EXERCISE (J-MAIN)

1. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27°C is :-   **[AIEEE-2011]**

    (A) 32.3 J mol^{-1} K^{-1} (B) 42.3 J mol^{-1} K^{-1}

    (C) 38.3 J mol^{-1} K^{-1} (D) 35.8 J mol^{-1} K^{-1}

Ans. (C)

$$\text{1.} \quad \Delta S = nR\ln\frac{V_2}{V_1} = 2 \times 8.314 \times \ln\frac{100}{10}$$
$$= 38.24 \ \text{J/K}$$

2. The incorrect expression among the following is :-

    (A) $K = e^{-\Delta G°/RT}$ **[AIEEE-2012]**

    (B) $\dfrac{\Delta G_{system}}{\Delta S_{total}} = -T$

    (C) In isothermal process, $W_{reversible} = -nRT \ln \dfrac{V_f}{V_i}$

    (D) $\ln K = \dfrac{\Delta H° - T\Delta S°}{RT}$

Ans. (D)

$$\text{2.} \quad \ln K = -\left(\frac{\Delta H° - T\Delta s°}{RT}\right)$$

$$\text{(D)} \rightarrow \text{Incorrect}$$

3. The entropy (S°) of the following substances are :   **[JEE-MAINS-(online) 2014]**

CH_4 (g) 186.2 J K^{-1} mol^{-1}

O_2 (g) 205.0 J K^{-1} mol^{-1}

CO_2 (g) 213.6 J K^{-1} mol^{-1}

H_2O (l) 69.9 J K^{-1} mol^{-1}

The entropy change (ΔS°) for the reaction

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O (\ell)$ is:-

(A) –312.5 JK^{-1} mol^{-1} (B) – 37.6 JK^{-1} mol^{-1} (C) – 108.1 JK^{-1} mol^{-1} (D) – 242.8 JK^{-1} mol^{-1}

Ans. (D)

$$\Delta S = \left\{ (S_m^0)_{CO_2} + 2(S_m^0)_{H_2O} \right\} - \left\{ (S_m^0)_{CH_4} + (S_m^0)_{O_2} \times 2 \right\}$$

$$= \{213.6 + 2(69.9)\} - \{186.2 + 2 \times 205\} = -242.8 \ J/K$$

4. The molar heat capacity (C_p) of CD_2O is 10 cals at 1000 K. The change in entropy associated with cooling of 32 g of CD_2O vapour from 1000 K to 100 K at constant pressure will be

(D = deuterium, at. mass = 2u)   **[JEE-MAINS-(online) 2014]**

(A) – 23.03 cal deg^{-1} (B) 2.303 cal deg^{-1} (C) 23.03 cal deg^{-1} (C) – 2.303 cal deg^{-1}

Ans. (A)

$$\Delta S = n \, C_p \ln \frac{T_2}{T_1} = \frac{32}{32} \times 10 \times \ln \frac{100}{1000} = -23.03 \ cal/K$$

node06\B0AH-AI\Kota\JEE(Advanced)\Enthusiast\Advance Batch\Che.\Sheet\thermodynamics-02

5 $\Delta_f G°$ at 500 K for substance 'S' in liquid state and gaseous state are + 100.7 kcal mol^{-1} and + 103 kcal mol^{-1}, respectively. Vapour pressure of liquid 'S' at 500 K is approximately equal to :

(R = 2 cal K^{-1} mol^{-1}) - **[JEE-MAINS-(online) 2018]**

(1) 0.1 atm (2) 10 atm (3) 100 atm (4) 1 atm

Ans. (1)

$$\Delta_r G° = 103 - 100.7 = -2.3 \times \frac{2}{1000} \times 500 \log P$$

$$\Rightarrow \quad P_1 = 0.1 \ bar \simeq 0.1 \ atm$$

6. For which of the following processes, ΔS is negative? **[JEE-MAINS-(online) 2018]**

(1) C(diamond) $\rightarrow$ C(graphite) (2) N_2(g, 273 K) $\rightarrow$ N_2(g, 300K)

(3) H_2(g) $\rightarrow$ 2H(g) (4) N_2(g, 1 atm) $\rightarrow$ N_2(g, 5 atm)

6. Ans.(4)

(1) $\Delta S > 0$ (2) $\Delta S = nC_v \ln \dfrac{T_2}{T_1} > 0$

(3) $\Delta n_g > 0 \Rightarrow \Delta_r S > 0$

(4) $\Delta S = nR \ln \dfrac{P_1}{P_2} = nR \ln \dfrac{1}{5} = -ve$

7. At 320 K, a gas A_2 is 20% dissociated to $A(g)$. The standard free energy change at 320 K and 1 atm in J mol^{-1} is approximately : **[JEE-MAINS-(online) 2018]**

(R = 8.314 JK^{-1} mol^{-1}; ℓn 2 = 0.693; ℓn 3 = 1.098)

(1) 4281   (2) 4763   (3) 2068   (4) 1844

7. **Ans.(2)**

$$\Delta_r G^\circ = -RT \ln K_p = -RT \ln\left(\frac{4\,P_{eq}\,\alpha^2}{1-\alpha^2}\right)$$

$$= -8.314 \times 320 \ln\left(\frac{4 \times 1 \times 0.20^2}{1-0.20^2}\right) = 4765\,\frac{J}{mol}$$

$$= 8.314 \times 320 \ln 6 = 8.314 \times 320 \times 1.791 = 4765 \; \frac{J}{mol}$$

8. Two blocks of the same metal having same mass and at temperature T_1 and T_2, respectively. are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy, ΔS, for this process is : **[JEE-MAINS-(online) 2019]**

(1) $2C_P \ln\left(\dfrac{T_1 + T_2}{4T_1T_2}\right)$ (2) $2C_P \ln\left[\dfrac{(T_1+T_2)^{\frac{1}{2}}}{T_1T_2}\right]$ (3) $C_P \ln\left[\dfrac{(T_1+T_2)^2}{4T_1T_2}\right]$ (4) $2C_P \ln\left[\dfrac{T_1+T_2}{2T_1T_2}\right]$

8. **Ans.(3)**

$$nC_p(T_f - T_1) + nC_p(T_f - T_2) = 0 \Rightarrow T_f = \frac{T_1 + T_2}{2}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = C_p \ln\frac{T_f}{T_1} + C_p \ln\frac{T_f}{T_2} = C_p \ln\frac{T_f^2}{T_1 \cdot T_2} = C_p \ln\frac{\left(\frac{T_1+T_2}{2}\right)^2}{T_1 \cdot T_2} = C_p \ln\frac{(T_1+T_2)^2}{4T_1T_2}$$

9. For the chemical reaction $X \rightleftharpoons Y$, the standard reaction Gibbs energy depends on temperature T (in K) as : **[JEE-MAINS-(online) 2019]**

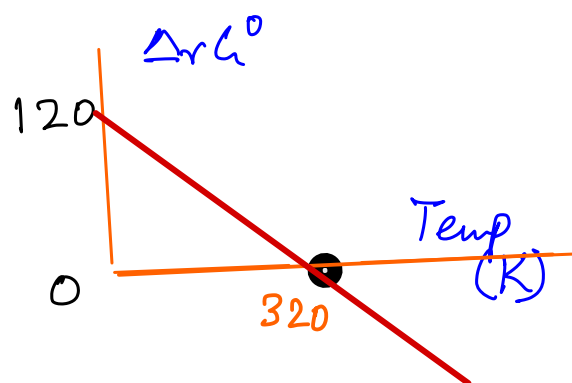$$\Delta_r G^\circ \text{ (in kJ mol}^{-1}) = 120 - \frac{3}{8}T$$

The major component of the reaction mixture at T is :

(1) X if T = 315 K   (2) X if T = 350 K   (3) Y if T = 300 K   (4) Y if T = 280 K

9. **Ans.(1)**

$$\Delta_r G^\circ > 0 \Rightarrow \overset{\varepsilon^m}{\underleftarrow{\quad}}$$

$$\Delta_r G^\circ < 0 \Rightarrow \overset{\varepsilon^m}{\underrightarrow{\quad}}$$

10. For the equilibrium, **[JEE-MAINS-(online) 2019]**
    $2H_2O \rightleftharpoons H_3O^+ + OH^-$, the value of ΔG° at 298 K is approximately :-
    (1) -80 kJ mol^{-1} (2) -100 kJ mol^{-1} (3) 100 kJ mol^{-1} (4) 80 kJ mol^{-1}
10. **Ans.(4)**

$$\Delta G^\bullet = -RT\ln K = -\frac{8.314}{1000} \times 298 \times 2.303 \log 10^{-14}$$

$$= 79.9 \text{ kJ/mol}$$

11. The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by
$$\Delta_r G^\circ = A - BT$$
Where A and B are non-zero constants. Which of the following is TRUE about this reaction ?

(1) Exothermic if B < 0   **[JEE-MAINS-(online) 2019]**

(2) Exothermic if A > 0 and B < 0

(3) Endothermic if A < 0 and B > 0

(4) Endothermic if A > 0

11. Ans.(4)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = A - BT$$

On comparing $\begin{cases} A = \Delta H^\circ \\ B = \Delta S^\circ \end{cases}$

(4) Correct

12. The reaction, $MgO(s) + C(s) \rightarrow Mg(S) + CO(g)$, for which $\Delta_r H^\circ = +491.1$ kJ mol^{-1} and $\Delta_r S^\circ = 198.0$ JK^{-1} mol^{-1}, is not feasible at 298 K. Temperature above which reaction will be feasible is :-

                                                         [JEE-MAINS-(online) 2019]

(1) 1890.0 K   (2) 2480.3 K   (3) 2040.5 K   (4) 2380.5 K

12. Ans.(2)

$$T_{eq} = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{491.1 \times 10^3}{198} = 2480.3 \text{ K}$$

13. A process has $\Delta H = 200$ Jmol^{-1} and

$\Delta S = 40$ JK^{-1}mol^{-1}. Out of the values given below, choose the minimum temperature above which the process will be spontaneous : **[JEE-MAINS-(online) 2019]**

(1) 5 K   (2) 4 K   (3) 20 K   (4) 12 K

13. **Ans.(1)**

$$T_{eq} = \frac{\Delta H}{\Delta S} = \frac{200}{40} = 5\,K.$$

14. The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is : **[JEE-MAINS-(online) 2019]**

(Specific heat of water liquid and water vapour are 4.2 kJ K^{-1} kg^{-1} and 2.0 kJ K^{-1} kg^{-1} ; heat of liquid fusion and vapourisation of water are 344 kJ kg^{-1} and 2491 kJ kg^{-1}, respectively).

(log 273 = 2.436, log 373 = 2.572, log 383 = 2.583)

(1) 7.90 kJ kg^{-1} K^{-1} (2) 2.64 kJ kg^{-1} K^{-1} (3) 8.49 kJ kg^{-1} K^{-1} (4) 9.26 kJ kg^{-1} K^{-1}

14. **Ans.(4)**

14

$$\Delta S_1 \qquad \Delta S_2 \qquad \qquad \Delta S_{Total} = ?$$

$$H_2O(s) \longrightarrow H_2O(l) \longrightarrow H_2O(l)$$

273K   273K   373K

$$\Delta S_3$$

$$\Delta S_4$$

$$H_2O(g) \longrightarrow H_2O(g)$$

373K   383 K
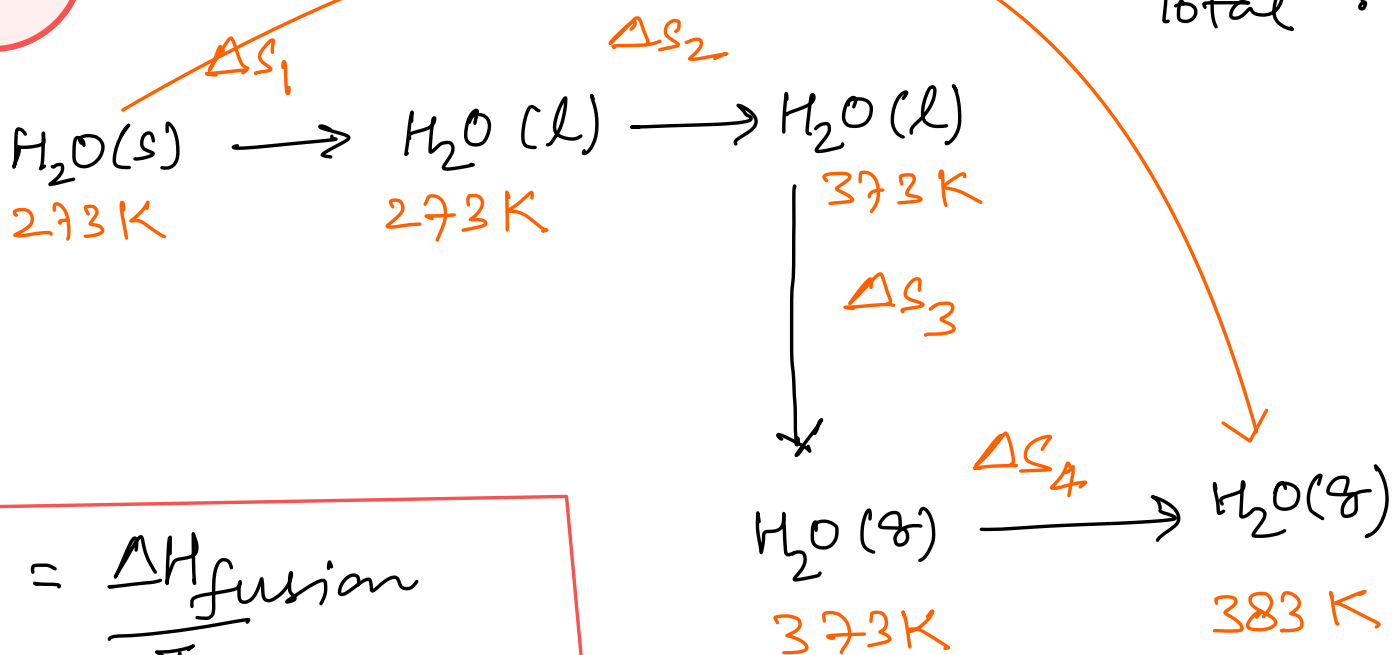
$$\Delta S_1 = \frac{\Delta H_{fusion}}{T_m}$$

$$= \frac{344}{273} = 1.26 \text{ kJ/K}$$

$$\Delta S_2 = 2.303 \, m \, \phi \log \frac{T_2}{T_1} = 2.303 \times 1 \times 4.2 \log \frac{373}{273}$$

$$= 1.32 \text{ kJ/K}$$

$$\Delta S_3 = \frac{\Delta H_{vap}}{T_b} = \frac{2491}{373} = 6.68 \text{ kJ/K}$$

$$\Delta S_4 = 2.303 \, ms \log \frac{T_2}{T_1} = 2.303 \times 1 \times 2 \log \frac{383}{373}$$

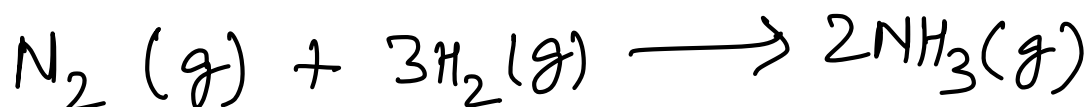$$= 2.303 \times 1 \times 2 \times 0.011$$

$$= 0.051 \text{ kJ/K}$$

$$\Delta S_{Total} = 9.31 \, \frac{kJ}{K}$$

15. The process with negative entropy change is :   **[JEE-MAINS-(online) 2019]**

(1) Dissolution of iodine in water

(2) Synthesis of ammonia from N_2 and H_2

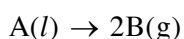(3) Dissolution of $CaSO_4(s)$ to $CaO(s)$ and $SO_3(g)$

(4) Subimation of dry ice

15. **Ans.(2)**

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

$$\Delta n_g < 0 \implies \Delta_r S < 0$$

16. For the reaction ;   **[JEE-MAINS-(online) 2020]**

$A(l) \rightarrow 2B(g)$

$\Delta U = 2.1$ kcal , $\Delta S = 20$ cal K^{-1} at 300 K

Hence ΔG in kcal is_____ .

16. **Ans.(–2.70 to –2.71)**

Sol. $A(\ell) \longrightarrow 2B(g)$

$\Delta U = 2.1$ Kcal , $\Delta S = 20$ cal K^{-1} at 300 K

$\Delta H = \Delta U + \Delta n_g RT$

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

$\Delta G = \Delta U + \Delta n_g RT - T\Delta S$

$= 2.1 + \dfrac{2 \times 2 \times 300}{1000} - \dfrac{300 \times 20}{1000}$
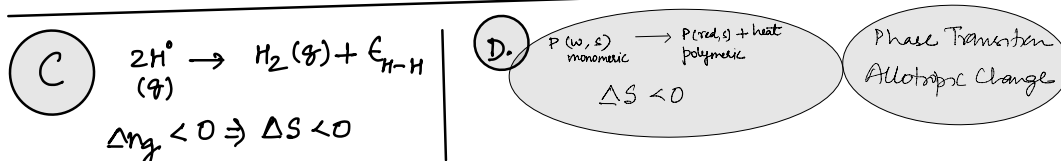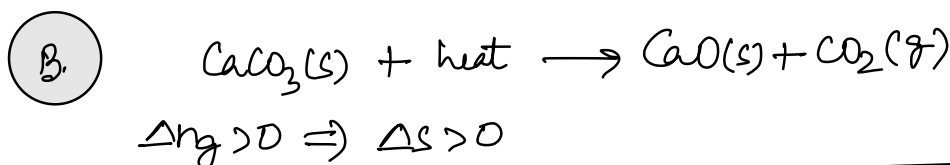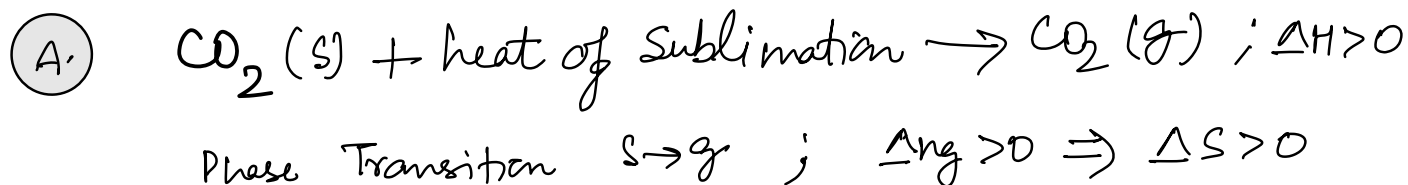
                        (R = 2 cal K^{-1} mol^{-1})

$= 2.1 + 1.2 - 6 = -2.70$ Kcal/mol

node06\B0AH-AI\Kota\JEE(Advanced)\Enthusiast\Advance Batch\Che.\Sheet\thermodynamics-02

EXERCISE (J-ADVANCE)

1. Match the transformations in **Column-I** with appropriate option in **Column-II**   **[JEE 2011]**

   Column-I   **Column-II**

   (A) $CO_2(s) \rightarrow CO_2(g)$ (p)   phase transition

   (B) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ (q)   allotropic change

   (C) $2H\bullet \rightarrow H_2(g)$ (r)   ΔH is positive

   (D) $P_{(white, \, solid)} \rightarrow P_{(red, solid)}$ (s)   ΔS is positive

                                                            (t)   ΔS is negative

Ans. (A)→(p, r, s) ; (B)→(r, s) ; (C)→(t) ; (D)→(p, q, t)

(A.) $CO_2(s) +$ heat of Sublimation $\rightarrow CO_2(g)$; $\Delta H > 0$

Phase Transition $s \rightarrow g$; $\Delta n_g > 0 \Rightarrow \Delta S > 0$

(B.) $CaCO_3(s) + $ heat $\rightarrow CaO(s) + CO_2(g)$

$\Delta n_g > 0 \Rightarrow \Delta S > 0$

(C) $2H^\bullet_{(g)} \rightarrow H_2(g) + \epsilon_{H-H}$

$\Delta n_g < 0 \Rightarrow \Delta S < 0$

(D.) $P_{(w, s)}$ monomeric $\rightarrow P_{(red, s)}$ polymeric $+$ heat

$\Delta S < 0$

Phase Transition
Allotropic Change

2. For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct ? [take ΔS as change in entropy and w as work done] **[JEE 2012]**
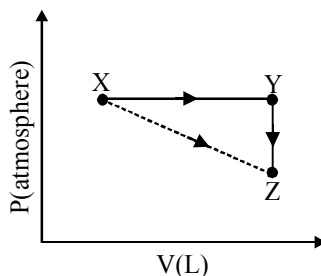
(A) $\Delta S_{x \to z} = \Delta S_{x \to y} + \Delta S_{y \to z}$

(B) $W_{x \to z} = W_{x \to y} + W_{y \to z}$

(C) $W_{x \to y \to z} = W_{x \to y}$

(D) $\Delta S_{x \to y \to z} = \Delta S_{x \to y}$

Ans. (A), (C)

A. $\Delta S_{x-z} = S_z - S_x$

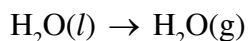$\Delta S_{xy} + \Delta S_{yz} = (S_y - S_x) + (S_z - S_y) = S_z - S_x$

C. $W_{x \to y \to z} = W_{xy} + W_{yz} = W_{xy}$

$= 0 \ (\text{Isochoric})$

3. For the process **[JEE 2014]**

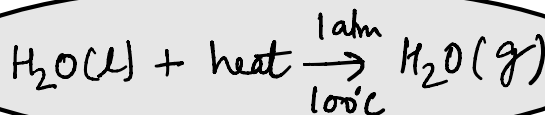$$H_2O(l) \to H_2O(g)$$

at T = 100°C 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 $\Delta S_{surroundings} < 0$

Ans. (B)

$H_2O(l) + heat \xrightarrow[100°C]{1 atm} H_2O(g)$

$\Delta S_{sys} + \Delta S_{surr} = 0 \ [Rev.]$

$\left[\dfrac{\Delta H_{vap,m}}{373} > 0\right]$ $\left[\dfrac{-q}{373} < 0\right]$

4. Match the thermodynamic processes given under Column-I with the expressions given under Column-II. **[JEE 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 temeprature and pressure in an isolated container

(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

Column - II

(P) q = 0

(Q) w = 0

(R) $\Delta S_{sys} < 0$

(S) $\Delta U = 0$

(T) $\Delta G = 0$

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

Ⓐ
$$H_2O(\ell) \xrightarrow[273K]{1atm} H_2O(s) + \text{heat of fusion}$$

$q = q_P = \Delta H < 0$

$w = -P\Delta V < 0$

$\Delta S = \dfrac{\Delta H}{T} < 0$

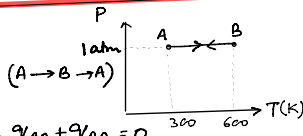$\Delta U \simeq \Delta H < 0 \quad [\because \Delta(PV) \simeq 0]$

$\Delta G = 0 \quad Eq^m$

Ⓑ
Isolated $\Rightarrow$ q=0 and w=0

$\Delta S = nR\ln\dfrac{V_2}{V_1} > 0$

$\Delta U = q + w = 0$

$dG = VdP < 0$

Ⓒ
$\underline{\Delta S_{mix}} = 2nR\ln 2$

$= +ve$

$\Delta G_{mix} = -\dfrac{\Delta S_{mix}}{T} = -ve$

Ⓓ

$q = q_{AB} + q_{BA} = 0$

$w = w_{AB} + w_{BA} = 0$

$\Delta U = \Delta G = \Delta S_{A\to B\to A} = 0$

5. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in J K^{-1} is - **[JEE 2016]**

(1 L atm = 101.3 J)

(A) 5.763   (B) 1.013   (C) –1.013   (D) –5.763

Ans. (C)

$$\Delta S_{surr} = \frac{-q}{T_{surr}} = \frac{w}{T} = -\frac{P_{ext}(V_2 - V_1)}{T} = -\frac{3(2-1)}{300}$$
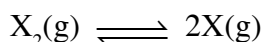
$$= -0.01 \frac{\ell \cdot atm}{K}$$

$$= -1.013 \text{ J/K}$$

Paragraph for Q.6 & Q.7

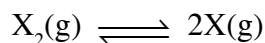Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation :   **[JEE 2016]**

$$X_2(g) \rightleftharpoons 2X(g)$$

The standard reaction Gibbs energy, $\Delta_r G°$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β . Thus, $\beta_{equilibrium}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally. (Given : R = 0.083 L bar K^{-1} mol^{-1})

6. The equilibrium constant K_P for this reaction at 298 K, in terms of $\beta_{equilibrium}$, is

(A) $\dfrac{8\beta_{equilibrium}^2}{2-\beta_{equilibrium}}$ (B) $\dfrac{8\beta_{equilibrium}^2}{4-\beta_{equilibrium}^2}$ (C) $\dfrac{4\beta_{equilibrium}^2}{2-\beta_{equilibrium}}$ (D) $\dfrac{4\beta_{equilibrium}^2}{4-\beta_{equilibrium}^2}$

6. **Ans.(B)**

$$X_2(g) \rightleftharpoons 2X(g)$$

$$1-\dfrac{\beta_{eq.}}{2} \qquad\qquad \beta_{eq.}$$

$$K_P = \dfrac{P_X^2}{P_{X_2}} = \dfrac{\left(\dfrac{\dfrac{\beta_{eq.}}{1+\dfrac{\beta_{eq}}{2}}P_T}{}\right)^2}{\left(\dfrac{1-\dfrac{\beta_{eq.}}{2}}{1+\dfrac{\beta_{eq}}{2}}P_T\right)}$$

$$K_P = \dfrac{\beta_{eq.}^2}{1-\dfrac{\beta_{eq.}^2}{4}}P_T = \dfrac{2\beta_{eq}^2}{1-\dfrac{\beta_{eq.}}{4}} \quad = \dfrac{8\beta_{eq.}^2}{4-\beta_{eq.}^2}$$

7. The **INCORRECT** statement among the following for this reaction is

(A) Decrease in the total pressure will result in formation of more moles of gaseous X

(B) At the start of the reaction, dissociation of gaseous X_2 takes place spontaneously

(C) $\beta_{equilibrium}$ = 0.7

(D) $K_C < 1$

7. **Ans.(C)**

(A) On decreasing P_T $\left[Q=\dfrac{n_{x^2}P_T}{n_{x_2}n_T}\right]$ Q will be less than Kp reaction will move in forward direction

(B) At the start of the reaction $\Delta G = \Delta G^0 + RT \ln Q$

   t = 0 , Q = 0 $\Rightarrow \Delta_{rxn} G = -ve$ (spontaneous)

(C) if β_{eq} = 0.7

$$K_p = \frac{8 \times 0.49}{4 - 0.49} = \frac{3.92}{3.51}$$

$$K_p > 1$$

Since it is given that

$$\Delta G^0 > 0 \implies K_p < 1$$

∴ This is incorrect

(D) $K_p = K_C \times (RT)^{\Delta n_g}$

$$K_C = \frac{K_P}{(R \times 298)^1}$$

$$K_C < 1$$

8. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at T = 298 K are **[JEE 2017]**

$$\Delta_f G^\circ \text{ [C(graphite)]} = 0 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ \text{ [C(diamond)]} = 2.9 \text{ kJ mol}^{-1}$$

The standard state means that the pressure should be 1 bar , and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by $2 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. If C(graphite) is converted to C(diamond) isothermally at T = 298 K, the pressure at which C(graphite) is in equilibrium with C(diamond), is

[Useful information : $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$; $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$; $1 \text{ bar} = 10^5 \text{ Pa}$]

(A) 14501 bar (B) 29001 bar (C) 58001 bar (D) 1405 bar

Ans. (A)

$$\Delta_r G^\circ_{P_2} - \Delta_r G^\circ_{P_1} = \Delta_r V (P_2 - P_1) \quad \nearrow 10^5 \text{ Pa}$$

$$= 0 \text{ (Eqm)} \quad (2.9 \times 10^3 - 0) \quad -2 \times 10^{-6}$$

$$P_1 = 14501 \times 10^5 \text{ Pa} = 14501 \text{ bar}$$

9. 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

(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

Ans. **(BC)**

$$\Delta H > 0 \Rightarrow T\uparrow \ K_{eq}\uparrow$$

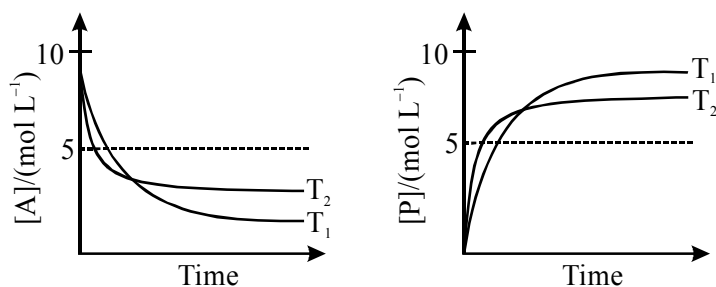$$\Delta H < 0 \Rightarrow T\uparrow \ K_{eq}\downarrow$$

$$\Delta S > 0 \ (fav) \qquad\qquad \Delta S < 0 \ (Unfav)$$

$$\Delta S_{surr} > 0 \ (fav) \qquad\qquad \Delta S_{surr} < 0 \ (Unfav.)$$

$$\Delta S_{surr} = -\frac{\Delta H}{T} \qquad \left(\begin{array}{c} At \ const \\ T \ and \ P \end{array}\right)$$

10. For a reaction, $A \rightleftharpoons P$, the plots of [A] and [P] with time at temperatures T_1 and T_2 are given below. **[JEE 2018]**

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

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

Ans. (A,C)

$$A = P \qquad \frac{\ln K_1}{\ln K_2} > \frac{T_2}{T_1} \implies -\Delta G_1^\circ > -\Delta G_2^\circ$$

$$T_1 \, \Delta S^\circ > T_2 \, \Delta S^\circ \implies \Delta S^\circ < 0$$

$$(\because T_2 > T_1)$$

11. The surface of copper gets tarnished by the formation of copper oxide. N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below

$2Cu(s) + H_2O(g) \rightarrow Cu_2O(s) + H_2(g)$

p_{H_2} is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln(p_{H_2})$ is ____.

(Given : total pressure = 1 bar, R (universal gas constant) = 8 $JK^{-1}mol^{-1}$, $\ln(10) = 2.3$. Cu(s) and $Cu_2O(s)$ are mutually immiscible.

At 1250 K : $2Cu(s) + 1/2O_2(g) \rightarrow Cu_2O(s)$; $\Delta G^\theta = -78,000$ J mol^{-1}

$H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)$; $\Delta G^\theta = -1,78,000$ J mol^{-1}; G is the Gibbs energy) **[JEE 2018]**

Ans. (−14.6)

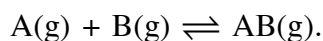$$\Delta G = \Delta G^0 + RT \ln Q$$

$$0 = 100 + \frac{8}{1000} \times 1250 \ln \frac{P_{H_2}}{P_{H_2O}}$$

$$0.01$$

$$\ln P_{H_2} = -14.6$$

12. Consider the following reversible reaction,   **[JEE 2018]**
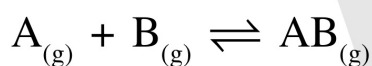
$$A(g) + B(g) \rightleftharpoons AB(g).$$

The activition energy of the backward reaction exceeds that of the forward reaction by 2RT (in J mol^{-1}). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of ΔG^θ (in J mol^{-1}) for the reaction at 300 K is____.

(Given ; ln (2) = 0.7, RT = 2500 J mol^{-1} at 300 K and G is the Gibbs energy)

Ans. (8500)

Sol. $A_{(g)} + B_{(g)} \rightleftharpoons AB_{(g)}$

$$E_{ab} - E_{af} = 2RT \qquad \Rightarrow \Delta H = -2RT \qquad \text{and} \quad \frac{A_f}{A_b} = 4$$

$$K_{eq} = \left(\frac{K_f}{K_b}\right) = \frac{A_f e^{-E_{af}/RT}}{A_b e^{-E_{ab}/RT}} = 4(e^2)$$

$$\Delta G^\circ = -RT \ln K = -2500 \times \ln(4 \times e^2) = -8500 \text{ J/mol}$$

$\therefore$ Absolute value of $\Delta G^\circ = 8500$ J/mol

Always ⊕