



# THE GURUKUL INSTITUTE

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## CHEMICAL EQUILIBRIUM

### Law of mass Action

1. One mole of  $\text{SO}_3$  was placed in a vessel of 1 L capacity at a certain temperature constant  $K_c$  for the following equilibrium was established.



At equilibrium, 0.6 moles of  $\text{SO}_2$  were formed. The equilibrium constant  $K_c$  for the reaction will be

- (A) 0.36                      (B) 0.45                      (C) 0.54                      (D) 0.675

2. At  $27^\circ\text{C}$   $K_p$  value for reaction  $\text{CaCO}_3(\text{s}) + \text{CO}_2(\text{g})$  is 0.1 atm, calculate its  $K_c$  value.

- (A)  $4 \times 10^{-3}$                       (B)  $6 \times 10^{-3}$                       (C)  $2 \times 10^{-3}$                       (D)  $9 \times 10^{-3}$

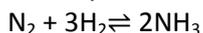
3. Solid  $\text{NH}_4\text{I}$  dissolves to the reaction at 400 K

$\text{NH}_4\text{I}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HI}(\text{g})$ ;  $K_p = 16$  atm. In presence of catalyst, HI dissociates into  $\text{H}_2$  and  $\text{I}_2$  as  $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ . If partial pressure of  $\text{H}_2$  at this temp is 1 atm in the container when both the equilibrium exist simultaneously, calculate  $K_p$  value of second equilibrium (for the dissociation of HI).

4. A vessel at 1000 K contains  $\text{CO}_2$  with a pressure of 0.5 atm. Some of the  $\text{CO}_2$  is converted into CO on addition of graphite. What is the value of  $K_p$  if the total pressure at equilibrium is 0.8 atm?

### Exercise – 1

1. Write the expression for  $K_p$  and  $K_c$  for the following reactions

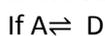


2. select the heterogeneous equilibrium from the following reaction

- (A)  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$   
(B)  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

### Exercise – 2

1. what is the value of equilibrium constant for the following reaction



$$K_1 = 2$$



$$K_2 = 5$$



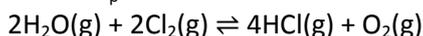
$$K_3 = 3$$

- (A) 60                      (B) 40                      (C) 20                      (D) 30

2. In an equilibrium  $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$ ; A and B are mixed in a vessel at temperature T. the initial concentration of A was twice the initial concentration of B. After the equilibrium has established, concentration of C was thrice the equilibrium concentration of B. Calculate  $K_c$ .

### Units of Equilibrium Constant

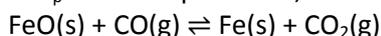
1. The value of  $K_p$  for the reaction



is 0.035 atm at  $400^\circ\text{C}$ , when the partial pressures are expressed in atmosphere.

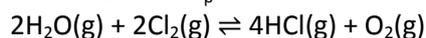
Calculate  $K_c$  for the reaction,  $\frac{1}{2}\text{O}_2(\text{g}) + 2\text{HCl}(\text{g}) \rightleftharpoons \text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$

2.  $K_p$  for the equilibrium,



At  $1000^\circ\text{C}$  is 0.4. if  $\text{CO}(\text{g})$  at a pressure of 1 atm and excess  $\text{FeO}(\text{s})$  are placed in a container at  $1000^\circ\text{C}$ , what are the pressure of  $\text{CO}(\text{g})$  and  $\text{CO}_2(\text{g})$  when equilibrium is attained?

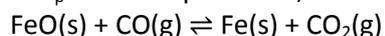
3. the value of  $K_p$  for the reaction



Is 0.035 atm at  $400^\circ\text{C}$ , when the partial pressures are expressed in atmosphere.

Calculate  $K_c$  for the reaction,  $\frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$

4.  $K_p$  for the equilibrium,



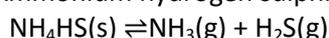
At  $1000^\circ\text{C}$  is 0.4. If  $\text{CO}(\text{g})$  at a pressure of 1 atm and excess  $\text{FeO}(\text{s})$  are placed in a container at  $1000^\circ\text{C}$ , what are the pressure of  $\text{CO}(\text{g})$  and  $\text{CO}_2(\text{g})$  when equilibrium is attained?

5. At 800 K a reaction mixture contained 0.5 mole of  $\text{SO}_2$ , 0.12 mole of  $\text{O}_2$  and 5 mole of  $\text{SO}_3$  at equilibrium  $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$  is 833 lit/ mole. If the volume of the container is 1 litre, calculate how much  $\text{O}_2$  is to be added at this equilibrium in order to get 5.2 moles of  $\text{SO}_3$  at the same temperature.

- (A) 2.34 moles      (B) 0.34 moles      (C) 1.43 moles      (D) 3.23 moles

### Exercise - 3

1. Ammonium hydrogen sulphite dissociates as follows



If solid  $\text{NH}_4\text{HS}$  is placed in an evacuated flask at certain temperature it will dissociate until the total pressure is 600 torr.

- (A) calculate the value of equilibrium constant for the dissociation reaction  
(B) Additional  $\text{NH}_3$  is introduced into the equilibrium mixture without changing the temperature until partial pressure of  $\text{NH}_3$  is 750 torr. What is the partial pressure of  $\text{H}_2\text{S}$  under these conditions? What is the total pressure in the flask?

2. At 700 K hydrogen and bromine react to form hydrogen bromide. The value of equilibrium constant for this reaction is  $5 \times 10^8$ . Calculate the amount of  $\text{H}_2$ ,  $\text{Br}_2$  and  $\text{HBr}$  at equilibrium, if a mixture of 0.6 mole of  $\text{H}_2$  and 0.2 mole of  $\text{Br}_2$  is heated to 700 K.

- (A) 1.4, 1, 1.4      (B) 2.2, 0, 0.4      (C) 0.4, 0, 0.4      (D) 2.3, 1, 2.4

### Reaction Quotient (Q)

1. For the reaction:  $\text{A}_{(\text{aq})} + \text{B}_{(\text{aq})} \rightleftharpoons \text{C}_{(\text{aq})} + \text{D}_{(\text{aq})}$ , the net rate of consumption of B at  $25^\circ\text{C}$  and at any time 't' is as given below

$$-\frac{d[\text{B}]}{dt} = \{4 \times 10^{-4} [\text{A}] [\text{B}] - 1.33 \times 10^{-5} [\text{C}] [\text{D}]\} \text{ mol L}^{-1} \text{ min}^{-1}$$

Predict whether the reaction will be spontaneous in the direction as written in reaction mixture in which each A, B, C and D is having a concentration of  $1 \text{ mol L}^{-1}$ ?

### Le chatelier's Principle

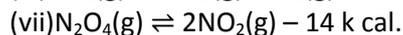
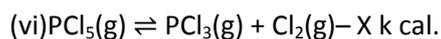
1.  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ :  $\Delta H = \text{negative}$

What are the conditions of temperature and pressure favourable for this reaction?

- (A) Low temperature, low pressure  
(B) high temperature, low pressure  
(C) high temperature, high pressure  
(D) low temperature, high pressure

2. under what conditions will the following reactions go in the forward direction?

- (i)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) + 23 \text{ k cal.}$   
(ii)  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) + 45 \text{ k cal.}$   
(iii)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) - 43.2 \text{ k cal.}$   
(iv)  $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) + 27.8 \text{ k cal.}$   
(v)  $\text{C}(\text{s}) + \text{HO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g}) + X \text{ k cal.}$



3. the equilibrium constant  $K_p$  for the reaction

$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$  is  $1.6 \times 10^{-4} \text{ atm}^{-2}$  at  $400^\circ \text{C}$ . what will be the equilibrium constant at  $500^\circ \text{C}$  if heat of the reaction in this temperature range is  $-25.14 \text{ k cal}$ ?

(A)  $1.231 \times 10^{-4} \text{ atm}^{-2}$

(B)  $1.876 \times 10^{-7} \text{ atm}^{-2}$

(C)  $1.462 \times 10^{-5} \text{ atm}^{-2}$

(D)  $3.462 \times 10^{-5} \text{ atm}^{-2}$

Calculation of the Degree of Dissociation from Density Measurement

4. When  $\text{PCl}_5$  is heated it dissociates into  $\text{PCl}_3$  and  $\text{Cl}_2$ . The density of the gas mixture at  $200^\circ \text{C}$  and at  $250^\circ \text{C}$  is 70.2 and 57.9 respectively. Find the degree of dissociation at  $200^\circ \text{C}$  and  $250^\circ \text{C}$ .

(A) 0.8

(B) 1.2

(C) 3.2

(D) 2.1

### Exercise - 5

1. How much  $\text{PCl}_5$  must be added to a one litre vessel at  $250^\circ \text{C}$  in order to obtain concentration of 0.1 mole of  $\text{Cl}_2$ ?  $K_c$  for  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$  is 0.0414 mol/litre.

### PROBLEMS

1. in an experiment 5 moles of HI were disclosed in a 5 liters container. At 717 K equilibrium constant for the gaseous reaction  $2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$  is 0.025. Calculate the equilibrium concentrations of HI,  $\text{H}_2$  and  $\text{I}_2$ . What is the fraction of HI that decomposes?

2. Calculate the volume percent of chlorine at equilibrium in  $\text{PCl}_5$  under a total pressure of 1.5 atm. ( $K_p = 0.202 \text{ atm}$ )

3. in a mixture of  $\text{N}_2$  and  $\text{H}_2$  initially in a mole ratio of 1 : 3 at 30 atm and  $300^\circ \text{C}$ , the equilibrium constant ( $K_p$ ) of the mixture, for the reaction  $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$

4. 256 g of HI was heated in a sealed bulb at  $444^\circ \text{C}$  till the equilibrium was attained. The acid was found to be 22% dissociated at equilibrium. Calculate equilibrium constants for synthesis and dissociation of HI?

5. Variation of equilibrium constant K with temperature T is given by Van't Hoff equation

$$\log K = \log A - \frac{\Delta H^0}{2.303 RT}$$

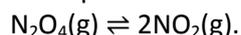
A graph between  $\log K$  and  $T^{-1}$  was a straight line as shown and having  $OP = 10$  and  $\tan \theta = 0.5$ .

Calculate

(i) equilibrium constant at 298 K, and

(ii) and equilibrium constant at 798 K, assuming  $\Delta H^0$  to be independent of temperature

6. The density of an equilibrium mixture of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  at 1 atm. And 348 K is  $1.84 \text{ gdm}^{-3}$ . Calculate the equilibrium constant of the reaction



### Objective

1. At a certain temperature 2 moles of carbonmonoxide and 3 moles of chlorine were allowed to reach equilibrium according to the reaction  $\text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2$  in a 5 lit vessel. At equilibrium if one mole of CO is present then equilibrium constant for the reaction is:

(A) 2

(B) 2.5

(C) 3.0

(D) 4

2.  $K_p$  for the reaction:  $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$  is found to be 16 at a given temperature. Originally equal numbers of moles of  $\text{H}_2$  and  $\text{CO}_2$  were placed in the flask. At equilibrium, the pressure of  $\text{H}_2$  is 1.20 atm. What is the partial pressure of  $\text{CO}$  and  $\text{H}_2\text{O}$ ?

- (A) 4.80 atm each (B) 9.60 atm each  
(C) 2.40 atm each (D) 1.20 atm each

3.  $K_c$  for the reaction  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$  is  $4.0 \times 10^{-6}$  at 400 K.  $K_p$  for the above reaction is

- (A)  $2.4 \times 10^{-3}$  (B)  $4.0 \times 10^{-6}$   
(C)  $4.0 \times 10^{-6} \times (\text{RT})^2$  (D) none of these

4.  $K_c$  for the reaction

$\text{A}_{(\text{g})} + \text{B}_{(\text{g})} \rightleftharpoons \text{C}_{(\text{g})} + \text{D}_{(\text{g})}$ , is 20 at  $25^\circ \text{C}$  if a container contains 1,2,4,5 moles per litre of  $\text{A}_{(\text{g})}$ ,  $\text{B}_{(\text{g})}$ ,  $\text{C}_{(\text{g})}$

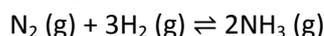
and  $\text{D}_{(\text{g})}$  respectively at  $25^\circ \text{C}$ , then the reaction shall

- (A) proceed from left to right  
(B) proceed from right to left  
(C) be at equilibrium  
(D) None of the above

5. When a sulphur in the form of  $\text{S}_8$  is heated at 900 K, the initial pressure of one atm falls by 29% at equilibrium.

- (A)  $1.16 \text{ atm}^3$  (B)  $0.71 \text{ atm}^3$  (C)  $2.55 \text{ atm}^3$  (D)  $5.1 \text{ atm}^3$

6. for the reversible reaction



At  $500^\circ \text{C}$ , the rate of  $K_p$  is  $1.44 \times 10^{-5}$  when partial pressure is measured in atmosphere. The corresponding value of  $K_c$  with concentration in mol/L is

- (A)  $\frac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$  (B)  $\frac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$   
(C)  $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^2}$  (D)  $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$

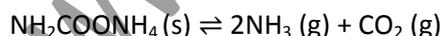
7. At temperature T, a compound  $\text{AB}_2(\text{g})$  dissociates according to the reaction



With degree of dissociation x, which is small compared with unity. The expression for x in terms of the equilibrium constant  $K_p$  and total pressure P is

- (A)  $x = \left(\frac{2K_p}{P}\right)^{1/3}$  (B)  $x = \left(\frac{2P}{K_p}\right)^{1/3}$   
(C)  $x = \left(\frac{2K_p}{P}\right)^{1/2}$  (D)  $\left(\frac{2K_p}{P}\right)$

8. Ammonium carbonate dissociates as

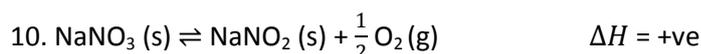


In a closed vessels containing ammonium carbonate ammonium carbonate in equilibrium, ammonia is added such that partial pressure of  $\text{NH}_3$  now equals to original total pressure. Calculate the ratio of total pressure now the original pressure.

- (A)  $\frac{35}{25}$  (B)  $\frac{25}{35}$  (C)  $\frac{31}{27}$  (D)  $\frac{27}{30}$

9. The reaction:  $3\text{O}_2 \rightleftharpoons 2\text{O}_3$ ,  $\Delta H = +69,000$  calories is favoured by:

- (A) high temperature and low pressure  
(B) high temperature and high pressure  
(C) low temperature and high pressure  
(D) low temperature and low pressure



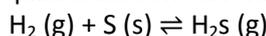
When  $\text{NaNO}_3$  is heated in a closed vessel, oxygen is liberated and  $\text{NaNO}_2$  is left behind. At equilibrium:

- (A) addition of  $\text{NaNO}_2$  favors reverse reaction
- (B) addition of  $\text{NaNO}_3$  favors forward reaction
- (C) increasing temperature favours forward reaction
- (D) decreasing pressure favours reverse reaction

11. The  $K_p$  of a reaction is 10 atm at 300K and 4 atm at 400K. the incorrect statement about the reaction is

- (A) the reaction is exothermic.
- (B) The  $E_a$  of forward reaction is more than that of backward reaction.
- (C) The rate of backward reaction increases more than that of forward reaction with increase of temperature.
- (D) The difference between heat of reaction at constant pressure and that at constant volume is  $RT$ .

12. The equilibrium constant for the reaction,



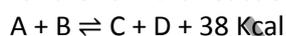
is 18.5 at 925 K and 9.25 at 1000 K respectively. Calculate the enthalpy of the reaction.

- (A) -10.20 kJ/mole
- (B) -7.18 kJ/mole
- (C) -2.15 kJ/mole
- (D) -4.30 kJ/mole

13. The enthalpies of two reaction are  $\Delta H_1$  and  $\Delta H_2$  (Both positive) with  $\Delta H_2 > \Delta H_1$ . If the temperature of reacting system is increased from  $T_1$  to  $T_2$ , predict which of the following alternatives is correct? ( $K_1, K_1'$  are eqbm. Constants for reaction 1 to  $T_1, T_2$  and  $K_2, K_2'$  are eqbm. Constants for reaction 2 at  $T_1, T_2$ .)

- (A)  $\frac{K_1'}{K_1} = \frac{K_2'}{K_2}$
- (B)  $\frac{K_1'}{K_1} > \frac{K_2'}{K_2}$
- (C)  $\frac{K_1'}{K_1} > \frac{K_2'}{K_2}$
- (D) None of these

14. The equilibrium constant at  $323^\circ \text{C}$  is 1000. What would be its value in the presence of a catalyst for the forward reaction?



- (A) 1000 x concentration of catalyst
- (B) 1000
- (C)  $\frac{1000}{\text{concentration of catalyst}}$
- (D) impossible to tell

15. A schematic plot of the  $K_{eq}$  vs inverse of temperature for a reaction is shown in the figure. The reaction must be

- (A) exothermic
- (B) endothermic
- (C) one with negligible enthalpy change
- (D) highly spontaneous at ordinary temperature

### Assignments

#### Section – 1

#### Part – A (Level – I)

- Why sealed soda water bottle on opening shows the evolution of gas with effervescence?
- for a gas phase reaction for which  $\Delta n_{gaseous} = 2$ . Unit of  $K_p$  is .....

- High pressure is favourable for those reversible reactions in which there is ..... in the number of molecules.
- Suggest four ways in which the concentration of hydrazine,  $N_2H_4$ , could be increase in an  $N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g)$   $\Delta H = 95 \text{ kJ}$
- Explain why an equilibrium between  $Br_2(l)$   $Br_2(g)$  would not be established if the bottle cap were removed from the bottle containing both these components.
- Higher the activation energy of a reaction, slower is the rate of reaction. [True/ false]
- Low pressure is favourable for melting of ice. [True/ False]
- The reactions having higher value of  $K_c$  are faster than the reactions having lower value of  $K_c$ , [True/ false]
- ice melts slowly at higher altitude, why?
- Under what vapour pressure of moisture in atmospheric conditions  $CuSO_4 \cdot 5H_2O$  will be efflorescent if  $CuSO_4 \cdot 5H_2O(s) + 2H_2O(g)$ ,  $K_p = 62.73 \text{ mm}^2$  of Hg.

## Level II

- The reaction  $2SO_2 + O_2 \rightleftharpoons 2SO_3$  is made to take place at  $t^\circ \text{C}$  in a closed vessel of 1 litre capacity and allowed to attain equilibrium. The equilibrium mixture contains 48 g  $SO_3$ , 12.8 g  $SO_2$  and 9.6 g of  $O_2$ . Determine  $K_c$ .
- One mole of  $H_2$ , 2 mol of  $I_2$  and 3 mol of  $HI$  are injected in a 1 litre flask. What will be the concentration of  $H_2$ ,  $I_2$  and  $HI$  at equilibrium?  $K_c$  for the equilibrium,  $H_2(g) + I_2(g) \rightleftharpoons 2HI$  is 45.9.
- 15 g sample of  $BaO_2$  is heated to  $794^\circ \text{C}$  in a closed evacuated vessel of 5 litres capacity. How many g of peroxide are converted to  $BaO(s)$ .  
 $2BaO_2(s) \rightleftharpoons 2BaO(s) + O_2(g)$ ,  $K_p = 0.5 \text{ atm}$ .
- Consider the vapour phase dissociation of an oxoacid  $HXO_3$  according to the equation:  
 $4HXO_3(g) \rightleftharpoons 4XO_2(g) + 2H_2O(g) + O_2(g)$ . Derive the expression:  $K_p = \dots \dots \dots$ ,  
Where  $P$  is the total pressure and  $P_{O_2}$  is partial pressure of  $O_2$ .
- $PCl_5(g)$  at  $500^\circ \text{K}$  at an initial pressure of 600 mm Hg dissociates as:  $PCl_5 \rightleftharpoons PCl_3 + Cl_2$  and the equilibrium pressure is 800 mm Hg at 500K. calculate  $K_p$  for the reaction assuming that no change in volume takes place.
- sulphide ions in alkaline solution react with solid sulphur to form polyvalent sulphide ions. The equilibrium constant for the formation of  $S_2^{2-}$  and  $S_3^{2-}$  from  $S$  and  $S^{2-}$  ions are 1.7 and 5.3 respectively. Calculate equilibrium constant  $K_c$  for the formation of  $S_3^{2-}$  from  $S_2^{2-}$  and  $S$ .
- The  $K_c$  for  $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$  at  $100^\circ \text{C}$  is 0. If one litre flask containing one mole of  $A_2$  is connected with a two litre flask containing 2 mole of  $B_2$ , how many moles of  $AB$  will be formed at  $100^\circ \text{C}$ ?
- At  $90^\circ \text{C}$  the following equilibrium is established,  $H_2(g) + S(s) \rightleftharpoons H_2S(g)$   $K = 6.8 \times 10^{-2}$  if 0.20 mole of hydrogen and 1.0 mol of sulphur are heated at  $90^\circ \text{C}$  in a 1.0 L vessel, what will be the partial pressure of  $H_2S$  at equilibrium?
- Solid ammonium carbonate decomposed according to the equation:  
 $(NH_4)_2 CO_3(s) \rightleftharpoons 2NH_3(g) + CO_2(g) + H_2O(g)$   
At a certain elevated temperature, the total pressure of the gases generated was 0.42 atm. At equilibrium. Calculate the equilibrium constant for the reaction.
- if a given quantity of phosphorus pentachloride is heated at  $250^\circ \text{C}$  and allowed to come to equilibrium at atmospheric pressure it is found to be dissociated to the extent of 80% into phosphorous trichloride and chlorine. If now, the pressure on this mixture is increased so that finally the equilibrium mixture occupies only one half of its original volume (temperature maintained constant).

- (i) what will be the % dissociation at the new pressure?  
(ii) What will be the effect of adding He gas keeping the volume fixed at V/2.
11. For the equilibrium  $\text{LiCl} \cdot 3\text{NH}_3(\text{s}) \rightleftharpoons \text{LiCl} \cdot \text{NH}_3(\text{s}) + 2\text{NH}_3$ ,  $K_p = 9\text{atm}^2$  at  $40^\circ\text{C}$ . A 5 litre vessel contains 0.1 mole  $\text{LiCl} \cdot \text{NH}_3$ . how many moles of  $\text{NH}_3$  would be added to the flask at the temperature to drive the backward reaction for nearly completion?
12. A sample of air consisting of  $\text{N}_2$  and  $\text{O}_2$  was heated to 2500 K until the equilibrium  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$  was established with an equilibrium constant  $K_c = 2.1 \times 10^{-3}$ . At equilibrium, the mole % of NO was 1.8. Estimate the initial composition of air in mole fraction of  $\text{N}_2$  and  $\text{O}_2$ .
65. in reaction:  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ , what will be the value of  $K_c$  at  $35^\circ\text{C}$  if  $\text{N}_2\text{O}_4$  is dissociated to the extent of 20% under a pressure of 1 atmosphere.
13. what is the vapour density of mixture of  $\text{PCl}_5$  at  $250^\circ\text{C}$  when it has dissociated to the extent of 80%.
14. Two solids components A and B dissociate into gaseous products at  $20^\circ\text{C}$  as  
(i)  $\text{A}(\text{s}) \rightleftharpoons \text{A}'(\text{g}) + \text{H}_2\text{S}(\text{g})$   
(ii)  $\text{B}(\text{s}) \rightleftharpoons \text{B}'(\text{g}) + \text{H}_2\text{S}(\text{g})$   
At  $20^\circ\text{C}$ , pressure over excess solid A is 50 mm Hg and that over excess solid B is 68 mm Hg. Find  
(i) The dissociation constants of A and B  
(ii) Ratio of number of moles of A' and B' in the vapour phase over a mixture of solids A and B  
(iii) The total pressure of gas over the solid mixture.

**Part – II**  
**(Multiple Choice Question)**  
**(single Option Correct)**

1. For the reaction,  $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ , which of the following facts hold good?  
(a)  $K_p = K_c$   
(b)  $K_p > K_c$   
(c)  $K_p < K_c$   
(d)  $K_p$  and  $K_c$  can not be correlated unless pressure of the system is given.
2. For the reaction  $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$ , the value of  $K_p$  at  $250^\circ\text{C}$  is  $0.61\text{atm}^{-1}$ . The value of  $K_c$  at this temperature will be  
(A)  $15(\text{mol/l})^{-1}$  (B)  $26.19(\text{mol/l})^{-1}$  (C)  $35(\text{mol/l})^{-1}$  (D)  $52(\text{mol/l})^{-1}$
3. for the reaction  $2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_5(\text{g})$  if the equilibrium constant  $K_p$ , then the equilibrium constant for the reaction  $2\text{N}_2\text{O}_5 \rightleftharpoons 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  would be  
(A)  $K_p^2$  (B)  $2/K_p$  (C)  $1/K_p^2$  (D)  $1/\sqrt{K_p}$
4. For the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ , the equilibrium constant  $K_p$  changes with  
(A) total pressure (B) catalyst  
(C) the amount amounts of  $\text{H}_2$  and  $\text{I}_2$  present (D) temperature
5. The equilibrium constant for the reaction  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$  is  $4 \times 10^{-4}$  at 200 K. in the presence of a catalyst the equilibrium is attained 10 times faster. Therefore the equilibrium constant in presence of the catalyst at 200 K is  
(A)  $4 \times 10^{-3}$  (B)  $4 \times 10^{-4}$  (C)  $4 \times 10^{-5}$  (D) None
6. For the reaction  $\text{Cu}(\text{s}) + 2\text{Ag}^+(\text{aq}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$  the equilibrium constant,  $K_c$  is given by  
(A)  $\frac{[\text{Cu}^{2+}][\text{Ag}]^2}{[\text{Cu}][\text{Ag}^+]^2}$  (B)  $\frac{[\text{Cu}][2\text{Ag}]}{[\text{Cu}^{2+}][2\text{Ag}^+]}$   
(C)  $\frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$  (D)  $\frac{[\text{Ag}^+]^2}{[\text{Cu}^{2+}]}$

7. In the gas phase reaction  $C_2H_4 + H_2 \rightleftharpoons C_2H_6$ , the equilibrium constant can be expressed in units  
 (A)  $l^{-1} \text{ mole}^{-1}$  (B)  $\text{lit mole}^{-1}$  (C)  $\text{mole}^2 \text{ lit}^{-2}$  (D)  $\text{mole lit}^{-1}$
8. for the reaction  $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$  the partial pressure of  $CO_2$  and  $CO$  are 2.0 and 4.0 atm respectively at equilibrium. The  $K_p$  for the reaction is  
 (A) 0.5 (B) 4.0 (C) 8.0 (D) 32.0
9.  $CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O$ . In this reaction one mole each of acetic acid and ethyl alcohol are heated in presence of little conc.  $H_2SO_4$ . On equilibrium being attained the value of  $K_c$  is 4. What amount of ethyl acetate is formed?  
 (A) 88 g (B) 176 g (C) 29.33 g (D) 58.67 g
10. For  $N_2 + 3H_2 \rightleftharpoons 2NH_3 + \text{heat}$   
 (A)  $K_p = K_c$  (B)  $K_p = K_c RT$  (C)  $K_p = K_c (RT)^{-2}$  (D)  $K_p = K_c (RT)^{-1}$
11. One mole of ethanol is treated with one mole of ethanoic acid at  $25^\circ \text{C}$ . One-fourth of the acid changes into ester at equilibrium. The equilibrium constant for the reaction will be  
 (A)  $1/9$  (B)  $4/9$  (C) 9 (D)  $9/4$
12. Given the following reaction at equilibrium:  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$   
 Some inert gas is added at constant volume. Predict which of the following facts will be affected?  
 (A) more of  $NH_3(g)$  is produced  
 (B) less of  $NH_3(g)$  is produced  
 (C) no effect on the degree of advancement of the reaction at equilibrium  
 (D)  $K_p$  of the reaction is increased
13. For which reaction high pressure and high temperature is helpful in obtaining a high equilibrium yield;  
 (A)  $2NF \rightleftharpoons N_2(g) + 3F_2(g) - 54.40 \text{ kcal}$   
 (B)  $N_2(g) + 3H_2 \rightleftharpoons 2NH_3(g) + 22.08 \text{ kcal}$   
 (C)  $Cl_2(g) + 2O_2(g) \rightleftharpoons 2ClO_2(g) - 49.40 \text{ kcal}$   
 (D)  $2Cl_2O_7(g) \rightleftharpoons 2Cl_2(g) + 7O_2(g) + 126.8 \text{ kcal}$
14. for the gas phase reaction  $C_2H_4(g) \rightleftharpoons C_2H_6(g)$ ;  $\Delta H = -32.7 \text{ kcal}$  carried out in a vessel, the equilibrium concentration of  $C_2H_4$  can be increased by  
 (A) increasing temperature (B) decreasing temperature  
 (C) removing some  $H_2$  (D) All of the above
15. For the reaction:  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ;  $\Delta H = -ve$   
 The formation  $NH_3$  is favoured at  
 (A) High pressure and low temperature  
 (B) low pressure and high temperature  
 (C) low pressure and low temperature  
 (D) high pressure and high temperature
16. For the reaction  $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ , the pressure of  $CO_2(g)$  depends on  
 (A) the mass of  $CaCO_3(s)$   
 (B) the mass of  $CaO(s)$   
 (C) the masses of both  $CaCO_3(s)$  and  $CaO(s)$   
 (D) temperature of the system
17. for the decomposition reaction:  $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$   
 The  $K_p = 2.9 \times 10^{-5} \text{ atm}^3$ . The total pressure of gases at equilibrium when 1 mole of  $NH_2COONH_4(s)$  was taken to start with would be

- (A) 0.0194 atm (B) 0.0388 atm  
(C) 0.0582 atm (D) 0.0766 atm

18. During thermal dissociation of a gas, the vapour density

- (A) remains the same  
(B) increase  
(C) decreases  
(D) increase in some cases and decrease in other

19. The equilibrium constant for the reaction  $\text{Br}_2 \rightleftharpoons 2\text{Br}$  at 500 K and 700 K are  $1 \times 10^{-10}$  and  $1 \times 10^{-5}$  respectively. The reaction is

- (A) endothermic (B) exothermic (C) fast (D) slow

20. The relationship between  $K_p$  and  $K_c$  is correctly shown as

- (A)  $K_c = K_p(RT)^{\Delta n}$  (B)  $K_p = K_c(RT)^{-\Delta n}$  (C)  $K_p = K_c(RT)^{\Delta n}$   
(D)  $K_c = K_p(RT)^{-\Delta n}$

21. The equilibrium constant of the reaction  $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SO}_3$  and  $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$  are  $K_1$  and  $K_2$  respectively. The relationship between  $K_1$  and  $K_2$  is

- (A)  $K_1 = K_2$  (B)  $K_2 = K_1^2$  (C)  $K_1 = \sqrt{K_2}$  (D)  $K_2 = \sqrt{K_1}$

22. Which of the following statement is/are correct for a reversible reaction?

- (A) Reaction quotient (Q) is the ratio of the product of arbitrary molar concentrations of the products to that of reactants  
(B) Q may be  $\leq K$   
(C) At a given temperature both Q and K vary with reaction progress  
(D) When  $Q > K$ , the reaction proceeds to backward direction before coming to stand still.

23. Which of the following will not affect the value of equilibrium constant of a reaction?

- (A) change in concentration of the reaction  
(B) change in temperature  
(C) change in pressure  
(D) addition of catalyst

24. Which of the following statement(s) is (are) wrong?

- (A) at equilibrium concentration of reactant and product become constant because the reaction stops  
(B) addition of catalyst speeds up the forward reaction more than the backward reaction  
(C) equilibrium constant of an exothermic reaction decreases with increase of temperature  
(D)  $K_p$  is always greater than  $K_c$

25. for the following two reaction equilibrium constants are given

- (i)  $\text{A (g)} + \text{B (g)} \rightleftharpoons \text{C (g)} + \text{D (g)}$   $K_1 = 1/3$   
(ii)  $\text{E (g)} + 2\text{B (g)} \rightleftharpoons \text{C (g)} + 4\text{D (g)}$   $K_2 = 6$

The equilibrium constant for the reaction

- (iii)  $\text{A (g)} + 3\text{B (g)} + \text{E (g)} \rightleftharpoons 2\text{C (g)} + 5\text{D (g)}$

26. Compound X dissociates according to the reaction  $2\text{X (g)} \rightleftharpoons 2\text{Y (g)} + \text{Z (g)}$  with degree of dissociation  $\alpha$  which is small compared with unity, if expression for  $\alpha$  in terms of equilibrium constant  $K_p$  and total pressure P is given as  $\alpha = \left(\frac{2K_p}{P}\right)^{1/n}$ . The value of n is

## COMPREHENSION TYPE

Read the paragraph carefully and answer the following questions

Bodenstein carried out the determination of equilibrium constant of phosgene equilibrium by introduction CO and Cl<sub>2</sub> at known pressure in a reaction bulb and measuring the equilibrium pressure from the attached monometer. In one experiment, CO at 342 mm and Cl<sub>2</sub> at 351.4 mm were introduced. The equilibrium pressure was found to be 439.5 mm. At equilibrium if partial pressure of COCl<sub>2</sub> is 'x' mm at 127° C.

Reaction is:  $\text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2$

- (i) Value of x is  
(A) 88.1 mm (B) 97.5 mm (C) 253.9 mm (D) 351.4 mm
- (ii) The K<sub>p</sub> for the above reaction is;  
(A) 0.029 atm<sup>-1</sup> (B) 760mm<sup>-1</sup> (C) 22.5 atm<sup>-1</sup> (D) 29.5 atm
- (iii) The volume of reacting vessel is decreased by 3 times, K<sub>p</sub> changes by:  
(A) 3 times increased (B) remains constant  
(C)  $\frac{1}{3}$  times decreased (D)  $\frac{1}{9}$  times increased

## MATCHING

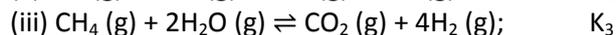
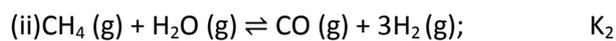
Match the following reaction in list – 1 with the factors in list – 2

List – 1	List – 2
(A) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ (Exothermic)	(p) Forward shift by rise in pressure
(B) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ (Exothermic)	(q) unaffected by change in pressure
(C) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ (Endothermic)	(r) Forward shift by rise in temperature
(D) $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$ (Endothermic)	(s) Forward shift by lowering the temperature
	(t) Backward shift by increasing the volume

## Section - II

1. One mole of N<sub>2</sub>O<sub>4</sub> (g) at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of N<sub>2</sub>O<sub>4</sub>(g) decompose to NO<sub>2</sub>(g). the resultant pressure is  
(A) 1.2 atm (B) 2.4 atm (C) 2.0 atm (D) 1.0 atm
2. At constant temperature, the equilibrium constant (K<sub>p</sub>) for the decomposition reaction  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$  is expressed by  $K_p = (4x^2 p)/(1-x^2)$ , where P = pressure, the following statements is true?  
(A) K<sub>p</sub> increases with increase of P  
(B) K<sub>p</sub> increases with increases of x  
(C) K<sub>p</sub> increases with decreases of x  
(D) K<sub>p</sub> remains constant with change in P and x.
3. for which of the following reaction, K<sub>p</sub> = K<sub>c</sub>?  
(A)  $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$   
(B)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$   
(C)  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$   
(D)  $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$
4. The rate constant of a reaction depends on  
(A) temperature (B) Mass  
(C) density (D) time
5. for the chemical reaction  $3\text{X}(\text{g}) + \text{Y}(\text{g}) \rightleftharpoons \text{X}_3\text{Y}(\text{g})$ , the amount of X<sub>3</sub>Y at equilibrium is affected by

- (A) Temperature and pressure  
 (B) temperature only  
 (C) Pressure only  
 (D) temperature, pressure and catalyst
6. The rate at which a substance reacts depends on its  
 (A) atomic mass (B) equivalent mass  
 (C) molecular mass (D) active mass
7. For the equilibrium,  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$   
 The forward reaction at constant temperature is favoured by  
 1. introducing an inert gas at constant volume  
 2. introducing chlorine gas at constant volume  
 3. introducing an inert gas at constant pressure  
 4. increasing the volume of the container  
 5. introducing  $\text{PCl}_5$  at constant volume  
 (A) 1,2 (B) 4,5 (C) 2,3,4 (D) 3,4,5
8. The equilibrium  $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$  is attained at  $25^\circ\text{C}$  in a closed container and inert gas helium is introduced, which of the following statements (s) is/are correct?  
 1. concentration of  $\text{SO}_2$ ,  $\text{Cl}_2$  and  $\text{SO}_2\text{Cl}_2$  change  
 2. more chlorine is formed  
 3. concentration of  $\text{SO}_2$  is reduced  
 4. More  $\text{SO}_2\text{Cl}_2$  is formed  
 (A) 1,2,3 (B) 2,3,4 (C) 3,4 (D) None
9. In what manner will increase of pressure affect the following equation?  
 $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$   
 (A) shift in the forward direction  
 (B) shift in the reverse direction  
 (C) increase in the yield of hydrogen  
 (D) No effect
10. the decomposition of phosgene  
 $\text{COCl}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$   
 Is an endothermic process. Which of the following factors will cause the value of equilibrium constant to increase?  
 (A) Adding  $\text{Cl}_2$  (B) Adding  $\text{He}(\text{g})$   
 (C) increasing the temperature  
 (D) Decreasing the total pressure
11.  $\text{KNO}_3(\text{s})$  dissociates on heating as  
 $\text{KNO}_3(\text{s}) \rightleftharpoons \text{KNO}_2(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \quad \Delta H = -ve$   
 At equilibrium in a closed container  
 (A) addition of  $\text{KNO}_3(\text{s})$  favours forward reaction  
 (B) addition of  $\text{KNO}_2(\text{s})$  favours reverse reaction  
 (C) increasing temperature favours forward reaction  
 (D) decreasing pressure favours reverse reaction
12. for the following three reaction (i), (ii) and (iii), equilibrium constants are given:  
 (i)  $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g}); \quad K_1$



Which of the following relation is correct?

(A)  $K_3 K_2^3 = K_1^2$

(B)  $K_1 \sqrt{K_2} = K_3$

(C)  $K_2 K_3 = K_1$

(D)  $K_3 = K_1 K_2$

13. for the reaction



Which one is correct representation?

(A)  $K_p = \dots\dots$

(B)  $\dots\dots\dots$

(C)  $K_p = K_c (RT)^2$

(D) All of these

14. the molecular weight of  $\text{PCl}_5$  is 208.32 but when heated to  $230^\circ\text{C}$ , it is reduced to 124. The extent of dissociation of  $\text{PCl}_5$  at this temperature will be

(A) 6.8%

(B) 68%

(C) 46%

(D) 64%

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