PHYSICAL CHEMISTRY

## CHEMICAL EQUILIBRIUM

## CHEMISTRY

#### SECTION-I : (ii) One or more options correct Type

This section contains 17 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE or MORE are correct. 4(-1)

1. Following two equilibrium is simultaneously established in a container

$$\begin{array}{rcl} PCl_{5}(g) & \rightleftharpoons & PCl_{3}(g) + & Cl_{2}(g) \\ CO(g) + & Cl_{2}(g) & \rightleftharpoons & COCl_{2}(g) \end{array}$$

If some Ni(s) is introduced in the container forming Ni (CO)<sub>4</sub> (g) then at new equilibrium

(A) PCl<sub>3</sub> concentration will increase (B) PCl<sub>3</sub> concentration will decrease

- (C) Cl<sub>2</sub> concentration will remain same (D) CO concentration will remain same
- When NaNO<sub>3</sub> is heated in a closed vessel, oxygen is liberated and NaNO<sub>2</sub> is left. At equilibrium 2.
  - (A) addition of NaNO<sub>2</sub> favours reverse reaction
  - (B) addition of NaNO<sub>3</sub> favours forward reaction
  - (C) increasing temperature favours forward reaction
  - (D) increasing pressure favours reverse reaction
- 3. Phase diagram of CO<sub>2</sub> is shown as following



Based on above find the correct statement(s)

- (A) 298K is the normal boiling point of liquid CO<sub>2</sub>
- (B) At 1 atm & 190 K CO<sub>2</sub> will exist as gas.
- (C)  $CO_2(s)$  will sublime above 195K under normal atmospheric pressure
- (D) Melting point & boiling point of CO<sub>2</sub> will increase on increasing pressure
- Consider the equilibrium HgO(s) + 4I<sup>-</sup> (aq) + H<sub>2</sub>O (l)  $\rightleftharpoons$  HgI<sub>4</sub><sup>2-</sup> (aq) + 2OH<sup>-</sup> (aq), which changes 4. will decrease the equilibrium concentration of  $HgI_4^{2-}$

(A) Addition of 0.1 M HI (aq)(B) Addition of HgO (s)(C) Addition of 
$$H_2O(l)$$
(D) Addition of KOH (aq)

- (D) Addition of KOH (aq)
- 5. Statement-1: Ammonia at a pressure of 10 atm and CO<sub>2</sub> at a pressure of 20 atm are introduced into an evacuated chamber. If  $K_p$  for the reaction

 $NH_2COONH_4$  (s)  $\rightleftharpoons 2NH_3$  (g) +  $CO_2$  (g) is 2020 atm<sup>3</sup>, the total pressure after a long time is less than 30 atm.

Statement-2 : Equilibrium can be attained from both directions.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

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6. Statement-1: Catalyst does not alter the equilibrium constant

**Statement-2**: Because for the catalysed reaction and uncatalysed reaction  $\Delta H$  remain same an equilibrium constant depend on  $\Delta H$ .

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.
- 7. For the decomposition of the compound, represented as [JEE-MAINS(online)-14]

$$NH_2COONH_4(s) \implies 2NH_3(g) + CO_2(g)$$

the K<sub>P</sub>= $2.9 \times 10^{-5}$  atm<sup>3</sup>.

If the reaction is started with 1 mol of the compound, the total pressure at equilibrium would be

- (A)  $38.8 \times 10^{-2}$  atm (B)  $1.94 \times 10^{-2}$  atm
- (C)  $5.82 \times 10^{-2}$  atm (D)  $7.66 \times 10^{-2}$  atm
- 8. Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction ? [JEE-MAINS(offline)-18]

(0,0)

(A)B and C (B) C and D (C) A and D (D) A and B

9. In which of the following reactions, an increase in the volume of the container will favour the formation of products ? [JEE-MAINS(online)-18]

 $(A)2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ 

 $(B)3O_2(g) \rightleftharpoons 2O_3(g)$ 

 $(C)H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$ 

- (D)  $4NH_3(g)+5O_2(g) \rightleftharpoons 4NO(g)+6H_2O(l)$
- 10. Consider the reaction equilibrium

 $2SO_{2(g)} + O_{2(g)} = 2 SO_{3(g)}; \Delta H^{\circ} = -198 \text{ kJ}$ 

On the basis of Le-Chatelier's principle, the condition favourable for the forward reaction is -

- (A) Lowering the temperature and increasing the pressure
- (B) Any value of temperature as well as pressure
- (C) Lowering of temperature as well as pressure
- (D) Increasing temperature as well as pressure



11. A schematic plot of  $ln K_{eq}$  verus inverse of temperature for a reaction is shown below. The reaction must be 6.0<sup>†</sup> [AIEEE-2005]

 $\ell_{n} \; K_{_{eq}}$ (A) endothermic 1 (B) exothermic 1.5 × 10<sup>-3</sup> 1/T (K<sup>-1</sup>) 2.0 × 10<sup>-3</sup> (C) highly spontaneous at ordinary temperature (D) one with negligible enthalpy change The equilibrium constants  $K_{p_1}$  and  $K_{p_2}$  for the reaction X  $\longrightarrow$  2Y and Z  $\longrightarrow$  P+Q, respectively are 12. in the ratio of 1:9. If the degree of dissociation of X and Z be equal then the ratio of total pressure at these equilibria is [AIEEE-2008] (A) 1 : 36 (C) 1 : 3 (D) 1 : 9 (B) 1 : 1 A vessel at 1000 K contains  $CO_2$  with a pressure of 0.5 atm. Some of the  $CO_2$  is converted into CO13. on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is (A) 0.3 atm (B) 0.18 atm [AIEEE-2011] (C) 1.8 atm (D) 3 atm 14. 8 mol of AB<sub>3</sub>(g) are introduced into a 1.0 dm<sup>3</sup> vessel. If it dissociates as  $2AB_3(g) \rightleftharpoons A_2(g) + 3B_2(g)$ At equilibrium, 2mol of A2 are found to be present. The equilibrium constant of this reaction is :-[JEE-MAINS(online)-12] (A) 36 (B) 3 (C) 27 (D) 2 15. The value of Kp for the equilibrium reaction  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$  is 2. The percentage dissociation of  $N_2O_4(g)$ at a pressure of 0.5 atm is [JEE-MAINS(online)-12] (C) 88 (D) 25 (A) 71 (B) 50 16.  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), K_1$  (A) [JEE-MAINS(online)-13]  $N_2(g) + O_2(g) \rightleftharpoons 2NO(g), K_2$ **(B)** 

$$H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g), K_3$$
 (C)

The equation for the equilibrium constant of the reaction

$$2 \operatorname{NH}_{3}(g) + \frac{5}{2} \operatorname{O}_{2}(g) \rightleftharpoons 2\operatorname{NO}(g) + 3\operatorname{H}_{2}\operatorname{O}(g), (\operatorname{K}_{4})$$

in terms of  $K_1$ ,  $K_2$  and  $K_3$  is :

(A) 
$$\frac{K_1 K_3^2}{K_2}$$
 (B)  $\frac{K_2 K_3^3}{K_1}$  (C)  $\frac{K_1 K_2}{K_3}$  (D)  $K_1 K_2 K_3$ 

#### SECTION–I(ii) : (Maximum Marks : 18)

- This section contains **3** questions of matching type.
- This section contains 1 table (having 3 columns and 4 rows)
- Based on table, there are **THREE** questions
- Each question has FOUR options (A), (B), (C) and (D). ONLY ONE of these four options is correct
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in <u>one of the following categories</u>:
  *Full Marks* : +3 If only the bubble corresponding to the correct option is darkened.
  *Zero Marks* : 0 In all other cases

Answer Q.No. 17, 18 and 19 by appropriately matching the information given in the three columns of the following table.

Column-I (Reaction)	Column-II (If α is negligiable w.r.t. 1)	Column-III
(A) $2X(g) \rightleftharpoons Y(g) + Z(g), \Delta H = -ve$	(P) $\alpha = 2 \times \sqrt{K_p}$ temperature	(I) K increase with increase in
(B) $X(g) \implies Y(g) + Z(g), \Delta H = +ve$	(Q) $\alpha = 3 \times \sqrt{K_{p}P}$ temperature	(II) K decrease with increase in
(C) $3X(g) \rightleftharpoons Y(g) + Z(g)$ , $\Delta H = +ve$	(R) $\alpha = \left(\frac{2Kp}{P}\right)^{1/3}$	(III) Pressure has no effect
(D) $2X(g) \rightleftharpoons Y(g) + 2Z(g), \Delta H = +ve$	(S) $\alpha = \sqrt{K_p / P}$	<ul><li>(IV) Addition of inert gas at constant pressure shift equilibrium in forward direction</li></ul>
<b>17.</b> Which of the following option is correct	ly matched ?	

(A) A-Q-III (B) B-S-II (C) C-Q-II (D) D-R-IV

18. Correct representation of reaction in option (A) is represented by graph



19. For the reaction of option (B) if degree of dissociation varies inversily as square root of pressure of the system. Suppose at constant temperature volume is increased 16 times of its initial volume the degree of dissociation ( $\alpha$ ) for this reaction will become :

(A) 4 times (B) 2 times (C) 1/4 times (D) 1/2 times

#### **SECTION-III : (Integer Value Correct Type)**

This section contains **2 questions**. The answer to each question is **a single digit Integer**, ranging from **0 to 9** (both inclusive) **4(-1)** 

- **1.** In the esterfication  $C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$  an equimolar mixture of alcohol and acid taken initially yields under equilibrium, the water with mole fraction = 0.333. Calculate the equilibrium constant.
- 2. Ammonia is a weak base that reacts with water according to the equation

 $NH_3 (aq) + H_2O (l) \rightleftharpoons NH_4^+ + OH^- (aq)$ 

Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?

(a) Addition of NaOH. (b) Addition of HCl. (c) Addition of  $NH_4Cl$ .

## **SECTION-IV : SUBJECTIVE**

1. Write down the expression for equilibrium constant  $K_{c}$  and  $K_{p}$  for the following reactions :

(a) 
$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

(b) 
$$H_2O(\ell) \rightleftharpoons H_2O(g)$$

(c) 
$$NH_2COONH_4(s) \implies 2NH_3(g) + CO_2(g)$$

(d) 
$$CH_3COOH(\ell) + C_2H_5OH(\ell) \Longrightarrow CH_3COOC_2H_5(\ell) + H_2O(\ell)$$

(e) 
$$\operatorname{NH}_3(\operatorname{aq}) + \operatorname{H}_2O(\ell) \rightleftharpoons \operatorname{NH}_4^+(\operatorname{aq}) + OH^-(\operatorname{aq})$$

(excess)

(f) 
$$\operatorname{Zn}(s) + 2\operatorname{H}^{+}(aq) \rightleftharpoons \operatorname{Zn}^{2+}(aq) + \operatorname{H}_{2}(g)$$

2. Write the relationship between  $K_p$  and  $K_c$  for the following reactions :

(a) 
$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
 (b)  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ 

(c) 
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
 (d)  $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$ 

(e) 
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

3. The value of  $K_c$  for the reaction  $2A \implies B + C$  is  $2 \times 10^{-3}$ . At a given time, the composition of reaction mixture is  $[A] = [B] = [C] = 3 \times 10^{-4}$  M. In which direction the reaction will proceed?

- 4. A sample of HI (9.6 × 10<sup>-3</sup> mol) was placed in an empty 2.00 L container at 1000 K. After equilibrium was reached, the concentration of I<sub>2</sub> was 4 × 10<sup>-4</sup> M. Calculate the value of K<sub>c</sub> at 1000 K for the reaction H<sub>2</sub> (g) + I<sub>2</sub> (g)  $\rightleftharpoons$  2HI (g).
- 5. One mole of  $H_2O$  and one mole of CO are taken in a 10 L vessel and heated to 725 K. At equilibrium 40 percent of water (by mass) reacts with carbon monoxide according to the equation.

 $H_2O_{(g)} + CO_{(g)} \implies H_{2(g)} + CO_{2(g)}$ 

Calculate the equilibrium constant for the reaction.

- 6. Calculate the equilibrium concentration of  $H_2$ ,  $I_2$  and HI at 300 K if initially 2 mol of  $H_2$  and  $I_2$  are taken in a closed container of having volume 10 lit. [Given :  $H_2 + I_2 \rightleftharpoons 2HI$ ; K = 100 at 300 K]
- 7. For the given reaction,

 $A(g) + B(g) \Longrightarrow C(g) + D(g)$ 

the number of moles at equilibrium was found to be 4, 4, 2 & 8 respectively in 1 L container. Find the new equilibrium concentration if 18 moles of D are added to above 1 L container.

**8.** For the given reaction,

 $PCl_5 \implies PCl_3 + Cl_2$ 

the number of moles at equilibrium was found to be 2, 6 & 4 respectively at 10 atm pressure. Find the new equilibrium moles & partial pressure, if it is restablished at an equilibrium pressure 50 atm.

- 9. For the reaction  $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$ Initially 5 moles of  $SO_3$  is taken and at equillibrium 4 moles of  $SO_3$  is dissociated then find out  $\alpha$  and the value of  $K_C$  (Volume = 2litre)
- 10. The degree of dissociation of  $N_2O_4$  into  $NO_2$  at 1.5 atmosphere and 40°C is 0.25. Calculate its  $K_p$  at 40°C. Also report degree of dissociation at 10 atmospheric pressure at same temperature.
- 11. 2 NOBr (g)  $\rightleftharpoons$  2 NO (g) + Br<sub>2</sub> (g). If nitrosyl bromide (NOBr) is 33.33% dissociated at 25° C & a total pressure of 0.28 atm. Calculate K<sub>p</sub> for the dissociation at this temperature.
- 12. Anhydrous calcium chloride is often used as a dessicant. In the presence of excess of  $CaCl_{2,}$ , the amount of the water taken up is governed by  $K_p = 6.4 \times 10^{85}$  for the following reaction at room temperature,  $CaCl_2(s) + 6H_2O(g) \rightleftharpoons CaCl_2 .6H_2O(s)$ . What is the equilibrium vapour pressure of water in a closed vessel that contains  $CaCl_2(s)$ ?
- 13.(a)Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst. Write the expression for the equilibrium constant for the reversible reaction.

 $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$   $\Delta H = -90.2 \text{ kJ}$ 

(b) Assume that equilibrium has been established and predict how the concentration of  $H_2$ , CO and  $CH_3OH$  will differ at a new equilibrium if (A) more  $H_2$  is added. (B) CO is removed. (C)  $CH_3OH$  is added. (D) the pressure on the system is increased. (5) the temperature of the system is increased. (6) more catalyst is added.

14. Listed in the table are forward and reverse rate constants for the reaction 2NO (g)  $\rightleftharpoons$  N<sub>2</sub>(g) +O<sub>2</sub>(g)

Геmperature (К)	$k_{f} (M^{-1}s^{-1})$	$k_r (M^{-1}s^{-1})$
1400	0.29	$1.1 \times 10^{-6}$
1500	1.3	$1.4 \times 10^{-5}$

Is the reaction endothermic or exothermic? Explain in terms of kinetics.

- 15. One mole of  $N_2O_4(g)$  at 300 K is left in a closed container under one atm. It is heated to 600 K when 20 % by mass of  $N_2O_4(g)$  decomposes to  $NO_2(g)$ . Calculate resultant pressure.
- 16. Solid Ammonium carbamate dissociates as:  $NH_2 COONH_4$  (s)  $\rightleftharpoons 2NH_3(g) + CO_2(g)$ . In a closed vessel solid ammonium carbamate is in equilibrium with its dissociation products. At equilibrium, ammonia is added such that the partial pressure of  $NH_3$  at new equilibrium now equals the original total pressure. Calculate the ratio of total pressure at new equilibrium to that of original total pressure.
- 17. A definite amount of solid  $NH_4HS$  is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure.  $NH_4HS$  decomposes to give  $NH_3$  and  $H_2S$  and at equilibrium total pressure in flask is 0.84 atm. Calculate equilibrium constant for the reaction :

# **18.** For the reaction $A(g) + 2B(g) \rightleftharpoons C(g) + D(g)$ ; $K_c = 10^{12}$ . If the initial moles of A,B,C and D are 0.5, 1, 0.5 and 3.5 moles respectively in a one litre vessel. What is the equilibrium concentration of B?

**19.** At certain temperature (T) for the gas phase reaction

 $2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$   $K_n = 12 \times 10^8 \text{ atm}$ 

If  $Cl_2$ , HCl &  $O_2$  are mixed in such a manner that the partial pressure of each is 2 atm and the mixture is brough into contact with excess of liquid water. What would be approximate partial pressure of  $Cl_2$  when equilibrium is attained at temperature (T)?

## [Given : Vapour pressure of water is 380 mm Hg at temperature (T)]

20. In a vessel, two equilibrium are simultaneously established at same temperature as follows,

$N_2(g) + 3H_2(g) \Longrightarrow 2NH_3(g)$	(i)
$N_2(g) + 2H_2(g) \implies N_2H_4(g)$	(ii)

Initially the vessel contains  $N_2$  and  $H_2$  in the molar ratio of 9 : 13. The equilibrium pressure is 7  $P_0$  in which pressure due to ammonia is  $P_0$  and due to hydrogen is  $2P_0$ . Find the values of equilibrium constants  $(K_p's)$  for both the reactions.