CHEMICAL EQUILIBRIUM [JEE ADVANCE PREVIOUS YEAR SOLVED PAPER]

JEE Advanced

Single Correct Answer Type

1. The oxidation of SO_2 by O_2 to SO_3 is an exothermic reaction. The yield of SO_3 will be maximum if

a. temperature is increased and pressure is kept constant
b. temperature is reduced and pressure is increased
c. both temperature and pressure are increased
d. both temperature and pressure are reduced

(IIT-JEE 1981)

2. For the reaction:

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

The equilibrium constant K_p changes with

a. total pressure
b. catalyst
c. the amounts of H_2 and I_2 present
d. temperature

(IIT-JEE 1981)

3. A liquid is in equilibrium with its vapour at its boiling point. On the average, the molecules in the two phases have equal

a. inter-molecular forces **b.** potential energy
c. total energy **d.** kinetic energy

(IIT-JEE 1984)

4. Pure ammonia is placed in a vessel at a temperature where its dissociation constant (α) is appreciable. At equilibrium:

a. K_p does not change significantly with pressure
b. α does not change with pressure
c. concentration of NH_3 does not change with pressure
d. concentration of hydrogen is less than that of nitrogen

(IIT-JEE 1984)

5. An example of a reversible reaction is

a. $Pb(NO_3)_2(aq) + 2NaI(aq) \rightarrow PbI_2(s) + 2NaNO_3(aq)$
b. $AgNO_3(aq) + HCl(aq) \rightarrow AgCl(s) + HNO_3(aq)$
c. $2Na(s) + H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$
d. $KNO_3(aq) + NaCl(aq) \rightarrow KCl(aq) + NaNO_3(aq)$

(IIT-JEE 1985)

6. The reaction which proceeds in the forward direction is

a. $Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$
b. $NH_3 + H_2O + NaCl \rightarrow NH_4Cl + NaOH$
c. $SnCl_4 + Hg_2Cl_2 \rightarrow SnCl_2 + 2HgCl_2$
d. $2CuI + I_2 + 4K^+ \rightarrow 2Cu^{2+} + 4KI$ **(IIT-JEE 1991)**

7. One mole of $N_2O_4(g)$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of $N_2O_4(g)$ decomposes to $NO_2(g)$. The resultant pressure is

a. 1.2 atm **b.** 2.4 atm **c.** 2.0 atm **d.** 1.0 atm

(IIT-JEE 1996)

8. For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$ the amount of X_3Y at equilibrium is affected by

a. temperature and pressure
b. temperature only
c. pressure only
d. temperature, pressure, and catalyst **(IIT-JEE 1999)**

9. For the reversible reaction.

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

at 500°C, the value of K_p is 1.44×10^{-5} when the partial pressure is measured in atmosphere. The corresponding value of K_c with concentration in mol/L is

a. $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$ **b.** $\dfrac{1.44 \times 10^{-5}}{(9.314 \times 773)^{-2}}$

c. $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^{2}}$ **d.** $K_c = \dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$

(IIT-JEE 2000)

10. 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

a. is zero **b.** decreases with time
c. is independent of time **d.** increases with time

(IIT-JEE 2000)

11. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction, $N_2O_4 \rightleftharpoons 2NO_2$, is expressed by $K_p = \dfrac{(4x^2P)}{(1-x)}$, where P = pressure and x = extent of decomposition. Which of the following statements is true?

a. K_p increases with increase in P
b. K_p increases with increase in x
c. K_p increases with decrease in x
d. K_p remains constant with change in P and x

(IIT-JEE 2001)

12. The set with correct order of acidity is

a. $HClO < HClO_2 < HClO_3 < HClO_4$
b. $HClO_4 < HClO_3 < HClO_2 < HClO$
c. $HClO < HClO_4 < HClO_3 < HClO_2$
d. $HClO_4 < HClO_2 < HClO_3 < HClO$ **(IIT-JEE 2001)**

13. Consider the following equilibrium in a closed container

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

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

a. Neither K_p nor α changes
b. Both K_p and α change
c. K_p changes but α does not change
d. K_p does not change but α changes **(IIT-JEE 2002)**

14. The Haber's process for the formation of NH_3 at 298 K is $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta H = -46.0$ kJ. Which of the following is the correct statement

a. The condition for equilibrium is

$$G_{N_2} + 3G_{H_2} = 2G_{NH_3}$$

where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure.

b. On adding N_2, the equilibrium will shift to forward direction because according to IInd law of thermodynamics the entropy must increase in the direction of spontaneous reaction

c. The catalyst will increase the rate of forward reaction by 2 times and that of backward reaction by 1.5 times

d. None of these **(IIT-JEE 2006)**

Multiple Correct Answers Type

1. For the gas phase reaction

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6 \qquad (\Delta H = -32.7 \text{ kcal})$$

carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by

a. increasing the temperature
b. decreasing the pressure
c. removing some H_2
d. adding some C_2H_6 **(IIT-JEE 1984)**

2. When $NaNO_3$ is heated in a closed vessel oxygen is liberated and $NaNO_2$ is left behind. At equilibrium:
   a. addition of $NaNO_2$ favours reverse reaction
   b. addition of $NaNO_3$ favours forward reaction
   c. increasing temperature favours forward reaction
   d. increasing pressure favours reverse reaction
(IIT-JEE 1986)

3. The equilibrium $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is attained at 25°C in a closed container and an inert gas, helium is introduced. Which of the following statements is/are correct?
   a. Concentrations of SO_2, Cl_2, and SO_2Cl_2 change
   b. More chlorine is formed
   c. Concentration of SO_2 is reduced
   d. All are incorrect **(IIT-JEE 1989)**

4. For the reaction

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

The forward reaction at constant temperature is favoured by
   a. introducing an inert gas at constant volume
   b. introducing chlorine gas at constant volume
   c. introducing an inert gas at constant pressure
   d. increasing the volume of the container
   e. introducing PCl_5 at constant volume
(IIT-JEE 1991)

5. For the reaction:

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

At a given temperature, the equilibrium amount of $CO_2(g)$ can be increased by
   a. adding a suitable catalyst
   b. adding an inert gas
   c. decreasing the volume of the container
   d. increasing the amount of CO(g) **(IIT-JEE 1998)**

6. The equilibrium

$$2Cu^{I} \rightleftharpoons Cu^{0} + Cu^{II}$$

in aqueous medium at 25°C shifts towards the left in the presence of

a. $NO_3^{\ominus}$ **b.** $Cl^{\ominus}$ **c.** $SCN^{\ominus}$ **d.** $CN^{\ominus}$
(IIT-JEE 2011)

7. The thermal dissociation equilibrium of $CaCO_3(s)$ is studied under different conditions $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. For this equilibrium, the correct statement(s) is(are)
   a. ΔH is dependent on T
   b. K is independent of the initial amount of $CaCO_3$
   c. K is dependent on the pressure of CO_2 at a given T
   d. ΔH is independent of the catalyst, if any
(JEE Advanced 2013)

Assertion-Reasoning Type

Each question contains Statement 1 (Assertion) and Statement 2 (Reason). Each question has 4 choices (a), (b), (c) and (d) out of which only one is correct. Mark your answer as

a. If both Statement 1 and Statement 2 are correct, and Statement 2 is the correct explanation of Statement 2.
b. If both Statement 1 and Statement 2 are correct, but Statement 2 is not the correct explanation of Statement 1.
c. If Statement 1 is correct but Statement 2 is incorrect.
d. If Statement 1 is incorrect but Statement 2 is correct.

1. **Statement 1:** The endothermic reactions are favoured at lower temperature and the exothermic reactions are favoured at higher temperature.
   Statement 2: When a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect on change. **(IIT-JEE 1991)**
2. **Statement 1:** For every chemical reaction at temperature, standard Gibbs energy of reaction is zero.
   Statement 2: At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. **(IIT-JEE 2008)**

Fill in the Blanks Type

1. For a given reversible reaction at a fixed temperature, equilibrium constants K_p and K_c are related by ______ . **(IIT-JEE 1994)**
2. A ten-fold increase in pressure on the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at equilibrium, results in ______ in K_p. **(IIT-JEE 1996)**
3. For a gaseous reaction $2B \rightarrow A$, the equilibrium constant K_p is ______ to/than K_c. **(IIT-JEE 1997)**

True / False Type

1. When a liquid and its vapour are at equilibrium and the pressure is suddenly decreased, cooling occurs. **(IIT-JEE 1984)**
2. If the equilibrium constant for the reaction

$$A_2 + B_2 \rightleftharpoons 2AB$$

is K, then the backward reaction,

$$AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$$

the equilibrium constant is $1/K$. **(IIT-JEE 1984)**

3. A catalyst makes a reaction more exothermic. **(IIT-JEE 1987)**
4. The rate of an exothermic reaction increases with increasing temperature. **(IIT-JEE 1993)**

Subjective Type

1. One mole of nitrogen is mixed with three moles of hydrogen in a 4 litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction

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

calculate the equilibrium constant (K_c) in concentration units. What will be the value of K_c for the following equilibrium?

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g) \quad \textbf{(IIT-JEE 1981)}$$

2. One mole of Cl_2 and 3 moles of PCl_5 are placed in a 100 L vessel heated to 227°C. The equilibrium pressure is 2.05 atmospheres. Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and K_p for the reaction,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \quad \textbf{(IIT-JEE 1984)}$$

3. The equilibrium constant of the reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ at 100°C is 50. If a one litre flask containing 1 mole of A_2 is connected to a two litre flask containing two moles of B_2, how many moles of AB will be formed at 373 K? **(IIT-JEE 1985)**

4. At a certain temperature, equilibrium constant (K_c) is 16 for the reaction:

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

If we take one mol of each of all the four gases in a one litre container, what would be the equilibrium concentrations of NO and NO_2? **(IIT-JEE 1987)**

5. N_2O_4 is 25% dissociated at 37°C and one atmosphere pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atmosphere and 37°C. **(IIT-JEE 1988)**

6. The equilibrium constant K_p of the reaction,

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

is 900 atm at 800 K. A mixture containing SO_3 and O_2 having initial pressure of 1 and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K. **(IIT-JEE 1989)**

7. For the reaction,

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

hydrogen gas is introduced into a five litre flask at 327°C, containing 0.2 mol of CO(g) and a catalyst, until the pressure is 4.92 atm. At point, 0.1 mol of $CH_3OH(g)$ is formed. Calculate the equilibrium constants K_p and K_c. **(IIT-JEE 1990)**

8. 0.15 moles of CO taken in a 2.5 L flask is maintained at 750 K along with a catalyst so that the following reaction can take place:

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

Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 moles of methanol is formed. Calculate (i) K_p and K_c and (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place. **(IIT-JEE 1993)**

9. At temperature T, a compound $AB_2(g)$ dissociates according to the reaction

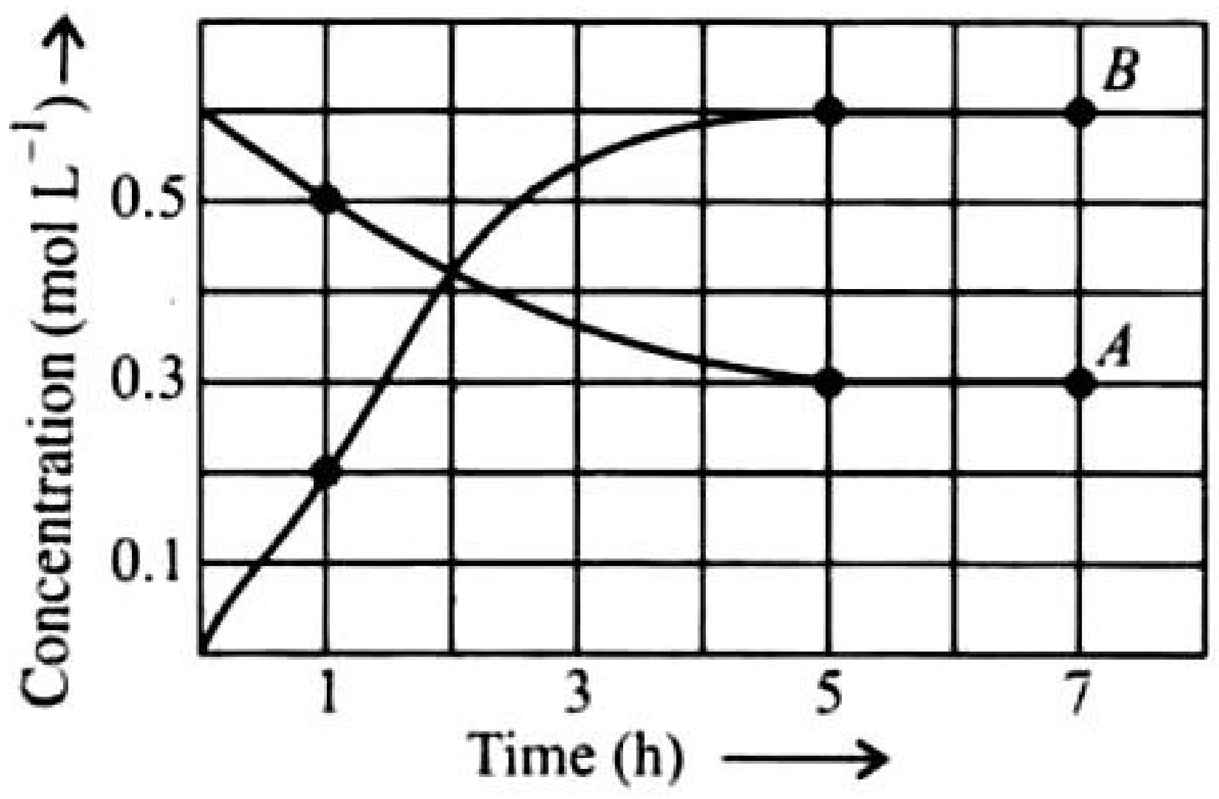
$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

with a degree of dissociation x which is small compared with unity. Deduce the expression for x in terms of the equilibrium constant K_p and the total pressure, P. **(IIT-JEE 1994)**

10. The progress of reaction

$$A \rightleftharpoons nB$$

with time, is presented in the figure given below.



Determine

a. The value of n.

b. The equilibrium constant K.

c. The initial rate of conversion of A. **(IIT-JEE 1994)**

11. A sample of air consisting of N_2 and O_2 was heated to 2500 K until the equilibrium

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

was established with an equilibrium constant, $K_c = 2.1 \times 10^{-3}$. At equilibrium, the mole% of NO was 1.8. Estimate the initial composition of air in mole fraction of N_2 and O_2. **(IIT-JEE 1997)**

12. The degree of dissociation is 0.4 at 400 K and 1.0 atm for the gaseous reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Assuming ideal behaviour of all the gases, calculate the density of equilibrium mixture at 400 K and 1.0 atmosphere (relative atomic mass of P is 31.0 and Cl is 35.5). **(IIT-JEE 1998)**

13. When 3.06 g of solid NH_4HS is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.

i. Calculate K_c and K_p for the reaction at 27°C.

ii. What would happen to the equilibrium when more solid NH_4HS is introduced into the flask? **(IIT-JEE 1999)**

14. a. In the following equilibrium

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

when 5 moles of each is taken, the temperature is kept at 298 K, the total pressure was found to be 20 bar. Given that

$$\Delta G_f^\circ(N_2O_4) = 100 \text{ kJ}$$

$$\Delta G_f^\circ \, NO_2 = 50 \text{ kJ}$$

i. Find ΔG of the reaction.

ii. The direction of the reaction in which the equilibrium shifts.

b. A graph is plotted for a real gas which follows van der Waals equation with PV_m taken on Y-axis and p on X-axis. Find the intercept of the line where V_m is molar volume. **(IIT-JEE 2004)**

Answer Key

JEE Advanced

Single Correct Answer Type

1. b. **2.** d. **3.** c. **4.** a. **5.** d.
6. a. **7.** b. **8.** a. **9.** d. **10.** d.
11. d. **12.** a. **13.** d. **14.** a.

True/False Type

1. True **2.** False **3.** False **4.** False

Multiple Correct Answers Type

1. a., b., c., d. **2.** c., d. **3.** d. **4.** c., d., e.
5. d. **6.** b., c., d. **7.** a., b., d.

Assertion–Reasoning Type

1. d. **2.** d.

Fill in the Blanks Type

1. $K_p = K_c(RT)^{\Delta n_g}$ **2.** no change **3.** less

Hints and Solutions

JEE Advanced

Single Correct Answer Type

1. b. **i.** According is Le-Chatelier's principle, exothermic reactions are favoured at low temperature.

ii. According to Le-Chatelier's principle, the reactions in which $n < 0$, are favoured at high pressure.

Given $2SO_2 + O_2 \rightleftharpoons 2SO_3$ + Heat

$\because$ It is an exothermic reaction

$\therefore$ Yield of SO_3 is maximum at low temperature

$n = 2 - 3 = -1$ or $n < 0$

Yield of SO_3 maximum at high pressure.

2. d Only temperature affects the equilibrium constant.

3. c. Vapours and liquid are at the same temperature.

4. a. At equilibrium, K_p does not change significantly with pressure. K_p only changes with temperature.

5. d. The reaction,

$$KNO_3(aq) + NaCl(aq) = KCl(aq) + NaNO_3(aq)$$

As none of the reactants or products is solid. Hence it is a reversible reaction.

6. a. Due to absence of hydrolysation of $FeCl_3$ backward reaction will not take place.

7. b.

$$\begin{array}{ccc} N_2O_4 & \rightleftharpoons & 2NO_2 \\ 1 & & 0 \\ (1-0.2) & & 2\times 0.2 = 0.4 \end{array}$$

Total pressure = 1.2

As the temperature is doubled, the pressure becomes double. Therefore, the total final pressure is $1.2 \times 2 = 2.4$ atm.

8. a. Equilibrium is affected by temperature and pressure due to change in heat as well as change in volume of substances (Le-Chatelier's principle).

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

Δn_g = No. of gaseous moles of right side – No. of gaseous moles of left side.

$$\Delta n_g = 2 - 4 = -2$$

As we know that

$$K_p = K_c(RT)^{\Delta n}$$

or $1.44 \times 10^{-5} = K_c \times (0.0821 \times 773)^{-2}$

or $K_c = \dfrac{1.44\times10^{-5}}{(0.0821\times773)^{-2}}(\text{mol/L}^{-2})$

10. d. Reaction quotient is equal to the ratio of the concentration of products to the ratio of the concentration of the reactants at any stage of the reaction, each concentration term being raised to the power of its stoichiometric coefficient. In the beginning of the reaction, $Q = 0$.

11. d. K_p is not based upon pressure and concentration.

12. a. **i.** For oxyacids containing similar central atom, the acid strength increases with the increase in the number of oxygen atom attached to the central atom and not attached to any other atom.

ii. Higher the oxidation number of the central atom, higher is the acidity of the species. Thus acidity follows the order:

Oxidation number of Cl $\underset{+1}{HClO} < \underset{+3}{HClO_2} < \underset{+5}{HClO_3} < \underset{+7}{HClO_4}$

13. d. For equilibrium

$$\begin{array}{llcl} & N_2O_4(s) & \rightleftharpoons & 2NO_2(g) \\ \text{At equilibrium} & (1-\alpha)\text{mole} & & 2\alpha\text{ mole} \\ \text{Total mole} & =1-\alpha+2\alpha=1+\alpha & & \end{array}$$

If P is total pressure at equilibrium therefore

$$P_{N_2O_4} = \frac{1-\alpha}{1+\alpha} \times P \quad \text{and} \quad P_{NO_2} = \frac{2\alpha}{1-\alpha} \times P$$

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_2}} = \frac{4\alpha^2 \times P}{(1-\alpha)(1+\alpha)} = \frac{4\alpha^2 P}{1-\alpha^2}$$

If volume is halved, therefore pressure is doubled but the value of K_p is not effected by pressure. Thus at higher P. K_p will be higher, but it is constant so for maintaining the constant value of K_p, α will be lowered. Hence K_p does not change, but α changes.

14. a. In a reversible reaction, a catalyst speeds up both the forward and backward reactions to the same extent, so (c) is wrong. At equilibrium,

$$\Delta G = G_{\text{products}} - G_{\text{reactants}} = 0$$

$$\Rightarrow \quad 2G_{NH_3} - (G_{N_2} + 3G_{H_2}) = 0 \quad \text{or} \quad 2G_{NH_3} = G_{N_2} + 3G_{H_2}$$

Multiple Correct Answers Type

1. a., b., c., d.

Applying Le-Chatelier's principle, when the temperature is increased, the equilibrium shifts in the direaction of less number of moles. The removal of a reactant and addition of a product shift the equilibrium in the backward direction.

2. c., d.

$$2NaNO_3(g) \rightleftharpoons 2NaNO_2(g) + O_2(g)$$

$$\Delta H = \text{positive, endothermic}$$

Addition of solids does not affect the equilibrium.
Endothermic reaction is favoured by increase in temperature.
Increased pressure shifts the equilibrium in the direaction of less gaseous moles.

3. d.

At constant volume, there is no effect on addition of inert gas to a reaction in equilibrium. At constant pressure, for the reactions for which $\Delta n = 0$. there is no effect on addition of inert gas to a reaction in equilibrium. At constant pressure, for the reactions for which $\Delta n \neq 0$, the equilibrium shifts in the direction of more number of moles.

4. c., d., e.

At constant volume, There is no effect on addition of inert gas to a reaction in equilibrium. At constant pressure, for the reactions for which $\Delta n = 0$, there is no effect on addition of inert gas to a reaction in equilibrium. At constant pressure, for the reactions for which $\Delta n \neq 0$, the equilibrium shifts in the direction of more number of moles. Addition of the reactant favours forward reaction. Increasing the volume means decreasing the pressure, which shifts the reaction in the direction of more number of gaseous moles.

5. d.

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

At constant volume, there is no effect on addition of inert gas to a reaction in equilibrium.
At constant pressure, for the reactions for which $\Delta n_g = 0$, there is no effect on addition of inert gas to a reaction in equilibrium. The presence of a catalyst just helps to achieve the equilibrium at a different pace. It does not affect the amount of a reactant or a product at equilibrium.
Only if the reactant concentration is increased, the equilibrium shifts forward and the product concentration is increased.

6. b., c., d.

$$2Cu^{I} \rightleftharpoons Cu^{0} + Cu^{II}$$

$Cl^{\ominus}$ and $CN^{\ominus}$ both make precipitate with Cu^{I} and hence drive the reaction to the left.
Cupric thicyanate $Cu(SCN)_2$, black powder, insoluble in water, readily turning into cuprous thiocyanate Cu(SCN) a whitish yellow powder, hence it also drives the equilibrium to the left.

7. a., b., d.

a. $\Delta H = C_{P(rxn)}\, \Delta T$
Hence enthalpy depends on temperature.

b. $CaCO_{3(g)} \rightleftharpoons CaO_{(s)} + CO_{2(g)} \qquad K_p = P_{CO_2}$

c. K_{eq} depends only on temperature and not on pressure.

d. Enthalpy of reaction is independent of the catalyst. A catalyst generally lowers activation energy.

Assertion-Reasoning Type

1. d. Statement 1 is clearly wrong in context with Le-Chatelier's principle, which states that "increase in temperature shifts the equilibrium in the forward direction of those reactions which proceed with absorption of heat (endothermic reactions), and in the backward direction of those reactions which proceed with the evolution of heat (exothermic reactions)." Statement 2 is clearly true again according to Le-Chatelier's principle.

2. d. We know that for every chemical reaction at equilibrium, Gibb's free energy ($\Delta G = 0$) is zero. However standard Gibb's free energy (ΔG°) may or may not be zero . Thus Statement 1 is false.
For a spontaneous reaction, at constant temperature and pressure, the reaction proceeds in the direction in which ΔG is < 0 i.e., in the direction of decreasing Gibb's energy (G) so the Statement 2 is true.
Thus, the only such option is (d) which is correct answer.

Fill in the Blanks Type

1. $K_p = K_c(RT)^{\Delta n_g}$
where Δn = No. of moles of gaseous products – No. of mole of gaseous reactants
R = Gas constant
T = Absolute temperature

2. No change. K_p doesn't get changed by 'p',
For reversible reaction

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

$$K_p = \frac{(2x^2)(a+b-2x)^2}{(a-x)(b-3x)^3 \times P^2},$$

where a and b are the moles of N_2 and H_2 at $t = 0$. x is the change in mole of N_2 into NH_3 and P is total pressure at equilibrium. On increasing in pressure on the reaction in equilibrium results in no change in K_p.

3. Less

$$K_p = K_c(RT)^{\Delta n_g}$$

For given reaction,

$$\Delta n_g = 1 - 2 = -1$$

$$\therefore \quad K_p = K_c(RT)^{-1} \quad \text{or} \quad K_p < K_c$$

True / False Type

1. **True:**

When the pressure is decreased, the boiling point decreases. Therefore, cooling occurs because evaporation is endothermic and cooling is caused.

2. **False:**

For, $A_2 + B_2 \rightleftharpoons 2AB$

If equation is reversed equilibrium constant reciprocal

If equation is divided by equilibrium constant $n\sqrt{K}$

$$K = \frac{[AB]^2}{[A_2][B_2]}$$

For $\quad AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$

$$K' = \frac{[A_2]^{1/2}[B_2]^{1/2}}{[AB]}$$

$\therefore \quad K' = \sqrt{\frac{1}{K}}$

3. **False:**

Catalyst does not make a reaction more exothermic. It only helps to achieve equilibrium at a different pace.

4. **False:**

The rate of an exothermic reaction decreases with increasing temperature. For endothermic reaction, the value of K increases with increase in temperature and vice versa. For exothermic, the value of K decreases with increase in temperature and vice versa.

Subjective Type

1.

Initial moles	$N_2(g)$ ·	$3H_2(g)$ →	$2NH_3(g)$
Eq. moles	$1 - 0.0025$	$3 - 0.0075$	2×0.0025
Eq. conc.	$\frac{1-0.0025}{4}$	$\frac{3-0.0075}{4}$	$\frac{2\times 0.0025}{4}$

Now we know that $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

Since 0.0025 and 0.0075 are very small, $1 - 0.0025$ and $3 - 0.0075$ may be taken as 1 and 3 respectively.

Substitute the various values

$$K_c = \frac{\left(\frac{2\times 0.0025}{4}\right)^2}{\left[\frac{1}{4}\right]\left[\frac{3}{4}\right]^3} = \frac{0.0025 \times 0.0025}{4} \times \frac{4\times4\times4\times4}{3\times3\times3}$$

$$= 1.48 \times 10^{-5}\,\text{litre}^2\text{mol}^{-2}$$

For the equilibrium,

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

$$K_c' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = \sqrt{K_c} = \sqrt{(1.48\times 10^{-5}\,\text{litre}^2\,\text{mol}^{-2})}$$

$$= 3.82 \times 10^{-3}\,\text{litre mol}^{-1}$$

2.

	PCl_5 ⇌	PCl_3 +	Cl_2
Moles at $t = 0$	3	0	1
Moles at equilibrium	$(3 - x)$	x	$x + 1$

$\therefore$ Total moles present at equilibrium $= 4 + x$

Given, total pressure at equilibrium = 2.05 atm

Now, $PV = nRT$ at equilibrium

$2.05 \times 100 = (4 + x) \times 0.0821 \times 500$

$\therefore \quad x = 0.9939$

Now the degree of dissociation for

$$PCl_5 = \frac{\text{Moles dissociated}}{\text{Total moles}} = \frac{0.9939}{3} = 0.313 \text{ or } 33.13\%$$

$$\therefore \quad K_p = \left[\frac{n_{PCl_3} \times n_{Cl_2}}{n_{PCl_5}}\right] \times \left[\frac{P}{\Sigma n}\right]^{+1} = \frac{x^2}{(3-x)} \times \left[\frac{2.05}{4+x}\right]$$

$$= \frac{(0.9939)^2}{(3-0.9939)} \times \left[\frac{2.05}{4+0.9939}\right] = 0.20$$

3.

	A_2g +	B_2g ⇌	$2AB(g)$
At $t = 0$	1	2	0
At equilibrium	$(1 - x)$	$(2 - x)$	$2x$

Total volume of both containers on joining becomes 3 L.

$\therefore \quad$ At equilibrium, $[A_2] = \frac{1-x}{3}$, $[B_2] = \frac{(2-x)}{3}$, $[AB] = \frac{2x}{3}$

$$\therefore \quad K_c = \frac{[AB]^2}{[A_2][B_2]} = \frac{4x^2}{9\left(\frac{1-x}{3}\right)\left(\frac{2-x}{3}\right)} = \frac{4x^2}{2 - 3x + x^2} = 50$$

$\therefore \quad 4x^2 = 100 - 150x + 50x^2 \quad$ or $\quad 46x^2 - 150x + 100 = 0$

or $\quad x = 0.93$ and 2.326 which is not valid since $x \times 2$

$\therefore \quad$ moles of $AB = 2x = 2 \times 0.93 = 1.86$

4.

	$SO_2(g)$ +	$NO_2(g)$ ⇌	$SO_3(g)$ +	$NO(g)$
At $t = 0$	1	1	1	1
At equilibrium	$(1 - x)$	$(1 - x)$	$(1 + x)$	$(1 + x)$

Let the total volume of the mixture is V litre.

$$\therefore \quad K_c = \frac{\left(\frac{1+x}{V}\right)\left(\frac{1+x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)} = \left(\frac{(1+x)^2}{(1-x)^2}\right)$$

$\therefore \quad \frac{(1+x)^2}{(1-x)^2} = 16 \quad (\because$ Given, $K_c = 16)$

$\therefore \quad \frac{(1+x)}{(1-x)} = 4 \quad$ or $\quad x = \frac{3}{5} = 0.6$

$\because \quad$ Volume = 1 L

$\therefore \quad [SO_2] = [NO_2] = 1 - x = 1 - 0.6 = 0.4$ mol/L

and $\quad [SO_3] = [NO] = 1 + x = 1 + 0.6 = 1.6$ mol/L

5.

	N_2O_4 ⇌	$2NO_2$
Before dissociation	1	0
After dissociation	$1 - a$	$2a$

Total moles after dissociation $(\Sigma n) = 1 - \alpha + 2\alpha = (1 - \alpha)$ where α is the degree of dissociation.

$$\therefore \quad K_p = \frac{(n_{NO_2})^2}{(n_{N_2O_4})} \times \left(\frac{P}{\Sigma n}\right)^{\Delta n} = \frac{(2\alpha)^2}{(1-\alpha)}\left[\frac{p}{1+\alpha}\right]^1$$

or $\quad K_p = \frac{4\alpha^2 P}{1-\alpha^2}$

$$\therefore \quad K_p = \frac{4(0.25)^2 \times 1}{1-(0.25)^2} \quad (\because \alpha = 25\%, \text{given} = 0.25)$$

$$= \frac{0.25}{0.9375} = 0.267$$

Again at 0.1 atm

$$K_p = \frac{4\alpha^2 P}{1-\alpha^2}$$

$$\alpha = \pm 0.65 \text{ or } 65\%$$

6. Consider the reaction,

$$\begin{array}{llll} & 2SO_3 \rightleftharpoons & 2SO_2 + & O_2, \quad K' = \frac{1}{K_p} = \frac{1}{900}\text{atm} \\ \text{Initial pressure} & 1 & 0 & 2 \\ \text{At equilibrium} & (1-x) & x & \left(2+\frac{x}{2}\right) \end{array}$$

$$\therefore \quad K' = \frac{(P'_{SO_2})^2 (P'_{O_2})^2}{(P'_{SO_3})^2}$$

$$\therefore \quad \frac{1}{900} = \frac{x^2\left(2+\frac{x}{2}\right)}{(1-x)^2}$$

$\therefore$ Since K_p of this reaction is small and thus $x < 1$.

$$\therefore \quad \frac{1}{900} = \frac{x^2(2)}{(1-x)^2} \quad \left(\because 2+\frac{x}{2} \approx 2\right)$$

$$= \frac{2x^2}{(1-x)^2}$$

$$\therefore \quad \frac{1}{30} = \frac{\sqrt{2}x}{(1-x)}$$

$\therefore \quad x = 0.0236$

$\therefore$ At equilibrium

$p'_{SO_3} = 1 - x = 1 - 0.0236 = 0.9764$ atm

$p'_{SO_2} = x = 0.0236$ atm

$p'_{O_2} = 2 + (x/2) = 2.0118$ atm

7. Let the number of moles of hydrogen introduced be n moles.

Total moles of CO and hydrogen $= 0.2 + n$

Applying, $PV = nRT$

$P = 4.92$ atm, $V = 5$, $R = 0.082$

$T = (273 + 327) = 600$ K

$4.92 \times 5 = 0.082 \times 600 \times (0.2 + n)$

$$\Rightarrow \quad 0.2 + n = \frac{4.92 \times 5}{0.082 \times 600}$$

$\Rightarrow \quad n = 0.3$ mol

$$\begin{array}{llll} & CO(g) + & 2H_2(g) \rightleftharpoons & CH_3OH(g) \\ \text{At equilibrium} & 0.2 - x & 0.3 - 2x & x \\ \text{or} & 0.2 - 0.1 & 0.3 - 0.2 & 0.1 \\ \text{or} & 0.1 & 0.1 & 0.1 \end{array}$$

$$\therefore \quad [CO] = \frac{0.1}{5}; [H_2] = \frac{0.1}{5}; [CH_3OH] = \frac{0.1}{5} \text{ (Active masses}$$

Applying the law of mass action

$$K_c = \frac{[CH_3OH]}{[CO]H_2]^2} = \frac{\frac{0.1}{5}}{\frac{0.1}{5} \times \left(\frac{0.1}{5}\right)^2} = 2500 \text{ mol}^{-2}\text{ L}^2$$

We know that $K_p = K_c(RT)^{\Delta n}$, $\Delta n = -2$

$\therefore \quad K_p = 2500\,(0.082 \times 600)^{-2}$

$$K_p = \frac{2500}{(49.2)^2} = 1.0327 \text{ atm}^{-2}$$

8. $PV = nRT$ (for gas)

Given that $P = 8.5$ atm. $\quad V = 2.5$ L, $\quad T = 750$ K,

$R = 0.0821$ L-atm/K/mol

$$\therefore \quad \text{moles } (n) = \frac{PV}{RT} = \frac{8.5 \times 2.5}{0.0821 \times 750} = 0.3451$$

Total moles at equilibrium = 0.3451

$$\begin{array}{llll} & CO(g) & + \; 2H_2(g) \rightleftharpoons & CH_3OH(g) \\ \text{At } t = 0 & 0.15 \text{ mole} & a \text{ moles} & 0 \\ \text{At equilibrium} & (0.15 - 0.08) \text{ mole} & (a - 0.16) \text{ mole} & 0.08 \text{ mole} \\ & = 0.077 \text{ mole} & & \end{array}$$

Total moles at equilibrium

$= 0.07 + (a - 0.16) + 0.08 = 0.3451$

So $\quad a = 0.3555$ mole

Moles of hydrogen at equilibrium $= (0.3555 - 0.1600) = 0.1955$

At equilibrium,

$$[CO] = \frac{0.07}{2.5} \text{ mol/L}$$

$$[H_2] = \frac{0.1955}{2.5} \text{ mol/L}$$

$$[CH_3OH] = \frac{0.08}{2.5} \text{ mol/L}$$

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{0.08/2.5}{\frac{0.07}{2.5} \times \left(\frac{0.1955}{2.5}\right)^2} = 186.88 \text{ L}^2 \text{ mol}^{-2}$$

$\therefore \quad K_p = K_c \times (RT)^{\Delta n}$

$\therefore \quad \Delta n$ for above reaction $= 1 - (1 + 2) = -2$

$\therefore \quad K_p = 186.88 \times (0.0821 \times 750)^{-2} = 0.0494$ atm^{-2}

Initially moles of CO = 0.15

Moles of $H_2 = 0.3555$

Total moles $= 0.15 + 0.3555 = 0.5055$

$PV = RT$

$$P = \frac{n}{V} \times RT = \frac{0.5055}{2.5} \times 0.0821 \times 750 \text{ atm} = 12.45 \text{ atm}$$

9.

$$\begin{array}{llll} & 2AB_2(g) \rightleftharpoons & 2AB(g) + & B_2(g) \\ \text{Initial mole} & 1 & 0 & 0 \\ \text{Mole at equb.} & 1 - x & x & \frac{x}{2} \end{array}$$

$$\text{Total moles at equilibrium} = 1 - x + x + \frac{x}{2} = 1 + \frac{x}{2} = \frac{2+x}{2}$$

$$p_{AB_2} = \frac{(1-x)}{2 + x/2}P = \frac{2(1-x)}{2+x}P$$

$$p_{AB} = \frac{x}{2 + x/2}P = \frac{2x}{2+x}P$$

$$p_{B_2} = \frac{x/2}{2 + x/2}P = \frac{x}{2+x}P$$

$$\therefore \quad K_p = \frac{(p_{AB})^2\,(p_{B_2})}{(p_{AB_2})^2} = \frac{\left(\frac{2x}{2+x}P\right)^2\left(\frac{x}{2+x}P\right)}{\left[\frac{2(1-x)}{(2+x)}P\right]^2}$$

$$= \frac{x^3 P}{(2+x)(1-x)^2}$$

$$K_p \approx \frac{x^3}{2}P \quad \text{or} \quad x = \left[\frac{2K_p}{P}\right]^{1/3}.$$

10. **i.** $A \rightleftharpoons nB$

From the graph, it is clear that in 4 h, decrease in concentration of $A = 0.2$ mol L^{-1}, increase in concentration of $B = 0.4$ mol L^{-1}, increase in concentration of B is double as compared to decrease in concentration of A.

Therefore, $n = 2$.

ii. $A \rightleftharpoons 2B$

At equilibrium,

$[A] = 0.3$

At equilibrium,

$[B] = 0.6$

$$K_c = \frac{[B]^2}{[A]} = \frac{(0.6)^2}{0.3} = 1.2 \text{ mol/L}$$

iii. For the first half hours, change in concentration of A is $0.6 - 0.5 = 0.1$ mol L^{-1}.

$$\frac{\Delta[A]}{\Delta t} = \frac{0.1}{1} = 0.1 \text{ mol } L^{-1} \text{ hr}^{-1}$$

11. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

Let the total number of moles of N_2 and O_2 at start = 100 and number of moles of N_2 at start = a

Further let the number of moles of NO present at equilibrium = x

	$N_2(g)$	+ $O_2(g)$	$\rightleftharpoons$ $2NO(g)$
At start	a	$100-a$	0
At equb.	$(a-x)$	$(100-a-x)$	$2x$

Given $\frac{2x}{100} = \frac{1.8}{100}$ $\therefore x = 0.9$

Substituting the values in the relation

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

$$2.1 \times 10^{-3} = \frac{(2x)^2}{(a-x)(100-a-x)} = \frac{(2 \times 0.9)^2}{(a-0.9)(100-a-0.9)}$$

On usual calculation, $a = 79$

% of N_2 air = 79%

% of O_2 in air = 100 − 79 = 21%.

12.

	$PCl_5(g)$	$\rightleftharpoons$ $PCl_3(g)$	+ $Cl_2(g)$
At $t = 0$	1	0	0
At equilibrium	$(1-0.4)$	0.4	0.4

Total moles at equilibrium = 1 − 0.4 + 0.4 + 0.4 = 1.4

$PV = nRT$

$1 \times V = 1.4 \times 0.0821 \times 400$

$$\therefore \quad V = \frac{1.4 \times 0.0821 \times 400}{1} = 45.976 \text{ L}$$

Thus, the density of equilibrium mixture $= \frac{208.5}{45.976}$ g/L = 4.54 g/L

13. **i.** Weight of $NH_4HS = 3.06$ g

$$\therefore \quad \text{Mole of } NH_4HS = \frac{3.06}{\text{mol. wt.}} = \frac{3.06}{51} = 0.06$$

	$NH_4HS_{(S)}$	$\rightleftharpoons$ $H_2S_{(g)}$ +	$NH_3(g)$
At $t = 0$	0.06 mole	0	0
At equilibrium (on 30% decomposition)	(0.06–0.018) mole	0.018 mole	0.018 mole

At equilibrium

$$[H_2S] = \frac{0.018}{2} = 0.009 \text{ mol/L}$$

$$[NH_3] = \frac{0.018}{2} = 0.009 \text{ mol/L} \quad (\therefore \text{Volume of flask is 2 L})$$

$\therefore \quad K_c = [H_2S][NH_3] = 0.009 \times 0.009 = 81 \times 10^{-6} \text{ (mol/L)}^2$

As NH_4HS is solid it is not considered.

As we know that

$K_p = K_c \times (RT)^{\Delta n}$

$\therefore \quad \Delta n$ for above reaction = 2

($\because$ Δn = number of gaseous mole of right side number of gaseous mole of left side = 2 − 0 = 2)

$T = 27°C + 273 = 300$ K

$R = 0.0821$ L-atom/K/mol

$\therefore \quad K_p = 81 \times 10^{-6} \times (0.0821 \times 300)^2 = 0.048 \text{ atm}^2$

14. **a.** **i.** ΔG_0 for reaction

$$\Delta G^\circ_{\text{reac.}} = 2\Delta G_f^\circ(NO_2) - \Delta G_f^\circ(N_2O_4)$$

$$\Delta G^\circ = 100 - 100 = 0$$

Now $\Delta G = 2.303RT \log Q_P + \Delta G_0$

Here $Q_P = \frac{P^2_{NO_2}}{P_{N_2O_4}} = \frac{100}{10} = 10$ atm

So, $\Delta G = 2.303RT \log Q_P + 0 = 2.303RT \log Q_P$

$= 2.303RT \log_{10} 10 = 2.303RT$

$= 2.303 \times 0.82 \times 298$

$= 56.276$ L-atm, approximately

ii. Since Q_P is more than K_P

(calculate K_P by putting the value of ΔG_0 in the equation 2.303 RT log K_P as $\Delta G_0 = 0$ that's why K_P comes as 1)

Hence, the reaction will proceed in backward direction.

b. The van der Waals equation (of 1 mole of a real gas)

$$\left[P + \frac{a}{V_m^2}\right](V_m - b) = RT$$

or
$$PV_m - Pb + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT$$

or
$$PV_m = RT + Pb - \frac{a}{V_m} + \frac{ab}{V_m^2} \quad \text{(i)}$$

To calculate the intercept $P \to 0$ due to which $V_m \to \infty$

Thus, we can ignore the last two terms of right-hand side of equation (i) hence

$$PV_m = RT + Pb$$

When $P = 0$, the intercept will be RT.