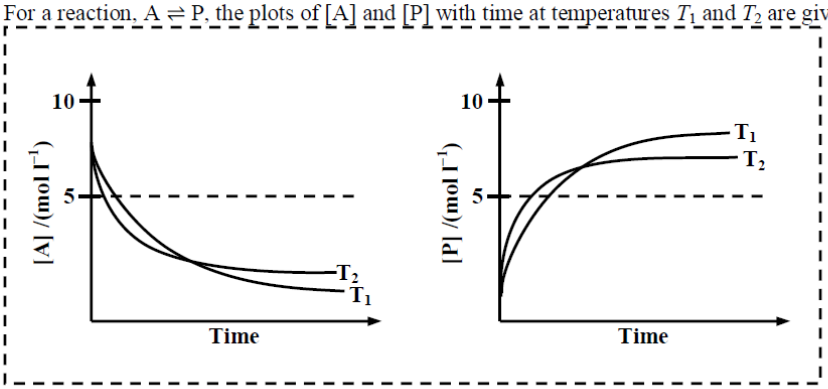
Q.6 For a reaction, A ⇌ P, the plots of [A] and [P] with time at temperatures T_1 and T_2 are given below.



If $T_2 > T_1$, the correct statement(s) is (are) (Assume ΔH^θ and ΔS^θ are independent of temperature and ratio of ln$K$ at T_1 to ln$K$ at T_2 is greater than T_2/T_1. Here H, S, G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.)

(A) $\Delta H^\theta < 0$, $\Delta S^\theta < 0$ (B) $\Delta G^\theta < 0$, $\Delta H^\theta > 0$

(C) $\Delta G^\theta < 0$, $\Delta S^\theta < 0$ (D) $\Delta G^\theta < 0$, $\Delta S^\theta > 0$

Sol. **A, C**

$A \rightleftharpoons P$

$(P)_{eq} > 5,\ (A)_{eq} < 5$

$K_{eq} = \dfrac{[P]}{[A]} > 1$

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

$\dfrac{\ln K_{T_1}}{\ln K_{T_2}} > \dfrac{T_2}{T_1} > 1$

$\Rightarrow \dfrac{K_{T_1}}{K_{T_2}} > 1$

$\Rightarrow K_{T_2} < K_{T_1}$ (exothermic)

$\Delta H^0 < 0$, since (P) at T_2 < at T_1.

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

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

$\Delta S^0 = \dfrac{\Delta H^0 - \Delta G^0}{T};\ (\Delta H^0) > (\Delta G^0)$

$\Delta S^0 < 0$

Also, $-T_1 \ln K_{T_1} < -T_2 \ln K_{T_2}$ II

$\Delta G^0_{T_1} < \Delta G^0_{T_2}$

$\Delta H^0_{T_1} - T\Delta S^0_{T_1} < \Delta H^0_{T_2} - T\Delta S^0_{T_2}$

It is possible only if $\Delta S^0 < 0$.