PRACTICAL PROBLEMS

PROBLEM 1 (practical)

A pH buffer solution has a well defined acidity which changes only very slightly upon addition of moderate quantities of strong acid or base. The larger is the quantity of acid or base that must be added to a certain volume of a buffer solution in order to change its pH by a specific amount, the better is its action. A buffer solution is prepared by mixing a weak acid and its conjugate base in appropriate amounts in a solution. An example of a useful buffer system in aqueous solution is the phosphate system.

Your task is to prepare a phosphate buffer with properties specified by the following two conditions:

(1) pH = 7.20 in the buffer solution,

(2) pH = 6.80 in a mixture of 50.0 cm^3 of the butter solution and 5.0 cm^3 hydrochloric acid with a concentration of 0.100 mol dm^{-3}.

Chemicals and equipment

Aqueous solution of phosphoric acid, sodium hydroxide solution of known concentration, hydrochloric acid (0.100 mol dm^{-3}), solution of bromocresol green, distilled water.

Burettes, pipettes (25 and 5 cm^3), Erlenmeyer flasks (100 and 250 cm^3), volumetric flask (100 cm^3), beaker, and funnel.

Procedure

Determine the concentration of the phosphoric acid solution by titration with a sodium hydroxide solution using bromocresol green as an indicator (pH range $3.8 < pH < 5.4$).

Make a buffer solution by mixing calculated volumes of phosphoric acid and sodium hydroxide solutions in the volumetric flask and filling the flask to the mark with distilled water.

Mix in an Erlenmeyer flask 50.0 cm^3 of the buffer solution with 5.0 cm^3 of the hydrochloric acid.

Hand in your answer sheet to the referee who will also measure the pH of your two solutions and note your results.

The pK_a values for phosphoric acid are:

$pK_{a1} = 1.75, \quad pK_{a2} = 6.73, \quad pK_{a3} = 11.50$

SOLUTION

The buffer solution must contain

$H_2PO_4^-$ (concentration **a** mol dm^{-3}) and

HPO_4^{2-} (concentration **b** mol dm^{-3}).

The concentrations should satisfy the condition

$$\frac{\mathbf{b}}{\mathbf{a}} = \frac{10^{-6.73}}{10^{-7.20}}$$

After addition of HCl the condition will be

$$\frac{50.0\,b - 0.50}{50.0\,a + 0.50} = \frac{10^{-6.73}}{10^{-6.80}}$$

From these equations,

a = 0.0122 **b** = 0.0361

Total concentration of the phosphate system = 0.0483 mol dm^{-3}

Total concentration of Na^+ = (**a** + 2 **b**) mol dm^{-3} = 0.0844 mol dm^{-3}

If the concentration of both phosphoric acid and sodium hydroxide solution are 0.500 mol dm^{-3}, then 100.0 cm^3 buffer solution will require:

$$\text{volume of } H_3PO_4 \text{ solution} = \frac{0.0483 \times 0.1000}{0.500\,dm^3} = 9.7\,cm^3$$

$$\text{volume of NaOH solution} = \frac{0.0844 \times 0.1000}{0.500\,dm^3} = 16.9\,cm^3$$

PROBLEM 2 (practical)

Each of 8 numbered test tubes contains a solution of one salt. In the solutions the following positive ions can be found (a maximum of one in each test tube):

Ag^+, Al^{3+}, Cu^{2+}, Na^+, NH_4^+, and Zn^{2+}

and the following negative ions (at most one in each test tube)

Br^-, Cl^-, I^-, NO_3^-, OH^-, and $S_3O_3^{2-}$.

A test plate, test tubes in a rack, dropping pipettes, indicator paper, and a gas burner are also provided.

Determine by means of mutual reactions which salt is dissolved in each test tube. Confirm your conclusions by carrying out as many reactions as possible. It may be necessary to use combinations of solutions and reagents.

Give a list of numbers and corresponding formulae of the substances, indicate the formation of a precipitate by a downward arrow, and gas evolution by an upward arrow in the square array provided for reporting the reactions.

Write chemical equations for all the reactions observed.

SOLUTION

Numbers of solutions mixed	Chemical equation for the observed reaction
1 + 2	$NH_4^+ + OH^- \rightarrow NH_3(g) + H_2O$
2 + 3	$2\ OH^- + 2\ Ag^+ \rightarrow Ag_2O(s) + H_2O$
2 + 3 + 1	$Ag_2O(s) + 4\ NH_4^+ + 2\ OH^- \rightarrow 2\ Ag(NH_3)_2^+ + 3\ H_2O$
2 + 4	$Zn^{2+} + 2\ OH^- \rightarrow Zn(OH)_2(s) \leftrightarrow Zn(OH)_2(s) + 2\ OH^- \rightarrow Zn(OH)_4^{2-}$
2 + 5	$Al^{3+} + 3\ OH^- \rightarrow Al(OH)_3(s) \leftrightarrow Al(OH)_3(s) + OH^- \rightarrow Al(OH)_4^-$

Reactions to distinguish Zn^{2+} from Al^{3+}:

Numbers of solutions mixed	Chemical equation for the observed reaction
2 + 4 + 1	$Zn(OH)_4^{2-} + 4\ NH_4^+ \rightarrow Zn(NH_3)_4^{2+} + 4\ H_2O$
2 + 5 + 1	$Al(OH)_4^- + 2\ NH_4^+ \rightarrow Al(OH)_3(s) + NH_3 + H_2O$
2 + 6	$Cu^{2+} + 2\ OH^- \rightarrow Cu(OH)_2(s)$

2 + 6 + 1	$Cu(OH)_2(s) + 4\ NH_4^+ + 2\ OH^- \rightarrow\ Cu(NH_3)_4^{2+} + 4\ H_2O$
3 + 4	$Ag^+ + Cl^- \rightarrow\ AgCl(s)$
3 + 6	$Ag^+ + Br^- \rightarrow\ AgBr(s)$
3 + 7	$Ag^+ + I^- \rightarrow\ AgI(s)$
3 + 8	$2\ Ag+ + S_2O_3^{2-} \rightarrow Ag_2S_2O_3(s) \leftrightarrow\ Ag_2S_2O_3(s) + 3\,S_2O_3^{2-} \rightarrow$ $\rightarrow 2\,Ag(S_2O_3)_2^{3-}$

Reactions to distinguish Cl^- from Br^- and from I^-

3 + 4 + 1 + 2	$AgCl(s) + 2\ NH_4^+ + 2\ OH^- \rightarrow\ Ag(NH_3)_2^+ + Cl^- + H_2O$
3 + 4 + 8	$AgCl(s) + 2\ S_2O_3^{2-} \rightarrow\ Ag(S_2O_3)_2^{3-} + Cl^-$
3 + 6 + 1 + 2	AgBr(s) does not dissolve
3 + 6 + 8	$AgBr(s) + 2\ S_2O_3^{2-} \rightarrow\ Ag(S_2O_3)_2^{3-} + Br^-$
3 + 7 + 8	AgI(s) does not dissolve
6 + 7	$2\ Cu^{2+} + 4\ I^- \rightarrow\ 2\ CuI(s) + I_2$
6 + 7 + 8	$I_2(s) + 2\ S_2O_3^{2-} \rightarrow\ 2\ I^- + S_4O_6^{2-}$

	1	2	3	4	5	6	7	8
1		↑						
2	↑		↓	↓	↓	↓		
3		↓		↓		↓	↓	↓
4		↓	↓					
5		↓						
6		↓	↓				↓	
7			↓			↓		
8			↓					

List of numbers and corresponding formulae for the substances:

1. NH_4NO_3
2. NaOH
3. $AgNO_3$
4. $ZnCl_2$
5. $Al(NO_3)_3$
6. $CuBr_2$
7. NaI
8. $Na_2S_2O_3$

PROBLEM 3 (practical)

Determination of the solubility product of lead(II) chloride

Shake solid lead(II) chloride:

a) with water,

b) with three solutions of sodium chloride of different concentrations,

until equilibrium is attained. Then determine the lead ion concentration by titration with EDTA. Calculate the solubility product of lead(II) chloride.

Equipment and chemicals

Volumetric flask (100 cm^3), pipettes (20 cm^3 and 10 cm^3), graduated cylinder (100 cm^3 and 25 cm^3), 4 Erlenmeyer flasks (200 – 250 cm^3) with stoppers, spatula, 4 filter funnels, filter papers, thermometer, 4 Erlenmeyer flasks (100 cm^3), titrating flasks (200 – 250 cm^3), beakers, stand with burette (50 cm^3), burette funnel, wash bottle with distilled water, glass rod.

Standard solutions of sodium chloride (0.1000 mol dm^{-3}) and EDTA (0.01000 mol dm^{-3}), solid lead(II) chloride, xylenol orange solution in a dropping bottle (0.5 % in water), solid hexamine (urotropine), nitric acid (2.5 mol dm^{-3}) in a dropping bottle.

Procedure

1. Prepare 100 cm^3 of sodium chloride solutions with concentrations of 0.0600 mol dm^{-3}, 0.0400 mol dm^{-3}, and 0.0200 mol dm^{-3}, respectively. Place the solutions in Erlenmeyer flasks with stoppers. Place 100 cm^3 of water in the fourth flask with a stopper. Add 5 spatulas of solid lead(II) chloride (about 2 g) to each, stopper the flasks and shake vigorously. Let the flasks stand for 30 minutes. Shake them occasionally. Prepare for filtration and titration in the meanwhile.
2. Measure the temperatures of the lead(II) chloride solutions and report them in the table of results. Filter the solutions through dry filters into small, dry Erlenmeyer flasks.
3. Using a pipette, transfer 10.00 cm^3 of the filtrate into a titration flask. Dilute with approximately 25 cm^3 of water, add 3 drops of xylenol orange (indicator) and 5 drops of nitric acid. Then add 5 spatulas (about 0.5 g) of solid hexamine (a weak base) and swirl gently until the solution is clear. Titrate with EDTA.

4. Calculate the concentration of lead ions and that of chloride ions in the solutions and give the solubility product K_s. Report the results in the table.
5. Answer the questions in the answer sheet.

Questions

3.1 Give the structure of EDTA. Mark those atoms which can coordinate to a metal ion with an asterisk (*).

3.2 Give the equation for the filtration reaction. EDTA may be written as H_2X^{2-}.

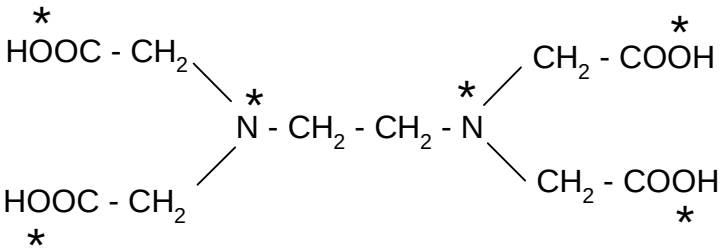
SOLUTION

A typical result:

c(NaCl) (mol dm^{-3})	Temperature (℃)	Volume EDTA solution (cm^3)	[Pb^{2+}] (mol dm^{-3})	[Cl^-] (mol dm^{-3})	K_s
0.0600	21	18.7	0.0187	0.0974	1.77×10^{-4}
0.0400	21	22.7	0.0227	0.0854	1.66×10^{-4}
0.0200	21	27.8	0.0278	0.0756	1.59×10^{-4}
-	21	34.2	0.0342	0.0684	1.60×10^{-4}

Answers to the questions:

3.1



3.2 $H_2Y^{2-} + Pb^{2+} \rightarrow PbY^{2-} + 2\ H^+$