29th International Chemistry Olympiad

29e Olympiade Internationale de la Chimie

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. <u>Do **NOT** write anything on the back of your answer sheets</u>. 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

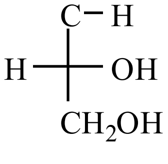
(15 points)

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**).

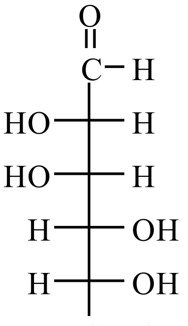
i) On the answer sheet, draw Fischer projection formulas of **A**, **B**, **C**, and **D**.

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

$E_B = - 20$ kJ mol^{-1} for Proposal B

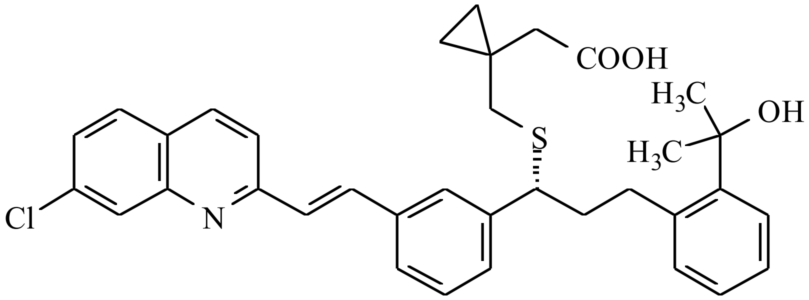
State the relationship between the rate constant and the temperature (Arrhenius relationship) for each proposal and predict the temperature dependence of the rate constants for each proposal.

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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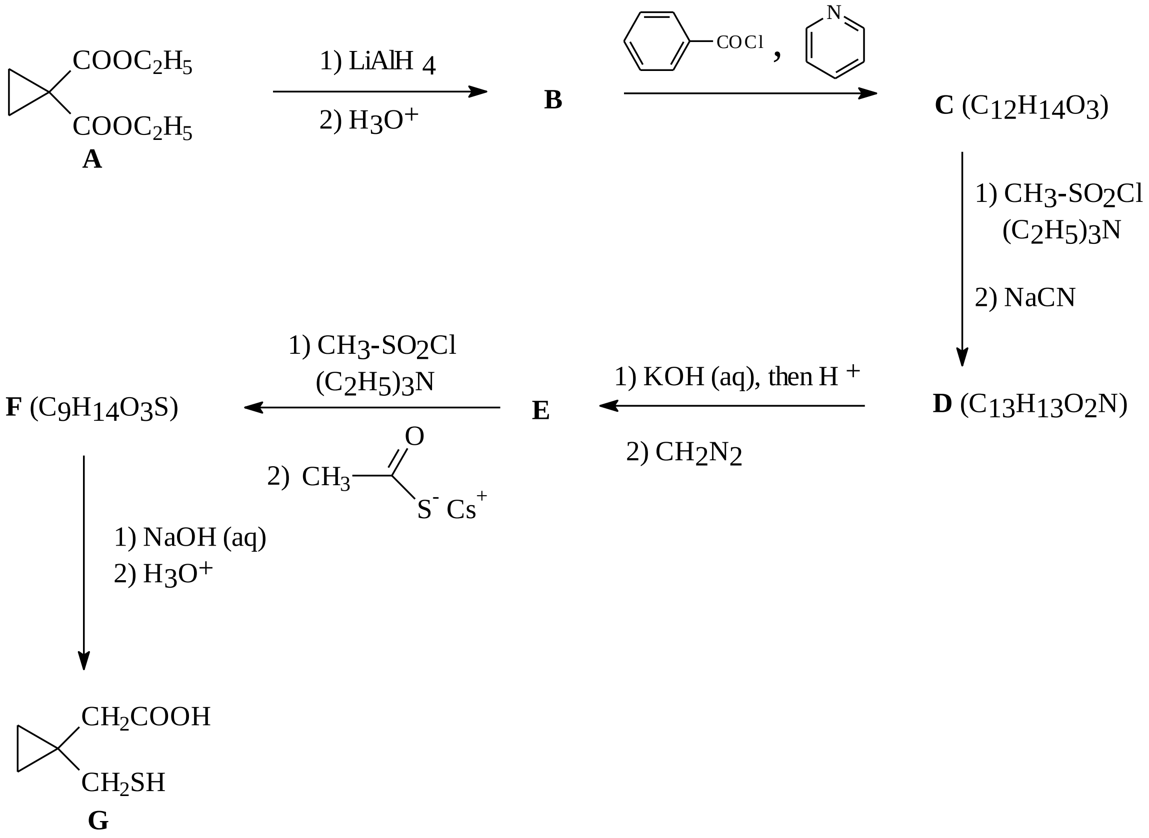
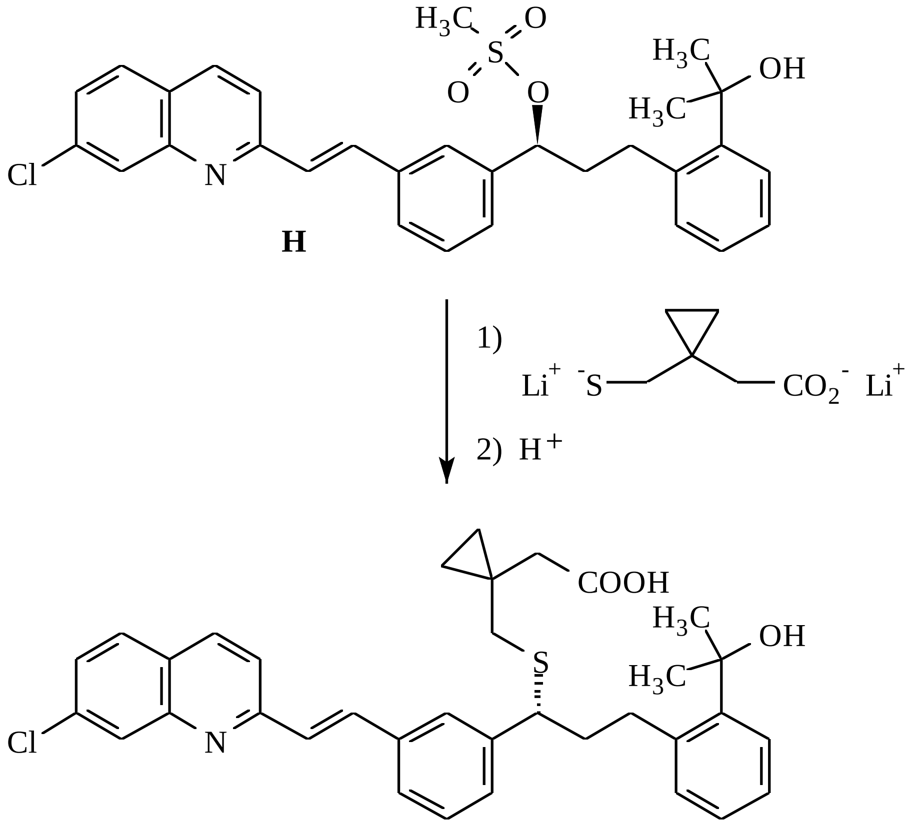


Problem 3 (continued)

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.



H

MK-0476

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.

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

also written as

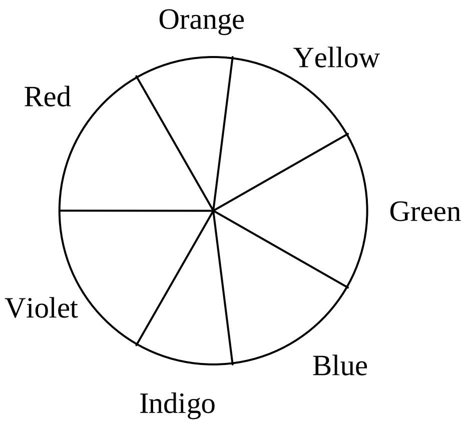
$$HIn \rightleftharpoons In^{-} + H^{+}$$

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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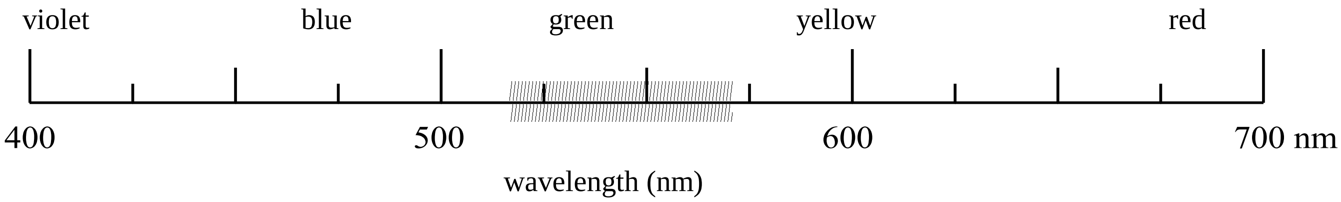
Problem 4 (continued)

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 1.00×10^{-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)	9.04×10^{2}	3.52×10^{2}
In^{-} (NaOH)	1.08×10^{2}	1.65×10^{3}

(M = mol dm^{-3})

Calculate the absorbance (1.00 cm cell) at the two wavelengths for an aqueous 1.80×10^{-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**.

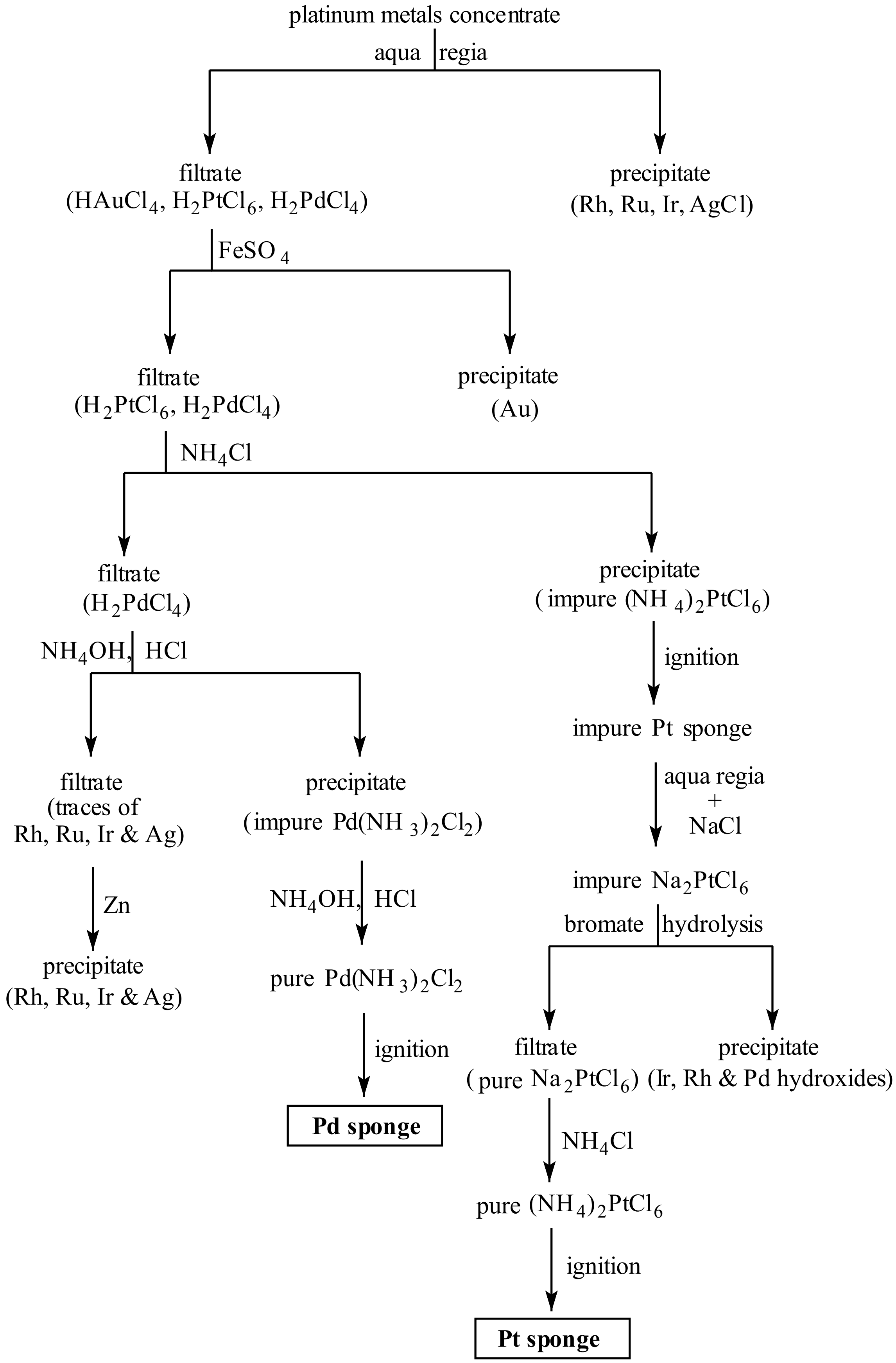
ii) Write a complete balanced equation for the reaction of the chloride with ammonia.

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

continued…

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:

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

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

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

$\ln K_c = 17.78$ and $\Delta H^o = -37.2$ 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):

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

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}

29th International Chemistry Olympiad

29e Olympiade Internationale de la Chimie

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Montreal, Thursday, July 17, 1997

ANSWER SHEETS

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- 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.

- There are a total of **18** pages in this answer booklet.

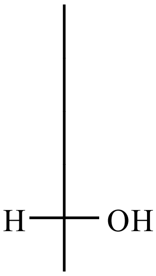
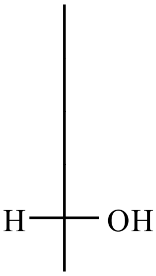
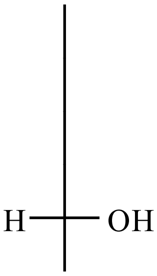
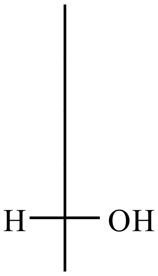
Name ____________________________

Identification Code ____________________________

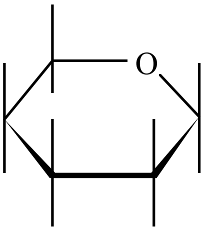
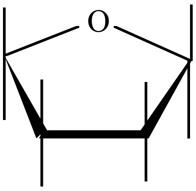
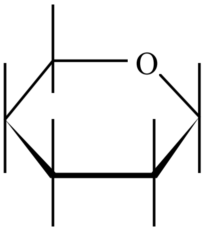
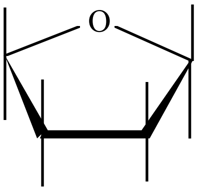
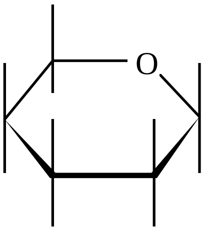
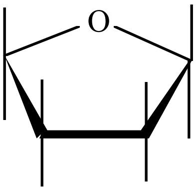
Team ____________________________

SOLUTION 1

i) Draw Fischer projection formulas of **A**, **B**, **C**, and **D**.

 **A**	 **B**	 **C**	 **D**

ii) Complete the appropriate Haworth projection formulas to clearly show the ring size and absolute stereochemistry of **E**, **F**, and **G**.

 **or**  **E**	 **or**  **F**	 **or**  **G**

iii) Underline the correct representation of the connectivity sequence of the three monosaccharides present in trisaccharide **X**.

Note: **A**$_5$ represents the furanose (5-membered ring) form of carbohydrate **A**.

A$_6$ represents the pyranose (6-membered ring) form of carbohydrate **A**.

B$_5$ represents the furanose (5-membered ring) form of carbohydrate **B**.

B$_6$ represents the pyranose (6-membered ring) form of carbohydrate **B**.

C$_5$ represents the furanose (5-membered ring) form of carbohydrate **C**.

C$_6$ represents the pyranose (6-membered ring) form of carbohydrate **C**.

A_6-B_6-C_5 A_6-B_5-C_6 A_5-B_6-C_6	B_6-C_6-A_5 B_6-C_5-A_6 B_5-C_6-A_6	C_6-A_6-B_5 C_6-A_5-B_6 C_5-A_6-B_6

Name ___________________________

Identification Code ___________________________

Team ___________________________

SOLUTION 2

i) Reaction order for Proposal A: _______

Reaction order for Proposal B: _______

ii) Reaction order for the two-step mechanism: _________

Derivation of the appropriate rate law:

SOLUTION 2 (continued)

iii) For Proposal A:

Arrhenius relationship: ____________________________

The rate constant for the reaction:

p Increases with increasing temperature

p Decreases with increasing temperature

p Is independent of the temperature

For Proposal B:

Arrhenius relationship: ____________________________

The rate constant for the reaction:

p Increases with increasing temperature

p Decreases with increasing temperature

p Is independent of the temperature

iv) The dominant mechanism in the upper atmosphere must be:

p Proposal A due to the temperature dependence of the rate constant

p Proposal B since $k_2 << k_1$ or k_{-1}

p Proposal A since the probability of the necessary collision in Proposal B is too small

p Proposal B due to the temperature dependence of the rate constant

Name ________________________

Identification Code ________________________

Team ________________________

SOLUTION 3

i) The structures of the intermediate products **B - F** are:

B	**C**	**D**
E	**F**	

ii) The mechanistic designation of this coupling is: _______________

iii) Mark the appropriate box and, if necessary, complete the phrase.

☐ The overall rate of the reaction would decrease by a factor of _____________.

☐ The overall rate of the reaction would increase by a factor of _____________.

☐ The overall rate of the reaction would remain unchanged.

continued…

Name ________________________

Identification Code ________________________

SOLUTION 3 (continued)

iv) a) Bromoethane and **G** plus 2 molar equivalents of base yields:

b) Bromoethane and **G** plus 1 molar equivalent of base yields:

v) Oxidative dimerization of **G** yields:

Name ______________________

Identification Code ______________________

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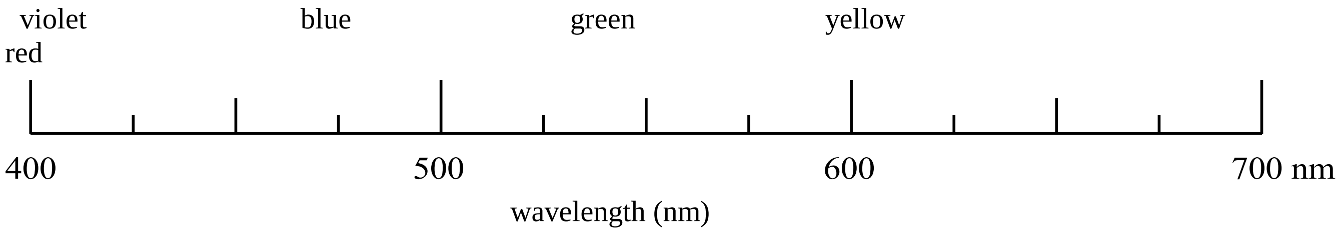
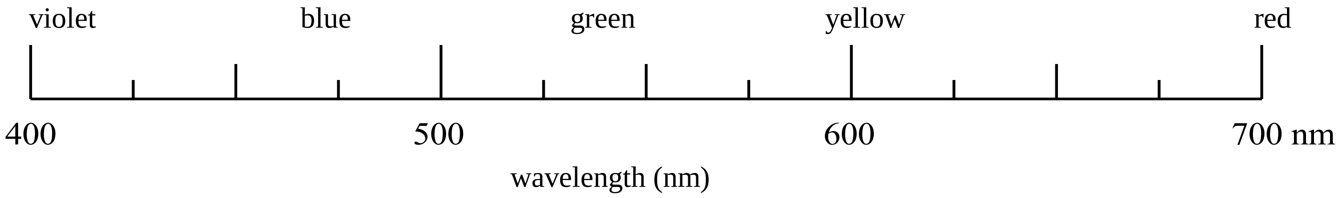
SOLUTION 4

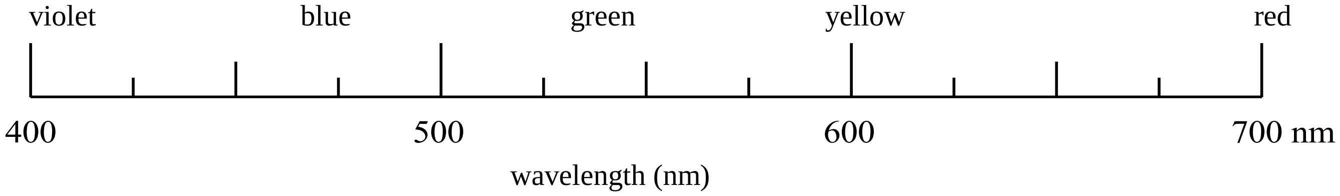
i) a) Indicator colour at pH 1.00:



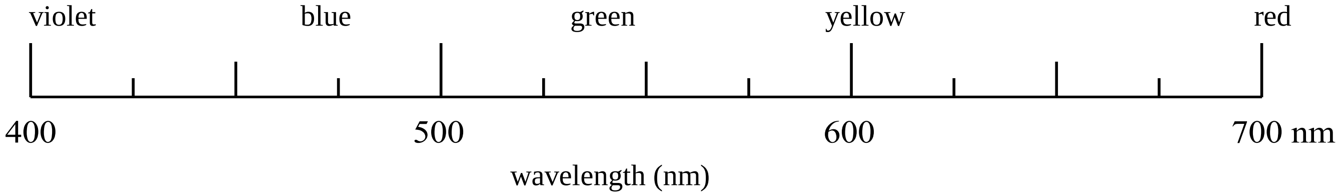
b) Indicator colour at pH 13.00:



ii) Appropriate colour filter:



iii) Appropriate wavelength range:



iv) Absorbance: ______________________

v) Absorbance at 490 nm: ________________________

Absorbance at 625 nm: ________________________

Name ____________________________

Identification Code ____________________________

Team ____________________________

SOLUTION 5

i) a) Atomic radius of Fe: ____________________ cm

b) Density of Fe (1250 K): ____________________ g cm^{-3}

Show your calculations for a and b:

ii) a) Average number of carbon atoms per unit cell: ______

b) Density of martensite: __________________ g cm^{-3}

Show your calculations for a and b:

Name ____________________________

Identification Code ____________________________

Team ____________________________

SOLUTION 5

i) a) Atomic radius of Fe: ____________________ cm

b) Density of Fe (1250 K): ____________________ g cm^{-3}

Show your calculations for a and b:

ii) a) Average number of carbon atoms per unit cell: ______

b) Density of martensite: __________________ g cm^{-3}

Show your calculations for a and b:

Name ____________________________

Identification Code ____________________________

Team ____________________________

SOLUTION 6

a) i)

$PtCl_6^{2-}$	**$PdCl_4^{2-}$**

ii) Structure(s) of monomeric $Pd(NH_3)_2Cl_2$ (and stereochemical descriptors)

iii) Underline the appropriate response:

$FeSO_4$ is acting as a: catalyst oxidizing agent reducing agent solvent

Balanced reaction involving $FeSO_4$:

iv) Balanced reaction involving ignition of $Pd(NH_3)_2Cl_2$:

What is being oxidized? ____

What is being reduced? ____

continued…

Name _________________________

Identification Code _________________________

SOLUTION 6 (continued)

b) i) Element **A** is: _______

ii) Balanced equation for the reaction of the chloride with ammonia:

iii) Redox half-reaction equations:

Name ____________________

Identification Code ____________________

Team ____________________

SOLUTION 7

a) I) Molecular Orbital description of Cl_2:

The bond order of Cl_2 is:______

The Cl_2 molecule is: diamagnetic ferromagnetic paramagnetic

(Underline the correct answer)

continued…

Name ___________________________

Identification Code ___________________________

SOLUTION 7 (continued)

a) ii) ΔE: __________________ kJ

ΔS_{sys}: _______________ J K^{-1}

Show your calculations.

continued…

Name _________________________

Identification Code _________________________

SOLUTION 7 (continued)

b) ΔG^o for Reaction 3: _ $kJ\ mol^{-1}$

ΔS^o for Reaction 3: _ $J\ K^{-1}$

K_c for Reaction 3: _______________________

Show your calculations:

Name __________________________

Identification Code __________________________

Team __________________________

SOLUTION 8

i) Reaction(s) at the anode:

Reactions(s) at the cathode:

ii) Moles of H_2: ______________________________

Moles of Cu: ______________________________

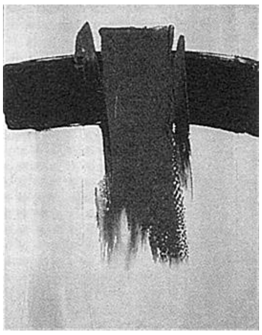
continued…

Name __________________________

Identification Code __________________________

SOLUTION 8 (continued)

iii) Monolayers of Cu: _________________________



29th International Chemistry Olympiad

29e Olympiade Internationale de la Chimie

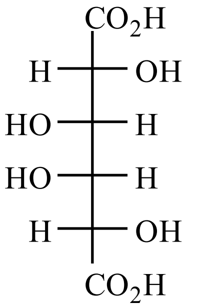
Theoretical Examination

Montreal, Thursday, July 17, 1997

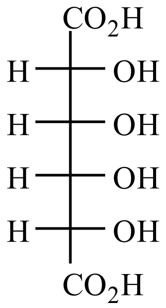
DETAILED SOLUTIONS

SOLUTION 1

Compound **X** is a trisaccharide which does not react with Benedict's solution nor does it mutarotate. This shows that **X** is a non-reducing sugar and therefore only acetal or ketal linkages exist at all of the anomeric carbons. Of the three monosaccharides, **A** and **B** give the same osazone and therefore have identical stereochemistry at C-3, C-4, and C-5 (and C-6). **A** and **B** are also different from compound **1** (i.e. D-mannose) yet give the same osazone, and thus one of them must be the C-2 epimer of D-mannose (i.e. D-glucose) and the other must be the corresponding keto sugar at C-2 (i.e. D-fructose). (This deduction is confirmed later in the oxidative cleavage reactions.) Compound **C**, after reaction with nitric acid, gives an optically inactive aldaric acid **D**. The two possible aldaric acids which could be **D** are thus:

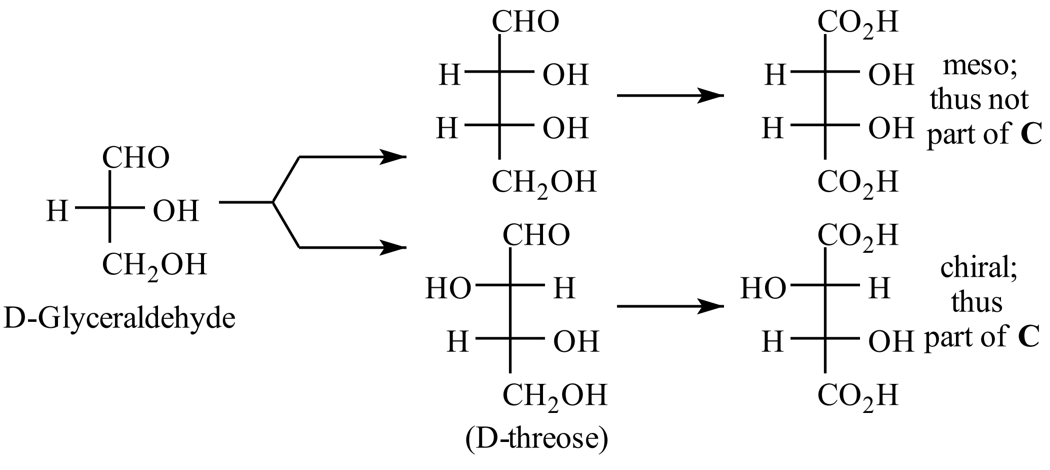


AA1 (=**D**)



AA2

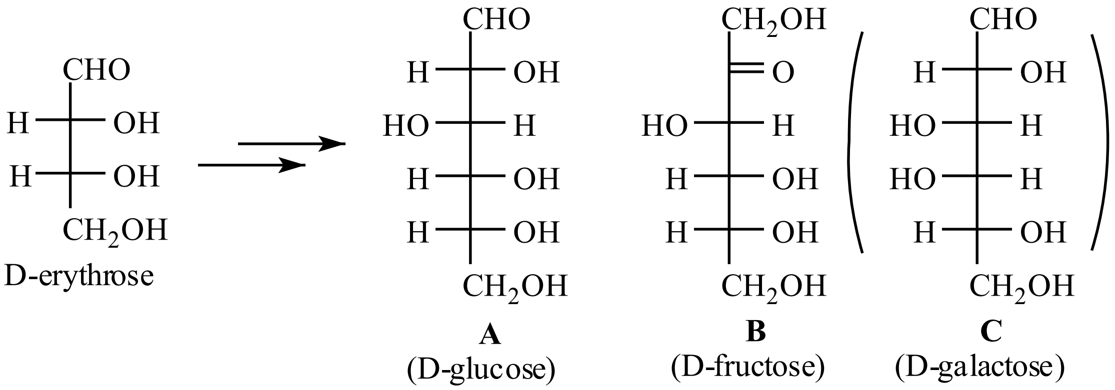
The aldotetrose which is the precursor of **C** (and thus also of **D)** does <u>not</u> give a meso compound after reaction with nitric acid and therefore must be the D-threose:



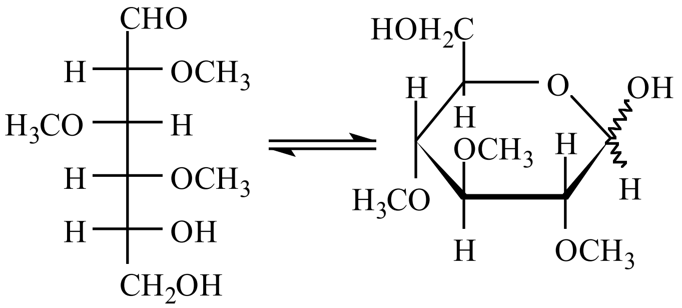
It follows from this that the aldaric acid **D** produced from **C** above is **AA1** and thus that **C** must be D-galactose. Compound **A** reacts with 5 moles of HI to give 5 moles of methanoic (formic) acid and one mole of methanal (formaldehyde) suggesting that it is an aldohexose while **B** reacts with 5 moles of HI to give 4 moles of methanoic (formic) acid, one mole of methanal (formaldehyde) and one mole of CO_2 suggesting that it is a ketohexose.

Compounds **A** and **B** are related to the same tetrose which is <u>not</u> the same as that of **C** (i.e.

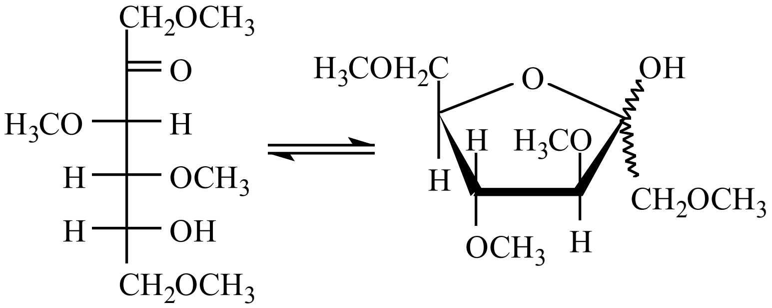
are related to D-erythrose). The tetrose which is related to **A** and **B** must therefore have the following structure and accordingly **A** is D-glucose and **B** is D-fructose.



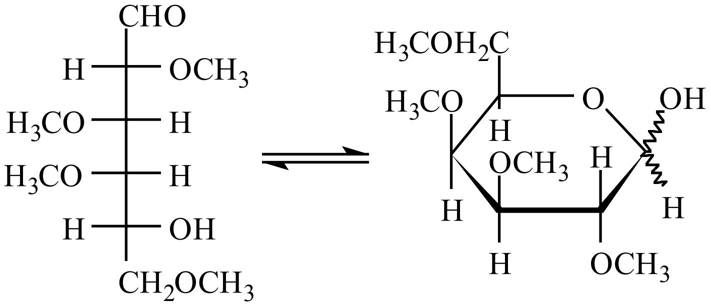
Methylation of **X** followed by hydrolysis yields **E**, **F** and **G** below:



E derived from **A**



F derived from **B**



G derived from **C**

SOLUTION 1 (continued)

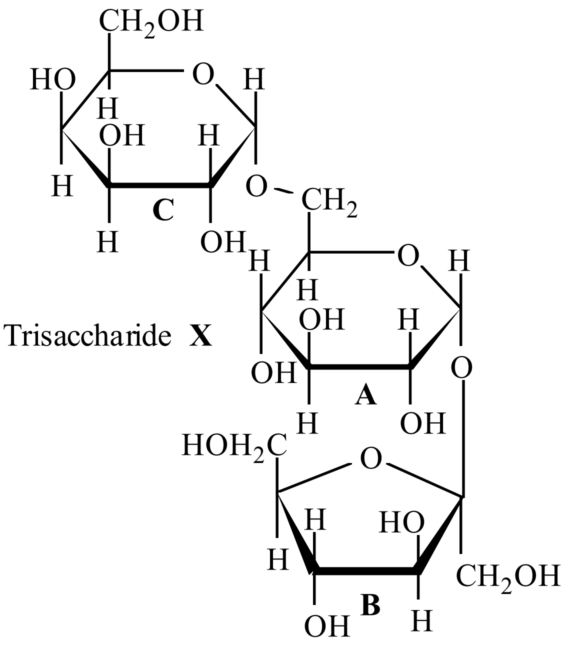
During methylation, only hydroxyl groups not involved in acetal/ketal formation (either intra- or intermolecular) will be etherified. From the methylation data, only **E** has two free hydroxyl groups with which to link to the other carbohydrates. Thus **A** must be the central carbohydrate.

These results indicate that the sequence of monosaccharides in **X** is **C-A-B** (or **B-A-C**).

If: $\mathbf{A}_5$ represents the furanose (5-membered ring) form of carbohydrate **A**.
$\mathbf{A}_6$ represents the pyranose (6-membered ring) form of carbohydrate **A**.
$\mathbf{B}_5$ represents the furanose (5-membered ring) form of carbohydrate **B**, etc.

then the trisaccharide **X** would be represented as: $\mathbf{C_6\text{-}A_6\text{-}B_5}$

One of the 4 possible variations in the structure of **X** is given below.



Trisaccharide **X**

Note: The nature of the anomeric linkages was not specified in the problem. The linkage arrangement of **A** to **B** and **C** may also be reversed (i.e. a 1,1' linkage between **C** and **A** and a 1,6 linkage betwen **A** and **B**.

SOLUTION 2

i) Proposal A: $\frac{d[H_2SO_4]}{dt} = k[H_2O]\,[SO_3]$

Summing the exponents gives a second order process

Proposal B: $\frac{d[H_2SO_4]}{dt} = k[SO_3][H_2O]^2$

Summing the exponents gives a third order process

ii) The steady state approximation gives:

The rate law here will be similar to that found for an enzymatic process which proceeds through a rapid reversible binding step followed by a slower reaction process.

$$\frac{d[SO_3 \bullet 2H_2O]}{dt} = k_1[SO_3][H_2O]^2 - k_{-1}[SO_3 \bullet 2H_2O] - k_2[SO_3 \bullet 2H_2O] = 0$$

Thus: $k_{-1}[SO_3 \bullet 2H_2O] + k_2[SO_3 \bullet 2H_2O] = k_1[SO_3]\,[H_2O]^2$

and therefore: $[SO_3 \bullet 2H_2O] = \frac{k_1[SO_3][H_2O]^2}{k_{-1} + k_2}$

Also: $\frac{d[H_2SO_4]}{dt} = k_2[SO_3 \bullet 2H_2O]$ and substituting from above yields

$$\frac{d[H_2SO_4]}{dt} = k_2[SO_3 \bullet 2H_2O] = \frac{k_1k_2[SO_3]\,[H_2O]^2}{k_{-1} + k_2}$$

However, since $k_2 << k_{-1}$ the above reduces to:

$$\frac{d[H_2SO_4]}{dt} = \frac{k_1k_2[SO_3][H_2O]^2}{k_{-1}} = K_{eq}k_2[SO_3][H_2O]^2 = k[SO_3][H_2O]^2$$

which is also third order

SOLUTION 2 (continued)

iii) Knowing the Arrhenius relationship: $k = Ae^{-E/RT}$

for Proposal A: $k = A\ e^{-E_A/RT} = Ae^{-83.6/RT}$ which increases with increasing T

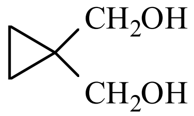
For Proposal B only the slow step is critical in determining the dependence of the rate constant on the temperature. The complexation step is very stable which explains the negative activation energy.

for Proposal B: $k = Ae^{-E_B/RT} = Ae^{+83.60/RT}$ which decreases with increasing T

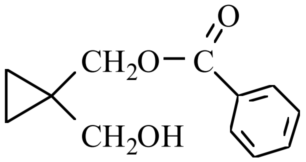
iv) Assuming that the pre-exponential factors are comparable in magnitude as is usually the case, the reaction will be faster at the lower temperatures found in the upper atmosphere due to the temperature dependence deduced above, and thus Proposal B must be operating. The rational for Proposal B which involves the relative sizes of the rate constants is nonsense and was included to balance the choices. The rational for Proposal A involving collision probabilities appears plausible but is not a factor — it is the massive negative activation energy which controls the situation.

SOLUTION 3

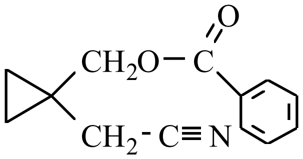
i)



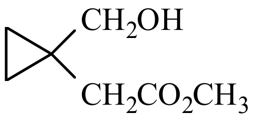
B



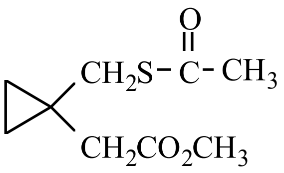
C ($C_{12}H_{14}O_3$)



D ($C_{13}H_{13}O_2N$)



E



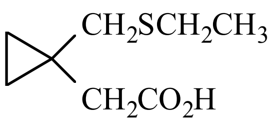
F ($C_9H_{14}O_3S$)

ii) S_N2 Bimolecular Nucleophilic Substitution

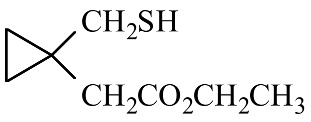
iii) Rate = k[substrate] [nucleophile]

The overall rate is directly dependent on the concentration of <u>both</u> the substrate and the nucleophile. Thus tripling the concentration of both of the reactants will result in a 9-fold increase in the overall reaction rate.

iv)

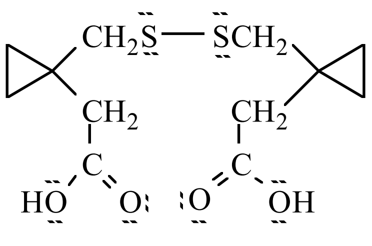


From 2 equiv base



From 1 equiv base

v)



oxidative coupled product

SOLUTION 4

i) The observed colour will be the complementary colour to that of the absorption maximum.

a) Acidic conditions (pH 1):

The sample absorbs at 490 ± 25 (blue-green) and thus will transmit the complementary colour and will appear to be yellow-orange (625 ± 25 nm).

b) Basic conditions (pH 13):

The sample absorbs at 625 ± 25 (yellow-orange) and thus will transmit the complementary colour and will appear to be blue-green (490 ± 25 nm).

ii) The filter should transmit the colour that the sample will absorb most efficiently. The acidic sample absorbs most strongly in the blue range (490 ± 25 nm) and thus a similar colour filter would be most suitable for the photometric analysis of the sample.

iii) The wavelength range to be used for maximum sensitivity should correspond to that at which the sample absorbs most strongly. The maximum absorbance for the basic form of the indicator in solution occurs at 625 ± 25 nm and this is the most suitable wavelength for the analysis.

iv) From a graph of A versus wavelength, the absorbance of a 5.00×10^{-4} M basic solution at 545 nm is 0.256. From the plot, it is clear that this region of the graph is linear and thus the above value can also be interpolated from the data table.

$A = \varepsilon\, l\, c$ (Beer's Law)

where, l = length of cell

c = concentration of analyte

ε = molar absorptivity

therefore, $$\varepsilon = \frac{A}{lc} = \frac{0.256}{1.0 \times 5.00 \times 10^{-4}} = 5.12 \times 10^{2}\ \mathrm{M^{-1}\ cm^{-1}}$$

Absorbance of a 1.00×10^{-4} M basic solution of the indicator using a 2.50 cm cell is:

$A = 5.12 \times 10^{2} \times 2.50 \times 1.0 \times 10^{-4} = 0.128$

SOLUTION 4 (continued)

v) The dissociation reaction of the indicator is:

$[HIn] = [H^+] + [In^-]$

accordingly,

$[H^+] = [In^-]$ (1)

and

$[HIn] + [In^-] = 1.80 \times 10^{-3}$ M (2)

$$K_a = \frac{[H^+][In^-]}{[HIn]} \qquad (3)$$

Substitute (1) and (2) into (3)

$$K_a = \frac{[In^-]^2}{1.8 \times 10^{-3} - [In^-]} = 2.93 \times 10^{-5}$$

Rearrangement yields the quadratic expression

$[In^-]^2 + 2.93 \times 10^{-5}[In^-] - 5.27 \times 10^{-8} = 0$

which results in

$[In^-] = 2.15 \times 10^{-4}$ M

$[HIn] = 1.80 \times 10^{-3}$ M $- 2.15 \times 10^{-4}$ M $= 1.58 \times 10^{-3}$ M

The absorbance at the two wavelengths are then:

$A_{490} = (9.04 \times 10^2 \times 1 \times 1.58 \times 10^{-3}) + (1.08 \times 10^2 \times 1 \times 2.15 \times 10^{-4}) = 1.45$

$A_{625} = (3.52 \times 10^2 \times 1 \times 1.58 \times 10^{-3}) + (1.65 \times 10^3 \times 1 \times 2.15 \times 10^{-4}) = 0.911$

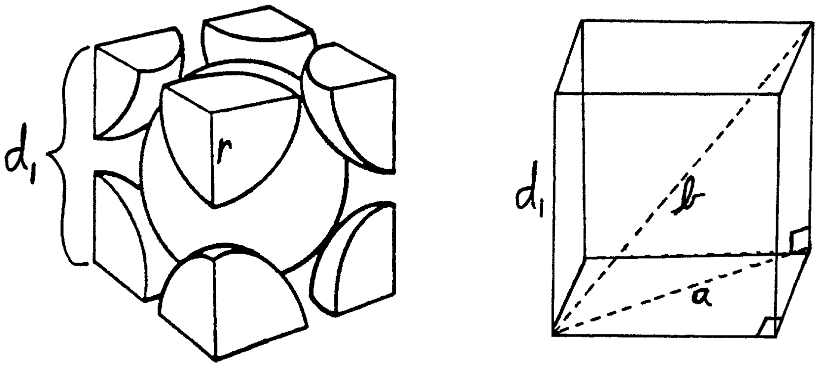
SOLUTION 5

i) Expected steps of the calculation:

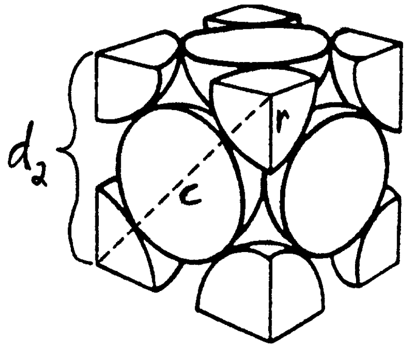
1. Define the length (a, b, c, d_1, d_2, and r) and volume (V_1 and V_2) parameters for both bcc and fcc structures of iron (*cf.* Details below).
2. Calculate the volume (V_1) of the unit cell of α-iron from its density (ρ_{bcc}) at 293 K, the molar weight (M_{Fe}) of iron, and Avogadro's number (N_A).
3. Calculate the length (d_1) of the edge of the bcc unit cell from its volume (V_1).
4. Calculate the atomic radius (r) of iron from the length "d_1".
5. Calculate the length (d_2) of the edge of the fcc unit cell (at 1250 K) from the atomic radius (r) of iron.
6. Calculate the volume (V_2) of the fcc unit cell of γ-iron from the length (d_2) of its edge.
7. Calculate the mass (m) of the number of iron atoms in a unit cell of γ-iron from the molar weight (M_{Fe}) of iron and Avogadro's number (N_A).
8. Calculate the density (ρ_{fcc}) of γ-iron from the values of "m" and "V_2".

An alternative route to ρ_{fcc} of γ-iron, involving the percent space filling ratios of both the bcc and fcc unit cells, can replace the aforementioned steps 5 through 8. In this route, these steps are labeled from 5' through 8' as listed below:

5'. Calculate the percent space filling ratio of the bcc unit cell.
6'. Calculate the percent space filling ratio of the fcc unit cell.
7'. Calculate the ρ_{fcc}/ρ_{bcc} density ratio from the fcc/bcc space filling ratios.
8'. Calculate the density (ρ_{fcc}) of γ-iron from the value found in step 7'.



Body centered cubic structure (bcc)



Face-centered cubic structure (fcc)

SOLUTION 5 (continued)

i) Details:

1. At 293 K, α-iron has a bcc crystal structure.
Each unit cell possesses 2 atoms and one of them is in the center of the cell.
At 1250 K, γ-iron has a fcc crystal structure.
Each unit cell possesses 4 atoms and each side has one-half an atom at its center.

r = atomic radius of iron.
a = length of the diagonal on one side of the bcc unit cell.
b = length of the diagonal passing through the center of the bcc unit cell.
c = length of the diagonal on one side of the fcc unit cell.
d_1 = length of the edge of the bcc unit cell of α-iron.
d_2 = length of the edge of the fcc unit cell of γ-iron.
V_1 = Volume of the bcc unit cell of α-iron.
V_2 = Volume of the fcc unit cell of γ-iron.
V_a = Volume of one atom.
V_{a1} = Volume occupied by 2 atoms in one bcc unit cell.
V_{a2} = Volume occupied by 4 atoms in one fcc unit cell.
R_1 = Percent space filling ratio in a bcc unit cell.
R_2 = Percent space filling ratio in a fcc unit cell.

$V_a = (4/3)\ \pi\ r^3$ $\quad\quad$ $V_{a1} = 2\ V_a$ $\quad\quad$ $V_{a2} = 4\ V_a$

$b = 4r;$ $\quad\quad$ $a^2 = 2d_1^2;$ $\quad\quad$ $b^2 = d_1^2 + a^2 = 3d_1^2$

$d_1 = (b^2/3)^{1/2} = (16r^2/3)^{1/2};$ $\quad\quad$ $V_1 = d_1^3 = [(16r^2/3)^{1/2}]^3$

$c = 4r;$ $\quad\quad$ $c^2 = 2d_2^2$

$d_2 = (c^2/2)^{1/2} = (16r^2/2)^{1/2};$ $\quad\quad$ $V_2 = d_2^3 = [(16r^2/2)^{1/2}]^3$

2. 1.000 cm^3 of iron weights 7.874 g at 293 K (ρ_{bcc}).
1 mole of iron weights 55.847 g (M_{Fe}).
So 0.1410 mol (7.874 g/55.847 g mol^{-1}) of iron occupy a volume of 1.000 cm^3 or
1 mol of iron will occupy a volume of 7.093 cm^3
1 mole corresponds to 6.02214×10^{23} atoms
$V_1 = (7.093\ cm^3\ mol^{-1}) \times (2\ atoms/unit\ cell) / (6.02214 \times 10^{23}\ atoms\ mol^{-1})$
$V_1 = 2.356 \times 10^{-23}\ cm^3$ per unit cell

3. $d_1 = (V_1)^{1/3} = (2.356 \times 10^{-23}\ cm^3)^{1/3}$
$d_1 = 2.867 \times 10^{-8}$ cm

SOLUTION 5 (continued)

4. For a bcc structure, the value of d_1 can be expressed as: $d_1 = [(16r^2)/3]^{1/2}$

   so the value of "r" will be: $r = (3d_1^2/16)^{1/2}$

   $r = [3\ (2.867 \text{ x } 10^{-8}\text{ cm})^2/16]^{1/2}$

   $r = 1.241 \text{ x } 10^{-8}\text{ cm}$

5. At 1250 K, in the fcc structure, the value of "d_2" is given by: $d_2 = (16r^2/2)^{1/2}$

   $d_2 = [16\ (1.241 \text{ x } 10^{-8}\text{ cm})^2/2]^{1/2}$

   $d_2 = 3.511 \text{ x } 10^{-8}\text{ cm}$

6. $V_2 = d_2^3 = (3.511 \text{ x } 10^{-8}\text{ cm})^3$

   $V_2 = 4.327 \text{ x } 10^{-23}\text{ cm}^3$

7. The mass "m" of the 4 iron atoms in the fcc unit cell will be:

   $m = (55.847\text{ g mol}^{-1}) \text{ x } (4\text{ atoms/unit cell}) / (6.02214 \text{ x } 10^{23}\text{ atoms mol}^{-1})$

   $m = 3.709 \text{ x } 10^{-22}$ g per unit cell

8. $\rho_{fcc} = m/V_2 = (3.709 \text{ x } 10^{-22}\text{ g}) / (4.327 \text{ x } 10^{-23}\text{ cm}^3)$

   $\rho_{fcc} = 8.572\text{ g/cm}^3$

Alternative route to ρ_{fcc} of γ-iron:

5'. $R_1 = [(V_{a1}) / (V_1)] \text{ x } 100\% = [(2\ V_a) / (V_1)] \text{ x } 100\%$

$R_1 = ([2 \text{ x } (4/3)\ \pi\ r^3] / [(16r^2/3)^{1/2}]^3) \text{ x } 100\%$

$R_1 = ([(8/3)\ \pi\ r^3] / [(16/3)^{3/2}\ r^3]) \text{ x } 100\%$

$R_1 = ([(8/3)\ \pi] / [(16/3)^{3/2}]) \text{ x } 100\%$

$R_1 = [(8.378) / (12.32)] \text{ x } 100\%$

$R_1 = 68.02\%$

6'. $R_2 = [(V_{a2}) / (V_2)] \text{ x } 100\% = [(4\ V_a) / (V_2)] \text{ x } 100\%$

$R_2 = ([4 \text{ x } (4/3)\ \pi\ r^3] / [(16r^2/2)^{1/2}]^3) \text{ x } 100\%$

$R_2 = ([(16/3)\ \pi\ r^3] / [8^{3/2}\ r^3]) \text{ x } 100\%$

$R_2 = ([(16/3)\ \pi] / [8^{3/2}]) \text{ x } 100\%$

$R_2 = [(16.76) / (22.63)] \text{ x } 100\%$

$R_2 = 74.05\%$

7'. $\rho_{fcc} / \rho_{bcc} = (74.05\%) / (68.02\%)$

$\rho_{fcc} / \rho_{bcc} = 1.089$

8'. $\rho_{fcc} = 1.089 \text{ x } \rho_{bcc}$

$\rho_{fcc} = 1.089 \text{ x } 7.874\text{ g cm}^{-3}$

$\rho_{fcc} = 8.572\text{ g cm}^{-3}$

SOLUTION 5 (continued)

ii) Expected Steps of the Calculation:

1. From the percent composition of martensite (by mass), calculate the relative amounts of moles of carbon and iron.
2. Bring the C/Fe molar ratio to one (1) unit cell (Note: 2 Fe atoms per unit cell).
3. Find the smallest whole number of C atoms for the smallest whole number of unit cell (facultative).
4. Calculate the mass of iron per unit cell.
5. Calculate the mass of carbon per unit cell.
6. Calculate the total mass of carbon and iron in one unit cell.
7. Calculate the density of martensite [ρ(martensite @ 4.3%C)] from the total mass of C and Fe and volume (V_1) of α-iron bcc unit cell.

ii) Details:

1. In 100.0 g of martensite at 4.3%C: (4.3 g C) / (12.011 g mol^{-1}) = 0.36 mol C
   (95.7 g Fe) / (55.847 g mol^{-1}) = 1.71 mol Fe

   So we have 1 carbon atom for 4.8 iron atoms or
   0.21 carbon atoms per iron atom

2. Martensite has a bcc crystal structure (2 iron atoms per unit cell).
   [(1 C atom) / (4.8 Fe atoms)] x (2 Fe atoms / unit cell)
   or: 0.42 carbon atoms per unit cell

3. 5 carbon atoms [(0.42 C atom/0.42) x 5] in 12 unit cells [(1 unit cell/0.42) x 5].
   5 carbon atoms dispersed in 12 unit cells

4. [(55.847 g/mol) / (6.02214 x 10^{23} atoms/mol)] x (2 atoms/unit cell of α-Iron)
   1.8547 x 10^{-22} g Fe per unit cell of α-Iron

5. (12.011 g/mol) / (6.02214 x 10^{23} atoms/mol)
   1.9945 x 10^{-23} g C per atom

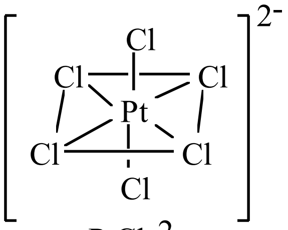
6. [1.8547 x 10^{-22} g Fe + (0.42 C at. x 1.9945 x 10^{-23} g/C at.)] per unit cell
   1.938 x 10^{-22} g C and Fe per unit cell

7. Each unit cell of α-Iron occupies a volume, V_1, of 2.356 x 10^{-23} cm^3
   (*cf.* Question i)
   ρ(martensite @ 4.3% C) = (1.938 x 10^{-22} g C and Fe) / (2.356 x 10^{-23} cm^3)
   ρ(martensite @ 4.3% C) = 8.228 g cm^{-3}

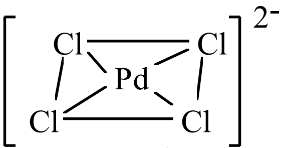
SOLUTION 6

a)

i) The $PtCl_6^{2-}$ anion consists of a Pt(IV) centered in a regular octahedron of Cl^- ions. The $PdCl_4^{2-}$ anion consists of a Pt(II) centered in a square of Cl^- ions.

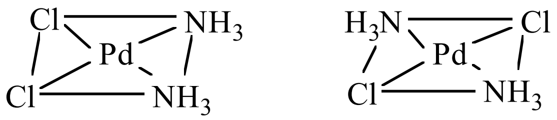


$PtCl_6^{2-}$



$PdCl_4^{2-}$

ii) Like $PdCl_4^{2-}$, $Pd(NH_3)_2Cl_2$ is also square planar. However, in this case there are two distinct ways in which the two different substituent groups (ligands) can be arranged. One places the two Cl^- on adjacent corners of the square (and axiomatically, the two NH_3 on the other two adjacent corners). This arrangement is called the *cis* isomer. The second arrangement has the pairs of the same ligand placed on diagonally opposite corners of the square. This arrangement is called the *trans* isomer. There are only these two stereoisomers possible for a monomeric form of the complex.



cis $Pd(NH_3)_2Cl_2$ trans

iii) The $FeSO_4$ [i.e. Fe(II)] acts as a reducing agent. Under the conditions used in the process, the Fe(II) is a strong enough reducing agent to reduce Au(III) to Au(0), but not to reduce Pd(II) or Pt(IV).

$$HAuCl_4 + 3\,FeSO_4 \rightarrow Au(0) + HCl + FeCl_3 + Fe_2(SO_4)_3$$

iv)

$$Pd(NH_3)_2Cl_2 + O_2 \rightarrow Pd(0) + N_2 + 2H_2O + 2HCl$$

$$Pd^{2+} + 2e \rightarrow Pd^0 \text{ reduction}$$

$$2O^0 + 4e \rightarrow 2O^{2-} \text{ reduction}$$

$$2N^{3-} - 6e \rightarrow 2N^0 \text{ oxidation}$$

or

SOLUTION 6 (continued)

$$Pd(NH_3)_2Cl_2 + 2O_2 \rightarrow Pd(0) + 2NO + 2H_2O + 2HCl$$

$$Pd^{2+} + 2e \rightarrow Pd^0 \text{ reduction}$$

$$4O^0 + 8e \rightarrow 4O^{2-} \text{ reduction}$$

$$2N^{3-} - 10e \rightarrow 2N^{2+} \text{ oxidation}$$

or

$$Pd(NH_3)_2Cl_2 + 3O_2 \rightarrow Pd(0) + 2NO_2 + 2H_2O + 2HCl$$

$$Pd^{2+} + 2e \rightarrow Pd^0 \text{ reduction}$$

$$6O^0 + 12e \rightarrow 6O^{2-} \text{ reduction}$$

$$2N^{3-} - 14e \rightarrow 2N^{4+} \text{ oxidation}$$

In this reaction the ammonia is oxidized to water and dinitrogen (or nitrogen oxides) and the Pd(II) and dioxygen are being reduced.

Part of the oxidation is due to the Pd(II) acquiring two electrons to go to Pd(0), and part by dioxygen which is reduced to water. In the presence of noble metal catalysts, NH_3 can also be oxidized to $(NO)_X$. Thus other nitrogen species are also in principle possible in the above ignition.

b)

i) **A** = sulfur

All Cl is located in the NH_4Cl, and thus the weight of Cl is found by:
53.492 g NH_4Cl → 35.453 g Cl
25.68 g NH_4Cl → ? g Cl
? = 25.68 x 35.453/53.492 =17.02 g Cl

Total amount of **A** in the reaction is 24.71 g Cl - 17.02 g Cl = 7.69 g **A**

There is 2.57 g free **A** and (7.69 - 2.57) = 5.12 g **A** in the nitride.

The amount of N bound in nitride is therefore
7.37 g nitride - 5.12 g **A** bound in nitride = 2.25 g N bound in nitride
The amount of nitrogen bound in NH_4Cl is 25.68 - 17.02 = 8.66 g

The rule of multiple proportions is applied:

SOLUTION 6 (continued)

PROPORTIONS OF 1:1

Chloride:	Nitride
7.69 g **A** binds → 17.02 g Cl	5.12 g **A** binds → 2.25 g N
? g **A** binds → 35.453 g Cl	? g **A** binds → 14.007 g N
? = 35.453 x 7.69/17.02 = 16.02 g	? = 14.007 x 5.12/2.25 = 31.87* g
A could be oxygen, but it is a main group element and it is a gas and thus it can be excluded	**A** could be is sulfur, fits the physical description and M_S=32.064

(*Phosphorus, M_P = 30.97, is also possible, but the highest degree of "polymerization" known is 4, in the P_4 molecule and thus P must also be excluded)

PROPORTIONS OF 1:2

Chloride:	Nitride
7.69 g **A** binds → 17.02 g Cl	5.12 g **A** binds → 2.25 g N
? g **A** binds → 2 x 35.453 g Cl	? g **A** binds → 2 x 14.007 g N
? = 2 x 35.453 x 7.69/17.02 = 32.03 g	? = 2 x 14.007 x 5.12/2.25 = 63.75 g
Again **A** could be sulfur	**A** could be Cu but it is a Group B element and thus can be excluded

Therefore element **A** must be sulfur.

ii) $SCl_2 + 2\,2/3\,NH_3 \rightarrow 2NH_4Cl + 1/3\,S + S_{2/3}N_{2/3}$

or

$3\,SCl_2 + 8\,NH_3 \rightarrow 6NH_4Cl + S + S_2N_2$

or

$6\,SCl_2 + 16NH_3 \rightarrow 12NH_4Cl + 2S + S_4N_4$

In fact the elemental S is in the form of S_8 and so the equation should be multiplied by a factor of 8. Although S_2N_2 roughly fits the description of colour and explosive instability, it is actually S_4N_4 that is produced in this reaction. Both of these ring compounds under carefully controlled heating polymerize to give the high molecular weight linear polymer $(SN)_n$, which is one of the rare examples of a metal containing only lighter p-group elements. The tendency of these ring compounds to polymerize is due to the relatively weak S-N bonds and the large amount of strain energy in the ring. The S-S bond is also quite weak and can be broken by heating. For this reason the S_8 ring also undergoes polymerization at high temperature. However, there is hardly any energy stored in the form of ring strain in this ring and so the polymerization is not highly exothermic or explosive. Other sulfur chlorides (S_2Cl_2 and SCl_4 do not fit the stoichiometry of the reaction.)

iii) A disproportionation reaction involving sulfur occurs:

$$2S^{2+} - 2e \rightarrow 2\,S^{3+}$$

$$S^{2+} + 2e \rightarrow S^0$$

SOLUTION 7

a)

i) Electronic configuration of a Cl atom:

$1s^22s^22p_x^22p_y^22pz^23s^23p_x^23p_y^23p_z^1$

Significant atomic orbitals (AO) = 1(K) + 4(L) + 4(M) = 9 AO

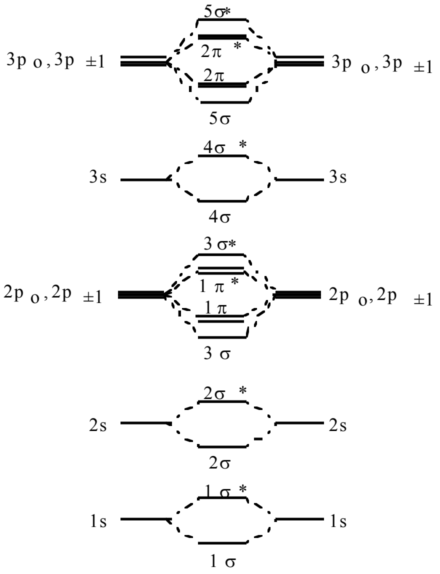
Number of electrons in these AOs: 17

Number of molecular orbitals (MO) equals number of AOs

Thus 2 x [1(K) + 4(L) + 4(M)] = 18 MOs are present in a Cl_2 molecule

In the formation of Cl_2: 2 x 17 = 34 electrons to go into the 18 MOs.

MO description of Cl_2:



$1\sigma^21\sigma^{*2}2\sigma^22\sigma^{*2}3\sigma^21\pi^41\pi^{*4}3\sigma^{*2}4\sigma^24\sigma^{*2}5\sigma^22\pi^42\pi^{*4}$

or

$(KK)(LL)(\sigma 3s)^2(\sigma^*3s)^2(\pi 3p)^4(\sigma 3p)^2(\pi^*3p)^4$

or

$1(\sigma s^2)(\sigma s^{*2})2(\sigma s^2)(\sigma s^{*2})(\sigma p_x^2)(\sigma p_x^{*2})(\pi p_y^2)(\pi p_y^{*2})(\pi p_z^2)(\pi p_z^{*2})3(\sigma s^2)(\sigma s^{*2})$

$(\pi p_x^2)(\pi p_x^{*2})(\pi p_y^2)(\pi p_y^{*2})(\sigma p_z^2)(\sigma p_z^{*0})$

or

$(KK)(LL)3(\sigma s^2)(\sigma s^{*2})(\pi p_x^2)(\pi p_y^{*2})(\pi p_y^2)(\pi p_y^{*2})(\sigma p_z^2)(\sigma p_z^{*2})$

*assumption: - bond formation is along the z-axis
(equivalent formulae for x or y axes are accepted)

Bond order is given by (n-n*)/2:

(2-2)/2 for (KK) + (8-8)/2 for (LL) + (2-2)/2 for 3s + (2-2)/2 for $3p_x$ + (2-2)/2 for $3p_y$ + (2-0)/2 for $3p_z$ = 0+0+0+0+0+1 = 1 (σ bond, not π bond)

The Cl_2 molecule has a bond order of 1.

The Cl_2 molecule is diamagnetic since there are no unpaired electrons.

SOLUTION 7 (continued)

a)

ii) Summary of the changes involved:

$$\begin{array}{ccccc} \mathrm{Cl_2\ (g)} & & \mathrm{Cl_2\ (g)} & & \mathrm{Cl_2\ (l)} \\ \text{1 mol} & \xrightarrow[\substack{\text{cooled} \\ 1.013 \times 10^7\ \text{Pa} \\ \text{(100 atm)}}]{\Delta E_1} & \text{1 mol} & \xrightarrow[\substack{1.013 \times 10^5\ \text{Pa} \\ \text{(1 atm)}}]{\Delta E_2} & \text{0.1 mol} \\ \text{300 K} & & \text{239 K} & & \text{239 K} \end{array}$$

The total process is an expansion plus an isobaric change of phase (gas to liquid) and since the internal energy (E) is a function of state, the total change in the internal energy is $\Delta E = \Delta E1 + \Delta E2$.

Process 1:

$$\Delta E_1 = \int nC_v dT = (1)(28.66)(239 - 300) = -1748.3\ \text{J}$$

Note: a) ΔE for a perfect gas is a function only of T

b) C_V is constant

c) “-” sign means a loss of energy due to the work needed for expansion of 1 mole of gas

Process 2: For convenience, the data were manipulated in atm; equivalent procedure in Pa will require the appropriate conversion factor

From an energetic point of view, the liquid formation Process 2 can be split into two separate steps :

- the vaporization heat loss (decreased internal energy, -) from the system into surroundings (since the process takes place at constant pressure, the heat is equal to the change in the enthalpy)
- the work done by the surroundings in compressing the system to a smaller volume (increased internal energy, +).

Volume of gas which condensed is $V = nRT/P = (0.1)(0.0820584)(239)/1 = 1.96$ L

Volume of liquid Cl_2: $(0.1)(2 \times 35.454)/1.56 = 4.54$ mL

$$\Delta E_2 = \Delta H_2 - \int P_{ext}\Delta V(\text{phase change}) = \Delta H_2 - P_{ext}(V_l - V_g)$$

but V_l is approximately 0 and can be neglected

(ca. 4.5 mL liquid volume vs. ca. 17.6 L; ca. 0.03% error)

$$\begin{aligned} \Delta E_2 &= (0.1)(-\Delta H_{vap}) + P_{ext}V_g \\ &= (0.1)(-20420) + 1(1.96\ \text{L})(101.325\ \text{J L}^{-1}\ \text{atm}^{-1}) \\ &= -2042.0 + 198.5 \\ &= -1843.5\ \text{J} \end{aligned}$$

$\Delta E = \Delta E_1 + \Delta E_2 = -1748.3 + (-1843.5) = -3591.8$ J

SOLUTION 7 (continued)

Entropy S is a function of two variables of state. Since in Process 1 the known variables are T and P, expression of S is chosen as S(T,P).

$\Delta S_{sys} = \Delta S_1 + \Delta S_2$ and $\overline{C}_p = \overline{C}_v + R = 28.66 + 8.314 = 36.97$ J K^{-1} mol^{-1}

$$\Delta S_1 = nC_p \ln\frac{T_2}{T_1} - nR\ln\frac{P_2}{P_1} = 1.0(36.97)\ln\frac{239}{300} - 8.314\ln\frac{1}{100}$$

$= -8.40 + 38.29 = 29.89$ J K^{-1}

For the phase transition (constant temperature), by definition $\Delta S_2 = Q/T$
Since the pressure is constant in this case, $Q/T = Q_p/T = \Delta H/T$

$$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{(0.1)(-20420)}{239} = -8.54$$

$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{(0.1)(-20420)}{239} = -8.54$ J K^{-1}

$\Delta S_{sys} = 29.89 - 8.54 = 21.35$ J K^{-1}

SOLUTION 7 (continued)

b) Beware of round-off errors in the variations to the solution to this problem: One can get small differences due to conversion into and out of the *ln* relationships. It is the approach which matters.

One reverses the signs of $\ln K_c$ and ΔH^o for Reaction 1 when it is reversed.
Equilibrium constants are multiplied when equations are added, thus lnK's will add.

Reaction 3 = Reaction 2 - Reaction 1
Thus $\Delta S_3 = \Delta S_2 - \Delta S_1$ and $\Delta G_3 = \Delta G_2 - \Delta G_1$

$\Delta G^o{}_1 = -RT\ln K_{c1} = -8.314(298)(11.60) = -28740 \text{ J mol}^{-1} = -28.74 \text{ kJ mol}^{-1}$
$\Delta H^o{}_1 = -33.5 \text{ kJ mol}^{-1}$
$\Delta S^o{}_1 = (\Delta H^o{}_1 - \Delta G^o{}_1)/T$
$= (-33.5) - (-28.74))/298 = -0.0161 \text{ kJ K}^{-1} \text{ mol}^{-1} = -16.1 \text{ J K}^{-1} \text{ mol}^{-1}$

Similarly:
$\Delta G^o{}_2 = -44.05 \text{ kJ mol}^{-1}$
$\Delta H^o{}_2 = -37.2 \text{ kJ mol}^{-1}$
$\Delta S^o{}_2 = -22.98 \text{ J K}^{-1} \text{ mol}^{-1}$

Reaction 3 = Reaction 2 - Reaction 1, thus
$\Delta H^o{}_3 = \Delta H^o{}_2 - \Delta H^o{}_1 = -3.7 \text{ kJ}$
$\Delta S^o{}_3 = \Delta S^o{}_2 - \Delta S^o{}_1 = 39.08 \text{ J K}^{-1}$
$\Delta G^o{}_3 = \Delta H^o{}_3 - T\Delta S^o{}_3 = -15.35 \text{ kJ mol}^{-1}$

Thus $K_{c3} = e^{\frac{15.35}{RT}} = 4.90 \times 10^2$

Alternatively:
$\Delta G^o{}_3 = \Delta G^o{}_2 - \Delta G^o{}_1 = -44.05 - (-28.74) = -15.31 \text{ kJ mol}^{-1}$ thus $K = 4.82 \times 10^2$)
$\Delta S^o = (\Delta H^o - \Delta G^o)/T = (-3700 - (-15311))/298 = 38.96 \text{ J K}^{-1}$

SOLUTION 8

Approach

- Determine the number of H_2 moles generated by the electrolysis
- Calculate the charge required for the H_2 production and the charge of the formation of the Cu deposit and thus the number of moles of Cu in the deposit.
- Calculate the surface concentration of atoms in the Pt (100) face thus the number of Pt atoms per $1\,\text{cm}^2$; during an epitaxial growth the number of Cu atoms per $1\,\text{cm}^2$ equals the number of Pt atoms
- Determine the charge necessary to form one monolayer of Cu and subsequently the number of Cu monolayers on Pt (100)

Calculations

i) Balanced electrode equations

(a) Anode: $2\,H_2O \rightarrow 4\,H^+ + O_2 + 4\,e$

(b) Cathode: $2\,H^+ + 2\,e \rightarrow H_2$ Two reactions occur simultaneously at the cathode
$Cu^{2+} + 2\,e \rightarrow Cu$

ii)

Determination of the charge necessary to generate 2.0000 cm^3 of H$_2$ gas (T = 273.15 K, P = 10.1325 kPa)

Two approaches to determination of the number of H_2 *gas moles*

(a) determination of n_{H_2} $P\,V_{H_2} = n_{H_2}\,R\,T$

$$n_{H_2} = \frac{10132.5 \times 2.0000 \times 10^{-6}}{8.314510 \times 273.15} = 8.9230 \times 10^{-6}\ \text{mol}$$

(b) $n_{H_2} = \dfrac{V_{H_2}}{V_m}$ $V_m = 22.4141\,\text{dm}^3$ (V_m refers to the pressure of 1 atm or at $P_{H_2} = 101.325\,\text{kPa}$ and because the H_2 pressure is ten times smaller, one knows right away that the volume occupied under 1 atm would be $0.20000\,\text{cm}^3$)

$$n_{H_2} = \frac{0.20000 \times 10^{-3}}{22.4141} = 8.9230 \times 10^{-6}\ \text{mol}$$

SOLUTION 8 (continued)

Determination of the charge necessary to generate 8.9230 x 10^{-6} moles of H_2 gas

Two approaches to determination of the charge

(a) the number of H atoms, N_H, equals twice the number of H_2 molecules; if one multiplies N_H by e, then one gets the sought charge, Q_H

$$Q_H = 2 \times 8.9230 \times 10^{-6} \times N_A \times 1.60218 \times 10^{-19}$$

$$Q_H = 1.7219 \text{ C}$$

(b) one may use the Faraday law

$$m_H = k_H\, Q_H$$

where k_H is the electrochemical equivalent of H thus the mass of H generated by 1 C; to use this formula one has to calculate k_H; knowing that the charge of $1\text{ F} = 96485.3$ C results in formation of 1 mole of H (1/2 mole of H_2), one may easily determine k_H

$$\frac{96\,485.3}{1.00795} = \frac{1.0000}{k_H}$$

$$k_H = 1.04467 \times 10^{-5} \text{ g C}^{-1}$$

Subsequently

$$Q_H = \frac{m_H}{k_H} = \frac{2 \times 8.9230 \times 10^{-6} \times 1.00795}{1.04467 \times 10^{-5}}$$

$$Q_H = 1.7219 \text{ C}$$

Determination of the Cu deposition charge

$$Q_{Cu} = 2.0000 - Q_H$$

$$Q_{Cu} = 2.0000 - 1.7219 = 0.2781 \text{ C}$$

The moles of Cu is thus 0.2781/2F = 1.4412 x 10^{-6}

SOLUTION8 (continued)

iii)

Determination of the charge of formation of 1 monolayer (ML) of the Cu deposit and the number of Cu monolayers on the Pt (100) substrate

Calculate the number of surface Pt atoms in the (100) face

Surface area of the fundamental unit:

$$A_u = a_{Pt}^2 = 1.5395 \times 10^{-15}\ \mathrm{cm}^2$$

Number of atoms per fundamental (100) unit: $n_u = 2$

Surface atom concentration:

$$s_{Pt(100)} = \frac{n_u}{A_u} = \frac{2}{1.5395 \times 10^{-15}\ \mathrm{cm}^2} = 1.2991 \times 10^{15}\ \mathrm{cm}^{-2}$$

The number of Cu atoms per $1\,\mathrm{cm}^2$ equals the number of Pt atoms - *epitaxial growth*

$$\sigma_{Cu\,(100)} = \sigma_{Pt(100)} = 1.2991 \times 10^{15}\ \mathrm{cm}^{-2}$$

The charge of formation of one monolayer (ML) of Cu equals:

$$q_{ML} = 2 \times e \times 1.2991 \times 10^{15}$$

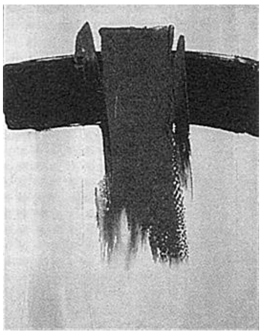
$$q_{ML} = 4.1628 \times 10^{-4}\ \mathrm{C}$$

Determination of the number of Cu monolayers on the Pt (100) substrate

$$n_{ML} = \frac{0.2780\ \mathrm{C}}{4.1628 \times 10^{-4}\ \mathrm{C}}$$

$$n_{ML} = 668\ \mathrm{ML}$$

One can also calculate the number of Cu atoms (8.6802 x 10^{17}) formed from the number of moles produced and divide this by the number of atoms (1.2991 x 10^{15}) on the exposed Pt surface to also arrive at 668 monolayers.



29th International Chemistry Olympiad

29e Olympiade Internationale de la Chimie

Theoretical Examination

Montreal, Thursday, July 17, 1997

ANSWER KEY

&

GRADING KEY

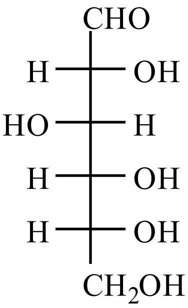
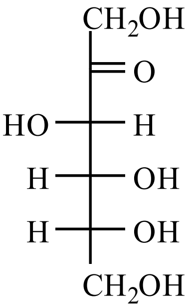
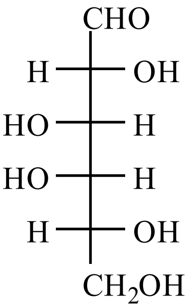
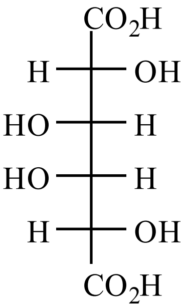
Name ____________________________

Identification Code ____________________________

Team ____________________________

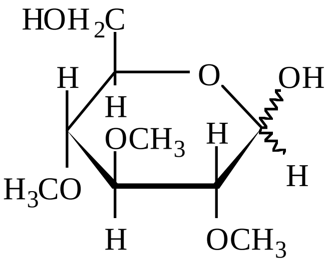
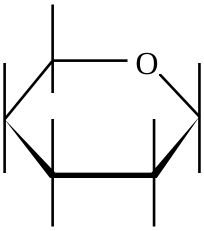
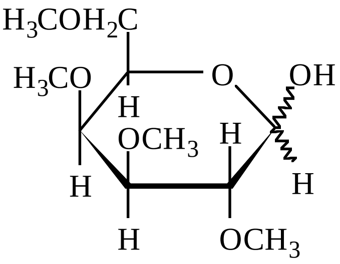
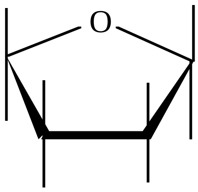
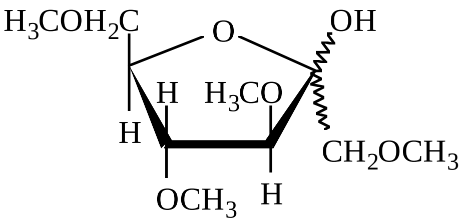
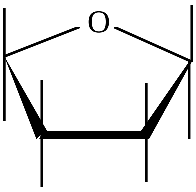
SOLUTION 1

i) Draw Fischer projection formulas of A, B, C, and D.

			
2 marks	*2 marks*	*2 marks*	*2 marks*
A	**B**	**C**	**D**

0.5 marks per stereocentre

ii) Complete the appropriate Haworth projection formulas to clearly show the ring size and absolute stereochemistry of **E**, **F**, and **G**.

		
or	**or**	**or**
		
2 marks	*2 marks*	*2 marks*
E	**F**	**G**

0.5 marks per stereocentre (not including the anomeric centre)

continued…

Name ____________________________

Identification Code ____________________________

SOLUTION 1 (continued)

iii) Underline the correct representation of the connectivity sequence of the three monosaccharides present in trisaccharide **X**.

Note: $\mathbf{A}_5$ represents the furanose (5-membered ring) form of carbohydrate **A**.
$\mathbf{A}_6$ represents the pyranose (6-membered ring) form of carbohydrate **A**.
$\mathbf{B}_5$ represents the furanose (5-membered ring) form of carbohydrate **B**.
$\mathbf{B}_6$ represents the pyranose (6-membered ring) form of carbohydrate **B**.
$\mathbf{C}_5$ represents the furanose (5-membered ring) form of carbohydrate **C**.
$\mathbf{C}_6$ represents the pyranose (6-membered ring) form of carbohydrate **C**.

$A_6\text{-}B_6\text{-}C_5$	$B_6\text{-}C_6\text{-}A_5$	$\underline{\underline{C_6\text{-}A_6\text{-}B_5}}$ *1 mark*
$A_6\text{-}B_5\text{-}C_6$	$B_6\text{-}C_5\text{-}A_6$	$C_6\text{-}A_5\text{-}B_6$
$A_5\text{-}B_6\text{-}C_6$	$B_5\text{-}C_6\text{-}A_6$	$C_5\text{-}A_6\text{-}B_6$

SOLUTION 2

i) Reaction order for Proposal A: ____2____ *2 marks*

Reaction order for Proposal B: ____3____ *2 marks*

ii) Reaction order for the two-step mechanism: ____3____ *1 mark*

Derivation of the appropriate rate law:
The steady state approximation gives:

$$\frac{d[SO_3 \bullet 2H_2O]}{dt} = k_1[SO_3][H_2O]^2 - k_{-1}[SO_3 \bullet 2H_2O] - k_2[SO_3 \bullet 2H_2O] = 0$$ *1 mark*

Thus: $k_{-1}[SO_3 \bullet 2H_2O] + k_2[SO_3 \bullet 2H_2O] = k_1[SO_3]\,[H_2O]^2$

and therefore: $[SO_3 \bullet 2H_2O] = \dfrac{k_1[SO_3][H_2O]^2}{k_{-1} + k_2}$ *1 mark*

Also: $\dfrac{d[H_2SO_4]}{dt} = k_2[SO_3 \bullet 2H_2O]$ and substituting from above yields

$$\frac{d[H_2SO_4]}{dt} = k_2[SO_3 \bullet 2H_2O] = \frac{k_1k_2[SO_3]\,[H_2O]^2}{k_{-1} + k_2}$$ *2 marks*

OR

However, since $k_2 << k_{-1}$ the above reduces to:

$$\frac{d[H_2SO_4]}{dt} = \frac{k_1k_2[SO_3][H_2O]^2}{k_{-1}} = K_{eq}k_2[SO_3][H_2O]^2 = k[SO_3][H_2O]^2$$

which is also third order

iii) For Proposal A:

Arrhenius relationship: $k = A\ e^{-E_A/RT} = Ae^{-80000/RT}$ *1 mark*

The rate constant for the reaction: *1 mark*

The answer must be consistent with the form of the Arrhenius equation given above.

☑ Increases with increasing temperature
☐ Decreases with increasing temperature
☐ Is independent of the temperature

For Proposal B:

Arrhenius relationship: $k = Ae^{-E_B/RT} = Ae^{+20000/RT}$ *1 mark*

The rate constant for the reaction: *1 mark*

The answer must be consistent with the form of the Arrhenius equation given above.

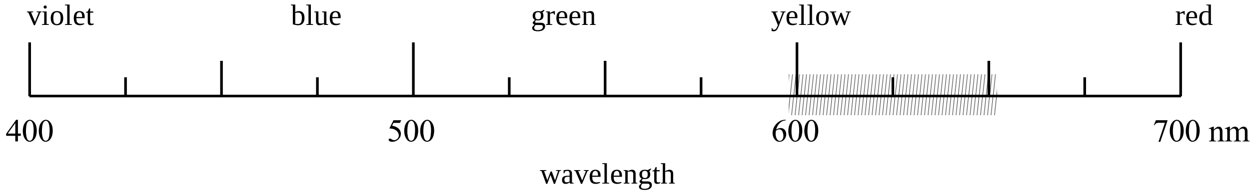
☐ Increases with increasing temperature
☑ Decreases with increasing temperature
☐ Is independent of the temperature

iv) The dominant mechanism in the upper atmosphere must be: *2 marks*

☐ Proposal A due to the temperature dependence of the rate constant
☐ Proposal B since $k_2 << k_1$ or k_{-1}
☐ Proposal A since the probability of the necessary collision in Proposal B is too small
☑ Proposal B due to the temperature dependence of the rate constant

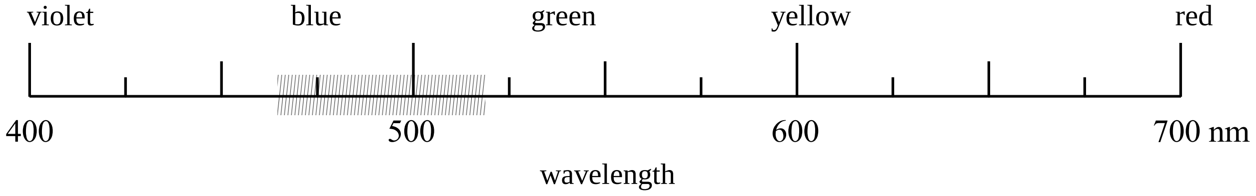
SOLUTION 4

i) a) Indicator colour at pH 1.00:



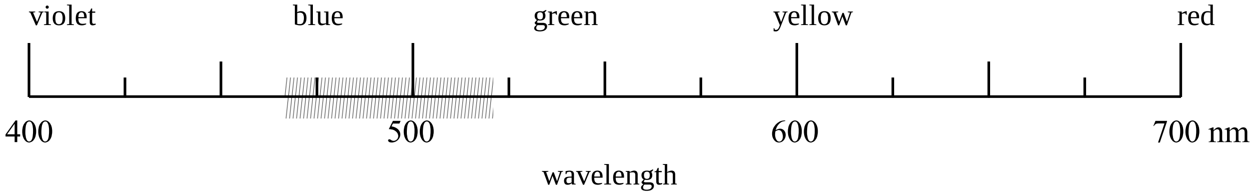
1 mark

b) Indicator colour at pH 13.00:



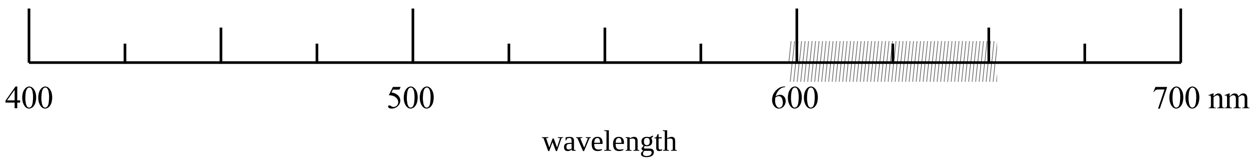
1 mark

ii) Appropriate colour filter:



1 mark

iii) Appropriate wavelength range:



1 mark

iv) Absorbance: A = 0.128 *(3 marks; see breakdown)*

From a graph of A versus wavelength, the absorbance of a 5.00 x 10^{-4} M basic solution at 545 nm is 0.256. *1 mark*

A = ε l c (Beer's Law) where,
l = length of cell;
c = concentration of analyte;
ε = molar absorptivity

therefore, $$\varepsilon = \frac{A}{lc} = \frac{0.256}{1.0 \times 5.00 \times 10^{-4}} = 5.12 \times 10^{2}\ M^{-1}\ cm^{-1}$$ *1 mark*

Therefore absorbance of a 1.00 x 10^{-4} M basic solution of the indicator using a 2.50 cm cell is: A = 5.12 x 10^{2} x 2.50 x 1.0 x 10^{-4} = 0.128 *1 mark*

v) a) Absorbance at 490 nm: A = 1.45 *(7 marks; see breakdown)*

The dissociation reaction of the indicator is: $[HIn] \rightleftharpoons [H^+] + [In^-]$ and thus

$[H^+] = [In^-]$ (1)

$[HIn] + [In^-] = 1.8 \times 10^{-3}$ M (2) *1 mark*

$$K_a = \frac{[H^+][In^-]}{[HIn]} \quad (3)$$

Substitute (1) and (2) into (3) $K_a = \frac{[In^-]^2}{1.8 \times 10^{-3} - [In^-]} = 2.93 \times 10^{-5}$ *1 mark*

Rearrangement yields: $[In^-]^2 + 2.93 \times 10^{-5}[In^-] - 5.27 \times 10^{-8} = 0$
which results in

$[In^-] = 2.15 \times 10^{-4}$ M *1.5 marks*

$[HIn] = 1.80 \times 10^{-3}$ M $- 2.15 \times 10^{-4}$ M $= 1.58 \times 10^{-3}$ M *1.5 marks*

The absorbance is thus

$A_{490} = (9.04 \times 10^2 \times 1 \times 1.58 \times 10^{-3}) + (1.08 \times 10^2 \times 1 \times 2.15 \times 10^{-4}) = 1.45$ *2 marks*

b) Absorbance at 625 nm: <u>A = 0.911</u> *1 mark*

Similar substitution to v-a above yields:

$A_{625} = (3.52 \times 10^2 \times 1 \times 1.58 \times 10^{-3}) + (1.65 \times 10^3 \times 1 \times 2.15 \times 10^{-4}) = 0.911$

SOLUTION 5

i) a) Atomic radius of Fe: ___1.241 x 10^{-8}___ cm *(4 marks; see breakdown)*

b) Density of Fe (1250 K): ___8.572___ g cm^{-3} *(4 marks; see breakdown)*

See the detailed solution for the definition of various symbols.

a) 1.000 cm^3 of iron weighs 7.874 g at 293 K (ρ_{bcc}).

1 mole of iron weighs 55.847 g (M_{Fe}).

So 0.1410 mol (7.874 g/55.847 g mol^{-1}) of iron occupy a volume of 1.000 cm^3 or

1 mol of iron will occupy a volume of 7.093 cm^3 *1 mark*

1 mole corresponds to 6.02214 x 10^{23} atoms

V_1 = (7.093 cm^3 mol^{-1}) x (2 atoms/unit cell) / (6.02214 x 10^{23} atoms mol^{-1})

V_1 = 2.356 x 10^{-23} cm^3 per unit cell *1 mark*

$d_1 = (V_1)^{1/3} = (2.356 \times 10^{-23}\ cm^3)^{1/3}$

d_1 = 2.867 x 10^{-8} cm *1 mark*

For a bcc structure, the value of d_1 can be expressed as: $d_1 = [(16r^2)/3]^{1/2}$

so the value of "r" will be: $r = (3d_1^2/16)^{1/2}$

$r = [3\ (2.867 \times 10^{-8}\ cm)^2/16]^{1/2}$

r = 1.241 x 10^{-8} cm *1 mark*

b) At 1250 K, in the fcc structure, the value of "d_2" is given by: $d_2 = (16r^2/2)^{1/2}$

$d_2 = [16\ (1.241 \times 10^{-8}\ cm)^2/2]^{1/2}$

d_2 = 3.511 x 10^{-8} cm *1 mark*

$V_2 = d_2^3 = (3.511 \times 10^{-8}\ cm)^3$

V_2 = 4.327 x 10^{-23} cm^3 *1 mark*

The mass "m" of the 4 iron atoms in the fcc unit cell will be:

m = (55.847 g mol^{-1}) x (4 atoms/unit cell) / (6.02214 x 10^{23} atoms mol^{-1})

m = 3.709 x 10^{-22} g per unit cell *1 mark*

$\rho_{fcc} = m/V_2 = (3.709 \times 10^{-22}\ g) / (4.327 \times 10^{-23}\ cm^3)$

ρ_{fcc} = 8.572 g/cm^3 *1 mark*

ALTERNATIVE SOLUTION

i) a) Atomic radius of Fe: ___1.241 x 10^{-8}___ cm *(4 marks; see breakdown above)*

b) Density of Fe (1250 K): ___8.572___ g cm^{-3} *(4 marks; see breakdown)*

See the detailed solution for the definition of various symbols.

a) Radius of an iron atom calculated as above. *4 marks*

b) Alternative calculation of the density of iron at 1250 K:

$R_1 = [(V_{a1}) / (V_1)] \times 100\% = [(2\ V_a) / (V_1)] \times 100\%$

$R_1 = ([2 \times (4/3)\ \pi\ r^3] / [(16r^2/3)^{1/2}]^3) \times 100\%$

$R_1 = ([(8/3)\ \pi\ r^3] / [(16/3)^{3/2}\ r^3]) \times 100\%$

$R_1 = ([(8/3)\ \pi] / [(16/3)^{3/2}]) \times 100\%$

$R_1 = [(8.378) / (12.32)] \times 100\%$

$R_1 = 68.02\%$ *1 mark*

$R_2 = [(V_{a2}) / (V_2)] \times 100\% = [(4\ V_a) / (V_2)] \times 100\%$

$R_2 = ([4 \times (4/3)\ \pi\ r^3] / [(16r^2/2)^{1/2}]^3) \times 100\%$

$R_2 = ([(16/3)\ \pi\ r^3] / [8^{3/2}\ r^3]) \times 100\%$

$R_2 = ([(16/3)\ \pi] / [8^{3/2}]) \times 100\%$

$R_2 = [(16.76) / (22.63)] \times 100\%$

$R_2 = 74.05\%$ *1 mark*

$\rho_{fcc} / \rho_{bcc} = (74.05\%) / (68.02\%)$

$\rho_{fcc} / \rho_{bcc} = 1.089$ *1 mark*

$\rho_{fcc} = 1.089 \times \rho_{bcc}$

$\rho_{fcc} = 1.089 \times 7.874$ g cm^{-3}

$\rho_{fcc} = 8.572$ g cm^{-3} *1 mark*

ii) a) Average number of carbon atoms per unit cell: 0.42 *2 marks; see breakdown*

b) Density of martensite: 8.228 g cm^{-3} *5 marks; see breakdown*

a) In 100.0 g of martensite at 4.3%C: (4.3 g C) / (12.011 g mol^{-1}) = 0.36 mol C

(95.7 g Fe) / (55.847 g mol^{-1}) = 1.71 mol Fe

So we have 1 carbon atom for 4.8 iron atoms or

0.21 carbon atoms per iron atom *1 mark*

Martensite has a bcc crystal structure (2 iron atoms per unit cell).

[(1 C atom) / (4.8 Fe atoms)] x (2 Fe atoms / unit cell)

or: 0.42 carbon atoms per unit cell *1 mark*

b) 5 carbon atoms [(0.42 C atom/0.42) x 5] in 12 unit cells [(1 unit cell/0.42) x 5]

5 carbon atoms dispersed in 12 unit cells

[(55.847 g/mol) / (6.02214 x 10^{23} atoms/mol)] x (2 atoms/unit cell of α-Iron)

1.8547 x 10^{-22} g Fe per unit cell of α-Iron *1 mark*

(12.011 g/mol) / (6.02214 x 10^{23} atoms/mol)

1.9945 x 10^{-23} g C per atom *1 mark*

[1.8547 x 10^{-22} g Fe + (0.42 C at. x 1.9945 x 10^{-23} g/C at.)] per unit cell

1.938 x 10^{-22} g C and Fe per unit cell *2 marks*

Each unit cell of α-Iron occupies a volume, V_1, of 2.356 x 10^{-23} cm^3

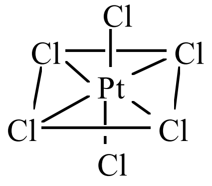
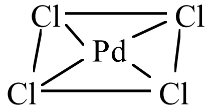
(*cf.* Question i)

ρ(martensite @ 4.3% C) = (1.938 x 10^{-22} g C and Fe) / (2.356 x 10^{-23} cm^3)

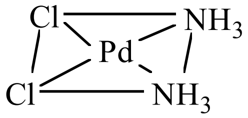
ρ(martensite @ 4.3% C) = 8.228 g cm^{-3} *1 mark*

SOLUTION 6

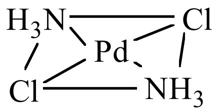
a) i)

 (octahedral) *0.5 mark* **$PtCl_6^{2-}$**	 (square planar) *0.5 mark* **$PdCl_4^{2-}$**

ii) Structure(s) of monomeric $Pd(NH_3)_2Cl_2$ (and stereochemical descriptors)



cis



trans

0.5 mark for each structure; 0.5 marks for each stereochemical descriptor

iii) Underline the appropriate response: *0.5 marks*

$FeSO_4$ is acting as a: catalyst oxidizing agent <u>reducing agent</u> solvent

Balanced reaction involving $FeSO_4$: *1 mark*

$$HAuCl_4 + 3\,FeSO_4 \rightarrow Au(0) + HCl + FeCl_3 + Fe_2(SO_4)_3$$

iv) Balanced reaction involving ignition of $Pd(NH_3)_2Cl_2$: *1 mark*

$$Pd(NH_3)_2Cl_2 + O_2 \rightarrow Pd(0) + N_2 + 2H_2O + 2HCl$$

What is being oxidized? ammonia (or N^{3-}) *0.5 marks*

What is being reduced? dioxygen, palladium(II) *1 mark*

b) i) Element **A** is: Sulfur *(4 marks; see breakdown)*

All Cl is located in the NH_4Cl, and thus the weight of Cl is found by:

53.492 g NH_4Cl → 35.453 g Cl

25.68 g NH_4Cl → ? g Cl

? = 25.68 x 35.453/53.492 =17.02 g Cl *0.5 marks*

Total amount of **A** in the reaction is 24.71 g Cl - 17.02 g Cl = 7.69 g **A** *0.5 marks*

There is 2.57 g free **A** and (7.69 - 2.57) = 5.12 g **A** in the nitride.

The amount of N bound in nitride is therefore

7.37 g nitride - 5.12 g **A** bound in nitride = 2.25 g N bound in nitride *0.5 marks*

The amount of ammonium ion bound in NH_4Cl is 25.68 - 17.02 = 8.66 g, therefore the amount of nitrogen present is 6.74 g.

The rule of multiple proportions is applied: *0.5 marks*

PROPORTIONS OF 1:1

Chloride:

7.69 g **A** binds → 17.02 g Cl

? g **A** binds → 35.45s g Cl

? = 35.453 x 7.69/17.02 = 16.02 g

A could be oxygen, but it is a main group element and it is a gas and thus it can be excluded*0.5 marks*

Nitride

5.12 g **A** binds → 2.25 g N

? g **A** binds → 14.007 g N

? = 14.007 x 5.12/2.25 = 31.87* g

A could be is sulfur, fits the physical description and M_S=32.064

0.5 marks

(*Phosphorus, Mp = 30.97, is also possible, but the highest degree of "polymerization" known is 4, in the P_4 molecule and thus P must also be excluded)

PROPORTIONS OF 1:2

Chloride:

7.69 g **A** binds → 17.02 g Cl

? g **A** binds → 2 x 35.453 g Cl

? = 2 x 35.453 x 7.69/17.02 = 32.03 g

Again **A** could be sulfur

0.5 marks

Nitride

5.12 g **A** binds → 2.25 g N

? g **A** binds → 2 x 14.007 g N

? = 2 x 14.007 x 5.12/2.25 = 63.75 g

A could be Cu but it is a Group B element and thus can be excluded

0.5 marks

ii) Balanced equation for the reaction of the chloride with ammonia: *2 marks*

$$3SCl_2 + 8NH_3 \rightarrow 6NH_4Cl + S + S_2N_2$$

(Other variations of SN species are possible)

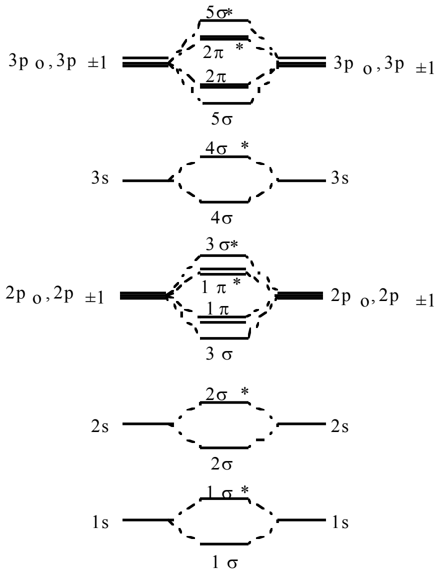
iii) Redox process: $2S^{2+} - 2e \rightarrow 2S^{3+}$ *2 marks*

$$S^{2+} + 2e \rightarrow S^0$$

SOLUTION 7

a) i) Molecular Orbital description of Cl_2:

In the formation of Cl_2: 2 x 17 = 34 electrons to go into the 18 MOs. *0.5 marks*



$1\sigma^2 1\sigma^{*2} 2\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 1\pi^{*4} 3\sigma^{*2} 4\sigma^2 4\sigma^{*2} 5\sigma^2 2\pi^4 2\pi^{*4}$ *1.5 marks*

or

$(KK)(LL)(\sigma 3s)^2(\sigma^*3s)^2(\pi 3p)^4(\sigma 3p)^2(\pi^*3p)^4$

or

$1(\sigma s^2)(\sigma s^{*2})2(\sigma s^2)(\sigma s^{*2})(\sigma p_x{}^2)(\sigma p_x{}^{*2})(\pi p_y{}^2)(\pi p_y{}^{*2})(\pi p_z{}^2)(\pi p_z{}^{*2})3(\sigma s^2)(\sigma s^{*2})$
$(\pi p_x{}^2)(\pi p_x{}^{*2})(\pi p_y{}^2)(\pi p_y{}^{*2})(\sigma p_z{}^2)(\sigma p_z{}^{*0})$

or

$(KK)(LL)3(\sigma s^2)(\sigma s^{*2})(\pi p_x{}^2)(\pi p_y{}^{*2})(\pi p_y{}^2)(\pi p_y{}^{*2})(\sigma p_z{}^2)(\sigma p_z{}^{*0})$

*assumption: - bond formation is along the z-axis
(equivalent formulas for x or y axes are accepted)

The bond order of Cl_2 is: 1 *0.5 marks*

Bond order is given by (n-n*)/2: Thus (2-2)/2 for (KK) + (8-8)/2 for (LL) +
(2-2)/2 for 3s + (2-2)/2 for $3p_x$ + (2-2)/2 for $3p_y$ + (2-0)/2 for $3p_z$ = 0+0+0+0+0+1 = 1

The Cl_2 molecule is: diamagnetic ferromagnetic paramagnetic *0.5 marks*

(Underline the correct answer)

The magnetism response must be consistent with the bond order response for marks.

a) ii) ΔE = -3591.8 kJ *(3.5 marks; see breakdown)*

ΔS_{sys} = 21.35 J K^{-1} *(2.5 marks; see breakdown)*

$$\underset{\substack{1\text{ mol}\\300\text{ K}}}{Cl_2\,(g)} \xrightarrow[\substack{\text{cooled}\\1.013\times10^7\text{ Pa}\\(100\text{ atm})}]{\Delta E_1} \underset{\substack{1\text{ mol}\\239\text{ K}}}{Cl_2\,(g)} \xrightarrow[\substack{1.013\times10^5\text{ Pa}\\(1\text{ atm})}]{\Delta E_2} \underset{\substack{0.1\text{ mol}\\239\text{ K}}}{Cl_2\,(l)}$$

Process 1:

$$\Delta E_1 = \int nC_v dT = (1)(28.66)(239 - 300) = -1748.3\text{ J}$$ *1 mark*

Process 2: For convenience, the data were manipulated in atm

Volume of gas which condensed is V = nRT/P = (0.1)(0.0820584)(239)/1 = 1.96 L

Volume of liquid Cl_2: (0.1)(2 x 35.454)/1.56 = 4.54 mL

$\Delta E_2 = \Delta H_2 - \int P_{ext}\Delta V(\text{phase change}) = \Delta H_2 - P_{ext}(V_l - V_g)$ *1 mark*

but V_l is approximately 0 and can be neglected
(ca. 4.5 mL liquid volume vs. ca. 17.6 L; ca. 0.03% error)

$\Delta E_2 = (0.1)(-\Delta H_{vap}) + P_{ext}V_g$
$= (0.1)(-20420) + 1(1.96\text{ L})(101.325\text{ J L}^{-1}\text{ atm}^{-1})$
$= -2042.0 + 198.5$
$= -1843.5\text{ J}$ *1 mark*

$\Delta E = \Delta E_1 + \Delta E_2 = -1748.3 + (-1843.5) = -3591.8\text{ J}$ *0.5 marks*

$\Delta S_{sys} = \Delta S_1 + \Delta S_2$ and $\bar{C}_p = \bar{C}_v + R = 28.66 + 8.314 = 36.97\text{ J K}^{-1}\text{ mol}^{-1}$ *0.5 marks*

$\Delta S_1 = nC_p \ln\frac{T_2}{T_1} - nR\ln\frac{P_2}{P_1} = 1.0(36.97)\ln\frac{239}{300} - 8.314\ln\frac{1}{100}$ *0.5 marks*

$= -8.40 + 38.29 = 29.89\text{ J K}^{-1}$ *0.5 marks*

$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{(0.1)(-20420)}{239} = -8.54 \quad \Delta S_2 = \frac{\Delta H_2}{T} = \frac{(0.1)(-20420)}{239} = -8.54\text{ J K}^{-1}$

0.5 marks

Thus $\Delta S_{sys} = 29.89 - 8.54 = 21.35\text{ J K}^{-1}$ *0.5 marks*

b) ΔG^o for Reaction 3: ___-15.35___ kJ mol^{-1} *(2 marks; see breakdown)*
ΔS^o for Reaction 3: ___39.08___ J K^{-1} *(2 marks; see breakdown)*
K_c for Reaction 3: ___490___ *(2 marks; see breakdown)*

One reverses the signs of $\ln K_c$ and ΔH^o for Reaction 1 when it is reversed.
Equilibrium constants are multiplied when equations are added, thus lnK's will add.
Reaction 3 = Reaction 2 - Reaction 1 *1 mark*
Thus $\Delta S_3 = \Delta S_2 - \Delta S_1$ and $\Delta G_3 = \Delta G_2 - \Delta G_1$ *0. 5 marks*

$\Delta G^o_1 = -RT\ln K_{c1} = -8.314(298)(11.60) = -28740\text{ J mol}^{-1} = -28.74\text{ kJ mol}^{-1}$ *1 mark*

$\Delta H^o_1 = -33.5\text{ kJ mol}^{-1}$

$\Delta S^o_1 = (\Delta H^o_1 - \Delta G^o_1)/T$ *0.5 marks*

$= (-33.5) - (-28.74))/298 = -0.0161\text{ kJ K}^{-1}\text{ mol}^{-1} = -16.1\text{ J K}^{-1}\text{ mol}^{-1}$ *0.5 marks*

Similarly:

$\Delta G^o_2 = -44.05\text{ kJ mol}^{-1}$ *0.5 marks*

$\Delta H^o_2 = -37.2\text{ kJ mol}^{-1}$

$\Delta S^o_2 = -22.98\text{ J K}^{-1}\text{ mol}^{-1}$ *0.5 marks*

Reaction 3 = Reaction 2 - Reaction 1, thus

$\Delta H^o_3 = \Delta H^o_2 - \Delta H^o_1 = -3.7\text{ kJ}$

$\Delta S^o_3 = \Delta S^o_2 - \Delta S^o_1 = 39.08\text{ J K}^{-1}$

$\Delta G^o_3 = \Delta H^o_3 - T\Delta S^o_3 = -15.35\text{ kJ mol}^{-1}$ *0.5 marks*

Since $\Delta G^o_3 = -RT\ln K_{c3}$ then $K_{c3} = e^{\frac{15.35}{RT}} = 4.90 \times 10^2$ *1 mark*

Alternatively:

$\Delta G^o_3 = \Delta G^o_2 - \Delta G^o_1 = -44.05 - (-28.74) = -15.31\text{ kJ mol}^{-1}$ thus $K = 4.82 \times 10^2$)

$\Delta S^o = (\Delta H^o - \Delta G^o)/T = (-3700 - (-15311))/298 = 38.96\text{ J K}^{-1}$

SOLUTION8

i) Reaction(s) at the anode: *1 mark*

$2\,H_2O \rightarrow 4\,H^+ + O_2 + 4\,e$

Reactions(s) at the cathode:

$2\,H^+ + 2\,e \rightarrow H_2$ Two reactions occur simultaneously at the cathode *2 marks*

$Cu^{2+} + 2\,e \rightarrow Cu$

ii) Moles of H_2: 8.9230 x 10^{-6} *1 mark*

$P\,V_{H_2} = n_{H_2}\,R\,T$

$$n_{H_2} = \frac{10132.5 \times 2.0000 \times 10^{-6}}{8.314510 \times 273.15} = 8.9230 \times 10^{-6}\ \text{mol}$$

Moles of Cu: 1.4412 x 10^{-6} *3 marks (see breakdown)*

charge necessary to generate 8.9230 x 10^{-6} moles H_2

Q_H = 2 x 8.9230 x 10^{-6} x N_A x 1.60218 x 10^{-19} = 1.7219 C *1 mark*

charge available for Cu deposition

Q_{Cu} = 2.0000 - Q_H = 2.0000 - 1.7219 = 0.2781 C *1 mark*

moles of Cu (requires 2e equivalents) = 0.2781 C/2 F = 1.4412 x 10^{-6} *1 mark*

iii) Monolayers of Cu: 668 (*8 marks; see breakdown)*

calculation of surface Pt atoms in the (100) face

surface area of the fundamental unit:

$A_u = (a_{Pt})^2$ = (3.9236 x $10^{-8})^2$ = 1.5395 x 10^{-15} cm^2 *1 mark*

number of atoms per fundamental (100) unit: n_u = 2 *1 mark*

surface atom concentration: $\sigma_{Pt(100)} = n_u/A_u$ = 1.2991 x 10^{15} cm^{-2} *1 mark*

for epitaxial growth the number of Cu atoms equals the number of Pt atoms

$\sigma_{Cu(100)} = \sigma_{Pt(100)}$ = 1.2991 x 10^{15} cm^{-2} *1 mark*

charge for the formation of one monolayer (ML) of Cu

q_{ML} = 2 x e x 1.2991 x 10^{15} = 4.1628 x 10^{-4} C *2 marks*

number of monolayers equals charge/charge per monolayer

0.2781/4.1628 x 10^{-4} = 668.1 = 668 *2 marks*

Alternate method:

Surface atom concentration and epitaxial requirement (as above) *4 marks*

One can also calculate the number of Cu atoms (1.4412 x 10^{-6} x N_A =8.6802 x 10^{17}) formed from the number of moles produced and divide this by the number of atoms (1.2991 x 10^{15}) on the exposed Pt surface to also arrive at 668 monolayers. *4 marks*