EXERCISE-01 CHECK YOUR GRASP

SELECT THE CORRECT ALTERNATIVE (ONLY ONE CORRECT ANSWER)

1. In a reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ degree of dissociation is 30%. If initial moles of PCl_5 is one then total moles at equilibrium is

(A) 1.3 (B) 0.7 (C) 1.6 (D) 1.0

2. For reaction $HI \rightleftharpoons \frac{1}{2} H_2 + \frac{1}{2} I_2$ value of K_c is 1/8 then value of K_c for $H_2 + I_2 \rightleftharpoons 2HI$.

(A) $\frac{1}{64}$ (B) 64 (C) $\frac{1}{8}$ (D) 8

3. In a equilibrium reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$\Delta H = -3000$ calories,

which factor favours dissociation of HI :-

(A) Low temp. (B) High Pressure (C) High temp. (D) Low pressure.

4. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

If temp. of following equilibrium reaction increase then -

(A) Shift Right side (B) Shift left side (C) Unchanged (D) Nothing say.

5. $C(s) + H_2O(g) \rightleftharpoons H_2(g) + CO(g)$

by increasing pressure following equilibrium

(A) Unaffected (B) Proceed in backward direction

(C) Proceed in forward direction (D) Unfixed

6. Unit of equilibrium constant K_c for following homogenous reaction :-

$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$ is

(A) $(Conc^n)^{-1}$ (B) $(Conc^n)^{+1}$ (C) $(Conc^n)^{+10}$ (D) Have no unit

7. Which of the following factor shifted the reaction $PCl_3 + Cl_2 \rightleftharpoons PCl_5$ at left side.

(A) Adding PCl_5 (B) Increase pressure (C) Constant temp. (D) Catalyst.

8. In which of the following process reaction is fastest complete.

(A) K = 10 (B) K = 1 (C) $K = 10^3$ (D) $K = 10^{-2}$

9. At 298 K equilibrium constant K_1 and K_2 of

following reaction $SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g)$ ----- (1)

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

The relation between K_1 and K_2 is

(A) $K_1 = K_2$ (B) $K_2 = K_1^2$ (C) $K_2 = 1/K_1^2$ (D) $K_2 = 1/K_1$

10. In the following reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ at constant temp. rate of backward reaction is increase by :

(A) Inert gas mixed at constant volume (B) Cl_2 gas mixed at constant volume

(C) Inert gas mixed at constant pressure (D) PCl_5 mixed in constant volume.

11. Some gaseous equilibrium are following :

$$CO + H_2O \overset{K}{\rightleftharpoons} CO_2 + H_2$$

$$2CO + O_2 \overset{K_1}{\rightleftharpoons} 2CO_2$$

$$2H_2 + O_2 \overset{K_2}{\rightleftharpoons} 2H_2O$$

then find out the relation between equilibrium constants :-

(A) $K = K_1K_2$ (B) $K = (K_1K_2)^2$ (C) $K = (K_1K_2)^{-1/2}$ (D) $K = (K_1/K_2)^{1/2}$

12. For the equilibrium process x + y $\rightleftharpoons$ xy. If the concⁿ. of x and y is doubled, then equilibrium constant.

(A) Become twice (B) Become half (C) Unchanged (D) Become thrice

13. Two moles of PCl_5 were heated in closed vessel of 2 litre capacity, at equilibrium 40% of PCl_5 was dissociated into PCl_3 and Cl_2. The value of equilibrium constant is :

(A) .267 (B) .53 (C) 2.67 (D) 5.3

14. The reaction A(g) + B(g) $\rightleftharpoons$ 2C(g) is occur by mixing of 3 moles of A and 1 mole of B in one litre Container. if α of B is $\frac{1}{3}$, then K_C for this reaction is :-

(A) 0.12 (B) 0.25 (C) 0.50 (D) 0.75

15. Reaction $2BaO_2(s) \rightleftharpoons 2BaO(s) + O_2(g)$; $\Delta H = +ve$. At equilibrium condition, Pressure of O_2 is depends on :-

(A) Increase mass of BaO_2

(B) Increase mass of BaO

(C) Increase temp. at Eq^m.

(D) Increase mass of BaO_2 and BaO both

16. Consider the following equilibrium in a closed container $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements held true regarding the equilibrium constant (K_p) and degree of dissociation (α) :-

(A) Neither K_p nor α changes

(B) Both K_p and α- changes

(C) K_p changes, but α does not change

(D) K_p does not change, but α - changes

17. $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$

According to above reaction, partial Pressure of CO_2 & CO are 4 & 8 respectively then find out K_p of the above reaction :-

(A) 6 (B) 2 (C) 16 (D) 32

18. For the reaction, A+B $\rightleftharpoons$ C + D, $K_c = 9$. If A and B are taken in equal amounts, then amount of C at equilibrium is :-

(A) 1 (B) 0.25 (C) 0.75 (D) None of these

19. At equilibrium 500mL vessel contains 1 5 M of each A, B, C, D. If 0 5M of C and D expelled out then what would be the K_C :-

(A) 1 (B) $\frac{1}{9}$ (C) $\frac{4}{9}$ (D) $\frac{5}{9}$

20. The following equilibrium are given

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ -------------- K_1

$N_2 + O_2 \rightleftharpoons 2NO$ -------------- K_2

$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$ -------------- K_3

The equilibrium constant of the reaction

$2NH_3 + \frac{5}{2}O_2 \rightleftharpoons 2NO + 3H_2O$, in terms of K_1, K_2 and K_3 is :

(A) $\frac{K_1K_2}{K_3}$ (B) $\frac{K_1K_3^2}{K_2}$ (C) $\frac{K_2K_3^3}{K_1}$ (D) $K_1K_2K_3$

21. The reaction A + B $\rightleftharpoons$ C + D is studied in a one litre vessel at 250 C. The initial concentration of A was 3n and that of B was n. When equilibrium was attained, equilibrium concentration of C was found to the equal to the equilibrium concentration of B. What is the concentration of D at equilibrium :

(A) n/2 (B) (3n – 1/2) (C) (n – n/3) (D) n

22. In a reversible reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$, the initial concentration of A and B are a and b in moles per litre and the equilibrium concentration are (a – x) and (b + x) respectively ; express x in terms of k_1, k_2, a and b :

(A) $\frac{k_1a - k_2b}{k_1 + k_2}$ (B) $\frac{k_1a - k_2b}{k_1 - k_2}$ (C) $\frac{k_1a - k_2b}{k_1k_2}$ (D) $\frac{k_1a + k_2b}{k_1 + k_2}$

23. The value of K_p for the reaction

$2H_2O\,(g) + 2Cl_2O\,(g) \rightleftharpoons 4HCl\,(g) + O_2\,(g)$

is 0.03 atm at 427 C, when the partial pressure are expressed in atmosphere then the value of K_C for the same reaction is :

(A) 5.23 10^{-4} (B) 7.34 10^{-4} (C) 3.2 10^{-3} (D) 5.43 10^{-5}

24. The equilibrium constant of the reaction $SO_2\,(g) + \frac{1}{2}O_2\,(g) \rightleftharpoons SO_3\,(g)$ is 4 $10^{-3}\,atm^{-1/2}$. The equilibrium constant of the reaction $2\,SO_3\,(g) \rightleftharpoons 2\,SO_2\,(g) + O_2\,(g)$ would be :

(A) 250 atm (B) 4 10^3 atm (C) 0.25 10^4 atm (D) 6.25 10^4 atm

25. When alcohol (C_2H_5OH) and acetic acid are mixed together in equimolar ratio at 27 C, 33% is converted into ester. Then the K_C for the equilibrium :

$C_2H_5OH\,(\ell) + CH_3COOH\,(\ell) \rightleftharpoons CH_3COOC_2H_2\,(\ell) + H_2O\,(\ell)$

(A) 4 (B) 1/4 (C) 9 (D) 1/9

26. 2 moles each of SO_3, CO, SO_2 and CO_2 is taken in a one lit. vessel. If K_C for $SO_3 + CO \rightleftharpoons SO_2 + CO_2$ is 1/9 then :

(A) total no. of moles at equilibrium are less than 8

(B) n (SO_3) + n(CO_2) = 4

(C) [n(SO_2)/n (CO)] < 1

(D) both (B) and (C)

27. An equilibrium mixture in a vessel of capacity 100 litre contain 1 mol N_2, 2 mol O_2 and 3 mol NO. No. of moles of O_2 to be added so that at new equilibrium the conc. of NO is found to be 0.04 mol/lit :

(A) (101/18) (B) (101/9) (C) (202/9) (D) None of these

28. Ammonia gas at 15 atm is introduced in a rigid vessel at 300 K. At equilibrium the total pressure of the vessel is found to be 40.11 atm at 300 C. The degree of dissociation of NH_3 will be :

(A) 0.6 (B) 0.4 (C) unpredictable (D) none of these

29. The degree of dissociation of SO_3 is α at equilibrium pressure P_0:

Kp for $2SO_3\,(g) \rightleftharpoons 2SO_2\,(g) + O_2\,(g)$

(A) $[(P_0\alpha^3)/2(1 - \alpha)^3]$ (B) $[(P_0\alpha^3)/(2 + \alpha)(1-\alpha)^2]$ (C) $[(P_0\alpha^2)/2(1 - \alpha)^2]$ (D) none of these

30. For the reaction $CO(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)$ at a given temperature the equilibrium amount of $CO_2\,(g)$ can be increased by :

(A) adding a suitable catalyst (B) adding an inert gas

(C) decreasing the volume of container (D) increasing the amount of CO (g)

31. For the reaction :

$PCl_5\,(g) \rightarrow PCl_3\,(g) + Cl_2\,(g)$

The forward reaction at constant temperature is favoured by

(A) introducing an inert gas at constant volume (B) introducing chlorine gas at constant volume

(C) introducing an inert gas at constant pressure (D) increasing the volume of the container

(E) introducing PCl_5 at constant volume

32. Given the following reaction at equilibrium $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$. Some inert gas at constant pressure is added to the system. Predict which of the following facts will be affected :

(A) more $NH_3\,(g)$ is produced
(B) less $NH_3\,(g)$ is produced
(C) no affect on the equilibrium
(D) K_p of the reaction is decreased

33. For an equilibrium $H_2O\,(s) \rightleftharpoons H_2O\,(\ell)$ which of the following statement is true :

(A) the pressure changes do not affect the equilibrium
(B) more of ice melts if pressure on the system is increased
(C) more of liquid freezes if pressure on the system is increase
(D) the pressure changes may increase or decrease the degree of advancement of the reaction depending upon the temperature of the system.

34. When a bottle of cold drink is opened, the gas comes out with a fizze due to :

(A) decrease in temperature
(B) increase in pressure
(C) decrease in pressure suddenly which results in decrease of solubility of CO_2 gas in water
(D) none

35. The equilibrium, $SO_2Cl_2\,(g) \rightleftharpoons SO_2\,(g) + Cl_2\,(g)$ is attained at 25 C in a closed container and an inert gas, helium, is introduced. Which of the following statements are correct :

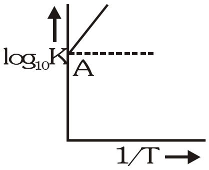
(A) concentrations of SO_2, Cl_2 and SO_2Cl_2 are changed
(B) no effect on equilibrium
(C) concentration of SO_2 is reduced
(D) K_p of reaction is increasing

36. For the reaction $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$

$K_C = 66.9$ at 350 C and $K_C = 50.0$ at 448 C. The reaction has :

(A) $\Delta H = +ve$
(B) $\Delta H = -ve$
(C) $\Delta H =$ Zero
(D) $\Delta H =$ Not found the signs

37. Variation of $\log_{10} K$ with $\frac{1}{T}$ is shown by the following graph in which straight line is at 45 , hence ΔH is :



(A) +4.606 cal
(B) –4.606 cal
(C) 2 cal
(D) – 2cal

CHECK YOUR GRASP						ANSWER KEY									EXERCISE -1
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	A	B	C	B	B	B	A	C	C	B	D	C	A	B	C
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	D	C	C	A	C	A	A	A	D	B	D	A	B	B	D
Que.	31	32	33	34	35	36	37								
Ans.	C,D,E	B	B	C	B	B	B								

EXERCISE–02 BRAIN TEASERS

SELECT THE CORRECT ALTERNATIVES (ONE OR MORE THEN ONE CORRECT ANSWERS)

1. Consider following reaction in equilibrium with equilibrium concentration 0.01 M of every species

(I) $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$

(II) $2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$

(III) $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

Extent of the reactions taking place is :

(A) I > II > III (B) I < II < III (C) II < III < I (D) III < I < II

2. For the reaction $3\,A\,(g) + B\,(g) \rightleftharpoons 2\,C\,(g)$ at a given temperature, $K_c = 9.0$. What must be the volume of the flask, if a mixture of 2.0 mol each of A, B and C exist in equilibrium?

(A) 6 L (B) 9 L (C) 36 L (D) None of these

3. Sulphide ion in alkaline solution reacts with solid sulphur to form polysulphide ions having formulae S_2^{2-}, S_3^{2-}, S_4^{2-} and so on. The equilibrium constant for the formation of S_2^{2-} is 12 (K_1) & for the formation of S_3^{2-} is 132 (K_2), both from S and S^{2-}. What is the equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S ?

(A) 11 (B) 12 (C) 132 (D) None of these

4. For the following gases equilibrium $N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$

K_p is found to be equal to K_c. This is attained when :

(A) 0 C (B) 273 K (C) 1 K (D) 12.19 K

5. 1 mole N_2 and 3 mol H_2 are placed in a closed container at a pressure of 4 atm. The pressure falls to 3 atm at the same temperature when the following equilibrium is attained

$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$. The equilibrium constant K_P for dissociation of NH_3 is :

(A) $\frac{1}{0.5}\times(1.5)^3\,\text{atm}^{-2}$ (B) $0.5\quad(1.5)^3\,\text{atm}^2$ (C) $\frac{0.5\times(1.5)^3}{3\times3}\,\text{atm}^2$ (D) $\frac{3\times3}{0.5\times(1.5)^3}\,\text{atm}^{-2}$

6. 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). The resultant pressure is :

(A) 1.2 atm (B) 2.4 atm (C) 2.0 atm (D) 1.0 atm

7. For the reaction : $2\,HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$, the degree of dissociation (α) of HI (g) is related to equilibrium constant K_P by the expression :

(A) $\frac{1+2\sqrt{K_P}}{2}$ (B) $\sqrt{\frac{1+2K_P}{2}}$ (C) $\sqrt{\frac{2K_P}{1+2K_P}}$ (D) $\frac{2\sqrt{K_P}}{1+2\sqrt{K_P}}$

8. The vapour density of N_2O_4 at a certain temperature is 30. What is the % dissociation of N_2O_4 at this temperature :

(A) 53.3% (B) 106.6% (C) 26.7% (D) None

9. For the reaction $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$, the forward reaction at constant temperature is favoured by :

(A) introducing an inert gas at constant volume

(B) introducing chlorine gas at constant volume

(C) introducing an inert gas at constant pressure

(D) introducing PCl_5 at constant volume

10. When N_2O_5 is heated at temp. T, it dissociates as $N_2O_5 \rightleftharpoons N_2O_3 + O_2$, $K_C = 2.5$. At the same time N_2O_3 also decomposes as : $N_2O_3 \rightleftharpoons N_2O + O_2$. If initially 4.0 moles of N_2O_5 are taken in 1.0 litre flask and allowed to attain equilibrium, concentration of O_2 was formed to be 2.5 M. Equilibrium concentration of N_2O is :

(A) 1.0 (B) 1.5 (C) 2.166 (D) 0.334

11. Densities of diamond and graphite are 3.5 and 2.3 g/mL.

C (diamond) $\rightleftharpoons$ C (graphite) $\Delta_r H = -1.9$ kJ/mole

favourable conditions for formation of diamond are :

(A) high pressure and low temperature

(B) low pressure and high temperature

(C) high pressure and high temperature

(D) low pressure and low temperature

12. When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left behind. At equilibrium:

(A) addition of $NaNO_2$ favours reverse reaction

(B) addition of $NaNO_3$ favours forward reaction

(C) increasing temperature favours forward reaction

(D) increasing pressure favours reverse reaction

13. The equilibrium SO_2Cl_2 (g) $\rightleftharpoons$ SO_2 (g) + Cl_2 (g) is attained at 25 C in a closed rigid container when an inert gas, helium is introduced. Which of the following statement is / are correct :

(A) concentrations of SO_2, Cl_2 and SO_2Cl_2 do not change

(B) more chlorine is formed

(C) concentration of SO_2 is reduced

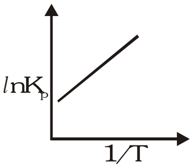
(D) more SO_2Cl_2 is formed

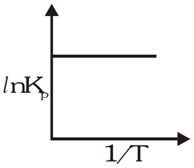
14. For the gas phase reaction, $C_2H_4 + H_2 \rightleftharpoons C_2H_6$ ($\Delta H = -32.7$ kcal), carried out in a closed vessel, the equilibrium moles of C_2H_4 can be increased by :

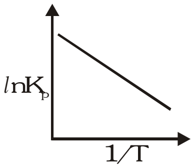
(A) increasing the temperature (B) decreasing the pressure

(C) removing some H_2 (D) adding some C_2H_6

15. An exothermic reaction is represented by the graph :

(A)


(B)


(C)


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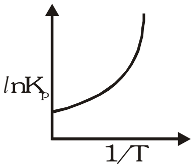


16. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K is :

(A) $-\Delta G = RT \ln K$ (B) $\Delta G = RT \ln K$ (C) $-\Delta G = RT \ln K$ (D) $\Delta G = RT \ln K$

17. The value of ΔG_f of gaseous mercury is 31 kJ/mole. At what external pressure mercury start boiling 25 C. [R = 8.3 J/K mole]

(A) $10^{-5.44}$ (B) $10^{-12.5}$ (C) $10^{-6.52}$ (D) $10^{-3.12}$

18. What is $\Delta_r G$ (kJ/mole) for synthesis of ammonia at 298 K at following sets of partial pressure :

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta_r G = -33$ kJ/mole. [Take R = 8.3 J/K mole, log 2 = 0.3 ; log 3 = 0.48]

Gas	N_2	H_2	NH_3
Pressure (atm)	1	3	0.02

(A) +6.5 (B) –6.5 (C) +60.5 (D) –60.5

19. In a 7.0 L evacuated chamber, 0.50 mol H_2 and 0.50 mol I_2 react at 427 C.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. At the given temperature, $K_C = 49$ for the reaction.

(i) What is the value of K_p ?

(A) 7 (B) 49 (C) 24.5 (D) None

(ii) What is the total pressure (atm) in the chamber ?

(A) 83.14 (B) 831.4 (C) 8.21 (D) None

(iii) How many moles of the iodine remain unreacted at equilibrium ?

(A) 0.388 (B) 0.112 (C) 0.25 (D) 0.125

(iv) What is the partial pressure (atm) of HI in the equilibrium mixture?

(A) 6.385 (B) 12.77 (C) 40.768 (D) 646.58

20. $N_2 + O_2 \rightleftharpoons 2NO,\ K_1\ ;\ \left(\frac{1}{2}\right)N_2 + \left(\frac{1}{2}\right)O_2 \rightleftharpoons NO,\ K_2$

$2NO \rightleftharpoons N_2 + O_2,\ K_3\ ;\ NO \rightleftharpoons \left(\frac{1}{2}\right)N_2 + \left(\frac{1}{2}\right)O_2,\ K_4$

Correct relation between K_1, K_2, K_3 and K_4 is :

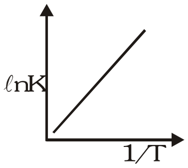
(A) $K_1 \quad K_3 = 1$ (B) $\sqrt{K_1} \times K_4 = 1$ (C) $\sqrt{K_3} \times K_2 = 1$ (D) None

21. The equation, $a = \frac{D - d}{(n-1)d}$ is correctly matched for :

(A) $A \rightleftharpoons nB/2 + nC/3$ (B) $A \rightleftharpoons nB/3 + (2n/3)C$

(C) $A \rightarrow (n/2)B + (n/4)C$ (D) $A \rightleftharpoons (n/2)B + C$

22. Variation of equilibrium constant K for the reaction ; $2A(s) + B(g) \rightleftharpoons C(g) + 2D(g)$ is plotted against absolute temperature T in figure as - ℓnK Vs (1/T) :



(ℓnK vs 1/T diagram)

(A) the forward reaction is exothermic (B) the forward reaction is endothermic

(C) the slope of line is proportional to ΔH (D) adding 'A' favours forward reaction

(E) removing C favours forward reaction

23. The equilibrium of which of the following reactions will not be disturbed by the addition of an inert gas at constant volume?

(A) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (B) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(C) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ (D) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

24. An industrial fuel, 'water gas', which consists of a mixture of H_2 and CO can be made by passing steam over red-hot carbon. The reaction is :

$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g),\ \Delta H = +131$ kJ

The yield of CO and H_2 at equilibrium would be shifted to the product side by

(A) raising the relative pressure of the steam

(B) adding hot carbon

(C) raising the temperature

(D) reducing the volume of the system

25. The dissociation of ammonium carbamate may be represented by the equation :

$$NH_4CO_2NH_2\ (s) \rightleftharpoons 2NH_3\ (g) + CO_2\ (g)$$

ΔH^0 for the forward reaction is negative. The equilibrium will shift from right to left if there is

(A) a decrease in pressure

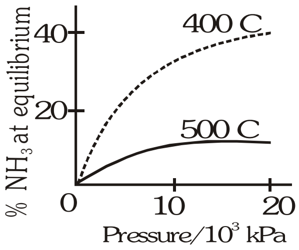
(B) an increase in temperature

(C) an increase in the concentration of ammonia

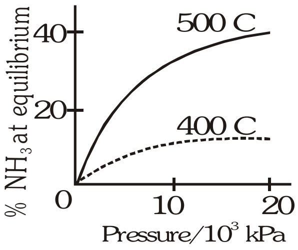
(D) an increase in the concentration of carbon dioxide

26. The percentage of ammonia obtainable, if equilibrium were to be established during the Haber process, is plotted against the operating pressure for two temperatures 400 C and 500 C. Which of the following correctly represents the two graphs ?

(A)



(B)



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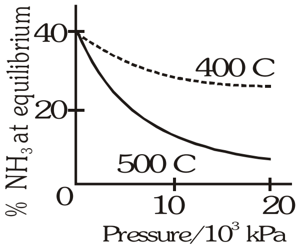
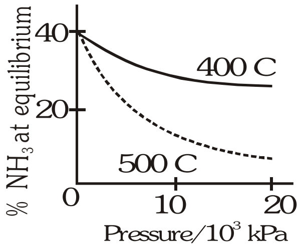


(D)



BRAIN TEASERS **ANSWER KEY** EXERCISE -2

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	B	A	A	D	B	B	D	A	C,D	D	C	C,D	A	A,B,C,D	A
Que.	16	17	18	19(i)	(ii)	(iii)	(iv)	20	21	22	23	24	25	26	
Ans.	A	A	D	B	C	B	A	A,B,C	B	A,C,E	A,B,C,D	A,C	B,C,D	A	

EXERCISE–03 MISCELLANEOUS TYPE QUESTIONS

TRUE / FALSE

1. Van't Hoff's equation gives the quantitative relation between change in value of K with change in temperature.
2. The larger value of K indicates that the product is more stable relative to reactants.
3. The value of equilibrium constant changes with change in the initial concentration of the reactants.
4. Extent of a reaction can always be increased by increasing the temperature.
5. K_P is related to K_C as $K_P = K_C\,(RT)^{\Delta n}$.
6. Introduction of inert gas in a gaseous reaction ($\Delta n_g \neq 0$) at equilibrium keeping pressure constant has no effect on equilibrium state.
7. For the reaction, $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$, $K_P = K_C\,(RT)$.
8. For a reaction the value of Q greater than K indicates that the net reaction is proceeding in backward direction.
9. Solubilities of all solids in water increase with increase in temperature.
10. Dissolution of all gases in water is accompained by evolution of heat.
11. For the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the equilibrium expression may be written as $K = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$.
12. For the reaction, $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$, $K_P = p_{CO_2}$.
13. A catalyst increases the value of the equilibrium constant for a reaction.
14. If concentration quotient of reaction is less than K, the net reaction is proceeding in the backward direction.
15. In case of endothermic reaction, the equilibrium shifts in backward direction on increasing the temperature.
16. The value of K increases with increase in pressure.
17. For the reaction, $H_2 + I_2 \rightleftharpoons 2HI$, the equilibrium constant, K is dimensionalless.
18. The reaction $2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$, $\Delta H = -X$ kJ, is favoured by high pressure and high temperature.
19. A very high value of K indicates that at equilibrium most of the reactants are converted into products.
20. The value of K for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, can be increased by applying high pressure or by using a catalyst.

FILL IN THE BLANKS

1. K for the reaction $2A + B \rightleftharpoons 2C$ is 1.5 10^{12}. This indicates that at equilibrium the concentration of .... would be maximum.
2. The reaction $N_2 + O_2 \rightleftharpoons 2NO$ – Heat, would be favoured by .... temperature.
3. K for the reaction $X_2 + Y_2 \rightleftharpoons 2XY$ is 100 K for this reaction $XY \rightleftharpoons \frac{1}{2}X_2 + \frac{1}{2}Y_2$ would be ....
4. Compared to K for the dissociation, $2H_2S \rightleftharpoons 2H^+ + 2HS^-$, then K' for the $H^+ + HS^- \rightleftharpoons H_2S$ would have ....
5. The equilibrium constant for a reaction decreases with increase in temperature, the reaction must be ....
6. For the reaction, $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$, K_P and K_C are related as ....
7. For the reaction, $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$, at equilibrium, increase in pressure shifts the equilibrium in .... direction.

8. ΔG is related to K by the relation ....

9. Vant Hoff's equation is ....

0. When the reaction is at equilibrium, the value of ΔG is ....

11. Dimensions of equilibrium constant, K_c for the reaction $2NH_3 \rightleftharpoons N_2 + 3H_2$, are ....

12. The value of K for a reaction can be changed by changing ....

13. The law of mass action was proposed by ....

14. The degree of dissociation of PCl_5 [$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$], ... with increase in pressure at equilibrium.

15. If concentration quotient, Q is greater than K_C, the net reaction in taking place in .... direction.

16. The reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ would be favoured by .... pressure.

17. K_P is related to K_C as ....

18. Solubility of a gas in water .... with increase in temperature.

19. Introduction of inert gas at constant volume to a gaseous reaction at equilibrium results in formation of .... product.

20. The product is more stable than reactants in reaction having .... K.

MATCH THE COLUMN

1.

	Column-I (Reactions)		Column-II (Favourable conditions)
(A)	Oxidation of nitrogen $N_2(g) + O_2(g) + 180.5\ kJ \rightleftharpoons 2NO(g)$	(p)	Addition of inert gas at constant pressure
(B)	Dissociation of $N_2O_4(g)$ $N_2O_4(g) + 57.2\ kJ \rightleftharpoons 2NO_2(g)$	(q)	Decrease in pressure
(C)	Oxidation of $NH_3(g)$ $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) + 905.6\ kJ$	(r)	Decrease in temperature
(D)	Formation of $NO_2(g)$ $NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g) + 200\ kJ$	(s)	Increase in temperature

2.

	Column-I (Reaction)		Column-II (If α is negligiable w.r.t. 1)
(A)	$2X(g) \rightleftharpoons Y(g) + Z(g)$	(p)	$\alpha = 2\sqrt{K_c}$
(B)	$X(g) \rightleftharpoons Y(g) + Z(g)$	(q)	$\alpha = 3\sqrt{K_c}$
(C)	$3X(g) \rightleftharpoons Y(g) + Z(g)$	(r)	$\alpha = (2K_c)^{1/3}$
(D)	$2X(g) \rightleftharpoons Y(g) + 2Z(g)$	(s)	$\alpha = \sqrt{K_c}$

ASSERTION & REASON

These questions contains, Statement I (assertion) and Statement II (reason).

(A) Statement-I is true, Statement-II is true ; Statement-II is correct explanation for Statement-I.

(B) Statement-I is true, Statement-II is true ; Statement-II is NOT a correct explanation for statement-I

(C) Statement-I is true, Statement-II is false

(D) Statement-I is false, Statement-II is true

1. **Statement-I** : The melting point of ice decreases with increase of pressure.

   Because

   Statement-II : Ice contracts on melting.

2. **Statement-I** : The equilibrium of $A(g) \rightleftharpoons B(g) + C(g)$ is not affected by changing the volume.

   Because

   Statement-II : K_c for the reaction does not depend on volume of the container.

3. **Statement-I** : For the reaction $A(g) \rightleftharpoons B(g) + C(g)$, $K_p = 1$ atm. If we start with equal moles of all gases at 9 atm of initial pressure, then at equilibrium partial pressure of A increases.

   Because

   Statement-II : Reaction quotient $Q_p > K_p$ hence equilibrium shifts in backward direction.

4. **Statement-I** : For a reaction at equilibrium, the Gibb's free energy of reaction is minimum at constant temp. and pressure.

   Because

   Statement-II : The Gibb's free energy of both reactants and products increases and become equal at equilibrium.

5. **Statement-I** : Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.

   Because

   Statement-II : Equilibrium constant depends upon the way in which the reaction is written.

6. **Statement-I** : For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ if the volume of vessel is reduced to half of its original volume, equilibrium concentration of all gases will be doubled.

   Because

   Statement-II : According to Le Chatelier's principle, reaction shifts in a direction that tends to minimized the effect of the stress.

7. **Statement-I** : For the reaction at certain temperature

   $$A(g) + B(g) \rightleftharpoons C(g)$$

   there will be no effect by addition of inert gas at constant volume.

   Because

   Statement-II : Molar concentration of all gases remains constant.

8. **Statement-I** : The catalyst does not alter the equilibrium constant.

   Because

   Statement-II : For the catalysed reaction and uncatalysed reaction ΔH remains same and equilibrium constant depends on ΔH.

COMPREHENSION BASED QUESTIONS

Comprehension # 1

On July, 1, 2000, the combined tunnel and bridge connecting Denmark and Sweden was officially opened. It consists of a tunnel from Copenhagen to an artificial Island and a bridge from the island to Malmo in Sweden. The major construction materials employed are concrete and steel. This problem deals with chemical reactions relating to production and degradation of such materials.

Concrete is produced from a mixture of cement, water, sand and small stones. Cement consists primarly of calcium silicates and calcium aluminates formed by heating and grinding of clay and limestone. In the later steps of cement production may lead to formation of unwanted hemihydrate, $CaSO_4 \cdot \frac{1}{2} H_2O$. Consider the following reaction :

$$CaSO_4 \,.\, 2H_2O(s) \longrightarrow CaSO_4 \cdot \frac{1}{2} H_2O(s) + 1\frac{1}{2} H_2O(g)$$

The following thermodynamic data apply at 25 C, standard pressure : 1.00 bar :

Compound	H /(kJ mol^{-1}) (ΔH_f)	S /(JK^{-1} mol^{-1})
$CaSO_4 \,.\, 2H_2O(s)$	–2021.0	194.0
$CaSO_4 \cdot \frac{1}{2} H_2O(s)$	–1575.0	130.5
$H_2O(g)$	–241.8	188.6

Gas constant ; R = 8.314 J mol^{-1} K^{-1}

1. ΔH for the transformation of 1.00 kg of $CaSO_4.2H_2O(s)$ to $CaSO_4 \cdot \frac{1}{2} H_2O(s)$ is :

(A) +446 kJ (B) +484 kJ (C) –446 kJ (D) –484 kJ

2. Equilibrium pressure (in bar) of water vapour in a closed vessel containing $CaSO_4 \,.\, 2H_2O(s)$, $CaSO_4(s) \cdot \frac{1}{2} H_2O(s)$ and H_2O (g) at 25 C is :

(A) 7.35 10^{-4} bar (B) 2.15 10^{-4} bar (C) 8.10 10^{-3} bar (D) 7.00 10^{-4} bar

3. Temperature at which the equilibrium water vapour pressure is 1.00 bar.

(A) 107 C (B) 380 C (C) 215 C (D) 240 C

Comprehension # 2

Questions are based on the manufacture of Na_2CO_3 by Solvay process :

In the manufacture of $Na_2CO_3(s)$ by Solvay process, $NaHCO_3(s)$ is decomposed by heating :

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

$$K_p = 0.23 \text{ at } 100\text{ C} \qquad \Delta H = 136 \text{ kJ}$$

1. If a sample of $NaHCO_3$ (s) is brought to a temperature of 100 C in a closed container total gas pressure at equilibrium is :

(A) 0.96 atm (B) 0.23 atm

(C) 0.48 atm (D) 0.46 atm

2. A mixture of 1.00 mol each of $NaHCO_3(s)$ and $Na_2CO_3(s)$ is introduced into a 2.5 L flask in which $P_{CO_2} = 2.10$ atm and $P_{H_2O} = 0.94$ atm.When equilibrium is established at 100 C, then partial pressure of :

(A) $CO_2(g)$ and $H_2O(g)$ will be greater than their initial pressure

(B) $CO_2(g)$ and $H_2O(g)$ will be less than their initial pressure

(C) $CO_2(g)$ will be larger and that of $H_2O(g)$ will be less than their initial pressure

(D) $H_2O(g)$ will be larger and that of $CO_2(g)$ will be less than their initial pressure

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MISCELLANEOUS TYPE QUESTION

ANSWER KEY

EXERCISE -3

- *True / False*

1\. T 2. T 3. F 4. F
5\. T 6. F 7. T 8. T
9\. F 10. T 11. T 12. T
13\. F 14. F 15. F 16. F
17\. T 18. F 19. T 20. F

- *Fill in the Blanks*

1\. C 2. high 3. $\frac{1}{10}$ 4. $\frac{1}{\sqrt{K}}$
5\. exothermic 6. $K_P = K_C (RT)$ 7. backward 8. $\Delta G = -RT \ln K$
9\. $\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$ 10. zero 11. $mol^2\ L^{-2}$
12\. temperature 13. Guldberg and Waage 14. decreases 15. backward
16\. high 17. $K_P = K_C (RT)^{\Delta n}$ 18. decreases 19. same amount of
20\. large value of

- *Match the Column*

1\. A - (s), B - (p,q,s), C - (p,q,r), D - (r) 2. A - (p), B - (s), C - (q), D - (r)

- *Assertion - Reason Questions*

1\. A 2. D 3. A 4. C
5\. A 6. B 7. A 8. A

- *Comprehension Based Questions*

Comprehension #1 : 1. B 2. C 3. A
Comprehension #2 : 1. A 2. B

EXERCISE–04 [A] CONCEPTUAL SUBJECTIVE EXERCISE

Reaction quotient and equillibrium constant

1. The initial concentration or pressure of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the directions in which each system will shift to reach equilibrium.

(a) $2NH_3\,(g) \rightleftharpoons N_2\,(g) + 3H_2\,(g)$ K = 17

$[NH_3] = 0.20$ M ; $[N_2] = 1.00$ M ; $[H_2] = 1.00$ M

(b) $2NH_3\,(g) \rightleftharpoons N_2\,(g) + 3H_2\,(g)$ $K_p = 6.8 \quad 10^4$ atm^2

Initial pressure : NH_3 = 3.0 atm ; N_2 = 2.0 atm ; H_2 = 1.0 atm

(c) $2SO_3(g) \rightleftharpoons 2SO_2\,(g) + O_2\,(g)$ K = 0.230 atm

$[SO_3] = 0.00$ M ; $[SO_2] = 1.00$ M ; $[O_2] = 1.00$ M

(d) $2SO_3\,(g) \rightleftharpoons 2SO_2\,(g) + O_2\,(g)$ K_p = 16.5 atm

Initial pressure : SO_3 = 1.0 atm ; SO_2 = 1.0 atm ; O_2 = 1.0 atm

(e) $2NO\,(g) + Cl_2\,(g) \rightleftharpoons 2NOCl\,(g)$ $K = 4.6 \quad 10^4$

$[NO] = 1.00$ M ; $[Cl_2] = 1.00$ M ; $[NOCl] = 0$ M

2. Among the solubility rules, the statement that all chlorides are soluble except Hg_2Cl_2, AgCl, $PbCl_2$, and CuCl.

(a) Write the expression for the equilibrium constant for the reaction represented by the equation

$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$

Is K greater than 1, less than 1, or about equal to 1? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation

$Pb^{2+}\,(aq) + 2Cl^-\,(aq) \rightleftharpoons PbCl_2\,(s)$

Is K greater than 1, less than 1, or about equal to 1? Explain your answer.

3. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene.

$3C_2H_2 \longrightarrow C_6H_6$

Would this reaction be most useful commercially if K were about 0.01, about 1, or about 10? Explain your answer.

4. For which of the following reactions will the equilibrium mixture contain an appreciable concentration of both reactants and products?

(a) $Cl_2\,(g) \rightleftharpoons 2Cl\,(g)$; $K_c = 6.4 \quad 10^{-39}$

(b) $Cl_2\,(g) + 2NO\,(g) \rightleftharpoons 2NOCl\,(g)$; $K_c = 3.7 \quad 10^8$

(c) $Cl_2\,(g) + 2NO_2\,(g) \rightleftharpoons 2NO_2Cl\,(g)$; $K_c = 1.8$

5. The value of K_c for the reaction $3\,O_2\,(g) \rightleftharpoons 2O_3\,(g)$ is $1.7 \quad 10^{-56}$ at 25 C. Do you expect pure air at 25 C to contain much O_3 (ozone) when O_2 and O_3 are in equilibrium ? If the equilibrium concentration of O_2 in air at 25 C is $8 \quad 10^{-3}$ M, what is the equilibrium concentration of O_3.

6. At 1400 K, $K_c = 2.5 \quad 10^{-3}$ for the reaction $CH_4\,(g) + 2H_2S \rightleftharpoons CS_2\,(g) + 4H_2\,(g)$. A 10.0 L reaction vessel at 1400 K contains 2.0 mol of CH_4, 3.0 mol of CS_2, 3.0 mol of H_2 and 4.0 mol of H_2S. Is this reaction mixture at equilibrium ? If not, in which direction does the reaction proceed to reach equilibrium ?

7. An equilibrium mixture of N_2, H_2 and NH_3 at 700 K contains 0.036 M N_2 and 0.15 M H_2. At this temperature, K_c for the reaction $N_2(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$ is 0.29. What is the concentration of NH_3?

8. The air pollutant NO is produced in automobile engines from the high temperature reaction $N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$; $K_c = 1.7 \quad 10^{-3}$ at 2300 K. If the initial concentrations of N_2 and O_2 at 2300 K are both 1.40 M, what are the concentration of NO, N_2 and O_2 when the reaction mixture reaches equilibrium?

9. At a certain temperature, the reaction $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$ has an equilibrium constant $K_c = 5.8 \quad 10^{-2}$. Calculate the equilibrium concentrations of PCl_5, PCl_3 and Cl_2 if only PCl_5 is present initially, at a concentration of 0.160 M.

10. At 700 K, $K_p = 0.140$ for the reaction $ClF_3\,(g) \rightleftharpoons ClF\,(g) + F_2\,(g)$. Calculate the equilibrium partial pressure of ClF_3, ClF and F_2 if only ClF_3 is present initially ; at a partial pressure of 1.47 atm.

Homogeneous equilibria degree of dissociation, vapour density and equilibrium constant

11. 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.

12. At 46 C, K_p for the reaction $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$ is 0.667 atm. Compute the percent dissociation of N_2O_4 at 46 C at a total pressure of 380 Torr.

13. When 36.8 g $N_2O_4\,(g)$ is introduced into a 1.0 - litre flask at 27 C. The following equilibrium reaction occurs :

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g) \;;\; K_p = 0.1642 \text{ atm.}$$

(a) Calculate K_c of the equilibrium reaction.

(b) What are the number of moles of N_2O_4 and NO_2 at equilibrium?

(c) What is the total gas pressure in the flask at equilibrium?

(d) What is the percent dissociation of N_2O_4?

14. At some temperature and under a pressure of 4 atm, PCl_5 is 10% dissociated. Calculate the pressure at which PCl_5 will be 20% dissociated, temperature remaining same.

15. In a mixture of N_2 and H_2 in the ratio of 1 : 3 at 64 atmospheric pressure and 300 C, the percentage of ammonia under equilibrium is 33.33 by volume. Calculate the equilibrium constant of the reaction using the equation.

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

16. The system $N_2O_4 \rightleftharpoons 2\,NO_2$ maintained in a closed vessel at 60 C & pressure of 5 atm has an average (i.e. observed) molecular weight of 69, calculate K_p. At what pressure at the same temperature would the observed molecular weight be (230/3) ?

17. The vapour density of N_2O_4 at a certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature. $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$.

18. In the esterification $C_2H_5OH\,(\ell) + CH_3COOH\,(\ell) \rightleftharpoons CH_3COOC_2H_5\,(\ell) + H_2O\,(\ell)$ an equimolar mixture of alcohol and acid taken initially yields under equilibrium, the water with mole fraction = 0.333. Calculate the equilibrium constant.

Hetrogeneous equilibrium

19. Solid Ammonium carbamate dissociates as : $NH_2COONH_4\ (s) \rightleftharpoons 2NH_3\ (g) + CO_2\ (g)$. 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.

20. A sample of $CaCO_3$ (s) is introduced into a sealed container of volume 0.821 litre & heated to 1000 K until equilibrium is reached. The equilibrium constant for the reaction $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$ is $4 \quad 10^{-2}$ atm at this temperature. Calculate the mass of CaO present at equilibrium.

21. 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 $K_p = 6.4 \quad 10^{85}$ for the following reaction at room temperature, $CaCl_2\ (s) + 6H_2O\ (g) \rightleftharpoons CaCl_2 \cdot 6H_2O\ (s)$. What is the equilibrium vapour pressure of water in a closed vessel that contains $CaCl_2$ (s) ?

22. 20.0 grams of $CaCO_3$ (s) were placed in a closed vessel, heated & maintained at 727 C under equilibrium $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$ and it is found that 75% of $CaCO_3$ was decomposed. What is the value of K_p? The volume of the container was 15 litres.

Changes in concentration at equilibrium Le Chatelier's principle

23. Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the equation

$$N_2\ (g) + 2H_2\ (g) \rightleftharpoons N_2H_4\ (g) \qquad \Delta H = 95\ kJ$$

24. How will an increase in temperature and increase in pressure affect each of the following equilibria?

(a) $2NH_3\ (g) \rightleftharpoons N_2\ (g) + 3H_2\ (g) \qquad \Delta H = 92\ kJ$

(b) $N_2\ (g) + O_2\ (g) \rightleftharpoons 2NO\ (g) \qquad \Delta H = 181\ kJ$

(c) $2O_3\ (g) \rightleftharpoons 3\ O_2\ (g) \qquad \Delta H = -285\ kJ$

(d) $CaO\ (s) + CO_2\ (g) \rightleftharpoons CaCO_3\ (s) \qquad \Delta H = -176\ kJ$

25. (a) Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red-hot coke,essentially pure carbon. Write the expression for the equilibrium constant for the reversible reaction.

$$C\ (s) + H_2O\ (g) \rightleftharpoons CO\ (g) + H_2\ (g) \qquad \Delta H = 131.30\ kJ$$

(b) Assume that equilibrium has been established and predict how the concentration of each reactant and product will differ at a new equilibrium if (1) more C is added. (2) H_2O is removed. (3) CO is added (4) the pressure on the system is increased. (5) the temperature of the system is increased.

26. Ammonia is weak base that reacts with water according to the equation

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

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.

27. Suggest two ways in which equilibrium concentration of Ag^+ can be reduced in a solution of Na^+, Cl^-, Ag^+ and NO_3^-, in contact with solid AgCl.

$$Na^+\ (aq) + Cl^-\ (aq) + Ag^+\ (aq) + NO_3^-\ (aq) \rightleftharpoons AgCl\ (s) + Na^+\ (aq) + NO_3^-\ (aq)\ \Delta H = -65.9\ kJ$$

Kinetics and equilibrium constant

28. Consider a general single-step reaction of the type $A + B \rightleftharpoons C$. Show that the equilibrium constant is equal to the ratio of the rate constant for the forward and reverse reaction, $K_c = K_f/K_r$.

29. Consider the reaction of chloromethane with OH^- in aqueous solution

$$CH_3Cl\ (aq) + OH^-\ (aq) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CH_3OH\ (aq) + Cl^-\ (aq)$$

At 25 C, the rate constant for the forward reaction is $6 \quad 10^{-6}\ M^{-1}\ s^{-1}$, and the equilibrium constant K_c is $1 \quad 10^{16}$. Calculate the rate constant for the reverse reaction at 25 C.

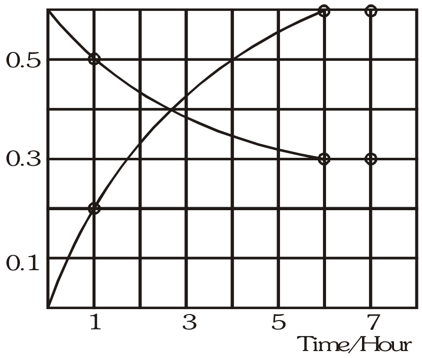
30. The progress of the reaction

$A \rightleftharpoons nB$ with time, is presented in figure, Determine

(i) the value of n.

(ii) the equilibrium constant K.

(iii) the initial rate of conversion of A.



Temperature dependence of equilibrium constant

31. Listed in the table are forward and reverse rate constants for the reaction $2NO\ (g) \rightleftharpoons N_2\ (g) + O_2\ (g)$

Temperature (K)	k_f ($M^{-1}s^{-1}$)	k_r ($M^{-1}s^{-1}$)
1400	0.29	$1.1 \quad 10^{-6}$
1500	1.3	$1.4 \quad 10^{-5}$

Is the reaction endothermic or exothermic?

32. Rate of disappearance of the reactant A at two different temperature is given by $A \rightleftharpoons B$

$$\frac{-d[A]}{dt} = (2 \quad 10^{-2}\ S^{-1})\ [A] - 4 \quad 10^{-3}\ S^{-1}\ [B]\ ;\ 300\ K$$

$$\frac{-d[A]}{dt} = (4 \quad 10^{-2}\ S^{-1})\ [A] - 16 \quad 10^{-4}\ S^{-1}\ [B]\ ;\ 400\ K$$

Calculate heat of reaction in the given temperature range. When equilibrium is set up.

33. The K_p for reaction $A + B \rightleftharpoons C + D$ is 1.34 at 60 C and 6.64 at 100 C. Determine the free energy change of this reaction at each temperature and ΔH for the reaction over this range of temperature?

Equilibrium expressions and equilibrium constants

34. If $K_c = 7.5 \quad 10^{-9}$ at 1000 K for the reaction $N_2\ (g) + O_2\ (g) \rightleftharpoons 2NO\ (g)$, what is K_c at 1000 K for the reaction $2NO\ (g) \rightleftharpoons N_2\ (g) + O_2\ (g)$?

35. A sample of HI ($9.30 \quad 10^{-3}$ mol) was placed in an empty 2.00 L container at 1000 K. After equilibrium was reached, the concentration of I_2 was $6.29 \quad 10^{-4}$ M. Calculate the value of K_c at 1000 K for the reaction $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$.

36. The vapour pressure of water at 25 C is 0.0313 atm. Calculate the values of K_p and K_c at 25 C for the equilibrium $H_2O\ (\ell) \rightleftharpoons H_2O\ (g)$.

37. For each of the following equilibria, write the equilibrium constant expression for K_c. Where appropriate, also write the equilibrium constant expression for K_p.

(a) $Fe_2O_3\ (s) + 3CO\ (g) \rightleftharpoons 2Fe\ (\ell) + 3\ CO_2\ (g)$

(b) $4Fe\ (s) + 3\ O_2\ (g) \rightleftharpoons 2Fe_2O_3\ (s)$

(c) $BaSO_4\ (s) \rightleftharpoons BaO\ (s) + SO_3\ (g)$

(d) $BaSO_4\ (s) \rightleftharpoons Ba^{2+}\ (aq) + SO_4^{2-}\ (aq)$

General problems

38. When 0.5 mol of N_2O_4 is placed in a 4.00 L reaction vessel and heated at 400 K, 79.3 % of the N_2O_4 decomposes to NO_2.

Calculate K_c and K_p at 400 K for the reaction $N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)$.

39. At 100 K, then value of K_c for the reaction $C(s) + H_2O\ (g) \rightleftharpoons CO\ (g) + H_2\ (g)$ is $3.0\quad 10^{-2}$. Calculate equilibrium concentrations of H_2O, CO_2 and H_2 in the reaction mixture obtained by heating 6.0 mole of steam and an excess of solid carbon in a 5.0 L container. What is the molar composition of the equilibrium mixture?

40. When 1.0 mol of PCl_5 is introduced into a 5.0 L container at 500 K, 78.5 % of the PCl_5 dissociates to given an equilibrium mixture of PCl_5, PCl_3 and Cl_2.

$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$

(a) Calculate the values of K_c and K_p.

(b) If the initial concentrations in a particular mixture of reactants and products are $[PCl_5] = 0.5$ M, $[PCl_3] = 0.15$ M, and $[Cl_2] = 0.6$ M, in which direction does the reaction proceed to reach equilibrium?

What are the concentrations when the mixture reaches equilibrium?

Thermodynamic and equilibrium constant

41. α-D-Glucose undergoes mutarotation to β-D-Glucose in aqueous solution. If at 298 K there is 60% conversion. Calculate ΔG of the reaction.

$\alpha\text{-D-Glucose} \rightleftharpoons \beta\text{-D-Glucose}$

42. For the reaction at 298 K

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

$\Delta H = -\ 29.8$ kcal ; $\Delta S = -\ 0.1$ kcal/K

Calculate ΔG and K.

43. The equilibrium constant of the reaction $2\ C_3H_6\ (g) \rightleftharpoons C_2H_4\ (g) + C_4H_8\ (g)$ is found to fit the expression

$$\ell nK = -\ 1.04 - \frac{1088}{T}$$

Calculate the standard reaction enthalpy and entropy at 400 K.

44. PCl_5 dissociates according to the reaction $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$. At 523 K, $K_p = 1.78$ atm. Find the density of the equilibrium mixture at a total pressure of 1 atm.

45. The following data for the equilibrium composition of the reaction

$2\ Na\ (g) \rightleftharpoons Na_2\ (g)$

at 1.013 MP_a pressure and 1482.53 K have been obtained.

mass % Na (monomer gas) = 71.3

mass % Na_2 (dimer gas) = 28.7

Calculate the equilibrium constant K_p.

46. A certain gas A polymerizes to a small extent at a given temperature & pressure, $nA \rightleftharpoons A_n$. Show that the gas obeys the approx equation $\frac{PV}{RT} = \left[1 - \frac{(n-1)K_c}{V^{n-1}}\right]$ where $K_c = \frac{[A_n]}{[A]^n}$ & V is the volume of the container. Assume that initially one mole of A was taken in the container.

47. When 1 mole of A (g) is introduced in a closed rigid 1 litre vessel maintained at constant temperature the following equilibria are established.

$$A(g) \rightleftharpoons B(g) + C(g) \quad : \quad K_{C_1}$$

$$C(g) \rightleftharpoons D(g) + B(g) \quad : \quad K_{C_2}$$

The pressure at equilibrium is twice the initial pressure. Calculate the value of $\frac{K_{C_2}}{K_{C_1}}$ if $\frac{[C]_{eq}}{[B]_{eq}} = \frac{1}{5}$

CONCEPTUAL SUBJECTIVE EXERCISE

ANSWER KEY

EXERCISE-4(A)

1. (a) 25, shifts left, (b) 0.22, shifts right, (c) ∞, shifts left, (d) 1, shifts right, (e) 0, shifts right

2. (a) K = $[Ag^+]$ $[Cl^-]$ is less than 1. AgCl is insoluble thus the concentration of ions are much less than 1 M

(b) K = $1/[Pb^{2+}]$ $[Cl^-]^2$ is greater than one because $PbCl_2$ is insoluble and formation of the solid will reduce the concentration of ions to a low level.

3. K about 10

4. c

5. $\simeq$ 9 10^{-32} mol/L

6. The reaction is not in equilibrium because $Q_c > K_c$. The reaction will proceed from right to left to reach equilibrium.

7. 5.9 10^{-3} M

8. [NO] = 0.056 M, $[N_2] = [O_2]$ = 1.37 M

9. $[PCl_3] = [Cl_2]$ = 0.071 M, $[PCl_5]$ = 0.089 M

10. $P_{ClF} = P_{F_2}$ = 0.389 atm, P_{ClF_3} = 1.08 atm

11. K_p = 0.4, $\alpha \simeq 0.1$

12. 50%

13. (a) 6.667 10^{-3}mol L^{-1} ; (b) n (N_2O_4) = 0.374 mol ; n (NO_2) = 0.052 mol ; (c) 10.49 atm (d) 6.44%

14. 0.97 atm

15. K_p = 1.3 10^{-3} atm^{-2}

16. K_p = 2.5 atm , P = 15 atm

17. 53.33%

18. K = 4

19. 31/27

20. 22.4 mg

21. P_{H_2O} = 5 10^{-15}atm

22. 0.821 atm

23. add N_2, add H_2, increase the pressure, heat the reaction

24. (a) shift right, shift left, (b) shift right, no effect, (c) shift left, shift left, (d) shift left, shift right

25. (a) K = $[CO][H_2] / [H_2O]$;

(b) in each of the following cases the mass of carbon will change, but its concentration (activity) will not change.

1. $[H_2O]$ no change, [CO] no change, $[H_2]$ no change ;
2. $[H_2O]$ decrease, [CO] decrease, $[H_2]$ decrease ;
3. $[H_2O]$ increase, [CO] increase, $[H_2]$ decrease ;
4. $[H_2O]$ increase, [CO] decrease, $[H_2]$ decrease ;
5. $[H_2O]$ decrease, [CO] increase, $[H_2]$ increase ;

26. b

27. Add NaCl or some other salt that produces Cl^- in the solution. Cool the solution

28. k_f [A][B] = k_r [C] ; $\dfrac{k_f}{k_r} = \dfrac{[C]}{[A][B]} = k_c$

29. 6 10^{-22}

30. (i) 2 ; (ii) 1.2 mol/L ; (iii) 0.1 moles/hr

31. The reaction is exothermic

32. 16.06 kJ

33. –810 J/mol ; –5872 J/mol and 41.3 kJ/mol

34. 1.3 10^8

35. 29.0

36. K_p = 0.0313 atm, K_c = 1.28 10^{-3}

37. (a) $K_c = \dfrac{[CO_2]^3}{[CO]^3}$, $K_p = \dfrac{\left(P_{CO_2}\right)^3}{\left(P_{CO}\right)^3}$, (b) $K_c = \dfrac{1}{[O_2]^3}$, $K_p = \dfrac{1}{(P_{O_2})^3}$; (c) $K_c = [SO_3]$, $K_p = P_{SO_3}$ (d) $K_c = [Ba^{2+}]\ [SO_4^{\,2-}]$

38. K_c = 1.51, K_p = 49.6

39. [CO] = $[H_2]$ = 0.18 M ; $[H_2O]$ = 1.02 M

40. (a) K_c = 0.573 and K_p = 23.5 ; (b) to the right, $[PCl_5]$ = 0.365 M ; $[PCl_3]$ = 0.285 M ; $[Cl_2]$ = 0.735 M

41. –1.005 kJ/mol

42. ΔG = 0 ; K = 1

43. ΔH = 9.04 kJ/mol ; ΔS = – 8.64 J / mol^{-1} K^{-1}

44. 2.71 g/L

45. P_{Na} = 0.843 M Pa, P_{Na_2} = 0.170 M Pa, k_P = 0.293

46. To be proved

47. 4

EXERCISE–04 [B] BRAIN STORMING SUBJECTIVE EXERCISE

1. 0.15 mole of CO taken in a 2.5 litre flask is maintained at 750 K along with a catalyst so that the following reaction can take place ;

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g).$$

Hydrogen is introduced untill the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed. Calculate :

(i) K_p & K_c ;

(ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place.

2. In a vessel, two equilibrium are simultaneously established at the same temperature as follows :

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ....(i)

$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g)$ ....(ii)

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

3. The decomposition of solid ammonium carbamete, $(NH_4)(NH_2CO_2)$, to gaseous ammonia and carbon dioxide is an endothermic reaction.

$(NH_4)\ (NH_2CO_2)\ (s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

(a) When solid $(NH_4)\ (NH_2CO_2)$ is introduced into an evacuated flask at 25 C, the total pressure of gas at equilibrium is 0.116 atm. What is the value of K_p at 25 C ?

(b) Given that the decomposition reaction is at equilibrium, how would the following changes affect the total quantity of NH_3 in the flask once equilibrium is re-established?

(i) Adding CO_2

(ii) Adding $(NH_4)\ (NH_2CO_2)$

(iii) Removing CO_2

(iv) Increasing the total volume

(v) Adding neon

(vi) Increasing the temperature

4. A container contains three gases. A, B and C in equilibrium $A \rightleftharpoons 2B + C$

At equilibrium the concentration of A was 3 M, and of B was 4 M. On doubling the volume of container, the new equilibrium concentration of B was 3M. Calculate K_C and initial equilibrium concentration of C.

5. The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm and 346 K is 1.8 g/L. Calculate K_C for the reaction.

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

6. At 90 C, the following equilibrium is established :

$H_2(g) + S(s) \rightleftharpoons H_2S(g)$ $K_p = 6.8\ \ 10^{-2}$

If 0.2 mol of hydrogen and 1.0 mol of sulphur are heated to 90 C in a 1.0 litre vessel, what will be the partial pressure of H_2S at equilibrium ?

7. At 817 C, K_p for the reaction between pure CO_2 and excess hot graphite to form 2CO(g) is 10 atm.

(a) What is the analysis of the gases at equilibrium at 817 C & a total pressure of 4.0 atm ? What is the partial pressure of CO_2 at equilibrium ?

(b) At what total pressure will the gas mixture analyze 6%, CO_2 by volume ?

8. For the reaction $N_2O_4 \rightleftharpoons 2NO_2$, equilibrium mixture contains NO_2 at P = 1.1 atm & N_2O_4 at P = 0.28 atm at 350 K. The volume of the container is doubled. Calculate the equilibrium pressures of the two gases when the system reaches new equilibrium.

9. The degree of dissociation of HI at a particular temperature is 0.8. Find the volume of 1.5 M sodium thiosulphate solution required to react completely with the iodine present at equilibrium in acidic conditions, when 0.135 mol each of H_2 and I_2 are heated at 440 K in a closed vessel of capacity 2.0 L.

10. A mixture of hydrogen & iodine in the mole ratio 1.5 : 1 is maintained at 450 C. After the attainment of equilibrium $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, it is found on analysis that the mole ratio of I_2 to HI is 1 : 18. Calculate the equilibrium constant & the number of moles of each species present under equilibrium, if initially, 127 g of iodine were taken.

11. The equilibrium constant for the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ is 7.3 at 450 C & 1 atm pressure. The initially concentration of water gas [CO & H_2 in equimolar ratio] & steam are 2 moles & 5 moles respectively. Find the number of moles of CO, H_2, CO_2 & H_2O (vapour) at equilibrium.

12. At 1200 C, the following equilibrium is established between chlorine atoms & molecule.

$$Cl_2(g) \rightleftharpoons 2Cl(g)$$

The composition of equilibrium mixture may be determined by measuring the rate of effusion of the mixture through a pin hold. It is found that at 1200 C and 1 atm pressure the mixture effuses 1.16 times as fast as krypton effuses under the same condition. Calculate the equilibrium constant K_c.

13. Two solids X and Y dissociate into gaseous products at a certain temperature as follows :

$X(s) \rightleftharpoons A(g) + C(g)$, and $Y(s) \rightleftharpoons B(g) + C(g)$. At a given temperature, pressure over excess solid X is 40 mm and total pressure over solid Y is 60 mm. Calculate :

(a) the values of K_p for two reactions (in mm)

(b) the ratio of moles of A and B in the vapour state over a mixture of X and Y.

(c) the total pressure of gases over a mixture of X and Y.

14. SO_3 decomposes at a temperature of 1000 K and at a total pressure of 1.642 atm. At equilibrium, the density of mixture is found to be 1.28 g/L in a vessel of 90 litres. Find the degree of dissociation of SO_3 for $SO_3 \rightleftharpoons SO_2 + 1/2O_2$.

15. The density of an equilibrium mixture of N_2O_4 and NO_2 at 101.32 KP_a is 3.62 g dm^{-3} at 288 K and 1.84 g dm^{-3} at 348 K. What is the heat of the reaction for $N_2O_4 \rightleftharpoons 2NO_2(g)$.

16. The equilibrium constant for the following reaction at 1395 K.

$2H_2O \rightleftharpoons 2H_2 + O_2$ $\quad K_1 = 2.1 \quad 10^{-13}$

$2CO_2 \rightleftharpoons 2CO + O_2$ $\quad K_2 = 1.4 \quad 10^{-12}$

Calculate the value of K for the reaction : $H_2 + CO_2 \rightleftharpoons CO + H_2O$

17. A saturated solution of iodine in water contains 0.33 g I_2/L. More than this can dissolve in a KI solution because of the equilibrium : $I_2\ (aq) + I^-\ (aq) \rightleftharpoons I_3^-\ (aq)$. A 0.10 M KI solution (0.10 MI^-) actually dissolves 12.5 g of iodine/L, most of which is converted to I_3^-. Assuming that the concentration of I_2 in all saturated solutions is the same, calculate the equilibrium constant for the above reaction. What is the effect of adding water to a clear saturated of I_2 in the KI solution ?

18. A mixture of N_2 & H_2 are in equilibrium at 600 K at a total pressure of 80 atm. If the initial ratio of N_2 and H_2 are 3 : 1 and at equilibrium NH_3 is 10% by volume, calculate K_p of reaction at given temperature.

19. ΔG (298 K) for the reaction $1/2N_2 + 3H_2 \overset{K_1}{\rightleftharpoons} NH_3$ is –16.5 kJ mol^{-1}. Find the equilibrium constant (K_1) at 25 C. What will be the equilibrium constants K_2 and K_3 for the following reactions :

$N_2 + 3H_2 \overset{K_2}{\rightleftharpoons} 2NH_3$

$NH_3 \overset{K_3}{\rightleftharpoons} 1/2\ N_2 + 3/2\ H_2$

20. When NO & NO_2 are mixed, the following equilibria are readily obtained ;

$2NO_2 \rightleftharpoons N_2O_4$ $\quad K_p = 6.8\ atm^{-1}$

$NO + NO_2 \rightleftharpoons N_2O_3$ $\quad K_p = ?$

In an experiment when NO & NO_2 are mixed in the ratio of 1 : 2, the total final pressure was 5.05 atm & the partial pressure of N_2O_4 was 1.7 atm. Calculate :

(a) the equilibrium partial pressure of NO. (b) K_p for $NO + NO_2 \rightleftharpoons N_2O_3$

21. Solid NH_4I on rapid heating in a closed vessel at 357 C develops a constant pressure of 275 mm Hg owing to partial decomposition of NH_4I into NH_3 and HI but the pressure gradually increases further (when the excess solid residue remains in the vessel) owing to the dissociation of HI. Calculate the final pressure developed at equilibrium.

$NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$

$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, $K_c = 0.065$ at 357 C

22. For the reaction $SO_2(g) + 1/2O_2(g) \rightleftharpoons SO_3(g)$ $\Delta H_{298} = -98.32$ kJ/mole,

$\Delta S_{298} = -95.0$ J/K/mole. Find the K_p for this reaction at 298 K.

23. Given are the following standard free energies of formation at 298 K.

	CO(g)	$CO_2(g)$	$H_2O(g)$	$H_2O(l)$
Δ_fG /kJ mole^{-1}	–137.17	–394.36	–228.57	–237.13

(a) Find Δ_rG and the standard equilibrium constant K_p^0 at 298 K for the reaction

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

(b) If CO, CO_2 and H_2 are mixed so that the partial pressure of each is 101.325 kPa and the mixture is brought into contact with excess of liquid water, what will be the partial pressure of each gas when equilibrium is attained at 298 K. The volume available to the gases is constant.

24. For the reaction

$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$

K_p^0 is 0.05 and Δ_rG is 22.384 kJ mol^{-1} at 900 K. If an initial mixture comprising 20 mol of C_2H_6 and 80 mol of N_2 (inert) is passed over a dehydrogenation catalyst at 900 K, what is the equilibrium percentage composition of the effluent gas mixture? The total pressure is kept at 0.5 bar. Given : $\Delta_rS = 135.143$ J K^{-1} mol^{-1} at 300 K. Calculate Δ_rG at 300 K. (Assume $\Delta_rC_p = 0$).

BRAIN STORMING SUBJECTIVE EXERCISE

ANSWER KEY

EXERCISE-4(B)

1. (i) $k_C = 187.85$ mol^{-2} lit^2 , $k_P = 0.05$ atm^{-2} (ii) P = 12.438 atm

2. $K_{P_1} = \frac{1}{20P_0^2}$, $K_{P_2} = \frac{3}{20P_0}$

3. (a) 2.31 10^{-4} (b) (i) decrease (ii) no change (iii) increase (iv) increase (v) no change (vi) increase

4. 28.8

5. 12.8

6. 0.379 atm

7. (i) $p(CO_2) = 0.938$ atm (ii) $P_{Total} = 0.68$atm

8. $P_{NO_2} = 0.64$ atm, $P_{N_2O_4} = 0.095$ atm

9. V = 144 mL

10. $k_C = 54$, $n_{HI} = 0.9$ mol, $n_{I_2} = 0.05$ mol, $n_{H_2} = 0.3$ mol

11. $n_{CO_2} = 0.938$, $n_{H_2} = 1.938$, $n_{CO} = 0.062$, $n_{H_2O} = 4.062$

12. 6.3 10^{-4}

13. (a) 400 mm^2, 900 mm^2 (b) 4 : 9 (c) 72.11 mmHg

14. $\alpha = 0.5$

15. $\Delta_rH = 75.68$ kJ mol^{-1}

16. k = 2.58

17. K = 707.2 backward reaction is favoured

18. 1.032 10^{-3}

19. $K_1 = 779.4$, $K_2 = 6.074$ 10^5 ; $K_3 = 1.283$ 10^{-3}

20. (a) 1.05 atm (b) 3.43 atm^{-1}

21. 337 mmHg

22. $K_P = 1.862$ 10^{12} atm $^{-1/2}$

23. (a) $\Delta G = -28.62$ kJ/mole (b) $P_{CO_2} = 202.44$ kPa, $P_{H_2O} = 3.16$ kPa, $P_{CO} = 0.2$ kPa, $K_P = 1.039$ 10^5

24. 103.47 kJ/mol

EXERCISE - 05 [A] JEE-[MAINS] : PREVIOUS YEAR QUESTIONS

1. Reaction $CO_{(g)} + \frac{1}{2} O_{2(g)} \rightleftharpoons CO_{2(g)}$. The value of $\frac{K_P}{K_c}$ is - [AIEEE-2002]

(A) $\frac{1}{RT}$ (B) $\sqrt{RT}$ (C) $\frac{1}{\sqrt{RT}}$ (D) RT

2. One of the following equilibrium is not affected by change in volume of the flask - [AIEEE-2002]

(A) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ (B) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(C) $N_2(g) + O_2 \rightleftharpoons 2NO(g)$ (D) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

3. For the reaction equilibrium,

$N_2O_4\ (g) \rightleftharpoons 2NO_2(g)$ the concentration of N_2O_4 and NO_2 at equilibrium are $4.8 \quad 10^{-2}$ and $1.2 \quad 10^{-2}$ mol L^{-1} respectively. The value of K_C for the reaction is- [AIEEE-2003]

(A) $3 \quad 10^{-3}$ mol L^{-1} (B) $3 \quad 10^{3}$ mol L^{-1} (C) $3.3 \quad 10^{2}$ mol L^{-1} (D) $3 \quad 10^{-1}$ mol L^{-1}

4. Consider the reaction equilibrium [AIEEE-2003]

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2\ SO_{3(g)}$; $\Delta H = -198$ 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

5. What is the equilibrium expression for the reaction $P_{4(s)} + 5O_{2(g)} \rightleftharpoons P_4O_{10(s)}$? [AIEEE-2004]

(A) $K_C = [P_4O_{10}] / [P_4] [O_2]^5$ (B) $K_C = [P_4O_{10}] / 5 [P_4] [O_2]$

(C) $K_C = [O_2]^5$ (D) $K_C = 1 / [O_2]^5$

6. For the reaction $CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$ the $\frac{K_P}{K_C}$ is equal to - [AIEEE-2004]

(A) $\frac{1}{RT}$ (B) RT (C) $\sqrt{RT}$ (D) 1.0

7. The equilibrium constant for the reaction $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ at temperature T is $4 \quad 10^{-4}$. The value of K_C for the reaction $NO_{(g)} \rightleftharpoons \frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)}$ [AIEEE-2004]

(A) $2.5 \quad 10^{2}$ (B) 50 (C) $4 \quad 10^{-4}$ (D) 0.02

8. For the reaction $2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}$, ($K_c = 1.8 \quad 10^{-6}$ at 184 C) (R = 0.831 kJ(mol.K)) When K_p and k_c are compared at 184 C it is found that [AIEEE-2005]

(A) K_p is less than K_c

(B) K_p is greater than K_c

(C) Whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure

(D) $K_p = K_c$

9. The exothermic formation of ClF_3 is represented by the equation [AIEEE-2005]

$Cl_{2(g)} + 3F_{2(g)} \rightleftharpoons 2ClF_{3(g)}$; $\Delta H_r = -329$ kJ

Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3?

(A) Removing Cl_2 (B) Increasing the temperature

(C) Adding F_2 (D) Increasing the volume of the container

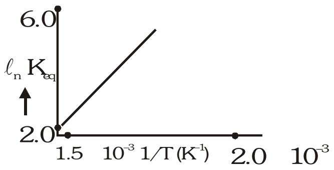
10. A schematic plot of $\ell n\ K_{eq}$ verus inverse of temperature for a reaction is shown below. The reaction must be [AIEEE-2005]

(A) endothermic

(B) exothermic

(C) highly spontaneous at ordinary temperature

(D) one with negligible enthalpy change



11. Phosphorus pentachloride dissociates as follows, in a closed reaction vessel, [AIEEE-2006]

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be-

(A) $\left(\frac{2x}{1-x}\right)P$ (B) $\left(\frac{x}{x-1}\right)P$ (C) $\left(\frac{x}{1-x}\right)P$ (D) $\left(\frac{x}{x+1}\right)P$

12. The equilibrium constant for the reaction $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$ is $K_C = 4.9\ 10^{-2}$. The value of K_C for the reaction [AIEEE-2006]

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ will be

(A) $2.40\ \ 10^{-3}$ (B) $9.8\ \ 10^{-2}$ (C) $4.9\ \ 10^{-2}$ (D) 416

13. The equlibrium constants K_{p_1} and K_{p_2} for the reaction $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively are 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 (B) 1 : 1 (C) 1 : 3 (D) 1 : 9

14. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is :- [AIEEE-2011]

(A) 0.3 atm (B) 0.18 atm (C) 1.8 atm (D) 3 atm

15. The equilibrium constant (K_C) for the reaction $N_2(g) + O_2(g) \longrightarrow 2NO(g)$ at temperature T is $4\ \ 10^{-4}$. The value of K_C for the reaction. $NO(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is :- [AIEEE-2012]

(A) 50.0 (B) 0.02 (C) $2.5\ \ 10^{2}$ (D) $4\ \ 10^{-4}$

JEE-[MAIN] : PREVIOUS YEAR QUESTIONS **ANSWER KEY** EXERCISE -5[A]

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans	C	C	A	A	D	A	B	B	C	B	D	D	A	C	A

EXERCISE - 05 [B] JEE-[ADVANCED] : PREVIOUS YEAR QUESTIONS

1. For the reaction $CO\ (g) + H_2O \rightleftharpoons CO_2\ (g) + H_2\ (g)$ at a given temperature the equilibrium amount of CO_2 (g) can be increased by : **[JEE 1998]**

(A) adding a suitable catalyst

(B) adding an inert gas

(C) decreasing the volume of the container

(D) increasing the amount of CO (g)

2. For the reaction, $N_2O_5\ (g) = 2\ NO_2\ (g) + 0.5\ O_2\ (g)$, calculate the mole fraction of N_2O_5 (g) decomposed at a constant volume & temperature, if the initial pressure is 600 mm Hg & the pressure at anytime is 960 mm Hg. Assume ideal gas behaviour. **[JEE 1998]**

3. The degree of dissociation is 0.4 at 400 K & 1.0 atm for the gaseous reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2\ (g)$. Assuming ideal behaviour of all gases. Calculate the density of equilibrium mixture at 400 K & 1.0 atm pressure. **[JEE 1999]**

4. When 3.06 g of solid NH_4HS is introduced into a two litre evacuated flask at 27 C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. **[JEE 2000]**

(i) Calculate K_C & K_P for the reaction at 27 C.

(ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?

5. When 1-pentyne (A) is treated with 4N alcoholic KOH at 175 C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) & 3.5 % of 1,2-pentadiene (C). The equilibrium was maintained at 175 C. Calculate ΔG for the following equilibria.

B = A $\Delta G_1 = ?$

B = C $\Delta G_2 = ?$

From the calculated value of ΔG_1 & ΔG_2 indicate the order of stability of A, B & C. Write a reasonable reaction mechanism sharing all intermediate leading to A, B & C. **[JEE 2001]**

6. $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

This reaction is carried out at 298 K and 20 bar. 5 mol each of N_2O_4 and NO_2 are taken initially :

Given : $\Delta G_{N_2O_4} = 100\ kJ\ mol^{-1}$; $\Delta G_{NO_2} = 50\ kJ\ mol^{-1}$

(i) Find ΔG for reaction at 298 K under given condition.

(ii) Find the direction in which the reaction proceeds to achieve equilibrium. **[JEE 2004]**

7. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Which is correct statement if N_2 is added at equilibrium condition?

(A) The equilibrium will shift to forward direction because according to II law of thermodynamics the entropy must increases in the direction of spontaneous reaction.

(B) The condition for equilibrium is $G_{N_2} + 3G_{H_2} \rightleftharpoons 2\,G_{NH_3}$ where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward reactions to the same extent.

(C) The catalyst will increase the rate of forward reaction by α and that of backward reaction by β.

(D) Catalyst will not alter the rate of either of the reaction. **[JEE 2006]**

8. The value of $\log_{10}K$ for a reaction $A \rightleftharpoons B$ is : **[JEE 2007]**

(Given : $\Delta_rH_{298K} = -54.07$ kJ mol^{-1}, $\Delta_rS_{298K} = 10$ $JK^{-1}\,mol^{-1}$ and

$R = 8.314$ $JK^{-1}\,mol^{-1}$; 2.303   8.314   298 = 5705)

JEE-[ADVANICE] : PREVIOUS YEAR QUESTIONS **ANSWER KEY** EXERCISE -5[B]

1. D   2. Fraction decomposed = 0.4   3. 4.54 g dm^{-3}

4. (i) $K_C = 8.1 \quad 10^{-5}$ mol^2 L^2 ; $K_P = 4.91 \quad 10^{-2}$ atm^2 ,(ii) No effect ;

5. 15991 J mol^{-1}, 12304 J mol^{-1} ; B > C > A

6. (i) $5.705 \quad 10^3$ J mol^{-1}

(ii) Since initial Gibbs free energy change of the reaction is positive, so the reverse reaction will take place.

7. B

8. B

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

$= -54.07 \quad 1000 - 298 \quad 10$

$= -54070 - 2980 = -57050$

$\Delta G = -2.303\ RT \log_{10}K$

$-57050 = -2.303 \quad 298 \quad 8.314 \log_{10}K$

$= -5705 \log_{10}K$

log10 K = 10