

CHAPTER

6

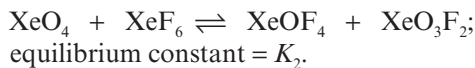
Chemical Equilibrium

EXERCISE I (JEE MAIN)

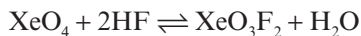
Basic

- The reaction which proceeds towards completion in the forward direction is
 - $\text{Fe}_2\text{O}_3 + 6\text{HCl} \rightleftharpoons \text{FeCl}_3 + 3\text{H}_2\text{O}$
 - $\text{SnCl}_4 + \text{Hg}_2\text{Cl}_2 \rightleftharpoons \text{SnCl}_2 + 2\text{HgCl}_2$
 - $\text{NH}_3 + \text{H}_2\text{O} + \text{NaCl} \rightleftharpoons \text{NH}_4\text{Cl} + \text{NaOH}$
 - $2\text{CuI} + \text{I}_2 + 4\text{K}^+ \rightleftharpoons 2\text{Cu}^{2+} + 4\text{KI}$
- The concentration of a pure solid or liquid phase is not included in the expression of equilibrium constant because
 - solid and liquid concentrations are independent of their quantities.
 - solid and liquids react slowly.
 - solid and liquids at equilibrium do not interact with gaseous phase.
 - the molecules of solids and liquids cannot migrate to the gaseous phase.
- For the reversible reaction: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ at 500°C , the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c , with concentration in mole litre⁻¹, is
 - $\frac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$
 - $\frac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$
 - $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^2}$
 - $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$
- 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
 - is zero
 - decreases with time
 - is independent of time
 - increases with time
- 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 $K_p = \frac{4x^2 P}{1-x^2}$, where P = total pressure at equilibrium, x = extent of decomposition. Which one of the following statements is true?
 - K_p increases with increase of P .
 - K_p increases with increase of x .
 - K_p increases with decrease of x .
 - K_p remains constant with change in P and x .
- For the reaction: $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, K_p is
 - P_{CO_2}
 - $\frac{P_{\text{CO}_2}}{P_{\text{CaCO}_3}}$
 - $\frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$
 - $\frac{P_{\text{CaCO}_3}}{P_{\text{CaO}} P_{\text{CO}_2}}$

7. $\text{XeF}_6 + \text{H}_2\text{O} \rightleftharpoons \text{XeOF}_4 + 2\text{HF}$;
equilibrium constant = K_1 .

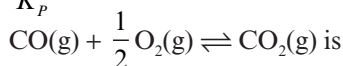


Then equilibrium constant for the following reaction will be:



- (a) $\frac{K_1}{K_2}$ (b) $K_1 + K_2$
(c) $\frac{K_2}{K_1}$ (d) $K_2 - K_1$
8. K_p for formation of ethane from hydrogen and ethylene is $5.5 \times 10^{18} \text{ atm}^{-1}$ and K_p for formation of ethylene from hydrogen and acetylene is $5 \times 10^{26} \text{ atm}^{-1}$ at 323 K. What is K_p for the reaction between hydrogen and acetylene to form ethane at 323 K?
- (a) $2.75 \times 10^{45} \text{ atm}^{-2}$
(b) 1.1×10^{-8}
(c) 9.09×10^7
(d) $3.63 \times 10^{-46} \text{ atm}^2$
9. For a reversible reaction: $\text{A} + \text{B} \rightleftharpoons \text{C}$, if the concentrations of the reactants are doubled at a definite temperature, then equilibrium constant will
- (a) be doubled
(b) be halved
(c) be one fourth
(d) remain same

10. $\frac{K_c}{K_p}$ for reaction:



- (a) $\frac{1}{\sqrt{RT}}$
(b) \sqrt{RT}
(c) $1/RT$
(d) 1

11. The equilibrium constant for the reaction: $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ is K_1 and the equilibrium constant for the reaction: $\text{NO}(\text{g}) \rightleftharpoons \frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$ is K_2 , both at the same temperature. K_1 and K_2 are related as

(a) $K_1 = \left(\frac{1}{K_2} \right)^2$ (b) $K_1 = K_2^2$

(c) $K_2 = \left(\frac{1}{K_1} \right)^2$ (d) $K_2 = K_1^2$

12. Equilibrium constants for some reactions are given. In which of the following case does the reaction go farthest to completion?

- (a) $K = 10^2$ (b) $K = 10^{-2}$
(c) $K = 10$ (d) $K = 1$

13. For a reversible reaction, the rate constants for the forward and backward reactions are 0.16 and 4×10^4 , respectively. What is the value of equilibrium constant of the reaction?

- (a) 0.25×10^6 (b) 2.5×10^5
(c) 4×10^{-6} (d) 4×10^{-4}

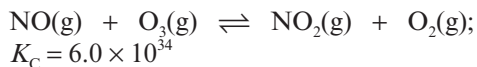
14. The following reaction has an equilibrium constant K_c equal to 3.07×10^{-4} at 24°C



The correct set of concentrations at which the rate of forward reaction is greater than that of backward reaction is

- (a) $[\text{NOBr}] = 0.06 \text{ M}$, $[\text{NO}] = 0.015 \text{ M}$, $[\text{Br}_2] = 0.01 \text{ M}$
(b) $[\text{NOBr}] = 0.15 \text{ M}$, $[\text{NO}] = 0.015 \text{ M}$, $[\text{Br}_2] = 0.014 \text{ M}$
(c) $[\text{NOBr}] = 0.18 \text{ M}$, $[\text{NO}] = 0.012 \text{ M}$, $[\text{Br}_2] = 0.02 \text{ M}$
(d) $[\text{NOBr}] = 0.045 \text{ M}$, $[\text{NO}] = 0.0105 \text{ M}$, $[\text{Br}_2] = 0.01 \text{ M}$

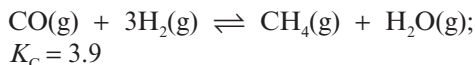
15. NO_2 is involved in the formation of smog and acid rain. It is formed importantly as:



The air over a metropolitan city contained 1.0×10^{-5} M-NO, 1.0×10^{-6} M- O_3 , 2.5×10^{-4} M- NO_2 and 8.2×10^{-3} M- O_2 . These data suggest that

- more of NO and O_3 tend to be formed
 - more of NO_2 and O_2 tend to be formed
 - more of NO_2 and O_3 tend to be formed
 - no tendency to change because the reaction is at equilibrium
16. For the reaction: $\text{I}_2\text{(g)} \rightleftharpoons 2\text{I(g)}$, $K_C = 1.0 \times 10^{-2} \text{ mol lit}^{-1}$. What volume of the vessel should be taken so that at equilibrium 1 mole of I_2 and 0.5 mole of 'I' are present at equilibrium?
- 25 l
 - 0.04 l
 - 0.25 l
 - 5 l
17. The equilibrium constant for the reaction: $3\text{C}_2\text{H}_2 \rightleftharpoons \text{C}_6\text{H}_6$ is 4.0 at T K. If the equilibrium concentration of C_2H_2 is 0.5 M, then the concentration of C_6H_6 at equilibrium is
- 0.5 M
 - 1.5 M
 - 5×10^{-2} M
 - 0.25 M
18. The equilibrium mixture for the reaction: $2\text{H}_2\text{S(g)} \rightleftharpoons 2\text{H}_2\text{(g)} + \text{S}_2\text{(g)}$ has 1 mole H_2S , 0.20 mole H_2 and 0.80 mole of S_2 in a 2 L vessel. K_C for the reaction is
- 0.16 M
 - 0.008 M
 - 0.016 M
 - 0.032 M

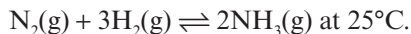
19. A gaseous mixture contains 0.30 moles CO, 0.10 moles H_2 , and 0.03 moles H_2O vapour and an unknown amount of CH_4 per litre. This mixture is at equilibrium at 1200 K.



What is the concentration of CH_4 in this mixture? The equilibrium constant K_C equals 3.92.

- 0.39 M
 - 0.039 M
 - 0.78 M
 - 0.078 M
20. For the reaction: $2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)}$, $\Delta H^\circ = 18 \text{ kcal}$ and $\Delta S^\circ = 30 \text{ cal/K}$ at 300 K. The equilibrium constant, K_P° of the reaction at 300 K is
- e^{15}
 - e^{-15}
 - e^{-18}
 - e^{-12}
21. For the gas phase reaction: $2\text{NO(g)} \rightleftharpoons \text{N}_2\text{(g)} + \text{O}_2\text{(g)}$; $\Delta H = -43.5 \text{ kcal}$. Which one of the following is true for the reaction: $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO(g)}$?
- K is independent of T
 - K decreases as T decreases
 - K increases as T decreases
 - K varies with addition of NO
22. The equilibrium constant for the reaction: $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO(g)}$ is 4.0×10^{-4} at 2000 K. In the presence of a catalyst, the equilibrium is attained 10 times faster. Therefore, the equilibrium constant in presence of the catalyst at 2000 K is
- 4×10^{-3}
 - 4×10^{-5}
 - 4×10^{-4}
 - Unpredictable

23. What is the approximate value of $\log K_p$ for the reaction:



The standard enthalpy of formation of $\text{NH}_3(\text{g})$ is -40.0 kJ/mol and standard entropies of $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$ and $\text{NH}_3(\text{g})$ are 191, 130 and $192 \text{ JK}^{-1} \text{ mol}^{-1}$, respectively.

- (a) 0.04 (b) 7.05
(c) 8.6 (d) 3.73
24. If K_1 and K_2 are the equilibrium constants for a reversible reaction at $T_1 \text{ K}$ and $T_2 \text{ K}$ temperature, respectively ($T_1 < T_2$) and the reaction takes place with neither heat evolution nor absorption, then
- (a) $K_1 > K_2$ at high temperature
(b) $K_1 < K_2$ at high temperature
(c) $K_1 = K_2$ only at high temperature
(d) $K_1 = K_2$ at any temperature
25. From the following data:
- (i) $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}); K_{2000 \text{ K}} = 4.4$
(ii) $2\text{H}_2\text{O}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}); K_{2000 \text{ K}} = 5.31 \times 10^{-10}$
(iii) $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g}); K_{1000 \text{ K}} = 2.24 \times 10^{22}$

Show whether the reaction (iii) is exothermic or endothermic or thermal?

- (a) Exothermic
(b) Endothermic
(c) Thermal
(d) Cannot say
26. In the decomposition equilibrium of a certain metallic carbonate, the partial pressure of CO_2 becomes a hundred fold when the temperature increased from

400 K to 500 K. What is the mean value of ΔH° for the given range of temperature?

- (a) 18.4 kcal/mol
(b) 13.84 kcal/mol
(c) 14.83 kcal/mol
(d) 10.83 kcal/mol
27. The equilibrium constants for the reaction: $\text{A}_2 \rightleftharpoons 2\text{A}$ at 500 K and 1000 K are 1×10^{-10} and 1×10^{-5} , respectively. The reaction is
- (a) Exothermic
(b) Very slow
(c) Very fast
(d) Endothermic
28. The activation energies for the forward and reverse elementary reactions in the system: $\text{A} \rightleftharpoons \text{B}$, are 10.303 and 8.000 kcal, respectively, at 500 K. Assuming the pre-exponential factor to be the same for both the forward and reverse steps, the equilibrium constant of the reaction at 500 K is
- (a) 1.00 (b) 10.0
(c) 100 (d) 0.1
29. ΔG° for the reaction: $\text{X} + \text{Y} \rightleftharpoons \text{C}$ is -4.606 kcal at 1000 K. The equilibrium constant for the reverse mode of the reaction is
- (a) 100 (b) 10
(c) 0.01 (d) 0.1
30. For a gaseous equilibrium: $2\text{A}(\text{g}) \rightleftharpoons 2\text{B}(\text{g}) + \text{C}(\text{g})$, K_p has a value 1.8 at 700 K. The value of K_c for the equilibrium: $2\text{B}(\text{g}) + \text{C}(\text{g}) \rightleftharpoons 2\text{A}(\text{g})$ at that temperature is about
- (a) 0.031
(b) 32
(c) 57.4
(d) 103.3

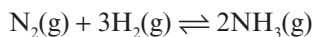
Application of Equilibrium Constant

31. Amounts of 0.8 mol of PCl_5 and 0.2 mole of PCl_3 are mixed in a 1 l flask. At equilibrium, 0.4 mole of PCl_3 is present. The equilibrium constant for the reaction, $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ will be
 (a) 0.05 mol l^{-1}
 (b) 0.13 mol l^{-1}
 (c) 0.013 mol l^{-1}
 (d) 0.60 mol l^{-1}
32. One mole of pure PCl_5 is placed in an evacuated container and maintained at 250°C . The equilibrium is established at total pressure of 2 atm. What is the partial pressure of chlorine at equilibrium?
 $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}); K_p = 1.6 \text{ atm}$
 (a) 0.4 atm (b) 0.67 atm
 (c) 0.80 atm (d) 0.64 atm
33. For the reaction: $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, if initial moles of PCl_5 is 'x', a is the degree of dissociation and P is total pressure at equilibrium, then P_{PCl_5} , P^{-1} is equal to
 (a) $\frac{x}{1+x}$ (b) $\frac{ax}{a+x}$
 (c) $\frac{a}{1+a}$ (d) $\frac{a}{x+ax}$
34. In a 5.76 l vessel, 0.5 moles of H_2 gas and 0.5 moles of I_2 vapours are allowed to react to form $\text{HI}(\text{g})$ at 447°C , then total pressure of gases at equilibrium would be ($R = 0.08 \text{ l-atm/K-mol}$)
 (a) 20 atm (b) 10 atm
 (c) 5 atm (d) 1 atm
35. In a closed tube, $\text{HI}(\text{g})$ is heated at 440°C up to establishment of equilibrium. If it dissociates into $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ up to 22%, the dissociation constant is
 (a) 0.282 (b) 0.0796
 (c) 0.0199 (d) 1.99
36. For the reaction: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$, the value of equilibrium constant is 9.0. The degree of dissociation of HI will be
 (a) 0.5 (b) 0.33
 (c) 0.4 (d) 0.67
37. At 444°C , HI is 30% dissociated. If initially 3 moles of HI are taken, the number of moles of HI at equilibrium is
 (a) 0.9 (b) 2.1
 (c) 0.45 (d) 1.8
38. One mole of $\text{N}_2\text{O}_4(\text{g})$ at 300 K is kept in a closed container under one atm. It is heated to 600 K when 20% by mass of $\text{N}_2\text{O}_4(\text{g})$ decomposes to $\text{NO}_2(\text{g})$. The resultant pressure is
 (a) 1.2 atm
 (b) 2.4 atm
 (c) 2.0 atm
 (d) 1.0 atm
39. For the reaction: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, the relation between the degree of dissociation, α , of $\text{N}_2\text{O}_4(\text{g})$ at pressure, P , with its equilibrium constant K_p is
 (a) $\alpha = \frac{K_p/P}{4 + K_p/P}$
 (b) $\alpha = \frac{K_p}{4 + K_p}$
 (c) $\alpha = \left[\frac{K_p/P}{4 + K_p/P} \right]^{1/2}$
 (d) $\alpha = \left[\frac{K_p}{4 + K_p} \right]^{1/2}$
40. At total pressure P_1 atm and P_2 atm, N_2O_4 is dissociated to an extent of 33.33% and 50.00%, respectively. The ratio of pressures P_1 and P_2 is
 (a) 3:8 (b) 2:1
 (c) 8:3 (d) 1:2

41. At 0°C and 1 atm pressure, 1 L of N_2O_4 decomposes to NO_2 according to the equation $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$. To what extent has the decomposition proceeded when the original volume is 25% less than that of existing volume?

(a) 0.67 (b) 0.33
(c) 0.25 (d) 0.75

42. Forty per cent of a mixture of 0.2 mol of N_2 and 0.6 mol of H_2 react to give NH_3 according to the equation:



at constant temperature and pressure. Then, the ratio of the final volume to the initial volumes of gases is

(a) 4:5 (b) 5:4
(c) 7:10 (d) 8:5

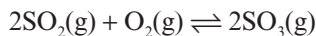
43. An amount of 4 moles of NH_3 gas is introduced with a previously evacuated 1 L container in which it is partially dissociated at high temperature as



At equilibrium, 2 mole of $\text{NH}_3(\text{g})$ remained. The value of K_C for the reaction is

(a) $1.5M^2$ (b) $0.75M^2$
(c) $0.44M^2$ (d) $2.25M^2$

44. In a closed container maintained at 1 atm pressure and 25°C, 2 moles of $\text{SO}_2(\text{g})$ and 1 mole of $\text{O}_2(\text{g})$ were allowed to react to form $\text{SO}_3(\text{g})$ under the influence of a catalyst.



At equilibrium, it was found that 50% of $\text{SO}_2(\text{g})$ was converted to $\text{SO}_3(\text{g})$. The partial pressure of $\text{O}_2(\text{g})$ at equilibrium will be

(a) 0.17 atm (b) 0.5 atm
(c) 0.33 atm (d) 0.20 atm

45. One mole of ethanol is treated with one mole of ethanoic acid at 25°C. One-fourth of the acid changes into ester at equilibrium. The equilibrium constant for the reaction will be

(a) 1/9 (b) 4/9
(c) 9 (d) 9/4

46. One mole each of A and B and 3 moles each of C and D are placed in 1 L flask. If equilibrium constant is 2.25 for the reaction: $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$, equilibrium concentrations of A and C will be in the ratio

(a) 2:3 (b) 3:2
(c) 1:2 (d) 2:1

47. For the reaction: $\text{XY}_2(\text{g}) \rightleftharpoons \text{XY}(\text{g}) + \text{Y}(\text{g})$, the reaction is started with initial pressure of XY_2 , 600 mm Hg. The total pressure for gases at equilibrium is 800 mm Hg. Assuming volume and temperature of the system remains constant, the value of K_p is

(a) 100 atm
(b) 100 mm Hg
(c) 0.01 atm
(d) 400 mm Hg

48. For the reaction: $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$, the initial concentration of A and B is equal, but the equilibrium concentration of C is twice that of equilibrium concentration of A. The equilibrium constant is

(a) 4 (b) 9
(c) 1/4 (d) 1/9

49. $\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$. This reaction is set up in aqueous medium. We start with 1 mol of I_2 and 0.5 mol of I^- in 1L flask. After equilibrium is reached, excess of AgNO_3 gave 0.25 mol of yellow precipitate. Equilibrium constant is

(a) 1.33 (b) 2.66
(c) 0.375 (d) 0.75

50. The equilibrium constant for the mutarotation, $\alpha\text{-D-glucose} \rightleftharpoons \beta\text{-D-glucose}$ is 1.8. What per cent of the α -form remains under equilibrium?

(a) 35.7 (b) 64.3
(c) 55.6 (d) 44.4

51. For the reaction:

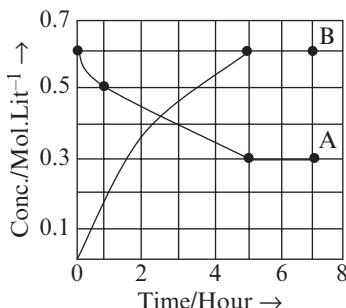


the ratio $\frac{K_p}{P}$, where P is the total pressure of gases at equilibrium and $P_{\text{Br}_2} = \frac{P}{9}$ at a certain temperature, is

(a) $\frac{1}{9}$ (b) $\frac{1}{81}$
(c) $\frac{1}{27}$ (d) $\frac{1}{3}$

52. The progress of the reaction $\text{A} \rightleftharpoons n\text{B}$, with time is represented by the graph given below.

The value of n is



(a) 1 (b) 2
(c) 3 (d) 4

53. K_p for the reaction: $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\text{NO}_2$ is 640 mm at 775 K. The percentage dissociation of N_2O_4 at equilibrium pressure of 160 mm is

(a) $\frac{100}{\sqrt{2}}$ (b) 50
(c) $\frac{50}{\sqrt{2}}$ (d) $10\sqrt{2}$

54. At 127°C and 1 atm pressure, $\text{PCl}_5\text{(g)}$ is partially dissociated into $\text{PCl}_2\text{(g)}$ and $\text{Cl}_2\text{(g)}$ as: $\text{PCl}_5\text{(g)} \rightleftharpoons \text{PCl}_3\text{(g)} + \text{Cl}_2\text{(g)}$. The density of the equilibrium mixture is 3.5 g/L. Percentage dissociation of PCl_5 is ($R = 0.08$ L-atm/K-mol, $P = 31$, $\text{Cl} = 35.5$)

(a) 46.28 (b) 86.16
(c) 15.86 (d) 53.72

55. At T K, a compound $\text{AB}_2\text{(g)}$ dissociates according to the reaction: $2\text{AB}_2\text{(g)} \rightleftharpoons 2\text{AB(g)} + \text{B}_2\text{(g)}$, with a degree of dissociation 'x' which is small compared with unity. The expression for 'x' in terms of the equilibrium constant, K_p and the total pressure, P , is

(a) $\frac{K_p}{P}$
(b) $(K_p)^{1/3}$
(c) $\left(\frac{2K_p}{P}\right)^{1/3}$
(d) $\left(\frac{K_p}{P}\right)^{1/3}$

Heterogeneous Equilibrium

56. A quantity of 25 g sample of BaO_2 is heated to 954 K in a closed and rigid evacuated vessel of 8.21 L capacity. What percentage of peroxide is converted into oxide?



(a) 20% (b) 50%
(c) 75% (d) 80%

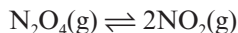
57. For the reaction: $\text{NH}_2\text{COONH}_4\text{(s)} \rightleftharpoons 2\text{NH}_3\text{(g)} + \text{CO}_2\text{(g)}$, $K_p = 3.2 \times 10^{-5} \text{ atm}^3$. The total pressure of the gaseous products when sufficient amount of reactant is allowed to achieve equilibrium, is

(a) 0.02 atm
(b) 0.04 atm
(c) 0.06 atm
(d) 0.095 atm

58. At a certain temperature, K_p for the dissociation of solid CaCO_3 is 4.5×10^{-2} atm and for the reaction $\text{C(s)} + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO(g)}$, the K_p value is 2.0 atm. The pressure of carbon monoxide at this temperature, when solid carbon, CaO and CaCO_3 are mixed together and allowed to attain equilibrium, is
- 0.09 atm
 - 0.30 atm
 - 2.1 atm
 - 0.47 atm
59. The value of K_p for the equilibrium: $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S(g)}$ at a certain temperature and total 2 atm pressure at equilibrium will be
- 0.25 atm^2
 - 1.0 atm^2
 - 4.0 atm^2
 - 1.0 atm
60. Iron fillings and water were placed in a 5 L vessel and sealed. The tank was heated to 1000°C . Upon analysis, the tank was found to contain 1.2 g of $\text{H}_2(\text{g})$ and 54.0 g of $\text{H}_2\text{O(g)}$. If the reaction is represented as: $3\text{Fe(s)} + 4\text{H}_2\text{O(g)} \rightleftharpoons \text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g})$, the value of equilibrium constant is
- 0.2
 - 0.04
 - 0.008
 - 0.0016
61. At 1000°C and a pressure of 16 atm, the equilibrium constant of the reaction:
- $$\text{CO}_2(\text{g}) + \text{C(s)} \rightleftharpoons 2\text{CO(g)}$$
- is such that for every nine moles of CO, there is one mole of CO_2 . For what pressure of the mixture, is the ratio $\text{CO}:\text{CO}_2 = 4:1$? The temperature remains 1000°C .
- 40.5 atm
 - 81 atm
 - 33.75 atm
 - 6.7 atm
62. At a certain temperature, K_p for the reaction: $2\text{CO(g)} \rightleftharpoons \text{CO}_2(\text{g}) + \text{C(graphite)}$ is 0.1 atm^{-1} . What is the ratio of partial pressures of CO and CO_2 at equilibrium, taking the total pressure to be 1.1 atm?
- 9:1
 - 10:1
 - 1:10
 - 1:9
63. For the equilibrium: $\text{LiCl} \cdot 3\text{NH}_3(\text{s}) \rightleftharpoons \text{LiCl} \cdot \text{NH}_3(\text{s}) + 2\text{NH}_3(\text{g})$; $K_p = 9 \text{ atm}^2$ at 27°C . A 8.21 L vessel contains 0.1 mole of $\text{LiCl} \cdot \text{NH}_3(\text{s})$. How many moles of $\text{NH}_3(\text{g})$ should be added to the flask at this temperature to derive the backward reaction for completion?
- 0.8
 - 1.0
 - 1.2
 - 1.1
64. The reaction, $\text{ZnO(s)} + \text{CO(g)} \rightleftharpoons \text{Zn(g)} + \text{CO}_2(\text{g})$, has an equilibrium constant of 1 atm at 1500 K. The equilibrium partial pressure of zinc vapour in a reaction vessel if an equimolar mixture of CO and CO_2 is brought into contact with solid ZnO at 1500 K and the equilibrium is achieved at 1 atm, is
- 0.68 atm
 - 0.76 atm
 - 0.24 atm
 - 0.5 atm
65. If 0.3 moles of hydrogen gas and 2.0 moles of sulphur solid are heated to 87°C in a 2.0 L vessel, what will be the partial pressure of H_2S gas at equilibrium? (Given: $R = 0.08 \text{ l-atm/K-mol}$)
- $$\text{H}_2(\text{g}) + \text{S(s)} \rightleftharpoons \text{H}_2\text{S(g)}; K_c = 0.08$$
- 0.32 atm
 - 0.43 atm
 - 0.62 atm
 - 0.48 atm

Le-Chatelier's Principle

66. Consider the following equilibrium in a closed container:



At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statement holds true regarding the equilibrium constant (K_p) and degree of dissociation (α)?

- (a) neither K_p nor α changes
 - (b) both K_p and α changes
 - (c) K_p changes, but α does not change
 - (d) K_p does not change, but α changes
67. Which of the following hypothetical reactions is favoured by increase of temperature as well as pressure?
- (a) $\text{A}(\text{s}) + 2\text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g}) + \text{D}(\text{g}); \Delta H = +\text{ve}$
 - (b) $\text{A}(\text{s}) + 2\text{B}(\text{g}) \rightleftharpoons 2\text{C}(\text{g}) + \text{D}(\text{g}); \Delta H = +\text{ve}$
 - (c) $2\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons 2\text{C}(\text{g}) + \text{D}(\text{s}); \Delta H = +\text{ve}$
 - (d) $2\text{A}(\text{s}) + 2\text{B}(\text{g}) \rightleftharpoons 2\text{C}(\text{g}) + 2\text{D}(\text{g}); \Delta H = -\text{ve}$
68. In the system $\text{AB}(\text{s}) \rightleftharpoons \text{A}(\text{g}) + \text{B}(\text{g})$, doubling the quantity of $\text{AB}(\text{s})$ would
- (a) increase the amount of A to double its value
 - (b) increase the amount of B to double its value
 - (c) increase the amounts of both A and B to some extent
 - (d) cause no changes in the amounts of A and B
69. In a system: $\text{A}(\text{s}) \rightleftharpoons 2\text{B}(\text{g}) + 3\text{C}(\text{g})$, if the concentration of C at equilibrium is increased by a factor of 2, it will cause

the equilibrium concentration of B to decrease by

- (a) two times the original value
 - (b) one half of its original value
 - (c) $2\sqrt{2}$ times its original value
 - (d) 8 times its original value
70. The reaction: $\text{MgCO}_3(\text{s}) \rightleftharpoons \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$ is in progress. If number of moles of MgO in the vessel is doubled at an instance
- (a) the reaction quotient, Q is halved
 - (b) the reaction quotient, Q is doubled
 - (c) the moles of CO_2 present at equilibrium is halved
 - (d) the partial pressure of CO_2 in the vessel remains unchanged
71. When pressure is applied to the equilibrium system: $\text{Ice} \rightleftharpoons \text{water}$, which of the following phenomenon will happen?
- (a) more ice will be formed
 - (b) ice will sublime
 - (c) more water will be formed
 - (d) equilibrium will not disturb
72. The equilibrium: $\text{SOCl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ is attained at 25°C in a closed container and helium gas is introduced. Which of the following statements is correct?
- (a) concentration of SO_2 is increased
 - (b) more Cl_2 is formed
 - (c) concentrations of all change
 - (d) concentrations will not change
73. When calcium acetate is dissolved in water, heat is evolved. If the temperature is raised, the solubility of calcium acetate
- (a) increases
 - (b) decreases
 - (c) is not affected
 - (d) first increases and then decreases

74. The Haber's process for the manufacture of ammonia is usually carried out at about 500°C . If a temperature of about 250°C was used instead of 500°C ,
- no ammonia would be formed at all
 - the percentage of ammonia in the equilibrium mixture would be too low
 - a catalyst would be of no use at all at this temperature
 - the percentage of ammonia in the equilibrium mixture would be too high
75. Densities of diamond and graphite are 3.5 and 2.4 g/ml, respectively. The increase in pressure (at the constant temperature) at the equilibrium in $\text{C (diamond)} \rightleftharpoons \text{C (graphite)}$ will
- favour the forward reaction
 - favour the backward reaction
 - have no effect
 - increases the equilibrium constant
76. In a flask, colourless N_2O_4 is in equilibrium with brown coloured NO_2 . At equilibrium, when the flask is heated at 100°C the brown colour deepens and on cooling it becomes less coloured. The change in enthalpy, ΔH , for the system is
- negative
 - positive
 - zero
 - undefined
77. For the chemical reaction: $3\text{X(g)} + \text{Y(g)} \rightleftharpoons \text{X}_3\text{Y(g)}$, the amount of X_3Y at equilibrium is affected by
- temperature and pressure
 - temperature only
 - pressure only
 - temperature, pressure and catalyst
78. What will the change on increasing the pressure at equilibrium: $\text{water} \rightleftharpoons \text{water vapour}$?
- The boiling point of water will increase.
 - The boiling point of water will decrease.
 - The boiling point of water will not change.
 - Boiling point is not related with pressure.
79. In equilibrium:
- $$\underset{\text{colourless}}{\text{SCN}^{-}(\text{aq})} + \underset{\text{yellow}}{\text{Fe}^{+3}(\text{aq})} \rightleftharpoons \underset{\text{deep red}}{[\text{Fe}(\text{SCN})^{2+}](\text{aq})}$$
- If thiocyanate ions are added in equilibrium mixture
- The solution becomes colourless.
 - The yellow colour of solution deepens.
 - The red colour of the solution deepens.
 - Concentration of $[\text{Fe}(\text{SCN})]^{2+}$ ion will decrease.
80. An aqueous solution of volume 500 ml, when the reaction: $2\text{Ag}^{+}(\text{aq}) + \text{Cu(s)} \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{Ag(s)}$, reached equilibrium, the concentration of Cu^{2+} ions was x M. To this solution, 500 ml of water is added. At the new equilibrium, the concentration of Cu^{2+} ions would be
- $2x$ M
 - x M
 - between x and $0.5x$ M
 - less than $0.5x$ M
81. $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$. In the above reaction, the partial pressure of PCl_3 , Cl_2 and PCl_5 are 0.3, 0.2 and 0.6 atm, respectively. If partial pressure of PCl_3 and Cl_2 was increased twice at the new equilibrium, what will be the new partial pressure of PCl_5 (in atm)?
- | | |
|---------|----------|
| (a) 0.3 | (b) 1.2 |
| (c) 2.4 | (d) 0.15 |

82. In the equilibrium mixture: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$, the mole ratio of gases are $\sqrt{2} : \sqrt{2} : 10$, respectively. What would be the effect on the mole ratio on adding 5 mole of He gas at constant pressure?
- No change
 - The new molar ratio becomes 1:1:5
 - The new molar ratio becomes 2:2:5
 - The new molar ratio becomes $2:2:5\sqrt{2}$
83. One mole of He (g, colourless) is added to the equilibrium mixture containing N_2O_4 (g, colourless) and NO_2 (g, red-brown) present in a cylinder piston arrangement maintained at constant pressure and temperature. It will result
- no change in colour of the equilibrium mixture.
 - lightening the colour of the equilibrium mixture.
 - darkening the colour of the equilibrium mixture.
 - no effect on the equilibrium composition.
84. Consider the formation of SO_3 according to the reaction: $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$; $\Delta H = -198 \text{ kJ}$. Which of the following may change the value of equilibrium constant of the above reaction?
- Adding He gas to reaction vessel
 - Adding more of O_2 to the reaction vessel
 - Increasing the temperature
 - Doubling the volume of reaction vessel
85. For the given chemical equation: $2\text{X}(\text{g}) + \text{Y}(\text{g}) \rightleftharpoons 2\text{Z}(\text{g}) + 8 \text{ kcal}$, which combination of pressure and temperature gives the highest yield of 'Z' at equilibrium?
- 1000 atm and 500°C
 - 500 atm and 500°C
 - 500 atm and 100°C
 - 1000 atm and 100°C

Answer Keys – Exercise I

Basic

1. (a) 2. (a) 3. (d) 4. (d) 5. (d) 6. (a) 7. (c) 8. (a) 9. (d) 10. (b)
 11. (a) 12. (a) 13. (c) 14. (c) 15. (b) 16. (a) 17. (a) 18. (c) 19. (b) 20. (b)
 21. (b) 22. (c) 23. (d) 24. (d) 25. (a) 26. (a) 27. (d) 28. (d) 29. (d) 30. (b)

Application of Equilibrium Constant

31. (b) 32. (c) 33. (c) 34. (b) 35. (c) 36. (c) 37. (b) 38. (b) 39. (c) 40. (c)
 41. (b) 42. (a) 43. (d) 44. (d) 45. (a) 46. (a) 47. (b) 48. (a) 49. (a) 50. (a)
 51. (b) 52. (b) 53. (a) 54. (b) 55. (c)

Heterogeneous Equilibrium

56. (d) 57. (c) 58. (b) 59. (b) 60. (d) 61. (a) 62. (c) 63. (c) 64. (c) 65. (a)

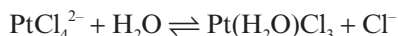
Le-Chatelier's Principle

66. (d) 67. (c) 68. (d) 69. (c) 70. (d) 71. (c) 72. (d) 73. (b) 74. (a) 75. (b)
 76. (b) 77. (a) 78. (a) 79. (c) 80. (d) 81. (c) 82. (a) 83. (b) 84. (c) 85. (d)

EXERCISE II (JEE ADVANCED)

Section A (Only one Correct)

1. The approach to the following equilibrium was observed kinetically from both directions:



At 25°C, it was found that

$$-\frac{d[\text{PtCl}_4^{2-}]}{dt} = (3.9 \times 10^{-5} \text{ s}^{-1}) [\text{PtCl}_4^{2-}] - (2.1 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}) [\text{Pt}(\text{H}_2\text{O})\text{Cl}_3][\text{Cl}^-]$$

The value of K_{eq} (equilibrium constant) for the complexation of the fourth Cl^- by $\text{Pt}(\text{II})$ is

- (a) 53.8 mol L⁻¹
 (b) 0.018 mol L⁻¹
 (c) 53.8 L mol⁻¹
 (d) 0.018 L mol⁻¹
2. The complexation of Fe^{2+} with the chelating agent dipyrityl has been studied kinetically in both the forward and reverse directions.
- $$\text{Fe}^{2+} + 3 \text{ dipy} \rightleftharpoons [\text{Fe}(\text{dipy})_3]^{2+}$$
- For this reaction, the rates of forward and reverse reactions are $(1.45 \times 10^{13} \text{ M}^{-3} \text{ s}^{-1}) [\text{Fe}^{2+}][\text{dipy}]^3$ and $(1.22 \times 10^{-4} \text{ s}^{-1}) [\text{Fe}(\text{dipy})_3]^{2+}$, at 25°C. What is the stability constant of the complex?
- (a) 1.77×10^9
 (b) 8.4×10^{-18}
 (c) 1.18×10^{17}
 (d) 5.65×10^{-10}
3. The rate constant for the forward reaction: $\text{A}(\text{g}) \rightleftharpoons 2\text{B}(\text{g})$ is $1.5 \times 10^{-3} \text{ s}^{-1}$ at 300 K. If 10^{-5} moles of 'A' and 100 moles of 'B' are present in a 10 litre vessel at equilibrium,

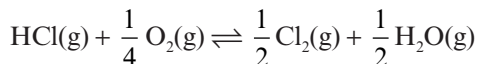
then the rate constant of the backward reaction at this temperature is

- (a) $1.5 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$
 (b) $1.5 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$
 (c) $1.5 \times 10^{-11} \text{ M}^{-1} \text{ s}^{-1}$
 (d) $1.5 \times 10^{-12} \text{ M}^{-1} \text{ s}^{-1}$
4. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O}(\text{s}) + 2\text{H}_2\text{O}(\text{g})$, K_p for this equilibrium is $1.0 \times 10^{-4} \text{ atm}^2$ at 25°C. What is the maximum pressure of water vapour (moisture) in the atmosphere, below which the pentahydrate is efflorescent?
- (a) 7.60 mm
 (b) 0.01 mm
 (c) 0.076 mm
 (d) 760 mm
5. Ammonia at a pressure of 10 atm and CO_2 at a pressure of 20 atm are introduced into an evacuated chamber. If K_p for the reaction: $\text{NH}_2\text{COONH}_4(\text{s}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$ is 2020 atm^3 , the total pressure after a long time is
- (a) less than 30 atm
 (b) more than 30 atm
 (c) equal to 30 atm
 (d) unpredictable
6. K_p for the process: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O}(\text{s}) + 2\text{H}_2\text{O}(\text{g})$ is $1.21 \times 10^{-4} \text{ atm}^2$ at certain temperature. If aqueous tension at that temperature is 40 torr, then at what relative humidity of air will $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ effloresces?
- (a) above 40.8%
 (b) below 40.8%
 (c) above 20.9%
 (d) below 20.9%

7. K_p for the reaction: $\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightleftharpoons 2\text{HI}(\text{g})$ is 6.4×10^{-4} atm. On close observation, it is found that the partial pressure of iodine present in vapour state is 1.6×10^{-4} atm, at the same temperature. The K_p for the reaction: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ is
 (a) 0.25
 (b) 4
 (c) 1.024×10^{-7}
 (d) 9.76×10^6
8. For the reaction: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$. The rate law expression is:
 (a) $-\frac{1}{2} \cdot \frac{d[\text{HI}]}{dt} = K_{-1}[\text{HI}]^2 - K_1[\text{H}_2][\text{I}_2]$
 (b) $-\frac{1}{2} \cdot \frac{d[\text{HI}]}{dt} = \frac{K_1[\text{HI}]^2}{K_{-1}[\text{H}_2][\text{I}_2]}$
 (c) $-\frac{1}{2} \cdot \frac{d[\text{HI}]}{dt} = K_1[\text{H}_2][\text{I}_2] - K_{-1}[\text{HI}]^2$
 (d) $-\frac{1}{2} \cdot \frac{d[\text{HI}]}{dt} = K_1 K_{-1}[\text{H}_2][\text{I}_2]$
9. At 200°C , PCl_5 dissociates as follows: $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$. It was found that the equilibrium vapours are 62 times as heavy as hydrogen. The percentage dissociation of PCl_5 at 200°C is
 (a) 34.1%
 (b) 70.3%
 (c) 40.5%
 (d) 68.1%
10. Under what pressure must an equimolar mixture of Cl_2 and PCl_3 be placed at 250°C in order to obtain 75% conversion of PCl_3 into PCl_5 ? Given: $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$; $K_p = 2 \text{ atm}^{-1}$
 (a) 12 atm
 (b) 6 atm
 (c) 15 atm
 (d) 30 atm
11. In the reaction: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{Heat}$. One mole of N_2 reacts with three moles of H_2 . If at equilibrium ' x ' moles of N_2 combined, then the value of ' x ' in terms of K_p and the total pressure of gases at equilibrium, P , is
 (a) $\frac{3P \cdot \sqrt{3 \cdot K_p}}{8}$
 (b) $\frac{8P}{3\sqrt{3 \cdot K_p}}$
 (c) $\frac{3\sqrt{3 \cdot K_p}}{8P}$
 (d) $\frac{8}{P} \cdot \sqrt{\frac{K_p}{3}}$
12. For the reaction: $\text{X}_2(\text{g}) + \text{Y}_2(\text{g}) \rightleftharpoons 2\text{XY}(\text{g})$, 2 moles of ' X_2 ' was taken in a 2 L vessel and 3 moles of ' Y_2 ' was taken in a 3 L vessel. Both vessels were then connected. At equilibrium, concentration of ' XY ' is 0.7 M. Equilibrium concentrations of ' X_2 ' and ' Y_2 ' would be
 (a) 0.65 M, 0.65 M
 (b) 0.30 M, 0.30 M
 (c) 0.25 M, 1.25 M
 (d) 0.05 M, 0.25 M
13. The equilibrium constant for the reaction: $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ is 0.09 at 3500 K . The fraction of equimolar mixture of N_2 and O_2 converted into NO is
 (a) 0.13
 (b) 0.23
 (c) 0.30
 (d) 0.357
14. At a certain temperature, the equilibrium constant of the reaction: $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ is 0.0004. Assuming air to be a mixture of four volumes of nitrogen with one volume of oxygen, the percentage of nitric oxide, by volume, in the gas produced by allowing air to reach equilibrium at this temperature, is
 (a) 3.0%
 (b) 0.8%
 (c) 0.04%
 (d) 8.0%

15. When a mixture of N_2 and H_2 in the volume ratio of 1:5 is allowed to react at 700 K and 10^3 atm pressure, 0.4 mole fraction of NH_3 is formed at equilibrium. The K_p for the reaction:
- $$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
- (a) $2.6 \times 10^{-5} \text{ atm}^{-2}$
 (b) $2.6 \times 10^{-4} \text{ atm}^{-2}$
 (c) $2.6 \times 10^3 \text{ atm}^{-2}$
 (d) $5.1 \times 10^{-3} \text{ atm}^{-2}$
16. An amount of 16 moles H_2 and 4 moles of N_2 is confined in a vessel of volume one litre. The vessel is heated to a constant temperature until the equilibrium is established. At equilibrium, the pressure was found to be $9/10^{\text{th}}$ of the initial pressure. The value of K_c for the reaction: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, is
- (a) 8100
 (b) 6.07×10^{-4}
 (c) 1647.75
 (d) 8.99×10^{-5}
17. An amount of 3 moles of N_2 and some H_2 is introduced into an evacuated vessel. The reaction starts at $t = 0$ and equilibrium is attained at $t = t_1$. The amount of ammonia at $t = 2t_1$ is found to be 34 g. It is observed that $\frac{w(\text{N}_2)}{w(\text{H}_2)} = \frac{14}{3}$ at $t = \frac{t_1}{3}$ and $t = \frac{t_1}{2}$. The only correct statement is
- (a) $w(\text{N}_2) + w(\text{H}_2) + w(\text{NH}_3) = 118 \text{ g}$ at $t = t_1$
 (b) $w(\text{N}_2) + w(\text{H}_2) + w(\text{NH}_3) = 102 \text{ g}$ at $t = 2t_1$
 (c) $w(\text{N}_2) + w(\text{H}_2) + w(\text{NH}_3) = 50 \text{ g}$ at $t = t_1/3$
 (d) $w(\text{N}_2) + w(\text{H}_2) + w(\text{NH}_3)$ cannot be predicted
18. Starting with 2 moles SO_2 and 1 mol of O_2 in 1 L flask, the equilibrium mixture required 0.4 moles of MnO_4^- for complete reaction in acidic medium. K_c for the reaction: $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ is
- (a) 2
 (b) 0.5
 (c) 0.25
 (d) 4
19. A quantity of 60 g CH_3COOH and 46 g $\text{CH}_3\text{CH}_2\text{OH}$ reacts in 5 L flask to form 44 g $\text{CH}_3\text{COOC}_2\text{H}_5$ at equilibrium. On taking 120 g CH_3COOH and 46 g $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{COOC}_2\text{H}_5$ formed at equilibrium is
- (a) 44 g
 (b) 29.33 g
 (c) 66 g
 (d) 58.67 g
20. Two moles of an equimolar mixture of two alcohols $\text{R}_1\text{-OH}$ and $\text{R}_2\text{-OH}$ are esterified with one mole of acetic acid. If only 80% of the acid is consumed till equilibrium and the quantities of ester formed under equilibrium are in the ratio 3:2. What is the value of equilibrium constant for the esterification of $\text{R}_1\text{-OH}$?
- (a) 0.48
 (b) 2.2
 (c) 0.32
 (d) 0.75
21. For the reaction: $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})$, NO and Cl_2 are initially taken in mole ratio of 2:1. The total pressure at equilibrium is found to be 1 atm. If the moles of NOCl are one-fourth of that of Cl_2 at equilibrium, K_p for the reaction is
- (a) $\frac{13}{36}$
 (b) $\frac{13}{256}$
 (c) $\frac{13}{512}$
 (d) $\frac{13}{128}$
22. When S in the form of S_8 is heated at 900 K, the initial pressure of 1 atm falls by 30% at equilibrium. This is because of conversion of some $\text{S}_8(\text{g})$ to $\text{S}_2(\text{g})$. The K_p of the reaction is
- (a) 0.011 atm^{-3}
 (b) 2.96 atm^3
 (c) 1.71 atm^3
 (d) 204.8 atm^3

23. The Deacon reaction is the oxidation of HCl by O_2 :

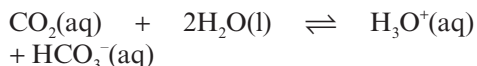


At a pressure of 730 mm and with an initial mixture containing 8% HCl and 92% O_2 , the degree of decomposition of the HCl is 0.08. What is the equilibrium partial pressure of oxygen?

- (a) 671.6 mm
(b) 659.92 mm
(c) 537.28 mm
(d) 670.43 mm
24. The equilibrium constant for the reaction: $H_3BO_3 + \text{glycerin} \rightleftharpoons (H_3BO_3 + \text{glycerin complex})$ is 0.90. How much glycerin should be added to 1 L of 0.10 M- H_3BO_3 solution, so that 60% of the H_3BO_3 is converted to boric acid-glycerin complex?
- (a) Infinite (b) 1.73 M
(c) 0.10 M (d) 2.27 M
25. The process: $2A(g) \rightleftharpoons A_2(g)$ has $K_p = 8 \times 10^8 \text{ atm}^{-1}$. If 'A' atoms are taken at 1 atm pressure, what should be the equilibrium pressure of 'A'?

- (a) 0
(b) $2.5 \times 10^{-5} \text{ atm}$
(c) $4 \times 10^4 \text{ atm}$
(d) $1.25 \times 10^{-5} \text{ atm}$

26. When $CO_2(g)$ is dissolved in water, the following equilibrium is established:



for which the equilibrium constant is 3.8×10^{-7} . If the pH of solution is 6.0, what would be the ratio of concentration of $HCO_3^-(aq)$ to $CO_2(aq)$?

- (a) 3.8×10^{-13} (b) 6.0
(c) 0.38 (d) 13.4

27. For the equilibrium: $A(g) \rightleftharpoons nB(g)$, the equilibrium constant, K_p , is related with the degree of dissociation, α , and the total pressure of gases at equilibrium, P , as

- (a) $\frac{(n\alpha)^n \cdot P^{n-1}}{(1-\alpha) \cdot [1 + (n-1)\alpha]^{n-1}}$
(b) $\frac{(n\alpha)^{n-1} \cdot P^{n-1}}{(1-\alpha) \cdot [1 + (n-1)\alpha]^{n-1}}$
(c) $\frac{\alpha^{n-1} \cdot P^{n-1}}{(1-\alpha) \cdot [1 + (n-1)\alpha]}$
(d) $\frac{n\alpha \cdot P^{n-1}}{(1-\alpha)^{n-1} \cdot [1 + (n-1)\alpha]}$

28. Reaction: $A(g) + B(g) \rightleftharpoons C(g) + D(g)$, occurs in a single step. The rate constant of forward reaction is $2.0 \times 10^{-3} \text{ mol}^{-1} \text{ L s}^{-1}$. When the reaction is started with equimolar amounts of A and B, it is found that the concentration of A is twice that of C at equilibrium. The rate constant of the backward reaction is

- (a) $5.0 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$
(b) $8.0 \times 10^{-3} \text{ mol}^{-1} \text{ L s}^{-1}$
(c) $1.25 \times 10^2 \text{ mol}^{-1} \text{ L s}^{-1}$
(d) $2.0 \times 10^3 \text{ mol}^{-1} \text{ L s}^{-1}$

29. Find the concentration of monomeric dichloroacetic acid in a CCl_4 solution which contains 0.0129 g of the acid in 100 ml of solution. The dissociation constant of the dimeric acid is 5.0×10^{-4} . Assume that the acids are unionized in CCl_4 solution.

- (a) $5.0 \times 10^{-4} \text{ M}$
(b) $2.5 \times 10^{-4} \text{ M}$
(c) $1.0 \times 10^{-3} \text{ M}$
(d) $2.5 \times 10^{-3} \text{ M}$

30. In an evacuated rigid vessel of volume V litre, one mole of solid ammonium carbonate, NH_2CONH_2 , is taken and the vessel is heated to T K. The equilibrium total pressure of gases is found to be P atm. The percentage dissociation of solid into $\text{NH}_3(\text{g})$ and $\text{CO}_2(\text{g})$ is
- (a) $\frac{100RT}{3PV} \%$ (b) $\frac{RT}{3PV} \%$
 (c) $\frac{100RT}{PV} \%$ (d) $\frac{300RT}{PV} \%$
31. For the equilibrium: $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{SrCl}_2 \cdot 2\text{H}_2\text{O}(\text{s}) + 4\text{H}_2\text{O}(\text{g})$, $K_p = 8.1 \times 10^{-7} \text{ atm}^4$ at 27°C . If 1.642L of air saturated with water vapour at 27°C is exposed to a large quantity of $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$, what mass of water vapour will be absorbed? Saturated vapour pressure of water at $27^\circ\text{C} = 30.4$ torr.
- (a) 12 mg (b) 6.67 mg
 (c) 9 mg (d) 48 mg
32. Two systems $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ and $\text{COCl}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$ are simultaneously in equilibrium in a vessel at constant volume. If some CO is introduced into the vessel, then at the new equilibrium, the moles of
- (a) PCl_5 increase
 (b) PCl_5 remain unchanged
 (c) PCl_5 decrease
 (d) Cl_2 increase
33. In the system, $\text{LaCl}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) + \text{heat} \rightleftharpoons \text{LaClO}(\text{s}) + 2\text{HCl}(\text{g})$, equilibrium is established. More water vapour is added to disturb the equilibrium. If the pressure of water vapour at new equilibrium is double of that at initial equilibrium, the factor by which pressure of HCl is changed is
- (a) 2 times (b) $\sqrt{2}$ times
 (c) $\frac{1}{\sqrt{2}}$ times (d) 4 times
34. Indicate the correct answer out of the following for the reaction:
- $$\text{NH}_4\text{Cl} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{HCl}$$
- (a) The reaction is retarded by the addition of KOH
 (b) The reaction is favoured by the addition of NH_4OH
 (c) The reaction is retarded by the addition of hydrogen ion
 (d) The reaction is favoured by the addition of hydrogen ion
35. The two equilibria, $\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^-$ and $\text{AB} + \text{B}^- \rightleftharpoons \text{AB}_2^-$ are simultaneously maintained in a solution with equilibrium constants K_1 and K_2 , respectively. The ratio of A^+ to AB_2^- in the solution is
- (a) Directly proportional to the concentration of B
 (b) Inversely proportional to the concentration of B
 (c) Directly proportional to the square of the concentration of B
 (d) Inversely proportional to the square of the concentration of B
36. Solid NH_4HS dissociates into NH_3 and H_2S at a certain temperature, the equilibrium pressure is P atm. If now, NH_3 is pumped into the system so that its partial pressure becomes P atm, what will be the partial pressure (in atm) of H_2S ?
- (a) $0.5 P$ (b) $0.25 P$
 (c) $0.33 P$ (d) $0.67 P$
37. In a closed rigid vessel, the following equilibrium partial pressures are measured: $\text{N}_2 = 100$ mm, $\text{H}_2 = 400$ mm and $\text{NH}_3 = 1000$ mm. Now, nitrogen is removed from the vessel until the pressure of hydrogen at equilibrium is equal to 700 mm. The new equilibrium partial pressure of N_2 is
- (a) 11.94 mm (b) 200 mm
 (c) 18.66 mm (d) 43.78 mm

38. Suppose the gas phase isomerization reactions: $A \rightleftharpoons B$, $A \rightleftharpoons C$ and $B \rightleftharpoons C$ achieve equilibrium simultaneously, at a fixed temperature. The equilibrium mole fraction of 'A' in terms of equilibrium constants, K_1 , K_2 and K_3 (respectively), is

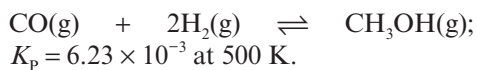
(a) $\frac{K_1}{K_1 + K_2 + K_3}$

(b) $\frac{1}{1 + K_1 + K_2}$

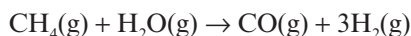
(c) $\frac{1}{K_1 + K_2 + K_3}$

(d) $\frac{1}{K_1 + K_2}$

39. Methanol, CH_3OH can be prepared from CO and H_2 as



What total pressure is required to convert 25% of CO to CH_3OH at 500 K, if CO and H_2 comes from the reaction:



- (a) 20.48 bar
(b) 21 bar
(c) 10.24 bar
(d) 5.12 bar

40. An amount of 1 mole each of A and D is introduced in 1L container. Simultaneously the following two equilibria are established:



The equilibrium concentration of A will be

- (a) 10^{-6} M (b) 10^{-3} M
(c) 10^{-12} M (d) 10^{-4} M

41. For a reversible reaction: $A \xrightleftharpoons[K_2]{K_1} B$, the initial molar concentration of A and B are $a \text{ M}$ and $b \text{ M}$, respectively. If $x \text{ M}$ of A is reacted till the achievement of equilibrium, then x is

(a) $\frac{K_1 a - K_2 b}{K_1 + K_2}$

(b) $\frac{K_1 a - K_2 b}{K_1 - K_2}$

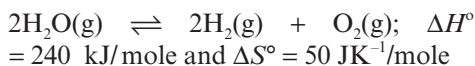
(c) $\frac{K_1 a - K_2 b}{K_1 K_2}$

(d) $\frac{K_1 a + K_2 b}{K_1 + K_2}$

42. For the given reaction: $2A(s) + B(g) \rightleftharpoons C(g) + 2D(s) + E(s)$, the extent of reaction of B was found to be 20% at 300 K and 24% at 500 K. The rate of backward reaction

- (a) increases with increase in pressure and temperature
(b) increases with increase in pressure and decrease in temperature
(c) depends on temperature only and decreases with increases in temperature
(d) depends on temperature only and increases with increase in temperature

43. Steam decomposes at high temperature according to the equation:



The temperature at which the equilibrium constant (K_p°) becomes 1.0, is

- (a) 4.8 K (b) 4800 K
(c) 480 K (d) Impossible

44. $\Delta_r G^\circ$ for the formation of HI(g) from its gaseous elements is -2.303 kcal/mol at 500 K. When the partial pressure of HI is 10 atm and of $I_2(g)$ is 0.001 atm, what must be the partial pressure of hydrogen be at this temperature to reduce the magnitude of ΔG for the reaction to zero?

(a) 1000 atm (b) 10000 atm
(c) 100 atm (d) 31.63 atm

45. When α -D-glucose is dissolved in water, it undergoes a partial conversion to β -D-glucose. This conversion, called mutarotation, stops when 64.0% of the glucose is in the β -form. Assuming that equilibrium has been attained, what is ΔG° for the reaction: α -D-glucose \rightleftharpoons β -D-glucose, at this experimental temperature?

(a) $-RT \log_{10}(1.6)$
(b) $-RT \log_{10}(1.78)$
(c) $-RT \log_e(1.78)$
(d) $-RT \log_e(1.6)$

46. At chemical equilibrium, a reaction is

(a) spontaneous in forward direction
(b) spontaneous in backward direction
(c) spontaneous in both direction
(d) spontaneous in neither direction

47. Rate of disappearance of the reactant 'A' in the reversible reaction: $A \rightleftharpoons B$, at two temperatures is given as

$$-\frac{d[A]}{dt} = (2.0 \times 10^{-3} \text{ s}^{-1})[A] - (5.0 \times 10^{-4} \text{ s}^{-1})[B] \text{ (at } 27^\circ\text{C)}$$

$$-\frac{d[A]}{dt} = (8.0 \times 10^{-2} \text{ s}^{-1})[A] - (4.0 \times 10^{-3} \text{ s}^{-1})[B] \text{ (at } 127^\circ\text{C)}$$

The enthalpy of reaction in the given temperature range is

(a) $-\frac{2.303 \times 8.314 \times 300 \times 400}{100} \cdot \log(50) \text{ J/mol}$
(b) $-\frac{2.303 \times 8.314 \times 300 \times 400}{100} \cdot \log(5) \text{ J/mol}$
(c) $\frac{2.303 \times 8.314 \times 300 \times 400}{100} \cdot \log(50) \text{ J/mol}$
(d) $\frac{2.303 \times 8.314 \times 300 \times 400}{100} \cdot \log(5) \text{ J/mol}$

48. A certain gas 'A' polymerizes to a very small extent at a given temperature as: $nA(g) \rightleftharpoons A_n(g)$. The reaction is started with one mole of 'A' in a container of capacity V . Which of the following is correct value of $\frac{PV}{RT}$, at equilibrium?

(a) $1 - \frac{(n-1).K_C}{V^{n-1}}$

(b) $\frac{(n-1).K_C}{V^{n-1}}$

(c) $1 - \frac{n.K_C}{V^{n-1}}$

(d) $1 - \frac{n.K_C}{V^n}$

49. PCl_5 (molecular mass = M) dissociates into PCl_3 and Cl_2 as: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. If the total pressure of the system at equilibrium is P and the density is 'd' at temperature, T K. The degree of dissociation of PCl_5 may be represented as

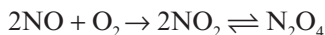
(a) $\frac{PM}{dRT}$

(b) $\frac{PM}{dRT} - 1$

(c) $\frac{dRT}{PM} - 1$

(d) $\frac{dRT}{PM}$

50. A 250 ml flask and 100 ml flask are separated by a stopcock. At 350 K, the nitric oxide in the larger flask exerts a pressure of 0.4 atm, and the smaller one contains oxygen at 0.8 atm. The gases are mixed by opening the stopcock. The reactions occurring are:



The first reaction is complete while the second one is at equilibrium. Assuming all the gases to behave ideally, calculate the K_p for the second reaction if the total pressure is 0.3 atm.

(a) 3.5 atm^{-1}
(b) 0.87 atm^{-1}
(c) 0.07 atm^{-1}
(d) 7.0 atm^{-1}

51. If 'a' is the fraction of ammonia present by volume in an equilibrium mixture made from one volume of N_2 and three volumes of H_2 and P is the total pressure, then
- $\frac{a}{1-a} \propto P$
 - $\frac{a}{(1-a)^2} \propto P$
 - $\frac{a}{(1+a)^2} \propto P$
 - $\frac{a}{1+a} \propto P$
52. At 525 K, $PCl_5(g)$ is 80% dissociated at a pressure of 1 atm. Now, sufficient quantity of an inert gas at constant pressure is introduced into the above reaction mixture to produce inert gas partial pressure of 0.9 atm. What is the percentage dissociation of $PCl_5(g)$ when equilibrium is re-established?
- 97.3%
 - 80%
 - 65.6%
 - 4.7%
53. For the reaction: $CuSO_4 \cdot 3H_2O(s) \rightleftharpoons CuSO_4 \cdot H_2O(s) + 2H_2O(g)$; $\Delta H = 3360$ cal. The dissociation pressure is 7×10^{-3} atm at $27^\circ C$. What will be the dissociation pressure at $127^\circ C$? ($\ln 2 = 0.7$)
- 9.8×10^{-3} atm
 - 1.4×10^{-2} atm
 - 1.4×10^{-3} atm
 - 9.8×10^{-2} atm
54. Carbon monoxide in water gas, reacts with steam according to the reaction:
- $$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g); K_{eq} = 0.3333$$
- If two volumes of water gas (containing 1:1 of CO and H_2) are mixed with five volumes of steam, then the volume ratio of the four gases present at equilibrium is
- 1:1:1:1
 - 1:3:1:1
 - 1:15:1:5
 - 1:9:1:3
55. If for the equilibria: $NH_2COONH_4(s) \rightleftharpoons N_2 + H_2 + CO + O_2$, the value of K_p at 800 K is $27 \times 2^{\lambda/2}$ and the equilibrium pressure is 22 atm. The value of λ is
- 21
 - 22
 - 11
 - 12
56. Solid ammonium carbamate dissociates as: $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$. In a closed vessel solid ammonium carbamate is in equilibrium with its dissociation products. At equilibrium ammonia is added such that the partial pressure of NH_3 at new equilibrium now equals the original total pressure. The ratio of total pressure at new equilibrium to that of original total pressure is
- 1:1
 - 27:31
 - 31:27
 - 3:4
57. The value of equilibrium constant for the following reaction at 300 K and constant pressure:
- $$A(g) + B(g) \rightleftharpoons C(g) + D(g) + E(g); \Delta E^\circ = -30 \text{ kcal and } \Delta S^\circ = 100 \text{ cal/K}$$
- e
 - $\frac{1}{e}$
 - e^2
 - $\frac{1}{e^2}$
58. $\Delta_r G^\circ$ are 30.426 kJ/mol for *trans*-1,2-dichloroethene and 22.112 kJ/mol for *cis*-1,2-dichloroethene, at $27^\circ C$. The molar ratio of *trans* and *cis* isomers at equilibrium at $27^\circ C$, is [$\ln 28 = 3.33$]
- 10:3
 - 3:10
 - 28:1
 - 1:28

59. The equilibrium constant for the reaction: $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$ is 3.0 at 500 K. In a 2.0 l vessel, 60 g of water gas [equimolar mixture of CO(g) and $\text{H}_2\text{(g)}$] and 90 g steam is initially taken. What is the equilibrium concentration of $\text{H}_2\text{(g)}$?
- (a) 1.75 M (b) 3.5 M
(c) 1.5 M (d) 0.75 M
60. The equilibrium: $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{H}_2\text{S(g)}$ is achieved at the equilibrium pressure of 'X' bar at T K. The value of $\Delta_r G^\circ$ for the reaction is
- (a) $-RT \ln X$
(b) $-2RT \ln X$
(c) $-2RT (\ln X - \ln 2)$
(d) $-2RT \ln(2X)$

Section B (One or More than one Correct)

1. When $\text{NH}_4\text{HS(s)}$ is vaporized in an empty vessel and maintained at 20°C , the equilibrium is established: $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{H}_2\text{S(g)}$ and the total pressure of gases at equilibrium is 0.4 atm. When $\text{NH}_4\text{HS(s)}$ is vaporized in the presence of $\text{NH}_3\text{(g)}$ in the same vessel at 20°C , the partial pressure of $\text{NH}_3\text{(g)}$ at equilibrium is 0.5 atm. Which of the following is/are correct statement(s)?
- (a) At second equilibrium, the final partial pressure of $\text{H}_2\text{S(g)}$ is 0.08 atm.
(b) In second experiment, the initial pressure of $\text{NH}_3\text{(g)}$ was 0.42 atm.
(c) In presence of $\text{NH}_3\text{(g)}$, the extent of dissociation of $\text{NH}_4\text{HS(s)}$ decreased.
(d) At second equilibrium, the mole-fraction of $\text{H}_2\text{S(g)}$ is 0.5.
2. Which of the following reaction(s) have $K_p = K_c$?
- (a) $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$
(b) $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO(g)}$
(c) $2\text{NO(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons 2\text{NOCl(g)}$
(d) $2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{SO}_3\text{(g)}$
3. For dissociation of a gas N_2O_5 as: $\text{N}_2\text{O}_5\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)}$. The reaction is performed at constant temperature and volume. If D is the vapour density of equilibrium mixture, P_o is initial pressure of $\text{N}_2\text{O}_5\text{(g)}$ and M is molecular mass of N_2O_5 , then the correct information(s) at the equilibrium is/are
- (a) The total pressure of gases at equilibrium is $\frac{P_o \cdot M}{2D}$.
(b) The degree of dissociation of $\text{N}_2\text{O}_5\text{(g)}$ is $\frac{M - 2D}{3D}$.
(c) The partial pressure of $\text{N}_2\text{O}_5\text{(g)}$ at equilibrium is $\frac{(5D - M) \cdot P_o}{3D}$.
(d) The partial pressure of $\text{O}_2\text{(g)}$ at equilibrium is $\frac{(M - 2D) \cdot P_o}{3D}$.
4. Which of the following is/are correct statement(s)?
- (a) The dissociation of CaCO_3 is suppressed at high pressure.
(b) The apparent molecular mass of PCl_5 shows lower value on dissociation.
(c) Low pressure is favourable for melting of ice.
(d) Combination of hydrogen atoms to form hydrogen molecule is favourable at high temperature.
5. What is/are true about equilibrium state?
- (a) Catalyst has no effect on equilibrium state.
(b) Equilibrium constant is independent of initial concentration of reaction.
(c) The reaction ceases at equilibrium.
(d) Equilibrium constant is independent of pressure.

6. A chemical system is in equilibrium. Addition of a catalyst would result in
- increase in the rate of forward reaction.
 - increase in the rate of reverse reaction.
 - a new reaction pathway to reaction.
 - increase the amount of heat evolved.
7. A cylinder fitted with a movable piston contains liquid water in equilibrium with water vapour at 25°C. Which operation results in a decrease in the equilibrium vapour pressure?
- moving the piston downward a short distance
 - removing a small amount of vapour
 - removing a small amount of the liquid water
 - dissolving salt in the water
8. Condition suitable for forming atomic chlorine from molecular chlorine is
- Low temperature
 - Low pressure
 - High temperature
 - High pressure
9. The position of equilibrium will shift in the given direction by the addition of inert gas at constant pressure in the following case(s):
- $\text{N}_2(\text{g}) + 3\text{F}_2(\text{g}) \rightleftharpoons 2\text{NF}_3(\text{g})$; forward direction
 - $\text{COCl}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$; forward direction
 - $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$; backward direction
 - $2\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$; backward direction
10. Two gases A and B, one being the dimer of the other, are at equilibrium. Decreases of pressure at constant temperature or increases of temperature at constant pressure favours the formation of more of B. The reaction could not be represented by
- $2\text{A} \rightleftharpoons \text{B} + q \text{ calories}$
 - $2\text{A} \rightleftharpoons \text{B} - q \text{ calories}$
 - $2\text{B} \rightleftharpoons \text{A} - q \text{ calories}$
 - $2\text{B} \rightleftharpoons \text{A} + q \text{ calories}$
11. The equilibrium constant for some reactions are given below against each of the reaction:
- $2\text{N}_2 + 5\text{O}_2 \rightleftharpoons 2\text{N}_2\text{O}_5$; $K = 5 \times 10^{-27}$
 - $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$; $K = 2 \times 10^{-15}$
 - $\text{N}_2 + 2\text{O}_2 \rightleftharpoons 2\text{NO}_2$; $K = 1.5 \times 10^{-29}$
- Which of the following statement is correct?
- The least stable oxide is NO_2
 - The most stable oxide is NO
 - The stability order is $\text{N}_2\text{O}_5 > \text{NO}_2 > \text{NO}$
 - The stability order is $\text{NO}_2 > \text{NO} > \text{N}_2\text{O}_5$
12. For the gaseous reaction: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, the following thermodynamical data are given
- $$\Delta H^\circ_{300 \text{ K}} = -41.0 \text{ kJ mol}^{-1};$$
- $$\Delta S^\circ_{300 \text{ K}} = -0.04 \text{ kJ K}^{-1} \text{ mol}^{-1}$$
- $$\Delta H^\circ_{1200 \text{ K}} = -33.0 \text{ kJ mol}^{-1};$$
- $$\Delta S^\circ_{1200 \text{ K}} = -0.03 \text{ kJ K}^{-1} \text{ mol}^{-1}$$
- Assuming partial pressure of each component is 1 bar, the direction of spontaneous reaction is/are
- Forward at 300 K
 - Forward at 1200 K
 - Backward at 300 K
 - Backward at 1200 K

13. Van't Hoff equations show the effect of temperature on equilibrium constants K_C and K_p . K_p and K_C varies with temperature according to the relations

$$(a) \log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303R} \left[\frac{T_1 - T_2}{T_1 T_2} \right]$$

$$(b) \log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

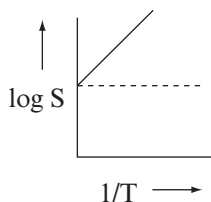
$$(c) \log \frac{K_{C_2}}{K_{C_1}} = \frac{\Delta U}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$(d) \log \frac{K_{C_2}}{K_{C_1}} = \frac{\Delta U}{2.303R} \left[\frac{T_1 - T_2}{T_1 T_2} \right]$$

14. For a chemical reaction at the state of equilibrium, which of the following statement(s) is/are correct?

- (a) None of the variables like temperature, pressure or volume appear to change.
- (b) Reaction system has maximum stability with minimum energy content.
- (c) Addition of catalyst disturbs the point of equilibrium.
- (d) Addition of inert gas at equilibrium for constant volume system will move the equilibrium in the direction, where more number of moles of gases is present.

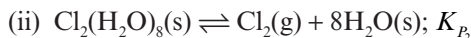
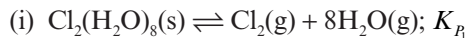
15. Solubility of a solute in a solvent (say, water) is dependent on temperature as given by $S = A \cdot e^{-\Delta H/RT}$, where ΔH is heat of reaction: solute + $H_2O \rightleftharpoons$ solution. For a given solution, variation of $\log S$ with temperature is shown graphically. The solute should be



- (a) $CuSO_4 \cdot 5H_2O$
- (b) NaCl
- (c) Sucrose
- (d) CaO

16. At chemical equilibrium, the
- (a) enthalpy of system is minimum.
 - (b) entropy of system is maximum.
 - (c) free energy of system is minimum.
 - (d) free energy of system is zero.

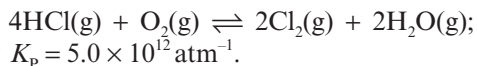
17. At $-10^\circ C$, the solid compound $Cl_2(H_2O)_8$ is in equilibrium with gaseous chlorine, water vapour and ice. The partial pressure of the two gases in equilibrium with a mixture of $Cl_2(H_2O)_8$ and ice are 0.20 atm for Cl_2 and 0.001 atm for water vapour. The processes may be represented as:



Identify the correct statement among the following regarding the processes.

- (a) The value of K_p is $2.0 \times 10^{-25} \text{ atm}^9$.
 - (b) The value of K_p is 0.2 atm.
 - (c) The vapour pressure of ice is 0.001 atm at 263 K.
 - (d) Process (i) must be exothermic.
18. In an evacuated vessel of capacity 112 L, 4 moles of $Ar(g)$ and 5 moles of $PCl_5(g)$, were introduced and temperature is maintained at $273^\circ C$. At equilibrium, the total pressure of the mixture was found to be 4.8 atm.
- (a) The degree of dissociation of $PCl_5(g)$ into $PCl_3(g)$ and $Cl_2(g)$ is 0.6.
 - (b) K_p for the reaction: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 2.7 atm.
 - (c) At equilibrium, the total moles of gases are 12.
 - (d) On removing $Ar(g)$ from the equilibrium mixture at constant pressure and temperature, the extent of dissociation of PCl_5 will increase.

19. In a vessel of 1.0 L capacity, $O_2(g)$ at 0.25 atm pressure and $HCl(g)$ at 1.0 atm pressure are allowed to react in presence of liquid water at $57^\circ C$.



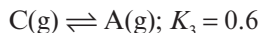
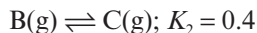
The volume occupied by liquid water is negligible but it is sufficient to achieve equilibrium with water vapour. The vapour pressure of water at $57^\circ C$ is 0.4 atm. Select the correct statement(s) regarding the equilibrium mixture.

- The partial pressure of water vapour at any stage of reaction is 0.4 atm.
 - The partial pressure of $Cl_2(g)$ at equilibrium is 0.5 atm.
 - The partial pressure of $O_2(g)$ at equilibrium is 5.0×10^{-4} atm.
 - The partial pressure of $HCl(g)$ at equilibrium is 2.0×10^{-3} atm.
20. In the following equilibrium: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, when 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar. Given: $\Delta_f G^\circ[N_2O_4(g)] = 100 \text{ kJ/mol}$; $\Delta_f G^\circ[NO_2(g)] = 50 \text{ kJ/mol}$.
- K_p for the reaction is 1.0 bar.
 - ΔG° for the reaction is zero at 298 K.
 - Under the given condition, the reaction is mainly occurring in backward direction.
 - The mixture taken is at equilibrium.
21. A gaseous substance $AB_2(g)$ converts to $AB(g)$ in the presence of solid A as: $AB_2(g) + A(s) \rightleftharpoons 2AB(g)$. The initial pressure and equilibrium pressure are 0.7 and 0.95 bar, respectively. Now, the equilibrium mixture is expanded reversibly and isothermally till the gas

pressure falls to 0.4 bar. Then, which of the following statements is correct?

- The volume per cent of $AB(g)$ at final equilibrium is nearly 27%.
 - The volume per cent of $AB_2(g)$ at final equilibrium is nearly 32.5%.
 - K_p for the equilibrium is $5/9$.
 - The ratio of equilibrium pressure of $AB_2(g)$ at initial and final equilibrium is more than 2 but less than 3.
22. An amount of 1 mole of $PCl_5(g)$ and 1 mole of $PCl_3(g)$ is taken in a vessel of 10 L capacity maintained at 400 K. At equilibrium, the moles of Cl_2 is found to be 0.004.
- K_c for the reaction: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 0.0004 M.
 - K_p for the reaction: $PCl_5(g) + Cl_2(g) \rightleftharpoons PCl_3(g)$ is $0.0004 \times (0.082 \times 400) \text{ atm}$.
 - If $PCl_3(g)$ is added to the equilibrium mixture, ΔG at the new equilibrium becomes greater than the ΔG at old equilibrium.
 - After equilibrium is achieved, moles of PCl_3 are doubled and moles of Cl_2 are halved simultaneously, then the partial pressure of PCl_5 remains unchanged.
23. A reaction at 300 K with $\Delta G^\circ = -1743 \text{ J}$ consists of 3 moles of $A(g)$, 6 moles of $B(g)$ and 3 moles of $C(g)$. If A, B and C are in equilibrium in 1L container, then the reaction may be ($\ln 2 = 0.7$, $R = 8.3 \text{ J/K-mol}$)
- $A + B \rightleftharpoons C$
 - $A \rightleftharpoons B + 2C$
 - $2A \rightleftharpoons B + C$
 - $A + B \rightleftharpoons 2C$

24. The equilibrium between gaseous isomers A, B and C can be represented as:



If one mole of A is taken in a closed vessel of volume 1L, then

- $[A] + [B] + [C] = 1$ M at any moment of reaction.
- Concentration of C is 1.2 M at equilibrium.
- The value of K_1 is 1/0.24.
- Isomer A is thermodynamically least stable.

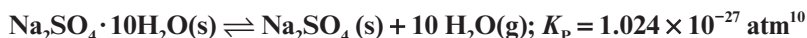
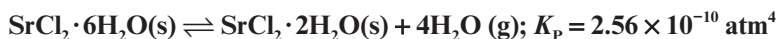
25. Consider the equilibrium: $\text{HgO}(s) + 4\text{I}^-(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HgI}_4^{2-}(\text{aq}) + 2\text{OH}^-(\text{aq})$, which changes will decrease the equilibrium concentration of $\text{HgI}_4^{2-}(\text{aq})$?

- Addition of 0.1 M-HI(aq)
- Addition of $\text{HgO}(s)$
- Addition of $\text{H}_2\text{O}(l)$
- Addition of $\text{KOH}(\text{aq})$

Section C (Comprehensions)

Comprehension I

Equilibrium constants are given for the following reactions at 27°C.



The vapour pressure of water at 27°C is 0.04 atm.

- Which is the most effective drying agent at 27°C?
 - $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$,
 - $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$
 - Na_2SO_4
 - All, equally
- At what relative humidity will $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(s)$ be efflorescent when exposed to the air at 27°C?
 - below 50%
 - above 50%
 - above 5%
 - below 5%
- At what relative humidity will $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}(s)$ deliquescent when exposed to the air at 27°C?
 - below 75%
 - above 75%
 - above 7.5%
 - below 7.5%

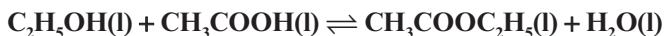
Comprehension II

An amount of 0.20 moles of CO taken in a 2.463 L flask is maintained at 750 K along with a catalyst so that the following reaction can take place: $\text{CO(g)} + 2\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_3\text{OH(g)}$. Hydrogen is introduced until the total pressure of the system is 7.5 atm at equilibrium and 0.1 mole of methanol is formed.

- For the reaction, K_p is
 (a) 0.16 atm^{-2} (b) 6.25 atm^{-2}
 (c) 0.04 atm^{-2} (d) 1.56 atm^{-2}
- For the reaction, K_c is [Given: $(2.463)^2 = 6.07$]
 (a) 6.07 M^{-2} (b) 607 M^{-2}
 (c) 151.75 M^{-2} (d) 2428 M^{-2}
- What is the final pressure if the same amount of CO and H_2 as before used, but with no catalyst so that the reaction does not take place?
 (a) 18.75 atm
 (b) 10.0 atm
 (c) 15.0 atm
 (d) 12.5 atm

Comprehension III

In the esterification reaction:



an equimolar mixture of alcohol and acid taken initially, yields under equilibrium, the ester with mole fraction = 0.333.

- The equilibrium constant is
 (a) 10 (b) 4
 (c) 100 (d) 16
- What fraction of the alcohol would be esterified if the initial mole fraction of the alcohol is 0.333? [Given: $\sqrt{12} = 3.45$]
 (a) 0.15 (b) 0.85
 (c) 0.28 (d) 0.72
- If in this esterification, initially equal moles of alcohol and acid are taken. At equilibrium, unreacted alcohol and acid, on treatment of sodium, produced H_2 which occupied 44.8 L at 0°C and 1 atm. The percentage esterification of acid and alcohol is
 (a) 25% (b) 33.3%
 (c) 50% (d) 66.7%

Comprehension IV

At 444°C , HI undergoes dissociation to the extent of 22.22% at equilibrium

- What is the equilibrium constant of the reaction: $2\text{HI(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$, at 444°C ?
 (a) 50 (b) 0.02
 (c) 0.143 (d) 3.14
- What is the percentage dissociation of HI at 444°C , if the experiment is started with one mole of HI(g) and one mole of $\text{I}_2\text{(g)}$?
 (a) less than 22.22%
 (b) more than 22.22%
 (c) equal to 22.22%
 (d) nothing can be said
- What is the percentage dissociation of HI at 444°C , if the experiment is started with one mole of HI(g) and 1 mole of He(g)?
 (a) less than 22.22%
 (b) more than 22.22%
 (c) equal to 22.22%
 (d) nothing can be said

Comprehension V

Le Chatelier performed an experiment in science academy. He introduced excess of solid NH_4HS into a closed 5.0 L vessel containing NH_3 gas at a partial pressure of P mm and at temperature 300 K. Due to it, dissociation of the solid takes place and at equilibrium, he measured the partial pressure of NH_3 gas equal to 625 mm and the total pressure of gases equal to 725 mm.

13. The value of P is
 (a) 725 (b) 625 (c) 525 (d) 100
14. K_p for the reaction: $\text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{NH}_4\text{HS}(\text{s})$, is
 (a) $6.25 \times 10^4 \text{ atm}^2$
 (b) $1.6 \times 10^{-5} \text{ atm}^{-2}$
 (c) $1.6 \times 10^{-3} \text{ atm}^{-2}$
 (d) $4.53 \times 10^5 \text{ atm}^2$
15. What would have been the partial pressure of NH_3 , if excess solid NH_4HS had been taken in an evacuated vessel of the same volume at the same temperature?
- (a) 1000 mm (b) 750 mm
 (c) 500 mm (d) 250 mm
16. The minimum mass of $\text{NH}_4\text{HS}(\text{s})$ needed to establish equilibrium in the same evacuated vessel at the same temperature is
 (a) $\frac{250 \times 5}{0.0821 \times 300} \text{ g}$
 (b) $\frac{250 \times 5 \times 51}{0.0821 \times 300} \text{ g}$
 (c) $\frac{250 \times 5 \times 51}{0.0821 \times 300 \times 760} \text{ g}$
 (d) $\frac{250 \times 5}{0.0821 \times 300 \times 760} \text{ g}$

Comprehension VI

For the system: $\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g}) + \text{D}(\text{g})$, ΔH for the forward reaction is -24.942 kJ/mol . The activation energies of forward and backward reactions are in the ratio 2:3. Assume that the pre-exponential factor is the same for the forward and backward reactions.

17. What is the equilibrium constant for the reaction at 27°C ?
 (a) e^4 (b) e^{-4}
 (c) e^{10} (d) e^{-10}
18. What is the ratio of rate constant of backward to forward direction?
 (a) e^4 (b) e^{-4}
 (c) e^{10} (d) e^{-10}
19. Identify the correct statement?
 (a) The rate constant of forward reaction is e^{30} .
 (b) The rate constant of forward reaction is e^{-30} .
 (c) The rate constant of backward reaction is e^{30} .
 (d) The rate constant of backward reaction is e^{-30} .

Comprehension VII

The degree of dissociation of NH_3 in a vessel V_1 (initially evacuated) at $T \text{ K}$ at an equilibrium pressure of 50 atm is same as that of $\text{SO}_3(\text{g})$ at a total equilibrium pressure equal to K_p for



A vessel V_2 (capacity 100 L and maintained at T K) initially contains equimolar mixture of NH_3 , N_2 , H_2 and Ne. The total mass of the mixture containing four gases is 0.134 kg. At equilibrium, N_2 was found to be 52.24%, by mass. (Ne = 20)

20. The degree of dissociation of NH_3 at T K, in the vessel of volume V_1 , is
 (a) 0.33
 (b) 0.50
 (c) 0.67
 (d) 0.75
21. K_p for the reaction: $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ at T K is
 (a) 2700 atm^2
 (b) 2500 atm^2
 (c) $3.7 \times 10^{-4} \text{ atm}^2$
 (d) $4.0 \times 10^{-4} \text{ atm}^2$
22. The total pressure of gases at equilibrium in the vessel V_2 is
 (a) $\sqrt{\frac{2700 \times 8}{2.5}} \text{ atm}$
 (b) $\sqrt{\frac{2700 \times 8}{2.5 \times 7}} \text{ atm}$
 (c) $\sqrt{\frac{2700 \times 81}{2.5 \times (3.5)^3}} \text{ atm}$
 (d) $\sqrt{\frac{2700 \times 81}{3.5 \times (2.5)^3}} \text{ atm}$

Comprehension VIII

In a vessel, the equilibria: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ and $\text{N}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{N}_2\text{H}_4(\text{g})$ are achieved simultaneously. Initially the vessel contains N_2 and H_2 in molar ratio of 9:13. The equilibrium pressure is $7P_0$ in which due to ammonia, the pressure is P_0 and due to hydrogen, pressure is $2P_0$.

23. The value of K_p for the reaction: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ is
 (a) $20 P_0^2$
 (b) $\frac{20 P_0^2}{3}$
 (c) $\frac{1}{20 P_0^2}$
 (d) $\frac{3}{20 P_0^2}$
24. The value of K_p for the reaction: $\text{N}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{N}_2\text{H}_4(\text{g})$ is
 (a) $20 P_0^2$
 (b) $\frac{20 P_0^2}{3}$
 (c) $\frac{1}{20 P_0^2}$
 (d) $\frac{3}{20 P_0^2}$

Section D (Assertion–Reason)

The following questions consist of two statements. Mark

- (a) If both statements are CORRECT, and **Statement II** is the CORRECT explanation of **Statement I**.
 (b) If both statements are CORRECT, and **Statement II** is NOT the CORRECT explanation of **Statement I**.
 (c) If **Statement I** is CORRECT, but **Statement II** is INCORRECT.
 (d) If **Statement I** is INCORRECT, but **Statement II** is CORRECT.

1. **Statement I:** For the reaction: $\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g})$, equilibrium moles of A and B are, respectively, 'a' and 'b' in 1 l container. If 5 moles of A and 3 moles of B are added, then reaction must move in forward direction.

Statement II: Even if the amount of reactant added to a system at equilibrium is more than amount of product added at the same time, the equilibrium can shift in any direction.

2. **Statement I:** 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 the system (reaction: $A(g) \rightleftharpoons B(g)$)

Statement II: The number of moles of the substance which is removed, is partially compensated as the system reaches to the new equilibrium.

3. **Statement I:** A net reaction can occur only if a system is not at equilibrium.

Statement II: All reactions occur to reach a state of equilibrium.

4. **Statement I:** A catalyst does not influence the value of equilibrium constant.

Statement II: Catalyst influence the rates of both forward and backward reactions by the same factor.

5. **Statement I:** Le Chatelier's principle predicts that an increase in temperature favours an endothermic process.

Statement II: An endothermic process is one that absorbs heat and hence tends to minimize the temperature increase.

6. **Statement I:** For a gaseous reversible reaction, K_p can be equal to or less than or even greater than the value of K_c .

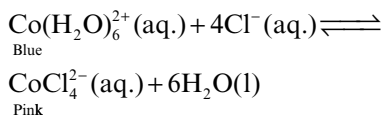
Statement II: The relation between K_p and K_c depends on the change in the number of moles of gaseous reactants and products as well as temperature.

7. **Statement I:** The system $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is said to be at equilibrium when

the intensity of brown colour does not change with time.

Statement II: $N_2O_4(g)$ is colourless while $NO_2(g)$ is coloured.

8. **Statement I:** On cooling in a freezing mixture, colour of the following mixture turns to pink from deep blue for the reaction:



Statement II: The reaction is endothermic.

9. **Statement I:** NaCl solution can be purified by passing excess of hydrogen chloride gas through NaCl solution.

Statement II: Increase in chloride ion concentration in the solution results precipitation of NaCl.

10. **Statement I:** Decrease in volume of the system at constant temperature at equilibrium results increase in molar concentration of all the gaseous components involved in the reaction: $A(g) + B(s) \rightleftharpoons 3C(g)$.

Statement II: Decrease in volume of the system at constant temperature at equilibrium results increase in moles of $A(g)$ and decrease in moles of $C(g)$ but no change in the moles of $B(s)$ in the reaction: $A(g) + B(s) \rightleftharpoons 3C(g)$.

Section E (Column Match)

1. Match the following

Column I	Column II
(A) $Q = K_{eq}$	(P) Reaction is near to completion
(B) $Q < K_{eq}$	(Q) Reaction is not at equilibrium
(C) $Q > K_{eq}$	(R) Reaction is fast in forward direction
(D) $K_{eq} \gg 1$	(S) Reaction at equilibrium

2. Match the following

Column I	Column II
(A) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$	(P) $K_p = K_c (RT)$
(B) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	(Q) $K_p = K_c (RT)^2$
(C) $\text{PCl}_3(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$	(R) $K_p = K_c (RT)^{-2}$
(D) $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$	(S) $K_p = K_c$

3. Match Column I with Column II

Column I	Column II
(A) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$	(P) Unaffected by inert gas addition
(B) $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	(Q) Forward shift by rise in pressure and backward shift by inert gas addition
(C) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	(R) Unaffected by increase in pressure
(D) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$	(S) Backward shift by rise in pressure and forward shift by inert gas addition

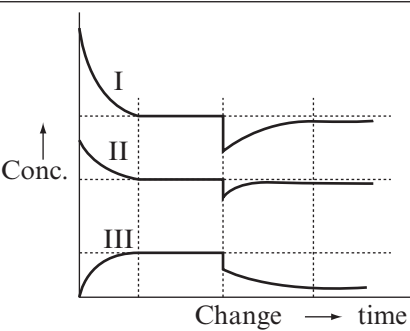
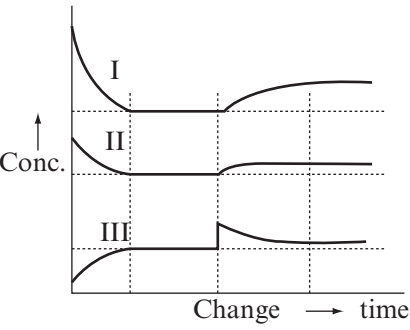
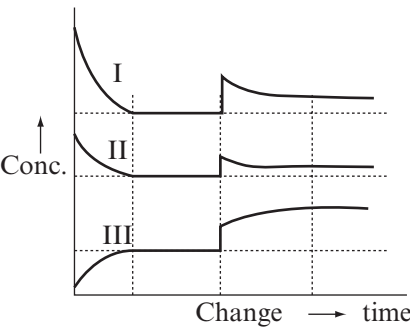
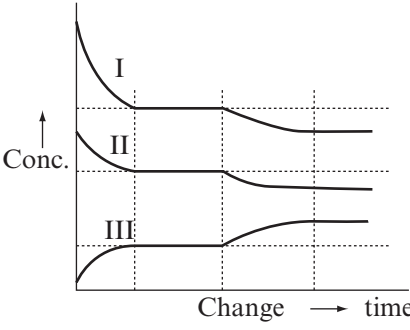
4. Match Column I with Column II

Column I	Column II
(A) $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$	(P) Extent of reaction will not increase with increase in pressure
(B) $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$	(Q) Concentration of product will increase with increase in temperature
(C) $2(\text{CH}_3\text{COOH})(\text{g}) \rightleftharpoons (\text{CH}_3\text{COOH})_2(\text{g})$	(R) Increase in volume will increase moles of reactant
	(S) Introduction of inert gas at constant pressure will shift the equilibrium in the product side.

5. Match Column I with Column II

Column I	Column II
(A) $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$	(P) Introduction of hydrogen gas at constant volume shift equilibrium back
(B) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$	(Q) α increases on increasing temperature
(C) $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$	(R) On adding inert gas at constant volume, equilibrium state does not change
(D) $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$	(S) On increasing the pressure, concentration of all reactants increases
	(T) α is independent of equilibrium pressure

6. For an endothermic reaction: $4A(g) + B_2(g) \rightleftharpoons 2A_2B(g)$

Column I	Column II
<p>(A) </p>	<p>(P) Increase in temperature</p>
<p>(B) </p>	<p>(Q) Increase in pressure</p>
<p>(C) </p>	<p>(R) Addition of A_2B at equilibrium</p>
<p>(D) </p>	<p>(S) Addition of inert gas at constant pressure</p> <p>(T) Increase in volume</p>

7. Match the following

Column I	Column II
(A) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$	(P) $K_p > K_c$ at 300 K
(B) $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$	(Q) $K_p < K_c$ at 300 K
(C) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$	(R) P is increased, reaction moves to right side
(D) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	(S) Inert gas added at constant volume, equilibrium will not be affected
	(T) Inert gas added at constant pressure, equilibrium will shift right

8. Match the following for the reaction: $2\text{A}(\text{g}) \rightleftharpoons 3\text{B}(\text{g}) + \text{C}(\text{s})$; $\Delta H = -ve$

Column I	Column II
(A) Increase in total pressure at equilibrium	(P) Increase in moles of A
(B) Increase in volume at equilibrium	(Q) Increase in moles of B
(C) Addition of $\text{He}(\text{g})$ at constant pressure	(R) Increase in moles of C
(D) Increase in temperature at constant volume	(S) Increase in molar concentration of A
	(T) Increase in molar concentration of B

9. For the reaction: $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$; $K_p = 2.463$ atm at 900 K. The reaction is performed in a rigid vessel of 15.0 l capacity maintained at 900 K, starting with the following amounts of $\text{CaCO}_3(\text{s})$ (given in Column I). Match the correct information given in Column II for the amount given in Column I.

Column I	Column II
(A) 100 g	(P) 50% dissociation of CaCO_3
(B) 50 g	(Q) 100% dissociation of CaCO_3
(C) 25 g	(R) Addition of small amount of $\text{CO}_2(\text{g})$ may result shift of equilibrium in backward direction
	(S) Addition of 10 g of $\text{CaCO}_3(\text{s})$ may result increase in moles of $\text{CO}_2(\text{g})$

10. Match the following

Column I (Reactions)	Column II (Effect on addition of water)
(A) $\text{A}(\text{aq}) \rightleftharpoons 2\text{B}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	(P) Moles of 'A' increases
(B) $3\text{A}(\text{aq}) \rightleftharpoons 2\text{B}(\text{aq})$	(Q) Moles of 'B' increases
(C) $2\text{A}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{B}(\text{aq})$	(R) Molar concentration of 'A' decreases
(D) $2\text{A}(\text{aq}) \rightleftharpoons 3\text{B}(\text{aq})$	(S) Molar concentration of 'B' decreases

Section F (Subjective)

Single-digit Integer Type

1. The per cent dissociation of $\text{H}_2\text{S}(\text{g})$ if 0.1 mole of H_2S is kept in 0.4 L vessel at 1000 K for the reaction: $2\text{H}_2\text{S}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{S}_2(\text{g})$; $K_c = 1.0 \times 10^{-6}$.
2. $\text{COF}_2(\text{g})$ passed over catalyst at 1000°C comes to equilibrium: $2\text{COF}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{CF}_4(\text{g})$. Analysis of the equilibrium mixture (after quick cooling to freeze the equilibrium) shows that 500 ml of the equilibrium mixture (STP) contains 300 ml (STP) of $(\text{COF}_2 + \text{CO}_2)$ taking the total pressure to be 10 atm. The value of K_p for the reaction is
3. The dissociation constant of PCl_5 is 5 atm at 200°C . What pressure (in atm) will be developed when 2.085 g of this substance is vaporized at 200°C in 448 ml vessel originally full of chlorine gas at 0°C and 1 atm pressure?
4. A mixture of equimolar quantities of ethyl alcohol and acetic acid is prepared. Immediately after mixing, 10 ml of mixture was neutralized by 10 ml of N-NaOH. When the mixture reaches the equilibrium, 10 ml requires 5 ml of N-NaOH for neutralization. What is the equilibrium constant for the formation of ester?
5. The degree of dissociation of HI at a particular temperature of 0.8. Calculate the volume (in litre) of 1.6 M- $\text{N}_2\text{S}_2\text{O}_3$ solution required to neutralize the iodine present in an equilibrium mixture of a reaction when 2 moles each of H_2 and I_2 are heated in a closed vessel of 2 l capacity.
6. It was found that when 1.0 mole of dichloroacetic acid and 4.0 moles of amylene were heated together at 363 K

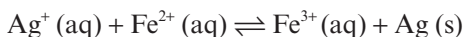
to equilibrium state, 0.5 moles of ester were formed and the total volume of the mixture was 700 ml. In another experiment, 1.0 mole of the acid was heated at the same temperature with some moles of amylene and the equilibrium mixture now occupied a volume of 480 ml. If the amount of ester at equilibrium is 0.6 mole in the second experiment, how many moles of amylene was taken initially? Amylene is one of the pentene.

7. The minimum mass (in g) of CaCO_3 required to establish the equilibrium:



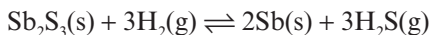
at a certain temperature in a 1.0 L container is

8. To 500 ml of 0.9 M- AgNO_3 solution was added 500 ml of 1.0M- Fe^{2+} solution and the reaction is allowed to achieve equilibrium at 25°C .



For 30 ml of the solution, 25 ml of 0.06 M- KMnO_4 was required for oxidation of Fe^{2+} present. The equilibrium constant (in M^{-1}) for the reaction at 25°C is

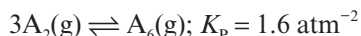
9. A vessel of 2.5 L was filled with 0.01 mole of Sb_2S_3 and 0.01 mole of H_2 to attain equilibrium at 440°C as:



After equilibrium, the H_2S formed was analysed by dissolving it in water and treating with excess of Pb^{2+} to give 1.19 g of PbS as precipitate. The value of K_c of the reaction at 440°C is ($\text{Pb} = 206$)

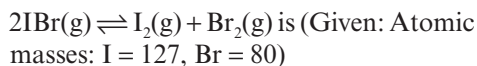
10. At 25°C, 560 g of deuterium oxide, D_2O ($d = 1.10$ g/ml) and 504 g H_2O ($d = 0.997$ g/ml) are mixed. The volumes are additive. Fifty per cent of the H_2O reacts to form HDO. The value of K_c at 25°C for the reaction: $H_2O + D_2O \rightleftharpoons 2HDO$ is

11. Following equilibria are established on mixing two gases A_2 and C:



When $A_2(g)$ and $C(g)$ are mixed in 2:1 molar ratio, the total pressure of gases at equilibrium is found to be 1.4 atm and partial pressure of $A_6(g)$, 0.2 atm. The value of ' $4x$ ' is

12. A 8.28 g sample of $IBr(g)$ is placed in a container of capacity 164.2 ml and heated to 500 K. The equilibrium pressure of $Br_2(g)$ in the system is 4.0 atm. The value of K_p for the reaction:

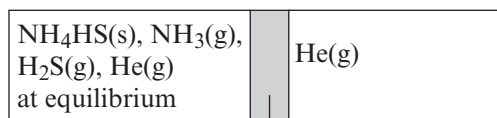


13. When 1.0 mole of $H_2(g)$ and 3.0 moles of I_2 vapours are allowed to react, ' x ' moles of $HI(g)$ is formed at equilibrium. Addition of a further 2.0 moles of $H_2(g)$

gave an additional ' x ' moles of $HI(g)$ at new equilibrium. The value of equilibrium constant for the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is

14. When $N_2O_5(g)$ is heated to 600 K, it dissociates as: $N_2O_5(g) \rightleftharpoons N_2O_3(g) + O_2(g)$; $K_c = 2.5$ M. Simultaneously, $N_2O_3(g)$ decomposes as: $N_2O_3(g) \rightleftharpoons N_2O(g) + O_2(g)$. When initially 4.0 moles of $N_2O_5(g)$ is taken in a 2.0 l flask and allowed to attain equilibrium, the equilibrium concentration of $O_2(g)$ is found to be 2.5 M. The equilibrium concentration of $N_2O(g)$ (in M) is

- 15.



Fixed SPM, which allows only $He(g)$ to cross it

The entire system is at equilibrium at 300 K. The volume of each chamber is 82.1 L. The total pressure in left chamber is 4 atm and in right chamber, 2 atm. $NH_3(g)$ and $H_2S(g)$ are obtained only from the dissociation of $NH_4HS(s)$. The value of K_p (in atm^2) for the reaction: $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$, is

Four-digit Integer Type

1. The equilibrium: p -xyloquinone + methylene white \rightleftharpoons p -xylohydroquinone + methylene blue, may be studied conveniently by observing the difference in colour between methylene blue and methylene white. One millimole of methylene blue was added to 1.00 l of solution that was 0.24 M in p -xylohydroquinone and 0.012 M in p -xyloquinone. It was then found that 4.0% of the added methylene blue was

reduced to methylene white. What is the equilibrium constant for the above reaction? The equation is balanced with 1 molecule of each of the four substances.

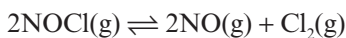
2. The theoretically computed equilibrium constant for the polymerization of formaldehyde to glucose in aqueous solution is $6.4 \times 10^{19} \text{ M}^{-5}$. If 1 M solution of glucose were taken, what would be the equilibrium concentration of formaldehyde, in milligram per litre?

3. A container of capacity V L contains an equilibrium mixture that consists of 2 moles each of PCl_5 , PCl_3 and Cl_2 (all as gases). The pressure is 30.3975 kPa and temperature is T K. A certain amount (' x ' mole) of $\text{Cl}_2(\text{g})$ is now introduced keeping the pressure and temperature constant, until the equilibrium volume becomes $2V$ L. The value of ' $90x$ ' is
4. The standard reaction enthalpy of the reaction: $\text{Zn}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{ZnO}(\text{s}) + \text{H}_2(\text{g})$ is +223 kJ/mol and the standard reaction Gibbs's functions is +33 kJ mol $^{-1}$ at 1520 K. Assuming that both ΔH° and ΔS° remain constant, estimate the minimum temperature (in Kelvin) above which the equilibrium constant becomes greater than one.
5. The diamonds are formed from graphite under very high pressure. Given that the densities of graphite and diamond are, respectively, 2.4 and 3.6 g/cm 3 and are independent of pressure. $\Delta_f G^\circ$ values for graphite and diamond are zero and 3.0 kJ/mol, respectively. If the equilibrium pressure at which graphite is converted into diamond at 25°C is P bar, then the value of $0.01P$ is
6. For the equilibrium: $\text{NiO}(\text{s}) + \text{CO}(\text{g}) \rightleftharpoons \text{Ni}(\text{s}) + \text{CO}_2(\text{g})$, $\Delta G^\circ(\text{cal/mol}^{-1}) = -5320 - 5.6T(\text{K})$. The temperature (in Kelvin) at which the gaseous mixture at equilibrium contains 400 ppm of CO, by mole, is [$\ln 10 = 2.3$, $\ln 2 = 0.7$]
7. Assume that the decomposition of HNO_3 can be represented as

$$4\text{HNO}_3(\text{g}) \rightleftharpoons 4\text{NO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$$
 and that at a given temperature of 400 K and pressure of 30 atm, the reaction approaches equilibrium. At equilibrium,

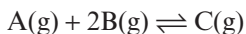
the partial pressure of $\text{HNO}_3(\text{g})$ is 2 atm. The value of K_c (in M^3) for the reaction at 400 K is

8. Gaseous nitrosyl chloride (NOCl) and N_2 are taken in a flask, sealed and heated to some temperature where the total pressure would have been 1.0 bar had not the following equilibrium been established

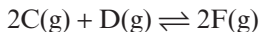


But the actual pressure was found to be 1.2 bar. Now, into the equilibrium mixture, some Cl_2 gas was introduced at constant volume and temperature so that the total pressure would have been 8.3 bar had no further reaction occurred but the actual pressure was found to be 8.2 bar. The equilibrium constant, K_p (in bar), for the decomposition reaction under the given experimental condition is (Answer by multiplying the K_p value with 10)

9. Three ideal gases A, B and D were taken in a vessel of constant volume in molar ratio of 1:2:3, respectively, causing the reaction:

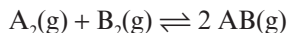


After a long time, when the equilibrium is established, the total pressure was $5/6^{\text{th}}$ of the initial total pressure. At this point, the volume was reduced to half and a catalyst was added starting the reaction:

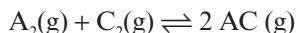


If at the second equilibrium, moles of A and C are equal and the ratio of equilibrium total pressure at second equilibrium to the equilibrium total pressure at the first equilibrium is ' $x:100$ ', then the value of ' x ' is

10. An amount of 0.2 mole of each $A_2(g)$ and $B_2(g)$ is introduced in a sealed flask and heated to 2000 K where following equilibrium is established:



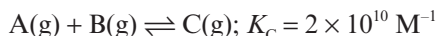
At equilibrium, moles of AB is 0.3. At this stage, 0.1 mole of $C_2(g)$ is added and a new equilibrium is also established as:



At the new equilibrium, the moles of AB becomes 0.24. What is the equilibrium constant for the second reaction?

11. At 27°C, the rate of forward reaction at time, t , is e^4 times greater than that of reverse reaction for the reaction: $A + B \rightleftharpoons P$. The magnitude of free energy change involved at that time (in cal) is

12. An amount of 5.0 moles of 'A', 'B' and 'D' is added to a 1.0 L container.



If at equilibrium, the moles of 'B' is 'x', then the value of '150x' is

13. For the reaction: $Br_2(l) + Cl_2(g) \rightleftharpoons 2BrCl(g)$; $K_p = 1$ atm. In a closed container of volume 164 L, initially 10 moles of $Cl_2(g)$ are present at 27°C. What minimum mass (in g) of $Br_2(l)$

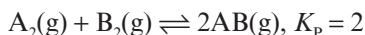
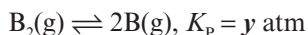
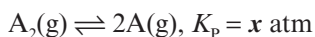
must be introduced into this container so that above equilibrium is maintained at a total pressure of 2.25 atm. Vapour pressure of $Br_2(l)$ at 27°C is 0.25 atm. Assume that volume occupied by the liquid is negligible. ($R = 0.082$ L-atm/K-mol, Atomic mass of Br = 80)

14. In a 10.0 L container, an equilibrium was established between SO_3 , SO_2 and O_2 gases, by starting with SO_3 only. The density of equilibrium mixture was found to be

16 g/litre at a temperature of $\frac{900}{0.0821}$ K.

If the degree of dissociation of SO_3 is 40%, then the value of K_p (in atm) for the reaction: $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$, is

15. Equimolar mixture of two gases A_2 and B_2 is taken in a rigid vessel at constant temperature 300 K. The gases achieve equilibrium as:



If the initial pressure in the container was 2 atm and the final pressure at equilibrium is 2.75 atm in which the partial pressure of AB(g) is 0.5 atm, the value of $y:x$ is

Answer Keys – Exercise II

Section A (Only one Correct)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (a) | 2. (c) | 3. (c) | 4. (a) | 5. (c) | 6. (d) | 7. (b) | 8. (a) | 9. (d) | 10. (a) |
| 11. (a) | 12. (d) | 13. (a) | 14. (b) | 15. (a) | 16. (b) | 17. (b) | 18. (a) | 19. (d) | 20. (b) |
| 21. (b) | 22. (b) | 23. (d) | 24. (b) | 25. (b) | 26. (c) | 27. (a) | 28. (b) | 29. (b) | 30. (a) |
| 31. (a) | 32. (c) | 33. (b) | 34. (c) | 35. (d) | 36. (b) | 37. (a) | 38. (b) | 39. (c) | 40. (a) |

41. (a) 42. (d) 43. (b) 44. (a) 45. (c) 46. (d) 47. (d) 48. (a) 49. (b) 50. (a)
 51. (b) 52. (a) 53. (b) 54. (d) 55. (a) 56. (c) 57. (b) 58. (c) 59. (a) 60. (c)

Section B (One or More than one Correct)

- | | | | |
|-------------------|-------------------|------------------------|-------------------|
| 1. (a), (b), (c) | 2. (a), (b) | 3. (a), (b), (c) | 4. (a), (b) |
| 5. (a), (b), (d) | 6. (a), (b), (c) | 7. (d) | 8. (b), (c) |
| 9. (b), (c) | 10. (a), (b), (d) | 11. (a), (b) | 12. (a), (d) |
| 13. (b), (c) | 14. (a), (b) | 15. (d) | 16. (a), (b), (c) |
| 17. (a), (b), (c) | 18. (a), (b), (c) | 19. (a), (b), (c), (d) | 20. (a), (b) |
| 21. (b), (c) | 22. (a), (d) | 23. (c) | 24. (a), (c), (d) |
| 25. (c), (d) | | | |

Section C

Comprehension I

1. (c) 2. (d) 3. (c)

Comprehension II

4. (a) 5. (b) 6. (d)

Comprehension III

7. (b) 8. (b) 9. (d)

Comprehension IV

10. (b) 11. (a) 12. (c)

Comprehension V

13. (c) 14. (b) 15. (d) 16. (c)

Comprehension VI

17. (c) 18. (d) 19. (d)

Comprehension VII

20. (c) 21. (a) 22. (c)

Comprehension VIII

23. (a) 24. (d)

Section D (Assertion – Reason)

1. (d) 2. (b) 3. (b) 4. (a) 5. (a) 6. (a) 7. (a) 8. (a) 9. (a) 10. (c)

Section E (Column Match)

- $A \rightarrow S; B \rightarrow Q, R; C \rightarrow Q; D \rightarrow P$
- $A \rightarrow S; B \rightarrow R; C \rightarrow P; D \rightarrow Q$
- $A \rightarrow P, R; B \rightarrow S; C \rightarrow Q; D \rightarrow S$
- $A \rightarrow P, Q, S; B \rightarrow P, Q; C \rightarrow R$
- $A \rightarrow P, Q, R, S; B \rightarrow Q, R, S; C \rightarrow P, Q, R, S, T; D \rightarrow Q, R, S$
- $A \rightarrow S, T; B \rightarrow R; C \rightarrow Q; D \rightarrow P$
- $A \rightarrow P, S, T; B \rightarrow Q, R, S; C \rightarrow S; D \rightarrow Q, R, S$
- $A \rightarrow P, S, T; B \rightarrow Q, R; C \rightarrow Q, R; D \rightarrow Q, R, T$
- $A \rightarrow P, R; B \rightarrow Q, R; C \rightarrow Q, S$
- $A \rightarrow Q, R, S; B \rightarrow P, R, S; C \rightarrow P, R, S; D \rightarrow Q, R, S$

Section F (Subjective)**Single-digit Integer Type**

1. (2) 2. (4) 3. (7) 4. (1) 5. (2) 6. (4) 7. (5) 8. (5) 9. (1) 10. (4)
11. (6) 12. (4) 13. (4) 14. (1) 15. (1)

Four-digit Integer Type

1. (0480) 2. (0015) 3. (0600) 4. (1784) 5. (0180)
6. (0532) 7. (0032) 8. (0032) 9. (0170) 10. (0018)
11. (2400) 12. (0250) 13. (0800) 14. (0016) 15. (0008)
-