

19th



5 theoretical problems
3 practical problems

THE NINETEENTH INTERNATIONAL CHEMISTRY OLYMPIAD 6–15 JULY 1987, VESZPRÉM – BUDAPEST, HUNGARY

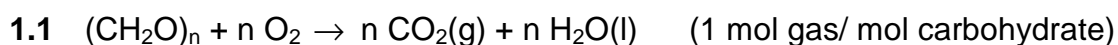
THEORETICAL PROBLEMS

PROBLEM 1

Treating waste water in a sewage plant, 45 % of its carbohydrate $(\text{CH}_2\text{O})_n$ is completely oxidized, 10 % undergoes anaerobic decomposition by fermentation (two components) and the rest remains in the sludge. The total gas formation is 16 m^3 per day ($25 \text{ }^\circ\text{C}$, 100 kPa).

- 1.1 What is the amount of carbohydrate remaining in the sludge measured in kg per day?
- 1.2 Using the heat of combustion of methane (-882 kJ mol^{-1}), calculate the amount of energy that can be produced by combustion of the methane formed per day.
- 1.3 Knowing that the concentration of the carbohydrate in the waste water is 250 mg dm^{-3} , calculate the daily amount of waste water processed in the plant in m^3 of water per day.

SOLUTION



For 16 m^3 of gases: $n(\text{gas}) = \frac{pV}{RT} = 646 \text{ mol}$ (55 %) with the rest (45 %) therefore

being in the sludge.

The amount in the sludge is $\frac{45}{55} \times 646 = 528 \text{ mol}$, that is 15.85 kg/day.

$$1.2 \quad n(\text{CH}_4) = \frac{5}{55} \times 646 = 58.71 \text{ mol}$$

$$\Delta H = -882 \times 58.71 = -5.178 \times 10^4 \text{ kJ/day}$$

1.3 The sum of CH₂O is $\frac{646}{0.55} = 1174$ mol. Since $250 \text{ mg dm}^{-3} = 0.25 \text{ kg m}^{-3}$, the daily

amount of water is: $V = \frac{1174 \times 30}{0.25 \times 10^3} = \underline{140.9 \text{ m}^3/\text{day}}$

PROBLEM 2

500 mg of a hydrated sodium salt of phosphoric acid are dissolved in 50.0 cm³ of 0.1 molar sulphuric acid. This solution is diluted with distilled water to 100.0 cm³ and 20.0 cm³ of it are titrated with 0.100 molar NaOH solution using thymolphthalein as indicator. The average of the burette reading is 26.53 cm³. The pH at the end-point is 10.00.

Problems:

- 2.1 Calculate the percentage distribution by moles of all protonated H_nPO₄ⁿ⁻³ species at the end-point.
- 2.2 What is the stoichiometric formula of the salt?

The cumulative protonation constants are given by

$$\beta_n = \frac{[\text{H}_n\text{PO}_4^{n-3}]}{[\text{PO}_4^{3-}][\text{H}^+]^n}$$

where $\log\beta_1 = 11.70$; $\log\beta_2 = 18.6$; $\log\beta_3 = 20.6$.

The relative atomic masses are: Na = 23.0; P = 31.0; H = 1.0; O = 16.0.

SOLUTION

2.1 $[\text{H}_3\text{PO}_4] + [\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + [\text{PO}_4^{3-}] = T_{\text{konst}}$; $[\text{H}^+] = 10^{-10} \text{ mol dm}^{-3}$

$$[\text{H}_3\text{PO}_4] = 1 \text{ mol dm}^{-3}$$

$$[\text{HPO}_4^{2-}] = \beta_1[\text{PO}_4^{3-}][\text{H}^+] = 1.25 \times 10^{10} \text{ mol dm}^{-3} = 97.97 \%$$

$$[\text{H}_2\text{PO}_4^-] = \beta_2[\text{PO}_4^{3-}][\text{H}^+]^2 = 1 \times 10^8 \text{ mol dm}^{-3} = 0.078 \%$$

$$[\text{PO}_4^{3-}] = (\beta_3[\text{H}^+]^3)^{-1} = 2.5 \times 10^9 \text{ mol dm}^{-3} = 1.955 \%$$

2.2 A general formula of the salt: $\text{Na}_{3-n}(\text{H}_n\text{PO}_4) \times m \text{ H}_2\text{O}$ ($n = 0, 1, 2$)

The titrated solution contains 100 mg (y mol) of the salt and 1.00 mmol of sulphuric acid. The reacted protons (in mmol) can be calculated using the results of a):

$$2 + (n - 0.9797 - 2 \times 0.00078) y = 2.653$$

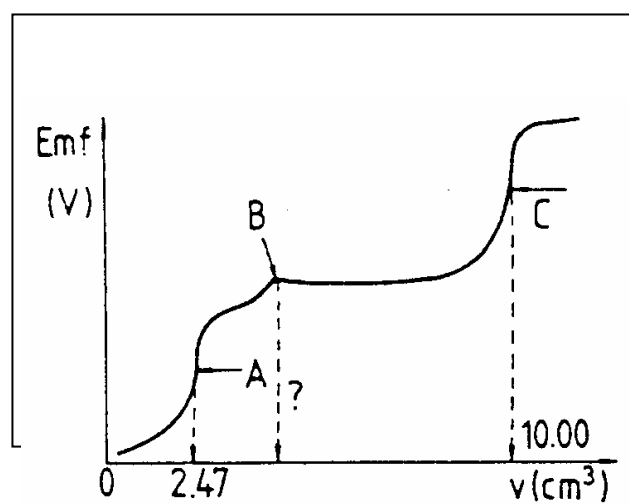
Since $y = 100/M$ (in mmol) but $M \geq 120 \text{ g mol}^{-1}$, the only real solution is $n = 2$.

Therefore $M = 156 \text{ g mol}^{-1}$, m is $(156-120)/18 = 2 \Rightarrow \underline{\text{NaH}_2\text{PO}_4 \cdot 2 \text{ H}_2\text{O}}$

PROBLEM 3

25.00 cm³ of a neutral solution containing potassium chloride and potassium cyanide are potentiometrically titrated with a standard 0.1000 molar silver nitrate solution at 25 °C using a silver electrode and a normal calomel half-cell with KNO₃ - salt bridge. The protonation of cyanide ions is negligible. The potentiometric curve obtained (emf (V)) vs. burette readings (in cm³) is shown in Fig. 1.

Fig. 1



- 3.1 The end points of the reactions taking place during the titration, are marked with A, B and C. Write the balanced ionic equation for each reaction.
- 3.2 What volume of the titrant is required to reach point B?
- 3.3 Calculate the concentrations of KCl and KCN (in mol dm⁻³) in the sample solution.
- 3.4 Calculate the emf readings at the points A and C in volts.
- 3.5 What is the molar ratio Cl⁻/CN⁻ in the solution and in the precipitate at point C?

Data:

$$E^{\circ}(\text{Ag}^+/\text{Ag}) = 0.800 \text{ V}$$

$$E^{\circ}(\text{Calomel}) = 0.285 \text{ V}$$

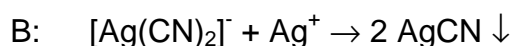
$$K_{sp}(\text{AgCN}) = 10^{-15.8}$$

$$K_{sp}(\text{AgCl}) = 10^{-9.75}$$

$$\beta_2 = \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = 10^{21.1}$$

SOLUTION

3.1 β_2 indicates that the complexation of Ag^+ with CN^- occurs easily. Thus A denotes the point where all Ag^+ is present in the complex form, having a higher potential than Ag^+ , B shows the point where the precipitation of AgCN starts, thus leading to a constant Ag^+ concentration until all CN^- is precipitated. Now at point C the precipitation of the more soluble AgCl begins:



$$3.2 \quad 2 \times 2.47 \text{ cm}^3 = \underline{4.94 \text{ cm}^3}$$

$$3.3 \quad [\text{CN}^-] = (4.94 \times 0.1 \times 40)/1000 \text{ mol dm}^{-3} = 1.98 \times 10^{-2} \text{ mol dm}^{-3}$$

$$[\text{Cl}^-] = ((10 - 4.94) \times 0.1 \times 40)/1000 \text{ mol dm}^{-3} = 2.02 \times 10^{-2} \text{ mol dm}^{-3}$$

3.4 For the system Ag/Ag^+ at point A: $E = E_o + 0.059 \log[\text{Ag}^+]$.

The following equations are derived from the equilibrium conditions:

$$[\text{Ag}^+] = \frac{[\text{Ag}(\text{CN}^-)_2]}{[\text{CN}^-]^2 \beta_2}$$

$$[\text{Ag}^+] + [\text{Ag}(\text{CN}^-)_2] = \frac{2.47 \times 0.1}{25 + 2.47}$$

$$[\text{CN}^-] = 2 [\text{Ag}^+]$$

It yields an equation of third degree in $[\text{Ag}^+]$:

$$4\beta_2[\text{Ag}^+]^3 + [\text{Ag}(\text{CN}^-)_2] = 0$$

$[\text{Ag}(\text{CN}^-)_2]$ can be assumed to be $(2.47 \times 0.1) / 27.47 \text{ mol dm}^{-3}$, and therefore $[\text{Ag}^+]$ equals $1.213 \times 10^{-8} \text{ mol dm}^{-3}$.

$$\text{The emf will be: } E = 0.8 + 0.059 \log[\text{Ag}^+] - 0.285 = \underline{0.048 \text{ V}}$$

$$\text{At point C: } [\text{Ag}^+] = \sqrt{K_{sp}(\text{AgCl})} = 1.333 \times 10^{-5} \text{ and}$$

$$E = 0.8 + 0.059 \log[\text{Ag}^+] - 0.285 = \underline{0.227 \text{ V}}$$

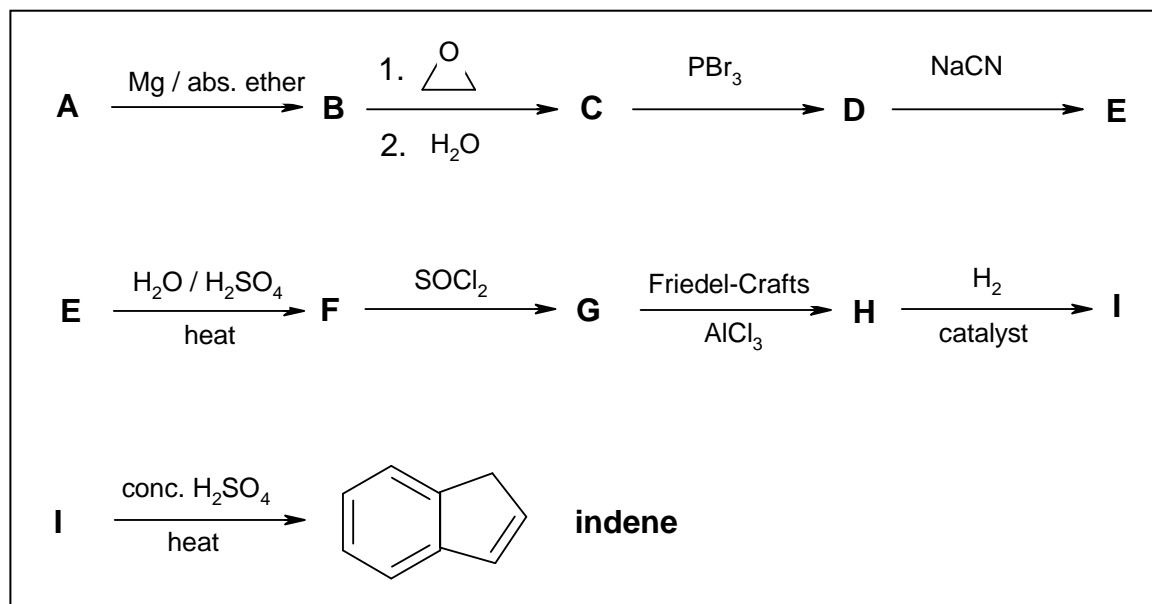
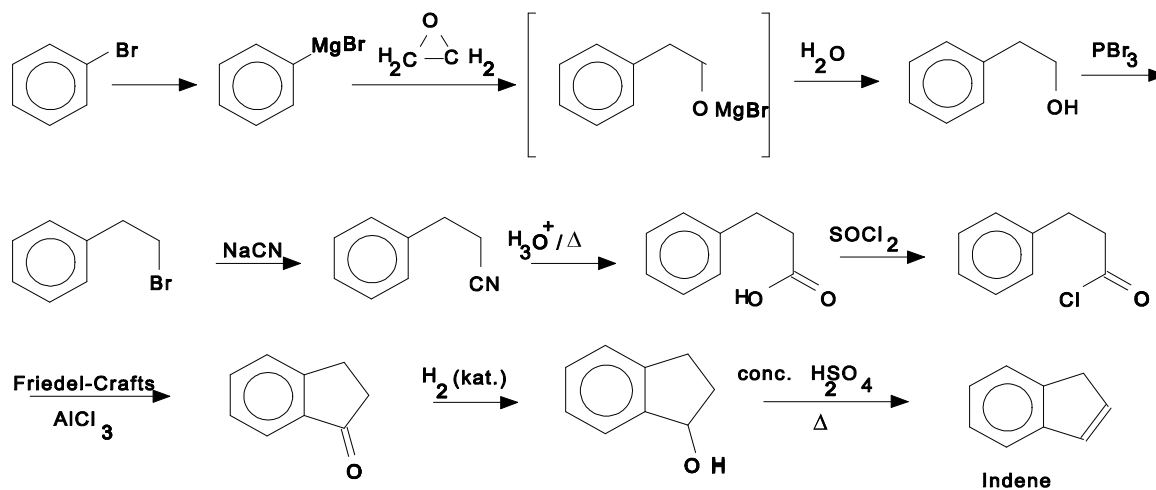
3.5 Since both AgCN and AgCl are present as the precipitate, the solution must be saturated:

$$\text{In the solution: } [\text{Cl}^-]/[\text{CN}^-] = K_{sp}(\text{AgCl})/K_{sp}(\text{AgCN}) = 10^{6.05} = \underline{1.222 \times 10^6}$$

$$\text{In the precipitate: } n(\text{AgCl}) / n(\text{AgCN}) = 2.02 / 1.98 = \underline{1.02}$$

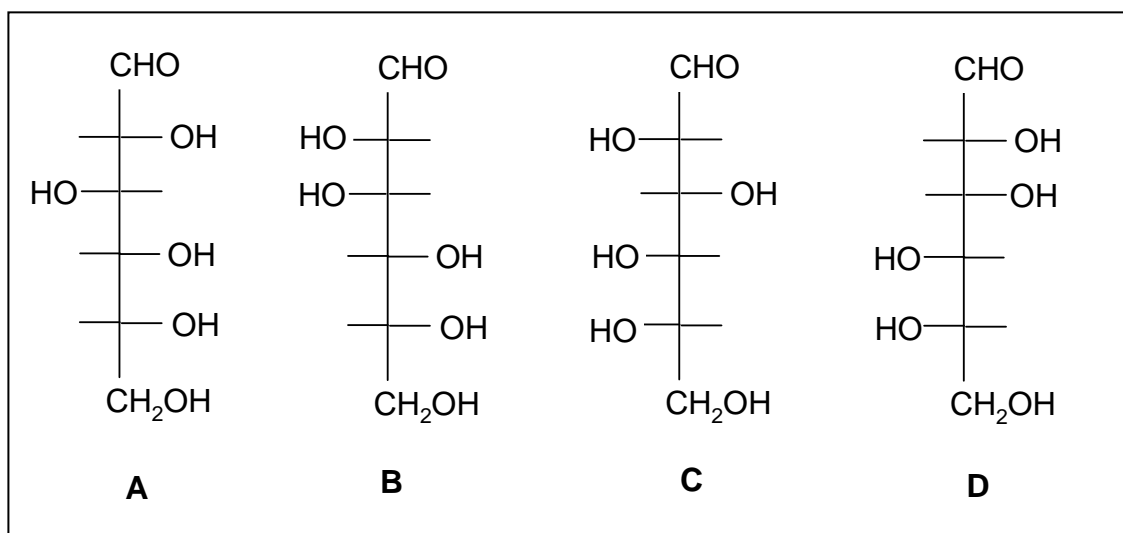
PROBLEM 4

Write the structural formulae of the compounds **A** to **I** in the following reaction sequence.

**SOLUTION**

PROBLEM 5

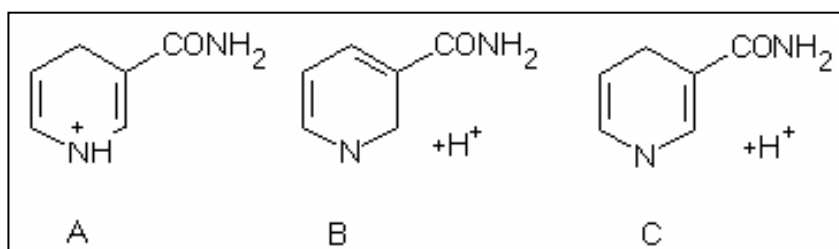
- 5.1** What ratio of primary / secondary / tertiary products can statistically be expected in the high temperature chlorination of methyl butane? Assume that the reaction rate of the substitution is equal for all C-H bonds.
- 5.2** Which of the following alcohols: pentan-1-ol, pentan-2-ol and 2-methyl-butan-2-ol react with the following reagents listed below?
1) cold, concentrated sulphuric acid; 2) $\text{CrO}_3 / \text{H}_2\text{SO}_4$; 3) $\text{ZnCl}_2 / \text{HCl}$; 4) I_2 / NaOH
- 5.3** Which of the following aldohexose structures are:
1) enantiomer pairs, 2) diastereomer pairs?



- 5.4** Two hydrocarbon compounds of the same molecular formula, C_4H_8 , easily react with hydrogen in the presence of a platinum catalyst. During ozonolysis only ethanal (acetaldehyde) is formed in both cases. The $^1\text{H-NMR}$ spectra of the two compounds show two types of protons in a ratio of 3 to 1. Draw the structures of the described compounds.
- 5.5** Select the components of the group listed below that can be obtained during complete hydrolysis of lecithin (a phospholipid): serine, phosphoric acid, sphingosine, choline, glycerol, myo-inositol, phosphatidic acid and fatty acids).
- 5.6** Which of the following carboxylic acid can be formed in the tricarboxylic acid cycle (Krebs' citric acid cycle):

maleic acid (cis-butenedioic acid), mandelic acid (α-hydroxy-phenylethanoic acid), malic acid (2-hydroxy-butanedioic acid), tricarb-allylic acid (propane-1,2,3-tricarboxylic acid), oxalacetic acid (2-oxo-butanedioic acid), keto-glutaric acid (2-oxo-pentanedioic acid), fumaric acid (trans-butenedioic acid) and acetoacetic acid (3-oxo-buta-noic acid).

- 5.7 To which structures is the nicotinamide moiety (part) of NAD⁺ converted during the uptake of hydrogen to form NADH (A, B or C)?



SOLUTION

- 5.1 The ratio of primary, secondary and tertiary products will be 9 : 2 : 1.

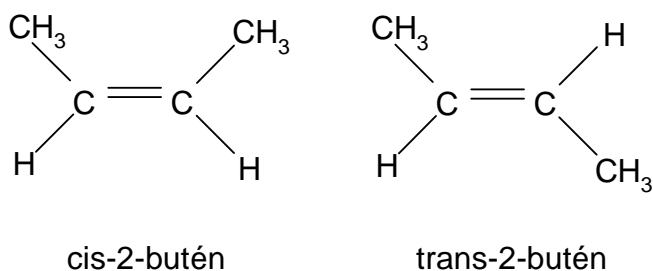
- 5.2 1-Pentanol reacts with 1) cold conc. sulphuric acid (elimination) and with 2) CrO₃/H₂SO₄ (oxidation).

2-Pentanol reacts with 1) under elimination, with 2) under oxidation, with 3) under reduction and with 4) (haloform oxidation).

2-Methyl-2-butanol reacts with 1) under elimination and with 3) under reduction.

- 5.3 a/c and b/d are enantiomers, a/b, a/d, b/c and c/d are diastereomers.

- 5.4



- 5.5** Glycerol, choline, phosphoric acid and fatty acids can be found during complete hydrolysis of lecithin.
- 5.6** maleic acid, oxalacetic acid, ketoglutaric acid, fumaric acid
- 5.7** c) is correct since the NAD^+ is converted into NADH/H^+
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PRACTICAL PROBLEMS**PROBLEM 1 (practical)**

You are required to investigate seven inorganic compounds.

Your test-tube rack is numbered 1 to 9. Two of the positions are empty. Each of the seven test-tubes provided contains only one compound in aqueous solution. Using only these solutions, pH indicator paper, and test-tubes, you are to identify as many of the ions present as you are able.

For your information, record in the table the observations you make on mixing the solutions. Use the following symbols:

elimination reactions: ↓ precipitate; ↑ gaseous product;

↓_s precipitate soluble in the excess of a precipitating agent.

colours: w - white or colourless, b - blue, g - green, y - yellow, p - pink, r - red, br - brown.

pH: a - acidic, b - alkaline, n - neutral.

Equipment:

A home-made rack contained 9 test-tubes with the unknown solutions, 30 empty Wassermann-tubes and one small beaker containing the pH indicator paper. Into each solution a dropper was inserted, and thus, the test-tubes need not to be removed from the rack while handling them. According to the original plan the following nine unknown solutions were expected to be given to the participants: CoCl_2 , $\text{Fe}(\text{SCN})_3$, NH_4OH , KI , AgNO_3 , Na_2HAsO_4 , HgCl_2 , NiCl_2 , CuCl_2 .

During the discussion of the International Jury it became known that in some countries the corresponding laws forbid the pupils in secondary schools to handle mercury and arsenic compounds. For this reason these two compounds were removed from the rack and consequently the number of ions to be detected - and the marks available - were reduced to 12 (from the original 15). (Under these conditions the alkali and nitrate ions cannot be detected.)

The order of the test-tubes varied individually, but the first two contained invariably red solutions (CoCl_2 and $\text{Fe}(\text{SCN})_3$), while the last two were the green NiCl_2 and CuCl_2 symbolizing the Hungarian national colours, red-white-green.

SOLUTION

The ions of the remaining seven solutions can easily be identified by mutual reactions. Out of the 21 possible reactions, 12 are common positive reactions. Additional information is available from the colour of 4, and the smell of one solution.

AgNO₃: reacts with all the six compounds;

NH₃: with the exception of iodide it gives a characteristic reaction with all the others salts;

Fe(SCN)₃: its colour and reaction with NH₃, I⁻, Ag⁺ are characteristic;

CoCl₂: can be detected from its colour and by adding NH₃ or Ag⁺;

KI: can be identified by its reaction with Ag⁺ and from the evolution of I₂ due to an addition of Fe³⁺ or Cu²⁺;

CuCl₂: can be detected from its colour and reaction with NH₃, I⁻ and Ag⁺;

NiCl₂: has a characteristic colour and reacts with NH₃ and Ag⁺.

PROBLEM 2 (practical)

You are required to estimate the heat (enthalpy) change on mixing a series of 5 liquids to produce equimolar mixtures and to explain the temperature changes.

Procedure:

1. A mixture of trichloromethane (chloroform) and propanone (acetone)

Measure 0.5 mol of trichloromethane in the measuring cylinder labelled A₁ and measure its temperature. Dry the thermometer with a piece of tissue paper. Measure 0.5 mol of propanone using measuring cylinder B₁, pour it into a beaker and measure its temperature. Record the average of the two temperatures as temperature t_1 (to 0.1 °C). Leave the thermometer in the beaker. Add the trichloromethane to the propanone, stir the mixture carefully and follow the temperature changes until a maximum or minimum is reached. Record this extreme temperature as temperature t_2 . Dispose the mixture into a special bottle labelled "waste solution", dry the reaction beaker and the thermometer and proceed to the next part of the experiment.

2. A mixture of methanol and propanone (acetone)

Measure 0.5 mol of propanone in measuring cylinder B₁ and 0.5 mol of methanol in measuring cylinder A₂, and continue as in part 1.

3. A mixture of methanol and n-hexane

Measure 0.5 mol of methanol into measuring cylinder A₂ and 0.5 mol of hexane into measuring cylinder B₂, and continue as in part 1.

4. A mixture of methanol and water

Measure 0.5 mol of methanol into measuring cylinder A₂, measure its temperature and pour it into the beaker. Rinse the cylinder thoroughly with distilled water and then measure 0.5 mole of water using this measuring cylinder. Continue as instructed in the above part 1.

Tasks:

Calculate the enthalpy (heat) changes involved in the mixings on the basis of the temperature changes observed. In your calculations you should neglect heat exchanges with the surroundings as well as the heat capacity of the beaker and thermometer. Briefly explain your results in terms of the molecular interactions in the pure liquids and in the mixture, preferably using sketches.

Data:

Substance	Relative molecular mass	Density (g cm ⁻³)	Molar heat capacity (J K ⁻¹ mol ⁻¹)
methanol	32.04	0.79	80.61
chloroform	119.38	1.49	114.94
acetone	58.08	0.79	124.96
n-hexane	86.18	0.66	190.10
water	18.02	1.00	75.35

PROBLEM 3 (practical)

You are required to determine the concentrations of hydrochloric acid and potassium iodate in the diluted solution containing both.

Procedure:

A solution containing potassium iodate and hydrochloric acid has already been measured into the volumetric flask provided. Fill the flask to the mark with distilled water using the wash bottle, close it with a stopper and shake it thoroughly. Fill the burette with the standard sodium thiosulphate solution using one of the beakers provided. (The exact concentration of the thiosulphate is given on the label of the bottle.)

a) First titration

Pipette a 10.00 cm³ aliquot (portion) of the solution from the volumetric flask into a glass stoppered conical flask. Dilute it with 10 cm³ of distilled water, add 1 g (a small spatula end-full) of potassium iodide and acidify with 10 cm³ of 10 % sulphuric acid using a measuring cylinder. Titrate immediately the iodine formed with the standard sodium thiosulphate solution until the solution in the flask is pale yellow. Add with a pipette 1 cm³ of starch indicator solution and continue the titration to completion. Repeat the titration twice more and record your readings on the result sheet.

b) Second titration

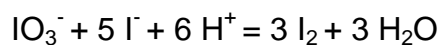
Pipette a 10.00 cm³ aliquot of the solution into another glass stoppered conical flask, dilute with 10 cm³ of distilled water, add 1 g of solid potassium iodide, and leave to stand for 10 minutes. Then titrate the iodine formed using the standard sodium thiosulphate solution, adding 1 cm³ of starch indicator solution when the mixture is pale yellow. Repeat the titration twice more, recording your readings on the result sheet.

Task:

Calculate the concentration of the HCl and the KIO₃ in the solution that you prepared by dilution (in mol dm⁻³).

SOLUTION

The reaction:



occurs to be quantitative both with respect to IO_3^- and H^+ . Consequently the first titration (in the presence of sulphuric acid) is suitable for the determination of iodate, while the second one for the determination of the hydrochloric acid content.
