- A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.
  - (a) What is the initial effect of the change on vapour pressure?
  - (b) How do rate of evaporation and condensation change initially?
  - (c) What happens when equilibrium is restored finally and what will be the final vapour pressure?

## Ans:

- (a) Initially, the vapour pressure will decrease because the same amount of vapour will be distributed in larger volume.
- (b) The rate of evaporation remains constant at constant temperature. But the rate of condensation will decrease initially because there are fewer molecules per unit volume in the vapour phase.
- (c) When equilibrium is restored, rate of evaporation becomes equal to the rate of condensation. The final vapour pressure will be the same as the original vapour pressure because vapour pressure depends only on temperature.
- 2. At a certain temperature and total pressure of  $10^5 Pa$ , iodine vapour contains 40% by volume

of iodine atoms. Calculate  $K_p$  for the equilibrium,  $I_2(g) \xrightarrow{2 I(g)} 2I(g)$ .

## Ans:

Percentage by volume of gaseous iodine atoms = 40%

- $\therefore$  Mole fraction of gaseous iddine atoms =  $\frac{40}{100}$
- :. Partial pressure of gaseous iddine atoms =  $\frac{40}{100} \times 10^5 Pa = 0.4 \times 10^5 Pa$

Partial pressure of gaseous  $I_2 = 0.6 \times 10^5 Pa$ 

$$\therefore K_p = \frac{P_I^2}{P_{I_2}} = \frac{(0.4 \times 10^5)^2}{0.6 \times 10^5} = 2.67 \times 10^4 Pa$$

3. Find out the value of  $K_c$  for each of the following equilibria from the value of  $K_p$ 

(i) 
$$2NOCl(g) \xrightarrow{2NO(g)} 2NO(g) + Cl_2(g)$$
;  $K_p = 1.8 \times 10^{-2}$  at 500 K

(ii)  $CaCO_3(s) \xrightarrow{\longrightarrow} CaO(s) + CO_2(g)$ ;  $K_p = 167$  at 1073 K

(i) 
$$\Delta n(g) = (2+1) - 2 = 1$$
,  
 $\therefore K_p = K_c RT$  or  $K_c = \frac{K_p}{RT} = \frac{1.8 \times 10^{-2}}{0.0821 \times 500} = 4.38 \times 10^{-2}$   
(ii)  $\Delta n(g) = 1 - 0 = 1$   
 $\therefore K_c = \frac{K_p}{RT} = \frac{167}{0.0821 \times 1073} = 1.895$ 

4. For the following equilibrium,  $K_c = 6.3 \times 10^{14}$  at 1000 K

$$NO(g) + O_3(g) \xrightarrow{\longrightarrow} NO_2(g) + O_2(g)$$

What is  $K_c'$  for the reverse reactions?

Ans:  $K_c'$  for the reverse reaction =  $\frac{1}{K_c} = \frac{1}{6.3 \times 10^4} = 0.159 \times 10^{-14} = 1.59 \times 10^{-15}$ 

5. Nitric oxide reacts with bromine to form nitrosyl bromide as follows

 $2NO(g) + Br_2(g) \implies 2NOBr(g)$ 

When 0.087 mol of NO and 0.0437 mole of  $Br_2$  are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and  $Br_2$ .

Ans: 2 moles of NO gives 2 moles of NOBr

:. Number of moles NO reacted to form 0.0518 mol of NOBr = 0.0518

Number of moles of  $Br_2$  reacted =  $\frac{0.0518}{2} = 0.0259$ 

- : Number of moles of NO remaining at equilibrium = 0.087 0.0518 = 0.0352 mol
- $\therefore$  Number of moles  $Br_2$  at equilibrium = 0.0437 0.0259 = 0.0178 mol
- 6. A sample of HI(g) is placed in a flask at a pressure of 0.2 atm. At equilibrium, the partial pressure of HI(g) is 0.04 atm. What is  $K_p$  for the equilibrium

$$2HI(g) \xrightarrow{} H_2(g) + I_2(g)$$

Ans:

Initial pressure of HI(g) = 0.2 atm

Partial pressure of HI(g) at equilibrium = 0.04 atm

 $\therefore$  Decrease in pressure of HI (g) = 0.2 - 0.04 = 0.16 atm

It is because of decomposition to  $H_2$  and  $I_2$ .

:. Partial pressure of  $H_2$  = Partial pressure of  $I_2(g) = \frac{0.16}{2} = 0.08$  atm

: 
$$K_p = \frac{P_{H_2} \times P_{I_2}}{P_{HI}^2} = \frac{0.08 \times 0.08}{0.04 \times 0.04} = 4.0$$

7. A mixture of 1.57 mol of  $N_2$ , 1.92 mol of  $H_2$  and 8.13 mol of  $NH_3$  is introduced into a 20L vessel at 500K.  $K_c$  for the reaction  $N_2 + 3H_2 \implies 2NH_3$  is  $1.7 \times 10^2$  at 500K. Is the reaction mixture at equilibrium. If not, what is the direction of the net reaction.

$$[N_2] = \frac{1.57}{20} \mod L^{-1}; \quad [H_2] = \frac{1.92}{20} \mod L^{-1}; \quad [NH_3] = \frac{8.13}{20} \mod L^{-1}$$
$$\therefore \ \mathcal{Q}_c = \frac{[NH_3]^2}{[N_2] [H_2]^3} = \frac{(8.13/20)^2}{\frac{1.57}{20} \times \left(\frac{1.92}{20}\right)^3} = 2.38 \times 10^3$$

Since  $Q_c \neq K_c$ , the reaction mixture is not at equilibrium. Since  $Q_c > K_c$ , the reaction will take place in the backward direction

- 8. One mole of  $H_2O$  and one mole of CO are taken in a 10L vessel and heated to 725K. At Solution Moles of  $H_2O$  reacted =  $1 \times \frac{40}{100} = 0.4$ 
  - :. Number of moles of  $H_2O$  at equilibrium = 1 0.4 = 0.6

$$\therefore [H_2 O] = \frac{0.6}{10} = 0.06 \text{ mol } L^{-1}$$

Similarly,  $[CO] = 0.06 \mod L^{-1}$ 

$$[H_2] = \frac{0.4}{10} = 0.04 \text{ mol } \text{L}^{-1}; \quad [CO_2] = 0.04 \text{ mol } \text{L}^{-1}$$

: 
$$K_c = \frac{[H_2] [CO_2]}{[H_2O] [CO]} = \frac{0.04 \times 0.04}{0.06 \times 0.06} = 0.44$$

9. What is the equilibrium concentration of each of the substance in the equilibrium when the initial concentration of *ICl* was 0.78 M.

$$2ICl(g) \xrightarrow{\longrightarrow} I_2(g) + Cl_2(g), \quad K_c = 0.14$$

Institute the equilibrium concentration of  $I_2$  and  $CI_2$  be x. Then equilibrium concentration of  $ICI_2$ 

- will be 0.78 2x  $K_c = \frac{[I_2] [CI_2]}{[ICI]^2}$  i.e.,  $0.14 = \frac{x \times x}{(0.78 - 2x)^2}$   $\therefore \frac{x}{0.78 - 2x} = \sqrt{0.14} = 0.37$   $\therefore x = (0.78 - 2x) 0.37 = 0.288 - 0.74 x$  x + 0.74 x = 0.288 i.e., 1.74 x = 0.288  $\therefore x = \frac{0.288}{1.74} = 0.165$ i.e.,  $[I_2] = [CI_2] = 0.165$  M  $[ICI] = 0.78 - 2 \times 0.165 = 0.45$  M
- 10. Do the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?

(a) 
$$PCl_5(g) \xrightarrow{} PCl_3(g) + Cl_2(g)$$
  
(b)  $CaO(s) + CO_2(g) \xrightarrow{} CaCO_3(s)$   
(c)  $3 Fe(s) + 4H_2O(g) \xrightarrow{} Fe_3O_4(s) + 4H_2(g)$ 

Ans:

- (a) Applying Le Chatelier's principle, as pressure decreases the system will favour the forward direction where there is increase in the number of moles of gaseous products.
   i.e., Number of moles of reaction products increase.
- (b) Decrease of pressure will favour backward direction because of the formation of more gaseous substance. i.e., number of moles of reaction products decrease.
- (c) In this reaction, there is no change in the number of moles of gaseous reactants and products. So pressure will not have any effect on the equilibrium. i.e., number of moles of the products will remain the same.
- 11. It has been found that pH of 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionisation constant of the acid and its pKa.

Ans: 
$$HA \xrightarrow{} A^- + H^+$$
  
(acid)  $A^- + H^+$   
 $pH = -\log [H^+]$ 

- $\therefore \log [H^+] = -pH = -4.15 = 5.85$   $\therefore [H^+] = \text{Antilog of } \overline{5}.85 = 7.08 \times 10^{-5} \text{ M}$ Concentration of  $A^-$  = Concentration of  $H^+ = 7.08 \times 10^{-5} \text{ M}$   $K_a = \frac{[A^-][H^+]}{[HA]} = \frac{7.08 \times 10^{-5} \times 7.08 \times 10^{-5}}{0.01} = 5.01 \times 10^{-7}$  $pKa = -\log K_a = -\log (5.01 \times 10^{-7}) = 7 - 0.699 = 6.301 = 6.3$
- 12. The degree of ionisation of 0.1 M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pKa of bromoacetic acid.

## Ans:

$$K_a = c\alpha^2 = 0.1 \times 0.132 \times 0.132 = 1.74 \times 10^{-3}$$
  

$$\therefore pKa = -\log K_a = -\log (1.74 \times 10^{-3}) = 3 - 0.2405 \approx 2.76$$
  

$$[H^+] = c\alpha = 0.1 \times 0.132 = 1.32 \times 10^{-2} M$$
  

$$\therefore pH = -\log (1.32 \times 10^{-2}) = 2 - 0.1205 \approx 1.88$$

13. If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K, calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

Ans: Mass of KOH is 1000 mL solution =  $0.561 \times 5g$ 

 $\therefore \text{ Concentration of } KOH \text{ solution} = \frac{0.561 \times 5}{56} = 0.05 \text{ M}$ 

Since KOH completely ionises to give  $K^{-1}$  and  $OH^{-1}$ ,  $[K^{+}] = [OH^{-}] = [KOH] = 0.05 \text{ M}$ 

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.05} = 2.0 \times 10^{-13} \,\mathrm{M}$$

:. 
$$pH = -\log(2 \times 10^{-13}) = 13 - 0.3010 = 12.699 \approx 12.7$$

14. The solubility of  $Sr(OH)_2$  at 298 K is 19.23 g/L of solution. Calculate the concentration of strontium and hydroxyl ions. What is its pH? (Atomic mass of Sr = 87.6)

Ans: Molar mass of  $Sr(OH)_2 = 87.6 + 34 = 121.6 \text{ g mol}^{-1}$ 

Solubility of  $Sr(OH)_2$  in mol/L =  $\frac{18.23}{121.6} = 0.158 \text{ mol } \text{L}^{-1}$   $Sr(OH)_2 \longrightarrow Sr^{2+} + 2OH^{-1}$  $\therefore [Sr^{2+}] = 0.158 \text{ mol } \text{L}^{-1} \text{ (or M)}$   $[OH] = 2 \times 0.158 = 0.316 \text{ mol } L^{-1} \text{ (or M)}$   $pOH = -\log 0.316 = 0.5$  $\therefore pH = 14 - 0.5 = 13.5$ 

15. The ionic product of water at 310 K is  $2.7 \times 10^{-14}$ . What is the *pH* of neutral water at this temperature.

Ans: 
$$K_w = [H^+] [OH^-] = 2.7 \times 10^{-14}$$
  
 $\therefore [H^+] = \sqrt{2.7 \times 10^{-14}} = 1.643 \times 10^{-7}$ 

- :  $pH = -\log(1.643 \times 10^{-7}) = 7 0.2156 = 6.7844 \approx 6.78$
- 16. The solubility product constant of  $Ag_2CrO_4$  and AgBr are  $1.1 \times 10^{-12}$  and  $5.0 \times 10^{-13}$  respectively. Calculate the ratio of the molarities of their saturated solution.

Ans: 
$$K_{sp}$$
 of  $Ag_2CrO_4 = 1.1 \times 10^{-12}$   
For  $Ag_2CrO_4$ ,  $K_{sp} = 4s^3$   
 $\therefore$  Solubility (s) of  $Ag_2CrO_4 = \sqrt[3]{\frac{1.1 \times 10^{-12}}{4}} = 0.65 \times 10^{-4} = 6.5 \times 10^{-5}$  M  
Solubility of  $AgBr = \sqrt{K_{sp}} = \sqrt{5 \times 10^{-13}} = \sqrt{50 \times 10^{-14}} = 7.07 \times 10^{-7}$  M

 $\therefore \text{ Ratio of concentration of } Ag_2CrO_4 \text{ to } AgBr \text{ solution} = \frac{6.5 \times 10^{-5}}{7.07 \times 10^{-7}} = 91.9$