PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Four aqueous solutions are available on the laboratory desk. These are solutions of HCl, NaOH, NH_3, and CH_3COOH whose concentrations are approximately 1 mol dm^{-3}. The concentration of HCl solution is the only one that is exactly determined and known.

Using the volumetric solution of HCl, determine the exact concentrations of the other solutions. A burette, pipette, titration flasks and indicators methyl orange and phenolphthalein are at your disposal. Perform twice each titration and calculate the mean value for concentration. The third determination is needed to be carried out only in such a case when the results of the previous two titrations differ more than by 2 %.

Now you will perform the following thermochemical measurements of neutralisation heat evolved in the reactions of the above given solutions of acids and bases:

a) Measure quantitatively exactly 50.0 cm^3 of the hydrochloric acid solution into a beaker. Measure into another equal beaker a volume of NaOH solution that contains such a number of moles of NaOH as that of HCl being present in the first beaker. Then measure the temperatures of both solutions with a precision of 0.2 K. Pour quickly the content of the first beaker into the other using the thermometers as a glass stick and stir the resulting solution with the thermometer. Determine the final highest temperature of the mixture.

b) Perform analogous measurement with the following pairs of acids and bases:
$HCl – NH_3$, $CH_3COOH – NaOH$, $CH_3COOH – NH_3$.

Problems:

1.1 What indicators have been used for the individual determinations? Give approximately pH regions in which the mentioned indicators show colour transitions. Give reasons for the use of the individual indicators using only ionic equations for the reactions which are characteristic of specific properties of salts being formed in the individual neutralisation reactions. Calculate the concentrations of all solutions under investigations.

1.2 Write the calorimetric equation in its general form by means of which the neutralisation heat can be calculated. Calculate the thermal effect for each neutralisation reaction under investigation and give the value in relation to one mole of the water formed.

Densities of the solutions are as follows:

$\rho(HCl) = 1.02$ g cm^{-3}

$\rho(NaOH) = 1.04$ g cm^{-3}

$\rho(NH_3) = 0.99$ g cm^{-3}

$\rho(CH_3COOH) = 1.01$ g cm^{-3}

In the calculations consider the specific heat capacity value for the solutions equal to 4.19 J g^{-1} K^{-1} whereas the heat capacity of glass and thermometer may be neglected.

1.3. Have you obtained equal results in all four cases? If not, order the particular reaction systems according to the decreasing value of reaction heat. What reactions cause the above mentioned differences? Express the reactions by means of chemical equations.

1.4 The exact methods showed that neutralisation heat in the reaction of the strong acid with a strong base (i. e. the reaction heat when 1 mole of water is formed from H^+ and OH^- ions) is equal to 57.57 kJ mol^{-1}. Calculate the relative error of your determination.

SOLUTION

1.1. In titrating a strong acid with a strong base, both phenolphthalein and methyl orange can be used as acid-base indicators. The drop on the titration curve covers the colour changes of both indicators (pH values from 4 – 10).

Only phenolphthalein can be used in the case when a weak acid is titrated with a strong base because the neutralisation occurs at higher pH values (the colour transition of phenolphthalein is in the region of pH = 8 – 10). A salt formed undergoes hydrolysis (more precisely its anion) and the solution exhibits a basic reaction:

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

In titrating a strong acid with a weak base or vice versa, methyl orange is used (pH = 3 – 4.5) and due to hydrolysis the resulting solution shows an acidic reaction:

$$NH_4^+ + 2\ H_2O \rightleftharpoons NH_3 \,.\, H_2O + H_3O^+$$

The exact concentrations of the aqueous solutions of sodium hydroxide and ammonia are determined by titrations with the volumetric solution of hydrochloric acid. The exact concentration of the acetic acid solution is then determined by a titration with the sodium hydroxide solution.

1.2 When the specific heat capacities of glass and thermometer are neglected the neutralisation heat can be then calculated according to a simple relation:

$\Delta H_{neutr.} = (m_1 + m_2)\ c\ (T_2 - T_1)$

m_1 – mass of the first solution,

m_2 – mass of the second solution,

c – specific heat capacity of the solutions,

T_1 – temperatures of the solutions before mixing,

T_2 – temperatures of the solutions after mixing.

If the temperatures of the solutions before mixing are not equal then T_1 will be the mean temperature of both. Finally, the neutralisation heat value should be related to 1 mole of water formed.

1.3 The results obtained for the neutralisation of a strong base with a weak acid and vice versa, as well as for the reaction of a weak acid with a weak base, are lower than those obtained for the neutralisation of a strong acid with a strong base. A part of the heat is consumed for ionisation of a weak electrolyte:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

A similar equation can be written for $NH_3.H_2O$.

PROBLEM 2 (practical)

The values of standard reduction potentials are given for the following redox systems:

$2\ S_2O_3^{2-} / S_4O_6^{2-}$ $\qquad E_1^0 = 0.17$ V

$2\ I^- / I_2$ $\qquad E_2^0 = 0.535$ V

$2\ SO_4^{2-} / S_2O_8^{2-}$ $\qquad E_3^0 = 2.05$ V

Problems:

2.1 Set in order the oxidation forms of the above given redox systems from the weakest to the strongest oxidising agent (write into Table 1)

In a similar way order the reduction forms from the weakest to the strongest reducing agent.

2.2 In the bellow given equations mark by arrows the expected possible course (direction) of the chemical reaction (Table 1).

$2\ I^- + S_4O_6^{2-} = I_2 + 2\ S_2O_3^{2-}$

$2\ I^- + S_2O_8^{2-} = I_2 + 2\ SO_4^{2-}$

$2\ S_2O_3^{2-} + S_2O_8^{2-} = S_4O_6^{2-} + 2\ SO_4^{2-}$

2.3 On the assumption that solutions of the same concentration are used, is it possible to tell without making any experiment which of the given reactions would run at a higher rate and which ones at a lower rate?

In order to confirm your hypothesis given under 3, perform the following three qualitative experiments:

Experiment 1

Pour 20.0 cm^3 of a 0.10-molar solution of $Na_2S_2O_3$ into an Erlenmeyer flask and quickly add under intense stirring 1.0 cm^3 of a 0.10-molar iodine solution.

Experiment 2

Measure 20.0 cm^3 of a 0.10-molar solution of $(NH_4)_2S_2O_8$ into an Erlenmeyer flask and quickly add under intense stirring 4.0 cm^3 of a 0.10-molar potassium iodide solution.

Experiment 3

Put 20.0 cm^3 of a 0.10-molar solution of $(NH_4)_2S_2O_8$ into an Erlenmeyer flask and then quickly add under intense stirring 2.0 cm^3 of a 0.10-molar sodium thiosulphate solution.

Since both the reactants and reactant products are colourless, the course of the reaction can be followed indirectly. For that purpose, add to the solution after 1 – 2 minutes two or three drops of a 0.10-molar iodine solution. If the result of your experiment is surprising, perform experiment No 3 again but allow solutions of $Na_2S_2O_3$ and $(NH_4)_2S_2O_8$ to react for 10 minutes.

Order the reactions from experiments No 1 – 3 (into Table 3) according to their increasing reaction rate and then answer the question whether it is possible on the basis of known values of the standard reduction potentials to guess, at least qualitatively, the reaction rate for the reaction mixture containing two pairs of redox systems.

Conclusions made on the above experiments make it possible to investigate the influence of concentration of each of the starting substances on the rate of the reaction between I^- and $S_2O_8^{2-}$ ions.

Perform experiment No 4 according to the following instructions:

Experiment 4

a) Measure successively into a 250 cm^3 Erlenmeyer flask: 25.0 cm^3 of a 0.20-molar potassium iodide solution, 10.0 cm^3 of a 0.01-molar sodium thiosulphate solution, 5.0 cm^3 of a starch paste, and stir the content of the flask.

b) Measure 25.0 cm^3 of a 0.20-molar $(NH_4)_2S_2O_8$ solution into a 100 cm^3 beaker. Pour the content of the beaker quickly into the flask, press a stop-watch and stir the content of the flask. Measure the time till the moment when the solution becomes blue.

Perform analogously experiment No 4 three times over, using the bellow given volumes of the 0.20-molar potassium iodide solution, while the volumes of $Na_2S_2O_3$ and $(NH_4)_2S_2O_8$ solutions as well as that of the starch paste remain unchanged. Moreover, add to the solution the bellow given volumes of a 0.20-molar potassium nitrate solution so that the volume of the resulting solution is always the same. Explain the use of potassium nitrate in this case.

4 (ii): 15.0 cm^3 0.20-molar KI + 10.0 cm^3 0.20-molar KNO_3

4 (iii): 10.0 cm^3 0.20-molar KI + 15.0 cm^3 0.20-molar KNO_3

4 (iv): 5.0 cm^3 0.20-molar KI + 20.0 cm^3 0.20-molar KNO_3

2.4 List the results of experiments No 1-4 briefly and clearly in the attached Tables.

Write formulas of the corresponding substances above the arrows in Table 1 (as required under 2.1) and mark the expected course of the mentioned chemical reactions by arrows in the equations.

For a qualitative evaluation of reaction rate (Table 2) use terms such as: very rapid, rapid, slow, very slow.

Fill in Table 3 exactly according to the titles of the columns.

2.5 Calculate the reaction rate according to the formula:

$$v = \frac{\Delta c(S_2O_8^{2-})}{\Delta \tau} \text{ (mol dm}^{-3}\text{ s}^{-1}\text{)}$$

$\Delta c(S_2O_8^{2-})$ - concentration change of $S_2O_8^{2-}$ in a time interval.

Plot (on the attached mm-paper) the dependence of reaction rate on the concentration of I^- anions at a constant concentration of $S_2O_8^{2-}$ anions in the solution.

2.6 Making use of the knowledge gained from the preceding experiment and the solutions which are at your disposal, suggest another experiment which would make it possible to investigate the reaction rate dependence on concentration of $S_2O_8^{2-}$ anions at a constant concentration of I^- anions in the solution.

Considering Table 3, fill in Table 4. Mark the columns in the Table, suggest a plan of the experiment and list experimental results as well as the calculated values. Similarly as before, plot the dependence under investigation on a mm-paper.

2.7 Write a general relation for the reaction rate dependence on the concentration of reactants and then using the diagrams attached, calculate the values for the reaction rate constant for both cases and determine their mean value.

SOLUTION

2.1 $S_4O_6^{2-}$ I_2 $S_2O_8^{2-}$ →

Increase of oxidising properties of oxidised forms

SO_4^{2-} I^- $S_2O_3^{2-}$ →

Increase of reducing properties of reduced forms

2.2 The expected course of the chemical reactions:

$$2\,I^- + S_4O_6^{2-} \leftarrow I_2 + 2\,S_2O_3^{2-} \qquad \text{(a)}$$

$$2\,I^- + S_2O_8^{2-} \rightarrow I_2 + 2\,SO_4^{2-} \qquad \text{(b)}$$

$2\ S_2O_3^{2-} + S_2O_8^{2-} \rightarrow S_4O_6^{2-} + 2\ SO_4^{2-}$ (c)

2.3 The formulation of any hypothesis either supporting or neglecting the possibility of predicting the reaction rate, should be accepted as correct.

Results of experiments Nos 1-3:

1 - reaction (a) is very rapid;

2 - reaction (b) is slow;

3 - reaction (c) is very slow, its course can hardly be observed.

Conclusion: The known differences between the values of standard reduction potentials of two pairs of redox systems do not allow to guess even qualitatively the proper relations between the rates of the corresponding reactions.

2.4 You are required to fill in the following data into Table 3:

- volumes of individual solutions,
- the total volume of the solution (65 cm^3),
- calculated values for I^- and $S_2O_8^{2-}$ concentrations,
- reaction time,
- calculated values for the reaction rate.

The addition of 0.20-molar KNO_3 solution is needed to keep the constant ionic strength of the resulting solution.

In plotting the reaction rate in dependence on the values of $[I^-]^2$ (at the constant concentration of $S_2O_8^{2-}$ anions) we get a straight line crossing the beginning of the coordinate system.

Table 4 should be filled in analogously as Table 3 where, moreover, the individual columns should be specified.

Solutions for the experiment are prepared in the same way but the solution of KI (25 cm^3) will form a constant addition, whereas those of $(NH_4)_2S_2O_8$ and $(NH_4)_2SO_4$ will form a changeable addition in the resulting solution and the other conditions are equal. Ammonium sulphate plays the same role in the solution as potassium nitrate in the preceding experiment.

In this case the reaction rate versus the concentration of $S_2O_8^{2-}$ anions is plotted (at a constant concentration of I^- anions) to give also a straight line crossing the beginning of the coordinate system.

2.5 The rate of the reaction:

$v = k\,[S_2O_8^{2-}]\,[I^-]^2$

a) $[I^-] = \text{const} \Rightarrow v = k'\,[S_2O_8^{2-}]$

$$k = \frac{k'}{[I^-]^2}$$

k' is the slope of the straight line.

b) $[S_2O_8^{2-}] = \text{const}$ $v = k''\,[I^-]^2$

$k'' = k\,[S_2O_8^{2-}]$

$$k = \frac{k''}{[S_2O_8^{2-}]}$$

k'' is the slope of the straight line.

The values of the rate constants obtained from the procedures a) and b) should be theoretically equal. If they partly differ, calculate the mean value of the rate constant.