

**Q1.** When a sample of radioactive sugar is added to a saturated solution of ordinary sugar it is observed that the solution and rest of the undissolved sugar also show radioactivity.  
 (a) What conclusion do you draw from the observation?  
 (b) What should be the effect of addition of radioactive sugar on the concentration of saturated solution.

**Q2.** The equilibrium constant expression for a gas reaction is

$$K_c = \frac{[\text{NH}_3]^4 [\text{O}_2]^5}{[\text{NO}]^4 [\text{H}_2\text{O}]^6}$$

Write the balanced chemical equation corresponding to this expression.

**Q3.** Mention the condition when  $K_p = K_c = K_x$  for a reaction.

**Q4.** A saturated solution is in equilibrium with a large amount of undissolved solid solute. Tell what will happen to the concentration when:  
 (a) More solute is added.  
 (b) A few millilitres of the saturated solution are removed.  
 (c) A few millilitres of similar type of unsaturated solution are added.  
 (d) A few millilitres of pure solvent are added to the saturated solution.

**Q5.** Which of the following reactions represent homogeneous equilibria and which involve heterogeneous equilibria?

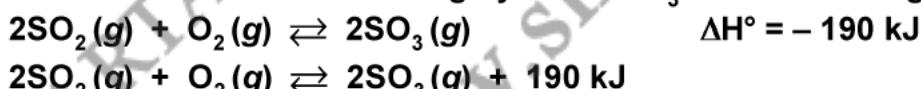
(a) $2\text{N}_2\text{O}(g) \rightleftharpoons 2\text{N}_2(g) + \text{O}_2(g)$	(b) $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$
(c) $2\text{Cu}(\text{NO}_3)_2(\text{s}) \rightleftharpoons 2\text{CuO}(\text{s}) + 4\text{NO}_2(g) + \text{O}_2(g)$	
(d) $\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOH}(\text{aq}) + \text{C}_2\text{H}_5\text{OH}(\text{aq})$	
(e) $\text{Fe}^{3+}(\text{aq}) + 3\text{OH}(\text{aq}) \rightleftharpoons \text{Fe}(\text{OH})_3(\text{s})$	

**Q6.** Give two examples of chemical reactions for which  $K_p = K_c = K_x$ . Justify your answer.

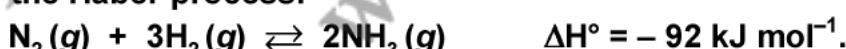
**Q7.** Find a relation between equilibrium constants of the following reaction:

(a)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$       (b)  $\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$

**Q8.** What are the factors that will favour a high yield of  $\text{SO}_3$  in the following reaction?



**Q9.** Apply the Le Chatelier's principle to know the factors which would favour a high yield of ammonia in the Haber process:



**Q10.** The solution of bromine in water is brown and has weak acidic character because of the following equilibrium:



In solution  $\text{Br}_2(\text{aq})$  is brown,  $\text{Br}^-(\text{aq})$  is colourless and  $\text{HBrO}(\text{aq})$  (hypobromic acid) is also colourless.

Explain the following observations:

- (a) When sodium hydroxide is added to the solution, the solution becomes colourless.
- (b) The colour returns when hydrochloric acid is added to the colourless solution of experiment (i).

**Q11.** Hydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction.



- (a) Write an expression for  $K_p$  for the above reaction.
- (b) How will the value of  $K_p$  and composition of equilibrium mixture be affected by
  - (i) increasing the pressure
  - (ii) increasing the temperature
  - (iii) using a catalyst.

**Q12.** Which of the following reactions will get affected by increase of pressure? Also mention, whether change will cause the reaction to go into the right or left direction?

(a) $\text{CH}_4(\text{g}) + 2\text{S}_2(\text{g}) \rightleftharpoons \text{CS}_2(\text{g}) + 2\text{H}_2\text{S}(\text{g})$	(b) $\text{CO}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons 2\text{CO}(\text{g})$
(c) $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$	(d) $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{C}_2\text{H}_6(\text{g})$

**Q13.** 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 rates of evaporation and condensation change initially?
- (c) What happens when equilibrium is restored finally and what will be the final vapour pressure?

**Q14.** In the reaction  $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$  the concentrations of hydrogen, carbon monoxide and methanol become constant at equilibrium. What will happen if

- (a) volume of the reaction vessel containing reactants and products is suddenly reduced to half.
- (b) the partial pressure of hydrogen is suddenly doubled.
- (c) an inert gas is added to the system.

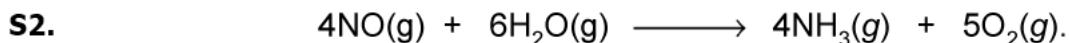
**Q15.** Write the expression for the equilibrium constant,  $K_c$  for each of the following reactions:

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

**Q16.** Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression?

**S1.** (a) The presence of radioactive sugar in the solution as well as in rest of the undissolved solid suggests that the process of dissolution and separation of sugar takes place at equilibrium. This equilibrium is **dynamic**.

(b) Addition of radioactive sugar will not change the concentration of saturated solution of sugar.



**S3.** For a reaction  $K_p = K_c = K_x$  when  $\Delta v_{\text{gas}} = 0$ , that is  $(m + n)$  gas =  $(a + b)$  gas. This implies that the sum of the stoichiometric coefficients of the gaseous products is equal to the sum of the stoichiometric coefficients of gaseous reactants.

**S4.** (a) Addition of more solute will not change the concentration of a saturated solution. But the total mass of the undissolved solid solute will be increased.

(b) Removal of a few millilitres of the solution will not cause any change in the concentration of solution. But volume of the solution will decrease.

(c) Addition of a few millilitres of unsaturated solution will dilute the saturated solution. Thus initially the resulting solution will become unsaturated. But more solid will dissolve and finally the solution will become saturated.

(d) Addition of a few millilitres of pure solvent will initially lower the concentration. This will make the solution unsaturated. But further dissolution of solid will make the solution saturated (provided the solid was in excess). Now this will cause a decrease in the mass of undissolved solid.

**S5.** (A) Homogeneous reactions: (a), (b), (d).

(b) Heterogeneous reactions: (c), (e).

**S6.** (a) For the reaction  $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$

$$K_p = K_c = K_x$$

because

$$\Delta v = 2 - (1 + 1) = 2 - 2 = 0.$$

(b) For the reaction  $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{CO}_2\text{(g)}$

$$K_p = K_c = K_x$$

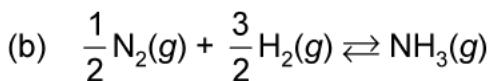
because

$$\Delta v = (1 + 1) - (1 + 1) = 2 - 2 = 0.$$

**S7.** For the reactions

(a)  $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$

$$K_c (i) = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$



$$K_c(ii) = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2} [\text{H}_2]^{3/2}}$$

Right hand side of equation (ii) may be written as:

$$\text{R.H.S.} = \left\{ \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \right\}^{1/2} = \{K_c(i)\}^{1/2}$$

Therefore,  $K_c(ii) = \{K_c(i)\}^{1/2}$

That is, when the chemical equation is multiplied by a factor, the equilibrium constant is raised to the power by the same factor.

**S8.** The forward reaction is exothermic and the mole of product is less than that of reactants. According to the Le Chatelier's principle the yield of  $\text{SO}_3$  can be increased by

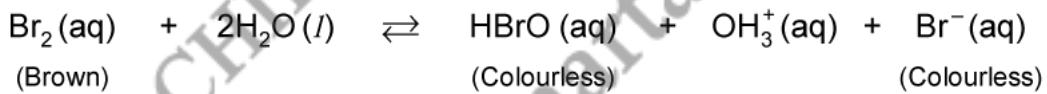
(a) Low temperature (b) High pressure  
(c) Adding more  $\text{SO}_2$  and  $\text{O}_2$  (d) Removing  $\text{SO}_3$  from the reaction mixture.



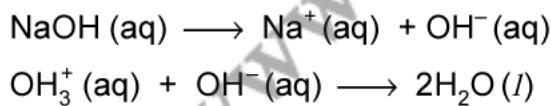
This reaction is exothermic in the forward direction and the number of moles on the right hand side is less than that on the left hand side. Application of Le Chatelier's principle suggests that the higher yield of ammonia is favoured by

(a) Low temperature  
(b) High pressure  
(c) Adding more nitrogen and hydrogen to the reaction mixture  
(d) Removing ammonia from the reaction mixture.

**S10.** It is given that

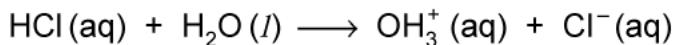


(a) When sodium hydroxide ( $\text{NaOH}$ ) is added to the above system at equilibrium the  $\text{OH}^-$  ions of  $\text{NaOH}$  combine with  $\text{OH}_3^+$  ions to form unionized water



Thus, the addition of  $\text{NaOH}$  removes  $\text{OH}_3^+$  ions from the solution. Now, according to the Le Chatelier's principle removal of  $\text{OH}_3^+$  ions shifts the reaction equilibrium to the **right** where  $\text{OH}_3^+$  ions are formed. This means more of brown  $\text{Br}_2$  is converted into **colourless products**  $\text{HBrO}$ ,  $\text{OH}_3^+$  and  $\text{Br}^-$ . Therefore, addition of sufficient  $\text{NaOH}$  makes the solution colourless.

(b) When hydrochloric acid (HCl) is added to the solution, hydronium ions ( $\text{OH}_3^+$ ) are produced.



Thus, addition of HCl increases the concentration of  $\text{OH}_3^+$  ions in the solution. Now, according to the Le Chatelier's principle increase of  $\text{OH}_3^+$  ions shifts the reaction equilibrium to the left so that colourless  $\text{OH}_3^+$ ,  $\text{Br}^-$  and  $\text{HBrO}$  combine to form brown  $\text{Br}_2$ .

**S11.** For the reaction  $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$ ;  $\Delta H > 0$  (endothermic) and  $\Delta v = (1 + 3) - (1 + 1) = 4 - 2 = 2$

(a) 
$$K_p = \frac{(p\text{CO}) \times (p\text{H}_2)^2}{(p\text{CH}_4) \times p(\text{H}_2\text{O})}$$

(b) **Change of  $K_p$  and composition of equilibrium mixture**

$K_p$  is independent of total pressure ( $\Delta G^\ominus = -RT \ln K_p$ ).

- (i) Increase of pressure will cause the reaction to proceed in the reverse direction. Therefore, the concentrations of reactants will **increase** and the concentrations of the products will **decrease**.
- (ii) The forward reaction is endothermic. Therefore, increase of temperature will increase the concentrations of the products. This will increase the value of  $K_p$ .
- (iii) Use of the catalyst will not affect the value of  $K_p$ . It will also not affect the concentration of equilibrium mixture.

**S12.** (a) For the reaction  $\text{CH}_4(\text{g}) + 2\text{S}_2(\text{g}) \rightleftharpoons \text{CS}_2(\text{g}) + 2\text{H}_2\text{S}(\text{g})$

$$\Delta v = (1 + 2) - (1 + 2) = 3 - 3 = 0$$

The equilibrium will not be affected by change of pressure.

(b) For the reaction  $\text{CO}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons 2\text{CO}(\text{g})$

$$\Delta v = 2 - 1 = 1$$

Increase of pressure will cause the reaction to proceed in the reverse direction (towards reactant side).

(c) For the reaction  $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

$$\Delta v = (4 + 6) - (4 + 5) = 10 - 9 = 1$$

Increase of pressure will cause the reaction to proceed in reverse direction (towards left).

(d) For the reaction  $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{C}_2\text{H}_6(\text{g})$

$$\Delta v = (1 - (1 + 1)) = -1$$

Increase of pressure will cause the reaction to proceed in the forward direction (towards right).

**S13.** (a) If the volume of the container is suddenly increased, then the vapour pressure would decrease initially. This is because the amount of vapour remains the same, but the volume increases suddenly. As a result, the same amount of vapour is distributed in a larger volume.

(b) Since the temperature is constant, the rate of evaporation also remains constant. When the volume of the container is increased, the density of the vapour phase decreases. As a result, the rate of collisions of the vapour particles also decreases. Hence, the rate of condensation decreases initially.

(c) When equilibrium is restored finally, the rate of evaporation becomes equal to the rate of condensation. In this case, only the volume changes while the temperature remains constant. The vapour pressure depends on temperature and not on volume. Hence, the final vapour pressure will be equal to the original vapour pressure of the system.

**S14.** In the reaction  $\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$ , the volume on the reactant side is more than the volume on the product side. Therefore,

- (a) Reduction of volume will cause the formation of more product.
- (b) Increase of partial pressure of hydrogen (reactant) will cause the reaction to proceed in the forward direction and more  $\text{CH}_3\text{OH}$  will be formed.
- (c) Addition of an inert gas will favour the formation of reactants.

**S15.** (i) 
$$K_c = \frac{[\text{NO}(g)]^2 [\text{Cl}_2(g)]}{[\text{NOCl}(g)]^2}$$

(ii) 
$$K_c = \frac{[\text{CuO}(s)]^2 [\text{NO}_2(g)]^4 [\text{O}_2(g)]}{[\text{Cu}(\text{NO}_3)_2(s)]^2}$$
  

$$= [\text{NO}_2(g)]^4 [\text{O}_2(g)]$$

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

(iv) 
$$K_c = \frac{[\text{Fe}(\text{OH})_3(s)]}{[\text{Fe}^{3+}(aq)][\text{OH}^-(aq)]^3}$$
  

$$= \frac{1}{[\text{Fe}^{3+}(aq)][\text{OH}^-(aq)]^3}$$

(v) 
$$K_c = \frac{[\text{IF}_5(I)]^2}{[\text{I}_2(s)][\text{F}_2(g)]^5} = \frac{1}{[\text{F}_2(g)]^5}$$

**S16.** [Pure liquid] or [Pure solid]

$$= \frac{\text{No. of moles}}{\text{Volume}} = \frac{\text{Mass}}{\text{Mol. mass} \times \text{Volume}}$$

$$= \frac{\text{Mass}}{\text{Volume}} \times \frac{1}{\text{Mol. mass}} = \frac{\text{Density}}{\text{Mol. mass}}$$

As density of a pure liquid or pure solid is constant at constant temperature and molecular mass is also constant, therefore, their molar concentrations are constant and are independent of the amount of the substance present. Hence, pure liquids and solids are ignored while writing equilibrium constant expression.

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Date: 16/10/2021

**Q1.** In an aqueous solutions  $[\text{OH}_3^+] = 6.2 \times 10^{-4} \text{ mol L}^{-1}$ . Calculate  $[\text{OH}^-]$  when  $K_w = 10^{-14}$ . 1

**Q2.** Calculate the pH of the following solutions: 2g of TIOH dissolved in water to give 2 litre of the solution. 1

**Q3.** The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion it. 1

**Q4.** The concentration of hydrogen ion in a sample of soft drink is  $3.8 \times 10^{-3} \text{ M}$ . What is its pH? 1

**Q5.** Write the conjugate acids for the following Bronsted bases: 1

$\text{NH}_2^-$ ,  $\text{NH}_3$  and  $\text{HCOO}^-$ .

**Q6.** What will be the conjugate bases for the Bronsted acids:  $\text{HF}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HCO}_3^-$ . 1

**Q7.** Which of the followings are Lewis acids? 1

$\text{H}_2\text{O}$ ,  $\text{BF}_3$ ,  $\text{H}^+$ ,  $\text{NH}_4^-$ .

**Q8.** The pH of a solution is 4.6 at 298 K. What is the pOH of the solution? Is this solution acidic, alkaline or neutral? 1

**Q9.** At 273 K the ionic product of water is  $5.0 \times 10^{-16}$  and at 298 K the value is  $1.0 \times 10^{-11}$ . From the given data predict whether the ionization of water into hydrogen and hydroxide ions is exothermic or endothermic? 1

**Q10.** Calculate the hydrogen ion concentration when 3.2 g hydrogen chloride is dissolved in 1.00 L of water at 298 K. What is  $[\text{OH}]$ ? 1

**Q11.** Write the formula of conjugate base of each of the following acids : 2

(a) $\text{OH}_3^+$	(b) $\text{NH}_4^+$	(c) $\text{H}_2\text{PO}_4^-$
(d) $\text{CH}_3\text{NH}_3^+$	(f) $\text{HSO}_4^-$	(g) $\text{H}_3\text{PO}_4$

**Q12.** Select the lowry-Bronsted acids and bases from the following: 2

$\text{NH}_3$ ,  $\text{NCN}$ ,  $\text{HCl}$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{OH}^-$ ,  $\text{HSO}_4^-$ ,  $\text{HCO}_3^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{Al(OH)}_2^+$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{NH}_4^+$ ,  $\text{Al(OH)}_2^+$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HS}^-$ ,  $\text{CH}_3\text{NH}_3^+$ ,  $\text{Mg(OH)}^+$ .

**Q13.** Assuming complete dissociation calculate the pH of the following solutions: (a) 0.003 M HCl (b) 0.005 M NaOH. 2

**Q14.** Assuming complete dissociation calculate the pH of the following solutions: (a) 0.002 M HBr (b) 0.002 M KOH. 2

**Q15.** A solution is prepared by dissolving 3.2 g of hydrogen chloride (HCl) in 1.0 L of water. Calculate the molarity,  $[\text{OH}_3^+]$  and pH of the solution. 2

**Q16.** Interpret the result when pH of a solution is 4.2. 2

**Q17.** The pH of solution is 8. What is the value of  $[\text{OH}]$ ? is this solution acidic? 2

**Q18.** Compute the pH of  $10^{-8}$  M HCl solution at 298 K. 2

**Q19.** Calculate  $[\text{OH}^-]$  and pOH of a solution which has pH = 4.75 at K; take  $pK_w = 14$ . 2

**Q20.** Calculate the pH of an aqueous solution if hydrogen ion concentration is  $3 \times 10^{-5}$  mol $^{-1}$ . 2  
What is the concentration of hydroxide ions in the solution? Is the solution acidic, basic (alkaline) or neutral?

**Q21.** The pH 0.1 M HCN solution is 5.2. Calculate the value of  $K_a$  of this acid. 2

**Q22.** Calculate the pH of the solution obtained when 0.2 molar solution of ammonia is exactly neutralized by calculated quantity of HCl,  $K_b$  ( $\text{NH}_4\text{OH}$ ) =  $1.8 \times 10^{-5}$ . 2

**Q23.** Calculate of pH of a 0.015 M solution of  $\text{NH}_4\text{Cl}$ . For  $\text{NH}_4\text{OH}$ ,  $K_b = 1.8 \times 10^{-5}$ . 2

**Q24.** A sample of 0.561 g KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxide ions. What is its pH? 2

**Q25.** Ionic product of water at 310 K is  $2.7 \times 10^{-14}$ . What is the pH of Neutral water at this temperature? 2

**Q26.** The pH of 0.1 M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution. 2

**Q27.** The pH of a given solution at 373 K is 7. Tell whether the solution is neutral, acidic or alkaline. It is given  $K_w$  at 100°C is 55 times its value at 25°C. 2

**Q28.** The pH of 0.3 molar solution of ammonium chloride is 5. What is the dissociation constant of  $\text{NH}_3$ ? 2

**Q29.** What is meant by the conjugate acid-base pair? Find the conjugate acid-base for the following species: 2  
 $\text{HNO}_2$ ,  $\text{CN}^-$ ,  $\text{HClO}_4$ ,  $\text{F}^-$ ,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{S}^{2-}$ .

**Q30.** Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base: 2  
(a)  $\text{OH}^-$       (b)  $\text{F}^-$       (c)  $\text{H}^+$       (d)  $\text{BCl}_3$

**Q31.** The ionization constants of HF,  $\text{HCOOH}$  and HCN at 298 K are  $6.8 \times 10^{-4}$ ,  $1.8 \times 10^{-4}$  and  $4.8 \times 10^{-9}$  respectively. Calculate the ionization constants of the corresponding conjugate base. 2

**Q32.** Compute the concentration of  $\text{OH}^-$  ions in a solution when  $[\text{OH}_3^+] = 10^{-2}$  mol L $^{-1}$ ,  $K_w = 10^{-14}$ . 2

**Q33.** Assuming complete dissociation, calculate the pH of the following solutions: 2  
(a) 0.002 M HBr      (b) 0.002 M KOH

**Q34.** Assuming complete dissociation, calculate the pH of the following solutions: 2  
(a) 0.003 M HCl      (b) 0.005 M NaOH

**Q35.** The ionization of acetic acid is  $1.74 \times 10^{-5}$ . Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH. 2

**Q36.** Calculate the hydrogen ion concentraton in the following biological fluids whose pH are given below: 2  
(a) Human muscle-fluid 6.83      (b) Human stomach fluid 1.2

**Q37. Calculate the hydrogen ion concentraton in the following biological fluids whose pH are given below:**

**(a) Human blood 7.38**

**(b) Human saliva 6.4**

**Q38. Calculate the pH of the resultant mixture of 10 mL of 0.01 M  $\text{H}_2\text{SO}_4$  + 10 mL of 0.01 M  $\text{Ca}(\text{OH})_2$ . 2**

**Q39. Calculate the pH of the resultant mixture of 10 mL of 0.2 M  $\text{Ca(OH)}_2$  + 25 mL of 0.1 M HCl. 2**

**Q40. Calculate the pH of the resultant mixture of 10 mL of 0.1 M  $\text{H}_2\text{SO}_4$  + 10 mL of 0.1 M KOH. 2**

**Q41.** Find  $[\text{OH}^-]$  and  $[\text{H}^+]$  in a solution which is prepared by dissolving 0.28 g of potassium hydroxide in 1.00 L of water at 25°C.

**Q42.** A solution prepared by dissolving 0.28 g of potassium hydroxide (KOH) in 1.00 L water at 298 K. Calculate the molarity,  $[\text{OH}^-]$ ,  $[\text{OH}_3^+]$  and pH of the solution.

(Take  $K_w = 1.0 \times 10^{-14}$ )

**Q43.** The degree of dissociation of water is  $1.8 \times 10^{-9}$  at 298 K. Calculate the ionization constant and ionic product of water at 298 K. 3

Q44. Complete the following by writing the formula of the correct conjugate base or acid. 3

(a) Acid 1 + Base 2  $\rightleftharpoons$  Acid 2 + ..... (b)  $\text{CH}_3\text{COOH} + \dots \rightleftharpoons \text{OH}^- + \text{CH}_3\text{COO}^-$

(c)  $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{OH}_3^+ + \dots$  (d)  $\text{H}_2\text{O} + \text{CN}^- \rightleftharpoons \text{HCN} + \dots$

(e)  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$  (f)  $\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-$

$$(c) \text{H}_2\text{S} \rightarrow \text{S}^\ddagger + \text{H}_2$$

$$(g) \dots + H_2O \rightleftharpoons OH_3^- OH^- \quad (h) H_2O + \dots \rightleftharpoons H_2CO_3^- + OH^-$$

(i)  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightleftharpoons \dots + \text{HSO}_4^-$

Q45. How many moles of  $\text{Ca}(\text{OH})_2$  must be dissolved to produce 250 mL of an aqueous solution of pH 10.65? Assume complete dissociation. 3

**Q46.**  $K_a$  for butyric acid is  $2 \times 10^{-5}$ . Calculate pH and hydroxide ion concentration of 0.2 M aqueous solution of sodium butyrate.

**Q47. What is the pH of a 1.0 M solution of acetic acid? To what volume must one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value?**

$$K_a = 1.8 \times 10^{-5}.$$

**Q48.** Calculate the pH of 0.20 M solution of methylamine ( $\text{CH}_3\text{NH}_2$ ) whose ionization constant is  $4.4 \times 10^{-5}$  at 298 K.

Q49. Calculate the pH of 0.1 M periodic acid ( $\text{HIO}_4$ ).  $K_a$  for the acid is  $2.3 \times 10^{-2}$  at 298 K. 3

Q50. When 0.1 M acetic acid ionizes the equilibrium is established at 298 K as

$$\text{CH}_3\text{COOH} \text{ (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{OH}^+ \text{ (aq)} + \text{CH}_3\text{COO}^- \text{ (aq)}$$

The ionization constant of the acid is  $1.82 \times 10^{-5}$  at 298 K. Compute  $\alpha$ ,  $[\text{OH}_3^+]$ , and pH. What is the concentration of acetate in the solution?

**Q51. What is the pH at the equivalence point when a solution 0.2 M HF is titrated with a solution of 0.2 M NaOH? The dissociation constant of HF is  $3.5 \times 10^{-4}$ .**

Q52. When 0.20 M acetic acid is neutralized with 0.20 M NaOH in 0.50 L of water the resulting solution is slightly alkaline. Calculate the pH of the resulting solution.  $K_a$  of acetic acid is  $1.8 \times 10^{-5}$ .

**Q53. The ionization constant of phenol is  $1.0 \times 10^{-10}$ . What is the concentration of phenate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01 M in sodium phenate?** 3

**Q54. Calcium lactate is a salt of a weak organic acid and represented as  $\text{Ca}(\text{Lac})_2$ . A saturated solution of  $\text{Ca}(\text{Lac})_2$  contains 0.13 mol of this salt in 0.50 L solution. The pOH of this solution is 5.60. Assuming a complete dissociation of the salt, calculate the  $K_a$  of lactic acid.** 3

**Q55. The first ionization constant of  $\text{H}_2\text{S}$  is  $9.1 \times 10^{-8}$ . Calculate the concentration of  $\text{HS}^-$  ion in its 0.1 M solution and how will this concentration be affected if the solution is 0.1 M in HCl also. If the second dissociation constant of  $\text{H}_2\text{S}$  is  $1.2 \times 10^{-13}$ , calculate the concentration of  $\text{S}^{2-}$  under both conditions.** 3

**Q56. Calculate the pH of the following solutions:** 3

- (a) 0.3 g of  $\text{Ca}(\text{OH})_2$  dissolved in water to give 500 mL of the solution.
- (b) 0.3 g of NaOH dissolved in water to give 200 mL of the solution.
- (c) 1 mL of 13.6 M HCl diluted with water to give 1 litre of the solution.

**Q57. What is the pH of 0.001 M aniline solution? The ionization constant of aniline is  $4.27 \times 10^{-10}$ . Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.** 3

**Q58. The ionization constant of dimethylamine is  $5.4 \times 10^{-4}$ . Calculate its degree of ionization in its 0.02 M solution. What percentage of dimethylamine is ionized if the solution is also 0.1 M NaOH?** 3

**Q59. The ionization constant of propanoic acid is  $1.32 \times 10^{-5}$ . Calculate the degree of ionization of the acid in its 0.05 M solution and also is pH. What will be its degree of ionization if the solution is 0.01 M in HCl also?** 3

Name : .....

Total Marks = 126

Time : 04:17

Date: 16/10/2021

**S1.** we know that

$$K_w = [\text{OH}_3^+] [\text{OH}^-]$$

1

$$[\text{OH}^-] = \frac{K_w}{[\text{OH}_3^+]} = \frac{10^{-14}}{6.2 \times 10^{-4}} = 1.6 \times 10^{-11} \text{ mol L}^{-1}$$

**S2.**

$$\text{Mole conc. of TIOH} = \frac{2 \text{ g}}{221 \text{ g mol}^{-1}} \times \frac{1}{2 \text{ L}} = 4.25 \times 10^{-3} \text{ M}$$

1

$$[\text{OH}^-] = [\text{TIOH}] = 4.25 \times 10^{-3} \text{ M}$$

$$[\text{H}^+] = 10^{-14} / (4.25 \times 10^{-3}) = 2.21 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log (2.21 \times 10^{-12})$$

$$= 12 - (0.3424) = 11.66.$$

**S3.**

$$\text{pH} = -\log [\text{H}^+]$$

1

or

$$\log [\text{H}^+] = -\text{pH} = -3.76 = \bar{4.24}$$

∴

$$[\text{H}^+] = \text{Antilog } \bar{4.25} = 1.738 \times 10^{-4} \text{ M}$$

$$= 1.74 \times 10^{-4} \text{ M.}$$

**S4.**

$$\text{pH} = -\log [\text{H}^+] = -\log (3.8 \times 10^{-3})$$

1

$$= -\log 3.8 + 3 = 3 - 0.5798$$

$$= 2.4202 = 2.42.$$

**S5.** A conjugate acid of a base is formed by gain of a proton ( $\text{H}^+$ ) by the base.

1

∴ The conjugated acids of the given bases are  $\text{NH}_3$ ,  $\text{NH}_4^+$ ,  $\text{HCOOH}$  respectively

**S6.** A conjugate base of an acid is formed by loss of  $\text{H}^+$  by the acid.

1

∴ Conjugate bases of the given acids will be  $\text{F}^-$ ,  $\text{HSO}_4^-$ ,  $\text{CO}_3^{2-}$  respectively.

**S7.**  $\text{BF}_3$ ,  $\text{H}^+$  and  $\text{NH}_4^+$ .

1

**S8.**  $\text{pH} + \text{pOH} = \text{p}K_w = 14$  at 298 K

1

$$\therefore \text{pOH} = \text{p}K_w - \text{pH} = 14 - 4.6 = 9.4$$

The given solution is acidic because  $\text{pH} = 4.6$  and thus  $[\text{H}^+] > 10^{-7}$

**S9.**  $K_w = 5.0 \times 10^{-16}$  at 273 K

1

$$K_w = 1.0 \times 10^{-14} \text{ at 298 K}$$

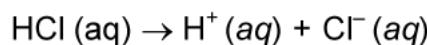
Since the value of  $K_w$  at a higher temperature is largest than its value at a lower temperature, the ionization of water into  $H^+$  and  $OH^-$  ions is an endothermic process.

**S10.**

$$\text{Molarity of HCl (aq)} = \frac{\text{Mole of HCl}}{\text{Volume of solution}}$$

$$= \frac{3.2 \text{ g}}{36.5 \text{ g mol}^{-1}} \times \frac{1}{1.00 \text{ L}} = 0.0876 \text{ mol L}^{-1}$$

1



$$\therefore [\text{H}^+] = \text{Molarity of HCl (aq)} = 0.0876 \text{ mol L}^{-1}$$

$$\text{Now, } [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14}}{0.0876} = 1.14 \times 10^{-13}$$

**S11.** A base has proton less than its conjugate acid

2



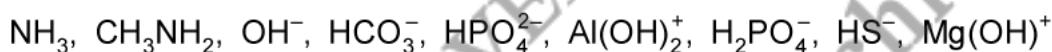
- (a)  $\text{OH}_3^+ \rightleftharpoons \text{H}^+ + \text{H}_2\text{O}$
- (b)  $\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3$
- (c)  $\text{N}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$
- (d)  $\text{CH}_3\text{NH}_3^+ \rightleftharpoons \text{H}^+ + \text{CH}_3\text{NH}_2$
- (e)  $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$
- (f)  $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$

**S12. Lowry-Bronsted acids:**

2



**Lowry-Bronsted bases:**



**S13. In case of complete dissociation**

2

The hydrogen ion concentration will be equal to the molarity of acid.

The hydroxide ion concentration will be equal to the molarity of base. Thus

(a) In 0.003 M-HCl

$$\begin{aligned} \text{pH} &= -\log [\text{H}^+] \\ &= -\log (0.003) = -\log (3 \times 10^{-3}) \\ &= -\log 3 + 3 \log 10 = 2.5 \end{aligned}$$

(b) In 0.005 M-NaOH

$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-] \\ &= -\log (0.005) = -\log (5 \times 10^{-3}) \\ &= -\log 5 + 3 \log 10 = 2.3 \\ \text{pH} &= \text{pK}_w - \text{pOH} = 14 - 2.3 = 11.7 \end{aligned}$$

**S14. (a)** In 0.002 M-HBr

$$pH = -\log [H^+]$$

$$= -\log (0.002) = -\log (2 \times 10^{-3})$$

$$= -\log 2 + 3 \log 10 = 2.7$$

**(b)** In 0.002 M-KOH

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

$$= -\log (0.002) = -\log (2 \times 10^{-3})$$

$$= -\log 2 + 3 \log 10 = 2.7$$

$$pH = pK_w - pOH = 14 - 2.7 = 11.3$$

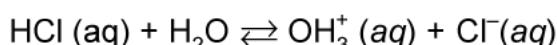
**S15.** Since the solution is dilute, the volume of solution may be taken equal to the volume of solvent (1.00 L). 2

The dissolution may be represented as



$$\text{Molarity} = \frac{3.2 \text{ g}}{36.5 \text{ g mol}} \times \frac{1}{1.00 \text{ L}} = 0.0876 \text{ mol L}^{-1}$$

Since HCl is a strong acid and ionizes completely as



$$\therefore [\text{OH}_3^+] = 0.0876 \text{ mol L}^{-1} = 8.76 \times 10^{-2} \text{ mol L}^{-1}$$

$$\begin{aligned} pH &= -\log [\text{OH}_3^+] = -\log (8.76 \times 10^{-2}) \\ &= -\log 8.76 + 2 \log 10 \\ &= -0.9425 + 2 \times 1 = 1.06 \end{aligned}$$

**S16.** pH = 4.2 means that in the given solution 2

(i)  $[\text{OH}_3^+] = 10^{-4.2} = 6.31 \times 10^{-5} \text{ mol/L}$

(ii)  $[\text{OH}^-] = 10^{-9.8} = 1.58 \times 10^{-10} \text{ mol/L}$

(iii) The solution is acidic.

**S17.**

$$pH = 8 = -\log [H^+]$$

and

$$[H^+] = \text{antilog} (-8) = 10^{-8}$$

$$\therefore [OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-8}} = 10^{-14} \times 10^8 = 10^{-6} \text{ mol/L}$$

The given solution is not acidic. It is alkaline solution, because  $[\text{OH}^-] > [\text{H}^+]$ .

**S18.** HCl is a strong acid and thus it is completely ionized. 2

$\text{HCl} + \text{H}_2\text{O} \rightarrow \text{OH}_3^+ + \text{Cl}^-$ . On ionization  $10^{-8} \text{ M HCl}$  will furnish  $10^{-8} \text{ M}$  of  $\text{OH}_3^+$  ions in solution. So, according to the definition the pH of the solution should be 8. But for an acid a pH value of 8 is meaningless. Its pH must be less than 7. In dilute solutions, therefore, we must consider the  $\text{OH}_3^+$  ion concentration from the ionization of water also.

Thus,  $[\text{OH}_3^+] = 10^{-8} \text{ (from HCl)} + 10^{-7} \text{ (from H}_2\text{O)}$   
 $= (1 + 10) \times 10^{-8} = 11 \times 10^{-8} \text{ mol L}^{-1}$   
 $\therefore \text{pH} = -\log(\text{OH}_3^+) = -\log(11 \times 10^{-8}) = \log 11 + 8 \log 10$   
 $= -1.0414 + 8 = 6.958$

The pH is less than 7, hence the solution is acidic.

**S19.** We know that  $\text{pH} + \text{pOH} = \text{pK}_w = 14$

2

$$\text{pOH} = \text{pK}_w - \text{pH} = 14.475 - 9.25$$

$\text{pOH}$  is defined as

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

$$\therefore [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-9.25} = 10^{-9} \times 10^{-0.25} \\ = 5.6 \times 10^{-10} \text{ mol L}^{-1}$$

**S20. (a)**  $\text{pH} = -\log(3 \times 10^{-5}) = -\log 3 + 5 \log 10 = -0.477 + 5 = 4.523$

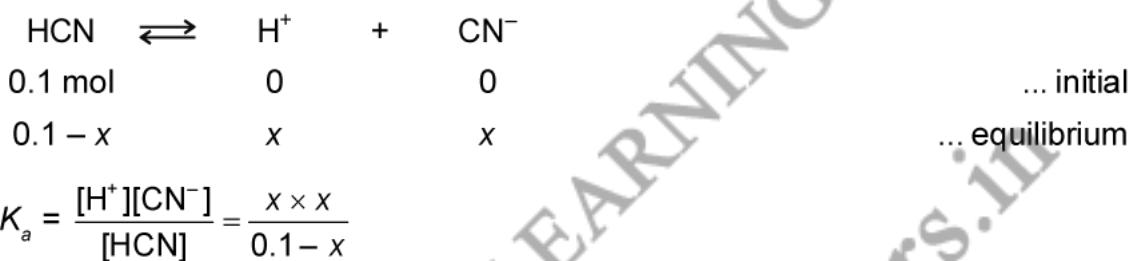
2

$$(b) [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14}}{3 \times 10^{-5}} = 3.33 \times 10^{-10}$$

(c) The given solution is acidic because  $\text{pH} < 7$  and  $[\text{H}^+] > 10^{-7}$ .

**S21.** Hydrocyanic acid is a weak electrolyte which dissociates as

2



To get the value of dissociation constant ( $K_a$ ) we must know  $x$  which is the concentration of  $\text{H}^+$  ions. Thus

$$\text{pH} = -\log[\text{H}^+]$$

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-5.2} = 6.31 \times 10^{-6}$$

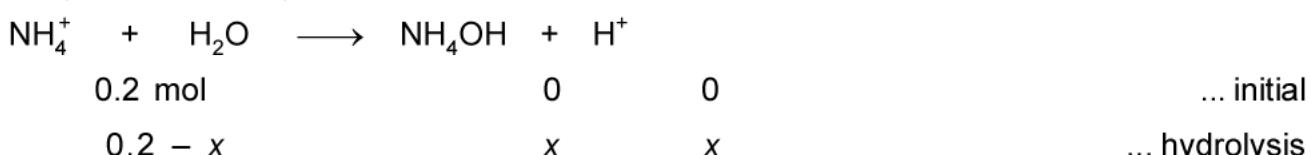
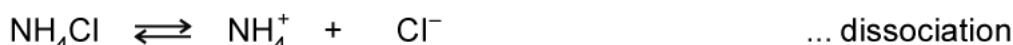
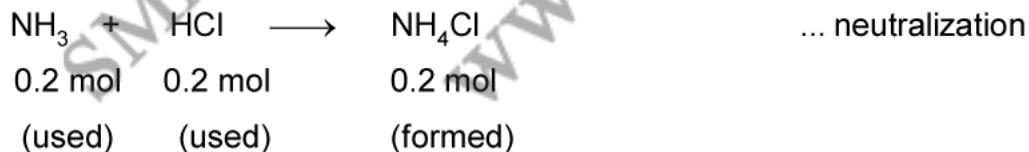
$$\therefore x = 6.31 \times 10^{-6} \text{ mol/L}$$

$$\text{and } 0.1 - x = 0.1 - 6.31 \times 10^{-6} = 0.1 \text{ mol/L}$$

$$\therefore K_a = \frac{x^2}{0.1 - x} = \frac{(6.31 \times 10^{-6})^2}{0.1} = 3.9816 \times 10^{-10} = 4 \times 10^{-10}.$$

**S22.** Neutralization reaction is described as

2



$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = \frac{x^2}{0.2} = \frac{x^2}{0.2}$$

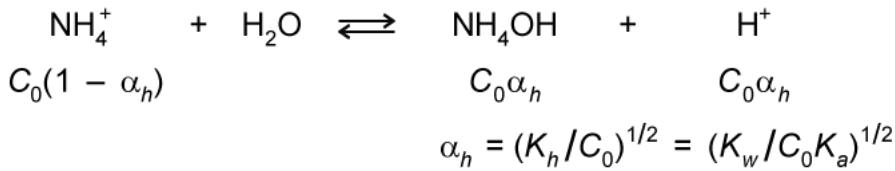
$$x^2 = K_h \times 0.2 = \frac{K_w}{K_a} \times 0.2 = \frac{10^{-14} \times 0.2}{18 \times 10^{-5}} = 1.11 \times 10^{-10}$$

$$x = (1.11 \times 10^{-10})^{1/2} = 1.054 \times 10^{-5} = [\text{H}^+]$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1.054 \times 10^{-5}) = 4.977 = 5$$

**S23.** For the hydrolysis of  $\text{NH}_4^+$  ion.

2



$$= \left( \frac{10^{-14}}{0.015 \times 1.8 \times 10^{-5}} \right)^{1/2} = 1.924 \times 10^{-4}$$

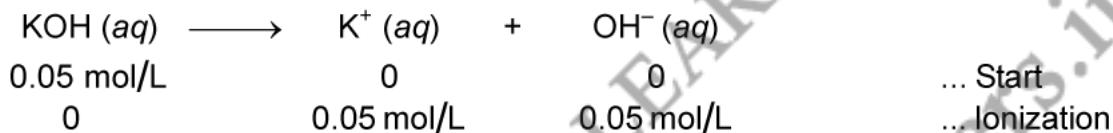
$$\therefore [\text{H}^+] = C_0\alpha = 0.015 \times 1.924 \times 10^{-4} = 2.887 \times 10^{-6}$$

$$\text{pH} = -\log [\text{H}^+] = -\log(2.887 \times 10^{-6}) = 5.54$$

**S24.**

$$\text{Molarity of KOH} = \frac{0.561 \text{ g}}{56.1 \text{ g mol}^{-1}} \times \frac{1000 \text{ mL/L}}{200 \text{ mL}} = 0.05 \text{ mol/L}$$

2



$$\therefore [\text{K}^+] = [\text{OH}^-] = 0.05 \text{ mol/L}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14} (\text{mol/L})^2}{0.05 \text{ mol/L}} = 2.0 \times 10^{-13} \text{ mol/L}$$

$$\text{pH} = -\log[\text{H}^+] = -\log 2 \times 10^{-13} = -\log 2 + 13 \log 10 = 12.7$$

**S25.**

$$\text{In water pH} = \text{pOH} = \frac{1}{2} \text{p}K_w$$

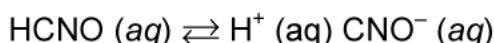
2

$$\text{Now, } \text{p}K_w = -\log K_w = -\log(2.7 \times 10^{-14}) = -\log 2.7 + 14 \log 10 = 13.5686$$

$$\therefore \text{pH} = \frac{1}{2} \times \text{p}K_w = \frac{1}{2} \times 13.5686 = 6.784$$

Note: At 310 K the pH of pure water is less than 7, but still water is neutral.

**S26.**



2

$$K_a = \frac{[\text{H}^+][\text{CNO}^-]}{[\text{HCNO}]} = \frac{[\text{H}^+]^2}{C_0 - [\text{H}^+]} = C_0\alpha^2$$

Now,  $[\text{H}^+] = 10^{-\text{pH}} = 10^{-2.34} = 4.57 \times 10^{-3} \text{ mol/L}$

$$\alpha = \frac{x}{C_0} = \frac{[\text{H}^+]}{C_0} = \frac{4.57 \times 10^{-4}}{0.1} = 4.57 \times 10^{-2} = 0.0457$$

$$\therefore K_a = C_0 \alpha^2 = 0.1 \times (4.57 \times 10^{-2})^2 = 2.09 \times 10^{-4}$$

**S27.**  $K_w(\text{at } 100^\circ \text{C}) = 55 \times K_w(\text{at } 25^\circ \text{C}) = 55 \times 10^{-14}$  2

$$\text{The pH (water)} = \frac{1}{2}(-\log K_w) = \frac{1}{2}(-\log K_w) = -\frac{1}{2} \log (55 \times 10^{-14}) = 6.13$$

The pH of water at  $100^\circ \text{C}$  is 6.13. Now, any solution with its pH value greater than 6.13 at  $100^\circ \text{C}$  is alkaline. Thus, the given solution is alkaline at 373 K.

**S28.** The dissociation constant of a weak base is related to the hydrolysis constant of its cation by the equation. 2

$$K_h = K_w / K_b$$

or

$$K_b = K_w / K_h = 10^{-14} K_h$$

The hydrolysis constant for the reaction



is given by

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = \frac{[\text{H}^+]^2}{[\text{NH}_4^+]}$$

Now,

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-5}$$

$$\therefore K_h = \frac{(10^{-5})^2}{(0.3)} = 3.33 \times 10^{-10}$$

$$K_b = \frac{10^{-14}}{K_h} = \frac{10^{-14}}{3.33 \times 10^{-10}} = 3 \times 10^{-5}$$

**S29.** An acid-base pair which differs by a proton is called conjugate acid-base pair. 2



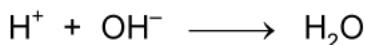
**S30. (a)**  $\text{OH}^-$  can donate electron pair. Hence, it is a Lewis base. 2



**(b)**  $\text{F}^-$  can also donate electron pair. Hence, it is a Lewis base.



**(c)**  $\text{H}^+$  can accept electron pair. Hence, it is a Lewis acid.



**(d)**  $\text{BCl}_3$  can accept electron pair and is, therefore, it is a Lewis acid.



**S31.** The relation between ionization constant of an acid and that of its conjugate base is

2

$$K_a \times K_b = K_w$$

$$\therefore K_b = \frac{K_w}{K_a}$$

The conjugate base of HF is  $F^-$

$$K_b(F^-) = \frac{K_w}{K_a(HF)} = \frac{1 \times 10^{-14}}{6.8 \times 10^{-4}} \\ = 1.5 \times 10^{-11}.$$

The conjugate base of HCOOH is  $HCOO^-$ .

$$K_b(HCOO^-) = \frac{K_w}{K_a(HCOOH)} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-4}} \\ = 5.6 \times 10^{-11}.$$

The conjugate base of HCN is  $CN^-$ .

$$K_b(CN^-) = \frac{K_w}{K_a(HCN)} = \frac{1 \times 10^{-14}}{4.8 \times 10^{-9}} \\ = 2.1 \times 10^{-6}.$$

**S32.** The ionic product of water is given as

2

$$K_w = [OH_3^+] [OH^-]$$

$$\therefore [OH^-] = \frac{K_w}{[OH_3^+]} = \frac{10^{-14}}{10^{-2}} = 10^{-12} \text{ mol L}^{-1}$$

Remarks.

$$K_w = \{[OH_3^+]/C^\circ\} \times \{[OH^-]/C^\circ\}$$

Thus:

$$[OH^-]/C^\circ = \frac{10^{-14}}{6.2 \times 10^{-4}} = 1.6 \times 10^{-11} \text{ mol L}^{-1}$$

and

$$[OH^-] = 10^{-12} \times C^\circ = 10^{-12} \times 1.0 \text{ mol L}^{-1} = 10^{-12} \text{ mol L}^{-1}.$$

**S33. (a)**

2



$$\therefore [H^+] = 2 \times 10^{-3} \text{ M},$$

$$pH = -\log(2 \times 10^{-3}) = 2.70$$

(b)



$$\therefore [OH^-] = 2 \times 10^{-3} \text{ M},$$

$$[H^+] = 10^{-14}/(2 \times 10^{-3}) = 2 \times 10^{-12},$$

$$pH = -\log(5 \times 10^{-12}) = 11.30.$$

S34. (a)



$$\therefore [\text{H}^+] = [\text{HCl}] = 3 \times 10^{-3} \text{ M},$$

$$\text{pH} = -\log (3 \times 10^{-3}) = 2.52$$

(b)

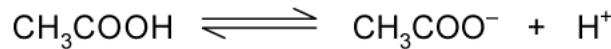


$$\therefore [\text{OH}^-] = 5 \times 10^{-3} \text{ M},$$

$$[\text{H}^+] = 10^{-14}/(5 \times 10^{-3}) = 2 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log (2 \times 10^{-12}) = 11.70$$

S35.



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]}$$

It may be noted that the equilibrium concentration of the  $\text{CH}_3\text{COOH}$  may be taken as the same as the initial concentration because acetic acid, being a weak acid undergoes only slight dissociation.

or

$$[\text{H}^+] = \sqrt{K_a[\text{CH}_3\text{COOH}]}$$

$$= \sqrt{(17.4 \times 10^{-5})(5 \times 10^{-2})}$$

$$= 9.33 \times 10^{-4} \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = [\text{H}^+] = 9.33 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log (9.33 \times 10^{-4}) = 4 - 0.9699$$

$$= 4 - 0.97 = 3.03.$$

S36. (a)

$$-\log [\text{H}^+] = 6.83$$

$$\log [\text{H}^+] = -6.83 = \bar{7.17}$$

$$[\text{H}^+] = \text{antilog} (\bar{7.17}) = 1.48 \times 10^{-7} \text{ M}$$

(b)

$$-\log [\text{H}^+] = 1.2$$

$$\log [\text{H}^+] = -1.2 = \bar{2.8}$$

$$[\text{H}^+] = \text{antilog} (\bar{2.8}) = 6.31 \times 10^{-2} \text{ M}$$

S37. (a)

$$-\log [\text{H}^+] = 7.38$$

$$\log [\text{H}^+] = -7.38 = \bar{8.62}$$

$$[\text{H}^+] = \text{antilog} (\bar{8.62}) = 4.17 \times 10^{-8} \text{ M}$$

(b)

$$-\log [\text{H}^+] = 6.4$$

$$\log [\text{H}^+] = -6.4 = \bar{7.6}$$

$$[\text{H}^+] = \text{antilog} (\bar{7.6}) = 3.98 \times 10^{-7} \text{ M}$$

S38.

$$10 \text{ mL of } 0.01 \text{ M H}_2\text{SO}_4 = 10 \times 0.01 \text{ millimole} = 0.1 \text{ millimole}$$

$$10 \text{ mL of } 0.01 \text{ M Ca(OH)}_2 = 10 \times 0.01 \text{ millimole}$$

$$= 0.1 \text{ millimole}$$

2

2

2

2

2



1 mole of  $\text{Ca(OH)}_2$  reacts with 1 mole of  $\text{H}_2\text{SO}_4$

∴ 0.1 millimole of  $\text{Ca(OH)}_2$  will react completely with 0.1 millimole of  $\text{H}_2\text{SO}_4$ . Hence, solution will be neutral with pH = 7.0.

**S39.** 10 mL of 0.2 M  $\text{Ca(OH)}_2$  =  $10 \times 0.2$  millimoles = 2 millimoles of  $\text{Ca(OH)}_2$  2

$$= 25 \times 0.1 \text{ millimoles} = 2.5 \text{ millimoles of HCl}$$



1 millimole of  $\text{Ca(OH)}_2$  reacts with 2 millimoles of HCl

∴ 2.5 millimoles of HCl will react with 1.25 millimoles of  $\text{Ca(OH)}_2$

$$\therefore \text{Ca(OH)}_2 \text{ left unreacted} = 2 - 1.25 = 0.75 \text{ millimoles}$$

$$\text{Total volume of the solution} = (10 + 25) \text{ mL} = 35 \text{ mL}$$

∴ Molarity of  $\text{Ca(OH)}_2$  in the mixture solution

$$= \frac{0.75}{35} \text{ M} = 0.0214 \text{ M}$$

$$\therefore [\text{OH}^-] = 2 \times 0.0214 \text{ M} = 0.0428 \text{ M} = 4.28 \times 10^{-2} \text{ M}$$

$$\text{pOH} = -\log (4.28 \times 10^{-2}) = 2 - 0.6314$$

$$= 1.3686 = 1.37$$

$$\therefore \text{pH} = \text{pK}_w - \text{pOH} = 14 - 1.37 = 12.63.$$

**S40.** 10 mL of 0.1 M  $\text{H}_2\text{SO}_4$  = 1 millimole 2

$$10 \text{ mL of 0.1 M KOH} = 1 \text{ millimole}$$



1 millimole of KOH will react with 0.5 millimole of  $\text{H}_2\text{SO}_4$

$$\therefore \text{H}_2\text{SO}_4 \text{ left unreacted} = 1 - 0.5 = 0.5 \text{ millimole}$$

$$\text{Volume of reaction mixture} = 10 + 10 = 20 \text{ mL}$$

∴ Molarity of  $\text{H}_2\text{SO}_4$  in the mixture solution

$$= \frac{0.5}{20} = 2.5 \times 10^{-2} \text{ M}$$

$$[\text{H}^+] = 2 \times 2.5 \times 10^{-2} = 5 \times 10^{-2} \text{ M}$$

$$\text{pH} = -\log (5 \times 10^{-2}) = 2 - 0.699 = 1.3.$$

**S41.** Molarity of KOH = 
$$\frac{\text{Mass of KOH/L}}{\text{Molar mass of KOH}} = \frac{0.28 \text{ g/L}}{(39 + 16 + 1) \text{ g/mol}}$$
 2

$$= \frac{0.28}{56} = 5.0 \times 10^{-3} \text{ mol L}^{-1}$$

$$[\text{OH}^-] = 5 \times 10^{-3} \text{ mol L}^{-1}$$

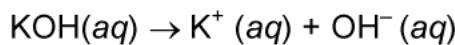
$$[\text{OH}^-] \times [\text{H}^+] = 10^{-14}$$

$$[\text{H}^+] = \frac{10^{-14}}{5 \times 10^{-3}} = 2 \times 10^{-12} \text{ mol L}^{-1}.$$

**S42.** Since the solution is dilute, the volume of solution may be taken equal to the volume of solvent (1.00 L). Thus 3

$$\text{Molarity} = \frac{0.28}{56 \text{ g mol}^{-1}} \times \frac{1}{1.00 \text{ L}} = 5.0 \times 10^{-3} \text{ mol L}^{-1}$$

Since KOH is a strong base, it is completely ionized in solution.



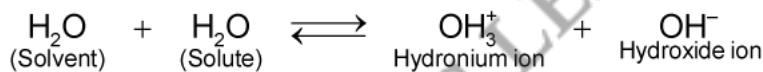
$$[\text{OH}^-] = 5.0 \times 10^{-3} \text{ mol L}^{-1}$$

In an aqueous solution:

$$[\text{OH}_3^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-3}} = 2 \times 10^{-12} \text{ mol L}^{-1}$$

$$\begin{aligned} \text{pH} &= -\log[\text{OH}_3^+] = -\log 2 \times 10^{-12} = -\log 2 + 12 \log 10 \\ &= -0.3010 + 12 = 11.7 \end{aligned}$$

**S43.** The ionization of water in water is represented by 3



The equilibrium constant :

$$K_{eq} = \frac{[\text{OH}_3^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{H}_2\text{O}]}$$

Ionization constant of  $\text{H}_2\text{O}$

$$K_{\text{ionization}} = \frac{[\text{OH}_3^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

One  $\text{H}_2\text{O}$  is considered as solvent so its concentration is unchanged.

Now, molarity of  $\text{H}_2\text{O}$  in water is given by

$$[\text{H}_2\text{O}] = \frac{\text{mole of H}_2\text{O}}{\text{Litres of water}} = \frac{1000/18}{1\text{L}} = 55.56 \text{ mol/L}$$

$$[\text{OH}_3^+] = [\text{OH}^-] = C_0\alpha = 55.56 \times 1.8 \times 10^{-9}$$

$$\therefore K_{\text{ionization}} = \frac{(55.56 \times 1.8 \times 10^{-9})}{55.56} = 1.8 \times 10^{-16}$$

Ionic product of water is given by

$$K_w = [\text{OH}_3^+]^2 = (C_0\alpha)^2 \\ = (55.56 \times 1.8 \times 10^{-9})^2 = 1.0 \times 10^{-14}$$

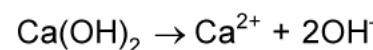
**S44.** (a) Base 1      (b)  $\text{H}_2\text{O}$       (c)  $\text{NH}_3$       (d)  $\text{OH}^-$       (e)  $\text{HCO}_3^-$       **3**  
 (f)  $\text{HCO}_3^-$       (g)  $\text{H}_2\text{O}$       (h)  $\text{HCO}_3^-$       (i)  $\text{OH}_3^+$

**S45.** We shall the pH values to know  $[\text{H}^+]$  and  $[\text{OH}^-]$  and from  $[\text{OH}^-]$ , we shall get the amount of **3**  $\text{Ca}(\text{OH})_2$ .

Now,  $[\text{H}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-10.65) = 2.24 \times 10^{-11}$

$$\therefore [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14}}{2.24 \times 10^{-11}} = 4.46 \times 10^{-4} \text{ mol L}^{-1}$$

According to the dissociation reaction :



$$2 \text{ mol OH}^- = 1 \text{ mol Ca}(\text{OH})_2$$

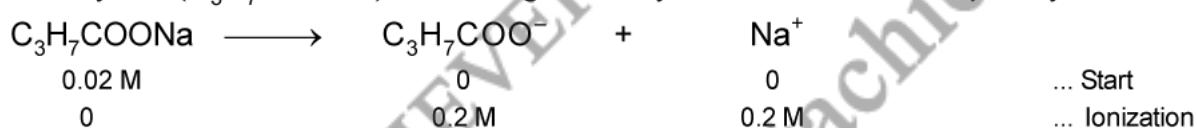
$$\therefore 4.46 \times 10^{-4} \text{ mol L}^{-1} = \frac{1}{2} \times 4.46 \times 10^{-4} \text{ mol L}^{-1} \text{ Ca}(\text{OH})_2 \\ = 2.23 \times 10^{-4} \text{ mol L}^{-1}$$

$$\text{Mole of Ca}(\text{OH})_2 \text{ in 1000 mL of solution} = 2.23 \times 10^{-4}$$

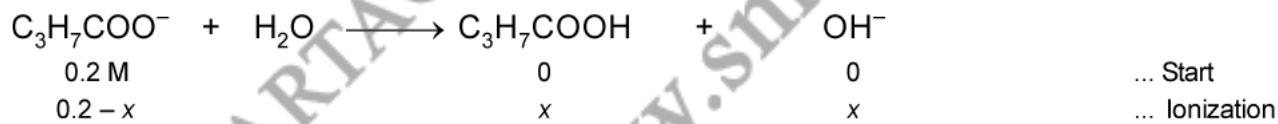
$$\text{Mole of Ca}(\text{OH})_2 \text{ in 250 mL of solution} = 2.23 \times 10^{-4} \times \frac{250}{1000} \\ = 5.575 \times 10^{-5}$$

Thus,  $5.575 \times 10^{-5}$  mole of  $\text{Ca}(\text{OH})_2$  should be dissolved to produce 250 mL of an aqueous solution of pH 10.65.

**S46.** Sodium butyrate ( $\text{C}_3\text{H}_7\text{COONa}$ ) is a strong electrolyte which ionizes completely in the solution. **3**



Butyrate ion hydrolyses to give weak butyric acid and  $\text{OH}^-$  ions. Let  $x$  be the mole of  $\text{C}_3\text{H}_7\text{COO}^-$  hydrolysed at equilibrium.



$$K_h = \frac{[\text{C}_3\text{H}_7\text{COOH}][\text{OH}^-]}{[\text{C}_3\text{H}_7\text{COO}^-]} = \frac{x \cdot x}{0.2 - x} = \frac{x^2}{0.2}$$

But  $K_h = K_w / K_a$ , therefore

$$x^2 = 0.2 \times K_h = 0.2 \times \frac{10^{-14}}{2 \times 10^{-5}} = 10^{-10}$$

$$x = 10^{-5} \text{ mol/L}$$

$$[\text{OH}^-] = x = 10^{-5} \text{ mol/L}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{10^{-5}} = 10^{-9}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 10^{-9} = -(-9 \log 10) = 9.$$

**S47.** Acetic acid ionizes as

3

$\text{CH}_3\text{COOH}$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{CH}_3\text{COO}^-$	
1 M		0		0	... initial
$1 - x$		$x$		$x$	... equilibrium

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x \cdot x}{1 - x} = \frac{x^2}{1}$$

$$\therefore x = \sqrt{K_a} = \sqrt{1.8 \times 10^{-5}} = 4.24 \times 10^{-3}$$

$$\therefore [\text{H}^+] = x = 4.24 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 4.24 \times 10^{-3} = -0.6274 + 3 = 2.37$$

In diluted solution

$$\text{pH} = 2 \times 2.37 = 4.74$$

$$\therefore [\text{H}^+] = \text{antilog}(-4.74) = \text{antilog}(5.26) = 1.8 \times 10^{-5}$$

This  $\text{H}^+$  ion given by the ionization of diluted solution of  $\text{CH}_3\text{COOH}$ .

$\text{CH}_3\text{COOH}$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{CH}_3\text{COO}^-$	
$C_0$		0		0	... Start
$C_0 - 1.8 \times 10^{-5}$		$1.8 \times 10^{-5}$		$1.8 \times 10^{-5}$	... equilibrium

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$1.8 \times 10^{-5} = \frac{(1.8 \times 10^{-5}) \times (1.8 \times 10^{-5})}{C_0 - 1.8 \times 10^{-5}}$$

$$C_0 - 1.8 \times 10^{-5} = 1.8 \times 10^{-5}$$

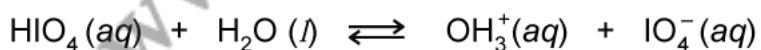
$$C_0 = 1.8 \times 10^{-5} + 1.8 \times 10^{-5} = 3.6 \times 10^{-5} \text{ M}$$

$$\text{Dilution factor} \quad 1 \text{ L} \times 1 \text{ mol} = V \times 3.6 \times 10^{-5} \text{ mol}$$

$$\therefore V = \frac{1}{3.6 \times 10^{-5}} = 2.78 \times 10^4 \text{ L}$$

**S48.** The ionization of  $\text{CH}_3\text{NH}_2$  in aqueous solution is represented by

3



Initial	0.1	0	0
Equilibrium	$0.1(1 - \alpha)$	$0.1\alpha$	$0.1\alpha$

Equilibrium law gives

$$K_a = \frac{[\text{OH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{(0.2\alpha)(0.2\alpha)}{0.2(1-\alpha)}$$

Let us suppose that  $\alpha \ll 1$  and  $1 - \alpha \approx 1$ ,

$$\therefore K_b = \frac{0.04\alpha^2}{0.2} = 0.2\alpha^2$$

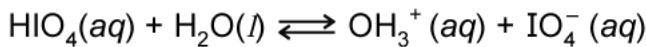
$$\therefore \alpha = (K_b/0.2)^{1/2} = (4.4^{-5}/0.2)^{1/2} = 0.0148$$

$$[\text{OH}^-] = 0.2\alpha = 0.2 \times 0.0148 = 2.96 \times 10^{-3} \text{ mol L}^{-1}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{2.96 \times 10^{-3}} = 3.378 \times 10^{-12}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 3.378 \times 10^{-12} = -0.5286 + 12 \\ = 11.47$$

**S49.** The ionization of periodic acid is shown as



initial	0.1	0	0
Equilibrium	0.1 (1 - $\alpha$ )	0.1 $\alpha$	0.1 $\alpha$

Equilibrium law gives

$$K_a = \frac{[\text{OH}_3^+][\text{IO}_4^-]}{[\text{HIO}_4]} = \frac{0.1\alpha^2}{1-\alpha}$$

$$\text{and, } 0.1\alpha^2 + K_a\alpha - K_a = 0$$

Using  $K_a = 2.3 \times 10^{-2}$  and solving for  $\alpha$ , we get

$$\alpha = \frac{-2.3 \times 10^{-2} \pm \{(2.3 \times 10^{-2})^2 + (4 \times 0.1 \times 2.3 \times 10^{-2})\}^{1/2}}{2 \times 0.1} =$$

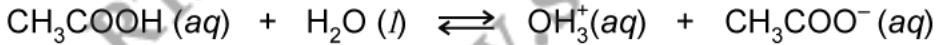
0.378

$$\therefore [\text{OH}_3^+] = 0.1\alpha = 0.1 \times 0.378 = 0.1 \times 1.378 \text{ mol L}^{-1}$$

$$\text{pH} = -\log [\text{OH}_3^+] = -\log (0.1 \times 1.378) = -0.5775 + 2 = 1.42$$

**Note:** Since the value of  $\alpha$  is appreciable, we cannot approximate  $\alpha = (K_a/C_0)^{1/2}$ .

**S50.** The ionization of acetic acid, and equilibrium concentrations may be shown as



Initial	$C_0$	0	0
Equilibrium	$C_0(1 - \alpha)$	$C_0\alpha$	$C_0\alpha$

$$K_a = \frac{[\text{OH}_3^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{C_0\alpha \times C_0\alpha}{C_0(1-\alpha)} = \frac{C_0\alpha^2}{1-\alpha}$$

When  $\alpha \ll 1$ , we can take  $1 - \alpha = 1$ , and

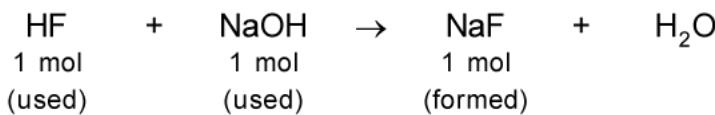
$$\alpha = (K_a/C_0)^{1/2} = (1.82 \times 10^{-5}/0.1)^{1/2} = 1.35 \times 10^{-2} \\ = 1.35 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{pH} = -\log [\text{OH}_3^+] = -\log 1.35 \times 10^{-3} = -0.1303 + 3 = 2.87$$

$$[\text{CH}_3\text{COO}^-] = C_0\alpha = [\text{OH}_3^+] = 1.35 \times 10^{-3} \text{ mol L}^{-1}$$

**S51.** The neutralization reaction is represented by

3



Since the solutions of acid and alkali have same initial concentrations, equal of each solution will be needed for complete neutralization. Now, at the equivalence point, the total volume of the final solution is twice the initial volume. Thus, the molarity of the salt formed

$$\text{Molarity of salt} = \frac{1}{2} (0.2 \text{ mol/L}) = 0.1 \text{ mol/L}$$

HF is weak acid, therefore, after neutralization  $\text{F}^-$  ion of the salt NaF undergo hydrolysis.



When  $x$  is small, we have  $0.1 - x = 0.1$  and

$$x = (K_h \times 0.1)^{1/2} = 2.857 \times 10^{-11}$$

$$\text{Now, } K_h = \frac{k_w}{k_a} = \frac{10^{-14}}{3.5 \times 10^{-4}} = 2.857 \times 10^{-11}$$

$$\therefore [\text{OH}^-] = x = (2.857 \times 10^{-11} \times 0.1)^{1/2} = 1.69 \times 10^{-6}$$

$$\text{pH} = \text{p}K_w - \text{pOH} = \text{pOH} = 14 - 5.77 = 8.23$$

The solution at the equivalence point will be alkaline.

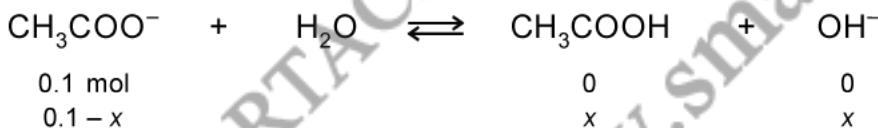
**S52.** The neutralization reaction between 0.2 M  $\text{CH}_3\text{COOH}$  and 0.2 M NaOH produces 0.2 M  $\text{CH}_3\text{COONa}$ . Since, the volume of the solution becomes double on mixing acid and base, therefore, mole of  $\text{CH}_3\text{COONa}$  in the solution is 0.1 mole.



... Stoichiometry

$$\therefore [\text{CH}_3\text{COOH}] = [\text{NaOH}] = [\text{CH}_3\text{COONa}] = 0.1 \text{ mol}$$

The hydrolysis of acetate ions may be described by



... initial  
... equilibrium

The hydrolysis constant ( $K_h$ ) is given by

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{x \times x}{0.1 - x} = \frac{x^2}{0.1 - x}$$

The hydrolysis constant is related to the ionic product of water ( $K_w$ ) and the dissociation constant of weak acid as

$$K_h = K_w / K_a$$

$$K_h = \frac{K_w}{K_a} = \frac{x^2}{0.1 - x} = \frac{x^2}{0.1} \quad (0.1 - x \approx 0.1)$$

$$x^2 = 0.1 \times \frac{K_w}{K_a} = \frac{0.1 \times 10^{-14}}{1.8 \times 10^{-5}} = 55.5 \times 10^{-12}$$

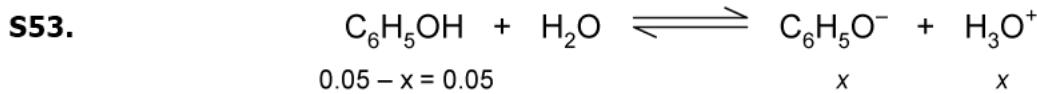
$$\therefore x = (55.5 \times 10^{-12})^{1/2} = 7.45 \times 10^{-6}$$

$$\therefore [\text{OH}^-] = x = 7.45 \times 10^{-6}$$

$$\text{p}(\text{OH}) = -\log [\text{OH}^-] = -\log (7.45 \times 10^{-6}) = -0.8722 + 6 = 5.13$$

$$\text{pH} = \text{p}K_w - \text{p}(\text{OH}) = 14 - 5.13 = 8.87$$

Exercise: Calculate the pH at the equivalence point when a solution of 0.10 M acetic acid is titrated with a solution of 0.10 M sodium hydroxide.  $K_a$  for acetic acid is  $1.9 \times 10^{-5}$ .



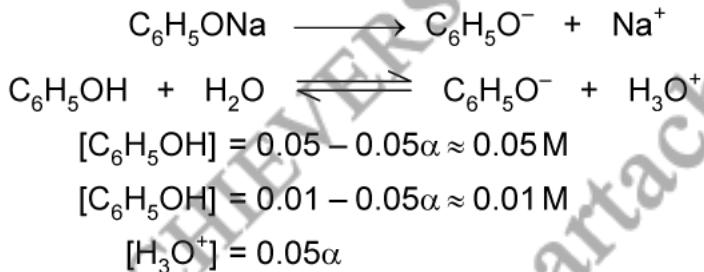
At equilibrium (molar):

$$K_a = \frac{[\text{C}_6\text{H}_5\text{O}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{OH}]} = \frac{[\text{H}_3\text{O}^+]^2}{[\text{C}_6\text{H}_5\text{OH}]}$$

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \sqrt{K_a \times [\text{C}_6\text{H}_5\text{OH}]} \\ &= \sqrt{1 \times 10^{-10} \times 0.05} = \sqrt{5 \times 10^{-12}} \\ &= 2.2 \times 10^{-6} \text{ M} \end{aligned}$$

$$[\text{Phenate}] = [\text{H}_3\text{O}^+] = 2.2 \times 10^{-6} \text{ M}$$

Let  $\alpha$  be the degree of ionization of phenol in the presence of 0.01 M sodium phenate.

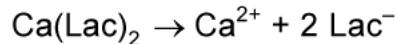


$$K_a = \frac{[\text{C}_6\text{H}_5\text{O}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{OH}]} = \frac{(0.01)(0.05\alpha)}{(0.05)}$$

$$1 \times 10^{-10} = 0.01\alpha$$

$$\alpha = 1 \times 10^{-8}$$

**S54.** The dissociation of salt gives

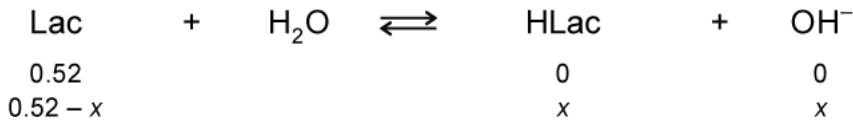


$$\text{Molarity of salt} = [\text{Ca}(\text{Lac})_2] = \frac{0.13 \text{ mol}}{0.5 \text{ L}} = 0.26 \text{ mol/L}$$

$\therefore 1 \text{ mol Ca}(\text{Lac})_2$  gives  $2 \text{ mol Lac}^-$ .

$$\therefore \text{Molarity of Lac}^- = [\text{Lac}^-] = 2 \times 0.26 \text{ mol/L} = 0.52 \text{ mol/L}$$

Hydrolysis of lactate ions ( $\text{Lac}^-$ ) is given by



Hydrolysis constant ( $K_h$ ) is given by

$$K_h = \frac{[\text{HLac}][\text{OH}^-]}{[\text{Lac}^-]} = \frac{x \times x}{0.52 - x} = \frac{x^2}{0.52 - x}$$

$K_h$  is related to  $K_w$  and  $K_a$  as

$$K_h = K_w / K_a$$

$$K_a = K_w / K_h = \frac{K_w}{x^2 / (0.52 - x)} = \frac{K_w \times (0.52 - x)}{x^2}$$

But  $x = [\text{OH}^-]$ , which is calculated from  $\text{pOH}$  as follows :

$$\text{pOH} = -\log[\text{OH}^-] = 5.6$$

$$\therefore [\text{OH}^-] = \text{antilog}(-5.60) = \text{antilog}(6.40) = 2.5 \times 10^{-6}$$

On substituting

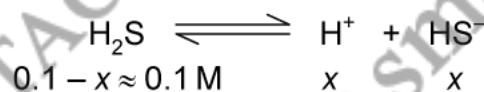
$$x = 2.5 \times 10^{-6} \text{ into expression for } K_a, \text{ we get}$$

$$K_a = 10^{-14} \times \frac{(0.52 - 2.5 \times 10^{-6})}{(2.5 \times 10^{-6})} = 8.3 \times 10^{-4}$$

Note: We have ignored  $2.5 \times 10^{-6}$  in comparison to 0.52 and taken  $0.52 - x$  equal to 0.52 which is justified.

**S55.** Calculation of concentration of  $\text{HS}^-$  ions.

**Case I:** Let the conc. of  $\text{HS}^-$  be  $x \text{ M}$



$$K_{a1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

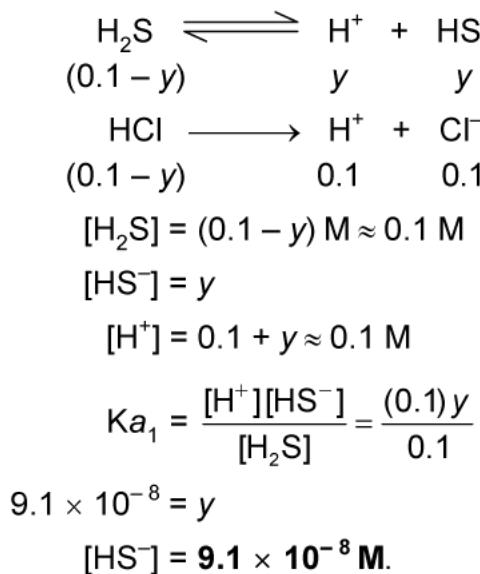
$$9.1 \times 10^{-8} = \frac{(x)(x)}{0.1}$$

$$x^2 = 9.1 \times 10^{-9}$$

$$x = 9.54 \times 10^{-5} \text{ M.}$$

$$[\text{HS}^-] = 9.54 \times 10^{-5} \text{ M.}$$

**Case II:** In the presence of 0.1 HCl, let the concentration of  $\text{HS}^-$  by  $y \text{ M}$



Calculation of concentration of  $\text{S}^{2-}$  ions.



**Case I:**  $[\text{HS}^-] \approx 9.54 \times 10^{-5} \text{ M}$  [From first stage ionization]  
 $[\text{S}^{2-}] = x' \text{ (say)}$   
 $[\text{H}^+] = 9.54 \times 10^{-5} \text{ M}$  [From first stage ionization]

$$\text{Ka}_2 = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} = \frac{(9.54 \times 10^{-5})(x')}{9.54 \times 10^{-5}}$$

$$1.2 \times 10^{-13} = x'$$

$$\therefore [\text{S}^{2-}] = \mathbf{1.2 \times 10^{-13} \text{ M.}}$$

**Case II:**  $[\text{HS}^-] = 9.1 \times 10^{-8} \text{ M}$  [From first stage ionization]  
 $[\text{H}^+] = 0.1 \text{ M}$  [Mainly from HCl]  
 $[\text{S}^{2-}] = y' \text{ (say)}$

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

$$1.2 \times 10^{-13} = \frac{(0.1)(y')}{9.1 \times 10^{-8}}$$

$$y' = 1.09 \times 10^{-20} \text{ M}$$

$$[\text{S}^{2-}] = \mathbf{1.09 \times 10^{-20} \text{ M.}}$$

**S56.** (a)  $[\text{Ca}(\text{OH})_2] = \frac{0.3 \text{ g}}{74 \text{ g mol}^{-1}} \times \frac{1}{0.5 \text{ L}} = 8.11 \times 10^{-3} \text{ M}$

$$\text{Ca}(\text{OH})_2 \longrightarrow \text{Ca}^{2+} + 2\text{OH}^-$$

$$\therefore [\text{OH}^-] = 2 [\text{Ca}(\text{OH})_2] = 2 \times (8.11 \times 10^{-3}) \text{ M}$$

$$= 1.622 \times 10^{-2} \text{ M}$$

$$\text{pOH} = -\log (1.622 \times 10^{-2})$$

$$= 2 - 0.2101 = 1.79$$

$$\text{pH} = 14 - \text{pOH} = 14 - 1.79 = 12.21$$

(b)  $[\text{NaOH}] = \frac{0.3 \text{ g}}{40 \text{ g mol}^{-1}} \times \frac{1}{0.2 \text{ L}} = 3.75 \times 10^{-2}$

$$[\text{OH}^-] = 3.75 \times 10^{-2}$$

$$\text{pOH} = -\log (3.75 \times 10^{-2}) = 2 - 0.0574 = 1.43$$

$$\therefore \text{pH} = 14 - \text{pOH} = 14 - 1.43 = 12.57$$

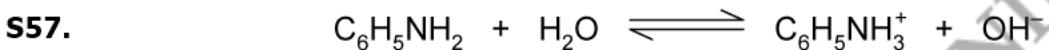
(c)  $M_1 V_1 = M_2 V_2$

$$\therefore 13.6 \text{ M} \times 1 \text{ mL} = M_2 \times 1000 \text{ mL}$$

$$M_2 = 1.36 \times 10^{-2} \text{ M}$$

$$[\text{H}^+] = [\text{HCl}] = 1.36 \times 10^{-2} \text{ M}, \text{pH}$$

$$= -\log (1.36 \times 10^{-2}) = 2 - 0.1335 \approx 1.87.$$



$$K_a = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = \frac{[\text{OH}^-]^2}{[\text{C}_6\text{H}_5\text{NH}_2]}$$

$$[\text{OH}^-] = \sqrt{K_a [\text{C}_6\text{H}_5\text{NH}_2]} = \sqrt{(4.27 \times 10^{-10})(10^{-3})}$$

$$= 6.534 \times 10^{-7} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (6.534 \times 10^{-7})$$

$$= 7 - 0.8152 = 6.18$$

$$\therefore \text{pH} = 14 - 6.18 = 7.82$$

$$\alpha = \sqrt{K_b/C} = \sqrt{4.27 \times 10^{-10}/10^{-3}}$$

$$= 6.53 \times 10^{-4}.$$

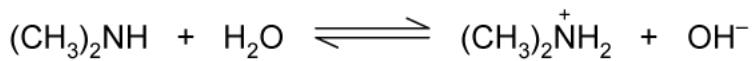
$$K_a (\text{conjugate acid}) = \frac{K_w}{K_b}$$

$$= \frac{1 \times 10^{-14}}{4.27 \times 10^{-10}} = 2.34 \times 10^{-5}.$$

**S58.**  $\alpha = \sqrt{K_b/C} = \sqrt{(5.4 \times 10^{-10})/(2 \times 10^{-2})}$

$$= 0.164$$

In presence of 0.1 M NaOH, if  $x$  is the amount of dimethyl amine dissociated, then



Initial	0.02 M		
After dissociation	0.02 - x	x	0.1 + x
	$\approx 0.02$		
$[(\text{CH}_3)_2\text{NH}] = (0.02 - x) \text{ M} \approx 0.02 \text{ M}$			
$[(\text{CH}_3)_2\text{NH}_2^+] = x \text{ M}$			

$$[\text{OH}^-] = [0.1 + x] \text{ M} \approx 0.1 \text{ M}$$

$$K_b = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]} = \frac{x(0.1)}{0.02}$$

or  $\frac{x}{0.02} = \frac{5.4 \times 10^{-4}}{10^{-1}} = 5.4 \times 10^{-3}$   
 $\therefore \alpha = 5.4 \times 10^{-3}$

Per cent dissociation =  $\alpha \times 100$   
 $= 5.4 \times 10^{-3} \times 100 = 0.54$ .

**S59.** Let us represent propanoic acid as HA. Let its degree of ionization be a.

3

	HA + H <sub>2</sub> O	$\rightleftharpoons$	H <sub>3</sub> O <sup>+</sup> + A <sup>-</sup>
More conc.	(0.05 - 0.5α)		0.05α 0.05α
At equilibrium			$\approx 0.05 \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+]}{[\text{HA}]} = \frac{(0.05\alpha)(0.05\alpha)}{(0.05)} = 0.05\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{0.05}} \times \sqrt{\frac{1.32 \times 10^{-5}}{0.05}}$$

$$[\text{H}_3\text{O}^+] = 0.05\alpha = 0.05 \times 1.63 \times 10^{-2} \\ = 8.15 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] \\ = -\log 8.15 \times 10^{-4} = 4 - \log 8.15 \\ = 4 - 0.91 = 3.09.$$

**In the presence of 0.01 M HCl, let a be the degree of ionization.**

$$[\text{H}_3\text{O}^+] = 0.01 \text{ M}$$

$$[\text{A}^-] = 0.05\alpha' \text{ M}$$

$$[\text{HA}] = 0.05 - 0.05\alpha' = 0.05 \text{ M}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(0.01)(0.05\alpha')}{(0.05)}$$

$$\alpha' = \frac{K_a}{0.01} = \frac{1.32 \times 10^{-5}}{0.01} = 1.32 \times 10^{-3}.$$

- Q1.** A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine.
- Q2.** Ionic product of water at 310 K is  $2.7 \times 10^{-14}$ . What is the pH of neutral water at this temperature?
- Q3.** It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its  $pK_a$ .
- Q4.** The pH of 0.005 M codeine ( $C_{18}H_{21}NO_3$ ) solution is 9.95. Calculate the ionization constant and  $pK_b$ .
- Q5.** The degree of ionization of a 0.1 M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the  $pK_a$  of bromoacetic acid.
- Q6.** The ionization constant of chloriacetic is  $1.35 \times 10^{-3}$ . What will be the pH of 0.1 M acid and its 0.1 M sodium salt solution?

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**S1.** Pyridinium hydrochloride is a salt of a weak base [pyridine and a strong acid (HCl)]. The pH of an aqueous solution of this salt is given by the relation:

$$pH = \frac{1}{2} [pK_w - pK_b - \log C]$$

$$3.44 = \frac{1}{2} [14 + \log K_b - \log (0.02)]$$

$$6.88 = 14 + \log K_b + 1.7$$

$$\log K_b = -8.82 = \bar{9.18}$$

$$K_b = 1.5 \times 10^{-9}.$$

**S2.**

For pure water,

$$K_w = [H_3O^+] [OH^-]$$

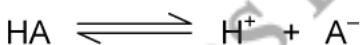
$$[H_3O^+] = [OH^-]$$

$$K_w = [H_3O^+]^2$$

$$[H_3O^+] = \sqrt{K_w} = \sqrt{2.7 \times 10^{-14}} \\ = 1.643 \times 10^{-7} \text{ mol L}^{-1}$$

$$pH = -\log [H_3O^+] \\ = -\log (1.643 \times 10^{-7}) = 7 - \log 1.643 \\ = 7 - 0.2156 = 6.78.$$

**S3.**



$$pH = -\log [H^+] \text{ or } \log [H^+] \\ = -pH = -4.15 = \bar{5.85}$$

$$[H^+] = \text{antilog} (\bar{5.85}) = 7.08 \times 10^{-5} \text{ M}$$

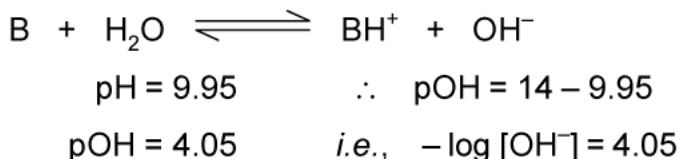
$$= 7.08 \times 10^{-5} \text{ M}$$

$$[A^-] = [H^+] = 7.08 \times 10^{-5} \text{ M}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(7.08 \times 10^{-5})(7.08 \times 10^{-5})}{10^{-2}} \\ = 5.01 \times 10^{-7}$$

$$pK_a = -\log K_a = -\log (5.01 \times 10^{-7}) \\ = -0.699 = 6.301.$$

**S4.** Condeine is a base. Its ionization may be represented as



or

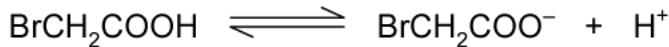
$$\log [\text{H}^+] = -4.05 = 5.95 \quad \text{or} \quad [\text{OH}^-] = 8.91 \times 10^{-5}$$

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} = \frac{[\text{OH}^-]^2}{[\text{B}]} = \frac{(8.91 \times 10^{-5})^2}{5 \times 10^{-3}}$$

$$= 1.588 \times 10^{-6}$$

$$\text{p}K_b = -\log (1.588 \times 10^{-6}) = 6 - 0.1987 = 5.8.$$

**S5.**



Initial conc.	C	0	0
Equilibrium conc.	C - C $\alpha$	C $\alpha$	C $\alpha$

$$K_a = \frac{[\text{BrCH}_2\text{COO}^-][\text{H}^+]}{[\text{BrCH}_2\text{COOH}]} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

$$\approx C\alpha^2 = 0.1 \times (0.132)^2 = 1.74 \times 10^{-3}$$

$$\text{p}K_a = -\log K_a = -\log (1.74 \times 10^{-3}) = 3 - 0.2405 = 2.76$$

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

$$\text{pH} = -\log (1.32 \times 10^{-2}) = 2 - 0.1206 = 1.88.$$

**S6. (a) Calculation of pH of 0.1 M acid.**

$$[\text{H}^+] = \sqrt{K_a \times C}$$

$$= \sqrt{1.35 \times 10^{-3} \times 0.1}$$

$$= 1.16 \times 10^{-2} \text{ M.}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (1.16 \times 10^{-2}) = 2 - \log 1.16 = 2 - 0.06 = 1.94.$$

**(b) Calculation of pH of 0.1 M sodium salt of the acid**

This would be a salt of strong base and weak acid. Its pH would be given by the relation:

$$\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_a - \log C]$$

$$= \frac{1}{2} [14 - \log (1.35 \times 10^{-3}) + \log (0.1)]$$

$$\begin{aligned}&= \frac{1}{2} [14 + (3 - \log 1.35) - 1] \\&= \frac{1}{2} [14 + (3 - 0.1303) - 1] = \mathbf{7.94}.\end{aligned}$$

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