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### 3.7 AQUEOUS SYSTEMS

AS 90700

Describe properties of aqueous systems

#### 3.7 1. Solubility

- relative equilibrium concentrations of dissolved species
- variability in solubility of a sparingly soluble salt due to the formation of a complex ion, the addition of a common ion, or the reaction of a basic anion with added acid.
- calculations involving  $K_s$  and solubility limited to:
  - AB,  $A_2B$  and  $AB_2$  type solids where neither of the ions A or B react further with water
  - calculating the concentration of one ion given the other
  - calculating the solubility in water and in solutions already containing one of the ions A or B (common ion)
  - predicting precipitation or dissolution

▶ (a) Describe what is meant by the term 'solubility'.

(b) The solubility product,  $K_s$ , of AgCl has a value of  $1.56 \times 10^{-10}$  at 25°C and this value increases to  $2.15 \times 10^{-8}$  at 100°C.

Explain why  $K_s$  is higher at 100°C. Include reference to the relevant equilibrium equation in your answer.

The chloride ion concentration in sea water can be determined by titrating a sample with aqueous silver nitrate ( $AgNO_3$ ) using potassium chromate ( $K_2CrO_4$ ) as the indicator.

As the silver nitrate is added, a precipitate of silver chloride, ( $AgCl$ ) forms. When most of the  $AgCl$  has precipitated, the  $Ag^+(aq)$  concentration becomes high enough for a red precipitate of  $Ag_2CrO_4$  to form.

(c) Show that the solubility of  $Ag_2CrO_4$  in pure water at 25°C is higher than that of AgCl.

$$K_s(AgCl) = 1.56 \times 10^{-10} \quad K_s(Ag_2CrO_4) = 1.30 \times 10^{-12}$$

(d) If the concentration of chromate ions is  $6.30 \times 10^{-3} \text{ mol L}^{-1}$  at the point when the  $Ag_2CrO_4$  starts to precipitate, calculate the concentration of  $Ag^+$  ions in the solution.

#### 3.7 2. Acids and Bases

- correlation between acid or base strength,  $K_a$  and pH
- calculations involving  $K_a$ ,  $K_w$  and pH limited to:
  - solutions of bases, monoprotic acids and buffers
  - those in which the extent of reaction is small that the equilibrium concentration of a dissolved weak acid can be approximated by the initial concentration
  - pH at a particular point in a titration

▶ When bromine is added to water, it forms hypobromous acid ( $HOBr$ ), a weak acid.

- (a) (i) Write an equation to show the equilibrium system that is formed with hypobromous acid and water.
- (ii) Write the  $K_a$  expression for hypobromous acid.
- (b) Calculate the pH of a  $0.0525 \text{ mol L}^{-1}$  hypobromous acid solution.

$$pK_a(HOBr) = 8.62$$

#### 3.7 3. Buffer Solutions

- the nature of buffer solutions

▶ Two solutions, A and B, were made as described below.

Solution A: 50 mL of aqueous  $1.00 \text{ mol L}^{-1}$  ammonium chloride was added to 50 mL of aqueous  $1.00 \text{ mol L}^{-1}$  ammonia.

Solution B: 25 mL of aqueous  $0.010 \text{ mol L}^{-1}$  hydrochloric acid was added to 50 mL of aqueous  $0.010 \text{ mol L}^{-1}$  ammonia.

- (a) (i) Write the  $K_a$  expression for  $NH_4^+$ .
- (ii) Show, by calculation, that the pH of each of the two solutions is 9.24.

$$pK_a(NH_4^+) = 9.24$$

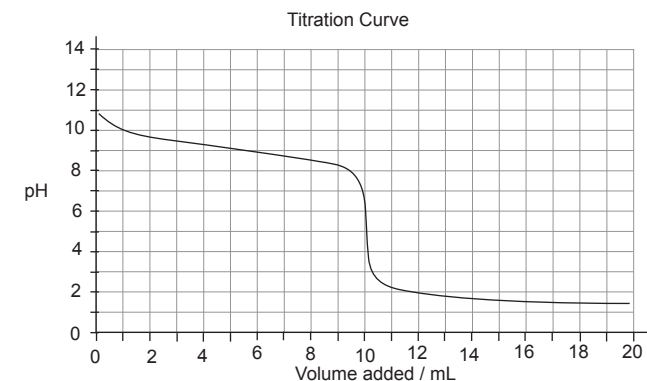
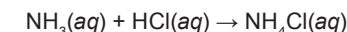
- (b) (i) Discuss the abilities of solutions A and B to act as buffers.
- (ii) Compare how the pH of each solution would be affected when  $1.00 \text{ mol L}^{-1}$  sodium hydroxide is added drop-wise to each solution. Calculations are not required, but you should include appropriate equations in your answer.

#### 3.7 4. Titration Curves

- features of titration curves include buffer region, equivalence point and selection of indicator
- titration of weak acids with weak bases are excluded

▶ The graph below shows the change in pH when 40.0 mL of  $0.0500 \text{ mol L}^{-1}$  aqueous  $NH_3$  is titrated with  $0.200 \text{ mol L}^{-1}$  aqueous HCl.

The equation for the reaction occurring during the titration is:



- (a) Use the curve to determine  $pK_a(NH_4^+)$  and hence calculate  $K_a(NH_4^+)$ .
- (b) Explain why the pH at the equivalence point for this titration is less than 7. (Include an equation to support your answer.)
- (c) A  $NH_4^+ / NH_3$  buffer solution is prepared with a pH of 9.6. Use the graph to describe how this buffer solution could be made from  $0.0500 \text{ mol L}^{-1}$   $NH_3$  solution and  $0.200 \text{ mol L}^{-1}$  HCl solutions.

A second titration is carried out – this time 40.0 mL of  $0.0500 \text{ mol L}^{-1}$   $NH_4Cl$  solution is titrated against  $0.200 \text{ mol L}^{-1}$  NaOH solution.

- (d) Write an equation for the titration reaction.
- (e) (i) Show that  $[NH_3]$  at the equivalence point is  $0.0400 \text{ mol L}^{-1}$ .
- (ii) Using  $K_a(NH_4^+)$  determined in part (a) above, determine the pH at the equivalence point of the second titration.