29th International Chemistry Olympiad

29e Olympiade Internationale de la Chimie

Experimental Examination

Montreal, Tuesday, July 15, 1997

In the laboratory you must wear safety eye glasses or your own glasses, and use the pipette filler bulb provided. You will receive a warning from the laboratory supervisor if you remove your glasses or fill a pipette by mouth. Repeated infractions will result in a penalty of 5 points subtracted from the total score of the current problem. The third violation is considered a major fault incompatible with further experimental work, and you will be dismissed from the laboratory with a resultant zero score for the entire experimental examination.

- Please carefully read the text of each experiment and study the layout of the answer forms before you begin your experimental work.
- Write your name, personal identification code (posted at your workstation), and team in the upper right corner of the first page of each problem's answer sheet. Write your name and code on all remaining answer sheets.
- The work must begin only when the START command is given.
- You have 5 hours to perform all of the experiments, including the time needed to fill in the answer sheets with your results. You must stop your work and give the completed answer sheets to the supervisor immediately after the STOP command is given. A delay in doing this by 3 minutes will lead to cancellation of the current problem and will result in zero points for this problem.
- All results must be written in the corresponding areas on the answer sheets. Data written elsewhere will not be marked. Do **NOT** write anything on the back of your answer sheets. If you need more paper for working or a replacement answer sheet, request it from the supervisor.
- Use only the pen and calculator provided or your own nonprogrammable calculator.
- Use only the distilled water, except for cooling purposes.
- Use the appropriate waste containers for disposal of chemical and other waste materials.
- The number of significant figures in numerical answers must conform to the rules of evaluation of experimental errors. The inability to perform calculations correctly will result in penalty points, even if your experiment is flawless.
- There are a total of **7** pages in this examination.

Experimental Problem 1

(16 points)

DETERMINATION OF Mg^{2+} AND Ca^{2+} IN BOTTLED WATER

- The K_{sp} for calcium oxalate is 2.3 x 10^{-9} and the K_{sp} for magnesium oxalate is 8.6 x 10^{-5}.

- In a solution buffered to maintain pH 10, Calmagite indicator is pink when bound to Mg^{2+} and blue in the absence of available magnesium ions. Calcium ions are not bound by Calmagite.

- EDTA binds to Mg^{2+} and Ca^{2+} even in the presence of Calmagite. The stoichiometry of the EDTA-metal complex formed with both Mg^{2+} and Ca^{2+} is 1:1.

- Molar masses: M_{Ca} = 40.08 g mol^{-1} M_{Mg} = 24.31 g mol^{-1}

<u>Chemicals Available</u>

500 mL sample of "Bottled Water"	(labeled BOTTLED WATER)
aqueous buffer (pH 10)	(labeled Buffer pH 10)
Calmagite indicator	(labeled Calmagite)
aqueous saturated ammonium oxalate	(in common burettes)
aqueous ethylenediaminetetraacetic acid	(labeled EDTA)
aqueous standardized* Mg^{2+}	(labeled Mg^{2+} Standard)
distilled water	(labeled DISTILLED WATER)

*0.928 mg Mg^{2+}/mL solution, 0.0382 moles Mg^{2+}/litre

<u>Procedure</u>

A. Precipitation of calcium ions

Precipitate the calcium ions in a 25.00 mL aliquot of the "Bottled Water" sample by accurately adding approximately 0.50 mL of saturated ammonium oxalate solution (from the common burettes in each lab room). Carefully swirl the solution to ensure uniform mixing. Allow at least 45 minutes for complete precipitation to occur.

B. Standardization of the EDTA solution

Using distilled water, dilute 5.00 mL of the standardized magnesium solution to a final volume of 100.0 mL.

Add 40 mL of distilled water, 5 mL of pH 10 buffer solution, and some Calmagite indicator to 5.00 mL of diluted magnesium solution. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

continued…

Experimental Problem 1 (continued)

C. Titration of Mg^{2+} and Ca^{2+}

Add 40 mL of distilled water, 5 mL of pH 10 buffer solution, and some Calmagite indicator to 5.00 mL of the "Bottled Water" sample. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

D. Titration of Mg^{2+}

Add 40 mL of distilled water, 5 mL of pH 10 buffer solution, and some Calmagite indicator to 5.00 mL of the calcium-free "Bottled Water" sample prepared in part **A**. The presence of a small amount of calcium oxalate will not interfer with your titration. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

Calculations

Calculate the concentration of Mg^{2+} (in mg L^{-1}) in the "Bottled Water" sample.

Calculate the concentration of Ca^{2+} (in mg L^{-1}) in the "Bottled Water" sample.

Experimental Problem 2

(12 points)

Organic Qualitative Analysis

You have six bottles containing six different organic compounds. From the list of eight compounds given below, identify the contents of each bottle using the reagents available.

Many of these compounds have strong odours. To prevent the laboratory from becoming too odorous, you must keep each bottle tightly capped when it is not in use. Dispose of any waste produced in the bottle labeled “ORGANIC WASTE” at your station. Also place used litmus paper in this bottle. Keep the waste bottle capped when not in use.

Chemicals Available

litmus paper, red and blue	
aqueous ceric ammonium nitrate	(labeled CERIC AMMONIUM NITRATE)
aqueous chromic-sulfuric acid	(labeled CHROMIC-SULFURIC ACID)
aqueous 2,4-dinitrophenylhydrazine	(labeled 2,4-DNPH)
aqueous 0.2% $KMnO_4$	(labeled 0.2% $KMnO_4$)
acetone (2-propanone)	(labeled ACETONE)

Possible Unknowns*

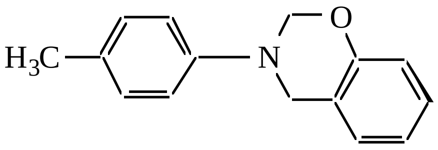
2-butanone
1-decene
2,3-diamino-2,3-dimethylbutane
hexane
3-methyl-1-butanol
2-methyl-2-butanol
nonanal
propanoic acid

*Several of the unknowns are present as dilute aqueous solutions.
This will not interfere with the test results.

Experimental Problem 3

(12 points)

SYNTHESIS OF THE SUBSTITUTED DIHYDRO-1,3-BENZOXAZINE (C)



C

Problem

Benzoxazines have long been recognized as useful biologically-active compounds. One such compound (**C**) will be prepared using the three-step synthesis described below. All of the product obtained in Step I should be used in Step II and similarly all of the product from Step II should be used in Step III. You will be evaluated on both the yield and purity of the final product.

Chemicals Available

5-mL reaction vial containing 2.5 mL of ethanolic 1-amino-4-methylbenzene (0.22 g)	(labeled i)
vial containing 0.25 g of 2-hydroxybenzaldehyde	(labeled ii)
vial containing 0.1 g of sodium borohydride	(labeled iii)
vial containing 0.042 g of paraformaldehyde	(labeled iv)
test tube containing dilute ethanolic KOH (50 mg of KOH dissolved in 10 mL of ethanol)	(labeled v)
wash bottle containing dry ethanol	(labeled ETHANOL)

Ice is available in each laboratory room.

Molar masses

$M_H = 1.008$ g mol^{-1}

$M_C = 12.011$ g mol^{-1}

$M_N = 14.007$ g mol^{-1}

$M_O = 15.999$ g mol^{-1}

$M_{Na} = 22.990$ g mol^{-1}

$M_B = 10.811$ g mol^{-1}

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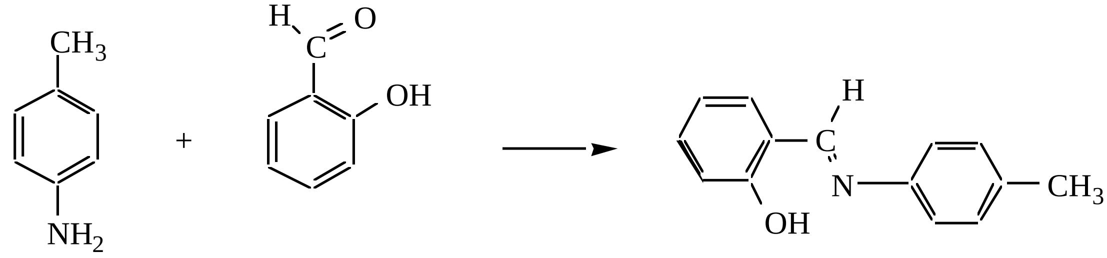
Procedure

STEP I



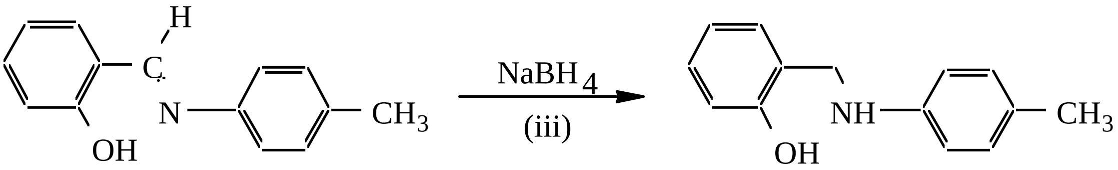
(i) (ii) **A**

1. Place the small magnetic stirbar in the 5 mL reaction vial containing solution (i) and stir.

2. Add the 2-hydroxybenzaldehyde from vial (ii) dropwise to the stirred solution in vial (i). After a short period of time a yellow solid will crystallize out. This is intermediate Product **A**.

3. Isolate the yellow solid (**A**) by vacuum (suction) filtration and wash it with ice-cold ethanol.

STEP II



A **B**

1. Add the impure Product **A** from Step I to a 5-mL reaction vial containing approximately 1.5 mL of ethanol.

2. Surround the vial with ice/water, and stir the reaction vigorously with the spatula while carefully adding small amounts of sodium borohydride (iii) over a period of about 5 minutes until the bright yellow colour disappears. The reaction will bubble and a white solid will form.
   Note that you have been given more sodium borohydride than is required for this reaction.

3. Isolate the intermediate Product **B** by vacuum (suction) filtration, wash it with ice-cold ethanol, and air dry the solid for approximately 5 minutes.

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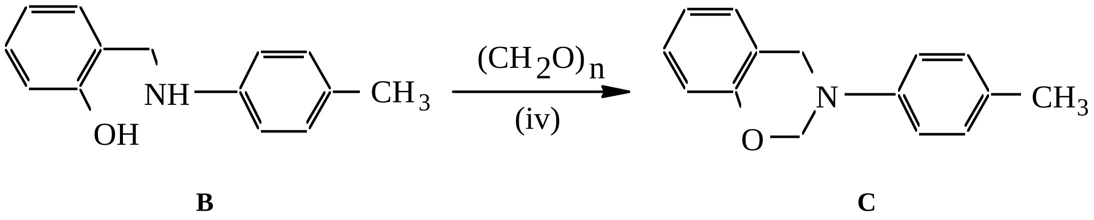
Experimental Problem 3 (continued)

STEP III



1. Dissolve all of the paraformaldehyde (iv) in approximately 2.5 mL of ethanolic potassium hydroxide (v) in a 5 mL vial. Stir to dissolve all of the solid.

2. Add all of Product **B** from Step II to the vial. Stir and gently reflux the mixture for 15 minutes. A clear solution should be obtained.

3. Concentrate the solution by carefully boiling off some of the ethanol leaving approximately 1 mL in the vial and allow the vial to cool. The crystals which form are the required Product **C**.

4. Isolate the crude Product **C** by vacuum (suction) filtration and air dry the crystals.

5. Recrystallize the crude product from ethanol. Air dry the crystals for 15 minutes.

6. Determine the melting point* and then mass of the final product.

7. Place all of your remaining product in the numbered vial labeled "PRODUCT C" and hand it in for evaluation.

* Note: A melting point is always recorded as a range -- from when the crystals first begin to melt until the last crystal has melted. The melting point apparatus should be allowed to cool to approximately 50 degrees before you use it. The supervisors will be rechecking both your reported melting point and mass for Product **C**.

* Caution: Do not leave the melting point and mass determinations until the end of the lab period.

Theoretical Examination

Montreal, Thursday, July 17, 1997

PROBLEMS

- Write your name, personal identification code, and team in the upper right corner of the first page of each problem's answer sheet. Write your name and code on all remaining answer sheets.

- Work must begin only when the START command is given.

- You have 5 hours to solve the problems, including the time needed to fill in the answer sheets with your results. You must stop your work and give the completed answer sheets to the supervisor immediately after the STOP command has been given.

- All solutions must be written in the corresponding areas on the answer sheets. Data written elsewhere will not be marked. Do **NOT** write anything on the back of your answer sheets. If you need more paper for working or a replacement answer sheet, request it from the supervisor.

- **Use only the pen and calculator provided or your own nonprogrammable calculator.**

- There are a total of **12** pages in this examination.

Problem 1

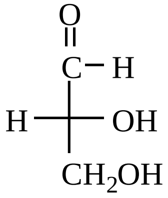
(15 points)

Compound **X** is a trisaccharide which occurs principally in cottonseed meal. Compound **X** does not react with Benedict's or Fehling's solutions nor does it mutarotate. Acid-catalyzed hydrolysis gives three different D-hexoses, **A**, **B**, and **C**. Compounds **A** and **B**, as well as compound **1** (see below), all give the same osazone upon reaction with excess acidic phenylhydrazine. Compound **C** reacts with nitric acid to give an optically inactive compound **D.** The Kiliani-Fischer approach is used to establish the configurational relationship between D-glyceraldehyde and **C.** The intermediate aldotetrose which leads to C does not give a meso compound when oxidized by nitric acid. When **A** is treated with nitric acid, the dicarboxylic acid (aldaric acid) produced is optically active. Both **A** and **B** react with 5 moles of HIO_4; one mole of **A** gives 5 moles of methanoic (formic) acid and one mole of methanal (formaldehyde) while one mole of **B** gives 3 moles of methanoic (formic) acid and 2 moles of methanal (formaldehyde) and one mole of carbon dioxide. Both **A** and **B** are related to the same aldotetrose which is the diastereoisomer of the one to which **C** is related. Methylation of **X** followed by hydrolysis gives a 2,3,4-tri-*O*-methyl-D-hexose (**E**) (derived from **A**), a 1,3,4,6-tetra-*O*-methyl-D-hexose (**F**) (derived from **B**), and a 2,3,4,6-tetra-*O*-methyl-D-hexose (**G**) (derived from **C**).

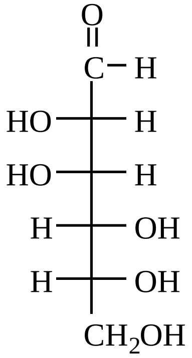
i) On the answer sheet, draw Fischer projection formulas of **A**, **B**, **C**, and **D**.

ii) On the answer sheet, complete the appropriate Haworth projection formulas to clearly show the ring size and absolute stereochemistry of **E**, **F**, and **G**. Either of the anomeric forms are acceptable as an answer.

iii) On the answer sheet, underline the correct representation of the connectivity sequence of the three monosaccharides present in trisaccharide **X**.



D-Glyceraldehyde



Compound **1**

Problem 2

(15 points)

Professor Molina of the Massachusetts Institute of Technology won the 1995 Nobel Prize in Chemistry for his work on atmospheric chemistry. One reaction that he has studied in detail is the acid rain reaction which produces H_2SO_4 in the atmosphere. He has proposed two possible stoichiometric reactions:

Proposal A: $H_2O(g) + SO_3(g) \rightarrow H_2SO_4(g)$

Proposal B: $2H_2O(g) + SO_3(g) \rightarrow H_2SO_4(g) + H_2O(g)$

i) Using simple collision theory, what reaction orders would be expected for Proposal A and for Proposal B?

Proposal B is thought to proceed by the following two-step process:

$$SO_3 + 2H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_3{\bullet}2H_2O \qquad \text{(fast)}$$

$$SO_3{\bullet}2H_2O \xrightarrow{k_2} H_2SO_4 + H_2O \qquad \text{(slow)}$$

($SO_3{\bullet}2H_2O$ is a complex which is stabilized by hydrogen bonds and $k_2 << k_1$ or k_{-1})

ii) By applying the principle of stationary (steady) states, derive the appropriate rate law and hence the reaction order of the two-step mechanism for Proposal B.

iii) Recent quantum chemical calculations have shown that the overall reaction activation energies for the two proposals are:

E_A = + 80 kJ mol^{-1} for Proposal A $\qquad$ E_B = - 20 kJ mol^{-1} for Proposal B

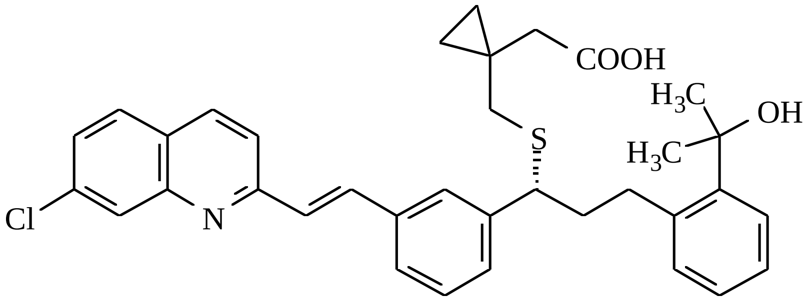
State the relationship between the rate constant and the temperature (Arrhenius relationship) for each proposal and predict the temperature dependence of the rate constants for each proposal.

iv) The formation of H_2SO_4 is faster in the upper atmosphere (T = 175 K) than at the earth's suface (T = 300 K). Which proposed pathway must dominate in the upper atmosphere given the activation energies in part (iii) and your understanding of the Arrhenius equation?

Problem 3

(15 points)

Chemists at Merck Frosst Canada in Montréal have developed a promising drug which is useful against asthma. The structure of MK-0476 is shown below.



MK-0476

During their investigation, they devised a simple and efficient synthesis, depicted below, for the thiolated portion of MK-0476 starting from diethyl ester **A**.

i) Give the structures of the intermediate products **B - F** prepared during this synthesis.

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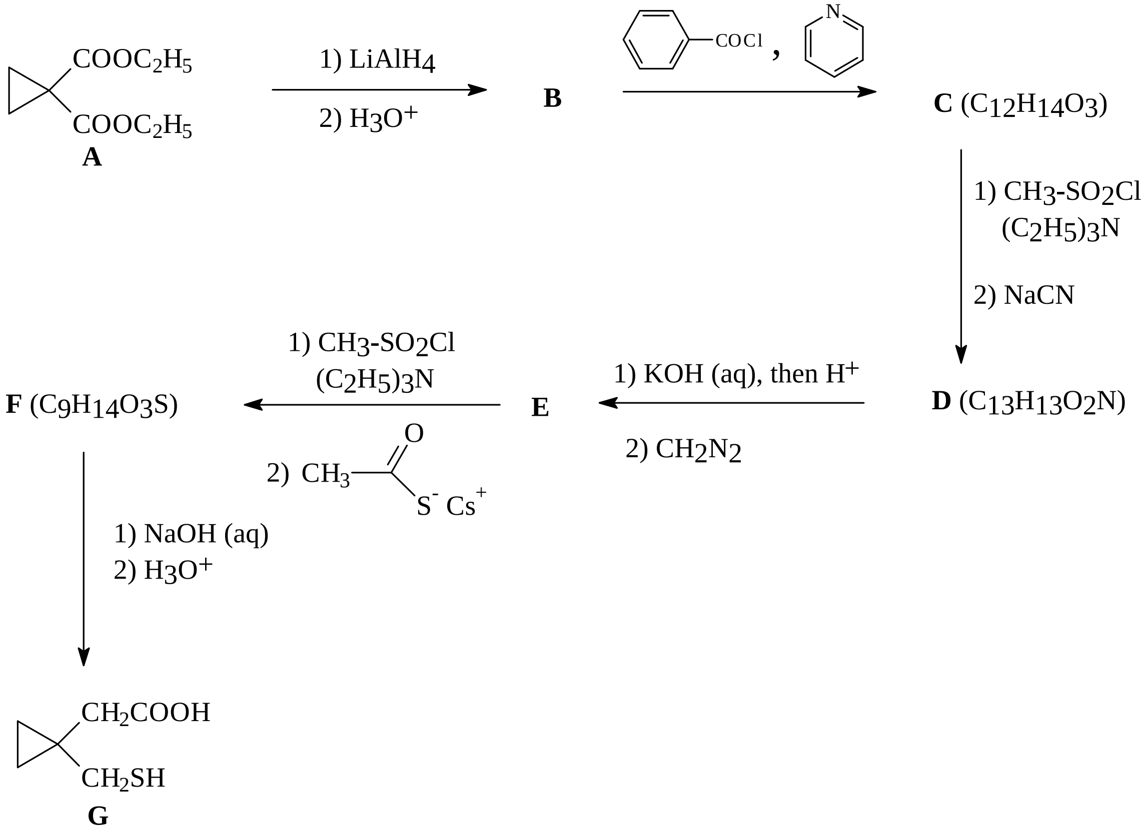
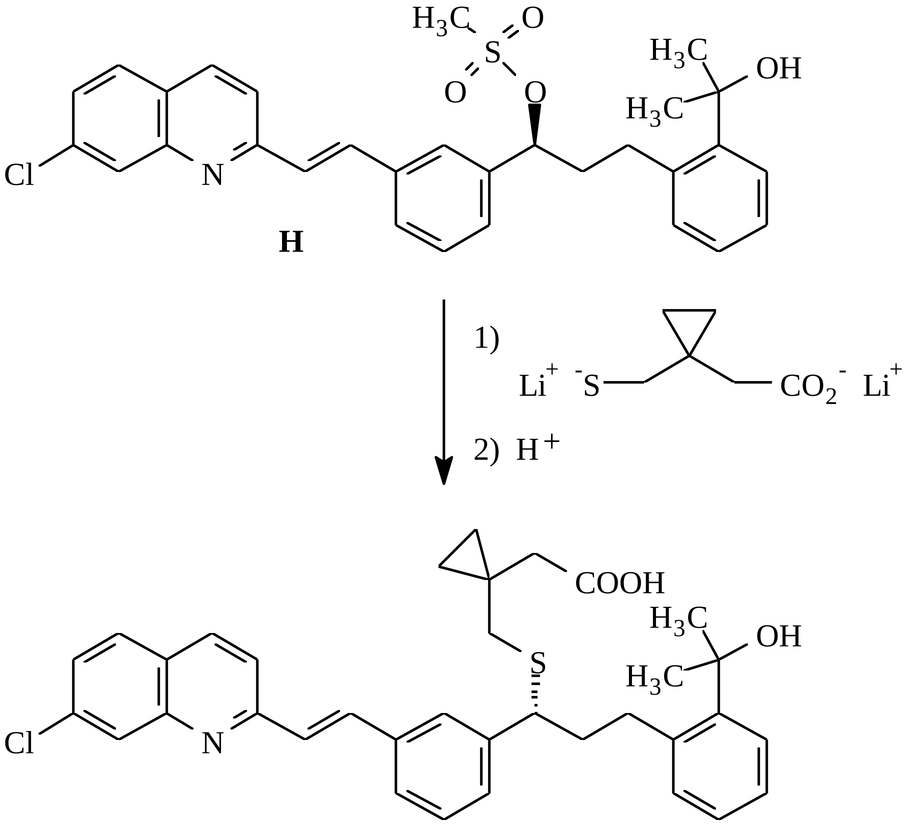


Problem 3 (continued)

In one of the last steps of the synthesis on MK-0476, the dilithium salt of the above thiol acid (**G**) was coupled with the side chain of the rest of the molecule as shown below.



ii) Based on the observed stereochemistry of the above reaction, what is the mechanistic designation of this coupling process?

iii) If the process proceeds by your proposed mechanism, what change would occur to the overall rate of the reaction if the concentration of both the thiolate salt and the substrate **H** were simultaneously tripled?

iv) For the nucleophilic substitution reaction, model studies were carried out using bromoethane as the substrate to perfect the above coupling. Draw only the structure of the major product of the reaction of one molar equivalent of bromoethane with:

a) **G** plus two molar equivalents of base

b) **G** plus one molar equivalent of base

v) A side reaction of **G** is its oxidative dimerization.
Draw the structure of the dimeric product, showing all non-bonded electrons.

Problem 4

(15 points)

Graph paper is provided for your optional use in this question.
If you choose to use it, print your name and identification
code in the upper right corner of the graph paper.

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HIn is a weakly acidic indicator.

$$\mathrm{HIn} + \mathrm{Na^{+}OH^{-}} \rightleftharpoons \mathrm{Na^{+}In^{-}} + \mathrm{H_2O}$$

also written as

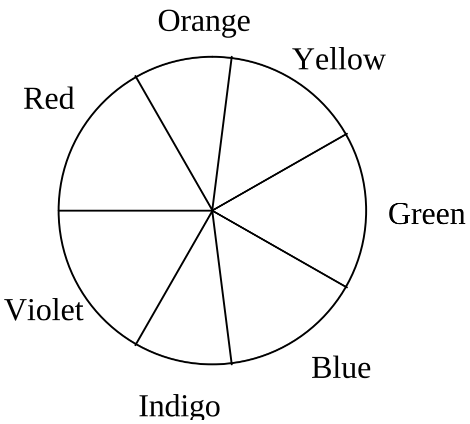
$$\mathrm{HIn} \rightleftharpoons \mathrm{In^{-}} + \mathrm{H^{+}}$$

At normal temperatures, the acid dissociation constant for this indicator is $K_a = 2.93 \times 10^{-5}$.

The absorbance data (1.00 cm cells) for 5.00×10^{-4} M (mol dm^{-3}) solutions of this indicator in strongly acidic and strongly alkaline solutions are given in the following table.

Absorbance Data (A)

λ, nm	pH = 1.00	pH = 13.00
400	0.401	0.067
470	0.447	0.050
485	0.453	0.052
490	0.452	0.054
505	0.443	0.073
535	0.390	0.170
555	0.342	0.342
570	0.303	0.515
585	0.263	0.648
615	0.195	0.816
625	0.176	0.823
635	0.170	0.816
650	0.137	0.763
680	0.097	0.588



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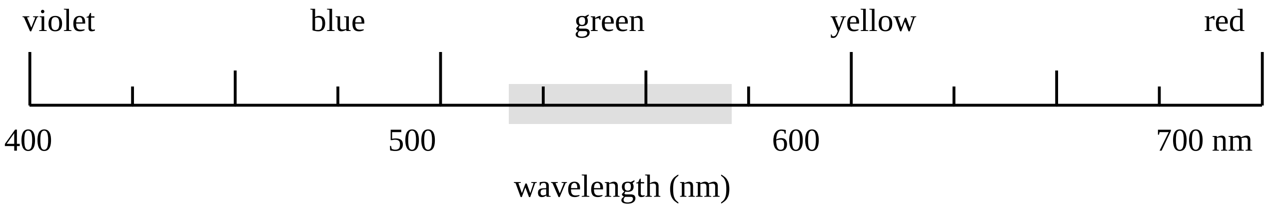
Problem 4 (continued)

i) Predict the observed colour of the a) acidic and b) basic forms of the indicator.

Using a “50 nm wide bar”, shade the appropriate area of the wavelength scale on the answer sheet which would correspond to the colour of the indicator at the pH values given in the table.
For example, if observed colour is green, your answer would appear as:



ii) A filter is located between the light source and the sample. What colour filter would be most suitable for the photometric analysis of the indicator in a strongly acidic medium?

iii) What wavelength range would be most suitable for the photometric analysis of the indicator in a strongly basic medium?

iv) What would be the absorbance of a 1.00 x 10^{-4} M (mol dm^{-3}) solution of the indicator in alkaline form if measured at 545 nm in a 2.50 cm cell?

v) Solutions of the indicator were prepared in a strongly acidic solution (HCl, pH = 1) and in a strongly basic solution (NaOH, pH = 13). Perfectly linear relationships between absorbance and concentration were observed in both media at 490 nm and 625 nm, respectively.

The molar absorptivities at the two wavelengths are:

	ε_{490}	ε_{625}
	M^{-1} cm^{-1}	M^{-1} cm^{-1}
HIn (HCl)	9.04 x 10^{2}	3.52 x 10^{2}
In^{-} (NaOH)	1.08 x 10^{2}	1.65 x 10^{3}

(M = mol dm^{-3})

Calculate the absorbance (1.00 cm cell) at the two wavelengths for an aqueous 1.80 x 10^{-3} M (mol dm^{-3}) solution of the indicator HIn.

Problem 5

(15 points)

Iron metal melts at 1811 K. Between room temperature and its melting point, iron metal can exist in different allotropic or crystalline forms. From room temperature to 1185 K, the crystal structure of iron metal exists as a body-centered cubic (bcc) lattice known as α-iron. From 1185 K to 1667 K, the structure becomes face-centered cubic (fcc) and is called γ-iron. Above 1667 K, and up to its melting point, iron reverts to a bcc structure similar to that of α-iron. The latter phase is called δ-iron.

i) Given that the density of pure iron metal is 7.874 g cm^{-3} at 293 K,

   a) Calculate the atomic radius of iron (expressed in cm)

   b) Calculate its density (expressed in g cm^{-3}) at 1250 K

Notes: Ignore the small effects due to the thermal expansion of the metal.

Clearly define any symbols which you use, e.g. r = atomic radius of Fe

Steel is an alloy of iron and carbon in which some of the interstitial spaces ("holes") of the crystal lattice (iron) are occupied by small atoms (carbon). Its carbon content typically ranges from 0.1% to 4.0%. In a blast-furnace, the melting of iron is facilitated when it contains 4.3% of carbon by mass. If this mixture is cooled too rapidly the carbon atoms remain dispersed within the α-iron phase. This new solid, called martensite, is extremely hard and brittle. Although is it slightly distorted, the size of the unit cell of this solid (martensite) is the same as that of α-iron (bcc).

ii) Assuming that the carbon atoms are evenly distributed in the iron structure,

   a) Calculate the average number of carbon atoms per unit cell of α-iron in martensite containing 4.3% C by mass.

   b) Calculate the density (expressed in g cm^{-3}) of this material.

Molar masses and constants

M_{Fe} = 55.847 g mol^{-1}

M_C = 12.011 g mol^{-1}

N_A = 6.02214 x 10^{23} mol^{-1}

Problem 6

(15 points)

a) Much of the world's supply of platinum group metals is derived from the residues recovered from the electrolytic refining of copper and nickel. A flow chart for the recovery of platinum and palladium is shown on the following page.

i) Clearly draw the shape (geometry) of both the $PtCl_6^{2-}$ and the $PdCl_4^{2-}$ anions.

ii) Clearly draw all possible stereoisomeric structures of monomeric $Pd(NH_3)_2Cl_2$. Label the structures that you have drawn with their correct stereochemical descriptors.

iii) What is the role of the $FeSO_4$ in the second step of the flow chart? Write a balanced equation for the reaction of $FeSO_4$ in this step.

iv) Write a complete balanced equation for the ignition of $Pd(NH_3)_2Cl_2$ in air to give Pd metal. In this reaction, what is being oxidized and what is being reduced?

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b) Reaction of a main group chloride (24.71 g) with ammonia (10.90 g) gave a mixture of products consisting of NH_4Cl (25.68 g), a solid element **A** (2.57 g) and a yellow crystalline nitride of this element (7.37 g) according to the equation below.

$$n\mathbf{A}_wCl_x + mNH_3 \rightarrow pNH_4Cl + q\mathbf{A} + r\mathbf{A}_yN_z$$

(where n, m, p, q, r, w, x, y and z are coefficients to be determined)

A sample of the nitride exploded violently when struck with a hammer, but it underwent controlled polymerization on heating to give a bronze-coloured, fibrous solid which exhibits metallic conductivity. Element **A** also undergoes polymerization to a high molecular weight linear polymer upon heating.

Molar masses: $M_{Cl} = 35.453$ g mol^{-1} $M_N = 14.007$ g mol^{-1} $M_H = 1.008$ g mol^{-1}

i) Identify element **A**.

ii) Write a complete balanced equation for the reaction of the chloride with ammonia.

iii) Assuming conventional oxidation states, write the balanced redox half-reaction equations involved in this reaction.

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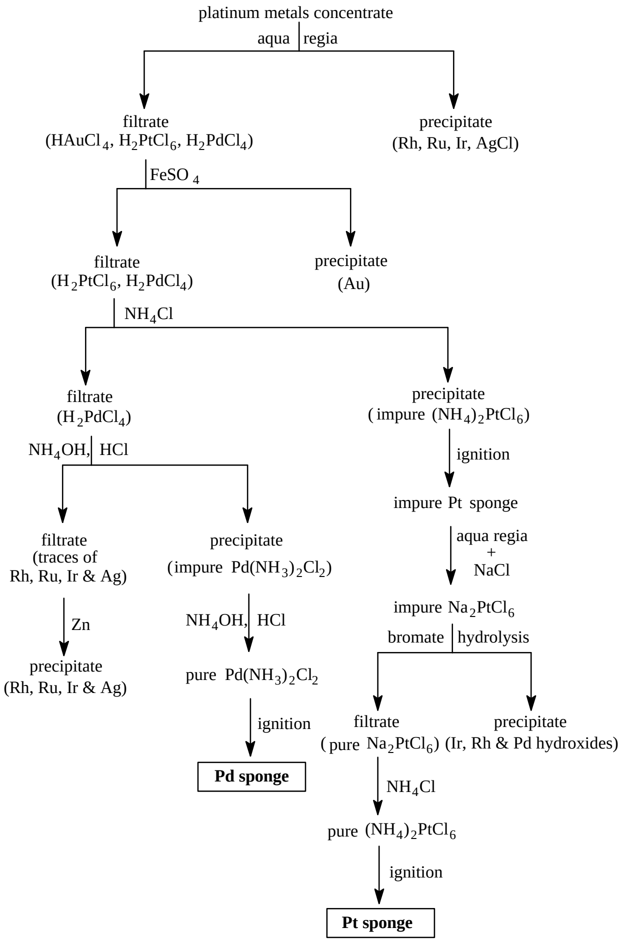
Problem 6 (continued)

Method of Purification of Platinum and Palladium



Problem 7

(15 points)

a) One mole of Cl_2 (g), which may be assumed to obey the ideal gas law, initially at 300 K and 1.01325×10^7 Pa, is expanded against a constant external pressure of 1.01325×10^5 Pa to a final pressure of 1.01325×10^5 Pa. As a result of the expansion, the gas cooled to a temperature of 239 K (which is the normal boiling point of Cl_2), and 0.100 mol of Cl_2 condensed.

The enthalpy of vaporization of Cl_2 (l) is 20.42 kJ mol^{-1} at the normal boiling point, the molar heat capacity of Cl_2 (g) at constant volume is $C_v = 28.66$ J K^{-1} mol^{-1} and the density of Cl_2 (l) is 1.56 g cm^{-3} (at 239 K). Assume that the molar heat capacity at constant pressure for Cl_2 (g) is $C_p = C_v + R$.

(1 atm = 1.01325×10^5 Pa, R = 8.314510 J K^{-1} mol^{-1} = 0.0820584 L atm K^{-1} mol^{-1})

i) **Either** draw a complete molecular orbital energy diagram **or** write the complete electronic configuration of Cl_2. Predict the bond order of Cl_2 and thus whether this molecule will be diamagnetic, ferromagnetic, or paramagnetic.

ii) For the changes described above, calculate the change in the internal energy (ΔE) and the change in the entropy (ΔS_{sys}) of the system.

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b) For the following reactions occurring in dilute aqueous solution at 298 K:

$$[Ni(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Ni(NH_3)_2(H_2O)_4]^{2+} + 2H_2O \qquad [1]$$

$$\ln K_c = 11.60 \text{ and } \Delta H^o = -33.5 \text{ kJ mol}^{-1}$$

$$[Ni(H_2O)_6]^{2+} + en \rightleftharpoons [Ni(en)(H_2O)_4]^{2+} + 2H_2O \qquad [2]$$

$$\ln K_c = 17.78 \text{ and } \Delta H^o = -37.2 \text{ kJ mol}^{-1}$$

Note: *en* is ethylenediamine (a neutral bidentate ligand)

(R = 8.314510 J K^{-1} mol^{-1} = 0.0820584 L atm K^{-1} mol^{-1})

Calculate ΔG^o, ΔS^o , and K_c at 298 K for reaction [3] occuring in a dilute aqueous solution:

$$[Ni(NH_3)_2(H_2O)_4]^{2+} + en \rightleftharpoons [Ni(en)(H_2O)_4]^{2+} + 2NH_3 \qquad [3]$$

Problem 8

(15 points)

An electrolyte is prepared from H_2SO_4, $CuSO_4$ and distilled water and its volume is 100.0 cm^3. The concentrations of H^+ and Cu^{2+} in the electrolyte are $c_{H^+} = 1.000$ M (mol dm^{-3}) and $c_{Cu^{2+}} = 1.000 \times 10^{-2}$ M (mol dm^{-3}), respectively. Two cubic platinum electrodes are immersed in the electrolyte. Both of the electrodes are single crystals with only one face (100) exposed to the electrolyte (the other five faces are blocked physically by an insulator which is stable in the electrolyte). The exposed surface area of each electrode is equal to 1.000 cm^2. During an electrolysis a total charge of 2.0000 C is passed between the cathode and the anode. At the cathode, two simultaneous processes are occurring: deposition of an epitaxial (layer-by-layer) Cu layer and H_2 gas generation. At the anode, O_2 gas is generated. The H_2 gas is collected in a flask under the following conditions (assume ideal gas behaviour):

$T = 273.15$ K and $P_{H_2} = 1.01325 \times 10^4$ Pa; the volume of H_2 is equal to 2.0000 cm^3

i) Write equations of the processes taking place at the electrodes.

ii) Calculate the number of moles of H_2 gas generated at the cathode and the number of moles of Cu deposited on the electrode.

iii) Calculate the number of Cu monolayers formed on the Pt (100) cathode.

Note that the lattice constant of Pt is $a_{Pt} = 3.9236 \times 10^{-8}$ cm.
Both Pt and Cu have the fcc (face centered cubic) crystallographic structure.

Molar masses and constants

$M_H = 1.00795$ g mol^{-1}
$M_{Cu} = 63.546$ g mol^{-1}
$e = 1.60218 \times 10^{-19}$ C
$F = 96485.3$ C mol^{-1}
$R = 8.314510$ J K^{-1} mol^{-1} = 0.0820584 L atm K^{-1} mol^{-1}
$V_m = 22.4141$ dm^3
1 atm = 1.01325×10^5 Pa
$N_A = 6.02214 \times 10^{23}$ mol^{-1}