1. For the reaction equilibrium:
\[ \text{N}_2\text{O}_5 (g) \rightleftharpoons 2\text{NO}_2 (g) \]; the concentration of \( \text{N}_2\text{O}_5 \) and \( \text{NO}_2 \) at equilibrium are \( 4.8 \times 10^{-3} \) and \( 1.2 \times 10^{-3} \) mol/L respectively. The value of \( K \) for the reaction is:
(A) \( 3 \times 10^{-1} \) M  
(B) \( 3 \times 10^{1} \) M  
(C) \( 3.3 \times 10^{1} \) M  
(D) \( 3 \times 10^{-1} \) M

2. What is the equilibrium constant for the reaction \( \text{P}_4\text{H}_8 (s) \rightleftharpoons \text{PH}_3 (g) \):
(A) \( K_c = \frac{1}{[\text{O}_2]^8} \)  
(B) \( K_c = \frac{[\text{P}_4\text{H}_8]}{[\text{P}_4][\text{H}_8]^3} \)  
(C) \( K_c = [\text{O}_2]^8 \)  
(D) \( K_c = \frac{[\text{P}_4\text{H}_8]}{[\text{P}_4][\text{H}_8]^3} \)

3. The equilibrium constant for the reaction:
\[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO(g)} \] at temperature \( T \) is \( 4 \times 10^4 \). The value of \( K \) for the reaction:
\[ \text{NO(g)} \rightleftharpoons \frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g) \] at the same temperature is:
(A) \( 0.02 \)  
(B) \( 50 \)  
(C) \( 4 \times 10^{-4} \)  
(D) \( 2.5 \times 10^2 \)

4. The equilibrium constant for the given reaction:
\[ \text{SO}_2(g) \rightleftharpoons \text{SO}_3(g) + \frac{1}{2}\text{O}_2(g) ; \] \( K_c = 4.9 \times 10^{-4} \); The value of \( K \) for the reaction:
\[ 2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \], will be:
(A) \( 416 \)  
(B) \( 2.40 \times 10^{-3} \)  
(C) \( 9.8 \times 10^{-4} \)  
(D) \( 4.9 \times 10^{-3} \)

5. For the following three reactions 1, 2 and 3, equilibrium constants are given:
(1) \( \text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) ; \) \( K_1 \)
(2) \( \text{CH}_3\text{O(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2(g) + 3\text{H}_2(g) ; \) \( K_2 \)
(3) \( \text{CH}_4(g) + 2\text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2(g) + 4\text{H}_2(g) ; \) \( K_3 \)
Which of the following relations is correct?
(A) \( K_1 \sqrt{K_2} = K_3 \)  
(B) \( K_1K_2 = K_3 \)  
(C) \( K_1 = K_2K_3 \)  
(D) \( K_1K_2K_3 \)

6. Consider following reactions in equilibrium with equilibrium concentration 0.01M of every species
(I) \( \text{PCI}_3(g) \rightleftharpoons \text{PCI}_2(g) + \text{Cl}_2(g) \)
(II) \( 2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g) \)
(III) \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \)
Extent of the reactions taking place is:
(A) I > II > III  
(B) I < II < III  
(C) II < III < I  
(D) III < I < II

7. A definite amount of solid \( \text{NH}_4\text{HS} \) is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. \( \text{NH}_4\text{HS} \) decomposes to give \( \text{NH}_3 \) and \( \text{H}_2\text{S} \) and at equilibrium total pressure in flask is 0.84 atm. The equilibrium constant for the reaction is:
(A) \( 0.30 \)  
(B) \( 0.18 \)  
(C) \( 0.17 \)  
(D) \( 0.11 \)

8. For the reaction \( 3\text{A(g)} + \text{B(g)} \rightleftharpoons 2\text{C(g)} \) 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

9. Sulfide ion in alkaline solution reacts with solid sulfur to form polysulfide ions having formulas \( \text{S}_2^{2-}, \text{S}_2^{3-}, \text{S}_3^{2-} \) and so on. The equilibrium constant for the formation of \( \text{S}_2^{2-} \) is 12 (\( K_c \)) & for the formation of \( \text{S}_3^{2-} \) is 132 (\( K_c \)), both from \( \text{S} \) and \( \text{S}^{2-} \). What is the equilibrium constant for the formation of \( \text{S}_4^{3-} \) from \( \text{S}_2^{2-} \) and \( \text{S}^{2-} \)?
(A) \( 11 \)  
(B) \( 12 \)  
(C) \( 132 \)  
(D) None of these

10. 1 mole \( \text{N}_2 \) and 3 mole \( \text{H}_2 \) 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.
\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]. The equilibrium constant \( K_p \) for dissociation of \( \text{NH}_3 \) is:
(A) \( \frac{1}{0.5} \times (1.5)^3 \) atm\(^{-2} \)  
(B) \( 0.5 \times (1.5)^3 \) atm\(^{-2} \)  
(C) \( \frac{0.5 \times (1.5)^3}{3} \) atm\(^{-2} \)  
(D) \( \frac{3 \times 3}{0.5 \times (1.5)^3} \) atm\(^{-2} \)
11. One mole of N₂O₅(g) at 300 K is left in a closed container under one atm. It is heated to 600 K when 20% by mass of N₂O₅(g) decomposes to NO₂(g). The resultant pressure is:
   (A) 1.2 atm    (B) 2.4 atm
   (C) 2.0 atm    (D) 1.0 atm

12. For the following gases equilibrium,
   N₂O₅(g) ⇌ 2NO₂(g)  Kₘ is found to be equal to Kₗ. This is attained when temperature is
   (A) 0°C    (B) 273 K
   (C) 1 K    (D) 12.19 K

13. For the reaction:
   CO(g) + \frac{1}{2} O₂(g) ⇌ CO₂(g), Kₚ/Kₗ is:
   (A) RT    (B) (RT)⁻¹
   (C) (RT)⁻¹/²  (D) (RT⁻¹/²)

14. For the reaction:
   2NO₂(g) ⇌ 2NO(g) + O₂(g)  Kₙ = 1.8 \times 10⁻⁴ at 184°C and R = 0.083 JK⁻¹ mol⁻¹. When Kₙ and Kₗ are compared at 184°C, it is found that:
   (A) Kₙ > Kₗ    (B) Kₙ < Kₗ
   (C) Kₙ = Kₗ    (D) None of these

15. PCl₅ dissociation in a closed container as:
   PCl₅(g) ⇌ PCl₃(g) + Cl₂(g)
   If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl₅ is α, the partial pressure of PCl₃ will be:
   (A) P [α/(α⁻¹)]    (B) P [2α/(1−α)]
   (C) P [α/(α⁻¹)]    (D) P [α/(1−α)]

16. For the reaction: 2HI(g) ⇌ H₂(g) + I₂(g), the degree of dissociated (α) of HI(g) is related to equilibrium constant Kₚ by the expression:
   (A) \frac{1+2\sqrt{Kₚ}}{2}    (B) \frac{1-2\sqrt{Kₚ}}{2}
   (C) \sqrt{\frac{2Kₚ}{1-2Kₚ}}    (D) \frac{2\sqrt{Kₚ}}{1+2\sqrt{Kₚ}}

17. The equilibrium constant for the reaction
   A(g) + 2B(g) ⇌ C(g) is 0.25 dm³ mol⁻². In a volume of 5 dm³, what amount of A must be mixed with 4 mol of B to yield 1 mol of C at 
   equilibrium.
   (A) 3 moles    (B) 24 moles
   (C) 26 moles   (D) None of these

18. For the reaction
   A(g) + 2B(g) ⇌ C(g) + D(g); Kₗ = 10⁻¹² If the initial moles of A, B, C and D are 0.5, 1, 0.5 and 3.5 moles respectively in a one litre vessel. What is the equilibrium concentration of B?
   (A) 10⁻⁴    (B) 2 \times 10⁻⁴
   (C) 4 \times 10⁻⁴  (D) 8 \times 10⁻⁴

19. The equilibrium constant Kₗ for the reaction,
   A(g) + 2B(g) ⇌ 3C(g) is 2 \times 10⁻¹
   What would be the equilibrium partial pressure of gas C if initial pressure of gas A & B are 1 & 2 atm respectively.
   (A) 0.0625 atm    (B) 0.1875 atm
   (C) 0.21 atm     (D) None of these

20. A 20.0 litre vessel initially contains 0.50 mole each of H₂ and I₂ gases. These substances react and finally reach an equilibrium condition. Calculate the equilibrium concentration of HI if Kₚ = 49 for the reaction H₂ + I₂ ⇌ 2HI.
   (A) 0.78 M    (B) 0.039 M
   (C) 0.033 M   (D) 0.021 M

21. A vessel of 250 litre was filled with 0.01 mole of Sb₂S₃, and 0.01 mole of H₂ to attain the equilibrium at 440°C as
   Sb₂S₃(s) + 3H₂(g) ⇌ 2Sb(s) + 3H₂S(g).
   After equilibrium the H₂S formed was analysed by dissolving it in water and treating with excess of Pb²⁺ to give. 1.195 g of PbS (Molecular weight = 239) precipitate.
   What is value of Kₚ of the reaction at 440°C?
   (A) 1    (B) 2
   (C) 4   (D) None of these
22. The equilibrium constant for the reaction \[ \text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \] is 3 at 500 K. In a 2 litre vessel 60 gm of water gas [equimolar mixture of CO(g) and H₂(g)] and 90 gm of steam is initially taken.
What is the equilibrium concentration of H₂(g) at equilibrium (mole/L)?
(A) 1.75 \hspace{1cm} (B) 3.5
(C) 1.5 \hspace{1cm} (D) 0.75

23. At 87°C, the following equilibrium is established
\[ \text{H}_2(g) + \text{S(s)} \rightleftharpoons \text{H}_2\text{S(g)} \] \[ K_p = 7 \times 10^{-3} \]
If 0.50 mole of hydrogen and 1.0 mole of sulfur are heated to 87°C in 1.0 L vessel, what will be the partial pressure of H₂S at equilibrium?
(A) 0.966 atm \hspace{1cm} (B) 1.38 atm
(C) 0.0327 \hspace{1cm} (D) 9.66 atm

24. At certain temperature (T) for the gas phase reaction
\[ 2\text{H}_2\text{O}(g) + 2\text{Cl}_2(g) \rightleftharpoons 4\text{HCl(g)} + \text{O}_2(g) \]
\[ K_p = 12 \times 10^{10} \text{atm} \]
If Cl₂, H₂O & O₂ are mixed in such a manner that the partial pressure of each is 2 atm and the mixture is brought into contact with excess of liquid water. What would be approximate partial pressure of Cl₂, when equilibrium is attained at temperature (T)?

[Given : Vapour pressure of water is 380 mm Hg at temperature (T)]
(A) 3.6 \times 10^{-3} \text{ atm} \hspace{1cm} (B) 10^{-4} \text{ atm}
(C) 3.6 \times 10^{-1} \text{ atm} \hspace{1cm} (D) 0.01 \text{ atm}

25. At 675 K, H₂(g) and CO₂(g) react to form CO(g) and H₂O(g), K_f for the reaction is 0.16.
If a mixture of 0.25 mole of H₂(g) and 0.25 mol of CO₂ is heated at 675 K, mole% of CO(g) in equilibrium mixture is:
(A) 7.14 \hspace{1cm} (B) 14.28
(C) 28.57 \hspace{1cm} (D) 33.33

26. In which of the following reactions, increase in the pressure at constant temperature does not affect the moles at equilibrium.
(A) \[ 2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g) \]
(B) \[ \text{C}(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{CO}(g) \]
(C) \[ \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) \]
(D) \[ \text{H}_2(g) + \frac{1}{2} \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g) \]

27. Change in volume of the system does not alter the number of moles in which of the following equilibria?
(A) \[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \]
(B) \[ \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \]
(C) \[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]
(D) \[ \text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g) \]

28. The conditions favorable for the reaction:
\[ 2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \] \[ \Delta H^\circ = -198 \text{ kJ} \]
are:
(A) low temperature, high pressure
(B) any value of T and P
(C) low temperature and low pressure
(D) high temperature and high pressure

29. The exothermic formation of CIF₃, is represented by the equation:
\[ \text{Cl}_2(g) + 3\text{F}_2(g) \rightleftharpoons 2\text{CIF}_3(g) \] \[ \Delta H = -329 \text{ kJ} \]
Which of the following will increase the quantity of CIF₃ in an equilibrium mixture of Cl₂, F₂ and CIF₃:
(A) Increasing the temperature
(B) Removing Cl₂
(C) Increasing the volume of container
(D) Adding F₂

30. Densities of diamond and graphite are 3.5 and 2.3 gm/ml, respectively and for the reaction:
\[ \text{C(diamond)} \rightleftharpoons \text{C(graphite)} \] \[ \Delta H = -1.9 \text{ kJ/mole} \]
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

31. The equilibrium \[ \text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g) \] is attained at 25°C in a closed rigid container and an inert gas, helium is introduced. Which of the following statements is/are correct.
(A) concentrations of SO₂, Cl₂ and SO₂Cl₂ do not change
(B) more chlorine is formed
(C) concentration of SO₂ is reduced
(D) more SO₂Cl₂ is formed
32. Following two equilibrium is simultaneously established in a container

$$\text{PCl}_3(g) \rightleftharpoons \text{PCI}_2(g) + \text{Cl}_2(g)$$

$$\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g)$$

If some Ni(s) is introduced in the container forming Ni(CO)_4(g) then at new equilibrium
(A) PCI concentration will increase
(B) PCI concentration will decrease
(C) Cl_2 concentration will remain same
(D) CO concentration will remain same

33. The yield of product in the reaction

$$2A(g) + B(g) \rightleftharpoons 2C(g) + Q \text{kJ}$$

would be lower at:
(A) low temperature and low pressure
(B) high temperature & high pressure
(C) low temperature and high pressure
(D) high temperature & low pressure

34. What is the effect of the reduction of the volume of the system for the equilibrium

$$2C(s) + O_2(g) \rightleftharpoons 2CO(g)$$

(A) The equilibrium will be shifted to the left by the increased pressure caused by the reduction in volume
(B) The equilibrium will be shifted to the right by the decreased pressure caused by the reduction in volume.
(C) The equilibrium will be shifted to the left by the increased pressure caused by the increase in volume.
(D) The equilibrium will be shifted to the right by the increased pressure caused by the reduction in volume.

35. 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

36. The equilibrium constant $K_p$ (in atm) for the reaction is 9 at 7 atm and 300 K.

$$A_2(g) \rightleftharpoons B_2(g) + C_2(g)$$

Calculate the average molar mass (in gm/mol) of an equilibrium mixture.

37. Vapour density of the equilibrium mixture of the reaction

$$2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$$

is 6.0

Percent dissociation of ammonia gas is:
(A) 18.88
(B) 58.82
(C) 41.66
(D) None of these

38. Equimolar mixture of two gases $A_2$ and $B_2$ is taken in a rigid vessel at temperature 300 K. The gases reacts according to given equations:

$$A_2(g) \rightleftharpoons 2A(g) \quad K_p - ?$$

$$B_2(g) \rightleftharpoons 2B(g) \quad K_p = ?$$

$$A_2(g) + B_2(g) \rightleftharpoons 2\text{AB}(g) \quad K_p = 2$$

If the initial pressure in the container was 2 atm and final pressure developed at equilibrium is 2.75 atm.

In which equilibrium partial pressure of gas AB was 0.5 atm, calculate the ratio of $K_p$.

[Given: Degree of dissociation of $B_2$ is greater than $A_2$.]
(A) 8
(B) 9
(C) 1/8
(D) None of these

39. The heat of reaction at constant volume for an endothermic reaction in equilibrium is 1200 cal more than at constant pressure at 300K. Calculate the ratio of equilibrium constant Kp and Kc.

(A) 1.648x10⁻³:
(B) 1 : 1.
(C) 1 : 3
(D) 1 : 9

40. When N_2O_4 is heated at temp. T, it dissociates as N_2O_4 $\rightleftharpoons$ N_2O_3 + O_2, $K_p = 2.5$. 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_4 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
41. An exothermic reaction is represented by the graph:

\[ \text{(A) } mK_p \quad \text{(B) } mK_p \]
\[ \text{(C) } \frac{mK_p}{1/T} \quad \text{(D) } \frac{mK_p}{1/T} \]

42. A chemical reaction \( A \rightleftharpoons B \) is said to be in equilibrium when -
   (A) Complete conversion of \( A \) to \( B \) has taken place
   (B) Conversion of \( A \) to \( B \) is only 50% complete
   (C) Only 10% conversion of \( A \) to \( B \) has taken place
   (D) The rate of transformation of \( A \) to \( B \) is just equal to rate of transformation of \( B \) to \( A \) in the system

43. According to Law of Mass action, the rate of reaction is directly proportional to -
   (A) molarities of the reactants
   (B) normalities of the reactants
   (C) molalities of the reactants
   (D) mole fractions of the reactants

44. In a chemical equilibrium, the equilibrium constant is found to be 2.5. If the rate constant of backward reaction is \( 3.2 \times 10^{-3} \), the rate constant of forward reaction is -
   (A) \( 8.0 \times 10^{-2} \)
   (B) \( 4.0 \times 10^{-2} \)
   (C) \( 3.5 \times 10^{-2} \)
   (D) \( 7.6 \times 10^{-3} \)

45. \( K_1 \) and \( K_2 \) are the rate constants of forward and backward reactions. The equilibrium constant \( K \) of the reaction is -
   (A) \( K_1 \times K_2 \)
   (B) \( K_1 - K_2 \)
   (C) \( \frac{K_1}{K_2} \)
   (D) \( \frac{K_1 + K_2}{K_1 - K_2} \)

46. The value of \( K_p \) for the reaction \( \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \) is 50. What is the value of \( K_C \)?
   (A) 30  (B) 40  (C) 50  (D) 70

47. For the reaction \( A(g) + B(g) \rightleftharpoons C(g) + D(g) \), the degree of dissociation \( \alpha \) would be -
   (A) \( \frac{\sqrt{K}}{\sqrt{K} + 1} \)
   (B) \( \sqrt{K} + 1 \)
   (C) \( \sqrt{K} - 1 \)
   (D) \( \sqrt{K} + 1 \)

48. An unknown compound \( A \) dissociates at 500°C to give products as follows -
   \( A(g) \rightleftharpoons B(g) + C(g) + D(g) \)
   Vapour density of the equilibrium mixture is 50 when it dissociates to the extent to 10%. What will be the molecular weight of Compound \( A \)?
   (A) 120  (B) 130  (C) 134  (D) 140

49. \( \text{N}_2\text{O}_4 \) dissociates as \( \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \) at 273 K and 2 atm pressure. The equilibrium mixture has a density of 41. What will be the degree of dissociation -
   (A) 14.2%  (B) 16.2%  (C) 12.2%  (D) None

50. At 250°C and 1 atmospheric pressure, the vapour density of \( \text{PCl}_5 \) is 57.9. What will be the dissociation of \( \text{PCl}_5 \)?
   (A) 1.00  (B) 0.90  (C) 0.80  (D) 0.65
EXERCISE – II

1. Which of the following statements is (are) correct?
   (A) An irreversible reaction goes to almost completion.
   (B) A reversible reaction always goes to completion if carried out in a closed vessel.
   (C) At equilibrium, the rate of forward reaction becomes equal to that of backward reaction.
   (D) In the beginning, the rate of backward reaction is much greater than that of forward reaction.

2. The value of equilibrium constant of a reversible reaction at a given temperature:
   (A) depends on the initial concentration of reactants.
   (B) depends on the concentration of products at equilibrium.
   (C) gets reversed when the mode of representation of the reaction is reversed.
   (D) changes when the unit of active mass is changed.

3. Which of the following statement is (are) correct?
   (A) The value of equilibrium constant for a particular reaction is constant under all conditions of temperature and pressure.
   (B) The unit of $K_c$ for the reaction.
   $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$ are mol L$^{-1}$.
   (C) In the reaction $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$.
   $[\text{CaCO}_3] = [\text{CaO}] = 1$
   (D) $K_c$ is always greater than $K'_c$ for a particular reaction.

4. If it is found that the equilibrium constant increases by a factor of four when the temperature is increased from 25°C to 40°C. The value of $\Delta H^\circ$ is
   (A) 25.46 kJ
   (B) 171.65 kJ
   (C) 89.43 kJ
   (D) 71.65 kJ

5. Ammonium carbamate dissociates as follows:
   $\text{NH}_2\text{COONH}_4(s) \rightleftharpoons 2\text{NH}_3(g) + \text{CO}_2(g)$
   The value of $K_c$ for this reaction is found to be equal to $2.92 \times 10^{-1} \text{ atm}^2$. If one mole of ammonium carbamate is heated in a sealed container, the total pressure developed in the container is
   (A) 0.0194 atm
   (B) 0.0388 atm
   (C) 0.0582 atm
   (D) 0.0667 atm

6. The equilibrium constant for the following reactions at 1400 K are given:
   $2\text{H}_2\text{O}(g) \rightleftharpoons 2\text{H}_2(g) + \text{O}_2(g)$; $K_c = 2.1 \times 10^{-13}$
   $2\text{CO}_2(g) \rightleftharpoons 2\text{CO}(g) + \text{O}_2(g)$; $K_c = 1.4 \times 10^{12}$
   Then, the equilibrium constant $K$ for the reaction
   $\text{H}_2(g) + \text{CO}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)$ is
   (A) 2.04
   (B) 2.6
   (C) 8.4
   (D) 20.5

7. Under what conditions of temperature and pressure, the formation of atomic hydrogen from molecular hydrogen will be favoured most?
   (A) High temperature and high pressure
   (B) Low temperature and low pressure
   (C) High temperature and low pressure
   (D) Low temperature and high pressure

8. For the reaction $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$, 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 $\text{PCl}_5$ at constant volume.

9. When $\text{NaNO}_3(s)$ is heated in a closed vessel, oxygen is liberated and $\text{NaNO}_2(s)$ is left behind. At equilibrium,
   (A) addition of $\text{NaNO}_2$ favours reverse reaction
   (B) addition of $\text{NaNO}_3$ favours forward reaction
   (C) increasing temperature favours forward reaction
   (D) increasing pressure favours reverse reaction

10. Phase diagram of $\text{CO}_2$ is shown as follows.
    Based on above find the correct statement(s)

   (A) 298 K is the normal boiling point of liquid $\text{CO}_2$
   (B) At 1 atm & 190 K $\text{CO}_2$ will exist as gas.
   (C) $\text{CO}_2(s)$ will sublime above 195 K under normal atmospheric pressure
   (D) Melting point & boiling point of $\text{CO}_2$ will increase on increasing pressure.
11. The equilibrium between, gaseous isomers A, B and C can be represented as

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(g) ⇌ B(g)</td>
<td>: $K_1 = ?$</td>
</tr>
<tr>
<td>B(g) ⇌ C(g)</td>
<td>: $K_2 = 0.4$</td>
</tr>
<tr>
<td>C(g) ⇌ A(g)</td>
<td>: $K_3 = 0.6$</td>
</tr>
</tbody>
</table>

If one mole of A is taken in a closed vessel of volume 1 litre, then
(A) [A] + [B] + [C] = 1 M at any time of the reactions.
(B) Concentration of C is 4.1 M at the attainment equilibrium in all the reactions.
(C) The value of $K_1$ is $\frac{1}{0.24}$. 
(D) Isomer [A] is least stable as per thermodynamics.

12. For the gas phase exothermic reaction.

$A_1 + B_1 \rightleftharpoons C_1$, carried out in a closed vessel, the equilibrium moles of $A_1$ can be increased by
(A) increasing the temperature  
(B) decreasing the pressure  
(C) adding inert gas at constant pressure  
(D) removing some $C_1$

13. Consider the equilibrium

$\text{HgO}(s) + 4\text{I}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HgI}_4^{2-} (aq) + 2\text{OH}^- (aq)$, which changes will decrease the equilibrium concentration of $\text{HgI}_4^{2-}$

(A) Addition of 0.1 M Hl (aq)  
(B) Addition of HgO(s)  
(C) Addition of $\text{H}_2\text{O}$ (l)  
(D) Addition of K$\text{OH}$ (aq)

14. In the laboratory the equilibrium constant for a particular reaction can be measured at different temperatures. Plotting the data yields the graph shown. Which of the following statements is false?
(Note: The notation $4.40 \times 10^{-4}$ is equivalent to $4.40 \times 10^{-4}$)

15. Decrease in the pressure for the following equilibria: $\text{H}_2\text{O}(s) \rightleftharpoons \text{H}_2\text{O}(l)$ result in the:
(A) formation of more $\text{H}_2\text{O}(s)$  
(B) formation of more $\text{H}_2\text{O}(l)$  
(C) increase in melting point of $\text{H}_2\text{O}(s)$  
(D) decrease in melting point of $\text{H}_2\text{O}(s)$

**ASSERTION - REASON**

In each sub-question below a statement S and an explanation E is given. Choose the correct answers from the codes A,B,C,D given for each question.

(A) $\Delta S^o$ can be obtained from the y-intercept  
(B) The slope of the line is equal to + $(\Delta H^o/R)$  
(C) The reaction is endothermic  
(D) The standard free energy change of the reaction is positive.


**Statement-2:** Increase in pressure leads to an increase in boiling point.

17. **Statement-1:** A decrease in pressure leads to an increase in freezing point of water.

**Statement-2:** For ice on melting volume decreases.

18. **Statement-1:** The solubility of gases always increases with increase in pressure.

**Statement-2:** High pressure favours the change where volume of gas decreases.

19. **Statement-1:** Total number of moles in a closed system at new equilibrium is less than the old equilibrium if some amount of a substance is removed from a system.  

**Statement-2:** The number of moles of the substance which is removed, is partially compensated as the system reached to new equilibrium.

20. **Statement-1:** An exothermic reaction, non-spontaneous at high temperature, may become spontaneous at low temperature.

**Statement-2:** Entropy of an exothermic reaction always decrease with decrease in temperature.
21. **Statement-1**: Ammonia at a pressure of 10 atm and CO₂ at a pressure of 20 atm are introduced into an evacuated chamber. If \( K_p \) for the reaction:
\[
\text{NH}_3\text{COONH}_4(s) \rightleftharpoons 2\text{NH}_3(g) + \text{CO}_2(g)
\]
is 20 atm⁻¹, the total pressure after a long time is less than 30 atm.
**Statement-2**: Equilibrium can be attained from both directions.

**COMPREHENSION**

**Paragraph for Questions No. 22 to 25**

In a 7.0 L evacuated chamber, 0.50 mol H₂ and 0.50 mol I₂, react at 427°C.

\[
\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)
\]
At the given temperature, \( K_p = 49 \) for the reaction.

22. What is the value of \( K_p \)?
(A) 7  
(B) 49  
(C) 24.5  
(D) None

23. What is the total pressure (atm) in the chamber?
(A) 83.14  
(B) 831.4  
(C) 8.21  
(D) None

24. How many moles of the iodine remain unreacted at equilibrium?
(A) 0.388  
(B) 0.112  
(C) 0.25  
(D) 0.125

25. What is the partial pressure (atm) of HI in the equilibrium mixture?
(A) 6.385  
(B) 12.77  
(C) 40.768  
(D) 646.58

**Paragraph for Question Nos. 26 to 28**

Equilibrium constants are given (in atm) for the following reactions at 0°C:

- \( \text{SrCl}_2 \cdot 6\text{H}_2\text{O}(s) \rightleftharpoons \text{SrCl}_2 \cdot 2\text{H}_2\text{O}(s) + 4\text{H}_2\text{O}(g) \)
  \( K_p = 5 \times 10^{-12} \)
- \( \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}(s) \rightleftharpoons \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}(s) + 5\text{H}_2\text{O}(g) \)
  \( K_p = 2.43 \times 10^{-11} \)
- \( \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(s) \rightleftharpoons \text{Na}_2\text{SO}_4(s) + 10\text{H}_2\text{O}(g) \)
  \( K_p = 1.024 \times 10^{-22} \)

The vapor pressure of water at 0°C is 4.56 torr.

26. Which is the most effective drying agent at 0°C?
(A) \( \text{SrCl}_2 \cdot 2\text{H}_2\text{O} \)  
(B) \( \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O} \)  
(C) \( \text{Na}_2\text{SO}_4 \)  
(D) All equally

27. At what relative humidities will \( \text{Na}_2\text{SO}_4 \) be efflorescent (release moisture) when exposed to air at 0°C?
(A) above 33.33 %  
(B) below 33.33 %  
(C) above 66.66%  
(D) below 66.66%

28. At what relative humidities will \( \text{Na}_2\text{SO}_4 \) be deliquescent (i.e. absorb moisture) when exposed to the air at 0°C?
(A) above 33.33 %  
(B) below 33.33 %  
(C) above 66.66%  
(D) below 66.66%

**Paragraph for Question Nos. 29 to 60**

If we know the equilibrium constant for a particular reaction, we can calculate the concentrations in the equilibrium mixture from the initial concentrations. Commonly only the initial concentration of reactants are given.

29. In a study of equilibrium
\[
\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)
\]
1 mole of \( \text{H}_2 \) and 3 mole of \( \text{I}_2 \) gave rise to equilibrium to \( x \) mol of \( \text{HI} \).

Addition of a further 2 mol of \( \text{H}_2 \) gave an additional \( x \) mol of \( \text{HI} \). What is \( x \)?
(A) 0.5  
(B) 1  
(C) 1.5  
(D) None of these

30. In above problem, what is \( K_p \) at the temperature of the experiment?
(A) 1  
(B) 2  
(C) 4  
(D) None of these

31. In a study of equilibrium
\[
2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)
\]
Starting with 2 mole \( \text{SO}_2 \) and 1.5 mole \( \text{O}_2 \) in 5 litre flask. Equilibrium mixture required 0.4 mole \( \text{K}_{\text{MnO}_4} \) in acidic medium. Hence \( K_p \) is:
(A) 0.2  
(B) 5.0  
(C) 675.0  
(D) None of these

**Match the column**

32. **Column I**
(A) \( K_p < K_f \)  
(B) Introduction  
(C) \( K_f \) is dimensionless  
(D) Temperature increase

**Column II**

(P) \( \text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 \)
(Q) \( \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \) of inert gas at pressure will decrease the constant concentration of reactants.
(R) \( 2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \)
(S) \( \text{NH}_3(g) + \text{HI(g)} \rightleftharpoons \) will shift the reaction \( \text{NH}_4\text{I} \) on product side.
33. **Column-I**  
   (A) \( A_{(g)} + 3B_{(g)} \rightleftharpoons 2AB_{(g)} \)  
   (B) \( A_{(g)} + B_{(g)} \rightleftharpoons 2AB_{(g)} \)  
   (C) \( A_{(g)} + 1.5B_{(g)} \rightleftharpoons 2AB_{(g)} \)  
   (D) \( AB_{(g)} + 0.5B_{(g)} \rightleftharpoons A_{(g)} \)  

   **Column-II**  
   \( K_p/K_c \)  

34. **Column-I**  
   (A) \( A_{2(g)} + B_{2(g)} \rightleftharpoons 2AB_{(g)} \)  
   (B) \( 2AB_{(g)} + B_{(g)} \rightleftharpoons 2AB_{(g)} \)  
   (C) \( 2AB_{(g)} \rightleftharpoons A_{(g)} + 3B_{(g)} \)  

   **Column-II factors affecting forward**  
   (p) High temperature  
   (q) Low temperature  
   (r) High pressure  
   (s) Low pressure  
   (t) Independent of pressure  

35. **INTEGER TYPE**  
   If a mixture of 3 mole of \( H_2 \) and 1 mole of \( N_2 \) is completely converted into \( NH_3 \), what would be the final volume at same \( p \) and \( T \)?  

36. For the reaction, \( C(s) + CO(g) \rightleftharpoons 2CO(g) \), the partial pressure of \( CO \) and \( CO_2 \) are 2 atm and 4.0 atm respectively at equilibrium. Find the \( K_p \) for the reaction.  

37. In the reaction, \( PCl_5 \rightleftharpoons PCl_3 + Cl_2 \), the amounts of \( PCl_5, PCl_3, \) and \( Cl_2 \) are 2 moles each at equilibrium and the total pressure is 3 atm. Find the equilibrium constant \( K_p \).  

38. For the equilibrium, \( 2NO_{(g)} + O_2_{(g)} \rightleftharpoons 2NO_2_{(g)} \), \( K_p \) is 1.24 \( \times \) 10^{-1} at 727°C. Find the value of \( K_c \) at 727°C.  

39. The equilibrium constant for, \( 2H_2S \rightleftharpoons 2H_2 + S_{(g)} \) is 0.469 atm at 1065°C and heat of dissociation is 42.4 kcal. Calculate the equilibrium constant at 1132°C.  

40. The molar concentration of \( A \) and \( B \) are 0.80 mol/litre each. On mixing them, the reaction starts to proceed as: \( A + B \rightarrow C + D \), and attain equilibrium. At equilibrium molar concentration of \( C \) is 0.60 mol/litre. Find the value of \( K_c \) of the reaction.  

41. In a reaction at equilibrium \( x \) mole of the reactant \( A \) decompose to give 1 mole of \( C \) and \( D \). It has been found that the fraction of \( A \) decomposed at equilibrium is independent of initial concentration of \( A \). Find the value of \( x \).  

42. In the reaction \( C(s) + CO(g) \rightleftharpoons 2CO(g) \), the equilibrium pressure is 6.75 atm. If 50% of \( CO \) reacts, then find the value of \( K_p \).  

43. \( N_2O_4 \) is 60% dissociated into \( NO_2 \) at 340K and 1 atm pressure. Find the volume of 10 g \( N_2O_4 \) occupy under these condition.  

44. Ammonium carbamate when heated to 473K gives a mixture of \( NH_3 \) and \( CO_2 \) vapour with a density of 13. Find the degree of dissociation of ammonium carbamate.  

45. In a experiment starting with 1 mole of \( C_2H_5OH \), 1 mole of \( CH_3COOH \) and 1 mole of water, the equilibrium mixture on analysis shows that 54.3% of the acid is esterified. Find the value of \( K_c \).  

46. Maximum number of phases at equilibrium of pure substance is  

47. The composition of the equilibrium mixture for the equilibrium \( Cl_2 \rightleftharpoons 2Cl \) at 1470 K, may be determined by the rate of diffusion of mixture through a pin hole. It is found that at 1470 K, the mixture diffuses 1.16 times as fast as krypton (83.8) diffuses under the same conditions. Calculate the % degree of dissociation of \( Cl_2 \) at equilibrium.  

48. \( 2A(g) + B(g) \rightleftharpoons 3C(g) \)  
   Initially only \( A \) & \( B \) are present in the container & moles of \( A \) and \( B \) at \( t = 0 \) are 4 & 2 respectively.  
   If the concentration of \( A \) at equilibrium is \( p \times 10^{-n} \) then find \( p + q - 2 \)  
   Given : Volume of container is 100 lit.  

49. Ammonium carbamate dissociates as \( NH_4COONH_4 \)  
   \( (s) \rightleftharpoons 2NH_3(g) + CO_2(g) \). In a closed vessel containing ammonium carbamate in equilibrium, ammonia is added such that partial pressure of \( NH_3 \) now equals to the original total pressure. Calculate the ratio of total pressure now to the original pressure as \( P/Q \).  

50. In a vessel of the reaction \( 2A + B \rightleftharpoons 3C + D \), \( A \) and \( B \) are mixed in a vessel at \( ^\circ \)C. The initial conc. of \( A \) is twice the initial conc. of \( B \). After equilibrium is reached, the conc. of \( C \) is three times the conc. of \( B \). Calculate the equilibrium constant \( K_c \) in terms of \( P/Q \) and report \( P + Q \).
Exercise – III

Subjective Problems (JEE Advanced)

Reaction quotient and equilibrium constant

1. The initial concentrations 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) \(2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)\) \(K = 17\)
      
      \([\text{NH}_3]\) = 0.20 M ; \([\text{N}_2]\) = 1.00 M ; \([\text{H}_2]\) = 1.00 M
   (b) \(2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)\) \(K_p = 6.8 \times 10^4\) atm
      
      Initial pressure : \(\text{NH}_3 = 3.0\) atm ; \(\text{N}_2 = 2.0\) atm ; \(\text{H}_2 = 1.0\) atm
   (c) \(2\text{SO}_2(g) \rightleftharpoons 2\text{SO}_3(g) + \text{O}_2(g)\) \(K = 0.230\) atm
      
      \([\text{SO}_2]\) = 0.00 M ; \([\text{SO}_3]\) = 1.00 M ; \([\text{O}_2]\) = 1.00 M
   (d) \(2\text{SO}_2(g) \rightleftharpoons 2\text{SO}_3(g) + \text{O}_2(g)\) \(K_p = 16.5\) atm
      
      Initial pressure : \(\text{SO}_2 = 1.0\) atm ; \(\text{SO}_3 = 1.0\) atm ; \(\text{O}_2 = 1.0\) atm
   (e) \(2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)\) \(K = 4.6 \times 10^4\)
      
      \([\text{NO}]\) = 1.00 M ; \([\text{Cl}_2]\) = 1.00 M ; \([\text{NOCl}]\) = 0 M

2. Among the solubility rules is the statement that all chlorides are soluble except Hg₂Cl₂, AgCl, PbCl₂, and CuCl₂.
   (a) Write the expression for the equilibrium constant for the reaction represented by the equation.
      \(\text{AgCl} (s) \rightleftharpoons \text{Ag}^+ (aq) + \text{Cl}^- (aq)\)
      
      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.
      \(\text{Pb}^2+ (aq) + 2\text{Cl}^- (aq) \rightleftharpoons \text{PbCl}_2(S)\)
      
      Is \(K\) greater than 1, less than 1, or about equal to 1? Explain your answer.

3. Among the solubility rules is the statement that carbonates, phosphates, borates, arsenates, and arsenites, except those of the ammonium ion and the alkal metal group, are insoluble.
   (a) Write the expression for the equilibrium constant for the reaction represented by the equation.
      \(\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+} (aq) + \text{CO}_3^{2-} (aq)\)

4. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene into benzene. \(3\text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6\)
   Would this reaction be most useful commercially if \(K\) were about 0.01, about 1, or about 10? Explain your answer.

5. Show the complete chemical equation and the net ionic equation for the reaction represented by the equation.
   \(\text{Kl} (aq) + \text{I}_2 (aq) \rightleftharpoons \text{Kl}_2 (aq)\)
   Give the same expression for the reaction quotient. \(\text{Kl}_2\) is composed of the ions \(\text{K}^+\) and \(\text{I}^-\).

Using the equilibrium constant

6. Which of the following reactions goes almost all the way to completion, and which proceeds hardly at all?
   (a) \(\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g); K = 2.7 \times 10^{-14}\)
   (b) \(2\text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g); K = 6.0 \times 10^{-11}\)

7. For which of the following reactions will the equilibrium mixture contain an appreciable concentration of both reactants and products?
   (a) \(\text{Cl}_2(g) \rightleftharpoons 2\text{Cl}(g); K = 6.4 \times 10^{-29}\)
   (b) \(\text{Cl}_2(g) + 2\text{NO}(g) \rightleftharpoons 2\text{NOCl}(g); K = 3.7 \times 10^6\)
   (c) \(\text{Cl}_2(g) + 2\text{NO}_2(g) \rightleftharpoons 2\text{NO}_2\text{Cl}(g); K = 1.8\)

8. The value of \(K\) for the reaction
   \(3\text{O}_2(g) \rightleftharpoons 2\text{O}_3(g)\) is \(1.7 \times 10^{-14}\) at 25°C. Do you expect pure air at 25°C to contain much \(\text{O}_3\) (ozone) when \(\text{O}_2\) and \(\text{O}_3\) are in equilibrium? If the equilibrium concentration of \(\text{O}_3\) in air at 25°C is \(8 \times 10^{-1} \text{ M}\), what is the equilibrium concentration of \(\text{O}_2\)?
9. At 1400 K, $K_p = 2.5 \times 10^{-1}$ for the reaction
\[ \text{CH}_4(g) + 2\text{H}_2\text{S} \rightleftharpoons \text{CS}_2(g) + 4 \text{H}_2(g) \]. 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$_2$S. Is the reaction mixture at equilibrium? If not, in which direction does the reaction proceed to reach equilibrium?

10. The first step in the industrial synthesis of hydrogen is the reaction of steam and methane to give water gas, a mixture of carbon monoxide and hydrogen.
\[ \text{H}_2\text{O}(g) + \text{CH}_4(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g) \]
$K_p = 4.7$ at 1400 K.
A mixture of reactants and product at 1400 K contains 0.035 M H$_2$O, 0.050 M CH$_4$, 0.15 M CO, and 0.20 M H$_2$. In which direction does the reaction proceed to reach equilibrium?

11. 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, $K_p$ for the reaction
\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \] is 0.29. What is the concentration of NH$_3$?

12. The air pollutant NO is produced in automobile engines from the high temperature reaction
\[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g) \]; $K_p = 1.7 \times 10^{-15}$ at 2300 K. If the initial concentrations of N$_2$ and O$_2$ are both 1.40 M, what are the concentrations of NO, N$_2$, and O$_2$ when the reaction mixture reaches equilibrium?

13. At a certain temperature, the reaction
\[ \text{PCl}_3(g) \rightleftharpoons \text{PCl}_2(g) + \text{Cl}_2(g) \] has an equilibrium constant $K_p = 5.8 \times 10^4$. Calculate the equilibrium concentrations of PCl$_3$, PCl$_2$, and Cl$_2$ if only PCl$_3$ is present initially, at a concentration of 0.160 M.

14. At 700 K, $K_p = 0.140$ for the reaction
\[ \text{Cl}_2\text{F}(g) \rightleftharpoons \text{ClF}(g) + \text{F}_2(g) \]. Calculate the equilibrium partial pressure of ClF, ClF, and F$_2$ if only ClF is present initially, at a partial pressure of 1.47 atm. Homogeneous equilibria degree of dissociation, vapour density and equilibrium constant.

15. The degree of dissociation of N$_2$O into NO 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.

16. At 46°C $K_p$ for the reaction
\[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \] is 0.667 atm. Compute the percent dissociation of N$_2$O$_4$ at 46°C at a total pressure of 380 Torr.

17. When 36.8 g N$_2$O$_4$(g) is introduced into a 1.0-litre flask at 27°C. The following equilibrium reaction occurs:
\[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \]; $K_p = 0.1642$ atm.
(a) Calculate $K_p$ of the equilibrium reaction.
(b) What are the number of moles of N$_2$O$_4$ 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$_2$O$_4$?

18. At some temperature and under a pressure of 4 atm, PCl$_3$ is 10% dissociated. Calculate the pressure at which PCl$_3$ will be 20% dissociated, temperature remaining same.

19. 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.
\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]

20. The system N$_2$O$_4$ maintained in a closed vessel at 60°C & a 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)?

21. The vapour density of N$_2$O$_4$ and NO$_2$ mixture at a certain temperature is 30. Calculate the percentage dissociation of N$_2$O$_4$ at this temperature. N$_2$O$_4$(g) $\rightleftharpoons$ 2NO$_2$(g)

22. In the esterification
\[ \text{C}_2\text{H}_5\text{OH}(1)+\text{CH}_2\text{COOH}(1) \rightarrow \text{CH}_2\text{COOC}_{2}\text{H}_5(l)+\text{H}_2\text{O}(l) \] an equimolar mixture of alcohol and acid taken initially yields under equilibrium, the water with molar fraction = 0.333. Calculate the equilibrium constant.

Heterogeneous equilibrium

23. Solid Ammonium carbamate dissociates as :
\[ \text{NH}_4\text{COO NH}_3\text{, (s)} \rightleftharpoons 2\text{NH}_3(g) + \text{CO}_2(g) \]. 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.
24. A sample of CaCO$_3$ (s) is introduced into a sealed container of volume 0.821 litre & heated to 1000K until equilibrium is reached. The equilibrium constant for the reaction

\[ \text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g}) \]

is $4 \times 10^{-2}$ atm at this temperature. Calculate the mass of CaO present at equilibrium.

25. Anhydrous calcium chloride is often used as a deoxidant. In the presence of excess of CaCl$_2$, the amount of the water taken up is governed by $K_r = 6.4 \times 10^4$ for the following reaction at room temperature,

\[ \text{CaCl}_2(\text{s}) + 6\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CaCl}_2\cdot 6\text{H}_2\text{O}(\text{s}) \]

What is the equilibrium vapour pressure of water in a closed vessel that contains CaCl$_2$ (s)?

26. 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 $K_r$? The volume of the container was 15 litres.

27. Suggest four ways in which the concentration of hydrazine, N$_2$H$_4$, could be increased in an equilibrium described by the equation.

\[ \text{N}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{N}_2\text{H}_4(\text{g}) \]

$\Delta H = 95$ kJ

28. How will an increase in temperature affect each of the following equilibria? An increase in pressure?

(a) 2NH$_3$(g) $\rightleftharpoons$ N$_2$(g) + 3H$_2$(g) $\Delta H = 92$ kJ

(b) N$_2$(g) + O$_2$(g) $\rightleftharpoons$ 2NO(g) $\Delta H = 181$ kJ

(c) 2O$_2$(g) $\rightleftharpoons$ 3O$_3$(g) $\Delta H = -285$ kJ

(d) CaO(s) + CO$_2$(g) $\rightleftharpoons$ CaCO$_3$(s) $\Delta H = -176$ kJ

29. (a) Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst. Write the expression for the equilibrium constant for the reversible reaction.

\[ 2\text{H}_2(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g}) \]

$\Delta H = -90.2$ kJ

(b) Assume that equilibrium has been established and predict how the concentration of H$_2$, CO and CH$_3$OH will differ at a new equilibrium if (i) more H$_2$ is added. (2) CO is removed. (3) CH$_3$OH is added. (4) the pressure on the system is increased. (5) the temperature of the system is increased. (6) more catalyst is added.

30. (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.

\[ \text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g}) \]

$\Delta H = 131.30$ 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$_2$O is removed. (3) CO is added. (4) the pressure on the system is increased. (5) the temperature of the system is increased.

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

\[ \text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_3^+ + \text{OH}^- + \text{aq} \]

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$_4$Cl.

32. Suggest two ways in which the equilibrium concentration of Ag$^+$ can be reduced in a solution of Na$^+$, Cl$^-$, Ag$^+$ and NO$_3^-$, in contact with solid AgCl.

\[ \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Ag}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \rightleftharpoons \text{AgCl(s}) + \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \]

$\Delta H = -65.9$ kJ

33. Additional solid silver sulfate, a slightly soluble solid, is added to a solution of silver ion and sulfate ion in equilibrium with solid silver sulfate. Which of the following will occur? (a) The Ag$^+$ and SO$_4^{2-}$ concentration will not change. (b) The added silver sulfate will dissolve. (c) Additional silver sulfate will form and precipitate from soluto into Ag$^+$ ions and SO$_4^{2-}$ ions combine. (d) The Ag$^+$ ion concentration will increase and the SO$_4^{2-}$ ion concentration will decrease.

Kinetics and equilibrium constant

34. 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, $K_e = \frac{k_f}{k_r}$.

35. Which of the following relative values of $k_f$ and $k_r$ results in an equilibrium mixture that contains large amounts of reactants and small amounts of product?

(a) $k_f > k_r$  (b) $k_f = k_r$  (c) $k_f < k_r$.
36. Consider the gas-phase hydration of hexafluoracetone, \((\text{CF}_3)_2\text{CO}\):
\[(\text{CF}_3)_2\text{CO} + \text{H}_2\text{O} \rightleftharpoons (\text{CF}_3)_2\text{C(OH)}\_\text{aq}\]
At 76°C, the forward and reverse rate constants are \(k_f = 0.13 \text{ M}^{-1} \text{s}^{-1}\) and \(k_r = 6.02 \times 10^{-4} \text{ s}^{-1}\). What is the value of the equilibrium constant \(K_e\)?

37. Consider the reaction of chloromethane with \(\text{OH}^-\) in aqueous solution
\[\text{CH}_3\text{Cl(aq)} + \text{OH}^-(aq) \rightleftharpoons \text{CH}_2\text{OH(aq)} + \text{Cl}^- (aq)\]
At 25°C, the rate constant for the forward reaction is \(6 \times 10^{-4} \text{ M}^{-1} \text{s}^{-1}\), and the equilibrium constant \(K_e\) is \(1 \times 10^{14}\). Calculate the rate constant for the reverse reaction at 25°C.

38. The progress of the reaction
\[\text{A} \rightleftharpoons \text{nB} \text{ with time, is presented in figure. Determine}
(i) the value of \(n\).
(ii) the equilibrium constant \(K_e\).
(iii) the initial rate of conversion of \(A\).

Temperature dependence of equilibrium constant

39. Listed in the table are forward and reverse rate constants for the reactions
\[2\text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g)\]

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(k_f(\text{M}^{-1}\text{s}^{-1}))</th>
<th>(k_r(\text{M}^{-1}\text{s}^{-1}))</th>
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<tr>
<td>1400</td>
<td>0.29</td>
<td>1.1 \times 10^{-4}</td>
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<tr>
<td>1500</td>
<td>1.3</td>
<td>1.4 \times 10^{-4}</td>
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Is the reaction endothermic or exothermic? Explain in terms of kinetics.

40. Forward and reverse rate constant for the reaction \(\text{CO}(g) + \text{N}_2(g) \rightleftharpoons \text{CO}(g) + \text{N}_2\text{O}\) exhibit the following temperature dependence.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(k_f(\text{M}^{-1}\text{s}^{-1}))</th>
<th>(k_r(\text{M}^{-1}\text{s}^{-1}))</th>
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<tbody>
<tr>
<td>1200</td>
<td>9.1 \times 10^{-11}</td>
<td>1.5 \times 10^{1}</td>
</tr>
<tr>
<td>1500</td>
<td>2.7 \times 10^{-9}</td>
<td>2.6 \times 10^{1}</td>
</tr>
</tbody>
</table>

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

41. The equilibrium constant \(K_e\) for the reaction \(\text{PCl}_3(g) \rightleftharpoons \text{PCl}_4(g) + \text{Cl}_2(g)\) is \(3.81 \times 10^7\) at 600 K and \(2.69 \times 10^7\) at 700 K. Calculate \(\Delta H\).

Temperature dependence of equilibrium constant

42. Rate of disappearance of the reactant \(A\) at two different temperature is given by
\[
\frac{d[A]}{dt} = 4 \times 10^{-2} \text{S}^{-1}[A] - 16 \times 10^{-7} [B] ; 300 \text{ K}
\]
\[
\frac{d[A]}{dt} = 2 \times 10^{-2} \text{S}^{-1}[A] - 4 \times 10^{-7} [B] ; 400 \text{ K}
\]
Calculate heat of reaction in the given temperature range. When equilibrium is set up.

43. The \(K_e\) for reaction \(A + B \rightleftharpoons C + D\) is 1.34 at 60°C and 6.64 at 100°C. Determine the standard free energy change of this reaction at each temperature and \(\Delta H^\circ\) for the reaction over this range of temperature?

Equilibrium expressions and equilibrium constants

44. If \(K_e = 7.5 \times 10^{-2}\) at 1000 K for the reaction \(\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)\), what is \(K_e\) at 1000 K for the reaction \(2\text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g)\)?

45. An equilibrium mixture of \(\text{PCl}_3\), \(\text{PCl}_4\), and \(\text{Cl}_2\) at a certain temperature contains \(8.3 \times 10^{-3} \text{ M} \text{PCl}_3\), \(1.5 \times 10^{-2} \text{ M} \text{PCl}_4\), and \(3.2 \times 10^{-1} \text{ M} \text{Cl}_2\). Calculate the equilibrium constant \(K_e\) for the reaction \(\text{PCl}_3(g) \rightleftharpoons \text{PCl}_4(g) + \text{Cl}_2(g)\).

46. A sample of HI (9.30 \times 10^{-3} \text{ mol}) was placed in an empty 2.00 L container at 1000 K. After equilibrium was reached, the concentration of I, was 6.29 \times 10^{-4} M. Calculate the value of \(K_e\) at 1000 K for the reaction \(\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)\).

47. The vapour pressure of water at 25°C is 0.0313 atm. Calculate the values of \(K_e\) and \(K_e\) at 25°C for the equilibrium \(\text{H}_2\text{O}(1) \rightleftharpoons \text{H}_2\text{O}(g)\).
EXERCISE - IV

LEVEL - I

PREVIOUS YEARS PROBLEMS

JEE MAIN

1. For the reaction \( \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \), 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. Which of the following equilibria is not affected by change in volume of the flask? [AIEEE-2002]

(A) \( \text{PCl}_5 (g) \rightleftharpoons \text{PCl}_3 (g) + \text{Cl}_2 (g) \)  
(B) \( \text{N}_2 (g) + 3\text{H}_2 (g) \rightleftharpoons 2\text{NH}_3 (g) \)  
(C) \( \text{N}_2 (g) + \text{O}_2 (g) \rightleftharpoons 2\text{NO} (g) \)  
(D) \( \text{SO}_2\text{Cl}_2 (g) \rightleftharpoons \text{SO}_2 (g) + \text{Cl}_2 (g) \)

3. For the reaction equilibrium \( \text{N}_2\text{O}_4 (g) \rightleftharpoons 2\text{NO}_2 (g) \) the concentrations of \( \text{N}_2\text{O}_4 \) and \( \text{NO}_2 \) at equilibrium are \( 4.8 \times 10^{-2} \) and \( 1.2 \times 10^{-2} \) mol L\(^{-1}\) respectively. The value of \( K_c \) for the reaction is - [AIEEE-2003]

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

4. Consider the reaction equilibrium

\( 2\text{SO}_2 (g) + \text{O}_2 (g) \rightleftharpoons 2 \text{SO}_3 (g); \Delta \text{H}^{\circ} = -198 \text{ kJ} \)

On the basis of Le Chatelier's principle, the condition favourable for the forward reaction is - [AIEEE-2003]

(A) Lowering the temperature and increasing the pressure  
(B) Any value of temperature and 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 \( \text{P}_4(\text{s}) + 5\text{SO}_2(\text{g}) \rightleftharpoons \text{P}_4\text{O}_{10}(\text{s}) ? \) [AIEEE-2004]

(A) \( K_c = \frac{[\text{P}_4\text{O}_{10}]}{[\text{P}_4][\text{O}_2]^5} \)

(B) \( K_c = \frac{[\text{P}_4\text{O}_{10}]}{5[\text{P}_4][\text{O}_2]} \)

(C) \( K_c = [\text{O}_2]^5 \)

(D) \( K_c = 1[\text{O}_2]^5 \)

6. For the reaction \( \text{CO}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{COCl}_2(\text{g}) \) 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 \( \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) \) at temperature \( T \) is \( 4 \times 10^{-4} \). The value of \( K_c \) for the reaction

\( \text{NO}(\text{g}) \rightleftharpoons \frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \) at the same temperature is - [AIEEE-2004]

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

8. For the reaction

\( 2 \text{NO}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \),

\( K_c = 1.8 \times 10^{-6} \) at 184\(^\circ\)C

\( R = 0.0831 \text{ kJ}/(\text{mol}.\text{K}) \)

When \( K_p \) and \( K_c \) are compared at 184\(^\circ\)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 ClF₃ is represented by the equation:
\[ \text{Cl}_2(\text{g}) + 3\text{F}_2(\text{g}) \rightleftharpoons 2\text{ClF}_3(\text{g}) \Delta H = -329 \text{ kJ} \]
Which of the following will increase the quantity of ClF₃ in an equilibrium mixture of Cl₂ and ClF₃?
(A) Removing Cl₂
(B) Increasing the temperature
(C) Adding F₂
(D) Increasing the volume of the container

[AIIEEE-2005]

10. A schematic plot of ln Kₑ versus inverse of temperature for a reaction is shown below.

\[ \begin{array}{c}
\text{6.0} \\
\text{2.0} \\
\text{1.5} \times 10^{-3} \\
\text{2.0} \times 10^{-3} \\
\end{array} \quad \begin{array}{c}
\text{1/T (K⁻¹)} \\
\text{1/T (K⁻¹)} \\
\end{array} \]
The reaction must be
(A) endothermic
(B) exothermic
(C) highly spontaneous at ordinary temperature
(D) one with negligible enthalpy change

[AIIEEE-2005]

11. An amount of solid NH₄HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH₃ and H₂S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for NH₄HS decomposition at this temperature is -

(A) 0.18  (B) 0.30  (C) 0.11  (D) 0.17

[AIIEEE-2005]

12. Phosphorus pentachloride dissociates as follows,
\[ \text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \]
If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl₅ is x, the partial pressure of PCl₃ will be

(A) \( \frac{2x}{1-x} \) P
(B) \( \frac{x}{x-1} \) P
(C) \( \frac{x}{1-x} \) P
(D) \( \frac{x}{x-1} \) P

[AIIEEE-2006]

13. The equilibrium constant for the reaction
\[ \text{SO}_3(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \]
Is \( K_c = 4.9 \times 10^{-2} \).
The value of \( K_c \) for the reaction
\[ 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) \]
will be \[ (A) 2.40 \times 10^{-3} \quad (B) 9.8 \times 10^{-2} \]
\[ (C) 4.9 \times 10^{-2} \quad (D) 416 \]

[AIIEEE 2006]

14. For the following three reactions a, b, and c, equilibrium constants are given

(a) \( \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \); \( K_1 \)
(b) \( \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \); \( K_2 \)
(c) \( \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + 4\text{H}_2(\text{g}) \); \( K_3 \)
Which of the following relations is correct
(A) \( K_2 K_3 = K_1 \)
(B) \( K_3 = K_1 K_2 \)
(C) \( K_3 K_2 = K_1^{-1} \)
(D) \( K_1 K_2 = K_3 \)

[AIIEEE 2008]

15. The equilibrium constants \( K_{p1} \) and \( K_{p2} \) for the reactions \( X \rightleftharpoons 2Y \) 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 pressures at these equilibria is -

(A) 1 : 1  (B) 1 : 3  (C) 1 : 9  (D) 1 : 36

[AIIEEE 2008]

16. 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 the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of \( K_{p1} \):

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

[AIIEEE 2011]

17. The equilibrium constant \( K_c \) for the reaction
\[ \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) \]
at temperature \( T \) is \( 4 \times 10^{-4} \). The value of \( K_c \) for the reaction,
\[ \text{NO}(\text{g}) \rightarrow \frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \]
at the same temperature is:

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

[AIIEEE 2012]
1. The degree of dissociation is 0.4 at 400 K & 1.0 atm for the gaseous reaction \( \text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2(g) \). Assuming ideal behaviour of all gases. Calculate the density of equilibrium mixture at 400 K & 1.0 atm pressure. [JEE 1999]

2. When 3.06 g of solid NH₃·HS is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.
(i) Calculate \( K_c \) & \( K_p \) for the reaction at 27°C.
(ii) What would happen to the equilibrium when more solid NH₃·HS is introduced into the flask? [JEE 2000]

3. When two reactants A and B are mixed to give products C and D, the reaction quotient \( Q \), at the initial stages of the reaction: [JEE 2000]
(A) is zero
(B) decreases with time
(C) independent of time
(D) increases with time

4. For the reversible reactions:
\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \] at 500°C. The value of \( K_c \) is \( 1.44 \times 10^{-4} \); when partial pressure is measured in atmospheres. The corresponding value of \( K_p \), with concentration in mol L⁻¹ is:
(A) \( 1.44 \times 10^{-4} \)
(B) \( 1.44 \times 10^{-5} \)
(C) \( 1.44 \times 10^{-4} \)
(D) \( 1.44 \times 10^{-5} \)

5. At constant temperature, the equilibrium constant \( K_p \) for the decomposition reaction.
\[ \text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 \] is expressed by \( K_p = \frac{4x^2P}{(1-x)^2} \)
where P is pressure, x is extent of decomposition. Which of the following statement is true?
(A) \( K_p \) increases with increase of P
(B) \( K_p \) increases with increase of x
(C) \( K_p \) increases with decrease of x
(D) \( K_p \) remains constant with change in P or x [JEE 2001]

7. Consider the following equilibrium in a closed container: \( \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \). At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant \( (K_p) \) and degree of dissociation \( (\alpha) \):
(A) Neither \( K_p \) nor \( \alpha \) changes
(B) Both \( K_p \) and \( \alpha \) change
(C) \( K_p \) changes, but \( \alpha \) does not change
(D) \( K_p \) does not change, but \( \alpha \) changes [JEE 2002]

8. If \( \text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag(NH}_3)_2]^+ \); \( K_p = 6.8 \times 10^4 \)
and
\[ [\text{Ag(NH}_3)_2]^+ + \text{NH}_3 \rightleftharpoons [\text{Ag(NH}_3)_3]^+ ; K_p = 6.8 \times 10^4 \]
The formation constant of \( [\text{Ag(NH}_3)_3]^+ \) is:
(A) \( 6.08 \times 10^{-4} \)
(B) \( 6.8 \times 10^4 \)
(C) \( 1.6 \times 10^4 \)
(D) \( 1.08 \times 10^4 \) [JEE 2006]

9. The equilibrium
\[ 2\text{Cu}^\text{II} \rightleftharpoons \text{Cu}^\text{II} + \text{Cu}^\text{II} \]
in aqueous medium at 25°C shifts towards the left in the presence of [JEE 2011]
(A) \( \text{NO}_3^- \)
(B) \( \text{Cl}^- \)
(C) \( \text{SCN}^- \)
(D) \( \text{CN}^- \)

10. The thermal dissociation equilibrium of \( \text{CaCO}_3(s) \) is studied under different conditions.
\( \text{CaCO}_3(s) \rightleftharpoons \text{CaO(s)} + \text{CO}_2(g) \)
For this equilibrium, the correct statement(s) is (are) [JEE 2013]
(A) \( \Delta H \) is dependent on T
(B) \( K \) is independent of the initial amount of \( \text{CaCO}_3 \)
(C) \( K \) is dependent on the pressure of \( \text{CO}_2 \) at a given T
(D) \( \Delta H \) is independent of the catalyst, if any

11. The thermal dissociation equilibrium of \( \text{CaCO}_3(s) \) is studied under different conditions.
\( \text{CaCO}_3(s) \rightleftharpoons \text{CaO(s)} + \text{CO}_2(g) \)
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(A) \( \Delta H \) is dependent on T
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(C) \( K \) is dependent on the pressure of \( \text{CO}_2 \) at a given T
(D) \( \Delta H \) is independent of the catalyst, if any
# Answers

## OBJECTIVE PROBLEMS (JEE MAIN)

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## OBJECTIVE PROBLEMS (JEE ADVANCED)

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## SUBJECTIVE PROBLEMS (JEE ADVANCED)

1. (a) 25, shifts left. (b) 0.22, shifts right. (c) x, shifts left. (d) 1, shifts right. (e) 0, shift 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) $K = \frac{1}{[Pb^{2+}][Cl^-]^2}$ 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. (a) incomplete (b) almost complete 7. c 8. ~ $9 \times 10^{-21}$ mol/L
5. The reaction is not an equilibrium because $Q_c > K_c$. The reaction will proceed from right to left to reach equilibrium
6. 5.9 x 10$^{-1}$ M 12. [NO] = 0.056 M, [N$_2$] = [O$_2$] = 1.37 M 13. [PCl$_5$] = [Cl$_2$] = 0.071 M, [PCl$_3$] = 0.089
7. $P_{Cr} = P_{PbCr} = 0.389$ atm, $P_{Pb} = 1.08$ atm 15. $K_c = 0.4$, $a = 0.1$ 16. 50%
8. (a) 6.667 x 10$^{-4}$ mol L$^{-1}$; (b) n(N$_2$O$_5$) = 0.374 mol; n(NO$_2$) = 0.052 mol; (c) 10.49 atm (d) 6.44%
18. 0.97 atm  19. $K_p = 1.3 \times 10^{-3}$ atm$^{-2}$  20. $K_p = 2.5$ atm  21. 53.33 %

22. $K = 4$  23. $\frac{31}{27}$  24. 22.4 mg  25. $P_{H_2O} = 5 \times 10^{-1}$ atm  26. 0.821 atm

27. add $N_2$, add $H_2$, increase the pressure, heat the reaction

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

29. (a) $K = \frac{[CH_3OH]}{[H_2]^{1}[CO]}$.
   (b) 1. $[H_2]$ increase, $[CO]$ decrease, $[CH_3OH]$ increase
   2. $[H_2]$ increase, $[CO]$ decrease, $[CH_3OH]$ decrease
   3. $[H_2]$ increase, $[CO]$ increase, $[CH_3OH]$ increase
   4. $[H_2]$ increase, $[CO]$ increase, $[CH_3OH]$ increase
   5. $[H_2]$ increase, $[CO]$ increase $[CH_3OH]$ decrease
   6. no change

30. (a) $K = \frac{[CO]}{[H_2][H_2O]}$ ;
   (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, $[CO]$ increase. $[H_2]$ increase; 5. $[H_2O]$ decrease, $[CO]$ increase, $[H_2]$ increase

31. b

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

33. a

34. $k_{f} / k_{b} = \frac{[C]}{[A][B]} = k_c$

35. 216

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

37. $k_f$ increase more than $k_c$, this means that $E_f$ (reverse) is greater than $E_f$ (forward). The reaction is exothermic when $E_f$ (reverse) > $E_f$ (forward).

38. 16.06 kJ

39. $-810$ J/mol; $-587.2$ J/mol and 41.3 KJ/mol

40. 1.3 $\times$ 10$^4$

41. 45. 0.056

42. 29.0

43. 47. $K_c = 0.0313$ atm, $K_c = 1.28 \times 10^{-1}$

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**Answer Ex-IV**

**PREVIOUS YEARS PROBLEMS**

**LEVEL – I**

| JEE MAIN |
|---|---|---|---|---|---|---|

**LEVEL – II**

| JEE ADVANCED |
|---|---|---|---|---|---|---|
| 1. 4.54 g dm$^{-3}$ | 2. (i) $K_c = 8.1 \times 10^{-4}$ mol$^2$L$^2$; $K_c = 4.91 \times 10^{-2}$ atm$^2$ (ii) No effect |
CHEMICAL EQUILIBRIUM

1. **A**
   Given: \( \text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 \)
   \( (g) \quad (g) \)
   conc. of \( \text{N}_2\text{O}_4 \) = \( 4.8 \times 10^{-2} \) mol/lit
   \( \text{NO}_2 \) = \( 1.2 \times 10^{-2} \) mol/lit

   \[ K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 3 \times 10^{-3} \]

2. **A**
   Given \( P_4(s) + 5\text{O}_2(g) \rightleftharpoons P_4\text{O}_{10}(s) \)
   Note: for solid conc. is 1

   \[ K_c = \frac{[\text{P}_4\text{O}_{10}]}{[P_4][\text{O}_2]^5} \]

   \[ \Rightarrow \frac{1}{[\text{O}_2]^5} \]

3. **B**
   Given: \( \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \)
   \( K_c = 4 \times 10^{-4} \)

   Now, \( \text{No} \) = \( \frac{1}{2} \text{N}_2(g) + \frac{1}{2} \text{O}_2(g) \)

   \[ K_c = \frac{1}{K_c} = \frac{1}{4 \times 10^{-4}} = 2.5 \times 10^2 \]

4. **A**
   Given: \( \text{SO}_3(g) \rightleftharpoons \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \)
   \( K_c = 4.9 \times 10^{-2} \)

   \[ 2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3 \]

   \( K_c = \frac{1}{(K_c)^2} = \frac{1}{(4.9 \times 10^{-2})^2} = 416.49 \]

5. **C**
   Rewrite the equation as
   \( \text{CO}(g) + 3\text{H}_2(g) \rightleftharpoons \text{CH}_4(g) + \text{H}_2\text{O}(g) \quad 1/K_2 \)
   \( \text{CH}_4(g) + 2\text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + 4\text{H}_2(g) \quad K_1 \)

   \( \frac{1}{K_2} \times K_3 = k_1 \)

   \( \Rightarrow K_3 = K_1 K_2 \)

6. **B**
   Given: \( \text{PCl}_3(g) \rightleftharpoons \text{PCl}_2(g) + \text{Cl}_2(g) \)

   \[ K_c, \quad \frac{[\text{PCl}_2] \times [\text{Cl}_2]}{[\text{PCl}_3]} = \frac{0.01 \times 0.01}{0.01} = 0.001 \]

   \( 2\text{H}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) + \text{I}_2(g) \)

   \[ K_c = 0.01 \]

   \( K_3 = \frac{(0.01)^2}{(0.01)^2} = 1 \)

   \[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \]

   \[ 0.01 \]

   \[ 0.01 \]

   \[ 0.01 \]

   \[ K_c = \frac{(0.01)^2}{(0.01)^2} = \frac{1}{10^{-2}} = 10^{-4} \]

   Extent of reaction \( K_c \quad (iii) > (ii) > (i) \)

7. **D**
   Given: \( \text{NH}_3 \text{HS} \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S}(g) \)

   \( (s) \quad (g) \quad (g) \)

   a mole
   \( 0.5 \text{ atm} \quad 0 \)

   at eq.
   \( 0.5 + x \quad x \quad \text{atm} \quad \text{atm} \)

   total pressure = \( 0.5 + x + x = 0.84 \)

   \[ 2x = 0.34 \]

   \[ x = 0.17 \]

   \[ P_{\text{NH}_3} = 0.5 + x \]

   \[ = 0.5 + 0.17 = 0.67 \]

   \[ P_{\text{H}_2\text{S}} = 0.17 \]

   \[ \text{K}_s = [P_{\text{NH}_3}][P_{\text{H}_2\text{S}}] = 0.67 \times 0.17 = 0.114 \]
8. A
Given \(3A(g) + B(g) \rightarrow 2C(g)\)
 portrayed at equil.
conc\(^n\) \[\begin{array}{c|c|c}
 2 & 2 & 2 \\
 v & v & v
\end{array}\]

\[K_c = 9.0 \text{(given)}\]

\[K_c = \frac{[C]^2}{[A]^3[B]}\]

\[\Rightarrow \frac{(2/v)^2}{(2/v)^3 (2/v)}\]

\[q = \frac{v^2}{4}\]

\[v^2 = 36\]

\[\Rightarrow v = 6L\]

9. A
Given that: \(-\)
Constant formation of \(S_{2}^{+}\) is \(K_1 = 12\)
\(S^{2-} + S \rightarrow S_{2}^{+}\) \(K_1 = 12\) \(\ldots (1)\)

Similarly:
Eq. (2) - Eq(1)
\(S_{2}^{+} + S \rightarrow S_{3}^{+}\)

\[\Rightarrow K_3 = \frac{1}{K_1} \times K_2 \Rightarrow \frac{132}{12} = 11\]

10. B
Given 1 mole \(N_2\), 3 mole \(H_2\),
total pressure = 4 atm
reaction \(N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)\)
initially \[\begin{array}{c|c|c}
 1 & 3 \\
\end{array}\]
at equilibrium \(1-x \rightarrow 3-3x \rightarrow 2x\)

\[P_{\text{tot}} = 1 - x + 3 - 3x + 2x\]

\[= 4 - 2x\] \(\ldots (1)\)

\(P_{\text{tot}}\) fall to 3 atm

\[\Rightarrow P_{\text{tot}} = 3\] \(\ldots (2)\)

from (1) & (2)

\[3 = 4 - 2x \Rightarrow x = \frac{1}{2}\]

\[P_{H_2} = \frac{1}{2} ; P_{H_2} = 3 - \frac{3}{2} ; P_{NH_3} (\text{eq.}) = 2 \times \frac{1}{2}\]

\[\Rightarrow \frac{3}{2} \Rightarrow 1\]

11. B
Given: 1 mole of \(N_2O_5\)
Initial temp. = 300 K
Final temp. = 600 K
\(N_2O_5\) decomposes
\(N_2O_5(g) \rightarrow 2NO_2(g)\)

\[\begin{array}{c|c|c}
 1 & 0 & 0.4 \\
 1-0.2 & & \\
 \Rightarrow 0.8 \\
\end{array}\]

as we know
PV = nRT

\[\frac{P_1}{n_1T_1} = \frac{P_2}{n_2T_2}\]

\[1 \times 300 = 1.2 \times 600\]

\[P_2 = 2.4 \text{ atm}\]

12. D
Given: \(N_2O_5(g) \rightarrow 2NO_2(g)\)

\[K_p = K_c \ldots (1)\]

\[K_p = K_c (RT)^{y_N}\]

\[\Delta n = 2 - 1 \Rightarrow 1\]

\[K_p = K_c \times RT\]

\[RT = 1\]

\[T = \frac{1}{R}\]

\[\Rightarrow \frac{1}{0.082} \Rightarrow 12.19 K\]

\[T = 12.19 K\]

13. C
Given: \(CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)\)

\[\Delta n = 1 - \left(\frac{1}{2} + 1\right)\]
\[ \Delta n_r = -\frac{1}{2} \]

as we know

\[ K_p = K_c (RT)^{\Delta n_r} \]

\[ \Rightarrow \frac{K_p}{K_c} = (RT)^{-1/2} \]

14. **A**

Given:

\[ 2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2 \]

\[ K_c = 1.8 \times 10^{-4} \text{ (g) (g) (g)} \]

\[ T = 184^\circ \text{C} \]

\[ = (184 + 273) \text{K} \Rightarrow 475 \text{K} \]

\[ R = 0.083 \text{ J K}^{-1} \text{ mol}^{-1} \]

Now, \[ \Delta n_r = 3 - 2 \Rightarrow 1 \]

\[ K_p = K_c (RT)^{\Delta n_r} \]

\[ K_p = K_c (RT)^{1} \Rightarrow \frac{K_p}{K_c} = (RT)^{1} \]

\[ \frac{K_p}{K_c} = 0.0821 \times 457 \]

\[ K_p > 1 \]

\[ \Rightarrow K_p > K_c \]

15. **A**

PCl₅ dissociation in a closed container

\[ \text{PCl}_5 (g) \rightleftharpoons \text{PCl}_3 (g) + \text{Cl}_2 (g) \]

\[ 1 \quad 0 \]

\[ 1 - \alpha \quad \alpha \quad \alpha \]

Total mole = \( 1 - \alpha + \alpha + \alpha \) \[ \Rightarrow 1 + \alpha \]

\[ K_{PCl_3} \] (mole fraction) = \[ \frac{\alpha}{1+\alpha} \]

\[ \therefore \] (partial pressure) \[ P_{PCl_3} = P \left[ \frac{\alpha}{1+\alpha} \right] \]

16. **D**

Given - Reaction:

\[ 2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g) \]

\[ 1 \quad 0 \quad 0 \]

\[ 1 - \alpha \quad \alpha \quad \alpha \] (where \( \alpha \) is degree of dissociation)

\[ C(1-\alpha) \quad \frac{C}{2} \quad \frac{C}{2} \]

as

\[ K_c = K_p = \frac{x^2}{4(1-x)^2} \]

\[ \sqrt{K_p} = \frac{x}{2(1-x)} \]

\[ 2\sqrt{K_p} = \frac{x}{1-x} \]

\[ \frac{1 - \alpha}{\alpha} = \frac{1}{2 \sqrt{K_p}} \Rightarrow \frac{1}{\alpha} - 1 = \frac{1}{2 \sqrt{K_p}} \]

\[ \frac{1}{\alpha} = 1 + \frac{1}{2 \sqrt{K_p}} \]

\[ \frac{1}{\alpha} = \frac{2\sqrt{K_p} + 1}{2\sqrt{K_p}} \]

\[ \Rightarrow \alpha = \frac{2\sqrt{K_p}}{2\sqrt{K_p} + 1} \]

17. **C**

Given - reaction

\[ \text{A}(g) + 2\text{B}(g) \rightleftharpoons \text{C}(g) \]

\[ a \quad 4 \quad 0 \]

(at equill.) \( a-x \quad 4-2x \quad x \)

as \( x = 1 \)

\[ \text{A}(g) = a - 1, \quad \text{B}(g) = 2, \quad \text{C}(g) = 1 \]

\[ \frac{[\text{A}]}{[\text{B}]} = \frac{\frac{a-1}{5}}{\frac{2}{5}}, \quad \frac{[\text{C}]}{[\text{B}]} = \frac{1}{5} \]

\[ K_c = \left( \frac{1}{5} \right) \left( \frac{2^4}{5^4} \right) \]

\[ K_c = \frac{25}{4(a-1)} \quad \ldots(1) \]

as \( K_c = 0.25 \)

\[ \ldots(2) \]

from (1) & (2)

\[ 0.25 = \frac{25}{4(a-1)} \]

\[ \Rightarrow 4(a-1) = 100 \]

\[ a - 1 = 25 \]

\[ \Rightarrow a = 26 \]

18. **B**

Given rxn -

\[ \text{A}(g) + 2\text{B}(g) \rightleftharpoons \text{C}(g) + \text{D}(g) : K_c = 10^{12} \]

\[ 0.5 \quad 1 \quad 0.5 \quad 3.5 \]

\[ K_c = 10^{12} \]

\[ Q_c = \frac{[\text{A}][\text{C}]}{[\text{B}][\text{D}]} = \frac{0.5 \times 3.5}{0.5} \]
Q_c = 3.5
\Rightarrow Q_c = K_c.

Forward shift
Now, \( A(g) + 2B(g) \rightleftharpoons C(g) + D(g) \)

\[ \gamma \quad 2\gamma \quad 1 \quad 4 \]

Let

\( K_c \) is very high
\therefore x \approx 0.5
as \( \Rightarrow \gamma = 0.5 - x \) and \( 1 - 2x = 2\gamma \)

\[ K_c = \frac{[C][D]}{[A][B]^2} \Rightarrow \frac{1 \times 4}{4 \times 4\gamma^2} \]
\[ = \frac{4}{4\gamma^2} \]

where \( K_c = 10^{11} \)
\therefore \[ 10^{11} = \frac{4}{4\gamma^2} \]
\[ \gamma = 10^{-4} \]
concent. of B = 2\gamma \Rightarrow 2 \times 10^{-4}

19. B

\( A(g) + 2B(g) \rightleftharpoons 3C(g) \)

\[ K_r = \frac{(3x)^3}{(2 - 2x)(1 - x)} \]

\[ K_r = \frac{(3x)^3}{4(1 - x)^3} \]

\( \therefore K_r = 2 \times 10^{-3} \)
\[ 2 \times 10^{-3} \times 4 = \frac{(3x)^3}{(1 - x)^3} \]
\[ 2 \times 10^{-1} = \frac{3x}{(1 - x)} \]
\[ 2(1 - x) = 3x \]
\[ x = \frac{0.2}{3} \]

Now \( P_c = 3x \)
\[ = 3 \times \frac{1}{16} \]
\[ \Rightarrow \frac{3}{16} \Rightarrow 0.1875 \]

20. B

Given:
V = 20.0 lit
0.50 mole of each gas that is \( H_2 + I_2 \)
Now, \( H_2 + I_2 \rightleftharpoons 2HI \)
initially \( 0.5 \quad 0.5 \quad 0 \)
at eq. \( 0.5 - x \quad 0.5 - x \quad 2x \)

\[ K_{eq} = \frac{[HI]^2}{[H_2][I_2]} \]
\[ 49 = \frac{(2x)^2}{(0.5 - x)^2} \]

(as \( K_{eq} = 49 \))

\[ 7 = \frac{2x}{0.5 - x} \]
\[ 2x = 3.5 - 7x \]
\[ 9x = 3.5 \]
\[ x = 0.39 \]

conc. of [HI] = \( 2x \frac{20 - x}{10} \)
\[ \Rightarrow 0.039 \]

21. A

Given:
\( V = 250 \) lit
\( SO_2S_2(S) + 3H_2(g) \rightleftharpoons 2Sb(S) + 3H_2S(g) \)

After equilibrium
\( H_2S \) treated with excess of Pb\(^{2-}\)
\( \Rightarrow H_2S + Pb^{2-} \rightleftharpoons PbS + H_2 \)

\( \therefore \) mole of PbS = \( \frac{1.195}{239} \)
\[ = 5 \times 10^{-1} \]
mole of \( H_2S = 5 \times 10^{-1} \)
mole of \( H_2 \) remaining = 0.01-0.005 = 0.005

\[ K_c = \frac{[H_2S]^3}{[H_2]^3} \]
\[ = \frac{0.005}{0.005} \]
\[ \Rightarrow K_c = 1 \]

22. A

Given:
\( CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2 \)

\( K_c = 3 \)
\[ \frac{[CO_2][H_2]}{[CO][H_2O]} \]

At eq. \( x \quad 5 - x \quad 2 + x \)
3 = \frac{(x)(2 + x)}{(5 - x)(2 - x)}
3[10 - 7x + x^2] = 2x + x^2
2x^2 - 23x + 30 = 0
\left( x - \frac{3}{2} \right) (x - 10) = 0
x = \frac{3}{2}, x = 10
conc. of H_2 = \left( 2 + \frac{3}{2} \right) / 2
\Rightarrow \frac{2 + 1.5}{2} = \frac{3.5}{2}
Now, \Rightarrow \frac{21.5}{2} = 1.75

23. A
Given :-
H_2(g) + S(s) \rightleftharpoons H_2S(g)
K_p = 7 \times 10^{-2}
as given - .50 mole of H_2
1.0 mole of S
Now, H_2(g) + S(s) \rightleftharpoons H_2S(g)
0.5 1.0
0.5-x 1-x x
as \quad K_p = K_c = \frac{x}{(0.5 - x)}
7 \times 10^{-2} = \frac{x}{(0.5 - x)} \quad \text{(as \; K_p = 7 \times 10^{-2})}
x = 0.035 - 0.07x
\Rightarrow x = \frac{0.035}{1.07}

R_{H_2S} = \frac{(0.035 \times 0.0821 \times 360)}{1}
= 0.966 \text{ atm.}

24. C
Given :-
K_p = 12 \times 10^4 \text{ atm for reaction}
2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)
2atm 2atm 2atm
380 = \frac{1}{2} 2-2y 2 + 4x 2 + x
K_p = 12 \times 10^4; \; K_p >> 1
\Rightarrow x = 1

\Rightarrow 12 \times 10^4 = \frac{(3 \times (6)^4)}{y^2 \times (1/2)^2}
\Rightarrow \frac{12 \times 10^4}{3 \times 36 \times 36 \times 4} = \frac{1}{y^2}
\Rightarrow y = \frac{36 \times 2}{2 \times 10^4} \quad 2 \times 18 \times 10^4
y = 36 \times 10^4 \text{ atm}
y = 3.6 \times 10^3 \text{ atm}

25. B
Given :- Reaction as
H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)
Here \quad K_p = K_c
initially 0.25 0.25 0 0
at eq. 0.25-x 0.25x x x
K_c = \frac{[CO][H_2O]}{[H_2][CO_2]} \Rightarrow \frac{x^2}{(0.25-x)^2}
\Rightarrow 0.16 \frac{x^2}{(0.25-x)^2} \quad \text{[as \; K_c = K_p = 0.16]}
x = 0.1 - 0.4 x
x = 0.1 \quad \frac{1}{1.4} = \frac{1}{14}
% mole of CO = \frac{(1/14)}{\text{total mole}} \times 100
% mole of CO = \frac{(1/14)}{0.5} \times 100
= 14.28%

26. D
H_2(g) + I_2(g) \rightleftharpoons 2HI(g)
If \lambda_n = 0
\Rightarrow (2 - 2) = 0
then no effect of Pressure change

27. A
H_2(g) + O_2(g) \rightleftharpoons 2NO(g) \Delta H_s = 0
If we change the volume the ultimate effect will be due to change in pressure
\Rightarrow If \lambda_n = 0
no effect of change in volume
28. **A**

\[ 2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \quad \Delta H^\circ = -198 \text{ KJ} \]

Exothermic reaction
favourable at low temperature \( \Delta n_\text{f} < 0 \)
\[ \Rightarrow \text{favourable at high pressure} \]

29. **D**

\[ \text{Cl}_2 + 3\text{F}_2(g) \rightleftharpoons 2\text{ClF}_3(g) \quad \Delta H = -329 \text{ KJ} \]

ClF\(_3\) will be increased when reaction shifted forward.
\[ \Rightarrow \text{Exothermic low temperature} \]
\[ \therefore \text{Addition of reactant} \]
\[ \Delta n_\text{f} < 0 \]
\[ \Rightarrow \text{Increase in pressure lowers the volume.} \]

30. **C**

C(diamond) \rightleftharpoons C(graphite) \quad \Delta H = -1.9 \text{ KJ/mole}

It is exothermic reaction
so it favours low temperature
density of graphite is less than diamond low pressure.
\[ \Rightarrow \text{but for formation of diamond Reverse condition high temperature & high pressure} \]

31. **A**

\[ \text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_3(g) + \text{Cl}_2(g) \]

Volume of container is constant
so no effect of addition of inert gas.

32. **B**

\[ \text{PCl}_3(g) \rightleftharpoons \text{PCl}_5(g) + \text{Cl}_2(g) \]

CO(g) + Cl\(_2\)(g) \rightleftharpoons COCl\(_2\)(g)
Ni will react will CO hence concentration of CO will reduces
\[ \Rightarrow \text{Second equilibrium shifted backward which increase the conc of Cl}_2 \therefore \text{first equilibrium also shifted backward.} \]

33. **D**

Exothermic
\[ \Rightarrow \text{low yield at high temperature} \]
\[ \Delta n_\text{f} < 0 \]
\[ \Rightarrow \text{low yield at low pressure} \]

34. **A**

\[ 2\text{C}(s) + \text{O}_2(g) \rightleftharpoons 2\text{CO}(g) \]

\[ \Delta n_\text{f} = 2 - 1 = 1 \]
\[ \Rightarrow \Delta n_\text{f} > 0 \]
\[ \Rightarrow \text{so on increasing the pressure equilibrium shifted left (or backward direction) as pressure increases volume decreases.} \]

35. **A**

Given - V.D of N\(_2\)O\(_4\) = 30

\[ \text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 \]

1 \[ \quad \text{0} \]

1 - \(\alpha\) \[ \quad 22 \]

Total mole = 1 + 2\(\alpha\) - \(\alpha\) \[ \Rightarrow 1 + \alpha \]

Mass conservation
wt. of N\(_2\)O\(_4\) at t = 0 \[ \text{wt. of mixture.} \]
\[ 1 \times (92) = (1 + \alpha) \times 2 \times 30 \]
\[ \Rightarrow 92 = (1 + \alpha) \times 60 \]
\[ \Rightarrow \alpha = \frac{32}{60} = \frac{8}{15} \]
\[ \alpha\% = \frac{8}{15} \times 100 \]
\[ = 53.3\% \]

36. **C**

Given :- \[ A_i(g) \rightleftharpoons B_j(g) + C_k(g) \]

At eq. \[ P = x \quad x \quad x \]

Total pressure \[ P = x + x + x \]
\[ \Rightarrow P + x = 7 \text{ as total pressure = 7} \ldots (1) \]

Now, \[ K_p = \frac{[P_{B_j}] [P_{C_k}]}{[P_{A_i}]} \]
\[ 9 = \frac{x^2}{(P - x)} \] \[ \text{as } K_p = 9 \]
\[ 9(7 - x - x) = x^2 \] \[ \text{[from eq. (1)]} \]
\[ \Rightarrow x^2 + 18x - 63 = 0 \]
\[ x = 3 \]
\[ x = 3 \]
\[ \text{then} \]
\[ p + x = 7 \]
\[ p = 4 \]

as we know
P.M. = dRT (volume cont.)
\[ \Rightarrow P \times 1 = \frac{1}{M} \]
\[ \Rightarrow \frac{P}{P_{eq}} = \frac{M_{eq}}{M_i} \]
\[ \Rightarrow \frac{4}{7} = \frac{M_{eq}}{70} \]
\[ \Rightarrow M_{eq} = 40 \]
37. **C**

Given: - Vapour density = 6

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Initially</th>
<th>At eq.</th>
<th>Total no. of moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\text{NH}_3(g) \rightleftharpoons \text{H}_2(g) + 3\text{H}_2(g)$</td>
<td>$t=0$</td>
<td>$1$</td>
<td>$1 - \alpha$</td>
</tr>
</tbody>
</table>

$\Rightarrow 1 + \alpha$

Apply Mass conservation

wt. of NH$_3$ at $t=0 = \text{wt. of mixture of equil.}$

$1 \times [14 + 3] = (1 + \alpha) \quad 2 \times \text{U.} \Delta$

$17 = (1 + \alpha) \times 2 \times 6$

$\frac{17}{12} = 1 - \alpha$

$\alpha = \frac{5}{12}$ $\Rightarrow \% \text{ of } \alpha = \frac{5}{12} \times 100 = 41.66$

$K_{p_2} = \frac{(P_{AB})^2}{P_{A_2} \times P_{B_2}} = \frac{(0.5)^2}{(0.75 - x)(0.75 - y)} \ldots (3)$

$K_{p_3} = \frac{(P_x)^2}{P_{A_2}} = \frac{(2x)^2}{(0.75 - x)}$

$K_{p_4} = \frac{(P_y)^2}{P_{B_2}} = \frac{(2y)^2}{(0.75 - y)}$

$K_{p_1} \times K_{p_2} = \frac{(2x)^2(2y)^2}{(0.75 - x)(0.75 - y)} \Rightarrow \frac{16x^2y^2}{(0.75 - x)(0.75 - y)} \ldots (4)$

Now equate with eq. (3)

$K_{p_1} \times K_{p_2} = K_{p_3}$

$\Rightarrow 0.5 = 4xy \Rightarrow xy = \frac{1}{8}$

$x + y = 0.75 \text{ [put } y = \frac{1}{8x} \text{ ]}$

$\Rightarrow 8x^2 - 6x + 1 = 0$

$x = \frac{1}{4}, x = \frac{1}{d}$

$y = \frac{1}{2} \quad [x > y]$

Now,

$\frac{K_{p_3}}{K_{p_2}} = \frac{(1/4)(1/2)}{1(1/4)} = \frac{1}{8}$

$\Rightarrow \frac{K_{p_3}}{K_p} = 8$

38. **A**

Given - Equimolar mixture of two gaven

$A_2$ and $B_2$

$A_2(g) \rightleftharpoons 2A(g) \quad K_p$

At eq. 1-$x$ | 2$x$
| $B_2(g) \rightleftharpoons 2B(g)$ |

At eq. 1-$4$ | 24

Now

$A_2(g)+B_2(g) \rightleftharpoons 2AB \quad K_p = 2$

| Initially | 1-$x$ | 1-$4$ | 2z
| $P_{eq} = P_{A_2} - P_{B_2} + P_B + P_{A} + P_{AB}$ |

$\Rightarrow 1-x-z+1-y-z+2x+24+2z$

$P_{eq} = 2 + x + y$

$2 + x + y = 2.75$

$x + y = 0.75 \quad \text{[as } P_{eq} = 2.75]\)$

$x + y = 0.75 \ldots (1)$

As partial pressure of $AB(g)$

$P_{AB} = 0.5$

$27 = 0.5$

$7 = 0.25 \ldots (2)$

39. **A**

Given: - Heat of reaction (at constant V) = 1200 cal

(at constant pressure) $\Rightarrow T = 300K$

$K_p$

$K_c = ?$

Now, $K_p = e^{\frac{-\Delta H}{RT}}$
40. \(D\)

Given: - When \(N_2O_5\) is heated \(T\), its dissociates
\[N_2O_5 \rightleftharpoons N_2O_4 + O_2 : K_c = 2.5\]

and
\[N_2O_4 \rightleftharpoons N_2O + O_2 : K_c\]

\(K_c = \frac{(x+y)(x-y)}{4-x}\)

\[\Rightarrow \frac{2.5(x-y)}{4-x} = 2.5 \ [\text{from eq. (1)}]\]

\[\Rightarrow x-y = 4-x\]

\[\Rightarrow \frac{2x-y = 4}{(2)\ (2)}\]

\(\Rightarrow\) from (1) and (2)

\(3x = 6.5\)

\(x = 2.17\)

from (1)

\(2.17 + y = 2.5\)

\(y = 2.5 - 2.17\)

\(y = 0.334\)

Equilibrium concentration of \(N_2O\) is 0.334.

41. \(A\)

\[\ln k_p = \frac{-\Delta H}{RT} + \ln A\]

Exothermic \(\Delta H < 0\)

slope +Ve

42. \(D\)

\(A \rightleftharpoons B\)

The rate transformation of \(A\) to \(B\) just equal to rate of transformation of \(B\) to \(A\) in the system.
\[
\frac{1-\alpha}{\alpha} = \frac{1}{\sqrt{K}}
\]
\[
\frac{1}{\alpha} = \frac{1}{\sqrt{K}} + \frac{\sqrt{K}}{K}
\]

Now,
\[
\alpha = \frac{\sqrt{K}}{1 + \sqrt{K}}
\]

48. A
Given:
\[A \rightleftharpoons B + C + D\]
initially
\[
\begin{array}{ccc}
1 & 0 & 0 \\
\end{array}
\]
at eq.
\[
\begin{array}{cccc}
1-x & x & x & x \\
\end{array}
\]
Total mole = 1 + 2x
Apply mass conservation
Wt. of A at t=0 = wt of mixture at eq.
\[1 \times M_{\text{m}} = [1+2x] \times 50 \]
\[M_{\text{m}} = (1+0.2) \times 100 \quad (\text{as } x = 0.1) \]
\[M_{\text{m}} = 120 \]

49. C
Given: \(\text{N}_2\text{O}_4\) dissociated
\[\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2\]
\[
\begin{array}{ccc}
1 & 0 \\
\end{array}
\]
at eq. \(1-x\)
\[
\begin{array}{cc}
2x \\
\end{array}
\]
Total mole = 1 - x + 2x
= 1 + x
Mass conservation
wt. of \(\text{N}_2\text{O}_4\) at t=0 = wt. of \(\text{NO}_2\) at eq.
\[1 \times 92 = (1+x) \times 82 \]
\[92 - 1 = x \]
\[82 \]
\[x \% = \frac{10}{82} \% = 12.2\% \]

50. C
Given: \(\text{PCl}_3 \rightleftharpoons \text{PCl}_4 + \text{Cl}_2\)
initially
\[
\begin{array}{ccc}
1 & 0 & 0 \\
\end{array}
\]
1. **A, C**

2. **C, D**

3. **B**

4. **D**
   
   As we know
   
   \[
   \ln \left( \frac{K_p}{K_p^0} \right) = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
   \]
   
   \[
   \ln 4 = \frac{8.314}{0.313} \left( \frac{1}{298} - \frac{1}{313} \right)
   \]
   
   \[
   \Delta H^\circ = 71.6 \text{ kJ}
   \]

5. **C**
   
   Given:
   
   \[
   \text{NH}_2\text{COONH}_4(s) \rightleftharpoons 2\text{NH}_3(g) + \text{CO}_2(g)
   \]
   
   \[
   (2x)^2x = 2.92 \times 10^{-5}
   \]
   
   \[
   x^2 = \frac{2.92}{4} \times 10^{-5}
   \]
   
   \[
   P_{\text{new}} = 3x = 0.0582
   \]

6. **B**
   
   Given:
   
   \[
   2\text{H}_2(g) + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}(g)
   \]
   
   \[
   2\text{CO}_2 \rightleftharpoons 2\text{CO}(g) + 2\text{O}_2
   \]
   
   \[
   2\text{H}_2(g) + 2\text{CO}(g) \rightleftharpoons 2\text{H}_2\text{O}(g) + 2\text{CO}_2
   \]
   
   \[
   \text{H}_2(g) + \text{CO}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) + \text{CO}(g)
   \]
   
   \[
   K_1 = \frac{K_2}{K_1}
   \]
   
   \[
   K = 2.58
   \]

7. **C**
   
   \[
   \text{H}_2(g) \rightleftharpoons 2\text{H}(g)
   \]
   
   reaction is endothermic
   
   \[
   \Delta H^\circ < 0 \rightarrow \text{High temperature}
   \]
   
   \[
   \Delta n > 0 \text{ low pressure}
   \]

8. **C, D**
   
   Introduction of inert gas at constant pressure will increase ↑ & volume ↓ the pressure of gases of equilibrium
   
   ⇒ equilibrium shifted forward

9. **C, D**
   
   \[
   \text{NaNO}_3(s) \rightleftharpoons \text{NaNO}_2(s) + \text{O}_2(g)
   \]
   
   \[
   \Delta H^\circ > 0 \text{ endothermic}
   \]
   
   High temperature
   
   ⇒ forward reaction favoured
   
   1000 pressure
   
   High pressure → Reverse reaction

10. **B, C**

11. **A, C, D**

12. **B, C**
   
   Exothermic → low temp
   
   ⇒ forward reaction favoured
   
   High temp backward

13. **D, C**
   
   As given:
   
   \[
   \text{HgO}(s) + 4\text{I}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HgI}_4^{2-}(aq) + 2\text{OH}^-(aq)
   \]
   
   \[
   K = \frac{[\text{HgI}_4^{2-}][\text{OH}^-]^2}{[\text{I}^-]^4}
   \]

   as, \[
   \text{OH}^+ \rightleftharpoons \text{HgI}_4^{2-} \downarrow
   \]
   
   \[
   \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^+ \rightleftharpoons \text{H}^+ + \text{OH}^-
   \]

14. **B, D**
   
   \[
   \Delta G = \Delta H^\circ + \Delta S
   \]
   
   \[
   \Delta G = RT \ln k
   \]
   
   from (1) & (2)
   
   \[
   \ln k = \frac{\Delta H^\circ}{R} + \frac{\Delta S}{R}
   \]

   slope of the line equal to \[
   \frac{\Delta H^\circ}{R}
   \]

15. **A, C**
   
   As given:
   
   \[
   \text{H}_2\text{O}(s) \rightleftharpoons \text{H}_2\text{O}(l)
   \]

   At 0°C density of \text{H}_2\text{O}(s) < \text{H}_2\text{O}(l)

   As P ↓ & V ↑
   
   ⇒ formation of more \text{H}_2\text{O}(s)

   and increase in melting point of \text{H}_2\text{O}(s)

16. **A**
   
   (A) Statement-1 is true, statement-2 is true and statement-3 is correct explanation for statement-1
17. A
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1

18. A
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1

19. B
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1

20. C
(C) Statement-1 is false, statement-2 is true.

21. D
(D) Statement-1 is true, statement-2 is false.

22. B
As we know, \( K_s = K_c (RT)^{\Delta n_s} \)
\[ \Delta n_s = 2 - 2 = 0 \]
\[ \Rightarrow \frac{49 \times \left(0.0802 \times 700\right)^6}{7} \]
\[ K_s = 49 \]

23. C
\( H_2 + I_2 \rightarrow 2HI \)
\[ \begin{align*}
0.5 & \quad \text{0.5} \\
0.5-x & \quad \text{0.5-x} \quad \text{2x} \\
\text{Total number of moles} & \quad 0.5 - x + 0.5 - x + 2x = 1 \\
\text{P} & \quad \frac{1 \times 0.0821 \times 700}{7} \\
\text{P} & \quad 8.21 \text{ atm} \\
\end{align*} \]

24. B
from above question
\[ K_c = \frac{4x^2}{(0.5 - x)^2} \]
\[ \frac{4x^2}{\left(\frac{2x}{7}\right)^2} \]
\[ \frac{4x^2}{\left(\frac{0.5 - x}{7}\right) \left(\frac{0.5 - x}{7}\right)} = 49 \]

25. A
At equilibrium mole of HI = 2x
\[ 2x / (0.5 - x) = 7 \Rightarrow x = 0.388 \]
remaining \( I_2 = 0.5 - 0.388 = 0.112 \)

26. A
Best drying agent reduces the moisture more effectively means reduces the
\( P_{H_2O} \) to the minimum
for \( SrCl_2 \), \( 2H_2O P_{H_2O} = (K_v)^{1/4} \)
\[ (5 \times 10^{-12})^{1/4} = 1.49 \times 10^{-3} \]
for \( NaOH \), \( 7H_2O \)
\[ P_{H_2O} = (2.43 \times 10^{-11})^{1/4} = 3 \times 10^{-3} \]
for \( Na_2SO_4 \)
\[ P_{H_2O} = (1.02 \times 10^{-27})^{1/4} = 2 \times 10^{-3} \]

27. B
\( Na_2SO_4 \cdot 10H_2O \) will release moisture
when \( P_{H_2O} < 2 \times 10^{-3} \)
\[ VP_{H_2O} = 6 \times 10^{-3} \text{ atm} \]
Relative humidity \( = \frac{P_{H_2O}}{VP_{H_2O}} = \frac{2 \times 10^{-3}}{6 \times 10^{-3}} \)
\[ = 33.33\% \]
if relative humidity < 33.33%
\[ P_{H_2O} < 2 \times 10^{-3} \]
it will releases the moles

28. A
above 33.33%
from previous question

29. C
Given as:
\( H_2(g) + I_2(g) \rightarrow 2 HI(g) \)
\[ \begin{align*}
\text{Initially} & \quad 1 \quad 3 \\
\text{At equilibrium} & \quad 1-x/2 \quad 3-x/2 \quad x \\
\text{addition of 2 mole} H_2 & \\
& \quad 3-x/2 \quad 3-x/2 \quad x+x \\
& \quad = 3-x \quad 3-x \quad 2x \\
\end{align*} \]
\[
\frac{(x)^2}{2} = \frac{(2x)^2}{3 - x} \Rightarrow \frac{1 - x}{2(3 - x)} = \frac{(2x)^2}{(3 - x)(3 - x)}
\]

\[2x = 3 \Rightarrow x = \frac{3}{2}
\]

30. \(C\)

\[K_c = \frac{(2x)^2}{(3 - x)(3 - x)} = \frac{9}{4} - 4
\]

\[K_p = K_c \text{ because } \Delta n_s = 0\]

31. \(B\)

Given:

\[2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)\]

\[\text{conc.} = \frac{2 - 2x}{5} \frac{1.5 - x}{5} \frac{2x}{5}
\]

\[\text{SO}_2 \rightarrow \text{SO}_3 \text{ (mf of SO}_2 = 2)\]

\[\text{m.eq of KMnO}_4 = \text{m.eq of SO}_2\]

\[0.4 \times 5 = 2(2.2x) \times 2\]

\[2 = 2(1 - x) \times 2\]

\[\Rightarrow 1 - x = 1/2 \Rightarrow x = \frac{1}{2}
\]

\[[\text{SO}_2] = \frac{1}{5} ; [\text{O}_2] = \frac{1}{5}
\]

\[[\text{SO}_3] = \frac{1}{5}
\]

32. As we know

\[\frac{K_p}{K_c} = (RT)^{\Delta n_s}
\]

\[K_p \& K_c \text{ ratio depend on } T \& \Delta n_s\]

\[\text{if we take } T = 0^\circ C \text{ than } (RT) > 1\]

33. \(C\)

Addition of inert gas at const pressure means pressure of equilibrium gases will decrease equilibrium shift where mole of gases are high due to the conc of reactant means equilibrium shifted to forward

\[\Rightarrow \Delta n_s > 0\]

But pressure is constant \(\Rightarrow\) volume \(\uparrow\)

\[\Rightarrow \text{conc. of reactants } \downarrow\]

34. \(A-P, B-Q, C-S, D-R\)

\[K_p = K_c (RT)^{\Delta n_s}\]

\[\frac{K_p}{K_c} = (RT)^{\Delta n_s}\]

35. \(A\)

\[3H_2 + N_2 \rightarrow 2NH_3\]

36. \(A\)

\[\frac{K_p}{K_c} = \frac{4^2}{2} = 8\]

\[\frac{P^2CO}{PCO_2}\]

37. \(1\)

Given:

\[K_p = \frac{2^2}{2} = 2\]

\[K_p = K_c \frac{2RT}{V} = \frac{2RT}{nT} \times 6 = 1\]

38. \(1\)

Given: \(2NO + O_2 \rightleftharpoons 2NO_2\)

\[\Delta n_s = -1 \quad \text{As } T = 727 + 273 \Rightarrow 1000\]

\[K_p = K_c (RT)^{\Delta n_s}\]

\[K_c = K_p (RT)\]

\[1.24 \times 10^{-2} \times 0.0821 \times 1000 = 1.018\]

39. \(1\)
40. 9
Given: \( A + B \rightleftharpoons C + D \)
Initially 0.8 0.8
at eq. 0.2 0.2 0.6 0.6
\[
K_c = \frac{[C][D]}{[A][B]}
\]
\[
= \frac{0.6 \times 0.6}{0.2 \times 0.2}
\]
\( K_c = 9 \)

41. 2

42. 9
\( C(s) + CO_2(g) \rightleftharpoons 2CO(g) \)
\[
\Rightarrow \frac{x^2}{1-x^2} P_{eq} = 9
\]

43. 5
\( PV = \frac{W}{RT} \)
\[
\Rightarrow 1 \times V = \frac{10}{92} \times R \times 340(1 + 6)
\]
\( V = 5 \)

44. 1
\( NH_4COONH_4 \rightarrow 2NH_3 + CO_2 \)
at eq. \( (1-x) \times 2x \times x \)
Total mole = \( 1-x+2x+x \)
\[
= 1 + 2x
\]
\[
\frac{78}{1 + 2x} = 26
\]
x = 1

45. 4
Given:
\( C_2H_4O + CH_3COOH \rightleftharpoons H_2O + CH_3COOC_2H_5 \)
at eq. \( 1-x \times 1-x \times 1+x \times x \)
x = 0.543
\[
K_c = \frac{(1+x)}{(1-x)} - 4
\]

46. 3
Maximum number of phase at equil. of pure
substance is 3.

47. 14
\[
\frac{83.8}{M_{\text{mix}}} = 1.16^2 \times \frac{1}{M_a}
\]
\[
\frac{71}{1 + x} = 62.27
\]
\% x = 14

48. 9
Given:
\( 2A(g) + B(g) \rightleftharpoons 3C(g) \)
\[
K_c = 2 \times 10^9
\]
\[
K_c = \frac{[C]^3}{[B][A]^2}
\]
\[
\frac{(3x)^3}{(4-2x)^2(2-x)} = 2 \times 10^9
\]
\[
\frac{x}{2-x} = \frac{2}{3} \times 10^9
\]
2-x=0.003
\[
[A]=6\times 10^{-5}
\]
\( A + q - 2 = 9 \)

50. 43
Given:
\( 2A + 2B \rightleftharpoons 3C + D \)
x-2y=8
3x \times x \times 0 \times 0 \times x=37
\[
K_c = \frac{37y^4}{x^2(x+y)^2} = \frac{27y^4}{(x+y)^2} P+Q=43
\]
\[
K_c = \frac{27}{16} \Rightarrow P+Q=43
\]
1. (A) \( Q = \frac{1}{0.04} = 25 > K \) 
   backward shift
(B) \( Q_o = \frac{(2)(1)^3}{(3)^3} = \frac{2}{9} < K_p \) 
   forward shift
(C) \( Q_c = \frac{(1)^2(1)}{0} > K \) 
   backward shift
(D) \( Q_r = \frac{(1)^2(1)}{(1)^2} = 1 < K_p \) 
   forward shift
(E) \( Q_c = \frac{(0)}{(1)^2(1)} < K \) 
   forward shift

2. (A) \( K = [\text{Ag}^+] [\text{Cl}^-] \)
   AgCl insoluble
   \[ [\text{Ag}^+] & [\text{Cl}^-] < 1 \]
(B) \( K = \frac{1}{[\text{Pb}^+] [\text{Cl}^-]^2} > 1 \)

3. (A) \( K = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] < 1 \)
(B) \( K = \frac{1}{[\text{Ba}^+] ^2 [\text{PO}_4^{3-}] } > 1 \)

4. more useful if \( K = 10 \)
   \( K_{\text{pred}} \) formation

5. Given:
   \[ K'I \rightleftharpoons K' + I^- \]
   \( K = \frac{[K'] [I^-]}{K'I} \)

6. Higher the \( K_c \) \( \Rightarrow \) higher reaction will be the extent of reaction
   (A) hardly proceed
   (B) Almost completion

7. (A) very high conc. of Reactant
(B) very low conc. of Reactant
(C) consider the conc. of Reactant & product

8. \( K_c = 1.7 \times 10^{-54} \) very low
   \( \Rightarrow [O_2] \) is very high
   \( O_2 \) contain is high in air compare to \( O_3 \)
   \[ 1.7 \times 10^{-54} = \frac{[O_3]^2}{(8 \times 10^{-3})^3} \]
   \( \Rightarrow [O_3] = 1.04 \times 10^{-10} \)

9. Given:
   \[ Q_c = \frac{[\text{H}_2]^4 [\text{CS}_2]}{[\text{CH}_4][\text{H}_2\text{S}]^2} \]
   \[ = \frac{(\frac{3}{10})^4 (\frac{3}{10})}{(\frac{4}{10})^2} = 7.59 \times 10^{-5} > K_c \]
   backward reaction

10. Given:
    \[ Q_c = \frac{[\text{H}_4\text{N}_2][0.15]^2}{[0.035]^2} = 3.43 < K_c \]
    reaction shifted forward direction

11. Given:
    \[ K_c = 0.29 = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \]
    \[ 0.29 = \frac{[\text{NH}_3]^2}{0.036(0.15)^3} \]
    \( \text{NH}_3 = 0.015 \)

12. Given:
    \[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO} \]
    initially 1.4  1.4
    at eq. 1.4x  1.4x  2x
    \[ K_c = 1.7 \times 10^{-3} = \frac{4x^2}{(1.4 - x)^2} \]
    \( \Rightarrow x = \frac{1.4}{1.4} = 0.02 \)
    \[ [\text{NO}] = 2x = 2 \times 0.02 \times 1.4 = 0.056 \]
    \[ [\text{O}_2] = [\text{N}_2] = 1.4 - 0.028 = 1.372 \]
13. Given:
\[ \text{PCI}_3 \rightleftharpoons \text{PCI}_4 + \text{Cl}_2 \]
at eq. 0.16x \hspace{1cm} x \hspace{1cm} x
\[ \frac{x^2}{0.16} - x = 5.8 \times 10^{-2} \]
\[ x^2 + 5.8 \times 10^{-2} - 9.28 \times 10^{-2} = 0 \]
\[ x = \frac{5.8 \times 10^{-2} - \sqrt{0.04}}{2} = 0.071 \]
\[ \text{PCI}_3 = 0.16 - 0.071 = 0.089 \]

14. Given:
\[ \text{ClF}_2(g) \rightleftharpoons \text{ClF}(g) + \text{F}_2(g) \]
Initially 1.47 \hspace{1cm} 0 \hspace{1cm} 0
at eq. 1.47-x \hspace{1cm} x \hspace{1cm} x
\[ K_p = 0.14 = \frac{x^2}{1.47 - x} \]
\[ x^2 + 0.14x - 0.2058 = 0 \]
x = 0.389
\[ \text{ClF}_2 = 1.47 - 0.389 = 1.08 \]

15. Given:
\[ \text{N}_2\text{O}_5 \rightleftharpoons 2\text{NO}_2 \]
P 4 \hspace{1cm} 2
P+\frac{P}{4} = 1.5 \hspace{1cm} P = 1.2 \hspace{1cm} \text{......(1)}
\[ \text{N}_2\text{O}_5 = 0.9 \hspace{1cm} \text{NO}_2 = 0.6 \]
\[ K_p = \frac{0.6 \times 0.6}{0.9} = 0.4 \]
At 10 atm
\[ \Rightarrow \frac{4P - 4x}{10} = 4x^2 \]
\[ \Rightarrow p - x = x^2 \]
10x^2 + x - p = 0
\[ \Rightarrow x = 0.904 \quad \text{[from (1)]} \]

16. Given:
\[ \text{N}_2\text{O}_5(g) \rightleftharpoons 2\text{NO}_2 \]
at eq.
\[ \text{total no. moles} \Rightarrow P + x = 0.5 \]
now,
\[ \frac{2x^2}{P - x} = K_p = \frac{2}{3} \]
\[ \Rightarrow \frac{2x^2}{0.5 - 2x} = \frac{1}{3} \Rightarrow 6x^2 + 2x - 0.5 = 0 \]
\[ x = \frac{1}{6} \Rightarrow P = \frac{1}{3} \]
% diss = 50%

17. (A) \[ K_c = \frac{P_t}{(RT)^{n_q}} = \frac{0.1642}{0.0821 \times 300} \]
\[ = \frac{2}{300} = 6.667 \times 10^{-3} \]

(B) Given:
\[ \text{N}_2\text{O}_5 \rightleftharpoons 2\text{NO}_2 \]
at eq. 0.4-x \hspace{1cm} 2x
\[ \frac{4x^2}{0.4 - x} = \frac{2}{300} \Rightarrow x < 0.4 \]
\[ 4x^2 = \frac{2}{0.4} \times 300 \Rightarrow x = 0.026 \]
\[ \text{NO}_2 = 2x = 0.026 \times 2 = 0.052 \]
\[ \text{N}_2\text{O}_5 = 0.4 - x = 0.374 \]

(C) \[ P = \frac{n \times R \times T}{V} = \frac{0.426 \times 0.821 \times T}{1} \]
\[ = 10.49 \text{ atm} \]

(D) 6.44%

18. Given:
\[ \text{PCI}_4 \rightleftharpoons \text{PCI} + \text{Cl}_2 \]
Initially P \hspace{1cm} 0 \hspace{1cm} 0
at eq. P-\frac{P}{10} \hspace{1cm} P \hspace{1cm} P
\[ P_{\text{total}} = P + \frac{P}{10} = 11P = 4 \]
\[ \Rightarrow P = \frac{40}{11} \quad \text{......(1)} \]

\[ K_p = \frac{P^2/100}{9P/10} = \frac{P}{90} = \frac{4}{99} \quad \text{[From (1)]} \]

If 20% dissociation
\[ P-\frac{P}{5} \hspace{1cm} P \hspace{1cm} P \]
\[ \frac{4}{99} = \frac{(P/5)^2}{(4P/5)} \Rightarrow P_1 = \frac{80}{99} \quad \text{......(2)} \]
\[ P_{\text{total}} = \frac{6P}{5} = \frac{6}{5} \times \frac{80}{99} \quad \text{[from (2)]} \]
\[ = 0.97 \]

19. Given:
20. As we know $D = 46$

$$d = \frac{D - d}{d(n - 1)}$$

$$= \frac{46 - 34.5}{34.5(2 - 1)}$$

$$= \frac{1}{3} \text{ at 5 atm}$$

as given $\text{NO}_2 \Rightarrow 2\text{NO}_3$

$$P(1 - u) = 2P u$$

$$= \frac{2P}{3}$$

$$K_p = \frac{\frac{2P}{3} \cdot \frac{2P}{3}}{\frac{2P}{3}} = \frac{2P}{3}$$

$$= \frac{4P}{9}$$

21. As we know

$$n = \frac{D - d}{d(n - 1)}$$

$$= \frac{46 - 30}{30(2 - 1)} = \frac{16}{30} = 0.5333$$

$$\% x = 53.33\%$$

22. Given:

$$\text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{COOH} \Rightarrow \text{ester} + \text{H}_2\text{O}$$

Initially $1 \quad 1 \quad 0 \quad 0$

at eq. $1 - n \quad 1 - n \quad n \quad n$

Total = 2

$$X_{\text{H}_2\text{O}} = \frac{n}{2} = \frac{1}{3} \quad \frac{n}{2} = \frac{2}{3}$$

$$K = \frac{n}{1 - n} = \frac{\frac{2}{3}}{\frac{1}{3}} = 4$$

23. Given:

$$A(s) \Rightarrow 2\text{B}(g) + \text{C}(g)$$

at eq. $2P \quad P$

$$P_{\text{eq}} = 3P$$

$$K_p = 4P^3$$

......(1)

$$A(s) \Rightarrow 2\text{B}(g) + \text{C}(g)$$

$$2P + P_{\text{eq}} - 2x = 3P$$

$$P - 2x - P$$

$$K_p = (P - x)(3P)^3$$

as we know

$$4P^3 = (P - x)(9P^3)$$

$$\frac{4}{9}P = P - x$$

$$x = \frac{9}{4}P$$

$$x = \frac{9}{4}P$$
\[ \Rightarrow P_{\text{total new}} = 4P_x = 4P - \frac{5P}{9} \]

\[ \frac{31P}{9} = 31, \quad \text{...(2)} \]

From (1) & (2)

\[ \text{ratio} = \frac{31/9}{27} = \frac{31}{27} \]

24. Given:

\[ \text{CaCO}_3(s) \rightleftharpoons \text{CaO(s)} + \text{CO}_2(g) \]

\[ K_p = 4 \times 10^{-3} \]

\[ n_{\text{CO}_2} = \frac{\text{PV}}{\text{RT}} \]

\[ = 4 \times 10^{-2} \times 0.821 \]

\[ = 0.0821 \times 1000 \]

\[ = 4 \times 10^{-4} \]

\[ \text{CaO mole} = 4 \times 10^{-4} \]

\[ \text{mass} = 0.0224 \text{g} = 22.4 \text{mg} \]

25. Given:

\[ K_f = 6.4 \times 10^{10} = \frac{1}{p_{\text{H}_2}^2} \]

\[ \Rightarrow \text{P}_{\text{H}_2} = 5 \times 10^{-15} \text{ atm} \]

26. Given:

\[ \text{CaCO}_3(s) \rightleftharpoons \text{CaO(s)} + \text{CO}_2(g) \]

\[ \frac{2}{100} = 0.2 \text{mole} \]

\[ 0.05 \quad 0.15 \quad 0.15 \text{ mole} \]

\[ P_{\text{CO}_2} = \frac{0.15 \times 0.082 \times 100}{15} \]

\[ = 0.821 \text{ atm} \]

\[ K_f = P_{\text{CO}_2} = 0.821 \text{ atm} \]

27. (a) By ↑ the conc of \( N_2 \)

(b) By ↑ the conc of \( H_2 \)

(c) By ↑ the temp

(d) By ↑ the pressure

28. (a) T ↑ forward as (temp. increases) (right)

(b) P ↑ (pressure increases) backward (left)

(c) T ↑ forward (temp. increases) (left); P (pressure increases) backward (right)

(d) T ↑ forward (temp. increases) (left); P (pressure increases) backward (right)

29. (a) \[ K_f = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{H}_2}^2 \times P_{\text{CO}}} \]

(b) (1) H, H₂ ↑, CO ↑, CH₃OH ↑

(2) co removed H₂ ↑, CO ↓, CH₃OH ↓

30. (a) \[ K = \frac{[\text{CO}][\text{H}_2]}{[\text{H}_2\text{O}]} \]

(b) (1) c added no effect

(2) CO ↑, H₂ ↑, H₂O ↓,

(3) H₂O ↑, CO ↑, H₂ ↓,

(4) Pressure ↑; volume ↓ conc. ↑

H₂O ↑, CO ↑, H₂ ↓,

(5) T ↑ Rxn forward

H₂O ↓, CO ↓, H₂↑

31. (a) backward shift (reaction move towards the backward direction)

(b) forward shift (reaction move towards the forward direction)

(c) backward shift (reaction move towards the backward direction)

32. Ag⁺ (aq) can be reduced if eq shifted forward due to the →

(a) Additon of Cl⁻

(b) Exothermic T

33. A

\[ 2\text{Ag}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{Ag}_2\text{SO}_4(s) \]

(aq.) (aq.)

The Ag⁺ and SO₄²⁻ concentration will not change.

34. \[ K_f = [\text{A}] [\text{B}] K [\text{C}] \]

\[ K_c = \frac{C}{(A)(B)c} K_f \]

35. \[ \frac{K_f}{K_r} > 1 \text{ large product & less reactant} \]

(b) \[ \frac{K_f}{K_r} > 1 \]

(c) \[ \frac{K_f}{K_r} < 1 \text{ less product & large reactant} \]

36. \[ \frac{K_c}{K_b} = \frac{0.13}{6.02 \times 10^{-4}} \]

\[ = 215.9 \approx 216 \]

37. \[ K_r = 1 \times 10^{14} = \frac{K_f}{K_b} \]

\[ 1 \times 10^{14} = \frac{6 \times 10^{-6}}{K_b} \]

\[ K_b = 6 \times 10^{-22} \]
38. Let at intersection point
   \[ A \rightleftharpoons nB \]
   at eq. 0.6 - x \ nx
   \[ 0.6 - x = nx \Rightarrow x = \frac{0.6}{n - 1} \]

   (B) = \frac{n \times 0.6}{n + 1} = 0.4
   \Rightarrow 3n = 2n + 2
   \Rightarrow n = 2

(ii) At equilibrium
   \[ A \rightleftharpoons 2B \]
   0.6 - x \ 2x
   2x = 0.6
   x = 0.3
   (B) = 2x = 0.6
   (A) = 0.3

   \[ K_p = \frac{[0.6]^2}{[0.3]} = 1.2 \]

(iii) 0.1 mole / hr

39. \[ K_{eq} \text{ at } 1400 \text{ K} = \frac{0.29}{1.1 \times 10^{-6}} = 2.6 \times 10^5 \]

   \[ K_{eq} \text{ at } 1500 \text{ K} = \frac{1.3}{1.4 \times 10^{-5}} = 9.2 \times 10^4 \]

   \[ T \uparrow K_{eq} \downarrow \Delta H < 0 \text{ exothermic} \]

40. K ↑ with much higher rate than K as temperature ↑
    \[ \text{endothermic} \]

   or \[ K_{eq}(T_2) = 6.06 \times 10^{-16} \]
   \[ K_{eq}(T_1) = 1.03 \times 10^{-14} \]
   \[ T \uparrow K_{eq} \downarrow \Delta H > 0 \text{ endothermic} \]

41. As we know \[ \ln \left( \frac{K_2}{K_1} \right) = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

   \[ \ln \left( \frac{2.69 \times 10^3}{3.81 \times 10^2} \right) = \frac{\Delta H}{8.314} \times \left( \frac{1}{600} - \frac{1}{700} \right) \]
   \[ \Delta H = 68.25 \text{ KJ} \]

42. As given : At 300 K
    \[ K_{eq} = \frac{2 \times 10^{-2}}{4 \times 10^{-3}} = 5 \]
    At 400 K
    \[ K_{eq} = \frac{4 \times 10^{-2}}{16 \times 10^{-4}} = 25 \]

   \[ \ln \left( \frac{25}{5} \right) = \frac{\Delta H}{8.314} \left( \frac{1}{300} - \frac{1}{400} \right) \]

   \[ \ln \left( \frac{5}{1} \right) = \frac{\Delta H}{8.314} \times \left( \frac{100}{1200} \right) \]

43. \[ \Rightarrow 16.06 \text{ KJ} \]

   As given : \[ \Delta G^{\circ} \text{160°C} = -8.314 \times 333 \ln \left( \frac{1.34}{373} \right) \]
   \[ = -810.271 \text{ mole} \]
   \[ \Delta G^{\circ} \text{100°C} = 8.314 \times 373 \ln \left( \frac{1.34}{373} \right) \]
   \[ = -5870.77 \text{ J/mole} \]

   \[ \ln \left( \frac{6.64}{1.34} \right) = \frac{\Delta H^o}{8.314} \times \left( \frac{1}{333} - \frac{1}{373} \right) \]
   \[ \Delta H^o = 41.32 \text{ KJ} \]

44. As given :
    \[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \]
    \[ K_c = \frac{1}{K_c} = \frac{1}{7.5 \times 10^{-9}} \]
    \[ = \frac{10^9}{7.5} \]
    \[ = 1.33 \times 10^4 \]

45. As given reaction :
    \[ \text{P}. \text{Cl}_3 \rightleftharpoons \text{PCl}_5 + \text{Cl}_2 \]
    \[ 8.3 \times 10^{-3} \quad 1.5 \times 10^{-2} \quad 3.2 \times 10^{-2} \]
    \[ K_c = \frac{3.2 \times 10^{-2}}{8.3 \times 10^{-3}} \]
    \[ = \frac{0.58 \times 10^2}{0.058} \]
    \[ K_c = 0.058 \]

46. As given :
    \[ \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \]
    \[ x \quad x \]
    \[ x = 8.29 \times 10^{-4} \left( \frac{9.3 \times 10^{-3}}{2} - 2x \right) \]

    \[ x = \ln \left( \frac{9.3 \times 10^{-3} - 2 \times 6.29 \times 10^{-4}}{6.29 \times 10^{-4}} \right) = 29 \]

47. As given :
    \[ \text{H}_2\text{O}(g) \rightleftharpoons \text{H}_2\text{O}(g) \]
    \[ T = 259^\circ \text{C} \]
    \[ = 25 + 273 \]
    \[ = 298 \text{ K} \]
    \[ K_c = K_{H_2O} = 0.0313 \]

    \[ K_c = \frac{K_p}{RT} = \frac{0.0313}{0.0821 \times 298} \text{ (as } \Delta n_s = 1) \]
    \[ = 1.28 \times 10^{-1} \]
EXERCISE – IV

LEVEL – I

1. C
Given: \( \text{Co}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g) \)
\( \Delta n_1 = 1 - (1 + 1/2) = \frac{1}{2} \)
\( \Delta n_s = -1/2 \)
\( K_p = (RT)^{\Delta n_1} \)
\( K_c = (RT)^{-\Delta n_s/2} \)
2. C
Given: \( \text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g) \)
\( \Delta n_s = 2 - 2 = 0 \)
So, there is no effect of change in volume
3. A
At given reaction
\( \text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g) \)
equilibrium conc. of \( \text{N}_2\text{O}_4 = 4.8 \times 10^{-2} \text{ mol/L} \)
\( \text{NO}_2 = 1.2 \times 10^{-2} \text{ mol/L} \)
now, \( K_c = \frac{(1.2 \times 10^{-2})^2}{4.8 \times 10^{-2} \times 3 \times 10^{-1} \text{ mol/L}} \)
4. A
As given reaction.
\( 2\text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{SO}_3(g) \)
\( \Delta H^0 = -198 \text{ kJ} \)
as \( \Delta H < 0 \) exothermic \( T^\circ \)
\( \Delta n_s < 0 \) \( p^\circ \)
5. D
As given reaction.
\( K_c = \frac{[\text{P}_4\text{O}_{10}]}{[\text{P}_4][\text{O}_2]^3} \)
\( K_c = \frac{1}{[\text{O}_2]^3} \) \[ as \ [\text{P}_4\text{O}_{10}] = 1, \text{ and } [\text{P}_4] = 1 \]
6. A
For the reaction
\( \text{Co}(g) + \text{Cl}_2(g) \rightarrow \text{CoCl}_2(g) \)
\( \Delta n_1 = 1 - 2 \)
\( \Delta n_s = -1 \)
\( K_p = K_c (RT)^{\Delta n_1} \)
\( K_c = K_p (RT)^{-\Delta n_s} \)
\( K_p/K_c = \frac{1}{RT} \)
7. B
As given reaction
\( \text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g) \)
\( K_c = 4 \times 10^{-4} \)
\( K_p = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \) \[ \text{Now, } \text{NO}(g) \rightarrow \frac{1}{2} \text{N}_2(g) + \frac{1}{2} \text{O}_2(g) \]
\( K_c = \frac{[\text{N}_2]^{1/2}[\text{O}_2]^{1/2}}{[\text{NO}]} \)
\( K_c = \frac{1}{\sqrt{K_c}} \)
\( = \frac{1}{\sqrt{1 \times 10^{-5}}} = \frac{1}{2 \times 10^{-25}} \)
\( = 50 \)
8. B
For the reaction
\( 2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g) \)
\( K_c = 1.8 \times 10^{-4} \)
\( T = 184^\circ C = 184 + 273 \)
\( T = 457 \text{ K} \)
\( \text{Now, } K_p = K_c (RT)^{\Delta n_1} \)
\( = 1.8 \times 10^{-4} \times 0.0831 \times 457 \)
\( K_p > K_c \)
9. C
By the equation
\( \text{Cl}_2(g) + 3\text{F}_2(g) \rightarrow 2\text{ClF}_2(g) \)
\( \Delta H = -329 \text{ kJ} \)
\( \text{ClF}_2 \) will increased when reaction shifted forward
Exothermic reaction favours low temperature.
addition of reactant $\Delta n_q < 0$.

$\Rightarrow$ increase in pressure
lowering in volume

10. B

\[ \frac{X}{1 - X} = K \]

In $K_w$ V/V

Now, $\ln K_w = \frac{-\Delta H}{RT}$

\[ \Delta H < 0 \] exothermic reaction

11. C

$NH_3$ + $H_2S(s) \rightleftharpoons NH_4S(g) + H_2(g)$

Initially 0.5 0

at eq. 0.5 + x x

Total pressure = 0.5 + x + x

$= 0.5 + 2x$

$= 0.5 + 2x = 0.84$ (Total pressure = 0.84)

$2x = 0.34$

$x = 0.17$

Now, $P_{NH_3} = 0.5 + x$

$= 0.5 + 0.17 = 0.67$

$K_p = P_{NH_3} \cdot P_{H_2S}$

$= 0.67 \times 0.17$

$= 0.113$

12. D

For given reaction

$PCl_3(g) \rightleftharpoons PCl_2 + Cl_2(g)$

Initially 1 0 0

at eq. 1 - x x x

Total mole = 1 - x + x + x

$= 1 + x$

Now, $P_{PCl_3} = \frac{PCl_3}{1 + x} \cdot P$

13. D

For given reaction

$SO_3 \rightleftharpoons SO_2(g) + 1/2 O_2(g)$

$K_C = 4.9 \times 10^{-2}$

$K_C = \frac{[SO_2][O_2]^{1/2}}{[SO_3]}$ ........(1)

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

$K_{C_1} = \frac{[SO_2]^2}{[SO_3]^2[O_2]}$ ........(2)

From (1) & (2)

$K_{C_1} = \frac{1}{K_C^2}$

$= \frac{1}{(4.9 \times 10^{-2})^2}$

$= 4.9 \times 10^{-9}$

$= 416$

14. B

(A) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) ; K_1$

(B) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) ; K_2$

(C) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g) ; K_3 + K_2$

For equation [C] $K_2$ is equilibrium constant.

15. D

$X \rightleftharpoons 2Y$

Initially 1 0

at eq. 1 - x 2x

$Z \rightleftharpoons P + Q$

1 0 0

at eq. 1 - x x x

$K_{P_1} = P_1 \times \frac{x^2}{1 - x}$

$= 4P_1 \times \frac{x^2}{1 - x}$ ....(1)

$K_{P_2} = P_2 \times \frac{x^2}{1 - x}$ ....(2)

from (1) & (2)
\[
\frac{K_{P_1}}{K_{P_2}} = \frac{4P_1}{P_2} \quad \text{[as } \frac{K_{P_1}}{K_{P_2}} = \frac{1}{9}] \\
P_1 : P_2 = 1 : 36
\]

16. **A**

As given CO, converted into CO

\[ \Rightarrow \text{CO}_2(g) + \text{C(s)} \rightleftharpoons 2\text{CO}(g) \]

0.5

at eq. \( 0.5 - x \quad 2x \)

Total pressure = \( 0.5 - x + 2x \)

= \( 0.5 + x \)

\[ \Rightarrow 0.5 + x = 0.8 \quad [\text{as total pressure} = 0.8] \]

Now,

\[ K_p = \frac{(2x)^2}{(0.5 - x)} \]

17. **B**

Reaction \( \text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g) \)

\[ K_c = 4 \times 10^{-4} \quad \text{.........(1)} \]

Now,

\[ \text{NO}(g) \rightarrow \frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g) \]

\[ K_a = ? \quad \text{.........(2)} \]

from eq. (1) & (2)

\[ K_{eq} = \frac{1}{\sqrt{K_c}} \]

\[ = \frac{1}{\sqrt{4 \times 10^{-4}}} = \frac{1}{2 \times 10^{-2}} \]

\[ = K_a = 50 \]

**Physicswallah**
1. \[ \text{PCl}_3 \rightleftharpoons \text{PCl}_4^+ + \text{Cl}_2 \]

at \( t = 0 \): \begin{align*}
1 & 0 & 0 \\
0.4 & 0.4 & 0.4
\end{align*}

Total molar after dissociation
\[ = 0.6 + 0.4 + 0.4 = 1.4 \]

\[ PV = nRT \]
\[ \frac{V}{1} = \frac{1.4 \times 0.082 \times 400}{1} = 45.92 \]

Density \[ \frac{\text{mole} \times \text{wt}}{\text{Volume}} = \frac{208.5}{45.92} = 4.5 \text{ g/dm}^3 \]

2. As given NH₄HS introduced in 2-litre

\[ \text{NH}_4\text{HS mole} = \frac{3.06}{57} = 0.06 \]

\[ \text{Now,} \]
\[ \text{NH}_4\text{HS} \rightarrow \text{NH}_4^+ + \text{H}_2\text{S} \]

\[ \begin{align*}
\text{(S)} & 0.06 & 0 \\
\text{(g)} & 0.06 & 0.018 \\
0.06-0.018 & 0.018 & 0.018
\end{align*} \]

Conc. of [NH₄⁺] \[ = \frac{0.018}{2} = 0.009 \]

Conc. of [H₂S] \[ = \frac{0.018}{2} = 0.009 \]

\[ K_c = (0.009)(0.009) = 0.0009 \]

\[ k_c = 81 \times 10^{-4} \]

\[ K_s = K_c \times (RT)^{\Delta \mu} \]

\[ \Delta \mu = 2 \]

\[ = 81 \times 10^{-4}(RT)^2 \]

\[ = 81 \times 10^{-4} \times (0.0821 \times 400) = 4.91 \times 10^{-2} \]

3. \( \text{D} \)

Given: \( A + B \rightleftharpoons C + D \)

\[ Q = \frac{[C][D]}{[A][B]} \]

As conc. \[ C \] \( \uparrow \) (increases)

\[ [A][B] \downarrow \) (decreases)

\[ [D] \uparrow \) (increases)

4. As given reversible reaction &

\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \]

\[ T = 500^\circ \text{C} \]

\[ = 500 + 273 = 773 \text{ K} \]

\[ K_p = 1.44 \times 10^{-5} \]

\[ \Delta n_q = 2 - 4 = -2 \]

We know,

\[ K_p = K_c \times (RT)^{\Delta \mu} \]

\[ K_p = K_c \times (0.082 \times 173)^{\Delta \mu} \]

\[ K_p = \frac{4.44 \times 10^{-5}}{(0.082 \times 773)^{\Delta \mu}} \]

5. \( \text{D} \)

As given

\[ \text{N}_2\text{O}_5(g) \rightleftharpoons 2\text{NO}_2(g) \]

Temperature is constant

\[ \Delta n_q = 2 - 1 = 1 \]

α change but \( K_p \) remains the same

6. \( \text{D} \)

As given

\[ \text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag(NH}_3)]^+ \]

\[ K_p = 1.6 \times 10^{13} \]

and

\[ [\text{Ag(NH}_3)]^+ \]

\[ K_p = 6.8 \times 10^7 \]

As \( K = K_p \times K_q \)

\[ = 1.088 \times 10^7 \]

BCD

Cu⁺⁺ four will react with CN⁻ and SCN⁻ forming \([\text{Cu(CN)}]_2\)³⁻ and \([\text{Cu(SCN)}]_2\)³⁻ leading the reaction in the backward direction.

\[ \text{Cu}^{2+} + 2\text{CN}^- \rightarrow \text{Cu(CN)}_2^- \]

\[ 2\text{Cu(CN)}_2^- \rightarrow 2\text{CuCN} + (\text{CN})_2 \]

\[ = \text{CuCN} + 3\text{CN}^- \rightarrow [\text{Cu(CN)}]_3^3^- \]

\[ = \text{Cu}^{2+} + 3\text{SCN}^- \rightarrow [\text{Cu(SCN)}]_3^3^- \]

Cu⁺⁺ also combines with CuCl₂, which reacts with Cu to produce CuCl, purting the reaction in the backward direction

\[ \text{CuCl}_2 + \text{Cu} \rightarrow 2\text{CuCl} \]

ABD

For the equilibrium

\[ \text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g) \]

the equilibrium constant \( k \) is independent of initial amount of CaCO₃, where as at a given temperature is independent of pressure of CO₂, AH is independent of catalyst and it depends on temperature.
### Answers

#### Answer Ex-I

<table>
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<th>Objective Problems (JEE Main)</th>
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<td>50. C</td>
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#### Answer Ex-II

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<tr>
<th>Objective Problems (JEE Advanced)</th>
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<tr>
<td>33. A→p; B→α; C→s; D→r</td>
</tr>
<tr>
<td>35. 2</td>
</tr>
<tr>
<td>42. 9</td>
</tr>
<tr>
<td>49. 56</td>
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#### Answer Ex-III

<table>
<thead>
<tr>
<th>Subjective Problems (JEE Advanced)</th>
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<tbody>
<tr>
<td>1. (a) 25. shifts left. (b) 0.22. shifts right. (c) −, shifts left. (d) 1, shifts right. (e) 0, shift right</td>
</tr>
<tr>
<td>2. (a) $\frac{1}{K_{sp}^{2}[Cl^-]}$ is less than 1. AgCl is insoluble thus the concentration of ions are much less than 1 M</td>
</tr>
<tr>
<td>(b) $K_{sp}^{2}[Cl^-] = 1$ is greater than one because PbCl₂ is insoluble and formation of the solid will reduce the concentration of ions to a low level</td>
</tr>
<tr>
<td>3. K about 10</td>
</tr>
<tr>
<td>9. The reaction is not an equilibrium because $Q &lt; K_{eq}$. The reaction will proceed from right to left to reach equilibrium</td>
</tr>
<tr>
<td>11. $5.9 \times 10^{-2}$ M</td>
</tr>
<tr>
<td>13. [P₄Cl₆] = [Cl₂] = 0.071 M, [PCl₅] = 0.089</td>
</tr>
<tr>
<td>14. $P_{Cl} = 0.389$ atm, $P_{P₄Cl₆} = 1.08$ atm</td>
</tr>
<tr>
<td>15. $K_p = 0.4$, $a = 0.1$</td>
</tr>
<tr>
<td>16. 50%</td>
</tr>
<tr>
<td>17. (a) $6.667 \times 10^{-3}$ mol L⁻¹ ; (b) $n(N₂O₅) = 0.374$ mol ; $n(NO₂) = 0.052$ mol</td>
</tr>
</tbody>
</table>
(c) 10.49 atm  (d) 6.44 %

18.  0.97 atm  19.  \( K_p = 1.3 \times 10^{-1} \text{ atm}^{-2} \)  20.  \( K_p = 2.5 \text{ atm} \)  21.  53.33 %

22.  \( K = 4 \)  23.  \( \frac{31}{27} \)  24.  22.4 mg  25.  \( P_{H_2O} = 5 \times 10^{-11} \text{ atm} \)  26.  0.821 atm

27.  Add \( N_2 \), add \( H_2 \). Increase the pressure, heat the reaction

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

29.  (a) \( K = \frac{[CO][H_2][CO]}{[H_2O]} \)

(b) 1. \( [H_2] \) increase, \( [CO] \) decrease, \( [CH_2OH] \) increase ; 2. \( [H_2] \) increase, \( [CO] \) decrease, \( [CH_2OH] \) decrease ; 3. \( [H_2] \) increase, \( [CO] \) increase, \( [CH_2OH] \) increase ; 4. \( [H_2] \) increase, \( [CO] \) increase, \( [CH_2OH] \) increase ; 5. \( [H_2] \) increase, \( [CO] \) increase \( [CH_2OH] \) decrease ; 6. no change

30.  (a) \( K = \frac{[CO][H_2][H_2O]}{[H_2]} \)

(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, \( [CO] \) increase. \( [H_2] \) increase ; 5. \( [H_2O] \) decrease, \( [CO] \) increase, \( [H_2] \) increase.

31.  32. Add NaCl or some other salt that produces \( Cl^- \) in the solution. Cool the solution.

33.  34. \( k_1[A][B] = k, [C] = \frac{[C]}{[A][B]} = k_2 \)

36.  216

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

39.  \( k_1 \) increase more than \( k_2 \), this means that \( E_r \) (reverse) is greater than \( E_f \) (forward). The reaction is exothermic when \( E_r \) (reverse) > \( E_f \) (forward).

42.  16.06 kJ  43.  -810 J/mol ; -5872 J/mol and 41.3 KJ/mol

44.  1.3 \times 10^8  45.  0.058

46.  29.0  47. \( K_r = 0.0313 \text{ atm} \), \( K_c = 1.28 \times 10^{-3} \)

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**Answer Ex-IV**

**PREVIOUS YEARS PROBLEMS**

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<td>3. A</td>
<td>4. A</td>
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<tr>
<td>5. D</td>
<td>6. A</td>
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<tr>
<td>7. B</td>
<td></td>
</tr>
<tr>
<td>12. D</td>
<td>13. D</td>
</tr>
<tr>
<td>14. B</td>
<td></td>
</tr>
<tr>
<td>15. D</td>
<td>16. A</td>
</tr>
<tr>
<td>17. B</td>
<td></td>
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<table>
<thead>
<tr>
<th>LEVEL – II</th>
<th>JEE ADVANCED</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 4.54 g dm(^{-3})</td>
<td>2. (i) ( K_c = 8.1 \times 10^{-4} \text{ mol}^2 \text{ L}^{-2} ); ( K_p = 4.91 \times 10^{-4} \text{ atm}^2 ) (ii) No effect ;</td>
</tr>
<tr>
<td>3. D</td>
<td>4. D</td>
</tr>
<tr>
<td>5. D</td>
<td>6. D</td>
</tr>
</tbody>
</table>