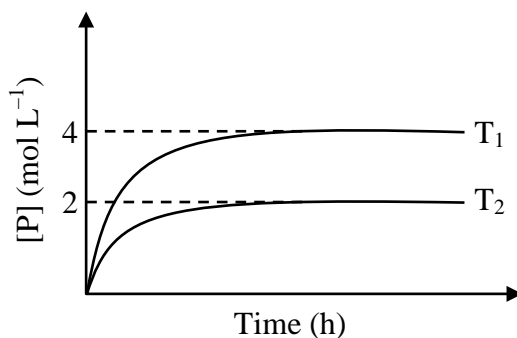


## PHYSICAL CHEMISTRY

## THERMODYNAMICS-II

1. In a one-litre flask, 6 moles of A undergoes the reaction  $A(g) \rightleftharpoons P(g)$ . The progress of product formation at two temperatures (in Kelvin),  $T_1$  and  $T_2$ , is shown in the figure: [JEE(Advanced) 2023]



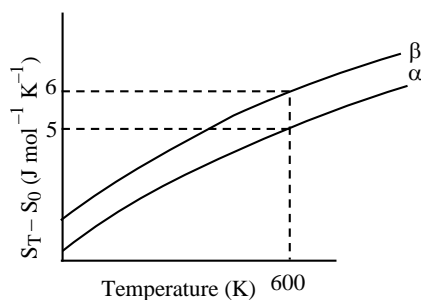
If  $T_1 = 2T_2$  and  $(\Delta G_2^\ominus - \Delta G_1^\ominus) = RT_2 \ln x$ , then the value of  $x$  is \_\_\_\_\_.

[ $\Delta G_1^\ominus$  and  $\Delta G_2^\ominus$  are standard Gibb's free energy change for the reaction at temperatures  $T_1$  and  $T_2$ , respectively.]

## "Paragraph I" for Question No. 2

The entropy versus temperature plot for phases  $\alpha$  and  $\beta$  at 1 bar pressure is given.

$S_T$  and  $S_0$  are entropies of the phases at temperatures  $T$  and 0 K, respectively.



The transition temperature for  $\alpha$  to  $\beta$  phase change is 600 K and  $C_{P,\beta} - C_{P,\alpha} = 1 \text{ J mol}^{-1} \text{ K}^{-1}$ . Assume  $(C_{P,\beta} - C_{P,\alpha})$  is independent of temperature in the range of 200 to 700 K.  $C_{P,\alpha}$  and  $C_{P,\beta}$  are heat capacities of  $\alpha$  and  $\beta$  phases, respectively. [JEE(Advanced) 2023]

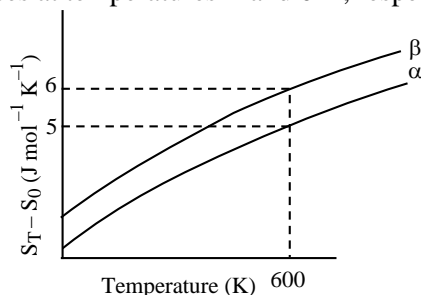
2. The value of entropy change,  $S_\beta - S_\alpha$  (in  $\text{J mol}^{-1} \text{ K}^{-1}$ ), at 300 K is \_\_\_\_\_.

[Use :  $\ln 2 = 0.69$

Given :  $S_\beta - S_\alpha = 0$  at 0 K]

"Paragraph I" for Question No. 3

The entropy versus temperature plot for phases  $\alpha$  and  $\beta$  1 bar pressure is given.  $S_T$  and  $S_0$  are entropies of the phases at temperatures  $T$  and 0 K, respectively

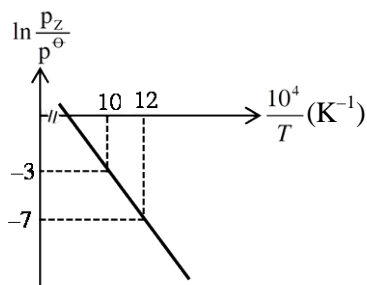


The transition temperature for  $\alpha$  to  $\beta$  phase change is 600 K and  $C_{P,\beta} - C_{P,\alpha} = 1 \text{ J mol}^{-1} \text{ K}^{-1}$ . Assume  $(C_{P,\beta} - C_{P,\alpha})$  is independent of temperature in the range of 200 to 700 K.  $C_{P,\alpha}$  and  $C_{P,\beta}$  are heat capacities of  $\alpha$  and  $\beta$  phases, respectively. [JEE(Advanced) 2023]

3. The value of enthalpy change,  $H_\beta - H_\alpha$  (in  $\text{J mol}^{-1}$ ), at 300 K is \_\_\_\_\_.

Question Stem for Question Nos. 4 and 5

For the reaction  $\text{X(s)} \rightleftharpoons \text{Y(s)} + \text{Z(g)}$ , the plot of  $\ln \frac{p_Z}{p^\ominus}$  versus  $\frac{10^4}{T}$  is given below (in solid line), where  $p_Z$  is the pressure (in bar) of the gas  $\text{Z}$  at temperature  $T$  and  $P^\ominus = 1$  bar.

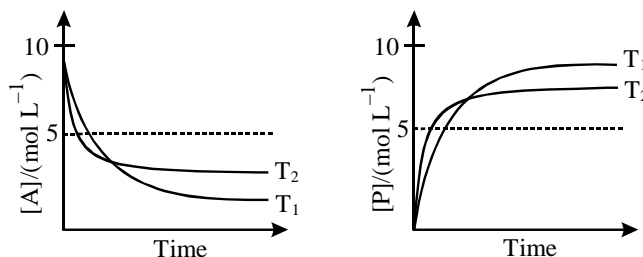


(Given,  $\frac{d(\ln K)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^\ominus}{R}$ , where the equilibrium constant,  $K = \frac{p_Z}{p^\ominus}$  and the gas constant,

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )

[JEE(Advanced) 2021]

4. The value of standard enthalpy,  $\Delta H^\ominus$  (in  $\text{kJ mol}^{-1}$ ) for the reaction is \_\_\_\_\_.  
 5. The value of  $\Delta S^\ominus$  (in  $\text{J K}^{-1} \text{ mol}^{-1}$ ) for the given reaction, at 1000 K is \_\_\_\_\_.  
 6. For a reaction,  $\text{A} \rightleftharpoons \text{P}$ , the plots of  $[\text{A}]$  and  $[\text{P}]$  with time at temperatures  $T_1$  and  $T_2$  are given below.



If  $T_2 > T_1$ , the correct statement(s) is (are)

[JEE(Advanced) 2018]

(Assume  $\Delta H^\ominus$  and  $\Delta S^\ominus$  are independent of temperature and ratio of  $\ln K$  at  $T_1$  to  $\ln K$  at  $T_2$  is greater than  $\frac{T_2}{T_1}$ . Here  $H$ ,  $S$ ,  $G$  and  $K$  are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.)

- (A)  $\Delta H^\ominus < 0, \Delta S^\ominus < 0$     (B)  $\Delta G^\ominus < 0, \Delta H^\ominus > 0$     (C)  $\Delta G^\ominus < 0, \Delta S^\ominus < 0$     (D)  $\Delta G^\ominus < 0, \Delta S^\ominus > 0$

7. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant  $K$  in terms of change in entropy is described by [JEE(Advanced) 2017]
- (A) With increase in temperature, the value of  $K$  for exothermic reaction decreases because the entropy change of the system is positive
- (B) With increase in temperature, the value of  $K$  for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases
- (C) With increase in temperature, the value of  $K$  for exothermic reaction decreases because favourable change in entropy of the surroundings decreases
- (D) With increase in temperature, the value of  $K$  for endothermic reaction increases because the entropy change of the system negative
8. Match the thermodynamic processes given under Column-I with the expressions given under Column-II. [JEE(Advanced) 2015]

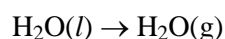
**Column-I**

- (A) Freezing of water at 273 K and 1 atm
- (B) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions
- (C) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container
- (D) Reversible heating of  $\text{H}_2(\text{g})$  at 1 atm from 300 K to 600 K followed by reversible cooling to 300 K at 1 atm

**Column-II**

- (P)  $q = 0$
- (Q)  $w = 0$
- (R)  $\Delta S_{\text{sys}} < 0$
- (S)  $\Delta U = 0$
- (T)  $\Delta G = 0$

9. For the process



at  $T = 100^\circ\text{C}$  and 1 atmosphere pressure, the correct choice is

- (A)  $\Delta S_{\text{system}} > 0$  and  $\Delta S_{\text{surroundings}} > 0$
- (B)  $\Delta S_{\text{system}} > 0$  and  $\Delta S_{\text{surroundings}} < 0$
- (C)  $\Delta S_{\text{system}} < 0$  and  $\Delta S_{\text{surroundings}} > 0$
- (D)  $\Delta S_{\text{system}} < 0$  and  $\Delta S_{\text{surroundings}} < 0$

[JEE(Advanced) 2014]

## SOLUTIONS

## 1. Ans. (8)



$$t = 0 \quad 6$$

$$t = \infty \quad 6 - x \quad x = 4 \text{ (from plot)}$$

$$\Rightarrow \text{At } T_1 \text{ K : } K_{P_1} = \frac{4}{2} = 2$$



$$t = 0 \quad 6$$

$$t = \infty \quad 6 - y \quad y = 2 \text{ (from plot)}$$

$$\Rightarrow \text{At } T_2 \text{ K : } K_{P_2} = \frac{2}{4} = \frac{1}{2}$$

$$\text{Now, } \Delta G_2^\circ = -RT_2 \ln K_{P_2} = -RT_2 \ln \frac{1}{2}$$

$$\Rightarrow \Delta G_2^\circ = RT_2 \ln 2$$

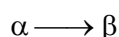
$$\Delta G_1^\circ = -RT_1 \ln K_{P_1} = -RT_1 \ln 2 = -2RT_2 \ln 2$$

$$\text{Given : } \Delta G_2^\circ - \Delta G_1^\circ = RT_2 \ln 2 + 2RT_2 \ln 2 = 3RT_2 \ln 2 = RT_2 \ln x$$

$$\Rightarrow x = 2^3 = 8$$

## 2. Ans. (0.30 to 0.32)

Sol. At 1 bar



$$S_{\alpha(600)}^\circ = S_{\alpha(300)}^\circ + C_{P(\alpha)} \ln \frac{600}{300}$$

$$S_{\beta(600)}^\circ = S_{\beta(300)}^\circ + C_{P(\beta)} \ln \frac{600}{300}$$

$$S_{\beta(600)}^\circ - S_{\alpha(600)}^\circ = S_{\beta(300)}^\circ - S_{\alpha(300)}^\circ + (C_{P(\beta)} - C_{P(\alpha)}) \ln 2$$

$$6 - 5 = S_{\beta(300)}^\circ - S_{\alpha(300)}^\circ + 1 \times \ln 2$$

$$1 = S_{\beta(300)}^\circ - S_{\alpha(300)}^\circ + 0.69$$

$$\text{So } S_{\beta(300)}^\circ - S_{\alpha(300)}^\circ = 0.31$$

3. Ans. (300.00)

Sol. As the phase transition temperature is 600 K

$$\text{So at 600 K } \Delta G^{\circ}_{\text{rxn}} = 0$$

$$\text{So } \Delta H^{\circ}_{\text{reaction (600)}} = T \Delta S^{\circ}_{\text{reaction (600)}}$$

$$\Delta H^{\circ}_{(600)} = 600 \times 1 = 600 \text{ Joule/mole}$$

$$\text{So } \Delta H_{600} - \Delta H_{300} = \Delta C_P (T_2 - T_1)$$

$$\Delta H_{600} - \Delta H_{300} = 1 \times 300$$

$$\Delta H_{300} = \Delta H_{600} - 300 = 600 - 300 = 300 \text{ Joule/mole.}$$

4. Ans. (166.28)

$$\text{Sol. } \Delta G^{\circ} = -RT \ln \left( \frac{P}{1} \right) = \Delta H^{\circ} - T \Delta S^{\circ}$$

$$\ln \left( \frac{P}{1} \right) = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

$$\text{Slope} = -\frac{\Delta H^{\circ}}{R} = 10^4 \times \left( -\frac{4}{2} \right)$$

$$\Rightarrow \Delta H^{\circ} = 2 \times 10^4 \times R$$

$$= 166.28 \text{ kJ/mole}$$

5. Ans. (141.33 or 141.34)

Sol. From the plot when,  $\frac{10^4}{T} = 10 \Rightarrow T = 1000 \text{ K}$

$$\ln \left( \frac{P_2}{1} \right) = -3$$

Substituting in equation :

$$\ln \left( \frac{P_2}{1} \right) = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

We get,

$$-3 = -\frac{2 \times 10^4 \times R}{R \times 1000} + \frac{\Delta S^{\circ}}{R}$$

$$\Rightarrow \Delta S^{\circ} = 17R$$

$$\Rightarrow \Delta S^{\circ} = 17 \times 8.314 \text{ J/K-mol}$$

$$\Rightarrow \Delta S^{\circ} = 141.34 \text{ J/K-mol}$$

6. Ans. (A, C)

Sol.  $A \rightleftharpoons P$

given  $T_2 > T_1$

$$\frac{\ln K_1}{\ln K_2} > \frac{T_2}{T_1}$$

$$\Rightarrow T_1 \ln k_1 > T_2 \ln k_2$$

$$\Rightarrow -\Delta G^\circ_1 > -\Delta G^\circ_2$$

$$\Rightarrow (-\Delta H^\circ + T_1 \Delta S^\circ) > (-\Delta H^\circ + T_2 \Delta S^\circ)$$

$$\Rightarrow T_1 \Delta S^\circ > T_2 \Delta S^\circ$$

$$\Rightarrow \Delta S^\circ < 0$$

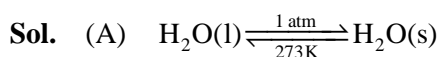
7. Ans. (B, C)

Sol.  $\Delta S_{\text{surr.}} = \frac{-q_{\text{process}}}{T_{\text{surr.}}}$

If  $\Delta H > 0$  on  $T \uparrow K_{\text{eq}} \uparrow$ ,  $\Delta S_{\text{surr.}} < 0$  (Surrounding is unfavourable)

If  $\Delta H < 0$  on  $T \uparrow K_{\text{eq}} \downarrow$ ,  $\Delta S_{\text{surr.}} > 0$  (Surrounding is favourable)

8. Ans. (A)  $\rightarrow$  R, T ; (B)  $\rightarrow$  P, Q, S ; (C)  $\rightarrow$  P, Q, S ; (D)  $\rightarrow$  P, Q, S, T



$$q < 0$$

$$w < 0 \text{ (expansion)}$$

$$\Delta S_{\text{sys}} < 0$$

$$\Delta U < 0$$

$$\Delta G = 0 \text{ (At equilibrium)}$$

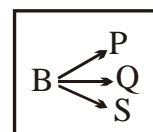
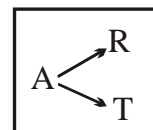
(B)  $q = 0$  (Isolated)

$$w = 0 \text{ (Isolated)}$$

$$\Delta S_{\text{sys}} > 0 \text{ (Expansion)}$$

$$\Delta U = q + w = 0$$

$$\Delta G = nRT \ln \frac{V_1}{V_2} < 0$$



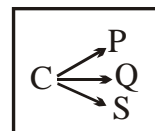
(C)  $q = 0$

$w = 0$

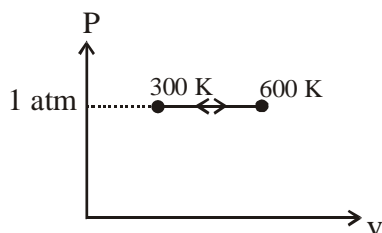
$\Delta S_{\text{sys}} > 0$  (mixing of gases)

$\Delta U = 0$

$(\Delta G)_{T,P} < 0$  (Process is feasible)



(D)



$q = 0$   
 $w = 0$  }  $q$  &  $w$  are path function but same path is re-traced

$\Delta S_{\text{sys}} = 0$   
 $\Delta U = 0$   
 $\Delta G = 0$  }  $S, U, G$  are state functiona

9. **Ans. (B)**

**Sol.** At  $100^\circ\text{C}$  &  $1 \text{ atm}$  vapourization of water is a reversible process, So

$\Delta S_{\text{Universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$

$\Rightarrow \Delta S_{\text{system}} = -\Delta S_{\text{surrounding}}$

During vapourization entropy of system increases

i.e.,  $\Delta S_{\text{system}} > 0$

i.e.,  $\Delta S_{\text{surrounding}} < 0$