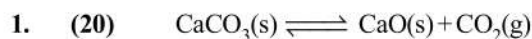


# Equilibrium

- Equilibrium constant  $K_p$  for the reaction  
 $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  is 0.82 atm at 727 °C.  
If 1 mole of  $\text{CaCO}_3$  is placed in a closed container of 20L and heated to this temperature, what amount of  $\text{CaCO}_3$  in grams would dissociate at equilibrium?
- An amount of solid  $\text{NH}_4\text{HS}$  is placed in a flask already containing ammonia gas at a certain temperature and 1.0 atm pressure. Ammonium hydrogen sulphide decomposes to yield  $\text{NH}_3$  and  $\text{H}_2\text{S}$  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  $\text{NH}_4\text{HS}$  decomposition at this temperature?
- 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  $1 \times 10^{-5}$ .
- 28 g  $\text{N}_2$  and 6.0 g of  $\text{H}_2$  are heated over catalyst in a closed one litre flask of 450 °C. The entire equilibrium mixture required 500 mL of 1.0 M  $\text{H}_2\text{SO}_4$  for neutralisation. Calculate the value of  $K_c$  in  $\text{L}^2 \text{mol}^2$  for the given reaction.  
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
- 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.
- For the reaction  $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$ ,  $K_p = 63$  atm at 1000 K. If at equilibrium :  $P_{\text{CO}} = 10 P_{\text{CO}_2}$ . Find the total pressure (atm) of the gases at equilibrium.
- The  $\text{p}K_a$  of  $\text{HCOOH}$  is 3.8 and  $\text{p}K_b$  of  $\text{NH}_3$  is 4.8, find the pH of aqueous solution of 1M  $\text{HCOONH}_4$ .
- In the reaction  $\text{AB}(\text{g}) \rightleftharpoons \text{A}(\text{g}) + \text{B}(\text{g})$  at 30° C,  $K_p$  for the dissociation equilibrium is  $1.6 \times 10^{-3}$  atm. If the total pressure at equilibrium is 1 atm, then calculate the percentage dissociation of AB.
- Calculate the pH at the equivalence point when a solution of 0.01 M  $\text{CH}_3\text{COOH}$  is titrated with a solution of 0.01 M NaOH.  $\text{p}K_a$  of  $\text{CH}_3\text{COOH}$  is 4.74.
- The value of  $K_p$  for the equilibrium reaction  
$$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$$
 is 2.  
Calculate the percentage dissociation of  $\text{N}_2\text{O}_4(\text{g})$  at a pressure of 0.5 atm.
- A buffer solution is prepared by mixing 10 mL of 1.0 M  $\text{CH}_3\text{COOH}$  and 20 mL of 0.5 M  $\text{CH}_3\text{COONa}$  and then diluted to 100 mL with distilled water. If  $\text{p}K_a$  of  $\text{CH}_3\text{COOH}$  is 4.76, what is the pH of the buffer solution?
- At a certain temperature and 2 atm pressure equilibrium constant ( $K_p$ ) is 25 for the reaction  
$$\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})$$
  
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  $\text{NO}_2$  in atm?
- Find the pH of a 2 litre solution which is 0.1 M each with respect to  $\text{CH}_3\text{COOH}$  and  $(\text{CH}_3\text{COO})_2\text{Ba}$ . ( $K_a = 1.8 \times 10^{-5}$ )
- On addition of increasing amount of  $\text{AgNO}_3$  to 0.1 M each of  $\text{NaCl}$  and  $\text{NaBr}$  in a solution, what % of  $\text{Br}^-$  ion gets precipitated when  $\text{Cl}^-$  ion starts precipitating?  
Given :  $K_{sp}(\text{AgCl}) = 1.0 \times 10^{-10}$ ;  $K_{sp}(\text{AgBr}) = 1 \times 10^{-13}$
- What can be the maximum possible molarity of  $\text{Co}^{2+}$  ions in 0.1 M  $\text{HCl}$  saturated with  $\text{H}_2\text{S}$  ( $K_a = 4 \times 10^{-21}$ )? Given that  $K_{sp}$  for  $\text{CoS}$  is  $2 \times 10^{-21}$  and concentration of saturated  $\text{H}_2\text{S} = 0.1$  M.

# SOLUTIONS

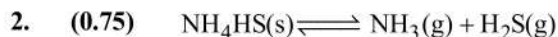


$$K_p = P_{\text{CO}_2} = 0.82 \text{ atm};$$

$$n_{\text{CO}_2} = \frac{PV}{RT} = \frac{0.82 \times 20}{0.082 \times 1000} = 0.2 \text{ mole}$$

$$\text{Mole of CaCO}_3 \text{ dissociated} = n_{\text{CO}_2} = 0.2$$

$$\text{Amount dissociated} = 0.2 \times 100 = 20 \text{ g}$$



Initial	1.0 atm	0 atm
At eqm.	1.0 + x atm	x atm

$$\text{Then } 1.0 + x + x = 2x + 1.0 = 2.0 \text{ (given)}$$

$$\Rightarrow x = 0.5 \text{ atm}$$

$$P_{\text{NH}_3} = 1.0 + 0.5 = 1.5 \text{ atm}; \quad P_{\text{H}_2\text{S}} = 0.5 \text{ atm}^2$$

$$K = P_{\text{NH}_3} \times P_{\text{H}_2\text{S}} = 1.5 \times 0.5 \text{ atm}^2 = 0.75 \text{ atm}^2$$



$$1 \times 0.10 = M_2 \times 100$$

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



C	0	0
C(1 - α)	Cα	Cα

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

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

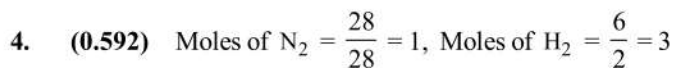
$$\alpha = \sqrt{K_b / C}$$

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

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

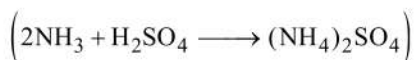
$$\therefore \text{pH} + \text{pOH} = 14$$

$$\therefore \text{pH} = 14 - 4 = 10$$

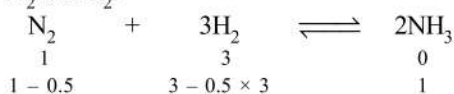


$$\text{Moles of H}_2\text{SO}_4 \text{ required} = \frac{500 \times 1}{1000} = 0.5$$

$$\text{Moles of NH}_3 \text{ neutralised by H}_2\text{SO}_4 = 1.0$$



Hence 1 mole of  $\text{NH}_3$  by the reaction between  $\text{N}_2$  and  $\text{H}_2$ .



initial conc.  
at equilibrium  
conc.

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

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

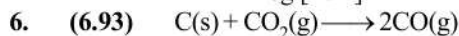
$$\therefore K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{10^{-7}} = 10^{-7}$$

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

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

$$\Rightarrow \text{pOH} = -\log [\text{OH}^-]$$

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



Apply law of mass action,

$$K_p = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}} \text{ or } 63 = \frac{(10P_{\text{CO}_2})^2}{P_{\text{CO}_2}}$$

$$\text{(Given } K_p = 63) \text{ and } P_{\text{CO}} = 10P_{\text{CO}_2}$$

$$\text{or } 63 = \frac{100(P_{\text{CO}_2})^2}{P_{\text{CO}_2}} \text{ or } 63 = 100 P_{\text{CO}_2}$$

$$P_{\text{CO}_2} = \frac{63}{100} = 0.63 \text{ atm}$$

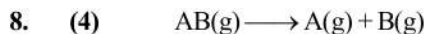
$$P_{\text{CO}} = 10P_{\text{CO}_2} = 10 \times 0.63 = 6.3 \text{ atm}$$

$$P_{\text{total}} = P_{\text{CO}_2} + P_{\text{CO}} = 0.63 + 6.3 = 6.93 \text{ atm}$$

7. (6.5)  $\text{HCOONH}_4$  is a salt of weak acid and weak base ;

$$\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$

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



Applying law of mass action

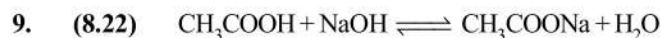
$$K_p = \frac{\alpha^2 p}{1-\alpha^2} \quad (\text{given } p = 1 \text{ atm})$$

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

$$(\because \alpha \ll 1)$$

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

% age dissociation = 4%.



Let acid be = V mL

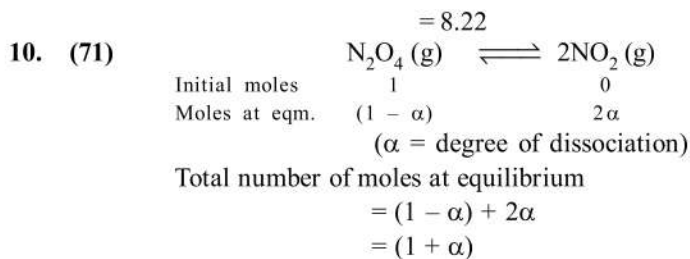
V mL of 0.01 M  $\text{CH}_3\text{COOH}$  will require V mL of 0.01 M NaOH. But  $\text{CH}_3\text{COONa}$  formed will make solution alkaline due to hydrolysis.



$$[\text{CH}_3\text{COONa}] = \frac{0.01}{2} = 0.005 \text{ M}$$

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

$$\text{pH} = 7 + \frac{\text{p}K_a}{2} + \frac{\log C}{2} = 7 + \frac{4.74}{2} + \frac{\log 0.005}{2}$$



$$P_{\text{N}_2\text{O}_4} = \frac{(1 - \alpha)}{(1 + \alpha)} \times P$$

$$P_{\text{NO}_2} = \frac{2\alpha}{(1 + \alpha)} \times P$$

$$K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{\left(\frac{2\alpha}{(1 + \alpha)} \times P\right)^2}{\left(\frac{1 - \alpha}{(1 + \alpha)} \times P\right)} = \frac{4\alpha^2 P}{1 - \alpha^2}$$

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

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

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

$$\alpha = 0.707 \approx 0.71$$

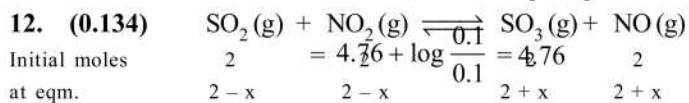
$$\therefore \text{Percentage dissociation} = 0.71 \times 100 = 71$$



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

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

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



$$(\because Q_p < K_p)$$

Total no. of moles of gases at equilibrium

$$= 8 + 2 = 10$$

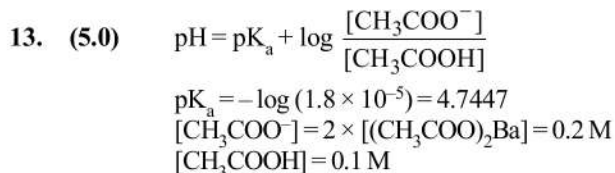
$$K_p = \frac{P_{\text{SO}_3} \cdot P_{\text{NO}}}{P_{\text{SO}_2} \cdot P_{\text{NO}_2}}$$

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

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

Partial Pressure of  $\text{NO}_2 = \frac{2-x}{10} \times P_{\text{total}}$

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



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



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

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

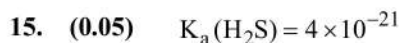
$[\text{Br}^-]$  remaining at this stage

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

% of  $\text{Br}^-$  remaining unprecipitated

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

$$\text{% of Br}^- \text{ precipitated} = 100 - 0.1 = 99.9$$



$$= \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]} = \frac{0.1^2 \times [\text{S}^{2-}]}{0.1}$$

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

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

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