43rd

8 theoretical problems
3 practical problems

THE FORTY-THIRD
INTERNATIONAL CHEMISTRY OLYMPIAD
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THEORETICAL PROBLEMS

PROBLEM 1

Nitrogen oxides, common pollutants in the ambient air, are primarily nitric oxide, NO, and nitrogen dioxide, NO_2. Atmospheric nitric oxide is produced mainly during thunderstorms and in the internal combustion engines. At high temperatures NO reacts with H_2 to produce nitrous oxide, N_2O, a greenhouse gas.

$$2\ NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$

To study the kinetics of this reaction at 820 °C, initial rates for the formation of N_2O were measured using various initial partial pressures of NO and H_2.

Exp.	Initial pressure, torr		Initial rate of production of N_2O, torr s^{-1}
	p_{NO}	p_{H_2}	
1	120.0	60.0	$8.66 \cdot 10^{-2}$
2	60.0	60.0	$2.17 \cdot 10^{-2}$
3	60.0	180.0	$6.62 \cdot 10^{-2}$

Throughout this problem do not use concentrations. Use units of pressure (torr) and time in seconds.

1.1 Determine the experimental rate law and calculate the rate constant.

1.2 Calculate the initial rate of disappearance of NO, if NO with a pressure of $2.00 \cdot 10^2$ torr and H_2 with $1.00 \cdot 10^2$ torr are mixed at 820 °C.

(If you have been unable to calculate the value for the rate constant, you can use the value of $2 \cdot 10^{-7}$ in appropriate unit.)

1.3 Calculate the time elapsed to reduce the partial pressure of H_2 to the half of its initial value, if NO with a pressure of $8.00 \cdot 10^2$ torr and H_2 with 1.0 torr are mixed at 820 °C.

(If you have been unable to calculate the value for the rate constant, you can use the value of $2 \cdot 10^{-7}$ in appropriate unit.)

A proposed mechanism for the reaction between NO and H_2 is given below:

$$2\,NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$$

$$N_2O_2(g) + H_2(g) \xrightarrow{k_2} N_2O(g) + H_2O(g)$$

1.4 Derive the rate law for the formation of N_2O from the proposed mechanism using the steady-state approximation for the intermediate.

1.5 Under what condition does this rate law reduce to the experimentally determined rate law found in Part 1.1? Tick the relevant answer.

☐ If $k_{-1} << k_2\, p_{H2}$

☐ If $k_{-1} >> k_2\, p_{H2}$

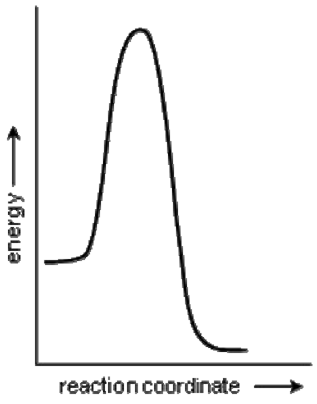
☐ If $k_{-1} > k_2$

☐ If $k_1 > k_{-1}$

1.6 Express the experimentally determined rate constant k in terms of k_1, k_{-1} and k_2.

1.7 Select the schematic energy diagram that is consistent with the proposed reaction mechanism and experimental rate law.

a.



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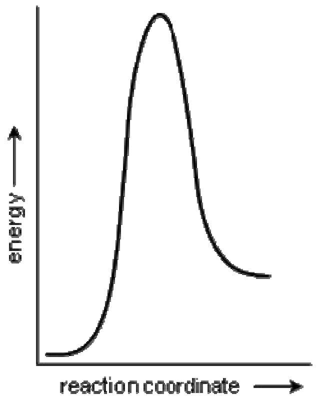

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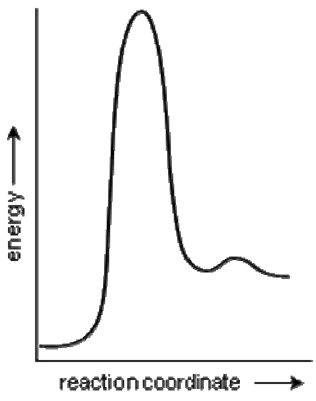

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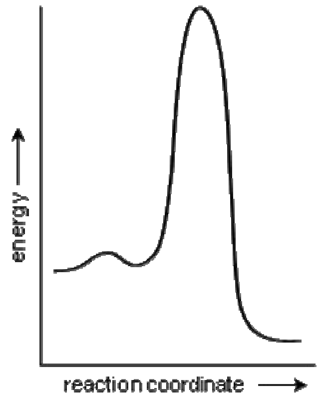
energy
reaction coordinate

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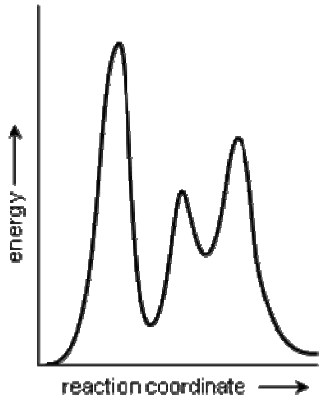
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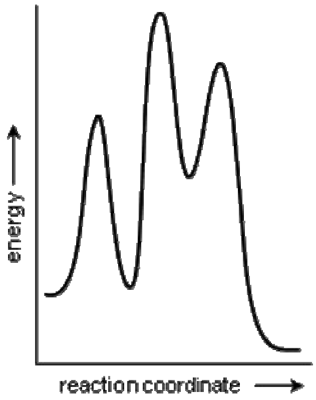

energy
reaction coordinate

SOLUTION

1.1 Rate = $R = k\,(p_{NO})^a\,(p_{H_2})^b$

$$\frac{R_1}{R_2} = \frac{8.66 \cdot 10^{-2}}{2.17 \cdot 10^{-2}} = 3.99 = \frac{k \times 120^a \times 60^b}{k \times 60^a \times 60^b} \qquad 2^a = 3.99 \;\Rightarrow\; a = 2$$

$$\frac{R_3}{R_2} = \frac{6.62 \cdot 10^{-2}}{2.17 \cdot 10^{-2}} = 3.05 = \frac{k \times 60^a \times 180^b}{k \times 60^a \times 60^b} \qquad 3^b = 3.05 \;\Rightarrow\; b = 1$$

Rate = $R = k\,(p_{NO})^2\,p_{H_2}$

$$k = \frac{8.66 \cdot 10^{-2}}{120^2 \times 60} = 1.00 \cdot 10^{-7}\ \text{torr}^{-2}\,\text{s}^{-1}$$

1.2 $$\text{Rate} = \frac{\Delta p_{N_2O}}{\Delta t} = -\frac{1}{2}\,\frac{\Delta p_{NO}}{\Delta t} = 1.0 \cdot 10^{-7} \times 200^2 \times 100 = 0.40\ \text{torr s}^{-1}$$

$$-\frac{\Delta p_{NO}}{\Delta t} = 0.80\ \text{torr s}^{-1}$$

1.3 Rate = $R = k\,(p_{NO})^2\,p_{H_2}$

Since $p_{NO} \gg p_{H_2}$

$$\text{Rate} = k'\,p_{H_2} \;\Rightarrow\; k' = k\,(p_{NO})^2$$

$k' = 1.0 \cdot 10^{-7} \times (8.00 \cdot 10^2)^2 = 0.064\ \text{s}^{-1}$

$$t_{1/2} = \frac{\ln 2}{k'} = 10.8\ \text{s}$$

1.4 $$\frac{\Delta p_{N_2O}}{\Delta t} = k_2\,p_{N_2O_2}\,p_{H_2}$$

Steady state approximation for N_2O_2:

$$\frac{\Delta p_{N_2O_2}}{\Delta t} = 0 = k_1\,(p_{NO})^2 - k_{-1}\,p_{N_2O_2} - k_2\,p_{N_2O_2}\,p_{H_2} = 0$$

$$p_{N_2O_2} = \frac{k_1\,(p_{NO})^2}{k_{-1} + k_2\,p_{H_2}}$$

$$\frac{\Delta p_{N_2O}}{\Delta t} = k_2\,p_{H_2}\,\frac{k_1\,(p_{NO})^2}{k_{-1} + k_2\,p_{H_2}}$$

$$\text{Rate} = \frac{\Delta p_{N_2O}}{\Delta t} = k_1 k_2\,\frac{(p_{NO})^2\,p_{H_2}}{k_{-1} + k_2\,p_{H_2}}$$

1.5 The correct answer: If $k_{-1} >> k_2\, p_{H_2}$

1.6 $k = \frac{k_1 k_2}{k_{-1}}$

1.7 Energy diagram **d** is correct.

PROBLEM 2

Anhydrous ammonia is an ultra-clean, energy-dense alternative liquid fuel. It produces no greenhouse gases on combustion.

In an experiment, gaseous NH_3 is burned with O_2 in a container of fixed volume according to the equation given below.

$$4\ NH_3(g) + 3\ O_2(g) \rightarrow 2\ N_2(g) + 6\ H_2O(l)$$

The initial and final states are at 298 K. After combustion with 14.40 g of O_2, some of NH_3 remains unreacted.

2.1 Calculate the heat released during the process.

$\Delta_f H^o(NH_3(g)) = -46.11$ kJ mol^{-1} and $\Delta_f H^o(H_2O(l)) = -285.83$ kJ mol^{-1}

To determine the amount of NH_3 gas dissolved in water, produced during the combustion process, a 10.00 cm^3 sample of the aqueous solution was withdrawn from the reaction vessel and added to 15.0 cm^3 of a H_2SO_4 solution (c = 0.0100 mol dm^{-3}). The resulting solution was titrated with a standard NaOH solution (c = 0.0200 mol dm^{-3}) and the equivalence point was reached at 10.64 cm^3.

($K_b(NH_3) = 1.8 \cdot 10^{-5}$; $K_a(HSO_4^-) = 1.1 \cdot 10^{-2}$)

2.2 Calculate pH of the solution in the container after combustion.

2.3 At the end point of titration, NH_4^+ and SO_4^{2-} ions are present in the solution. Write the equations for the relevant equilibria to show how the presence of these two ions affects the pH and calculate their equilibrium constant(s).

2.4 Tick the correct statement for the pH of the solution at the equivalence point.

☐ pH > 7 ☐ pH = 7 ☐ pH < 7

SOLUTION

2.1 $q_v = \Delta E = \Delta H - \Delta n_g RT$

For 1 mole of NH_3:

$\Delta H = 3/2 \times (-285.83) - (-46.11) = -382.64$ kJ

$\Delta n_g = -1.25$ mol

$\Delta E = -382.64\text{ kJ} - [(-1.25\text{ mol}) \times 8.314\text{ J mol}^{-1}\text{ K}^{-1} \times 298\text{ K}] = -379.5\text{ kJ}$

$$n(O_2) = \frac{14.4\text{ g}}{32.0\text{ g mol}^{-1}} = 0.450\text{ mol}$$

$n(NH_3)_{\text{reacted}} = 0.450\text{ mol} \times 4/3 = 0.600\text{ mol}$

$q_v = \Delta E = 0.600\text{ mol} \times (-379.5\text{ kJ mol}^{-1}) = \underline{-227.7\text{ kJ}}$

2.2 Total $n(H_2SO_4) = 15.00\text{ cm}^3 \times 0.0100\text{ mol dm}^{-3} = 0.150$ mmol

$H_2SO_4 + 2\text{ NaOH} \rightarrow Na_2SO_4 + 2\text{ H}_2O$

After back titration with NaOH:

$n(H_2SO_4)_{\text{reacted}} = ½\, n(\text{NaOH})_{\text{reacted}} = ½\,(0.01064\text{ dm}^3 \times 0.0200\text{ mol dm}^{-3}) =$

$= 1.064 \cdot 10^{-4}\text{ mol} = 0.1064\text{ mmol}$

$n(H_2SO_4)_{\text{reacted with NH}_3} = 0.0436$ mmol

$2\text{ NH}_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

$n(NH_3) = 2 \times n(H_2SO_4)_{\text{reacted with NH}_3} = 2 \times 0.0436\text{ mmol} = 0.0872\text{ mmol}$

$$c(NH_3) = \frac{0.0872\text{ mmol}}{0.0100\text{ dm}^3} = 8.72 \cdot 10^{-3}\text{ mol dm}^{-3}$$

$$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

$c - x \qquad\qquad x \qquad x$

$$K_b = 1.8 \cdot 10^{-5} = \frac{x^2}{0.00872 - x}$$

$x = [OH^-] = 3.96 \cdot 10^{-4}$

$pOH = 3.41$

$pH = 10.59$

2.3 $SO_4^{2-}(aq) + H_2O(l) \rightleftarrows HSO_4^-(aq) + OH^-(aq)$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \cdot 10^{-14}}{1.1 \cdot 10^{-2}} = 9.1 \cdot 10^{-13}$$

$NH_4^+(aq) + H_2O(l) \rightleftarrows NH_3(aq) + H_3O^+(aq)$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \cdot 10^{-14}}{1.8 \cdot 10^{-5}} = 5.6 \cdot 10^{-10}$$

2.4 The correct answer: $pH < 7.0$

PROBLEM 3

At a temperature of 0 K, the total energy of a gaseous diatomic molecule AB is approximately given by:

$E = E_o + E_{vib}$

where E_o is the electronic energy of the ground state, and E_{vib} is the vibrational energy.

Allowed values of the vibrational energies are given by the expression:

$$E_{\mathbf{vib}} = (\nu + \frac{1}{2})\,\varepsilon \qquad \nu = 0, 1, 2, \ldots \qquad \varepsilon = \frac{h}{2\,\pi}\sqrt{\frac{k}{\mu}} \qquad \mu(\text{AB}) = \frac{m_A\, m_B}{m_A + m_B}$$

where h is the Planck's constant, ν is the vibrational quantum number, k is the force constant, and μ is the reduced mass of the molecule. At 0 K, it may be safely assumed that ν is zero, and E_o and k are independent of isotopic substitution in the molecule.

Deuterium, D, is an isotope of hydrogen atom with mass number 2. For the H_2 molecule, k is 575.11 N m^{-1}, and the isotopic molar masses of H and D are 1.0078 and 2.0141 g mol^{-1}, respectively.

At a temperature of 0 K: $\varepsilon_{H_2} = 1.1546\,\varepsilon_{HD}$ and $\varepsilon_{D_2} = 0.8167\ \varepsilon_{HD}$.

3.1 Calculate the enthalpy change, ΔH, in kJ·mol^{-1} for the following reaction at 0 K:

$H_2(g) + D_2(g) \rightarrow 2\ HD(g)$

3.2 Calculate the frequency in s^{-1} of infrared photons that can be absorbed by HD molecule.

(If you have been unable to calculate the value for ε_{HD} then use $8.000 \cdot 10^{-20}$ J for the calculation.)

The allowed electronic energies of H atom are given by the expression:

$$E = -\frac{R_H}{n^2}, \quad n = 1, 2, \ldots$$ where R_H = 13.5984 eV, and 1 eV = $1.602 \cdot 10^{-19}$ J

The total energy of H_2 molecule in its ground state is –31.675 eV, relative to the same reference as that of hydrogen atom.

3.3 Calculate the dissociation energy, DE, in eV of a hydrogen molecule in its ground state such that both H atoms are produced in their ground states.

3.4 A molecule H_2 in the ground state dissociates into its atoms after absorbing a photon of wavelength 77.0 nm. Determine all possibilities for the electronic states of hydrogen atoms produced. For each case calculate the total kinetic energy, KE, in eV of the dissociated hydrogen atoms.

3.5 Calculate the electron affinity, EA, of H_2^+ ion in eV if its dissociation energy is 2.650 eV. If you have been unable to calculate the value for the dissociation energy of H_2 then use 4.500 eV for the calculation.)

SOLUTION

3.1 $H_2(g) + D_2(g) \rightarrow 2\ HD(g) \qquad \Delta H = ?$

$\Delta H = \Delta E + \Delta n_g\ R\ T$

$\Delta n_g = 0$, thus $\Delta H = \Delta E$

$\Delta E = 2\ E(HD) - E(H_2) - E(D_2)$

$E_{vib} = \frac{1}{2}\varepsilon$ as $v = 0$ at 0 K.

$$\Delta E = 2\left(E_0 + \frac{\varepsilon_{HD}}{2}\right) - \left(E_0 + \frac{\varepsilon_{H_2}}{2}\right) - \left(E_0 + \frac{\varepsilon_{D_2}}{2}\right) = \varepsilon_{HD} - \frac{1}{2}(\varepsilon_{H_2} + \varepsilon_{D_2})$$

$$\Delta E = \varepsilon_{HD}(1 - \frac{1}{2}(1.1546 + 0.8167)) = 0.01435\ \varepsilon_{HD}$$

$$\mu(HD) = \frac{m_H\ m_D}{m_H + m_D} =$$

$$= \frac{\dfrac{1.0078\cdot 10^{-3}\ \text{kg mol}^{-1} \times 2.0141\cdot 10^{-3}\ \text{kg mol}^{-1}}{N_A^2}}{\dfrac{1.0078\cdot 10^{-3}\ \text{kg mol}^{-1} + 2.0141\cdot 10^{-3}\ \text{kg mol}^{-1}}{N_A}} = 1.1154\cdot 10^{-27}\ \text{kg}$$

For one molecule HD:

$$\varepsilon_{HD} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{6.6261\cdot 10^{-34}\ \text{J s}}{2\pi}\sqrt{\frac{575.11\ \text{N m}^{-1}}{1.1154\cdot 10^{-27}\ \text{kg}}} = 7.5724\cdot 10^{-20}\ \text{J}$$

For 1 mol of HD:

$$\varepsilon_{HD} = 7.5724\cdot 10^{-20}\ \text{J} \times N_A = 7.5724\cdot 10^{-20}\ \text{J} \times 6.0221\cdot 10^{23}\ \text{mol}^{-1} = 45\,600\ \text{kJ mol}^{-1}$$

$$\Delta H = \Delta E = 0.01435\,\varepsilon_{HD} = 0.6544\ \text{kJ mol}^{-1}$$

3.2 $h\nu = \Delta E$

$$\Delta E = E_{\nu 1} - E_{\nu 0} = \left(\frac{3}{2} - \frac{1}{2}\right)\varepsilon_{HD} = \varepsilon_{HD}$$

$$h\nu = \varepsilon_{HD} \ \Rightarrow\ \nu = \frac{\varepsilon_{HD}}{h}$$

From part 3.1:

$$\varepsilon_{HD} = 7.5724\cdot 10^{-20}\ \text{J}$$

Thus: $\nu = \dfrac{7.5724 \cdot 10^{-20}\ \text{J}}{6.6261 \cdot 10^{-34}\ \text{J s}} = 1.1428 \cdot 10^{-14}\ \text{s}$

3.3 $H_2 \rightarrow 2\ H$

For $n = 1$: $\Delta E = 2\ (-13.5984) - (-31.675) = 4.478$ eV

3.4 $H_2 + h\nu \rightarrow \quad H \quad + \quad H$

$$\begin{array}{rcc} n = & 1 & 1 \\ & 1 & 2 \\ & 2 & 1 \\ & 2 & 2 \\ & . & . \\ & . & . \\ & . & . \end{array}$$

The energy of H_2 molecule in its ground state is –31.675 eV.

$\lambda = 77.0$ nm

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.6261 \cdot 10^{-34} \times 3.00 \cdot 10^{8}}{77.0 \cdot 10^{-9}} = 2.58 \cdot 10^{-18}\ \text{J}$$

$$E_{\text{photon}} = \frac{6.6261 \cdot 10^{-34}}{1.602 \cdot 10^{-19}} = 16.1\ \text{eV}$$

$$\Delta E = E_{n_1} + E_{n_2} - E_{n_{H_2}} = -\frac{R_H}{n_1^2} - \frac{R_H}{n_2^2} - (31.675) < 16.1\,\text{eV}$$

$n_1 = 1 \qquad n_2 = 1$

$$\Delta E = -\frac{13.5984}{1^2} - \frac{13.5984}{1^2} + 31.675 = 4.478\ \text{eV}$$

KE = 16.1 – 4.478 = 11.6 eV

$n_1 = 1$, $n_2 = 2$ or $n_1 = 2$, $n_2 = 1$

$$\Delta E = -\frac{13.5984}{1^2} - \frac{13.5984}{2^2} + 31.675 = 14.677\ \text{eV}$$

KE = 16.1 – 14.677 = 1.4 eV

$n_1 = 2, \quad n_2 = 2$

$$\Delta E = -\frac{13.5984}{2^2} - \frac{13.5984}{2^2} + 31.675 = 24.880 \text{ eV} > 16.1 \text{ eV}$$

K.E. = 16.1 – 14.677 = 1.4 eV

Thus, the possibilities are:

$H_2 + h\nu \rightarrow H + H$

n = 1 1
1 2
2 1

3.5 IP(H) = $\Delta E_{n \rightarrow \infty} = -\frac{13.5984}{\infty^2} - \frac{13.5984}{1^2} = 13.598$ eV (ionization potential)

$H_2^+ + e \rightarrow H_2$ $\quad$ $EA(H_2^+) = -IP(H_2)$

$H_2^+ \rightarrow H^+ + H$ $\quad$ $DE(H_2^+) = 2.650$ eV

$H \rightarrow H^+ + e$ $\quad$ $IP(H) = 13.598$ eV

$H_2 \rightarrow H + H$ $\quad$ $DE(H_2) = 4.478$ eV

$EA(H_2^+) = DE(H_2^+) - IP(H) - DE(H_2) = 2.650 - 13.598 - 4.478 = -15.426$ eV

Electron affinity H_2^+ = – 15.426 eV

PROBLEM 4

For sustainable energy, hydrogen appears to be the best energy carrier. The most efficient way of using hydrogen is generation of electrical energy in a fuel cell. However, storing hydrogen in large quantities is a challenge in fuel cell applications. Among the chemical hydrides considered as solid hydrogen storage materials, sodium borohydride ($NaBH_4$), being non-toxic, stable and environmentally benign, appears to be the most promising one. The hydrolysis of sodium borohydride that releases H_2 gas is a slow reaction at ambient temperature and, therefore, needs to be catalyzed.

$$NaBH_4(aq) + 2\,H_2O(l) \xrightarrow{\text{catalyst}} Na^+(aq) + BO_2^-(aq) + 4\,H_2(g)$$

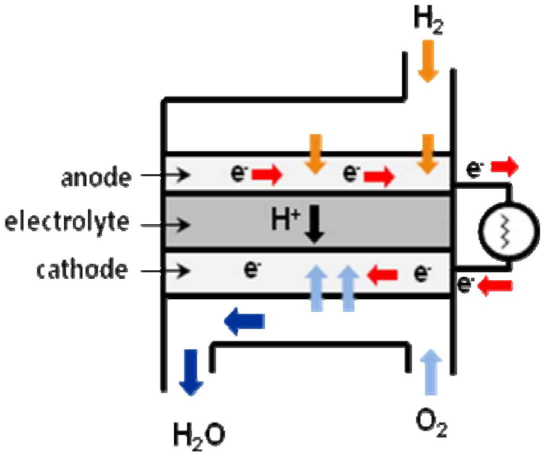
Colloidal ruthenium(0) nanoclusters are the most active catalysts in this hydrolysis even at room temperature and lead to a complete H_2 release from sodium borohydride. Kinetic studies show that the catalytic hydrolysis of $NaBH_4$ is a first order reaction with respect to the catalyst, but a zero order with respect to the substrate. The rate of hydrogen production per mole of ruthenium is 92 mol $H_2\cdot(\text{mol Ru})^{-1}\cdot\text{min}^{-1}$ at 25 °C.

4.1 Calculate the amount of ruthenium catalyst (in mg) which must be added to 0.100 dm^3 of $NaBH_4$ solution with a concentration of 1.0 mol dm^{-3} to supply the hydrogen gas at a rate of 0.100 $dm^3\cdot min^{-1}$ at 25 °C and 1.0 atm, that is required for a portable fuel cell.

4.2 For how many minutes will this system supply hydrogen gas at this rate?

4.3 The Arrhenius activation energy for this catalytic hydrolysis of sodium borohydride is E_a = 42.0 kJ mol^{-1}. Calculate the temperature required to achieve the same rate of hydrogen evolution by using a half of the amount of ruthenium catalyst used at 25.0 °C.

4.4 A fuel cell (see figure) is made up of three segments sandwiched together: the anode, the electrolyte, and the cathode. Hydrogen is used as fuel and oxygen as oxidant. Two chemical reactions occur at the interfaces of the three different segments:



$$O_2(g) + 2\,H_2O(l) + 4\,e^- \rightarrow 4\,OH^-(aq)$$

$H_2(g) + 2\ OH^-(aq) \rightarrow 2\ H_2O(l) + 2\ e^-$

The net result of the two reactions is

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

The hydrogen for the fuel cell is supplied from the hydrolysis of sodium borohydride.

Calculate the standard potential for the cathode half reaction if the standard reduction potential for the anode half reaction is –0.83 V and $\Delta_f G^o(H_2O(l))$ is –237 kJ mol^{-1}.

4.5 Calculate the volume of air at a temperature of 25 °C and a pressure of 1.0 atm needed to generate a constant current of 2.5 A for 3.0 hours in this fuel cell. Assume that air contains 20 % by volume O_2(g).

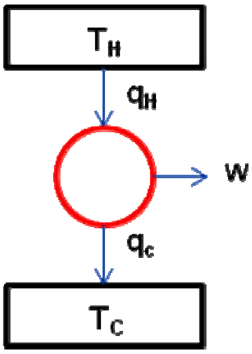
4.6 The efficiency of a fuel cell is given by the ratio of the work produced to the heat dissipated by the cell reaction. Thus, the maximum efficiency for a fuel cell is given by:

$$\eta_{\text{fuel cell}} = \frac{\text{work}}{\text{heat}}$$

Calculate the maximum efficiency for the fuel cell using the data given below at 25 °C and a standard pressure.

	S° (J mol^{-1} K^{-1})
$H_2(g)$	130.7
$O_2(g)$	205.2
$H_2O(l)$	70.0

The second law of thermodynamics states that it is impossible to convert all of the heat, q_H, from a high-temperature reservoir at T_H into work. At least, some of the energy, q_C, must be transferred to a low-temperature reservoir at T_C. Thus, a heat engine with 100% efficiency is thermodynamically impossible. When the heat engine is working reversibly, as in a Carnot cycle, the efficiency will be a maximum.



For a heat engine working reversibly between two reservoirs the following relations are applied:

$$q_H = w + q_C$$

and

$$\frac{q_H}{T_H} = \frac{q_C}{T_C}$$

4.7 What should be the temperature of the hot reservoir, T_H, of a Carnot heat engine to maintain the efficiency of the fuel cell calculated in part 4.6, if the temperature of cold reservoir T_C is 40 °C?

(If you have been unable to calculate the value for the efficiency then use the value 0.80 for the calculation.)

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SOLUTION

4.1 $n(H_2) = \dfrac{0.100\ \text{dm}^3\ \text{min}^{-1} \times 101.325\ \text{kPa}}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times\ 298\ \text{K}} = 4.1 \cdot 10^{-3}\ \text{mol min}^{-1}$

$$n(\text{Ru}) = \frac{4.1 \cdot 10^{-3}\ \text{mol H}_2\ \text{min}^{-1}}{\dfrac{92\ \text{mol H}_2\ \text{min}^{-1}}{1\ \text{mol Ru}}} = 4.5 \cdot 10^{-5}\ \text{mol}$$

$$m(\text{Ru}) = 4.5 \cdot 10^{-5}\ \text{mol} \times 101.07\ \text{g mol}^{-1} = 4.5 \cdot 10^{-3}\ \text{g} = 4.5\ \text{mg}$$

4.2 $n(NaBH_4)$ = 1.0 mol dm^{-3} × 0.100 dm^3 = 0.10 mol

0.04 mol of H_2 are released from 0.10 mol $NaBH_4$.

Thus:

$$t = \frac{0.40\ \ \text{mol H}_2}{4.1 \cdot 10^{-3}\ \ \text{mol H}_2\ \text{min}^{-1}} = 98\ \text{min}$$

4.3 Rate = k [Ru] = $A\, e^{-E_a/RT}$ [Ru]

$$\frac{e^{-E_a/R \times 298}}{e^{-E_a/RT}} = \frac{1}{2}$$

$$-\frac{E_a}{R}\left(\frac{1}{298} - \frac{1}{T}\right) = \ln\frac{1}{2}$$

$$\frac{4.20 \cdot 10^4\ \text{J mol}^{-1}}{8.314\ \text{J mol}^{-1}\text{K}^{-1}}\left(\frac{1}{298} - \frac{1}{T}\right) = \ln 2$$

T = 311 K or 38 °C

4.4 Since $\Delta G^o = -\,n\,F\,E^o$

$2\,(-2.37 \cdot 10^5) = -\,4 \times 96485 \times E^0_{\text{cell}}$ $\qquad E^0_{\text{cell}} = 1.23\ \text{V}$

$$1.23\ \text{V} = E^0_{\text{cathode}} - (-0.83\ \text{V})$$

$$E^0_{\text{cathode}} = 0.40\ \text{V}$$

4.5 2.5 A × 3 × 3600 s = 27000 C

$$n(O_2) = 27000\ \text{C} \times \frac{1\ \text{mol}}{4 \times 96485\ \text{C}} = 0.070\ \text{mol}$$

$V(O_2) = \dfrac{0.070\ \text{mol} \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}}{101.325\ \text{kPa}} = 1.7\ \text{dm}^3$ $\qquad V(\text{air}) = 8.6\ \text{dm}^3$

4.6 $\Delta_{rxn}G^o = \Delta_{rxn}H^o - T\,\Delta_{rxn}S^o$

$\Delta_{rxn}S^o = 2\,S^o\,(H_2O_{(l)}) - [\,2S^o\,(H_2(g)) + S^o(O_2\,(g))\,] = 2 \times 70.0 - (2 \times 130.7 + 205.2)$

$= -326.6$ J mol^{-1} K^{-1}

$\Delta_{rxn}H^o = \Delta_{rxn}G^o + T\,\Delta_{rxn}S^o = -474 + 298.15 \times (-326.6 \cdot 10^{-3}) = -571.4$ kJ

maximum w = $\Delta_{rxn}G^o = -474$ kJ

$$\eta = \frac{-474000\text{ J}}{-571400\text{ J}} = 0.83$$

4.7 $$\eta_{\text{engine}} = \frac{w}{q_H} = \frac{q_H - q_C}{q_H} = 1 - \frac{q_C}{q_H}$$

Since $\dfrac{q_H}{T_H} = \dfrac{q_C}{T_C} \qquad \dfrac{q_C}{q_H} = \dfrac{T_C}{T_H}$

Thus: $\eta_{\text{engine}} = 1 - \dfrac{T_C}{T_H}$

$0.83 = 1 - \dfrac{313}{T_H}$

$T_H = 1.8 \cdot 10^3$ K or $T_H \approx 1.5 \cdot 10^3$ °C

PROBLEM 5

Polynitrogen compounds have great potential for being used as high energy density materials. They are thermodynamically unstable. Huge amount of energy is released from their decomposition or reactions leading to more stable products. The only known polynitrogen species are N_2, N_3^- and N_5^+, isolated in 1772, 1890 and 1999, respectively, and recently reported cyclic anion, N_5^-.

5.1 Write the Lewis structure for N_5^+ with three energetically favourable resonance forms. Indicate the lone pairs and formal charges. Draw the molecular geometry of N_5^+.

5.2 Write the Lewis structures for cyclic N_5^- with five energetically favourable resonance forms. Indicate the lone pairs and formal charges. Draw the molecular geometry of cyclic N_5^-.

5.3 The synthesis of $[N_5^+][AsF_6^-]$, a white ionic solid, was achieved by reacting $[N_2F^+][AsF_6^-]$ with hydrazoic acid, HN_3, in liquid HF at –78 °C. Write the balanced chemical equation for this reaction.

The preparation of $[N_2F^+][AsF_6^-]$ requires the reaction of N_2F_2 with strong Lewis acid AsF_5 as follows:

$x\,C(\text{graphite}) + AsF_5 \rightarrow C_x \cdot AsF_5$ (graphite intercalate with x = 10 – 12)

$2\,C_x \cdot AsF_5 + N_2F_4 \rightarrow 2\,[C_x^+][AsF_6^-] + trans\text{-}N_2F_2$

$trans\text{-}N_2F_2 + AsF_5 \rightarrow [N_2F^+][AsF_6^-]$

In the synthesis of N_2F_2, the *trans* isomer is formed which is thermodynamically less stable than *cis*-N_2F_2. However, conversion of *trans*-N_2F_2 to *cis*-N_2F_2 requires surmounting a high energy barrier of 251 kJ mol^{-1}, so that equilibration between the *cis* and the *trans* isomers does not significantly take place without a suitable catalyst.

When *trans*-N_2F_2 is maintained in a closed container for six days at room temperature in the presence of a small amount of SbF_5 as a catalyst, *cis-trans* thermal equilibrium is established.

$$trans\text{-}N_2F_2 \xrightleftharpoons{25\ °C} cis\text{-}N_2F_2$$

The standard enthalpies of formation of *trans*- and *cis*-N_2F_2 are 67.31 and 62.03 kJ mol^{-1}, respectively, and their standard entropies at 25 °C are 262.10 and 266.50 J K^{-1} mol^{-1}, respectively.

5.4 Find the ratio of the number of *cis*-N_2F_2 molecules over that of the *trans*-N_2F_2 molecules in an equilibrium mixture at 25 °C.

5.5 Write the Lewis structures showing the geometry of N_2F^+ ion and those of *trans*- and *cis*-isomers of N_2F_2. Include all lone pairs and formal charges. Suggest an appropriate hybridization for each nitrogen atom in N_2F_2 and N_2F^+.

Solid $[N_5^+][AsF_6^-]$ is marginally stable at room temperature but reacts explosively with water to produce arsenic pentafluoride, hydrogen fluoride, molecular nitrogen and oxygen.

5.6 Write a balanced equation for the reaction between $[N_5^+][AsF_6^-]$ and water.

Conversion of $[N_5^+][SbF_6^-]$ into other N_5^+ salts can be achieved by a metathesis reaction:

$[N_5^+][SbF_6^-] + [M^+][X^-] \longrightarrow [N_5^+][X^-] + [M^+][SbF_6^-]$

where $M^+ = Na^+, K^+, Cs^+$, and X^- = large anion such as SnF_6^{2-} and $B(CF_3)_4^-$.

Since $[Cs^+][SbF_6^-]$ has a low solubility in anhydrous HF, and $[K^+][SbF_6^-]$ has a low solubility in SO_2, these two solvents were used extensively to carry out metathesis reactions at –78 °C and –64 °C, respectively.

5.7 Write the balanced equation for the preparation of $[N_5^+]_2[SnF_6^{2-}]$ and $[N_5^+][B(CF_3)_4^-]$ in solution starting with $[Cs^+]_2[SnF_6^{2-}]$ and $[K^+][B(CF_3)_4^-]$, respectively. Indicate the appropriate solvent.

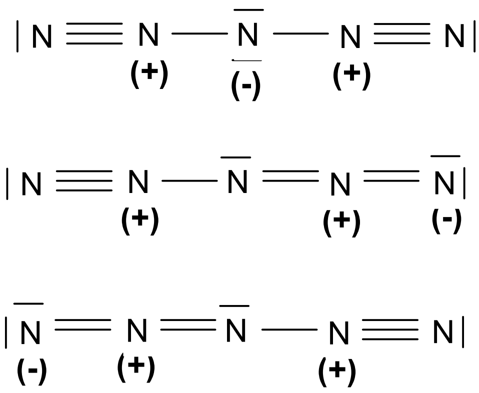
When $[N_5^+]_2[SnF_6^{2-}]$ decomposes under carefully controlled conditions at 25 – 30 °C, $[N_5^+][SnF_5^-]$ and N_5F are formed. The $[N_5^+][SnF_5^-]$ salt is a white solid and has a thermal stability comparable to that of $[N_5^+][SbF_6^-]$ (50 – 60 °C). The solution ^{119}Sn NMR spectrum has shown that the SnF_5^- anion in this compound is, in fact, a mixture of dimeric and tetrameric polyanions. In both of these polyanions the coordination number of Sn atom is 6 and there are bridging fluorine atoms.

5.8 Draw the structures of dimeric and tetrameric polyanions.

SOLUTION

5.1 Formula: N_5^+

Lewis structure:

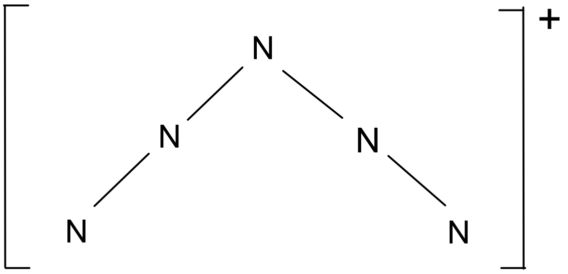


$$|N\equiv\underset{(+)}{N}-\underset{(-)}{\overline{\underline{N}}}-\underset{(+)}{N}\equiv N|$$

$$|N\equiv\underset{(+)}{N}-\overline{N}=\underset{(+)}{N}=\underset{(-)}{\overline{N}}|$$

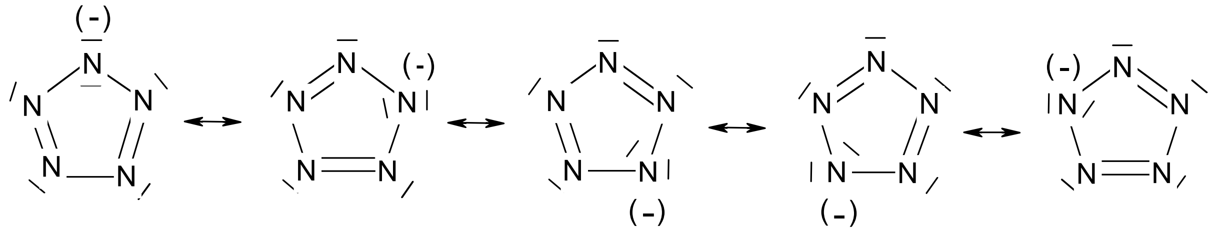
$$|\underset{(-)}{\overline{N}}=\underset{(+)}{N}=\overline{N}-\underset{(+)}{N}\equiv N|$$

Molecular geometry:

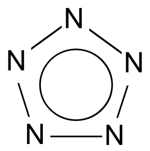


5.2 Cyclic N_5^+:

Lewis structure:



Molecular geometry:



5.3 $$[N_2F^+][AsF_6^-] + HN_3 \xrightarrow[\text{in HF}(l)]{-78\ ^\circ C} [N_5^+][AsF_6^-] + HF$$

5.4 The desired ratio is the value of the equilibrium constant *K* of the trans $\rightleftarrows$ cis reaction shown above:

$$K = \frac{[cis]}{[trans]}$$

$$\Delta G^o = -\,RT \ln K$$

$$\Delta G^o = \Delta H^o - T\,\Delta S^o$$

$$\Delta H^o = 62.03 - 67.31 = -5.28 \text{ kJ mol}^{-1}$$

$$\Delta S^o = 266.50 - 262.10 = 4.40 \text{ J mol}^{-1}\text{ K}^{-1}$$

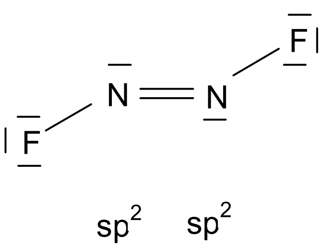
$$\Delta G^o = -5.28{\cdot}10^3 - (298 \times 4.40) = -6.59\cdot 10^3 \text{ J mol}^{-1}$$

$$K = e^{-\Delta G^o / RT} = \; = e^{-(-6.59\,\cdot\,10^3)/(8.314\times 298)} = 14.3$$

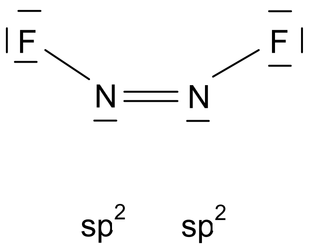
$$K = \frac{[cis]}{[trans]} = 14.3 \text{ at } 25\ \text{°C}$$

5.5

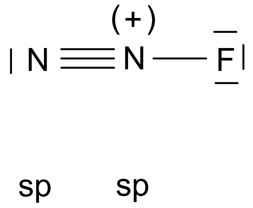
trans - N_2F_2



cis- N_2F_2



N_2F^+



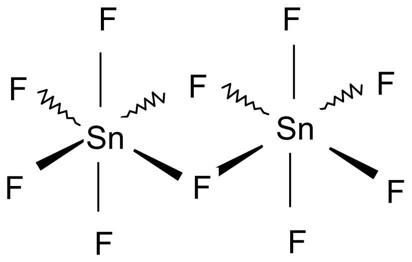
5.6 $4\,[N_5^+][AsF_6^-] + 2\,H_2O \rightarrow 4\,AsF_5 + 4\,HF + 10\,N_2 + O_2$

5.7 $2\,[N_5^+][AsF_6^-] + Cs_2SnF_6 \xrightarrow{\text{HF, }-78\text{ °C}} [N_5^+]_2[SnF_6^{2-}] + 2\,CsSbF_6$

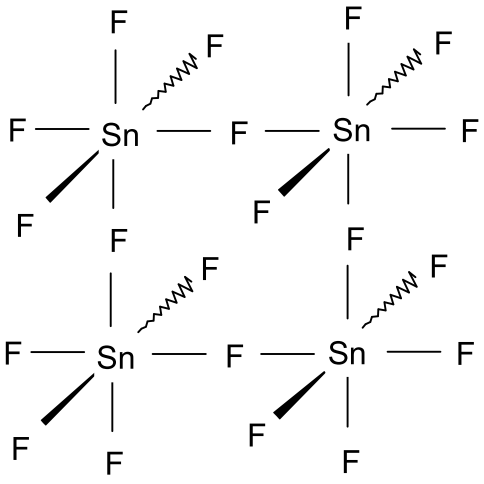
$[N_5^+]\,[SbF_6^{\,-}] + K^+[B(CF_3)_4^-] \xrightarrow{SO_2,\ -64\text{ °C}} [N_5^+]\,[B(CF_3)_4^-] + 2\,KSbF_6$

5.8

dimer, $Sn_2F_{10}^{2-}$



tetramer, $Sn_4F_{20}^{4-}$



PROBLEM 6

Extraction of gold using sodium cyanide, a very poisonous chemical, causes environmental problems and gives rise to serious public concern about the use of this so called "cyanide process". Thiosulfate leaching of gold has been considered as an alternative. In this process, the main reagent is ammonium thiosulfate, $(NH_4)_2S_2O_3$, which is relatively non-toxic. Although this process appears to be environmentally benign, the chemistry involved is very complex and needs to be studied thoroughly. The solution used for leaching gold contains $S_2O_3^{2-}$, Cu^{2+}, NH_3, and dissolved O_2. The solution must have a pH greater than 8.5 to allow free ammonia to be present.

According to the proposed mechanism, a local voltaic micro-cell is formed on the surface of gold particles during the leaching process and operates as follows:

Anode:

$Au(s) + 2\ NH_3(aq) \longrightarrow [Au(NH_3)_2]^+(aq) + e^-$

$[Au(NH_3)_2]^+(aq) + 2\ S_2O_3^{2-}(aq) \longrightarrow [Au(S_2O_3)_2]^{3-}(aq) + 2\ NH_3(aq)$

Cathode:

$[Cu(NH_3)_4]^{2+}(aq) + e^- \longrightarrow [Cu(NH_3)_2]^+(aq) + 2\ NH_3(aq)$

$[Cu(NH_3)_2]^+(aq) + 3\ S_2O_3^{2-}(aq) \longrightarrow [Cu(S_2O_3)_3]^{5-}(aq) + 2\ NH_3(aq)$

6.1 Write the overall cell reaction for this voltaic cell.

6.2 In the presence of ammonia $[Cu(S_2O_3)_3]^{5-}$ is oxidized by O_2 back to $[Cu(NH_3)_4]^{2+}$. Write a balanced equation for this oxidation-reduction reaction in basic solution.

6.3 In this leaching process, the $[Cu(NH_3)_4]^{2+}$ complex ion functions as catalyst and speeds up the dissolution of gold. Write the net overall oxidation-reduction reaction for dissolution of the gold metal, which is catalyzed by $[Cu(NH_3)_4]^{2+}$ complex ion.

6.4 Draw the coordination geometries of the metal in $[Au(NH_3)_2]^+$ and $[Au(S_2O_3)_2]^{3-}$ complex ions, indicating the coordinating atoms.

The formation constants, K_f, of $[Au(NH_3)_2]^+$ and $[Au(S_2O_3)_2]^{3-}$ complexes are $1.00 \cdot 10^{26}$ and $1.00 \cdot 10^{28}$, respectively. Consider a leaching solution in which the equilibrium concentrations of the species are as follows:

$[S_2O_3^{2-}] = 0.100$; $[NH_3] = 0.100$ and the total concentration of gold(I) species = $5.50 \cdot 10^{-5}$ mol dm^{-3}.

6.5 Calculate the percentage of gold(I) ion that exists in the form of thiosulfate complex.

When the concentration of O_2 is not high enough and pH > 10, $S_2O_3^{2-}$ reduces $[Cu(NH_3)_4]^{2+}$ to $[Cu(S_2O_3)_3]^{5-}$ with the formation of tetrathionate ion $S_4O_6^{2-}$:

$$2\ [Cu(NH_3)_4]^{2+}(aq) + 8\ S_2O_3^{2-}\ (aq) \rightarrow 2\ [Cu(S_2O_3)_3]^{5-}\ (aq) + S_4O_6^{2-}\ (aq) + 8\ NH_3(aq)$$

In basic solution tetrathionate disproportionates to trithionate, $S_3O_6^{2-}$, and thiosulfate.

6.6 Write a balanced equation for this disproportionation reaction.

6.7 When the O_2 concentration is too high, $S_2O_3^{2-}$ is oxidized by oxygen to yield trithionate and sulfate ions. Write a balanced equation for this reaction.

SOLUTION

6.1 Net anode half reaction:

$Au(s) + 2\ S_2O_3^{2-}(aq) \rightarrow [Au(S_2O_3)_2]^{3-}(aq) + e^-$

Net cathode half reaction:

$[Cu(NH_3)_4]^{2+}(aq) + 3\ S_2O_3^{2-}(aq) + e^- \rightarrow [Cu(S_2O_3)_3]^{5-}(aq) + 4\ NH_3(aq)$

erall cell reaction:

$Au(s) + [Cu(NH_3)_4]^{2+}(aq) + 5\ S_2O_3^{2-}(aq) \rightarrow [Au(S_2O_3)_2]^{3-}(aq) + [Cu(S_2O_3)_3]^{5-}(aq)$
$+ 4\ NH_3(aq)$

6.2 Oxidation half reaction:

$[Cu(S_2O_3)_3]^{5-}(aq) + 4\ NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq) + 3\ S_2O_3^{2-}(aq) + e^-$

Reduction half reaction:

$O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-\ (aq)$

Redox reaction:

$4\ [Cu(S_2O_3)_3]^{5-}(aq) + 16\ NH_3(aq) + O_2(g) + 2\ H_2O(l) \rightarrow$
$\rightarrow 4\ [Cu(NH_3)_4]^{2+}(aq) + 12\ S_2O_3^{2-}(aq) + 4\ OH^-(aq)$

6.3 $Au(s) + [Cu(NH_3)_4]^{2+}(aq) + 5\ S_2O_3^{2-}(aq) \rightarrow [Au(S_2O_3)_2]^{3-}(aq) + [Cu(S_2O_3)_3]^{5-}(aq) +$
$+ 4\ NH_3(aq)$

$4\ [Cu(S_2O_3)_3]^{5-}(aq) + 16\ NH_3(aq) + O_2(g) + 2\ H_2O(l) \rightarrow$
$\rightarrow 4\ [Cu(NH_3)_4]^{2+}(aq) + 12\ S_2O_3^{2-}(aq) + 4\ OH^-(aq)$

Summarizing the above equations:

$4\ Au(s) + 8\ S_2O_3^{2-}(aq) + O_2(g) + 2\ H_2O(l) \rightarrow 4\ [Au(S_2O_3)_2]^{3-}(aq) + 4\ OH^-(aq)$

6.4	$[Au(NH_3)_2]^+$	$[Au(S_2O_3)_2]^{3-}$
Coordination geometry:	$[H_3N\text{-}Au\text{-}NH_3\ ]^+$	$[O_3S\text{-}S\text{-}Au\text{-}S\text{-}SO_3\ ]^{3-}$

6.5 $Au^+(aq) + 2\ NH_3(aq) \rightarrow [Au(NH_3)_2]^+(aq)$ $K_{f,1} = 1.00\ .\ 10^{26}$

$Au^+(aq) + 2\ S_2O_3^{2-}\ (aq) \rightarrow [Au(S_2O_3)_2]^{3-}(aq)$ $K_{f,2} = 1.00\ .\ 10^{28}$

$[Au(NH_3)_2]^+(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow [Au(S_2O_3)_2]^{3-}(aq) + 2\ NH_3(aq)$

$$K_{eq} = \frac{K_{f,2}}{K_{f,1}} = 1.00 \cdot 10^2$$

$[Au(NH_3)_2]^+ + [Au(S_2O_3)_2]^{3-} = 5.50 \cdot 10^{-5}$ mol dm^{-3}

$$K_{eq} = \frac{(0.100)^2\ x}{(5.50 \cdot 10^{-5} - x)\,(0.100)^2} = 1.00 \cdot 10^2$$

$x = 5.445 \cdot 10^{-5}$

$$\frac{5.445 \cdot 10^{-5}}{5.50 \cdot 10^{-5}} \times 100 = 99.0\ \%$$

Thus, 99.0 % of Au(I) is in the form of $[Au(S_2O_3)_2]^{3-}$.

6.6 $S_4O_6^{2-}(aq) + 2\ e^- \rightarrow 2\ S_2O_3^{2-}(aq)$

$12\ OH^-(aq) + 3\ S_4O_6^{2-}(aq) \rightarrow 4\ S_3O_6^{2-}(aq) + 6\ H_2O(l) + 10\ e^-$

$4\ S_4O_6^{2-}(aq) + 6\ OH^-(aq) \rightarrow 5\ S_2O_3^{2-}(aq) + 2\ S_3O_6^{2-}(aq) + 3\ H_2O(l)$

disproportionation

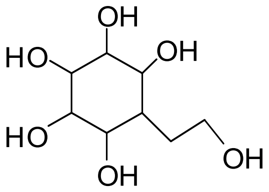
6.7 $2\ S_2O_3^{2-}(aq) + 2\ O_2(g) \rightarrow SO_4^{2-}(aq) + S_3O_6^{2-}(aq)$

PROBLEM 7

Synthesis of a carbasugar

Carbohydrates are essential components of living cells and a source of energy for animals. They include simple sugars with small molecules as well as macromolecular substances. When the ring oxygen (endocyclic oxygen) in sugars is replaced by a methylene group, the compounds formed are called as *pseudosugars* or *carbasugars*. Since carbasugars are hydrolytically stable towards acids and enzymes, several carbasugars have found application in the field of glycosidase inhibition.

The total syntheses of two isomeric carbasugars having skeleton **1** are described below.

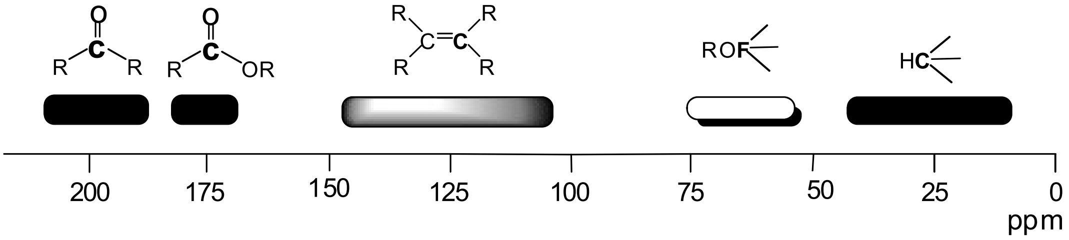


1

The total synthesis of **1** starts with a reduction of benzene by sodium in liquid ammonia to give **A**. The C-13 NMR spectrum of **A** consists of two signals at 124.0 and 26.0 ppm.

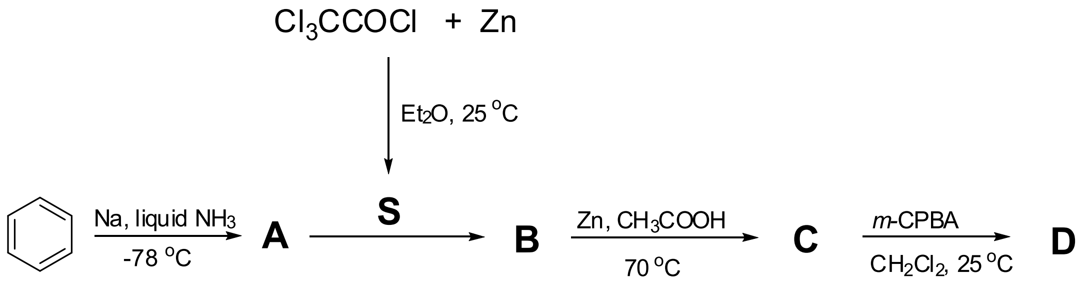
Trichloroacetyl chloride in the presence of Zn gives a reactive species **S** (see the Scheme 7.1). One equivalent of **S** undergoes [2+2]cycloaddition with **A** to form a racemic product **B**. The reaction of **B** with Zn in acetic acid gives **C**. Compound **C** contains only carbon, hydrogen and oxygen. The C-13 NMR spectrum of **C** exhibits three sp^2 carbon signals at 210.0, 126.5 and 125.3 ppm.

The reaction of **C** with one equivalent *m*-chloroperbenzoic acid (*m*-CPBA) in methylene chloride gives **D** as a major product. The C-13 NMR spectrum of **D** exhibits also three signals in the sp^2 region at 177.0, 125.8, 124.0 ppm.



^{13}C-NMR chemical shift ranges of typical functional groups

Scheme 7.1:

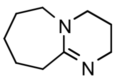


7.1 Draw the structures of **A**, **B**, **C**, **D**, and the intermediate **S**.

Reduction of **D** with $LiAlH_4$ yields **E** which reacts with an excess of acetyl chloride in pyridine to give **F** (Scheme 7.2).

Scheme 7.2:

$$\mathbf{D} \xrightarrow[25\ ^\circ C]{LiAlH_4,\ Et_2O} \mathbf{E} \xrightarrow[\text{Pyridine, } 25\ ^\circ C]{CH_3COCl} \mathbf{F} \xrightarrow[CH_2Cl_2,\ 0\ ^\circ C]{Br_2} \mathbf{G_1} + \mathbf{G_2} \xrightarrow[\text{Benzene, reflux}]{\text{DBU (2 eq)}} \mathbf{H}$$

DBU =


7.2 Draw the structures (use one enantiomer) of **E** and **F** using dashed-wedged line notation. Assign the configurations (*R* or *S*) at the asymmetric carbon atoms in **E**.

The compound **F** (use the drawn enantiomer) reacts with bromine to give the stereoisomers $\mathbf{G_1}$ and $\mathbf{G_2}$.

7.3 Draw the structures of $\mathbf{G_1}$and $\mathbf{G_2}$ using dashed-wedged line notation.

A mixture of $\mathbf{G_1}$ and $\mathbf{G_2}$ reacts with two equivalents of 1,8-diazabicyclo- [5.4.0]undec-7-ene (DBU), which is a strong amine base, to afford **H**.

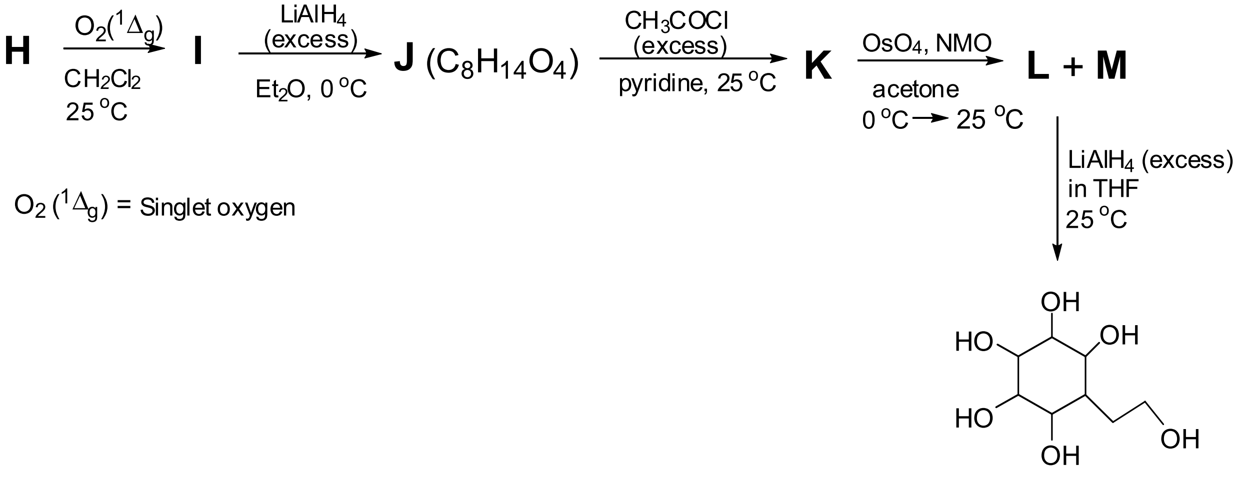
7.4 Draw the structure of **H** using dashed-wedged line notation.

Reaction of **H** with singlet oxygen (in situ generated) affords **I**. Although two isomers are theoretically possible, **I** is formed as the single isomer due to steric hindrance and electronic repulsion.

The reaction of **I** with excess of $LiAlH_4$ results in the formation of **J** (see the Scheme 7.3). The C-13 NMR spectrum of **J** shows 8 signals, two in the sp^2 region.

Reaction of **J** with excess acetyl chloride in the presence of pyridine yields **K**. Subsequent reaction of **K** with OsO_4 in the presence of 4-methylmorpholine 4-oxide (NMO) gives stereoisomers **L** and **M.** Upon reduction with excess $LiAlH_4$, **L** and **M** give the stereoisomers **1a** and **1b**, respectively.

Scheme 7.3:



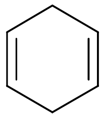
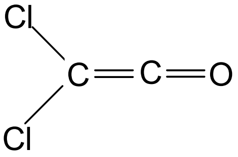
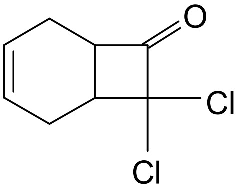
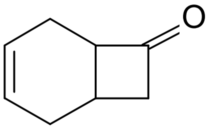
1a and **1b**

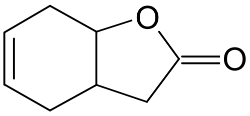
7.5 Draw the structures of **I, J, K, L, M, 1a**, and **1b** using dashed-wedged line notation.

____

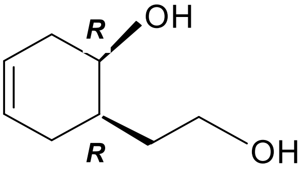
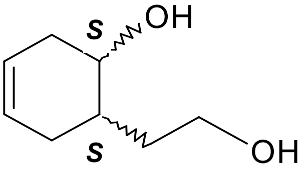
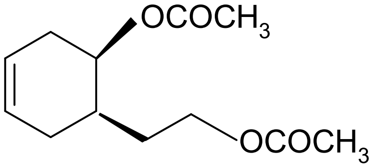
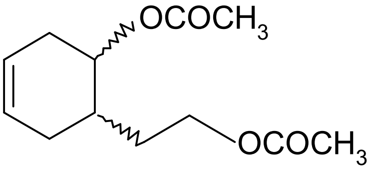
SOLUTION

7.1

A 	**S** 
B  	**C** 

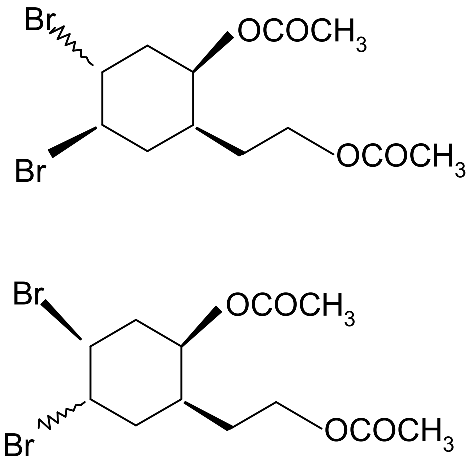
D 

7.2

E  or  	**F**  or 

7.3

G$_1$ and **G$_2$**



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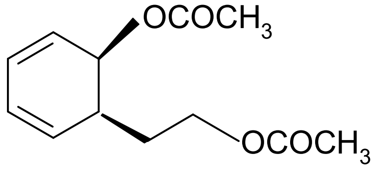
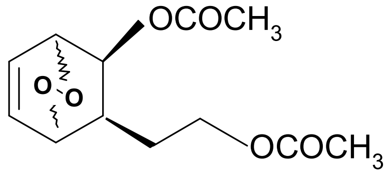
H



7.5

I



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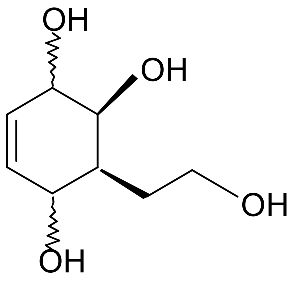
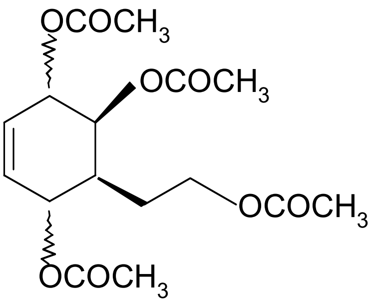
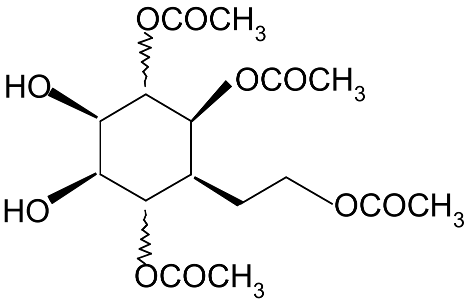
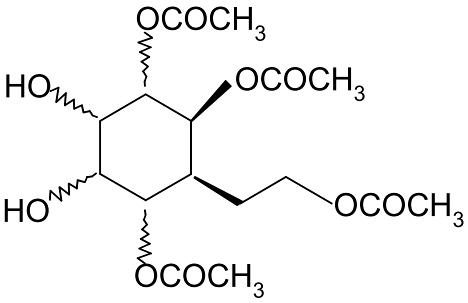


K

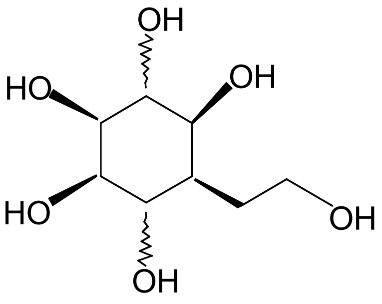


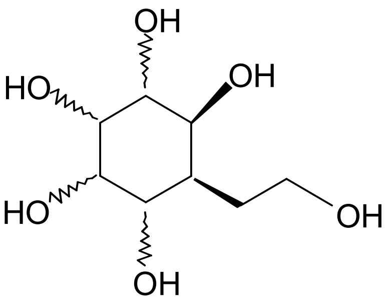
L and **M**





1a and **1b**

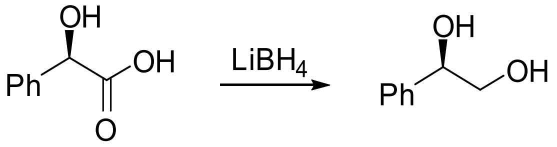




PROBLEM 8

Click chemistry is a chemical concept introduced by K. B. Sharpless in 2001 and describes a set of chemical reactions that generate substances quickly, reliably and quantitatively by joining molecules through small units under mild conditions. This methodology has recently been applied as a key step in the following synthesis of bicyclic compounds.

Mandelic acid is a versatile natural compound and widely used as a "chiral pool" in synthesis. The reduction of (*R*)-mandelic acid with $LiBH_4$ affords **A**.



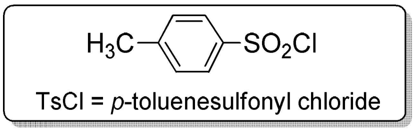
(*R*)-Mandelic acid

A

Reaction of **A** with one equivalent of *p*-toluenesulfonyl chloride gives **B** (Scheme 8.1). Heating **B** in pyridine yields **C**. During this transformation, compounds **B** and **C** retain their absolute configurations.

Scheme 8.1:

$$\mathbf{A} \xrightarrow[\text{CH}_2\text{Cl}_2,\ 0\ ^\circ\text{C}]{\text{TsCl (1 eq), Et}_3\text{N (1.2 eq)}} \mathbf{B} \xrightarrow{\text{Pyridine, heat}} \mathbf{C}$$



TsCl = *p*-toluenesulfonyl chloride

8.1 Draw the structures of **B** and **C** with the correct stereochemistry. Use dashed-wedged line notation throughout this problem.

Reaction of **C** with sodium azide in aqueous acetonitrile gives a mixture of enantiopure regioisomers **D** and **E** in a ratio of 3 : 1 (Scheme 8.2). On the other hand, the compound **B** affords **E** as the sole product under the same condition.

Scheme 8.2:

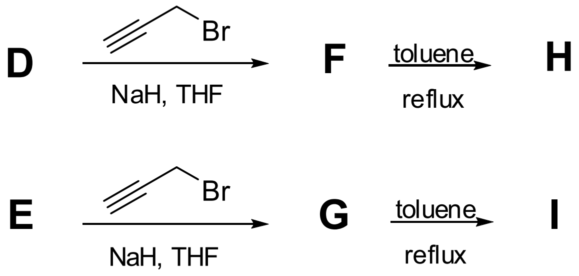
$$\mathbf{C} \xrightarrow[\text{reflux}]{\text{NaN}_3,\ \text{aq. CH}_3\text{CN}} \mathbf{D} + \mathbf{E}$$

$$\mathbf{B} \xrightarrow[\text{reflux}]{\text{NaN}_3,\ \text{aq. CH}_3\text{CN}} \mathbf{E}$$

8.2 Draw the structures of **D** and **E** with the correct stereochemistry.

Part I: Compounds **D** and **E** are separately subjected to NaH mediated reaction with 3-bromoprop-1-yne to afford **F** and **G**, respectively (Scheme 8.3). Heating **F** and **G** separately in toluene gives the bicyclic products **H** and **I**, respectively.

Scheme 8.3:



8.3 Draw the structure of compounds **F**, **G**, **H** and **I** with the correct stereochemistry.

Part II: Reaction of **D** and **E** separately with dimethyl acetylenedicarboxylate in water at 70 °C forms the optically active monocyclic regioisomers **J** and **K**, respectively (Scheme 8.4). Subsequent treatment of **J** and **K** with NaH gives final bicyclic products **L** and **M**, respectively, both having the formula $C_{13}H_{11}N_3O_4$.

Scheme 8.4:

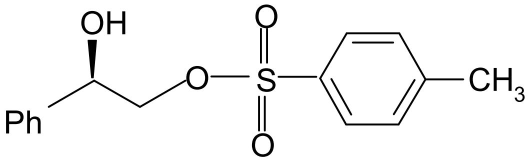
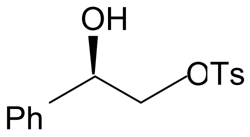
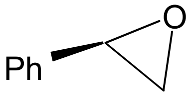
$$\mathbf{D} + \text{H}_3\text{CO}_2\text{C}{-}{\equiv}{-}\text{CO}_2\text{CH}_3 \xrightarrow[70\,^\circ\text{C}]{\text{H}_2\text{O}} \mathbf{J} \xrightarrow[\text{reflux}]{\text{NaH, dry THF}} \mathbf{L}$$

$$\mathbf{E} + \text{H}_3\text{CO}_2\text{C}{-}{\equiv}{-}\text{CO}_2\text{CH}_3 \xrightarrow[70\,^\circ\text{C}]{\text{H}_2\text{O}} \mathbf{K} \xrightarrow[\text{reflux}]{\text{NaH, dry THF}} \mathbf{M}$$

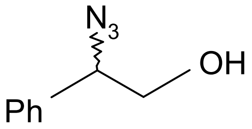
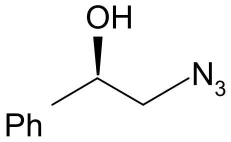
8.4 Draw the structures of compound **J**, **K**, **L** and **M** with the correct stereochemistry.

SOLUTION

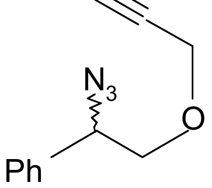
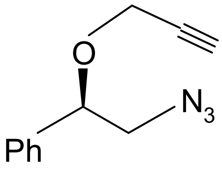
8.1

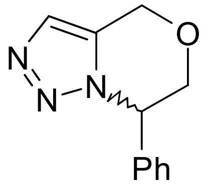
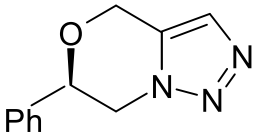
B	**C**
 or 	

8.2

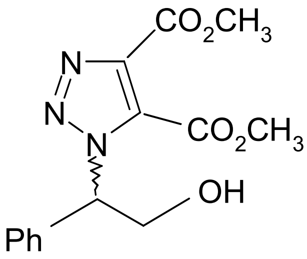
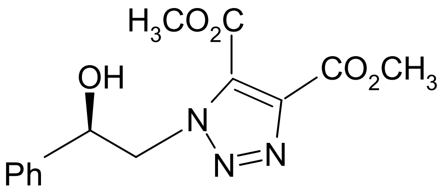
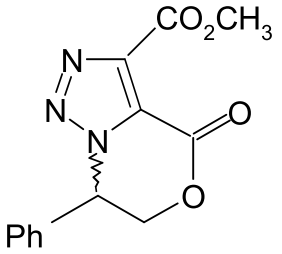
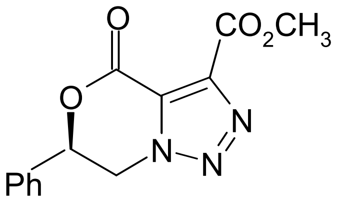
D	**E**
	

8.3

F	**G**
	

H 	**I** 

8.4

J 	**K** 
L 	**M** 

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Analysis of Chloride Mixtures

Introduction

Composition of a solution containing only $MgCl_2$ and NaCl can be determined by an indirect titration method by performing a precipitation titration to determine the total amount of chloride present, followed by a complex formation titration to determine the amount of magnesium ions. A common precipitation titration technique used to determine the amount of chloride ions present in a solution is the Fajans method. In this argentometric procedure, silver nitrate is used as the titrant to precipitate the chloride ions present in the solution. The end point is detected through the use of an adsorption indicator, typically dichlorofluorescein, a weak organic acid. Prior to the end point, silver chloride particles are negatively charged because of the adsorption of excess chloride ions present in solution. The indicator anions are repelled by the negatively charged surface of the silver chloride particles imparting a yellow-green colour to the solution. Beyond the equivalence point, however, silver chloride particles adsorb silver ions. Thus a positively charged layer is formed and it attracts the dichlorofluoresceinate ions displaying a pink-red colour. Dextrin is used to stabilize the silver chloride particles against the coagulation.

On the other hand, the amount of magnesium ions present in a solution can be determined by complexometric titration with ethylenediaminetetraacetic acid, EDTA. As a hexadentate ligand, EDTA forms chelates with all metal ions, except alkali metal ions, in a 1 : 1 mole ratio regardless of the charge of the cation. Eriochrome Black T (EBT) is a common indicator used for EDTA titrations. When pH > 7.00 EBT imparts a blue colour to the solution in the absence of metal ions and forms a red colour when coordinated to metal ions.

In this experiment the chloride content of the solution containing $MgCl_2$ and NaCl will be determined by Fajans method. Magnesium ion concentration will be determined by EDTA titration.

A 100 cm^3 solution prepared by dissolving $MgCl_2$ and NaCl in water is given as the unknown sample. The task is to determine the mass concentration (in g/100 cm^3) of both $MgCl_2$ and NaCl in the unknown solution.

Reagents

- Unknown solution, 100 cm^3
- Dextrin in Eppendorf tubes (3) in a zipper bag
- Dichlorofluorescein, indicator
- $AgNO_3$ solution, c = 0.1 mol dm^{-3} *), 100 cm^3
- EDTA solution, c = 0.01 mol dm^{-3} *), 100 cm^3
- pH 10 buffer (NH_3/NH_4Cl), 5 cm^3
- Eriochrome Black T, indicator

---

*) The exact value of the concentration is given on the label.

A. Determination of total chloride concentration by Fajans method

1. Using a 10 cm^3 pipette, transfer 10.0 cm^3 aliquot from the bottle labelled as unknown solution into a 250 cm^3 Erlenmeyer flask. Complete the volume to approximately 100 cm^3 by adding distilled water.
2. Take one of the Eppendorf tubes given in the zipper bag labelled as "dextrin" and transfer all its content into the Erlenmeyer flask.
3. Add 5 drops of dichlorofluorescein indicator solution.
4. Record the exact concentration of $AgNO_3$ in standard solution.
5. Fill one of the burettes with the standard $AgNO_3$ solution.
6. Titrate the unknown solution until the whole solution has pink-red colour.
7. Record the volume of $AgNO_3$ used in cm^3.
8. Use the same Erlenmeyer flask when repeating the titration. Before doing this, pour the content of Erlenmeyer flask into the "Aqueous Waste" container and rinse it twice with distilled water.

B. Determination of Mg^{2+} by direct titration with EDTA

1. Fill the second burette with the standard EDTA solution.
2. Record the exact concentration of EDTA in standard solution.

3. Using a 25 cm^3 pipette, transfer a 25.0 cm^3 aliquot of the unknown solution into a 250 cm^3 Erlenmeyer flask. Complete the volume to approximately 100 cm^3 by adding distilled water.
4. Using a 1 cm^3 pipette, add 1.0 cm^3 of pH 10 buffer.
5. Add 3 – 4 drops of EBT indicator solution.

6. Titrate the unknown solution with standard EDTA solution until the colour changes from red to blue.
7. Record the volume of EDTA solution used, in cm^3.
8. Use the same Erlenmeyer flask when repeating the titration. Before doing this, pour the content of Erlenmeyer flask into the "Aqueous Waste" container and rinse it twice with water.

Treatment of Data

1.1 Determine the amount of Cl^- ions (in mmol) in 100 cm^3 of the unknown solution.

1.2 Determine the amount of Mg^{2+} ions (in mmol) in 100 cm^3 of the unknown solution.

1.3 Calculate the concentration of both $MgCl_2$ and NaCl in g/100 cm^3 in the unknown solution.

SOLUTION

1.1 – 1.3

- Some distribution graphs were proposed by the organizer and approved by the International Jury that could be applied for evaluating of accuracy of the titrations and, consequently, for awarding points.
- For determinations of amounts of substance of Cl^- and Mg^{2+} ions, as well concentrations of both $MgCl_2$ and NaCl in the unknown solution, simple stoichiometric calculations can be applied.

PROBLEM 2 (practical)

Hydrogen generation from ammonia borane

Hydrogen has been considered as a clean and environmentally benign new energy carrier in the way towards a sustainable energy future. An effective and safe storage of hydrogen is one of the key issues of the hydrogen economy. Among the chemical hydrides, considered as potent solid hydrogen storage materials, ammonia-borane ($H_3N{\cdot}BH_3$) has been attracting a great deal of attention due to its high hydrogen content and stability under fuel cell operating conditions. Ammonia borane can release hydrogen upon hydrolysis, (Equation 1):

$$H_3N.BH_3(aq) + 2\ H_2O(l) \rightarrow NH_4BO_2(aq) + 3\ H_2(g) \qquad (1)$$

Aqueous solution of ammonia borane is stable and its hydrolysis occurs only in the presence of a suitable catalyst. Recent studies have shown that palladium(0) nanoclusters stabilized by water soluble polymers are highly active catalyst in the hydrolysis of ammonia borane. Palladium(0) nanoclusters are generated in situ by the reduction of potassium tetrachloropalladate(II) with ammonia borane in the presence of poly(4-styrenesulfonic acid-co-maleic acid).

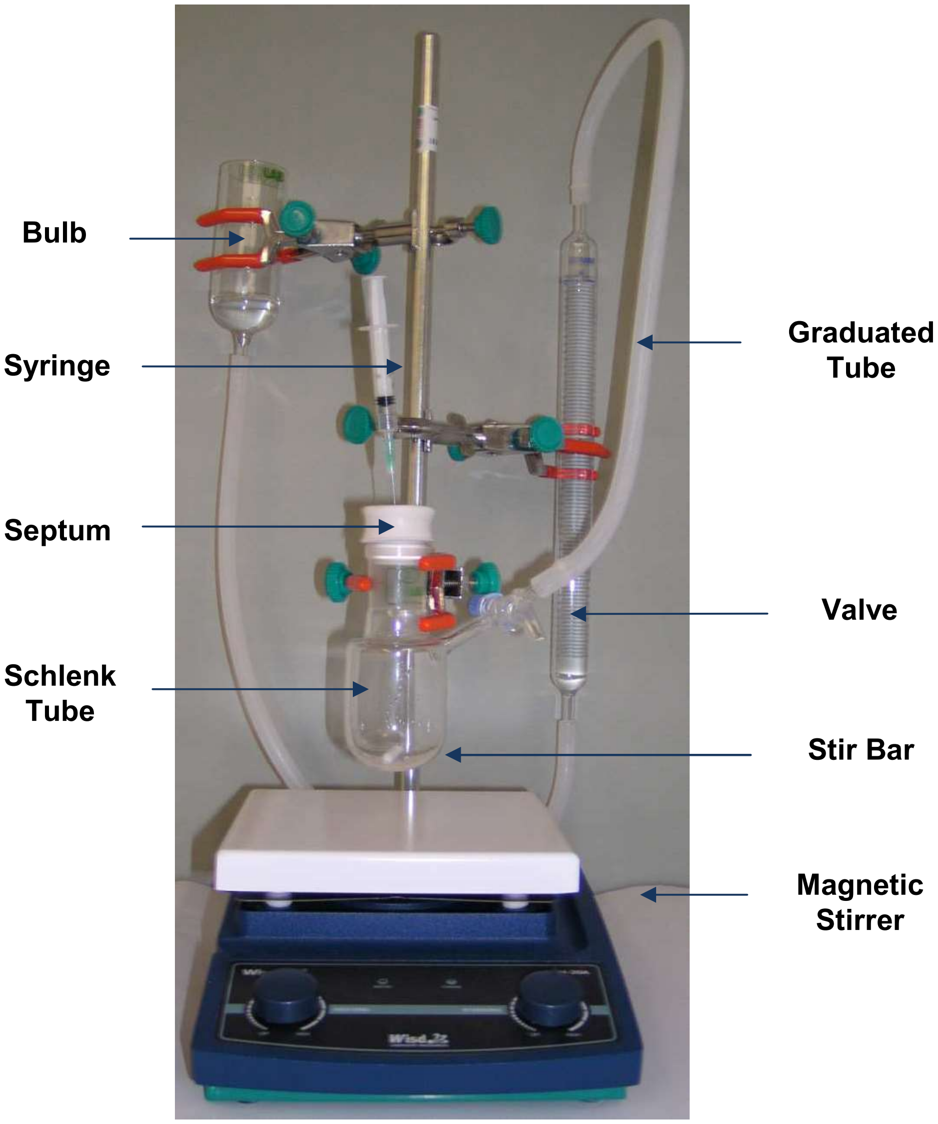
In this experiment, the catalytic hydrolysis of ammonia borane will be carried out starting with potassium tetrachloropalladate(II) in a solution containing poly(4-styrenesulfonic acid-co-maleic acid). Potassium tetrachloropalladate(II) will be used as precatalyst, which will be reduced by ammonia borane and palladium(0) nanoclusters will be formed and stabilized by poly(4-styrenesulfonic acid-co-maleic acid). These nanoclusters will catalyze the hydrolysis of ammonia borane.

Chemicals

- Solution A: H_3NBH_3 , 29.5 mg dissolved in 10 cm^3 H_2O,
- Solution B: poly(4-styrenesulfonic acid-co-maleic acid), 137.7 mg in 9 cm^3 H_2O,
- Solution C: Potassium tetrachloropalladate(II), $K_2[PdCl_4]$, 6.7 mg in 1 cm^3 H_2O.

I. Preparation of the Experimental Set-up

1. Check that the experimental setup, shown below, is held on a support, the graduated tube is connected to the Schlenk tube by Tygon tubing, and a stir bar is in the Schlenk tube.
2. Make sure that the septum is off and the valve is open.
3. By changing the bulb height adjust the water level in the graduated tube to zero.
4. Close the valve on the Schlenk tube.



Experimental Set-up

II. Hydrolysis of ammonia borane

A. In the absence of catalyst

1. Transfer all of the ammonia-borane solution (Solution A) from the glass vial to the Schlenk tube through the funnel,
2. Add the polymer solution (Solution B) from the glass vial to the Schlenk tube through the funnel.
3. Close the Schlenk tube with the septum, turn the stirring on at 600 rpm (as marked on the stirrer), and open the valve connecting to the graduated tube. Record the water level as V_o at time zero. Start the timer.
4. Every minute read the total volume of gas produced and write in the Table given on the answer sheet. Do this for 10 minutes. Stop the timer.

B. In the presence of catalyst

1. While stirring, transfer all of the potassium tetrachloropalladate(II) solution (Solution C) from the glass vial to the Schlenk tube by injecting through the septum using a 2.0 cm^3 syringe. Keep the syringe inserted in the septum throughout the experiment. Start the timer.
2. Every minute read the total volume of gas produced and write in the Table given on the answer sheet. Do this for 10 minutes. Stop the timer.

Treatment of Data

A. Reaction of ammonia-borane without catalyst

2.1 Plot the volume of gas recorded versus time in Graph 2.1.

2.2 Report the volume of gas evolved as $V_{uncatalyzed}$.

B. Reaction of ammonia-borane with catalyst

2.3 Plot the volume of the gas generated versus time in Graph 2.2.

2.4 Calculate the maximum amount of substance (mol) and the maximum volume (cm^3) of hydrogen gas which will be evolved theoretically from the hydrolysis of 29.5 mg ammonia borane with a purity of 97 % w/w at 25 °C. The atmospheric pressure is 690 torr.

2.5 Calculate the rate of hydrogen generation in your experiment

i) in cm^3 H_2/ min.

ii) in mmol H_2/min by assuming that the temperature is 25 °C. The atmospheric pressure is 690 torr.

2.6 Based on your experiment calculate the rate of hydrogen production per mole of palladium in (mol H_2)×(mol Pd)$^{-1}$×(min)$^{-1}$. The purity of potassium tetrachloropalladate(II) is 98 % w/w.

SOLUTION

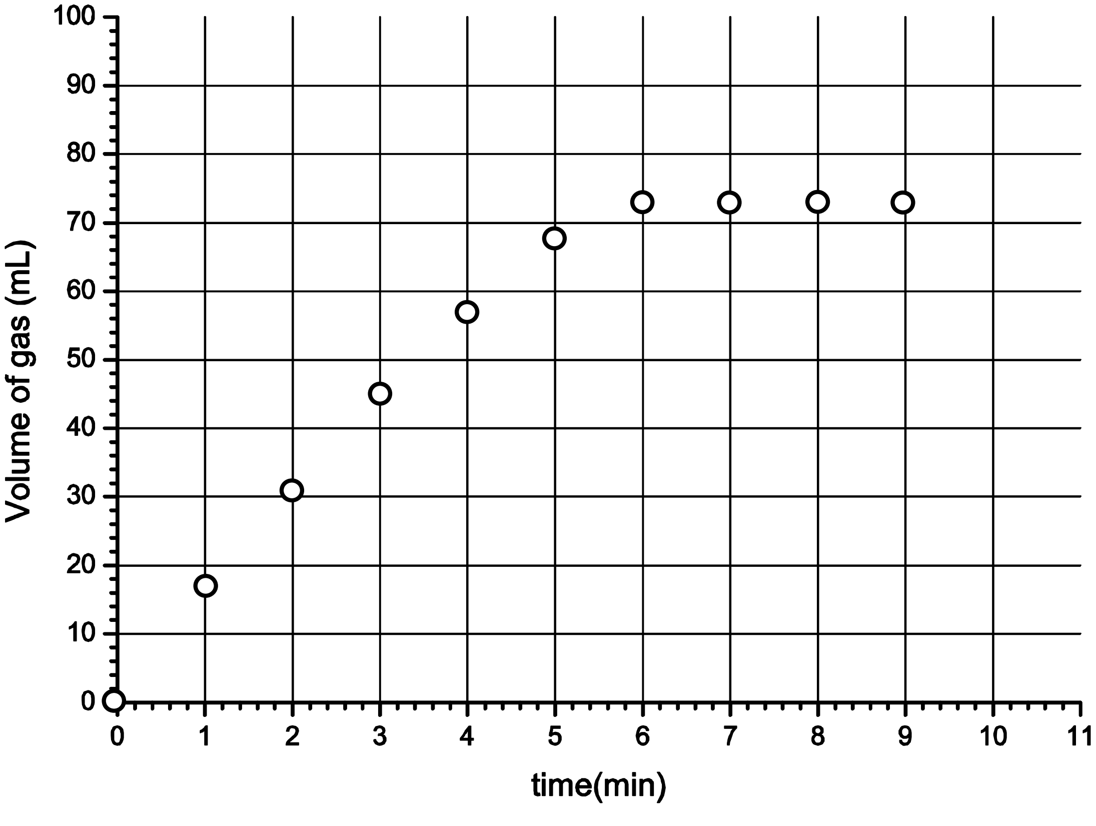
2.1 **Part A.** The volume of the gas evolved stays within a range of 0 – 2 cm^3 (maximum).

2.2 $V(H_2)_{uncatalyzed} = 0\ cm^3$

2.3 **Part B.** The gas volume versus time data for the reaction of ammonia borane in the presence of catalyst, are given in the table below.

Time (min)	0	1	2	3	4	5	6	7	8	9
Volume (cm^3)	0	17	31	45	57	68	73	73	73	73

Graph of gas volume versus time in the presence of catalyst:



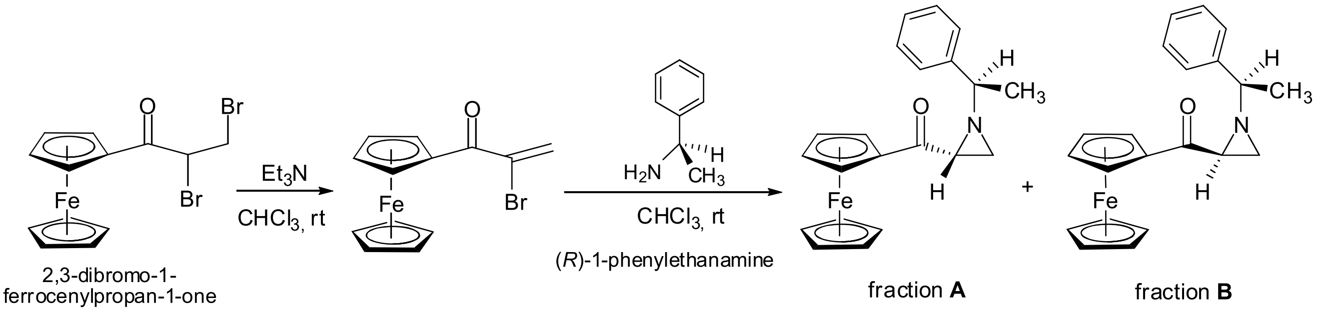
2.4 – 2.6

The required calculations are based on the experimental data obtained in practical problem 2. The well known relations between the mass, molar mass, amount of substance, and the volume of a gaseous substance at a certain pressure and temperature, as well as the experimental volume data in dependence on time (part 2.3) should be used to solve the tasks 2.4 – 2.6.

PROBLEM 3 (practical)

Synthesis, purification and separation of a diastereomeric mixture

Nature has many compounds in the form of a single enantiomer or diastereomer such as sugars, amino acids, steroids, etc. Some of these compounds are biologically active and used as drugs. Therefore, the asymmetric synthesis of organic compounds is important. One of the methods for the asymmetric synthesis of organic compounds employes a metal-catalyst, in which the metal is coordinated to a chiral organic molecule named as chiral ligand. In this experiment two chiral ligands will be synthesized.



Chemicals

- 2,3-dibromo-1-ferrocenylpropan-1-one, 0.50 mmol, labelled as "Rxn RB"
- Triethylamine, 1.0 mmol in 1.0 cm^3 of $CHCl_3$, label: "V 1"
- (*R*)-1-phenylethanamine, 1.0 mmol in 0.5 cm^3 of $CHCl_3$, label: "V 2"
- 2,3-dibromo-1-ferrocenylpropan-1-one, reference starting material for TLC, label: "SM"
- Heptane : ethyl acetate mixture in a volume ration 3 : 2, 500 cm^3, label: "ELUENT",

A. Synthesis

1. Using a syringe, transfer through the septum the triethylamine solution in vial 1 (V 1) to the 10 cm^3 round bottom reaction flask (Rxn RB) containing 0.50 mmol 2,3-dibromo-1-ferrocenylpropan-1-one.
2. Stir the mixture at room temperature for 30 minutes using the magnetic stirrer at 600 rpm (as marked on the stirrer).
3. After 30 minutes, transfer through the septum the (*R*)-1-phenylethanamine solution in vial 2 (V2) to the reaction flask using the same syringe.
4. Stir the mixture for additional 60 minutes at room temperature.

5. After 60 minutes turn off the magnetic stirrer and perform a thin layer chromatography, TLC, analysis as follows:
   - i) Check your TLC plates before use. Damaged plates will be replaced upon request without penalty.
   - ii) Draw a start line on the lower portion of TLC plate with a pencil (Fig. 3.1).
   - iii) Apply starting material from the vial labelled as SM two times to the spot on the left and then two times to the spot in the middle of plate. To the same plate, apply the reaction mixture (RM) taken from the reaction flask once to the spot on the right and then once to the spot in the middle as shown in Figure 3.1 (use a different capillary tube for each sample).
   - iv) Develop TLC plate in the TLC chamber with the eluent. Mark the solvent front with the pencil (Fig. 3.2).
   - v) When the TLC plate is dry, place it in a zipper storage bag marked as TLC1.

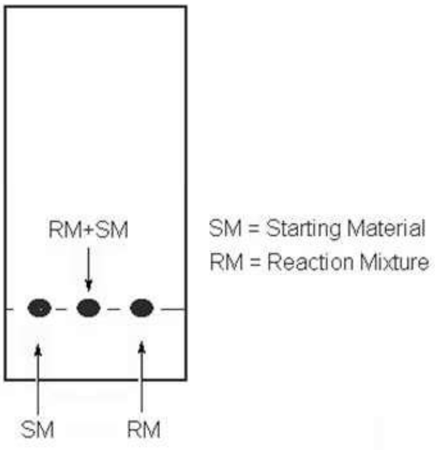


Figure 3.1. TLC plate

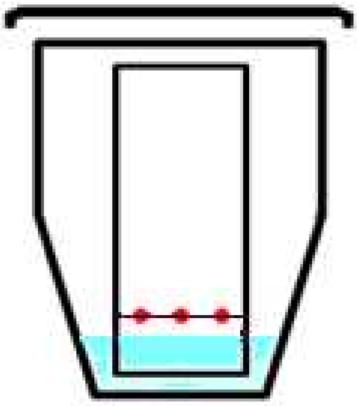


Fig. 3.2 TLC plate placed in the TLC developing chamber.

B. Flash Column Chromatography

1. Remove the stopper, open the valve, and bring the eluent level at top of column to the upper level of silica gel. (Fig. 3.3).
2. Close the valve and load the content of reaction flask on the top of flash column using a Pasteur pipette.
3. Rinse the reaction flask with 0.5 cm^3 eluent taken from the bottle labelled as ELUENT using a clean syringe. Using the same Pasteur pipette, load the washings also on the top of column.
4. Open the valve of the column and let the solvent run down to the upper level of silica gel.

5. Close the valve and add 1.0 cm^3 eluent by a Pasteur pipette. Open the valve. When the eluent is at the upper level of silica gel, add 2 - 3 cm^3 eluent slowly without closing the valve.
6. Fill the column by adding more eluent.

   CAUTION: Be careful during the addition of eluent; do not disturb silica gel.

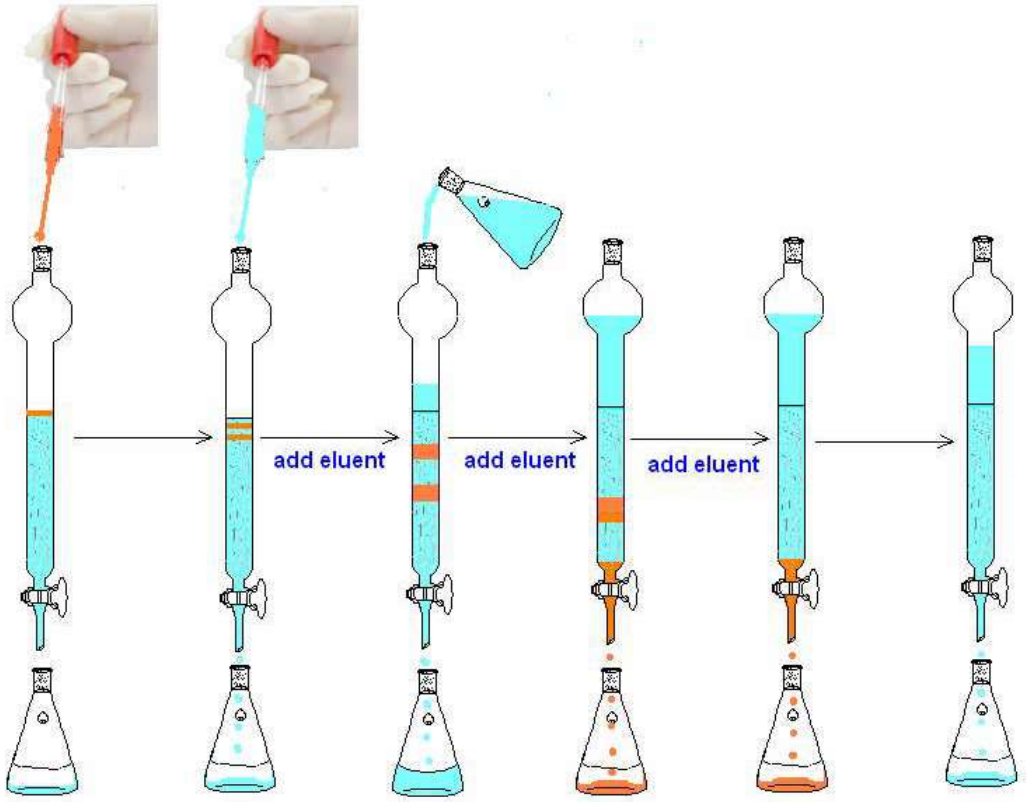


Figure 3.3. Flash Column Chromatography

7. In order to speed up the purification, apply little pressure by connecting the pressure applying bulb with an adapter on top of the column.

   CAUTION: Be careful not to apply too much pressure. Add eluent time to time to avoid silica gel run dry.
8. You are expected to collect two major fractions **A** and **B**. Discard any material which elutes before major fraction **A** and between **A** and **B** into the container labeled as Organic Waste.

9. Collect the first major fraction into a 100 cm^3 Erlenmeyer flask and label it as fraction **A**.
10. Collect the second major fraction into a 250 cm^3 Erlenmeyer flask and label it as fraction **B**.
11. After collecting fraction **B** stop the elution by closing the valve.

C. Analysis. Perform

1 Perform another TLC by applying the starting material (**SM**) two times to the spot on the left, apply fraction **A** two times to the spot in the middle, and then fraction **B** five times to the spot on the right. After development, when the TLC plate is dry, place it in a zipper storage bag marked **TLC2**.

2. Measure the volume of fraction **A** using 50 cm^3 graduated cylinder and record the volume to your answer sheet.
3. Measure the volume of fraction **B** using 250 cm^3 graduated cylinder and record the volume to your answer sheet.
4. Using a 2 cm^3 pipette transfer 2.0 cm^3 of fraction **A** into the 10 cm^3 volumetric flask and complete the volume to 10 cm^3 by adding eluent. After shaking the flask, fill out the UV-visible cell (at least ¾ of its volume) by using a Pasteur pipette. Ask the assistant to measure the absorbance at 450 nm using the spectrophotometer and record the result to your answer sheet.
5. Using fraction **B**, fill out (at least ¾ of its volume) the other UV-visible cell by a Pasteur pipette (no need for dilution). Ask the assistant to measure the absorbance at 450 nm using the spectrophotometer and record the result to your answer sheet.

Treatment of Data

3.1 Copy (sketch) the TLC1 plate on your answer sheet.

3.2 Copy (sketch) the TLC2 plate on your answer sheet.

3.3 Calculate and record the R_f values of the spots (fraction **A**, fraction **B**, and starting material **SM**) using the TLC2 plate.

3.4 The molar extinction coefficient, molar absorptivity, ε, is 404 M^{-1}cm^{-1} for **A** and 400 M^{-1}cm^{-1} for **B** at 450 nm (M = mol dm^{-3}). Calculate in percent:

i) the yield of fraction **A** based on the starting material.

ii) the yield of fraction **B** based on the starting material.

SOLUTION

3.1 – 3.2

Maximum points are given:

- for the appearance of three spots loaded on the base line,
- for the well developed and separated spots on the TLC,
- for the solvent front line and the base line,
- for the accurate presentation of the sketch of the TLC,
- in part 3.2, moreover, for the absence of fraction **B** in fraction **A** and vice versa.

3.3 Maximum points if calculated and recorded R_f values fall within those given in the following table:

Spots	R_f value
Fraction **A**	0.40 – 0.50
Fraction **B**	0.20 – 0.30
Starting material **SM**	0.65 – 0.75

3.4 Points were awarded in accordance with some distribution graphs proposed by the organizer and approved by the International Jury. The graphs were applied for fraction **A** and **B**, when evaluating their volumes, absorbance and yields.