CHAPTER - 05
THERMODYNAMICS AND CHEMICAL ENERGETICS

SYNOPSIS

Thermodynamics may be defined as the branch of science which 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.

System: A system is defined as that part of the universe which is under investigation.

Surroundings: The part of the universe other than the system is known as surroundings. Systems may be classified into three types.

a) Open system: One which can exchange mass as well as energy with the surroundings.

b) Closed system: One which can exchange energy with the surroundings but not mass.

c) Isolated system: One which can neither exchange mass nor energy with the surroundings.

Extensive properties: The properties of the system which depend upon the quantity or size of matter present in it. Examples are internal energy, heat capacity, enthalpy etc.

Intensive properties: The properties of the system which are independent of the quantity or size of matter present in it. Examples are temperature, pressure, viscosity etc.

State functions: The thermodynamic properties whose values depend only upon the initial and final states of the system and are independent of the path by which the change is brought about. Examples are internal energy, enthalpy, entropy, pressure, temperature etc.

Path functions: Properties whose values depend only on the path and not on the states of the system. Examples are heat (q) and work (w).

Isothermal process: A process carried out at constant temperature. ($\Delta T = 0$)

Adiabatic process: A process in which no heat exchange occurs between system and surroundings.

Isobaric process: A process carried out at constant pressure. ($\Delta P = 0$)

Isochoric process: A process carried out at constant volume. ($\Delta V = 0$)

Cyclic process: A process in which the system returns to the original state after undergoing series of changes.

Reversible process: A process is thermodynamically reversible if it can be reversed at any stage by a very small change in temperature, pressure or concentration. At every stage of the process the system will be in thermodynamic equilibrium and the process will take place infinitesimally slowly.

Irreversible process: A process which cannot be reversed by a small change in such properties is called an irreversible process. An irreversible process proceeds to one direction and it does not remain in equilibrium.

Zeroth law of thermodynamics: *The law states as follows.*

If the bodies (A and B) are in thermal equilibrium with another body C, then the bodies A and B will also be in thermal equilibrium with each other.

Modes of exchange of energy

1. **Heat (q):** Energy is exchanged between the system and the surroundings as heat if they are at different temperatures. According to international conventions, heat absorbed by the system is positive and heat given out by the system is given negative sign.

2. **Work (w):** Energy transfer may take place in the form of work if the system and surroundings have different pressures. Work done on the system is positive and work done by the system is negative.

Expression for PV-work: This work is also called expansion work. The general expression for all type of PV-work can be written as,

$$w = -P_{ex}\Delta V \quad \text{or} \quad w = -P\Delta V$$

(Work done during irreversible expansion)

Work done in reversible isothermal expansion of ideal gas

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

Internal energy or Intrinsic energy (U or E)

Every substance possesses a definite amount of energy which depends upon its chemical nature and its state of existence. This is called internal energy. The absolute value of internal energy cannot be determined, however the change in internal energy ΔU can be determined.

$$\Delta U = \Sigma U_{products} - \Sigma U_{reac\,tan\,ts}$$

First Law of Thermodynamics (Law of conservation of energy)

Energy can neither be created nor destroyed although it can be changed from one form to another.

OR

The total energy of the universe remains constant.

Consider a system having internal energy U_1.

Let q = heat absorbed from surroundings and w = work done on the system. The internal energy now changes to U_2.

$$\therefore U_2 = U_1 + q + w \quad \text{or} \quad U_2 - U_1 = q + w \quad \text{or} \quad \Delta U = q + w$$

This is the mathematical expression for the Ist law of Thermodynamics.

Enthalpy of Heat content (H)

This is used to study the heat changes of chemical reactions at constant temperature and constant pressure. The sum of internal energy and PV energy of any system is called enthalpy denoted by H.

$$H = U + PV \quad \text{and} \quad \Delta H = \Sigma H_P - \Sigma H_R$$

It can be shown that 1) $\Delta U = q_V$ and 2) $\Delta H = q_P$

Relationship between ΔH and ΔU

$$H = U + PV$$

$$\Delta H = \Delta U + P\Delta V \quad \text{(at constant pressure)}$$

For an ideal gas, PV = nRT.

At constant pressure and constant temperature,

$$P\Delta V = \Delta n.RT \quad \text{ie,} \quad \Delta H = \Delta U + \Delta n \cdot RT$$

where Δn = no. of moles of gaseous products – no. of moles of gaseous reactants.
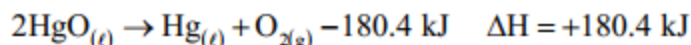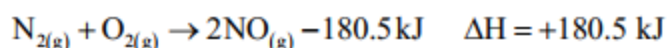
Exothermic reactions

Reactions which proceed with the evolution of heat energy are called exothermic reactions. Examples are,

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} + 393.5 kJ \quad \Delta H = -393.5 \text{ kJ}$$

For exothermic reactions carried out at constant volume and constant temperature, ΔU will be negative.

Endothermic reactions

Reactions which proceed with absorption of heat energy are called endothermic reactions.

$$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)} - 180.5 kJ \quad \Delta H = +180.5 \text{ kJ}$$

$$2HgO_{(\ell)} \rightarrow Hg_{(\ell)} + O_{2(g)} - 180.4 \text{ kJ} \quad \Delta H = +180.4 \text{ kJ}$$

Heat of formation or Enthalpy of formation $\left(\Delta H_f \right)$

It is the heat change accompanying the formation of one mole of a compound from its constituent elements.

When the species are in the standard states, it is called the standard heat of formation, denoted by ΔH^0_f.

$$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)} \quad \Delta H^0_f = -74.8 \text{ kJ}$$

The standard heat of formation of all elements in their stable state is zero.

$$\Delta H^0_f \text{ of } C_{(graphite)} = 0$$

$$\Delta H^0_f \text{ of } O_{2(g)} = 0$$

ΔH_f^0 of $S_{(rhombic)} = 0$ etc.

$$\Delta H_{reaction}^0 = \Sigma \Delta H_{f(products)}^0 - \Sigma \Delta H_{(reactants)}^0$$

Enthalpy of combustion (ΔH_c)

It is the enthalpy change accompanying the complete combustion of one mole of a substance in excess of oxygen or air.

Combustion reactions are accompanied by evolution of heat. $\therefore \Delta H_c$ is always negative.

Enthalpy of Neutralisation (ΔH_n)

It is the enthalpy change accompanying the complete neutralisation of one gram equivalent of an acid by a base or vice versa in dilute aqueous solutions.

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(\ell)}; \Delta H_n = -57.1kJ$$
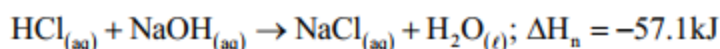
The heat of neutralisation of all strong acids and strong bases is always constant. If either the acid or base is weak, the value is less than 57.1 kJ.

$$CH_3COOH + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + H_2O; \Delta H = -56.1kJ$$

Enthalpy of solution (ΔH_{sol})

It is the enthalpy change accompanying the dissolution of one mole of a substance in large excess of solvent so that further addition of solvent does not produce any more heat change. ΔH_{sol} of hydrated salts like $CuSO_4.5H_2O$ or salts which do not form hydrates like KCl is generally positive. ΔH_{sol} of anhydrous salts which form hydrates like $CuSO_4$ is negative.

$$KCl_{(s)} + aq \rightarrow KCl_{(aq)} ; \Delta H = +18.6kJ$$

$$CuSO_{4(s)} + aq \rightarrow CuSO_{4(aq)}; \Delta H = -66.5 \text{ kJ}$$
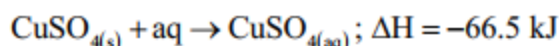
Enthalpy of hydration (ΔH_{hyd})

It is the enthalpy change accompanying the hydration of one mole of an anhydrous salt by combining with specific number of moles of water.

$$CuSO_{4(s)} + 5H_2O_{(\ell)} \rightarrow CuSO_4.5H_2O_{(s)} ; \Delta H = -78.2 \text{ kJ}$$
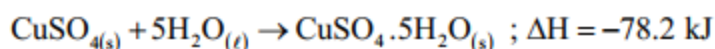
Hess's law of constant heat summation

It states that the total enthalpy change in a chemical reaction is the same whether the reaction takes place in one step or several steps.

Bond Enthalpy (Bond energy)

The energy required to break a particular bond in a gaseous molecule is called bond dissociation energy. Bond enthalpy may be defined as the average amount of energy required to break one mole bonds of that type in gaseous molecules. The standard enthalpies of reactions can be calculated using bond enthalpy values.

$$\Delta H_{reaction}^0 = \Sigma \text{ Bond enthalpies}_{(reactants)} - \Sigma \text{ Bond enthalpies}_{(products)}$$

Spontaneous process

It is an irreversible process which has a natural tendency to occur.

Examples are 1) Dissolution of sugar in water   2) Melting of ice at room temperature etc.

A negative value of ΔH may be the criterion of spontaneity.

Entropy

The disorder or degree of randomness in a system is called entropy, denoted by S.

$$\Delta S = \frac{q_{rev.}}{T}$$

Entropy of fusion

It is the entropy change taking place when one mole of the substance changes from solid state to liquid state at its melting point.

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

Entropy of vapourisation $\Delta S_v = \dfrac{\Delta H_v}{T_v}$

For isolated systems, the process will be spontaneous only if ΔS_{system} is positive.

Second Law of Thermodynamics

The entropy of the universe always increases in the course of every spontaneous change.

The entropy criterion can be summed up as follows:

1) $\Delta S_{total} > 0$; process is spontaneous

2) $\Delta S_{total} = 0$; equilibrium state

3) $\Delta S_{total} < 0$; process is non-spontaneous.

Third Law of Thermodynamics

At absolute zero, the entropy of a perfectly crystalline substance is zero.

Gibb's energy (G)

It is the amount of energy available from a system at a given set of conditions that can be put into useful work.

$$G = H - TS \quad \text{or} \quad \Delta G_{T,P} = \Delta H - T\Delta S$$

1) If ΔG is negative, the process is spontaneous.

2) If ΔG is positive, the process is non spontaneous

3) If $\Delta G = 0$, the process will be in equilibrium state.

Useful equations

1) $\Delta G^0 = -2.303 RT \log K$

2) $\Delta G^0 = -nFE^0_{cell}$

3) $E^0_{cell} = \dfrac{.0591}{n} \log K$

PART-I (JEE MAIN)

SECTION-I- Straight objective type questions

1. Assertion: Both mass and volume are extensive properties.

    Reason: The ratio of mass and volume is an extensive property.

    1) Both assertion and reason are true and the reason is the correct explanation of the assertion.

    2) Both assertion and reason are true but reason is not the correct explanation of the assertion.

    3) Assertion is true but reason is false.

    4) Assertion is false but reason is true.

2. Heat exchanged in a process at constant pressure is called as

    1) Internal energy of the process

    2) Enthalpy of the process

    3) Entropy of the process

    4) Free energy of the process

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

    1) 0.9 kJ   2) 900 kJ   3) -0.9 kJ   4) -900 kJ

4. Among the following, the set of parameters that represents path function, is:

    (A) q + w   (B) q   (C) w   (D) H – TS

    1) A and D   2) B, C and D   3) B and C   4) A, B and C

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

    1) 3RT   2) – 3RT   3) – 4RT   4) 4RT

6. The enthalpies of formation of Al_2O_3 and Cr_2O_3 are -1596 kJ and -1134 kJ, respectively. ΔH for the reaction $2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$ is

    1) -2730 kJ   2) -462 kJ   3) -1365 kJ   4) $+2730$ kJ

7. The standard heat of formation $(\Delta_f H^0_{298})$ of ethane if the heat of combustion of ethane, hydrogen and graphite are -1560, -393.5 and -286 kJ/mol, respectively, is

   1) -192.5 kJ mol^{-1}
   2) 192.5 kJ mol^{-1}
   3) 129.2 kJ mol^{-1}
   4) -129.2 kJ mol^{-1}

8. The lattice enthalpy and hydration enthalpy of NaCl are 788 and -784 kJ mol^{-1}, respectively. Enthalpy of solution of NaCl will be

   1) 4 kJ mol^{-1}
   2) -784 kJ mol^{-1}
   3) 1572 kJ mol^{-1}
   4) -1572 kJ mol^{-1}

9. The reaction, $MgO(s) + C(s) \longrightarrow Mg(s) + CO(g)$ for which $\Delta_r H^0 = 491.1$ kJ mol^{-1} and $\Delta_r S^0 = 198.0$ JK^{-1}mol^{-1} is not feasible at 298 K. The temperature above which reaction will be feasible is:

   1) 1890.0 K
   2) 2480.3 K
   3) 2040.5 K
   4) 2380.5 K

10. The process with negative entropy change is:

    1) Dissolution of iodine in water

    2) Synthesis of ammonia from N_2 and H_2.

    3) Dissociation of $CaSO_4(s)$ to $CaO(s)$ and $SO_3(g)$.

    4) Sublimation of dry ice

SECTION-II - Numerical Type Questions

11. A system absorbs 600 J of heat and does work equivalent to 300 J on its surroundings. The magnitude of internal energy change of the system is .... J

12. Consider the following thermochemical equations

    $$C + O_2 \rightarrow CO_2; \Delta H = -X$$

    $$CO + \frac{1}{2}O_2 \rightarrow CO_2; \Delta H = -Y$$

    If $\Delta_f H$ for CO is aX + bY, find the value of |a + b|

13. The enthalpy of combustion of methane at 25°C is -890 kJ mol^{-1}. The heat liberated when 3.2 g of methane is burnt in air at this temperature is .... kJ

PART-II (JEE ADVANCED)

Section-III - Only one option correct type

14. Work done in the following process ABCD on a monoatomic gas is
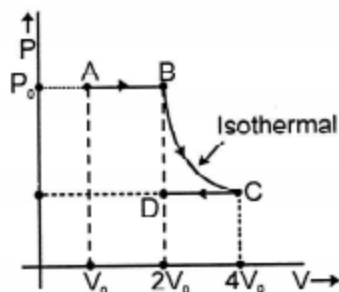
A) $w = -2P_0V_0 \ln 2$

B) $w = +2P_0V_0 \ln 2$

C) $w = -P_0V_0(1 + \ln 2)$

D) $w = -P_0V_0 \ln 2$

15. An ideal gas undergoes isothermal compression from $5\,m^3$ to $1m^3$ against a constant external pressure of $4Nm^{-2}$. If heat released in this process is used to increase the temperature of 1 mole of aluminium, the temperature of aluminium will increase by: (molar heat capacity of aluminium is $24\,J\,mol^{-1}K^{-1}$)

A) $\dfrac{3}{2}K$

B) $\dfrac{2}{3}K$

C) 1 K

D) 2 K

16. Choose the correct statement from the following

A) Adiabatic expansion of an ideal gas always has $q = 0$

B) Work done in the irreversible free expansion of an ideal gas is not equal to zero

C) Isothermal free expansion of an ideal gas may not be adiabatic

D) Adiabatic expansion of an ideal gas always involves a decrease in temperature

Passage-I (17-18)

For a system of ideal gas, an illustration of three different paths, A, (B + C) and (D + E) from an initial state (P_1, V_1, T_1) to a final state (P_2, V_2, T_1) is shown in the given figure.
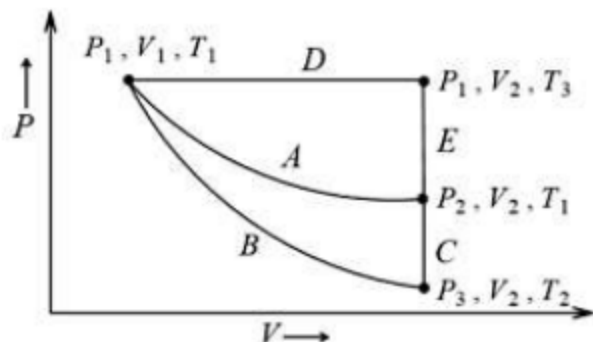
Path (A) represents a reversible isothermal expansion. Path (B + C) represents a reversible adiabatic expansion (B) followed by a reversible heating of the gas at constant volume (C). Path (D + E) represents a reversible expansion at constant pressure (D) followed by a reversible cooling at constant volume (E).

17. What is q_{system} for path (A)?

A) zero

B) $-nR \ln \dfrac{V_2}{V_1}$

C) $-nRT_1 \ln \dfrac{V_2}{V_1}$

D) $nRT_1 \ln \dfrac{V_2}{V_1}$
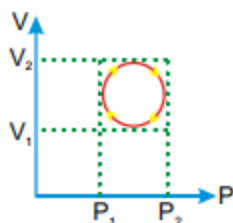
18. What is ΔS_{system} for path (D + E)?

A) zero

B) $\displaystyle\int_{T_1}^{T_2} \dfrac{C_V(T)}{T}\, dT$

C) $-nR \ln \dfrac{V_2}{V_1}$

D) $nR \ln \dfrac{V_2}{V_1}$

Section IV - One or more option correct type

19. The P-V diagram for a cyclic process is a circle as shown below. The magnitude of the work done during the process is equal to :

A) $\pi\left(\dfrac{P_2 - P_1}{2}\right)^2$

B) $\pi\left(\dfrac{V_2 - V_1}{2}\right)^2$

C) $\dfrac{\pi}{4}(P_2 - P_1)(V_2 - V_1)$

D) $\dfrac{\pi}{2}(P_2 - P_1)(V_2 - V_1)$

20. A 250 W electric heater raised the temperature of a calorimeter by 4.22°C in 55 s. When the oxidation of a methanol sample was carried out in the same calorimeter, the temperature rose from 22.49°C to 26.77°C. Then,

A) The amount of heat supplied by the electric heater is 13.75 kJ

B) The amount of heat supplied by the electric heater is 4.6 kJ

C) The enthalpy change for the oxidation is 1.39 kJ

D) The enthalpy change for the oxidation is 13.9 kJ

21. Choose the correct statement(s) from the following

    A) $\Delta G^0 < 0$ for the equilibrium $H_2O_{(\ell)} \rightleftharpoons H_2O_{(g)}$ at 1 atm and 298 K

    B) ΔU does not descriminate between reversible and irreversible processes

    C) $\Delta S_{total} \neq 0$ for irreversible process

    D) Enthalpy is the contributory factor for spontaneity in the case of diffusion of two gases into each other

22. For which of the following reactions, $\Delta_r H^0$ is not equal to $\Delta_f H^0$ for the product?

    A) $Xe_{(g)} + 2F_{2(g)} \longrightarrow XeF_{4(g)}$

    B) $2C_{(graphite,s)} + O_{2(g)} \longrightarrow 2CO_{(g)}$

    C) $2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)}$

    D) $S_{(monoclinic, s)} + \frac{3}{2}O_{2(g)} \longrightarrow SO_{3(g)}$

23. Consider the following thermochemical equations

    $2Fe_2O_{3(s)} \rightarrow 4Fe_{(s)} + 3O_{2(g)}; \Delta_r G_1^0 = +1487 \ kJ \ mol^{-1}$,

    $6CO_{(g)} + 3O_{2(g)} \rightarrow 6CO_{2(g)}; \Delta_r G_2^0 = -1543.2 \ kJmol^{-1}$

    The correct statement(s) is/are:

    A) $\Delta_r G^0$ for reduction of iron oxide to metallic iron by CO is +56.2 kJ mol⁻¹

    B) Fe_2O_3 can be reduced by CO spontaneously

    C) Fe_2O_3 cannot be reduced by CO spontaneously

    D) $\Delta_r G^0$ for reduction of iron oxide to metallic iron by CO is –28.1 kJ mol⁻¹

Section V - Numerical type questions

24. The heat liberated on complete combustion of 7.8 g of benzene is 327 kJ. This heat has been measured at constant volume and at 27°C. The magnitude of heat of combustion of 7.8 g of benzene at constant pressure will be .... kJ (Use R = 8.314 JK⁻¹ mol⁻¹)

25. Standard enthalpy change of neutralisation of a strong acid and a strong base is –57.1 kJ mol⁻¹. The heat liberated when 200 mL, 0.6 M CH_3COOH reacts with 400 mL, 0.8 M NaOH will be........ kJ (Dissociation energy of CH_3COOH = 17.1 kJ mol⁻¹)

26. What is the entropy change (in JK⁻¹ mol⁻¹) when one mole of ice is converted into water at 0°C? (The enthalpy change for the conversion of ice to water is 6.0 kJ mol⁻¹ at 0°C)

27. The reaction $CH_{4(g)} + Cl_{2(g)} \longrightarrow CH_3Cl_{(g)} + HCl_{(g)}$ has $\Delta H = -25$ kcal. From the following data, what is the bond energy of Cl–Cl bond (in kcal mol⁻¹)? (Given, $x : y = 9 : 5$)

Bond	C-Cl	H-Cl	C-H	Cl-Cl
Bond energy (in kcal mol⁻¹)	84	103	x	y

28. Calculate the magnitude of free energy change (in kJ) at 27°C for the reaction, $H_2 + Cl_2 \longrightarrow 2HCl$. (Use : Bond enthalpies of H_2, Cl_2 and HCl are 435, 240 and 430 kJ mol⁻¹ respectively; Entropies of H_2, Cl_2 and HCl are 131, 223 and 187 JK⁻¹ mol⁻¹ respectively)

Section-VI - Matrix match type

29. Match the following

    Column-I (Process for ideal gas)

    I) Reversible isothermal expansion

    II) Reversible adiabatic compression

    III) Adiabatic free expnansion

    IV) Irreversible isothermal compression

    Column-II (Entropy change)

    P) $\Delta S_{surrounding} = 0$

    Q) $\Delta S_{surrounding} < 0$

    R) $\Delta S_{surrounding} > 0$

    S) $\Delta S_{system} = 0$

    A) I → Q; II → PS; III → P; IV → R

    B) I → R; II → S; III → R; IV → Q

    C) I → Q; II → S; III → P; IV → R

    D) I → R; II → PS; III → R; IV → Q