

**(ACTC) ADVANCED CHEMISTRY TUITION CENTRE, 41/1 PWD ROAD, NAGERCOIL, 9952340892.**

about a minute, the gases diffuse far enough to meet and a ring of solid ammonium chloride is formed near the HCl end.

## 7.THERMODYNAMICS

### IMPORTANT FORMULA

1. For an adiabatic process  $q = 0$
2. For an isothermal process  $dT = 0$
3. For an isobaric process  $dP = 0$
4. For an isochoric process  $dV = 0$
5. For an cyclic process  $dU = 0$ ,  $dH = 0$ ,  $dP = 0$ ,  $dV = 0$ , and  $dT = 0$ .
6. Internal energy  $U = U_t + U_v + U_r + U_b + U_e + U_i$
7. Change in internal energy  $\Delta U = U_f - U_i$
8. Work =  $-w = Fx$  (or)  $w = P_{\text{ext}} \Delta V$
9.  $w_{\text{rev}} = -2.303 nRT \log \frac{V_f}{V_i}$
10. First law of thermodynamics =  $\Delta U = q + w$
11. For a cyclic process, first law of thermodynamics  $q = -w$
12. For an isochoric process, first law of thermodynamics  $\Delta U = q_v$
13. For an adiabatic process, first law of thermodynamics  $\Delta U = w$

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14. For an isobaric process, first law of thermodynamics  $\Delta U = q - P\Delta V$

15. Relationship between  $\Delta H$  and  $\Delta U$

$$\Delta H = \Delta U + P\Delta V \text{ (or) } \Delta H = \Delta U + \Delta n_{(g)}RT$$

16. Standard enthalpy of reaction  $\Delta H_r^0$

$$\Delta H_r^0 = \sum \Delta H_r^0 (\text{Products}) - \sum \Delta H_r^0 (\text{Reactants})$$

17. Heat capacity (C)  $C = \left[ \frac{q}{m(T_2 - T_1)} \right]$

18. Heat capacity at constant volume  $C_V = \left( \frac{\partial U}{\partial T} \right)_V$

19. Heat capacity at constant pressure  $C_P = \left( \frac{\partial U}{\partial T} \right)_P$

20. Relation between  $C_P$  and  $C_V$  for an ideal gas:  $C_P - C_V = nR$

21.  $\Delta U = n.C_V [T_2 - T_1]$

$$\Delta H = n.C_P [T_2 - T_1]$$

22. Hess's law  $= \Delta H_r = \Delta H_1 + \Delta H_2 + \Delta H_3 \dots\dots\dots$

23. Efficiency in percentage  $= \left[ 1 - \frac{T_2}{T_1} \right] \times 100$

24. Standard entropy change  $= \Delta S_f^0$

$$\Delta S_r^0 = \sum S^0 (\text{Products}) - \sum \Delta S^0 (\text{Reactants})$$

25. Change in entropy  $\Delta S = \frac{q_{rev}}{T} = \frac{\Delta H_{rev}}{T}$

26. Entropy of fusion  $= \Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_f}$

27. Entropy of vapourisation  $= \Delta S_v = \frac{\Delta H_v}{T_b}$

28. Entropy of transition  $= \Delta S_t = \frac{\Delta H_t}{T_i}$

29. Gibbs free energy  $= G = H - TS$  (or)  $\Delta G = \Delta H - T\Delta S$

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

30. Relation between Gibbs free energy and net work done by the system  $= -\Delta G = -w - P\Delta V$

31. Relationship between standard free energy change  $\Delta G^0$  and equilibrium constant  $K_{eq}$ :

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln K_{eq}$$

32. Third law of thermodynamics  $\lim_{T \rightarrow 0} S = 0$  for a perfectly ordered crystalline state.

**IMPORTANT POINT**

- ❖ **Thermodynamics** – It means flow of heat. It is a branch of science which deals the relation between energy, heat, work and accompanying changes in the nature and behaviour of various substances around us.
- ❖ **Macroscopic properties** – Heat and work.
- ❖ **First law of Thermodynamics** – It states that “The total energy of an isolated system remains constant though it may change from one form to another”.  
 $\Delta U = q + w$   
 $\Delta U$  – Change in the internal energy  
 $q$  – Amount of heat supplied to the system  
 $w$  – Amount of work done on the system
- ❖ **System** – It is defined as any portion of matter under thermodynamic consideration, which is separated from the rest of the universe by real or imaginary boundaries.
- ❖ **Homogeneous system** – If the physical states of all its matter are uniform, it is called homogeneous system.
- ❖ **Heterogeneous system** – If the physical states of all its matter are not uniform, it is called heterogeneous system.
- ❖ **Surroundings** – Everything in the universe that is not the part of system is called surroundings.
- ❖ **Boundary** – Anything which separates the system from its surrounding is called boundary.
- ❖ **Isolated system** – A system which can exchange neither matter nor energy with its surrounding is called an isolated system. e.g., Hot water contained in a thermos flask.
- ❖ **Closed system** – A system which can exchange only energy but not matter with its surroundings is called a closed system. e.g., Hot water contained in a closed beaker.
- ❖ **Open system** – A system which can exchange both matter and energy with its surroundings is called an open system. e.g., Hot water contained in an open beaker.
- ❖ **Intensive properties** – The properties that are independent of the mass or size of the system is called as intensive property. e.g., Refractive index, surface tension, density, temperature, boiling point and freezing point etc.
- ❖ **Extensive properties** – The properties that are depended on the mass or size of the system is called as extensive property. e.g., Volume, number of moles, mass and internal energy etc.
- ❖ **Thermodynamic process** – The method of operation which can bring about the change in the system is called thermodynamics process. e.g., Heating, cooling and fusion.
- ❖ **Reversible processs** – The process in which the system and surroundings can be restored to the initial state from the final state without producing any changes in the thermodynamic properties of the universe is called a reversible process.

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- ❖ **Irreversible process** – The process in which the system and surroundings cannot be restored to the initial state from the final state is called an irreversible process.
- ❖ **Adiabatic process** – It is defined as one in which there is no exchange of heat ( $q$ ) between the system and surrounding during process. [ $q = 0$ ]
- ❖ **Isothermal process** – It is defined as one in which the temperature of the system remains constant, during the change from its initial to final state. [ $dT = 0$ ]
- ❖ **Isobaric process** – It is defined as one in which the pressure of the system remains constant during its change from the initial to final state. [ $dP = 0$ ]
- ❖ **Isochoric process** – It is defined as one in which the volume of system remains constant during its change from initial to final state. [ $dV = 0$ ]
- ❖ **Cyclic process** – When a system returns to its original state after completing a series of changes the process is known as a cyclic process. For a cyclic process.  $dU = 0$ ,  $dH = 0$ ,  $dP = 0$ ,  $dV = 0$  and  $dT = 0$ .
- ❖ **State functions** – The properties of  $P$ ,  $V$ ,  $T$  and ' $n$ ' that are used to describe the state of a system are called as state functions.
- ❖ **Path functions** – A path function is a thermodynamic property of the system whose value depends on the path by which the system goes from its initial to final states. e.g., Work and heat.
- ❖ **Internal energy** – Internal energy of a system is equal to the energy possessed by all its constituents namely atoms, ions and molecules.  

$$U = \text{Internal energy} = U_t + U_v + U_r + U_b + U_e + U_i$$
- ❖  $\Delta U$  – Change in internal energy =  $U_f - U_i$
- ❖ **Heat ( $q$ )** – It is regarded as an energy in transit across the boundary separating a system from its surrounding. It is a path function.
- ❖ **Unit of heat** – SI unit of heat is joule (J). The other unit is calories (cal).
- ❖ **Calories (cal)** – It is defined as the quantity of heat required to raise the temperature of 1 gram of water by  $1^\circ\text{C}$  in the vicinity of  $15^\circ\text{C}$ .
- ❖ **Work ( $w$ )** – It is defined as the force ( $F$ ) multiplied by the displacement ( $x$ ). [ $-w = F \cdot x$ ]
- ❖ **Unit of work** – SI unit of work is joule (J) or kilojoule (kJ).
- ❖ **Joule** – It is defined as the work done by a force of one Newton through a displacement of one meter ( $J = \text{Nm}$ ).
- ❖ **Gravitational work** – When an object is raised to a certain height against the gravitational field, gravitational work is done on the object. [ $w = m \cdot g \cdot h$ ]
- ❖ **Electrical work** – When a charged body moves from one potential region to another, electrical work is done. [ $w = QV$ ]

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- ❖ **Mechanical work** – It is defined as force multiplied by the displacement through which the force acts.  $[w = F \cdot x]$
- ❖ **Pressure – Volume work** – The work done in expansion or compression of a gas. PV work (or) expansion work.
- ❖ **Work involved in expansion and compression process** –  $[w = -P\Delta V]$
- ❖ **Expansion** – During expansion, work is done by the system. Since  $V_f > V_i$ , the sign obtained for work will be negative.
- ❖ **Compression** – During compression, work is done on the system. Since  $V_f < V_i$ , the sign obtained for work will be positive.
- ❖ **For reversible process** –  $w_{rev} = -2.303 nRT \log \frac{V_f}{V_i}$
- ❖ **Zeroth law of thermodynamics** – This law states that ‘If two systems are separately in thermal equilibrium with a third one, then they tend to be in thermal equilibrium with themselves’.
- ❖ **First law of thermodynamics** – “Energy can neither be created nor destroyed, but may be converted from one form to another”.

(or)

The total energy of a system and surroundings remains constant (or conserved).

$$\Delta U = q + w$$

- ❖ **Mathematical statement of first law –**

	$\Delta U = q + w$	
Cyclic process	$\Delta U = 0$	$\therefore q = -w$
Isochoric process	$\Delta V = 0$ $w = 0$	$\therefore \Delta U = q_v$
Adiabatic process	$q = 0$	$\therefore \Delta U = w$
Isobaric process	$\Delta U = q + w$	$\Delta U = q - P\Delta V$

- ❖ **Enthalpy (H)** – It is defined as the sum of the internal energy (U) of a system and the product of pressure and volume of the system.

$$H = U + PV$$

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

- ❖ **Relation between enthalpy ‘H’ and internal energy ‘U’ –**

$$\Delta H = \Delta U + \Delta n_{(g)} RT$$

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❖ **Standard heat of formation** – It is defined as “the change in enthalpy that takes place when one mole of a compound is formed from its elements, present in their standard states (298K and 1 bar pressure).

❖ **Thermochemical equations** – It is a balanced stoichiometric chemical equation that includes the enthalpy change ( $\Delta H$ ).

❖ **Standard enthalpy of reaction** ( $\Delta H_r^0$ ) - It is the enthalpy change for a reaction when all the reactants and products are present in their standard states.

$$\Delta H_r^0 = \sum \Delta H_r^0 (\text{Products}) - \sum \Delta H_r^0 (\text{reactants})$$

❖ **Heat of combustion** ( $\Delta H_c$ ) – It is defined as the change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen.

❖ **Specific heat capacity** (C) – It is defined as the heat absorbed by one kilogram of a substance in raising its temperature by one Kelvin at a specified temperature.

$$C = \left[ \frac{q}{m(T_2 - T_1)} \right]$$

❖ **Molar heat capacity** – It is defined as the amount of heat absorbed by one mole of the substance to raise its temperature by 1 Kelvin.

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

❖ **Unit of heat capacity** –  $\text{JK}^{-1} \text{mol}^{-1}$ .

❖  **$C_V$  : (Molar heat capacity at constant volume)** – It is defined as the rate of change of internal energy with respect to temperature at constant volume.

$$C_V = \left( \frac{dU}{dT} \right)_V$$

❖  **$C_P$  : (Molar heat capacity at constant pressure)** – It is defined as the rate of change of enthalpy with respect to temperature at constant pressure.

$$C_P = \left( \frac{dU}{dT} \right)_P$$

❖ **Relation between  $C_P$  and  $C_V$  for an ideal gas** –

$$C_P - C_V = nR$$

❖ **Calorimetry** – It is the science associated with determining the changes in energy of a system by measuring the heat exchanged with the surroundings.

❖ **Exothermic reaction** – The reaction in which heat is evolved and system loses heat to the surroundings. [ $\Delta H_r = -ve$ ]

❖ **Endothermic reaction** – The reaction in which heat is absorbed and system gains heat from the surroundings. [ $\Delta H_r = +ve$ ]



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- ❖ **Calorific value** – It is defined as the amount of heat produced in calories (or joules) when one gram of a substance is completely burnt. The SI unit is J kg<sup>-1</sup>.
- ❖ **Heat of solution** – It is defined as the change in enthalpy of the system when one mole of a substance is dissolved in a specified quantity of a solvent at a given temperature.
- ❖ **Heat of neutralization** – It is defined as the change in enthalpy of the system when one gram equivalent of an acid is completely neutralized by one gram equivalent of a base in dilute solution.
- ❖ **Molar heat of fusion** – It is defined as the change in enthalpy when one mole of a solid substance is converted into the liquid state at its melting point.
- ❖ **Molar heat of vapourisation** – It is defined as the change in enthalpy when one mole of a liquid is converted into vapour or gaseous state at its boiling point.
- ❖ **Molar heat of sublimation** – It is defined as the change in enthalpy when one mole of a solid is directly converted into the gaseous state at its sublimation temperature..
- ❖ **Heat of transition** – It is defined as the change in enthalpy when one mole of an element change from one allotropic form to another.
- ❖ **Hess's law of constant heat summation** – It states that “the enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single step or multiple steps provided the initial and final states are same”.
- ❖ **Lattice energy** – It is defined as the amount of energy required to completely remove the constituent ions from its crystal lattice to an infinite distance.
- ❖ **Born Haber's cycle** – It applies Hess's law to calculate lattice enthalpy.
- ❖ **Second law of thermodynamics** –
  - (i) **Entropy statement** : “Whenever a spontaneous process takes place, it is accompanied by an increase in the total entropy of the Universe”.
 
$$\Delta S_{\text{universe}} > \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$
  - (ii) **Kelvin-Planck statement** – It is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of heat to a cooler reservoir.
- ❖ **% Efficiency** -  $\left[ \frac{T_1 - T_2}{T_1} \right] \times 100$
- ❖ **Clausius statement** – It states that heat flows spontaneously from hot objects to cold objects and to get it flow in the opposite direction, we have to expend some work.
- ❖ **Spontaneous process** – A reaction that does occur under the given set of conditions without any external driving force is called a spontaneous reaction.
- ❖ **Non-spontaneous process** – A reaction that does not occur under given set of conditions without any external driving force is called a non-spontaneous reaction.

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❖ **Entropy (S)** – It is defined as “for a reversible change taking place at a constant temperature (T), the change in entropy ( $\Delta S$ ) of the system is equal to heat energy absorbed or evolved (q) by the system divided by the constant temperature (T)”.  $\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}$

❖ **Unit of entropy** –  $\text{JK}^{-1}$  (SI unit).

❖ **Standard entropy of formation** – It is defined as the entropy of formation of 1 mole of a compound from the elements under standard conditions. It is denoted as  $\Delta S_f^0$ .

❖ **Standard entropy change  $\Delta S^0$**  –

$$\Delta S_r^0 = \sum S^0_{\text{(Products)}} - \sum \Delta S^0_{\text{(reactants)}}$$

❖ **Entropy of fusion** – When one mole of the solid melts at its melting point reversibly, the heat absorbed is called molar heat of fusion.

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

$\Delta H_f$  = Molar heat of fusion

$T_f$  = Melting point

❖ **Entropy of vapourisation** – When one mole of liquid is boiled at its boiling point reversibly, the heat absorbed is called molar heat of vapourisation.

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

$\Delta H_v$  = Molar heat of vapourisation

$T_b$  = Boiling point

❖ **Entropy of transition** – The heat change, when one mole of a solid changes reversibly from one allotropic form to another at its transition temperature.

$$\Delta S_t = \frac{\Delta H_t}{T_t}$$

$\Delta H_t$  = Molar heat of transition

$T_t$  = Transition temperature

❖ **Gibbs free energy** – It is the available energy to do the work. It is defined as the part of total energy of a system that can be converted (or) available for conversion into work.

$$G = H - TS$$

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

$$-\Delta G = -w - P\Delta V$$

Spontaneous (irreversible)	Equilibrium (reversible)	Non-spontaneous (non-feasible)
$\Delta H < 0$	$\Delta H = T\Delta S$	$\Delta H > 0$



$\Delta S < 0$	$\Delta S = \frac{\Delta H}{T}$	$\Delta S > 0$
$\Delta G < 0$	$\Delta G = 0$	$\Delta G > 0$

❖ **Reaction quotient (Q)** – It is defined as the ratio of concentration of the products to the concentrations of the reactants under non equilibrium conditions.

❖  **$\Delta G^0$  = Standard free energy change of the reaction.**

$$\Delta G^0 = \Delta G^0 + RT \ln Q$$

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

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

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln k_{eq}$$

❖ **Third law of thermodynamics** – It states that the entropy of pure crystalline substance at absolute zero is zero (or) it is impossible to lower the temperature of an object to absolute zero in a finite number of steps.  $\lim_{T \rightarrow 0} S = 0$ .

### I. Choose the best answer

1. The amount of heat exchanged with the surrounding at constant temperature and pressure is given by the quantity

- a)  $\Delta E$                                       b)  $\Delta H$                                       c)  $\Delta S$                                       d)  $\Delta G$

2. All the naturally occurring processes proceed spontaneously in a direction which leads to

- a) decrease in entropy                                      b) increase in enthalpy  
c) increase in free energy                                      d) **decrease in free energy**

3. In an adiabatic process, which of the following is true ?

- a)  $q = w$                                       b)  **$q = 0$**                                       c)  $\Delta E = q$                                       d)  $P \Delta V = 0$

4. In a reversible process, the change in entropy of the universe is

- a)  $> 0$                                       b)  $> 0$                                       c)  $< 0$                                       d)  **$= 0$**

5. In an adiabatic expansion of an ideal gas

- a)  **$w = -\Delta u$**                                       b)  $w = \Delta u + \Delta H$                                       c)  $\Delta u = 0$                                       d)  $w = 0$

6. The intensive property among the quantities below is

- a) mass                                      b) volume                                      c) enthalpy                                      d)  $\frac{\text{mass}}{\text{volume}}$

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7. An ideal gas expands from the volume of  $1 \times 10^{-3} \text{ m}^3$  to  $1 \times 10^{-2} \text{ m}^3$  at 300 K against a constant pressure at  $1 \times 10^5 \text{ Nm}^{-2}$ . The work done is

- a) – 900 J                      b) 900 kJ                      c) 270 kJ                      d) – 900 kJ

8. Heat of combustion is always

- a) positive                      b) **negative**                      c) zero                      d) either positive or negative

9. The heat of formation of CO and  $\text{CO}_2$  are – 26.4 kCal and – 94 kCal, respectively. Heat of combustion of carbon monoxide will be

- a) + 26.4 kcal                      b) – **67.6 kcal**                      c) – 120.6 kcal                      d) + 52.8 kcal

10.  $\text{C}(\text{diamond}) \rightarrow \text{C}(\text{graphite})$ ,  $\Delta H = -\text{ve}$ , this indicates that

- a) **graphite is more stable than diamond**                      b) graphite has more energy than diamond  
c) both are equally stable                      d) stability cannot be predicted

11. The enthalpies of formation of  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  are – 1596 kJ and – 1134 kJ, respectively.  $\Delta H$  for the reaction  $2\text{Al} + \text{Cr}_2\text{O}_3 \rightarrow 2\text{Cr} + \text{Al}_2\text{O}_3$  is

- a) – 1365 kJ                      b) 2730 kJ                      c) – 2730 kJ                      d) – **462 kJ**

12. Which of the following is not a thermodynamic function ?

- a) internal energy                      b) enthalpy                      c) entropy                      d) **frictional energy**

13. If one mole of ammonia and one mole of hydrogen chloride are mixed in a closed container to form ammonium chloride gas, then

- a)  $\Delta H > \Delta U$                       b)  $\Delta H - \Delta U = 0$                       c)  $\Delta H + \Delta U = 0$                       d)  **$\Delta H < \Delta U$**

14. Change in internal energy, when 4 kJ of work is done on the system and 1 kJ of heat is given out by the system is

- a) +1 kJ                      b) – 5 kJ                      c) **+3 kJ**                      d) – 3 kJ

15. The work done by the liberated gas when 55.85 g of iron (molar mass  $55.85 \text{ g mol}^{-1}$ ) reacts with hydrochloric acid in an open beaker at  $25^\circ\text{C}$

- a) – **2.48 kJ**                      b) – 2.22 kJ                      c) + 2.22 kJ                      d) + 2.48 kJ

16. The value of  $\Delta H$  for cooling 2 moles of an ideal monatomic gas from  $125^\circ\text{C}$  to  $25^\circ\text{C}$  at constant pressure will be  $\left[ \text{given } C_p = \frac{5}{2} R \right]$

- a) – 250 R                      b) – **500 R**                      c) 500 R                      d) + 250 R

17. Given that  $\text{C}_{(\text{g})} + \text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})}$   $\Delta H^0 = -a \text{ kJ}$ ;  $2 \text{CO}_{(\text{g})} + \text{O}_{2(\text{g})} \rightarrow 2\text{CO}_{2(\text{g})}$   $\Delta H^0 = -b \text{ kJ}$ ; Calculate the  $\Delta H^0$  for the reaction  $\text{C}_{(\text{g})} + \frac{1}{2} \text{O}_{2(\text{g})} \rightarrow \text{CO}_{(\text{g})}$

- a)  $\frac{b+2a}{2}$                       b)  $2a-b$                       c)  $\frac{2a-b}{2}$                       d)  $\frac{b-2a}{2}$

18. When 15.68 litres of a gas mixture of methane and propane are fully combusted at  $00^\circ\text{C}$  and 1 atmosphere, 32 litres of oxygen at the same temperature and pressure are consumed. The amount of heat of released from this combustion in kJ is ( $\Delta H^\circ \text{C}(\text{CH}_4) = -890 \text{ kJ mol}^{-1}$  and  $\Delta H^\circ \text{C}(\text{C}_3\text{H}_8) = -2220 \text{ kJ mol}^{-1}$ )

- a) – 889 kJ                      b) – 1390 kJ                      c) – 3180 kJ                      d) – **653.66 kJ**

19. The bond dissociation energy of methane and ethane are  $360 \text{ kJ mol}^{-1}$  and  $620 \text{ kJ mol}^{-1}$  respectively. Then, the bond dissociation energy of C-C bond is

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- a)  $170 \text{ kJ mol}^{-1}$     b)  $50 \text{ kJ mol}^{-1}$     c)  $80 \text{ kJ mol}^{-1}$     d)  $220 \text{ kJ mol}^{-1}$

20. The correct thermodynamic conditions for the spontaneous reaction at all temperature is (NEET Phase - I)

- 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  $\Delta S > 0$

21. The temperature of the system, decreases in an \_\_\_\_\_

- a) Isothermal expansion    b) Isothermal Compression  
c) **adiabatic expansion**    d) adiabatic compression

22. In an isothermal reversible compression of an ideal gas the sign of  $q$ ,  $\Delta S$  and  $w$  are respectively

- a) +, -, -    b) -, +, -    c) +, -, +    d) -, -, +

23. Molar heat of vapourisation of a liquid is  $4.8 \text{ kJ mol}^{-1}$ . If the entropy change is  $16 \text{ J mol}^{-1} \text{ K}^{-1}$ , the boiling point of the liquid is

- a) 323 K    b)  **$27^\circ \text{C}$**     c) 164 K    d) 0.3 K

24.  $\Delta S$  is expected to be maximum for the reaction

- a)  $\text{Ca(S)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CaO(S)}$     b)  $\text{C(S)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$   
c)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO(g)}$     d)  **$\text{CaCO}_3(\text{S}) \rightarrow \text{CaO(S)} + \text{CO}_2(\text{g})$**

25. The values of  $\Delta H$  and  $\Delta S$  for a reaction are respectively  $30 \text{ kJ mol}^{-1}$  and  $100 \text{ JK}^{-1} \text{ mol}^{-1}$ . Then the temperature above which the reaction will become spontaneous is

- a) **300 K**    b) 30 K    c) 100 K    d)  $20^\circ \text{C}$

### Question and Answer

#### 25.State the first law of thermodynamics.

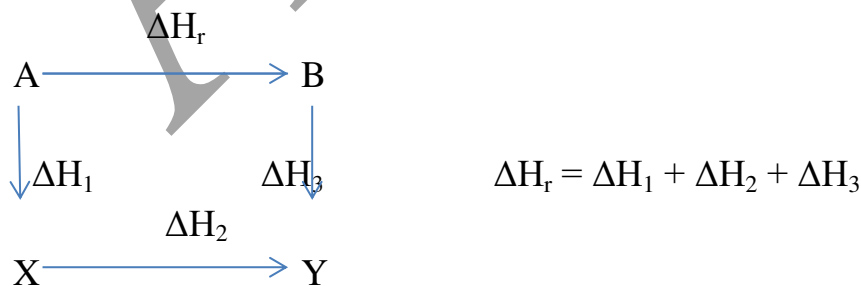
The first law of thermodynamics, also known as the law of conservation of energy, states that "The total energy of an isolated system remains constant though it may change from one form to another."

The mathematical statement of the Frist Law is:  $\Delta U = q + w$

Where  $q$ - the amount of heat supplied to the system;  $w$  – work done on the system

#### 27.Define Hess's law of constant heat summation.

The enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single or multiple steps provided the initial and final states are same.



28. Explain intensive properties with two examples

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The property that is independent of the mass or the size of the system is called an intensive property. Examples: Refractive index, Surface tension, density, temperature, Boiling point, Freezing point, molar volume, etc.,

## 29. Define the following terms:

**(a) isothermal process (b) adiabatic process (c) isobaric process (d) isochoric process**

**(a) Isothermal process:** An isothermal process is defined as one in which the temperature of the system remains constant, during the change from its initial to final state. The system exchange heat with its surrounding and the temperature of the system remains constant.

For an isothermal process  $dT = 0$

## **(b) Adiabatic process**

An adiabatic process is defined as one in which there is no exchange of heat ( $q$ ) between the system and surrounding during the process.

For an adiabatic process  $q = 0$

## **(c) Isobaric process**

An isobaric process is defined as one in which the pressure of the system remains constant during its change from the initial to final state.

For an Isochoric process  $dP = 0$

## **(d) Isochoric process**

An isochoric process is defined as the one in which the volume of system remains constant during its change from initial to final state.

For an isochoric process,  $dV = 0$

## 30. What is the usual definition of entropy? What is the unit of entropy?

**(i)** Entropy is a measure of the molecular disorderliness (randomness) of a system.

$$\Delta S = dq_{\text{rev}} / T$$

**ii)** The entropy ( $S$ ) is equal to heat energy exchanged ( $q$ ) divided by the temperature ( $T$ ) at which the exchange takes place. Therefore, The SI unit of entropy is  $\text{JK}^{-1}$

## 31. Predict the feasibility of a reaction when

**i) both  $\Delta H$  and  $\Delta S$  positive    ii) both  $\Delta H$  and  $\Delta S$  negative**

**iii)  $\Delta H$  decreases but  $\Delta S$  increases**

**(i)** the reaction is not feasible. (Non-spontaneous)

**(ii)** the reaction is not feasible. (Non-spontaneous)

**(iii)** the reaction is feasible. (Spontaneous )

## 32. Define is Gibbs's free energy.

**Gibbs free energy** is defined as the part of total energy of a system that can be converted (or) available for conversion into work.

Gibb's free energy is defined as  **$G = H - TS$**

**Where,**  $H$  = enthalpy or heat content of the system,

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T = Temperature in Kelvin and

S = Entropy

### 33. Define enthalpy of combustion.

The heat of combustion of a substance is defined as “The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen”. It is denoted by  $\Delta H_c$ .

### 34. Define molar heat capacity. Give its unit.

Molar heat capacity is define as “The amount of heat absorbed by one mole of the substance to raise its temperature by 1 kelvin”. It is denoted as  $C_m$ .

The SI unit of molar heat capacity is  $\text{JK}^{-1} \text{mol}^{-1}$

### 35. Define the calorific value of food. What is the unit of calorific value?

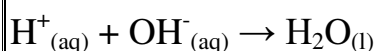
The calorific value is defined as “The amount of heat produced in calories (or joules) when one gram of the substance is completely burnt.”

The SI unit of calorific value is  $\text{J Kg}^{-1}$ .

It is usually expressed in  $\text{cal g}^{-1}$

### 36. Define enthalpy of neutralization.

The heat of neutralization is defined as “The change in enthalpy when one gram equivalent of an acid is completely neutralized by one gram equivalent of a base or vice versa in dilute solution”.



$$\Delta H = -57.32 \text{ kJ}$$

### 37. What is lattice energy?

Lattice energy is defined as “ The amount of energy required to completely remove the constituent ions from its crystal lattice to an infinite distance”.

It is also referred as lattice enthalpy.

### 38. What are state and path functions? Give two examples.

**(i) State Function:** A state function is a thermodynamic property of a system, which has a specific value for a given state and does not depend on the path (or manner) by which the particular state is reached.

**Example:** Pressure (P), Volume (V), Temperature (T)

**(ii) Path Functions:** A path function is a thermodynamic property of the system whose value depends on the path by which the system changes from its initial to final states.

**Examples:** Work (w), Heat (q).

### 39. Give Kelvin statement of second law of thermodynamics.

It is impossible to construct a machine that absorbs heat from a hot source and converts it completely into work by a cyclic process without transferring a part of heat to a cold sink.

**40. The equilibrium constant of a reaction is 10, what will be the sign of  $\Delta G$ ? Will this reaction be spontaneous?**

**Given**  $K_{\text{eq}} = 10$       Gas constant  $R = 8.314 \text{ JK}^{-1} \text{mol}^{-1}$        $T = 300\text{K}$

The relationship between Free energy change  $\Delta G$  and equilibrium constant K is

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$$\Delta G^\circ = -RT \ln K$$

Since K, T and R are positive values,  $\Delta G^\circ$  will be negative.

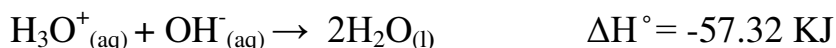
When  $\Delta G$  is -ve, the process is spontaneous and feasible.

**41. Enthalpy of neutralization is always a constant when a strong acid is neutralized by a strong base: account for the statement.**

Strong acids and strong bases exist in the fully ionized form in aqueous solutions as below:



(or)



The  $\text{H}^+$  ions produced in water by the acid molecules exist as  $\text{H}_3\text{O}^+$ . Thus, enthalpy change per mole of water formed from  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions. Therefore, irrespective of the chemical nature, the enthalpy of neutralization of strong acid by strong base is a constant value which is equal to -57.32 KJ.

**42. State the third law of thermodynamics.**

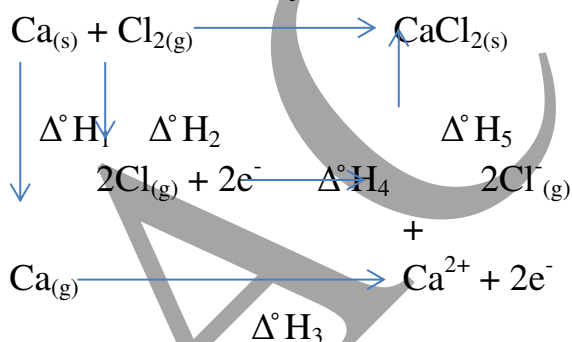
(i) The third law of thermodynamics states that the entropy of pure crystalline substance at absolute zero is zero.

(ii) It can also be stated as it is impossible to lower the temperature of an object to absolute zero in a finite number of steps.

(iii) Mathematically,  $\lim_{T \rightarrow 0} S = 0$  for a perfectly ordered crystalline state.

**43. Write down the Born-Haber cycle for the formation of  $\text{CaCl}_2$ .**

- Born – Haber cycle for the formation of  $\text{CaCl}_2$
- Born – Haber cycle is used to calculate the lattice enthalpy of  $\text{CaCl}_2$ .



**44. Identify the state and path functions out of the following: a) Enthalpy b) Entropy c) Heat d) Temperature e) Work f) Free energy.**

**State Function:** Enthalpy, entropy, temperature, free energy

**Path Function:** Heat, Work.

**45. State the various statements of second law of thermodynamics.**

(i) **Kelvin-Planck statement:** It is impossible to construct a machine that absorbs heat from a hot source and converts it completely into work by a cyclic process without transferring a part of heat to a cold sink.



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(ii) **Clausius statement:** It is impossible to transfer heat from a cold reservoir to a hot reservoir without doing some work.

iii) **Entropy statement:** The entropy of an isolated system increases during a spontaneous process.

(iv) **Efficiency statement:** Even an ideal, frictionless engine cannot convert 100% of its input heat into work.

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**46. What are spontaneous reactions? What are the conditions for the spontaneity of a process?**

(i) **Spontaneous reaction:** A reaction that occurs under the given set of conditions without any external driving force is called a spontaneous reaction.

(ii) **Criteria for spontaneity of a process:** The spontaneity of any process depends on three different factors.

$$\Delta H = -ve,$$

$$\Delta S = +ve,$$

$$\Delta G = -ve.$$

**47. List the characteristics of internal energy.**

- The internal energy of a system is an extensive property
- The internal energy of a system is a state function
- The change in internal energy of a system is expressed as  $\Delta U = U_f - U_i$
- In a cyclic process, there is no internal energy change.  $\Delta U_{(cyclic)} = 0$
- If the internal energy of the system in the final state ( $U_f$ ) is less than the internal energy of the system in its initial state ( $U_i$ ), then  $\Delta U$  would be negative.  $\Delta U = U_f - U_i = -ve$  ( $U_f < U_i$ )
- If the internal energy of the system in the final state ( $U_f$ ) is greater than the internal energy of the system in its initial state ( $U_i$ ), then  $\Delta U$  would be positive.  $\Delta U = U_f - U_i = +ve$  ( $U_f > U_i$ )

**48. Explain how heat absorbed at constant volume is measured using bomb calorimeter with a neat diagram.**

(i) Heat evolved at constant volume, is measured in a bomb calorimeter.

(ii) **Apparatus setup:** The inner vessel (the bomb) and its cover are made of strong steel. The cover is fitted tightly to the vessel by means of metal lid and screws.

(iii) **Experiment:** A weighed amount of the substance is taken in a platinum cup connected with electrical wires for striking an arc instantly to kindle combustion. The bomb is then tightly closed and pressurized with excess oxygen. The bomb is immersed in water, in the inner volume of the calorimeter. A stirrer is placed in the space between the wall of the calorimeter and the bomb, so that water can be stirred the substance through electrical heating.

(iv) **Calculation:** A known amount of combustible substance is burnt oxygen in the bomb. Heat evolved during the reaction is absorbed by the calorimeter as well as the water in which the bomb is immersed. The change in temperature is measured using a Beckman thermometer. Since the bomb is sealed its volume does not change and hence the heat measurement is equal to the heat of combustion at a constant volume ( $\Delta U_c$ ).

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The amount of heat produced in the reaction ( $\Delta U$ )<sub>c</sub> is equal to the sum of the heat absorbed by the calorimeter and water.

Heat absorbed by the calorimeter  $q_1 = k \cdot \Delta T$

Where  $m_w$  is molar mass of water  $C_w$  is molar heat capacity of water ( $4,184 \text{ kJ K}^{-1} \text{ mol}^{-1}$ )

Therefore  $\Delta U_c = q_1 + q_2$

$$= k \cdot \Delta T + m_w C_w \Delta T$$

$$= (k + m_w C_w) \Delta T$$

Calorimeter constant can be determined by burning a known mass of standard sample (benzoic acid) for which the heat of combustion is known ( $-3227 \text{ kJ mol}^{-1}$ ) The enthalpy of combustion at constant pressure of the substance is calculated from the equation

$$\Delta H^0_{C(\text{pressure})} = \Delta U^0_{C(\text{vol})} + \Delta n_g RT$$

#### 49. Calculate the work involved in expansion and compression process.

- For understanding pressure-volume work, let us consider a cylinder which contains 'n' moles of an ideal gas fitted with a frictionless piston of cross sectional area A. The total volume of the gas inside is  $V_i$  and pressure of the gas inside is  $P_{\text{int}}$ .
- If the external pressure  $P_{\text{ext}}$  is greater than  $P_{\text{int}}$ , the piston moves inward till the pressure inside becomes equal to  $P_{\text{ext}}$ . Let this change be achieved in a single step and the final volume be  $V_f$ .
- In this case, the work is done on the system (+w). It can be calculated as follows
- where  $dx$  is the distance moved by the piston during the compression and F is the force acting on the gas.

$$w = -F \cdot \Delta x \quad \text{----- (1)}$$

$$F = P_{\text{ext}} A \quad \text{---- (2)}$$

Substituting 2 in 1

$$w = -P_{\text{ext}} \cdot A \cdot \Delta x$$

$$A \cdot \Delta x = \text{change in volume} = V_f - V_i$$

$$w = -P_{\text{ext}} \cdot (V_f - V_i) \quad \text{----- (3)}$$

$$w = -P_{\text{ext}} \cdot (-\Delta V) \quad \text{----- (4)}$$

$$= P_{\text{ext}} \cdot \Delta V$$

- Since work is done on the system, it is a positive quantity.
- If the pressure is not constant, but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount,  $dV$ . In such a case we can calculate the work done on the gas by the relation

$$w_{\text{rev}} = \int_{V_i}^{V_f} P_{\text{int}} dV$$

- In a compression process,  $P_{\text{ext}}$  the external pressure is always greater than the pressure of the system. **i.e**  $P_{\text{ext}} = (P_{\text{int}} + dP)$ .
- In an expansion process, the external pressure is always less than the pressure of the system

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$$\text{i.e. } P_{\text{ext}} = (P_{\text{int}} - dP).$$

ix. When pressure is not constant and changes in infinitesimally small steps (reversible conditions) during compression from  $V_i$  to  $V_f$ , the P-V plot looks like in fig Work done on the gas is represented by the shaded area. In general case we can write,

x.  $P_{\text{ext}} = (P_{\text{int}} + dP)$ . Such processes are called reversible processes. For a compression process work can be related to internal pressure of the system under reversible conditions by writing equation

$$w_{\text{rev}} = \int_{v_i}^{v_f} P_{\text{int}} dV$$

For a given system with an ideal gas

$$P_{\text{int}} V = nRT$$

$$P_{\text{int}} = \frac{nRT}{V}$$

$$W_{\text{rev}} = \int_{v_i}^{v_f} \frac{nRT}{V} dV$$

$$W_{\text{rev}} = -nRT \int_{v_i}^{v_f} \left(\frac{dV}{V}\right)$$

$$W_{\text{rev}} = -nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$W_{\text{rev}} = -2.303 nRT \log\left(\frac{V_f}{V_i}\right)$$

xi. If  $V_f > V_i$  (expansion), the sign of work done by the process is negative.

xii. If  $V_f < V_i$  (compression) the sign of work done on the process is positive.

**50. Derive the relation between  $\Delta H$  and  $\Delta U$  for an ideal gas. Explain each term involved in the equation.**

When the system at constant pressure undergoes changes from an initial state with  $H_1$ ,  $U_1$  and  $V_1$  to a final state with  $H_2$ ,  $U_2$  and  $V_2$  the change in enthalpy  $\Delta H$ , can be calculated as follows:

$$H = U + PV$$

In the initial state

$$H_1 = U_1 + PV_1 \quad \text{----- (1)}$$

In the final state

$$H_2 = U_2 + PV_2 \quad \text{----- (2)}$$

change in enthalpy is (2) - (1)

$$(H_2 - H_1) = (U_2 - U_1) + P(V_2 - V_1)$$

$$\Delta H = \Delta U + P\Delta V \quad \text{----- (3)}$$

As per first law of thermodynamics,

$$\Delta U = q + w$$

Equation (3) becomes

$$\Delta H = q + w + P\Delta V$$

$$W = -P\Delta V$$

$$\Delta H = q_p - P\Delta V + P\Delta V$$

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$$\Delta H = q_p \quad \text{———— (4)}$$

$q_p$  – is the heat absorbed at constant pressure and is considered as heat content.

Consider a closed system of gases which are chemically reacting to form gaseous products at constant temperature and pressure with  $V_i$  and  $V_f$  as the total volumes of the reactant and product gases

respectively, and  $n_i$  and  $n_f$  as the number of moles of gaseous reactants and products, then,

**For reactants (initial state) :**

$$PV_i = n_i RT \quad \text{———— (5)}$$

**For products (final state) :**

$$PV_f = n_f RT \quad \text{———— (6)}$$

(6) - (5)

$$P(V_f - V_i) = (n_f - n_i) RT$$

$$P \Delta V = \Delta n_{(g)} RT \quad \text{———— (7)}$$

Substituting in (7) in (3)

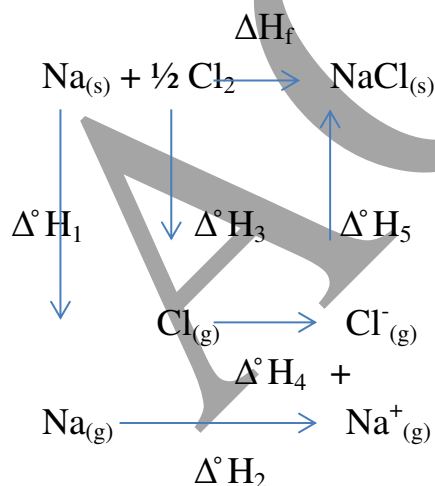
$$\Delta H = \Delta U + \Delta n_{(g)} RT \quad \text{———— (8)}$$

**51. Suggest and explain an indirect method to calculate lattice enthalpy of sodium chloride crystal.**

Let us use the Born - Haber cycle for determining the lattice enthalpy of NaCl as follows:

Since the reaction is carried out with reactants in elemental forms and products in their standard states, at 1 bar, the overall enthalpy change of the reaction is also the enthalpy of formation for NaCl. Also, the formation of NaCl can be considered in 5 steps. The sum of the enthalpy changes of these steps is equal to the enthalpy change for the overall reaction from which the lattice enthalpy of NaCl is calculated.

Let us calculate the lattice energy of sodium chloride using Born-Haber cycle



$\Delta^\circ H_f$  = heat of formation of sodium chloride =  $-411.3 \text{ kJ mol}^{-1}$

$\Delta^\circ H_1$  = heat of sublimation of Na<sub>(s)</sub> =  $108.7 \text{ kJ mol}^{-1}$

$\Delta^\circ H_2$  = ionisation energy of Na<sub>(s)</sub> =  $495.0 \text{ kJ mol}^{-1}$

$\Delta^\circ H_3$  = dissociation energy of Cl<sub>2(s)</sub> =  $244 \text{ kJ mol}^{-1}$

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$$\Delta^\circ H_4 = \text{Electron affinity of Cl}_{(s)} = -349.0 \text{ kJ mol}^{-1}$$

$$\Delta^\circ H_f = \Delta^\circ H_1 + \Delta^\circ H_2 + \frac{1}{2} \Delta^\circ H_3 + \Delta^\circ H_4 + \Delta^\circ H_5$$

$$\therefore \Delta^\circ H_5 = (\Delta^\circ H_f) - (\Delta^\circ H_1 + \Delta^\circ H_2 + \Delta^\circ H_3 + \Delta^\circ H_4)$$

$$\Rightarrow \Delta^\circ H_5 = (-411.3) - (108.7 + 495.0 + 122 - 349)$$

$$\Delta^\circ H_5 = (-411.3) - (376.7)$$

$$\therefore \Delta^\circ H_5 = -788 \text{ kJ mol}^{-1}$$

This negative sign in lattice energy indicates that the energy is released when sodium is formed from its constituent gaseous ions  $\text{Na}^+$  and  $\text{Cl}^-$

## 52. List the characteristics of Gibbs free energy.

(i) Free energy is defined as  $G = H - TS$ . 'G' is a state function

(ii) G- Extensive property;  $\Delta G$  – intensive property. When mass remains constant between initial and final states of system

(iii) 'G' has a single value for the thermodynamic state of the system

(iv) Gibbs free energy is defined as the part of total energy of a system that can be converted (or) available for conversion into work.

(v) G and  $\Delta G$  values correspond to the system only.

Process	Spontaneous	Equilibrium	Non-spontaneous
$\Delta G$	-Ve	Zero	+Ve

(vi) Gibbs free energy and the network done by the system:

For any system at constant pressure and temperature

$$\Delta G = \Delta H - T\Delta S \text{ ---- (1)}$$

We know that,

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

$$\therefore \Delta G = \Delta U + P\Delta V - T\Delta S$$

from first law of thermodynamics

$$\Delta U = q + w$$

from second law of thermodynamics

$$\Delta S = \frac{q}{T} \quad \Delta G = q + w + P\Delta V - T\left(\frac{q}{T}\right)$$

$$\Delta G = w + P\Delta V$$

$$-\Delta G = -w - P\Delta V \text{ ----- (2)}$$

But  $-P\Delta V$  represents the work done due to expansion against a constant external pressure.

**53. Calculate the work done when 2 moles of an ideal gas expands reversibly and isothermally from a volume of 500 ml to a volume of 2 L at 25°C and normal pressure.**

**Given :**

$$n = 2 \text{ moles; } V_i = 500 \text{ ml} = 0.5 \text{ lit; } V_f = 2 \text{ lit}$$

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

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$$w = -2.303 nRT \log \left( \frac{V_f}{V_i} \right)$$

$$w = -2.303 \times 2 \times 8.314 \times 298 \times \log \left( \frac{2}{0.5} \right)$$

$$w = -2.303 \times 2 \times 8.314 \times 298 \times \log(4)$$

$$w = -2.303 \times 2 \times 8.314 \times 298 \times 0.6021$$

$$w = -6871 \text{ J}$$

$$w = -6.871 \text{ kJ}$$

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54. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298 K. The temperature of the calorimeter was found to increase from 298 K to 298.45 K due to the combustion process. Given that the calorimeter constant is  $2.5 \text{ kJ K}^{-1}$ . Calculate the enthalpy of combustion of the gas in  $\text{kJ mol}^{-1}$ .

Given :

$$T_i = 298 \text{ K}; T_f = 298.45 \text{ K}; \quad k = 2.5 \text{ kJ K}^{-1}; \quad m = 3.5 \text{ g}; \quad M_m = 28$$

$$\text{heat evolved} = k \Delta T$$

$$= k (T_f - T_i)$$

$$= 2.5 \text{ kJ K}^{-1} (298.45 - 298) \text{ K}$$

$$= 1.125 \text{ kJ}$$

$$\Delta H_c = \frac{1.125}{3.5} \times 28 \text{ kJ mol}^{-1}$$

$$\Delta H_c = 9 \text{ kJ mol}^{-1}$$

55. Calculate the entropy change in the system, and surroundings, and the total entropy change in the universe during a process in which 245 J of heat flow out of the system at  $77^\circ\text{C}$  to the surrounding at  $33^\circ\text{C}$ .

Given :

$$T_{\text{sys}} = 77^\circ\text{C} = (77 + 273) = 350 \text{ K}$$

$$T_{\text{surr}} = 33^\circ\text{C} = (33 + 273) = 306 \text{ K}$$

$$q = 245 \text{ J}$$

$$\Delta S_{\text{sys}} = q$$

$$T_{\text{sys}} = \frac{q}{T_{\text{sys}}} = \frac{-245}{350} = -0.7 \text{ JK}^{-1}$$

$$\Delta S_{\text{surr}} = \frac{q}{T_{\text{surr}}} = \frac{+245}{306} = +0.8 \text{ JK}^{-1}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{univ}} = -0.7 \text{ JK}^{-1} + 0.8 \text{ JK}^{-1}$$

$$\Delta S_{\text{univ}} = 0.1 \text{ JK}^{-1}$$

56. 1 mole of an ideal gas, maintained at 4.1 atm and at a certain temperature, absorbs heat 3710J and expands to 2 litres. Calculate the entropy change in expansion process.

Given :

$$n = 1 \text{ mole}; \quad P = 4.1 \text{ atm}; \quad V = 2 \text{ Lit}; \quad T = ?; \quad q = 3710 \text{ J}$$

$$\Delta S = \frac{q}{T}; \quad \Delta S = \frac{q}{\left( \frac{PV}{nR} \right)}; \quad \Delta S = \frac{nRq}{PV}$$



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$$\Delta S = \frac{1 \times 0.082 \text{ lit atm K}^{-1} \times 3710 \text{ J}}{4.1 \text{ atm} \times 2 \text{ lit}}$$

$$\Delta S = 37.10 \text{ JK}^{-1}$$

57. 30.4 kJ is required to melt one mole of sodium chloride. The entropy change during melting is  $28.4 \text{ JK}^{-1} \text{ mol}^{-1}$ . Calculate the melting point of sodium chloride.

$$\Delta H_f(\text{NaCl}) = 30.4 \text{ kJ} = 30400 \text{ J mol}^{-1}$$

$$\Delta S_f(\text{NaCl}) = 28.4 \text{ JK}^{-1} \text{ mol}^{-1}; \quad T_f = ?$$

$$\Delta S_f = \frac{\Delta H_f}{T_f}; \quad T_f = \frac{\Delta H_f}{\Delta S_f}$$

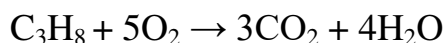
$$T_f = \frac{30400 \text{ J mol}^{-1}}{28.4 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$T_f = 1070.4 \text{ K}$$

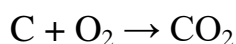
58. Calculate the standard heat of formation of propane, if its heat of combustion is  $-2220.2 \text{ kJ mol}^{-1}$ . the heats of formation of  $\text{CO}_{2(g)}$  and  $\text{H}_2\text{O(l)}$  are  $-393.5$  and  $-285.8 \text{ kJ mol}^{-1}$  respectively.

SOLUTION :

Given



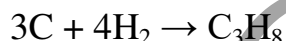
$$\Delta H_c^\circ = -2220.2 \text{ kJ mol}^{-1} \quad \text{-----(1)}$$



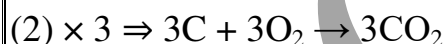
$$\Delta H_f^\circ = -393.5 \text{ kJ mol}^{-1} \quad \text{-----(2)}$$



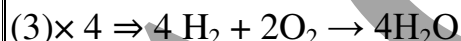
$$\Delta H_f^\circ = -285.8 \text{ kJ mol}^{-1} \quad \text{-----(3)}$$



$$\Delta H_c^\circ = ?$$



$$\Delta H_f^\circ = -1180.5 \text{ kJ} \quad \text{-----(4)}$$



$$\Delta H_f^\circ = -1143.2 \text{ kJ} \quad \text{-----(5)}$$



$$\Delta H_f^\circ = -1180.5 - 1143.2 - (-2220.2) \text{ kJ}$$



$$\Delta H_f^\circ = -103.5 \text{ kJ}$$

Standard heat of formation of propane is  $\Delta H_f^\circ(\text{C}_3\text{H}_8) = -103.5 \text{ kJ}$

59. You are given normal boiling points and standard enthalpies of vapourisation. Calculate the entropy of vapourisation of liquids listed below.

S.No	Liquid	Boiling points ( $^\circ\text{C}$ )	$\Delta H$ (KJ $\text{mol}^{-1}$ )
1.	Ethanol	78.4	+ 42.4
2.	Toluene	110.6	+ 35.2

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For ethanol :

Given :

$$T_b = 78.4^\circ \text{C} = (78.4 + 273) \\ = 351.4 \text{ K}$$

$$\Delta H_v (\text{ethanol}) = + 42.4 \text{ kJ mol}^{-1}$$

$$\Delta S_v = \frac{\Delta H_v}{T_b} ; \quad \Delta S_v = \frac{+ 42.4 \text{ KJ mol}^{-1}}{351.4 \text{ K}}$$

$$\Delta S_v = \frac{+42400 \text{ J mol}^{-1}}{351.4 \text{ K}};$$

$$\Delta S_v = + 120.66 \text{ JK}^{-1} \text{ mol}^{-1}$$

For Toluene :

Given :

$$T_b = 110.6^\circ \text{C} = (110.6 + 273) \\ = 383.6 \text{ K}$$

$$\Delta H_v (\text{toluene}) = + 35.2 \text{ kJ mol}^{-1}$$

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

$$\Delta S_v = \frac{+35.2 \text{ KJ mol}^{-1}}{383.6 \text{ K}} ;$$

$$\Delta S_v = \frac{+ 35200 \text{ J mol}^{-1}}{383.6 \text{ K}}$$

$$\Delta S_v = + 91.76 \text{ JK}^{-1}$$

60. For the reaction  $\text{Ag}_2\text{O(s)} \rightarrow 2\text{Ag(s)} + \frac{1}{2} \text{O}_2\text{(g)}$  :  $\Delta H = 30.56 \text{ kJ mol}^{-1}$  and  $\Delta S = 6.66 \text{ JK}^{-1} \text{ mol}^{-1}$  (at 1 atm). Calculate the temperature at which  $\Delta G$  is equal to zero. Also predict the direction of the reaction (i) at this temperature and (ii) below this temperature.

Solution :

$$\text{Given : } \Delta H = 30.56 \text{ kJ mol}^{-1} = 30560 \text{ J mol}^{-1}$$

$$\Delta S = 6.66 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$T = ? \text{ at which } \Delta G = 0$$

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

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

$$T = \frac{\Delta H}{\Delta S} ; \quad T = \frac{30.56 \text{ kJ mol}^{-1}}{6.66 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}}$$

$$T = 4589 \text{ K}$$

(i) At 4589 K ;  $\Delta G = 0$  the reaction is in equilibrium.

(ii) at temperature below 4598 K ,  $\Delta H > T \Delta S$   $\Delta G = \Delta H - T \Delta S > 0$ , the reaction in the forward direction, is nonspontaneous. In other words the reaction occurs in the backward direction.

61. What is the equilibrium constant  $K_{eq}$  for the following reaction at 400K.

$2\text{NOCl (g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)}$ , given that  $\Delta H^0 = 77.2 \text{ kJ mol}^{-1}$  ; and  $\Delta S^0 = 122 \text{ JK}^{-1} \text{ mol}^{-1}$ .

Solution :

Given

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$$T = 400\text{K} ; \Delta H^\circ = 77.2 \text{ kJ mol}^{-1} = 77200 \text{ J mol}^{-1} ;$$

$$\Delta S^\circ = 122 \text{ JK}^{-1} \text{ mol}^{-1}$$

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

$$\log K_{eq} = \frac{\Delta G^\circ}{2.303 RT}$$

$$\log K_{eq} = \frac{(\Delta H^\circ - T \Delta S^\circ)}{2.303 RT}$$

$$\log K_{eq} = - \left( \frac{77200 - 400 \times 122}{2.303 \times 8.314 \times 400} \right)$$

$$\log K_{eq} = \frac{(28400)}{7659}$$

$$\log K_{eq} = -3.7080$$

$$K_{eq} = \text{antilog}(-3.7080)$$

$$K_{eq} = 1.95 \times 10^{-4}$$

62. Cyanamide ( $\text{NH}_2\text{CN}$ ) is completely burnt in excess oxygen in a bomb calorimeter,  $\Delta U$  was found to be  $-742.4 \text{ kJ mol}^{-1}$ , calculate the enthalpy change of the reaction at 298K.  
 $\text{NH}_2\text{CN(s)} + 3/2 \text{ O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O(l)}$   $\Delta H = ?$

**Solution :**

**Given:**  $T = 298\text{K} ; \Delta U = -742.4 \text{ kJ mol}^{-1} \Delta H = ?$

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

$$\Delta H = \Delta U + (n_p - n_r) RT$$

$$\Delta H = -742.4 + \left(2 - \frac{3}{2}\right) \times 8.314 \times 10^{-3} \times 298$$

$$= -742.4 + (0.5 \times 8.314 \times 10^{-3} \times 298)$$

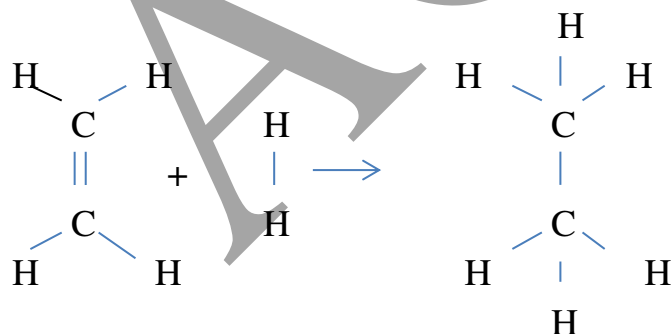
$$= -742.4 + 1.24$$

$$\Delta H = -741.16 \text{ kJ mol}^{-1}$$

63. Calculate the enthalpy of hydrogenation of ethylene from the following data. Bond energies of C-H, C-C, C=C and H-H are 414, 347, 618 and 435  $\text{kJ mol}^{-1}$ .

**Given :**  $E_{\text{C-H}} = 414 \text{ kJ mol}^{-1}$   $E_{\text{C-C}} = 347 \text{ kJ mol}^{-1}$   $E_{\text{C=C}} = 618 \text{ kJ mol}^{-1}$

$$E_{\text{H-H}} = 435 \text{ kJ mol}^{-1}$$



Ethylene

Ethane

$$\Delta H_r = \Sigma (\text{Bond energy})_r - \Sigma (\text{Bond energy})_p$$

$$\Delta H_r = (E_{\text{C=C}} + 4E_{\text{C-H}} + E_{\text{H-H}}) - (E_{\text{C-C}} + 6E_{\text{C-H}})$$

$$\Delta H_r = (618 + (4 \times 414) + 435) - (347 + (6 \times 414))$$

$$\Delta H_r = 2709 - 2831; \Delta H_r = -122 \text{ kJ mol}^{-1}$$

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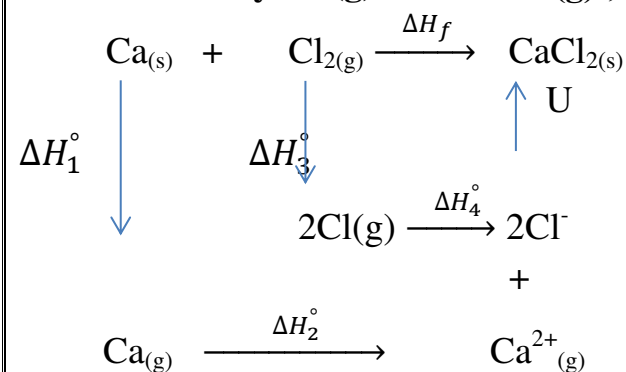
64. Calculate the lattice energy of  $\text{CaCl}_2$  from the given data  $\text{Ca (s)} + \text{Cl}_2(\text{g}) \rightarrow \text{CaCl}_2(\text{s})$  ;  $\Delta H_f^\circ = -795 \text{ kJ mol}^{-1}$

Atomization :  $\text{Ca(s)} \rightarrow \text{Ca(g)}$  ;  $\Delta H_1^\circ = +121 \text{ kJ mol}^{-1}$

Ionisation :  $\text{Ca(g)} \rightarrow \text{Ca}^{2+}(\text{g}) + 2\text{e}^-$  ;  $\Delta H_2^\circ = +2422 \text{ kJ mol}^{-1}$

Dissociation :  $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl(g)}$  ;  $\Delta H_3^\circ = +242.8 \text{ kJ mol}^{-1}$

Electron affinity :  $\text{Cl(g)} + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$  ;  $\Delta H_4^\circ = -355 \text{ kJ mol}^{-1}$



$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + U$$

$$-795 = 121 + 2422 + 242.8 + (2 \times -355) + U$$

$$-795 = 2785.8 - 710 + U$$

$$-795 = 2075.8 + U$$

$$U = -795 - 2075.8$$

$$U = -2870.8 \text{ KJmol}^{-1}$$

65. Calculate the enthalpy change for the reaction  $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$  from the following data.

$2\text{Fe} + 3/2 \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$ ;  $\Delta H = -741 \text{ kJ}$

$\text{C} + 1/2 \text{O}_2 \rightarrow \text{CO}$ ;  $\Delta H = -137 \text{ kJ}$

$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ ;  $\Delta H = -394.5 \text{ kJ}$

Given:

$$\Delta H_f(\text{Fe}_2\text{O}_3) = -741 \text{ kJmol}^{-1}$$

$$\Delta H_f(\text{CO}) = -137 \text{ kJmol}^{-1}$$

$$\Delta H_f(\text{CO}_2) = -394.5 \text{ kJmol}^{-1}$$



$$\Delta H_f = ?$$

$$\Delta H_r = \Sigma (\Delta H_f)_{\text{products}} - \Sigma (\Delta H_f)_{\text{reactants}}$$

$$\Delta H_r = [2\Delta H_f(\text{Fe}) + 3\Delta H_f(\text{CO}_2)] - [\Delta H_f(\text{Fe}_2\text{O}_3) + 3\Delta H_f(\text{CO})]$$

$$\Delta H_r = [0 + 3(-394.5)] - [-741 + 3(-137)]$$

$$\Delta H_r = [-1183.5] - [-1152]$$

$$\Delta H_r = -1183.5 + 1152 \quad \Delta H_r = -31.5 \text{ kJmol}^{-1}$$

66. When 1-pentyne (A) is treated with 4N alcoholic KOH at  $175^\circ\text{C}$ , it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne(A), 95.2% 2-pentyne(B) and 3.5% of 1,2 pentadiene (C) the equilibrium was maintained at  $175^\circ\text{C}$ , calculate  $\Delta G^\circ$  for the following equilibria.

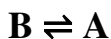
Dedication!

Determination!!

Distinction!!!

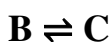
**(ACTC) ADVANCED CHEMISTRY TUITION CENTRE, 41/1 PWD ROAD, NAGERCOIL, 9952340892.****Solution:****Given:**  $T = 175^\circ\text{C} = 175 + 273 = 448 \text{ K}$ Concentration of 1-pentyne  $[A] = 1.3\%$ Concentration of 2-pentyne  $[B] = 95.2\%$ Concentration of 1,2 -pentyne  $[C] = 3.5\%$ 

At equilibrium



95.2%      1.3%

$$K_1 = \frac{1.3}{95.2} = 0.0136$$



95.2%      3.5%

$$K_2 = \frac{3.5}{95.2} = 0.0367$$

$$\Delta G_1^0 = -2.303RT \log K_1$$

$$\Delta G_1^0 = -2.303 \times 8.314 \times 448 \times \log 0.0136$$

$$\Delta G_1^0 = +16010 \text{ J}$$

$$\Delta G_1^0 = +16 \text{ KJ}$$

$$\Delta G_2^0 = -2.303 RT \log K_2$$

$$\Delta G_2^0 = -2.303 \times 8.314 \times 448 \times \log 0.00367$$

$$\Delta G_2^0 = +12312 \text{ J} = +12.312 \text{ kJ}$$

**67. At 33K,  $\text{N}_2\text{O}_4$  is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.****Solution:****Given:**  $T = 33 \text{ K}$ 

Initial Concentration      1              0

Dissociated                  0.5              1

At equilibrium              0.5              1

$$K_{eq} = \frac{1}{0.5} = 2$$

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

$$\Delta G^0 = -2.303 \times 8.314 \times 33 \times \log 2$$

$$\Delta G^0 = -190.18 \text{ J mol}^{-1}$$

**68. The standard enthalpies of formation of  $\text{SO}_2$  and  $\text{SO}_3$  are  $-297 \text{ kJ mol}^{-1}$  and  $-396 \text{ kJ mol}^{-1}$  respectively. Calculate the standard enthalpy of reaction for the reaction:****Solution:**

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Given:  $\Delta G_f^\circ(\text{SO}_2) = -297 \text{ kJ mol}^{-1}$   $\Delta G_f^\circ(\text{SO}_3) = -396 \text{ kJ mol}^{-1}$   $\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3$   $\Delta H_f^\circ = ?$

$$\Delta H_r^\circ = (\Delta H_f^\circ) \text{ Compound} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta H_r^\circ = \Delta H_f^\circ(\text{SO}_3) - (\Delta H_f^\circ(\text{SO}_2) + \frac{1}{2} \Delta H_f^\circ(\text{O}_2))$$

$$\Delta H_r^\circ = -396 \text{ kJ mol}^{-1} - (-297 \text{ kJ mol}^{-1} + 0)$$

$$\Delta H_r^\circ = -396 \text{ kJ mol}^{-1} + 297$$

$$\Delta H_r^\circ = -99 \text{ kJ mol}^{-1}$$

69. For the reaction at 298 K:  $2\text{A} + \text{B} \rightarrow \text{C}$   $\Delta H = 400 \text{ J mol}^{-1}$  ;  $\Delta S = 0.2 \text{ JK}^{-1} \text{ mol}^{-1}$

Determine the temperature at which the reaction would be spontaneous.

Solution:

Given:  $T = 298 \text{ K}$   $\Delta H = 400 \text{ J mol}^{-1}$   $\Delta S = 0.2 \text{ JK}^{-1} \text{ mol}^{-1}$

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

If  $T = 2000 \text{ K}$

$$\Delta G = 400 - (0.2 \times 2000) = 0$$

If  $T > 2000 \text{ K}$

$\Delta G$  will be negative

The reaction would be spontaneous only beyond 2000 K.

70. Find out the value of equilibrium constant for the following reaction at 298K,

$2 \text{NH}_3(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{NH}_2\text{CONH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$  Standard Gibbs energy change,  $\Delta G_r^\circ$  at the given temperature is  $-13.6 \text{ kJ mol}^{-1}$ .

Solution:

Given:

$T = 298 \text{ K}$

$$\Delta G_r^\circ = -13.6 \text{ kJ mol}^{-1}$$

$$= -13600 \text{ J mol}^{-1}$$

$$\Delta G_r^\circ = -2.303 RT \log K_{\text{eq}}$$

$$\log K_{\text{eq}} = \frac{-\Delta G^\circ}{2.303 RT}$$

$$\log K_{\text{eq}} = \frac{13.6 \text{ kJ mol}^{-1}}{2.303 \times 8.314 \times 10^{-3} \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}$$

$$\log K_{\text{eq}} = 2.38$$

$$K_{\text{eq}} = \text{antilog}(2.38)$$

$$K_{\text{eq}} = 239.88$$

71. A gas mixture of 3.67 lit of ethylene and methane on complete combustion at  $25^\circ\text{C}$  and at 1 atm pressure produce 6.11 lit of carbon dioxide. Find out the amount of



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heat evolved in kJ, during this combustion. ( $\Delta H_c(\text{CH}_4) = -890 \text{ kJ mol}^{-1}$  and  $\Delta H_c(\text{C}_2\text{H}_4) = -1423 \text{ kJ mol}^{-1}$ )

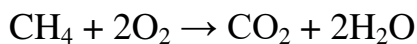
**Solution:**

**Given:**

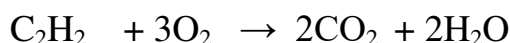
$$\Delta H_c(\text{CH}_4) = -890 \text{ KJmol}^{-1}$$

$$\Delta H_c(\text{C}_2\text{H}_4) = -1423 \text{ KJmol}^{-1}$$

Let the mixture contain x lit of  $\text{CH}_4$  and  $(3.67 - x)$  lit of ethylene.



x lit                  x lit



$(3.67 - x)$  lit                  2  $(3.67 - x)$

Volume of carbon dioxide formed =  $x + 2(3.67 - x) = 6.11$  lit

$$= x + 7.34 - 2x = 6.11$$

$$= 7.34 - x = 6.11$$

$$x = 1.23 \text{ lit}$$

Given mixture contains 1.23 lit of Methane and 2.44 lit of ethylene, hence

$$\Delta H_c = \left[ \frac{\Delta H_c(\text{CH}_4)}{22.4 \text{ lit}} \times (x) \text{ lit} \right] + \left[ \frac{\Delta H_c(\text{C}_2\text{H}_4)}{22.4 \text{ lit}} \times (3.67 - x) \text{ lit} \right]$$

$$\Delta H_c = \left[ \frac{-890 \text{ KJmol}^{-1}}{22.4 \text{ lit}} \times 1.23 \text{ lit} \right] + \left[ \frac{-1423}{22.4 \text{ lit}} \times (3.67 - 1.23) \text{ lit} \right]$$

$$\Delta H_c = [-48.87 \text{ kJmol}^{-1}] + [-155 \text{ kJmol}^{-1}]$$

$$\Delta H_c = -203.87 \text{ kJmol}^{-1}$$

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