61.(BD) Reaction spontaneous at higher temperatures and non-spontaneous at lower temperatures, $\Delta_r H > 0$ and $\Delta_r S > 0$.

62.(ABCD) $\Delta G^\circ = -RT \ln K_{eq} = \Delta H^\circ - T\Delta S^\circ$

$$\ln K_{eq} = \frac{-\Delta H^\circ}{R} \cdot \frac{1}{T} + \frac{\Delta S^\circ}{R}$$

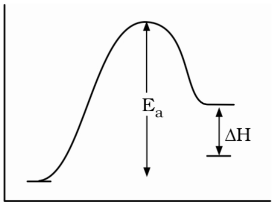
$$\text{slope} = \frac{-\Delta H^\circ}{R}, \text{y intercept} = \frac{\Delta S^\circ}{R}$$

63.(BCD) $C(\text{Graphite}) \longrightarrow C(\text{Diamond}) \qquad \Delta H = +\text{ve}$

i.e. $C(\text{Graphite})$ is thermodynamically more stable.

64.(AB) Internal energy and molar enthalpy do not depend on path. So both are state function

65.(C)



$\Delta H =$ heat of reaction (endothermic)

$E_a =$ energy of activation

Thus, $E_a > \Delta H$

66. **[A : 1, 2] ; [B : 1, 2] ; [C : 3] ; [D : 1, 2]**

(A) $CO_2(g) + C(s) \longrightarrow 2CO(g) \qquad \Delta_r H^o = 2(-220) - (-394)$ and $\Delta_r S^o > 0$

$\Rightarrow \quad \Delta_r G^o < 0$ and $\Delta_r H^o - \Delta_r U^o = \Delta n_g RT = (2-1)RT > 0$

(B) $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g) \qquad \Delta_r S > 0$ and $\Delta_r H - \Delta_r U = \Delta n_g RT = (2-1)RT > 0$

(C) $CO(g) + Cl_2(g) \longrightarrow COCl_2(g) \qquad \Delta_r S < 0$ and $\Delta_r H - \Delta_r U = (2-1)RT < 0$

(D) $Cl(g) \longrightarrow 2Cl(g) \qquad \Delta_r S > 0$ and $\Delta_r H - \Delta_r U = (2-1)RT > 0$

67. **[A : 1, 3] ; [B : 2] ; [C : 1, 3] ; [D : 2, 4]**

$\Rightarrow$ In standard state heat of formation (ΔH_f) and free energy change of formation (ΔG_f) will be zero.

68.(D) $PCl_5(g) \rightleftharpoons PCl_3(g) - Cl_2(g) \Rightarrow \Delta G = 0$

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

Since gaseous moles are increasing $\Delta S > 0$

Thus $\Delta H = T\Delta S \Rightarrow \Delta H > 0$

69.(B) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -95 \times 1000 - 500 \times (-190) = -95000 + 95000 = 0$

Upto $T = 500\,K$ the synthesis of ammonia is spontaneous. After 500 K synthesis becomes non-spontaneous, so ammonia will dissociate spontaneously.

70.(C) Internal energy of a gas depends upon its pressure and temperature. Thus, if a gas expands at constant temperature and pressure, then its internal energy remains same.

71.(D) $\Delta H = -\text{ve}$ (combustion reaction)

$\Delta S = +\text{ve}$ (spontaneous at all temperature)

$\Delta G = -\text{ve}$ (because reaction is spontaneous)

72.(A) For spontaneous process, system and surrounding entropy should be positive

$\Rightarrow \quad \Delta S_{\text{sys.}} + \Delta S_{\text{surr.}} > 0$

73.(A) $A(\ell) \rightleftharpoons A(g)$ at boiling point

$\Delta H = -100 - (-130) = 30 \text{ kJ / mol}$; $\Delta S = 200 - 100 = 100 \text{ kJ / mol}$

For equilibrium $\Delta G = 0 \quad \Rightarrow \quad T_b = \dfrac{\Delta H}{\Delta S} = 300\,\text{K}$

74.(A) For equilibrium $\Delta G = 0$

75.(A) $H_2O(1\,\text{bar}, 373\,\text{K}) \longrightarrow H_2O(g)(1\,\text{bar}, 373\,\text{K})$

$\Rightarrow$ equilibrium $\Rightarrow$ $\Delta G = 0$

Since liquid $\longrightarrow$ gaseous phase $\Delta S > 0$