K}}{\underset{\downarrow}{\Delta T}}$$

Q.



Ice at −20°C

$Q_{s_1} + Q_{L_1} + Q_{s_2}$

$Q_{total} = ?$

Water at 20°C

$Q_{s_1} = n_{ice} C_{ice} \Delta T$

ice at 0°C

$Q_L = n_{ice} L_{fus}$

Water at 0°C

$Q_{s_2} = n_w C_w \Delta T$

Specific heat, also called **specific heat capacity** is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin)

The **molar heat capacity** of a substance, Cm , is the heat capacity for one mole of the substance and is the quantity of heat needed to raise the temperature of one mole by one degree celsius (or one kelvin)

QUESTION

NCERT

Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C.

Molar heat capacity of Al is 24 J mol⁻¹ K⁻¹

Sol:

$$Q_S = n\, C_m\, \Delta T$$

$$= \frac{\overset{20}{\cancel{60}}}{\underset{\underset{3}{\cancel{9}}}{\cancel{27}}} \times \overset{8}{\cancel{24}} \times 20 = \frac{3200}{3} = 1066.66\ \text{J}$$

$$= 1.067\ \text{KJ}$$

QUESTION NCERT

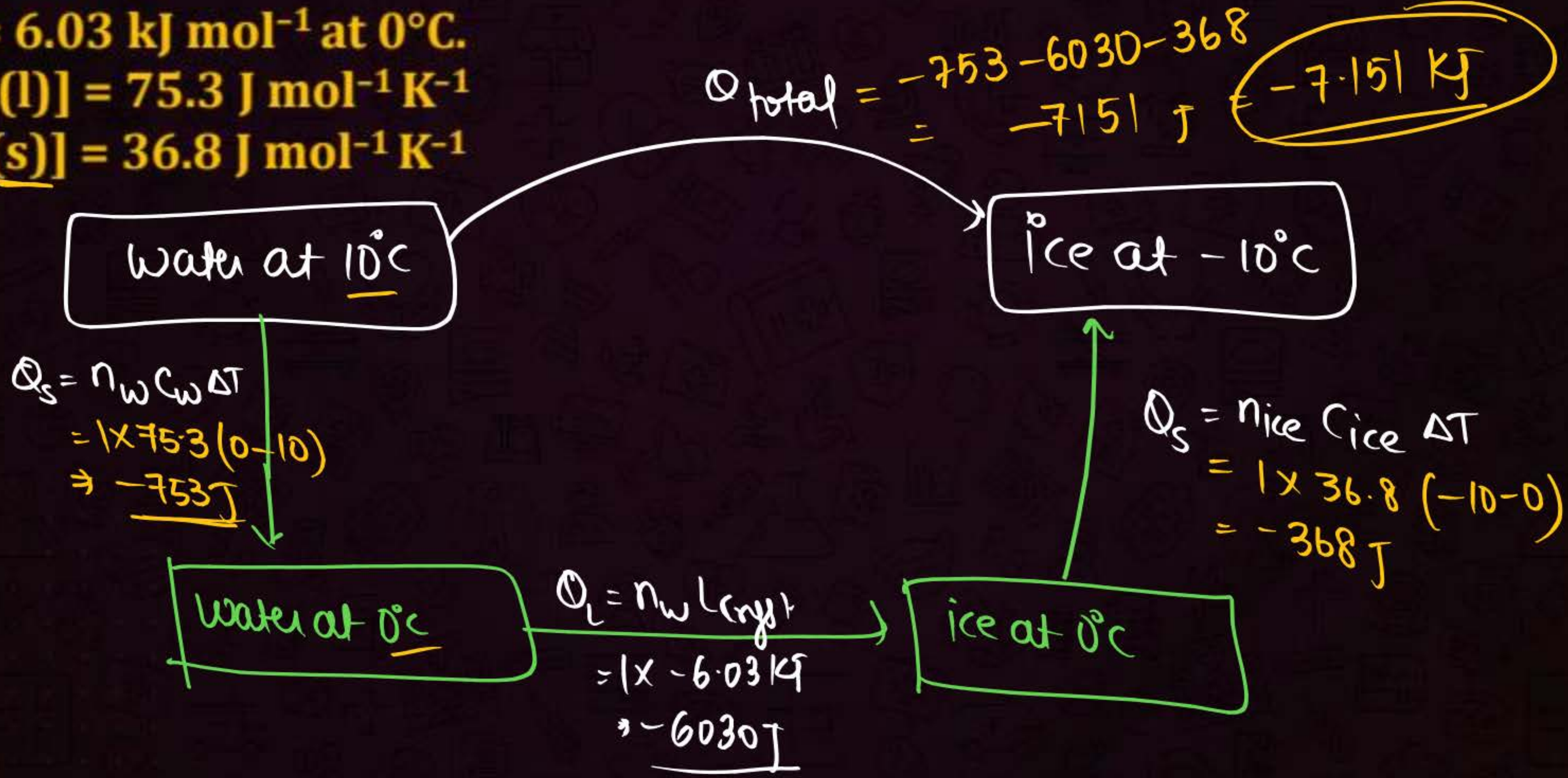
Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to ice at –10.0°C.

$\Delta_{fus}H = 6.03$ kJ mol^{-1} at 0°C.

$C[H_2O(l)] = 75.3$ J mol^{-1} K^{-1}

$C[H_2O(s)] = 36.8$ J mol^{-1} K^{-1}

Sol:



$Q_{total} = -753 - 6030 - 368$

$= -7151$ J $= \boxed{-7.151 \text{ kJ}}$

$Q_s = n_w C_w \Delta T$

$= 1 \times 75.3(0-10)$

$\Rightarrow -753$ J

$Q_L = n_w L_{(cryst)}$

$= 1 \times -6.03$ kJ

$\Rightarrow -6030$ J

$Q_s = n_{ice} C_{ice} \Delta T$

$= 1 \times 36.8(-10-0)$

$= -368$ J

Work (W)

→ path function
→ ordered from of energy
→ Higher from of energy.

In Physics

$$\boxed{W = F \cdot \Delta x}$$

$$= \frac{F}{A} \cdot \underbrace{A \cdot \Delta x}$$

$$\boxed{W = \underset{\text{Presure}}{P} \cdot \underset{\text{vol. change.}}{\Delta V}}$$

expansion (workdone by the system)

→ $V_{final} > V_{initial}$

→ $\Delta V > 0$

$$W_{\text{by the system}} = \underset{+ve}{-P} \times \underset{+ve}{\Delta V} = -ve$$

sign convention

$W_{\text{by the system}} = -ve$

$W_{\text{on the system}} = +ve$

According to IUPAC.

$$W = -P\Delta V = -P(V_{final} - V_{initial})$$

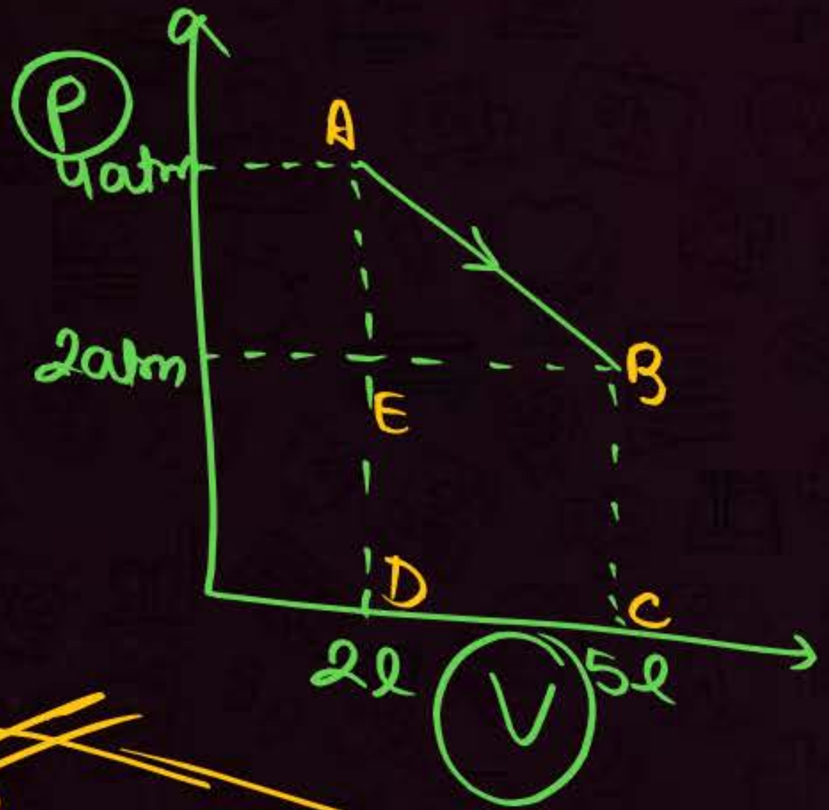
$$\boxed{\begin{aligned} W &= -P\Delta V \\ &= -P(V_{final} - V_{initial}) \end{aligned}}$$

$$\boxed{|W| = \text{area under P-V curve}}$$

Units of W/ Energy → Joule, Cal, l-atm.

$$\boxed{1\,l\text{-atm} = 101.3\,J \simeq 100\,J}$$

Q Calculate (W) for



$$\boxed{W = -911.7\,J}$$

$|w|$ = area under curve.

= area of △ABE + area of □ BCDE

$= \frac{1}{\cancel{2}} \times 3 \times \cancel{2} + 3 \times 2$

⇒ 9 l-atm

⇒ 9 × 101.3 J

⇒ 911.7 J

QUESTION

Quantity of work (in joules) done by the gas if it expands against a constant pressure of 0.980 atm and the change in volume (ΔV) is 25.0 L, is

(A) 24.5 J

(B) 2.48 J

[✓ (C)] 2.48×10^3 J

(D) 0.0245 J

$$|W| = P\Delta V$$

$$\Rightarrow 0.980 \times 25 \ l\cdot atm$$

$$= \underline{0.980 \times 25 \times 101.3 \ J}$$

QUESTION

One mole of an ideal gas at 25°C expands in volume from 1.0 L to 4.0 L at constant temperature. What work (in J) is done if the gas expands against vacuum ($P_{external} = 0$)?

A -4.0×10^2

$W = -P_{ext}\Delta V$

B -3.0×10^2

C -1.0×10^2

[✓ D Zero]

QUESTION

An ideal gas expands in volume from 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300 K against a constant pressure of 1×10^{5} Nm^{-2}. The work done is-

[✓ A] –900 J

(B) –900 kJ

(C) 270 kJ

(D) 900 kJ

$$W = -P_{ext}\,\Delta V$$

$$= -10^{5}\times\left(10^{-2}-10^{-3}\right)$$

$$\Rightarrow -10^{5}\times 10^{-3}\left(10-1\right)$$

$$\Rightarrow -9\times 10^{2}\,J$$

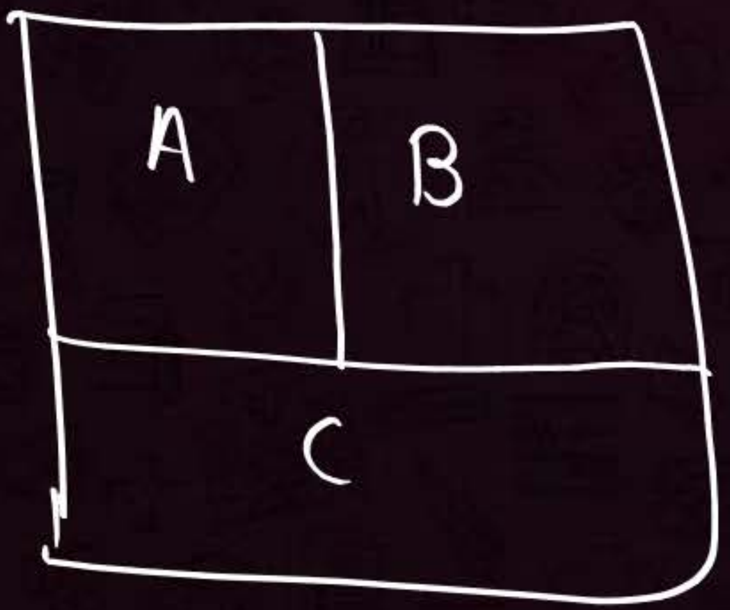
$$\Rightarrow -900\,J$$

Laws of Thermodynamics

- → Zeroth law of Thermodynamics
- → Ist law " "
- → 2nd law " "
- → 3rd law " "

⇒ $\boxed{\text{Zeroth law of Thermodynamics}}$ ⇒ Based on $\boxed{\text{thermal equilibrium}}$

(Temp = equal)



$T_A = T_B$ (A & B are in thermal eq^m)

$T_A = T_C$ (A & C are in thermal eq^m)

<u>then</u> $T_B = T_C$ (B & C are in thermal eq^m)

Zeroth Law of Thermodynamics

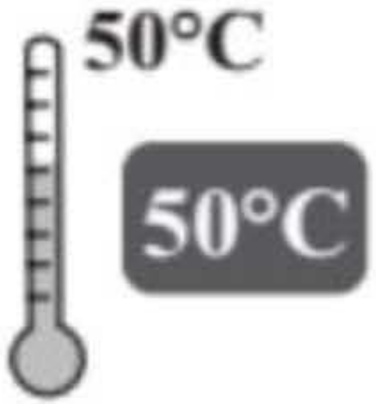
This law states that.

“Two objects at different temperatures in thermal contact with each other tend to move towards the same temperature”

or

“When two bodies A and B have equality of temperature with a third body C, they in turn have equality of temperature with each other”.

Thermodynamic Equilibrium

Mechanical Equilibrium → $F_{net} = 0$	Chemical Equilibrium → net rate = 0	Thermal Equilibrium → $\Delta T = 0$
When there is no macroscopic movement in the system. 	When Rate of forward reaction = Rate of backward reaction. 	When temperature of system = temperature of surroundings. 

Internal Energy (U)/(E)

⇒ All the possible forms of energy that are associated with a system are referred to as internal energy.

⇒ It is impossible to measure the exact value of the internal energy of a system. However, change in internal energy (U) can be measured when the system changes its state.

U = Kinetic energy + potential energy + Vibrational energy + electronic energy + rotational energy - - -

↳ state function

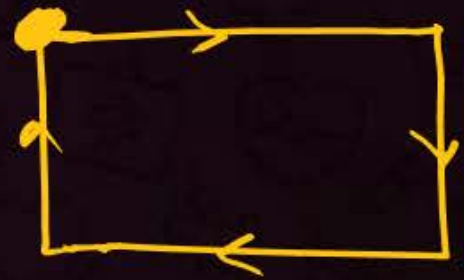
↳ extensive property.

Characteristics of Internal Energy

- Extensive property
- State property
- Does not depend on the path
- No change in a cyclic process.

$$\boxed{\Delta U = U_{final} - U_{initial}}$$

Cyclic process ⇒ (initial state = final state)



$$(\Delta \text{ state function}) = 0$$

QUESTION

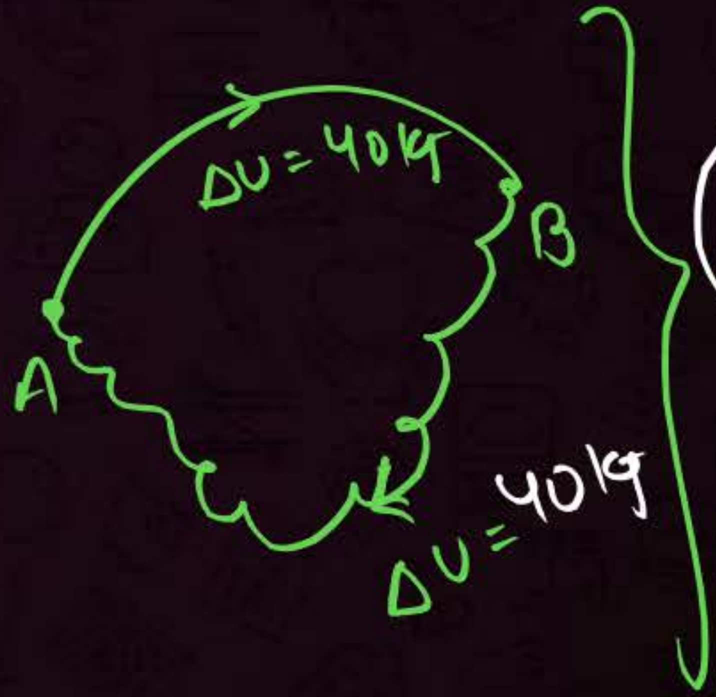
The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy.

A) < 40 kJ

[✓ B) Zero]

C) 40 kJ

D) > 40 kJ



$\Delta U_{\text{net change}} \doteq 0$

First Law of Thermodynamics

Time-table X

Target-table ✓

It is simply the law of conservation of energy.

It was given by Robert Mayer and Helmholtz.

The different statements of the law are as follows:

(i) "Energy cannot be created or destroyed but it can be transformed from one form to another".

(ii) "The total energy of the universe is constant"

(iii) "Total energy of an isolated system remains constant though it may change from one form to another".

Mathematical Formulation

The change in internal energy can be brought about in two ways.

(i) Either by allowing the heat to flow into the system (absorption) or out of system (evolution).

(ii) By doing work on the system or the work done by the system.

$$\boxed{\Delta U = \underset{\text{Heat}}{Q} + \underset{\text{work}}{W}} \leftarrow \text{alert} \rightarrow \text{Use sign convention correctly.}$$

Q A system absorbs 300 J of heat and does a work of 50 J. What will be ΔU?

Sol:

$$\Delta U = Q + W$$
$$= +300 - 50 = \underline{+250}$$

QUESTION

Identify the state functions among the following-

A $+q$ ✗

B $q - w$

[✓ C] $\boxed{q + w = \Delta U}$

D q/w

QUESTION NCERT

In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

Sol:

$$\Delta U = 701 - 394$$

$$^{7}307$$

NOTE → For ideal gas, $\Delta U \propto \boxed{\Delta T}$

Temp. increases, $(\Delta T = T_{final} - T_{initial}) > 0$, $\Delta U > 0$ (internal energy inc.)

Temp. decreases $(\Delta T = T_{final} - T_{initial}) < 0$, $\Delta U < 0$ (internal energy dec.)

QUESTION

$Q = 0$

A sample of liquid in a thermally insulated container (a calorimeter) is stirred for 2 hr. by a mechanical linkage to a motor in the surrounding, for this process

- (A) $w < 0 ; q = 0 ; \Delta U = 0$
- (B) $w > 0 ; q > 0 ; \Delta U > 0$
- (C) $w < 0 ; q > 0 ; \Delta U = 0$
- [✓ (D)] $w > 0 ; q = 0 ; \Delta U > 0$

$$\Delta U = \overset{0}{\cancel{Q}} + \underbrace{W}_{\text{on the system}}$$

+ve

+ve

Types of Thermodynamic Process

① Isothermal Process : $\boxed{\text{Temp} = \text{Constant}}$ $\boxed{\Delta T = 0}$

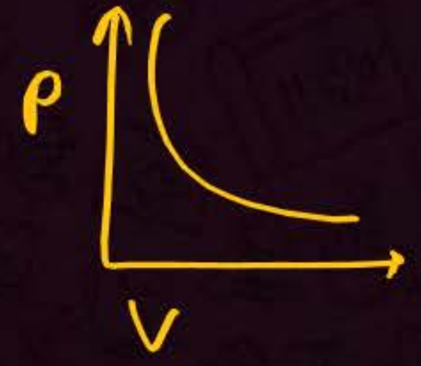
↓

for ideal gas ⇒ $\boxed{\Delta U_{\text{isothermal}} = 0}$

→ $PV = nRT$

→ $\boxed{PV = \text{Constant}}$

→ $\boxed{P_1V_1 = P_2V_2}$



Applying Ist law

$\Delta U = Q + W$

$\boxed{0 = Q + W}$ → $\boxed{+Q = -W}$

$\boxed{0 = Q + W}$ → $\boxed{-Q = +W}$

$PV = \text{Constant} = K$

$PdV + VdP = 0$

$$\boxed{\left(\frac{dP}{dV}\right)_{\text{isothermal}} = -\frac{P}{V}}$$ → slope of isothermal graph.

$P \propto \frac{1}{V}$ → at Constant (T), (n)

→ Boyle's law

② Isochoric Process :- $\boxed{\text{Volume} = \text{Constant}}$

$\Delta V = 0$

$$\boxed{\text{Workdone} = -P\Delta V = 0}$$

Applying I^{st} law of thermo

$$\Delta U = Q + \cancelto{0}{w}$$

max. value of internal energy ← $\boxed{\Delta U = Q_V = \text{heat at constant volume}}$

$$\Delta U = nC_V\Delta T$$

↓ Molar heat capacity at constant volume

ideal gas equation

$PV = nRT$

Gay-Lussac's law ↔ $\boxed{P \propto T}$ → in kelvin

$\frac{P}{T} = \text{constant}$ $\quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$

For 1 mole

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

$$\left(\frac{\Delta U}{\Delta T}\right)_{V=\text{constant}} = C_V = \left(\frac{dU}{dT}\right)_{V=\text{constant}}$$

for a reaction

$$\frac{(\Delta U)}{(\Delta T)} = (\Delta C_V)_{rxn} = \sum (C_V)_{\text{Products}} - \sum (C_V)_{\text{reactu}}$$

$$\left\{\frac{(\Delta U)_{T_2} - (\Delta U)_{T_1}}{T_2 - T_1} = (\Delta C_V)_{rxn}\right\}$$

③ Adiabatic Process ⇒ $\boxed{Q=0}$

Applying F.L.O.T

$$\Delta U = \cancelto{0}{Q} + W$$

$$\boxed{nC_v\Delta T} = \boxed{\Delta U = W_{adi}}$$

In adiabatic process

W done by the system, $\Delta U = -ve$

$\boxed{W = -ve}$ $\boxed{\Delta T = -ve}$

Temp. decreases.

(Cooling effect)

④ Free expansion/Vaccum ⇒ $P_{ext} = 0$

→ $W = -P\Delta U = 0$

F.L.O.T

$$\Delta U = Q + \cancelto{0}{W}$$

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

⑤ Cyclic Process :- $\boxed{\Delta U = 0}$

F.L.O.T

$$\cancelto{0}{\Delta U} = Q + W$$

$$\begin{tikzcd}
 & \boxed{0 = Q + W} \arrow[dl] \arrow[dr] & \\
\boxed{+Q = -W} & & \boxed{-Q = +W}
\end{tikzcd}$$

⑥ Isobaric Process ⇒ Pressure = constant

F.L.O.T

$$\Delta U = Q + W$$

$$\Delta U = Q - P\Delta V$$

$$\boxed{\Delta U + P\Delta V = Q_p} \rightarrow \text{enthalpy } (\Delta H)$$

$$\boxed{\Delta U + P\Delta V = Q_p = \Delta H = nC_p\Delta T}$$

C_p → molar heat capacity at constant Pressure

$$\Delta H = nC_p\Delta T$$

for 1 mole, $\Delta H = C_p\Delta T$

$$\left(\frac{\Delta H}{\Delta T}\right)_{P=\text{constant}} = C_p = \left(\frac{dH}{dT}\right)_{P=\text{constant}}$$

For rxn

$$\frac{\Delta H}{\Delta T} = (\Delta C_p)_{rxn} = \sum (C_p)_{product} - \sum (C_p)_{reactan}$$

$$\boxed{\frac{(\Delta H)_{T_2} - (\Delta H)_{T_1}}{T_2 - T_1} = (\Delta C_p)_{rxn}}$$

$$PV = nRT \Big\} \boxed{V \propto T}$$

→ charle's law

→ (in kelvin)

$$\frac{V}{T} = \text{contant}$$

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

⑦ Reversible Process

infinitely slow process with infinitely small step.

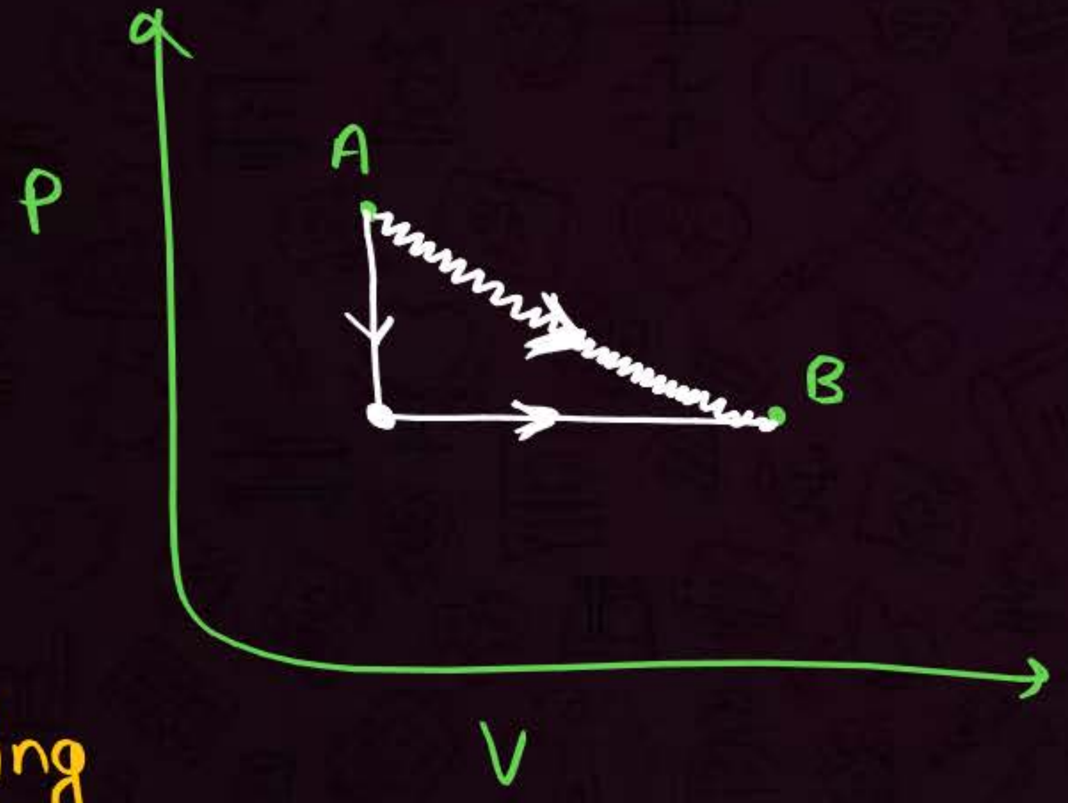
Completion time = ∞

No practical use

$\Rightarrow \underbrace{F_{ext}}_{\text{Driving force}} \cong \underbrace{F_{int}}_{\text{Opposing force}}$

Driving force ≃ Opposing force

$(P_{ext} \simeq P_{int})$

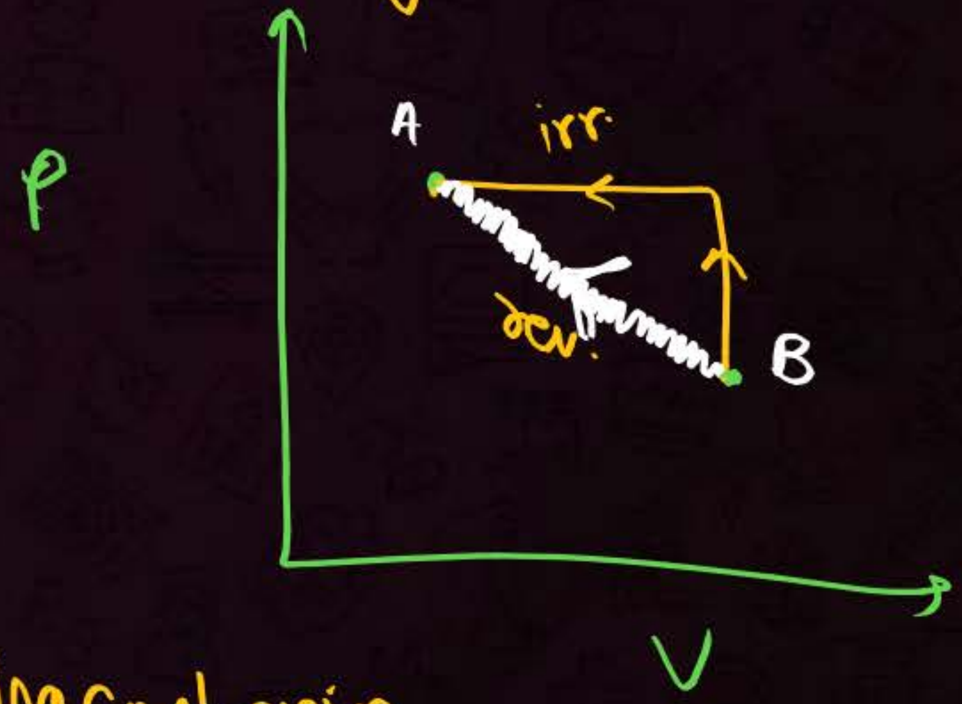


during expansion

$$|W_{rev}| > |W_{irrev}|$$

⑧ Irreversible Process

- finite step.
- practical world
- $F_{ext}/P_{ext} >>> P_{int}$
- $F_{driving} >>> F_{opposing}$.



during compression

$$|W_{rev}| < |W_{irr.}|$$

Reversible Process	Irreversible Process
It is a slow process going thorught a series of small stages with each stage maintaining equilibrium between the system and surroundings.	In this process the system attains final stage from the initial state with a measurable speed. During the transformation, there is no equilibrium maintained between the systems and the surroundings.
A reversible process can be made to proceed in forward or backward direction.	Irreversible process can take place in one direction only.
The driving force for the reversible process is small since the process proceeds in smaller steps.	There is a definite driving force required for the progress of the irreversible process.

Reversible Process	Irreversible Process
Work done in a reversible process is greater than the corresponding work done in irreversible process.	Work done in an irreversible process is lower than the same kind of work done in a reversible process.
A reversible process can be brought back to the initial state without making a change in the adjacent surroundings.	An irreversible process cannot be brought back to its initial state without making a change in the surroundings.

QUESTION

One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litres. The Change in Internal Energy for this process is ($R = 2$ cal $mol^{-1}K^{-1}$)

A 163.7 cal

B [✓ zero]

C 138.1 cal

D 9 lit atm.

QUESTION

In which process net work done is zero?

A Isochoric

B Free expansion

C Adiabatic

[✓ D] Both A & B

QUESTION

When 1 mole of gas is heated at constant volume. $\rightarrow W=0$ **Temperature is raised from 298 to 308 K. Heat supplied to the gas is 500 J. then which statement is correct?**

(A) $q = -W = 500$ J, $\Delta U = 0$ ✗

(B) [✓ $q = \Delta U = 500$ J, $W = 0$]

(C) $q = W = 500$ J, $\Delta U = 0$ ✗

(D) $\Delta U = 0$, $q = W = -500$ J ✗

QUESTION

The net internal energy change in reversible cyclic process is:

- (A) 3/2 RT
- [✓ (B)] Zero
- (C) Greater than zero
- (D) Less than zero

QUESTION

In a given process on an ideal gas, $\boxed{dw = 0}$ and $\underbrace{dq < 0}$. Then for the gas,

[✓ A] The temperature will decrease.

B The volume will increase.

C The pressure will remain constant.

D The temperature will increase.

$$\underbrace{\Delta U}_{\boxed{-ve}} = \underbrace{Q}_{-ve} + \cancel{W} \to 0$$

QUESTION

A piston filled with 0.04 mol 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, $\ln 7.5 = 2.01$)

$\Delta U = 0$

$Q = -w$

$w = -Q$

$Q = +208$ J

$W = -208$ J

(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

QUESTION

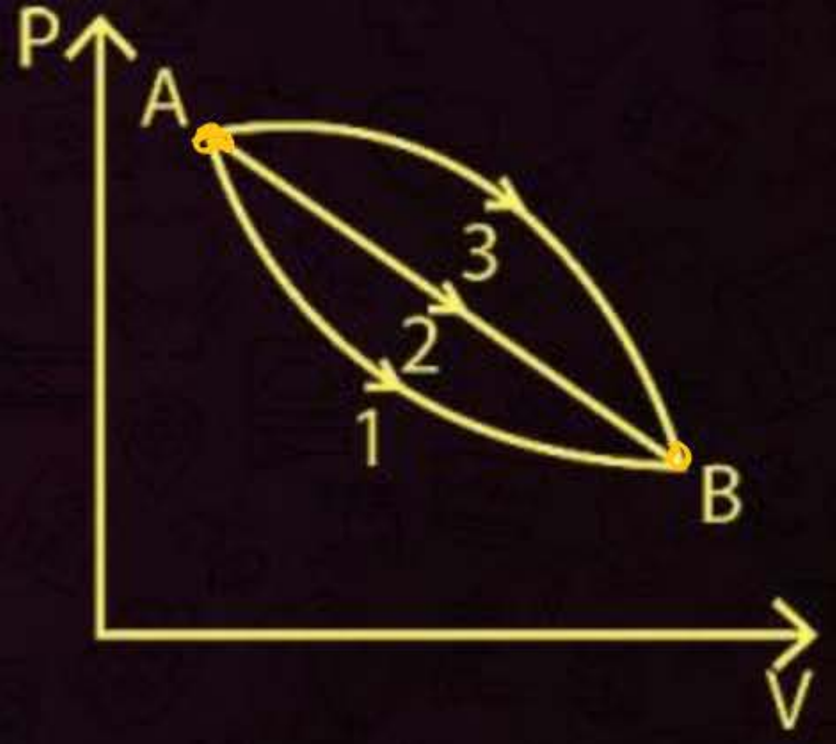
A given mass of gas expands from the state A to the state B by three paths 1, 2 and 3 as shown in the figure. If w_1, w_2, and w_3 respectively be the magnitudes work done by the gas along three paths then

A $w_1 > w_2 > w_3$

B $w_1 < w_2 < w_3$

[✓ C $w_1 = w_2 = w_3$]

D $w_2 < w_3 < w_1$



QUESTION

One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litres. The E for this process is (R = 2 cal mol^{-1}K^{-1})

- **A** 163.7 cal
- **B** [✓ zero]
- **C** 138.1 cal
- **D** 9 lit atm.

QUESTION

In which process net work done is zero?

- (A) Cyclic ✗
- [✓ (B) Isochoric]
- [✓ (C) Free expansion]
- (D) Adiabatic ✗

QUESTION

$\rightarrow w = 0$

When 1 mole of gas is heated at constant volume. Temperature is raised from 298 to 308 K. Heat supplied to the gas is 500 J. then which statement is correct?

(A) $q = -W = 500\ \text{J}, \Delta U = 0$

[✓ (B) $q = \Delta U = 500\ \text{J}, W = 0$]

(C) $q = W = 500\ \text{J}, \Delta U = 0$

(D) $\Delta U = 0, q = W = -500\ \text{J}$

QUESTION

A system is in thermodynamic equilibrium if it is in:

A only thermal equilibrium.

B chemical, mechanical and thermal equilibrium. ✓

C only chemical equilibrium.

D only mechanical equilibrium.

QUESTION

A cup of tea placed in the room eventually acquires room temperature by losing heat. The process may be considered close to:

- **A** cyclic process.
- [✓ **B** reversible process.]
- **C** isothermal process.
- **D** None of these

QUESTION

Match List-I with List-II to find out the correct option.

List-I		List-II	
A.	A process carried out infinitesimally slowly.	I.	Adiabatic
B.	A process in which no heat enters or leaves the system.	II.	$\Delta E = 0, \Delta H = 0$
C.	A process carried out at constant temperature.	III.	Reversible
D.	Cyclic process.	IV.	Isothermal

(A) A-II, B-I, C-IV, D-III

(B) A-IV, B-II, C-I, D-III

(C) A-IV, B-I, C-III, D-II

[✓ (D)] A-III, B-I, C-IV, D-II

QUESTION

An irreversible process is characterized by;

A the system returning to its initial state after completion of the process.

B a continuous decrease in temperature of the system.

[✓ C] the inability to completely restore both the system and its surroundings to their initial states.

D the absence of any heat transfer during the process.

QUESTION

In which of the following processes, the pressure of an ideal gas remain constant?

(A) Isothermal expansion

[✓ (B) Isobaric compression]

(C) Adiabatic expansion

(D) Isochoric heating

QUESTION

During an isochoric process, 400 J of heat is added to a system. How much work is done by the system?

[✓ A] 0 J

B 400 J

C –400 J

D Cannot be determined

Enthalpy

→ represented by $\textcircled{H}$

→ state function.

→ extensive property.

→ heat at constant pressure.

$$\boxed{\begin{array}{l} \Delta H = Q_p = nC_p\Delta T \\ \Delta H = \Delta U + P\Delta V \\ \Delta H = \Delta U + (P_2V_2 - P_1V_1) \end{array}}$$

valid for all

Mathematically

$$\boxed{H = U + PV}$$

$$\Delta H = \Delta U + \Delta(PV) \longrightarrow \Delta H = \Delta U + P\Delta U + \cancel{V\Delta P} \rightarrow \text{negligible}$$

$$\boxed{\Delta H = \Delta U + (P_2V_2 - P_1V_1)} \qquad \boxed{\Delta H = \Delta U + P\Delta V}$$

For ideal gas: $PV = nRT$

$P\Delta V = \Delta nRT$

$$\boxed{\Delta H = \Delta U + \Delta n_gRT}$$

Δn_g = no. of gaseous moles of (product - reactant)

$$\boxed{\Delta H = \Delta U + \Delta n_g RT} \Rightarrow \boxed{Q_p - Q_v = \Delta n_g RT}$$

Case-I → $\Delta n_g = 0$, $\boxed{\underset{Q_p}{\Delta H} = \underset{Q_v}{\Delta U}}$

→ both sids of rxn have equal gaseous moles.

→ both sides of rxn, there are solids & liquid.

Case-II → $\Delta n_g > 0$ $\quad \Delta H > \Delta U$

Case-III → $\Delta n_g < 0$ $\quad \Delta H < \Delta U$

$$R = \left(8.314 = \frac{25}{3}\right) \text{J mol}^{-1} \text{K}^{-1}$$

$$R = \frac{8.314}{1000} \text{kJ mol}^{-1} \text{K}^{-1}$$

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

$$R = \frac{2}{1000} \text{kcal mol}^{-1} \text{K}^{-1}$$

QUESTION

Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta U$?

(A) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$ → $\Delta n_g = 2 - 1 = 1$

(B) $2CO(g) + O_2(g) \rightarrow \underline{2}CO_2(g)$ → $\Delta n_g = 2 - 3 = \boxed{-1}$

[✓ (C)] $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ → $\Delta n_g = 2 - 2 = 0$

(D) $\underline{C(s)} + 2H_2O(g) \rightarrow 2H_2(g) + CO_2(g)$ → $\Delta n_g = 3 - 2 = 1$

QUESTION

For the reaction, $C_3H_5(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ at constant temperature, $\Delta H - \Delta U$ is

A +RT

B –3RT ✓

C +3RT

D –RT

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

$$\downarrow$$

$$(3-6)RT$$

$$-3RT$$

QUESTION

The value of enthalpy change (H) for the reaction $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ at 27°C is –1366.5 kJ mol^{-1}. The value of internal energy change for the above reaction at this temperature will be:

(A) –1371.5 kJ

(B) –1369.0 kJ

[✓ (C)] –1364.0 kJ

(D) –1361.5 kJ

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

$$\Delta U = -1366.5 - (-1) \times \frac{8.314}{1000} \times 300$$

$$\Delta U = -1366.5 + 2.5$$

$$\underline{\Delta U = -1364.0}$$

QUESTION

One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) → (4.0 atm, 5.0 L, 245 K) with a change in internal energy, $\Delta U = 30.0$ L atm. The change in enthalpy (ΔH) is the process in L atm is:

A 40.0

B 42.3

[✓ **C**] 44.0

D Not defined, because process is not constant

$$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$$

$$\Delta H = 30\ \text{l-atm} + (4\times5 - 3\times2)$$

$$= 30 + 14 = \underline{44}$$

QUESTION

For a gaseous reaction; $N_2O_4(g) \rightarrow 2NO_2(g)$ → $\underline{\Delta n_g = 2-1=1}$

(A) ΔH and ΔU are equal.

[✓ (B)] $\Delta H - \Delta U = RT$

(C) $\Delta H - \Delta U = 2R$

(D) $\Delta H - \Delta U = 0$

QUESTION

The latent heat of vapourisation of a liquid at 500 K and 1 atm pressure is 10.0 kcal/mol. What will be the change in internal energy of 3 moles of the liquid at the same temperature and pressure?

[✓ A] 27.0 kcal

B 13.0 kcal

C –27.0 kcal

D –13.0 kcal

$$\boxed{A(l) \rightleftharpoons A(g)}$$

$\Delta n_g = 1 - 0 = 1$

$\Delta H = 10 \text{ kcal/mol}$

$$\boxed{\begin{aligned} \Delta U &= \Delta H - \Delta n_g RT \\ &= \underbrace{3\times10} - (3\times1)\times\frac{\cancel{2}}{\cancel{1000}}\times\cancel{500} \\ &= 30 - 3 = 27 \text{ kcal} \end{aligned}}$$

QUESTION

For which of the following reactions, ΔH and ΔU are equal?

(i) $H_2(g) + \frac{1}{2}O2(g) \rightarrow H_2O(l)$

(ii) $H_2(g) + I_2(g) \rightarrow 2HI(g)$ $\longrightarrow \Delta n_g = 2-2=0$

(iii) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\longrightarrow \Delta n_g = 1-1=0$

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

A (i) only

[✓ B] (ii) and (iii) only

C (iii) only

D (iv) only

$$\boxed{\underbrace{\Delta H}_{Q_p} = \underbrace{\Delta U}_{Q_V} + P\Delta V}$$

$$C_p \cancel{\Delta T} = C_v \cancel{\Delta T} + R \cancel{\Delta T}$$

$$C_p = C_v + R$$

$$\boxed{C_p - C_v = R} \rightarrow \text{for 1 mole}$$

$$\boxed{C_p - C_v = nR} \rightarrow \text{for 'n' mole}$$

C_p → molar heat capacity at constant Ⓟ

C_v → molar heat capacity at constant Ⓥ

for 1 mole

$$\Delta H = C_p \Delta T$$

$$\Delta U = C_v \Delta T$$

$$PV = RT$$

$$P\Delta V = R\Delta T$$

In terms of specific heat capacity,

$$\boxed{c_p - c_v = \frac{R}{M}}$$

M → molar mass of gas.

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

$C_p - C_v = R$

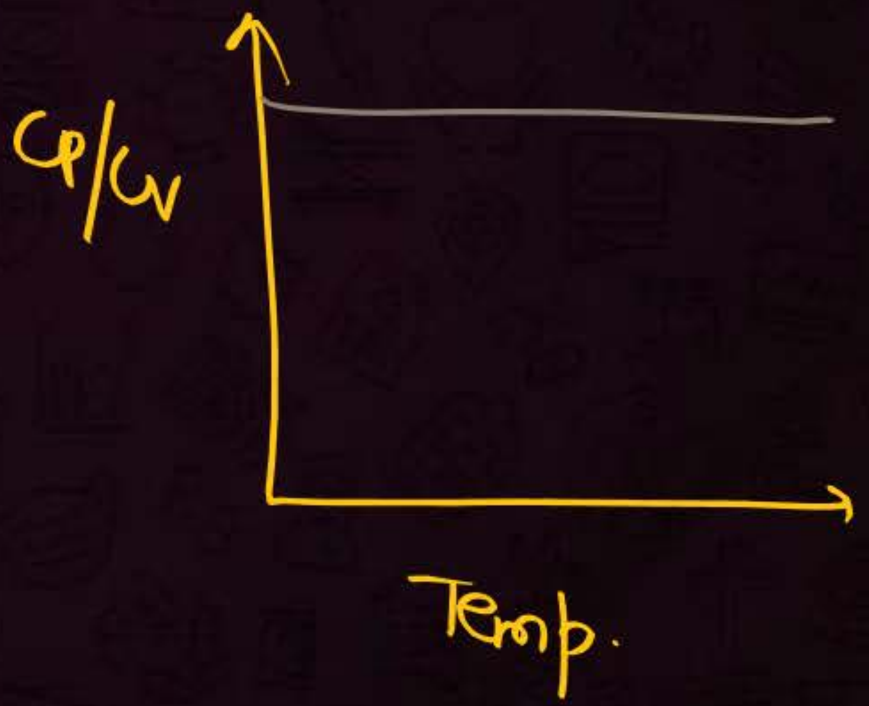
Gas	C_v	C_p	γ
Monoatomic He, Ne	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{3} = 1.66$
Diatomic (O_2, N_2)	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{5} = 1.4$
Polyatomic (linear) CO_2	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{5} = 1.4$
Polyatomic (non-linear)	$\frac{6}{2}R = 3R$	$\frac{8}{2}R = 4R$	$\frac{4}{3} = 1.33$

$$\gamma C_v - C_v = R$$

$$C_v(\gamma - 1) = R$$

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

$$\boxed{\begin{aligned} C_p &= \gamma C_v \\ C_p &= \frac{\gamma R}{\gamma - 1} \end{aligned}}$$



Work Done

$$W = -P_{ext}\,\Delta V = -P_{ext}\left(V_{final} - V_{initial}\right)$$ → valid fr all processes

$$|W| = \text{area under P-V curve}$$

= Isothermal Reversible Process

- $\Delta U = 0$
- $Q = -W$
- $-Q = +W$
- $P_1V_1 = P_2V_2$

$P_{ext} \cong P_{int}$

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

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

Adiabatic Process

$$W_{adi} = \Delta U = nC_v \Delta T = \frac{nR\,\Delta T}{\gamma-1} = \frac{nR(T_2-T_1)}{\gamma-1}$$

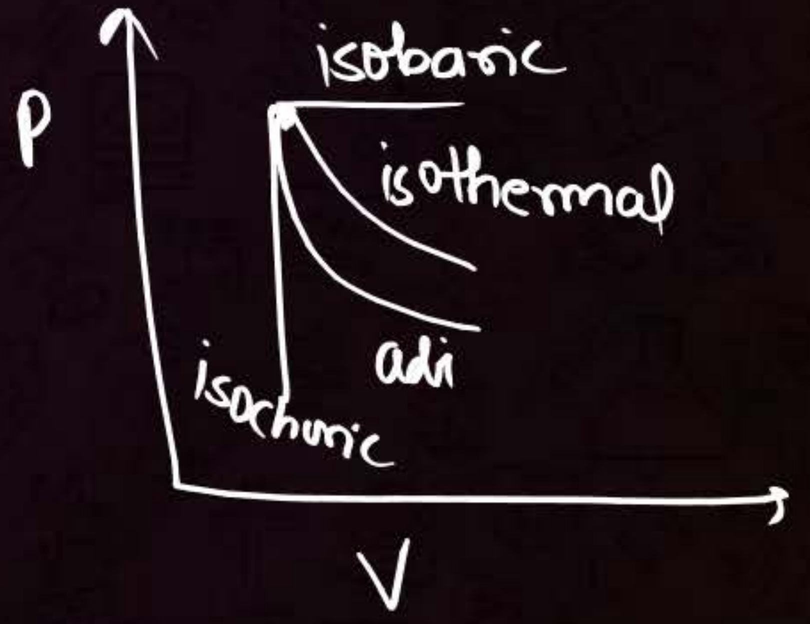
$$= \frac{P_2V_2 - P_1V_1}{\gamma-1}$$

$$P_1V_1 = nRT_1$$
$$P_2V_2 = nRT_2$$

$$P \times V^{\gamma} = \text{constant}$$

Slope of adiabatic process $= \left(\frac{dP}{dV}\right)_{adi} = -\underline{\gamma}\cdot\frac{P}{V}$

Slope of isothermal Process $= -\frac{P}{V} = \left(\frac{dP}{dV}\right)_{iso}$



QUESTION

The maximum work obtained by an isothermal reversible expansion of 1 mole of an ideal gas at 27°C from 2.24 to 22.4 L is ($R = 2$ cal K^{-1} mol^{-1})

[✓ A] –1381.8 cal

B –600 cal

C –138.18 cal

D –690.9 cal

$$W_{iso,rev} = -2.303 \times 1 \times 2 \times 300 \log\left(\frac{22.4}{2.24}\right)$$

$$= \underline{-2.303 \times 600 \text{ cal}}$$

QUESTION

2 mole of an ideal gas at 27°C expands isothermally and reversibly from a volume of 4 litres to 40 litres. The work done (in kJ) is:

(A) w = –28.72 kJ

[✓ (B)] w = –11.488 Kj

(C) w = –5.736 kJ

(D) w = –4.988 kJ

$$W_{iso,rev} = -2.303\, nRT \log \frac{V_2}{V_1}$$

$$= -2.303 \times 2 \times \frac{8.314}{10\cancel{00}} \times 3\cancel{00} \log\left(\frac{\overset{10}{\cancel{40}}}{\cancel{4}}\right)$$

$$= -2.303 \times \underbrace{2 \times 2.5}_{}\ kJ$$

QUESTION

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

- A –12.5 kJ
- [✓ B] –2.5 kJ
- C –625 kJ
- D 500 kJ

$W_{adi} = nC_V \Delta T$

$= 2 \times 12.5 \times (200 - 300)$

$\Rightarrow -25 \times 100 \text{ J}$

$\Rightarrow -2500 \text{ J}$

$\Rightarrow -2.5 \text{ kJ}$

QUESTION

What is the final temperature of 0.10 mole monoatomic ideal gas that performs 75 cal of work adiabatically if the initial temperature is 227°C? (use R = 2 cal/K-mol)

$\rightarrow \gamma = \frac{5}{3}$

$\boxed{W_{adi} = -75\,cal}$

$T_1 = 227 + 273$
$= 500K$

- **A** $\boxed{250\text{ K}}$
- **B** 300 K ✗
- **C** 350 K
- **D** 750 K ✓

$$W_{adi} = \frac{nR(T_2 - T_1)}{\gamma - 1} = \frac{0.1 \times 2 \times (T_2 - 500)}{\left(\frac{5}{3} - 1 = \frac{2}{3}\right)}$$

$$+75 = \frac{+0.1 \times \cancel{2} \times (T_2 - 500) \times 3}{\cancel{2}}$$

$$\frac{750}{0.3} = T_2 - 500$$

$$250 = T_2 - 500$$

$$\boxed{T_2 = 750\,K}$$

Adiabatic Process

$$\boxed{P \times V^{\gamma} = \text{constant}}$$

$$PV = nRT$$

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

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

$$\frac{nRT}{V} \times V^{\gamma} = \text{constant}$$

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

$$P \times \left(\frac{nRT}{P}\right)^{\gamma} = \text{constant}$$

$$P \times (nR)^{\gamma} \cdot \frac{T^{\gamma}}{P^{\gamma}} = \text{constant}$$

$$\boxed{P^{1-\gamma} \cdot T^{\gamma} = \text{constant}}$$

$$\left\{ \begin{aligned} & P^{1}\, T^{\frac{\gamma}{1-\gamma}} = \text{constant} \\ & P^{\frac{1-\gamma}{\gamma}} \cdot T = \text{constant} \end{aligned} \right\}$$

QUESTION

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

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

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

A gas expands adiabatically at constant pressure such that $TV^{1/2}$. The value of (C_p/C_v) of the gas will be:

- A 1.30
- [✓ B] 1.50
- C 1.70
- D 2

$TV^{1/2} = \text{constant}$

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

$\gamma - 1 = \frac{1}{2}$

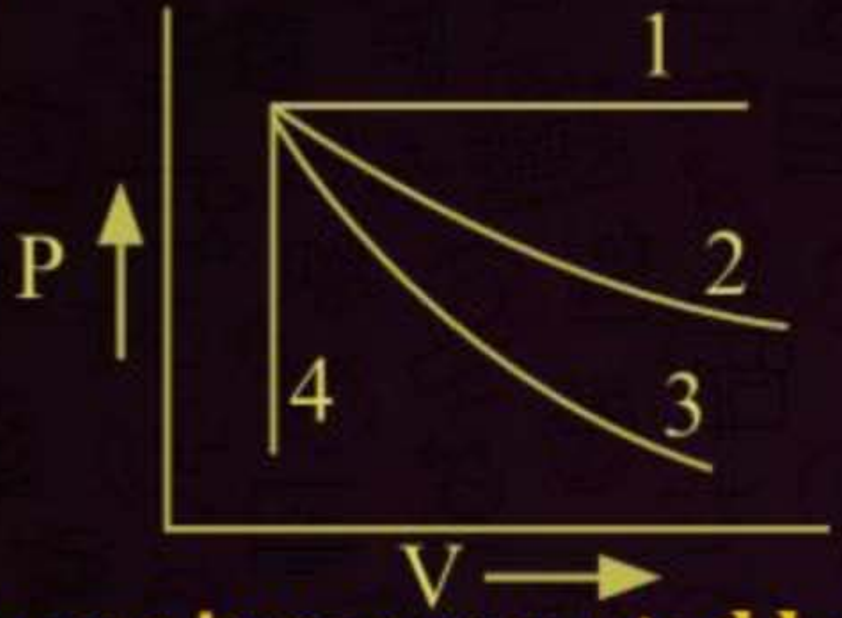
$\boxed{\gamma = \frac{3}{2}}$

QUESTION

Which amongst the following options is the correct relation between change in enthalpy and change in internal energy? [2023]

- (A) $\Delta H + \Delta U = \Delta nR$
- (B) $\Delta H = \Delta U - \Delta n_g RT$
- [✓ (C) $\Delta H = \Delta U + \Delta n_g RT$]
- (D) $\Delta H - \Delta U = -\Delta nRT$

QUESTION



Isobaric process is represented by:

(A) 3

(B) 4

[✓ (C) 1]

(D) 2

QUESTION

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

- A) 500 kcal
- B) 15.1 kcal
- C) 25.03 kcal
- [✓ D)] 2.303 kcal

$V_1 = V$

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

$$W_{iso,rev} = -2.303 \times 1 \times 2 \times 500 \log\left(\frac{1}{10}\right)$$

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

$$\Rightarrow \underline{+2.303 \text{ kcal}}$$

QUESTION

At constant temperature for the reaction $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(\ell)$, $\Delta E - \Delta H$ is:

- **A** +RT
- **B** −3RT
- **C** [✓ +3RT]
- **D** −RT

$\Delta n_g = 3 - 6 = \boxed{-3}$

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

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

$= -(-3)RT$

$\Rightarrow \underline{3RT}$

QUESTION

Heat of reaction for $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ at constant V is –67.71 kCal at 17°C. The heat of reaction at constant P at 17°C is:

[✓ (A)] –68.0 kCal

(B) +68.0 kCal

(C) –67.42 kCal

(D) None

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

$$= -67.71 - \frac{1}{\cancel{2}} \times \frac{\cancel{2}}{1000} \times 290$$

$$= -67.71 - 0.29$$

QUESTION

For which change $\Delta H \neq \Delta E$:

A $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

B $HCl(\ell) + NaOH(\ell) \rightarrow NaCl(s) + H_2O(\ell)$

C $C(s) + O_2(g) \rightarrow CO_2(g)$

[✓ D] $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

QUESTION

When 229 J of energy is supplied as heat at constant pressure to 3 mol Ar(g), the temperature of the sample is increased by 2.55K. Calculate the molar heat capacity at constant volume:

A 30 kJ K^{-1} mol^{-1}

B 30 J K^{-1} mol^{-1}

[✓ **C**] 21.7 J K^{-1} mol^{-1}

D 21.7 kJ K^{-1} mol^{-1}

$$Q_p = 229\,J = n\,C_p\,\Delta T$$

$$229 = 3 \times C_p \times 2.55$$

$$C_p = \frac{229}{3 \times 2.55} = 29.93\,J$$

$$C_p - C_v = R$$

$$\boxed{\begin{aligned} C_v &= C_p - R \\ &\Rightarrow 29.93 - 8.314 \\ &= 21.62 \end{aligned}}$$

QUESTION

Calculate w for the isothermal reversible expansion of 1 mol of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K:

- [✓ A] −5227.2 J
- B +5227.2 J ✗
- C −2257 J ✗
- D +2257 J ✗

$$W_{iso,rev} = -2.303\,nRT\log\left(\frac{P_1}{P_2}\right)$$

$$= -2.303 \times 1 \times 8.314 \times 273 \underbrace{\log\left(\frac{1}{0.1}\right)}$$

$$\Rightarrow -\underbrace{2.303 \times 8.314} \times 273$$

QUESTION

For a reversible process at T = 300K, the volume is increased from $V_i = 1L$ to $V_f = 10L$. Calculate ΔH if the process is isothermal-

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

(A) 11.47 kJ

(B) 4.98 kJ

[✓ (C)] 0

(D) –11.47 kJ

Limitations of First Law of Thermodynamics

① doesnot explain about feasibility of Process.

② does not explain of direction of flow of heat.

Process

Spontaneous Process
or
Feasible Process

→ occurs by itself without help of any external force.

Non-spontaneous Process
or
Non-feasible Process

→ Occurs with the help of external force

Driving force

→ maximum stability (min energy) $\Delta H<0$

→ Maximum Randomness

Entropy (S)

→ degree of measure of randomness / disorderness

→ $S_{gas} > S_{liquid} > S_{solid}$

→ state function.

→ extensive property

→ $\boxed{\Delta S = \frac{Q_{rev}}{T} \text{ or } \frac{\Delta H}{T}}$ ← for a process

$$\begin{tikzcd} \text{Solid} \arrow[r, "\Delta S>0"] & \text{liquid} \arrow[l, bend left, "\Delta S<0"] \arrow[r, "\Delta S>0"] & \text{Gas} \arrow[l, bend left, "\Delta S<0"] \end{tikzcd}$$

⇒ $S_{soft} > S_{hard}$

⇒ $S_{CH_4} < S_{C_2H_6} < S_{C_3H_8}$

⇒ Temp. ↑ S. ↑

ΔS ↓

for a rxn

$aM + bN \longrightarrow cR$

$(\Delta S)_{rxn} = [c(\Delta S)_R] - [a(\Delta S)_M + b(\Delta S)_N]$

$$\boxed{(\Delta S)_{rxn} = \sum(\Delta S)_{product} - \sum(\Delta S)_{Reactant}}$$

Entropy (S)

- Entropy is a thermodynamic state quantity which is a measure of randomness or disorder of the system.
- More is the randomness in the system, more is the entropy of the system.
- Entropy is a state function and depends only on initial and final states of the system.

⇒ If the temperature of a system increases, entropy increases.

⇒ If the temperature of a system decreases, entropy decreases.

⇒ For a fixed volume system, entropy increases if the number of molecules is increased in the system.

⇒ For a system with fixed number of molecules, entropy increases as volume increases and vice – versa.

⇒ Entropy of more complex molecules is larger than those of simpler molecules as in more complex molecules there are more ways of arranging atoms in 3D (i.e. more randomness).

⇒ Entropy of compounds with similar molecular masses increases (with increase) in their sizes.

$\boxed{\text{size}\uparrow \quad S\uparrow}$

⇒ Entropies of ionic solids becomes larger as the attraction amongst the ions become weaker.-

$S_{NaCl} > S_{MgCl_2}$

IMF ⇒ $NaCl < MgCl_2$

⇒ Harder substances have smaller entropies than softer substances.

e.g. $S_{C(diamond)} < S_{C(graphite)} < S_{Fe} < S_{Al} < S_{Na}$

\# $$\boxed{\Delta S = \frac{Q_{rev}}{T_{(in\ K)}} \text{ or } \frac{\Delta H}{T}} \begin{matrix}\rightarrow J/mol \\ \rightarrow K\end{matrix}$$

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

$$\boxed{\Delta S > 0}$$

$$R_{(s)} \rightleftharpoons P_{(l)} \quad \Delta S > 0$$

$$2H_{2}(g) + O_{2(g)} \longrightarrow 2H_{2}O_{(l)} \quad \Delta S < 0$$

$$\boxed{\text{Unit of entropy} = J\ mol^{-1}\ K^{-1}}$$

Phase transformation → at Constant Ⓣ

Fusion → $\Delta S_{fusion} = \dfrac{\Delta H_{fusion}}{M.pt (in\ k)}$

Vaporisation → $\Delta S_{vap.} = \dfrac{\Delta H_{vap}}{B.pt (in\ k)}$

$$\boxed{\Delta S_{Transition} = \frac{\Delta H_{Transition}}{T_{Transition\ (in\ k)}}}$$

QUESTION

In which reaction ΔS is positive:

A $H_2O_{(\ell)} \rightarrow H_2O_{(s)} \rightarrow \Delta S < 0$

B $\underline{3}O_{2(g)} \rightarrow \underline{2}O_{3(g)} \rightarrow \Delta S < 0$

C $H_2O_{(\ell)} \rightarrow H_2O_{(g)} \} \; \Delta S > 0$

D $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)} \} \; \Delta S < 0$

QUESTION

Which of the following reactions is associated with negative change in entropy?

(A) $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$ → $\Delta S > 0$

(B) $C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$ → $\Delta S > 0$

(C) $2C(s, \text{graphite}) + O_2(g) \rightarrow 2CO(g)$ $\Delta S > 0$

[✓ (D)] $3C_2H_2(g) \rightarrow C_6H_6(l)$ → $\Delta S < 0$

Entropy Change

$$\boxed{\Delta S = \frac{\Delta H}{T} \text{ or } \frac{Q_{rev}}{T}}$$

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

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T_{surr}}$$

$$\boxed{\Delta S_{\underset{\text{total}}{\underset{\text{or}}{universe}}} = \Delta S_{sys} + \Delta S_{surr}}$$

For a rxn

$$\boxed{\Delta S_{rxn} = \sum(\Delta S)_{product} - \sum(\Delta S)_{Reactants}}$$

For a process

$$\boxed{\begin{aligned}\Delta S &= nC_v \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right) \\ &= nC_p \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{P_1}{P_2}\right)\end{aligned}}$$

Isothermal Process $(T_2 = T_1)$

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right) = nR \ln\left(\frac{P_1}{P_2}\right)$$

isochoric Process $(V_2 = V_1)$

$$\Delta S = nC_v \ln \frac{T_2}{T_1}$$

isobaric Process $(P_1 = P_2)$

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

QUESTION

The enthalpy of vaporization for water is 186.5 kJ mol^{-1}, the entropy of its vaporization will be-

[✓ A] 0.5 kJ K^{-1} mol^{-1}

B 1.0 kJ K^{-1} mol^{-1}

C 1.5 kJ K^{-1} mol^{-1}

D 2.0 kJ K^{-1} mol^{-1}

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{B.pt}$$

$$= \frac{186.5}{373} = \frac{1}{2}$$

QUESTION

Calculate the entropy change in melting of one gm ice at 0°C if latent heat of ice is 80 cal/g-

$$\Delta S = \frac{Q}{T} = \frac{80}{273}$$

A 80 Cal K^{-1}

B 20 Cal K^{-1}

C 4.4 Cal K^{-1}

[✓ **D** 0.3 Cal K^{-1}]

QUESTION

If S° for H_2, Cl_2 and HCl are 0.13, 0.22 and 0.19 KJ K^{-1} mol^{-1} respectively. The total change in standard entropy for the reaction $H_2 + Cl_2 \longrightarrow 2HCl$ is:

[✓ (A)] 30 JK^{-1} mol^{-1}

(B) 40 JK^{-1} mol^{-1}

(C) 60 JK^{-1} mol^{-1}

(D) 20 JK^{-1} mol^{-1}

$$(\Delta S)_{rxn} = \left[2(\Delta S)_{HCl}\right] - \left[(\Delta S)_{H_2} + (\Delta S)_{Cl_2}\right]$$

$$(\Delta S)_{rxn} = (2 \times 0.19) - (0.13 + 0.22)$$

$$= 0.38 - 0.35$$

$$\Rightarrow \underline{0.03\ KJ/mol\text{-}K}$$

$$\Rightarrow \underline{30\ J/mol^{-1}\text{-}K^{-1}}$$

QUESTION

5 mole of an ideal gas expand reversibly from a volume of 8 dm^3 to 80 dm^3 at a temperature of 27°C. The change in entropy is:

A) 41.57 JK^{-1}

B) –95.73 JK^{-1}

[✓ C)] 95.73 JK^{-1}

D) –41.57 JK^{-1}

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow 2.303 \times 5 \times 8.314 \log\left(\frac{80}{8}\right)$$

$$\boxed{\Delta S \Rightarrow 2.303 \times 5 \times 8.314}$$

QUESTION

1 mole of a diatomic ideal gas at 25°C is subjected to expand reversibly and adiabatically to ten times of its initial volume. Calculate the change in entropy during expansion (in JK^{-1} mol^{-1})

A R ln 10

B –R ln 10

C 2.5 R ln 10

[✓ **D**] Zero

$\boxed{Q=0}$

$\Delta S = 0$

Adiabatic Reversible process

sys & surr. are always in equilibrium

$\Delta S_{sys} = \Delta S_{surr} = 0$

isoentropic process

QUESTION

If one mole of an ideal gas is expanded isothermally at 300 K until it's volume is tripled, then change in entropy of gas is:

A Zero

B Infinity

C 5/2R ln3

D [✓ R ln3]

$V_1 = V$

$V_2 = 2V$

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow 1 \times R \ln \frac{3\cancel{V}}{\cancel{V}}$$

$$\Rightarrow R \ln 3$$

Reversible Process

↳ sys & surr. are always in equilibrium.

$$\boxed{T_{sys} = T_{surr}}$$

$$\boxed{\Delta S_{total} = 0 = \Delta S_{sys} + \Delta S_{surr}}$$

For irreversible Process

$$\boxed{\Delta S_{total} > 0}$$

Adiabatic Reversible

$$\Delta S_{sys} = \frac{Q_{sys}}{T_{sys}} = \frac{0}{T} = 0$$

$$\Delta S_{surr} = \frac{Q_{surr}}{T_{surr}} = \frac{0}{T} = 0$$

$$\Delta S_{total} = 0$$

Isothermal Reversible Process

$$\Delta S_{sys} = nR\ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S_{surr} = \frac{Q_{rev}}{T_{surr}} = \frac{-nR\cancel{T}\ln\left(\frac{V_2}{V_1}\right)}{\cancel{T}} = -nR\ln\left(\frac{V_2}{V_1}\right)$$

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

Process	ΔS_{system}	$\Delta S_{surrouding}$	Sign of ΔS_{total}
Reversible Isothermal	$nR\ln\left(\frac{V_2}{V_1}\right)$	$-nR\ln\left(\frac{V_2}{V_1}\right)$	$= 0$
Irreversible isothermal	$-nR\ln\left(\frac{V_2}{V_1}\right)$	$\frac{-P_{ext}\Delta V}{T}$	> 0
Reversible Adiabatic	0	0	$= 0$
Irreversible Adiabatic	$nC_V\ell n\left(\frac{T_2}{T_1}\right)+nR\ell n\left(\frac{V_2}{V_1}\right)$	0	> 0

Second Law of Thermodynamics

1. It states about the direction of flow of heat
2. All-natural process in universe are ir-reversible process or natural processes are spontaneous process.
3. Due to spontaneous process entropy of universe is increasing continuously i.e. entropy of an isolated system increases.

$(\Delta S)_T = +\text{ve}$ or $(\Delta S)_T = 0$ or $(\Delta S)_{\text{System}} + (\Delta S)_{\text{surr.}} > 0$

for spontaneous process ⇒ $\boxed{\Delta S_{\text{total}} > 0}$

for non-spontaneous process ⇒ $\boxed{\Delta S_{\text{total}} < 0}$

$\boxed{\Delta S_{\text{total}} = 0}$ → Reversible process
→ at equilibrium

QUESTION

In a spontaneous irreversible process, the total entropy of the system and surroundings

A Remains constant

B [✓ Increases]

C Decreases

D Zero

QUESTION

Match the column:

	Column – I		Column – II
a.	Adiabatic process	i.	$q = 0$
b.	Isothermal process	ii.	$\Delta H = 0$
c.	Isoenthalipic process	iii.	$\Delta T = 0$
d.	Isoentropic process	iv.	$\Delta S = 0$

A a-(i); b-(iv); c-(ii); d-(iii)

B a-(ii); b-(i); c-(iv); d-(iii)

C [✓ a-(i); b-(iii); c-(ii); d-(iv)]

D a-(i); b-(iii); c-(iv); d-(ii)

Some Famous or Extra Ordinary Examples of Entropy Change

(soft) (hard)

1. Entropy of graphite > Entropy of diamond.
2. $NH_4Cl(s) + aq \rightarrow NH_4^+(aq) + Cl^-(aq)$

   In this process NH_4^+ and Cl^- ions are free to move in solution where as they are not free to move in solid NH_4Cl.

exception

Hence ΔS is positive for this type of dissolution process.

1. On boiling of egg : Denaturation of proteins occur. Thus entropy increases.
2. Stretching of rubber : During stretching of rubber band its long flexible macromolecules get uncoiled. The uncoiled form has more specific geometry and more ordered arrangement. Thus entropy decreases.

$\Delta S < 0$

$$\boxed{\Delta S = \frac{Q_{rev}}{T} = \frac{\Delta H}{T}} \rightarrow \text{Reversible process}$$

$$\boxed{\text{irreversible process} \Rightarrow \Delta S > \frac{Q}{T} \text{ or } \frac{\Delta H}{T}}$$

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

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

For any spontaneous process

$$\left\{\begin{aligned} &\Delta S_{total} > 0 \\ &\Delta S_{sys} + \Delta S_{surr} > 0 \end{aligned}\right\}$$

$$\boxed{\Delta S_{total} = 0} \rightarrow \text{at equilibrium}$$

$$\Delta S_{total} < 0 \rightarrow \text{non-spontaneous process}$$

Third Law of Thermodynamics (Also Knows as Nernst Heat Theorem)

1. All substance have same heat capacities at 0 K.
2. Heat capacity of every substance is zero at 0 K.
3. Entropy of a perfectly crystalline substance is zero at 0 K.

for a perfect crystalline substance, entropy at Temp T K = $\boxed{S_{T K} = nC_p \ln T}$

Gibbs Free Energy 'G'

⇒ Gibb's energy is defined at constant temperature and pressure to predict spontaneity of a process.

⇒ Gibb's energy is a thermodynamic quantity which is used to measure the capacity of system to do useful work

OR

⇒ Gibb's energy is that part of the total energy of system which can be converted into useful work

$$\boxed{G = H - TS}$$

$$\Delta G = \Delta H - T\Delta S - \cancel{S\Delta T} \rightarrow \text{negligible}$$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

$$\boxed{\Delta G = \underbrace{(\Delta U + \Delta n_g RT)} - T\Delta S}$$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

$$\left\{\begin{array}{l} \Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}. \\ \Delta G_{surr} = \Delta H_{surr} - T\Delta S_{surr} \end{array}\right\}$$

ΔG → state function

→ extensive property.

for a rxn

$$\boxed{\Delta G_{rxn} = \sum(\Delta G)_{product} - \sum(\Delta G)_{Reactant}}$$

$$\# \boxed{\Delta G = \underbrace{V\Delta P}_{\text{non-mechanical work}} - S\Delta T}$$

$$\boxed{\Delta G_{sys} = -T\Delta S_{total}}$$

For spontaneous Process

$$\left\{\begin{array}{l} \Delta S_{total} > 0 \\ \Delta S_{sys} + \Delta S_{surr} > 0 \end{array}\right\} \quad \boxed{\Delta G_{sys} < 0}$$

For non-spontaneous Process

$$\left.\begin{array}{l} \Delta S_{total} < 0 \\ \Delta S_{sys} + \Delta S_{surr} < 0 \end{array}\right\} \quad \boxed{\Delta G_{sys} > 0}$$

at equilibrium

$$\Delta S_{total} = 0 \quad \boxed{\Delta G_{sys} = 0}$$

$$\boxed{\Delta G = V\Delta P - S\Delta T} \rightarrow \text{Constant Ⓣ} \quad \boxed{\Delta T = 0}$$

$$\left(\frac{\Delta G}{\Delta P}\right) = V$$

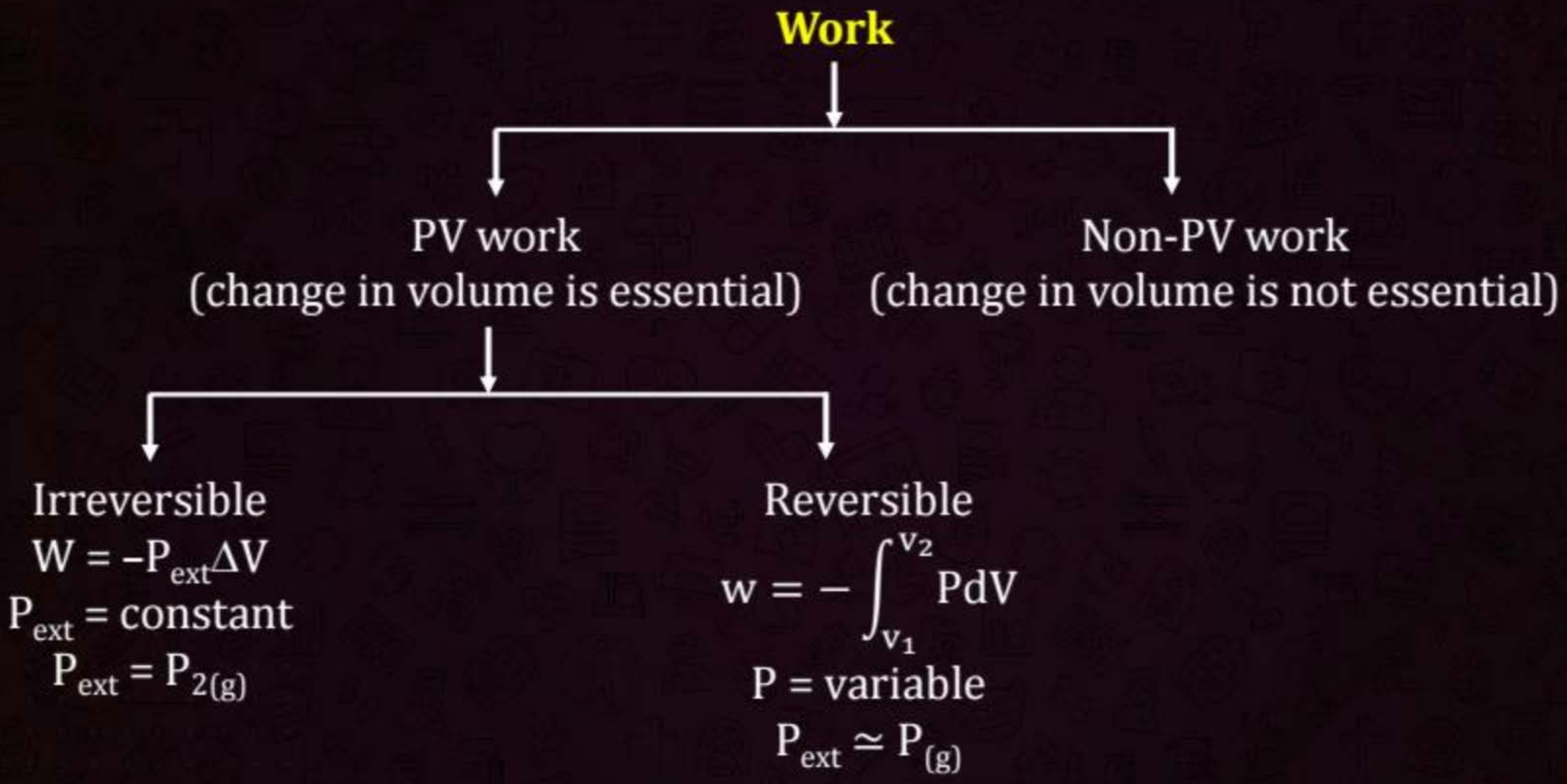
$\downarrow$

at Constant Ⓟ

$$\left(\frac{\Delta G}{\Delta T}\right) = -S$$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

$$\boxed{\Delta G_{sys} = -T\Delta S_{total}}$$



Work

- PV work
  (change in volume is essential)
  - Irreversible
    $W = -P_{ext}\Delta V$
    $P_{ext} = \text{constant}$
    $P_{ext} = P_{2(g)}$
  - Reversible
    $w = -\int_{V_1}^{V_2} PdV$
    $P = \text{variable}$
    $P_{ext} \simeq P_{(g)}$
- Non-PV work
  (change in volume is not essential)

QUESTION

For the reaction at 300 K.

$A(g) + B(g) \rightarrow C(g)$

$\Delta U = -3.0$ kcal $\Delta S = -10.0$ cal/K

($R \approx 2$ cal mol^{-1} K^{-1})

ΔG is:

[✓ A] –600 cal

B –3600 cal

C 2400 cal

D 3000 cal

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

$$= (\Delta U + \Delta n_g RT) - T\Delta S$$

$$= (-3000 - 1\times 2\times 300) - 300 \times -10$$

$$= -3000 - 600 + 3000$$

$$= \underline{\underline{-600}}$$

QUESTION

For a spontaneous process:

A $\boxed{\Delta G = 0} \rightarrow$ at eqm

[✓ B] $\boxed{\Delta G < 0} \rightarrow$ spontaneous

C $\boxed{\Delta G > 0} \rightarrow$ non-spontaneous.

D Any of the above

$\boxed{\Delta G = \Delta H - T\Delta S}$

<u>Case-I</u> ⇒ $\Delta H < 0$, $\Delta S > 0$

$$\underbrace{\Delta G} = \underbrace{\Delta H}_{\text{-ve}} \underbrace{- T\underbrace{\Delta S}_{\text{+ve}}}_{\text{-ve}}$$

$\boxed{\Delta G = \text{-ve} \text{ always}}$

} → always spontaneous at all temp.

<u>Case-II</u> $\Delta H < 0$ $\Delta S < 0$

$$\underbrace{\Delta G} = \underbrace{\Delta H}_{\text{-ve}} \underbrace{- T\underbrace{\Delta S}_{\text{-ve}}}_{\text{+ve}}$$

$\boxed{\Delta G = \text{-ve}}$ when $|\Delta H| > |T\Delta S|$

} spontaneous at low temp.

<u>Case-III</u> $\Delta H > 0$ $\Delta S > 0$

$$\Delta G = \underbrace{\Delta H}_{\text{+ve}} \underbrace{- T\underbrace{\Delta S}_{\text{+ve}}}_{\text{-ve}}$$

} spontaneous at high temp.

$\boxed{\Delta G = \text{-ve}}$ when $|T\Delta S| > |\Delta H|$

<u>Case-IV</u> $\Delta H > 0$ $\Delta S < 0$

$$\Delta G = \underbrace{\Delta H}_{\text{+ve}} \underbrace{- T\underbrace{\Delta S}_{\text{-ve}}}_{\text{+ve}}$$

} always non-spontaneous

$\boxed{\Delta G = \text{+ve} \text{ always}}$

QUESTION

In which of the following cases, the reaction is spontaneous at all temperatures?

$$\boxed{\begin{array}{l}\Delta H<0\\ \Delta S>0\end{array}}$$

(A) $\Delta H > 0, \Delta S > 0$

[✓ (B)] $\Delta H < 0, \Delta S > 0$

(C) $\Delta H < 0, \Delta S < 0$

(D) $\Delta H > 0, \Delta S < 0$

QUESTION

The value of ΔH and ΔS for the reaction $C_{graphite} + O_2(g) \rightarrow CO_2(g)$ are –100 kJ and –100 JK^{-1} respectively. The reaction will be spontaneous at:

A 1000 K

[✓ B] 900 K

C 1100 K

D At any temperature

$$\Delta G < 0$$

$$\Delta H - T\Delta S < 0$$

$$\underline{-100000} + \underline{T \times 100} < 0$$

$$100\ T < 100000$$

$$T < \frac{1000\cancel{00}}{1\cancel{00}}$$

$$\boxed{T < 1000 K}$$

QUESTION

Standard entropy of N_2, H_2 and NH_3 is are 60, 40 and 50 JK^{-1} mol^{-1} respectively. For the reaction $1/2N_2 + 3/2H_2 \rightleftharpoons NH_3$, $\Delta H = -30$ kJ to be at equilibrium, the temperature should be:

- A 500 K
- [✓ B 750 K]
- C 1000 K
- D 1250 K

$$\Delta G = 0$$

$$\Delta H - T\Delta S = 0$$

$$T = \frac{\Delta H}{\Delta S} = \frac{\cancel{-}3000\cancel{0} J}{\cancel{-}4\cancel{0}}$$

$$\boxed{T = 750 k}$$

$$\Delta S_{rxn} = \left[(\Delta S)_{NH_3}\right] - \left[\frac{1}{2}\Delta S_{N_2} + \frac{3}{2}(\Delta S)_{H_2}\right]$$

$$\Delta S_{rxn} = 50 - \left(\frac{1}{\cancel{2}} \times \overset{30}{\cancel{60}} + \frac{3}{\cancel{2}} \times \overset{20}{\cancel{40}}\right)$$

$$= 50 - (30 + 60)$$

$$= -40 J$$

QUESTION

A reaction occur spontaneously. If

(A) TΔS = ΔH and both ΔH and ΔS are positive → $\Delta G = \underset{+ve}{\Delta H} \boxed{-T\underset{+ve}{\Delta S}}_{-ve} = 0$

[✓ (B)] TΔS > ΔH and both ΔH and ΔS are positive → $\Delta G = \underbrace{\Delta H}_{+ve} \boxed{-T\underbrace{\Delta S}_{+ve}}_{-ve} \Rightarrow \boxed{\Delta G = -ve}$

(C) TΔS > ΔH and both ΔH and ΔS are negative

(D) TΔS = ΔH and both ΔH is positive and ΔS is negative ⇒ $\Delta G = \underbrace{\Delta H}_{+ve} \boxed{-T\underbrace{\Delta S}_{-ve}}_{+ve}$

$\boxed{\Delta G = \text{always } +ve}$

Standard Gibbs free energy (ΔG°) ⇒ Gibbs free energy at standard condition

($P = 1$ bar) ($\text{Temp} = 273\,K$)

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

$$\boxed{\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ}$$

$$\boxed{\Delta G = \Delta G^\circ + RT \ln Q_c}$$

where Q_c = Reaction Quotient

$$= \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

at equilibrium $\Delta G = 0$

$Q_c = K_c$ = equilibrium constant

$$\boxed{\Delta G^\circ = -RT \ln K_c = -2.303\,RT \log K_c}$$

$$\Delta H^\circ - T\Delta S^\circ = -RT \ln K_c$$

$$\frac{\Delta H^\circ}{-RT} + \frac{\cancel{T}\Delta S^\circ}{+R\cancel{T}} = \frac{\cancel{-RT} \ln K_c}{\cancel{-RT}}$$

$$\boxed{\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}}$$

$K_c > 1 \Rightarrow \underbrace{\Delta G^\circ < 0}$ → spontaneous process

$K_c = 1 \rightarrow \Delta G^\circ = 0$

$K_c < 1 \rightarrow \boxed{\Delta G^\circ = +ve}$ → non spontaneous process

QUESTION

Which is always correct at equilibrium:

A $\Delta G^\circ = 0$

[✓ B $\Delta G = 0$]

C $\Delta S_{system} = 0$

D $\Delta E = 0$

QUESTION

For the water gas reaction

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

The standard Gibb's energy of reaction (at 1000 K) is – 8.1 kJ mol^{-1}. Value of equilibrium constant is–

[✓ A] 2.6

B 6.2

C 8.2

D 10

$$\Delta G^\circ = -2.303 RT \log K_c$$

$$+8100 = +2.303 \times 8.314 \times 1000 \log K_c$$

$$\log K_c = \frac{81\cancel{00}}{2.303 \times 8.314 \times 10\cancel{00}}$$

$$\log K_c = 0.423$$

$$\underline{K_c = \text{antilog}(0.423)}$$

QUESTION

Calculate ΔG° for the conversion of oxygen to ozone,

$3/2O_2(g) \rightarrow O_3(g)$ at 298 K.

If K_P for this conversion is $\underbrace{3 \times 10^{-29}}$.

A $+175.3$ kJ mol^{-1}

[✓ **B** $+162.7$ kJ mol^{-1}]

C -162.7 kJ mol^{-1}

D -140.5 kJ mol^{-1}

$$\log(3\times10^{-29}) = -29 + \log 3$$
$$\rightarrow -29 + 0.48$$
$$\rightarrow -28.52$$

$$\Delta G^\circ = -2.303\, RT \log K_P$$
$$= -2.303 \times \frac{8.314}{1000} \times 298 \log(3\times10^{-29})$$

$$\Delta G^\circ = +2.303 \times \frac{8.314}{1000} \times 298 \times 28.52$$

$$\boxed{\Delta G^\circ = 162.73\, kJ}$$

Thermochemistry

→ used to find statefunction for rxn.

$\boxed{\Delta G, \Delta H, \Delta S}$

Thermochemistry is the branch of physical chemistry which deals with the transfer of heat between a chemical system and its surrounding when a change of phase or chemical reaction takes place within the system.

For a rxn

$$\left\{\begin{aligned} \Delta S_{rxn} &= \sum(\Delta S)_{product} - \sum(\Delta S)_{reactant} \\ \Delta G_{rxn} &= \sum(\Delta G)_{product} - \sum(\Delta G)_{Reactant} \end{aligned}\right\}$$

$$\checkmark \left(\Delta H_{rxn} = \sum \Delta H_{product} - \sum(\Delta H)_{Reactant}\right)$$

→ valid for all type of enthalpies except combustion enthalpy and bond dissociation enthalpy.

Thermochemical Reaction

- Balanced Chemical rx^n
- physical state mentioned.
- ΔH/Energy change is mentioned.

✗ $\boxed{CaCO_3 \longrightarrow CaO + CO_2}$

✓ $\boxed{CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)} \quad \Delta H = -200\ kJ/mol}$

Thermochemical Reaction

The balanced chemical reaction which give information about the physical states of reactants & products and heat change is called as thermochemical reaction

Eg. $2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$, $\Delta H = + x$ Cal

It is also important to specify the states of all reactants and products in a reaction.

[‘*s*’ for solids, ‘*l*’ for liquids, ‘*g*’ for gases (or free atoms), ‘*aq*’ for solution in water].

Heat of Reaction or (Enthalpy of Reaction) or (ΔH_R)

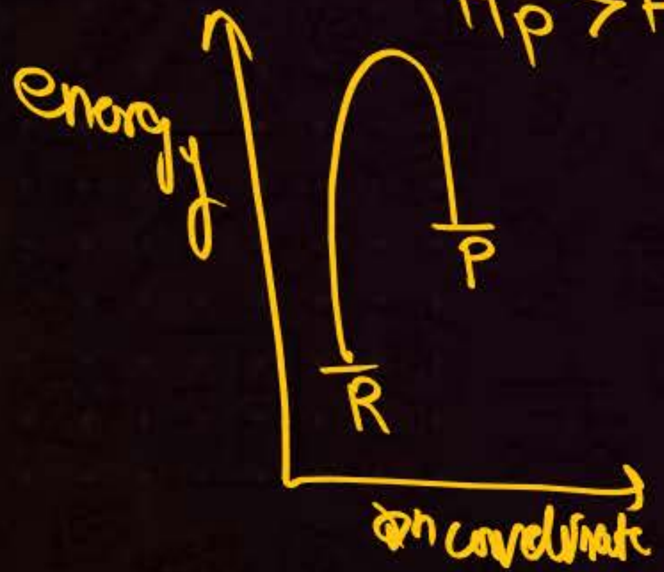
$$\boxed{\Delta H_{rxn} = H_P - H_R}$$

endothermic

$\Delta H_{rxn} > 0$

$H_P - H_R > 0$

$H_P > H_R$

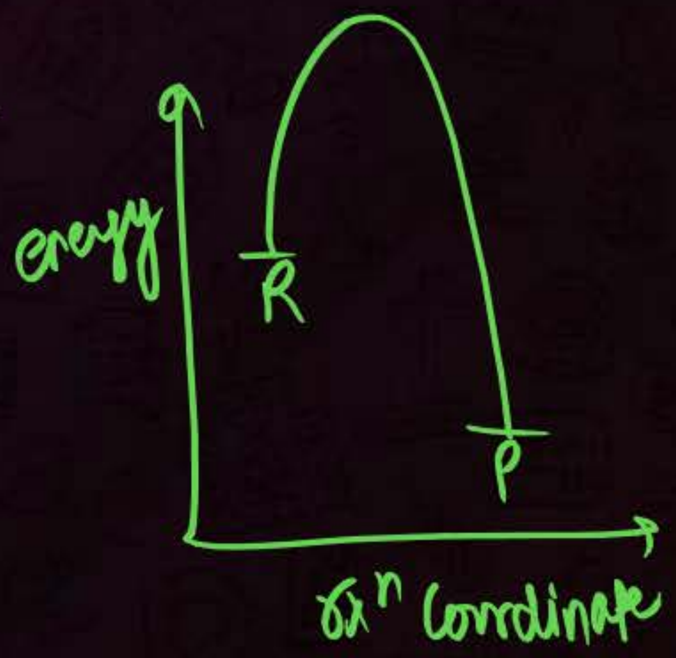


exothermic

$\Delta H_{rxn} < 0$

$H_P - H_R < 0$

$H_P < H_R$



Heat of Reaction or (Enthalpy of Reaction) or (ΔH_R)

The amount of heat evolved or absorbed when number of moles of the reactant according to the balanced chemical reaction had completely reacted is called as heat of reaction.

Example: $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}, \Delta H_R =$ ✓

$$\boxed{H_{2(g)} + O_{2(g)} \rightarrow H_2O_{(g)}, \Delta H_R = \text{✗}}$$

$H_{2(g)} + O_{2(g)} \rightarrow H_2O_{2(g)}, \Delta H_R =$ ✓

Note: Heat of reaction at constant pressure is ΔH and heat of reaction at constant volume of ΔE.

Laws of Thermochemistry

① $A \longrightarrow B \quad \Delta H_{rxn} = x \text{ kJ/mol}$

$B \longrightarrow A \quad \Delta H_{rxn} = -x \text{ kJ/mol}$

② $A \longrightarrow B \quad \Delta H = x \text{ kJ/mol}$

$nA \longrightarrow nB \quad \Delta H = nx \text{ kJ/mol}$

$\frac{1}{m}A \longrightarrow \frac{1}{m}B \quad \Delta H = \frac{x}{m} \text{ kJ/mol}$

③ $A \longrightarrow B \quad \Delta H_{rxn} = ?$

$$\left.\begin{array}{ll} A \longrightarrow \cancel{C} & \Delta H_{rxn} = x_1 \\ \cancel{C} \longrightarrow \cancel{D} & \Delta H_{rxn} = x_2 \\ \cancel{D} \longrightarrow B & \Delta H_{rxn} = x_3 \end{array}\right\}$$

$\boxed{A \longrightarrow B} \longrightarrow \Delta H_{rxn} = x_1 + x_2 + x_3$

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.

Q. $N_2 + 3H_2 \longrightarrow 2NH_3 \quad \Delta H = y$

$3N_2 + 9H_2 \longrightarrow 6NH_3 \quad \Delta H = 3y$

$\frac{1}{5}N_2 + \frac{3}{5}H_2 \longrightarrow \frac{2}{5}NH_3 \quad \Delta H = \frac{y}{5}$

$2NH_3 \longrightarrow N_2 + 3H_2 \quad \Delta H = \boxed{-y}$

$NH_3 \longrightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2 \quad \boxed{\Delta H = \frac{-y}{2}}$

Q. $H_2 + Br_2 \longrightarrow 2HBr \quad \Delta H = z$ kJ/mol

$\{6HBr \longrightarrow 3H_2 + 3Br_2\} \quad \Delta H = (-z) \times 3$

$\Rightarrow \underline{-3z}$

$\boxed{\text{Substract(i)} \times 3}$

QUESTION

A hypothetical reaction , A → 2B, proceed through following sequence of steps -

$A \rightleftharpoons 2C$; $H = q_1$

$2C \rightleftharpoons 2D$; $H = q_2$

$D \rightleftharpoons B$; $H = q_3$

The heat of reaction is:

Ⓐ $q_1 - q_2 + 2q_3$

Ⓑ $q_1 + q_2 - 2q_3$

Ⓒ $q_1 + q_2 + 2q_3$ ✓

Ⓓ $q_1 + 2q_2 - 2q_3$

$$A \rightleftharpoons \cancel{2C} \quad \Delta H = q_1$$

$$\cancel{2C} \rightleftharpoons \cancel{2D} \quad \Delta H = q_2$$

$$\cancel{2D} \rightleftharpoons 2B \quad \Delta H = 2q_3$$

$$\boxed{A \rightleftharpoons 2B} \; - \; \boxed{\Delta H = q_1 + q_2 + 2q_3}$$

QUESTION

The heat of reaction for $A + \frac{1}{2}O_2 \rightarrow AO$ is –50 kcal/mol and $AO + \frac{1}{2}O_2 \rightarrow AO_2$ is 100 kcal/mol. The heat of reaction (in kcal/mol) for $\boxed{A + O_2 \rightarrow AO_2}$ will be:

(A) –50

[✓ (B)] +50

(C) 100

(D) 150

$A + \frac{1}{2}O_2 \longrightarrow \cancel{AO}$ $\Delta H = -50$

$\cancel{AO} + \frac{1}{2}O_2 \longrightarrow AO_2$ $\Delta H = 100$

$\boxed{A + O_2 \longrightarrow AO_2}$, $\Delta H = \underline{+50}$

QUESTION

Consider the following process:

$$A \rightarrow 2B;\ \Delta H = +150\ \text{kJ}$$
$$3B \rightarrow 2C + D;\ \Delta H = -125\ \text{kJ}$$
$$G + A \rightarrow 2D;\ \Delta H = +350\ \text{kJ}$$

For $B + D \rightarrow G + 2C$; ΔH will be

- (A) +525 kJ
- (B) +325 kJ
- (C) −175 kJ
- (D) ✓ −325 kJ

$\cancel{A} \longrightarrow 2\cancel{B}$ $\quad \Delta H = +150$

$^{1}\cancel{2}D \longrightarrow G + \cancel{A}$ $\quad \Delta H = -350$

$^{1}\cancel{3}B \longrightarrow 2C + \cancel{D}$ $\quad \Delta H = -125$

$\boxed{B + D \longrightarrow G + 2C} \rightarrow \Delta H = \underline{-325}$

Factors Affecting Heat of Reaction

Factors Affecting Heat of Reaction

(i) Reaction Condition:

The chemical reaction sare carried out at constant temperature with either pressure or volume constant.

At constant pressure $q_p = \Delta H_{reaction}$

At constant volume $q_v d = \Delta E_{reaction}$

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

(ii) Quantity of Reactant:

Example: $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$ $\quad \Delta H_2 = -\times \text{ kCal mol}^{-1}$

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$ $\quad \Delta H_2 = 2 \times (-x \text{ kCal})$

Factors Affecting Heat of Reaction

(iii) Physical State of Products and Reactants:

Example: $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$ $\Delta H = -285.8 \text{ kJ mol}^{-1}$

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$ $\Delta H_2 = -242 \text{ kJ mol}^{-1}$

If the physical state of product is different then the value of ΔH is different.

Note: For H_2O (liq.), ΔH is more negative in comparision to the formation of H_2O(vap.) because when vapours convert into liquid than some heat is released.

(iv) Allotropic form: (Physical nature of reactant)

$C_{graphite} + O_2 \rightarrow CO_2$ $\Delta H_R = \underline{-393.5 \text{ kJ}} \text{ mol}^{-1}$

$C_{diamond} + O_2 \rightarrow CO_2$ $\Delta H_R = \underline{-399.5 \text{ kJ}} \text{ mol}^{-1}$

Factors Affecting Heat of Reaction

(v) Temperature:

Effect of temperature on heat of reaction is given by **Kirchoff equation**

(i) At constant pressure:

$$\boxed{\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_{pm}}$$

$$\Delta C_{Pm} = \Sigma(C_{Pm})_P - \Sigma(C_{Pm})_R$$

ΔH_{T_1} = Heat of reaction at T_1 temperature

ΔH_{T_2} = Heat of reaction at T_2 temperature

(ii) At constant volume:

$$\boxed{\frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_{Vm}}$$

$$\Delta C_{Vm} = \Sigma(C_{Vm})_P - \Sigma(C_{Vm})_R$$

- Heat change of a reaction does not depend on the **number of steps** used in the reaction.
- Heat change of a reaction does not depend on **intermediate position,** it depend only on initial and final state.
- Heat change of a chemical reaction does not depend on **time of reaction.**

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.

element	Standard/Reference state
Metal	Metal(s) except Hg(l)
H	$H_2(g)$
N	$N_2(g)$
O	$O_2(g)$
F	$F_2(g)$
Cl	$Cl_2(g)$
Br	$Br_2(l)$
I	$I_2(s)$

$C \longrightarrow C_{graphite}$

$S \longrightarrow S_{rhombic}$

NOTE → elements in their standard state have zero formation enthalpy.

→ Combustion enthalpy of $O_2 = 0$

Thermochemical Standard State

The reference/standard state of an element is its most stable state at 25°C and 1 bar pressure

C : Graphite ; S : Rhombic;

Br as $Br_2(g)$; I as $I_2(s)$;

H as $H_2(g)$; Cl as $Cl_2(g)$;

N as $N_2(g)$; O as $O_2(g)$;

P : White

(Exception : Red Phosphorus is more stable than White Phosphorus)

Elements	**Reference State**
C	$C_{(graphite)}$
S	$S_{8(Rhombic)}$ (Rhombic sulpur is energy wise more stable as compared to nonoclinic sulphur)
P	$P_{4(white)}$
O	$O_{2(g)}$
H	$H_{2(g)}$
Br	$Br_{2(\ell)}$
Metal	$M_{(s)}$[except $Hg_{(\ell)}$]

The formation reaction may be exothermic or endothermic.

Different Types of Enthalpies

Standard Heat of Formation: (ΔH_f°)

It is the enthalpy change when one mole of a substance is formed from its elements in their most abundant naturally occurring form or in their standard and stable state form (also called reference states).

$$\left. C_{\text{graphite}} + O_{2}(g) \longrightarrow CO_{2}(g) \right\} \Delta H_{rxn} = (\Delta H_f^\circ)_{CO_2}$$

$$\boxed{CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}} \times$$

$$\boxed{\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \longrightarrow \underbrace{NH_{3(g)}}_{1\,mol}}$$

$$\Delta H_{rxn} = (\Delta H_f^\circ)_{NH_3}$$

for any rxn, if (ΔH_f°) of Reactants and Products are given,

then, $$\boxed{\Delta H_{rxn} = \sum (\Delta H_f)_{Product} - \sum (\Delta H_f^\circ)_{Reactant}}$$

ΔH_f° → can be exo, endo

$$\boxed{4\,C_{graphite} + 5H_{2(g)} \longrightarrow \underbrace{C_4H_{10(g)}}_{1\ mol}}$$

$$\Delta H_{rxn} = (\Delta H_f^\circ)_{C_4H_{10}}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_f \qquad ✓$$

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}N_{2(g)} + \frac{3}{2}O_{2(g)} \longrightarrow \underset{1\text{mole}}{HNO_3} \qquad \Delta H_f \qquad ✓$$

$$Na_{(s)} + \frac{1}{2}O_{2(g)} + \frac{1}{2}H_{2(g)} \longrightarrow \underset{1\text{mole}}{NaOH} \qquad \Delta H_f \qquad ✓$$

QUESTION

The enthalpies of all elements in their standard states are:

(i) unity

[✓ (ii) zero]

(iii) < 0

(iv) different for each element

QUESTION

Which of the reaction defines molar ΔH_f^o?

(A) $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$ ✗

(B) $\frac{1}{2}Br_2\underset{\sim}{(g)} + \frac{1}{2}H_2(g) \rightarrow HBr(g)$ ✗

(C) $N_2(g) + 2H_2(g) + \frac{3}{2}O_2(g) \rightarrow NH_4NO_3(s)$ ✓

(D) $I_2\underset{\sim}{(g)} + H_2(g) \rightarrow 2HI(g)$ ✗

QUESTION

ΔH for the reaction,

$SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g); \Delta H = -98.3$ kJ

If the enthalpy of formation of $SO_3(g)$ is −395.4 kJ then the enthalpy of formation of $SO_2(g)$ is:

[✓ A] −297.1 kJ

B 493.7 kJ

C −493.7 kJ

D 297.1 kJ

$$\Delta H_{rxn} = \left[(\Delta H_f^\circ)_{SO_3}\right] - \left[(\Delta H_f^\circ)_{SO_2} + \cancel{\frac{1}{2}(\Delta H_f^\circ)_{O_2}}^{\,0}\right]$$

$$-98.3 = -395.4 - (\Delta H_f^\circ)_{SO_2}$$

$$(\Delta H_f^\circ)_{SO_2} = -395.4 + 98.3$$

$$\Rightarrow$$

QUESTION

The heat of formation of $Fe_2O_3(s)$ is -824.2 kJ mol^{-1}.
ΔH for the reaction.
$2Fe_2O_3,(s) \rightarrow 4Fe(s) + 3O_2(g)$ is:

$$\boxed{2Fe_{(s)} + \frac{3}{2}O_{2(g)} \longrightarrow Fe_2O_{3(s)}}$$

$$\Delta H_f^\circ = -824.2\ KJ/mol$$

$$(+824.2)\times 2 \Rightarrow \underline{+1648.4}$$

A –412.1 kJ

B –1648.4 kJ

C –3296. 8kJ

[✓ D] 1648.4 kJ

QUESTION

The ΔH° for the reaction,

$$4S(s) + 6O_2(g) \rightarrow 4SO_3\,(g) \text{ is } -1583.2 \text{ kJ.}$$

Standard enthalpy of formation of sulphur trioxide is:

A –3166.4 kJ

B 3166.4 kJ

C [✓ –395.8 kJ]

D 395.8 kJ

$$\boxed{S + \frac{3}{2}O_2 \longrightarrow SO_3}$$

$$\rightarrow \Delta H_{rxn} = (\Delta H_f^\circ)_{SO_3}$$

$$= \frac{-1583.2}{4}$$

$$= \underline{-395.8}$$

QUESTION

Calculate the heat of formation of $PCl_5(s)$ from the following data:

$2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(l) \quad \Delta H = -151.8$ kcal

$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s) \quad \Delta H = -32.8$ kcal

[✓ (A) −108.7 kcal]

(B) 108.7 kcal

(C) −184.6 kcal

(D) 184.6 kcal

$$\boxed{P + \frac{5}{2}Cl_2 \longrightarrow PCl_5} \rightarrow \Delta H_{rxn} = (\Delta H_f^\circ)_{PCl_5}$$

$$\boxed{\frac{(i)}{2} + (ii)} \rightarrow \Delta H = \frac{-151.8}{2} - 32.8$$

$$\Rightarrow -75.9 - 32.8$$

$$\Rightarrow$$

Standard Heat of Combustion

$\underbrace{(\Delta H_c^\circ)}$

Amount of heat evolved when 1 mole of substance is completely burnt (or oxidised in excess of oxygen.)

Example:

$$\boxed{\underbrace{C_4H_{10}}_{\text{Butane}}{}_{(g)} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O} \longrightarrow \Delta H_{rxn} = (\Delta H_c^\circ)_{C_4H_{10}}$$

1 mol

⇒ for any rxn, if combustion enthalpy of reactants and products are given,

then $\boxed{\Delta H_{rxn} = \sum(\Delta H_c^\circ)_{Reactant} - \sum(\Delta H_c^\circ)_{product}}$

$(\Delta H_c^\circ)_{\text{graphite}}$ $(\Delta H_f^\circ)_{CO_2}$

$\underset{1\text{mole}}{C_{\text{graphite}}} + O_2 \longrightarrow CO_2$, $\boxed{\Delta H_{\text{comb}}}$ ✓ and $\boxed{\Delta H_f}$ ✓

$\underset{1\text{mole}}{C_{\text{diamond}}} + O_2 \longrightarrow CO_2$, $\boxed{\Delta H_{\text{comb}}}$ ✓ and $\boxed{\Delta H_f}$ ×

(ΔH_c°) diamond

incomplete combustion

$\underset{1\text{mole}}{C} + \frac{1}{2}O_2 \longrightarrow CO$, $\boxed{\Delta H_{\text{comb}} \quad \times}$ and $\boxed{(\Delta H_f)_{CO} \quad ✓}$

$\underset{1\text{mole}}{CO} + \frac{1}{2}O_2 \longrightarrow CO_2$, $\boxed{(\Delta H_{\text{comb}})_{CO} \quad ✓}$ and $\boxed{(\Delta H_f)_{CO_2} \quad \times}$

QUESTION

The enthalpies of combustion of carbon and carbon monoxide are –393.5 and –283 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide per mole-

$$\boxed{C_{\text{graphite}} + \frac{1}{2}O_2 \longrightarrow CO_{(g)}} \rightarrow \Delta H_{rxn} = (\Delta H_f^\circ)_{CO}$$

$$\Delta H_{rxn} = (\Delta H_C^\circ)_{C\,\text{graphite}} - (\Delta H_C^\circ)_{CO}$$

$$= -393.5 - (-283)$$

$$\Rightarrow -393.5 + 283$$

$$\Rightarrow \underline{-110.5\ \text{kJ}}$$

- (A) 110.5 kJ
- (B) 676.5 kJ
- (C) –676.5 kJ
- [✓ (D)] –110.5 kJ

QUESTION

The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, –890.3 kJ mol^{-1} –393.5 kJ mol^{-1}, and –285.8 kJ mol^{-1} respectively. Enthalpy of formation of $CH_4(g)$ will be

[✓ (A)] –74.8 kJ mol^{-1}

(B) –52.27 kJ mol^{-1}

(C) +74.8 kJ mol^{-1}

(D) +52.26 kJ mol^{-1}

$$\boxed{C + 2H_2 \longrightarrow CH_4} \rightarrow \Delta H_{rxn} = (\Delta H_f^\circ)_{CH_4}$$

$$\Delta H_{rxn} = \left[(\Delta H_c^\circ)_C + 2(\Delta H_c^\circ)_{H_2}\right] - \left[(\Delta H_c^\circ)_{CH_4}\right]$$

$$= \left[-393.5 + 2(-285.8)\right] - \left[-890.3\right]$$

$$= -393.5 - 571.6 + 890.3$$

$$= \underline{-74.8}$$

QUESTION

The enthalpy of formation for $C_2H_4(g)$, $CO_2(g)$ and $H_2O(l)$ at 25°C and 1 atm, pressure be 52, –394 and –286 kJ mol^{-1} respectively. The enthalpy of combustion of $C_2H_4(g)$ will be-

(A) $+1412$ kJ mol^{-1}

[✓ (B)] -1412 kJ mol^{-1}

(C) $+141.2$ kJ mol^{-1}

(D) -141.2 kJ mol^{-1}

$$\boxed{C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O}$$

$$\downarrow$$

$$\Delta H_{rxn} = (\Delta H_c^\circ)_{C_2H_4}$$

$$\Delta H_{rxn} = \left[2(\Delta H_f^\circ)_{CO_2} + 2(\Delta H_f^\circ)_{H_2O}\right] - \left[(\Delta H_f^\circ)_{C_2H_4}\right]$$

$$= \left[2\times(-394) + 2(-286)\right] - [52]$$

$$= -788 - 572 - 52$$

$$\Rightarrow \underline{-1412}$$

Bond Enthalpy

→ In general ⇒ Bond dissociation enthalpy

↳ always endothermic

The bond dissociation enthalpy is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase

$$A_2(g) \longrightarrow 2A(g) \Big\} (\Delta H_b^\circ)_{A_2} = x$$

$$2A(g) \longrightarrow A_2 \Big\} \Delta H_{\text{bond formation}} = -x$$

Bond formation enthalpy

⇓

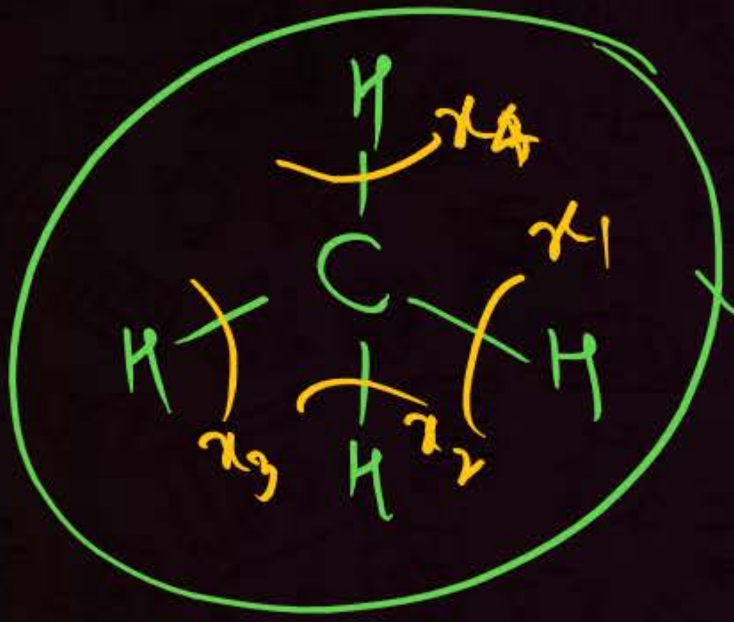
always exothermic

$$O_{2(g)} \longrightarrow 2O_{(g)} \Big\} (\Delta H_b^\circ)_{O_2}$$

$$H_{2(g)} \longrightarrow 2H_{(g)} \Big\} (\Delta H_b^\circ)_{H_2}$$

For polyatomic molecules

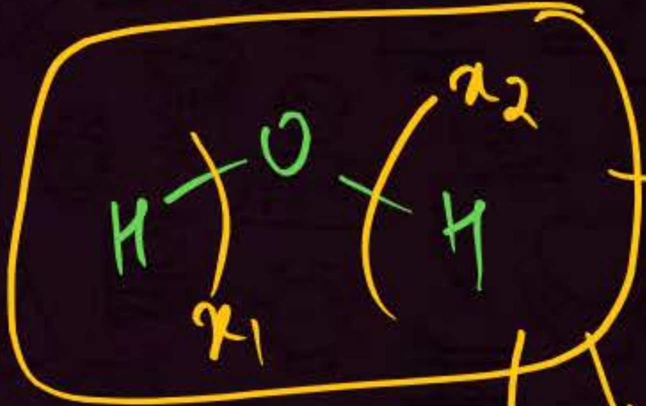
$$\boxed{CH_4 \longrightarrow C_{(g)} + 4H_{(g)}}$$



$x_1 \neq x_2 \neq x_3 \neq x_4$

Avg./Mean Bond enthalpy $= \dfrac{x_1+x_2+x_3+x_4}{4}$

$= \dfrac{\Delta H_{rxn}}{4}$



$H_2O \longrightarrow 2H_{(g)} + O_{(g)}$

$\Delta H_{rxn} = x_1 + x_2$

avg. Bond enthalpy of O-H bond $= \dfrac{x_1+x_2}{2}$

for any rxn, if bond enthalpy / bond dissociation enthalpy of reactants and products are given, then

$$\boxed{\Delta H_{rxn} = \sum(\Delta H_b)_{Reactant} - \sum(\Delta H_b)_{product}}$$

QUESTION

The Bond-energies of C ≡ C, C–H, H–H and C = C are 198, 98, 103, 145 kcal respectively. The enthalpy change of the reaction

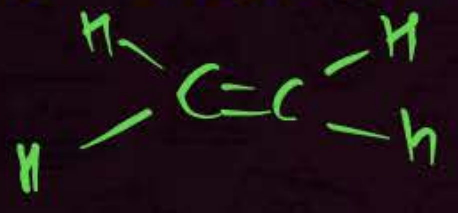
$HC \equiv CH + H_2 \rightarrow C_2H_4$ is-

A –152 kcal

B 96 kcal

C 48 kcal

[✓ **D**] –40 kcal



$$\Delta H_{rxn} = \left[2(\Delta H_b^\circ)_{C-H} + (\Delta H_b^\circ)_{C\equiv C} + (\Delta H_b^\circ)_{H_2}\right] - \left[4(\Delta H_b^\circ)_{C-H} + (\Delta H_b^\circ)_{C=C}\right]$$

$$= (2\times 98 + 198 + 103) - (4\times 98 + 145)$$

$$= 196 + 198 + 103 - 392 - 145$$

$$\Rightarrow \underline{-40}$$

QUESTION

Heat evolved in the reaction $H_2 + Cl_2 \xrightarrow{\Delta H = -182} 2HCl$ is 182 KJ. Bond energies of H - H and Cl - Cl are 430 and 242 KJ/mol respectively. The H - Cl bond energy is:

A) 245 kJ mol^{-1}

[✓ B) 427 kJ mol^{-1}]

C) 336 kJ mol^{-1}

D) 154 kJ mol^{-1}

$$\Delta H_{rxn} = -182 = \left[(\Delta H_b^\circ)_{H_2} + (\Delta H_b^\circ)_{Cl_2}\right] - \left[2(\Delta H_b^\circ)_{HCl}\right]$$

$$-182 = (430 + 242) - 2(\Delta H_b^\circ)_{HCl}$$

$$2(\Delta H_b^\circ)_{HCl} = \underline{672 + 182} = 854$$

$$(\Delta H_b^\circ)_{HCl} = \frac{854}{2} = \underline{427}$$

QUESTION

If bond dissociation energies of $N \equiv N$, $H - H$ and $N - H$ are x_1, x_2 and x_3 respectively, hence enthalpy of formation of $NH_3(g)$ is.

- **(A)** $x_1 + 3x_2 - 6x_3$
- **(B)** $3x_3 - \frac{1}{2}x_1 - \frac{3}{2}x_2$
- [✓ **(C)** $\frac{x_1}{2} + \frac{3}{2}x_2 - 3x_3$]
- **(D)** $6x_3 - x_1 - 3x_2$

$$\boxed{\frac{1}{2}N_2 + \frac{3}{2}H_2 \longrightarrow NH_3}$$

$$(\Delta H_f^\circ)_{NH_3} = \Delta H_{rxn} = \left[\left(\frac{1}{2}\Delta H_B^\circ\right)_{N_2} + \frac{3}{2}(\Delta H_B^\circ)_{H_2}\right] - \left[3(\Delta H_B^\circ)_{N-H}\right]$$

$$\Delta H_{rxn} = \frac{1}{2}x_1 + \frac{3}{2}x_2 - 3x_3$$

QUESTION

The enthalpy change for the following reaction is 368 kJ. Calculate the average O–F bond energy

$$OF_2(g) \rightarrow O(g) + 2F(g)$$

[✓ (A) 184 kJ/mol]

(B) 368 kJ/mol

(C) 536 kJ/mol

(D) 736 kJ/mol

avg. Bond enthalpy of O-F $= \frac{368}{2} = \underline{184}$

Heat of Atomization

It is the amount of energy required to break the bonds in a molecule (in gas phase) into gaseous atoms.

$Na(s) \longrightarrow Na(g)$; $(\Delta H_a^\circ)_{Na} = 108$ kJ/mol

$H - H(g) \longrightarrow 2H(g)$; $(\Delta H_a^\circ)_{H_2} = 435$ kJ/mol $= (\Delta H_b^\circ)_{H_2}$

$CH_4(g) \longrightarrow C(g) + 4H(g)$; $(\Delta H_a^\circ)_{CH_4} = 1665$ kJ/mol $= 4 \times (\Delta H_b^\circ)_{avg\ C-H}$

$$\boxed{\begin{array}{c} Br_2(g) \longrightarrow 2Br(g) \\ (\Delta H_b^\circ)_{Br_2} \end{array}}$$

$$\boxed{Br_2(l) \longrightarrow 2Br(g)}$$
$$\downarrow$$
$$(\Delta H_a^\circ)_{Br_2}$$

QUESTION

Match the column:

A	$C_{(s, graphite)} + O_2 \rightarrow CO_{2(g)}$	P	$\Delta H^o_{Combustion}$
B	$CO(g) + 1/2O_{2(g)} \rightarrow CO_{2(g)}$	Q	$\Delta H^o_{sublimation}$
C	$CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)}$	R	$\Delta H^o_{formation}$
D	$C_{(s, graphite)} \rightarrow C_{(g)}$	S	$\Delta H^o_{atomisation}$

(A) A → R, B → S, C → P, D → Q ✗

(B) A → R, B → P, C → Q, D → S

(C) A → P, B → S, C → Q, D → R ✗

[✓ (D)] A → R, B → P, C → S, D → Q

A → P, R
B → P
C → Q, S
D → S

Heat of Ionisation

→ for weak electrolytes

→ always endothermic

It is the amount of heat absorbed when one mole of a compound completely dissociates into ions in a solution.

$$\boxed{NH_4OH \longrightarrow NH_4^{\oplus} + OH^{\ominus}} \rightarrow \Delta H \text{ ionisation}$$

Heat of Neutralisation

→ always exothermic

It is the amount of heat liberated when one gm-equivalent of acid completely neutralises by one gm-equivalent of base.

$$\boxed{\underbrace{H^{\oplus}}_{\text{acid}} + \underbrace{OH^{\ominus}}_{\text{Base}} \longrightarrow \underbrace{H_2O}}$$

- is constant for strong acid and base neutralization and is equal to -13.7 kcal/mol or -57.27 kJ/mol.

$$\boxed{S.A + S.B} \longrightarrow \left.\begin{aligned}\Delta H_{new} &= -13.7\ \text{Kcal/eq} \\ &= -57.3\ \text{kJ/eq}\end{aligned}\right\}$$

$$\boxed{\Delta H_{\text{ionisation}} = (\Delta H_{new})_{\text{given}} - (\Delta H_{new})_{S.A + S.B}}$$

in case of

$$\boxed{\begin{matrix} W.A + S.B \\ W.B + S.A \\ W.B + W.A \end{matrix}}$$

→ ΔH neutralisation will be less negative as some part of energy is used for ionisation of weaker part.

QUESTION

How much heat is liberated when 100 mL of 0.1 M NaOH are completed neutralised by 100 mL of 0.1 M HCl-

$[OH^{\ominus}] = 100 \times 0.1 = 10\ \text{mmol}$

$[H^{+}] = 100 \times 0.1 = 10\ \text{mmol}$

- (A) −57 kJ
- [✓ (B)] −0.57 kJ
- (C) −5.7 kJ
- (D) −0.05 kJ

$$\left.\begin{array}{ccccc} H^{\oplus} & + & OH^{\ominus} & \longrightarrow & H_2O \\ 10 & & 10 & & 10\ \text{mmol} \end{array}\right\} \Delta H_{new} = -57.3 \times 10 \times 10^{-3}\ \text{kJ}$$

$$\Rightarrow -0.573\ \text{kJ}$$

QUESTION

W.B W.A

The enthalpy of neutralization of NH_4OH and CH_3COOH is –10.5 kcal/mole and enthalpy of neutralization of strong base and CH_3COOH is –12.5 kcal/mole. Calculate the enthalpy of dissociation of base NH_4OH

(A) 3.0

(B) 4.0

[✓ (C)] 2.0

(D) 10.0

$$(\Delta H_{ionisation})_{NH_4OH} = -10.5 - (-12.5)$$

$$\Rightarrow -10.5 + 12.5$$

$$\Rightarrow \underline{2.}$$

QUESTION

The heat of neutralization of $\underbrace{HCN}_{W.A}$ by $\underbrace{NaOH}_{S.B}$ is -13.3 KJ/mole, the energy of dissociation of HCN is-

A 43.8 KJ

B –43.8 KJ

C –68 KJ

D 68 KJ

$$\Delta H_{ionisation} = -13.3 - (-57.3)$$

$$\Rightarrow -13.3 + 57.3$$

$$\Rightarrow \underline{+44.0}$$

QUESTION

Enthalpy of neutralisation of CH_3COOH by NaOH is –50.6 kJ/mol and the heat of neutralisation of a strong acid with NaOH is –55.9 kJ/mol. The value of ΔH for the ionisation of CH_3COOH is

(A) 3.5 kJ/mol

(B) 4.6 kJ/mol

[✓ C] 5.3 kJ/mol

(D) 6.4 kJ/mol

$$(\Delta H_{\text{ionisation}})_{CH_3COOH} = -50.6 - (-55.9)$$

$$\Rightarrow -50.6 + 55.9$$

$$= \underline{+5.3}$$

QUESTION

Heat of neutralisation of an acid by a base is maximum when:

- **A** Both the acid and base are weak
- **B** [✓ Both the acid and base are strong]
- **C** The acid is strong and the base is weak
- **D** The acid is weak and the base is strong

QUESTION

If $H^+ + OH^- \rightarrow H_2O + 13.7$ kCal, then heat of complete neutralisation of 1 gm mol of H_2SO_4 with base in excess will be:

A –13.7 kCal

[✓ B] –27.4 kCal

C –6.85 kCal

D –3.425 kCal

$H_2SO_4 \longrightarrow 2H^{\oplus}$

ΔH_f°
ΔH_c°
ΔH_b°
ΔH_a°
ΔH_{neu}°

Lattice Enthalpy ($\Delta_{lattice}H^\circ$)

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.

$$NaCl_{(s)} \longrightarrow Na^{\oplus}_{(g)} + Cl^{\ominus}_{(g)} \Big\} \ \Delta H_{rxn} = \left(\Delta H_{\text{lattie}}\right)_{NaCl}$$

Hydration Enthalpy

It is the energy released when atoms (gaseous) in one mole of an ionic compound gets hydated.

$$\boxed{Na^{\oplus}_{(g)} \longrightarrow Na^{\oplus}_{(aq.)}} \longrightarrow \Delta H_{rxn} = (\Delta H_{hyd})_{Na^{\oplus}}$$

Heat of Hydration (ΔH_{hydra})

Amount of heat evolved when one mole of anhydrous salt combines with fixed number of water molecules to convert into its specific hydrated crystal is called as heat of hydration.

Example :

- $1\ CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4 .5\ H_2O(s) \quad \Delta H = -\ ve$

  anhydrous salt — hydrated salt

- $1\ MgSO_4(s) + 7H_2O\ (\ell) \longrightarrow MgSO_4.7H_2O(s) \quad \Delta H = -\ ve$

  anhydrous salt — hydrated salt

- $1\ CaCl_2(s) + 6H_2O(\ell) \longrightarrow CaCl_2 .6\ H_2O(s) \quad \Delta H = -\ ve$

  anhydrous salt — hydrated salt

Special Note : Heat of hydration is exothermic

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

$$\begin{tikzcd}
NaCl_{(s)} \arrow[rr, "\Delta H_{sol}^\circ"] \arrow[dr, "\underbrace{\Delta H_{lattice}}_{endo}"'] & & Na^{\oplus}_{(aq.)} + Cl^{\ominus}_{(aq.)} \\
& Na^{\oplus}_{(g)} + Cl^{\ominus}_{(g)} \arrow[ur, "\Delta H_{hyd} = exo."'] &
\end{tikzcd}$$

$$\boxed{\Delta H_{sol}^\circ = \Delta H_{lattice} + \Delta H_{hyd}}$$

Heat of Solution (ΔH_{Sol})

Amount of heat absorbed or evolved when one mol of substance is dissolved in such a large volume of solvent that further addition of solvent does not produce any more heat change is called as 'Heat of solution'.

$1\ CuSO_{4(s)} + aq \longrightarrow CuSO_4(aq)$ $\Delta H_{solution}$ ✓

$1\ CuSO_{4(s)} + 5H_2O\ (\ell) \longrightarrow CuSO_4.5H_2O(s)$ $\Delta H_{hydration}$ ✓

$MgSO_{4(s)} + 7H_2O\ (\ell) + aq \longrightarrow MgSO_4(aq)$ $\Delta H_{solution}$ ✓

$MgSO_4.7H_2O(s) + aq \longrightarrow MgSO_4(aq)$ $\Delta H_{solution}$ ✓

Heat of solution may be endothermic or exothermic.

Heat of Hydrogenation ($\Delta H_{Hydrogenation}$)

The heat evolved during the complete hydrogenation of one mol unsaturated organic compound into its saturated compound is called as heat of hydrogenation.

Unsaturated organic compound $\xrightarrow{\text{Change}}$ Saturated organic compound

(= or ≡ Bond) **(– Bond)**

$C_2H_2 + 2H_2 \longrightarrow C_2H_6,$ ΔH_{hydro} ✓

$C_2H_2 + H_2 \longrightarrow C_2H_4,$ ΔH_{hydro} ×

$C_2H_4 + H_2 \longrightarrow C_2H_6,$ ΔH_{hydro} ✓

Note : Heat of hydrogenation is exothermic process.

Enthalpy of Dilution

Let us consider the following set of enthalpy changes:

$HCl(g) + 25\ aq. \rightarrow HCl.25\ aq.\quad \Delta H = -72.03\ kJ / mol$

$HCl(g) + 40\ aq. \rightarrow HCl.40\ aq.\quad \Delta H = -72.79\ kJ / mol$

$$\Delta H_{dilution} = -72.79 - (-72.03)$$

$$\Rightarrow \underline{-0.76\ kJ/mol}$$

The enthalpy of dilution of a solution is dependent on the original concentration of the solution and the amount of solvent added.

Summary

↳ Thermodynamics

+

Thermochemistry

FOR NOTES & DPP CHECK DESCRIPTION

Homework

- DPP
- PyQs

FOR NOTES & DPP CHECK DESCRIPTION

THANK YOU