Equilibrium

1. Equilibrium constant K_p for the reaction

   $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ is 0.82 atm at 727 °C.

   If 1 mole of $CaCO_3$ is placed in a closed container of 20L and heated to this temperature, what amount of $CaCO_3$ in grams would dissociate at equilibrium ?

2. An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 1.0 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 2 atm. What will be the equilibrium constant for NH_4HS decomposition at this temperature?

3. Calculate the pH of a solution obtained by diluting 1 mL of 0.10 M weak monoacidic base to 100 mL at constant temperature if K_b of the base is 1×10^{-5}.

4. 28 g N_2 and 6.0 g of H_2 are heated over catalyst in a closed one litre flask of 450 °C. The entire equilibrium mixture required 500 mL of 1.0 M H_2SO_4 for neutralisation. Calculate the value of K_c in $L^2\,mol^2$ for the given reaction.

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

5. The equilibrium constant of the reaction of weak acid HA with strong base is 10^{-7}. Find the pOH of the aqueous solution of 0.1M NaA.

6. For the reaction $C(s) + CO_2(g) \rightarrow 2CO(g)$, $K_p = 63$ atm at 1000 K. If at equilibrium : $P_{CO} = 10\,P_{CO_2}$. Find the total pressure (atm) of the gases at equilibrium.

7. The pK_a of HCOOH is 3.8 and pK_b of NH_3 is 4.8, find the pH of aqueous solution of 1M $HCOONH_4$.

8. In the reaction $AB(g) \rightleftharpoons A(g) + B(g)$ at 30° C, K_p for the dissociation equilibrium is 1.6×10^{-3} atm. If the total pressure at equilibrium is 1 atm, then calculate the percentage dissociation of AB.

9. Calculate the pH at the equivalence point when a solution of 0.01 M CH_3COOH is titrated with a solution of 0.01 M NaOH. pK_a of CH_3COOH is 4.74.

10. The value of K_p for the equilibrium reaction

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

    Calculate the percentage dissociation of $N_2O_4(g)$ at a pressure of 0.5 atm.

11. A buffer solution is prepared by mixing 10 mL of 1.0 M CH_3COOH and 20 mL of 0.5 M CH_3COONa and then diluted to 100 mL with distilled water. If pK_a of CH_3COOH is 4.76, what is the pH of the buffer solution?

12. At a certain temperature and 2 atm pressure equilibrium constant (K_p) is 25 for the reaction

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

    Initially if we take 2 moles of each of the four gases and 2 moles of inert gas, what would be the equilibrium partial pressure of NO_2 in atm?

13. Find the pH of a 2 litre solution which is 0.1 M each with respect to CH_3COOH and $(CH_3OO)_2Ba$. ($K_a = 1.8 \times 10^{-5}$)

14. On addition of increasing amount of $AgNO_3$ to 0.1 M each of NaCl and NaBr in a solution, what % of Br^- ion gets precipitated when Cl^- ion starts precipitating?

    Given : K_{sp} (AgCl) = 1.0×10^{-10}; K_{sp} (AgBr) = 1×10^{-13}

15. What can be the maximum possible molarity of Co^{2+} ions in 0.1 M HCl saturated with H_2S ($K_a = 4 \times 10^{-21}$)? Given that K_{sp} for CoS is 2×10^{-21} and concentration of saturated H_2S = 0.1 M.

SOLUTIONS

1. **(20)** $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$K_p = P_{CO_2} = 0.82$ atm ;

$$n_{CO_2} = \frac{PV}{RT} = \frac{0.82 \times 20}{0.082 \times 1000} = 0.2 \text{ mole}$$

Mole of $CaCO_3$ dissociated $= n_{CO_2} = 0.2$

Amount dissociated $= 0.2 \times 100 = 20$ g

2. **(0.75)** $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

	$NH_3(g)$	$H_2S(g)$
Initial	1.0 atm	0 atm
At eqm.	$1.0 + x$ atm	x atm

Then $1.0 + x + x = 2x + 1.0 = 2.0$ (given)

$\Rightarrow x = 0.5$ atm

$p_{NH_3} = 1.0 + 0.5 = 1.5$ atm ; $p_{H_2S} = 0.5\ atm^2$

$K = p_{NH_3} \times p_{H_2S} = 1.5 \times 0.5\ atm^2 = 0.75\ atm^2$

3. **(10)** $M_1V_1 = M_2V_2$

$1 \times 0.10 = M_2 \times 100$

$M_2 = 0.001 = 10^{-3}$

$BOH(g)$	$\rightleftharpoons$	B^+	+	OH^-
C		0		0
$C(1-\alpha)$		$C\alpha$		$C\alpha$

$$K_b = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$K_b = C\alpha^2$ $\quad (\because 1 - \alpha \approx 1)$

$\alpha = \sqrt{K_b / C}$

$$[OH^-] = C\alpha = \sqrt{\frac{K_b}{C}} \times C = \sqrt{K_bC}$$

$= \sqrt{10^{-5} \times 10^{-3}} = 10^{-4}$

$\therefore pH + pOH = 14$

$\therefore pH = 14 - 4 = 10$

4. **(0.592)** Moles of $N_2 = \frac{28}{28} = 1$, Moles of $H_2 = \frac{6}{2} = 3$

Moles of H_2SO_4 required $= \frac{500 \times 1}{1000} = 0.5$

Moles of NH_3 neutralised by $H_2SO_4 = 1.0$

$\left(2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4\right)$

Hence 1 mole of NH_3 by the reaction between N_2 and H_2.

	N_2	+	$3H_2$	$\rightleftharpoons$	$2NH_3$
initial conc.	1		3		0
at equilibrium conc.	$1 - 0.5$		$3 - 0.5 \times 3$		1

$$K_c = \frac{1 \times 1}{0.5 \times (1.5)^3} = 0.592 \text{ mol}^{-2} L^2$$

5. **(4)** Hydrolysis of a salt is reverse reaction of acid base neutralization reaction.

$$\therefore K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{10^{-7}} = 10^{-7}$$

$$[OH^-] = h = C \times \sqrt{\frac{K_h}{C}} = \sqrt{C \times K_h}$$

$= \sqrt{10^{-8}} = 10^{-4}$

$\Rightarrow pOH^- = -\log[OH^-]$

$= -\log[10^{-4}] = 4$

6. **(6.93)** $C(s) + CO_2(g) \longrightarrow 2CO(g)$

Apply law of mass action,

$$K_P = \frac{(P_{CO})^2}{P_{CO_2}} \text{ or } 63 = \frac{(10P_{CO_2})^2}{P_{CO_2}}$$

(Given $K_P = 63$) and $P_{CO} = 10P_{CO_2}$

$$\text{or } 63 = \frac{100(P_{CO_2})^2}{P_{CO_2}} \text{ or } 63 = 100\ P_{CO_2}$$

$$P_{CO_2} = \frac{63}{100} = 0.63 \text{ atm}$$

$P_{CO} = 10P_{CO_2} = 10 \times 0.63 = 6.3$ atm

$P_{total} = P_{CO_2} + P_{CO} = 0.63 + 6.3 = 6.93$ atm

7. **(6.5)** $HCOONH_4$ is a salt of weak acid and weak base ;

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

$$\therefore pH = \frac{1}{2} \times 14 + \frac{1}{2} \times 3.8 - \frac{1}{2} \times 4.8 ; pH = 6.5$$

8. **(4)** $AB(g) \longrightarrow A(g) + B(g)$

Applying law of mass action

$$K_p = \frac{\alpha^2 p}{1 - \alpha^2} \quad (\text{given } p = 1 \text{ atm})$$

$$\therefore \frac{\alpha^2}{1-\alpha} = 1.6 \times 10^{-3} \Rightarrow \alpha^2 = 1.6 \times 10^{-3}$$

$(\because \alpha <<< 1)$

$\Rightarrow \alpha = \sqrt{1.6 \times 10^{-3}} \Rightarrow \alpha = 0.04$

% age dissociation = 4%.

9. **(8.22)** $CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$

Let acid be = V mL

V mL of 0.01 M CH_3COOH will require V mL of 0.01 M NaOH. But CH_3COONa formed will make solution alkaline due to hydrolysis.

$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$

$$[CH_3COONa] = \frac{0.01}{2} = 0.005 \text{ M}$$

Using equation for pH of salt of weak acid and strong base.

$$pH = 7 + \frac{pK_a}{2} + \frac{\log C}{2} = 7 + \frac{4.74}{2} + \frac{\log 0.005}{2}$$

$= 8.22$

10. (71)

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

	N_2O_4 (g)	$2NO_2$ (g)
Initial moles	1	0
Moles at eqm.	$(1-\alpha)$	2α

(α = degree of dissociation)

Total number of moles at equilibrium

$= (1-\alpha) + 2\alpha$

$= (1+\alpha)$

$$p_{N_2O_4} = \frac{(1-\alpha)}{(1+\alpha)} \times P$$

$$p_{NO_2} = \frac{2\alpha}{(1+\alpha)} \times P$$

$$K_P = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{\left(\frac{2\alpha}{(1+\alpha)} \times P\right)^2}{\left(\frac{1-\alpha}{1+\alpha}\right) \times P} = \frac{4\alpha^2 P}{1-\alpha^2}$$

Given, $K_P = 2$, $P = 0.5$ atm

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

$$= \frac{4\alpha^2 \times 0.5}{1-\alpha^2}$$

$\alpha = 0.707 \approx 0.71$

$\therefore$ Percentage dissociation $= 0.71 \times 100 = 71$

11. (4.76) Total volume = 100 mL

$$[\text{acid}] = 10\text{ mL} \times \frac{1.0}{100} = 0.1$$

$$[\text{salt}] = 20\text{ mL} \times \frac{0.5}{100} = 0.1$$

$$\text{pH of acidic buffer} = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$$= 4.76 + \log\frac{0.1}{0.1} = 4.76$$

12. (0.134)

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

	SO_2 (g)	NO_2 (g)	SO_3 (g)	NO (g)
Initial moles	2	2	2	2
at eqm.	2 – x	2 – x	2 + x	2 + x

$(\because Q_p < K_p)$

Total no. of moles of gases at equilibrium
$= 8 + 2 = 10$

$$K_p = \frac{P_{SO_3} \cdot P_{NO}}{P_{SO_2} \cdot P_{NO_2}}$$

$$\Rightarrow\ 25 = \frac{\left(\frac{2+x}{10} \times P\right)^2}{\left(\frac{2-x}{10} \times P\right)^2}$$

$$\Rightarrow\ 5 = \frac{2+x}{2-x};\ x = 1.33$$

$$\text{Partial Pressure of } NO_2 = \frac{2-x}{10} \times P_{total}$$

$$= \frac{2-1.33}{10} \times 2$$

13. (5.0)

$$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$

$pK_a = -\log(1.8 \times 10^{-5}) = 4.7447$

$[CH_3COO^-] = 2 \times [(CH_3COO)_2Ba] = 0.2$ M

$[CH_3COOH] = 0.1$ M

$$pH = 4.7447 + \log\frac{0.2}{0.1} = 5.046 \approx 5.0$$

14. (99.9) $[Ag^+]$ required for commencement of precipitation

$$\text{of AgCl} = \frac{K_{sp}(AgCl)}{[Cl^-]} = \frac{1.0 \times 10^{-10}}{0.1}$$

$$= 1.0 \times 10^{-9}\text{ M}$$

$[Br^-]$ remaining at this stage

$$= \frac{K_{sp}(AgBr)}{[Ag^+]} = \frac{1.0 \times 10^{-13}}{1.0 \times 10^{-9}} = 1.0 \times 10^{-4}\text{ M}$$

% of Br^- remaining unprecipitated

$$= \frac{1.0 \times 10^{-4}}{0.1} \times 100 = 0.1$$

% of Br^- precipitated $= 100 - 0.1 = 99.9$

15. (0.05) $K_a(H_2S) = 4 \times 10^{-21}$

$$= \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{0.1^2 \times [S^{2-}]}{0.1}$$

$$\Rightarrow [S^{2-}] = 4 \times 10^{-20}\text{ M}$$

$K_{sp}(CoS) = 2 \times 10^{-21} = [Co^{2+}]\,[S^{2-}]$

$= [Co^{2+}] \times 4 \times 10^{-20} \Rightarrow [Co^{2+}] = 0.05$ M