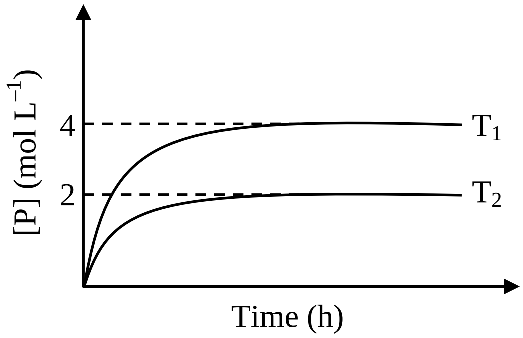
PHYSICAL CHEMISTRY

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]**



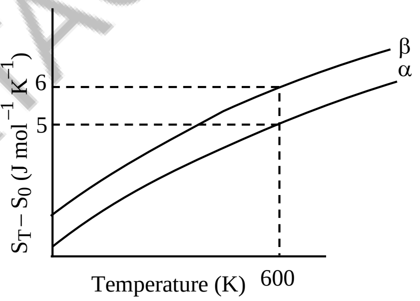
If $T_1 = 2T_2$ and $(\Delta G_2^\ominus - \Delta G_1^\ominus) = RT_2 \ln x$, then the value of x is ______.

[$\Delta G_1^\ominus$ 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 α and β 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 α to β phase change is 600 K and $C_{P,\beta} - C_{P,\alpha} = 1$ J mol^{-1} 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 α and β phases, respectively. **[JEE(Advanced) 2023]**

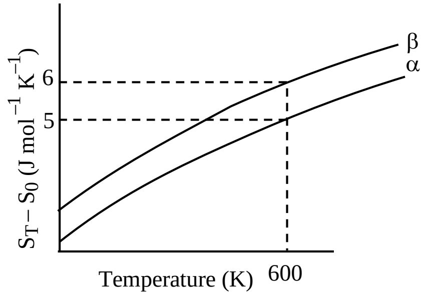
2. The value of entropy change, $S_\beta - S_\alpha$ (in J mol^{-1} K^{-1}), at 300 K is ______.

[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 α and β 1 bar pressure is given.
S_T and S_0 are entropies of the phases at temperatures T and 0 K, respectively



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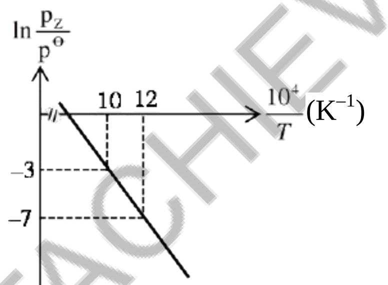
3. The value of enthalpy change, $H_\beta - H_\alpha$ (in J mol^{-1}), at 300 K is _______.

Question Stem for Question Nos. 4 and 5

For the reaction $\mathbf{X}(s) \rightleftharpoons \mathbf{Y}(s) + \mathbf{Z}(g)$, 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 **Z** at temperature T and $P^\ominus = 1$ bar.

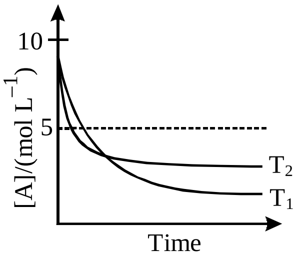


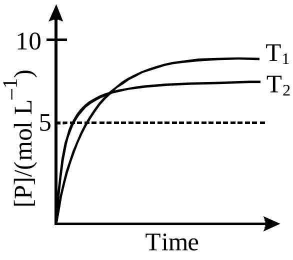
(Given, $\frac{d(\ln K)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^\ominus}{R}$, where the equilibrium constant, K = $\frac{p_z}{p^\ominus}$ and the gas constant,
R = 8.314 J K^{-1} mol^{-1}) **[JEE(Advanced) 2021]**

4. The value of standard enthalpy, $\Delta H^\ominus$ (in kJ mol^{-1}) for the reaction is________.

5. The value of $\Delta S^\ominus$ (in J K^{-1} mol^{-1}) for the given reaction, at 1000 K is________.

6. For a reaction, A $\rightleftharpoons$ 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) **[JEE(Advanced) 2018]**
(Assume ΔH^θ and ΔS^θ are independent of temperature and ratio of lnK at T_1 to lnK 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) $\Delta G^\theta < 0, \Delta S^\theta > 0$

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		**Column-II**
(A)	Freezing of water at 273 K and 1 atm	(P)	$q = 0$
(B)	Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(Q)	$w = 0$
(C)	Mixing of equal volumes of two ideal gases at constant temeprature and pressure in an isolated container	(R)	$\Delta S_{sys} < 0$
(D)	Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K followed by reversible cooling to 300 K at 1 atm	(S)	$\Delta U = 0$
		(T)	$\Delta G = 0$

9. For the process **[JEE(Advanced) 2014]**

$$H_2O(l) \rightarrow H_2O(g)$$

at T = 100ºC and 1 atmosphere pressure, the correct choice is

(A) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} > 0$

(B) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} < 0$

(C) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} > 0$

(D) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} < 0$

SOLUTIONS

1. **Ans. (8)**

Sol. At T_1 K : $A(g) \rightleftharpoons P(g)$

t = 0 6

t = ∞ 6 – x x = 4 (from plot)

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

At T_2 K : $A(g) \rightleftharpoons P(g)$

t = 0 6

t = ∞ 6 – y y = 2 (from plot)

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

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

$\Rightarrow \Delta G_2^o = RT_2\, ln\, 2$

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

Given : $\Delta G_2^o - \Delta G_1^o = RT_2\, ln\, 2 + 2RT_2\, ln\, 2 = 3RT_2\, ln\, 2 = RT_2\, ln\, x$

$\Rightarrow x = 2^3 = 8$

2. **Ans. (0.30 to 0.32)**

Sol. At 1 bar

$\alpha \longrightarrow \beta$

$S^o_{\alpha(600)} = S^o_{\alpha(300)} + C_{P(\alpha)} \ell n \frac{600}{300}$

$S^o_{\beta(600)} = S^o_{\beta(300)} + C_{P(\beta)} \ell n \frac{600}{300}$

$S^o_{\beta(600)} - S^o_{\alpha(600)} = S^o_{\beta(300)} - S^o_{\alpha(300)} + (C_{P(\beta)} - C_{P(\alpha)})\ \ell n 2$

$6 - 5 = S^o_{\beta(300)} - S^o_{\alpha(300)} + 1 \times \ell n 2$

$1 = S^o_{\beta(300)} - S^o_{\alpha(300)} + 0.69$

So $S^o_{\beta(300)} - S^o_{\alpha(300)} = 0.31$

3. **Ans. (300.00)**

Sol. As the phase transition temperature is 600 K

So at 600 K $\Delta G°_{rxn} = 0$

So $\Delta H°_{reaction\ (600)} = T\ \Delta S°_{reaction\ (600)}$

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

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

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

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

4. **Ans. (166.28)**

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

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

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

$\Rightarrow \Delta H^o = 2 \times 10^4 \times R$

$= 166.28$ kJ/mole

5. **Ans. (141.33 or 141.34)**

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

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

Substituting in equation :

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

We get,

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

$\Rightarrow \Delta S^o = 17R$

$\Rightarrow \Delta S^o = 17 \times 8.314$ J/K-mol

$\Rightarrow \Delta S^o = 141.34$ J/K-mol

6. Ans. (A, C)

Sol. $A \rightleftharpoons P$

given $T_2 > T_1$

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

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

$\Rightarrow -\Delta G^{o}_1 > -\Delta G^{o}_2$

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

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

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

7. Ans. (B, C)

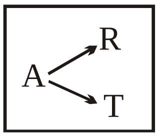
Sol. $\Delta S_{surr.} = \dfrac{-q_{process}}{T_{surr.}}$

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

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

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

Sol. (A) $H_2O(l) \underset{273K}{\overset{1\ atm}{\rightleftharpoons}} H_2O(s)$



$q < 0$

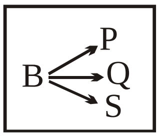
$w < 0$ (expansion)

$\Delta S_{sys} < 0$

$\Delta U < 0$

$\Delta G = 0$ (At equilibrium)

(B) $q = 0$ (Isolated)



$w = 0$ (Isolated)

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

$\Delta U = q + w = 0$

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

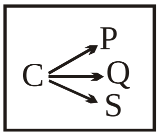
(C) $q = 0$

$w = 0$

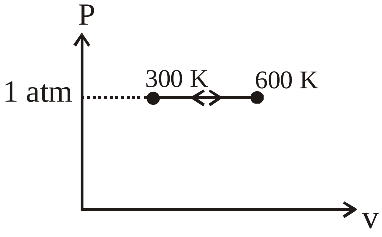
$\Delta S_{sys} > 0$ (mixing of gases)

$\Delta U = 0$

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



(D)



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

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

9. **Ans. (B)**

Sol. At 100ºC & 1 atm vapourization of water is a reversible process, So

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

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

During vapourization entropy of system increases

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

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