NEET CHEMISTRY PRACITCE PAPER

Time : 60 Mins **12 THERMODYNAMICS 1** **Marks : 200**

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1. For a reaction to be spontaneous at any temperature, the conditions are
   a) $\triangle H = +ve, \triangle S = +ve$ b) $\triangle H = -ve, \triangle S = -ve$ c) $\triangle H = +ve, \triangle S = -ve$
   d) $\triangle H = -ve, \triangle S = +ve$

   Solution : -
   We know,
   $\triangle G = \triangle H - T\triangle S$
   For a reaction to be spontaneous at any temperature, ΔG should be negative and ΔG is always negative if ΔH=−ve and ΔS=+ve

2. **Assertion:** For the change, $H_2O_{(l)} \longrightarrow H_2O_{(s)}$, $\triangle H = \triangle U$.
   Reason: No enthalpy change is involved in this process.
   a) If both assertion and reason are true and reason is the correct explanation of assertion.
   b) If both assertion and reason are true but reason is not the correct explanation of assertion.
   c) If assertion is true but reason is false. d) If both assertion and reason are false

   Solution : -
   For the change, $H_2O_{(l)} \longrightarrow H_2O_{(s)}$ there is negligible change in volume.
   $\therefore \triangle PV = \triangle n_gRT=0$
   Now, substituting the above value in eqn
   $\triangle H = \triangle U + \triangle n_gRT$
   we get, $\triangle H = \triangle U$.

3. Which of the following statements is not correct?
   a) For a spontaneous process, $\triangle G$ must be negative.
   b) Enthalpy, entropy, free energy etc. are state variables.
   c) A spontaneous process is reversible in nature.
   d) Total of all possible kinds of energy of a system is called its internal energy.

   Solution : -
   For a spontaneous process, $\Delta G<0$
   The variables which depend only on the initial and final states of the system are state variables.
   Therefore, enthalpy, entropy and free energy are state variables.
   A spontaneous process is not reversible in nature as for opposite reaction to occur, a force has to be applied.
   The internal energy is the total of all possible kinds of energy in the system.

4. The enthalpy of formation of ammonia when calculated from the following bond energy data is (B.E. of N - H, H - H, N≡N is 389 kJ mort, 435 kJ mol^{-1}, 945.36 kJ mol^{-1} respectively)
   a) 41.82 kJ mol^{-1} b) + 83.64 kJ mol^{-1} c) - 945.36 kJ mol^{-1} d) - 833 kJ mol^{-1}

   Solution : -
   $N_2+3H_2 \longrightarrow 2NH_3$
   $\triangle H=\triangle H(N\equiv N)+3\times\triangle H(H-H)-2\times3\triangle H(N-H)$
   = 945.36 + 3 x 435.0 - 6 x 389.0 = - 83.64 kJ
   Heat of formation of $NH_3 = \frac{-83.64}{2}$ =- 41.82 kJ/mol

5. The statement" The change of enthalpy of a chemical reaction is same whether the reaction takes place in one or several steps" is
   a) Le Chatelier's law b) van't Hoff's law c) first law of thermodynamics **d) Hess's law.**

Solution : -

The statement "The change of enthalpy of a chemical reaction is same whether the reaction takes place in one or several steps" is Hess's law of constant heat summation.

6. A reaction having equal energies of activation for forward and reverse reactions has:

a) $\Delta S = 0$ b) $\Delta G = 0$ **c) $\Delta H = 0$** d) $\Delta H = \Delta G = \Delta S = 0$

Solution : -

For a general reaction,
ΔH = Activation energy of forward reaction - Activation energy of backward reaction. As, both the energies of activation have same value thus, $\Delta H = 0$. ΔG is not equal to zero because if it is so the reaction must be in equilibrium which is not in this case.

7. Which of the following statements is correct for the spontaneous absorption of a gas?

a) ΔS is negative and therefore, ΔH should be highly positive
b) ΔS is negative and therefore, ΔH should be highly negative.
c) ΔS is positive and therefore, ΔH should be negative.
d) ΔS is positive and therefore, ΔH should also be highly positive.

Solution : -

For adsorption of the gas its entropy decreases that is, ΔS is negative. Now, the adsorption is spontaneous, too that means, change in Gibbs, energy ΔG should be negative. According to the relation,
$\Delta G = \Delta H - T\Delta S$
or $\Delta G + T\Delta S = \Delta H$
-ve + T(-ve) = ΔH
Thus, ΔH should be highly negative.

8. **Assertion:** The solubility of must salts in water increases with rise of temperature.

Reason: For most of the ionic compounds, $\triangle_{sol} H^o$ is positive and the dissociation process is endothermic.
a) If both assertion and reason are true and reason is the correct explanation of assertion.
b) If both assertion and reason are true but reason is not the correct explanation of assertion.
c) If assertion is true but reason is false. d) If both assertion and reason are false

Solution : -

Solubility of the most of the salt rises with increase in temperature.This is because with increase in temperature, kinetic energy of the molecules increases and the solvent molecules break apart the solute molecules that are held together by intermolecular attractions more effectively. Also for most of the ionic compounds, change in enthalpy is positive and hence the dissolution process is endothermic. For endothermic reaction, increase in temperature leads the reaction to forward reaction.

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

a) $H_{2(g)} + Br_{2(g)} \longrightarrow 2HBr_{(g)}$ b) $C_{(s)} + 2H_2O_{(g)} \longrightarrow 2H_{2(g)} + CO_{2(g)}$ c) $PCl_{5(g)} \longrightarrow PCl_{3(g)} + Cl_{2(g)}$
d) $2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)}$

Solution : -

As we know, $\Delta H = \Delta E + \Delta n_g RT$
So, the reaction for which Δn_g is zero, i.e., number of gaseous moles are same on reactant and product side then $\Delta H = \Delta E$.
Among the given reaction, only formation of HBr has $\Delta n_g = 0$

$$\underbrace{H_2(g) + Br_2(g)}_{Two gaseous moles} \longrightarrow \underbrace{2HBr(g)}_{Two gaseous moles}$$

$\Delta n_g = 2-2 = 0$
Hence, $\Delta H = \Delta E + \Delta n_g RT$
$\Delta H = \Delta E + 0 \Rightarrow \Delta H = \Delta E$

10. For a reaction,

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

$\triangle \int H^0(CaO) = -635.1kJmol^{-1}$

$\triangle \int H^0(CO_2) = -393.5kJmol^{-1}$ and

$\triangle \int H^0(CaCO_3) = -1206.9kJmol^{-1}$

Which of the following is a correct statement?

a) A large amount of heat is evolved during the decomposition of $CaCO_3$

b) Decomposition of $CaCO_3$ is an endothermic process and heat is provided for decomposition.

c) The amount of heat evolved cannot be calculated from the data provided.

d) $\triangle_r H^o = \sum \triangle_f H^o(\text{reactants}) - \sum \triangle_f H^o(\text{products})$

Solution : -

$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

$\therefore \triangle H_{decomposition} = \sum \triangle_f H^\circ_{products} - \sum \triangle_f H^\circ_{reactants} = \triangle_f H^\circ\ (CaO(s)) + \triangle_f H^\circ\ (CO_2(g)) - \triangle_f H^\circ\ (CaCO_3(s)) = -635.1 - 393.5 + 1206.9$

$\therefore \triangle H_{decomposition}$ of $CaCO_3 = 178.3kJmol^{-1}$

Therefore, $\triangle H$ is positive for decomposition of $CaCO_3$, so it is anendothermic process and heat is provided for decomposition.

11. If, ΔE is the heat of reaction for $C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ at constant volume, the ΔH (heat of reaction at constant pressure), then the correct relation is :

a) ΔH = ΔE + RT **b) ΔH = ΔE - RT** c) ΔH = ΔE - 2RT d) ΔH = ΔE + 2RT

Solution : -

As we know, $\Delta H = \Delta E + \Delta n_g RT$

Now, Δn_g = Number of gaseous moles of products - number of gaseous moles of reactions

= 2 - 3 = -1

ΔH = ΔE + (-1) RT

ΔH = ΔE - RT

12. If the heat change at constant volume for decomposition of silver oxide is 80.25 kJ, what will be the heat change at constant pressure?

a) 80.25 kJ **b) > 80.25 kJ** c) < 80.25 kJ d) 160.50 kJ

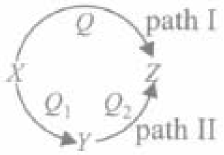
Solution : -

$Ag_2O_{(s)} \longrightarrow 2Ag_{(s)} + \frac{1}{2}O_{2(g)}$; $q_v = \triangle U = 80.25$ kJ

$q_p = q_v + \triangle n_g RT$

$\triangle n_g > 0 \left(\frac{1}{2} - 0 = \frac{1}{2}\right)$ or $q_p > q_v$ or $q_p > 80.25$ KJ

13. A reaction proceeds through two paths I and II to convert X → Z.



What is the correct relationship between Q, Q_1 and Q_2?

a) $Q = Q_1 \times Q_2$ **b) $Q = Q_1 + Q_2$** c) $Q = Q_2 - Q_1$ d) $Q = Q_1/Q_2$

Solution : -

Hess's Law of Constant Heat Summation (or just Hess's Law) states that regardless of the multiple stages or steps of a reaction, the total enthalpy change for the reaction is the sum of all changes.

So, $Q = Q_1 + Q_2$

14. The amount of heat evolved when 0.50 mole of HCl is mixed with 0.30 mole of NaOH solution is
    a) 57.1 kJ b) 28.55 kJ c) 11.42 kJ **d) 17.13 kJ**

    Solution : -
    0.50 mol of HCl == 0.50 mol of H+
    0.30 mol of NaOH == 0.30 mol of Ol-F
    $H^+ + OH^- \longrightarrow H_2O$ (Neutralisation)
    0.30 mol of HCl == 0.30 mol of H^+ or 0.30 mol of H^+ == 0.30 mol of OH^-
    Heat evolved with 1 mol H^+ = 57.1 kJ
    Heat evolved with 0.30 mol H^+ = 57.1 x 0.30 = 17.13 kJ

15. For the reactions, $N_2 + 3H_2 \longrightarrow 2NH_3$, ΔH = ?
    a) $\Delta E + 2RT$ **b) $\Delta E - 2RT$** c) $\Delta H = RT$ d) $\Delta E - RT$

    Solution : -
    For the given reaction,
    $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$
    $\Delta n_g = 2 - (1 + 3) = -2$
    Now, $\Delta H = \Delta E + \Delta n_g RT$
    $\Delta H = \Delta E - 2 RT$

16. Which of the following expressions is correct to calculate enthalpy of a reaction?
    a) $\triangle H_{reaction} = \sum B.E_{reactants} - \sum B.E_{products}$ b) $\triangle H_{reaction} = \triangle H_1 x \triangle H_2 x \triangle H_3 ...$
    c) $\triangle H_{reaction} = \sum \triangle_f H_{reactants} - \sum \triangle_f H_{products}$ d) $\triangle H_{reaction} = \sum B.E_{products} - \sum B.E_{reactants}$

    Solution : -
    Enthalpy change for a reaction expressions:
    1. $\triangle H_{reaction} = \Sigma. B. E_{reactant} - \Sigma. B. E_{product}$
    2. $\triangle H_{reaction} = \Sigma \triangle H_{products} - \Sigma \triangle H_{reactants}$
    3. $\triangle H_{reaction} = \triangle H_1 + \triangle H_2 + \triangle H_3 + ..$

17. Read the following statements regarding spontaneity of a process and mark the appropriate choice.
    (i) When enthalpy factor is absent then randomness factor decides spontaneity of a process.
    (ii) When randomness factor is absent then enthalpy factor decides spontaneity of a process.
    (iii) When both the factors take place simultaneously, the magnitude of both of factors decide spontaneity of a process.
    a) Statements (i) and (ii) are correct and (iii) is incorrect. b) Statement (iii) is correct, (i) and (ii) are incorrect.
    c) Statements (i), (ii) and (iii) are correct. d) Statements (i), (ii) and (iii) are incorrect

    Solution : -
    We know,
    $\triangle G = \triangle H - T \triangle S$
    Now,
    1. $\triangle G = \triangle H$ when $\triangle S = 0$.
    2. $\triangle G = T \triangle S$ when $\triangle H = 0$.
    3. $\triangle G = \triangle H - T \triangle S$ when $\triangle H = 0 = \triangle S$

18. The factor of ΔG values is important in metallurgy. The ΔG values for the following reactions at 800° C are given as
    $S_2(g) + 2O_2(g) \rightarrow 2SO_2(g); \Delta G = -544kJ$
    $2Zn(S) + S_2(g \rightarrow 2Z_nS_{(s)}; \Delta G = -293kJ$
    $2Zn(s) + O_2(g) \rightarrow 2ZnO(s); \Delta G = -480kJ$
    The ΔG for the reaction,
    $2ZnS(g) + 3O_2(g) \rightarrow 2ZnO(g) + 2SO_2(g)$ Will be:

a) -357 kJ **b) -731 kJ** c) -773 kJ d) - 229 kJ

Solution : -

$S_2(g) + 2O_2(g) \rightarrow 2SO_2(g)$; $\Delta G = -544kJ = \Delta H_1$
$2Zn(s) + S_2(g \rightarrow 2ZnS(s)$; $\Delta G = -293kJ = \Delta H_2$
$2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$; $\Delta G = -480kJ = \Delta H_3$
$\Delta H = \Delta H_1 + \Delta H_3 - \Delta H_2 = -731kJ$

19. For the gas phase reaction, $PCl_{5(g)}$ $^{-}PCl_{3(g)} + Cl_{2(g)}$ Which of the following conditions are correct?
    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 $\Delta S < 0$

Solution : -

$\Delta H = \Delta E + \Delta n_g RT$
$\Delta n_g = (1 + 1) - (1) = 1$
$=> \Delta H = \Delta E + RT$
Thus, m is a positive quantity i.e., $\Delta H > 0$. Now one mole of gaseous reactant dissociate into two moles of gaseous products thus, entropy increases i.e., $\Delta S > 0$.

20. For the reaction, $C_3H_{8(g)} + 5O_{2(g)} \longrightarrow 3CO_{2(g)}\, 4H_2O_{(l)}$ at constant temperature, $\Delta H - \Delta E$ is :
    a) + 3RT b) - RT c) + RT **d) - 3RT**

Solution : -

$\Delta H = \Delta E + \Delta n_g RT$
$\Delta n_g = 3 - (1 + 5) = -3$
$\Rightarrow \Delta H = \Delta E + -3RT$
$\Delta H - \Delta E = -3RT$

21. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy $\triangle U$ of the gas in joules will be:
    a) -500 J **b) -505 J** c) +505 J d) 1136.25 J

Solution : -

According to question the system is in isolated state.
For an adiabatic process, q = 0 ....(1)

$$\Delta \mathrm{U} = \mathrm{q} + \mathrm{w}$$
$$\therefore \Delta \mathrm{U} = \mathrm{w}$$
$$= -\mathrm{p}\Delta \mathrm{V}$$
$$= -2.5 \text{ atm} \times (4.5 - 2.5)\mathrm{L}$$
$$= -2.5 \times 2 \text{ L} - \text{atm}$$
$$= -5 \times 101.3 \text{ J}$$
$$= -506.5 \text{ J} \approx -505 \text{ J}$$

22. Which of the following does not represent enthalpy change during phase transformation?
    a) Standard enthalpy of fusion b) Standard enthalpy of vaporisation c) Standard enthalpy of sublimation **d) Standard enthalpy of formation**

Solution : -

There is no phase change in formation. A new product is formed during the reaction.

23. The value of ΔH and ΔS for the reaction, $C_{(graphite)} + CO_{2(g)} \longrightarrow 2CO_{(g)}$ are 170 kJ and 170 JK^{-l}, retpectively. This reaction will be spontaneous at:
    a) 710 K b) 910 K **c) 1010 K** d) 510 K

Solution : -

$\Delta G = 6H - T\Delta S$
For reaction to be spontaneous, $\Delta G < 0$
$0 > \Delta H - T\Delta S$

$0 > 170\text{kJ} - T(170\text{JK}^{-l})$
$\Rightarrow T(170\text{JK}^{-1}) > 170000 \text{ J}$
$T > 1000\text{K}$
Among the given temperatures, only 1110 K is greater than 1000 K thus, at this temperate the reaction will be spontaneous.

24. What will be the work done when one mole of a gas expands isothermally from 15 L to 50 L against a constant pressure of 1 atm at 25°C?
a) - 3542 cal b) - 843.3 cal **c) - 718 cal** d) - 60.23 cal

Solution : -
As we know that, work done in isothermal expansion is given as-

$$W = -nRT\ In\ \frac{V_2}{V_1} = -2.303\ nRT\ log\ \frac{V_2}{V_1}$$

Given:-
n = No. of moles = 1 mole
R = Gas constant = 2 cal
T = constant temperature associated with the process = 25℃ = (25 + 273) K = 298K
V_1 = Initial volume = 15 L
V_2 = Final volume = 50 L

$$\therefore W = -2.303 \times 1 \times 2 \times 298 \times log\left(\frac{50}{15}\right)$$

$\Rightarrow$ W = -1372.588 $\times$ (log 10 - log 3)
$\Rightarrow$ W = -1372.588 $\times$ 0.523 = -717.86 ≈= -718 cal
Hence the work done will be -718 cal.

25. Consider the following reaction:
(i) $\mathrm{H^+}_{\mathrm{(aq)}} + \mathrm{OH^-}_{\mathrm{(aq)}} = \mathrm{H_2O}(l)$
$\Delta\mathrm{H} = -\mathrm{X_1\ kJ\ mol^{-1}}$
(ii) $\mathrm{H_{2(g)}} + \frac{1}{2}\mathrm{O_{2(g)}} = \mathrm{H_2O}(l)$
$\Delta\mathrm{H} = -\mathrm{X_2\ kJ\ mol^{-1}}$
(iii) $\mathrm{CO_{2(g)}} + \mathrm{H_{2(g)}} = \mathrm{CO_{(g)}} + \mathrm{H_2O_2}$
$\Delta\mathrm{H} = -\mathrm{X_3\ kJ\ mol^{-1}}$
(iv) $\mathrm{C_2H_{2(g)}} + \frac{5}{2}\mathrm{O_{2(g)}} = 2\mathrm{CO_{2(g)}} + \mathrm{H_2O}(l)$
$\Delta\mathrm{H} = +4\mathrm{X_4\ kJ\ mol^{-1}}$
Enthalpy of formation of H_2On is
a) $+\mathrm{X_3\ kJ\ mol^{-1}}$ b) $-X_4 kJmol^{-1}$ c) $+X_1 kJmol^{-1}$ **d)** $-X_2 kJmol^{-1}$

Solution : -
It reaction shows the formation of H_2O, and the H, represents the enthalpy of formation of H_2O. Thi enthalpy of formation is the heat evolved or absorbed when one mole of substance is formed from its constitucnt atoms.

26. For the cell reaction
$2\mathrm{Fe^{3+}(aq)2I^-(aq)} \rightarrow 2\mathrm{Fe^{2+}(aq)I_2(aq)E^{-}_{cell}} = 0.24\ \mathrm{V}$ at 298 k The standard Gibbs energy $(\Delta_r G^-)$ of the cell reaction is:
[Given that Faraday constant F = 96500 C mol^{-1}]
a) $-23.16\ \mathrm{kJ\ mol^{-1}}$ b) $46.32\ \mathrm{kJ\ mol^{-1}}$ c) $23.16\ \mathrm{kJ\ mol^{-1}}$ **d)** $-46.32\ \mathrm{kJ\ mol^{-1}}$

Solution : -
$\Delta\mathrm{G^-} = -\mathrm{nFE^-_{cell}}$
$= -2 \times 96500 \times 0.24\ \mathrm{J\ mol^{-1}}$
$= -46320\ \mathrm{J\ mol^{-1}}$
$= -46.32\ \mathrm{kJ\ mol^{-1}}$

27. Identify the correct statement for change of Gibbs energy for a system $(\Delta G_{\text{system}})$ at constant temperature and pressure :

a) If $\Delta G_{\text{system}} = 0$, the system has attained equilibrium.

b) If $\Delta G_{\text{system}} = 0$ the system is still moving in a particular direction

c) If $\Delta G_{\text{system}} < 0$, the process is not spontaneous d) If $\Delta G_{\text{system}} > 0$, the process is not spontaneous

Solution : -

If $\Delta G_{\text{system}} = 0$ the process of system is equilibrium.

If $\Delta G < 0$ the process is spontaneous

If $\Delta G > 0$ the process does not occur in the forward direction. It may occur in negative direction.

28. For a sample of perfect gas when its pressure is changed isothermally from P_i to P_f, the entropy change is given by :

a) $\Delta S = nR \ln\left(\frac{p_f}{p_i}\right)$ **b) $\Delta S = nR \ln\left(\frac{p_i}{p_f}\right)$** c) $\Delta S = nRT \ln\left(\frac{p_f}{p_i}\right)$ d) $\Delta S = RT \ln\left(\frac{p_i}{p_f}\right)$

Solution : -

For reversible expansion of an ideal gas, change in entropy can be related to initial and final pressure and temperature as follows:

$\Delta S = nC_p \ln\frac{T_f}{T_i} + nR \ln\frac{P_i}{P_f}$

As, the reaction is isothermal. Thus, T_i, and T_f are same

$\Delta S = nC_p \ln 1 + nR \ln\frac{P_i}{P_f} = 0 + nR \ln\frac{P_i}{P_f}$

$\Delta S = nR \ln\left(\frac{P_i}{P_f}\right)$

29. A reaction is at equilibrium at 100°C and the enthalpy change for the reaction is 42.6 kJ mol^{-1}. What will be the value of $\triangle S$ in J K^{-1} mol^{-1}.

a) 120 b) 426.2 c) 373.1 **d) 114.2**

Solution : -

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

At equilibrium, $\triangle G = 0$, $\triangle H = T\triangle S$

$\triangle S = \frac{\triangle H}{T} = \frac{426000 Jmol^{-1}}{373 \quad K} = 114.2$ J k^{-1} mol^{-1}

30. Which of the following are not state functions?

(I) q + W, (II) q, (III) W, (IV) H - TS

a) I and IV b) II, III and IV c) I, II and III **d) II and III**

Solution : -

Enthalpy (H = q + W) and Gibbs energy, (G = H - TS) are state functions which depend only on the initial and final states of system. While, heat (q) and work done (W) are the path function which depends on the path followed in bringing the change between two states of the system.

31. **Assertion:** $\triangle H$ for an exothermic reaction is negative and for an endothermic reaction is positive.

Reason: Enthalpy is an extensive property.

a) If both assertion and reason are true and reason is the correct explanation of assertion.

b) If both assertion and reason are true but reason is not the correct explanation of assertion.

c) If assertion is true but reason is false. d) If both assertion and reason are false

Solution : -

In an exothermic reaction, heat is evolved and the system loses heat to the surrounding. Therefore, q_p will be negative and hence ΔH will be negative.

[$\therefore q_p = H - H_1 = \Delta H$].

Similarly is an endothermic reaction heat is absorbed, q_p is positive hence ΔH will be positive.
Enthalpy is an extensive property as it depends on the quantity of matter.

32. Bond energies of some bonds are given below:
Cl- Cl = 242.8 kJ mol^{-1}, H - Cl = 431.8 kJ mol^{-1},
O- H = 464 kJ mol^{-1},O = O = 442 kJ mol^{-1}
Using the B.E., calculate tlH for the following reactoin, $2Cl_2 + 2H_2O \longrightarrow 4HCl + O_2$
a) 906 kJ mol^{-1} **b) 172.4 kJ mol^{-1}** c) 198.8 kJ mol^{-1} d) 442 kJ mol^{-1}

Solution : -
$2Cl_2 + 2H_2O \longrightarrow 4HCl + O_2$
From Hess' Law, $\triangle$H = B.E. of (2 x Cl- Cl) + (2 x 2 x O - H) - (4x H - Cl) + (O = O)
= 2 x 242.8 + 4 x 464 - 4 x 431.8 - 442
= 172.4 kJ mol^{-1}

33. The entropy change can be calculated by using the expression, $\triangle S = \frac{q_{rev}}{T}$. When water freezes in a glass beaker, choose the correct statement amongst the following:
a) Δ S (system) decreases but Δ S (surroundings) remains the same
b) Δ S (system) increases but Δ S (surroundings) decreases
c) Δ S (system) decreases but Δ S (surroundings) increases
d) $\triangle$ S (system) decreases but $\triangle$ S (surroundings) also decreases

Solution : -
Freezing is exothermic process. The heat released increases the entropy of surrounding. Randomness of water molecules decreases as they are converting into solid.

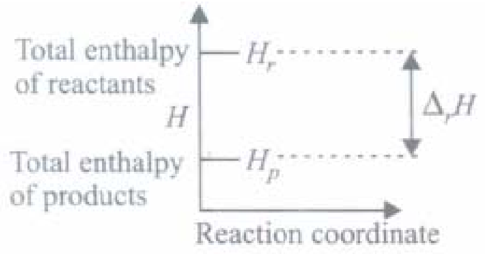
34. The enthalpy of hydrogenation of cyclohexane is - 119.5 kJ mol^{-1}. If resonance energy of benzene is -150.4 kJ mol^{-l}, its enthalpy of hydrogenation would be:
a) -208.1 kJ mol^{-1} b) -269.9 kJ mol^{-1} c) -358.5 kJ mol^{-1} d) -508.9 kJ mol^{-1}

Solution : -
Enthalpy of hydrogentaion of cyclohexene =−119.5kJ/mol
∴ calculated enthalpy of benzene =3×(−119.5)=−358.5kJ/mol
Resonance energy of benzene =−150.4kJ/mol
As we know that
Actual value of enthalpy = calculated enthalpy − resonance energy
∴ Actual enthalpy of benzene =(−358.5)−(−150.4)=−208.1kJ/mol
Hence the enthalpy of hydrogenation of benzene is −208.1kJ/mol.

35. For the gas phase reaction,
$\mathrm{PCl_5}(g) \rightleftharpoons \mathrm{PCl_3}(g) + \mathrm{Cl_2}(g)$
which of the following conditions are correct?
a) $\Delta \mathrm{H} = 0$ and $\Delta \mathrm{S} < 0$ **b)** $\Delta \mathrm{H} > 0$ and $\Delta \mathrm{S} > 0$ c) $\Delta \mathrm{H} < 0$ and $\Delta \mathrm{S} < 0$
d) $\Delta \mathrm{H} > 0$ and $\Delta \mathrm{S} < 0$

Solution : -
Given reaction,
$\mathrm{PCl_5}(g) \rightleftharpoons \mathrm{PCl_3}(g) + \mathrm{Cl_2}(g)$
The reaction given is an example of decomposition reaction and know that decomposition reactions are endothermic in nature, i.e., H > 0.
Further $\Delta \mathrm{n} = (1+1) - 1 = +1$
Thus, more number of molecules are present in products which shows more randomness i.e., $\Delta \mathrm{S} > 0$
($\Delta \mathrm{S}$ is positive)

36. The given enthalpy diagram represents which of the following reactions?



a) Enthalpy diagram for endothermic reaction **b) Enthalpy diagram for exothermic reaction**
c) Enthalpy diagram for reversible reaction d) Enthalpy diagram for non-spontaneous reaction

Solution : -
For an exothermic reaction, $\sum H_R > \sum H_p$. In the given graph, $\sum H_R > \sum H_p$. so it is an enthalpy diagram for exothermic reaction.

37. Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction?
a) Exothermic and decreasing disorder b) Endothermic and increasing disorder
c) Exothermic and increasing disorder d) Endothermic and decreasing disorder

Solution : -
For a reaction to become spontaneous, ΔG must be negative. For case (a) exothermic and decreasing disorder. For exothermic reaction, ΔH = -ve and for decreasing disorder,
ΔS = -ve
=> ΔG = -ve - T(-ve)
Thus, ΔG is not negative for all temperature range. For case (b) endothermic and increasing disorder. For endothermic reaction, ΔH = +ve and increasing disorder,
ΔS = +ve
Thus, ΔG is not negative for all temperature range. For case (c) exothermic and increasing disorder For exothermic reaction,
ΔH = -ve
and increasing disorder,
ΔS = +ve
ΔG = -ve -T(+ve)
Thus, ΔG is negative for all temperature range For case (d) endothermic and decreasing disorder For endothermic reaction,
ΔH = +ve
and decreasing disorder,
Δ5 = -ve
ΔG = +ve - T (-ve)
Thus, ΔG is positive for all temperature range.

38. For a given reaction, $\Delta \mathrm{H} = 35.5\ \mathrm{kJ\ mol}^{-1}$ and $\Delta \mathrm{S} = 83.6 \mathrm{JK}^{-\ 1}\ \mathrm{mol}^{-1}$. The reaction is spontaneous at : (Assume that $\Delta \mathrm{H}$ and $\Delta \mathrm{S}$ do not vary with temperature:
a) T > 425 K b) All temperatures c) T > 298 K d) T < 425 K

Solution : -
Given $\Delta \mathrm{H} 35.5\ \mathrm{kJ\ mol}^{-1}$
$\Delta \mathrm{S} = 83.6 \mathrm{JK}^{-1}\ \mathrm{mol}^{-1}$
$Then\ \Delta \mathrm{G} = \Delta \mathrm{H} - \mathrm{T} \Delta \mathrm{S}$
For a reaction to be spontaneous
$= -\ \mathrm{ve}$ i.e., $\Delta \mathrm{H} < \mathrm{T} \Delta \mathrm{S}$
$\therefore \mathrm{T} > \frac{\Delta \mathrm{H}}{\Delta \mathrm{S}} = \frac{35.5 \times 10^3\ \mathrm{J\ mol}^{-1}}{83.6 \mathrm{JK}^{-1}}$
Hence, the given reaction will be spontaneous at T > 425K

39. For the reaction,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3, \quad \Delta H = ?$$

a) $\Delta E + 2RT$ **b)** $\Delta E - 2RT$ c) $\Delta H = RT$ d) $\Delta E - RT$

Solution : -

According to enthalpy equation

$$\underset{\text{Enthalpy change}}{\Delta H} = \underset{\text{Internal energy}}{\Delta E} + \Delta n_g RT$$

$$\Delta n = 2 - (1+3)$$

$$[\Delta n = n_P - n_R]$$

Product Reactant

mole mole

= 2 - 4 = -2

$$\Delta H = \Delta E + (-2)RT$$

$$\Delta H = \Delta E - 2RT$$

40. The heat of combustion of carbon to CO_2 is - 393.5 kJ/mol. The heat released upon formation of 35.2 g of CO_2 from carbon and oxygen gas is :

a) + 315 kJ b) - 630 kJ c) - 3.15 kJ **d) - 315 kJ**

Solution : -

Formation of CO_2 from carbon and dioxygen gas can be represented as :

C (s) + O_2 (g) ⟶ CO_2 (g), ΔH_f = - 393.5 kJ/mole

Since, 1 mole CO_2 = 44 g

Heat released on formation of 44 g of CO_2 = - 393.5 kJ mole

Heat released on 35.2 g = $\frac{-393.5 kj/mole}{44g}$ x 35.2 g = - 315 kJ

41. The value for $\triangle U$ for the reversible isothermal evaporation of 90 g water at 100°C will be ($\triangle H_{evap}$ of water = 40.8 kJ mol^{-1} , R = 8.314 J K^{-l} mol^{-1})

a) 125.03 kJ **b) 4800 kJ** **c) 188.494 kJ** d) 40.8 kJ

Solution : -

$\triangle H$ for 18 g water = 40.8 kJ

For 90 g water = $\frac{40.8}{18} \times 90$=204 KJ

$\triangle n$ for 90 g water = 90/18 = 5

$\triangle n_g$ = 5 - 0 = 5

$\triangle H = \triangle U + \triangle ngRT$

$\triangle U$ = 204000 - (5 x 8.314 x 373) = 188494 J or 188.494 kJ

42. Bond dissociation enthalpies of $H_{2(g)}$ and $N_{2(g)}$ are 436.0 kJ mol^{-1} and 941.8 kJ mol^{-1}, respectively, and enthalpy of formation of $NH_{3(g)}$ is -46 kJ mol^{-1} . What are the enthalpy of atomisation of $NH_{3(g)}$ and the average bond enthalpy of N - H bond respectively (in kJ mol^{-1})?

a) 1170.9,390.3 b) 117,300 c) 300,200 d) 2000,1975

Solution : -

$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$; ΔH = -2X46 kJ mol^{-1}

$$\triangle H = \sum(BE)_{reactants} - \sum(BE)_{products}$$

= (941.8 + 3 × 436) - (6x) = -2 × 46

(Here x = BE of N - H bonds)

x = 390.3 kJ mol^{-1}

$NH_3 \rightarrow N + 3(H)$

Heat of atomisation = 3 × 390.3 = 1170.9 kJ mol^{-1}

43. Which of the following statements is correct?

a) The presence of reacting species in a covered beaker is an example of open system.

b)

There is an exchange of energy as well as matter between the system and the surroundings in a closed system.

c) The presence of reactants in a closed vessel made up of copper is an example of a closed system.

d)

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

Solution : -

In a closed system (e.g., the presence of reactants in a closed vessel made of conducting material i.e.copper) there is no exchange of matter, but exchange of energy is possible between system and the surroundings.

44. **Assertion:** There is no change in internal energy in a cyclic process.

Reason: Internal energy is a state function.

a) If both assertion and reason are true and reason is the correct explanation of assertion.

b) If both assertion and reason are true but reason is not the correct explanation of assertion.

c) If assertion is true but reason is false. d) If both assertion and reason are false

Solution : -

A function that depends only on the initial and final states of the system and is independent of the path are known as state functions.

Therefore, internal energy is a state function.

A cyclic process has the same initial and final states. Therefore, internal energy change is zero for a cyclic process.

45. What is the enthalpy change for ,

$2\mathrm{H_2O_2(l)} \rightarrow 2\mathrm{H_2O(l)} + \mathrm{O_2(\,g)}$ if heat of formation of $\mathrm{H_2O_2(l)}$

$\text{and } \mathrm{H_2O(l)} \text{ are } -188 \text{ and } -286\ \mathrm{kJ/mol} \text{ respectively?}$

a) $-196\ \mathrm{kJ/mol}$ b) $+948\ \mathrm{kJ/mol}$ c) $+196\ \mathrm{kJ/mol}$ d) $-948\ \mathrm{kJ/mol}$

Solution : -

$$\text{Reaction: } 2\mathrm{H_2O_2}(l) \rightarrow 2\mathrm{H_2O_2}(l) + \mathrm{O_2(\,g)}$$

$$\Delta\mathrm{H} = ?$$

$$\Delta\mathrm{H} = \left[2 \times \Delta\mathrm{H_f} \text{ of } \mathrm{H_2O}_{(l)} + (\Delta\mathrm{H_f} \text{ of } \mathrm{O}\ _2) - \left(2 \times \Delta\mathrm{H_f} \text{ of } \mathrm{H_2O}_{2(I)}\right)\right.$$

$$= [(2 \times -286) + (0) - (2 \times -188)]$$

$$= [-572 + 376] = -196\ \mathrm{kJ/mole}$$

46. Bond energies of H - H and Cl-Cl are 430 kJ mol^{-1} and 242 kJ mol^{-1} respectively. $\triangle H_f$ for HCl is 91 kJ mol^{-1}. What will be the bond energy of H - Cl?

a) 672 kJ b) 182 kJ **c) 245 kJ** d) 88 kJ

Solution : -

$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$

$\triangle H_f$(HCl)=91 kJ mol, H-H = 430 kJ mol^{-1}, Cl-Cl = 242 kJ mol^{-1}

91 = $\frac{1}{2} \times 430 + \frac{1}{2} \times 242$-B.E.(H-Cl)

91 = 336 - B.E. (H - Cl)

B.E. (H - Cl) = 336 - 91 = 245 kJ

47. **Assertion:** Third law of thermodynamics is confined to pure crystalline solids.

Reason: Theoretical arguments and practical evidences have shown that entropy of solutions and super cooled liquids is not zero at 0 K.

a) If both assertion and reason are true and reason is the correct explanation of assertion.

b) If both assertion and reason are true but reason is not the correct explanation of assertion.

c) If assertion is true but reason is false. d) If both assertion and reason are false.

Solution : -

According to the third law of thermodynamics, "The entropy of a perfectly crystalline substance at zero K or absolute zero is taken to be zero".

So according to the statement , both assertion and reason are correct and the reason is the correct explanation of assertion.

48. The equilibrium constant for a reaction is 10. What will be the value of $\triangle G^{\theta}$?

R = 8.314 JK^{-1} $mol^{-1}T$ = 300K.

a) -5.744 kJ b) -574 kJ c) + 11.48 kJ d) + 5.74 kJ

Solution : -

From the expression,

$\triangle G^{\theta}$ = -2.303RTlog K_{eq}

$\triangle$ G^{θ} for the reaction,

=(2.303)(8.314$JK^{-1}mol^{-1}$)(300K)$\log_{10}$

=-5744.14 J mol^{-1}

=-5.744 kJ mol^{-1}

49. Standard.entropies of $\mathrm{X2, Y2 \text{ and } XY3}$ are 60,40 and $50 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$ respectively. For the reaction $\frac{1}{2} X_2+\frac{3}{2} Y_2 \rightleftharpoons X Y_3, \Delta H=-30 \mathrm{~kJ}$ to be at equilibriurn, at temperature should be:

a) 750 K b) 1000 K c) 1250 K d) 500 K

Solution : -

Given for the reaction $\frac{1}{2} \mathrm{X}_2+\frac{3}{2} \mathrm{Y}_2 \rightleftharpoons \mathrm{XY}_3$

$\Delta \mathrm{S}=50-(30+60)=-40 \mathrm{~J}$

$\text{ For equilibrium } \Delta \mathrm{G}=0=\Delta \mathrm{H}-\mathrm{T} \Delta \mathrm{S}$

$\mathrm{T}=\frac{\Delta \mathrm{H}}{\Delta \mathrm{S}}=\frac{-3000}{-40}=750 \mathrm{~K}$

50. Consider the following reaction occurring in an automobile

$2 \mathrm{C}_8 \mathrm{H}_{18}(\mathrm{~g})+25 \mathrm{O}_2(\mathrm{~g}) \rightarrow 16 \mathrm{CO}_2(\mathrm{~g})+18 \mathrm{H}_2 \mathrm{O}(\mathrm{g})$ The sign of $\Delta \mathrm{H}, \Delta \mathrm{S} \text{ and } \Delta \mathrm{G}$ would be

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

Solution : -

The given reaction is combustion reaction, so it takes place by evolution of heat and hence, the sign of H = negative and there is a increase in the number of moles of gaseous products, so entropy also increases and hence, $\Delta S=\text{ positive. Thus, } \Delta \mathrm{G}=\Delta H-T \Delta S=-\text{ ve }-T(+\text{ ve })$

= - ve at any temperature