CHAPTER
7

Equilibrium

TRY YOURSELF ANSWERS

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1. In the soda water bottle, the pressure of the gas is very high above the liquid, so the mass of the CO_2 gas dissolved is also high. As soon as the bottle is opened, the pressure tends to decrease to atmospheric pressure, so the solubility decreases, *i.e.*, the dissolved gas escapes out.

2. $NH_4Cl_{(solid)} \rightleftharpoons NH_4Cl_{(vapour)}$

$I_{2(solid)} \rightleftharpoons I_{2(vapour)}$

3. **Irreversible reaction :** The reactions in which the products do not react under any condition to give back reactants are called irreversible reactions, *e.g.*, potassium chlorate decomposes on heating and forms potassium chloride and oxygen. But, the products cannot combine to form potassium chlorate.

$2KClO_3 \longrightarrow 2KCl + 3O_2$

Reversible reaction : The reactions in which the products under suitable condition react to give back reactants are called reversible reactions, *e.g.*, the reaction of hydrogen gas and iodine vapour to from hydrogen iodide.

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

4. It proceeds to completion because CO_2 escapes to atmosphere thus, reverse reaction cannot take place.

5. For reaction, $CaCO_3 \rightleftharpoons CaO + CO_2$,

$K_c = [CaO][CO_2]/[CaCO_3] = x$ ...(i)

For reaction, $2CaCO_3 \rightleftharpoons 2CaO + 2CO_2$,

$K_c' = [CaO]^2[CO_2]^2/ [CaCO_3]^2 = y$ ...(ii)

From eq (i) and (ii), $y = x^2$

6.

	$2HI$	$\rightleftharpoons H_2$	$+\ I_2$
Initial moles	2	0	0
At equilibrium	2 – 0.6 = 1.4	0.3	0.3

$K_c = [H_2][I_2]/[HI]^2 = 0.3 \times 0.3/1.4 \times 1.4 = 0.0459$

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

Here, $\Delta n_g = 2 - 3 = -1$

or $\dfrac{K_p}{K_c} = (RT)^{-1} = \dfrac{1}{0.082 \times 298} = 0.041$

8. $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$; $K_p = 1.3 \times 10^{-2}$

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

$\Delta n_g = 3 - 2 = 1$

$1.3 \times 10^{-2} = K_c\,(0.0821 \times 300)^1$

$K_c = 1.3 \times 10^{-2} / (0.0821 \times 300) = 5.28 \times 10^{-4}$

9. For the reaction,

let 'x' be the decrease in pressure of CO_2, then

	$CO_{2(g)}$	$+\ C_{(s)} \rightleftharpoons$	$2CO_{(g)}$
Initial pressure :	0.36 bar		0 bar
At eqm.	$(0.36 - x)$ bar		$2x$ bar

$K_p = (p_{CO})^2 / p_{CO_2}$

$K_p = (2x)^2/(0.36 - x) = 4$

$4x^2 = 4(0.36 - x)$

$4x^2 = 1.44 - 4x$

$4x^2 + 4x - 1.44 = 0$

$x = 0.28$

The equilibrium partial pressures are,

$p_{CO} = 2x = 2 \times 0.28 = 0.56$ bar

$p_{CO_2} = 0.36 - x = 0.36 - 0.28 = 0.08$ bar

10. $K_c = \dfrac{[AgNO_3]^2}{[HNO_3]^2}$

11. $Q_c = [NO_2]^2/[N_2O_4] = (0.5)^2/0.125 = 2$

Q_c value is greater than K_c. Hence, the reaction will proceed in the reverse direction until the Q value reaches 0.213.

12. Let x be the no. of moles of reactants reacted.

	A	$+\ B$	$\rightleftharpoons C$	$+\ D$
Initial conc.	1	1	1	1
At equilibrium	$1 - x$	$1 - x$	$1 + x$	$1 + x$

$K_c = [C][D]/[A][B] = (1 + x)(1 + x) / (1 - x)(1 - x) = 100$

or $10 = (1 + x)/(1 - x)$ or $10(1 - x) = 1 + x$

or $10 - 10x = 1 + x$ or $11x = 9$ or $x = 9/11 = 0.818$

$[D] = 1 + x = 1 + 0.818 = 1.818$ mol litre^{-1}

13. Higher the value of K, greater is the yield of products. Hence, yield of R will be maximum.

14. $Q = p_C$; $\Delta_r G = \Delta_r G^\circ + RT \ln p_C$

At 300 K, $\Delta_r G^\circ = 100 - (4 \times 10^{-2}) \times 300 = 100 - 12 = 88$ kJ

$\Delta_r G = 88 + 8.314 \times 300 \times 2.303 (\log 5) \times 10^{-3}$

$\Delta_r G = 92.014$ kJ/mol

15. $\Delta G^\circ = -2.303\,RT \log K_p \Rightarrow \log K_p = -\dfrac{\Delta G^\circ}{2.303\,RT}$

$= -\dfrac{(-16.5 \times 10^3)}{2.303 \times 8.314 \times 298} = 2.892$ or $K_p = 779.83$

K_p for the reaction, $N_{2(g)} + 3H_{(g)} \rightleftharpoons 2NH_{3(g)}$

$= (779.83)^2 = 6.08 \times 10^5$

$\Delta G^\circ = -2.303 \times 8.314 \times 298 \times \log (6.08 \times 10^5)$

$= 33000$ J/mol $= 33$ kJ/mol

16. Le Chatelier's principle states that changes in pressure are attributable to changes in volume. If we increase the volume, the reaction will shift toward the side that has more moles of gas. If we decrease the volume, the reaction will shift toward the side that has less moles of gas. Since the product side has only two moles of gas, compared to the reactant side with four moles, the reaction would shift toward the product side, and more NH_3 would form.

17. With increased pressure, each reaction will favour the side with the least amount of moles of gas. Thus, any reaction with less number of moles at product side will be favoured.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

18. We know, weaker the acid, stronger is its conjugate base. As CH_3COOH it a stronger acid than H_2O, hence OH^- is a stronger base than CH_3COO^-.

19. When a Lewis acid reacts with a Lewis base, a dative or coordinate bond is formed between them.

e.g., $\underset{\text{Lewis base}}{NH_3} + \underset{\text{Lewis acid}}{BF_3} \longrightarrow H_3N\!:\rightarrow BF_3$

20. $pH = -\log[H^+] = -\log 10^{-5} = +5 \log 10$

$pH = 5$

21. (a) $[H^+] = \text{Antilog }[-pH]$

$= \text{Antilog }[-7.26] = 5.495 \times 10^{-8}$ M

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{5.495\times10^{-8}} = 1.819 \times 10^{-7}\text{ M}$$

(b) $[H^+] = \text{Antilog}[-pH]$

$= \text{Antilog}[-11.25] = 5.623 \times 10^{-12}$ M

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{5.623\times10^{-12}} = 1.778 \times 10^{-3}\text{ M}$$

22. For ionization of acetic acid :

$$\begin{array}{llll} & CH_3COOH & \rightleftharpoons CH_3COO^- & + \; H^+ \\ t_0 & C & 0 & 0 \\ t_{eqm.} & C - C\alpha & C\alpha & C\alpha \end{array}$$

$$K_a = \frac{C\alpha \times C\alpha}{C - C\alpha} = \frac{C\alpha^2}{1-\alpha}$$

$$K_a = \frac{0.01\times(0.05)^2}{1-0.05} = 2.63\times10^{-5}$$

23. $pH = 2.85 \Rightarrow [H^+] = 1.41 \times 10^{-3}$

For weak monobasic acid, $[H^+] = \sqrt{K_a.C}$

or $K_a = \dfrac{[H^+]^2}{C} = \dfrac{(1.41\times10^{-3})^2}{0.08} = 2.485\times10^{-5}$

24. (i) $KCl + H_2O \rightarrow \underset{\text{Strong base}}{KOH} + \underset{\text{Strong acid}}{HCl}$

Hence, the solution is neutral.

(ii) $NH_4NO_3 + H_2O \rightarrow \underset{\text{Weak base}}{NH_4OH} + \underset{\text{Strong acid}}{HNO_3}$

Hence, the solution is acidic.

25. Ammonium acetate is a salt of weak acid and weak base.

$$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$$

$$= \frac{1}{2}[14 - \log(1.8\times10^{-5}) + \log(1.8\times10^{-5})] = 7.0$$

26. pH of our blood remains almost constant at 7.4 because of the buffer system present in the blood. The buffer for maintaining acid-base balance in the blood is the carbonic acid-bicarbonate buffer. So, pH of blood remains constant after eating spicy food.

27. pH of a buffer changes with temperature because concentration of H^+ ions increases, thus pH decreases with increase of temperature.

28. Solubility of $Mg(OH)_2 = 8.352 \times 10^{-3}$ gL^{-1}

$$= \frac{8.352\times10^{-3}}{58}\text{ mol L}^{-1} = 1.44 \times 10^{-4}\text{ mol L}^{-1}$$

Let s be the solubility of $Mg(OH)_2$.

$$Mg(OH)_2 \rightleftharpoons \underset{s}{Mg^{2+}} + \underset{2s}{2OH^-}$$

$K_{sp} = [Mg^{2+}][OH^-]^2 = s \times (2s)^2 = 4s^3$

$= 4 \times (1.44 \times 10^{-4})^3 = 1.194 \times 10^{-11}$ mol^3 L^{-3}

29. On mixing 50 mL of 0.01 M NaCl and 50 mL of 0.01 M $AgNO_3$ the total volume becomes 100 mL.

Therefore,

Conc. of NaCl in 100 mL $= \dfrac{0.01\times50}{100} = 0.005$ M

Conc. of $AgNO_3$ in 100 mL $= \dfrac{0.01\times50}{100} = 0.005$ M

Now, $NaCl_{(aq)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$

and $AgNO_{3(aq)} \rightleftharpoons Ag^+_{(aq)} + NO^-_{3(aq)}$

$[Cl^-] = [NaCl] = 0.005$ M

$[Ag^+] = [AgNO_3] = 0.005$ M

∴ Ionic product of $[Ag^+][Cl^-] = 0.005 \times 0.005 = 2.5 \times 10^{-5}$

Since, ionic product is greater than its solubility product, precipitation will occur.

30. Let the concentration of AgCl be x mol/litre and that of CuCl be y mol/litre

$$AgCl \rightleftharpoons \underset{x}{Ag^+} + \underset{x}{Cl^-}$$

$$\underset{y\,=\,0.1}{CuCl} \rightleftharpoons \underset{y}{Cu^+} + \underset{y}{Cl^-}$$

K_{sp} of AgCl $= [Ag^+][Cl^-] = x(x + y)$ ...(i)

K_{sp} of CuCl $= [Cu^+][Cl^-] = y(x + y)$ ...(ii)

On solving (i) and (ii), we get

$$\frac{K_{sp}\text{ of AgCl}}{K_{sp}\text{ of CuCl}} = \frac{x}{y} \Rightarrow \frac{1.6\times10^{-10}}{1.0\times10^{-6}} = \frac{x}{0.1}$$

$\Rightarrow x = 1.6 \times 10^{-5}$ mol/litre

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