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**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 HIO4; 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 H2SO4 in the atmosphere. He has proposed two possible stoichiometric reactions:

Proposal A: H2O(g) + SO3(g)  H2SO4(g)

Proposal B: 2H2O(g) + SO3(g)  H2SO4(g) + H2O(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:

k1

SO3 + 2H2O  SO3•2H2O (fast)

k -1

k2

SO3•2H2O  H2SO4 + H2O (slow)

(SO3•2H2O is a complex which is stabilized by hydrogen bonds and k2 << k1 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:

EA = + 80 kJ mol-1 for Proposal A EB = - 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 H2SO4 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.



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.

continued…



**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.

\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*

HIn is a weakly acidic indicator.

HIn + Na+OH-  Na+In- + H2O

also written as

HIn  In- + H+

At normal temperatures, the acid dissociation constant for this indicator is Ka = 2.93 x 10-5.

The absorbance data (1.00 cm cells) for 5.00 x 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)

Green

Blue

Indigo

Violet

Red

Orange

Yellow

, 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

continued…

**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:

violet blue green yellow red

wavelength (nm)

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:

490 625

M-1 cm-1 M-1 cm-1

HIn (HCl) 9.04 x 102 3.52 x 102

In- (NaOH) 1.08 x 102 1.65 x 103

(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 -iron. From 1185 K to 1667 K, the structure becomes face-centered cubic (fcc) and is called ‑iron. Above 1667 K, and up to its melting point, iron reverts to a bcc structure similar to that of ‑iron. The latter phase is called -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 -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 -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 -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**

MFe = 55.847 g mol-1

MC = 12.011 g mol-1

NA = 6.02214 x 1023 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 PtCl62- and the PdCl42- anions.

ii) Clearly draw all possible stereoisomeric structures of monomeric Pd(NH3)2Cl2. Label the structures that you have drawn with their correct stereochemical descriptors.

iii) What is the role of the FeSO4 in the second step of the flow chart? Write a balanced equation for the reaction of FeSO4 in this step.

iv) Write a complete balanced equation for the ignition of Pd(NH3)2Cl2 in air to give Pd metal. In this reaction, what is being oxidized and what is being reduced?

\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*

b) Reaction of a main group chloride (24.71 g) with ammonia (10.90 g) gave a mixture of products consisting of NH4Cl (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**A**wClx + mNH3  pNH4Cl + q**A** + r**A**yNz

(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: MCl = 35.453 g mol-1 MN = 14.007 g mol-1 MH = 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 Cl2 (g), which may be assumed to obey the ideal gas law, initially at 300 K and 1.01325 x 107 Pa, is expanded against a constant external pressure of  
1.01325 x 105 Pa to a final pressure of 1.01325 x 105 Pa. As a result of the expansion, the gas cooled to a temperature of 239 K (which is the normal boiling point of Cl2), and 0.100 mol of Cl2 condensed.

The enthalpy of vaporization of Cl2 (l) is 20.42 kJ mol-1 at the normal boiling point, the molar heat capacity of Cl2 (g) at constant volume is Cv = 28.66 J K-1 mol-1 and the density of Cl2 (l) is 1.56 g cm-3 (at 239 K). Assume that the molar heat capacity at constant pressure for Cl2 (g) is Cp = Cv + R.

(1 atm = 1.01325 x 105 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 Cl2. Predict the bond order of Cl2 and thus whether this molecule will be diamagnetic, ferromagnetic, or paramagnetic.

ii) For the changes described above, calculate the change in the internal energy (E) and the change in the entropy (Ssys) of the system.

\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*

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



lnKc = 11.60 and Ho = -33.5 kJ mol-1



lnKc = 17.78 and Ho = -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 Go, So , and Kc at 298 K for reaction [3] occuring in a dilute aqueous solution:



**Problem 8**

**(15 points)**

An electrolyte is prepared from H2SO4, CuSO4 and distilled water and its volume is  
100.0 cm3. The concentrations of H+ and Cu2+ in the electrolyte are cH+ = 1.000 M   
(mol dm-3) and cCu2+ = 1.000 x 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 cm2. 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 H2 gas generation. At the anode, O2 gas is generated. The H2 gas is collected in a flask under the following conditions (assume ideal gas behaviour):

T = 273.15 K and PH2 = 1.01325 x 104 Pa; the volume of H2 is equal to 2.0000 cm3

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

ii) Calculate the number of moles of H2 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 aPt = 3.9236 x 10-8 cm.

Both Pt and Cu have the fcc (face centered cubic) crystallographic structure.

**Molar masses and constants**

MH = 1.00795 g mol-1

MCu = 63.546 g mol-1

e = 1.60218 x 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

Vm = 22.4141 dm3

1 atm = 1.01325 x 105 Pa

NA = 6.02214 x 1023 mol-1

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**Theoretical Examination**

Montreal, Thursday, July 17, 1997

**\*\*\*ANSWER SHEETS\*\*\***

• 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.

• 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**.

|  |  |  |
| --- | --- | --- |
| A6-B6-C5  A6-B5-C6  A5-B6-C6 | B6-C6-A5  B6-C5-A6  B5-C6-A6 | C6-A6-B5  C6-A5-B6  C5-A6-B6 |

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:

Name

Identification Code

**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 k2 << k1 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.

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

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

p 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

Team

**SOLUTION 4**

i) a) Indicator colour at pH 1.00:

violet blue green yellow red

wavelength (nm)

b) Indicator colour at pH 13.00:

violet blue green yellow red

wavelength (nm)

ii) Appropriate colour filter:

violet blue green yellow red

wavelength (nm)

iii) Appropriate wavelength range:

violet blue green yellow red

wavelength (nm)

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) | **PtCl62-** | **PdCl42-** |

ii) Structure(s) of monomeric Pd(NH3)2Cl2 (and stereochemical descriptors)

iii) Underline the appropriate response:

FeSO4 is acting as a: catalyst oxidizing agent reducing agent solvent

Balanced reaction involving FeSO4:

iv) Balanced reaction involving ignition of Pd(NH3)2Cl2:

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 Cl2:

The bond order of Cl2 is:

The Cl2 molecule is: diamagnetic ferromagnetic paramagnetic

(Underline the correct answer)

continued… Name

Identification Code

**SOLUTION 7** (continued)

a) ii) E: kJ

Ssys: J K-1

Show your calculations.

continued… Name

Identification Code

**SOLUTION 7** (continued)

b) Go for Reaction 3: kJ mol-1

So for Reaction 3: J K-1

Kc 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 H2:

Moles of Cu:

continued…

Name

Identification Code

**SOLUTION 8** (continued)

iii) Monolayers of Cu:

|  |  |
| --- | --- |
|  |  |

**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, givesan 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 not 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 CO2 suggesting that it is a ketohexose.

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

**SOLUTION 1** (continued)

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:







**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: **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**, etc.

then the trisaccharide **X** would be represented as: **C**6-**A**6-**B**5

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



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: 

Summing the exponents gives a second order process

Proposal B: 

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.



Thus: 

and therefore: 

Also:  and substituting from above yields



However, since k2 << k-1 the above reduces to:



which is also third order

**SOLUTION 2** (continued)

iii) Knowing the Arrhenius relationship: 

for Proposal A:  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:  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)



ii) SN2 Bimolecular Nucleophilic Substitution

iii) Rate = k[substrate] [nucleophile]

The overall rate is directly dependent on the concentration of both 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)



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 x 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 = l c (Beer’s Law)

where, l = length of cell

c = concentration of analyte

= molar absorptivity

therefore, = A = 0.256 = 5.12 x 102 M-1 cm-1

lc 1.0 x 5.00 x 10-4

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 102 x 2.50 x 1.0 x 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 x 10-3 M (2)

 (3)

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



Rearrangement yields the quadratic expression

[In-]2 + 2.93 x 10-5[In-] - 5.27 x 10-8 = 0

which results in

[In-] = 2.15 x 10-4 M

[HIn] = 1.80 x 10-3 M - 2.15 x 10-4 M = 1.58 x 10-3 M

The absorbance at the two wavelengths are then:

A490 = (9.04 x 102 x 1 x 1.58 x 10-3) + (1.08 x 102 x 1 x 2.15 x 10-4 ) = 1.45

A625 = (3.52 x 102 x 1 x 1.58 x 10-3) + (1.65 x 103 x 1 x 2.15 x 10-4) = 0.911

**SOLUTION 5**

i) Expected steps of the calculation:

1. Define the length (a, b, c, d1, d2, and r) and volume (V1 and V2) parameters for both bcc and fcc structures of iron (*cf.* Details below).

2. Calculate the volume (V1) of the unit cell of -iron from its density (bcc) at 293 K, the molar weight (MFe) of iron, and Avogadro’s number (NA).

3. Calculate the length (d1) of the edge of the bcc unit cell from its volume (V1).

4. Calculate the atomic radius (r) of iron from the length “d1”.

5. Calculate the length (d2) of the edge of the fcc unit cell (at 1250 K) from the atomic radius (r) of iron.

6. Calculate the volume (V2) of the fcc unit cell of -iron from the length (d2) of its edge.

7. Calculate the mass (m) of the number of iron atoms in a unit cell of -iron from the molar weight (MFe) of iron and Avogadro’s number (NA).

8. Calculate the density (fcc) of -iron from the values of “m” and “V2”.

An alternative route to fcc of -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 fcc/bcc density ratio from the fcc/bcc space filling ratios.

8'. Calculate the density (fcc) of -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, -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, -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.

d1 = length of the edge of the bcc unit cell of -iron.

d2 = length of the edge of the fcc unit cell of -iron.

V1 = Volume of the bcc unit cell of -iron.

V2 = Volume of the fcc unit cell of -iron.

Va = Volume of one atom.

Va1 = Volume occupied by 2 atoms in one bcc unit cell.

Va2 = Volume occupied by 4 atoms in one fcc unit cell.

R1 = Percent space filling ratio in a bcc unit cell.

R2 = Percent space filling ratio in a fcc unit cell.

Va = (4/3)  r3 Va1 = 2 Va Va2 = 4 Va

b = 4r; a2 = 2d12; b2 = d12 + a2 = 3d12

d1 = (b2/3)1/2 = (16r2/3)1/2; V1 = d13 = [(16r2/3)1/2]3

c = 4r; c2 = 2d22

d2 = (c2/2)1/2 = (16r2/2)1/2; V2 = d23 = [(16r2/2)1/2]3

2. 1.000 cm3 of iron weights 7.874 g at 293 K (bcc).

1 mole of iron weights 55.847 g (MFe).

So 0.1410 mol (7.874 g/55.847 g mol-1) of iron occupy a volume of 1.000 cm3 or

1 mol of iron will occupy a volume of 7.093 cm3

1 mole corresponds to 6.02214 x 1023 atoms

V1 = (7.093 cm3 mol-1) x (2 atoms/unit cell) / (6.02214 x 1023 atoms mol-1)

V1 = 2.356 x 10-23 cm3 per unit cell

3. d1 = (V1)1/3 = (2.356 x 10-23 cm3)1/3

d1 = 2.867 x 10-8 cm

**SOLUTION 5** (continued)

4. For a bcc structure, the value of d1 can be expressed as: d1 = [(16r2)/3]1/2

so the value of “r” will be: r = (3d12/16)1/2

r = [3 (2.867 x 10-8 cm)2/16]1/2

r = 1.241 x 10-8 cm

5. At 1250 K, in the fcc structure, the value of “d2” is given by: d2 = (16r2/2)1/2

d2 = [16 (1.241 x 10-8 cm)2/2]1/2

d2 = 3.511 x 10-8 cm

6. V2 = d23 = (3.511 x 10-8 cm)3

V2 = 4.327 x 10-23 cm3

7. 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 1023 atoms mol-1)

m = 3.709 x 10-22 g per unit cell

8. fcc = m/V2 = (3.709 x 10-22 g) / (4.327 x 10-23 cm3)

fcc = 8.572 g/cm3

Alternative route to fcc of -iron:

5'. R1 = [(Va1) / (V1)] x 100% = [(2 Va) / (V1)] x 100%

R1 = ([2 x (4/3)  r3] / [(16r2/3)1/2]3) x 100%

R1 = ([(8/3)  r3] / [(16/3)3/2 r3]) x 100%

R1 = ([(8/3) ] / [(16/3)3/2]) x 100%

R1 = [(8.378) / (12.32)] x 100%

R1 = 68.02%

6'. R2 = [(Va2) / (V2)] x 100% = [(4 Va) / (V2)] x 100%

R2 = ([4 x (4/3)  r3] / [(16r2/2)1/2]3) x 100%

R2 = ([(16/3)  r3] / [83/2 r3]) x 100%

R2 = ([(16/3) ] / [83/2]) x 100%

R2 = [(16.76) / (22.63)] x 100%

R2 = 74.05%

7'. fcc / bcc = (74.05%) / (68.02%)

fcc / bcc = 1.089

8'. fcc = 1.089 x bcc

fcc = 1.089 x 7.874 g cm-3

fcc = 8.572 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 [(martensite @ 4.3%C)] from the total mass of C and Fe and volume (V1) of -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 1023 atoms/mol)] x (2 atoms/unit cell of -Iron)

1.8547 x 10-22 g Fe per unit cell of -Iron

5. (12.011 g/mol) / (6.02214 x 1023 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 -Iron occupies a volume, V1, of 2.356 x 10-23 cm3

(*cf.* Question i)

(martensite @ 4.3% C) = (1.938 x 10-22 g C and Fe) / (2.356 x 10-23 cm3)

(martensite @ 4.3% C) = 8.228 g cm-3

**SOLUTION 6**

a)

i) The PtCl62- anion consists of a Pt(IV) centered in a regular octahedron of Cl- ions. The PdCl42- anion consists of a Pt(II) centered in a square of Cl- ions.



ii) Like PdCl42-, Pd(NH3)2Cl2 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 NH3 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.



iii) The FeSO4 [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).

HAuCl4 + 3 FeSO4  Au(0) + HCl + FeCl3 + Fe2(SO4)3

iv)

Pd(NH3)2Cl2 + O2  Pd(0) + N2 + 2H2O + 2HCl

Pd2+ + 2e  Pd0 reduction

2O0 + 4e  2O2- reduction

2N3- - 6e  2N0 oxidation

or

**SOLUTION 6** (continued)

Pd(NH3)2Cl2 + 2O2  Pd(0) + 2NO + 2H2O + 2HCl

Pd2+ + 2e  Pd0 reduction

4O0 + 8e  4O2- reduction

2N3- - 10e  2N2+ oxidation

or

Pd(NH3)2Cl2 + 3O2  Pd(0) + 2NO2 + 2H2O + 2HCl

Pd2+ + 2e  Pd0 reduction

6O0 + 12e  6O2- reduction

2N3- - 14e  2N4+ 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, NH3 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 NH4Cl, and thus the weight of Cl is found by:

53.492 g NH4Cl  35.453 g Cl

25.68 g NH4Cl  ? 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 NH4Cl is 25.68 - 17.02 = 8.66 g

The rule of multiple proportions is applied:

**SOLUTION 6** (continued)

Proportions OF 1:1

|  |  |
| --- | --- |
| Chloride:  7.69 g **A** binds  17.02 g Cl  ? g **A** binds  35.453 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 | 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 MS=32.064 |

(\*Phosphorus, MP = 30.97, is also possible, but the highest degree of “polymerization” known is 4, in the P4 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 | 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 |

Therefore element **A** must be sulfur.

ii) SCl2 + 2 2/3 NH3  2NH4Cl + 1/3 S + S2/3N2/3

or

3 SCl2 + 8 NH3  6NH4Cl + S + S2N2

or

6 SCl2 + 16NH3  12NH4Cl + 2S + S4N4

In fact the elemental S is in the form of S8 and so the equation should be multiplied by a factor of 8. Although S2N2 roughly fits the description of colour and explosive instability, it is actually S4N4 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 S8 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 (S2Cl2 and SCl4 do not fit the stoichiometry of the reaction.)

iii) A disproportionation reaction involving sulfur occurs:

2S2+ - 2e  2 S3+

S2+ + 2e  S0

**SOLUTION 7**

a)

i) Electronic configuration of a Cl atom:

1s22s22px22py22pz23s23px23py23pz1

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 Cl2 molecule

In the formation of Cl2: 2 x 17 = 34 electrons to go into the 18 MOs.

MO description of Cl2:



121\*2222\*232141\*43\*2424\*252242\*4

or

(KK)(LL)(3s)2(\*3s)2(3p)4(3p)2(\*3p)4

or

1(s2)(s\*2)2(s2)(s\*2)(px2)(px\*2)(py2)(py\*2)(pz2)(pz\*2)3(s2)(s\*2) (px2)(px\*2)(py2)(py\*2)(pz2)(pz\*0)

or

(KK)(LL)3(s2)(s\*2)(px2)(py\*2)(py2)(py\*2)(pz2)(pz\*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 3px + (2-2)/2 for 3py + (2-0)/2 for 3pz = 0+0+0+0+0+1 = 1 ( bond, not  bond)

The Cl2 molecule has a bond order of 1.

The Cl2 molecule is diamagnetic since there are no unpaired electrons.

**SOLUTION 7** (continued)

a)

ii) Summary of the changes involved:



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 E = E1 + E2.

Process 1:

 = -1748.3 J

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

b) Cv 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 Cl2: (0.1)(2 x 35.454)/1.56 = 4.54 mL



but Vl is approximately 0 and can be neglected

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

E2 = (0.1)(-Hvap) + PextVg

= (0.1)(-20420) + 1(1.96 L)(101.325 J L-1 atm-1)

= -2042.0 + 198.5

= -1843.5 J

E = E1 + E2 = -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).

Ssys = S1 + S2 and  J K-1 mol-1



= -8.40 + 38.29 = 29.89 J K-1

For the phase transition (constant temperature), by definition S2 = Q/T

Since the pressure is constant in this case, Q/T = Qp/T = H/T

 J K-1

Ssys = 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 lnKc and Ho 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 S3 = S2 - S1 and G3 = G2 - G1

Go1 = -RTlnKc1 = -8.314(298)(11.60) = -28740 J mol-1 = -28.74 kJ mol-1

Ho1 = -33.5 kJ mol-1

So1 = (Ho1 - Go1)/T

= (-33.5) - (-28.74))/298 = -0.0161 kJ K-1 mol-1 = -16.1 J K-1 mol-1

Similarly:

Go2 = -44.05 kJ mol-1

Ho2 = -37.2 kJ mol-1

So2 = -22.98 J K-1 mol-1

Reaction 3 = Reaction 2 - Reaction 1, thus

Ho3 = Ho2 - Ho1 = -3.7 kJ

So3 = So2 - So1 = 39.08 J K-1

Go3 = Ho3 - TSo3 = -15.35 kJ mol-1

Thus  = 4.90 x 102

Alternatively:

Go3 = Go2 - Go1 = -44.05 - (-28.74) = -15.31 kJ mol-1 thus K = 4.82 x 102)

So = (Ho - Go)/T= ( - (-15311))/298 = 38.96 J K-1

**SOLUTION 8**

***Approach***

• Determine the number of  moles generated by the electrolysis

• Calculate the charge required for the  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 ; during an epitaxial growth the number of Cu atoms per  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: 

(b) Cathode:  Two reactions occur simultaneously at the cathode



***ii)***

***Determination of the charge necessary to generate*** ***2.0000 cm3 of H2 gas (T = 273.15 K,   
P = 10.1325 kPa)***

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

(a) determination of  



(b)   ( refers to the pressure of 1 atm or at  and because the  pressure is ten times smaller, one knows right away that the volume occupied under 1 atm would be )



**SOLUTION 8** (continued)

***Determination of the charge necessary to generate 8.9230 x 10-6 moles of*** ***H2*** ***gas***

*Two approaches to determination of the charge*

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





(b) one may use the Faraday law



where  is the electrochemical equivalent of H thus the mass of H generated by 1 C; to use this formula one has to calculate ; knowing that the charge of  results in formation of 1 mole of H (1/2 mole of ), one may easily determine 





Subsequently





***Determination of the Cu deposition charge***





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:



Number of atoms per fundamental (100) unit: 

Surface atom concentration:



The number of Cu atoms per  equals the number of Pt atoms - *epitaxial growth*



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





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





One can also calculate the number of Cu atoms (8.6802 x 1017) formed from the number of moles produced and divide this by the number of atoms (1.2991 x 1015) on the exposed Pt surface to also arrive at 668 monolayers.

|  |  |
| --- | --- |
|  |  |

**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*  **A** | *2 marks*  **B** | *2 marks*  **C** | *2 marks*  **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**    *2 marks*  **E** | **or**    *2 marks*  **F** | **or**    *2 marks*  **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: **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**.

|  |  |  |
| --- | --- | --- |
| A6-B6-C5  A6-B5-C6  A5-B6-C6 | B6-C6-A5  B6-C5-A6  B5-C6-A6 | C6-A6-B5  *1 mark*  C6-A5-B6  C5-A6-B6 |

**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:

 *1 mark*

Thus: 

and therefore:  *1 mark*

Also:  and substituting from above yields

 *2 marks*

**OR**

However, since k2 << k-1 the above reduces to:



which is also third order

iii) For Proposal A:

Arrhenius relationship:  *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

p Decreases with increasing temperature

1. Is independent of the temperature

For Proposal B:

Arrhenius relationship:  *1 mark*

The rate constant for the reaction: *1 mark*

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

p Increases with increasing temperature

Decreases with increasing temperature

p Is independent of the temperature

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

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

p Proposal B since k2 << k1 or k-1

p 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:

violet blue green yellow red

wavelength

*1 mark*

b) Indicator colour at pH 13.00:

violet blue green yellow red

wavelength

*1 mark*

ii) Appropriate colour filter:

violet blue green yellow red

wavelength

*1 mark*

iii) Appropriate wavelength range:

wavelength

*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 = l c (Beer’s Law) where,

l = length of cell;

c = concentration of analyte;

= molar absorptivity

therefore, = A = 0.256 = 5.12 x 102 M-1 cm-1 *1 mark*

lc 1.0 x 5.00 x 10-4

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 102 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][H+] + [In-] and thus

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

[HIn] + [In-] = 1.8 x 10-3 M (2) *1 mark*

 (3)

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

Rearrangement yields: [In-]2 + 2.93 x 10-5[In-] - 5.27 x 10-8 = 0

which results in

[In-] = 2.15 x 10-4 M *1.5 marks*

[HIn] = 1.80 x 10-3 M - 2.15 x 10-4 M = 1.58 x 10-3 M *1.5 marks*

The absorbance is thus

A490 = (9.04 x 102 x 1 x 1.58 x 10-3) + (1.08 x 102 x 1 x 2.15 x 10-4 ) = 1.45 *2 marks*

b) Absorbance at 625 nm: A = 0.911 *1 mark*

Similar substitution to v-a above yields:

A625 = (3.52 x 102 x 1 x 1.58 x 10-3) + (1.65 x 103 x 1 x 2.15 x 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 cm3 of iron weighs 7.874 g at 293 K (bcc).

1 mole of iron weighs 55.847 g (MFe).

So 0.1410 mol (7.874 g/55.847 g mol-1) of iron occupy a volume of 1.000 cm3 or

1 mol of iron will occupy a volume of 7.093 cm3 *1 mark*

1 mole corresponds to 6.02214 x 1023 atoms

V1 = (7.093 cm3 mol-1) x (2 atoms/unit cell) / (6.02214 x 1023 atoms mol-1)

V1 = 2.356 x 10-23 cm3 per unit cell *1 mark*

d1 = (V1)1/3 = (2.356 x 10-23 cm3)1/3

d1 = 2.867 x 10-8 cm *1 mark*

For a bcc structure, the value of d1 can be expressed as: d1 = [(16r2)/3]1/2

so the value of “r” will be: r = (3d12/16)1/2

r = [3 (2.867 x 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 “d2” is given by: d2 = (16r2/2)1/2

d2 = [16 (1.241 x 10-8 cm)2/2]1/2

d2 = 3.511 x 10-8 cm *1 mark*

V2 = d23 = (3.511 x 10-8 cm)3

V2 = 4.327 x 10-23 cm3 *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 1023 atoms mol-1)

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

fcc = m/V2 = (3.709 x 10-22 g) / (4.327 x 10-23 cm3)

fcc = 8.572 g/cm3 *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:

R1 = [(Va1) / (V1)] x 100% = [(2 Va) / (V1)] x 100%

R1 = ([2 x (4/3)  r3] / [(16r2/3)1/2]3) x 100%

R1 = ([(8/3)  r3] / [(16/3)3/2 r3]) x 100%

R1 = ([(8/3) ] / [(16/3)3/2]) x 100%

R1 = [(8.378) / (12.32)] x 100%

R1 = 68.02% *1 mark*

R2 = [(Va2) / (V2)] x 100% = [(4 Va) / (V2)] x 100%

R2 = ([4 x (4/3)  r3] / [(16r2/2)1/2]3) x 100%

R2 = ([(16/3)  r3] / [83/2 r3]) x 100%

R2 = ([(16/3) ] / [83/2]) x 100%

R2 = [(16.76) / (22.63)] x 100%

R2 = 74.05% *1 mark*

fcc / bcc = (74.05%) / (68.02%)

fcc / bcc = 1.089 *1 mark*

fcc = 1.089 x bcc

fcc = 1.089 x 7.874 g cm-3

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 1023 atoms/mol)] x (2 atoms/unit cell of -Iron)

1.8547 x 10-22 g Fe per unit cell of -Iron *1 mark*

(12.011 g/mol) / (6.02214 x 1023 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 -Iron occupies a volume, V1, of 2.356 x 10-23 cm3

(*cf.* Question i)

(martensite @ 4.3% C) = (1.938 x 10-22 g C and Fe) / (2.356 x 10-23 cm3)

(martensite @ 4.3% C) = 8.228 g cm-3 *1 mark*

**SOLUTION 6**

|  |  |  |
| --- | --- | --- |
| a) i) | (octahedral)  *0.5 mark*  **PtCl62-** | (square planar)  *0.5 mark*  **PdCl42-** |

ii) Structure(s) of monomeric Pd(NH3)2Cl2 (and stereochemical descriptors)



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

iii) Underline the appropriate response: *0.5 marks*

FeSO4 is acting as a: catalyst oxidizing agent reducing agent solvent

Balanced reaction involving FeSO4: *1 mark*

HAuCl4 + 3 FeSO4  Au(0) + HCl + FeCl3 + Fe2(SO4)3

iv) Balanced reaction involving ignition of Pd(NH3)2Cl2: *1 mark*

Pd(NH3)2Cl2 + O2  Pd(0) + N2 + 2H2O + 2HCl

What is being oxidized? ammonia (or N3-)  *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 NH4Cl, and thus the weight of Cl is found by:

53.492 g NH4Cl  35.453 g Cl

25.68 g NH4Cl  ? 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 NH4Cl 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 MS=32.064  *0.5 marks* |

(\*Phosphorus, MP = 30.97, is also possible, but the highest degree of “polymerization” known is 4, in the P4 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*

3SCl2 + 8NH3  6NH4Cl + S + S2N2

(Other variations of SN species are possible)

iii) Redox process: 2S2+ - 2e  2S3+ *2 marks*

S2+ + 2e  S0

**SOLUTION 7**

a) i) Molecular Orbital description of Cl2:

In the formation of Cl2: 2 x 17 = 34 electrons to go into the 18 MOs. *0.5 marks*



121\*2222\*232141\*43\*2424\*252242\*4 *1.5 marks*

or

(KK)(LL)(3s)2(\*3s)2(3p)4(3p)2(\*3p)4

or

1(s2)(s\*2)2(s2)(s\*2)(px2)(px\*2)(py2)(py\*2)(pz2)(pz\*2)3(s2)(s\*2) (px2)(px\*2)(py2)(py\*2)(pz2)(pz\*0)

or

(KK)(LL)3(s2)(s\*2)(px2)(py\*2)(py2)(py\*2)(pz2)(pz\*0)

\*assumption: - bond formation is along the z-axis

(equivalent formulas for x or y axes are accepted)

The bond order of Cl2 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 3px + (2-2)/2 for 3py + (2-0)/2 for 3pz = 0+0+0+0+0+1 = 1

The Cl2 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) E = -3591.8 kJ *(3.5 marks; see breakdown)*

Ssys = 21.35 J K-1 *(2.5 marks; see breakdown)*



Process 1:

 = -1748.3 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 Cl2: (0.1)(2 x 35.454)/1.56 = 4.54 mL

 *1 mark*

but Vl is approximately 0 and can be neglected

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

E2 = (0.1)(-Hvap) + PextVg

= (0.1)(-20420) + 1(1.96 L)(101.325 J L-1 atm-1)

= -2042.0 + 198.5

= -1843.5 J *1 mark*

E = E1 + E2 = -1748.3 + (-1843.5) = -3591.8 J *0.5 marks*

Ssys = S1 + S2 and  J K-1 mol-1 *0.5 marks*

 *0.5 marks*

= -8.40 + 38.29 = 29.89 J K-1 *0.5 marks*

 J K-1

*0.5 marks*

Thus Ssys = 29.89 - 8.54 = 21.35 J K-1 *0.5 marks*

b) Go for Reaction 3: -15.35 kJ mol-1 (*2 marks; see breakdown)*

So for Reaction 3: 39.08 J K-1 *(2 marks; see breakdown)*

Kc for Reaction 3: 490 *(2 marks; see breakdown)*

One reverses the signs of lnKc and Ho 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 S3 = S2 - S1 and G3 = G2 - G1 *0. 5 marks*

Go1 = -RTlnKc1 = -8.314(298)(11.60) = -28740 J mol-1 = -28.74 kJ mol-1 *1 mark*

Ho1 = -33.5 kJ mol-1

So1 = (Ho1 - Go1)/T *0.5 marks*

= (-33.5) - (-28.74))/298 = -0.0161 kJ K-1 mol-1 = -16.1 J K-1 mol-1 *0.5 marks*

Similarly:

Go2 = -44.05 kJ mol-1 *0.5 marks*

Ho2 = -37.2 kJ mol-1

So2 = -22.98 J K-1 mol-1 *0.5 marks*

Reaction 3 = Reaction 2 - Reaction 1, thus

Ho3 = Ho2 - Ho1 = -3.7 kJ

So3 = So2 - So1 = 39.08 J K-1

Go3 = Ho3 - TSo3 = -15.35 kJ mol-1 *0.5 marks*

Since Go3 = -RTlnKc3 then  = 4.90 x 102 *1 mark*

Alternatively:

Go3 = Go2 - Go1 = -44.05 - (-28.74) = -15.31 kJ mol-1 thus K = 4.82 x 102)

So = (Ho - Go)/T= ( - (-15311))/298 = 38.96 J K-1

**SOLUTION8**

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



Reactions(s) at the cathode:

 Two reactions occur simultaneously at the cathode *2 marks*



ii) Moles of H2: 8.9230 x 10-6 *1 mark*





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

charge necessary to generate 8.9230 x 10-6 moles H2

QH = 2 x 8.9230 x 10-6 x NA x 1.60218 x 10-19 = 1.7219 C *1 mark*

charge available for Cu deposition

QCu = 2.0000 - QH = 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:

Au = (aPt)2 = (3.9236 x 10-8)2 = 1.5395 x 10-15 cm2 *1 mark*

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

surface atom concentration: Pt(100) = nu/Au = 1.2991 x 1015 cm-2 *1 mark*

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

Cu(100) = Pt(100) = 1.2991 x 1015 cm-2 *1 mark*

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

qML = 2 x e x 1.2991 x 1015 = 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 NA =8.6802 x 1017) formed from the number of moles produced and divide this by the number of atoms (1.2991 x 1015) on the exposed Pt surface to also arrive at 668 monolayers. *4 marks*