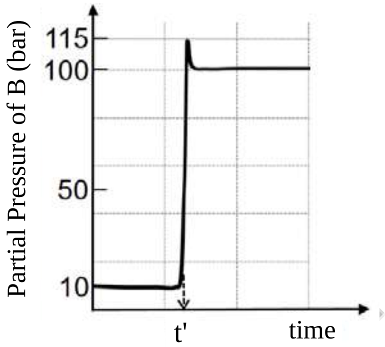
PHYSICAL CHEMISTRY

CHEMICAL EQUILIBRIUM

1. Consider the reaction **A** $\rightleftharpoons$ **B** at 1000 K. At time t', the temperature of the system was increased to 2000 K and the system was allowed to reach equilibrium. Throughout this experiment the partial pressure of **A** was maintained at 1 bar. Given below is the plot of the partial pressure of **B** with time. What is the ratio of the standard Gibbs energy of the reaction at 1000 K to that at 2000 K? **[JEE(Advanced) 2020]**



2. For the following reaction, the equilibrium constant K_c at 298 K is 1.6×10^{17}.

$Fe^{2+}(aq) + S^{2-}(aq) \rightleftharpoons FeS(s)$

When equal volumes of 0.06 M $Fe^{2+}(aq)$ and 0.2 M $S^{2-}(aq)$ solutions are mixed, the equilibrium concentration of $Fe^{2+}(aq)$ is found to be $\mathbf{Y} \times 10^{-17}$ **M**. The value of Y is ______. **[JEE(Advanced) 2019]**

3. Consider the following reversible reaction,

$A(g) + B(g) \rightleftharpoons AB(g)$.

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) **[JEE(Advanced) 2018]**

Paragraph For Question No. 4 and 5

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation :

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

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}) **[JEE(Advanced) 2016]**

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

(A) $\dfrac{8\beta^2_{\text{equilibrium}}}{2-\beta_{\text{equilibrium}}}$ (B) $\dfrac{8\beta^2_{\text{equilibrium}}}{4-\beta^2_{\text{equilibrium}}}$

(C) $\dfrac{4\beta^2_{\text{equilibrium}}}{2-\beta_{\text{equilibrium}}}$ (D) $\dfrac{4\beta^2_{\text{equilibrium}}}{4-\beta^2_{\text{equilibrium}}}$

5. 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

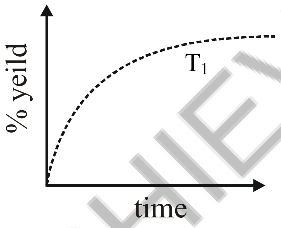
(B) At the start of the reaction, dissociation of gaseous X_2 takes place spontaneously

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

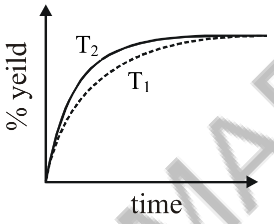
(D) $K_C < 1$

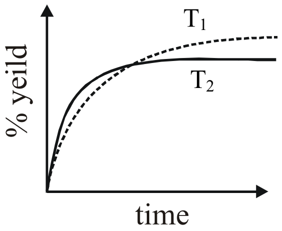
6. The % yield of ammonia as a function of time in the reaction **[JEE(Advanced) 2015]**

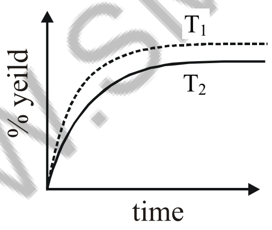
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H < 0$ at (P, T_1) is given below -

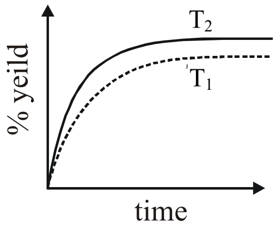


If this reaction is conducted at (P, T_2), with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by -

(A)


(B)


(C)


(D)


SOLUTIONS

1. **Ans. (0.25)**

Sol. $K_{eq.} = \frac{[B]}{[A]}$

$K_{1000} = \frac{10}{1} = 10$ and $K_{2000} = \frac{100}{1} = 100$

Now, $\frac{\Delta G^0_{1000}}{\Delta G^0_{2000}} = \frac{(-RT\ell nk_{eq})_{1000}}{(-RT\ell nK_{eq})_{2000}} = \frac{1000 \times \ell n10}{2000 \times \ell n100} = 0.25$

2. **Ans. (8.70 or 9.10)**

Sol. $Fe^{+2}_{(aq.)} \quad + \quad S^{-2}_{(aq.)} \quad \rightleftharpoons \quad FeS(s)$

$0.03\ M \qquad 0.1\ M$

$(0.03-x) \quad (0.1-x)$

$\simeq y \qquad \simeq 0.07$

$K_c >> 10^3 \Rightarrow 0.03-x \simeq 0 \simeq y$

$\Rightarrow x = 0.03$

$K_c = 1.6 \times 10^{17} = \frac{1}{y \times 0.07}$

$y = \frac{10^{-17}}{1.6 \times 0.07} = 8.928 \times 10^{-17} = Y \times 10^{-17} \qquad \Rightarrow \boxed{y \simeq 8.93}$

3. **Ans. (8500)**

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

$E_{ab} - E_{af} = 2RT$

$\Rightarrow \Delta H = -2RT$ and $\frac{A_f}{A_b} = 4$

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

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

Absolute value of $\Delta G° = 8500$ J/mol

4. Ans. (B)

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

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

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

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

5. Ans. (C)

Sol. (A) On decreasing P_T $\left[Q = \frac{n_{x^2}P_T}{n_{x_2}n_T}\right]$ 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 $\beta_{eq} = 0.7$

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

$K_p > 1$

Since it is given that

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

$\therefore$ This is incorrect

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

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

$K_C < 1$

6. Ans. (B)

Sol. At t = 0 $\Rightarrow r_{net} = k_f [N_2][H_2]^3 = r_f$

$\therefore$ % yield will increase in initial stages due to increase in net speed

As time proceeds $\Rightarrow r_{net} = k_f [N_2][H_2]^3 - k_b [NH_3]^2$

On increasing temp., k_f & k_b increase but increase of k_b is more. so % yield will decrease

% yield will increase in initial stage due to enhance speed but as time proceeds , final yield is governed by thermodynamics due to which yield decrease since reaction is exothermic