



TEXTBOOK QUESTIONS SOLVED

Question 1. A liquid is in equilibrium with its vapours in a sealed container at a fixed temperature. The volume of the container is suddenly increased,

- (i) What is the initial effect of the change on the vapour pressure?
- (ii) How do the rates of evaporation and condensation change initially?
- (iii) What happens when equilibrium is restored finally and what will be the final vapour pressure?

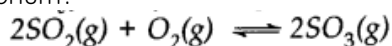
Answer:

(i) On increasing the volume of the container, the vapour pressure will initially decrease because the same amount of vapours are now distributed over a larger space.

(ii) On increasing the volume of the container, the rate of evaporation will increase initially because now more space is available. Since the amount of the vapours per unit volume decrease on increasing the volume, therefore, the rate of condensation will decrease initially.

(iii) Finally, equilibrium will be restored when the rates of the forward and backward processes become equal. However, the vapour pressure will remain unchanged because it depends upon the temperature and not upon the volume of the container.

Question 2. What is K_c for the following reaction in state of equilibrium?



Given: $[\text{SO}_2] = 0.6 \text{ M}$; $[\text{O}_2] = 0.82 \text{ M}$; and $[\text{SO}_3] = 1.90 \text{ M}$

Answer:



$$\begin{aligned} K_c &= \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{(1.9 \text{ M}) \times (1.9 \text{ M})}{(0.6 \text{ M}) \times (0.6 \text{ M}) \times (0.82 \text{ M})} \\ &= 12.229 \text{ M}^{-1} = 12.229 \text{ L mol}^{-1} \end{aligned}$$

Question 3.

At a certain temperature and total pressure of 10^5 Pa , iodine vapours contain 40% by volume of iodine atoms in the equilibrium $\text{I}_2(\text{g}) \rightleftharpoons 2\text{I}(\text{g})$. Calculate K_p for the equilibrium.

Answer:

According to available data:

Total pressure of equilibrium mixture = 10^5 Pa

Partial pressure of iodine atoms (I) = $\frac{40}{100} \times (10^5 \text{ Pa}) = 0.4 \times 10^5 \text{ Pa}$

Partial pressure of iodine molecules (I_2) = $\frac{60}{100} \times (10^5 \text{ Pa}) = 0.6 \times 10^5 \text{ Pa}$

$$\begin{array}{ccc} \text{I}_2(\text{g}) & \rightleftharpoons & 2\text{I}(\text{g}) \\ (0.6 \times 10^5 \text{ Pa}) & & (0.4 \times 10^5 \text{ Pa}) \end{array}$$
$$K_p = \frac{p_{\text{I}_2}}{p_{\text{I}}^2} = \frac{(0.4 \times 10^5 \text{ Pa})^2}{(0.6 \times 10^5 \text{ Pa})} = 2.67 \times 10^4 \text{ Pa}$$

Question 4. Write the expression for the equilibrium constant for each of the following reactions

- (i) $2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)}$
 (ii) $2\text{Cu(NO}_3)_2\text{(s)} \rightleftharpoons 2\text{CuO(s)} + 4\text{NO}_2\text{(g)} + \text{O}_2\text{(g)}$
 (iii) $\text{CH}_3\text{COOC}_2\text{H}_5\text{(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{CH}_3\text{COOH(aq)} + \text{C}_2\text{H}_5\text{OH(aq)}$
 (iv) $\text{Fe}^{3+}\text{(aq)} + 3\text{OH}^-\text{(aq)} \rightleftharpoons \text{Fe(OH)}_3\text{(s)}$
 (v) $\text{I}_2\text{(s)} + 5\text{F}_2\text{(g)} \rightleftharpoons 2\text{IF}_5\text{(l)}$

Answer:

- (i) $K_c = \frac{[\text{NO(g)}]^2 [\text{Cl}_2\text{(g)}]}{[\text{NOCl(g)}]^2}$
 (ii) $K_c = \frac{[\text{CuO(g)}]^2 [\text{NO}_2\text{(g)}]^4 [\text{O}_2\text{(g)}]}{[\text{Cu(NO}_3)_2\text{(s)}]^2} = [\text{NO}_2\text{(g)}]^4 [\text{O}_2\text{(g)}]$
 (iii) $K_c = \frac{[\text{CH}_3\text{COOH(aq)}][\text{C}_2\text{H}_5\text{OH(aq)}]}{[\text{CH}_3\text{COOC}_2\text{H}_5\text{(aq)}][\text{H}_2\text{O(l)}]}$

$$= \frac{[\text{CH}_3\text{COOH(aq)}][\text{C}_2\text{H}_5\text{OH(aq)}]}{[\text{CH}_3\text{COOC}_2\text{H}_5\text{(aq)}]}$$

 (iv) $K_c = \frac{[\text{Fe(OH)}_3\text{(s)}]}{[\text{Fe}^{3+}\text{(aq)}][\text{OH}^-\text{(aq)}]^3} = \frac{1}{[\text{Fe}^{3+}\text{(aq)}][\text{OH}^-\text{(aq)}]^3}$
 (v) $K_c = \frac{[\text{IF}_5\text{(l)}]^2}{[\text{I}_2\text{(s)}][\text{F}_2\text{(g)}]^5} = \frac{[\text{IF}_5\text{(l)}]^2}{[\text{F}_2\text{(g)}]^5}$

Question 5. Find the value of K_c for each of the following equilibria from the value of K

- (a) $2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)} ; K_p = 1.8 \times 10^{-2} \text{ atm at } 500 \text{ K}$
 (b) $\text{CaCO}_3\text{(s)} \rightleftharpoons \text{CaO(s)} + \text{CO}_2\text{(g)} ; K_p = 167 \text{ atm at } 1073 \text{ K}$

Answer:

K_p and K_c are related to each other as $K_p = K_c (RT)^{\Delta n_g}$

The value of K_c can be calculated as follows:

- (a) $2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)}$
 $K_p = 1.8 \times 10^{-2} \text{ atm,}$
 $\Delta n_g = 3 - 2 = 1 ; R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1} ; T = 500 \text{ K}$

$$\therefore K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{(1.8 \times 10^{-2} \text{ atm})}{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 500 \text{ K})^1}$$

$$= 4.4 \times 10^{-4} \text{ mol L}^{-1}$$

- (b) $\text{CaCO}_3\text{(s)} \rightleftharpoons \text{CaO(s)} + \text{CO}_2\text{(g)}$
 $K_p = 167 \text{ atm, } \Delta n_g = 1$
 $R = 0.0821 \text{ liter atm K}^{-1} \text{ mol}^{-1} ; T = 1073 \text{ K}$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{(167 \text{ atm})}{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 1073 \text{ K})^1}$$

$$= 1.9 \text{ mol L}^{-1}$$

Question 6. For the following equilibrium, $K = 6.3 \times 10^{14}$ at 1000 K. $\text{NO(g)} + \text{O}_3 \rightarrow \text{NO}_2\text{(g)} + \text{O}_2\text{(g)}$ Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c for the reverse reaction ?

Answer:

For the reverse reaction $K_c = \frac{1}{K_c} = \frac{1}{6.3 \times 10^{14}} = 1.59 \times 10^{-15}$.

Question 7. Explain why pure liquids and solids can be ignored while writing the value of equilibrium constants.

Answer: This is because molar concentration of a pure solid or liquid is independent of the amount present.

$$\text{Molar concentration} = \frac{\text{No. of moles}}{\text{volume}} \times \frac{\text{Mass}}{\text{volume}} \times \text{Density}$$

Since density of pure liquid or solid is fixed and molar mass is also fixed. Therefore molar concentration are constant.

Question 8. Reaction between nitrogen and oxygen takes place as follows:



If a mixture of 0.482 mol of N_2 and 0.933 mol of O_2 is placed in a reaction vessel of volume 10 L and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of the equilibrium mixture.

Answer: Let x moles of $\text{N}_2(\text{g})$ take part in the reaction. According to the equation, $x/2$ moles of $\text{O}_2(\text{g})$ will react to form x moles of $\text{N}_2\text{O}(\text{g})$. The molar concentration per litre of different species before the reaction and at the equilibrium point is:

	$2\text{N}_2(\text{g})$	+	$\text{O}_2(\text{g})$	\rightleftharpoons	$2\text{N}_2\text{O}(\text{g})$
Initial mole/litre:	$\frac{0.482}{10}$		$\frac{0.933}{10}$		Zero
Mole/litre at eqm. point:	$\frac{0.482-x}{10}$		$\frac{0.933-\frac{x}{2}}{10}$		$\frac{x}{10}$

The value of equilibrium constant (2.0×10^{-37}) is extremely small. This means that only small amounts of reactants have reacted. Therefore, is extremely small and can be omitted as far as the reactants are concerned.

Applying Law of Chemical Equilibrium $K_c = \frac{[\text{N}_2\text{O}(\text{g})]^2}{[\text{N}_2(\text{g})]^2[\text{O}_2(\text{g})]}$

$$2.0 \times 10^{-37} = \frac{\left(\frac{x}{10}\right)^2}{\left(\frac{0.482}{10}\right)^2 \times \left(\frac{0.933}{10}\right)} = \frac{0.01 x^2}{2.1676 \times 10^{-4}}$$

$$x^2 = 43.352 \times 10^{-40} \quad \text{or} \quad x = 6.6 \times 10^{-20}$$

As x is extremely small, it can be neglected.

Thus, in the equilibrium mixture

Molar conc. of $\text{N}_2 = 0.0482 \text{ mol L}^{-1}$

Molar conc. of $\text{O}_2 = 0.0933 \text{ mol L}^{-1}$

Molar conc. of $\text{N}_2\text{O} = 0.1 \times x = 0.1 \times 6.6 \times 10^{-20} \text{ mol L}^{-1}$
 $= 6.6 \times 10^{-21} \text{ mol L}^{-1}$

Question 9. Nitric oxide reacts with bromine and gives nitrosyl bromide as per reaction given below:



When 0.087 mole of NO and 0.0437 mole of Br_2 are mixed in a closed container at constant temperature, 0.0518 mole of NOBr is obtained at equilibrium. Determine the compositions of the equilibrium mixture.

Answer: The balanced chemical equation for the reaction is:
 According to the equation, 2 moles of $\text{NO}(\text{g})$ react with 1 mole of $\text{Br}_2(\text{g})$ to form 2 moles of $\text{NOBr}(\text{g})$. The composition of the equilibrium mixture can be calculated as follows:

No. of moles of $\text{NOBr}(\text{g})$ formed at equilibrium = 0.0518 mol (given)

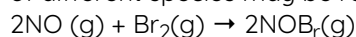
No. of moles of $\text{NO}(\text{g})$ taking part in reaction = 0.0518 mol

No. of moles of $\text{NO}(\text{g})$ left at equilibrium = $0.087 - 0.0518 = 0.0352$ mol

No. of moles of $\text{Br}_2(\text{g})$ taking part in reaction = $1/2 \times 0.0518 = 0.0259$ mol

No. of moles of $\text{Br}_2(\text{g})$ left at equilibrium = $0.0437 - 0.0259 = 0.0178$ mol

The initial molar concentration and equilibrium molar concentration of different species may be represented as:

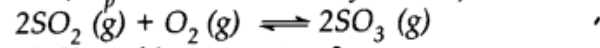


Initial moles 0.087 0.0437 0

Moles at eqm. point: 0.0352 0.0178 0.0518

Question 10.

At 450 K, $K_p = 2.0 \times 10^{10} \text{ bar}^{-1}$ for the equilibrium reaction:



What is K_c at this temperature?

Answer:

$$K_p = K_c (RT)^{\Delta n_g} \text{ or } K_c = \frac{K_p}{(RT)^{\Delta n_g}} = K_p (RT)^{-\Delta n_g}$$

$$K_p = 2.0 \times 10^{10} \text{ bar}^{-1}; R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}; T = 450 \text{ K}; \Delta n_g = 2 - 3 = -1$$

$$K_c = (2.0 \times 10^{10} \text{ bar}^{-1}) \times [(0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K})]^{-(-1)}$$

$$= 7.47 \times 10^{11} \text{ mol}^{-1} \text{ L} = 7.47 \times 10^{11} \text{ M}^{-1}$$

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