Inorganic Chemistry

PROBLEM 2

Write down equations for the following reactions:

2.1 Oxidation of chromium(III) chloride with bromine in alkaline solution (KOH).

2.2 Oxidation of potassium nitrite with potassium permanganate in acid solution (H_2SO_4).

2.3 Action of chlorine on lime water ($Ca(OH)_2$) in a cold reaction mixture.

SOLUTION

2.1 $2\ CrCl_3 + 3\ Br_2 + 16\ KOH \rightarrow 2\ K_2CrO_4 + 6\ KBr + 6\ KCl + 8\ H_2O$

2.2 $5\ KNO_2 + 2\ KMnO_4 + 3\ H_2SO_4 \rightarrow 2\ MnSO_4 + K_2SO_4 + 5\ KNO_3 + 3\ H_2O$

2.3. $Cl_2 + Ca(OH)_2 \rightarrow CaOCl_2 + H_2O$

PROBLEM 2

A compound **A** contains 38.67 % of potassium, 13.85 % of nitrogen, and 47.48 % of oxygen. On heating, it is converted to a compound **B** containing 45.85 % of potassium, 16.47 % of nitrogen, and 37.66 % of oxygen.

Problem:

2.1 What are the stoichiometric formulas of the compounds?

2.2 Write the corresponding chemical equation.

SOLUTION

2.1 Compound **A**:

$K_xN_yO_z$ $$x : y : z = \frac{38.67}{39.1} = \frac{13.85}{14} = \frac{47.48}{16} = 0.989 : 0.989 : 2.968 = 1 : 1 : 3$$

A : KNO_3

Compound **B**:

$K_pN_qO_r$ $$p : q : r = \frac{45.85}{39.1} = \frac{16.47}{14} = \frac{37.66}{16} = 1.173 : 1.176 : 2.354 = 1 : 1 : 2$$

B : KNO_2

2.2 Equation: $2\ KNO_3 \rightarrow 2\ KNO_2 + O_2$

PROBLEM 4

Calcium carbide and water are the basic raw materials in the production of:

a) ethanol

b) acetic acid

c) ethylene and polyethylene

d) vinyl chloride

e) benzene

Problem:

Give basic chemical equations for each reaction by which the above mentioned compounds can be obtained.

SOLUTION

Basic reaction: $CaC_2 + 2\ H_2O = Ca(OH)_2 + C_2H_2$

From acetylene can be obtained:

a) ethanol

$$CH{\equiv}CH + H_2O \xrightarrow[\text{diluted } H_2SO_4]{HgSO_4\ \text{(catalyst)}} \underset{\text{vinyl alcohol}}{CH_2{=}CH{-}OH} \longrightarrow$$

$$\xrightarrow{\text{rearrangement}} \underset{\text{acetaldehyde}}{CH_3{-}CH{=}O} \xrightarrow{\text{reduction}} \underset{\text{ethanol}}{CH_3{-}CH_2{-}OH}$$

b) acetic acid

$$CH{\equiv}CH + H_2O \xrightarrow[\text{diluted } H_2SO_4]{HgSO_4\ \text{(catalyst)}} \underset{\text{vinyl alcohol}}{CH_2{=}CH{-}OH} \longrightarrow$$

$$\xrightarrow{\text{rearrangement}} \underset{\text{acetaldehyde}}{CH_3{-}CH{=}O} \xrightarrow{\text{oxidation}} \underset{\text{acetic acid}}{CH_3{-}COOH}$$

c) ethylene, polyethylene

$$CH{\equiv}CH + H_2O \xrightarrow{\text{catalyst}} CH_2{=}CH_2$$

ethylene

$$CH_2{=}CH_2 \xrightarrow[\text{catalyst}]{\text{pressure, temperature}} (\text{-}\ CH_2\ \text{-}\ CH_2\ \text{-}\ )_n$$

polyethylene

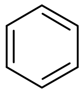
d) vinyl chloride

$$CH{\equiv}CH + HCl \longrightarrow CH_2{=}CH{-}Cl$$

vinyl chloride

e) benzene

$$3\ CH{\equiv}CH \xrightarrow{400\ \text{-}500\ ^\circ C}$$



PROBLEM 3

Carbon monoxide was mixed with 1.5 times greater volume of water vapours. What will be the composition (in mass as well as in volume %) of the gaseous mixture in the equilibrium state if 80 % of carbon monoxide is converted to carbon dioxide?

SOLUTION

$CO + H_2O \rightleftharpoons CO_2 + H_2$

Assumption:

$n(CO) = 1$ mol

$n(H_2O) = 1.5$ mol

After reaction:

$n(CO) = 0.2$ mol

$n(H_2O) = 0.7$ mol

$n(CO_2) = 0.8$ mol

$n(H_2) = 0.8$ mol

$$\varphi(CO) = \frac{V(CO)}{V} = \frac{0.2\text{ mol}}{2.5\text{ mol}} = 0.08 \text{ i.e. 8 vol. \% of CO}$$

$$\varphi(H_2O) = \frac{V(H_2O)}{V} = \frac{0.7\text{ mol}}{2.5\text{ mol}} = 0.28 \text{ i.e. 28 vol. \% of } H_2O$$

$$\varphi(CO_2) = \frac{V(CO_2)}{V} = \frac{0.8\text{ mol}}{2.5\text{ mol}} = 0.32 \text{ i.e. 32 vol. \% of } CO_2$$

$$\varphi(H_2) = \frac{V(H_2)}{V} = \frac{0.8\text{ mol}}{2.5\text{ mol}} = 0.32 \text{ i.e. 32 vol. \% of } H_2$$

Before reaction:

$m(CO) = n(CO) \times M(CO) = 1 \text{ mol} \times 28 \text{ g mol}^{-1} = 28 \text{ g}$

$m(H_2O) = 1.5 \text{ mol} \times 18 \text{ g mol}^{-1} = 27 \text{ g}$

After reaction:

$m(\text{CO}) = 0{,}2 \text{ mol} \times 28 \text{ g mol}^{-1} = 5.6 \text{ g}$

$m(\text{H}_2\text{O}) = 0.7 \text{ mol} \times 18 \text{ g mol}^{-1} = 12.6 \text{ g}$

$m(\text{CO}_2) = 0.8 \text{ mol} \times 44 \text{ g mol}^{-1} = 35.2 \text{ g}$

$m(\text{H}_2) = 0.8 \times 2 \text{ g mol}^{-1} = 1.6 \text{ g}$

$$w(\text{CO}) = \frac{m(\text{CO})}{m} = \frac{5.6 \text{ g}}{55.0 \text{ g}} = 0.102 \text{ i.e. } 10.2 \text{ mass \% of CO}$$

$$w(\text{H}_2\text{O}) = \frac{m(\text{H}_2\text{O})}{m} = \frac{12.6 \text{ g}}{55.0 \text{ g}} = 0.229 \text{ i.e. } 22.9 \text{ mass \% of H}_2\text{O}$$

$$w(\text{CO}_2) = \frac{m(\text{CO}_2)}{m} = \frac{35.2 \text{ g}}{55.0 \text{ g}} = 0.640 \text{ i.e. } 64.0 \text{ mass \% of CO}_2$$

$$w(H_2) = \frac{m(\text{H}_2)}{m} = \frac{1.6 \text{ g}}{55.0 \text{ g}} = 0.029 \text{ i.e. } 2.9 \text{ mass \% of H}_2$$

PROBLEM 5

An amount of 20 g of cooper (II) oxide was treated with a stoichiometric amount of a warm 20% sulphuric acid solution to produce a solution of copper (II) sulphate.

Problem:

How many grams of crystalline copper(II) sulphate ($CuSO_4 . 5 H_2O$) have crystallised when the solution is cooled to 20 °C?

Relative atomic masses: $A_r(Cu) = 63.5$; $A_r(S) = 32$; $A_r(O) = 16$; $A_r(H) = 1$

Solubility of $CuSO_4$ at 20 °C: s = 20.9 g of $CuSO_4$ in 100 g of H_2O.

SOLUTION

$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$

$$n(\text{CuO}) = \frac{m(\text{CuO})}{M(\text{CuO})} = \frac{20\text{ g}}{79.5\text{ g mol}^{-1}} = 0.2516\text{ g}$$

$$n(\text{H}_2\text{SO}_4) = n(\text{CuSO}_4) = 0.2516\text{ mol}$$

Mass of the $CuSO_4$ solution obtained by the reaction:

m(solution $CuSO_4$) = m(CuO) + m(solution H_2SO_4) =

$$= m(\text{CuO}) + \frac{n(\text{H}_2\text{SO}_4)\times M(\text{H}_2\text{SO}_4)}{w(\text{H}_2\text{SO}_4)} = 20\text{ g} + \frac{0.2516\text{ mol}\times 98\text{ g mol}^{-1}}{0.20}$$

m(solution $CuSO_4$) = 143.28 g

Mass fraction of $CuSO_4$:

a) in the solution obtained:

$$w(\text{CuSO}_4) = \frac{m(\text{CuSO}_4)}{m(\text{solution CuSO}_4)} = \frac{n(\text{CuSO}_4)\times M(\text{CuSO}_4)}{m(\text{solution CuSO}_4)} = 0.28$$

b) in saturated solution of $CuSO_4$ at 20 °C:

$$w(\text{CuSO}_4) = \frac{20.9\text{ g}}{120.9\text{ g}} = 0.173$$

c) in crystalline $CuSO_4 . 5\ H_2O$:

$$w(CuSO_4) = \frac{M(CuSO_4)}{M(CuSO_4 . 5H_2O)} = 0.639$$

Mass balance equation for $CuSO_4$:

$0.28\ m = 0.639\ m_1 + 0.173\ m_2$

m - mass of the $CuSO_4$ solution obtained by the reaction at a higher temperature.

m_1 - mass of the crystalline $CuSO_4 . 5H_2O$.

m_2 - mass of the saturated solution of $CuSO_4$ at 20 °C.

$0.28 \times 143.28 = 0.639\ m_1 + 0.173 \times (143.28 - m_1)$

$m_1 = 32.9$ g

The yield of the crystallisation is 32.9 g of $CuSO_4 . 5H_2O$.

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THEORETICAL PROBLEMS

PROBLEM 1

A mixture of two solid elements with a mass of 1.52 g was treated with an excess of hydrochloric acid. A volume of 0.896 dm^3 of a gas was liberated in this process and 0.56 g of a residue remained which was undissolved in the excess of the acid.

In another experiment, 1.52 g of the same mixture were allowed to react with an excess of a 10 % sodium hydroxide solution. In this case 0.896 dm^3 of a gas were also evolved but 0.96 g of an undissolved residue remained.

In the third experiment, 1.52 g of the initial mixture were heated to a high temperature without access of the air. In this way a compound was formed which was totally soluble in hydrochloric acid and 0.448 dm^3 of an unknown gas were released. All the gas obtained was introduced into a one litre closed vessel filled with oxygen. After the reaction of the unknown gas with oxygen the pressure in the vessel decreased by approximately ten times (T = *const*).

<u>Problem:</u>

1.1 Write chemical equations for the above reactions and prove their correctness by calculations.

In solving the problem consider that the volumes of gases were measured at STP and round up the relative atomic masses to whole numbers.

SOLUTION

1.1 a) Reaction with hydrochloric acid:

1.52 g – 0.56 g = 0.96 g of a metal reacted and 0.896 dm^3 of hydrogen (0.04 mol) were formed.

$$\text{combining mass of the metal: } 11.2 \times \frac{0.96}{0.896} = 12 \text{ g}$$

Possible solutions:

Relative atomic mass of the metal	Oxidation number	Element	Satisfying?
12	I	C	No
24	II	Mg	Yes
36	III	Cl	No

Reaction: $Mg + 2 HCl \rightarrow MgCl_2 + H_2$

b) Reaction with sodium hydroxide:

1.52 g – 0.96 g = 0.56 g of an element reacted, 0.896 dm^3 (0.04 mol) of hydrogen were formed.

$$\text{combining mass of the metal: } 11.2 \times \frac{0.56}{0.896} = 7 \text{ g}$$

Possible solutions:

Relative atomic mass of the element	Oxidation number	Element	Satisfying?
7	I	Li	No
14	II	N	No
21	III	Ne	No
28	IV	Si	Yes

Reaction: $Si + 2 NaOH + H_2O \rightarrow Na_2SiO_3 + 2 H_2$

c) Combining of both elements:

0.96 g Mg + 0.56 g Si = 1.52 g of silicide Mg_xSi_y

$$w(\text{Mg}) = \frac{0.96 \text{ g}}{1.52 \text{ g}} = 0.63 \qquad w(\text{Si}) = \frac{0.56 \text{ g}}{1.52 \text{ g}} = 0.37$$

$$x : y = \frac{0.63}{24} : \frac{0.37}{28} = 2 : 1$$

silicide: Mg_2Si

d) Reaction of the silicide with acid:

$Mg_2Si + 4\ HCl \rightarrow 2\ MgCl_2 + SiH_4$

$$n(Mg_2Si) = \frac{1.52\ g}{76\ g\ mol^{-1}} = 0.02\ mol$$

$$n(SiH_4) = \frac{0.448\ dm^3}{22.4\ dm^3\ mol^{-1}} = 0.02\ mol$$

e) Reaction of silane with oxygen:

$SiH_4 + 2\ O_2 \rightarrow SiO_2 + 2\ H_2O$

$V = 1\ dm^3$

On the assumption that $T = const$: $p_2 = \frac{n_2}{n_1} p_1$

$$n_1(O_2) = \frac{1\ dm^3}{22.4\ dm^3\ mol^{-1}} = 0.0446\ mol$$

Consumption of oxygen in the reaction: $n(O_2) = 0.04\ mol$

The remainder of oxygen in the closed vessel:

$n_2(O_2) = 0.0446\ mol - 0.04\ mol = 0.0046\ mol$

$$p_2 = \frac{0.0046\ mol}{0.0446\ mol} \times p_1 \approx 0.1\ p_1$$

PROBLEM 2

A mixture of metallic iron with freshly prepared iron (II) and iron (III) oxides was heated in a closed vessel in the atmosphere of hydrogen. An amount of 4.72 g of the mixture when reacted, yields 3.92 g of iron and 0.90 g of water.

When the same amount of the mixture was allowed to react with an excess of a copper(II) sulphate solution, 4.96 g of a solid mixture were obtained.

Problems:

2.1 Calculate the amount of 7.3 % hydrochloric acid ($\rho = 1.03$ g cm^{-3}) which is needed for a total dissolution of 4.72 g of the starting mixture.

2.2 What volume of a gas at STP is released?

Relative atomic masses:

$A_r(O) = 16$; $A_r(S) = 32$; $A_r(Cl) = 35.5$; $A_r(Fe) = 56$; $A_r(Cu) = 64$

SOLUTION

2.1 a) Reduction by hydrogen:

$FeO + H_2 \rightarrow Fe + H_2O$

$n(Fe) = n(FeO)$; $n(H_2O) = n(FeO)$

$Fe_2O_3 + 3\, H_2 \rightarrow 2\, Fe + 3\, H_2O$

$n(Fe) = 2\, n(Fe_2O_3)$; $n(H_2O) = 3\, n(Fe_2O_3)$

The mass of iron after reduction: 3.92 g

The total amount of substance of iron after reduction:

$$n(\text{Fe}) + n(\text{FeO}) + 2\, n(\text{Fe}_2\text{O}_3) = \frac{3.92 \text{ g}}{56 \text{ g mol}^{-1}} = 0.07 \text{ mol} \qquad (1)$$

b) Reaction with copper(II) sulphate:

$Fe + CuSO_4 \rightarrow Cu + FeSO_4$

Increase of the mass: 4.96 g – 4.72 g = 0.24 g

After reaction of 1 mol Fe, an increase of the molar mass would be:

$M(Cu) - M(Fe) = 64 \text{ g mol}^{-1} - 56 \text{ g mol}^{-1} = 8 \text{ g mol}^{-1}$

Amount of substance of iron in the mixture:

$$n(\text{Fe}) = \frac{0.24\ \text{g}}{8\ \text{g mol}^{-1}} = 0.03\ \text{mol} \qquad (2)$$

c) Formation of water after reduction:

0.90 g H_2O, i.e. 0.05 mol

0.05 mol = n(Fe) + 3 $n(Fe_2O_3)$ (3)

By solving equations (1), (2), and (3):

n(FeO) = 0.02 mol

$n(Fe_2O_3)$ = 0.01 mol

d) Consumption of acid:

$Fe + 2\ HCl \rightarrow FeCl_2 + H_2$

$FeO + 2\ HCl \rightarrow FeCl_2 + H_2O$

$Fe_2O_3 + 6\ HCl \rightarrow 2\ FeCl_2 + 3\ H_2O$

$n(HCl) = 2\ n(Fe) + 2\ n(FeO) + 6\ n(Fe_2O_3) =$

$= 0.06\ \text{mol} + 0.04\ \text{mol} + 0.06\ \text{mol} = 0.16\ \text{mol}$

A part of iron reacts according to the equation:

$Fe + 2\ FeCl_3 \rightarrow 3\ FeCl_2$

$n(Fe) = 0.5 \times n(FeCl_3) = n(Fe_2O_3)$

n(Fe) = 0.01 mol

It means that the consumption of acid decreases by 0.02 mol.

The total consumption of acid: n(HCl) = 0.14 mol

$$V(7.3\%\ \text{HCl}) = \frac{n\ M}{w\ \rho} = \frac{0.14\ \text{mol} \times 36.5\ \text{g mol}^{-1}}{0.073 \times 1.03\ \text{g cm}^{-3}} = 68\ \text{cm}^3$$

2.2 Volume of hydrogen:

$Fe + 2\ HCl \rightarrow FeCl_2 + H_2$

Iron in the mixture: 0.03 mol

Iron reacted with $FeCl_3$: 0.01 mol

Iron reacted with acid: 0.02 mol

Hence, 0.02 mol of hydrogen, i.e. 0.448 dm^3 of hydrogen are formed.

PROBLEM 4

When solutions of two unknown substances are mixed together in stoichiometric ratio, 1.25 g of a precipitate are formed which contain a salt of a bivalent metal M. The precipitate when heated to 1100 °C is decomposed to 0.70 g of a solid metal oxide MO and another gaseous oxide. After evaporation of the filtrate, a dry residue with a mass of 2.0 g remains which yields two products by thermal decomposition at 215 °C: a gaseous oxide and 0.90 g of water vapour. The total volume of the gaseous mixture is 1.68 dm^3 (at STP).

Problem:

4.1 Determine the unknown compounds and write chemical equations for the above mentioned reactions.

SOLUTION

4.1 a) Dry residue: 2.0 g

H_2O: 0.90 g, i. e. 0.05 mol

Gaseous oxide A_xO_y: 1.1 g

$$n(\text{mixture}) = \frac{1.68\ \text{dm}^3}{22.4\ \text{dm}^3\ \text{mol}^{-1}} = 0.075\ \text{mol}$$

$n(A_xO_y) = n(\text{mixture}) - n(H_2O) = 0.025$ mol

$$M(A_xO_y) = \frac{1.1\ \text{g}}{0.025\ \text{mol}} = 44\ \text{g mol}^{-1}$$

$x\,M(A) = M(A_xO_y) - y\,M(O)$

Solution 1:

If x = 1 and y = 1, then $M(A) = M(A_xO_y) - M(O) = (44 - 16)\ \text{g mol}^{-1} = 28\ \text{g mol}^{-1}$

A = Si. It does not satisfy the requirements of the task.

Solution 2:

If x = 2 and y = 1 then $M(A) = 14\ \text{g mol}^{-1}$

A = N and the gaseous oxide is N_2O.

Solution 3:

If x = 1 and y = 2 then $M(A) = 12\ \text{g mol}^{-1}$

A = C and the gaseous oxide is CO_2.

Solution 2 is correct, since it is known that gaseous N_2O is formed by thermal decomposition of NH_4NO_3. This conclusion is supported by the following calculation:

$$M(\text{dry residue}) = \frac{2.0\text{ g}}{0.025\text{ mol}} = 80\text{ g mol}^{-1} = M(NH_4NO_3)$$

Reaction of the thermal decomposition:

$NH_4NO_3 \rightarrow N_2O + 2\ H_2O$

b) The precipitation reaction can be described by the following equation:

$M(NO_3)_2 + (NH_4)_2B \rightarrow MB + 2\ NH_4NO_3$

$$M(\text{MB}) = \frac{1.25\text{ g}}{0.0125\text{ mol}} = 100\text{ g mol}^{-1}$$

$$M(\text{MO}) = \frac{0.70\text{ g}}{0.0125\text{ mol}} = 56\text{ g mol}^{-1}$$

$M(\text{M}) = M(\text{MO}) - M(\text{O}) = 56 - 16 = 40\text{ g mol}^{-1}$

M = Ca

Since

- the decomposition temperature of the precipitate is 1100 °C,
- the product of thermal decomposition is CaO,
- the molar mass of the precipitate is 100 g mol^{-1},
- the precipitate is $CaCO_3$.

Reaction:

$Ca(NO_3)_2 + (NH_4)_2CO_3 \rightarrow CaCO_3 + 2\ NH_4NO_3$

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THEORETICAL PROBLEMS

PROBLEM 1

By electrochemical decomposition of water, there are in an electric circuit a voltmeter, platinum electrodes and a battery containing ten galvanic cells connected in series, each of it having the voltage of 1.5 V and internal resistance of 0.4 Ω. The resistance of the voltmeter is 0.5 Ω and the polarisation voltage of the battery is 1.5 V. Electric current flows for 8 hours, 56 minutes and 7 seconds through the electrolyte. Hydrogen obtained in this way was used for a synthesis with another substance, thus forming a gaseous substance **A** which can be converted by oxidation with oxygen via oxide to substance **B**.

By means of substance **B** it is possible to prepare substance **C** from which after reduction by hydrogen substance **D** can be obtained. Substance **D** reacts at 180 °C with a concentration solution of sulphuric acid to produce sulphanilic acid. By diazotization and successive copulation with p-N,N-dimethylaniline, an azo dye, methyl orange is formed.

Problems:

1. Write chemical equations for all the above mentioned reactions.
2. Calculate the mass of product **D**.
3. Give the exact chemical name for the indicator methyl orange. Show by means of structural formulas what changes take place in dependence on concentration of H_3O^+ ions in the solution.

Relative atomic masses: $A_r(N) = 14$; $A_r(O) = 16$; $A_r(C) = 12$; $A_r(H) = 1$.

SOLUTION

1. $N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$

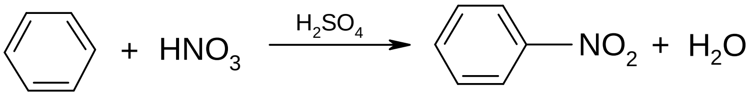
(**A**)

$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O$

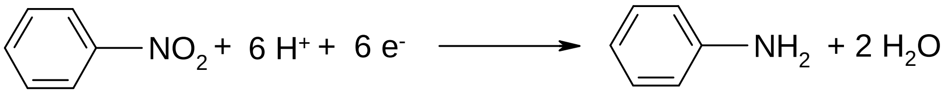
$2\,NO + O_2 \rightarrow 2\,NO_2$

$2\,NO_2 + H_2O + 1/2\,O_2 \rightarrow 2\,HNO_3$

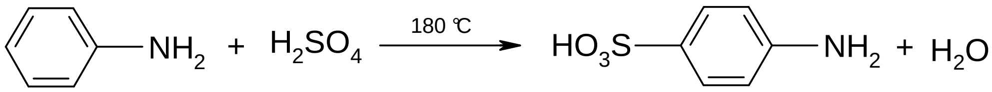
(**B**)

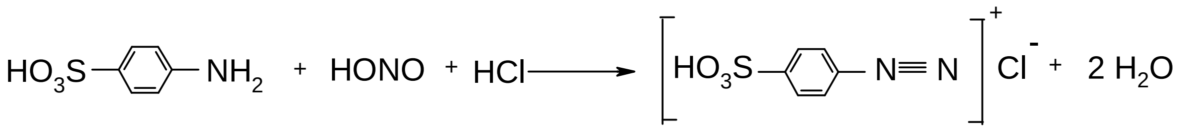


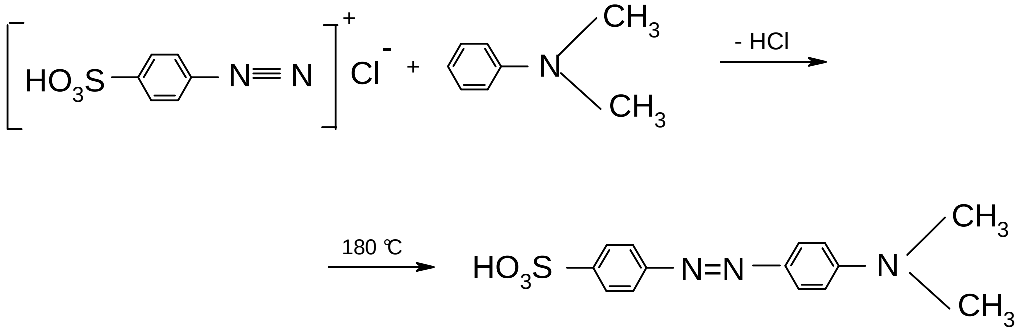
(**C**)



(**D**)







4'-dimethyl amino 4-azo benzene sulphonic acid

2. $$m = \frac{M}{F\,z}\,I\,t$$

$F = 96500$ C mol^{-1}

$$I = \frac{\text{b}\,E_b - E_p}{R_v + \text{b}\,R_i} = \frac{(10 \times 1.5\ \text{V}) - 1.5\ \text{V}}{0.5\ \Omega + (10 \times 0.4\ \Omega)} = 3\ \text{A}$$

b - number of batteries,

E_b - voltage of one battery,

E_p - polarisation voltage,

R_v - resistance of voltmeter,

R_i - internal resistance of one battery

$$m(\text{H}_2) = \frac{1\ \text{g mol}^{-1}}{96500\ \text{C mol}^{-1}} \times 3\ \text{A} \times 32167\ \text{s} = 1\ \text{g}$$

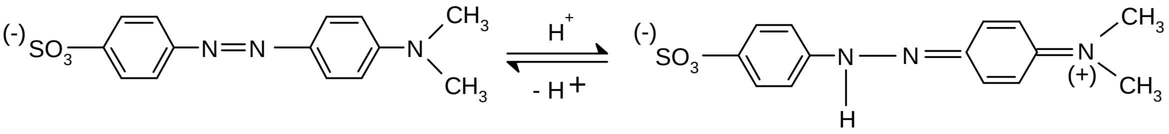
From equations:

1 g H_2 i. e. 0.5 mol H_2 corresponds $\frac{1}{3}$ mol NH_3 .... $\frac{1}{3}$ mol HNO_3 .... $\frac{1}{3}$ mol $C_6H_5NO_2$ .... $\frac{1}{3}$ mol $C_6H_5NH_2$ (**D**)

The mass of product **D**:

$m = n\,M = 31$ g $C_6H_5NH_2$

3.



PROBLEM 5

A mixture of two metals found in Mendelejev's periodical table in different groups, reacted with 56 cm^3 of hydrogen on heating (measured at STP conditions) to produce two ionic compounds. These compounds were allowed to react with 270 mg of water but only one third of water reacted. A basic solution was formed in which the content of hydroxides was 30 % by mass and at the same time deposited a precipitate with a mass that represented 59.05 % of a total mass of the products formed by the reaction. After filtration the precipitate was heated and its mass decreased by 27 mg.

When a stoichiometric amount of ammonium carbonate was added to the basic solution, a slightly soluble precipitate was obtained, at the same time ammonia was liberated and the content of hydroxides in the solution decreased to 16.81 %.

Problem:

5.1 Determine the metals in the starting mixture and their masses.

SOLUTION

Ionic hydrides are formed by combining of alkali metals or alkaline earth metals with hydrogen. In relation to the conditions in the task, there will be an alkali metal (M^I) as well as an alkaline earth metal (M^{II}) in the mixture.

Equations:

(1) $M^I + 1/2\ H_2 \rightarrow M^IH$

(2) $M^{II} + H_2 \rightarrow M^{II}H_2$

(3) $M^IH + H_2O \rightarrow M^IOH + H_2$

(4) $M^{II}H_2 + 2\ H_2O \rightarrow M^{II}(OH)_2 + 2\ H_2$

reacted: 0.09 g H_2O, i. e. 0.005 mol

unreacted: 0.18 g H_2O, i. e. 0.01 mol

Since all hydroxides of alkali metals are readily soluble in water, the undissolved precipitate is $M^{II}(OH)_2$, however, it is slightly soluble in water, too.

Thus, the mass of hydroxides dissolved in the solution:

(5) $m'(M^IOH + M^{II}(OH)_2) = Z$

Therefore:

$$30 = \frac{Z}{Z + 0.18} \times 100 \qquad\qquad Z = 0.077 \text{ g}$$

(6) $m'(M^IOH + M^{II}(OH)_2) = 0.077$ g

It represents 40.95 % of the total mass of the hydroxides, i. e. the <u>total mass of hydroxides</u> is as follows:

(7) $m'(M^IOH + M^{II}(OH)_2) = \dfrac{0.077 \text{ g} \times 100}{40.95} = 0.188$ g

The mass of solid $M^{II}(OH)_2$:

(8) 0.188 g – 0.077 g = 0.111 g

Heating:

(9) $M^{II}(OH)_2 \rightarrow M^{II}O + H_2O$

Decrease of the mass: 0.027 g (H_2O)

(10) <u>Mass of $M^{II}O$</u>: 0.084 g

In relation to (8), (9), and (10):

$$\frac{M_r(M^{II}O)}{M_r(M^{II}O) + 18} = \frac{0.084}{0.111}$$

$M_r(M^{II}O) = 56 \text{ g mol}^{-1}$

$M_r(M^{II}) = M_r(M^{II}O) - M_r(O) = 56 - 16 = 40$

<u>M^{II} = Ca</u>

Precipitation with (NH_4CO_3):

(11) $Ca(OH)_2 + (NH_4)_2CO_3 \rightarrow CaCO_3 + 2\ NH_3 + 2\ H_2O$

According to (5) and (6) the mass of the solution was:

0.18 g + 0.077 g = 0.257 g

After precipitation with $(NH_4)_2CO_3$:

$$16.81 = \frac{m(M^IOH)}{m(\text{solution})} \times 100$$

Let us mark as n' the amount of substance of $Ca(OH)_2$ being present in the solution.

$M(Ca(OH)_2) = 74 \text{ g mol}^{-1}$

Taking into account the condition in the task as well as equation (11), we get:

$$16.81 = \frac{(0.077 - 74n') \times 100}{0.257 - 74n' + 2n' \times 18}$$

$n' = 5 \times 10^{-4}$ mol

The total amount of substance of $Ca(OH)_2$ (both in the precipitate and in the solution):

(12) $$n(Ca(OH)_2) = \frac{0.111\text{ g}}{74\text{ g mol}^{-1}} + 5 \times 10^{-4}\text{ mol} = 0.002\text{ mol} \quad \text{(i. e. 0.148 g)}$$

According to equations (3) and (4):

$n(H_2O) = 0.004$ mol (for $M^{II}H_2$)

$n(H_2O) = 0.001$ mol (for $M^{I}H$)

$n(M^{I}OH) = 0.001$ mol

According to equations (7) and (11):

$m(M^{I}OH) = 0.188\text{ g} - 0.148\text{ g} = 0.04\text{ g}$

$$M(M^{I}OH) = \frac{m(M^{I}OH)}{n(M^{I}OH)} = \frac{0.04\text{ g}}{0.001\text{ mol}} = 40\text{ g mol}^{-1}$$

$M^{I}OH = NaOH$

Composition of the mixture:

0.002 mol Ca + 0.001 mol Na

or

0.080 g Ca + 0.023 g Na

THE SEVENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
1–10 JULY 1975, VESZPRÉM, HUNGARY

THEORETICAL PROBLEMS

PROBLEM 1

How many grams of alum $KAl(SO_4)_2 . 12\ H_2O$ are crystallised out from 320 g $KAl(SO_4)_2$ solution saturated at 20 °C if 160 g of water are evaporated from the solution at 20 °C?

(The solution saturated at 20 °C contains 5.50 % of $KAl(SO_4)_2$ by mass.)

Relative atomic masses:

$A_r(K) = 39.10$; $A_r(Al) = 26.98$; $A_r(S) = 32.06$; $A_r(O) = 16.0$; $A_r(H) = 1.01$

SOLUTION

Let us mark

x - mass of crystallised alum,

y - mass of the saturated solution of $AlK(SO_4)_2$ which remains after crystallisation

Mass fraction of $KAl(SO_4)_2$ in the crystallohydrate is equal to 0.544.

Then: $320 = x + y + 160$

i. e. $y = 160 - x$

Mass balance equation for $AlK(SO_4)_2$:

$$320 \times 0.055 = x \,.\, 0.544 + (160 - x)\, 0.055$$

$$x = 18.0 \text{ g}$$

PROBLEM 8

a) Mark by the "+" in a corresponding window those molecules for which the assertions written on the left side of the Table, are true.

Assertion	Molecule			
	C_2H_4	N_2H_4	H_2O_2	H_2F_2
There is a covalent bond between two equal atoms				
The molecule contains a double bond				
The molecule is planar				
The molecule is polar				
There is also a hydrogen bond in the molecule				
It has basic properties in relation to water				

b) The following assertion and Table are incomplete. Fill in the dotted places by a missing word and the missing formulas, respectively.

Assertion: The electronic structures of the molecules (ions) being placed in the Table one under the other are . . . .

CH_4	C_2H_6	CO_3^{2-}	. . . . . .	$C_2O_4^{2-}$	. . . . . .
NH_4^+	$N_2H_6^{2+}$	. . . . . .	NO_2^+	. . . . . .	N_2

SOLUTION

a)

Assertion	Molecule			
	C_2H_4	N_2H_4	H_2O_2	H_2F_2
There is a covalent bond between two equal atoms	+	+	+	
The molecule contains a double bond	+			
The molecule is planar	+			+
The molecule is polar		+	+	+
There is also a hydrogen bond in the molecule				+
It has basic properties in relation to water		+		

b) **Assertion**: The electronic structures of the molecules (ions) being placed in the Table under the other are **isoelectronic**.

CH_4	C_2H_6	CO_3^{2-}	$\mathbf{CO_2}$	$C_2O_4^{2-}$	$\mathbf{C_2^{2-}}$
NH_4^+	$N_2H_6^{2+}$	$\mathbf{NO_3^-}$	NO_2^+	$\mathbf{N_2O_4}$	N_2

THE EIGHTH
INTERNATIONAL CHEMISTRY OLYMPIAD
10–19 JULY 1976, HALLE, GERMAN DEMOCRATIC REPUBLIC

THEORETICAL PROBLEMS

PROBLEM 1

1.1 Explain by means of generally used international symbols and formulas which compounds are named as peroxo compounds. Write summary formulas for six of them.

1.2 Write chemical equations for two methods of quantitative determination of the content of peroxide in calcium(II) peroxide.

1.3 By means of chemical equations express the following chemical reactions:

a) $[Cr(H_2O)_6]Cl_3$ dissolved in water, is mixed with an excess of sodium hydroxide solution. A clear green solution is formed. The colour of the solution changes to yellow when an aqueous hydrogen peroxide solution is added.

b) If an aqueous solution of a violet manganese compound is mixed with a hydrogen peroxide solution, the resulting solution is decolourised and a gas is released from it.

SOLUTION

1.1 Peroxo compounds contain the functional group: O_2^{2-}

Examples: H_2O_2, Na_2O_2, BaO_2, H_2SO_5, $H_2S_2O_8$, $K_2C_2O_6$, CrO_5, $[VO_2]^{3+}$

1.2 Calcium(II) peroxide is decomposed by an aqueous solution of a suitable acid, and H_2O_2 which is liberated, is determined by:

a) manganometric method,

b) iodometric method.

Equations:

a) $5\ H_2O_2 + 2\ MnO_4^- + 6\ H_3O^+ \rightarrow 2\ Mn^{2+} + 5\ O_2 + 14\ H_2O$

b) $H_2O_2 + 2\ I^- + 6\ H_3O^+ \rightarrow I_2 + 4\ H_2O$

$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

1.3 a) $[Cr(H_2O)_6]^{3+} + 4\ OH^- \rightarrow [Cr(OH)_4(H_2O)_2]^- + 4\ H_2O$

$2\ [Cr(OH)_4(H_2O)_2]^- + 3\ H_2O_2 + 2\ OH^- \rightarrow 2\ CrO_4^{2-} + 12\ H_2O$

b) Equation is given in 2a.

PROBLEM 2

A sample of 2.3793 g of crystallohydrate of the type M_xA_y .z H_2O, where M is a metal, reacted with an excess of $SOCl_2$. Gaseous products formed by the reaction were introduced into a barium chloride solution containing hydrochloric acid and hydrogen peroxide. Small quantities of $SOCl_2$ carried by the gaseous products were removed by freezing out. The mass of the precipitate that is deposited from the solution, was 14.004 g. It was found to contain 13.74 mass % of sulphur.

In another experiment, 1.1896 g of the initial substance were dissolved in water and the solution was diluted to a volume of 100 cm^3. One fifth of this solution required to react with 10 cm^3 of a 0.2-molar $AgNO_3$ solution. The mass of the precipitate formed by the titration was 0.28664 g. (The end point of the titration was determined by the conductometric method.)

Problems:

2.1 Calculate the summary formula of the crystallohydrate. (Use the relative atomic mass values given in the attached Periodical Table of Elements.)

2.2 If you know that the sample can contain a maximum of seven moles of water per one mole of the crystallohydrate, give an example of another possible hydrate that cannot come into consideration due to the given limitation.

SOLUTION

2.1 a) The content of sulphur confirms that the precipitate is $BaSO_4$.

Reactions:

$M_xA_y \,.\, z\, H_2O + z\, SOCl_2 \rightarrow z\, SO_2 + 2\, z\, HCl + M_xA_y$

$z\, SO_2 + z\, H_2O_2 + z\, Ba^{2+} \rightarrow z\, BaSO_4 + 2\, z\, H^+$

$$n(BaSO_4) = \frac{m(BaSO_4)}{M(BaSO_4)} = \frac{14.004 \text{ g}}{233.4 \text{ g mol}^{-1}} = 0.06 \text{ mol}$$

<u>Amount of substance of H_2O in the hydrate</u>:

$n(H_2O) = 0.06$ mol

b) Amount of substance of A^- in the sample:

Reaction: $Ag^+ + A^- \rightarrow AgA$

$n(Ag^+) = c\,V = 0.2 \text{ mol dm}^{-3} \times 0.01 \text{ dm}^3 = 0.002 \text{ mol}$

$n(AgA) = 0.002 \text{ mol}$

$$M(AgA) = \frac{m(AgA)}{n(AgA)} = \frac{0.28664 \text{ g}}{0.002 \text{ mol}} = 143.32 \text{ g mol}^{-1}$$

A = Cl

The precipitate being formed by the titration is AgCl, thus the hydrate is a chloride.

$\frac{1.1896}{5}$ g, i. e. 0.23792 g of the hydrate contain 0.002 mol Cl^-

2.3792 g of the hydrate contain 0.02 mol Cl^-.

The molar ratio of Cl^- to H_2O in the hydrate:

$n(Cl^-) : n(H_2O) = 0.02 : 0.06 = 1 : 3$

Assumption:

i) $MCl . 3 H_2O$

$n(Cl^-) = 0.02 \text{ mol}$

$n(MCl . 3 H_2O) = 0.02 \text{ mol}$

$$M(MCl_3 . 3 H_20) = \frac{2{,}3793 \text{ g}}{0{,}02 \text{ mol}} = 118.965 \text{ g mol}^{-1}$$

$M(M) = M(MCl . 3 H_2O) - M(Cl) - 3\,M(H_2O) =$

$= 118.965 - 35.453 - 54.046 = 29.466 \text{ g mol}^{-1}$

Elements with similar molar masses are non-metals, therefore the first assumption is not suitable.

ii) $MCl_2 . 6 H_2O$

$n(Cl^-) = 0.02 \text{ mol}$

$n(MCl_2 . 6 H_2O) = 0.01 \text{ mol}$

$$M(MCl_2 . 6 H_20) = \frac{2{,}3793 \text{ g}}{0{,}01 \text{ mol}} = 237.93 \text{ g mol}^{-1}$$

$M(M) = M(MCl_2 . 6 H_2O) - 2\,M(Cl) - 6\,M(H_2O) =$

$= 237.93 - 70.906 - 108.092 = 58.932 \text{ g mol}^{-1}$

M = Co

The second assumption satisfies the conditions of the task.

The formula of the hydrate is: **$CoCl_2 . 6 H_2O$**

iii) $\underline{MCl_3 . 9 H_2O}$

$n(Cl^-) = 0.02$ mol

$$n(MCl_3 . 9 H_2O) = \frac{0.02}{3}\text{ mol}$$

$$M(MCl_3 . 9 H_2O) = 356.895\text{ g mol}^{-1}$$

$$M(M) = M(MCl_3 . 9 H_2O) - 3\,M(Cl) - 9\,M(H_2O) =$$

$$= 356.895 - 106.359 - 162.138 = 88.398\text{ g mol}^{-1}$$

<u>M = Y</u>

2.2 The hydrate $YCl_3 . 9 H_2O$ as well as the other hydrate $SnCl_4 . 12 H_2O$ cannot come into account because of the limitation in the task (a maximum of seven moles of H_2O pre one mole of the hydrate).

PROBLEM 3

A sample of 5 g of a technical iron(II) sulphide FeS, which contains 5 % metallic iron reacted with hydrochloric acid.

Problems:

3.1 Calculate the volume of the gaseous products at STP conditions.

3.2 What is the composition (in volume %) of the gaseous mixture?

SOLUTION

3.1 Reactions:

$Fe + 2\ HCl \rightarrow FeCl_2 + H_2$

$FeS + 2\ HCl \rightarrow FeCl_2 + H_2S$

$$n(\text{Fe}) = \frac{m(\text{Fe})}{M(\text{Fe})} = \frac{0.25\ \text{g}}{55.85\ \text{g mol}^{-1}} = 4.48 \times 10^{-3}\ \text{mol}$$

$$n(\text{FeS}) = \frac{m(\text{FeS})}{M(\text{FeS})} = \frac{4.75\ \text{g}}{87.91\ \text{g mol}^{-1}} = 5.40 \times 10^{-2}\ \text{mol}$$

$$V(\text{H}_2) = n(\text{H}_2) \times V_0 = 4.48 \times 10^{-3}\ \text{mol} \times 22.4\ \text{dm}^3\ \text{mol}^{-1} = \underline{0.1\ \text{dm}^3}$$

$$V(\text{H}_2\text{S}) = n(\text{H}_2\text{S}) \times V_0 = 5.40 \times 10^{-2}\ \text{mol} \times 22.4\ \text{dm}^3\ \text{mol}^{-1} = 1\underline{.21\ \text{dm}^3}$$

3.2 Composition of the gaseous mixture:

$$\frac{0.1\ \text{dm}^3}{1.31\ \text{dm}^3} \times 100 = 7.63\ \text{volume \% of H}_2$$

$$\frac{1.21\ \text{dm}^3}{1.31\ \text{dm}^3} \times 100 = 92.37\ \text{volume \% of H}_2\text{S}$$

THE NINTH
INTERNATIONAL CHEMISTRY OLYMPIAD
4–14 JULY 1977, BRATISLAVA, CZECHOSLOVAKIA

THEORETICAL PROBLEMS

PROBLEM 1

Compare three salts of a composition $M_2S_2O_x$ where x are three different small integers and M is an alkali metal. To each of the three salts apply some of the following assertions:

a) The O–O bond is characteristic for the anion.
b) The S–S bond is characteristic for the anion.
c) The S–O–S bond is characteristic for the anion.
d) It is formed by thermal decomposition of hydrogen sulphate.
e) It is formed by anodic oxidation of hydrogen sulphate.
f) It is formed by the reaction of an aqueous solution of sulphite with sulphur.
g) Its aqueous solution dissolves silver bromide.
h) Neutralisation of its aqueous solution with hydroxide MOH yields sulphate M_2SO_4.
i) In aqueous solution, it is able to oxidise Mn(II) salt to permanganate.

Problems:

1.1 Fill in the correct x values in the formulas given in the Table and indicate in the corresponding square by appropriate letters those assertions that may be applied to each of the given salts:

M_2S_2O☐					
M_2S_2O☐					
M_2S_2O☐					

1.2 Write structural formulas of the anions of the above three salts and assign σ-bonds and π-bonds in them.

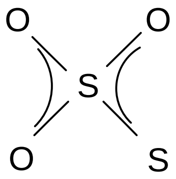
1.3 Write the chemical equations expressing the processes involved in the assertions under the letters d, e, f, g, h, i.

SOLUTION

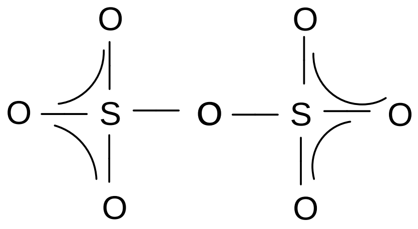
1.1

$M_2S_2O_3$	b	f	g		
$M_2S_2O_7$	c	d	h		
$M_2S_2O_8$	a	e	i		

1.2



$S_2O_3^{2-}$



$S_2O_7^{2-}$

1.3 d) $2\,HSO_4^- \rightarrow H_2O + S_2O_7^{2-}$

$2\,MHSO_4 \rightarrow H_2O + M_2S_2O_7$

e) $2\,HSO_4^- - 2e \rightarrow 2\,H^+ + S_2O_8^{2-}$

$2\,MHSO_4 - 2e \rightarrow 2\,H^+ + M_2S_2O_8$

f) $SO_3^{2-} + S \rightarrow S_2O_3^{2-}$

$M_2SO_3 + S \rightarrow M_2S_2O_3$

g) $AgBr + 2\,S_2O_3^{2-} \rightarrow [Ag(S_2O_3)_2]^{3-} + Br^-$

$AgBr + 2\,M_2S_2O_3 \rightarrow M_3[Ag(S_2O_3)_2] + MBr$

h) $S_2O_7^{2-} + 2\ OH^- \rightarrow 2\ SO_4^{2-} + H_2O$

$M_2S_2O_7 + 2\ MOH \rightarrow 2\ M_2SO_4 + H_2O$

i) $2\ Mn^{2+} + 5\ S_2O_8^{2-} + 8\ H_2O \rightarrow 2\ MnO_4^- + 10\ SO_4^{2-} + 16\ H^+$

$2\ MnSO_4 + 5\ M_2S_2O_8 + 8\ H_2O \rightarrow 2\ MMnO_4 + 4\ M_2SO_4 + 8\ H_2SO_4$

PROBLEM 2a

Note: The International Jury did not choose Task 2a for the competition but the alternative Task 2b.

Attention

Make sure to open only the correct envelopes.

You lose points for an incorrectly opened envelope.

Return unopened envelopes together with your solution.

Halogen X reacts with an aqueous solution of another halogen compound KYO_3 according to the equation:

$X_2 + 2\ KYO_3 \rightarrow 2\ KXO_3 + Y_2$

1. The atomic number of halogen X is greater than that of halogen Y. (If you find this answer correct open envelope 1.)
2. The atomic number of halogen X is smaller than that of halogen Y. (If you find this assertion correct open envelope 2.)

Choose the correct answer 1 or 2, open the correct envelope and continue in the solution according to the text in the opened envelope.

Text in envelope 1:

Your answer is correct. Continue.

Compound KXO_3 is oxidised in alkaline solution by halogen Y forming a compound $KX^{VII}O_4$ whereas halogen Y is reduced to halide KY:

$KXO_3 + 2\ KOH + Y_2 \rightarrow KXO_4 + 2\ KY + H_2O$

An aqueous solution of potassium halide KY yields with $AgNO_3$ solution a white precipitate AgY insoluble in water but readily soluble in aqueous ammonia solution.

3. Halogen Y is fluorine (envelope 3).
4. Halogen Y is chlorine (envelope 4).
5. Halogen Y is bromine (envelope 5).

Choose the correct answer 3, 4 or 5, open the corresponding envelope and carry on according to the instructions inside.

Text in envelope 2:

Your answer is incorrect. Choose envelope 1.

Text in envelope 3:

Your answer is incorrect. Choose answers 4 or 5.

Text in envelope 4:

Your answer is correct. Choose the final correct answer by indicating the correct alternative 6 or 7:

6. X = Br; $KXO_4 = KBrO_4$
7. X = I; $KXO_4 = KIO_4$

Text in envelope 5:

Your answer is incorrect. Choose answers 3 or 4.

SOLUTION

The correct answers are as follows: 1, 4, 7.

PROBLEM 2b

The reaction of permanganate ions with hydrogen peroxide in an acidic solution gives Mn(II) salt and at the same time oxygen is released:

$$2\ MnO_4^- + 1\ H_2O_2 + 6\ H^+ \rightarrow 2\ Mn^{2+} + 3\ O_2 + 4\ H_2O$$

$$2\ MnO_4^- + 3\ H_2O_2 + 6\ H^+ \rightarrow 2\ Mn^{2+} + 4\ O_2 + 6\ H_2O$$

$$2\ MnO_4^- + 5\ H_2O_2 + 6\ H^+ \rightarrow 2\ Mn^{2+} + 5\ O_2 + 8\ H_2O$$

$$2\ MnO_4^- + 7\ H_2O_2 + 6\ H^+ \rightarrow 2\ Mn^{2+} + 6\ O_2 + 10\ H_2O$$

Problems:

1. The possible ratios of the reactants in the above equations express:
   - a) all equations ☐
   - b) only some of the equations ☐
   - c) only one equation ☐
   - d) none ☐

Indicate the correct assertion by a cross in the corresponding square and explain your decision.

2. Which of the reactants is an oxidising agent and which is a reducing one?
3. How much potassium permanganate is needed to release 112 cm^3 of oxygen at STP conditions from an excess of hydrogen peroxide in acidic solution?

SOLUTION

1. Correct is **c**.

Explanation on the basis of electron balance:

$Mn^{VII} + 5\ e \rightarrow Mn^{II}$

$(O_2)^{-II} - 2\ e \rightarrow O_2^0$

$2\ Mn^{VII} + 5\ (O_2)^{-II} \rightarrow 2\ Mn^{II} + 5\ O_2^0$

2. Oxidising agent: MnO_4^- or Mn^{VII}

Reducing agent: H_2O_2 or $(O_2)^{-II}$

3. $V(O_2) = 112\ cm^3$

$$n(O_2) = \frac{0.112\ dm^{-3}}{22.4\ dm^3\ mol^{-1}} = 0.005\ mol$$

$$n(KMnO_4) = 0.005\ mol \times \frac{2}{5} = 0.002\ mol$$

$m(KMnO_4) = 0.316\ g$

PROBLEM 8a

Note: The International Jury did not choose Task 8a for the 9th IChO but the alternative Task 8b.

Due to the lack of other methods in the middle of the 19th century a chemist determining the molar mass of a new element **X** chose the following procedure:

He succeeded in preparing four compounds **A**, **B**, **C**, and **D** containing the element **X** and determined its content (in mass %) in each of the compounds. At 250 °C all four compounds were in gaseous state. They were individually transferred into previously evacuated flasks until the pressure reached the value of 1.013 .10^5 Pa and then the flasks were weighed. After subtracting the weight of the empty flask, the mass of the gas inside was determined. This procedure was repeated with nitrogen. Thus the following Table of data was obtained:

Gas	Total mass of gas	Content of element X in gas (mass %)
N_2	0.652 g	0
A	0.849 g	97.3
B	2.398 g	68.9
C	4.851 g	85.1
D	3.583 g	92.2

Problem:

8.1 Determine the probable molar mass of element **X**.

SOLUTION

8.1 $n(N_2) = \frac{m(N_2)}{M(N_2)} = \frac{0.652\text{ g}}{28\text{ g mol}^{-1}} = 0.0233\text{ mol}$

At a temperature of 250 °C all the substances **A**, **B**, **C**, and **D** are considered to behave as ideal gases and according to Avogadro's law:

$n(N_2) = n(\mathbf{A}) = n(\mathbf{B}) = n(\mathbf{C}) = n(\mathbf{D})$

$$M(\mathbf{A}) = \frac{m(\mathbf{A})}{n(\mathbf{A})}$$

$$M(\mathbf{B}) = \frac{m(\mathbf{B})}{n(\mathbf{B})}$$

$$M(\mathbf{C}) = \frac{m(\mathbf{C})}{n(\mathbf{C})}$$

$$M(\mathbf{D}) = \frac{m(\mathbf{D})}{n(\mathbf{D})}$$

The mass of element **X** in one mole of **A**, **B**, **C** or **D**:

A: $M(\mathbf{A}) \times 0.973 = 35.45$ g mol^{-1}

B: $M(\mathbf{B}) \times 0.689 = 70.91$ g mol^{-1}

C: $M(\mathbf{C}) \times 0.851 = 177.17$ g mol^{-1}

D: $M(\mathbf{D}) \times 0.922 = 141.78$ g mol^{-1}

Because in one molecule of a compound there must be at least one atom **X** or its integer multiple, we must calculate the highest common measure of the molar masses obtained. It is in our case equal to 35.45 g mol^{-1} in average which can be considered as the probable molar mass of element **X**. It is only the most probable value because its integer fraction cannot be excluded.

THE ELEVENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
2–11 JULY 1979, LENINGRAD, SOVIET UNION

THEORETICAL PROBLEMS

PROBLEM 1

When carrying out this programmed assignment, encircle those letters which in your opinion correspond to the correct answers to each of the 20 questions.

1. Which element is oxidized in the reaction between ethylene and an aqueous solution of potassium permanganate?

   A) carbon, B) hydrogen, C) potassium, D) manganese, E) oxygen.

2. How many litres of CO_2 will approximately be evolved in the reaction of 18 g of potassium hydrogen carbonate with 65 g of 10 % sulphuric acid?

   A) 1, B) 2, C) 3, D) 4, E) 5.

3. Which of the following hydrocarbons gives the maximum heat yield on complete combustion of 1 litre of the gas:

   A) propane, B) methane, C) acetylene, D) ethylene, E) all give the same yield.

4. How many isomers can have a compound if its formula is C_3H_5Br?

   A) 1, B) 2, C) 3, D) 4, E) 5.

5. Which of the following hydrocarbons will be the best engine fuel?

   A) cyclooctane, B) 2,2-dimethylhexane, C) normal octane, D) 3-ethylhexane, E) 2,2,4-trimethylpentane.

6. With which of the following compounds will an aqueous solution of a higher oxide of element No 33 react?

   A) CO_2, B) K_2SO_4, C) HCl, D) NaOH, E) magnesium.

7. What must be the minimum concentration (% by mass) of 1 kg of a potassium hydroxide solution for a complete neutralisation of 3.57 moles of nitric acid?

   A) 5 %, B) 10 %, C) 15 %, D) 20 %, E) 25 %.

8. How many compounds with the formula C_3H_9N can exist?

   A) 1, B) 2, C) 3, D) 4, E) 5.

9. In which of the following compounds has the nitrogen content (in mass %) a maximum value?

   A) potassium nitrate, B) barium nitrate, C) aluminium nitrate, D) lithium nitrate, E) sodium nitrate.

10. To which carbon atom (indicate the serial number) will chlorine mainly add in the reaction of HCl with penten-2-oic acid?

    A) 1, B) 2, C) 3, D) 4, E) 5.

11. How many moles of water are there per mole of calcium nitrate in a crystallohydrate if the water content is 30.5 % by mass?

    A) 1, B) 2, C) 3, D) 4, E) 5.

12. Which of these organic acids is the strongest?

    A) benzoic, B) 2-chlorobenzoic, C) 4-methylbenzoic, D) 2-aminobenzoic, E) 4-bromobenzoic.

13. Which of these acids has the highest degree of dissociation?

    A) HClO, B) $HClO_2$, C) $HClO_3$, D) $HClO_4$, E) all have the same degree.

14. Which of the salts given below do not undergo hydrolysis?

    A) potassium bromide, B) aluminium sulphate, C) sodium carbonate, D) iron(III) nitrate, E) barium sulphate.

15. How many litres of air are approximately required for complete combustion of 1 litre of ammonia?

    A) 1, B) 2, C) 3, D) 4, E) 5.

16. Which element is oxidised in the thermal decomposition of sodium hydrogen carbonate?

    A) sodium, B) hydrogen, C) oxygen, D) carbon, E) none.

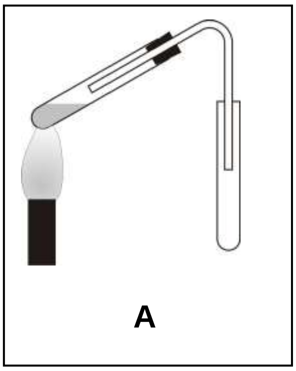
17. Which of the following changes have no effect on the chemical equilibrium in the thermal decomposition of $CaCO_3$?

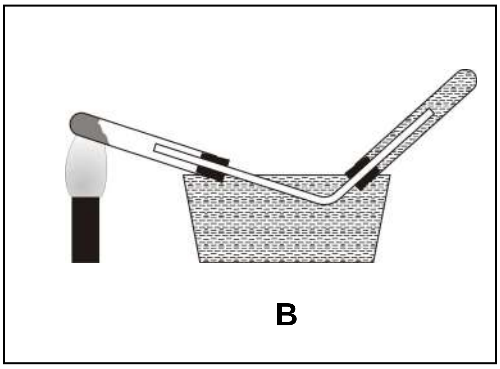
    A) temperature elevation, B) pressure decrease, C) addition of catalyst, D) a change in the CO_2 concentration, E) an increase in the amount of the initial substance.

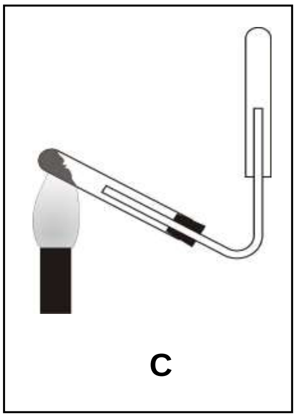
18. Which of the substances given bellow will be formed at the Pt-anode in the electrolysis of an aqueous solution of aluminium chloride?

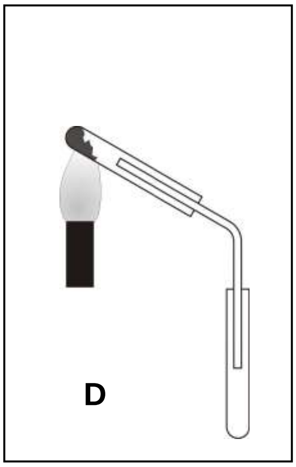
    A) aluminium, B) oxygen, C) hydrogen, D) aluminium hydroxide, E) chlorine.

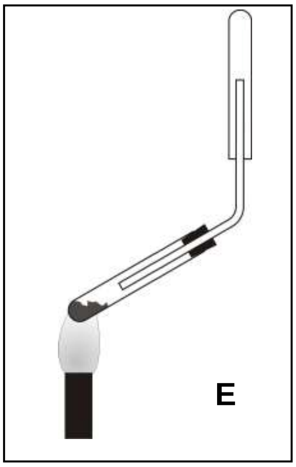
19. The apparatus shown in the figures is intended for preparing ammonia under laboratory conditions. The test tube being heated contains a mixture of NH_4Cl and $Ca(OH)_2$. Which of the figures is correct?



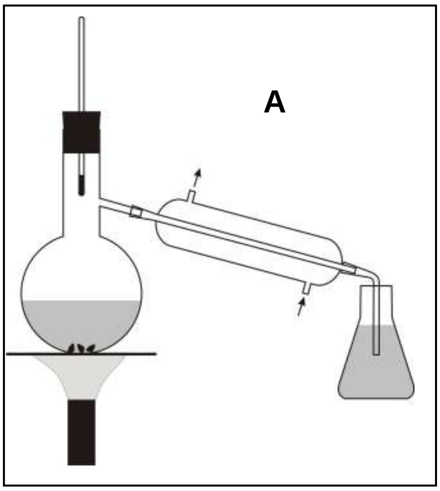


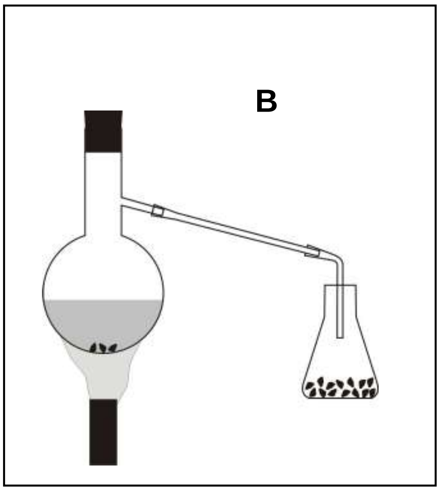


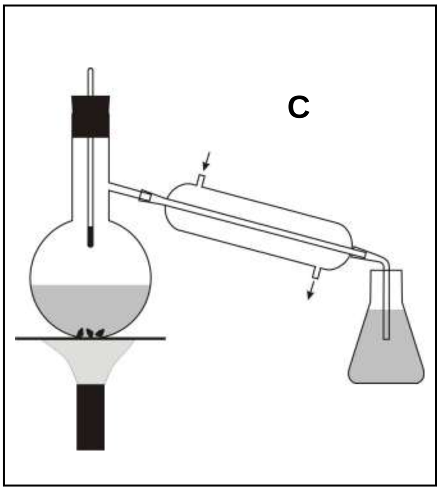


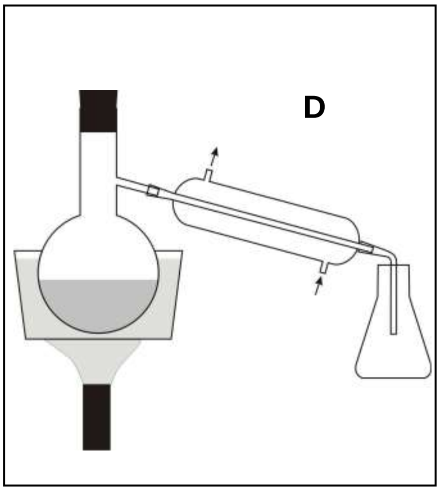


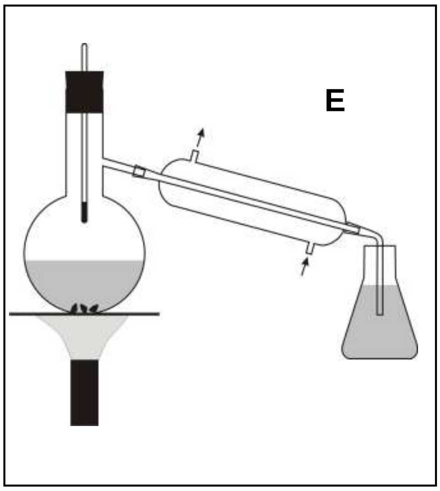
20. Which of the apparatuses shown in the figures is the best one for the synthesis of bromethane from potassium bromide, concentrated sulphuric acid and ethanol?











SOLUTION

1 –	A	6 –	D and E	11 –	D	16 –	E
2 –	C	7 –	D	12 –	B	17 –	C and E
3 –	A	8 –	D	13 –	D	18 –	B and E
4 –	E	9 –	D	14 –	A and E	19 –	C
5 –	E	10 –	C	15 –	D	20 –	A

PROBLEM 3

Which chemical processes can take place in the interaction of:

a) aluminium ammonium sulphate with baryta water,

b) potassium chromate, ferrous chloride and sulphuric acid,

c) calcinated soda and sodium hydrogen sulphate,

d) 4-bromoethyl benzene and chlorine,

e) n-propyl alcohol, phenol and concentrated sulphuric acid?

Write ionic equations for the reactions that proceed in aqueous solutions. For the other chemical reactions write complete equations and indicate the type of the reaction. Indicate the differences in the reaction conditions for those reactions that may lead to the formation of various substances.

SOLUTION

(a) a-1 $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow$

a-2 $NH_4^+ + OH^- \rightarrow NH_3.H_2O \rightarrow NH_3\uparrow + H_2O$

a-3 $Al^{3+} + 3\ OH^- \rightarrow Al(OH)_3\downarrow$

a-4 $Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$

a-5 possibly: $Ba^{2+} + 2\ [Al(OH)_4]^- \rightarrow Ba[Al(OH)_4]_2\downarrow$

(b) b-1 $2\ CrO_4^{2-} + 2\ H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

b-2 $6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \rightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$

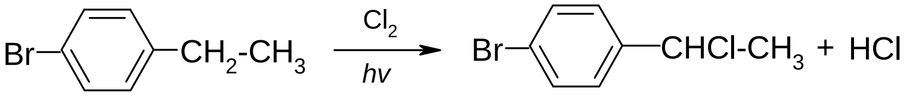
b-3 with high concentrations of Cl^- and H_2SO_4:

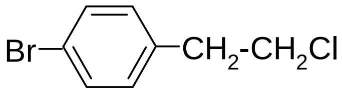
$Cr_2O_7^{2-} + 4\ Cl^- + 6\ H^+ \rightarrow CrO_2Cl_2 + 3\ H_2O$

(c) c-1 with excess of H^+: $CO_3^{2-} + 2\ H^+ \rightarrow H_2O.CO_2 \rightarrow H_2O + CO_2\uparrow$

c-2 with excwss of CO_3^{2-}: $CO_3^{2-} + H^+ \rightarrow HCO_3^-$

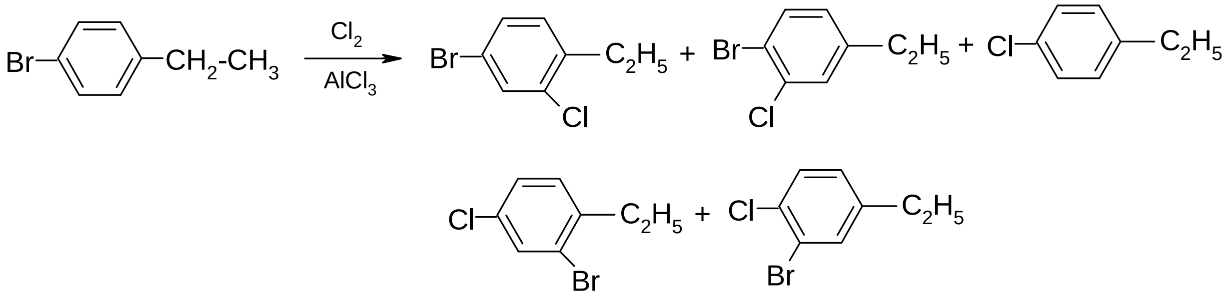
(d) d-1 free radical substitution (upon exposure to light or on heating)



small quantity of  and polychlorination

d-2 in the presence of electrophilic substitution catalysts:

and as side reaction products:



(e) e-1

$$CH_3CH_2CH_2OH + H_2SO_4 \xrightarrow[heat]{-\ H_2O} C_3H_7OSO_3H + H_2O \longrightarrow (C_3H_7O)_2SO_2 + H_2O$$

e-2

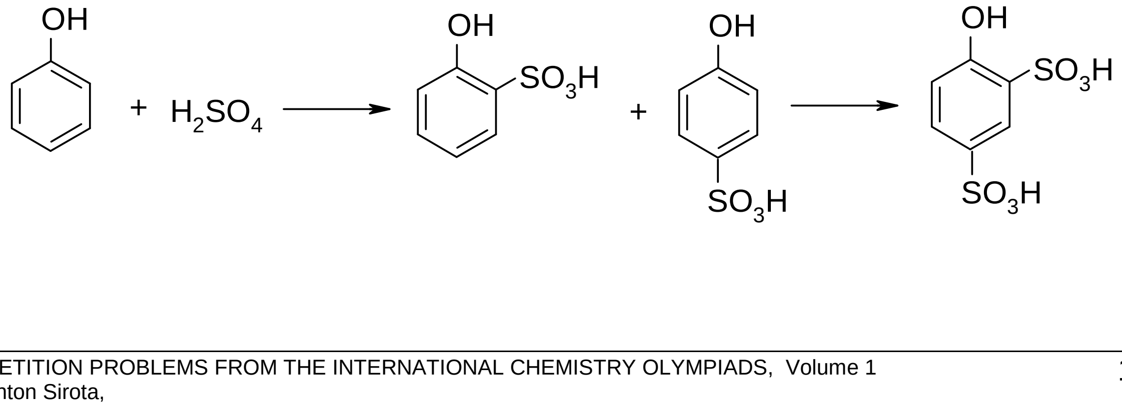
$$2\ C_3H_7OH + H_2SO_4 \xrightarrow[heat]{} C_3H_7OC_3H_7 \text{ (excess of } C_3H_7OH) + H_2O$$

e-3

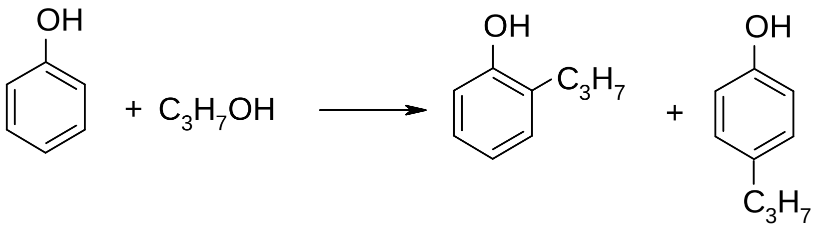
$$3\ CH_3CH_2CH_2OH \xrightarrow[heat]{H_2SO_4} CH_3CH{=}CH_2 \xrightarrow[H_2SO_4]{.H_2O} CH_3CH(OH)CH_3$$

(in e-1 and e-2)

e-4



e-5



polyalkylation n- and iso-

e-6 partial oxidation of C_3H_7OH and C_6H_5OH with subsequent condensation or esterification

PROBLEM 4

Compound **X** contains nitrogen and hydrogen. Strong heating of 3.2 g of **X** leads to its decomposition without the formation of a solid residue. The resulting mixture of gases is partially absorbed by sulphuric acid (the volume of the gaseous mixture decreased by a factor of 2.8). The non-absorbed gas, that is a mixture of hydrogen and nitrogen, occupies under normal conditions a volume of 1.4 dm^3 and has a density of 0.786 g dm^{-3}.

Determine the formula of compound **X**.

SOLUTION

If the density of the mixture of N_2 and H_2 is known, its composition can be determined as

$$0.786 \times 22.4 \times (n + 1) = 28\ n + 2$$

Hence n = 1.5. The mass of the mixture is 0.786 g $dm^{-3} \times 1.4 \approx 1.1$ g. Consequently, the mixture of gases absorbed by sulphuric acid (these gases could be NH_3 and N_2H_4) had an average molar mass of

$$\frac{3.2\ \text{g} - 1.1\ \text{g}}{1.4\ \text{dm}^3 \times (2.8 - 1)} \times 22.4\ \text{dm}^3\ \text{mol}^{-1} \cong 18.67\ \text{g mol}^{-1}$$

while NH_3 corresponds to 17 g mol^{-1}.

This means that the absorbed gaseous products consist of a mixture of NH_3 and N_2H_4. The composition of the absorbed fraction is

$$\frac{32 + 17\ n}{n + 1} = 18.67$$

n = 8, i. e. 8 NH_3 + N_2H_4.

As a result, the overall ratio of the components of the mixture is as follows:

8 NH_3 + N_2H_4 + 3 N_2 + 2 H_2 which corresponds to a composition of the initial substance X: N : H = (2 + 8 + 6) : (4 + 24 + 4) = 1 : 2.

The initial substance X is hydrazine N_2H_4.

PROBLEM 6

130 g of an unknown metal M were treated with excess of a dilute nitric acid. Excess hot alkaline solution was added to the resulting solution and 1.12 dm^3 of a gas evolved (normal conditions).

What metal M was dissolved in the nitric solution?

SOLUTION

The gas that evolved during the reaction with the alkaline solution was ammonia. Therefore, one of the products resulting from dissolution of the metal M in the acid is ammonium nitrate. Thus, the reaction equations will have the form:

$$8\ M + 10\ n\ HNO_3 \rightarrow 8\ M(NO_3)_n + n\ NH_4NO_3 + 3\ n\ H_2O$$

$$n\ NH_4NO_3 + n\ NaOH \rightarrow n\ NH_3 + n\ H_2O + NaNO_3$$

Hence, the scheme:

$$\begin{array}{lcl} x & & 1.12\ dm^3 \\ 8\ M & \longrightarrow & n\ NH_3 \\ 8\ A_r(M) & & n\ 22{,}4\ dm^3 \end{array}$$

where n is the valency of the metal (oxidation number of M^{n+}) and A_r(M) is the relative atomic mass of the metal.

$$8\ A_r(M) \quad \Rightarrow \quad 22.4 \times n$$

$$13\ g \quad \Rightarrow \quad 1.12\ dm^3$$

$$A_r(M) = \frac{13\ g \times 22.4\ dm^3 \times n}{8\ g \times 1{,}12\ dm^3} = 32.5\ n$$

If	n = 1	then	A_r(M) = 32.5	no metal
	n = 2		A_r(M) = 65	zinc
	n = 3		A_r(M) = 97,5	none
	n = 4		A_r(M) = 130	none

Answer: The unknown metal is zinc.

PROBLEM 3

(Chemistry of ions, stoichiometry, redox reactions)

A white crystalline solid compound **A** exhibits the following reactions:

1) The flame of a Bunsen burner is intensively yellow coloured.
2) An aqueous solution of **A** is neutral. Dropwise addition of sulphurous acid (an SO_2 solution) leads to a deep brown solution that is discoloured in the presence of excess of sulphurous acid.
3) If an $AgNO_3$ solution is added to the discoloured solution obtained by 2) and acidified with HNO_3, a yellow precipitate is obtained that is insoluble on addition of NH_3, but can be readily dissolved by adding CN^- or $S_2O_3^{2-}$.
4) If an aqueous solution of **A** is treated with KI and dilute H_2SO_4 a deep brown solution is formed that can be discoloured by addition of sulphurous acid or a $Na_2S_2O_3$ solution.
5) An amount of 0.1000 g of **A** is dissolved in water, then 0.5 g KI and a few cm^3 of dilute H_2SO_4 are added. The deep brown solution formed is titrated with 0.1000 M $Na_2S_2O_3$ solution until the solution is completely discoloured. The consumption is 37.40 cm^3.

Problems:

3.1 What elements are contained in the compound **A**?

3.2 What compounds can be considered as present on the basis of reactions 1) to 4)? Calculate their molar masses.

3.3 Formulate the reactions corresponding to 2) to 4) for the compounds considered and write the corresponding equations in the ionic form.

3.4 Decide on the basis of 5) which compound is present.

SOLUTION

3.1 The solid must contain Na and I. The yellow colouration of the flame of the Bunsen burner indicates the presence of Na. A yellow silver salt that is dissolved only by strong complexing agents such as CN^- or $S_2O_3^{2-}$, must be AgI.

3.2 Reactions 1) to 4) indicate an Na salt of an oxygen containing acid of iodine:

Both SO_2 and I^- are oxidised. While in the first case I^- is formed with an intermediate of I_2 (or I_3^-, brown solution), in the second I_2 (or I_3^-) is formed.

As the solution of **A** is neutral, $NaIO_3$ and $NaIO_4$ come into consideration.

$M(NaIO_3) = 22.99 + 126.905 + 3 \times 16.000 = 197.895 = 197.90 \text{ g mol}^{-1}$

$M(NaIO_4) = 22.99 + 126.905 + 4 \times 16.000 = 213.895 = 213.90 \text{ g mol}^{-1}$

3.3 $2\,IO_3^- + 4\,H_2O + 5\,SO_2 = 5\,HSO_4^- + 3\,H^+ + I_2$

$I_2 + SO_2 + 2\,H_2O = HSO_4^- + 3\,H^+ + 2\,I^-$

$IO_4^- + 7\,I^- + 8\,H^+ = 4\,I_2 + 4\,H_2O$

$IO_3^- + 5\,I^- + 6\,H^+ = 3\,I_2 + 3\,H_2O$

$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-}$

3.4 Experiment: 0.1000 g of the compound **A** ...... 3.740×10^{-3} moles $S_2O_3^{2-}$

1st hypothesis: The compound is $NaIO_3$.

1 mole $NaIO_3$ . . . . 197.90 g $NaIO_3$ . . . . 6 moles $S_2O_3^{2-}$

0.1000 g $NaIO_3$ . . . . $\dfrac{0.1000 \times 6}{197.90} = 3.032 \times 10^{-3}$ moles $S_2O_3^{2-}$

The hypothesis is false.

2nd hypothesis: The compound is $NaIO_4$.

mole $NaIO_4$ . . . . 213.90 g $NaIO_4$ . . . . 8 moles $S_2O_3^{2-}$

0.1000 g $NaIO_4$ . . . . $\dfrac{0.1000 \times 8}{213.90} = 3.740 \times 10^{-3}$ moles $S_2O_3^{2-}$

The compound **A** is $NaIO_4$.

PROBLEM 5

(Inorganic chemistry)

From 20 mg of partially methylated disilane, $Si_2H_{6-x}(CH_3)_x$, 27.8 cm^3 of hydrogen are evolved during alkaline hydrolysis at 294 K and 97400 Pa.

5.1 Why the Si-Si bond of the disilane reacts during hydrolysis?

5.2 Why the Si-H bonds of the disilane react during hydrolysis?

5.3 Calculate the degree of substitution x of the methylated disilane.

5.4 Write the complete reaction equation for the hydrolysis.

5.5 How many isomers can form the calculated compound? Give the structural formula for each isomer.

SOLUTION

5.1 The Si-Si bond is coordination unsaturated and thus, has a tendency to react with nucleophilic reagents with the bond breakage.

5.2 Similar to all compounds with negatively polarised hydrogen, this bond also reacts with protons from water with formation of elemental hydrogen.

5.3 $(CH_3)_xSi_2H_{6-x}$

Molecular mass: 2 Si 2×28.086

(6-x) H $(6-x) \times 1.008$

x CH_3 $x \times 15.035$

$56.172 + 1.008\,(6 - x) + 15.035\,x = 62.22 + 14.027\,x$

Sample mass**:** 20 mg $\Rightarrow \dfrac{20}{62.22 + 14.027\,x}$ mmol

Hydrogen evolved: $n = \dfrac{pV}{RT}$ mmol H_2 (V in cm^3)

$$n = \frac{0.974 \times 27.8}{0.08314 \times 294} \text{ mmol}$$

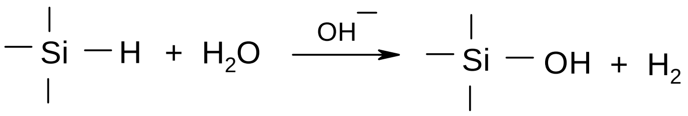
(SiH) (SiSi)

$$(6 - x + 1) \times \frac{20}{62.22 + 14.027\,x} = \frac{0.974 \times 27.8}{0.08314 \times 294}$$

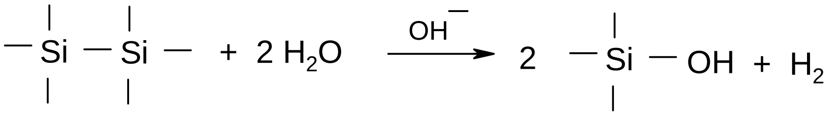
x = 1.9999

Hence, the degree of substitution = 2

5.4



$$-\text{Si}-\text{H} + H_2O \xrightarrow{OH^-} -\text{Si}-\text{OH} + H_2$$



$$-\text{Si}-\text{Si}- + 2\,H_2O \xrightarrow{OH^-} 2\ -\text{Si}-\text{OH} + H_2$$

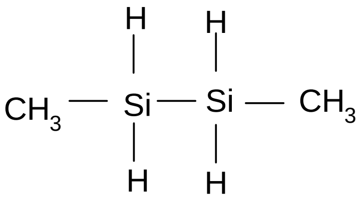
Hence (for a symmetrical isomer):

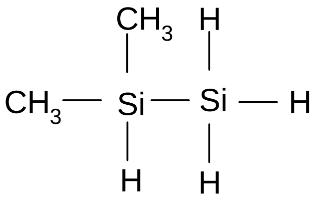
$Si_2H_4(CH_3)_2 + 6\ H_2O \rightarrow 2\ Si(OH)_3CH_3 + 5\ H_2$ / n

$2\ n\ Si(OH)_3CH_3 \rightarrow [Si_2O_3(CH_3)_2]_n + 3\ n\ H_2O$

$n\ Si_2H_4(CH_3)_2 + 3\ n\ H_2O \rightarrow [Si_2O_3(CH_3)_2]_n + 5\ n\ H_2$

5.5 Two:





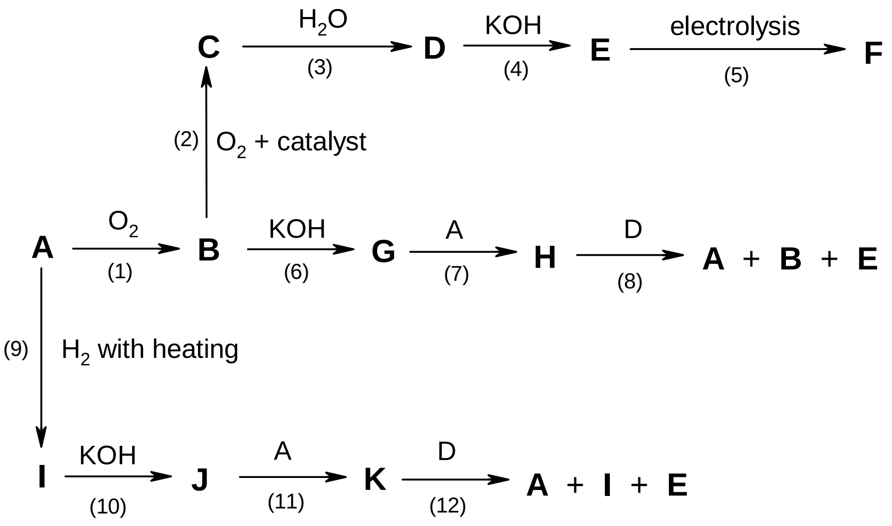
THE THIRTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
13–23 JULY 1981, BURGAS, BULGARIA

THEORETICAL PROBLEMS

PROBLEM 1

The sample **A** participates in the transformations in scheme 1. Only the products containing **A** are shown in the scheme 1.

Scheme 1



a) Substance **A** is a solid and is insoluble in water.

b) Substances **B** and **I** are gases soluble in water.

c) Substances **E**, **F**, **J** and **K** are solid and soluble in water.

d) Aqueous solutions of **B**, **G**, **H**, **I**, **J** and **K** react with **F**, the products in all cases being **E** and **D**.

e) The following transformations occur during the interaction with an aqueous solution of iodine:

$$\mathbf{B} \xrightarrow{(19)} \mathbf{D} \qquad \mathbf{G} \xrightarrow{(20)} \mathbf{E} \qquad \mathbf{H} \xrightarrow{(21)} \mathbf{L}$$

$$\mathbf{I} \xrightarrow[(22)]{} \mathbf{A} \qquad \mathbf{J} \xrightarrow[(23)]{} \mathbf{A} \qquad \mathbf{K} \xrightarrow[(24)]{} \mathbf{A}$$

Write the chemical equations for the above interactions and balance them.

SOLUTION

Schéma:

(1) $S + O_2 \rightarrow SO_2$

(2) $2\ SO_2 + O_2 \rightarrow 2\ SO_3$

(3) $SO_3 + H_2O \rightarrow H_2SO_4$

(4) $2\ KOH + H_2SO_4 \rightarrow K_2SO_4 + 2\ H_2O$

(5) $2\ SO_4^{2-} - 2\ e- \rightarrow S_2O_8^{2-}$

(6) $SO_2 + 2\ KOH \rightarrow K_2SO_3 + H_2O$

(7) $K_2SO_3 + S \rightarrow K_2S_2O_3$

(8) $K_2S_2O_3 + H_2SO_4 \rightarrow K_2SO_4 + S + SO_2 + H_2O$

(9) $H_2 + S \rightarrow H_2S$

(10) $H_2S + 2\ KOH \rightarrow K_2S + 2\ H_2O$

(11) $K_2S + x\ S \rightarrow K_2S_{(x+1)}$

(12) $K_2S_{(x+1)} + H_2SO_4 \rightarrow K_2SO_4 + x\ S + H_2S$

d)

(13) $SO_2 + 2\ H_2O + K_2S_2O_8 \rightarrow K_2SO_4 + 2\ H_2SO_4$

(14) $K_2SO_3 + H_2O + K_2S_2O_8 \rightarrow 2\ K_2SO_4 + H_2SO_4$

(15) $K_2S_2O_3 + 5\ H_2O + 4\ K_2S_2O_8 \rightarrow 5\ H_2SO_4 + 5\ K_2SO_4$

(16) $H_2S + 4\ H_2O + 4\ K_2S_2O_8 \rightarrow 5\ H_2SO_4 + 4\ K_2SO_4$

(17) $K_2S + 4\ H_2O + 4\ K_2S_2O_8 \rightarrow 4\ H_2SO_4 + 5\ K_2SO_4$

(18) $K_2S_{(x+1)} + (4x + 1)\ H_2O + 4\ x\ K_2S_2O_8 \rightarrow 5\ x\ H_2SO_4 + (4x + 1)\ K_2SO_4$ (+S)

e)

(19) $SO_2 + 2\ H_2O + I_2 \rightarrow H_2SO_4 + 2\ HI$

(20) $K_2SO_3 + H_2O + I_2 \rightarrow K_2SO_4 + 2\ HI$

(21) $2\ K_2S_2O_3 + I_2 \rightarrow 2\ KI + K_2S_4O_6$

(22) $H_2S + I_2 \rightarrow 2\ HI + S$

(23) $K_2S + I_2 \rightarrow 2\ KI + S$

(24) $K_2S_x + I_2 \rightarrow 2\ KI + x\ S$

A: S

B: SO_2

C: SO_3

D: H_2SO_4

E: K_2SO_4

F: $K_2S_2O_8$

G: K_2SO_3

H: $K_2S_2O_3$

I: H_2S

J: K_2S

K: K_2S_x

L: $K_2S_4O_6$

PROBLEM 4

The thermal decomposition of water

$H_2O \rightleftharpoons H_2 + ½\,O_2$

can be traced ($\alpha = 10^{-3}$) at temperature above 1700 K. This process can be realized at temperatures 800 – 900 K as well as through subsequent stages carried out in a cycle. Suggest such a process on the basis of the reactions:

$CuO(s) + MgCl_2(s) + H_2O(g) \xrightarrow{840\text{ K}} CuCl(s) + MgO(s) + HCl(g) + O_2(g)$

and

$Ag(s) + HCl(g) \xrightarrow{430\text{ K}} AgCl(s) + H_2(g)$

satisfying the following requirements:

a) Only water should be consumed during the process.

b) Oxygen and hydrogen alone should be the end products of the process.

c) In addition to the above substances, a 25 % ammonia solution is needed for the cycle.

d) The temperature for each step in the cycle should not exceed 840 K.

SOLUTION

1. $2\,CuO + 2\,MgCl_2 + H_2O \xrightarrow{840\text{ K}} 2\,CuCl + 2\,MgO + 2\,HCl + 0.5\,O_2$
2. $Ag + 2\,HCl \xrightarrow{430\text{ K}} 2\,AgCl + H_2$
3. $2\,CuCl + 4\,NH_3 \longrightarrow 2\,[Cu(NH_3)_2]^+ + 2\,Cl^-$
4. $2\,AgCl + 4\,NH_3 \longrightarrow 2\,[Ag(NH_3)_2]^+ + 2\,Cl^-$
5. $2\,[Cu(NH_3)_2]^+ + 2\,[Ag(NH_3)_2]^+ \longrightarrow 2\,Ag\downarrow + 2\,[Cu(NH_3)_4]^{2+}$
6. $2\,[Cu(NH_3)_4]^{2+} + 2\,MgO \xrightarrow{\text{boiling}} 2\,CuO\downarrow + 2\,Mg^{2+} + 8\,NH_3\uparrow$
7. $2\,Mg^{2+} + 4\,Cl^- \xrightarrow{\text{evaporation}} 2\,MgCl_2$
8. $H_2O \longrightarrow H_2 + 0.5\,O_2$

THE FOURTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
3–12 JULY 1982, STOCKHOLM, SWEDEN

THEORETICAL PROBLEMS

PROBLEM 1

A. The IUPAC name of the compound $[Co(NH_3)_6]Cl_2$ is

a) cobalt(II) hexaammonia dichlorine,

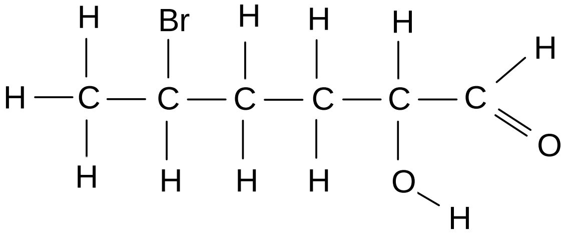
b) cobalt(II) hexaammonia dichloride,

c) hexaamminecobalt(II) chloride.

d) hexaamminedichlorocobalt(II)

e) cobalt(II) chloride-hexaammonia

B. The IUPAC name of the compound



is:

a) 5-bromo-1-hexanoic acid

b) 5-bromo-2-hydroxy-1-hexanal

c) 2-bromo-5-hydroxy-6-hexanal

d) 2-bromo-2-hydroxy-1-hexanal

e) 5-bromo-2-hydroxy-1-hexanone

C. Which of the following acid-base pairs is most suitable for keeping the pH constant at 9 in an aqueous solution?

a) CH_3COOH — CH_3COO^-

b) NH_4^+ — NH_3

c) H_2CO_3 — HCO_3^-

d) $H_2PO_4^- — HPO_4^{2-}$

e) $H_2C_2O_4 — HC_2O_4^-$

D. One of the following statements cannot be correct. State which one.

a) A water-soluble solid contains Mg^{2+}, Cr^{3+}, and $Br^–$.

b) A solid soluble in a sodium hydroxide solution contains Al^{3+}, K^+, and SO_4^{2-}.

c) A solid soluble in aqueous ammonia solution contains Ag^+, Cu^{2+}, and $Cl^–$.

d) A solid soluble in nitric acid contains Ba^{2+}, Fe^{2+}, and CO_3^{2-}.

e) A solution neutral to litmus contains Na+, Ca^{2+}, and PO_4^{3-}.

E. Complete the following equation:

$H_3AsO_4 + Zn \rightarrow AsH_3 + Zn^{2+}$

The reaction is carried out in an acid solution. Fill in the missing particles and balance the reaction equation.

F. State the degree of protolysis of acetic acid with concentration of 0.25 mol dm^{-3}.

$K_a(HAc) = 1.8 \times 10^{-5}$.

a) 0.021 %; b) 0.21 %; c) 0.84 %; d) 1.3 %; e) 8.4 %

G. A solution with a volume of 1.00 dm^3 is saturated with lead iodide, PbI_2. The concentration of iodide ions is 2.7 mol dm^{-3}. Determine the solubility product of PbI_2.

a) 3.6×10^{-6}; b) 2.0×10^{-8}; c) 9.8×10^{-9}; d) 2.5×10^{-9}; e) 4.9×10^{-9}.

H. The following standard enthalpies of formation are given:

Compound	ΔH^0
Acetic acid	- 0.50 MJ mol^{-1}
Carbon dioxide	- 0.40 MJ mol^{-1}
Water	- 0.30 MJ mol^{-1}

The ΔH^0 of combustion of acetic acid is:

a) 0.90 MJ mol^{-1}; b) - 0.90 MJ mol^{-1}; c) - 0.20 MJ mol^{-1};

d) - 2.1 MJ mol^{-1}; e) 0.20 MJ mol^{-1}

I. $COCl_2(g)$ is introduced in an empty vessel at a pressure of *a*. It dissociates and the following equilibrium is established at constant temperature:

$2\ COCl_2(g) \rightleftharpoons C(graphite) + CO_2(g) + 2\ Cl_2(g)$

If x represents the partial pressure of $CO_2(g)$ at equilibrium, what is the equilibrium expression?

a) $\frac{4x^3}{(a-2x)^2} = K_p$ b) $\frac{2x^4}{(a-2x)^2} = K_p$ c) $\frac{2x^3}{(a-x)^2} = K_p$

d) $\frac{4x^3}{(a-x)^2} = K_p$ e) $\frac{x^3}{(a-3x)^2} = K_p$

K. For a metal M the following redox data are known:

E^0 = - 0.60 V for $M^{2+}(aq) + e- \rightarrow M^+(aq)$

E^0 = 0.40 V for $M^{4+}(aq) + 2\ e- \rightarrow M^{2+}(aq)$

The E^0 for $M^{4+}(aq) + 3\ e- \rightarrow M^+(aq)$ is then:

a) - 0.20 V b) - 1.00 V c) 1.00 V d) 0.07 V e) - 0.07 V

SOLUTION

A. c) B. b) C. b) D. e)

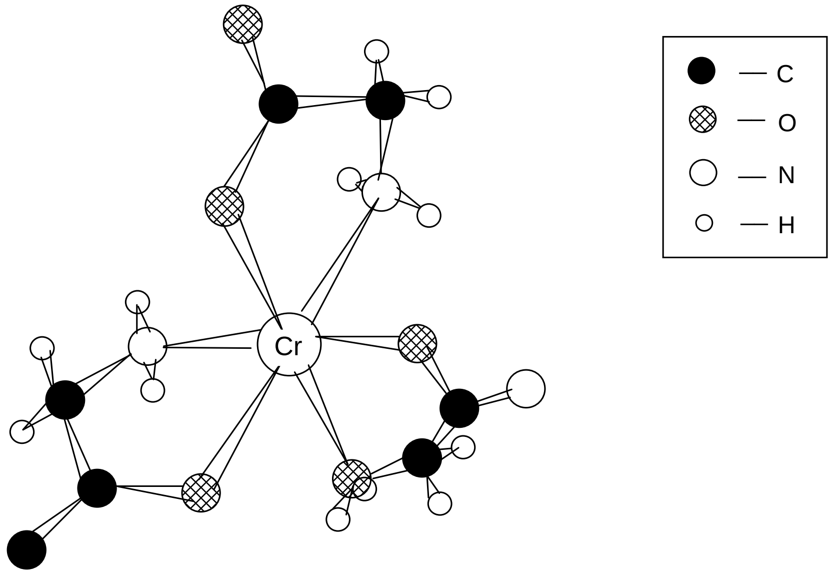
E. $H_3AsO_4 + 4\ Zn + 8\ H^+ \rightarrow AsH_3 + 4\ Zn^{2+} + 4\ H_2O$

F. c) G. c) H. b) I. a) K. d)

PROBLEM 4

A transition metal atom or ion may be directly bonded to a number of atoms or molecules that surround it (ligands), forming a characteristic pattern. This is the essential structural feature of an important class of so-called coordination or complex compounds. If two or more atoms from one individual ligand form bonds to the same central atom then the ligand is said to form a chelate (Greek chele = crab' claw).

The glycinate ion, NH_2–CH_2–COO^-, is a bidentate chelate ligand which can form, for instance, tris-glycinato-chromium(III) complexes. The figure shows one possible structure of such a complex. Oxygen and nitrogen are forced to coordinate to adjacent octahedral positions, as the N – C – C – O chain is too short to "embrace" the chromium ion.



4.1 How many different configurational isomers of the complex are possible, not counting optical isomers?

4.2 Which of these isomers can be further resolved into optical isomers?

Another coordination compound of chromium was analyzed and found to have the following mass composition: 19.5 % Cr, 40.0 % Cl, 4.5 % H, and 36.0 % O. A 0.533 g sample of the compound was dissolved in 100 cm^3 of water, and 10 cm^3 of nitric acid (2 mol dm^{-3}) was added. Excess of silver nitrate solution was then added and the precipitate formed was then filtered, washed, dried and weighed. Its mass was found to be 0.287 g.

When a 1.06 g sample was gently heated to 100 °C in a stream of dry air, 0.144 of water was driven off.

The freezing point of a solution prepared from 1.33 g of the compound and 100 cm^3 of water, was found to be –0.18 °C. (Molar freezing point depression of water is 1.82 K kg mol^{-1}).

Use all the experimental information to solve the following problems:

4.3 Derive the empirical formula of the compound.

4.4 Deduce formula for the compound showing the ligands of the chromium ion. Give molar ratios to support your result.

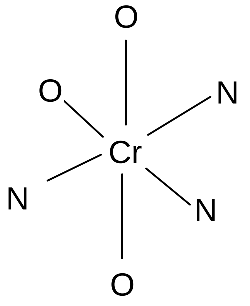
4.5 Sketch all possible steric arrangements of the ligands about the chromium ion.

SOLUTION

4.1 Two geometrical isomers of the complex are possible:

i) the facial, which is the one illustrating the problem,

ii) the meridional, with oxygen and nitrogen positions as shown:



4.2 It is clearly seen that any complex with three bidentate ligands attached octahedrally as shown, lacks mirror symmetry. Hence, both stereoisomers are further resolvable into optical isomers.

4.3 The empirical formula is $CrCl_3H_{12}O_6$.

4.4 The reaction with silver ions indicates that

1 mol $CrCl_3H_{12}O_6 \; \hat{=} \;$ 1 mol Cl^-

Gentle heating gives

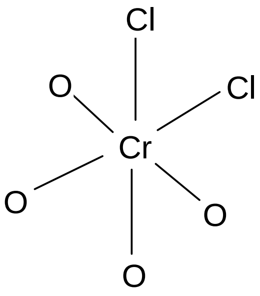
1 mol $CrCl_3H_{12}O_6 \; \hat{=} \;$ 2 mol H_2O

These results support the coordination $[CrCl_2(H_2O)_4]Cl \cdot 2\,H_2O$.

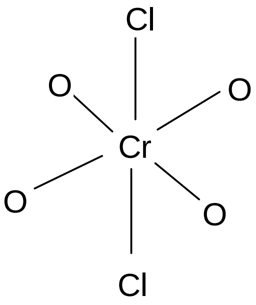
This formula is supported by the freezing point experiment showing that

1 mol $CrCl_3H_{12}O_6 \; \hat{=} \;$ 2 mol ions in solution

4.5 Possible steric arrangements of the ligands about the chromium atom:



cis-form



trans-form

THE FIFTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
2–11 JULY 1983, TIMISOARA, ROMANIA

THEORETICAL PROBLEMS

PROBLEM 1

A) Describe the thermal decomposition of the following ammonium salts in terms of chemical equations:

a) $NH_4ClO_4 \xrightarrow{t\ ^\circ C}$

b) $(NH_4)_2SO_4 \xrightarrow{t\ ^\circ C}$

c) $(NH_4)_2S_2O_8 \xrightarrow{t\ ^\circ C}$

d) $NH_4NO_2 \xrightarrow{t\ ^\circ C}$

B) Indicate the right answer:

a) Can the molar mass be determined by measuring the density of a gaseous compound at a given temperature and pressure?

1. Yes, under any conditions.
2. Yes, if the gaseous compound does not dissociate and associate.
3. Yes, if the gaseous compound does not dissociate.
4. Yes, if the gaseous compound does not associate.

b) Is a liquid boiling at a constant temperature (at a given pressure) a pure substance?

1. Yes, if the liquid is not azeotropic.
2. Yes, if the liquid is azeotropic.

C) Complete and balance the following equation: (in H_2O)

$K_2Cr_2O_7 + SnCl_2 +$ .... $\rightarrow CrCl_3 +$ ....+ KCl + ...

D) The solubility of Hg_2Cl_2 in water is 3.0×10^{-5} g/100 ml solution.

a) What is the solubility product?

b) What is the solubility (in mol dm^{-3}) of this substance in a 0.01 M NaCl solution?

c) What is the volume of a 0.01 M NaCl solution which dissolves the same quantity of mercurous chloride as that dissolved in one litre of pure water?

A_r(Hg) = 200.61 A_r(Cl) = 35.45

E) Which of the following groups contains solid compounds at 10 °C?

a) H_2O, NH_3, CH_4

b) F_2, Cl_2, Br_2

c) SO_3, I_2, NaCl

d) Si, S_8, Hg

F) Which of the following salts forms an acidic aqueous solution?

a) CH_3COONa

b) NH_4Cl

c) Na_2HPO_4

d) Na_2CO_3

e) $NaHCO_3$

G) Write the electronic formulas for the following compounds so that the nature of the chemical bonds is evident:

a) $NaClO_3$, b) $HClO_3$, c) SiF_4, d) NH_3, e) CaF_2, f) H_2O

H) Solid perchloric acid is usually written as $HClO_4.H_2O$. Based on experimental data showing four equal bonds, suggest a structure accounting for the experimental result.

I) The compounds of the second row elements with hydrogen are as follows: LiH, BeH_2, B_2H_6, CH_4, NH_3, H_2O, HF.

a) Which compounds are solid at room temperature? Explain.

b) Which of them are ionic?

c) Which are polymeric?

d) Which ones do not react with water under normal conditions?

e) Give products of the following reactions.

$BeH_2 + H_2O \rightarrow$

$B_2H_6 + H_2O \rightarrow$

$B_2H_6 + LiH$

f) Supposing that NH_3, H_2O and HF are acids under some conditions, write their corresponding conjugated bases and arrange them in order of increasing basic strength.

J) The following E^0 values are given for the half-reactions:

$MnO_4^- + 8\,H^+ + 5\,e^- = Mn^{2+} + 4\,H_2O \qquad E_1^0 = 1.52\ V$

$MnO_4^- + 4\,H^+ + 3\,e^- = MnO_2 + 2\,H_2O \qquad E_2^0 = 1.69\ V$

Calculate E^0 for the following reaction:

$MnO_2 + 4\,H^+ + 2\,e^- = Mn^{2+} + 2\,H_2O \qquad E_3^0 = ?$

SOLUTION

A) a) $4\,NH_4ClO_4 \xrightarrow{t\,°C} 4\,HCl + 6\,H_2O + 2\,N_2 + 5\,O_2$

b) $3\,(NH_4)_2SO_4 \xrightarrow{t\,°C} SO_2 + N_2 + 4\,NH_3 + 6\,H_2O$

c) $2\,(NH_4)_2S_2O_8 \xrightarrow{t\,°C} 4\,SO_2 + 2\,N_2 + 8\,H_2O$

d) $NH_4NO_2 \xrightarrow{t\,°C} N_2 + 2\,H_2O$

B) a) 1, 2, 3, 4

b) 1, 2

C) $K_2Cr_2O_7 + 3\,SnCl_2 + 14\,HCl \rightarrow 2\,CrCl_3 + 3\,SnCl_4 + 2\,KCl + 7\,H_2O$

D) a) $s = 3.0 \times 10^{-5}$ g/100 cm^3 = 3.0×10^{-4} g dm^{-3} =

$$= \frac{3.0 \times 10^{-4}\ \text{g dm}^{-3}}{472\ \text{g mol}^{-1}} = 6.3 \times 10^{-7}\ \text{mol dm}^{-3}$$

$Hg_2Cl_2 \rightarrow Hg_2^{2+} + 2\,Cl^-$

$K_s = 4\,s^3 = 4\,(6.3 \times 10^{-7})^3 = 1.0 \times 10^{-18}$

b) $c(Cl^-) = 0.01$ mol dm^{-3}

$$s = \frac{K_s}{[\text{Cl}^-]^2} = \frac{1.0\times10^{-18}}{(0.01)^2} = 1.0\times10^{-14}$$

$$s = 1.0\times10^{-14}\ \text{mol dm}^{-3}$$

c) The volume of 0.01 M NaCl solution in which dissolves the same quantity of Hg_2Cl_2 as in 1 dm^3 of water, is as follows:

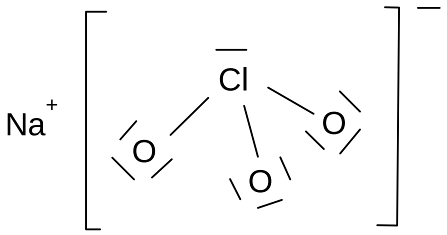
$$V = \frac{6.3\times10^{-7}}{1.0\times10^{-14}} = 6.3\times10^{7}\ \text{dm}^3$$

E) c) SO_3, I_2, NaCl

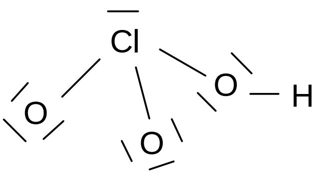
F) b)

G)

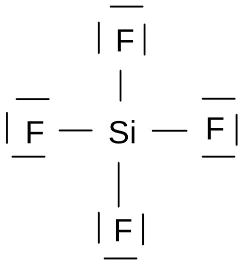
a)



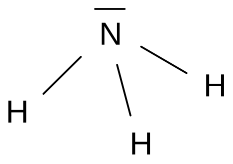
b)



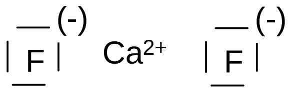
c)



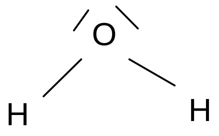
d)



e)

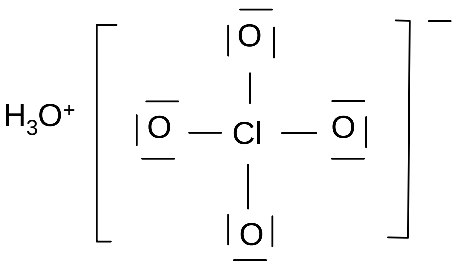


f)



H)

$H_3O^+ + ClO_4^-$ or



I) a) LiH, $(BeH_2)_n$ polymer

b) LiH

c) $(BeH_2)_n$

d) CH_4

e) $BeH_2 + 2\ H_2O \rightarrow Be(OH)_2 + 2\ H_2$

$B_2H_6 + 6\ H_2O \rightarrow 2\ B(OH)_3 + 6\ H_2$

$B_2H_6 + 2\ LiH \rightarrow 2\ Li[BH_4]$

f) $NH_2^- > OH^- > F^-$

J) $MnO_4^- + 4\ H^+ + 3\ e^- = MnO_2 + 2\ H_2O$ $\quad E_2^0 = 1.69\ V$

$MnO_2 + 4\ H^+ + 2\ e^- = Mn^{2+} + 2\ H_2O$ $\quad E_3^0 = ?$

$MnO_4^- + 8\ H^+ + 5\ e^- = Mn^{2+} + 4\ H_2O$ $\quad E_1^0 = 1.52\ V$

$5\,E_1^0 = 3\,E_2^0 + 2\,E_3^0$

7.60 = 5.07 + 2 x

x = 1.26 V

PROBLEM 2

In a gaseous mixture of CO and CO_2, a mass ratio of carbon : oxygen = 1 : 2 was determined.

2.1 Calculate the mass percent composition.

2.2 Calculate the volume percent composition.

2.3 Indicate values of the carbon: oxygen ratios for which both gases cannot be present simultaneously.

SOLUTION

Write x = number of moles of CO in 100 g

y = number of moles of CO_2 in 100 g

$28x + 44y = 100$

$$\frac{12(x+y)}{16(x+2y)} = \frac{1}{2}$$

x = 1.389 mol CO

y = 1,389 mol CO_2

2.1 $\frac{1.389\times 44}{100}\times 100 = 61.11\,\%\,CO_2$

$$\frac{1.389\times 28}{100}\times 100 = 38.89\,\%\,CO$$

2.2 X = y 50 % CO_2 + 50 % CO (by volume)

2.3 The two gases cannot be simultaneously present in the mixture if:

$$\frac{\text{carbon mass}}{\text{oxygen mass}} = \frac{12}{16} \text{ which correspeonds to pure CO}$$

$$\frac{12}{32} \text{ which correspeonds to pure } CO_2$$

PROBLEM 2

Ludwig Mond discovered before the turn of this century that finely divided nickel reacts with carbon monoxide forming tetracarbonylnickel, $Ni(CO)_4$, a colourless, very volatile liquid. The composition of $Ni(CO)_4$ provides an example of the noble gas rule ("EAN rule").

Problems:

2.1 Use the eighteen-electron rule (noble gas rule) to predict the formula of the binary carbonyls of Fe(0) and Cr(0).

2.2 What composition would the eighteen-electron rule predict for the most simple binary chromium(0)-nitrosyl compound?

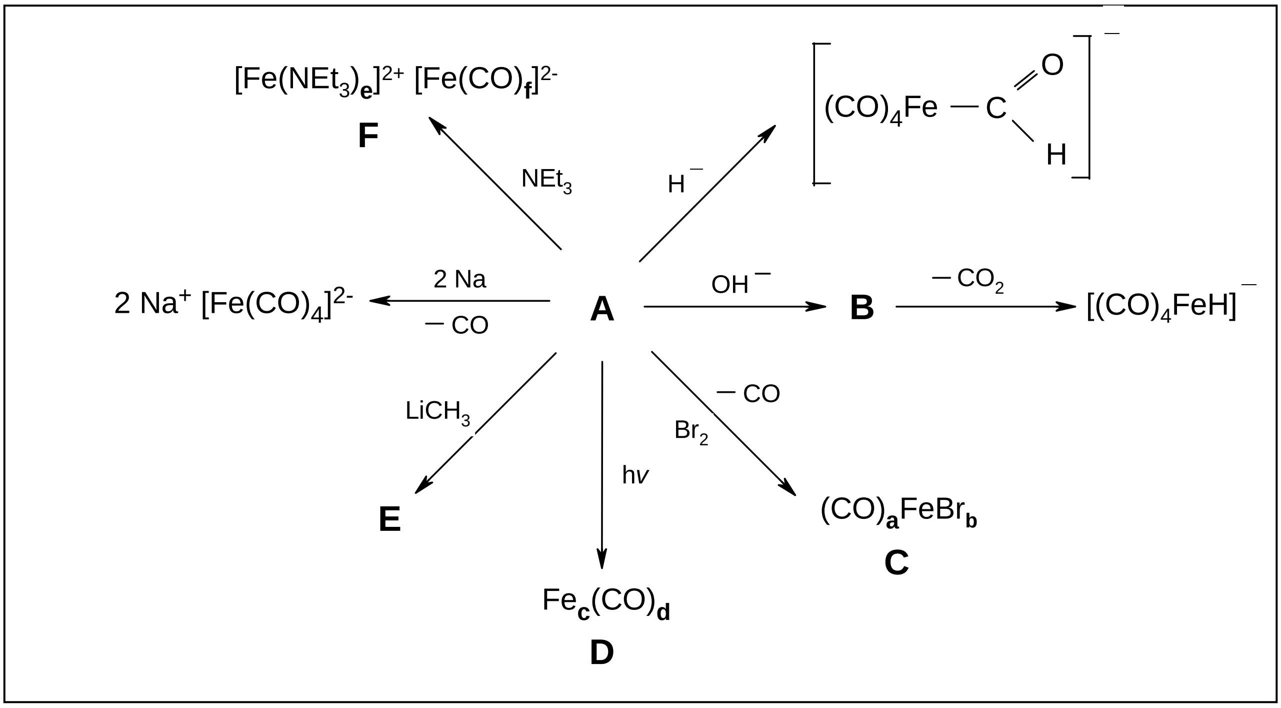
2.3 Explain why Mn(0) and Co(0) do not form so-called mononuclear carbonyl complexes of the type $M(CO)_x$ (M = metal), but rather compounds with metal-metal bonding.

2.4 Suggest structures of $Ni(CO)_4$, $Mn_2(CO)_{10}$ and $Co_2(CO)_8$.

2.5 State whether $V(CO)_6$ and the compounds mentioned in a) and d) are diamagnetic or paramagnetic.

2.6 Why are the carbon monoxide ligands bound to metals much more strongly than to boron in borane adducts (e.g. R_3B-CO; R = alkyl)?

2.7 Determine the composition of the compounds labeled **A** - **F** in the following reaction scheme:



Hints:

a) **C** has the following analysis: C, 14.75 % ; Br, 48.90 % .

b) **D** contains 30.70 % Fe; the molecular mass is 363.8 a.m.u.

c) Excess triethylamine is used for the synthesis of **F**. **F** contains 5.782 % C and 10.11 % N.

2.8 Why is the compound **F** formed in the disproportional reaction (given in g)), and not the compositional isomer $[Fe(CO)_f]^{2+}[Fe(NEt_3)_e]^{2-}$?

2.9 The eighteen-electron rule is also satisfied by a compound prepared from elementary chromium and benzene.

i) Draw the formula of this complex.

ii) Which complex with the analogous structure is prepared by the reaction of iron powder with cyclopentadiene? Write the chemical equation for its formation.

SOLUTION

2.1 $Fe(CO)_5$, $Cr(CO)_6$

2.2 $Cr(NO)_4$

2.3 Explanation: the odd number of electrons in the $Mn(CO)_5$ and $Co(CO)_4$ fragments.

2.4 $Ni(CO)_4$: tetrahedral geometry

$Mn_2(CO)_{10}$: - octahedral $Mn(CO)_5$-structure having a Mn-Mn bond,

- relative orientation (conformation) of the carbonyl groups.

$Co_2(CO)_{10}$: CO-bridges and Co-Co bond

2.5 $Fe(CO)_5$, $Cr(CO)_6$, $Ni(CO)_4$, $Mn_2(CO)_{10}$, $Co_2(CO)_{10}$ are diamagnetic, $V(CO)_6$ is paramagnetic.

2.6 Explanation using the so-called "back-bonding concept"

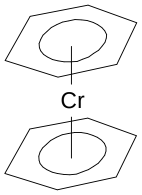
2.7 **A** = $[Fe(CO)_5]$ **B** = $[HOCOFe(CO)_4]$ **C** = $[FeBr_2(CO)_4]$

D = $[Fe_2(CO)_9]$ **E** = $[(CO)_4Fe{=}C(OLi)CH_3]$ **F** = $[Fe(NEt_3)_6]$ $[Fe(CO)_4]$

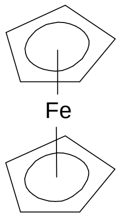
2.8 This observation is due to differing back bonding capability of NEt_3 and CO.

2.9

i) Structural formula of dibenzenechromium



ii) Structural formula of ferrocene.



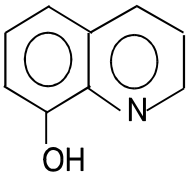
THE SEVENTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
1–8 JULY 1985, BRATISLAVA, CZECHOSLOVAKIA

THEORETICAL PROBLEMS

PROBLEM 1

A solution was formed from 0.5284 g of a sample of an alloy containing aluminium. The aluminium was then precipitated as aluminium 8-hydroxyquinolate. The precipitate was separated, dissolved in hydrochloric acid and the 8-hydroxyquinoline formed was titrated with a standard solution of potassium bromate containing potassium bromide. The concentration of the standard potassium bromate solution was 0.0200 M and 17.40 cm^3 of it were required. The resultant product is a dibromo derivative of 8-hydroxyquinoline.

The structural formula of 8-hydroxiquinoline is:



The relative atomic mass of aluminium is 26.98.

Problems:

1.1 Write the balanced equation for the reaction of the aluminium (III) ion with 8-hydroxyquinoline, showing clearly the structure of the products.

1.2 Give the name of the type of compound which is formed during the precipitation.

1.3 Write the balanced equation for the reaction in which bromine is produced.

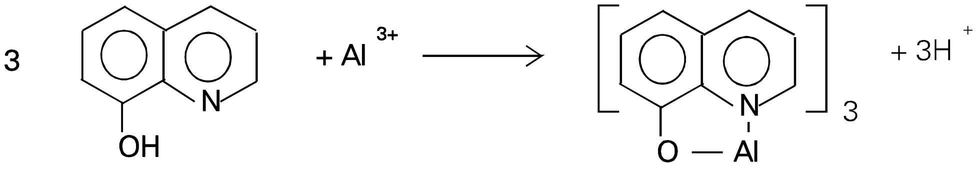
1.4 Write the balanced equation for the reaction of bromine with 8-hydroxyquinoline.

1.5 Calculate the molar ratio of aluminium ions to bromate ions.

1.6 Calculate the percentage by weight of aluminium in the alloy.

SOLUTION

1.1



1.2 Chelate

1.3

$BrO_3^- + 5\,Br^- + 6\,H^+ \rightarrow 3\,Br_2 + 3\,H_2O$

1.4

1.5 As Al $\triangleq$ Al(oxine)$_3$ $\triangleq$ 3 oxine $\triangleq$ 12 Br $\triangleq$ 12 e,

the chemical equivalent of Al equals 26.98/12 = 2.248.

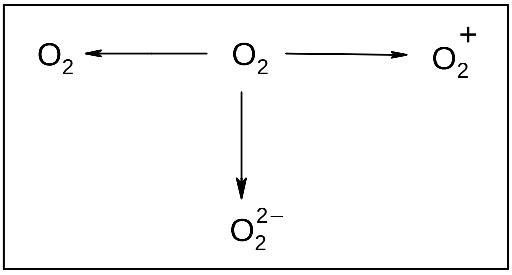
1.6 The percentage of the aluminium in the sample is

$$\%\,Al = \frac{17.40 \times 0.1000 \times 2.248 \times 100}{528.4} = 0.74$$

The alloy contains 0.74% of aluminium.

PROBLEM 2

It is possible to prepare compounds containing ions O_2^-, O_2^{2-} or even O_2^+. These ions are usually formed from molecules of oxygen during various reactions, as indicated in the scheme below:



2.1 Indicate clearly which of the above reactions correspond to the oxidation and which to the reduction of the oxygen molecule.

2.2 For each of the ions in the scheme give the formula of a compound containing that particular ion.

2.3 It has been found that one of the species in the scheme is diamagnetic. Which one is it?

2.4 Copy out the following table:

Species	Bond order	Interatomic distance	Bonding energy
O_2			
O_2^+			
O_2^-			
O_2^{2-}			

The interatomic distances, O-O, in the above species have the values 112, 121, 132 and about 149 pm. Write these values in the appropriate column in the table.

1 pm = 10^{-12} m.

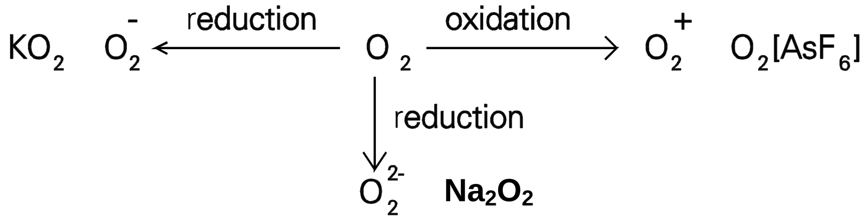
2.5 Three of the bond energies, $E_{o\text{-}o}$, have the values approximately 200, 490 and 625 kJ mol^{-1}. The value for one of the species is uncertain and, therefore, not given. Write the values in the appropriate spaces in the table.

2.6 Determine the bond order for the individual species and write the answers in the table.

2.7 Is it possible to prepare compounds containing the F_2^{2-} ion? Give reasons for your answer.

SOLUTION

2.1 and **2.2**



2.3 O_2^{2-}

2.4 - **2.6**

Species	Bond order	Interatomic distance (pm)	Bonding energy (kJ mol^{-1})
O_2	2	121	490
O_2^+	2.5	112	625
O_2^-	1.5	132	–
O_2^{2-}	1	149	200

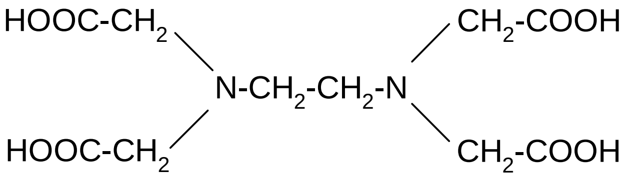
2.7 Ion F_2^{2-} does not exist. The number of electrons in the bonding and antibonding orbitals would be the same and thus, the bonding F–F cannot be formed. Therefore, there exists no compound containing ion F_2^{2-}.

PROBLEM 3

Calcium sulphate is a sparingly soluble compound. Its solubility product is given by:

$K_s(CaSO_4) = [Ca^{2+}][SO_4^{2-}] = 6.1 \times 10^{-5}$

Ethylenediaminetetraacetic acid (EDTA) has the formula $C_{10}H_{16}N_2O_8$ and the structure:



The anion of this acid, $C_{10}H_{12}N_2O_8^{4-}$, forms a stable complex $CaC_{10}H_{12}N_2O_8^{2-}$ with calcium ions. The stability constant of this complex ion is given by:

$$K = \frac{[CaC_{10}H_{12}N_2O_8^{2-}]}{[Ca^{2+}][C_{10}H_{12}N_2O_8^{4-}]} = 1.0 \times 10^{11}$$

EDTA is completely dissociated in strongly alkaline solution. The equation for this dissociation is:

$C_{10}H_{16}N_2O_8 \rightarrow 4\ H^+ + C_{10}H_{12}N_2O_8^{4-}$

Problems:

3.1 Calculate the concentration of calcium ions in a saturated solution of calcium sulphate.

3.2 Calculate the concentration of free Ca^{2+} cations in a solution of 0.1 M $Na_2(CaC_{10}H_{12}N_2O_8)$. You should ignore any protonation of the ligand.

3.3 How many moles of calcium sulphate will dissolve in 1 litre of a strongly alkaline solution of 0.1 M $Na_4C_{10}H_{12}N_2O_8$?

What would be the concentrations of the calcium and sulphate ions in the resulting solution?

3.4 Suggest a structure for the complex ion $[CaC_{10}H_{12}N_2O_8]^{2-}$ assuming that it is approximately octahedral.

3.5 Is the structure you have suggested in 4) optically active?

If your answer is "yes" then draw the structure of the other optical isomer enantiomer).

3.6 Explain why the complexes formed by the anion $C_{10}H_{12}N_2O_8^{4-}$ are exceptionally table.

SOLUTION

3.1 [Ca^{2+}] = 7.8×10^{-3} mol dm^{-3}

3.2 [Ca^{2+}] = 1.0×10^{-6} mol dm^{-3}

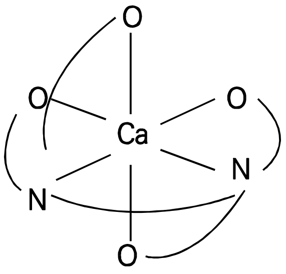
3.3 The $CaSO_4$ amount dissolved is 0.1 mol.

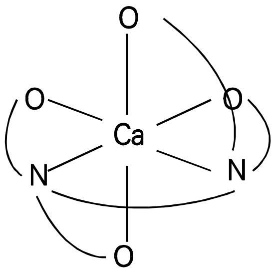
[SO_4^{2-}] = 0.10 mol dm^{-3}.

[Ca^{2+}] = 6.1×10^{-4} mol dm^{-3}

3.4 + **3.5**

The complex is optically active. The structures of both enantiomers are





3.6 The high number of the chelate rings. Other factors also contribute to the complex ability, e.g. the character of the donor atoms, the magnitude and distribution of the charges in the anion, etc.

THE EIGHTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
6–15 JULY 1986, LEIDEN, NETHERLANDS

THEORETICAL PROBLEMS

PROBLEM 1

Compounds containing divalent platinum with the general formula $PtX_2(amine)_2$ (X = Cl_2, SO_4^{2-}, malonate, etc.) have met a lot of scientific interest because of their biological activity, particularly in view of their properties in the treatment of tumours. The best known compound used clinically is $PtCl_2(NH_3)_2$. This compound, in which platinum is coordinated in a planar square, has two geometrical isomers of which only one shows the antitumour activity.

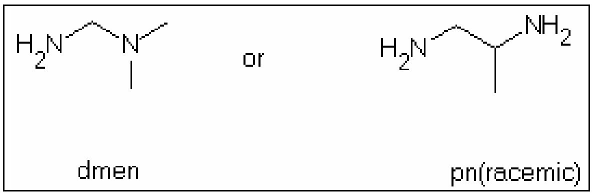
1.1 Sketch the spatial structures of the two possible isomers.

1.2 How many isomers has $PtBrCl(NH_3)_2$? Sketch all of them.

It is possible to replace the amine ligands by one ligand containing two donor atoms (N). Then one obtains a chelating ligand, such as 1,2-diaminoethane (en).

1.3 Show graphically that PtBrCl(en) has only one stable structure.

The ligand en can be substituted via methylation to form dmen or pn (racemic).



1.4 Give spatial structures of all isomers of the following compounds: $PtCl_2(dmen)$, $PtCl_2(pn)$, PtBrCl(dmen) and PtBrCl(pn).

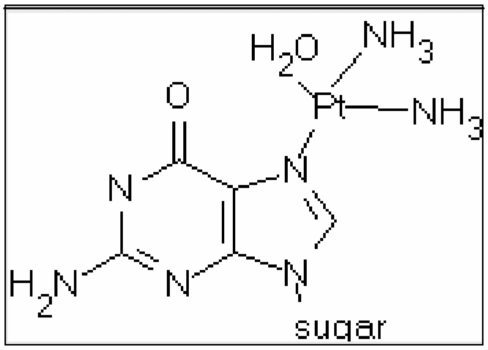
These compounds can isomerise in aqueous solution through dissociation of a ligand and transient replacement of the stronger ligands by the weak ligand water. Cl^- and Br^- are replaced relatively easily, but it is more difficult to replace the amine ligands, which usually requires heating.

1.5 Considering each of the isomers in the previous questions a-d, indicate which Isomers can be converted to another at room temperature. Give both the original molecule and the products.

1.6 $PtCl_2(en)$ reacts with Br^- in a molar proportion of 1:2 at room temperature. Which compound would you expect to form in what proportion? You can assume that the Pt-Br and Pt-Cl bonds are equally strong and that there is no perturbing influence from hydrolysis.

1.7 Using the equation to express chemical equilibrium, show that hydrolysis hardly ever occurs in blood but that it does occur in the cells. Note: $PtCl_2(NH_3)_2$ hydrolyses to and 2 Cl^-. In cells the Cl^- concentration is low; in blood it is fairly high.

After hydrolysis in the tumour cell a reactive platinum ion is formed to which two NH_3 groups are still bound, as it was found in the urine of patients treated with this compound. The reactive platinum ion appears to be bound to cellular DNA, where the bonding occurs via guanine to one of the N-atoms.

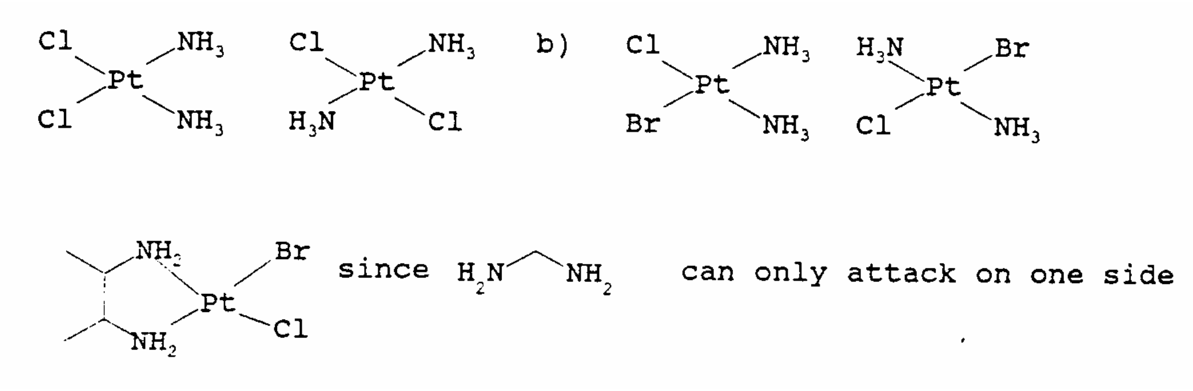


As a result of the two reactive sites of platinum and the two unreactive NH_3 ligands, it can form additionally a second bond to DNA. Research has shown that this happens in particular with a second guanine base from the same strand of DNA.

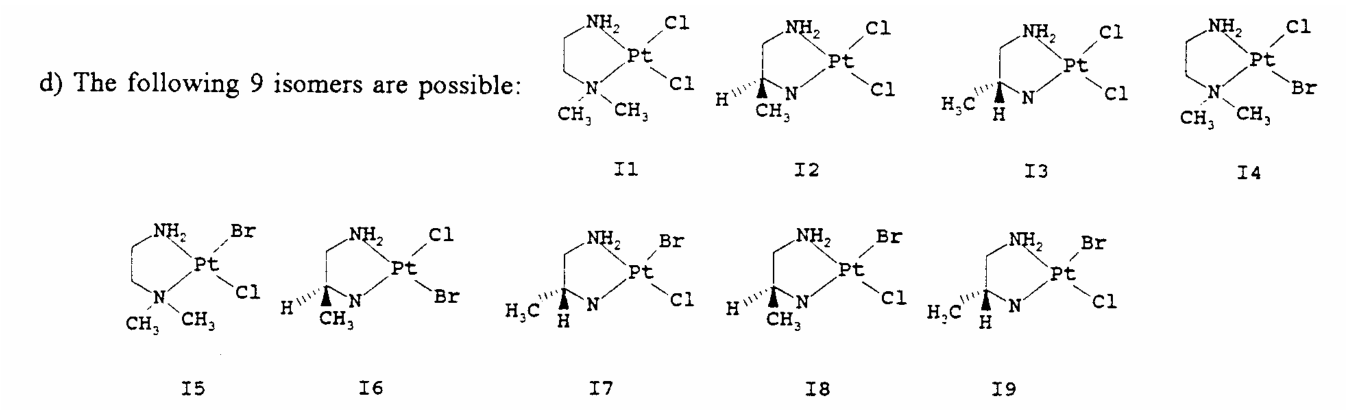
1.8 Show by calculations which of the two isomers in question a) can form this bond. (Note: Pt-N distance = 210 pm, DNA base distance = 320 pm).

SOLUTION

1.1 - 1.3 The isomers are:



1.4



d) The following 9 isomers are possible:

1.5 In a-c) there is no change possible;

in d) I4 and I5, I6 and I7, I8 and I9 transform one into another. Via this isomerization also $PtCl_2$(dmen), $PtBr_2$(dmen), $PtCl_2$ (pn) and $PtBr_2$(pn) can be formed, even though they are not isomers.

1.6 $PtCl_2(en) : PtBr_2(en) : PtBrCl(en) = 1 : 1 : 2$

1.7 $PtCl_2(NH_3)_2 \rightleftharpoons (PtCl(H_2O)(NH_3)_2)^+ \rightleftharpoons Pt(H_2O)_2(NH_3)_2)^{2+}$

In blood the hydrolysis does not occur, because the concentration of Cl^- is rather high and the equilibrium is shifted to the left side.

1.8 The bond is formed by the cis-isomer, because in that case the distance between the bases (320 pm) has to change only to $210\sqrt{2} =$ 297 nm, whereas in the case of the trans-compound the distant would be $210 \times 2 = 420$ nm.

PROBLEM 2

The compound $Na_5P_3O_{10}$ is used as an additive for detergents to bind the Ca^{2+} and Mg^{2+} ions present in water in order to prevent the precipitation of their fatty acid salts on the laundry.

2.1 Draw the structure of the ions $(P_3O_{10})^{5-}$ and $(P_3O_9)^{3-}$ assuming that P-P bonds do not occur.

2.2 Assuming an octahedral coordination of the Mg^{2+} ion give a drawing of the $Mg(P_3O_{10})(H_2O)_n)^{3-}$ ion also indicating the value for n.

The complex ions of Mg^{2+} and Ca^{2+} and triphosphate are well soluble in water. They are, among other things, responsible for the wild growth of algae in surface waters. They could be removed by precipitation as an insoluble compound.

2.3 Give some possibilities (ions) to precipitate the triphosphates bound to Ca^{2+} or Mg^{2+}.

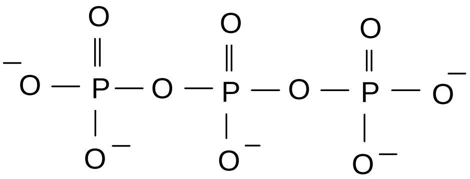
2.4 Calculate the mass of $Na_5P_3O_{10}$ (in grams) necessary in a washing machine to reduce the amount of Ca^{2+} in 20 litres of city water (0.225 g/l) to an acceptable maximum of 0.02 g/l. Effects of pH, the precipitation of $Ca(OH)_2$, and possible effects by other positive ions, can be neglected. The following data is given:

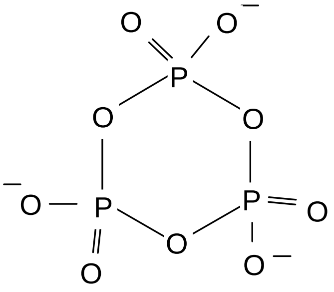
$$K_1 = \frac{[Ca^{2+}][P_3O_{10}^{5-}]}{[CaP_3O_{10}^{3-}]} = 1.0\times10^{-6}$$

Molar mass of $Na_5P_3O_{10}$ is 366 g mol^{-1}, the molar mass of Ca is 40 g mol^{-1}.

SOLUTION

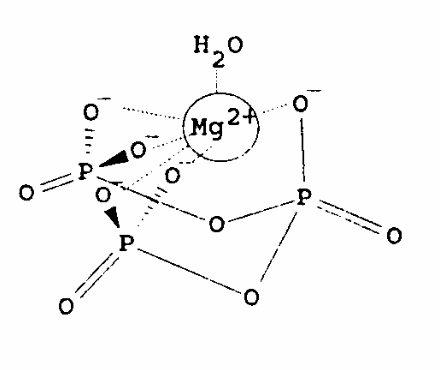
2.1 The structures are:





$P_3O_{10}^{5-}$ $P_3O_9^{3-}$

2.2 Since Mg^{2+} has the coordination number 6, one water molecule serves as the sixth ligand among the five O^- ligands already present in the $[P_3O_{10}]^{5-}$ - ligand:



2.3 Possible ions are Al^{3+} or Fe^{2+} because of their equal charge and similar size. The triphosphates are not soluble in water.

2.4 $[Ca^{2+}] + [CaP_3O_{10}]^{3-} = \frac{0.225}{40}\ mol\,dm^{-3}$;

$[Ca^{2+}] = \frac{0.020}{40}\ mol\,dm^{-3} \Rightarrow [CaP_3O_{10}^{3-}] = \frac{0.205}{40}\ mol\,dm^{-3}$

$[P_3O_{10}^{5-}] = \frac{K_1[CaP_3O_{10}^{3-}]}{[Ca^{2+}]} = 1.025 \times 10^{-5}\ mol\ dm^{-3}$

$[CaP_3O_{10}^{3-}] + [P_3O_{10}^{5-}] = 5.135 \times 10^{-3}\ mol\ dm^{-3} \equiv$ 37.6 g $Na_3P_3O_{10}$ in 20 dm^3 H_2O

THE TWENTIETH
INTERNATIONAL CHEMISTRY OLYMPIAD
2–9 JULY 1988, ESPOO, FINLAND

THEORETICAL PROBLEMS

PROBLEM 1

The periodic system of the elements in our three-dimensional world is based on the four electron quantum numbers n = 1, 2, 3,....; l = 0, 1,....,n – 1, m = 0, ± 1, ± 2,...., ± 1; and s = ± 1/2. In Flatlandia, a two-dimensional world, the periodic system is thus based on three electron quantum numbers: n = 1,2,3,...; m_l = 0, ±1, ±2, ..., ± (n-1); and s = ±1/2 where m_l plays the combined role of l and m_l of the three dimensional world. The following tasks relate to this two-dimensional world, where the chemical and physical experience obtained from our world is supposed to be still applicable.

1.1 Draw the first four periods of the Flatlandian periodic table of the elements. Number them according to their nuclear charge. Use the atomic numbers (Z) as symbols of the specific element. Write the electron configuration for each element.

1.2 Draw the hybrid orbitals of the elements with n = 2. Which element is the basis for the organic chemistry in Flatlandia? Find the Flatlandian analogous for ethane, ethene and cyclohexane. What kind of aromatic ring compounds are possible?

1.3 Which rules in Flatlandia correspond to the octet and the 18-electron rules in the three dimensional world?

1.4 Predict graphically the trends in the first ionization energies of the Flatlandian elements with n = 2. Show graphically how the electronegativities of the elements increase in the Flatlandian periodic table.

1.5 Draw the molecular orbital energy diagrams of the neutral homonuclear diatomic molecules of the elements with n = 2. Which of these molecules are stable in Flatlandia?

1.6 Consider simple binary compounds of the elements (n = 2) with Z = 1. Draw their Lewis structure, predict their geometries and propose analogues for them in the three dimensional world.

1.7 Consider elements with n ≤ 3. Propose an analogue and write the chemical symbol from our world for each of these Flatlandian elements. On the basis of this chemical and physical analogue predict which two-dimensional elements are solid, liquid or gaseous at normal pressure and temperature.

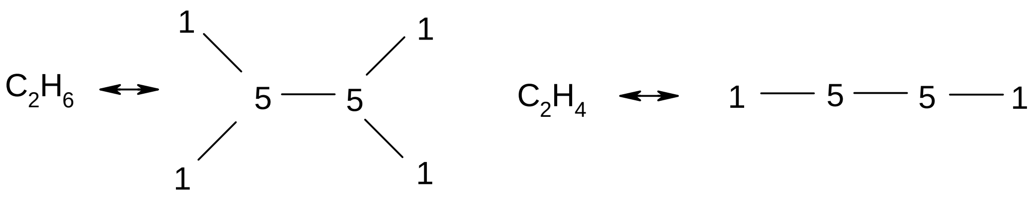
SOLUTION

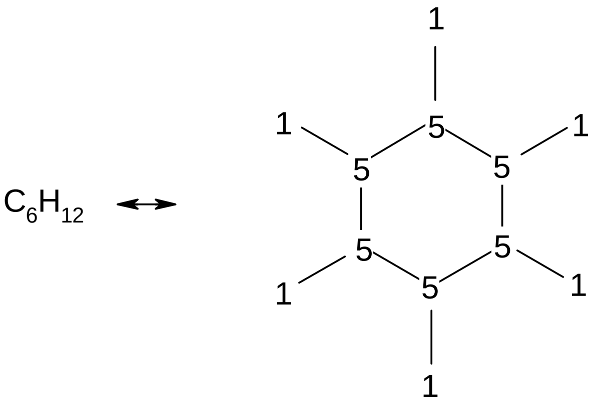
1.1 In the two dimensional world and the electron quantum numbers given, we obtain the following Flatlandian periodic table:

1 $1s^1$									**2** $1s^2$
3 [ ]$2s^1$	**4** [ ]$2s^2$					**5** [ ]$2s^2 2p^1$	**6** [ ]$2s^2 2p^2$	**7** [ ]$2s^2 2p^3$	**8** [ ]$2s^2 2p^4$
9 [ ]$3s^1$	**10** [ ]$3s^2$					**11** [ ]$3s^2 3p^1$	**12** [ ]$3s^2 3p^2$	**13** [ ]$3s^2 3p^3$	**14** [ ]$3s^2 3p^4$
15 [ ]$4s^1$	**16** [ ]$4s^2$	**17** [ ]$4s^2 3d^1$	**18** [ ]$4s^2 3d^2$	**19** [ ]$4s^2 3d^3$	**20** [ ]$4s^2 3d^4$	**21** [ ]$4s^2 3d^4$ $4p^1$	**22** [ ]$4s^2 3d^4$ $4p^2$	**23** [ ]$4s^2 3d^4$ $4p^3$	**24** [ ]$4s^2 3d^4$ $4p^4$

1.2 sp^1 and sp^2 hybrid orbitals are possible:

The element of life is the element with Z = 5. The corresponding compounds of ethane, ethene and cyclohexane are:

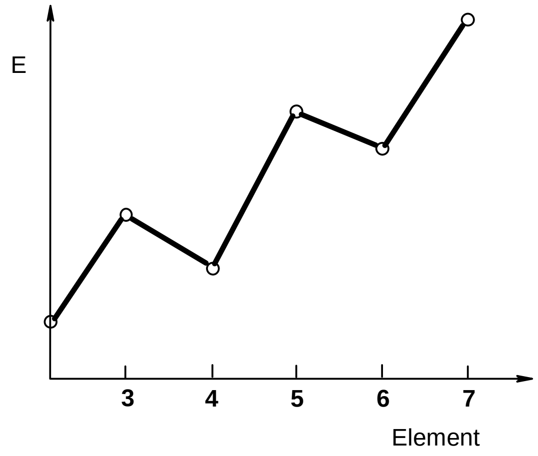


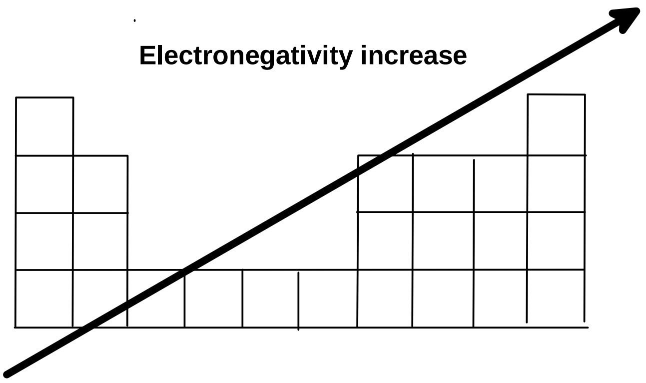


Aromatic ring compounds are not possible since there are no electron orbitals left that may overlap in the case of sp^2.

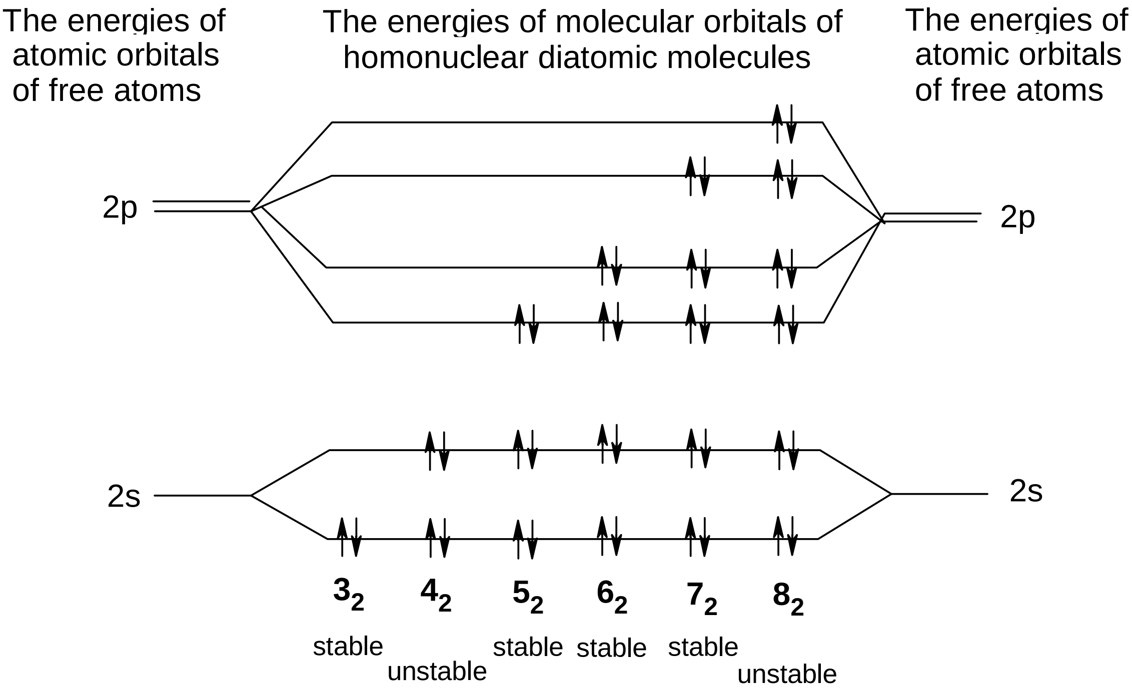
1.3 The Octet rule is changed to a Sextet rule, the 18-electron rule corresponds to a 10-electron rule.

1.4 The ionization energies and the trends in electronegativity

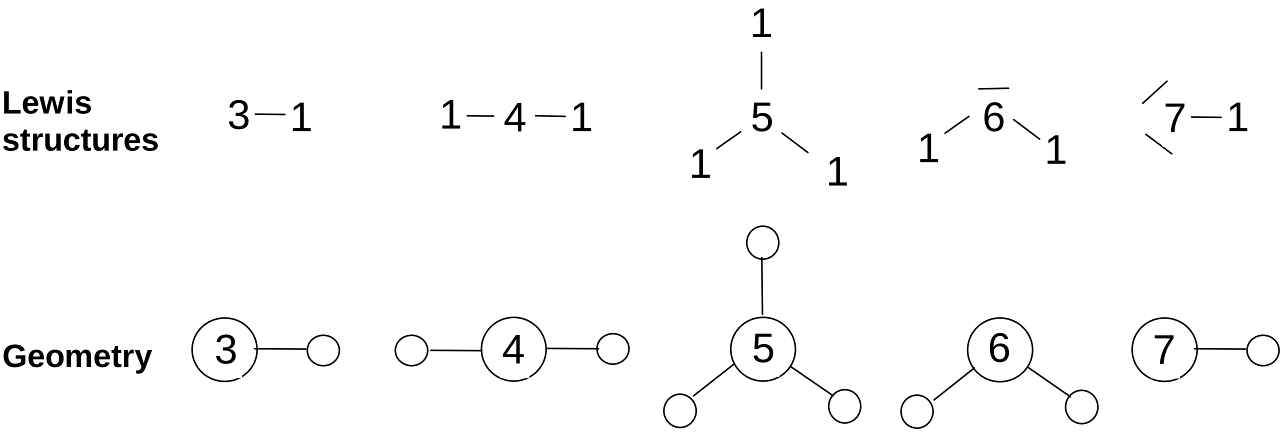




1.5 The molecular orbital diagram of the homonuclear X_2 molecules:



1.6 The Lewis structures and geometries:



1.7 The three-dimensional analogues of Flatlandian elements are:

1: H, gas
2: He, gas
3: Li, solid
4: Be, solid
5: B or C, solid
6: N or O, gas
7: F, gas
8: Ne, gas
9: Na, solid
10: Mg, solid
11: Al or Si, solid
12: P or S, solid
13: Cl, gas
14: Ar, gas

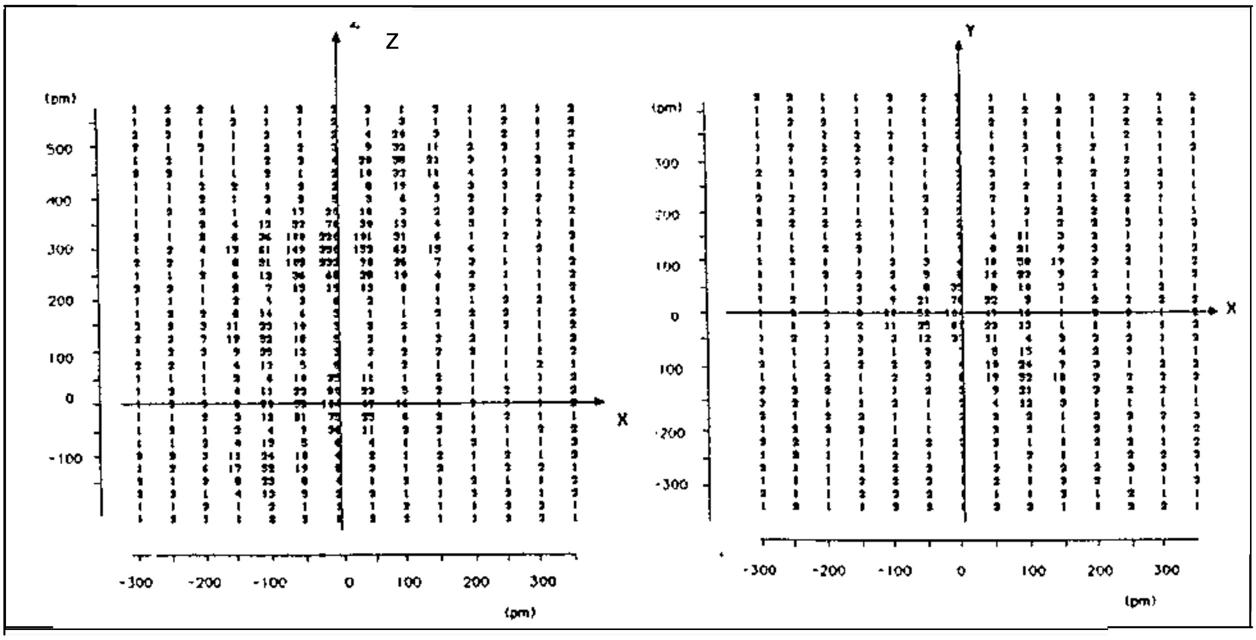
PROBLEM 2

Upon heating of a mixture of **A** and fluorine (molar ratio 1 : 9, pressure approximately 1 MPa) to 900 °C three compounds (**B**, **C** and **D**) are formed. All three products are crystalline solids at ambient temperature with melting points below 150 °C. The fluorine content of **C** is found to be 36.7 % and that of **D** 46.5 % (by weight). When **B** is treated with anhydrous $HOSO_2F$ at -75 °C a compound **E** is formed:

$$\mathbf{B} + HOSO_2F \rightarrow \mathbf{E} + HF$$

E is a solid which is stable for weeks at 0 °C, but decomposes in days at room temperature. The electron density distribution of **E** obtained through X-ray diffraction studies is shown on two intersecting, mutually perpendicular planes (see Fig. 1).

Fig. 1



The numbers indicated on the maps relate to the electron density in the neighbourhood of the atoms of **E** as a function of the spatial coordinates. The maxima found in these maps coincide with the locations of the atoms and the values are approximately proportional to the number of electrons in the atom in question.

2.1 Show where the maxima lie by drawing the contour curves around the maxima, connecting points of equal electron densities. Label each maximum to show the identities of the atoms in **E**.

2.2 When 450.0 mg of **C** was treated with an excess of mercury, 53.25 ml of **A** was liberated at a pressure of 101.0 kPa and a temperature of 25 °C. Calculate the relative atomic mass of **A**.

2.3 Identify **A**, **B**, **C**, **D** and **E**.

2.4 Use the valence-shell electron-pair repulsion theory (VSEPR) to propose electron-pair geometries for **B** and **C**. Using the two electron density maps, sketch the molecular geometry of **E**.

The original mixture was hydrolysed in water. **B** reacts to **A** while liberating oxygen and producing aqueous hydrogen fluoride. Hydrolysis of **C** leads to **A** and oxygen (in molar ratio of 4 : 3) and yields an aqueous solution of AO_3 and hydrogen fluoride. **D** hydrolyses to an aqueous solution of AO_3 and hydrogen fluoride.

2.5 Write the equations for the three hydrolysis reactions.

2.6 Quantitative hydrolysis of a mixture of **B**, **C** and **D** gives 60.2 ml of gas (measured at 290 K and 100 kPa). The oxygen content of this gas is 40.0% (by volume). The amount of AO_3 dissolved in water is titrated with an aqueous 0.1 molar $FeSO_4$ solution and 36.0 ml used thereby. During the titration Fe^{2+} is oxidized to Fe^{3+} and AO_3 is reduced to **A**. Calculate the composition (% by moles) of the original mixture of **B**, **C** and **D**.

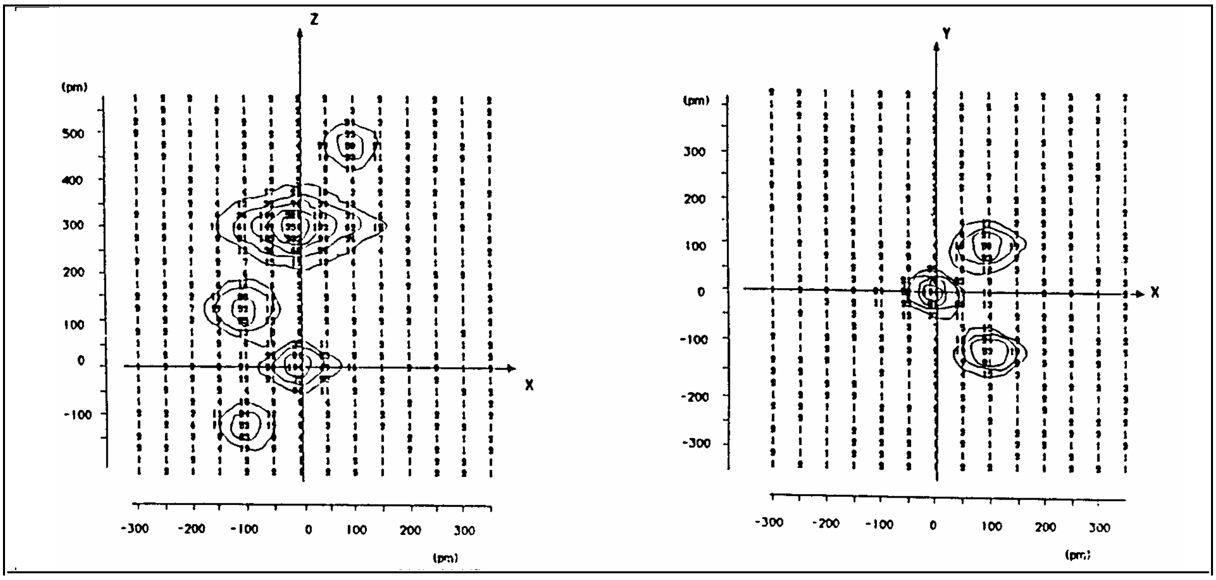
SOLUTION

2.1 Fig. 2 shows the electron densities with maxima 52, 58, 104, and 350. Since compound **E** is supposed to contain the atoms of fluorine, oxygen, sulphur, and **A**, the above maxima can be assign to particular atoms as follows:

Maximum	Element	Atomic number
52	O	8
58	F	9
104	S	16
350	**A**	?

The atomic number of **A** is 54. Thus, the element **A** is xenon.

Fig. 2



2.2 $\mathbf{A}F_n + n/2\ Hg \rightarrow \mathbf{A} + n/2\ HgF_2$

$$n_{gas} = \frac{pV}{RT} = \frac{101\,000\ \text{Pa} \times 53.25 \times 10^{-6}\ \text{m}^3}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}} = 2.17 \times 10^{-3}\ \text{mol} \ = n(\mathbf{A}) = n(\mathbf{A}F_n)$$

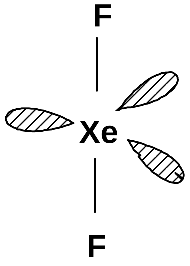
$$\underline{M(\mathbf{A}F_n)} = \frac{0.45}{2.17 \times 10^{-3}} = \underline{207.4\ \text{g mol}^{-1}} = M(\mathbf{A}) + n\,M(F)$$

$$n\,M(F) = 0.367\ M(\mathbf{A}F_n) \Rightarrow n = \frac{207 \times 0.367}{19} = 4.0055 \Rightarrow \underline{\mathbf{A}F_4};$$

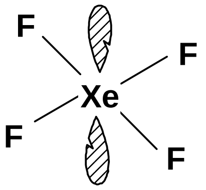
$$\underline{M(\mathbf{A})} = M(\mathbf{A}F_n) - n\,M(F) = 207.4 - 76.1 = \underline{131.3\ \text{g mol}^{-1}}$$

2.3 **A**: Xe **B**: XeF_2 **C**: XeF_4 **D**: XeI_6 **E**: $XeF(OSO_2F)$

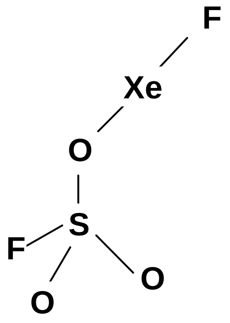
2.4



B



C



E

2.5 $XeF_2 + H_2O \rightarrow Xe + 2\ HF + 0.5\ O_2$

$XeF_4 + 2\ H_2O \rightarrow 2/3\ Xe + 4\ HF + 1/3\ XeO_3 + 0.5\ O_2$

$XeF_6 + 3\ H_2O \rightarrow XeO_3 + 6\ HF$

2.6 $$n_{gas} = \frac{pV}{RT} = \frac{100\ 000\ \text{Pa} \times 60.2 \times 10^{-6}\ \text{m}^3}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 290\ \text{K}} = 2.50 \times 10^{-3}\ \text{mol}$$

$n(O_2) = 0.4 \times n_{gas} = 1.00 \times 10^{-3}$ mol

$n(Xe) = 1.50 \times 10^{-3}$ mol

Assume $n(XeF_2) = a$; $n(XeF_4) = b$; $n(XeF_6) = c$

$n(Xe) = a + 2/3\ b$;

$n(O_2) = 1/2\ a + 1/2\ b$;

$n_{gas} = n(Xe) + n(O_2) = 3/2\ a + 7/6\ b = 2.50 \times 10^{-3}$ mol

$n(O_2) = 1/2\ a + 1/2\ b = 1.00 \times 10^{-3}$ mol

Solution of the equations:

$a = 0.5 \times 10^{-3}$ mol; $b = 1.5 \times 10^{-3}$ mol

$6\ Fe^{2+} + XeO_3 + 3\ H_2O \rightarrow 6\ Fe^{3+} + 6\ OH^- + Xe$

$n(XeO_3) = 1/6\ n(Fe^{2+}) = 1/6\ [c(Fe^{2+})\ V(Fe^{2+})] = 1/6 \times 0.100 \times 36.0 \times 10^{-3}$ mol =

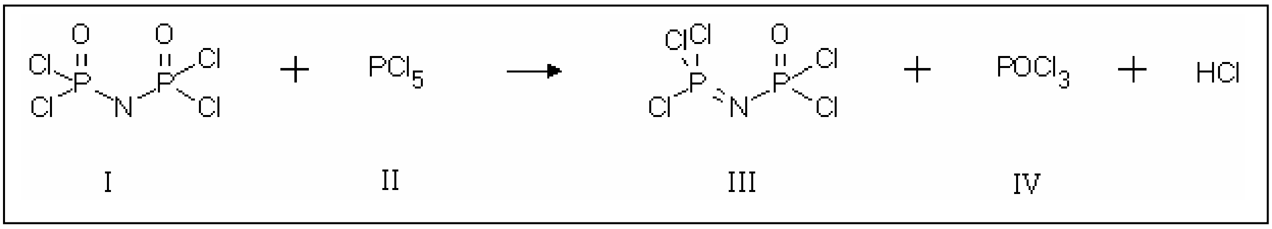
$= 6.00 \times 10^{-4}$ mol $= 1/3\ b + c$

$c = 0.6\ 10^{-3} - 0.5\ 10^{-3} = 1\ 10^{-4}$

<u>molar composition:</u>			
	XeF_2:	0.5×10^{-3} mol	(23.8 %)
	XeF_4:	1.5×10^{-3} mol	(71.4 %)
	XeF_6:	1×10^{-4} mol	(4.8 %)

PROBLEM 4

^{32}P labelled phosphorus pentachloride (half-life $t_{1/2}$ = 14.3 days) is used to study the electrophilic attack of a PCl_4^+ cation on nitrogen or on oxygen.



The reaction is carried out in CCl_4 and the solvent and product **IV** distilled off. Samples of **III** (remaining in the distillation flask), of **IV** (in the distillate) and samples of the starting material **II** are hydrolyzed by heating with a strong sodium hydroxide solution. The phosphate ions formed are precipitated as ammonium magnesium phosphate. Purified samples of the three precipitates are then dissolved by known volumes of water and the radioactivity measured.

4.1 Write the balanced equations for the reaction of red phosphorus forming PCl_5

4.2 Write the reaction equations for complete hydrolysis of the compounds **II** and **III** using sodium hydroxide.

4.3 How long does it take in order to lower the initial radioactivity to 10^{-3} of the initial value?

4.4 Write two alternative mechanisms for the reaction of labelled PCl_4^- with the anion of **I**.

4.5 After hydrolysis the precipitated ammonium magnesium phosphates show the following values for radioactivity:

II. 2380 Bq for 128 mg of $Mg(NH_4)PO_4$

III. 28 Bq for 153 mg of $Mg(NH_4)PO_4$

IV. 2627 Bq for 142 mg of $Mg(NH_4)PO_4$

Using these data, what can you say about the nucleophilic centre attacked by PCl_4^-?

Data: For H_3PO_4: $pK_1 = 2.2$; $pK_2 = 7.2$; $pK_3 = 12.4$

Solubility product of $Mg(NH_4)PO_4$: $pK_s = 12.6$

Equilibrium concentration of NH_4^+ = 0.1 mol dm^{-3}

4.6 Calculate the solubility for $Mg(NH_4)PO_4$ at pH equal to 10 under idealized conditions (activity coefficients can be neglected).

SOLUTION

4.1 $2\ {}^{32}P + 5\ Cl_2 \rightarrow 2\ {}^{32}PCl_5$

4.2 $PCl_5 + 2\ OH^- \rightarrow POCl_3 + 2\ Cl^- + H_2O$

$POCl_3 + 6\ OH^- \rightarrow PO_4^{3-} + 3\ Cl^- + 3\ H_2O$

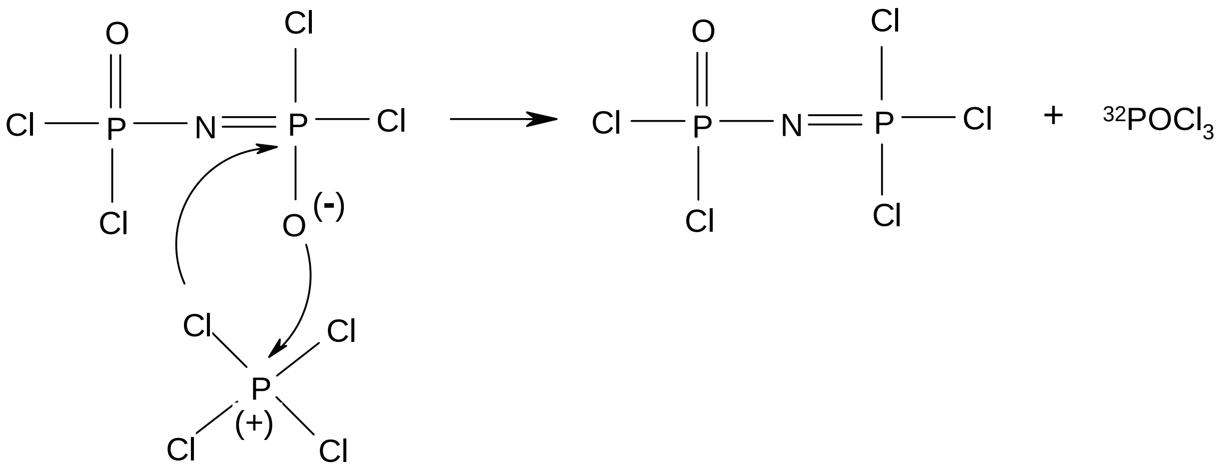
$PCl_5 + 8\ OH^- \rightarrow PO_4^{3-} + 5\ Cl^- + 4\ H_2O$

$Cl_3PNPOCl_2 + 11\ OH^- \rightarrow 2\ PO_4^{3-} + NH_3 + 5\ Cl^- + 4\ H_2O$

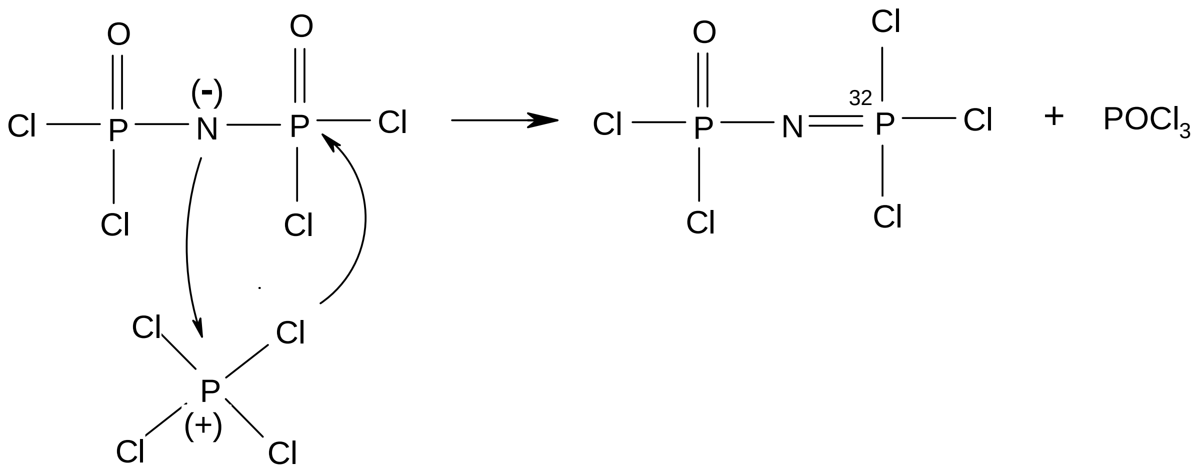
4.3 $A = A_0\ e^{-\lambda t}$ $t_{1/2}$: $A = 0.5\ A_0 \Rightarrow \lambda = \ln 2 / t_{1/2}$ $A = 10^{-3}\ A_0$

$$t = \frac{\ln A\ \ \ln A_0}{\lambda} = \frac{\ln 10^3}{\frac{\ln 2}{14.3}}\ \text{d} = 142.5\ \text{d}$$

4.4



1st mechanism



2nd mechanism

4.5 Specific activities $A_{sp}(\textbf{II}) = 18.6$ Bq/mg,

$A_{sp}(\textbf{III}) = 0.18$ Bq/mg,

$A_{sp}(\textbf{IV}) = 18.5$ Bq/mg.

Because of $A_{sp}(\textbf{II}) \approx A_{sp}(\textbf{IV})$ the first mechanism, proposed in d), is probable and therefore it is PCl_4^+ that attacks the O-atom.

4.6 Given data: $K_{sp} = [Mg^{2+}][NH_4^+][PO_4^{3-}] = 10^{-12.6}$; $[NH_4^+] = 0.1$; $pH = 10$; $pK_1 = 2.2$; $pK_2 = 7.2$; $pK_3 = 12.4$.

Exact solution:

$$2\,[Mg^{2+}] + [NH_4^+] + [H_3O^+] = [H_2PO_4^-] + 2\,[HPO_4^{2-}] + 3\,[PO_4^{3-}] + [OH^-]$$

$$[HPO_4^{2-}] = \frac{[PO_4^{3-}]\,[H^+]}{K_3}$$

$$[H_2PO_4^-] = \frac{[HPO_4^{2-}]\,[H^+]}{K_2} = \frac{[PO_4^{3-}]\,[H^+]^2}{K_2\,K_3}$$

$$[PO_4^{3-}] = \frac{K_{sp}}{[NH_4^+]\,[Mg^{2+}]}$$

$$\Rightarrow\; 2\,[Mg^{2+}] = \left(\frac{[H^+]^2}{K_1\,K_3} + \frac{2\,[H^+]}{K_3} + 3\right)\frac{K_{sp}}{[NH_4^+]} - [Mg^{2+}]\left([NH_4^+] + [H^+] - [OH^-]\right)$$

etc.

A simpler solution:

At pH = 10 the main component is HPO_4^{2-}:

$$[HPO_4^{2-}] = \frac{[PO_4^{3-}]\,[H^+]}{K_3} = 10^{2.4}\ [PO_4^{3-}]$$

$$[H_2PO_4^-]\ =\ \frac{[HPO_4^{2-}][H^+]}{K_2}\ =\ 10^{-2.8}\ [HPO_4^{2-}]$$

$S = [Mg^{2+}]\ [HPO_4^{2-}]$ and $K_{sp} = [NH_4^+] \times S \times K_3 \times \dfrac{S}{[H^+]}$

$pS = 0.5\ (pK_{sp} + pH - pK_3 - p[NH_4^+]) = 0.5\ (12.6 + 10.0 - 12.4 - 1.0) = 4.6$;

$S = 2.5 \times 10^{-5}$ mol dm^{-3}

THE TWENTY-SECOND
INTERNATIONAL CHEMISTRY OLYMPIAD
8–17 JULY 1990, PARIS, FRANCE

THEORETICAL PROBLEMS

PROBLEM 1

PHOSPHORIC ACID

The elemental phosphorus is present in the nature as phosphate in a complex mineral apatite. This mineral contains, in addition to phosphate, silica and the following ions: Ca^{2+}, CO_3^{2-}, SO_4^{2-}, SiO_3^{2-}, and $F^–$.

Let us assume that this mineral is a mixture of tricalcium phosphate, $Ca_3(PO_4)_2$, calcium sulphate, calcium fluoride, calcium carbonate and silica.

For uses as fertilizer the calcium bis(dihydrogenphosphate), $Ca(H_2PO_4)_2$, which is soluble in water, has been prepared. For this purpose, apatite is treated with a mixture of phosphoric and sulphuric acid. At the same time this operation eliminates the majority of impurities.

The elemental analysis of an apatite gave the following results in which, except of fluorine, the elemental composition is expressed as if the elements were in the form of oxides:

	CaO	P_2O_5	SiO_2	F	SO_3	CO_2
% by mass	47.3	28.4	3.4	3.4	3.5	6.1

Operation 1 - A sample of m_0 of this mineral is treated with 50.0 cm^3 of a solution containing 0.500 mol dm^{-3} phosphoric and 0.100 mol dm^{-3} sulphuric acids. The mixture is completely dehydrated by heating up to about 70 °C avoiding temperature rising above 90 °C. This operation is carried out under the hood since toxic gaseous substances are emitted. The dry residue is ground and weighed; m_1 is the mass of the residue obtained.

In these conditions only dihydrogenphosphate, $Ca(H_2PO_4)_2$, is formed while silica and silicate do not react.

Operation 2 - 1.00 g of this residue is treated with 50.0 cm^3 of water at 40 ℃, then filtered, dried and weighed. The mass of the residue obtained is m_2. This new residue is mainly containing gypsum, $CaSO_4 \cdot 2\,H_2O$, whose solubility can be considered as constant between 20 ℃ and 50 ℃ and is equal to 2.3 g dm^{-3}.

1.1 Write the balanced equations for the reactions that are involved.

1.2 From what mass of apatite should one start if all the reactions are stoichiometric?

Starting with m_0 of obtained apatite, m_1 = 5.49 g of residue are obtained.

1.3 What mass should theoretically be obtained?

1.4 This result is due to the presence of products that are not expected to be found in the residue. Give two of them that under these experimental conditions can plausibly account for the data.

Traditionally, in industry the analysis and the yield are expressed as percentage of oxide. The phosphorous content is expressed as if it were P_2O_5.

If n_2 is the amount of a soluble product obtained, n_1 the amount of a substance added as acid, n_0 the amount of apatite added, the yield is:

$$r_{\exp} = \frac{n_2}{n_1 + n_0} 100$$

m_2 = 0.144 g of residue is obtained on the filter.

1.5 Calculate $r_{\exp}$.

1.6 The experimental yield is over 100 %. Calculate a value of r nearer to the real yield.

Relative atomic masses of P: 31; Ca: 40; O: 16; H: 1; F: 19; C: 12; Si: 28; S: 32.

Values of pK: $\frac{HSO_4^-}{SO_4^{2-}} = 2$ $\frac{HF}{F^-} = 3$ $\frac{H_3PO_4}{H_2PO_4^-} = 2$ $\frac{H_2PO_4^-}{HPO_4^{2-}} = 7$ $\frac{HPO_4^{2-}}{PO_4^{3-}} = 12$

SOLUTION

1.1 $Ca_3(PO_4)_2 + 4\ H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + 2\ HF$

$CaCO_3 + 2\ H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + CO_2\uparrow + H_2O$

$Ca_3(PO_4)_2 + 2\ H_2SO_4 + 4\ H_2O \rightarrow 2\ CaSO_4 + 2\ H_2O + Ca(H_2PO_4)_2$

$CaF_2 + H_2SO_4 + 2\ H_2O \rightarrow CaSO_4 \cdot 2\ H_2O + 2\ HF\uparrow$

$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2\ H_2O + CO_2\uparrow$

1.2 1 g of apatite contains $\frac{0.284}{142} = 2.00\times10^{-3}$ mol of $Ca_3(PO_4)_2$

$\frac{0.034}{2+19} = 0.89\times10^{-3}$ mol of CaF_2

$\frac{0.061}{44} = 1.39\times10^{-3}$ mol of $CaCO_3$

$\frac{0.035}{80} = 0.44\times10^{-3}$ mol of $CaSO_4$

$\frac{0.473}{56} - \frac{3\times0.284}{142} - \frac{0.034}{38} - \frac{0.061}{44} - \frac{0.035}{80} = 2.72\times10^{-4}$ mol CaO that remain.

The amount of H_3PO_4 needed to react with 1 g of apatite is equal to $n(H_3PO_4) = 4\ n(Ca_3(PO_4)_2 + 2\ n(CaF_2) + 2\ n(CaCO_3) = 12.56\times10^{-3}$ mol.

50 cm^3 of the acid contains 25×10^{-3} mol of H_3PO_4, therefore 25 / 12.56 = <u>1.99 g</u> apatite is needed to neutralize the H_3PO_4 present.

The amount of H_2SO_4 needed to react with 1 g of apatite can be calculated in the same way:

$n(H_2SO_4) = 2\ n(Ca_3(PO_4)_2) + n(CaF_2) + n(CaCO_3) = 6.28\times10^{-3}$ mol. 50 cm^3 of the acid contains 5.00×10^{-3} mol of sulphuric acid. Therefore 5 / 6.28 = 0.80 g of apatite is needed to neutralize the H_2SO_4.

The total amount of apatite is m_0 = 1.99 + 0.80 = <u>2.79 g</u>

1.3 Formation of $Ca(H_2PO_4)_2$:

1.99 g of apatite needed to neutralize the H_3PO_4 contains $1.9 \times 2.00\times10^{-3}$ mol of $Ca_3(PO_4)_2$, thus $3 \times 2 \times 2\times10^{-3} = 1.2\times10^{-2}$ mol of dihydrogen phosphate is being formed.

From CaF_2, 1.99 × 0.89 = 1.80 mol and from $CaCO_3$, 1.99 × 1.39 = 2.77 mol of $Ca(H_2PO_4)_2$ are formed.

0.8 g of apatite that reacts with 50 cm^3 of the sulphuric acid yields $2 \times 0.8\times10^{-3} = 1.6\times10^{-3}$ mol of $Ca(H_2PO_4)_2$.

$m(Ca(H_2PO_4)_2 = 18.07\times10^{-3}$ mol = 4.230 g

Formation of gypsum: $n(CaSO_4) = n(H_2SO_4) = 5.00\times10^{-3}$ mol $\triangleq$ 0.86 g

The amount of $CaSO_4$ that was already present in 1 g of apatite and yielded gypsum is $0.434\times10^{-3} \times 172 = 0.075$ g. There remain also 0.034 g of silica, and thus the theoretical mass of the residue should be:

m_{th} = 4.230 + 0.86 + (0.0753 + 0.034) × 2.79 = $\underline{5.39\text{ g}}$

1.4 The difference of 0.1 g may be due to water and unreacted CaF_2 in the residue.

1.5 The second reaction is intended to dissolve $Ca(H_2PO_4)_2$, while all the other products remain on the filter.

According to the yielded residue of 0.144 g, 1 g of residue contains 1 – 0.144 = = 0.856 g of soluble product. If it were all $Ca(H_2PO_4)_2$ it would correspond to 0.856 / 234 = 3.66×10^{-3} mol. For 5.49 g of residue it is 0.0201×10^{-3} mol of soluble product (n_2). The amount of acid used is 0.500 / 20 = 0.025 mol H_3PO_4 (equals 0.0125 mol P_2O_5) and 0.005 mol H_2SO_4. The amount of $Ca_3(PO_4)_2$ in 2.79 g apatite is 0.00558 mol (equals 0.00558 mol P_2O_5). So, r_{exp} = 100 × [0.0201/(0.0125 + 0.00558)] = $\underline{111\ \%}$

Since 50 cm^3 water dissolve 0.115 g of gypsum, the real quantity of $Ca(H_2PO_4)_2$ is 0.856 – 0.115 = 0.741 mol, so that the real yield gives: r_{exp} = 100 × [0.0174/(0.0125 + 0.00558)] = $\underline{96\ \%.}$

1.6 The theoretical value for r_{exp} is: r_{exp} = 100 × [4.23/234 / (0.0125 + 0.00558)] = 100 %, so this calculation makes sense.

PROBLEM 4

The energy of stable states of the hydrogen atom is given by: $E_n = -2.18\times10^{-18}/n^2$ [J] where n denotes the principal quantum number.

4.1 Calculate the energy differences between n = 2 (first excited state) and n = 1 (ground state) and between n = 7 and n = 1.

4.2 In what spectral range is the Lyman series lying?

4.3 Can a single photon, emitted in the first and/or sixth line of the Lyman series, ionize:

a) another hydrogen atom in its ground state?

b) a copper atom in the Cu crystal?

The electron work function of Cu is $\Phi_{Cu} = 7.44\times10^{-19}$ J.

4.4 Calculate the de Broglie wavelength of the electrons emitted from a copper crystal when irradiated by photons from the first line and the sixth line of the Lyman series.

$h = 6.6256\times10^{-34}$ J s; $m_e = 9.1091\times10^{-31}$ kg; $c = 2.99792\times10^{8}$ m s^{-1}

SOLUTION

4.1 $\Delta E_{n\to1} = E_n - E_1 = 2.18\times10^{-18}\ (1 - n^2)$

$\Delta E_{2\to1} = 1.635\times10^{-18}$ J

$\Delta E_{7\to1} = 2.135\times10^{-18}$ J

4.2 The Lyman series is due to $\Delta E_{n\to1}$ varying from 1.635×10^{-18} J (n = 1) to 2.135×10^{-18} J ($n\to\infty$), which corresponds to 121.5 nm and to 93.0 nm, respectively. This is in the UV-region.

4.3 a) The ionisation energy is equal to $\Delta E_{\infty\to1} = 2.18\times10^{-18}$ J. Both $\Delta E_{2\to1}$ and $\Delta E_{7\to1}$ are smaller than $\Delta E_{\infty\to1}$ and a single photon emitted from these transitions is not able to ionize a hydrogen atom.

b) Ionization of copper in a Cu-crystal is related to the photoelectric effect:

$h\nu = \Phi_{Cu} + E_{kin} = \Phi_{Cu} + \frac{1}{2} m_e v^2$

Because $\Delta E_{2\to1} > \Phi_{Cu}$ and $\Delta E_{7\to1} > \Phi_{Cu}$ both photons are indeed able to ionize a Cu-atom in the crystal.

The kinetic energy of the emitted electrons is:

$\Delta E_{\text{kin}}\ (2\rightarrow1) = \Delta E_{2\rightarrow1} - \Phi_{\text{Cu}} = 8.91\times10^{-19}$ J

$\Delta E_{\text{kin}}\ (7\rightarrow1) = \Delta E_{7\rightarrow1} - \Phi_{\text{Cu}} = 13.91\times10^{-19}$ J

4.4 The wavelength of an electron is:

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2\ E_{\text{kin}}\ m_e}}$$

$(p = m_e v_e$ and $E_{\text{kin}} = \dfrac{p^2}{2\ m_e})$

$\Delta E_{2\rightarrow1}$: $\lambda_1 = 4.16\times10^{-10}$ m = 4.16 Å

$\Delta E_{7\rightarrow1}$: $\lambda_2 = 5.20\times10^{-10}$ m = 5.20 Å

PROBLEM 6

Sulphuric acid is produced by catalytic oxidation of SO_2 to SO_3, absorption of SO_3 in concentrated sulphuric acid forming oleum (containing 20 % SO_3 by mass) and appropriate dilution hereafter. The gas leaving the catalyst chamber contains nitrogen, oxygen, a trace of SO_2 and 10 % (by volume) of SO_3. Sulphur trioxide, SO_3, is converted into sulphuric acid (98 % by mass) and/or oleum.

6.1 Assuming that oleum is the only product formed, calculate the mass of water which is required for 1000 m^3 of gas leaving the catalyst chamber (273 K, 101.3 kPa).

6.2 Assuming that only 98 % sulphuric acid is produced, calculate the necessary mass of water and the mass of product produced thereby.

6.3 In the industry both oleum and 98 % sulphuric acid are produced in a mass ratio of $x = m_1/m_2$, where m_1 denotes the mass of oleum, m_2 the mass of 98 % sulphuric acid. Find an expression $y = f(x)$ to describe the relation between the mass of water consumed for 1000 m^3 gas (denoted y) and the value of x. Show that the results of 6.1) and 6.2) are in good agreement with your mathematical expression.

SOLUTION

6.1 1000 m^3 of gas contain 4.462 kmol SO_a

100 kg 20 % oleum contain 0.2498 kmol SO_3 and 0.8157 kmol H_2SO_4

1.0655 kmol SO_a and 0.8157 kmol (14.70 kg) H_2O are necessary for production of 100 kg 20 % oleum.

61.56 kg H_2O are necessary for 1000 m^3 of gas.

6.2 Assumption that only 98 % sulphuric acid is produced:

100,0 kg 98 % H_2SO_4 contain 0,9992 kmol H_2SO_4 and 1,1102 kmol H_2O.

100,0 kg 98 % H_2SO_4 contain 0.9992 kmol SO_3 and 1,1102 kmol (20,01 kg) H_2O.

89.36 kg H_2O are necessary for 1000 m^3 of gas and 446.56 kg 98 % H_2SO_4 are obtained.

6.3 To obtain 1 kg 20 % oleum, 0,1470 kg H_2O are necessary,

To obtain 1 kg 98 % H_2SO_4, 0,2001 kg H_2O are necessary.

Thus, for mass of water for production of m_1 kg 20 % oleum and m_2 kg 98 % H_2SO_4:

y = 0,1470 m_1 + 0,2001 m_2 .

Analogically for mass balance of SO_a:

4,462 = 1,0655 m_1 + 0,9992 m_2

Then: $$\frac{y}{4.462} = \frac{14.70\, m_1 + 20.01 m_2}{1.0655\, m_1 + 0.9992\, m_2}$$

After substitution: $m_1 l m_2 = x$ the above relation may written in the form of a function $y =$ f(x):

$$y = \frac{61.65\, x + 83.79}{x + 0.9378}$$

Production of oleum: $m_2 = 0$, y = 61,56,

production of the acid: $m_1 = 0$, y = 89,35,

Results are similar to those obtained in parts **6.1** and **6.2**.

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THEORETICAL PROBLEMS

PROBLEM 1

Diatoms, microscopic organisms, are an abundant food source in the oceans producing carbohydrates from carbon dioxide and water by photosynthesis:

$6\ CO_2 + 6\ H_2O + \text{solar energy} \rightarrow C_6H_{12}O_6 + 6\ O_2$

1.1 During the first five years of life blue whales gain 75 kg of mass per day by feeding on krill. The whale must consume ten times this mass of krill each day. The krill must consume 10.0 kg of diatoms to produce 1.0 kg of krill. Assuming that the mass gain in the first years of a whale's life is due to the consumption of carbohydrates ($C_6H_{12}O_6$), calculate the volume of CO_2 at STP (0 °C, 101 kPa) that must be used by the diatoms to produce the carbohydrates consumed by a blue whale in its first five years of life.

1.2 There is 0.23 cm^3 of dissolved CO_2 per one litre sea water (at 24 °C and 101 kPa).

i) If diatoms can completely remove carbon dioxide from the water they process, what volume of water would they process to produce the carbohydrates required by a blue whale during the first five years of life?

ii) What fraction of the total volume of the oceans will be needed to supply the carbon dioxide for the first five years of growth of 1000 blue whales? The volume of the oceans is 1.37×10^{18} m^3.

1.3 Three percent of the mass of a 9.1×10^4 kg adult whale is nitrogen. When a 9.1×10^4 kg blue whale dies, what is the maximum mass of NH_4^+ that can become available for other marine organisms?

1.4 Eighteen percent of a 9.1×10^4 kg whale's mass is carbon. Carbon can be returned to the atmosphere as CO_2 and then removed from the atmosphere by weathering of rocks containing calcium silicate.

$CaSiO_3(s) + 2\ CO_2(g) + 3\ H_2O(l) \rightarrow Ca^{2+}(aq) + 2\ HCO_3^-(aq) + H_4SiO_4(aq)$

What are the maximum number of grams of $CaSiO_3$ that can be weathered by the carbon dioxide produced from the decomposition of 1000 blue whales, the number estimated to die annually?

SOLUTION

1.1 In five years a whale eats carbohydrates coming from $5 \times 365 \times 75 \times 10 = 1.4\times10^6$ kg krill which themselves need 1.4×10^7 kg of carbohydrates coming from diatoms.

For 180 g $C_6H_{12}O_6$, 6×44 g CO_2 are necessary, and thus

for 1.4×10^7 kg carbohydrates $1.4\times10^7 \times (264/180) = 2.00\times10^7$ kg of CO_2 are needed, i. e. 1.0×10^{10} dm^3 CO_2

1.2 i) The amount of water is 4×10^{13} dm^3.

ii) 3×10^{-5} of the total ocean volume (0.03 ‰).

1.3 The mass of nitrogen from a whale is $0.03 \times 9.1\times10^4$ kg = 2.7×10^6 g.

$$n(N) = n(NH_4^+) = \frac{2.7\times10^6\ g}{14\ g\,mol^{-1}} = 1.9\times10^5\ mol$$

$$m(NH_4^+) = 1.9\times10^5\ mol \times 18\ g\ mol^{-1} = 3\times10^6\ g\ NH_4^+ = 3\times10^3\ kg\ NH_4^+$$

1.4 One whale contains 1.6×10^4 kg of carbon. It corresponds to 1.3×10^6 mol of CO_2.

From the equation: $n(CaSiO_3) = 6.5\times10^5$ mol

$$m(CaSiO_3) = 6.5\times10^5\ mol \times 116\ g\ mol^{-1} = 7.5\times10^7\ g\ CaSiO_3$$

1000 whales therefore produce 7.5×10^{10} g $CaSiO_3$.

PROBLEM 2

Many streams drain in areas where coal or metallic ores are mined. These streams have become acidic and contain high concentrations of dissolved iron and sulphate, due to sulphur-containing ores being exposed to the atmosphere or to oxygenated waters. The most common sulphur-containing mineral is pyrite, FeS_2, in which the oxidation state of iron is +2. As the iron-rich streams mix with other waters, the dissolved iron precipitates as goethite, FeO(OH), which coats the stream bottom while the water remains acidic.

2.1 Draw the electron dot structure that illustrates the bonding in the ion S_2^{2-}, showing all valence electrons.

2.2 Write a balanced chemical equation to show how hydrogen ions (H^+) are generated during the oxidation of pyrite to form a solution of iron(II) and sulphate ions.

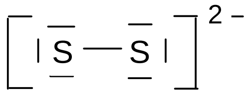
2.3 Write a balanced equation to show how many additional moles of hydrogen are generated when iron(II) ions are oxidized to form the mineral goethite, FeO(OH).

2.4 Calculate how many moles of pyrite would be required to bring 1.0 dm^3 of pure water to a pH of 3.0 if the pyrite was completely converted into FeO(OH) and H^+ ions. Neglect the formation of HSO_4^-.

2.5 The concentration of iron as Fe(II) in a stream is 0.00835 M. At a very narrow point in the stream it empties into a large pond, with a flow rate of 20.0 l each minute. The water in this stream is sufficiently aerated that 75 % of the Fe(II) is oxidized to Fe(III). The pH of the pond is high enough (> 7) that the iron(III) precipitates immediately as $Fe(OH)_3$ which on aging becomes Fe_2O_3. What mass of Fe_2O_3 will be deposited on the bottom of the pond in two years?

SOLUTION

2.1



2.2 $FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$

2.3 $Fe^{2+} + 1/4\ O_2 + 3/2\ H_2O \rightarrow FeOOH + 2\ H^+$

2.4 $[H^+] = 1\times10^{-3}$

$n[H^+] = 1\times10^{-3}$ mol

From both equations: $n(FeS_2) = 2.5\times10^{-4}$ mol

2.5 Total flow into pond in 2 years =

$2 \text{ yr} \times 365 \text{ days yr}^{-1} \times 24 \text{ h day}^{-1} \times 60 \text{ min h}^{-1} \times 20.0 \text{ dm}^3 \text{ min}^{-1}$ =

= 2.10×10^7 dm^3 of water

$n(Fe^{2+})$ into pond = $2.10\times10^7 \text{ dm}^3 \times 8{,}35\times10^{-3} \text{ mol dm}^{-3} = 1.76\times10^5$ mol

$n(Fe^{3+})$ produced = $0.75 \times 1.76\times10^5 \text{ mol} = 1.32\times10^5$ mol

mass of deposited Fe_2O_3:

$m(Fe_2O_3) = 0.5 \times 1.32\times10^5 \text{ mol} \times 159.7 \text{ g mol}^{-1} = 1.05\times10^7$ g

PROBLEM 8

The Pourbaix diagrams for water, nitrogen and manganese are depicted in Fig. 1.

8.1 Write the formula of the species of nitrogen that is predominant

i) in O_2-rich lakes of pH ≈ 6,

ii) in highly O_2-depleted lakes that are strongly contaminated with acid rain (pH ≈ 3),

8.2 Which species of manganese is predominant

i) in O_2-rich lakes of pH ≈ 6,

ii) in highly O_2-depleted lakes that are strongly contaminated with bases (pH ≈ 12)?

8.3 People often find that clear, slightly acidic (pH ≈ 5) water drawn from wells deposits a black manganese-containing solid on standing in toilet bowls.

i) Write the chemical formula of the black solid?

ii) Write the formula for the species of manganese found in well water while it is still underground ?

8.4 According to Pourbaix diagrams two species of nitrogen should oxidize Mn(s) to Mn^{2+}(aq).

i) Write the formulas of these two nitrogen species.

ii) Which of the two species of nitrogen does not oxidize Mn(s) (in practice) at room temperature ?

8.5 According to the Poubaix diagrams, some of the chemical forms of manganese should oxidize NH_3(aq) or NH_4^+(aq) to N_2(g).

Choose in the following list the forms of Mn that should do it:

Mn, $Mn(OH)_2$, Mn^{2+}, Mn_3O_4, Mn_2O_3, MnO_2, MnO_4^{2-} , MnO_4^-

8.6 Ammonium permanganate, NH_4MnO_4, is a well-known salt, but ammonium manganate, $(NH_4)_2MnO_4$, is a rarely known salt.

i) Is NH_4MnO_4 expected to be thermodynamically stable? (YES or NO)

ii) Is $(NH_4)_2MnO_4$ expected to be thermodynamically stable? (YES or NO)

iii) Write and balance an equation for the decomposition of NH_4MnO_4 to give MnO_2 a N_2.

iv) Write and balance an equation for the decomposition of $(NH_4)_2MnO_4$ to give Mn a N_2.

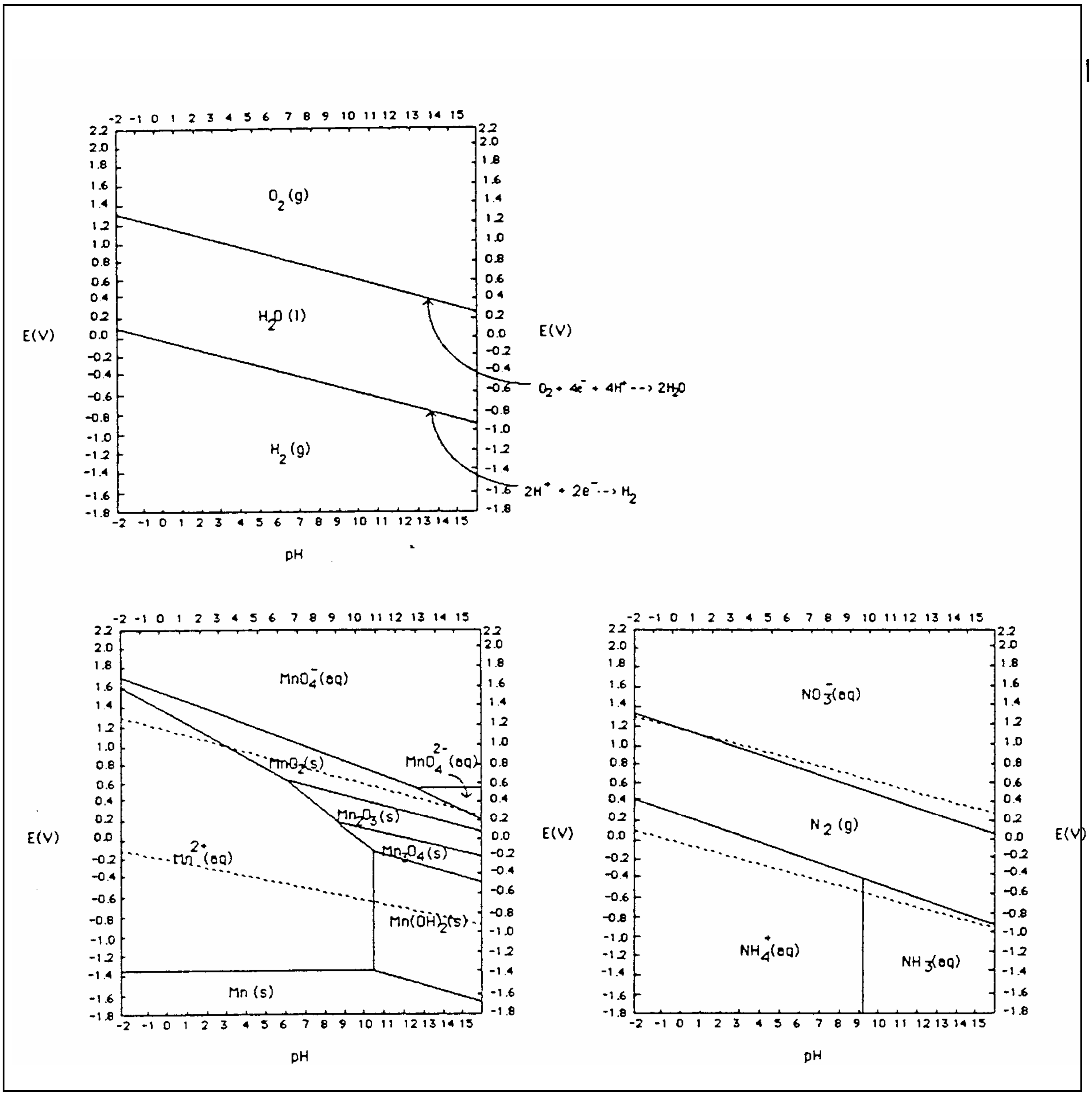
8.7 According to the Pourbaix diagrams, is it dangerous to grind together in a mortar and pestle

i potassium nitrate and manganese metal,

ii) potassium nitrate and manganese dioxide?

8.8 The standard reduction potential, E^0, for the reduction of MnO_4^- to MnO_2 is 1.692 V. Applying the Nernst equation calculate the reduction potential, E, for the reduction of 0.00100 M MnO_4^- solution at a pH = 4.0.

Figure 1



SOLUTION

8.1 i) N_2 ii) NO_3^-

8.2 i) MnO_2 ii) $Mn(OH)_2$

8.3 i) MnO_2, ii) Mn^{2+}

8.4 NO_3^- and N_2. In practice only NO_3^- would oxidize Mn, since the activation energy for N_2 in order to break the triple bonds is very high.

8.5 Mn_3O_4, Mn_2O_3, MnO_2, MnO_4^{2-}, MnO_4^-

8.6 i) NH_4MnO_4: YES

ii) $(NH_4)_2MnO_4$: NO

iii) $2\ NH_4MnO_4 \rightarrow 4\ H_2O + 2\ MnO_2 + N_2$

iv) $(NH_4)_2MnO_4 \rightarrow 4\ H_2O + Mn + N_2$

8.7 According to the diagrams, KNO_3 is easily reduced by Mn whereas the potential of MnO_2 is more positive than the potential of NO_3^-. So a mixture of KNO_3 and Mn could be explosive.

8.8 $$E = E^o + \frac{0.0591}{3}\log[MnO_4^-] + \frac{0.0591}{3}\log[H^+]^4) =$$

$$= 1.692 + 0.0197 \log 0.001 - 0.0788\ pH = 1.633 - 0.0788\ pH = \underline{1.34\ V}$$

THE TWENTY-FIFTH

INTERNATIONAL CHEMISTRY OLYMPIAD

11–22 JULY 1993, PERUGIA, ITALY

THEORETICAL PROBLEMS

PROBLEM 1

^{131}I is a radioactive isotope of iodine (e$^{–}$ emitter) used in nuclear medicine for analytical procedures to determine thyroid endocrine disorders by scintigraphy. The decay rate constant, *k*, of ^{131}I is 9.93×10^{-7} s^{-1}.

Questions:

1.1 Write the decay reaction of ^{131}I.

1.2 Calculate the half-life of ^{131}I expressed in days.

1.3 Calculate the time necessary (expressed in days) for a sample of ^{131}I to reduce its activity to 30 % of the original value.

1.4 Knowing that a Geiger counter detects activities of the order of 10^{-4} μc , calculate the minimum amount of ^{131}I (in grams) which could be detected by this counter.

1 Curie (c) is the amount of a radioisotope that produces 3.7×10^{10} disintegrations s^{1}.

SOLUTION

1.1 $^{131}\text{I} = {}^{131}\text{Xe} + \text{e}$

1.2 Decay reactions are first order reactions. Then:

$$k = \frac{\ln 2}{t_{1/2}} \qquad t_{1/2} = \frac{\ln 2}{k}$$

$$t_{1/2} = \frac{0.693}{9.93\times10^{-7}\times 86400\,\text{s}\,\text{d}^{-1}} = 8.08\,\text{d}$$

1.3 For a first order reaction:

$$\ln\frac{c_0}{c} = k\,t$$

where c_0 and c are the concentrations at time 0 and time t, respectively. Then:

$$\ln\frac{100}{30} = 9.93\times10^{-7}\times t$$

$$t = \frac{1.212\times10^{6}}{8.64\times10^{4}} = 14.03 \text{ d}$$

1.4 1 Curie (c) is the amount of a radioisotope that produces 3.7×10^{10} disintegrations s^{-1}

1 mc = 3.7×10^{7} dis s^{-1}

1 μc = 3.7×10^{4} dis s^{-1}

Then:

$$10^{-4}\ \mu c \times 3.7\times10^{4}\ \text{dis s}^{-1} = 3.7\ \text{dis s}^{-1} = -\frac{dN}{dt}$$

$t_{1/2}$ of ^{131}I expressed in seconds is = 8.08 d × 86400 s d^{-1} = 6.98×10^{5} s

$$m = -\frac{dN}{dt}\times\frac{t_{1/2}\times A_r(\text{I})}{\ln 2\times N_A} = \frac{3.7\times6.98\times10^{5}\times131}{0.693\times6.02\times10^{23}} = 8.11\times10^{-16}\ \text{g}$$

PROBLEM 3

Sulphur forms many different compounds with oxygen and halogens (sulphur as the central atom). These compounds are mainly molecular, and many are easily hydrolysed in water.

3.1 Write Lewis structures for molecules SCl_2, SO_3, SO_2ClF, SF_4, and $SBrF_5$.

3.2 Carefully draw the geometries of the 5 molecules. (Disregard small deviations from "ideal" angles.)

3.3 A compound, consisting of sulphur (one atom per molecule), oxygen and one or more atoms of the elements F, Cl, Br, and I, was examined. A small amount of the substance reacted with water. It was completely hydrolyzed without any oxidation or reduction, and all reaction products dissolved. 0.1 M solutions of a series of test reagents were added to separate small portions of a diluted solution of the substance.

Which ions are being tested for in the following tests?

i) Addition of HNO_3 and $AgNO_3$.

ii) Addition of $Ba(NO_3)_2$.

iii) Adjustment to $pH = 7$ with NH_3 and addition of $Ca(NO_3)_2$.

Write the equations for the possible reactions in the tests:

iv) Addition of $KMnO_4$ followed by $Ba(NO_3)_2$ to an acid solution of the substance.

v) Addition of $Cu(NO_3)_2$.

3.4 In practice, the tests in 3.3 gave the following results:

i) A yellowish precipitate.

ii) No precipitate.

iii) No visible reaction.

iv) The main features were that the characteristic colour of permanganate disappeared, and a white precipitate was formed upon addition of $Ba(NO_3)_2$.

v) No precipitate.

Write the formulas of the possible compounds, taking the results of these tests into account.

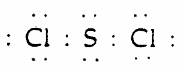
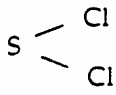
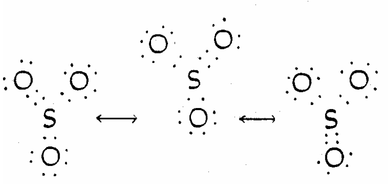
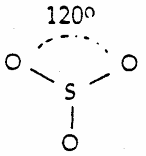
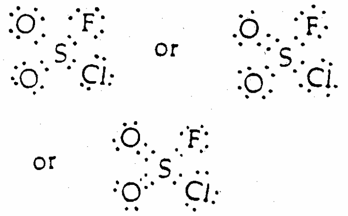
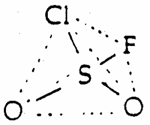
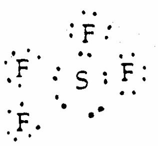
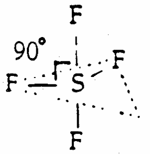
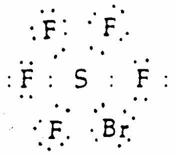
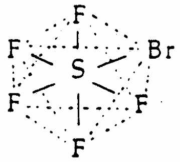
3.5 Finally, a simple quantitative analysis was undertaken:

7.190 g of the substance was weighed out and dissolved in water to give 250.0 cm^3 of a solution. To 25.00 cm^3 of this solution, nitric acid and enough $AgNO_3$ was added to secure complete precipitation. After washing and drying the precipitate weighed 1.452 g. Determine the formula of the compound.

3.6 Write the equation describing the reaction of the substance with water.

If you have not found the formula for the compound, use SOClF.

SOLUTION

	3.1	**3.2**
SCl_2		Bent 
SO_3		Trigonal planar 
SO_2ClF		Tetrahedral 
SF_4		Trigonal bipyramidal÷1 corner 
$SBrF_5$		Octahedral 

3.3 i) Cl^-, Br^-, I^-

ii) SO_4^{2-}

iii) F^-

iv) $2\ MnO_4^- + 5\ HSO_3^- + H^+ \rightarrow 5\ SO_4^{2-} + 2\ Mn^{2+} + 3\ H_2O$

$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\,(s)$

v) $2\ Cu^{2+} + 4\ I^- \rightarrow 2\ CuI(s) + I_2$

3.4 SOClBr and $SOBr_2$

3.5 SOClBr

[SOClBr: 1.456g, and $SOBr_2$: 1.299g]

3.6 $SOClBr + 2\ H_2O \rightarrow HSO_3^- + Cl^- + Br^- + 3\ H^+$

$SOClF + 2\ H_2O \rightarrow HSO_3^- + Cl^- + HF + 2\ H^+$

PROBLEM 4

Platinum(IV) oxide is not found in the nature, but it can be prepared in a laboratory. Solid platinum(IV) oxide is in equilibrium with platinum metal and oxygen gas at 1 atm (= 1.01325×10^5 Pa) and 650 °C.

4.1 This suggests that the conditions on the Earth, when the minerals we know were formed, were:

[1] $p(O_2) = 1$ atm, t = 650 °C;

[2] $p(O_2) < 1$ atm, t < 650 °C;

[3] $p(O_2) > 1$ atm, t < 650 °C;

[4] $p(O_2) < 1$ atm, t > 650 °C;

[5] $p(O_2) > 1$ atm, t > 650 °C

Mark the most probable alternative [1] – [5] on the answer sheet. Please note that the marking of only one alternative will be accepted.

4.2 What are ΔG and K_p for the formation of platinum(IV) oxide at oxygen pressure of 1 atm and temperature of 650 °C?

The preparation of platinum(IV) oxide involves boiling of a solution which contains hexachloroplatinate(IV) ions with sodium carbonate. In this process $PtO_2 \cdot n\ H_2O$ is formed and this is in turn converted to platinum(IV) oxide upon subsequent filtering and heat treatment. In the following we assume n = 4.

$PtO_2 \cdot 4\ H_2O$ or $Pt(OH)_4 \cdot 2\ H_2O$ can be dissolved in acids and strong bases.

4.3 Write the balanced equations for the preparation of platinum(IV) oxide according to the procedure given above.

4.4 Write the balanced equations for the dissolution of $PtO_2 \cdot 4\ H_2O$ in both hydrochloric acid and sodium hydroxide.

Platinum is mainly found in the nature as the metal (in mixture or in alloying with other precious metals). Platinum is dissolved in aqua regia under the formation of hexachloroplatinate(IV) ions. Aqua regia is a mixture of concentrated hydrochloric and nitric acids in proportion 3 : 1, and of the nitrosylchloride (NOCl) and the atomic chlorine which are formed upon the mixing. The latter is believed to be the active dissolving component.

The hexachloroplatinate(IV) ions can be precipitated as diammonium hexachloroplatinate(IV) and by thermal decomposition of this compound, finely powdered platinum and gaseous products are formed.

4.5 Write the balanced equations for the formation of aqua regia and its reaction with platinum.

4.6 Write the balanced equation of the thermal decomposition of diammonium hexachloroplatinate(IV) at elevated temperature.

From diammonium hexachloroplatinate(IV) we can prepare $Pt(NH_3)_2Cl_2$ which occurs in *cis* (ΔH_f^0 = – 467.4 kJ mol^{-1}, ΔG_f^0 = – 228.7 kJ mol^{-1}) and *trans* (ΔH_f^0 = – 480.3 kJ mol^{-1}, ΔG_f^0 = – 222.8 kJ mol^{-1}) form.

4.7 The occurrence of the isomers shows that $Pt(NH_3)_2Cl_2$ hasgeometry:

[1] linear,

[2] planar,

[3] tetrahedral,

[4] octahedral geometry.

Mark the correct alternative of [1] – [4] on the answer sheet.

4.8 Is the *cis* form or *trans* form thermodynamically more stable?

Platinum is used as a catalyst in modern automobiles. In the catalyst carbon monoxide (ΔH_f^0 = –110.5 kJ mol^{-1}, ΔG_f^0 = –137.3 kJ mol^{-1}) reacts with oxygen to carbon dioxide (ΔH_f^0 = –393.5 kJ mol^{-1}, ΔG_f^0 = –394.4 kJ mol^{-1}).

4.9 Is the reaction spontaneous at 25 °C?

[1] yes, or

[2] no.

Is the reaction:

[3] endothermic, or

[4] exothermic?

Calculate $\Delta S°$ for the reaction.

Establish whether the entropy of the reaction system

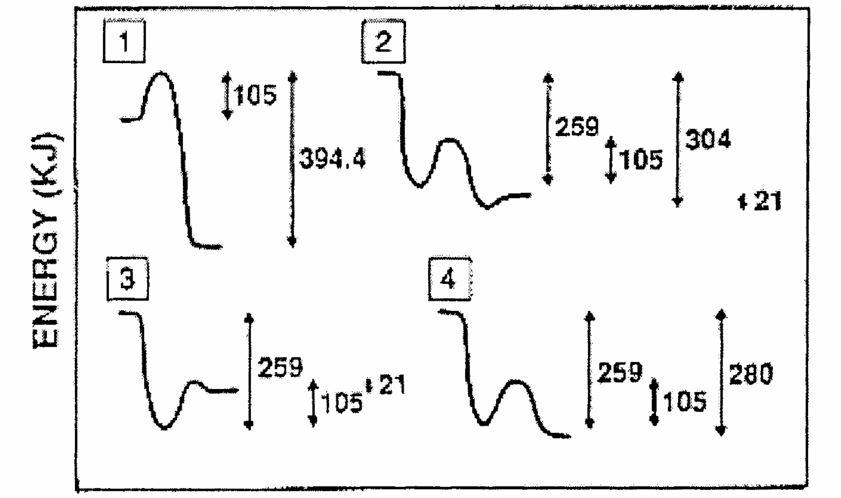
[5] increases, or

[6] decreases.

4.10 Establish an expression for the temperature dependence of the equilibrium constant in this case.

The overall catalytic reaction is simple, whereas the reaction mechanism in the homogeneous phase is very complicated with a large number of reaction steps, and the course is difficult to control owing to a distinct chain character. With platinum as catalyst the significant reaction steps are: (i) Adsorption of CO and adsorption/dissociation of O_2 (ΔH = –259 kJ per mol CO + O), (ii) their activation (105 kJ per mol CO + O) and (iii) the reaction and the desorption of CO_2 (ΔH = 21 kJ per mol CO_2).

A one-dimensional energy-diagram for the platinum catalyzed oxidation of carbon monoxide to dioxide can be represented as:



4.11 Mark the correct alternative of [1] – [4] on the answer sheet.

SOLUTION

4.1 Correct answer is No 4.

4.2 ΔG = 0 kJ and K_p = 1 according to the chemical equation

$Pt(s) + O_2(g) \rightarrow PtO_2(s)$

4.3 $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$

$PtCl_6^{2-}(aq) + 4\ OH^-(aq) + 2\ H_2O(l) \rightarrow Pt(OH)_4 \cdot 2\ H_2O(s) + 6\ Cl^-(aq)$

Alternative I: $PtO_2 \cdot 4\ H_2O(s) + 6\ Cl^-(aq)$

Alternative II: $(n–2)\ H_2O \rightarrow PtO_2 \cdot n\ H_2O(s) + 6\ Cl^-(aq)$

$PtO_2 .\ 4\ H_2O(s) \rightarrow PtO_2(s) + 4\ H_2O(g)$

$[PtO_2 \cdot 4\ H_2O(s) \rightarrow Pt(OH)_4 \cdot 2\ H_2O(s)]$

4.4 In hydrochloric acid:

$PtO_2 \cdot 4\ H_2O(s) + 4\ H^+(aq) + 6\ Cl^-(aq) \rightarrow PtCl_6^{2-}(aq) + 6\ H_2O$

In sodium hydroxide:

$PtO_2 \cdot 4\ H_2O(s) + 2\ OH^-(aq) \rightarrow Pt(OH)_6^{2-}(aq) + 2\ H_2O$

4.5 $3\ HCl(sol) + HNO_3(sol) \rightarrow NOCl(sol) + 2\ Cl(sol) + 2\ H_2O(sol)$

$Pt(s) + 4\ Cl(sol) + 2\ HCl(sol) \rightarrow PtCl_6^{2–}(sol) + 2\ H^+(sol)$

4.6 $(NH_4)_2PtCl_6(s) \rightarrow Pt(s) + 2\ NH_3(g) + 2\ HCl(g) + 2\ Cl_2(g)$

4.7 Correct is No 2.

4.8 The cis form is thermodynamically more stable.

4.9 [1] Yes. ($\Delta G° = – 257.1$ kJ for $CO(g) + 1/2\ O_2(g) \rightleftharpoons CO_2(g)$)

[4] The reaction is exothermic.

($\Delta H° = – 283.0$ kJ for $CO(g) + 1/2\ O_2(g) \rightleftharpoons CO_2(g)$)

[6] is correct.

$\Delta S° = – 0.0869$ kJ K^{-1} for $CO(g) + 1/2\ O_2(g) \rightleftharpoons CO_2(g)$;

As seen from the sign for $\Delta S°$ as well as for the reaction enthalpy the entropy of the system decreases.

4.10 ln K_p = 34037 / T – 10.45 for $CO(g) + 1/2\ O_2(g) \rightleftharpoons CO_2(g)$

Alternative: $K_p = \exp^{(34037\ /\ T\ –\ 10.45)}$

4.11 No 2 is correct.

PROBLEM 5

The action of nitric oxide upon human body is dual. The nitric oxide generated in nerve cells will damage the cells, while the nitric oxide generated in endothelial cells of blood vessels can relax the vessels and control blood pressure.

5.1 Indicate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of NO molecule using one of symbols π, σ, π***** or σ*, and indicate the electron(s) residing in the corresponding orbital using symbols ↑ and/or ↓.

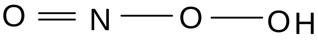
5.2 The relaxation of blood vessels is caused by a series of changes which are mediated by the coordination of NO molecule to iron ion, the latter being a component of an enzyme containing heme. It was known that the coordinated NO behaves as CO molecule (isoelectronic), which one of the following species really exists in the iron complex?

a) NO b) NO^+ c) NO^-

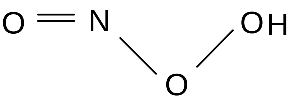
5.3 The cell damage is caused by free radical OH, which is one of the product of reaction between O_2^- and NO:

$$O_2^- + NO + H^+ \rightarrow HOONO \rightarrow \bullet NO_2 + \bullet OH$$

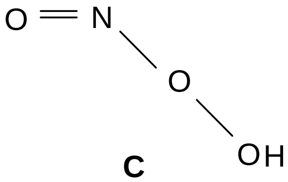
in which an intermediate with composition of HOONO is evolved. HOONO is a weak acid. Choose the structural formula with correct bond angles for the intermediate.



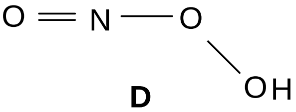
A



B

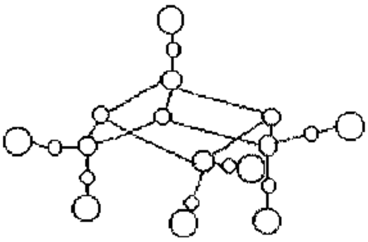


C



D

5.4 For preservation of meat, sodium nitrite is usually added and as a result NO is, then, formed. Consequently, NO reacts with the sulphur and iron atoms from decomposition of proteins, forming $[Fe_4S_3(NO)_7]^-$. The complex anion is bacteriostatic and antiseptic. X-ray crystallography shows that the complex anion has a structure as shown below:



i) Blacken all the circles corresponding to iron atoms and add symbols Fe(A), Fe(B), Fe(C) and Fe(D) beside the circles in the sequence of top → left → right.

ii) The configuration of 3d electron shell of the iron atoms has been studied with modern structural analysis. Knowing that the mean oxidation number of the four iron atoms is –0.5, give their configurations of 3d shell, respectively. Assume that each iron atom adopt sp hybridization.

5.5 $[Fe_4S_3(NO)_7]^-$ anion can be reduced and a new complex $[Fe_2S_2(NO)_4]^{2-}$ is formed which contains a cyclic structure unit of Fe_2S_2.

i) Write the structural formula for the anion $[Fe_2S_2(NO)_4]^{2-}$.

ii) Give the oxidation state of each iron atom with Arabic numerals.

iii) $[Fe_2S_2(NO)_4]^{2-}$ can be converted into $[Fe_2(SCH_3)_2(NO)_4]^n$, a carcinogen. Which of the following three species is added to $[Fe_2S_2(NO)_4]^{2-}$: CH_3^+, $\bullet CH_3$ or CH_3^-? Assign the value of n.

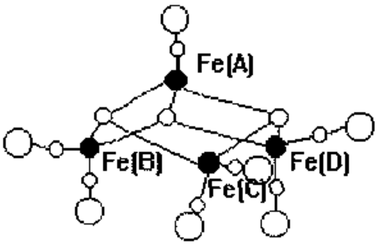
SOLUTION

5.1 The HOMO of NO molecule is π*, its electron arrangement ↑;
The LUMO of NO molecule is π*.

5.2 (b)

5.3 B

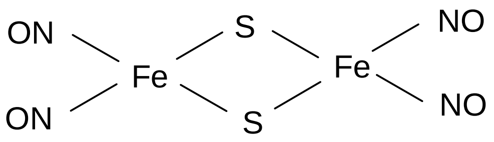
5.4



Fe(A) has $3d^7$ configuration;

Fe(B), Fe(C) , and F(D) have 3d^9 configuration.

5.5 i)



ii) Fe(-1) Fe(-1)

iii) The species added to S atom is CH_3^+; n = 0.

THE TWENTY-EIGHTH
INTERNATIONAL CHEMISTRY OLYMPIAD
14–23 JULY 1996, MOSCOW, RUSSIAN FEDERATION

THEORETICAL PROBLEMS

PROBLEM 1

The stereoregular polymerization of unsaturated hydrocarbons is usually considered as one of the most important for the industrial organic chemistry. The salts of big nonlinear cations carrying a sufficiently high charge to attack the electron density distributed along the π-bonds of the olefin molecules are usually used as the catalysts in these processes. Chloroaluminate anions (like $AlCl_4^-$) possessing a highly delocalized negative charge are used usually as the anions. The necessity to develop new catalysts of this kind urged the chemists to study the interaction in the system A - B, where A = Te(cryst.) and B = ($TeCl_4$ + 4 $AlCl_3$). The second component B was considered as an analog of Te(IV) chloroaluminate $Te[AlCl_4]_4$ which, however, cannot be isolated as an individual compound. It was found out that the interaction of the components A and B can lead to the formation of three new compounds (**I**, **II** and **III**) in the systems containing initially 77.8, 87.5 and 91.7 mol. % of the component A, respectively. It was also noticed that while in the case of compounds **II** and **III** no side products were formed, the formation of **I** was accompanied by the evolution of 1 mole of volatile $TeCl_4$ per two moles of **I**.

The compounds **I** and **II** attracted a particular interest of investigators. They both have pinkish-purple color and both dissociate into three ions as the conductivity studies in melted $NaAlCl_4$ showed. The cryoscopic measurements in $NaAlCl_4$ melt enabled to determine the molecular weights of these compounds being equal to 1126 ± 43 g mol^{-1} and 867 ± 48 g mol^{-1} for **I** and **II**, respectively. In the IR spectra of both compounds there is only one band observed which can be attributed to a vibration mode of a bond formed by Te atom. This band lies at 133 cm^{-1} and is therefore so low in energy that this bond undoubtedly is a kind of Te – Te interaction. The ^{27}Al NMR data for the complexes **I** and **II** show that in each compound there is only one type of tetrahedrally coordinated aluminum. However, the observed chemical shifts of aluminium for the compounds **I** and **II** are different, thus manifesting that Al atoms are different in them.

1.1 Determine Te : Al : Cl minimal atomic ratio for the complexes **I**, **II** and **III**.

1.2 Write the molecular-formulae of the compounds **I** and **II**.

1.3 Write the formulae of the anions and cations in compounds **I** and **II**.

1.4 Draw stereochemical formulae of cations and anions in the structures of **I** and **II** assuming that the cations in **I** and **II** are examples of inorganic aromatic systems.

1.5 Which compound has a higher thermal stability, **I** or **II**, taking into account that $AlCl_3$ is extremely volatile compound.

1.6 If one of the compounds **I** or **II** can be transformed into the other by heating, write the corresponding reaction equation.

SOLUTION

1.1 Te : Al : Cl ratios:

Compound I 2 : 2 : 7
Compound II 2 : 1 : 4
Compound III 3 : 1 : 4

solution:

The determination of the Te : Al : Cl ratios can be made using the data on the content of Te(cryst.) thus:

77.8 % of Te(cryst.) corresponds to Te(cryst.) + 2 $TeCl_4$ + 8 $AlCl_3$ and the minimum atomic ratio for the composition from which the excess of $TeCl_4$ is not substracted is Te : Al : Cl = 9 : 8 : 32, where the contents of Al and Cl are even and can be divided by 4, while that of Te exceeding the analogous even number by 1. Substracting one mole of $TeCl_4$ from the obtained ratio and dividing by 2 we obtain 4 Te + 4 Al + 14 Cl and the ratio is Te : Al : Cl = 2 : 2 : 7, which can be then verified by comparison with the molecular weight given 87.5 % of Te(cryst.) corresponds to 7 Te(cryst.) + $TeCl_4$ + 4 $AlCl_3$ = 8 Te + 4 Al + 16 Cl and the ratio is Te : Al : Cl = 2 : 1 : 4. 91.7 % of Te(cryst.) corresponds to 11 Te(cryst.) + $TeCl_4$ + 4 $AlCl_3$ = 12 Te + 4 Al + 16 Cl and the ratio is Te : Al : Cl = 3 : 1 : 4.

1.2 The molecular formulae of compounds **I** and **II**:

Compound **I**: $Te_4Al_4Cl_{14}$

Compound **II**: $Te_4Al_2Cl_8$

Molecular formulae can be deduced from the data on molar weights. Both correspond to double simplest formula.

For compound I: 2 ($Te_2Al_2Cl_7$) gives calculated M_r = 1114.7 while experimental value is 1126 ± 43.

For compound II: 2 (Te_2AlCl_4) gives calculated M_r = 848 while experimental value is 867 ± 48.

1.3 Cations and anions in compounds I and II:

Compound **I**: $[Te_4]^{2+}$ $[Al_2Cl_7]^-$

Compound **II**: $[Te_4]^{2+}$ $[AlCl_4]^-$

The compositions of the ions included in the structures of **I** and **II** can be determined by taking into consideration that both **I** and **II** are tri-ionic electrolytes, and the fact that all the tellurium atoms should be equivalent according to IR and are bonded only to each other. The Al atoms are in both compounds tetrahedrally coordinated and equivalent. At least in one case this can be $AlCl_4^-$ anion which seems probable for **II**, which therefore can be formulated as $[Te_4]^{2+}[AlCl_4]_2^-$. As according to similar colouration the cations are likely to be the same in both cases, the structure of **I** should contain $[Te_4]^{2+}$ cations and $[Al_2Cl_7]^-$ anions, which seems also to be in a good agreement with NMR data, assigning to Al atoms in **I** with a different tetrahedral geometry than that in **II**.

1.4 The geometry of the cation:

$[Te_4]^{2+}$ is a plane square due to proclaimed aromaticity.

The plane square configuration appears to be more favourable because the cation is mentioned to be aromatic, which means planar and possessing equal bond lengths for the sides of the corresponding aromatic ring.

The geometry of anions:

$AlCl_4^-$ is a single tetrahedron;

$Al_2Cl_7^-$ - there are two tetrahedra sharing a common vertex (a chlorine atoms).

1.5 The thermal stability of **II** should be higher than that of **I**. They both are ionic compounds with high melting points, but compound **I** can be transformed into **II** by the elimination of $AlCl_3$. which is a volatile solid and can be relatively easily removed on heating.

1.6 The reaction equation:

$Te_4[Al_2Cl_7]_2 = Te_4[AlCl_4]_2 + 2\ AlCl_3$

PROBLEM 6

6.1 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?

6.2 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.

$n\,\mathbf{A}wClx + m\,NH_3 \rightarrow p\,NH_4Cl + q\,\mathbf{A} + r\,\mathbf{A}yNz$

(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:

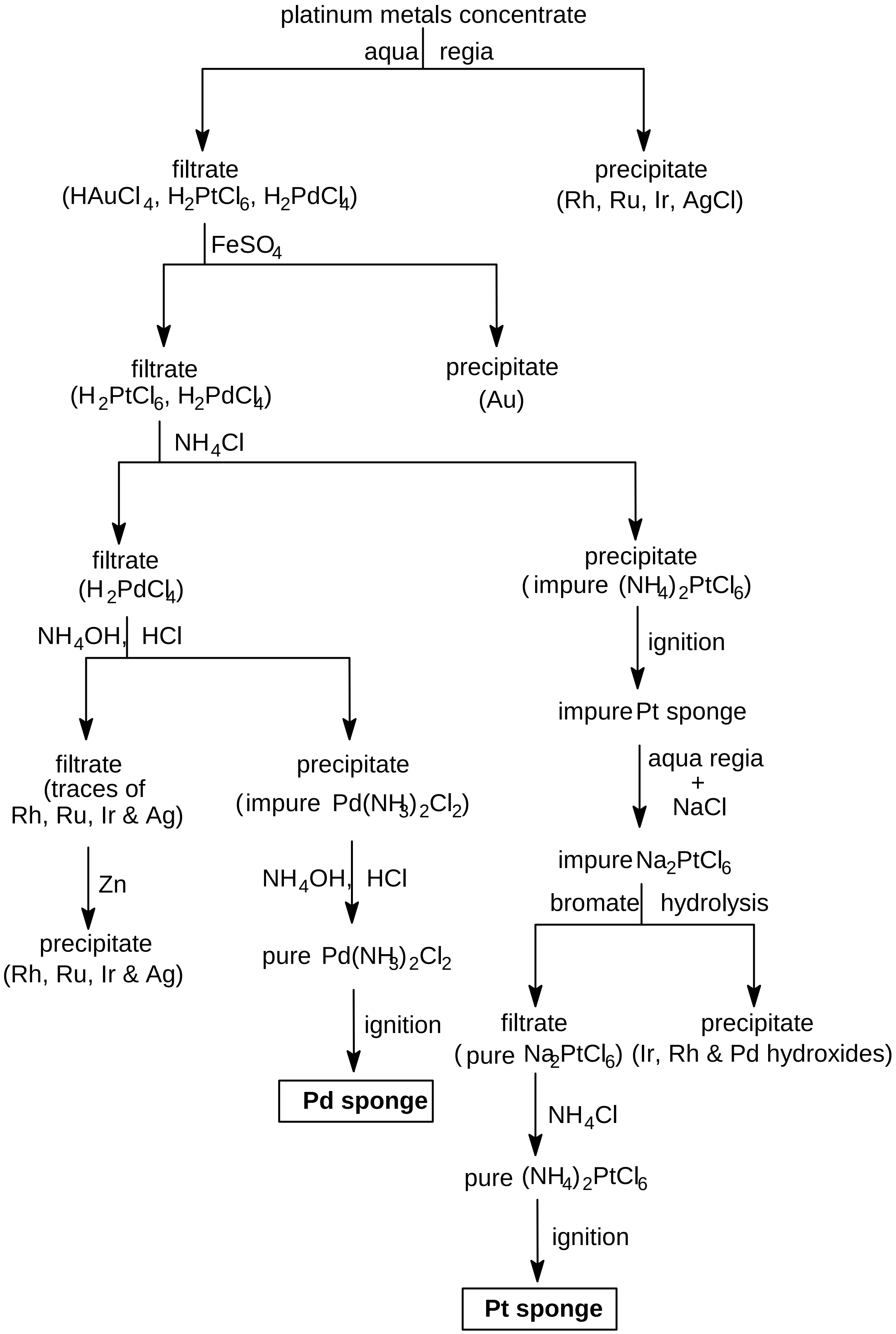
$M(Cl) = 35.453$ g mol^{-1} $M(N) = 14.007$ g mol^{-1} $M(H) = 1.008$ g mol^{-1}

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.

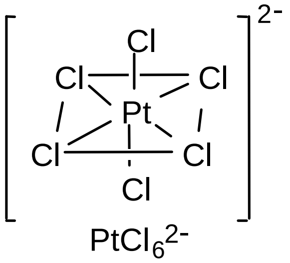
Method of Purification of Platinum and Palladium



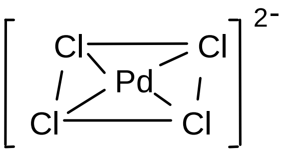
SOLUTION

6.1

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

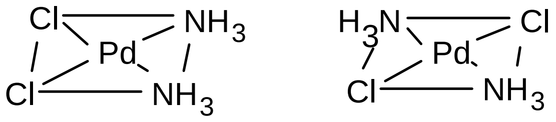


$PtCl_6^{2-}$



$PdCl_4^{2-}$

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

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

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

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

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

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

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

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

or

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

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

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

$2\,N^{3-} - 14\,e^- \rightarrow 2\,N^{4+}$ 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.

6.2

i) A = sulphur

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 × 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:

Proportions of 1 : 1

Chloride:

7.69 g A binds → 17.02 g Cl

? g A binds → 35.453 g Cl

? = 35.453 × 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 × 5.12/2.25 = 31.87* g

A could be is sulphur, fits the physical description and M_r(S) = 32.064

(*Phosphorus, M_r(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:

7.69 g A binds → 17.02 g Cl

? g A binds → 2 × 35.453 g Cl

? = 2 × 35.453 × 7.69 / 17.02 = 32.03 g. Again A could be sulphur.

Nitride:

5.12 g A binds → 2.25 g N

? g A binds → 2 × 14.007 g N

? = 2 × 14.007 × 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 sulphur.

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

or

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

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 sulphur chlorides (S_2Cl_2 and SCl_4) do not fit the stoichiometry of the reaction.)

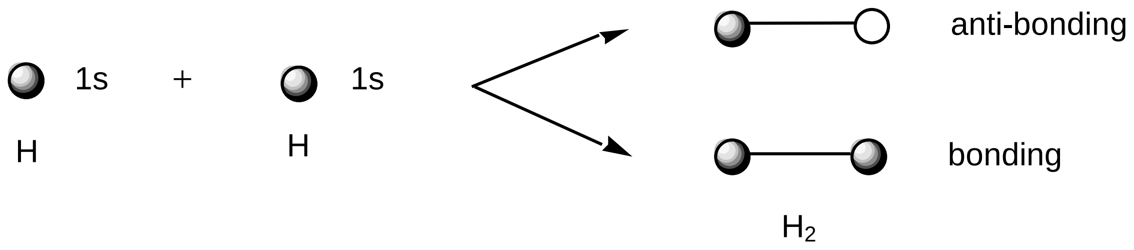
iii) A disproportionation reaction involving sulphur occurs:

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

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

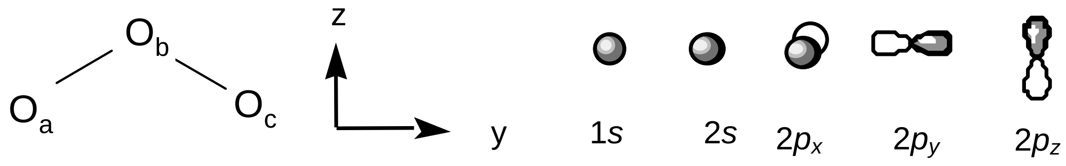
PROBLEM 4

When two hydrogen atoms come together, the 1s atomic orbitals combine to form bonding and anti-bonding molecular orbitals:



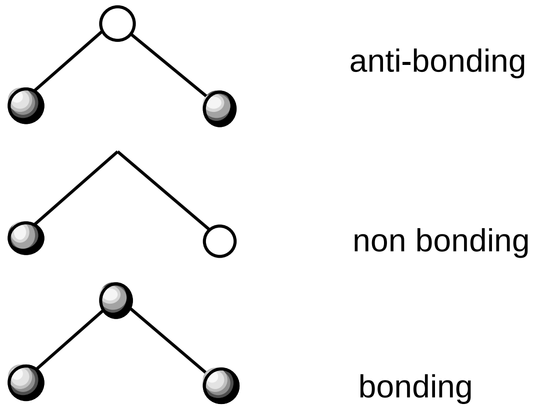
In a similar way, we may combine the atomic orbitals of more complicated atoms to form molecular orbitals, taking into account the symmetry of the molecule.

Consider the ozone molecule, O_3, which is shaped like an Australian boomerang. We can arrange the oxygens as follows (in the *yz* plane) and assume that there are 1*s*, 2*s*, 2p_x, 2p_y and 2p_z orbitals on each atom.



The atoms O_a and O_c are "related by symmetry" and the 1*s* orbitals on these atoms form symmetric and anti-symmetric combinations:

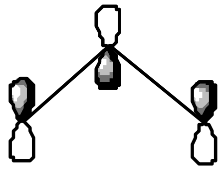
In this molecule the 1*s* atomic orbital on O_b is classified as symmetric. It can combine with the symmetric combination of O_a and O_c given above (but not with the anti-symmetric combination) to form bonding and anti-bonding molecular orbitals. The anti-symmetric combination is non-bonding. The final three molecular orbitals are:



4.1 On the answer sheet, use a similar approach to construct the molecular orbitals arising from the separate interaction of the 2*s*, 2p_x, 2p_y, and 2p_z atomic orbitals. (Remember to form the symmetric and anti-symmetric combinations of Oa and Oc first.)

We may now rearrange these molecular orbitals in order of increasing energy. This can be generalised to other triatomic molecules. The energy of these orbitals is different in a bent triatomic molecule (like ozone) compared to a linear molecule (like carbon dioxide). The variation in orbital energy may be represented in a "Walsh diagram" for XY_2 molecules as shown on the answer sheet. It shows a plot of the energy of each orbital versus the Y–X–Y bond angle. The orbitals have been given labels which we call "symmetry labels".

The $6a_1$ orbital referred to in the Walsh diagram is shown below.



4.2 Why does the energy of the $6a_1$ orbital increase so rapidly as the bond angle changes from 90° to 180°?

Only occupied molecular orbitals affect the geometry, and a doubly occupied orbital has more influence than a singly occupied orbital. For example, O_3 has 24 electrons and so at a bond angle of 135° the orbitals are doubly occupied up to $6a_1$. Thus, the lowest-energy geometry of ozone (taking into account steric repulsion and the contrasting energy behaviour of the $4b_2$, $1a_2$ and $6a_1$ orbitals) is probably towards the left of the Walsh diagram, which is consistent with the observed bond angle of 116°.

4.3 At a bond angle of 135°, what are the highest occupied orbitals for the molecules BO_2, CO_2, NO_2 and FO_2?

4.4 The bond angles of BO_2, CO_2 and O_3 are known experimentally to be 180°, 180° and 116°, respectively. Use the Walsh diagram on the answer sheet to predict whether NO_2 and FO_2 are more or less bent than O_3.

SOLUTION

4.1 Construction of the molecular orbitals arising from the separate interaction of the 2*s*, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals is shown on the next page.

4.2 Why does the energy of the $6a_1$ orbital increase so rapidly as the bond angle changes from 90° to 180°? (Choose one)

a) Because the bonding character decreases.

b) Because the anti-bonding character increases.

c) Both (a) and (b).

d) Because the overlap decreases.

The correct answer is c).

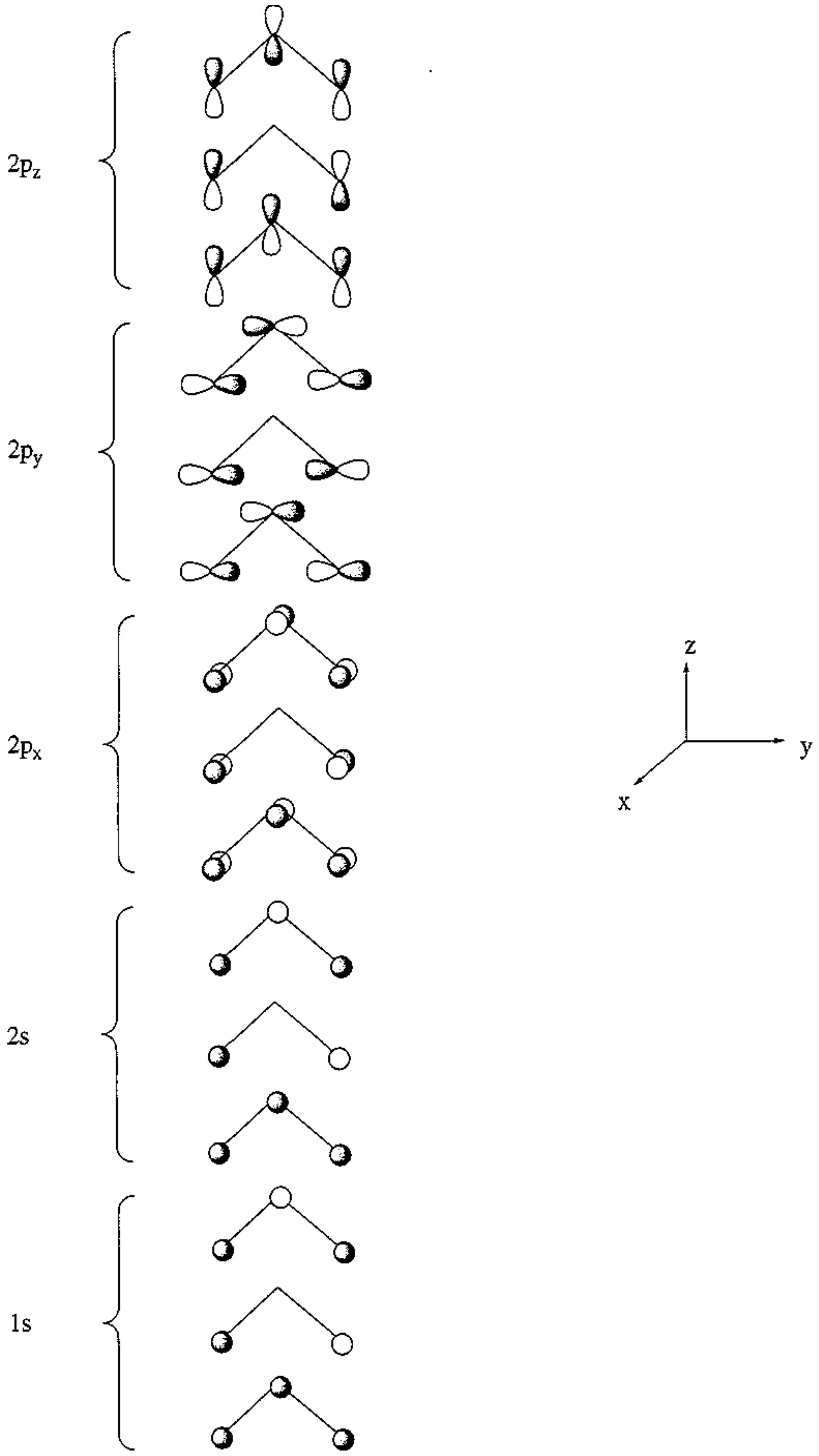
Reasoning: The energy changes so rapidly because the overlap is bonding between all three atoms in the bent molecule, but becomes more and more anti-bonding as the molecule approaches linearity:

4.3

O_3	BO_2	CO_2	NO_2	FO_2
$6a_x$ (24e-)	$4b_2$ (21e-)	$4b_2$ (22e-)	*$6a_1$* (23e-)	2bx (25e-)

4.4 The correct answer is (d): NO_2 is less bent than O_3, and FO_2 is more bent than O_3.

Atomic orbitals   Molecular orbitals



PROBLEM 6

Unlike carbon, tin can increase its coordination number beyond four. Like carbon, tin forms a chloride, $SnCl_4$.

6.1 Draw two alternative geometries for $SnCl_4$.

Lewis acids such as $SnCl_4$ react with Lewis bases such as chloride ion or amines. In the case of chloride the following two reactions are observed.

$SnCl_4 + Cl^- \rightarrow SnCl_5^-$

and

$SnCl_4 + 2\ Cl^- \rightarrow SnCl_6^{2-}$

6.2 Draw three alternative geometries for $SnCl_5^-$.

6.3 Use Valence Shell Electron Pair Repulsion (VSEPR) theory to predict which geometry is likely to be preferred for $SnCl_5^-$.

6.4 Draw three alternative geometries for $SnCl_6^{2-}$.

6.5 Use VSEPR theory to predict which of these geometries is likely to be preferred for $SnCl_6^{2-}$.

A solution containing $SnCl_6^{2-}$ (as the tetrabutylammonium salt) was examined by negative ion electrospray mass spectrometry (ESMS). The spectrum contains a single peak at m/z = 295.

You may assume that the only isotopes observed in this species are ^{120}Sn and ^{35}Cl.

6.6 Write the empirical formula for the tin-containing species detected by this technique.

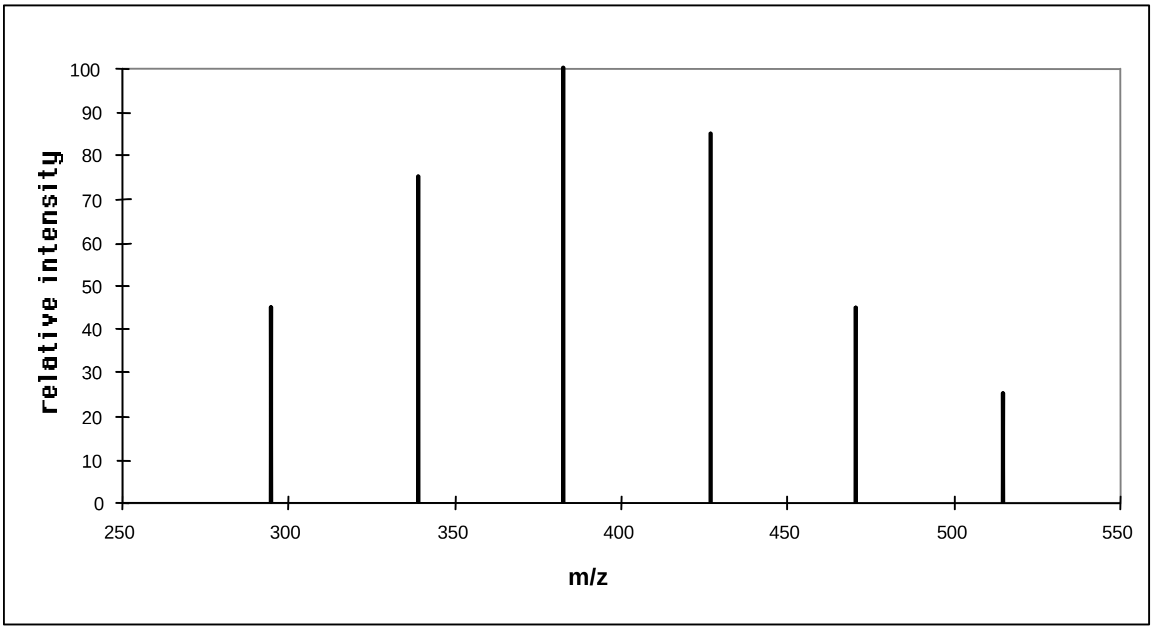
A solution containing $SnBr_6^{2-}$ (as the tetrabutylammonium salt) was examined by negative ion electrospray mass spectrometry (ESMS). The spectrum contains a single peak at m/z=515.

You may assume that the only isotopes observed in this species are ^{120}Sn and ^{79}Br.

6.7 Write the formula for the tin-containing species detected by this technique.

The ESMS spectrum of a solution made by mixing equimolar amounts of $SnCl_6^{2-}$ and $SnBr_6^{2-}$ (as tetrabutylammonium salts) shows six major species (Fig. 1).

Fig. 1



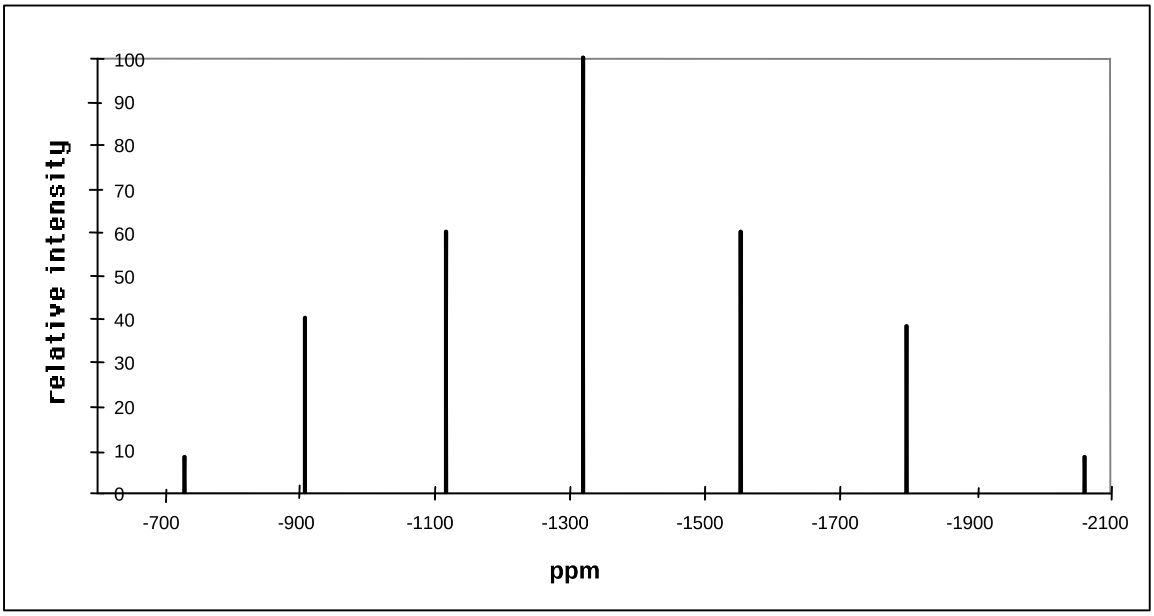
6.8 Write the empirical formula for each of the four new species.

^{1}H and ^{13}C NMR spectroscopy of molecules enable detection of a separate signal for each proton and ^{13}C nucleus which is in a different environment. These signals are recorded on dimensionless parts per million (ppm) scale relative to some agreed standard reference compound. Similarly, ^{119}Sn NMR gives a signal for each tin atom which is in a different environment.

The ^{119}Sn NMR spectrum of a solution of $SnCl_6^{2-}$ (as the tetrabutylammonium salt) contains only one signal which occurs at –732 ppm (relative to tetramethyltin, Me_4Sn). The ^{119}Sn NMR spectrum of a solution of $SnBr_6^{2-}$ (as the tetrabutylammonium salt) occurs at 2064 ppm. The ^{119}Sn NMR spectrum at 60 °C of a solution formed by mixing equimolar amounts of $SnCl_6^{2-}$ and $SnBr_6^{2-}$ contains seven peaks (Fig. 2).

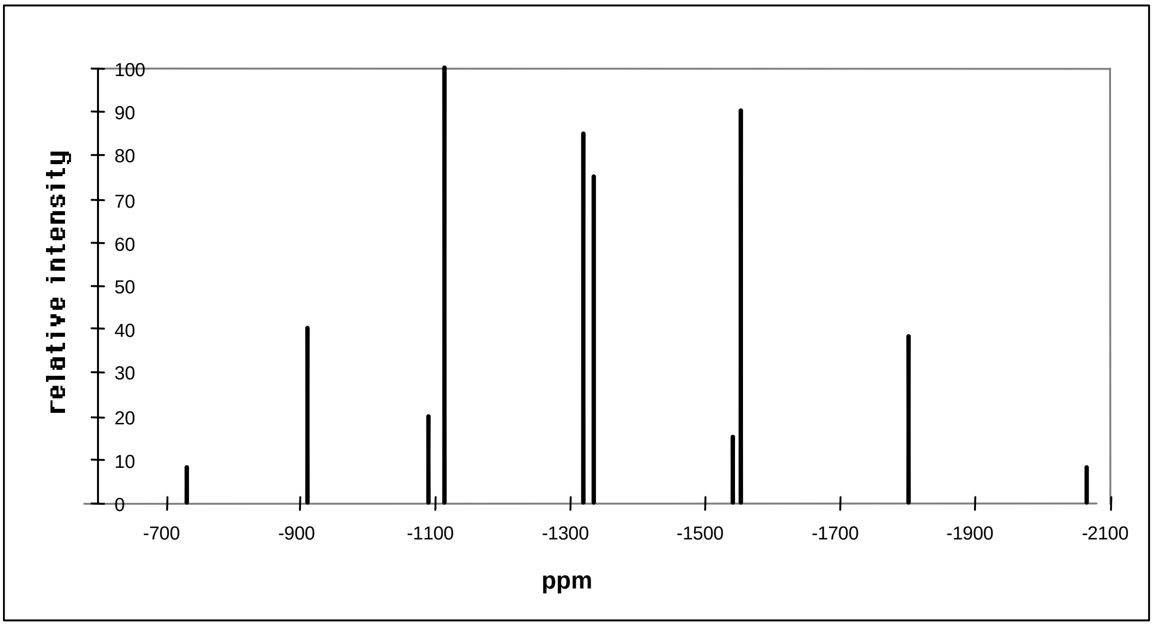
6.9 Write the empirical formula for the tin-containing species in this mixture that give rise to the peaks listed on the answer template.

Fig. 2



Cooling the solution causes a change to this ^{119}Sn NMR spectrum and at -30 °C ten peaks are observed (Fig. 3).

Fig. 3

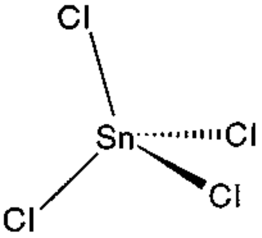


6.10 Draw the geometry for the four tin-containing species present in this solution at –30 °C that give rise to the peaks at –1092 and –1115, –1322 and –1336 ppm.

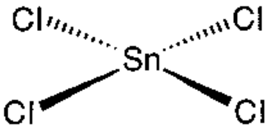
SOLUTION

6.1

A

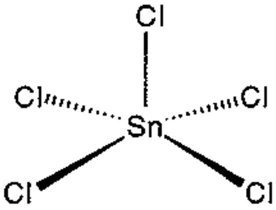


B

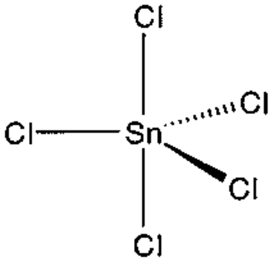


6.2

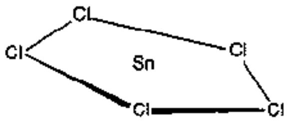
C



D



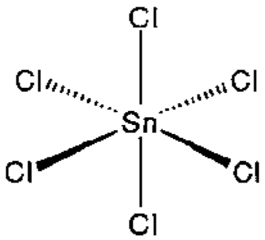
E



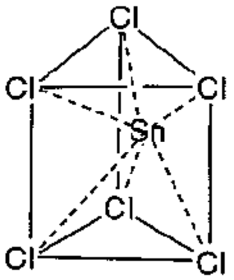
6.3 In accordance with VSEPR theory geometry D is likely to be preferred for $SnCl_5^-$.

6.4

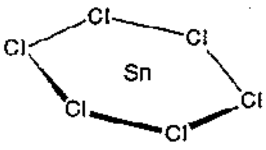
F



G



H



6.5 In accordance with VSEPR theory geometry of F is likely to be preferred for $SnCl_5^-$

6.6 $SnCl_5^-$

6.7 $SnBr_5^-$

6.8 m/z = 339: $SnCl_4Br^{--}$ m/z = 427: $SnCl_2Br_3^-$

m/z = 383: $SnCl_3Br_2^-$ - m/z = 471: $SnClBr_4^-$

6.9

- 912 ppm: $SnCl_5Br^{2-}$
-1117 ppm: $SnCl_4Br_2^{2-}$
-1322 ppm: $SnCl_3Br_3^{2-}$
-1554 ppm: $SnCl_2Br_4^{2-}$
-1800 ppm: $SnClBr_5^{2-}$

6.10

-1092 ppm and -1115 ppm (2 compounds)

-1322 ppm and -1336 ppm (2 compounds)

PROBLEM 3

One of naturally occurring radioactive decay series begins with $^{232}_{90}\text{Th}$ and ends with a stable $^{208}_{82}\text{Pb}$.

3.1 How many beta (β^-) decays are there in this series? Show by calculation.

3.2 How much energy in MeV is released in the complete chain?

3.3 Calculate the rate of production of energy (power) in watts (1 W = J s^{-1}) produced by 1.00 kilogram of ^{232}Th ($t_{½}$ = 1.40×10^{10} years).

3.4 ^{228}Th is a member of the thorium series. What volume in cm^3 of helium at 0 °C and 1 atm collected when 1.00 gram of ^{228}Th ($t_{1/2}$ = 1.91 years) is stored in a container for 20.0 years. The half-lives of all intermediate nuclides are short compared to the half-life of ^{228}Th.

3.5 One member of thorium series, after isolation, is found to contain 1.50×10^{10} atoms of the nuclide and decays at the rate of 3440 disintegrations per minute. What is the half-life in years?

The necessary atomic masses are :

$^{4}_{2}\text{He}$ = 4.00260 u, $^{208}_{82}\text{Pb}$ = 207.97664 u, $^{232}_{90}\text{Th}$ = 232.03805 u; and 1u = 931.5 MeV

1 MeV = 1.602×10^{-13} J

$N_A = 6.022\times10^{23}$ mol^{-1}

The molar volume of an ideal gas at 0 °C and 1 atm is 22.4 dm^3 mol^{-1}.

SOLUTION

3.1 A = 232 – 208 = 24; 24/4 = 6 alpha particles

The nuclear charge is therefore reduced by 2 × 6 = 12 units, however, the difference in nuclear charges is only 90 – 82 = 8 units. Therefore there must be

12 – 8 = 4 β^- emitted.

Number of beta decays = 4

3.2 $^{232}_{90}\text{Th} \rightarrow {}^{208}_{82}\text{Pb} + 6\,{}^{4}_{2}\text{He} + 4\beta^-$

Energy released is Q value

$Q = [m(^{232}\text{Th}) - m(^{208}\text{Pb}) - 6\ m(^{4}\text{He})]\ c^2$

(the mass of 4e$^-$ are included in daughters)

$= [232.03805\ u - 207.97664\ u - 6 \times 4.00260\ u] \times 931.5\ \text{MeV u}^{-1} =$

$= (0.04581u) \times (931.5\ \text{MeV}) = 42.67\ \text{MeV}$

3.3 The rate of production of energy (power) in watts (1 W = J s$^{–1}$) produced by 1.00 kilogram of ^{232}Th ($t_{\text{tl/2}} = 1.40\times10^{10}$ years).

1.00 kg contains = $\dfrac{1000\ \text{g} \times 6.022\times10^{23}\ \text{mol}^{-1}}{232\ \text{g mol}^{-1}} = 2.60\times10^{24}$ atoms

Decay constant for ^{232}Th:

$$\lambda = \frac{0.693}{1.40\times10^{10}\ \text{y} \times 3.154\times10^{7}\ \ \text{s y}^{-1}} = 1.57\times10^{-18}\ \text{s}^{-1}$$

For activity: $A = N\,\lambda = 2.60\times10^{24} \times 1.57\times10^{-18} = 4.08\times10^{6}$ dis s$^{–1}$

(disintegrations s$^{–1}$)

Each decay liberates 42.67 MeV

Rate of production of energy (power):

4.08×10^{6} dis s^{-1} × 42.67 MeV dis^{-1} × 1.602×10^{-13} J MeV^{-1} =

$= 2.79\times10^{-5}$ J s^{-1} = 2.79×10^{-5} W

3.4 The volume in cm^3 of helium at 0 °C and 1 atm collected when 1.00 gram of ^{228}Th ($t_{1/2}$ = 1.91 years) is stored in a container for 20.0 years.

$^{228}\text{Th} \rightarrow {}^{208}\text{Pb} + 5\ {}^{4}\text{He}$

The half-lives of various intermediates are relatively short compared with that of ^{228}Th.

$$A = \lambda N = \frac{0.693}{1.91\ \text{y}} \times \frac{1.000\ \text{g} \times 6.022\times10^{23}\ \text{mol}^{-1}}{228\ \text{g mol}^{-1}} = 9.58\times10^{20}\ \text{y}^{-1}$$

Number of He collected:

$N_{\text{He}} = 9.58\times10^{20}\ \text{y}^{-1} \times 20.0\ \text{y} \times 5$ particles = 9.58×10^{22} particles of He

$$V_{\text{He}} = \frac{9.58\times10^{22} \times 22{,}4\ \text{dm}^3\ \text{mol}^{-1}}{6.022\times10^{23}\ \text{mol}^{-1}} = 3.56\ \text{dm}^3 = 3.56\times10^{3}\ \text{cm}^3$$

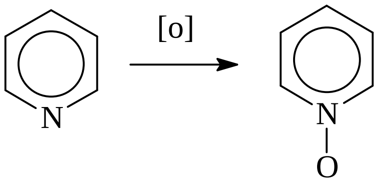
3.5 The half-life:

$$A = \lambda N$$

$$t_{½} = \frac{0.693}{\lambda} = \frac{0.693\,N}{A} = \frac{0.693 \times 510 \times 10^{10}\ \text{atoms}}{3440\ \text{atoms min}^{-1}} = 3.02 \times 10^{6}\ \text{min} = 5.75\ \text{years}$$

PROBLEM 4

Ligand **L** can form complexes with many transition metals. **L** is synthesized by heating a mixture of a bipyridine, glacial acetic acid and hydrogen peroxide to 70 – 80 °C for 3 hrs. The final product **L** crystallizes out as fine needles and its molecular mass is 188. An analogous reaction with pyridine is ;



Complexes of **L** with Fe and Cr have the formulae of $FeL_m(ClO_4)_n.\ 3\ H_2O$ (**A**) and $CrL_xCl_y(ClO_4)_z.H_2O$ (**B**), respectively. Their elemental analyses and physical properties are given in Tables 4a and 4b. The relationship of colour and wavelength is given in Table 4c.

Table 4a: Elemental analyses.

Complex	Elemental analyses , (wt. %)
A	Fe 5.740, C 37.030, H 3.090 , Cl 10.940, N 8.640
B	Cr 8.440, C 38.930, H 2.920, Cl 17.250, N 9.080

Use the following data:

Atomic number: Cr = 24, Fe = 26

Relative atomic mass: H = 1, C = 12, N = 14, O = 16, Cl = 35.45, Cr = 52, Fe = 55.8

Table 4b: Physical properties

Complex	Magnetic moment , μ B.M.	Colour
A	6.13	Yellow
B	Not measured	Purple

Table 4c Relationship of wavelength to colour.

Wavelength (nm) and colour absorbed	Complementary colour
400 (violet)	Yellow Green
450 (blue)	Yellow
490 (blue green)	Orange
500 (green)	Red
570 (yellow green)	Violet
580 (yellow)	Blue
600 (orange)	Blue green
650 (red)	Green

4.1 Write down the molecular formula of **L**.

4.2 If **L** is a bidentate chelating ligand, draw the structure of the bipyridine used. Also draw the structure of **L** .

4.3 Does the ligand **L** have any charge, i. e. net charge?

4.4 Draw the structure when one molecule of **L** binds to metal ion (M).

4.5 From the data in Table 4a, determine the empirical formula of **A**. What are the values of m and n in $FeL_m(ClO_4)_n$ .3 H_2O? Write the complete formula of **A** in the usual IUPAC notation. What is the ratio of cation to anion when **A** dissolves in water?

4.6 What is the oxidation number of Fe in **A**? How many d-electrons are present in Fe ion in the complex? Write the high spin and the low spin configurations that may exist for this complex. Which configuration, high or low spin, is the correct one? What is the best evidence to support your answer?

4.7 From Table 4c, estimate λ_{max} (nm) of **A**.

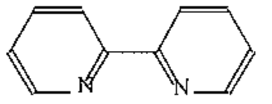
4.8 Detail analysis of **B** shows that it contains Cr^{3+} ion. Calculate the 'spin-only' magnetic moment of this compound.

4.9 Compound **B** is a 1 : 1 type electrolyte. Determine the empirical formula of **B** and the values of x, y, z in $CrL_xCl_y(ClO_4)_z$. H_2O.

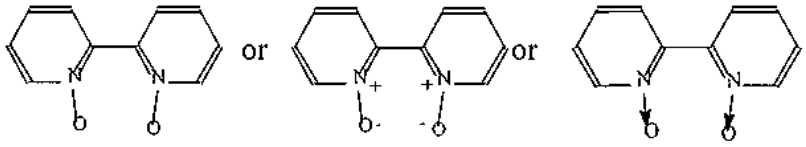
SOLUTION

4.1 Knowing that L was synthesized from bipyridine and during the reaction bipyridine was simply oxidized to bipyridine oxide. The molecular mass of bipyridine is 156 (for $C_{10}H_8N_2$) while the molecular mass of **L** is 188. The difference of 32 is due to 2 atoms of oxygen. Therefore, the molecular formula of **L** is $C_{10}H_8N_2O_2$.

4.2 The structures of bipyridine and **L**:



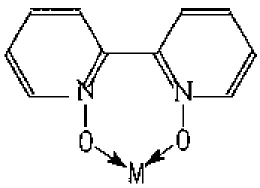
Structure of bipyridine



structure of L

4.3 The ligand **L** has no charge.

4.4 The structure when one molecule of **L** binds to metal ion (M):



4.5 The empirical formula of **A**. Calculation:

	Fe	C	H	Cl	N	O
%	5.740	37.030	3.090	10.940	8.640	34.560*
mol	0.103	3.085	3.090	0.309	0.617	2.160
mol ratio	1.000	29.959	30.00	2.996	5.992	20.971
atom ratio	1	30	30	3	6	21

*) Percentage of O is obtained by difference.)

The empirical formula of **A** is $FeC_{30}H_{30}Cl_3N_6C_{21}$

The values of m and n in $FeL_m(C104)_n . 3 H_2O$:

Since the molecular formula contains one atom of Fe, so in this case the empirical formula is equivalent to the molecular formula. The molecular formula of **L** has been obtained previously in (4a) and (4b), therefore we can work to find m = 3. Having obtained the value of m , one can work out for n and find that n = 3.

The complete formula of **A** is $[FeL_3](ClO_4)_3 . 3 H_2O$

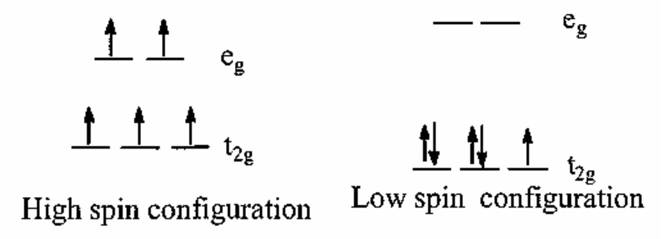
The ratio of cation to anion is equal to 1 : 3.

The three ClO_4^- groups will dissociate as free ion in solution. So the entire complex will be in the ion forms as $[FeL_3]^{3+}$ and 3 ClO_4^- in solution.

4.6 The oxidation number of Fe in complex **A** is +3 or III.

The number of *d*-electrons in Fe^{3+} ion in the complex = 5.

The high spin and the low spin configuration that may exist for this complex:



The correct answer is high spin configuration.

The best evidence to support your answer for this high/low spin selection is magnetic moment.

There exist a simple relation between number of unpaired electrons and the magnetic moment as follows:

$$\mu = \sqrt{n(n+2)}$$

where μ is the so-called 'spin-only' magnetic moment and n is the number of unpaired electrons. Thus, for high spin configuration in the given case,

$$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ B.M.}$$

For low spin case:

$$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ B.M.}$$

The measured magnetic moment, for **A** is 6.13 B.M. (Table 4b) which is in the range for high spin configuration. Therefore, we can conclude that **A** can exist as a high spin complex.

4.7 From Table 4c, the color absorbed is complementary to the color seen. Thus, λ_{max} for complex A is 450 nm.

4.8 The 'spin-only' magnetic moment of complex **B**.

For Cr^{3+}: n = 3

Therefore, $\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87$ B.M.

4.9 The empirical formula of B is $Cr_{20}H_{18}N_4Cl_3O_9$, i.e. x = 2, y = 2, z = 1.

PROBLEM 3

Bioinorganic Chemistry

The square planar complex *cis*-diammine dichloroplatinum(II) is an important drug for the treatment of certain cancers.

3.1 Draw the structures of *cis*- and *trans*-diammine dichloroplatinum(II) and label each structure as *cis* or *trans*.

A number of ionic compounds also have the empirical formula $Pt(NH_3)_2Cl_2$.

3.2 Write molecular formulas for all possible ionic compounds which comply with the following conditions: each compound has

1) empirical formula $Pt(NH_3)_2Cl_2$,
2) an anion and a cation and is composed of discrete, monomeric square planar platinum(II) complex,
3) only one type of cation and one type of anion. The answer must clearly reveal the composition of each discrete platinum(II) complex entity in each compound

3.3 How many *5d* electrons are there in the platinum(II) ion?

The valence d-orbital energy splitting diagram for a square planar complex can be regarded as being derived from that for an octahedral complex in which the metal-ligand interactions due to the two ligands coordinated along the *z* axis vanish, while the bonds to the four remaining ligands (coordinated along the *x* and *y* axes) become stronger.

3.4 Which of the five *5d* orbitals attain the highest energy (*i. e.* is the least likely to be occupied by electrons) in the general case of a square-planar Pt(II) complex?

Serum transferrin (abbreviated: Tf) is a monomeric protein whose main function in the human body is the transport of iron(III). Each transferrin molecule can bind up to two iron(III) ions with stepwise binding constants K_1 and K_2 at biological conditions except that the temperature is 25 °C corresponding to the reactions:

$Fe^{III} + Tf \rightarrow (Fe^{III})Tf$ $\qquad K_1 = 4.7\times10^{20}$

$Fe^{III} + (Fe^{III})Tf \rightarrow (Fe^{III})_2Tf$ $\qquad K_2 = 2.4\times10^{19}$

In the diferric protein, $(Fe^{III})_2Tf$, the two iron(III) ions are bound at two similar, but non-identical sites, and the two possible monoferric protein products, $(Fe^{III})Tf$, can be denoted $\{Fe^{III} . Tf\}$ and $\{Tf . Fe^{III}\}$. Their relative abundance at equilibrium is given by the constant

$K = [\{Tf . Fe^{III}\}] [\{Fe^{III} . Tf\}]^{-1} = 5.9$.

3.5 Calculate the values of the two constants $K_1' = [\{Fe^{III} . Tf\}] [Fe^{III}]^{-1} [Tf]^{-1}$ and $K_1'' = [\{Tf . Fe^{III}\}] [Fe^{III}]^{-1} [Tf]^{-1}$, respectively, corresponding to the formation of each monoferric form of transferrin.

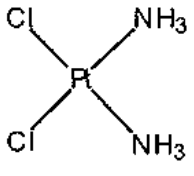
3.6 Calculate the values of the two constants $K_2' = [(Fe^{III})_2Tf] [Fe^{III}]^{-1} [\{Fe^{III} . Tf\}]^{-1}$ and $K_2'' = [(Fe^{III})_2Tf] [Fe^{III}]^{-1} [\{Tf . Fe^{III}\}]^{-1}$ respectively, corresponding to the formation of diferric transferrin from each of the monoferric forms.

The bound iron(III) ion at each binding site is surrounded by six donor atoms from various ligands. Thus, two oxygen atoms of a carbonate anion coordinate to the metal, and the following amino acid side chains from the protein primary structure also coordinate to the iron(III) ion with one potential donor atom each: one aspartate, one histidine and two tyrosine residues.

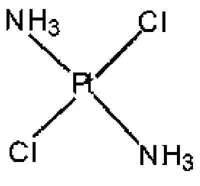
3.7 What is the total number of oxygen donor atoms that surround a 6-coordinate iron(III) ion in transferrin?

SOLUTION

3.1 The structures of *cis*- and *trans*-diammine dichloroplatinum(II)



cis



trans

3.2 $[Pt(NH_3)_4] [PtCl_4]$

$[Pt(NH_3)_3Cl] [Pt(NH_3)Cl_3]$

$[Pt(NH_3)_3Cl]_2 [PtCl_4]$

$[Pt(NH_3)_4] [Pt(NH_3)Cl_3]_2$

3.3 Eight *d*-electrons.

3.4 Orbital $5\,d_{x^2-y^2}$. In a square planar complex the four ligand atoms fall on the *x* and *y* axes along which this orbital, if filled, would also have electron density concentrated.

3.5 The concentration of monoferric forms of transferrin is

$[(Fe^{m})Tf = [\{Fe^{m}\text{ -}Tf\}] + [\{Tf\text{-}Fe^{III}\}]$

$K'_1 + K''_1 = K_1 \qquad K'_1 K = K''_1$

$$K'_1 = \frac{K_1}{1+K} = \frac{4.7\times10^{20}}{1+5.9} = 6.8\times10^{19}$$

$$K''_1 = K_1 - K'_1 = (4.7 - 0.68)\times10^{20} = 4.0\times10^{20}$$

3.6 $K'_1 K'_2 = K''_1 K''_2 = K_1 K_2$

$$K'_1 = \frac{K_1 K_2}{K'_1} = \frac{4.7\times10^{20}\times2.19\times10^{19}}{6.8\times10^{19}} = 1.7\times10^{20}$$

$$K''_1 K''_2 = K_1 K_2$$

$$K''_2 = \frac{K_1 K_2}{K''_1} = \frac{4.7\times10^{20}\times2.4\times10^{19}}{4.0\times10^{20}} = 2.8\times10^{19}$$

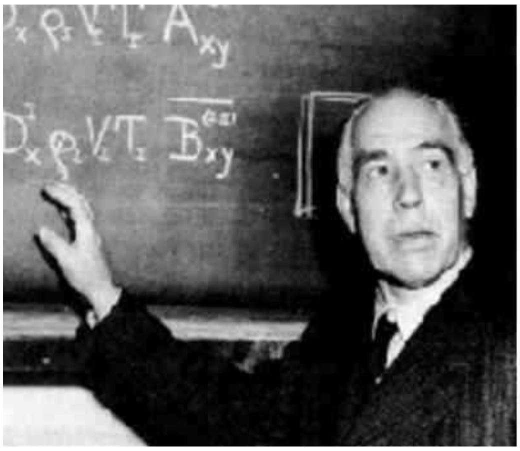
3.7 (= 2 $(CO_3^{2-}) + 1$ (Asp(O$^-$)) + 2 (2 × Tyr(O$^-$))

THE THIRTY-THIRD
INTERNATIONAL CHEMISTRY OLYMPIAD
6–15 JULY 2001, MUMBAI, INDIA

THEORETICAL PROBLEMS

PROBLEM 1

Hydrogen Atom and Hydrogen Molecule



Niels Bohr (1885-1962)

The observed wavelengths in the line spectrum of hydrogen atom were first expressed in terms of a series by Johann Jakob Balmer, a Swiss teacher. Balmer's empirical formula is

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2}\right); \quad n = 3, 4, 5, ...$$

Here,

$$R_H = \frac{m_e\, e^4}{8\, \varepsilon_0^2\, h^3\, c} = 109\,678\ \text{cm}^{-1}$$

is the Rydberg konstant, m_e is the mass of an electron. Niels Bohr derived this expression theoretically in 1913. The formula is easily generalized to any one electron atom/ion.

1.1 Calculate the longest wavelength in Å (1 Å = 10^{-10} m) in the 'Balmer series' of singly ionized helium (He^+). Ignore nuclear motion in your calculation.

1.2 A formula analogous to Balmer's formula applies to the series of spectral lines which arise from transitions from higher energy levels to the lowest energy level of hydrogen atom. Write this formula and use it to determine the ground state energy of a hydrogen atom in eV.

A 'muonic hydrogen atom' is like a hydrogen atom in which the electron is replaced by a heavier particle, the muon. The mass of a muon is about 207 times the mass of an electron, while its charge is the same as that of an electron. A muon has a very short lifetime, but we ignore its unstable nature here.

1.3 Determine the lowest energy and the radius of the first Bohr orbit of the muonic hydrogen atom. Ignore the motion of the nucleus in your calculation. The radius of the first Bohr orbit of a hydrogen atom

(called the Bohr radius, $a_0 = \dfrac{\varepsilon_0 \, h^2}{m_e \, e^2 \, \pi}$) is 0.53 Å.

The classical picture of an "orbit" in Bohr's theory has now been replaced by the quantum mechanical notion of an 'orbital'. The orbital $\psi_{1\sigma_{1s}}$ (r) for the ground state of a hydrogen atom is given by

$$\Psi_{1s}(r) = \frac{1}{\sqrt{\pi \, a_0^3}} \, e^{-\frac{r}{a_0}}$$

where r is the distance of the electron from the nucleus and a_0 is the Bohr radius.

1.4 Consider a spherical shell of radius a_0 and thickness $0.001a_0$. Estimate the probability of finding the electron in this shell. Volume of a spherical shell of inner radius r and small thickness Δr equals $4\pi r^2 \, \Delta r$.

The H_2 molecule can dissociate through two different channels:

(i) $H_2 \rightarrow H + H$ (two separate hydrogen atoms)

(ii) $H_2 \rightarrow H^+ + H^-$ (a proton and a hydride ion)

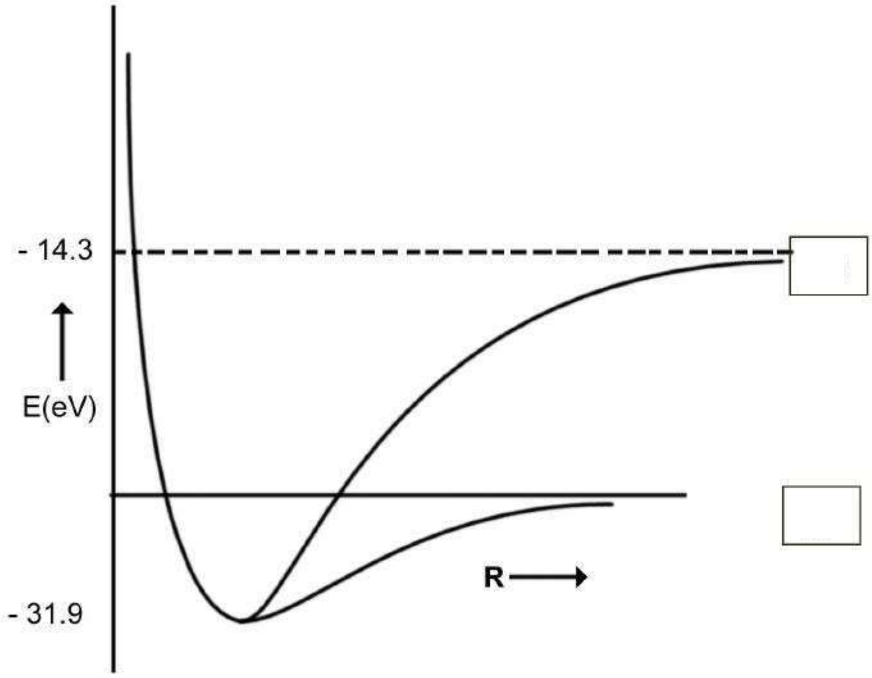
The graph of energy (E) vs internuclear distance (R) for H_2 is shown schematically in the figure. The atomic and molecular energies are given in the same scale.

1.5 Put appropriate channel labels (i) or (ii) in the boxes below.

1.6 Determine the values of the dissociation energies (D_e in eV) of the H_2 molecule corresponding to

channel (i) ☐

channel (ii) ☐



1.7 From the given data, calculate the energy change for the process

$H^- \rightarrow H + e^-$

1.8 H^- is a two-electron atomic system. Assuming that the Bohr energy formula is valid for each electron with nuclear charge Z replaced by Z_{eff}, calculate Z_{eff} for H^-.

SOLUTION

1.1 Longest wavelength A_L corresponds to n = 3

For He^+

$$\frac{1}{\lambda} = 4R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

λ_L = 1641.1 Å

1.2 $\frac{1}{\lambda} = 4R_H\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \qquad n = 2, 3, 4, ...$

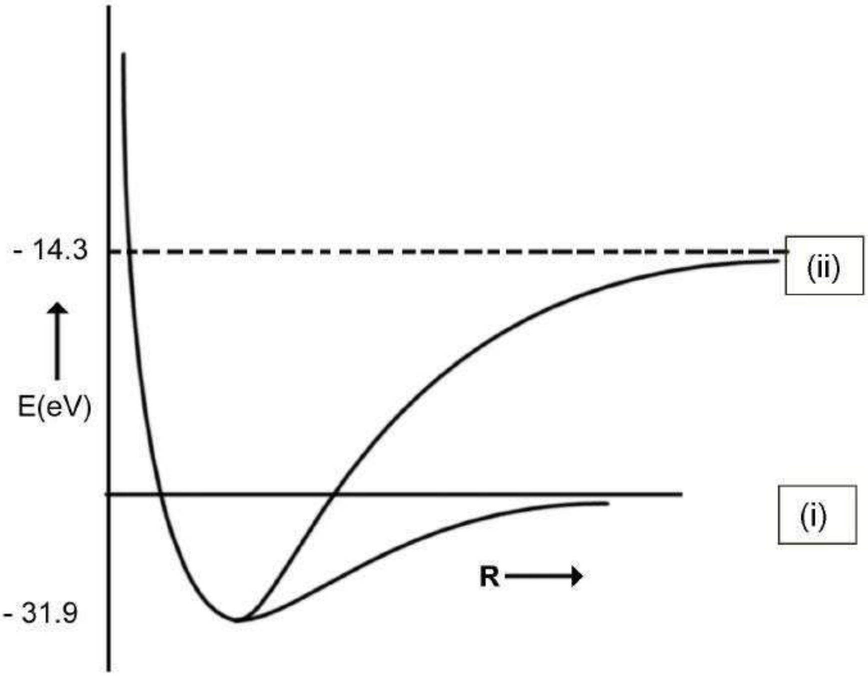
$E = -hcR_H = -13.6$ eV

1.3 Lowest energy = – 207 × 13.6 = –2.82 keV

Radius of the first Bohr orbit = 0.53 / 207 = 2.6×10^{-3} Å

1.4 Probability = $|\psi(a_0)|^2\ 4\pi a_0^2 \times 0.001a_o = 0.004\ e^{-2} = 5.41\times10^{-4}$

1.5



1.6 Channel (i): 4.7 eV

Channel (ii): 17.6 eV

1.7 Electron affinity = – 13.6 – (– 14.3) = 0.7 eV

1.8 $Z_{eff} = -13.6 + 27.2\ Z^2_{eff} = 0.7$

PROBLEM 4

Beach Sand Mineral in Kerala

Beach sand mineral, monazite, is a rich source of thorium, available in large quantities in the state of Kerala in India. A typical monazite sample contains about 9 % ThO_2 and 0.35 % U_3O_8. ^{208}Pb a ^{206}Pb are the stable end-products in the radioactive decay series of ^{232}Th and ^{238}U, respectively. All the lead (Pb) found in monazite is of radiogenic origin.

The isotopic atom ratio $^{208}Pb/^{232}Th$, measured mass spectrometrically, in a monazite sample was found to be 0.104. The half-lives of ^{232}Th and ^{238}U 1.41×10^{10} years and 4.47×10^{9} years, respectively. Assume that ^{208}Pb, ^{206}Pb, ^{232}Th and ^{238}U remained entirely in the monazite sample since the formation of monazite mineral.

4.1 Calculate the age (time elapsed since its formation) of the monazite sample.

4.2 Estimate the isotopic atom ratio $^{206}Pb/^{238}U$ in the monazite sample.

4.3 Thorium-232 is a fertile material for nuclear energy. In thermal neutron irradiation, it absorbs a neutron and the resulting isotope forms ^{233}U by successive β^- decays. Write the nuclear reactions for the formation of ^{233}U from ^{232}Th.

In nuclear fission of ^{233}U a complex mixture of radioactive fission products is formed. The fission product ^{101}Mo initially undergoes radioactive decay as shown below:

$$^{101}_{42}\text{Mo} \xrightarrow[t_{1/2}\,=\,14.6\,\text{min}]{} {}^{101}_{43}\text{Tc} \xrightarrow[t_{1/2}\,=\,14.3\,\text{min}]{} {}^{101}_{44}\text{Ru}$$

4.4 A freshly prepared radiochemically pure sample of ^{101}Mo contains 5000 atoms of ^{101}Mo initially. How many atoms of

i) ^{101}Mo

ii) ^{101}Tc

iii) ^{101}Ru

will be present in the sample after 14.6 min?

SOLUTION

4.1 $N = N_0\,\mathrm{e}^{-\frac{0.6931\,t}{t_{1/2}}}$

$$\frac{N_0 - N}{N} = \mathrm{e}^{\frac{+0.6931\,t}{t_{1/2}}} - 1$$

(N_0 - N) = Total number of ^{232}Th atoms decayed. = Total number of ^{208}Pb atoms formed.

$$\frac{N_0 - N}{N} = 0.104$$

$$\mathrm{e}^{\frac{0.6931\,t}{1.41\times10^{10}}} = 1.104$$

t = 2.01×10^{9} years.

4.2 Let x be the required ratio.

$$\mathrm{x} = \mathrm{e}^{\frac{+0.6931\,t}{t_{1/2}}} - 1$$

where t = 2.01×10^{9} years, and $t_{1/2}$ = 4.47×10^{9} years.

x = 0.366

4.3 $^{232}\mathrm{Th} \xrightarrow{(\mathrm{n},\,\gamma)} {}^{233}\mathrm{Th} \xrightarrow{\beta^-} {}^{233}\mathrm{Pa} \xrightarrow{\beta^-} {}^{233}\mathrm{U}$

4.4 (i) The number of atoms of ^{101}Mo (N_1) in the sample after one half-life is :

N_1 = 2500

(ii) The number of atoms of ^{101}Tc (N_2) is given by

$$N_2 = \frac{\lambda_1 N_0}{\lambda_2 - \lambda_1}(\mathrm{e}^{-\lambda_1 t} - e^{-\lambda_2 t})$$

where N_0 (= 5000) is the initial number of atoms of ^{101}Mo.

$$\lambda_1 = \frac{0.693}{14.6}\ \mathrm{min}^{-1}$$

$$\lambda_2 = \frac{0.693}{14.3}\ \mathrm{min}^{-1}$$

At t = 14.6 min

N_2 = 1710

(iii) Number of atoms of ^{101}Ru (N_3) at t = 14.6 min is :

$N_3 = N_0 - N_1 - N_2$ = 790 atoms

PROBLEM 5

Halogen Chemistry

Halogens in their reactions among themselves and with a variety of other elements give rise to a large number of compounds with diverse structure, bonding and chemical behaviour. Metal halides, halogen derivatives and interhalogens represent major types of halogen compounds.

(A) Photography

A "black and white" photographic film contains a coating of silver bromide on a support such as cellulose acetate.

5.1 Write the photochemical reaction that occurs when light falls on AgBr(s) coated on a film.

5.2 During the developing process, unexposed AgBr is washed away by complexation of Ag(I) by sodium thiosulphate solution. Write down this chemical reaction.

5.3 These washings are often disposed of as waste. However, metallic silver can be recovered from them by adding cyanide, followed by zinc. Write down the reactions involved.

(B) Shapes, spectra and reactivity

The most reactive halogen, fluorine, reacts with other halogens Cl_2, Br_2 and I_2 under controlled conditions giving a tetra-atomic, hexa-atomic and an octa-atomic molecule, respectively.

5.4 Write the formulae and 3-dimensional structures of these interhalogen molecules on the basis of VSEPR theory. Show the disposition of the lone pairs on the central atom, where appropriate.

A mixture of iodine vapour and chlorine gas when fed into a mass spectrometer gave two sets (A and B) of mass spectral peaks corresponding to molecular ions of two chemical species at *m*/*z*:

A: 162, 164

B: 464, 466, 468, 470, 472, 474, 476

5.5 Identify the molecular species corresponding to m/z = 162, 164, 466 and 476. Draw the structure of the heaviest species (m/z = 476) indicating clearly the lone pairs on atom(s) of I (iodine). Show the isotopic composition of each species.

In aqueous medium chlorine gas oxidises sodium thiosulphate to an ion containing the highest oxidation state of sulphur.

5.6 Write down the chemical equation for this reaction.

5.7 Write down the Lewis dot structure of the thiosulphate ion. Circle the sulphur atom that has the lower oxidation state.

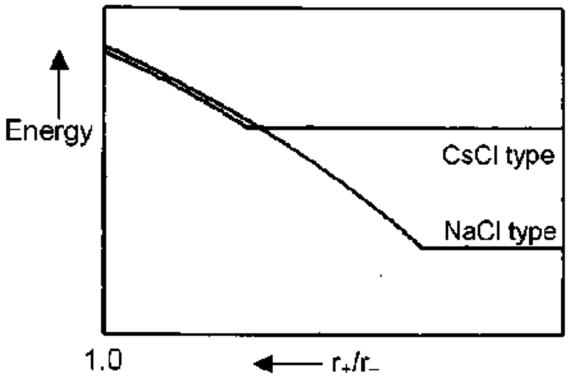
5.8 Chlorine dioxide reacts with sodium hydroxide as shown below. Identify the products X and Y (both containing chlorine) and balance the equation.

5.9 Reaction of chlorine an alkali is used by manufacturing bleach. Write the chemical reaction for its formation.

5.10 Write the oxidation state(s) of chlorine in bleach.

(C) Alkali metal halides and X-ray crystallography

X-ray crystallography reveals many aspects of the structure of metal halides. The radius ratio (r_+/r_-) is a useful parameter to rationalise their structure and stability. A table of radius ratio (r_+/r_-) for some alkali halides with radius ratio (r_- kept constant) is shown schematically for NaCl-type and CsCl-type crystal structures.



	Li^+	Na^+	K^+	Rb^+	Cs^+
Cl^-	0.33	0.52	0.74	0.82	0.93
Br^-	0.31	0.49	0.68	0.76	0.87
I^-	0.28	0.44	0.62	0.69	0.78

5.11 For a given anion, the graph for NaCl-type structure levels off at low r_+/r_- values because of

(a) cation-cation contact along the face diagonal. ☐

(b) anion-anion contact along the face diagonal. ☐

(c) cation-anion contact along the cell edge. ☐

(Mark X in the correct box.)

5.12 Which among the halides LiBr, NaBr and RbBr is likely to undergo phase transition from NaCl-type to CsCl-type structure with change of temperature and / or pressure?

5.13 Show by calculation the radius ratio ($r_+/r_–$) at which the energy of CsCl-type structure levels off.

5.14 Using CuKα X-rays (λ = 154 nm), diffraction by a KCl crystal (fcc structure) is observed at an angle (θ) of 14.2 °. Given that (i) diffraction takes place from the planes with $h^2 + k^2 + l^2 = 4$, (ii) in a cubic crystal $d_{hkl} = a / (h^2 + k^2 + l^2)^{1/2}$, where "d" is the distance between adjacent hkl planes and "a" is a lattice parameter, and (iii) reflections in an fcc structure can occur only from planes with "all odd" or "all even" hkl (Miller) indices, calculate the lattice parameter "a" for KCl.

5.15 Indicate in the table given below the required information for the 2nd and 3rd nearest neighbours of a K^+ ion in the KCl lattice.

2nd nearest neighbours			3rd nearest neighbours		
number	sign of the charge	distance (pm)	number	sign of the charge	distance (pm)

5.16 Determine the lowest value of diffraction angle θ possible for the KCl structure.

SOLUTION

5.1 $2\ AgBr\ (s) \xrightarrow{h\nu} 2\ Ag\ (s) + Br_2\ /2\ Br\ \bullet$

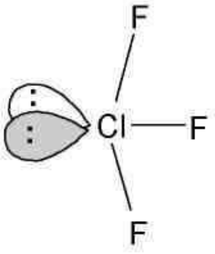
5.2 $AgBr(s) + 2\ Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

5.3 $[Ag(S_2O_3)_2]^{3-} + 2\ CN^- \rightarrow [Ag(CN)_2]^- + 2\ S_2O_3^{2-}$

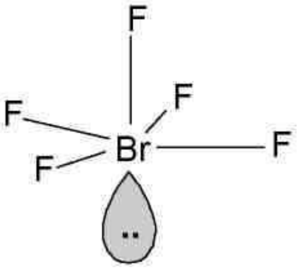
$2\ [Ag(CN)_2]^- + Zn \rightarrow [Zn\ (CN)_4]^{2-} + 2\ Ag\downarrow$

5.4

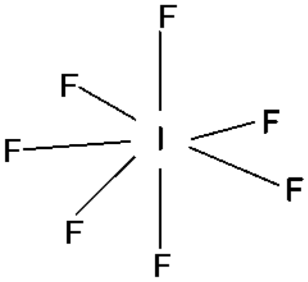
ClF_3



BrF_5



IF_7

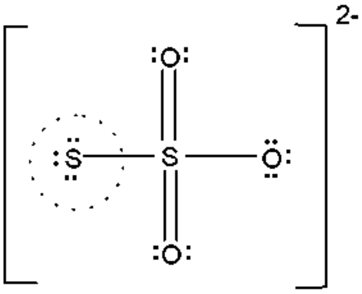


5.5.

Mass:	162	164	466	476
Species:	$I\,^{35}Cl$	$I\,^{37}Cl$	$I_2{}^{35}Cl_5{}^{37}Cl$	$I_2{}^{37}Cl_6$

5.6 $4\ Cl_2 + S_2O_3^{2-} + 5\ H_2O \rightarrow 8\ Cl^- + 2\ SO_4^{2-} + 10\ H^+$

5.7



5.8 $2\,ClO_2 + 2\,NaOH \rightarrow NaClO_2 + NaClO_3 + H_2O$

X Y

5.9 $Cl_2 + Ca(OH)_2 \rightarrow Ca(Cl)(OCl) + H_2O$

or

$Cl_2 + CaO \rightarrow Ca(Cl)(OCl)$

or

$2\,OH^- + Cl_2 \rightarrow Cl^- + OCl^- + H_2O$

5.10 The oxidation state(s) of chlorine in bleach is (are): -I and I

5.11 Correct answer: (b) anion–anion contact along the face diagonal.

5.12 RbBr

5.13 In CsCl-type structure,

Cell edge, a = 2 r

Body diagonál: $\sqrt{3}\,a = 2(r_+ + r_-)$

$$\frac{r_+}{r_-} = \sqrt{3} - 1 = 0.732$$

5.14 $\lambda = 2d \sin\theta$

$$d_{200} = \frac{\lambda}{2\sin\theta} = 314\text{ pm}$$

$$d_{200} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} = \frac{a}{(2^2 + 0^2 + 0^2)^{1/2}} = \frac{a}{2}$$

a = 628 pm

5.15 The 2nd and 3rd nearest neighbours of a K^+ ion in the KCl lattice.

2nd nearest neighbours			3rd nearest neighbours		
number	sign of the charge	distance (pm)	number	sign of the charge	distance (pm)
12	+	444	8	-	544

5.16 Lowest θ value is for the plane with hkl = (111)

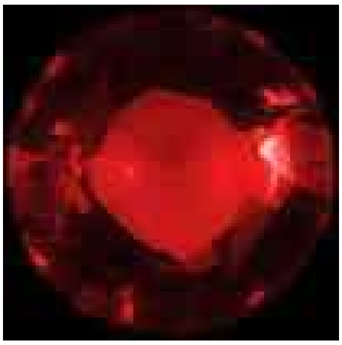
$$d = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{628}{\sqrt{3}} = 363\ \text{pm}$$

$$\sin\theta_{111} = \frac{\lambda}{2\,d_{111}} = \frac{154\ \text{pm}}{2 \times 363\ \text{pm}} = 0.212$$

$$\theta_{111} = 12.2\,^{\circ}$$

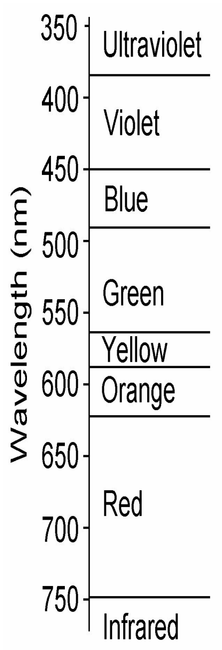
PROBLEM 9

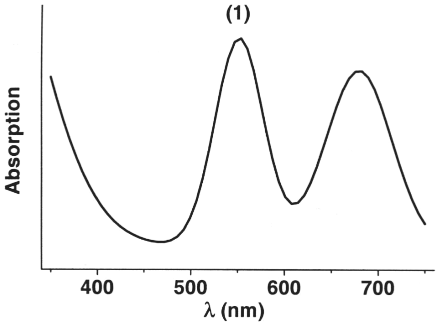
RED RUBY



Ruby crystals have a deep red colour and are well known for their use in jewellery. Not many people know that the heart of the first laser, built in 1960 by Maiman, was a big ruby crystal. The red colour of ruby originates from the absorption of light by Cr^{3+} ions that are incorporated in colourless aluminium oxide (Al_2O_3) crystals. The Cr^{3+} ion has 3 electrons in the 3*d* shell and the absorption of light is due to electronic transitions between 3*d* orbitals of lower and higher energy.

9.1 Indicate which of the four absorption spectra belongs to ruby.





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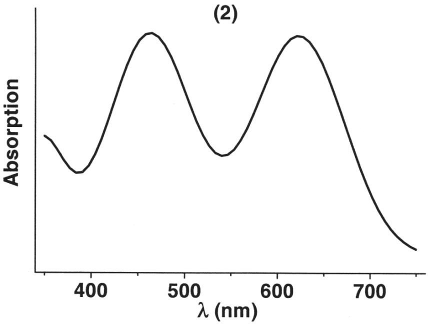

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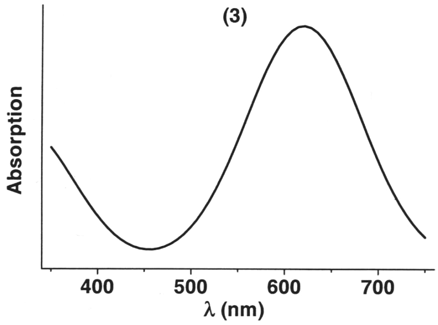

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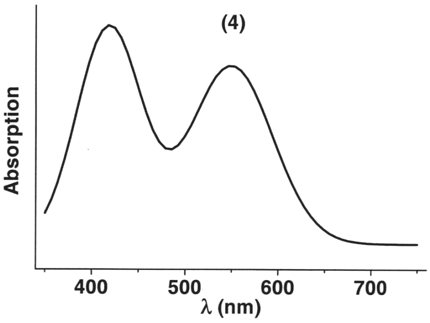

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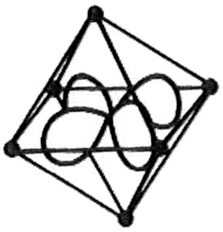
Figure 1

The rod used in ruby lasers is a cylinder with a length of 15.2 cm and a diameter of 1.15 cm. The amount of Cr^{3+} ions is 0.050 mass %. The density of Al_2O_3 is 4.05 g cm^{-3}. The atomic mass of Cr = 52u. (1u = 1.67×10^{-27} kg).

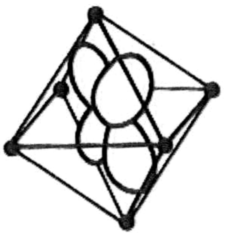
9.2 Calculate how many Cr^{3+} ions are in this laser rod.

In rubies the Cr^{3+} ions are coordinated by an octahedron of 6 oxygen ions. The shape of the five 3*d* orbitals is shown below. The box below shows the splitting of the five 3*d* orbitals into a group of three orbitals at lower energy (t_{2g}) and a group of two at higher energy (e_g)..

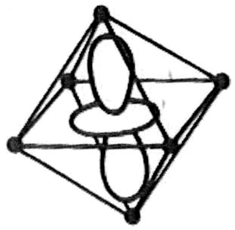
9.3 Indicate in the boxes below which of the 3*d* orbitals (d_{z^2}, d_{xy}, d_{yz}, $d_{x^2-y^2}$, d_{xz}) belong to the t_{2g} group and which belong to the e_g group.



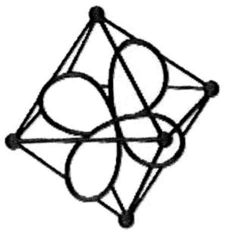
$d_{x^2-y^2}$



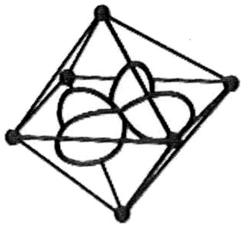
d_{yz}



d_{z^2}



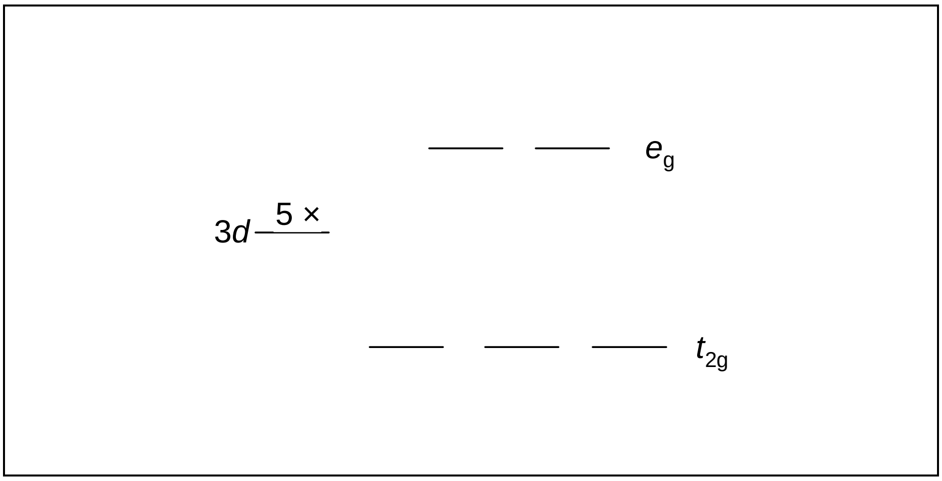
d_{xz}



d_{xy}

☐ ☐ ☐ ☐ ☐

9.4 Indicate with arrows the distribution and the direction of the magnetic spin moment of the three 3*d* electrons of Cr^{3+} over the five *d* orbitals in the lowest energy state of Cr^{3+}.



The ruby is placed on a (non-magnetic) scale. When the scale is in balance (Figure 2) a magnet is placed directly under the side with the ruby.

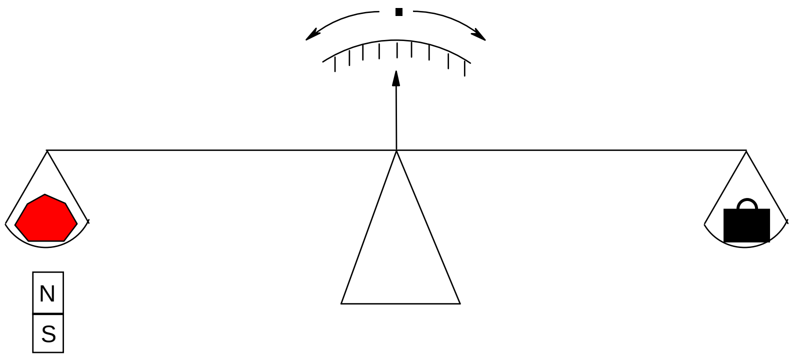


Figure 2

9.5 Indicate what will happen with the ruby (mark the correct answer)

- ☐ The magnet attracts the ruby (the ruby moves down)
- ☐ The magnet has no influence on the ruby (the ruby does not move)
- ☐ The magnet repels the ruby (the ruby moves up)
- ☐ The magnet has an oscillating effect on the ruby (the ruby moves up and down)

SOLUTION

9.1 The fourth spectrum is correct.

9.2 Volume of the rod = $\pi \times r^2 \times l$

$V = \pi \times 0.575^2 \times 15.2\ \text{cm}^3 = 15.79\ \text{cm}^3$

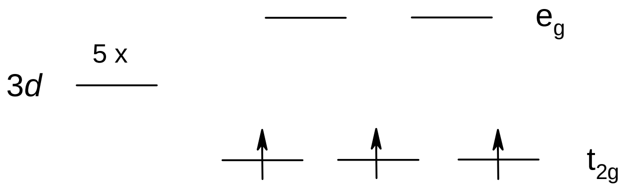
Mass of the rod: $m = 15.79 \times 4.05\ \text{g} = 63.94\ \text{g}$

Mass of chromium in the rod: $m_{\text{Cr}} = 63.94\ \text{g} \times 0.05 / 100 = 0.0319\ \text{g}$

Number od chromium ions: $N = 0{,}0319 \times 10^{-3}\ \text{kg} / (52 \times 1{,}67 \times 10^{-27}) = 3{,}68 \times 10^{20}$.

9.3 $d_{x^2-y^2}$: e_g d_{yz}: t_{2g} d_{z^2}: e_g d_{xz}: t_{2g} d_{xy}: t_{2g}

9.4



9.5 The correct answer: The magnet attracts the ruby (the ruby moves down).

THE THIRTY-FIFTH
INTERNATIONAL CHEMISTRY OLYMPIAD
5–14 JULY 2003, ATHENS, GREECE

THEORETICAL PROBLEMS

SECTION A: General Chemistry

QUESTION 1

The molar solubility s (mol dm^{-3}) of $Th(IO_3)_4$ as a function of the solubility product K_{sp} of this sparingly soluble thorium salt is given by the equation:

(a) $s = (K_{sp} / 128)^{1/4}$ ( )
(b) $s = (K_{sp} / 256)^{1/5}$ ( )
(c) $s = 256\ K_{sp}^{1/4}$ ( )
(d) $s = (128\ K_{sp})^{1/4}$ ( )
(e) $s = (256\ K_{sp})^{1/5}$ ( )
(f) $s = (K_{sp} / 128)^{1/5} / 2$ ( )

QUESTION 2

Which one of the following equations must be used for the exact calculation of [H$^+$] of an aqueous HCl solution at any concentration c_{HCl}? ($K_w = 1\times10^{-14}$).

(a) $[H^+] = c_{\text{HCl}}$ ( )
(b) $[H^+] = c_{\text{HCl}} + K_w / [H^+]$ ( )
(c) $[H^+] = c_{\text{HCl}} + K_w$ ( )
(d) $[H^+] = c_{\text{HCl}} - K_w / [H^+]$ ( )

QUESTION 3

The molar mass of glucose ($C_6H_{12}O_6$) is 180 g mol^{-1} and N_A is the Avogadro constant. Which one of the following statements is not correct?

(a) An aqueous 0.5 M solution of glucose is prepared by dissolving 90 g of glucose to give 1000 cm^3 of solution. ( )

(b) 1.00 mmol amount of glucose has a mass of 180 mg. ( )

(c) 0.0100 mol of glucose comprises of $0.0100 \times 24 \times N_A$ atoms. ( )

(d) 90.0 g glucose contain $3 \times N_A$ atoms of carbon. ( )

(e) 100 cm^3 of a 0.10 M solution contain 18 g of glucose. ( )

QUESTION 4

If the density of a liquid compound B is ρ (in g cm^{-3}), M is the molar mass of B and N_A is the Avogadro constant, then the number of molecules of B in 1 dm^3 of this compound is:

(a) $(1000 \times \rho) / (M \times N_A)$ ( )

(b) $(1000 \times \rho \times N_A) / M$ ( )

(c) $(N_A \times \rho) / (M \times 1000)$ ( )

(d) $(N_A \times \rho \times M) / 1000$ ( )

QUESTION 5

The equilibrium constant of the reaction:

$Ag_2CrO_4(s) + 2\ Cl(aq)^- \rightleftharpoons 2\ AgCl(s) + CrO_4^{2-}(aq)$

is given by the equation:

(a) $K = K_{sp}(Ag_2CrO_4) / K_{sp}(AgCl)^2$ ( )

(b) $K = K_{sp}(Ag_2CrO_4) \times K_{sp}(AgCl)^2$ ( )

(c) $K = K_{sp}(AgCl) / K_{sp}(Ag_2CrO_4)$ ( )

(d) $K = K_{sp}(AgCl)^2 / K_{sp}(Ag_2CrO_4)$ ( )

(e) $K = K_{sp}(Ag_2CrO_4) / K_{sp}(AgCl)$ ( )

QUESTION 6

How many cm^3 of 1.00 M NaOH solution must be added to 100.0 cm^3 of 0.100 M H_3PO_4 solution to obtain a phosphate buffer solution with pH of about 7.2? (The pK values for H_3PO_4 are $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.0$)

(a) 5.0 cm^3 ( )

(b) 10.0 cm^3 ( )

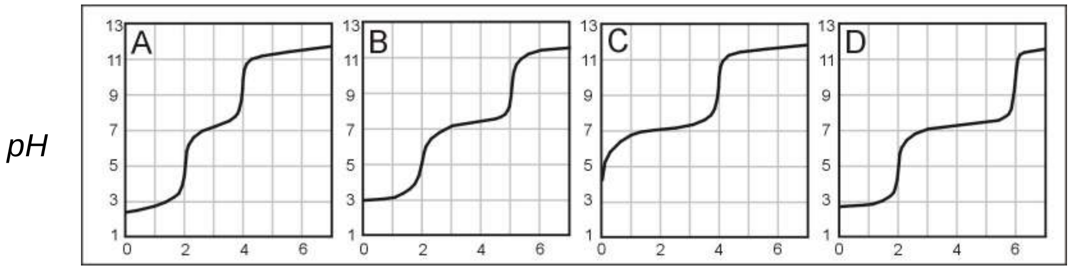
(c) 15.0 mL ( )

(d) 20.0 mL ( )

QUESTION 7

Solutions containing H_3PO_4 and/or NaH_2PO_4 are titrated with a strong base standard solution. Associate the contents of these solutions with the titration curves (*pH vs*. volume of titrant) shown in the figure:

(For H_3PO_4: $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.0$)



Volume of titrant (cm^3)

a) The sample contains H_3PO_4 only.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

b) The sample contains both in a mole ratio $H_3PO_4 : NaH_2PO_4 = 2 : 1$.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

c) The sample contains both in a mole ratio $H_3PO_4 : NaH_2PO_4 = 1 : 1$.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

QUESTION 8

A fuel/oxidant system consisting of N,N-dimethylhydrazine $(CH_3)_2NNH_2$ and N_2O_4 (both liquids) is commonly used in space vehicle propulsion. Components are mixed stoichiometrically so that N_2, CO_2 and H_2O are the only products (all gases under the same reaction conditions). How many moles of gases are produced from 1 mol of $(CH_3)_2NNH_2$?

(a) 8 ( )

(b) 9 ( )

(c) 10 ( )

(d) 11 ( )

(e) 12 ( )

QUESTION 9

The complete electrolysis of 1 mol of water requires the following amount of electric charge (F is the Faraday constant):

(a) F ( )
(b) (4/3) F ( )
(c) (3/2) F ( )
(d) 2 F ( )
(e) 3 F ( )

QUESTION 10

Identify particle X in each of the following nuclear reactions:

a) ${}^{68}_{30}\text{Zn} + {}^{1}_{0}\text{n} \rightarrow {}^{65}_{28}\text{Ni} + \text{X}$ alpha ( ), beta ( ), gamma ( ), neutron ( )

b) ${}^{130}_{..52}\text{Te} + {}^{2}_{1}\text{H} \rightarrow {}^{131}_{..53}\text{I} + \text{X}$ alpha ( ), beta ( ), gamma ( ), neutron ( )

c) ${}^{214}_{..82}\text{Pb} \rightarrow {}^{214}{}_{83}\text{Bi} + \text{X}$ alpha ( ), beta ( ), gamma ( ), neutron ( )

d) ${}^{23}_{11}\text{Na} + {}^{1}_{0}\text{n} \rightarrow {}^{24}_{11}\text{Na} + \text{X}$ alpha ( ), beta ( ), gamma ( ), neutron ( )

e) ${}^{19}_{..9}\text{F} + {}^{1}_{0}\text{n} \rightarrow {}^{20}_{..9}\text{F} + \text{X}$ alpha ( ), beta ( ), gamma ( ), neutron ( )

QUESTION 11

10.0 cm^3 of 0.50 M HCl and 10.0 cm^3 of 0.50 M NaOH solutions, both at the same temperature, are mixed in a calorimeter. A temperature increase of ΔT is recorded. Estimate the temperature increase if 5.0 cm^3 of 0.50 M NaOH were used instead of 10.0 cm^3. Thermal losses are negligible and the specific heats of both solutions are taken as equal.

(a) (1/2) ΔT ( )
(b) (2/3) ΔT ( )
(c) (3/4) ΔT ( )
(d) ΔT ( )

QUESTION 12

Natural antimony consists of the following 2 stable isotopes: ^{121}Sb, ^{123}Sb. Natural chlorine consists of the following 2 stable isotopes: ^{35}Cl, ^{37}Cl. Natural hydrogen consists of the following 2 stable isotopes: ^{1}H, ^{2}H. How many peaks are expected in a low resolution mass spectrum for the ionic fragment $SbHCl^+$?

(a) 4 ( )
(b) 5 ( )
(c) 6 ( )
(d) 7 ( )
(e) 8 ( )
(f) 9 ( )

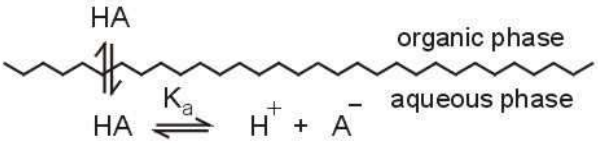
QUESTION 13

The smallest diffraction angle of a monochromatic beam of X-rays in a certain experiment is 11.5°. Based on this we must expect a beam of X-rays diffracted at:

(a) 22.0 degrees ( )
(b) 22.5 degrees ( )
(c) 23.0 degrees ( )
(d) 23.5 degrees ( )
(e) 24.0 degrees ( )
(f) 24.5 degrees ( )

QUESTION 14

The undissociated form of a weak organic acid HA can be extracted from the aqueous phase by a water-immiscible organic solvent according to the scheme:



Regarding this extraction, are the following statements correct (Y) or not (N)?

(a) The distribution constant (K_D) of the acid HA depends on the *pH* of the aqueous phase. (Y) (N)
(b) HA can be efficiently extracted only from acidic aqueous solutions. (Y) (N)

(c) The distribution ratio (D) of the acid HA depends on the pH of the aqueous phase. (Y) (N)

(d) The distribution ratio (D) of the acid HA depends mainly on its concentration. (Y) (N)

QUESTION 15

Regarding Beer's law, are the following statements correct (Y) or not (N)?

(a) The absorbance is proportional to the concentration of the absorbing compound. (Y) (N)

(b) The absorbance is linearly related to the wavelength of the incident light. (Y) (N)

(c) The logarithm of transmittance is proportional to the concentration of the absorbing compound. (Y) (N)

(d) The transmittance is inversely proportional to the logarithm of absorbance. (Y) (N)

(e) The transmittance is inversely proportional to the concentration of the absorbing compound. (Y) (N)

QUESTION 16

Calculate the corresponding wavelength in nanometers (nm) for monochromatic radiation with the following numerical characteristics:

a) 3000 Å 150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )

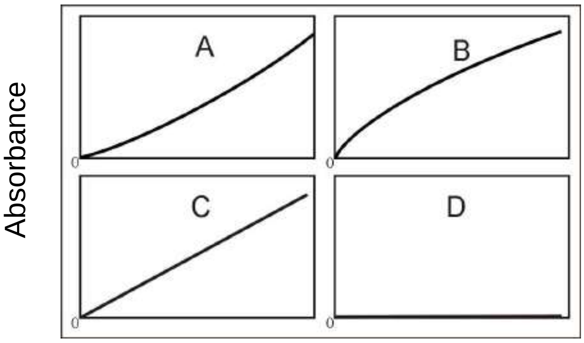
b) 5×10^{14} Hz 150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )

c) 2000 cm^{-1} 150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )

d) 2×10^{6} GHz 150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )

QUESTION 17

The absorbance of solutions of the weak acid HX were obtained. Associate the expected form of the resulting working curve with those shown in figure, under the following conditions:



Total concentration of HX

a) Pure aqueous solutions of HX were used. Only the undissociated species HX absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

b) Pure aqueous solutions of HX were used. Only the anionic species X^- absorb.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

c) All solutions of HX contain an excess of a strong base. Only the undissociated HX species absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

d) All solutions of HX contain an excess of a strong acid. Only the undissociated HX species absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

e) Pure aqueous solutions of HX were used. Both HX and X^- absorb. Measurements were obtained at a wavelength where the molar absorptivities of X^- and HX are equal and different than zero. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

QUESTION 18

Which of the following acids is the strongest?

a) perchloric acid, $HClO_4$ ( )

b) chloric acid, $HClO_3$ ( )

c) chlorous acid, $HClO_2$ ( )

d) hypochlorous, $HClO$ ( )

(e) All of them are equally strong because they all contain chlorine ( )

QUESTION 19

Which structure describes best the crystal system of iron in which the coordination number is 8?

a) simple cubic ( )

b) body-centered cubic ( )

c) cubic closest packed ( )

d) hexagonal closest packed ( )

e) none of the above ( )

QUESTION 20

Which of the following elements has the largest third ionization energy?

a) B ( )

b) C ( )

c) N ( )

d) Mg ( )

e) Al ( )

QUESTION 21

Which second period (row) element has the first six ionization energies (*IE* in electron volts, eV) listed below?

IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
11	24	48	64	392	490

a) B ( )

b) C ( )

c) N ( )

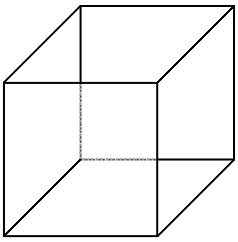
d) O ( )

e) F ( )

QUESTION 22

Silver metal exists as a face-centered cubic (fcc) packed solid.

a) Draw an fcc unit cell.



b) How many atoms are present in the fcc unit cell?

c) The density of silver has been determined to be 10.5 g cm^{-3} . What is the length of each edge of the unit cell?

d) What is the atomic radius of the silver atoms in the crystal?

QUESTION 23

Are the following statements correct (Y) or not (N)?

a) HF boils at a higher temperature than HCl. (Y) (N)

b) HBr boils at a lower temperature than HI (Y) (N)

c) Pure HI can be produced by reacting concentrated sulfuric acid with KI. (Y) (N)

d) Ammonia solutions are buffer solutions because they contain the conjugate pair $NH_3 – NH_4^+$. (Y) (N)

e) Pure water at 80 ℃ is acidic. (Y) (N)

f) During electrolysis of an aqueous KI solution with graphite electrodes, the *pH* near the cathode is below 7. (Y) (N)

QUESTION 24

Under certain conditions of concentration and temperature HNO_3 reacts with Zn and its reduction products are NO_2 and NO in a molar ratio 1 : 3. How many moles of HNO_3 are consumed by 1 mol of Zn?

a)	2.2	( )	d)	2.8	( )
b)	2.4	( )	e)	3.0	( )
c)	2.6	( )	f)	3.2	( )

SOLUTIONS FOR SECTION A

1: (b); :

2: (b);

3: (e) is not correct;

4: (b);

5: (a);

6: (c);

7: **a)** curve A;
b) curve B;
c) curve D;

8: (b);

9: (d);

10: **a)** alpha;
b) neutron;
c) beta;
d) gamma;
e) gamma;

11: (b);

12: (c);

13: (d);

14: **a)** N;
b) Y;
c) Y;
d) N;

15: **a)** Y;
b) N;
c) Y;
d) N;
e) N;

16: **a)** 300 nm;
b) 600 nm;
c) 5000 nm;
d) 150 nm;

17: **a)** Curve A;
b) Curve B;
c) Curve D;
d) Curve C;
e) Curve C;

18: (a);

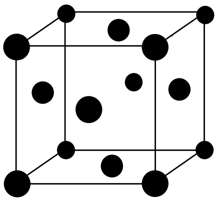
19: (b);

20: (d);

21: (b);

22:

a)



b) 4 atoms,

c) The length of each edge of the unit cell is 0.409 nm,

d) The atomic radius of the silver atoms in the crystal is 0.145 nm.

23: **a)** Y;
b) Y;
c) N;
d) N;
e) N;
f) N;

24: (d)

SECTION D: Inorganic Chemistry

PROBLEM 34 Aluminium

One of the largest factories in Greece, located near the ancient city of Delphi, produces alumina (Al_2O_3) and aluminium metal using the mineral bauxite mined from the Parnassus mountain. Bauxite is a mixed aluminium oxide hydroxide – $AlO_x(OH)_{3-2x}$ where $0<x<1$.

Production of Al metal follows a two-stage process:

(i) Bayer process: Extraction, purification and dehydration of bauxite (typical compositions for industrially used bauxites are Al_2O_3 40 – 60 %, H_2O 12 – 30 %, SiO_2 free and combined 1 – 15 %, Fe_2O_3 7 – 30 %, TiO_2 3 – 4 %, F, P_2O_5, V_2O_5, etc., 0.05 – 0.2 %). This involves dissolution in aqueous NaOH, separation from insoluble impurities, partial precipitation of the aluminium hydroxide and heating at 1200 °C. Complete and balance the following chemical reactions:

$Al_2O_3 + OH^- + \qquad \rightarrow \quad [Al(OH)_4(H_2O)_2]^-$

$SiO_2 + OH^- \quad \rightarrow \quad SiO_2(OH)_2^{2-}$

$SiO_2(OH)_2^{2-} + \qquad \rightarrow \quad CaSiO_3\downarrow +$

$[Al(OH)_4(H_2O)_2]^- \rightarrow \qquad \downarrow + OH^- + H_2O$

$Al(OH)_3 \rightarrow Al_2O_3 +$

ii) Héroult-Hall process: Electrolysis of pure alumina dissolved in molten cryolite, Na_3AlF_6. Typical electrolyte composition ranges are Na_3AlF_6 (80 – 85 %), CaF_2 (5 – 7 %), AlF_3 (5 – 7 %), Al_2O_3 (2 – 8 % intermittently recharged). Electrolysis is carried out at 940°C, under constant pressure of 1 atm, in a carbon-lined steel cell (cathode) with carbon anodes. Balance the main reaction of the electrolysis:

$Al_2O_3(l) + C(anode) \rightarrow Al(l) + CO_2(g)$

Since cryolite is a rather rare mineral, it is prepared according to the following reaction.

Complete and balance this reaction:

$HF + Al(OH)_3 + NaOH \rightarrow Na_3AlF_6 +$

During the electrolysis process several parallel reactions take place that degrade the graphite (C) anodes or reduce the yield.

iii) By using the thermodynamic data given below, which are taken to be independent on temperature, determine the thermodynamic quantities ΔH, ΔS and ΔG at 940 °C for the reaction:

$C(graphite) + CO_2(g) \rightarrow 2\ CO(g)$.

	Al(s)	Al_2O_3(s)	C (graphite)	CO(g)	CO_2(g)	O_2(g)
$\Delta_f H^o$ (kJ mol^{-1})	0	–1676	0	–111	–394	
S^o (J.K^{-1} mol^{-1})	28	51	6	198	214	205
$\Delta_{fus} H$ (kJ mol^{-1})	11	109				

iv) At the same temperature and using the data from the table in part (iii) determine the quantities ΔH and ΔG for the reaction

$2\ Al(l) + 3\ CO_2(g) \rightarrow Al_2O_3(l) + 3\ CO(g)$

given that ΔS = –126 J K^{-1} mol^{-1}. (Show your calculations)

v) Pure aluminium is a silvery-white metal with a face-centered cubic (fcc) crystal structure. Aluminium is readily soluble in hot concentrated hydrochloric acid producing the cation $[Al(H_2O)_6]^{3+}$, as well as in strong bases at room temperature producing hydrated tetrahydroxyaluminate anion, $[Al(OH)_4]^-$(aq). In both cases liberation of H_2 occurs. AlF_3 is made by treating Al_2O_3 with HF gas at 700 °C, while the other trihalides, AlX_3, are made by the direct exothermic reaction of Al with the corresponding dihalogen. Write all 4 chemical reactions described above.

vi) The $AlCl_3$ is a crystalline solid having a layer lattice with 6-coordinate Al(III), but at the melting point (192.4 °C) the structure changes to a 4-coordinate molecular dimer, Al_2Cl_6. The covalently bonded molecular dimer, in the gas phase and at high temperature, dissociates into trigonal planar $AlCl_3$ molecules.

For the molecular dimer Al_2Cl_6, in the gas phase, two different Al–Cl distances (206 and 221 pm) were measured. Draw the stereostructure of the dimer, and write down the corresponding Al–Cl distances.

vii) What is the hybridization of the Al atom(s) in Al_2Cl_6 and $AlCl_3$?

SOLUTION

i) $Al_2O_3 + 2\ OH^- + 7\ H_2O \rightarrow 2\ [Al(OH)_4(H_2O)_2]^-$

$SiO_2 + 2\ OH^- \rightarrow SiO_2(OH)_2^{2-}$

$SiO_2(OH)_2^{2-} + Ca^{2+} \rightarrow CaSiO_3\downarrow + H_2O$

$[Al(OH)_4(H_2O)_2]^- \rightarrow Al(OH)_3\downarrow + 2\ OH^- + 2\ H_2O$

$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O$

ii) $2\ Al_2O_3(l) + 3\ C(anode) \rightarrow 4\ Al(l) + 3\ CO_2(g)$

$6\ HF + Al(OH)_3 + 3\ NaOH \rightarrow Na_3AlF_6 + 6\ H_2O$

iii) $\Delta_r H^0_{1213} = 2\Delta_f H^0_{1213}(\mathrm{CO}) - \Delta_f H^0_{1213}(\mathrm{CO_2}) = 2\times(-111) - (-394) = 172\ \mathrm{kJ}$

$\Delta_r S^0_{1213} = 2S^0_{1213}(\mathrm{CO}) - S^0_{1213}(\mathrm{CO_2}) - S^0_{1213}(\mathrm{C}) = 2\times(-198) - 214 - 6 = 176\ \mathrm{J\ K^{-1}}$

$\Delta_r G^0_{1213} = \Delta_r H^0_{1213} - T\Delta S^0_{1213} = 172 - 1213\times 0.176 = -\ 41.5\ \mathrm{kJ\ K^{-1}}$

iv)

$$\begin{aligned}\Delta_r H^0_{1213} &= 3\Delta_f H^0_{1213}(\mathrm{CO}) + \Delta_f H^0_{298}(\mathrm{Al_2O_3}) + \Delta_{melt} H(\mathrm{Al_2O_3}) - 3\Delta_f H^0_{1213}(\mathrm{CO_2}) - 2\Delta H_{melt} H(\mathrm{Al}) = \\ &= 3\times(-111) - (-1676) + 109 - 3\times(-394) - 2\times 11 = -740\ \mathrm{kJ}\end{aligned}$$

$$\begin{aligned}\Delta_r H^0_{1213} &= 3\Delta_f H^0_{1213}(\mathrm{CO}) + \Delta_f H^0_{298}(\mathrm{Al_2O_3}) + \Delta_{melt} H(\mathrm{Al_2O_3}) - 3\Delta_f H^0_{1213}(\mathrm{CO_2}) - 2\Delta H_{melt} H(\mathrm{Al}) = \\ &= 3\times(-111) - (-1676) + 109 - 3\times(-394) - 2\times 11 = -740\ \mathrm{kJ}\end{aligned}$$

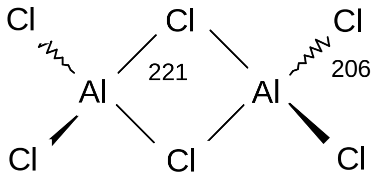
v) $2\ Al + 6\ H^+ + 12\ H_2O \rightarrow 2\ [Al(H_2O)_6]^{3+} + 3\ H_2$

$2\ Al + 2\ OH^- + 6\ H_2O \rightarrow 2[Al(OH)_4]^- + 3\ H_2$

$Al_2O_3 + HF \rightarrow 2\ AlF_3 + 3\ H_2O$

$2\ Al + 3\ X_2 \rightarrow 2\ AlX_3$

vi)



vii) Al_2Cl_6 - sp^3 hybridization

$AlCl_3$ - sp^2 hybridization

PROBLEM 3

Monovalent alkaline earth compounds?

In the past there have been several reports on compounds of monovalent calcium. Until recently the nature of these "compounds" was not known but they are still of great interest to solid state chemists.

Attempts to reduce $CaCl_2$ to CaCl have been made with

(a) Calcium (b) Hydrogen (c) Carbon

3.1 Give the corresponding reaction equations that could potentially lead to the formation of CaCl.

After an attempt to reduce $CaCl_2$ with the stoichiometric 1 : 1 molar amount of Ca one obtains an inhomogeneous grey substance. A closer look under the microscope reveals silvery metallic particles and colourless crystals.

3.2 What substance are the metallic particles and the colourless crystals?

When $CaCl_2$ is attempted to be reduced with elemental hydrogen a white product forms. Elemental analysis shows that the sample contains 52.36 % (by mass) of calcium and 46.32 mass % of chlorine.

3.3 Determine the empirical formula of the compound formed.

When $CaCl_2$ is attempted to be reduced with elemental carbon a red crystalline product forms. The molar ratio of Ca and Cl determined by elemental analysis is $n(\text{Ca}) : n(\text{Cl}) = 1.5 : 1$. During the hydrolysis of the red crystalline substance the same gas is evolved as during the hydrolysis of Mg_2C_3.

3.4 a) Show the two acyclic constitutional isomers of the gas that are formed by hydrolysis.

b) What compound is formed by the reaction of $CaCl_2$ with carbon?
(Provided that monovalent calcium does not exist.)

As none of these attempts lead to the formation of CaCl more consideration has to be given as to the hypothetical structure of CaCl. One can assume that CaCl is likely to crystallize in a simple crystal structure.

It is the radius ratio of cation $r(M^{m+})$ and anion $r(X^{x-})$ of salts that often determines the crystal structure of a particular compound as shown for MX compounds in the table below.

Coordination number of M	Surrounding of X	Radius ratio r_M/r_X	Structure type	estimated $\Delta_L H^0$ for CaCl
3	Triangular	0.155 – 0.225	BN	–663.8 kJ mol^{-1}
4	Tetrahedral	0.225 – 0.414	ZnS	–704.8 kJ mol^{-1}
6	Octahedral	0.414 – 0.732	NaCl	–751.9 kJ mol^{-1}
8	Cubic	0.732 – 1.000	CsCl	–758.4 kJ mol^{-1}

$\Delta_L H^0$(CaCl) is defined for the reaction $Ca^+(g) + Cl^-(g) \rightarrow CaCl(s)$

3.5 a) What type of structure is CaCl likely to have?

[$r(Ca^+) \approx 120$ pm (estimated), $r(Cl^-) \approx 167$ pm)]

Not only the lattice energy $\Delta_L H^0$ for CaCl is important for the decision whether CaCl is thermodynamically stable or not. In order to decide whether it is stable against decomposition into its elements, the standard enthalpy of formation $\Delta_f H^0$ of CaCl has to be known.

b) Calculate the value of $\Delta_f H^0$ (CaCl) with the aid of a Born-Haber-cycle.

heat of fusion	$\Delta_{fusion} H^0$(Ca)		9.3 kJ mol^{-1}
ionization enthalpy	$\Delta_{1.\ IE} H$(Ca)	$Ca \rightarrow Ca^+$	589.7 kJ mol^{-1}
ionization enthalpy	$\Delta_{2.\ IE} H$(Ca)	$Ca^+ \rightarrow Ca^{2+}$	1145.0 kJ mol^{-1}
heat of vaporization	$\Delta_{vap} H^0$(Ca)		150.0 kJ mol^{-1}
dissociation energy	$\Delta_{diss} H(Cl_2)$	$Cl_2 \rightarrow 2\ Cl$	240.0 kJ mol^{-1}

enthalpy of formation	$\Delta_f H^0(CaCl_2)$		–796.0 kJ mol^{-1}
electron affinity	$\Delta_{EA}H(Cl)$	$Cl + e^- \rightarrow Cl^-$	–349.0 kJ mol^{-1}

To decide whether CaCl is thermodynamically stable to disproportionation into Ca and $CaCl_2$ the standard enthalpy of this process has to be calculated. (The change of the entropy ΔS is very small in this case, so its influence is negligible.)

3.6 Does the disproportionation of CaCl take place from a thermodynamic point of view? Base your decision on a calculation!

SOLUTION

3.1 Chemical equations:

(a) $CaCl_2 + Ca \rightarrow 2\ CaCl$

(b) $2\ CaCl_2 + H_2 \rightarrow 2\ CaCl + 2\ HCl$

(c) $4\ CaCl_2 + C \rightarrow 4\ CaCl + CCl_4$

3.2

Silvery metallic particles:	Ca
Colourless crystals:	$CaCl_2$

Note: CaCl cannot be obtained by a conventional solid state reaction of Ca and $CaCl_2$

3.3 Empirical formula:

100 % –(mass % Ca + mass % Cl) = mass % X

100 % –(52.36 % + 46.32 %) = 1.32 % X

mol % of Ca = 52.36 mass % / M(Ca)

= 52.36 mass % / 40.08 g mol^{-1} = 1.31 mol %

mol % of Cl = 46.32 mass % / M (Cl)

= 46.32 mass % / 35.45 g mol^{-1} = 1.31 mol %

mol % of X = 1.32 % X / M (H)

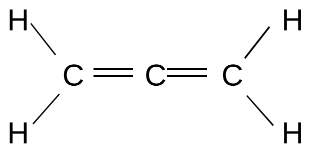
= 1.32 % X / 1.01 g mol^{-1} = 1.31 mol %

$n(Ca) : n(Cl) : n(H) = 1 : 1 : 1$

Empirical formula: CaClH

Notes: The reaction of $CaCl_2$ *with hydrogen does not lead to CaCl. The hydride CaClH is formed instead. The structure of this compound was determined by X-ray structure analysis which is not a suitable method to determine the position of light elements like hydrogen. Thus, the presence of hydrogen was missed and CaClH was thought to be CaCl for quite a long time.*

3.4 a) Structures only:



$H-C\equiv C-CH_3$

b) Empirical formula of the compound formed:

$Ca_3C_3Cl_2$

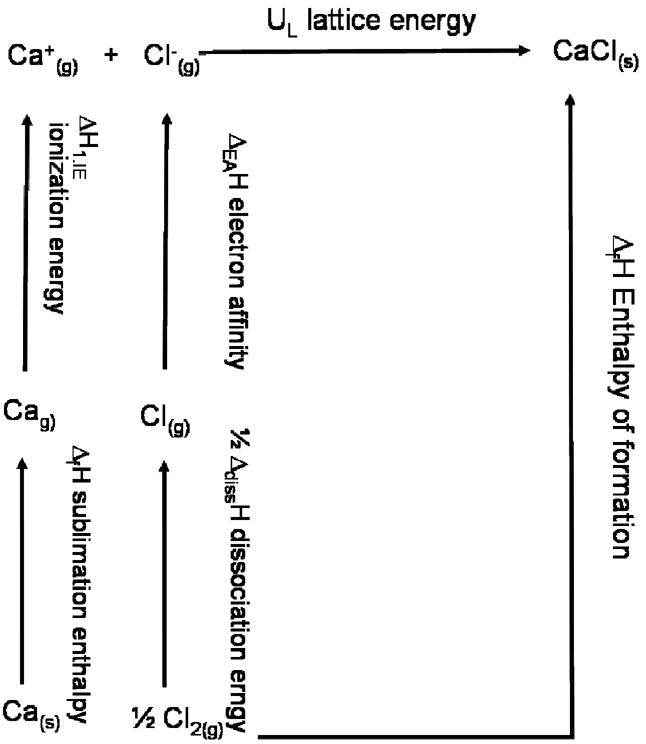
Notes: If the ratio of n(Ca) : n(Cl) = 1.5 : 1 [or better = 3 : 2 which can be rewritten as $CaCl_2 \cdot 2\ Ca^{2+} = Ca_3Cl_2^{4+}$ *] is given and the reduction product must contain a* C_3^{4-} *anion which needs two* Ca^{2+} *cations for electroneutrality, the composition* $Ca_3C_3Cl_2$ *will follow.*

3.5 a) Structure type CaCl likely to have:

$r(Ca^+)/r(Cl^-) = 120\ \text{pm} / 167\ \text{pm} = 0.719$

NaCl	CsCl	ZnS	BN	no decision possible
☒	☐	☐	☐	☐

b) $\Delta_f H^0$(CaCl) with a Born-Haber-cycle:



Summing up of all the single steps of the Born-Haber-cycle:

$$\Delta_f H^0\,(CaCl) = \Delta_{subl}H^0(Ca) + \Delta_{1.\,IE}H(Ca) + \tfrac{1}{2}\,\Delta_{diss}H(Cl_2) + \Delta_{EA}H(Cl) + \Delta_L H(CaCl)$$

$$= (159.3 + 589.7 + 120 - 349.0 - 751.9)\text{ kJ mol}^{-1}$$

$$= -231.9\text{ kJ mol}^{-1}$$

3.6 Stability to disproportionation:

$2\,CaCl \rightarrow CaCl_2 + Ca$

$\Delta H = \Delta_f H^0(CaCl_2) - 2\,\Delta_f H^0(CaCl) = -796.0\text{ kJ mol}^{-1} + 463.8\text{ kJ mol}^{-1} = -332.2\text{ kJ mol}^{-1}$

Disproportionation:	yes	no	no decision possible, more information needed
	☐	☒	☐

PROBLEM 4

Determining atomic masses

The reaction of the element X with hydrogen leads to a class of compounds that is analogous to hydrocarbons. 5.000 g of X form 5.628 g of a molar 2 : 1 mixture of the stoichiometric X-analogues of methane and ethane, respectively.

4.1 Determine the molar mass of X from this information. Give the chemical symbol of X, and the 3D-structure of the two products.

The following more complex case is of great historical interest.

The mineral Argyrodite is a stoichiometric compound that contains silver (oxidation state +1), sulphur (oxidation state -2) and an unknown element Y (oxidation state +4). The ratio between the masses of silver and Y in Argyrodite is m(Ag) : m(Y) = 11.88 : 1. Y forms a reddish brown lower sulfide (oxidation state of Y is +2) and a higher white sulfide (oxidation state of Y is +4). The coloured lower sulfide is the sublimate obtained by heating Argyrodite in a flow of hydrogen. The residues are Ag_2S and H_2S. To convert 10.0 g of Argyrodite completely, 0.295 dm^3 of hydrogen are needed at 400 K and 100 kPa.

4.2 Determine the molar mass of Y from this information. Give the chemical symbol of Y, and the empirical formula of Argyrodite.

The atomic masses are correlated with spectroscopic properties. To determine the vibrational frequency $\tilde{\nu}$ expressed in wave numbers of chemical bonds in IR spectra chemists use Hooke's law which focuses on the frequency of the vibration (attention to units!):

$$\tilde{\nu} = \frac{1}{2\pi c} \cdot \sqrt{\frac{k}{\mu}}$$

$\tilde{\nu}$ - vibrational frequency of the bond, in wavenumbers (cm^{-1})

c - speed of light

k - force constant, indicating the strength of the bond (N m^{-1}= kg s^{-2})

μ reduced mass in AB_4, which is given by $\mu = \dfrac{3\,m(A)\,m(B)}{3\,m(A) + 4\,m(B)}$

m(A), m(B) - the masses of the two bond atoms

The vibrational frequency of the C-H bond of methane is known to be 3030.00 cm^{-1}. The vibrational frequency of the Z-analogue of methane is known to be 2938.45 cm^{-1}. The bond enthalpy of a C-H bond in methane is 438.4 kJ mol^{-1}. The bond enthalpy of a Z-H bond in the Z-analogue of methane is known to be 450.2 kJ mol^{-1}.

4.3 Determine the force constant *k* of a C-H bond using Hooke's law.

Estimate the force constant *k* of a Z-H bond, assuming that there is a linear proportionality between force constant and bond enthalpy.

Determine the atomic mass of Z from this information.

Give the chemical symbol of Z.

SOLUTION

4.1 Atomic mass of X, symbol of X, structures:

1) $X + 2\,H_2 \rightarrow XH_4$

2) $2\,X + 3\,H_2 \rightarrow X_2H_6$

i) $5.0\text{ g} = [n_1(X) + n_2(X)] \cdot M(X)$

ii) $5.628\text{ g} =$

$= n_1(XH_4)\times[M(X) + 4\times1.01\text{ g mol}^{-1}] + n_2(X_2H_6)y \times [2\,M(X) + 6\times1.01\text{ g mol}^{-1}]$

iii) $n_1(XH_4) = 2\,n_2(X_2H_6)$

iii,i) → i') $2\,n_1(X) \times M(X) = 5.0\text{ g}$

iii,ii) → ii') $n_1(X) \times [2M(X) + 7.07\text{ g mol}^{-1}] = 5.628\text{ g}$

i',ii') → vi) $(5.0\text{ g}) \times [2\,M(X)]^{-1} = (5.628\text{ g}) \times [2\,M(X) + 7.07\text{ g mol}^{-1}]^{-1}$

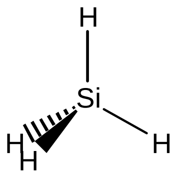
$M(X) = 3.535\text{ g mol}^{-1} \times (5.628\text{ g})^{-1} \times [(5.0\text{ g})^{-1} – (5.628\text{ g})^{-1}]^{-1}$

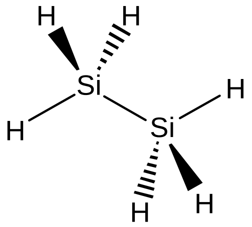
$M(X) = 28.14\text{ g mol}^{-1}$

Atomic mass of X: $M(X) = 28.14\text{ g mol}^{-1}$

Chemical symbol of X: Si

3D structures of the two products:





4.2 Atomic mass of Y and empirical formula of Argyrodite:

$Ag_aY_bS_{0.5\cdot a + 2\cdot b} + b\ H_2 \rightarrow 0.5a\ Ag_2S + b\ YS + b\ H_2S$

i) $10\ g = n(Ag_aY_bS_{0.5\cdot a+2\cdot b}) \times [a\ 107.87\ g\ mol^{-1} + b\ M(Y) +$

$+ (0.5\ a + 2\ b) \times 32.07\ g\ mol^{-1}]$

ii) $n(H_2) = \dfrac{p\,V(H_2)}{RT}$ $\qquad n(H_2) = \dfrac{100\ kPa \times 0.295 \times 10^{-3}\ m^3}{8.314\ J\ K^{-1} mol^{-1} \times 400\ K}$

$n(H_2) = 8.871 \times 10^{-3}\ mol$ $\qquad n(Ag_aY_bS_{0.5\cdot a + 2\cdot b}) = b^{-1} \times 8.871\cdot 10^{-3}\ mol$

iii) $11.88 = \dfrac{a \times 107.87\ g\ mol^{-1}}{b \times M(Y)}$ $\qquad a\ 107.87\ g\ mol^{-1} = 11.88 \times b \times M(Y)$

ii,i) → ii')

$b \times 10\ g \times (8.871\cdot 10^{-3}\ mol)^{-1} =$

$= a\ 107.87\ g\ mol^{-1} + b\ M(Y) + (0.5\ a + 2\ b) \times 32.07\ g\ mol^{-1}$

$b\ 1127\ g\ mol^{-1} = a\ 107.87\ g\ mol^{-1} + b\ M(Y) + (0.5\ a + 2\ b) \times 32.07\ g\ mol^{-1}$

iii,ii')→iv)

$b\cdot 1127\ g\ mol^{-1} = 11.88\cdot b\cdot M(Y) + b\cdot M(Y) + (0.5\cdot a + 2b)\cdot 32.07\ g\ mol^{-1}$

$b\cdot 1127\ g\ mol^{-1} =$

$= 11.88\ b\ M(Y) + b\ M(Y) + (0.5\ \dfrac{11.88 \times b \times M(Y)}{107.87\ g mol^{-1}} + 2\ b) \times 32.07\ g\ mol^{-1}$

$M(Y) = 72.57\ g\ mol^{-1} \rightarrow iii$ $\qquad a : b = 8 : 1$

Chemical symbol of Y: Ge

Empirical formula of Argyrodite: Ag_8GeS_6

4.3 The force constants of a C-H bond:

$$k(\text{C-H}) = [2\pi\, c\ \tilde{\nu}\ (\text{C-H})]^2 \cdot \frac{1}{N_A} \cdot \frac{3\,M(\text{C}) \times M(\text{H})}{3\,M(\text{C}) + 4\,M(\text{H})}$$

$$= [2\pi \times\ 3{\cdot}10^{10}\text{ cm s}^{-1} \times 3030\text{ cm}^{-1}]^2 \frac{1}{6.022 \times 10^{23}\text{ mol}^{-1}} \times \frac{3 \times 12.01 \times 1.01}{3 \times 12.01 + 4 \times 1.01}\text{ g mol}^{-1}$$

$k(\text{C-H}) = 491.94\text{ N m}^{-1}$

The force constants of a Z-H bond:

$$k(\text{Z-H}) = k(\text{C-H}) \cdot \frac{\Delta_b H(\text{Z-H})}{\Delta_b H(\text{C-H})}$$

$= 491.94\text{ N m}^{-1}{\cdot}450.2\text{ kJ mol}^{-1}{\cdot}[438.4\text{ kJ mol}^{-1}]^{-1} = 505.18\text{ N m}^{-1}$

The atomic mass and symbol of Z:

$$\frac{3\,M(\text{Z}) \times M(\text{H})}{3\,M(\text{Z}) + 4\,M(\text{H})} = \frac{k(\text{Z-H}) \times N_A}{[2\pi\, c\, \tilde{\nu}(\text{Z-H})]^2}$$

$$M(\text{Z}) = \frac{4}{3}\left(\frac{[2\pi\, c\, \tilde{\nu}(\text{Z-H})]^2}{k(\text{Z-H}) \cdot N_A} - \frac{1}{M(\text{H})}\right)^{-1}$$

$$M(\text{Z}) = \frac{4}{3}\left(\frac{[2\pi \times 3 \cdot 10^{10} \times 2938.45]^2}{505180 \times 6.022 \cdot 10^{23}} - \frac{1}{1.01}\right)^{-1}\text{ g mol}^{-1}$$

Atomic mass of Z: $M(\text{Z}) = 72.68\text{ g mol}^{-1}$

Chemical symbol of Z: Ge

PROBLEM 4

A

Gold Capital of Asia

Chiufen, the old mining town located within the hills in the northeast Taiwan, is a place where you can really experience Taiwan's historical legacy. It was the site of one of the largest gold mines In Asia. Accordingly, Chiufen is often referred to as the Gold Capital of Asia. The compound KCN is traditionally used to extract gold from ore. Gold dissolves in cyanide (CN^-) solutions in the presence of air to form $Au(CN)_2^-$, which is stable in aqueous solution.

$$4\,Au(s) + 8\,CN^-(aq) + O_2(g) + 2\,H_2O\,(l) \rightleftharpoons 4\,Au(CN)_2^-(aq) + 4\,OH^-(aq)$$

4.A-1 Draw a structure for $Au(CN)_2^-$ showing the spatial arrangements of the atoms.

4.A-2 How many grams of KCN are needed to extract 20 g of gold from ore? Show your work.

Aqua regia, a 3 : 1 mixture (by volume) of concentrated hydrochloric acid and nitric acid, was developed by the alchemists as a means to “dissolve” gold. The process is actually a redox reaction with the following simplified chemical equation:

$$Au(s) + NO_3^-(aq) + Cl^-(aq) \rightleftharpoons AuCl_4^-(aq) + NO_2(g)$$

4.A-3 Write down the half reactions, and use them to obtain a balanced redox reaction for this process.

4.A-4 What are the oxidizing and reducing agents for 4.A-3 process?

Gold is too noble to react with nitric acid. However, gold does react with aqua regia because the complex ion $AuCl_4^-$ forms. Consider the following half-reactions:

$Au^{3+}(aq) + 3\,e^- \rightarrow Au(s)$ $\qquad E^0 = +\,1.50\text{ V}$

$AuCl_4^-(aq) + 3\,e^- \rightarrow Au(s) + 4\,Cl^-$ $\qquad E^0 = +\,1.00\text{ V}$

An electrochemical cell can be formed from these two redox couples.

4.A-5 Calculate the formation constant for $AuCl_4^-$ at 25 °C:

$$K = \frac{[AuCl_4^-]}{[Au^{3+}]\,[Cl^-]^4}$$

4.A-6 The function of HCl is to provide Cl^{-}. What is the purpose of the Cl^{-} for the above reaction. Select your answer from the following choices.

(a) Cl^{-} is an oxidizing agent
(b) Cl^{-} is a reducing agent
(c) Cl^{-} is a complexing agent
(d) Cl^{-} is a catalyst

B

Gold Nanoparticles

The synthesis and characterization of gold nanoparticles is currently an active research area. The Brust-Schiffrin method for the synthesis of gold nanoparticle (AuNP) allows the facile preparation of thermally stable and air-stable AuNPs of reduced polydispersity with a controlled size distribution ranging in diameter between 1.5 and 5.2 nm. The preparative procedure is briefly described as follows. An aqueous solution of $HAuCl_4$ is mixed with a toluene solution of tetra-n-octylammonium bromide. The solution is mixed with dodecanethiol and is treated with an excess of $NaBH_4$. Formation of the AuNPs is evidenced by the immediate, pronounced darkening of the toluene phase. After ca. 24 h, the toluene solvent is removed with a rotary evaporator and the resulting solid washed on a frit with ethanol and hexane to remove excess thiol. These AuNPs can be repeatedly isolated and re-dissolved in common organic solvents without irreversible aggregation or decomposition.

4.B-1 Is the methodology for this fabrication referred to a top-down or a bottom-up approach? Select your answer from the following choices.

(a) top-down approach, which entails reducing the size of the smallest structures to the nanoscale
(b) bottom-up approach, which involves manipulating individual atoms and molecules into nanostructures

4.B-2 The trimethyl-n-octylammonium bromide can also be used as a phase-transfer reagent. It can carry $AlCl_4^{-}$ from an aqueous phase to an organic phase. Which property does trimethyl-n-octylammonium bromide possess to function as an efficient phase-transfer reagent? Select your answer from the following choices.

(a) one side of the molecule is electropositive, the other side is electronegative.

(b) one side of the molecule is hydrophilic, the other side is hydrophobic.

(c) one side of the molecule is acidic, the other side is basic.

4.B-3 What is the function of $NaBH_4$ in this preparation? Select your answer from the following choices.

(a) reducing agent

(b) oxidizing agent

(c) neutralization agent

(d) complexing agent

4.B-4 If the average diameter of a gold nanoparticle is 3 nm, what is the estimated number of Au atoms in each nanoparticle? (the atomic radius of Au is 0.144 nm). Select your answer from the following choices and show your work.

(a) 10^2

(b) 10^3

(c) 10^4

(d) 10^5

4.B-5 What is the estimated percentage of Au atoms on the surface of a nanoparticle? Select your answer from the following choices and show your work.

(a) 20 – 30 %

(b) 40 – 50 %

(c) 60 – 70 %

(d) 80 – 90 %

SOLUTION

4.A-1 $|N\equiv C-Au-C\equiv N|^{(-)}$

The structure of $Au(CN)_2^-$ is linear.

4.A-2 $4\ Au + 8\ KCN + O_2 + 2\ H_2O \rightleftharpoons 4\ KAu(CN)_2 + 4\ KOH$

$20\ g \div 197\ g\ mol^{-1} \approx 0.10\ mol\ (Au)$

$0.10\ mol \times (8/4) \times 65.12\ g\ mol^{-1} = 13.024\ g\ KCN$

4.A-3 Oxidation: $Au(s) + 4\ Cl^-(aq) \rightarrow AuCl_4^-(aq) + 3\ e^-$

Reduction: $3\ NO_3^-(aq) + 6\ H^+(aq) + 3\ e^- \rightarrow 3\ NO_2(g) + 3\ H_2O(l)$

$Au(s) + 3\ NO_3^-(aq) + 6\ H^+(aq) + 4\ Cl^-(aq) \rightleftharpoons AuCl_4^-(aq) + 3\ NO_2(g) + 3\ H_2O(l)$

4.A-4 Oxidizing agent: HNO_3 or nitric acid

Reducing agent: Au

4.A-5 $Au^{3+}(aq) + 3\ e^- \rightarrow Au(s)$ $E° = 1.50\ V$

$Au(s) + 4\ Cl^-(aq) \rightarrow AuCl_4^-(aq) + 3\ e^-$ $E° = 1.00\ V$

$- 3\ e^-$

$Au(s) + Au^{3+}(aq) + 4\ Cl^-(aq) \rightarrow AuCl_4^-(aq) + Au(s)$ $E° = +0.50\ V$

$+ 3\ e^-$

$E = E° - (0.059 / n) \log Q$

At equilibrium, $Q = K$, $E = 0$, $K = [AuCl_4\ ] / [Au^{3+}]\ [Cl^-]^4$

$E = (0.059 / n) \log K$, $0.50 = (0.059 / 3) \log K$, $K = 10^{25.42} = 2.6\times10^{25}$

$\Delta G^0_1 + \Delta G^0_2 = \Delta G^0_3$

$(-n\ F\ E^0_1) + (-n\ F\ E^0_2) = -RT \ln K$

$E° = (RT / nF) \ln K = (0.059 / n) \log K,$

$0.50 = (0.059 / 3) \log K,$

$K = 10^{2542} = 2.6\times10^{25}$

4.A-6 Answer for multiple choice question: (c)

4.B-1 Answer for multiple choice question: (b)

4.B-2 Answer for multiple choice question: (b)

4.B-3 Answer for multiple choice question: (a)

4.B-4 Answer for multiple choice question**:** (b)

Calculation:

$$V_{\text{AuNPs}} = \frac{4}{3}\pi\, r_{\text{AuNPs}}^3$$

$$V_{\text{Au}} = \frac{4}{3}\pi\, r_{\text{Au}}^3$$

$$N_{\text{Au}} = \frac{V_{\text{AuNPs}}}{V_{\text{Au}}} = \frac{\frac{4}{3}\pi\, r_{\text{AuNPs}}^3}{\frac{4}{3}\pi\, r_{\text{Au}}^3} = \left(\frac{r_{\text{AuNPs}}^3}{r_{\text{Au}}^3}\right)^3 = \left(\frac{15\text{ A}}{1{,}44\text{ A}}\right)^3 \approx 1000$$

4B-5 Calculation:

Method 1:

$4/3 \times \pi \times r_{\text{AuNPs}}{}^3 = 4/3 \times \pi \times r_{\text{Au}}{}^3 \times N_{\text{Au}}$

$r_{\text{AuNPs}}{}^3 = \text{r}_{\text{Au}}{}^3 \times N_{\text{Au}}$

Surface area of a gold nanoparticle: $\text{S}_{\text{AuNPs}} = 4\,\pi\, r_{\text{AuNPs}}{}^2$

$\text{S}_{\text{AuNPs}} = 4\,\pi\, r_{\text{Au}}{}^2\, \text{N}_{\text{Au}}{}^{2/3}$

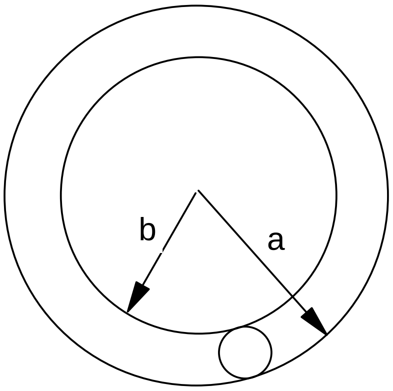
$N_{\text{S}} \approx \text{S}_{\text{AuNPs}} / \pi\, r_{\text{Au}}{}^2 = 4\; N_{\text{Au}}{}^{2/3}$

$\text{P} \approx N_{\text{S}} / N_{\text{Au}} = 4/ N_{\text{Au}}{}^{1/3}$

$\text{N}_{\text{Au}} \approx 1000$

$\text{P} \approx 40\ \%$

or Method 2:



$a = r_{\text{AuNPs}}$

$b = r'_{\text{AuNPs}} = r_{\text{AuNPs}} - 2\, r_{\text{Au}}$

$$\text{P}\ \% = \frac{\dfrac{V_{\text{AuNPs}}}{V_{\text{Au}}} - \dfrac{V'_{\text{AuNPs}}}{V_{\text{Au}}}}{\dfrac{V_{\text{AuNPs}}}{V_{\text{Au}}}} \times 100\ \% = \frac{\left(\dfrac{r_{\text{AuNPs}}}{r_{\text{Au}}}\right)^3 - \left(\dfrac{r'_{\text{AuNPs}}}{r_{\text{Au}}}\right)^3}{\left(\dfrac{r'_{\text{AuNPs}}}{r_{\text{Au}}}\right)^3} \times 100\ \% =$$

$$= \frac{(15\ \text{A})^3 - (12.12\ \text{A})^3}{(15\ \text{A})^3} \times 100\ \% = 47\ \%$$

PROBLEM 5

Lewis Structure

5.1 Draw one Lewis structure for each of the following molecules.

a) N_2

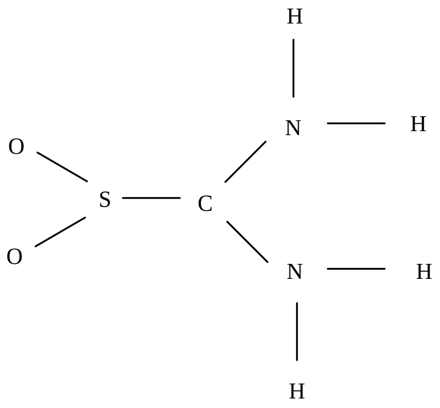
b) NH_3

c) O_3

d) SO_3

5.2 Draw the Lewis structure of carbon monoxide and assign formal charges and oxidation states to both the carbon and oxygen atoms in carbon monoxide.

Thiourea-S,S-dioxide, $O_2SC(NH_2)_2$, has the following skeletal structure



5.3 Draw the Lewis structure of thiourea-S,S-dioxide with zero formal charges on all atoms.

5.4 Based on the Valence Shell Electron Pair Repulsion (VSEPR) model, what is the geometry around the sulfur, carbon, and nitrogen according to the Lewis structure you predicted from 5.3?

5.4a What is the geometry around the sulfur atom? Select your answer from the following choices.

a) trigonal pyramidal

b) triangular planar

c) T-shape

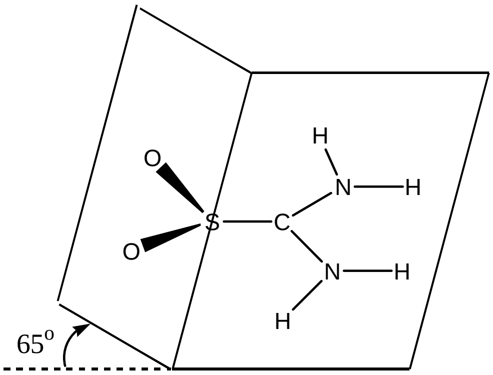
5.4b Similarly, what is the geometry around the C-atom? Select your answer from the following choices.

a) trigonal pyramidal
b) triangular planar
c) T-shape

5.4c Finally, what is the geometry around the N-atom? Select your answer from the following choices.

a) trigonal pyramidal
b) triangular planar
c) T-shape

Molecular structure in the solid state is usually determined by X-ray diffraction analysis. According to this method, the structure of thiourea-S,S-dioxide is shown below:



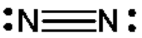
All the N, H atoms are coplanar with S, C atoms, and the dihedral angle between the OSO plane and the $SC(NH_2)_2$ plane is 65°.

5.5 Draw the Lewis structure and resonance forms that are consistent with the geometry determined.

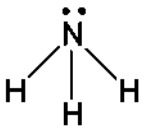
SOLUTION

5.1

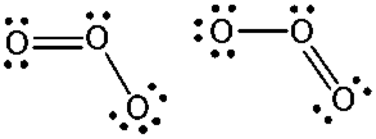
(a)



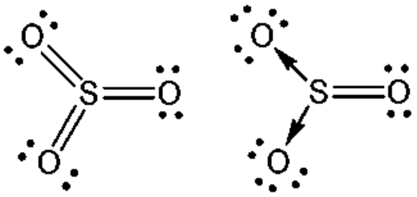
(b)

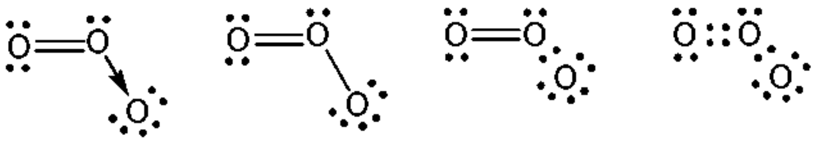


(c)



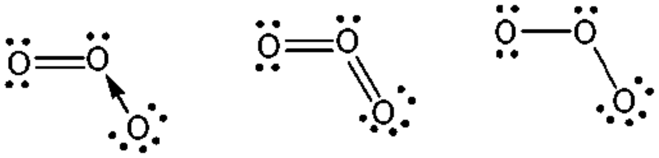
(d)



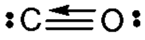


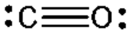
are all correct answers

But



are incorrect answers





acceptable

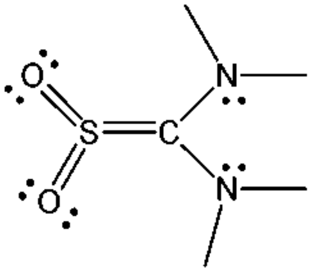
5.2

Formal charge C^{-1} ; O^{+1}

Oxidation state C^{2+} ; O^{2-}

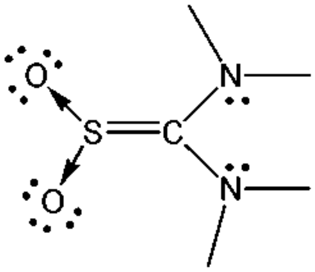
5.3

The structure



is correct.

The structure



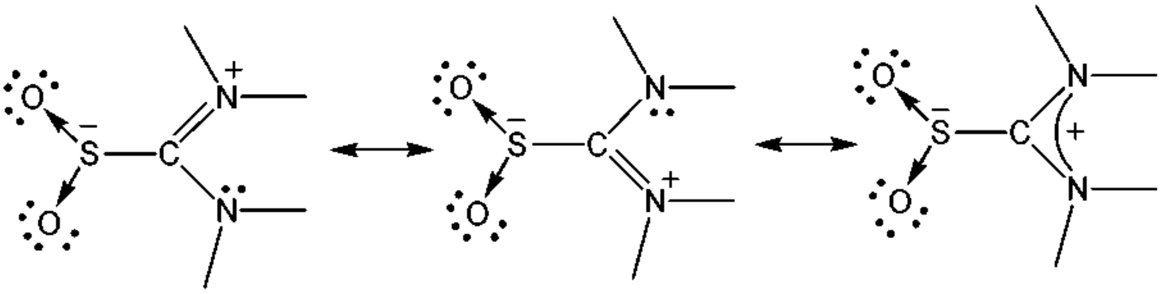
would have a formal charge and is incorrect.

5.4 Sulphur: (b) trigonal planar

Carbon: (b) trigonal planar

Nitrogen: (a) trigonal pyramidal

5.5



PROBLEM 8

Chemistry of Iron Oxides

The nucleus of iron is the most stable among all elements and, therefore, iron accumulates at the core of massive red giant stars where nucleosynthesis of many elements essential for life (such as C, N, O, P, S, etc.) takes place. As a result, among heavy elements iron is quite abundant in the universe. Iron is also abundant on Earth.

Development of a technology for reducing iron oxide to iron was a key step in human civilization. Key reactions taking place in the blast furnace are summarized below.

$C(s) + O_2(g) \rightarrow CO_2(g)$ ΔH^0 = –393.51 kJ(/mol) (1)

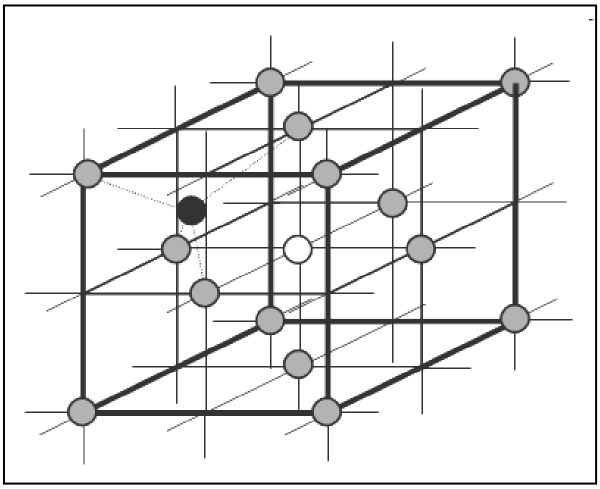
$CO_2(g) + C(s) \rightarrow 2\ CO(g)$ ΔH^0 = 172.46 kJ(/mol) (2)

$Fe_2O_3(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$ ΔH^0 = ? (3)

8.1 Indicate the reducing agent in each reaction.

8.2 Balance reaction (3) and calculate the equilibrium constant of reaction (3) at 1200 °C. $\Delta H_f^\circ(Fe_2O_3(s)$ = –824.2 kJ mol^{-1},
S°(J mol^{-1} K^{-1}): Fe(s) = 27.28, Fe_2O_3(s) = 87.40, C(s) = 5.74, CO(g) = 197.674, CO_2(g) = 213.74

In the manufacture of celadon pottery, Fe_2O_3 is partially reduced in a charcoal kiln to mixed oxides of Fe_3O_4 and FeO. The amount of the different oxides seems to be related to the "mystic" color of celadon ceramics. Fe_3O_4 (magnetite) itself is a mixed oxide containing Fe^{2+} and Fe^{3+} ions and belongs to a group of compounds with a general formula of AB_2O_4. The oxide ions form a face-centered cubic array. The figure shows the array of oxygens (gray circles) and representative sites for divalent A and trivalent B cations. The dark circle represents a tetrahedral site and the white circle an octahedral site.



8.3 How many available octahedral sites for iron ions are there in one AB_2O_4 unit? Certain sites are shared by neighbouring units.

AB_2O_4 can adopt a normal- or an inverse-spinel structure. In normal-spinel structure, two B ions occupy two of the octahedral sites and one A occupies one of the tetrahedral sites. In an inverse-spinel structure, one of the two B ions occupies a tetrahedral site. The other B ion and the one A ion occupy octahedral sites.

8.4 What percentage of available tetrahedral sites is occupied by either Fe^{2+} or Fe^{3+} ion in Fe_3O_4?

8.5 Fe_3O_4 has an inverse-spinel structure. Draw the crystal field splitting pattern of Fe^{2+} and fill out the electrons. The electron pairing energy is greater than the octahedral field splitting.

SOLUTION

8.1 (1): C (2): C (3): CO

8.2 Balanced equation (3): $Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(s) + 3\ CO_2(g)$

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^0_{(1)} = -393.51\ kJ = \Delta H_f^0\ (CO_2(g))$

(2) $CO_2(g) + C(s) \rightarrow 2\ CO(g)$ $\Delta H^0_{(2)} = 172.46\ kJ$

From (1) and (2):

$\Delta H_f^0(CO(g)) = (1/2)\ \{172.46 + (-393.51)\} = -110.525\ kJ$

$\Delta H_f^0(Fe_2O_3) = –824.2$ kJ

$\Delta H^0_{(3)} = 3 \times \Delta H_f^0(CO_2(g)) – \Delta H_f^0(Fe_2O_3) – 3 \times \Delta H_f^0(CO(g))$

$= [3 \times (–393.51)] – (–824.2) – [3 \times (–110.525)] = –24.8$ kJ

$\Delta S°_{(3)} = (2 \times 27.28) + (3 \times 213.74) – 87.4 – (3 \times 197.674) = 15.36$ J K^{-1}

$\Delta G^0_{(3)} = \Delta H^0 – T\Delta S^0 = –24.8$ kJ – (15.36 J K^{-1} $\times$ 1 kJ /1000 J x 1473.15 K) =

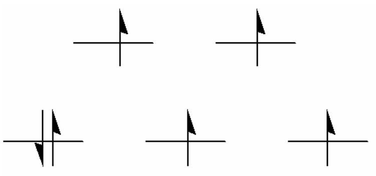
= – 47.43 kJ

$$K = e^{(-\Delta G°/RT)} = e^{(47430\,\text{J}\ /\ (8.314\ \text{J K}^{-1} \times 1473.15\ \text{K}))} = 48$$

8.3 One AB_2O_4 unit has available 4 (= 1 + (1/4 $\times$ 12) octahedral sites.

8.4 Since one face-centered cube in AB_2O_4 represents one Fe_3O_4 unit in this case, it has 8 available tetrahedral sites. In one Fe_3O_4 unit, 1 tetrahedral site should be occupied by either one Fe^{2+} (normal-spinel) or one Fe^{3+} (inverse-spinel). Therefore, in both cases, the calculation gives (1/8) x 100 % = 12.5 % occupancy in available tetrahedral sites.

8.5



THE THIRTY-NINTH
INTERNATIONAL CHEMISTRY OLYMPIAD
15–24 JULY 2007, MOSCOW, RUSSIAN FEDERATION

THEORETICAL PROBLEMS

PROBLEM 1

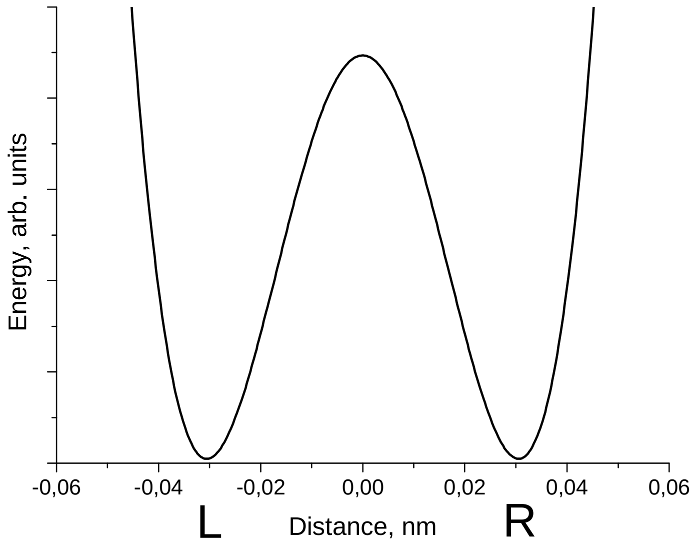
Proton tunneling

Proton tunneling through energy barriers is an important effect, which can be observed in many complex species containing hydrogen bonds (DNA, proteins, etc.). Propanedial (malonaldehyde) is one of the simplest molecules for which intramolecular proton transfer can occur.

1.1 Draw the condensed formula of propanedial and the structures of two of its isomers, which can exist in equilibrium with propanedial.

1.2 In a water solution propanedial is a weak acid, its strength being comparable with that of acetic acid. Specify the acidic hydrogen atom. Explain its acidity (choose one version in the Answer Sheet).

On the plot below an energy profile of the intramolecular proton transfer is given (the dependence of energy on the distance of proton motion (in nm)). Energy curve has a symmetric double-well form.

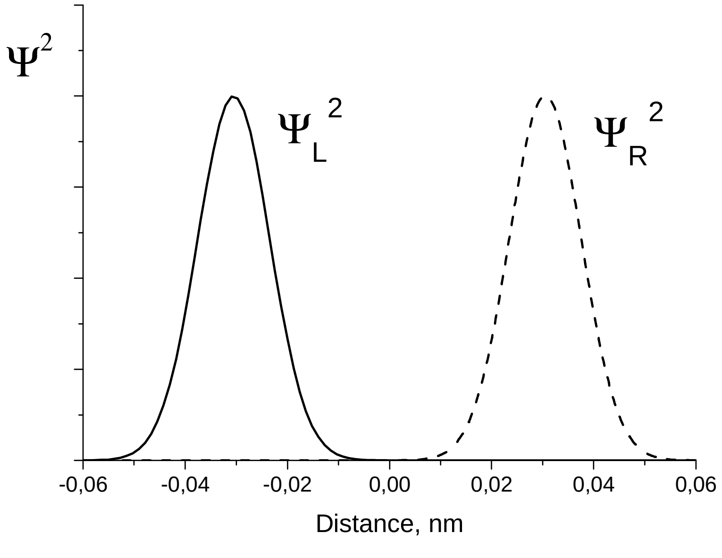


1.3 Draw the structures corresponding to two minima on this curve.

A proton is delocalized between two atoms and oscillates between two minima L and R with an angular frequency $\omega = 6.48 \times 10^{11}$ s^{-1}. Probability density for a proton depends on time as follows:

$$\Psi^2(x,t) = \frac{1}{2}\left[\Psi_L^2(x) + \Psi_R^2(x) + \left(\Psi_L^2(x) - \Psi_R^2(x)\right)\cos\left(\omega t\right)\right],$$

wavefunctions $\Psi_L(x)$ and $\Psi_R(x)$ describe a proton localized in the left and right wells, respectively:



1.4 Write down the expressions for the probability density at three moments: (a) $t = 0$, (b) $t = \pi/(2\omega)$, (c) $t = \pi/\omega$. Sketch the graphs of these three functions.

1.5 Without calculations, determine the probability of finding the proton in the left well at $t = \pi/(2\omega)$

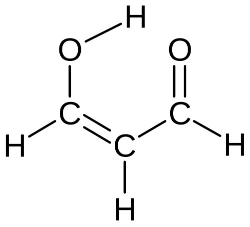
1.6 How much time is required for a proton to move from one well to another? What is the proton mean speed during the transfer?

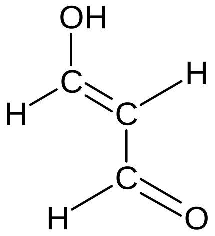
1.7 From the energy curve, estimate the uncertainty of the position of proton forming hydrogen bonds. Estimate the minimal uncertainty of the proton speed. Compare this value with that obtained in **1.6** and draw a conclusion about the proton tunneling (choose one of the versions in the Answer Sheet).

SOLUTION

1.1 The structures of propanedial and two of its isomers:

O=CH–CH$_2$–CH=O





1.2 Acidic hydrogen atom is in CH$_2$ (in enol forms acidic hydrogen is in OH).

The stability of propanedial is caused by (one of the following answers had to be chosen):

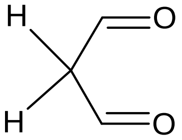
a) the stability of carbanion due to conjugation with two carbonyl groups,

b) weakness of C – H bond in a carbonyl group,

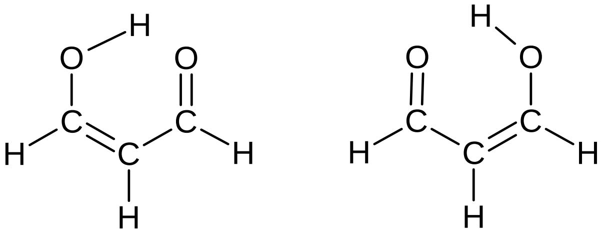
c) hydrogen bonds between two propanedial molecules.

The first answer is correct.

1.3 The distance between two minima on the energy curve is 0.06 nm. In a purely aldehyde form



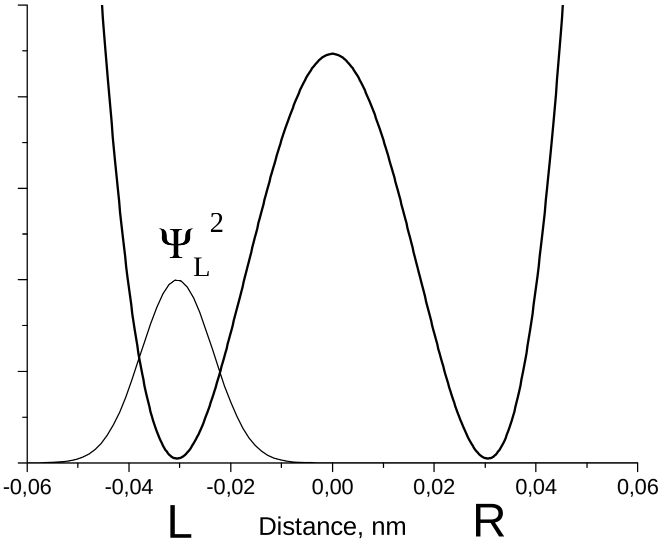
such distance between two possible positions of proton is impossible. Tunneling takes place only in enol Z-form:



1.4 Expressions and plots of probability density

(a) $\Psi^2(x,0) = \frac{1}{2}\left[\Psi_L^2(x) + \Psi_R^2(x) + \Psi_L^2(x) - \Psi_R^2(x)\right] = \Psi_L^2(x)$

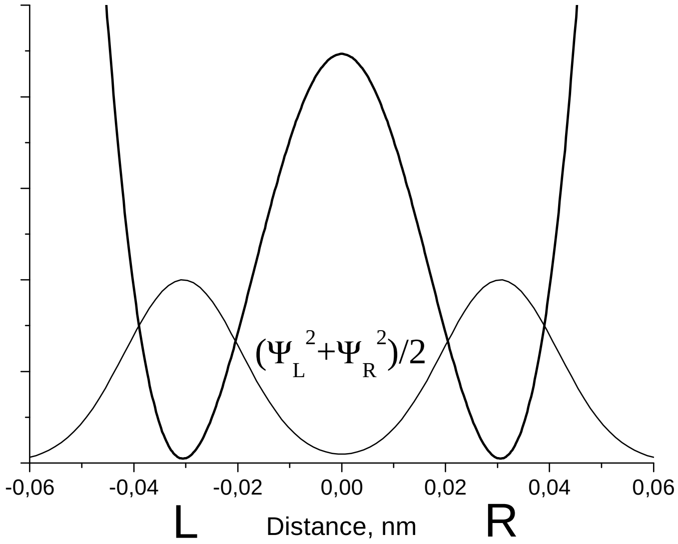
The probability density is concentrated in the left well:



(b) In the middle of the time interval

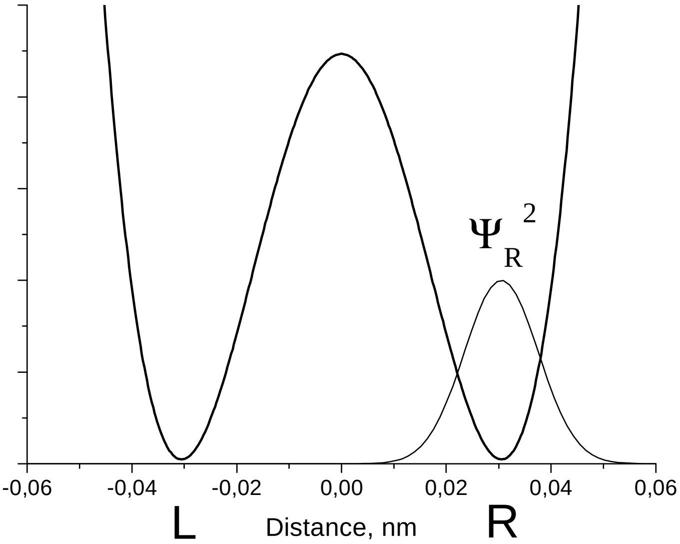
$$\Psi^2\left(x, \frac{\pi}{2\omega}\right) = \frac{1}{2}\left[\Psi_L^2(x) + \Psi_R^2(x)\right]$$

The probability density has a symmetric form, a proton is delocalized between two wells:



(c) $\Psi^2\left(x,\dfrac{\pi}{\omega}\right) = \dfrac{1}{2}\left[\Psi_L^2(x)+\Psi_R^2(x)-\Psi_L^2(x)+\Psi_R^2(x)\right] = \Psi_R^2(x)$

The probability density is concentrated in the right well:



1.5 The probability of finding the proton in the left well is 1/2, because probability function is symmetric, and both wells are identical.

1.6 The time of transfer from one well to another is $t = \pi / \omega$.

$t = \dfrac{3.14}{6.48\times10^{11}} = 4.85\times10^{-12}$ s.

The proton velocity:

$$v = \frac{0.06\times10^{-9}}{4.85\times10^{-12}} = 12 \text{ m s}^{-1}.$$

1.7 The uncertainty of proton position is approximately equal to half of the distance between minima, that is 0.03 nm (<u>0.06 nm will be also accepted</u>).

The minimal uncertainty of velocity can be obtained from the uncertainty relation:

$$\Delta v = \frac{h}{2\,m\,\Delta x} = \frac{1.055\times10^{-34}}{2\times\dfrac{0.001}{6.02\times10^{23}}\times0.03\times10^{-9}} \approx 1000 \text{ m s}^{-1}.$$

Comparing this uncertainty with the velocity 12 m s^{-1} we see that the notion of proton velocity during transfer from one well to another is senseless. Therefore, proton tunneling is a purely quantum phenomenon and cannot be described in classical terms. The second conclusion is correct.

PROBLEM 6

Silicates as the base of the Earth crust

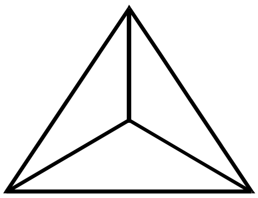
Silica and compounds derived from it, silicates, constitute ca. 90 % of the Earth crust substances. Silica gives rise to a beautiful material – glass. Nobody knows exactly how glass was discovered. There is a well-favored story related to Phoenician sailors who fused occasionally sea sand and soda ash. It is likely that they discovered the secret of “liquid glass” (LGL) – sodium metasilicate (Na_2SiO_3) soluble in water.

6.1 The solution of LGL was used earlier as office glue. Write down the net ionic equation accounting for the ability of LGL to set in air.

Hydrolysis of LGL in water allows obtaining a colloidal solution of silicic acid.

6.2 Complete the Table in the Answer Sheet. Write down the net ionic equations matching the processes enumerated in the Table. For each process check the “Yes” box if it leads to changes of pH. Otherwise check the “No” box.

The structure of species occurring in aqueous solutions of silicates is rather complex. However, it is possible to distinguish the main building block of all species – orthosilicate tetrahedron (SiO_4^{4-}, **1**):



(**1**)

For $[Si_3O_9]^{n-}$ ion found in aqueous solutions of silicates:

6.3 Determine the charge (n).

6.4 Determine the number of oxygen atoms bridging adjacent tetrahedra.

6.5 Depict its structure joining together several tetrahedra (**1**). Take into account that any adjacent tetrahedron shares one vertex.

Charged monolayers with the composition $[Si_4O_{10}]^{m-}$ are found in kaolinite (clay).

6.6 Using the same strategy as in **6.3 - 6.5**, depict <u>a fragment</u> of the layered structure joining 16 tetrahedra **(1)**. Note that 10 tetrahedra have shared vertices with 2 neighbours each, and the rest 6 have shared vertices with 3 neighbours each.

Being placed into the LGL solution, salts of transition metals give rise to fancy “trees” tinted relevant to the colour of the salt of the corresponding transition metal. Crystals of $CuSO_4 \cdot 5\ H_2O$ produce “trees” of blue colour, whereas those of $NiSO_4 \cdot 7\ H_2O$ form green “trees”.

6.7 Determine the pH of 0.1 M aqueous solution of copper sulphate at 25 °C assuming that its hydrolysis occurs in small degree only. Use the value of the first acidity constant of $[Cu(H_2O)_4]^{2+}$ $K_a^{I} = 1\times10^{-7}$.

6.8 Write down equation of a reaction between aqueous solutions of $CuSO_4$ and sodium metasilicate (LGL). Take into account the pH values of aqueous solutions of the salts.

SOLUTION

6.1 $SiO_3^{2-} + 2\ CO_2 + 2\ H_2O \rightarrow$ “H_2SiO_3”↓ (Silica acid gel) + 2 HCO_3^- or

$SiO_2(OH)_2^{2-} + 2\ CO_2 + H_2O \rightarrow$ “H_2SiO_3”↓+ 2 HCO_3^- or

$SiO_3^{2-} + CO_2 + H_2O \rightarrow$ “H_2SiO_3”↓ + CO_3^{2-}

6.2 a) protonation of ortho-silicate ions leading to the formation of Si-OH groups:

$SiO_4^{4-} + H_2O \rightarrow [SiO_3(OH)]^{3-} + OH^-$ or

$SiO_4^{4-} + H^+ \rightarrow [SiO_3(OH)]^{3-}$ or YES ☑

$[SiO_2(OH)_2]^{2-} + H^+ \rightarrow [SiO(OH)_3]^-$

b) formation of hydrated $[SiO_4(H_2O)_2]^{4-}$ anions NO ☑

$SiO_4^{4-} + 2\ H_2O \rightarrow [SiO_4(H_2O)_2]^{4-}$

c) polycondensation of ortho-silicate ions leading to the formation of Si-O-Si bonds

$2\ SiO_4^{4-} + H_2O = [O_3Si\text{-}O\text{-}SiO_3]^{6-} + 2\ OH^-$ or

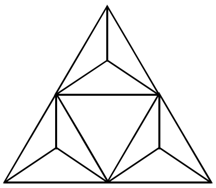
$2\ SiO_4^{4-} + 2\ H^+ = [O_3Si\text{-}O\text{-}SiO_3]^{6-} + H_2O$ or YES ☑

$2\ SiO_2(OH)_2^{2-} + H_2O = [O\text{-}Si(OH)_2\text{-}O\text{-}Si(OH)_2\text{-}O]^{2-} + 2\ OH^-$

6.3 n = 6 (assuming oxidation numbers of silicon (+4) and oxygen (-2), or taking into account its structure and the charge of orthosilicate ion (-4))

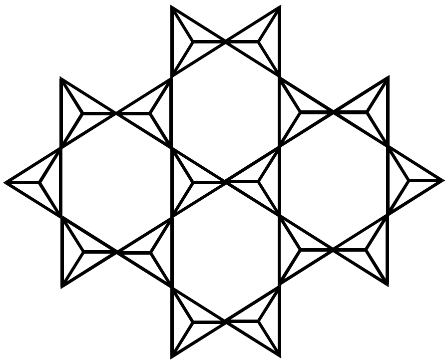
6.4 $Si_3O_9 \equiv 3\ [SiO_4] - 3\ O$, i.e. there are 3 oxygen atoms bridging adjacent tetrahedra

6.5



6.6 m = 4 (assuming oxidation numbers of silicon (IV) and oxygen (-II), or taking into account its structure and the charge of orthosilicate ion (-4))

$Si_4O_{10} \equiv 4[SiO_4] - 6\ O$, i. e. the formula of the tetrahedron is now $SiO_{2.5}$, which is possible if 1 O atom belongs to this tetrahedron and the other three are shared between 2 tetrahedra (their contribution = 3/2). This is possible if the tetrahedra are set on a plane and joined together through all apexes of their bases.



6.7 $Cu(H_2O)_4^{2+} + H_2O \rightleftharpoons Cu(OH)(H_2O)_3^{+} + H_3O^{+}$,

$[H^+] \approx (c\ K_a^{I})^{1/2} = 1\times10^{-4}$, $pH = -\log[H^+] = 4$

$pH = 4$

6.8 $CuSO_4 + Na_2SiO_3 + 2\ H_2O \rightarrow Cu(OH)_2\downarrow + \text{“}H_2SiO_3\text{”}\downarrow + Na_2SO_4$

or

$2\ CuSO_4 + Na_2SiO_3 + 2\ H_2O \rightarrow Cu_2(OH)_2SO_4\downarrow + \text{“}H_2SiO_3\text{”}\downarrow + Na_2SO_4$

This (or those) reaction(s) (apart from formation of copper silicate) can be deduced from the fact that the reaction describes mutual (self-amplifying) hydrolysis. It comes from the previous parts of the task: pH of LGL is greater than 7 (see questions **6.2**), and pH of copper sulfate solution is less than 7 (see **6.7**).

PROBLEM 5

A and **B** are white crystalline substances. Both are highly soluble in water and can be moderately heated (up to 200 ℃) without change but both decompose at higher temperatures. If an aqueous solution of 20.00 g **A** (which is slightly basic, *pH* ≈ 8.5-9) is added to an aqueous solution of 11.52 g **B** (which is slightly acidic, *pH* ≈ 4.5-5) a white precipitate **C** forms that weighs 20.35 g after filtering, washing and drying. The filtrate is essentially neutral and gives a brown colour reaction with an acidified KI solution. When boiled, the filtrate evaporates without the appearance of any residue.

The white solid **D** can be prepared by the heating of **A** in the absence of air. The exothermic reaction of **D** with water gives a colourless solution. This solution, if kept in an open container, slowly precipitates a white solid **E** and leaves water. Upon prolonged exposure to air at room temperature, solid **D** is transformed into **E** as well. However, heating **D** in air at 500 ℃ produces a different white substance **F**, which is barely soluble in water and has a mass of only 85.8% of the **E** formed from the same amount of **D**. **F** gives a brown colour reaction with an acidified solution of KI.

E can be converted back into **D** but ignition above 1400 ℃ is required for this purpose. The reaction of **B** and **D** in water forms the precipitate **C** and is accompanied by a characteristic odour.

5.1 Give the formulae of the substances **A** - **F**

5.2 Write balanced equations for all the reactions mentioned. (The equation for the thermal decomposition of **B** is not required.)

SOLUTION

5.1 The formulae of the substances **A** – **F:**

A	**B**	**C**
$Ba(NO_2)_2$	$(NH_4)_2SO_4$	$BaSO_4$
D	**E**	**F**
BaO	$BaCO_3$	BaO_2

5.2 Equations:

$Ba(NO_2)_2 = BaO + NO + NO_2$

$(NH_4)_2SO_4 = NH_4HSO_4 + NH_3$

$Ba^{2+} + SO_4^{2-} = BaSO_4$

$2\ NO_2^- + 2\ I^- + 4\ H^+ = 2\ NO + I_2 + 2\ H_2O$

$NH_4^+ + NO_2^- = N_2 + 2\ H_2O$

$BaO + H_2O = Ba^{2+} + 2\ OH^-$

$Ba^{2+} + 2\ OH^- + CO_2 = BaCO_3 + H_2O$

$BaO + CO_2 = BaCO_3$

$2\ BaO + O_2 = 2\ BaO_2$

$BaO_2 + 2\ I^- + 4\ H^+ = Ba^{2+} + I_2 + 2\ H_2O$

$BaCO_3 = BaO + CO_2$

$NH_4^+ + OH^- = NH_3 + H_2O$

Detailed solution:

The problem contains quite a number of clues to the identification of the compounds. It is clear that **A**, **D**, **E**, and **F** all contain the same element; with a water-soluble solid compound stable at 1400 °C, probably a metal. The aqueous solution of a metal compound giving a precipitate and pure water upon standing in the air strongly hints at the formation of a carbonate, possibly from a soluble hydroxide. A likely conclusion is that **D** is an oxide, limiting the choice of the metal to Sr or Ba. (One might also consider Li, Ca, or Tl which are less satisfactory because $Ca(OH)_2$ is poorly soluble while the solubilities of Li_2CO_3 and Tl_2CO_3 are quite significant.) If **E** is an alkaline earth metal carbonate, then the molar mass of **F** could be either M_{Ca} + 45.8, or M_{Sr} + 39.05, or M_{Ba} + 32. Since **F** is formed by heating the oxide in air, the former two do not make any sense while the latter is consistent with BaO_2. This is confirmed by the oxidative capability of **F**.

The odour appearing in the reaction of **B** with $Ba(OH)_2$ indicates that the former might be an ammonium salt. Assuming that the reaction of **A** and **B** is a simple precipitation between a barium salt and an ammonium salt, we get an equivalent mass of 48 for the anion of the precipitate. This might be either SO_4^{2-} or HPO_4^{2-} but the acidity of **B** is consistent with the former and, in addition, $(NH_4)_2HPO_4$ would not give the same $BaHPO_4$ precipitate with $Ba(OH)_2$ as with $Ba(NO_2)_2$. If we accept that **B** is $(NH_4)_2SO_4$, we obtain an equivalent mass of 46 for the anion of **A**. This and the surrounding chemistry are consistent with the nitrite ion.

THE FORTY-FIRST
INTERNATIONAL CHEMISTRY OLYMPIAD
18–27 JULY 2009, CAMBRIDGE, UNITED KINGDOM

THEORETICAL PROBLEMS

PROBLEM 1

Estimating the Avogadro constant

Many different methods have been used to determine the Avogadro constant. Three different methods are given below.

Method A – from X-ray diffraction data (modern)

The unit cell is the smallest repeating unit in a crystal structure. The unit cell of a gold crystal is found by X-ray diffraction to have the face-centred cubic unit structure (i.e. where the centre of an atom is located at each corner of a cube and in the middle of each face). The side of the unit cell is found to be 0.408 nm.

1.1 Sketch the unit cell and calculate how many Au atoms the cell contains.

1.2 The density of Au is $1.93 \cdot 10^4$ kg m^{-3}. Calculate the volume and mass of the cubic unit cell.

1.3 Hence calculate the mass of a gold atom and the Avogadro constant, given that the relative atomic mass of Au is 196.97.

Method B – from radioactive decay (Rutherford, 1911)

The radioactive decay series of ^{226}Ra is as follows:

$$^{226}\text{Ra} \xrightarrow{t} {}^{222}\text{Rn} \xrightarrow{3.825\ \text{d}} {}^{218}\text{Po} \xrightarrow{3.10\ \text{m}} {}^{214}\text{Pb} \xrightarrow{26.8\ \text{m}} {}^{214}\text{Bi} \xrightarrow{19.9\ \text{m}}$$

$$^{214}\text{Po} \xrightarrow{164.3\ \mu\text{s}} {}^{210}\text{Pb} \xrightarrow{22.3\ \text{y}} {}^{210}\text{Bi} \xrightarrow{5.013\ \text{d}} {}^{210}\text{Po} \xrightarrow{138.4\ \text{d}} {}^{206}\text{Pb}$$

The times indicated are half-lives, the units are y = years, d = days, m = minutes. The first decay, marked *t* above, has a much longer half-life than the others.

1.4 In the table below, identify which transformations are α-decays and which are β-decays.

	α-decay	β-decay
$^{226}Ra \longrightarrow {}^{222}Rn$		
$^{222}Rn \longrightarrow {}^{218}Po$		
$^{218}Po \longrightarrow {}^{214}Pb$		
$^{214}Pb \longrightarrow {}^{214}Bi$		
$^{214}Bi \longrightarrow {}^{214}Po$		
$^{214}Po \longrightarrow {}^{210}Pb$		
$^{210}Pb \longrightarrow {}^{210}Bi$		
$^{210}Bi \longrightarrow {}^{210}Po$		
$^{210}Po \longrightarrow {}^{206}Pb$		

1.5 A sample containing 192 mg of ^{226}Ra was purified and allowed to stand for 40 days. Identify the first isotope in the series (excluding Ra) that has not reached a steady state.

1.6 The total rate of α-decay from the sample was then determined by scintillation to be 27.7 GBq (where 1 Bq = 1 count s^{-1}). The sample was then sealed for 163 days. Calculate the number of α particles produced.

1.7 At the end of the 163 days the sample was found to contain 10.4 mm^3 of He, measured at 101325 Pa and 273 K. Calculate the Avogadro constant from these data.

1.8 Given that thee relative isotopic mass of ^{226}Ra measured by mass spectrometry is 226.25, use the textbook value of the Avogadro constant ($6.022 \cdot 10^{23}$ mol^{-1}) to calculate the number of ^{226}Ra atoms in the original sample, n_{Ra}, the decay rate constant, λ, and the half-life, t, of ^{226}Ra (in years). You need only consider the decays up to but not including the isotope identified in 1.5.

Method C – dispersion of particles (Perrin, 1909)

One of the first accurate determinations of the Avogadro constant was carried out by studying the vertical distribution under gravity of colloidal particles suspended in water. In one such experiment, particles with radius $2.12 \cdot 10^{-7}$ m and density $1.206 \cdot 10^{3}$ kg m^{-3} were suspended in a tube of water at 15 °C. After allowing sufficient time to equilibrate, the mean numbers of particles per unit volume observed at four heights from the bottom of the tube were:

height / 10^{-6} m	5	35	65	95
mean number per unit volume	4.00	1.88	0.90	0.48

1.9 Assuming the particles to be spherical, calculate:

i) the mass, *m*, of a particle;

ii) the mass, m_{H_2O}, of the water it displaces;

iii) the effective mass, *m**, of the particle in water accounting for buoyancy (i.e. taking account of the upthrust due to the displaced volume of water).

Take the density of water to be 999 kg m^{-3}.

At equilibrium, the number of particles per unit volume at different heights may be modelled according to a Boltzmann distribution:

$$\frac{n_h}{n_{h_0}} = \exp\left[-\frac{E_h - E_{h_0}}{RT}\right]$$

where

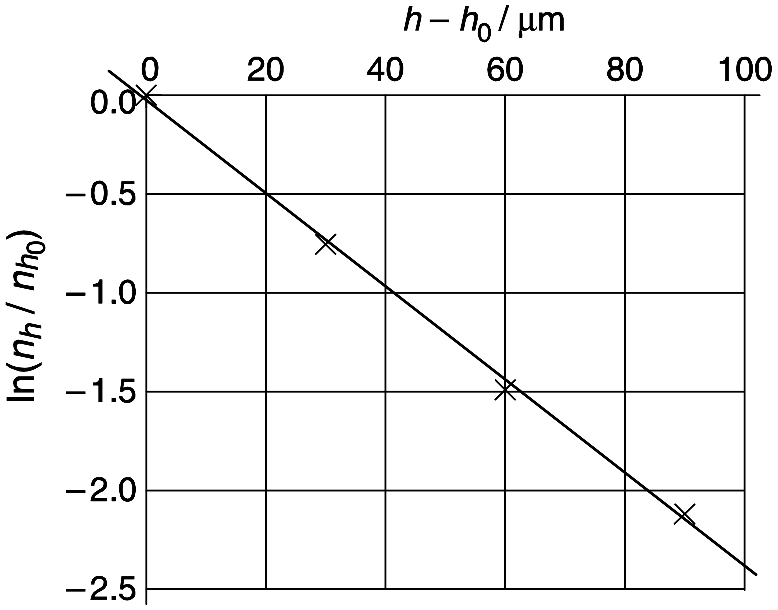
n_h is the number of particles per unit volume at height *h*,

n_{h0} is the number of particles per unit volume at the reference height h_0,

E_h is the gravitational potential energy per mole of particles at height *h* relative to the particles at the bottom of the tube,

R is the gas constant, 8.3145 J K^{-1} mol^{-1}.

A graph of $\ln(n_h / n_{h0})$ against $(h - h_0)$, based on the data in the table above, is shown below. The reference height is taken to be 5 μm from the bottom of the tube.

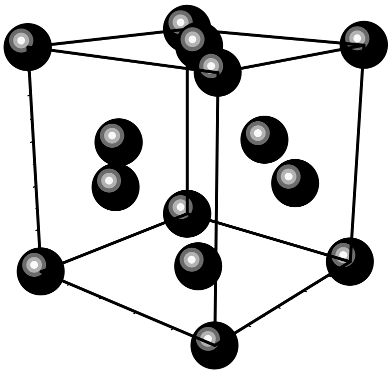


1.10 Derive an expression for the gradient (slope) of the graph.

1.11 Determine the Avogadro constant from these data.

SOLUTION

1.1 Unit cell:



Number of Au atoms in the unit cell:

8 × 1/8 from each corner = 1

6 × ½ from each face = 3

Total = 4 atoms

1.2 Volume:

V = (0.408 nm)^3 = 6.79 ·10^{-29} m^3

Mass:

$m = \rho V$ = 1.93 ·10^4 kg m^{-3} × 6.79 ·10^{-29} m^3 = 1.31 ·10^{-24} kg

1.3 Mass of Au atom:

$$m = \frac{1.31 \cdot 10^{-24}\ \text{kg}}{4} = 3.28 \cdot 10^{-25}\ \text{kg}$$

Avogadro constant:

$$N_A = \frac{196.97\ \text{g mol}^{-1}}{3.28 \cdot 10^{-22}\ \text{g}} = 6.01 \cdot 10^{23}\ \text{mol}^{-1}$$

1.4

	α-decay	β-decay
$^{226}\mathrm{Ra} \longrightarrow {}^{222}\mathrm{Rn}$	✓	
$^{222}\mathrm{Rn} \longrightarrow {}^{218}\mathrm{Po}$	✓	
$^{218}\mathrm{Po} \longrightarrow {}^{214}\mathrm{Pb}$	✓	
$^{214}\mathrm{Pb} \longrightarrow {}^{214}\mathrm{Bi}$		✓
$^{214}\mathrm{Bi} \longrightarrow {}^{214}\mathrm{Po}$		✓
$^{214}\mathrm{Po} \longrightarrow {}^{210}\mathrm{Pb}$	✓	
$^{210}\mathrm{Pb} \longrightarrow {}^{210}\mathrm{Bi}$		✓
$^{210}\mathrm{Bi} \longrightarrow {}^{210}\mathrm{Po}$		✓
$^{210}\mathrm{Po} \longrightarrow {}^{206}\mathrm{Pb}$	✓	

1.5 Answer: $^{210}\mathrm{Pb}$

1.6 $2.77 \cdot 10^{10}\ \mathrm{s}^{-1} \times 163 \times 24 \times 60 \times 60\ \mathrm{s} = 3.90 \cdot 10^{17}$

1.7 Answer:

$$n = \frac{pV}{RT} = 4.64 \cdot 10^{-7}\ \mathrm{mol}$$

$$N_A = \frac{3.90 \cdot 10^{17}}{4.64 \cdot 10^{-7}\ \mathrm{mol}} = 8.4 \cdot 10^{23}\ \mathrm{mol}^{-1}$$

1.8 $$n_{\mathrm{Ra}} = \frac{0.192\ \mathrm{g} \times 6.022 \cdot 10^{23}\ \mathrm{mol}^{-1}}{226.25\ \ \mathrm{g\,mol}^{-1}} = 5.11 \cdot 10^{20}\ \text{atoms}$$

$$\lambda = \frac{2.77 \cdot 10^{10}\ \mathrm{s}^{-1}}{5.11 \cdot 10^{20} \times 4} = 1.36 \cdot 10^{-11}\ \mathrm{s}^{-1}$$

(only ¼ of the decays are from $^{226}\mathrm{Ra}$)

$$t = \frac{\ln 2}{\lambda} = 5.12 \cdot 10^{10}\ \mathrm{s} = 1620\ \text{years}$$

1.9 $V = 3.99 \cdot 10^{-20}$ m^3

$m = 4.81 \cdot 10^{-17}$ kg

$m_{H_2O} = 3.99 \cdot 10^{-17}$ kg

$m^* = 8.3 \cdot 10^{-18}$ kg

1.10 gradient = $\dfrac{-m^* N_A\, g}{R\, T}$

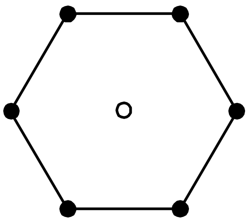
1.11 Acceptable range of slopes is 0.0235 ± 0.002 μm

Hence $N_A = (6.9 \pm 0.8) \cdot 10^{23}$ mol^{-1} (error range needs widening here).

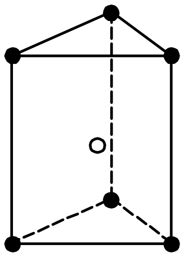
PROBLEM 6

Transition metal complexes

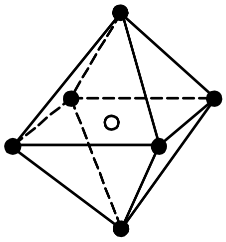
Alfred Werner used the technique of ‘isomer counting’ to deduce the structure of metal complexes with coordination number six. Three of the shapes he considered are shown below.



X



Y



Z

In each structure, the empty circle shows the location of the central metal atom and the filled circles show the location of the ligands. Structure **X** is hexagonal planar, structure **Y** is trigonal prismatic and structure **Z** is octahedral.

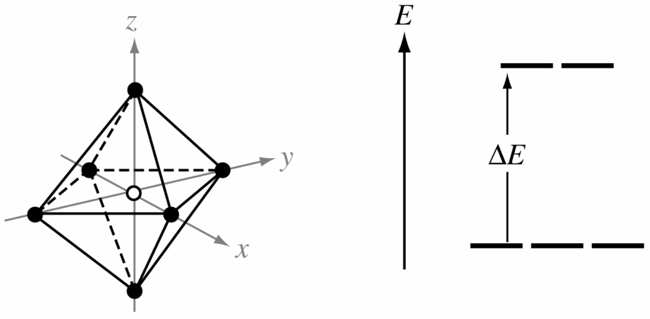
For each of the three shapes, there is just one structure when all of the ligands are the same, i.e. when the complex has the general formula MA_6 where A is the ligand. However, when achiral ligands A are substituted by one or more achiral ligands, it may be possible for each structure to form geometrical isomers. It might also be possible for one or more of the geometrical isomers to be optically active and exist as pairs of enantiomers.

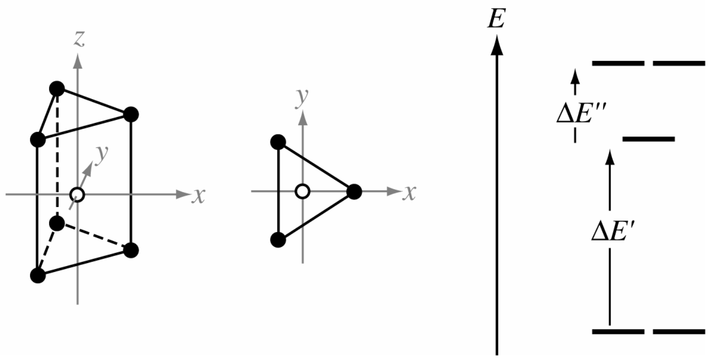
6.1 Fill in the table below to indicate how many geometrical isomers may be formed for each structure **X**, **Y**, and **Z** as the monodentate ligands A are substituted by monodentate ligands B or by symmetrical bidentate ligands, denoted C–C. Bidentate ligand C–C can only link between two atoms on adjacent positions, i.e. those positions connected by a line in the structures **X**, **Y**, and **Z**.

In each case write the number of geometrical isomers in the space provided. If one of the isomers exists as a pair of enantiomers, include an asterisk, *****, in the box. If two exist as two pairs of enantiomers, include two asterisks and so on. For example, if you think there are five geometrical isomers of a particular structure, three of which exist as pairs of enantiomers, write 5 *******

	Number of predicted geometrical isomers		
	Hexagonal planar **X**	Trigonal Prismatic **Y**	Octahedral **Z**
MA_6	1	1	1
MA_5B			
MA_4B_2			
MA_3B_3			
MA_4(C-C)			
MA_2(C-C)$_2$			
M(C-C)$_3$			

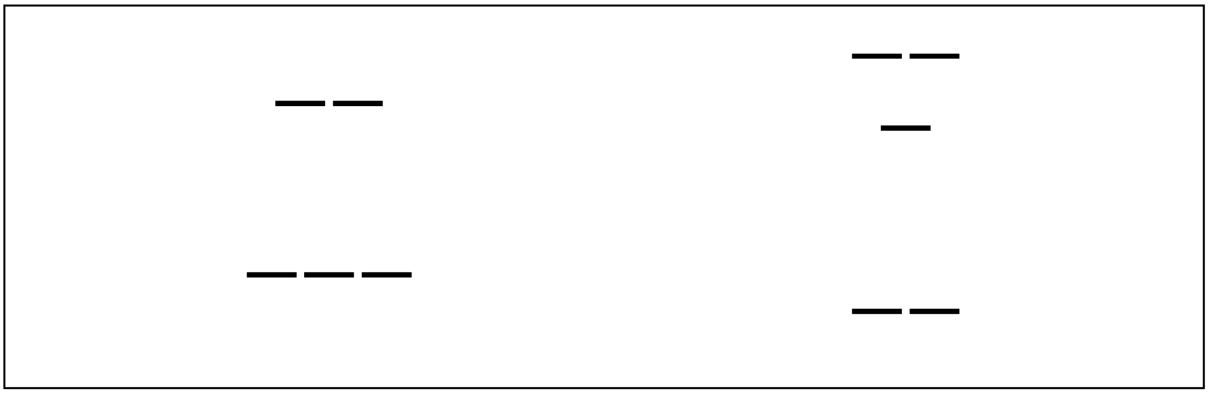
There are no known complexes that adopt the hexagonal planar geometry **X**, but structures are known for both the trigonal prismatic geometry **Y** and the octahedral geometry **Z**. In these complexes, the orbitals derived from the metal d orbitals have different energies depending on the geometry of the complex. The splitting patterns for the trigonal prismatic geometry and for the octahedral geometry are shown below.





The separations in energy, ΔE, $\Delta E'$ and $\Delta E''$ depend on the particular complex.

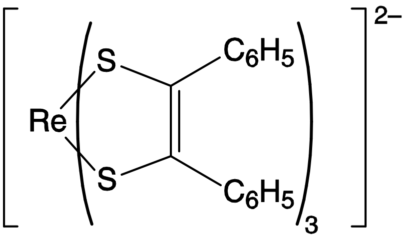
6.2 For each of the splitting patterns shown below label which d orbitals are which.



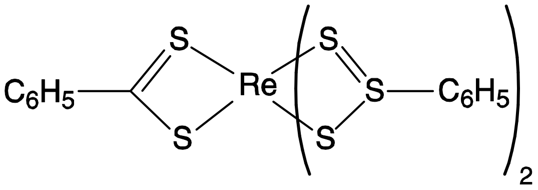
The two complexes $[Mn(H_2O)_6]^{2+}$ and $[Mn(CN)_6]^{2-}$ are both octahedral. One has a magnetic moment of 5.9 BM, the other has a magnetic moment of 3.8 BM but you must decide which is which.

6.3 On the diagram below, draw the electronic arrangements for each of the complexes.

The magnetic moments of complexes **A** and **B** shown below have been measured and found to be 1.9 and 2.7 BM but you must decide which is which.



A



B

6.4 Draw the orbital splitting diagrams for the two complexes, including the arrangements of the electrons.

Octahedral complexes are far more common than trigonal prismatic. Werner isolated five compounds **C** – **G** containing Co(III), Cl, and NH_3 only, each of which contained one octahedral complex. (There is actually a sixth compound but Werner could not isolate it.) Werner's five compounds had the molar conductivities shown below. The conductivities are extrapolated to infinite dilution and are expressed in arbitrary units. Compound **G** does not react with aqueous $AgNO_3$; compounds **C**, **D**, and **E** react with different stoichiometric ratios of aqueous $AgNO_3$; **E** and **F** react with the same stoichiometric ratio of aqueous $AgNO_3$.

	C	**D**	**E**	**F**	**G**
molar conductivity	510	372	249	249	~0

6.5 As far as you are able, suggest a structure for each of the compounds **C** – **G**.

Werner was also the first person to separate the enantiomers of an octahedral compound, **H**, which contained no carbon atoms. The compound, **H**, is composed of only cobalt, ammonia, chloride and an oxygen species which could be either H_2O, or HO^- or O^{2-}. The compound contains octahedrally coordinated cobalt ions. All of the chloride is easily removed from the compound by titration with aqueous silver nitrate. A 0.2872 g sample of **H** (containing no water of crystallization) required 22.8 cm^3 of a silver nitrate solution (c = 0.100 mol dm^{-3}) to exchange all of the chloride.

6.6 Calculate the percentage, by mass, of chloride in **H**.

H is stable to acids, but is hydrolysed in alkali. A 0.7934 g sample of **H** (containing no water of crystallization) was heated with excess aqueous sodium hydroxide. Cobalt(III) oxide was formed and ammonia gas given off. The ammonia produced was distilled off and absorbed into 50.0 cm^3 of aqueous HCl (c_{HCl} = 0.500 mol dm^{-3}). The residual HCl required 24.8 cm^3 of aqueous KOH solution (c_{KOH} = 0.500 mol dm^{-3}) to be neutralized.

The remaining suspension of cobalt(III) oxide was allowed to cool, approximately 1 g of potassium iodide was added, and then the mixture was acidified with aqueous HCl. The liberated iodine was then titrated with aqueous solution of sodium thiosulfate (c = 0.200 mol dm^{-3}) and required 21.0 cm^3 for complete reaction.

6.7 Calculate the percentage, by mass, of ammonia in **H**.

6.8 Give the equation for the reaction of cobalt(III) oxide with potassium iodide in aqueous acid.

6.9 Calculate the percentage, by mass, of cobalt in **H**.

6.10 Calculate the identity of the oxygen species contained in **H**. Show your working.

6.11 Give the empirical formula of **H**.

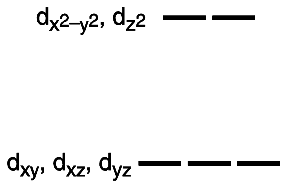
6.12 Suggest a structure for the chiral compound **H**.

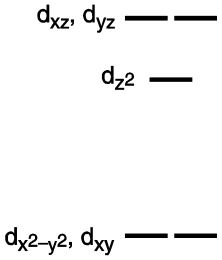
SOLUTION

6.1

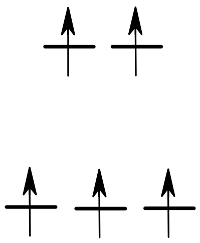
	Number of predicted geometrical isomers		
	Hexagonal planar **X**	Trigonal Prismatic **Y**	Octahedral **Z**
MA_6	1	1	1
MA_5B	1	1	1
MA_4B_2	3	3*	2
MA_3B_3	3	3*	2
$MA_4(C\text{-}C)$	1	2	1
$MA_2(C\text{-}C)_2$	2	4*	2*
$M(C\text{-}C)_3$	1	2	1*

6.2

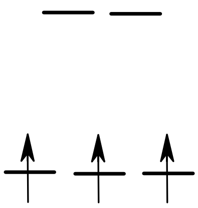




6.3



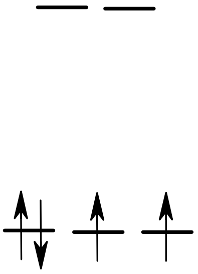
$[Mn(H_2O)_6]^{2+}$



$[Mn(CN)_6]^{2-}$

6.4

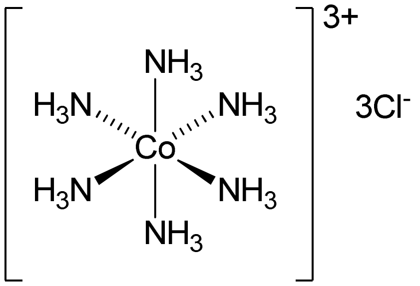
A



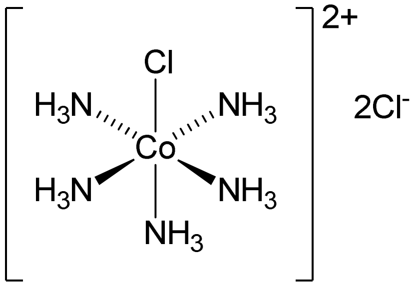
B

6.5

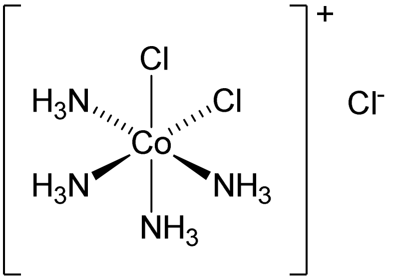
C



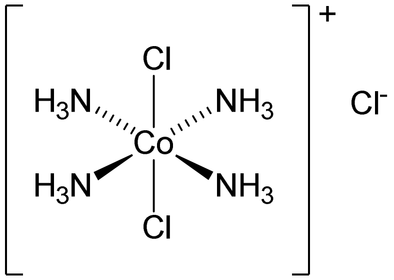
D



E

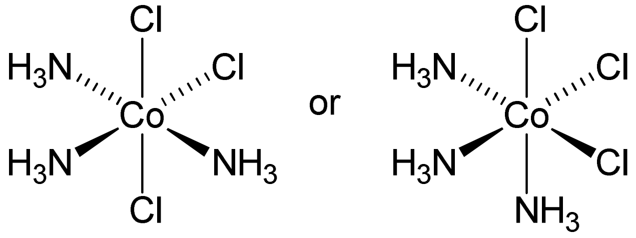


F



E and F could be either way round

G



6.6 $n(Ag^+) = 0.100 \text{ mol dm}^{-3} \times 0.0228 \text{ dm}^3 = 2.28 \cdot 10^{-3} \text{ mol}$

$n(Cl^-) = 2.28 \cdot 10^{-3} \text{ mol}$

$m(Cl) = 8.083 \cdot 10^{-2} \text{ g}$

$$\% \text{ Cl} = \frac{8.083 \cdot 10^{-2} \text{ g}}{0.2872 \text{ g}} \times 100 = 28.1$$

6.7 $n(KOH) = 0.0124 \text{ mol}$

$n(HCl)$ neutralised by ammonia = 0.025 mol – 0.0124 mol = 0.0126 mol

$m(NH_3) = 17.034 \text{ g mol}^{-1} \times 0.0126 \text{ mol} = 0.2146 \text{ g}$

$$\% \ NH_3 = \frac{0.2146 \text{ g}}{0.7934 \text{ g}} \times 100 = 27.1 \ \%$$

6.8 $Co_2O_3 + 2\ KI + 6\ HCl \rightarrow 2\ CoCl_2 + I_2 + 3\ H_2O + 2\ KCl$

6.9 $2\ Na_2S_2O_3 + I_2 \rightarrow 2\ NaI + Na_2S_4O_6$

$n(Na_2S_2O_3) = 0.200 \text{ mol dm}^{-3} \times 0.021 \text{ dm}^3 = 4.20 \cdot 10^{-3} \text{ mol}$

$n(I_2) = 2.10 \cdot 10^{-3} \text{ mol}$

$n(Co^{2+}) = 4.20 \cdot 10^{-3} \text{ mol}$

$m(Co) = 4.20 \cdot 10^{-3} \text{ mol} \times 58.93 \text{ g mol}^{-1} = 0.2475 \text{ g}$

$$\% \text{ Co by mass} = \frac{0.2475 \text{ g}}{0.7934 \text{ g}} \times 100 = 31.2$$

6.10 Assuming 100 g of complex, there is 13.6 g unaccounted. for molar ratio of

$$n(Co) : n(NH_3) : n(Cl) = \frac{31.2}{58.93} : \frac{27.1}{17.034} : \frac{28.1}{35.453} = 0.529 : 1.591 : 0.7926 = 2 : 6 : 3.$$

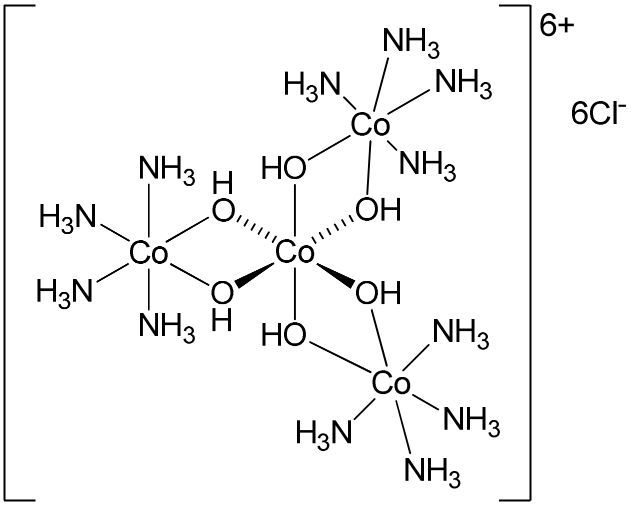
Missing species is either O^{2-}, OH^- or H_2O with similar molar mass ≈ 17 g mol^{-1}.

Molar fraction of missing oxygen species ≈ 13.6 / 17 = 0.8 i.e. the same as the Cl.

Considering charge balance, 2(+3) + 6(0) + 3(–1) = +3, it is needed –3 to balance i.e. the missing species must be OH^-.

6.11 Empirical formula of H: $Co_2\ N_6\ H_{21}\ O_3\ Cl_3$

6.12 Structure must fit the empirical formula worked out above, contain only octahedral cobalt, and be chiral. Some marks deducted if chloride is directly coordinated to cobalt, or if any single ammonia molecule is coordinated to more than one cobalt atom.



2.4 Calculate the enthalpy of the lattice formation of NaCl [kJ mol^{-1}] by using the following enthalpy data of the respective steps in the above Born-Haber cycle.

Formation of NaCl(*s*)	Sublimation of Na(*s*)	Ionization of Na(*g*)	Dissociation of Cl_2(*g*)	Electron gain by Cl(*g*)
–411 kJ mol^{-1}	109 kJ mol^{-1}	496 kJ mol^{-1}	242 kJ mol^{-1}	–349 kJ mol^{-1}

Synthesis of sodium carbonate by the ammonia-soda process (Solvay process)

Sodium carbonate (anhydrous soda ash) is a raw material in the manufacture of glass, medicaments, alkaline detergents, etc.

2.5 The total chemical reaction in the ammonia-soda process is represented as follows:

$2\ NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$

This reaction between sodium chloride and calcium carbonate does not proceed directly. The process comprises the following five reactions involving ammonia:

$CaCO_3 \xrightarrow{\Delta} [\ A\ ] + [\ B\ ]$

$NaCl + NH_3 + [\ B\ ] + H_2O \rightarrow [\ C\ ] + [\ D\ ]$

$2\ [\ C\ ] \xrightarrow{\Delta} Na_2CO_3 + H_2O + [\ B\ ]$

$[\ A\ ] + H_2O \rightarrow [\ E\ ]$

$[\ E\ ] + 2\ [\ D\ ] \rightarrow CaCl_2 + 2\ H_2O + 2\ NH_3$

where Δ represents applying heat treatment. Insert the chemical formulas of the appropriate compounds instead of [A] – [E] in the above reactions.

SOLUTION

2.1

Number of ions	$Na^+ = 4$	$Cl^- = 4$
Coordination number of ions	$Na^+ = 6$	$Cl^- = 6$

2.2 Length of lattice *l*: $l = 0.102 \times 2 + 0.181 \times 2 = 0.566$ nm

Density ρ:

$$\rho = \frac{(22.99 + 35.45) \times 4}{(0.566 \cdot 10^{-9})^3 \times 6.022 \cdot 10^{23}} = 2.1408 \cdot 10^6 \text{ g m}^{-3} = 2.14 \cdot 10^3 \text{ kg m}^{-3}$$

2.3 **A**: $Na(s) + ½\, Cl_2(g) \rightarrow NaCl(s)$

F: $NaCl(s) \rightarrow Na(g) + Cl^-(g)$

2.4 Enthalpy conservation condition: – **A** + **B** + **C** + **D**/2 = **F** – **E**

From the above equation: – (–411) + 109 + 496 + (242 / 2) = F + 349

Thus: F = 788

Lattice formation enthalpy of NaCl is –**F**, thus –788 kJ mol^{-1}.

2.5 **A**: CaO

B: CO_2

C: $NaHCO_3$

D: NH_4Cl

E: $Ca(OH)_2$

PROBLEM 8

The esterification reaction between bi-functional molecules gives one of the typical linear chain polymers, as shown in equation (1), by polycondensation (often called "condensation polymerization"). The control of polymerization conditions and procedures determines the length of polymer strands, i. e. *the average degree of polymerization,* ***X*** (note that $\boldsymbol{X} = 2\boldsymbol{n}$ in the present instance). Because $\boldsymbol{X}$ (and also $\boldsymbol{n}$) is an averaged number, it is not always an integer but a value with decimal figures.

$$n\ \text{HOOC-R}^1\text{-COOH} + n\ \text{HO-R}^2\text{-OH} \rightarrow \text{HO-[COR}^1\text{CO-OR}^2\text{O]}_n\text{-H} + (2n-1)\ \text{H}_2\text{O} \qquad (1)$$

$\boldsymbol{X}$ can be estimated from the consumption of functional groups (here, -COOH and -OH). Let us define the degree of reaction, $\boldsymbol{p}$, as $\boldsymbol{p} = (N_0 - N) / N_0$ (≤ 1), where N_0 and N denote the total numbers of functional groups before and after the polymerization, respectively. For each functional group of the dicarboxylic acid molecules (**A**) and diol molecules (**B**), we add the suffixes of "A" or "B" such as N_{A0}, N_{B0}, N_A or N_B, respectively, i. e. $N_0 = N_{A0} + N_{B0}$ and $N = N_A + N_B$. When the initial feed is unbalanced such as $N_{A0} \leq N_{B0}$, $\boldsymbol{X}$ is expressed by $\boldsymbol{p}_A$ and $\boldsymbol{r}$ as shown in equation 2, where $\boldsymbol{r} = N_{A0} / N_{B0}$ (≤ 1) and $\boldsymbol{p}_A = (N_{A0} - N_A) / N_{A0}$. If $\boldsymbol{r} = 1$, $\boldsymbol{p}_A$ is identical to $\boldsymbol{p}$ and equation 2 becomes the same to the Carothers equation.

$$X = \frac{1+r}{1+r-2\,p_A r} \qquad (2)$$

Some nylon-6,6 sample was prepared by polycondensation between an e*quimolar* mixture of adipic acid (hexanedioic acid) and hexamethylenediamine (hexane-1,6-diamine).

8.1 Show the chemical structure of this nylon-6,6 sample.

[Caution: What are the end groups when polycondensation was started from the *equimolar* mixture?]

8.2 When an average molar weight, $\boldsymbol{M}$, of this nylon-6,6 sample is 5507.25 (g mol^{-1}), calculate its $\boldsymbol{X}$ value to *the second decimal place*.

8.3 Give the $\boldsymbol{p}$ value to *the fifth decimal place* that is necessary to prepare the above nylon-6,6 sample. If you get no numerical answer in **8.2** use the value 52.50 instead.

The low-molecular-weight polyester (oligoester) is prepared from the mixture of 36.54 g of adipic acid (hexanedioic acid) and an unknown amount [***W*** (g)] of butane-1,4-diol (Bdiol). Under the condition of $\boldsymbol{p}_A \rightarrow 1$, the oligoester with ***X*** = 11.00 carrying Bdiol units in both chain ends, is obtained.

8.4 Show the *precise* chemical structure of this oligoester of ***X*** = 11.00.

8.5 Calculate the unknown amount, ***W*** (g), to the first decimal place.

SOLUTION

8.1 $HO–[CO(CH_2)_4CO–NH(CH_2)_6NH]_n–H$ or equivalent structures.

8.2 The unit molecular weight, M_u, is calculated as follows:

$$M_u = \frac{12.01\times 12 + 1.01\times 22 + 14.01\times 2 + 16.00\times 2}{2} = \frac{226.36}{2} = 113.18$$

$$X = \frac{5507.25 - 18.02}{M_u} = \frac{5507.25 - 18.02}{113.18} = 48.50$$

or

$$X = 2\,n = 2\times\frac{5507.25 - 18.02}{226.36} = 48.50$$

8.3 From equation 2 at r = 1 (Carothers eq.):

$$X = 48.50 = \frac{1}{1-p}$$

$p = 0.97938$

($p = 0.98095$ when $\boldsymbol{X} = 52.50$ was used instead of $X = 48.50$.)

8.4 $[HO(CH_2)_4O]_{1.000}–[CO(CH_2)_4CO–O(CH_2)_4O]_{5.000}–H$ or

$HO(CH_2)_4O–[CO(CH_2)_4CO–O(CH_2)_4O]_{5.000}–H$ is accurate

However,

$HO(CH_2)_4O–[CO(CH_2)_4CO–O(CH_2)_4O]_5–H$ is acceptable.

8.5 M(adipic acid) = 146.16 g mol^{-1}; M(Bdiol) = 90.14 g mol^{-1}

Answer 1:

Since $X = 11.00$, the oligoester contains 5.00 units of adipate and 6.00 units of the Bdiol. When $p_A \to 1$, the initial molar feed ratio of the monomers is equal to the molar composition of the resulting oligoester.

$$\frac{[\text{adipic acid}]_0}{[\text{Bdiol}]_0} = \frac{5.00}{6.00},$$

$$\boldsymbol{W} = 90.14\times\frac{6.00}{5.00}\times\frac{36.54}{146.16} = 27.0\text{ g}$$

Answer 2:

From eq. 2, when $p_A \rightarrow 1$, $X = (1 + r) / (1 - r)$. Therefore,

$$11.00 = \{1 + [(36.54 / 146.16) / \boldsymbol{W} / 90.14)]\} / \{1 - [(36.54 / 146.16) / \boldsymbol{W} / 90.14)]\} =$$

$$= [(\boldsymbol{W} / 90.14) + 0.2500] / [(\boldsymbol{W} / 90.14) - 0.2500]$$

$$11.00 \times [(\boldsymbol{W} / 90.14) - 0.2500] = [(\boldsymbol{W} / 90.14) + 0.2500],$$

$$10.00 \times [(\boldsymbol{W} / 90.14)] = 3.000$$

$$\boldsymbol{W} = 3.000 \times 90.14 / 10.00 = 27.0 \text{ g}$$

PROBLEM 3

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

$E = E_o + E_{vib}$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

SOLUTION

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

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

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

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

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

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

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

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

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

For one molecule HD:

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

For 1 mol of HD:

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

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

3.2 $h\nu = \Delta E$

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

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

From part 3.1:

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

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

3.3 $H_2 \rightarrow 2\ H$

For n = 1: ΔE = 2 (–13.5984) – (–31.675) = 4.478 eV

3.4

$$\begin{array}{lccc} H_2 + h\nu \rightarrow & H & + & H \\ n = & 1 & & 1 \\ & 1 & & 2 \\ & 2 & & 1 \\ & 2 & & 2 \\ & . & & . \\ & . & & . \\ & . & & . \end{array}$$

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

λ = 77.0 nm

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

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

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

$n_1 = 1$ $\quad n_2 = 1$

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

KE = 16.1 – 4.478 = 11.6 eV

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

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

KE = 16.1 – 14.677 = 1.4 eV

$n_1 = 2, \quad n_2 = 2$

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

K.E. = 16.1 – 14.677 = 1.4 eV

Thus, the possibilities are:

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

n =	1	1
	1	2
	2	1

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

$H_2^+ + e \rightarrow H_2 \qquad \text{EA}(H_2^+) = -\text{IP}(H_2)$

$H_2^+ \rightarrow H^+ + H \qquad \text{DE}(H_2^+) = 2.650 \text{ eV}$

$H \rightarrow H^+ + e \qquad \text{IP(H)} = 13.598 \text{ eV}$

$H_2 \rightarrow H + H \qquad \text{DE}(H_2) = 4.478 \text{ eV}$

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

Electron affinity $H_2^+ = -15.426$ eV

PROBLEM 5

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

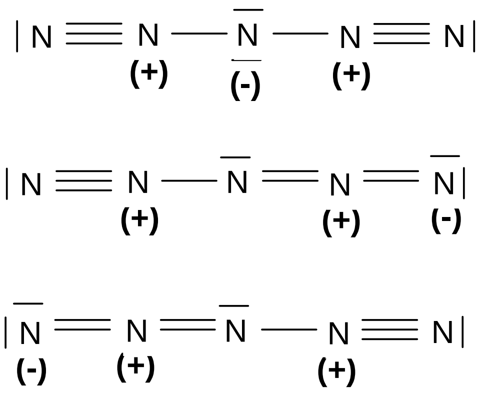
When $[N_5^+]_2[SnF_6^{2-}]$ decomposes under carefully controlled conditions at 25 – 30 °C, $[N_5^+][SnF_5^-]$ and N_5F are formed. The $[N_5^+][SnF_5^-]$ salt is a white solid and has a thermal stability comparable to that of $[N_5^+][SbF_6^-]$ (50 – 60 °C). The solution ^{119}Sn NMR spectrum has shown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

5.8 Draw the structures of dimeric and tetrameric polyanions.

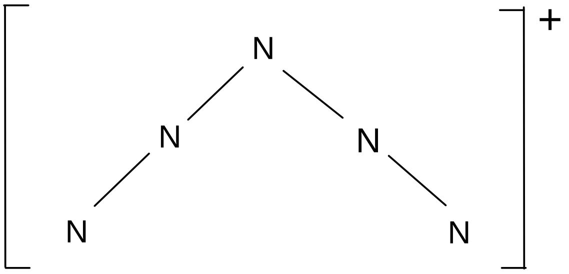
SOLUTION

5.1 Formula**:** N_5^+

Lewis structure:

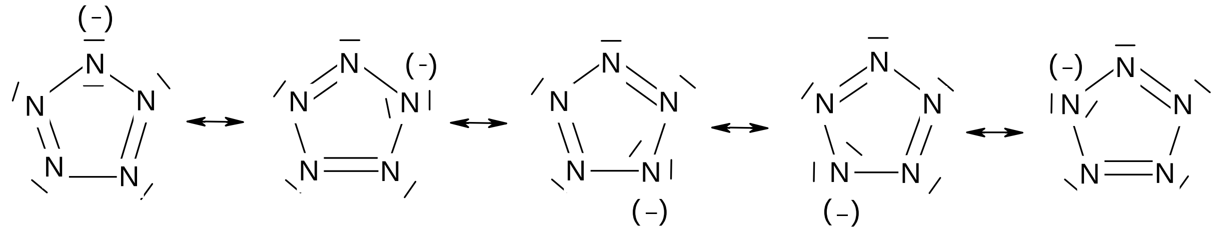


Molecular geometry:

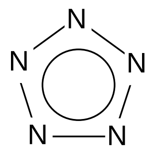


5.2 Cyclic N_5^+:

Lewis structure:



Molecular geometry:



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

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

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

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

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

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

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

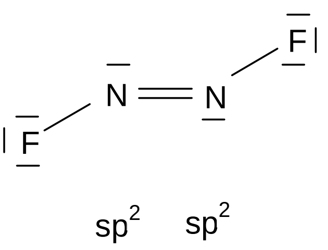
$$\Delta G^o = -5.28 \cdot 10^3 - (298 \times 4.40) = -6.59 \cdot 10^3 \text{ J mol}^{-1}$$

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

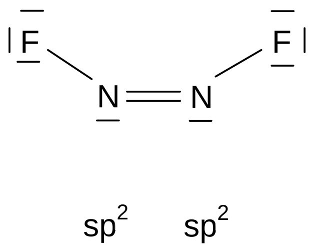
$$K = \frac{[cis]}{[trans]} = 14.3 \text{ at } 25\ ^\circ\text{C}$$

5.5

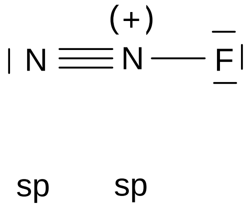
trans - N_2F_2



cis - N_2F_2



N_2F^+



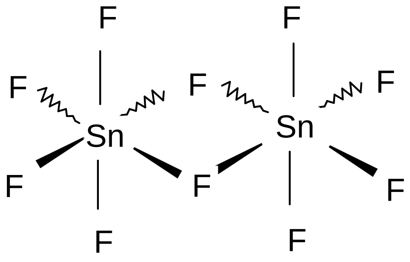
5.6 $4\,[N_5^+][AsF_6^-] + 2\,H_2O \rightarrow 4\,AsF_5 + 4\,HF + 10\,N_2 + O_2$

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

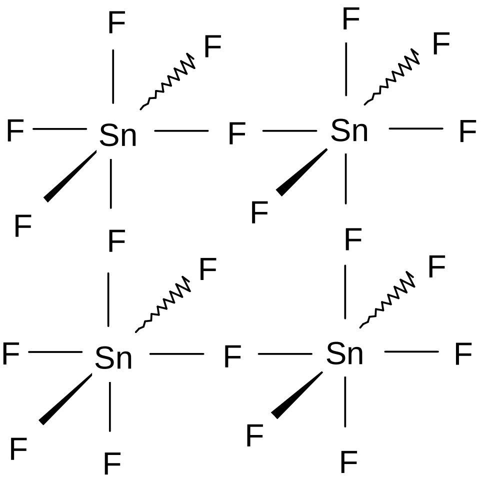
$[N_5^+]\,[SbF_6^-] + K^+[B(CF_3)_4^-] \xrightarrow{SO_2,\ -64\ ^\circ\text{C}} [N_5^+]\,[B(CF_3)_4^-] + 2\,KSbF_6$

5.8

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



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



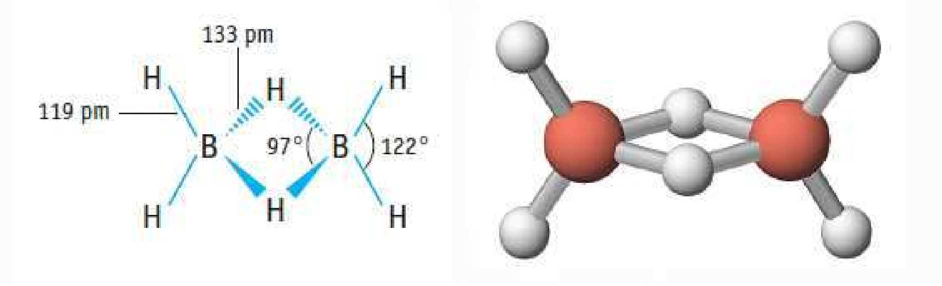
THE FORTY-FOURTH
INTERNATIONAL CHEMISTRY OLYMPIAD
21–30 JULY 2012, WASHINGTON, U.S.A.

THEORETICAL PROBLEMS

PROBLEM 1

A. Boron Hydrides and Other Boron Compounds

Boron hydride chemistry was first developed by Alfred Stock (1876 - 1946). More than 20 neutral molecular boron hydrides with the general formula B_xH_y have been characterized. The simplest boron hydride is B_2H_6, diborane.



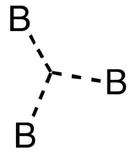
1.1 Using the data below derive the molecular formulae for two other members of this series of boron hydrides, **A** and **B**.

Substance	State (25 ˚C, 1 bar)	Mass Percent of Boron	Molar mass (g mol^{-1})
A	Liquid	83.1	65.1
B	Solid	88.5	122.2

William Lipscomb received the Nobel Prize in Chemistry in 1976 for “studies on the structures of boron hydrides illuminating the problems of chemical bonding.” Lipscomb recognized that, in all boron hydrides, each B atom has a normal 2-electron bond to at least one H atom (B–H). However, additional bonds of several types occur, and he developed a scheme for describing the structure of a borane by giving it a styx number where:

s = number of B–H–B bridges in the molecule,

t = the number of 3-center BBB bonds in the molecule,



y = the number of two-center B–B bonds in the molecule,

x = the number of BH_2 groups in the molecule.

The *styx* number for B_2H_6 is 2002.

1.2 Propose a structure for tetraborane, B_4H_{10}, with a *styx* number of 4012.

1.3 A boron-based compound is composed of boron, carbon, chlorine, and oxygen. Spectral measurements indicate that the molecule has two types of B atoms, with tetrahedral and trigonal planar geometry, in a 1 : 3 ratio, respectively. These spectra are also consistent with a CO triple bond. The molecular formula of the compound is B_4CCl_6O. Suggest a structure for its molecule.

B. Thermochemistry of Boron Compounds

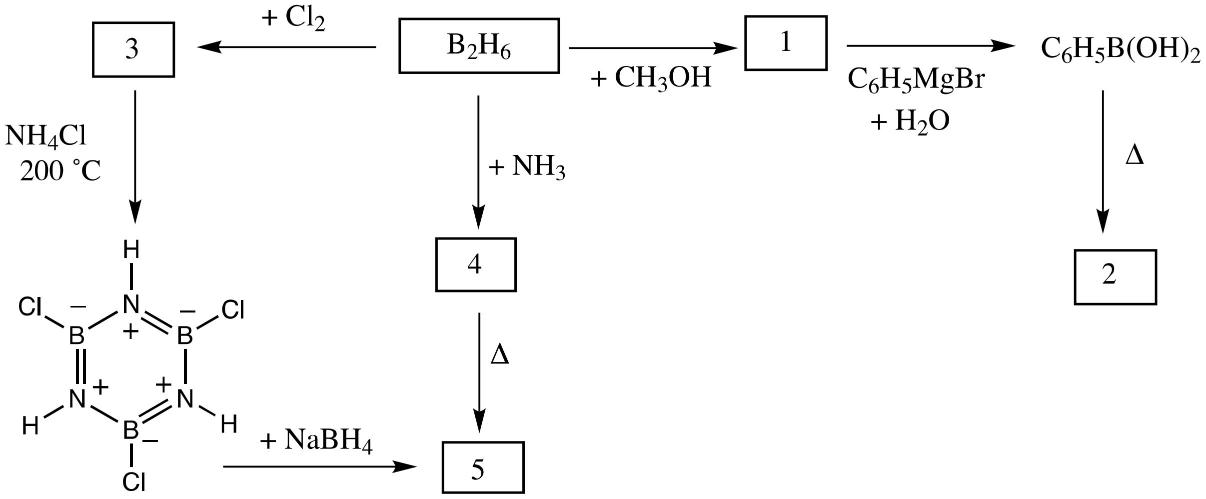
1.4 Estimate the B-B single bond dissociation enthalpy in $B_2Cl_4(g)$ using the following information:

Bond	Bond dissociation enthalpy (kJ mol^{-1})
B–Cl	443
Cl–Cl	242

Compound	$\Delta_f H°$ (kJ mol^{-1})
$BCl_3(g)$	–403
$B_2Cl_4(g)$	–489

C. Chemistry of Diborane

1.5 Give the structure for each numbered compound in the scheme below. Each numbered compound is a boron-containing compound.



NOTES:

i. The boiling point of compound 5 is 55 ˚C.

ii. Excess reagents used in all reactions.

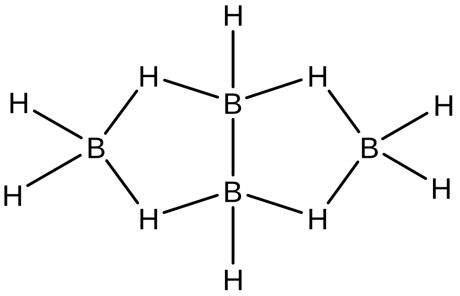
iii. The freezing point depression for 0.312 g of compound 2 in 25.0 g of benzene, is 0.205 ˚C. The freezing point depression constant for benzene is 5.12 kg K mol^{-1}.

SOLUTION

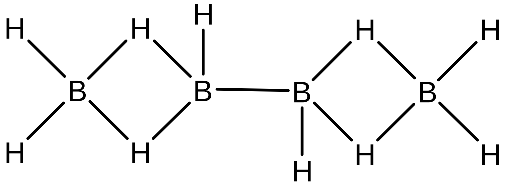
1.1 **A** = B_5H_{11}

B = $B_{10}H_{14}$

1.2



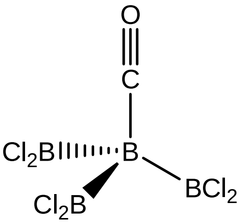
actual structure



unknown but acceptable structure

1.3

Structure:

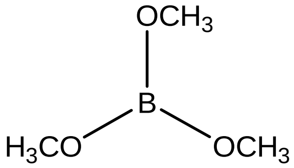
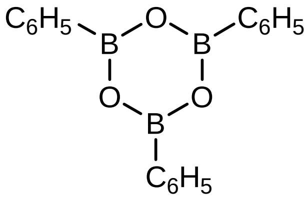
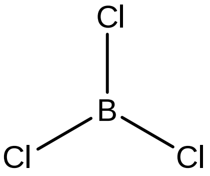
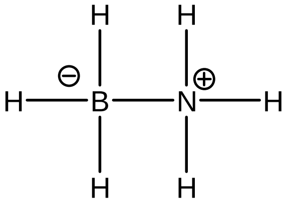
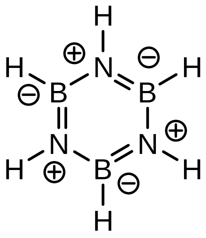


1.4

$$\begin{tikzcd}
 & 2B + 6Cl \arrow[dr, "\Delta_r H^o = -4 \times 443 - 242\ \text{kJ} - \text{BB}"] & \\
2BCl_3 \arrow[ur, "\Delta_r H^o = 6 \times 443\ \text{kJ}"] \arrow[rr, "\Delta_r H^o = +317\ \text{kJ}"'] & & B_2Cl_4 + Cl_2
\end{tikzcd}$$

A Born-Haber cycle gives a B–B bond dissociation enthalpy of 327 kJ mol^{-1}.

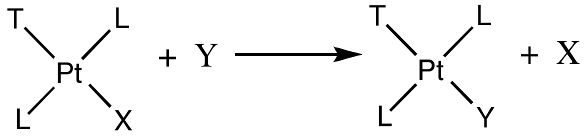
1.5

Number	Formula	Molecular Structure of the Compound
1	$B(OCH_3)_3$	
2	$B_3O_3(C_6H_5)_3$	 A dimer or tetramer $[C_6H_5BO]_x$ are also acceptable (x = 2, 4).
3	BCl_3	
4	BNH_6	 Formal charges are not necessary.
5	$B_3N_3H_6$	 Formal charges are not necessary.

PROBLEM 2

A. Platinum(II) Compounds, Isomers, and the *Trans* Effect.

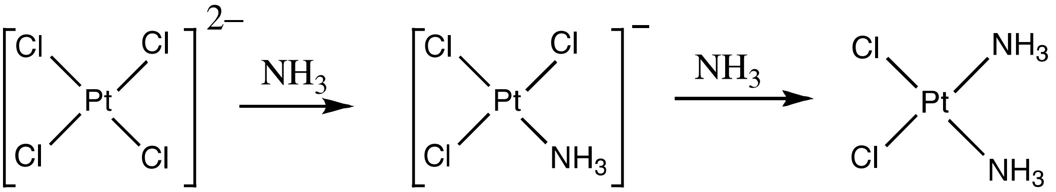
Platinum and other Group 10 metals form square planar complexes and the mechanisms of their reactions have been studied extensively. For example, it is known that substitution reactions of these complexes proceed with retention of stereochemistry.



It is also known that the rate of substitution of ligand X by Y depends on the nature of the ligand *trans* to X, that is, on ligand T. This is known as the ***trans effect.*** When T is one of the molecules or ions in the following list, the rate of substitution at the trans position decreases from left to right.

$$CN^- > H^- > NO_2^-, I^- > Br^-, Cl^- > \text{pyridine}, NH_3, OH^-, H_2O$$

The preparations of *cis*- and *trans*-$Pt(NH_3)_2Cl_2$ depend on the *trans* affect. The preparation of the *cis* isomer, a cancer chemotherapy agent commonly called cisplatin, involves the reaction of K_2PtCl_4 with ammonia.



2.1 Draw all possible stereoisomers for square planar platinum(II) compounds with the formula $Pt(py)(NH_3)BrCl$ (where py = pyridine, C_5H_5N).

2.2 Write reaction schemes including intermediate(s), if any, to show the preparation in aqueous solution for each of the stereoisomers of $[Pt(NH_3)(NO_2)Cl_2]^-$ using, as reagents, $PtCl_4^{2-}$, NH_3, and NO_2^-. The reactions are controlled kinetically by the *trans* effect.

B. Kinetic Studies of Substitution Reactions of Square Planar Complexes

Substitutions of the ligand X by Y in square planar complexes

$$ML_3X + Y \rightarrow ML_3Y + X$$

can occur in either or both of two ways:

i) *Direct substitution:* The incoming ligand Y attaches to the central metal, forming a five-coordinate complex, which then rapidly eliminates a ligand, X, to give the product, ML_3Y.

$$ML_3X \xrightarrow[**]{+\,Y} [ML_3XY] \xrightarrow{-\,X} ML_3Y$$

** = rate determining step, rate constant = k_Y

ii) *Solvent-assisted substitution:* A solvent molecule S attaches to the central metal to give ML_3XS, which eliminates the X to give ML_3S. Y rapidly displaces S to give ML_3Y.

$$ML_3X \xrightarrow[**]{+\,S} [ML_3XS] \xrightarrow{-\,X} [ML_3S] \xrightarrow[-\,S]{+\,Y} ML_3Y$$

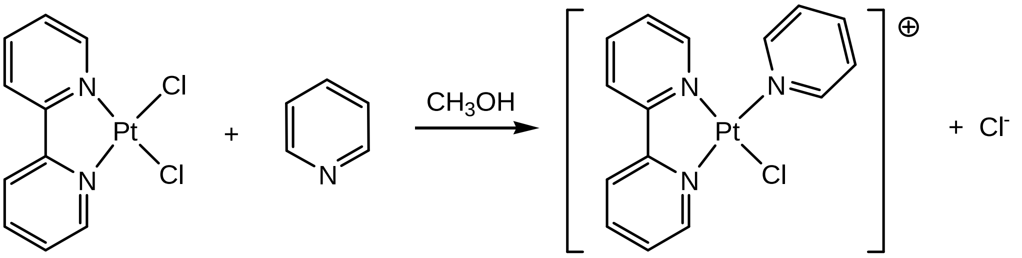
** = rate determining step, k_S = rate constant

The overall rate law for such substitutions is

$$\text{Rate} = k_s\,[ML_3X] + k_Y\,[Y]\,[ML_3X]$$

When [Y] >> $[ML_3X]$, then Rate = $k_{obs}\,[ML_3X]$.

The values of k_s and k_Y depend on the reactants and solvent involved. One example is the displacement of the Cl^- ligand in a square planar platinum(II) complex, ML_2X_2, by pyridine (C_5H_5N). (The ML_3X scheme above applies to ML_2X_2.)



Data for reaction at 25 °C in methanol where [pyridine] >> the concentration of the platinum complex, are given in the table below.

Concentration of pyridine (mol dm^{-3})	k_{obs} (s^{-1})
0.122	$7.20 \cdot 10^{-4}$
0.061	$3.45 \cdot 10^{-4}$
0.030	$1.75 \cdot 10^{-4}$

2.3 Calculate the values of k_S and k_Y. Give the proper unit for each constant.

(A grid is given if you wish to use it.)

2.4 When [pyridine] = 0.10 mol dm^{-3}, which of the following is true? (Tick the box next to the correct answer.)

☐ Most pyridine product is formed by the solvent-assisted (k_S) substitution pathway.

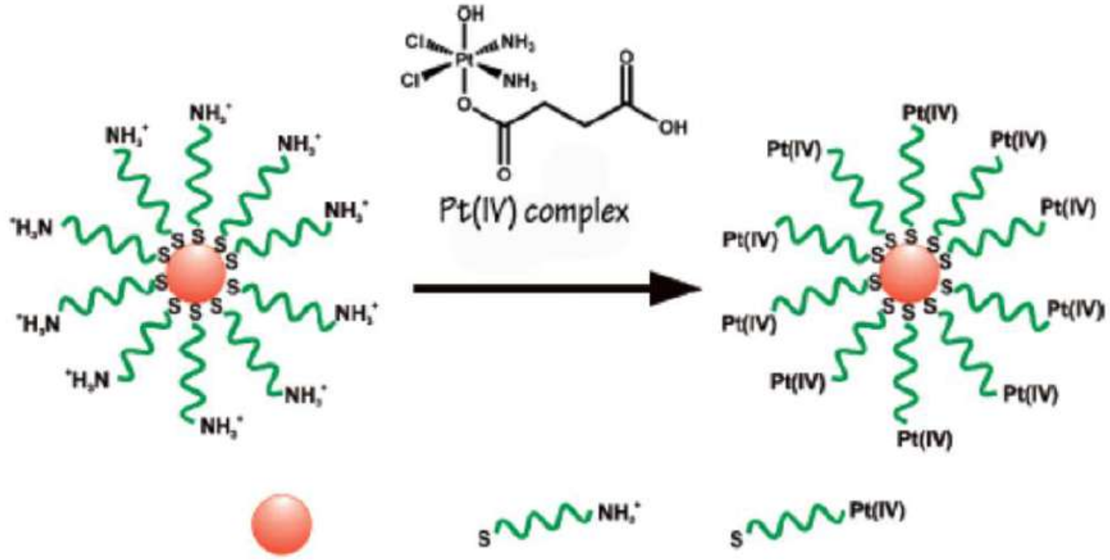
☐ Most pyridine product is formed by the direct substitution (k_Y) pathway

☐ Comparable amounts of product are formed by the two pathways.

☐ No conclusions may be drawn regarding the relative amounts of product produced by the two pathways.

C. A chemotherapy agent

In an effort to better target cisplatin to cancer cells, Professor Lippard's group at MIT attached a platinum(IV) complex to oligonucleotides bound to gold nanoparticles.



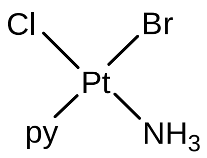
Gold nanoparticle Oligonucleotide Pt(IV) complex attached

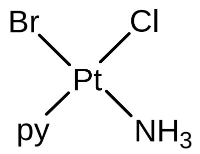
2.5 Experiments showed that the diameter of a gold nanoparticle was 13 nm. Attached to this nanoparticle are 90 oligonucleotide groups, with 98 % of them being bound to a Pt(IV) complex. Suppose that the reaction vessel used for treating cells with the Pt(IV) nanoparticle reagent had a volume of 1.0 cm^3 and the concentration of the solution was $1.0 \cdot 10^{-6}$ mol dm^{-3} in Pt. Calculate the mass of platinum and that of gold used in this experiment.

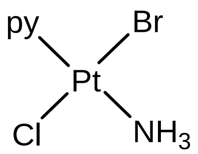
(The density of gold = 19.3 g cm^{-3}, the volume of a sphere = $(4/3)\pi r^3 = 4.18879\ r^3$.)

SOLUTION

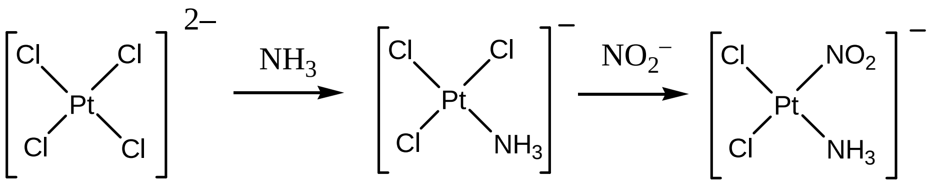
2.1



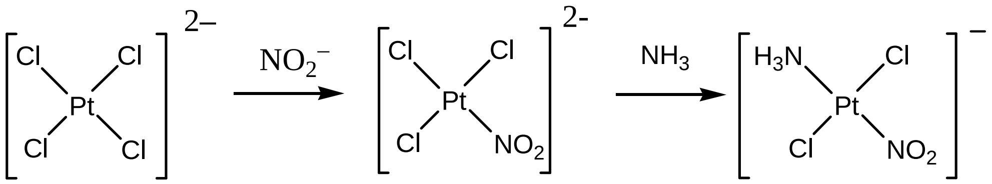




2.2 *cis*-isomer:



trans-isomer:



2.3

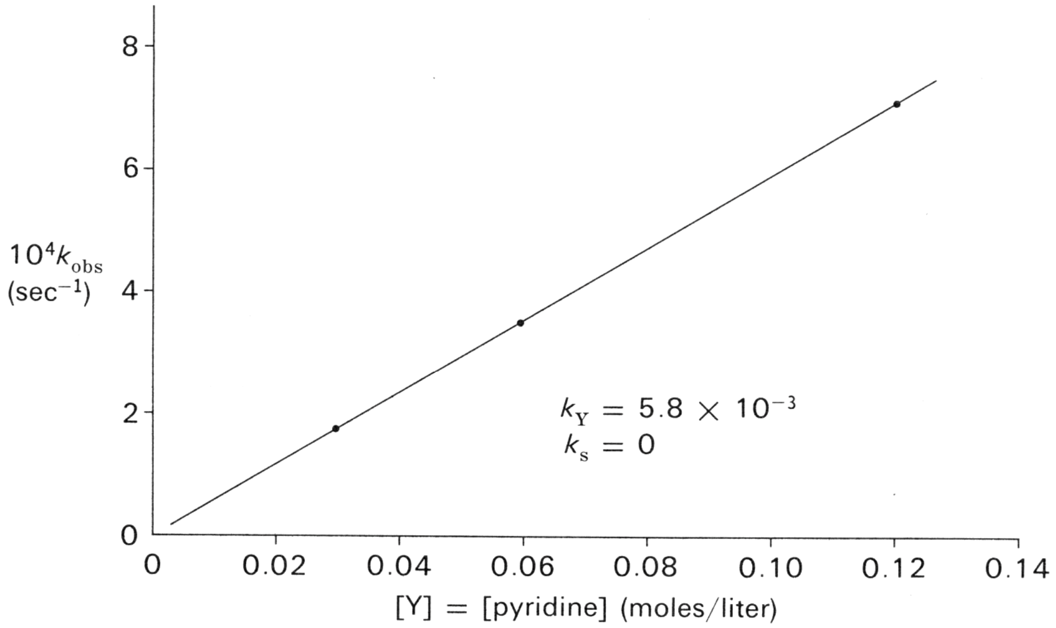


Fig. 2.3 Verification of the rate law $k_{obs} = k_s + k_Y$[pyridine] for the reaction of Pt(bipy)Cl_2 with pyridine to give Pt(bipy)(py)Cl^+. Data taken from L. Cattalini, A. Orio, and A. Doni, *Inorg. Chem.*, **5**, 1517 (1966).

$k_Y = 5.8 \cdot 10^{-3}\ s^{-1} mol^{-1}\ dm^3$

$k_S = 0\ s^{-1}$ (allow small range of values, $\pm\ 0.2 \cdot 10^{-3}$)

2.4 ☑ Most pyridine product is formed by the direct substitution (k_Y) pathway.

2.5 Mass of platinum

$n(Pt) = 1.0 \cdot 10^{-6}\ mol\ dm^{-3} \times 0.001\ dm^3 = 1.0 \cdot 10^{-9}\ mol$

This is equivalent to $2.0 \cdot 10^{-7}$ g Pt.

Mass of gold

- (90 groups/nanoparticle)(0.98 Pt bound complexes)

  = 88 Pt complexes/nanoparticle or 88 Pt atoms per nanoparticle
- $1.0 \cdot 10^{-9}$ mol Pt is equivalent to $6.0 \cdot 10^{14}$ Pt atoms
- ($6.0 \cdot 10^{14}$ Pt atoms)(1 nanoparticle/88 Pt atoms) = $6.8 \cdot 10^{12}$ nanoparticles
- Size of gold nanoparticles:

  Radius = $6.5 \cdot 10^{-7}$ cm and volume of gold nanoparticle = $1.2 \cdot 10^{-18}\ cm^3$

  Mass of gold nanoparticle = $2.3 \cdot 10^{-17}$ g

  Amount of gold in a nanoparticle = $1.2 \cdot 10^{-19}$ mol

  Atoms of gold in a nanoparticle = $7.1 \cdot 10^4$ atoms
- Mass of gold:

  Total number of gold atoms = ($6.8 \cdot 10^{12}$ particles)($7.1 \cdot 10^4$ atoms/particle)

  = $4.8 \cdot 10^{17}$ atoms of gold

  Equivalent to $1.5 \cdot 10^{-4}$ g of gold

PROBLEM 4

A simple inorganic experiment

Compound **A** which contains metal **X** is a colourless crystalline solid and highly soluble in water. It is used as a reagent in analysis and gives in alkali media a binary compound **B** containing 6.9 % (mass) of oxygen. Under heating **A** decomposes with a mass loss of 36.5 %.

4.1 Determine the metal **X** and compounds **A** and **B**.

Upon adding some amount of sodium thiosulfate to the solution of **A** the colour immediately becomes red, then changes to reddish-brown, and after some minutes a dark-brown precipitate **C** forms (reaction 1). The solution over it is colourless. Being heated on air at 600 ºC, **C** gives a grey powder **X** (reaction 2), so as 0.90 g of residue can be obtained from 1.10 g of **C**. A gas evolved by heating **C** in vacuum (reaction 3) can be absorbed by calcium hydroxide suspension (reaction 4). Being stored for a long time under saturated solution of barium perchlorate in $HClO_4$ (c = 0.1 mol dm^{-3}), the colour of the precipitate becomes lighter, while the use of magnesium perchlorate does not give such an effect.

4.2 What is **C**? Write the equations of the reactions 1 – 4.

The compound **C** being stored under the mother liquor (containing an excess of **A**) changes its colour to yellow due to the transformation into **D**. If barium ions are added to the suspension of **C** in the mother liquor, a mixture of **D** and of a white precipitate is formed.

4.3 Propose the formula of **D**, taking into account that it contains 77.5 mass % of **X**. Give the equation of **D** formation.

SOLUTION

4.1 A general formula of a binary compound is XO_n. The molar ratios of X and O should be:

$$\frac{93.1}{A_r(\text{X})} : \frac{6.9}{16} = \frac{1}{n},$$

where $A_r(\text{X})$ is a relative atomic mass of metal **X** and n = 0.5; 1; 1.5; 2; etc.

n = 0.5 gives $A_r(\text{X})$ = 107.9. That is the relative atomic mass of silver.

X: Ag, **B**: Ag_2O.

The heating of silver salts generally results in reduction of the metal. According to the mass loss, the molar mass of **A** is 170 g mol^{-1} and corresponds to silver nitrate: **A**` – $AgNO_3$.

4.2 The residue formed by heating on air is metallic silver, as the silver compounds readily decompose. Substance **C** contains silver and probably sulfur and oxygen as it evolves sulfur oxide by heating in vacuum.

1.10 g of **C** contains 0.90 g of Ag, thus, 1 mol of Ag is in 132 g of **C**. The mass of the elements other than Ag is 132 -108 = 24 g which corresponds to ½ S and ½ O. Thus, the empirical formula is $AgS_{1/2}O_{1/2}$ or Ag_2SO.

The light brown colour of the precipitate after the addition of barium salt means the formation of barium sulfate which is insoluble in acids. The sulfate groups on the surface of the precipitate are substituted by perchlorate ions from solution. Thus, based on the formula Ag_2SO and assuming the presence of sulfate, the formula $Ag_8S_3SO_4$ can be suggested.

The equations are listed below:

Equation 1:

$$16\ AgNO_3 + 6\ Na_2S_2O_3 + 6\ H_2O \rightarrow 2\ [Ag_8S_3]SO_4\downarrow + 4\ Na_2SO_4 + 4\ NaNO_3 + 12\ HNO_3$$

Equation 2:

$$[Ag_8S_3]SO_4 + 2\ O_2 \rightarrow 8\ Ag + 4\ SO_2$$

Equation 3:

$$[Ag_8S_3]SO_4 \rightarrow 2\ Ag_2S + 4\ Ag + 2\ SO_2.$$

Equation 4:

$$SO_2 + Ca(OH)_2 = CaSO_3 + H_2O \quad \text{or}$$

$$2\ SO_2 + Ca(OH)_2 = Ca(HSO_3)_2$$

4.3 We can assume that the sulfate ions in **C** are substituted by nitrate ions.

For a formula unit containing n silver atoms, molar mass is 108 n / 0.775 = 139.35 n. For $n = 3$ we get $M = 418$ g mol^{-1}. It corresponds to $418 - (108 \times 3) = 94$ that is NO_3 + S. Thus, the formula of **D** is $[Ag_3S]NO_3$.

Equation:

$[Ag_8S_3]SO_4 + AgNO_3 + 2\ NaNO_3 \rightarrow 3\ [Ag_3S]NO_3 + Na_2SO_4$

Student name **Student code**

Theoretical **Problem 3** **9.0 %** of the total	**Code:**		Question	1	2	3	4	Total
	Examiner		Marks	8	14	2	12	**36**
			Grade					

Problem 3. High-valent Silver Compounds

Silver chemistry is dominated by Ag (I) compounds. Compounds of silver in higher oxidation state (from +2 to +5) are not very abundant due to their instability with respect to reduction. High-valent silver compounds are very reactive and can be synthesized from Ag(I) compounds in electro-chemical oxidations or in chemical oxidations using powerful oxidizing agents.

1. In some peroxydisulfate ($S_2O_8^{2-}$) oxidations catalyzed by Ag^+, black solid (**A**) with the composition AgO can be isolated.

1a. **Choose** the appropriate magnetic behaviour of **A** if it exists as $Ag^{II}O$.

☐ Diamagnetic ☐ Paramagnetic

Single crystal X - ray studies reveal that the lattice of **A** contains two nonequivalent Ag atom sites (in equal proportions) of which one denoted as Ag1 and the other denoted as Ag2. Ag1 shows a linear O atom coordination (O-Ag-O) and Ag2 shows a square-planar O atom coordination. All O atoms are in equivalent environments in the structure. Thus, **A** should be assigned as $Ag^{I}Ag^{III}O_2$ rather than $Ag^{II}O$.

1b. **Assign** the oxidation number of Ag1 and Ag2.

Oxidation number of Ag1 : ……….

Oxidation number of Ag2 : ………

1c. What is the coordination number of O atoms in the lattice of **A**?

The coordination number of O atoms =………

Student name **Student code**

1d. **How many** Ag^{I} and Ag^{III} bond to one O atom in the lattice of **A**?

Number of Ag^{I} = ………

Number of Ag^{III} = …….

1e. **Predict** the magnetic behaviour of **A.** **Check** the appropriate box below.

☐ Diamagnetic ☐ Paramagnetic

1f. The compound **A** can also be formed on warming a solution of Ag^{+} with peroxydisulfate. **Write down** the equation for the formation of **A**.

2. Among the silver oxides which have been crystallographically characterized, the most surprising is probably that compound **A** is not a $Ag^{II}O$. Thermochemical cycles are useful to understand this fact. Some standard enthalpy changes (at 298 K) are listed:

Atom	Standard enthalpy of formation ($kJ \cdot mol^{-1}$)	1st ionization ($kJ \cdot mol^{-1}$)	2nd ionization ($kJ \cdot mol^{-1}$)	3rd ionization ($kJ \cdot mol^{-1}$)	1st electron affinity ($kJ \cdot mol^{-1}$)	2nd electron affinity ($kJ \cdot mol^{-1}$)
Cu(g)	337.4	751.7	1964.1	3560.2		
Ag(g)	284.9	737.2	2080.2	3367.2		
O(g)	249.0				-141.0	844.0

Compounds	ΔH^{o}_{f} ($kJ \cdot mol^{-1}$)
$Ag^{I}Ag^{III}O_{2\,(s)}$	–24.3
$Cu^{II}O_{\,(s)}$	–157.3

The relationship between the **lattice dissociation energy** (U_{lat}) and the **lattice dissociation enthalpy** (ΔH_{lat}) for monoatomic ion lattices is: $\Delta H_{lat} = U_{lat} + nRT$, where n is the number of ions in the formula unit.

Student name **Student code**

2a. Calculate U_{lat} at 298 K of $Ag^{I}Ag^{III}O_2$ and $Cu^{II}O$. Assume that they are ionic compounds.

U_{lat} of $Ag^{I}Ag^{III}O_2$

U_{lat} ($Ag^{I}Ag^{III}O_2$)

U_{lat} ($Cu^{II}O$)

*If you can not calculate the U_{lat} of $Ag^{I}Ag^{III}O_2$ and $Cu^{II}O$, use following values for further calculations: U_{lat} of $Ag^{I}Ag^{III}O_2$ = **8310.0** kJ·mol^{-1}; U_{lat} of $Cu^{II}O$ = **3600.0** kJ·mol^{-1}.*

The lattice dissociation energies for a range of compounds may be estimated using this simple formula:

$$U_{lat} = \mathrm{C} \times \left(\frac{1}{V_m} \right)^{\frac{1}{3}}$$

Where: V_m (nm^3) is the volume of the formula unit and C (kJ·nm·mol^{-1}) is an empirical constant which has a particular value for each type of lattice with ions of specified charges.

The formula unit volumes of some oxides are calculated from crystallographic data as the ratio between the unit cell volume and the number of formula units in the unit cell and listed as below:

Oxides	V_m (nm^3)
$Cu^{II}O$	0.02030
$Ag^{III}{}_2O_3$	0.06182
$Ag^{II}Ag^{III}{}_2O_4$	0.08985

2b. **Calculate** U_{lat} for the hypothetical compound $Ag^{II}O$. Assume that $Ag^{II}O$ and $Cu^{II}O$ have the same type of lattice, and that $V_m(Ag^{II}O) = V_m(Ag^{II}Ag^{III}{}_2O_4) - V_m(Ag^{III}{}_2O_3)$.

U_{lat} ($Ag^{II}O$)

2c. By constructing an appropriate thermodynamic cycle or otherwise, **estimate** the enthalpy change for the solid-state transformation from $Ag^{II}O$ to 1 mole of $Ag^{I}Ag^{III}O_2$.

(Use U_{lat} $Ag^{II}O$ = 3180.0 kJ·mol^{-1} and U_{lat} $Ag^{I}Ag^{III}O_2$ = 8310.0 kJ·mol^{-1} if you cannot calculate U_{lat} $Ag^{II}O$ in Part 2b).

ΔH_{rxn} =

2d. <u>Indicate</u> which compound is thermodynamically more stable by checking the appropriate box below.

$Ag^{II}O$ ☐	$Ag^{I}Ag^{III}O_2$ ☐

3. When $Ag^{I}Ag^{III}O_2$ is dissolved in aqueous $HClO_4$ solution, a paramagnetic compound (**B**) is first formed then slowly decomposes to form a diamagnetic compound (**C**). Given that **B** and **C** are the only compounds containing silver formed in these reactions, **<u>write down</u>** the equations for the formation of **B** and **C**.

For **B**:

For **C:**

4. Oxidation of Ag^+ with powerful oxidizing agents in the presence of appropriate ligands can result in the formation of high-valent silver complexes. A complex **Z** is synthesized and analyzed by the following procedures:

An aqueous solution containing 0.500 g of $AgNO_3$ and 2 mL of pyridine (d = 0.982 g/mL) is added to a stirred, ice-cold aqueous solution of 5.000 g of $K_2S_2O_8$. The reaction mixture becomes yellow, then an orange solid (**Z**) is formed which has a mass of 1.719 g when dried.

Elemental analysis of **Z** shows the mass percentages of C, H, N elements are 38.96%, 3.28%, 9.09%, respectively.

A 0.6164 g **Z** is added to aqueous NH_3. The suspension is boiled to form a clear solution during which stage the complex is destroyed completely. The solution is acidified with excess aqueous HCl and the resulting suspension is filtered, washed and dried (in darkness) to obtain 0.1433 g of white solid (**D**). The filtrate is collected and treated with excess $BaCl_2$ solution to obtain 0.4668 g (when dry) of white precipitate (**E**).

4a. **Determine** the empirical formula of **Z** and calculate the percentage yield in the preparation.

4b. Ag (IV) and Ag (V) compounds are extremely unstable and found only in few fluorides. Thus, the formation of their complexes with organic ligands in water can be discounted. To confirm the oxidation number of silver in **Z**, the effective magnetic moment (μ_{eff}) of **Z** was determined and found to be 1.78 BM. Use the spin only formula to **determine** the number of unpaired electrons in Z and the molecular formula of **Z.** (**Z** contains a mononuclear complex with only one species of Ag and only one type of ligand in the ligand sphere.)

4c. **Write down** all chemical equations for the preparation of **Z**, and its analysis.

Formation of **Z**:

Destruction of **Z** with NH_3:

Formation of **D**:

Formation of **E**:

Theoretical	**Code:**		Question	1	2	3	4	Total
Problem 3	**Examiner**		Marks	8	14	2	12	**36**
9.0 % of the total			**Grade**					

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1a. **Choose** the appropriate magnetic behaviour of **A** if it exists as $Ag^{II}O$.

☐ Diamagnetic

☐ Paramagnetic
x

1 point

Single crystal X - ray studies reveal that the lattice of **A** contains two nonequivalent Ag atom sites (in equal proportions) of which one denoted as Ag1 and the other denoted as Ag2. Ag1 shows a linear O atom coordination (O-Ag-O) and Ag2 shows a square-planar O atom coordination. All O atoms are in equivalent environments in the structure. Thus, **A** should be assigned as $Ag^{I}Ag^{III}O_2$ rather than $Ag^{II}O$.

1b. **Assign** the oxidation number of Ag1 and Ag2.

Oxidation number of Ag1 : ....+1
Oxidation number of Ag2 : .... +3

2 points

1c. What is the coordination number of O atoms in the lattice of **A**?

The coordination number of O atoms =……… 3 1 point

1d. How many Ag^{I} and Ag^{III} bond to one O atom in the lattice of **A**?

Number of Ag^{I} = ……… 1
Number of Ag^{III} = ……. 2 2 points

1e. Predict the magnetic behaviour of **A. Check** the appropriate box below.

☐ Diamagnetic ☐ Paramagnetic

x 1 point

The Ag^{I} is d^{10} hence diamagnetic; the Ag^{III} is square planar d^{8} also diamagnetic

1f. The compound **A** can also be formed on warming a solution of Ag^{+} with peroxydisulfate. **Write down** the equation for the formation of **A**.

$$S_2O_8^{2-}{}_{(aq)} + 2Ag^{+}{}_{(aq)} + 2H_2O_{(l)} \longrightarrow 2SO_4^{2-}{}_{(aq)} + Ag^{I}Ag^{III}O_{2\,(s)} + 4H^{+}{}_{(aq)}$$

1 point

2. Among the silver oxides which have been crystallographically characterized, the most surprising is probably that compound **A** is not a $Ag^{II}O$. Thermochemical cycles are useful to understand this fact. Some standard enthalpy changes (at 298 K) are listed:

Atom	Standard enthalpy of formation ($kJ\cdot mol^{-1}$)	1st ionization ($kJ\cdot mol^{-1}$)	2nd ionization ($kJ\cdot mol^{-1}$)	3rd ionization ($kJ\cdot mol^{-1}$)	1st electron affinity ($kJ\cdot mol^{-1}$)	2nd electron affinity ($kJ\cdot mol^{-1}$)
Cu(g)	337.4	751.7	1964.1	3560.2		
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O(g)	249.0				-141.0	844.0

Compounds	$\Delta H^o{}_f$ (kJ·mol^{-1})
$Ag^IAg^{III}O_{2\,(s)}$	–24.3
$Cu^{II}O_{\,(s)}$	–157.3

The relationship between the **lattice dissociation energy** (U_{lat}) and the **lattice dissociation enthalpy** (ΔH_{lat}) for monoatomic ion lattices is: $\Delta H_{lat} = U_{lat} + nRT$, where n is the number of ions in the formula unit.

2a. **Calculate** U_{lat} at 298 K of $Ag^IAg^{III}O_2$ and $Cu^{II}O$. Assume that they are ionic compounds.

U_{lat} of $Ag^IAg^{III}O_2$

Calculations:

$\Delta H_{lat}(Ag^IAg^{III}O_2) = 2\,\Delta H^o{}_f(O^{2-}) + \Delta H^o{}_f(Ag^+) + \Delta H^o{}_f(Ag^{3+}) - \Delta H^o{}_f(Ag^IAg^{III}O_2)$

$= (2\times249 - 2\times141 + 2\times844) + (284.9 + 737.2) + (284.9 + 737.2 + 2080.2 + 3367.2) - (-24.3)$

$= +9419.9$ (kJ·mol^{-1})

$U_{lat}(Ag^IAg^{III}O_2) = \Delta H_{lat}(Ag^IAg^{III}O_2) - 4RT$

$= +9419.9 - 10.0 = +\mathbf{9409.9}$ (kJ·mol^{-1}) 3 points

(no penalty if negative sign)

U_{lat} of $Cu^{II}O$

Calculations for: **U_{lat} of $Cu^{II}O$**

$\Delta H_{lat}(Cu^{II}O) = \Delta H^o{}_f(O^{2-}) + \Delta H^o{}_f(Cu^{2+}) - \Delta H^o{}_f(Cu^{II}O)$

$= (249 - 141 + 844) + (337.4 + 751.7 + 1964.1) - (-157.3)$

$= 4162.5$ (kJ·mol^{-1})

$U_{lat}(Cu^{II}O)$ $= \Delta H_{lat}(Cu^{II}O) - 2RT = 4162.5 - 5.0 = \mathbf{4157.5}$ (kJ·mol^{-1})

3 points

(no penalty if negative sign)

*If you can not calculate the U_{lat} of $Ag^IAg^{III}O_2$ and $Cu^{II}O$, use following values for further calculations: U_{lat} of $Ag^IAg^{III}O_2$ = **8310.0** kJ·mol^{-1}; U_{lat} of $Cu^{II}O$ = **3600.0** kJ·mol^{-1}.*

The lattice dissociation energies for a range of compounds may be estimated using this simple formula:

$$U_{lat} = \mathrm{C} \times \left(\frac{1}{V_m}\right)^{\frac{1}{3}}$$

Where: V_m (nm^3) is the volume of the formula unit and C (kJ·nm·mol^{-1}) is an empirical constant which has a particular value for each type of lattice with ions of specified charges.

The formula unit volumes of some oxides are calculated from crystallographic data as the ratio between the unit cell volume and the number of formula units in the unit cell and listed as below:

Oxides	V_m (nm^3)
$Cu^{II}O$	0.02030
$Ag^{III}{}_2O_3$	0.06182
$Ag^{II}Ag^{III}{}_2O_4$	0.08985

2b. <u>Calculate</u> U_{lat} for the hypothetical compound $Ag^{II}O$. Assume that $Ag^{II}O$ and $Cu^{II}O$ have the same type of lattice, and that $V_m(Ag^{II}O) = V_m(Ag^{II}Ag^{III}{}_2O_4) - V_m(Ag^{III}{}_2O_3)$.

Calculations:

$V_m(Ag^{II}O) = V_m(Ag^{II}Ag^{III}{}_2O_4) - V_m(Ag^{III}{}_2O_3) = 0.08985 - 0.06182 =$ **0.02803 nm^3**

From the relationship $U_{lat} = C\times(V_m)^{-1/3}$ we have

$$\frac{U_{lat}(\text{Ag oxide})}{U_{lat}(\text{Cu oxide})} \approx \left[\frac{V_m(\text{Cu oxide})}{V_m(\text{Ag oxide})}\right]^{1/3}$$

$U_{lat}(Ag^{II}O) = 4157.5\times\sqrt[3]{\frac{0.02030}{0.02803}} =$ **3733.6** (kJ·mol^{-1}) 3 points

Answer: **3733.6** (kJ.mol^{-1}) [or 3232.9 kJ·mol^{-1} if using U_{lat} $Cu^{II}O$ = 3600 kJ·mol^{-1}]

2c. By constructing an appropriate thermodynamic cycle or otherwise, **<u>estimate</u>** the enthalpy change for the solid-state transformation from $Ag^{II}O$ to 1 mole of $Ag^{I}Ag^{III}O_2$.

(Use U_{lat} $Ag^{II}O$ = 3180.0 kJ·mol^{-1} and U_{lat} $Ag^{I}Ag^{III}O_2$ = 8310.0 kJ·mol^{-1} if you cannot calculate U_{lat} $Ag^{II}O$ in Part 2b).

$$\begin{tikzcd}[column sep=huge, row sep=huge]
2Ag^{II}O_{(s)} \arrow[r, "\Delta H_{rxn}"] \arrow[d, "2U_{lat}\,(AgO)\ +\ 4RT"] & Ag^{I}Ag^{III}O_{2\,(s)} \\
2Ag^{2+}_{(g)} + 2O^{2-}_{(g)} \arrow[r, "IE_3\,(Ag) - IE_2\,(Ag)"] & Ag^{+}_{(g)} + Ag^{3+}_{(g)} + 2O^{2-}_{(g)} \arrow[u, "-\ U_{lat}\,(Ag^{I}Ag^{III}O)\ -\ 4RT"']
\end{tikzcd}$$

Calculations:

$$\Delta H_{rxn} = 2U_{lat}\,(Ag^{II}O) + 4RT + IE_3 - IE_2 - U_{lat}\,(Ag^{I}Ag^{III}O_2) - 4RT$$

$$= 2 \times 3733.6 + 3367.2 - 2080.2 - 9409.9$$

= **– 655.7 (kJ/mol)** or **- 663.0 kJ/mol** using given U_{lat} values 4 pts

2d. Indicate which compound is thermodynamically more stable by checking the appropriate box below.

$Ag^{II}O$	$Ag^{I}Ag^{III}O_2$	
☐	☐	
	x	1 point

3. When $Ag^{I}Ag^{III}O_2$ is dissolved in aqueous $HClO_4$ solution, a paramagnetic compound (**B**) is first formed then slowly decomposes to form a diamagnetic compound (**C**). Given that **B** and **C** are the only compounds containing silver formed in these reactions, **write down** the equations for the formation of **B** and **C**.

For **B**:

$$Ag^{I}Ag^{III}O_{2\,(s)} + 4\ HClO_{4\,(aq)} \longrightarrow 2Ag(ClO_4)_{2\,(aq)} + 2\ H_2O_{\,(l)}$$ 1 point

For **C**: $$4Ag(ClO_4)_{2\,(aq)} + 2\ H_2O_{\,(l)} \longrightarrow 4\ AgClO_{4\,(aq)} + 4\ HClO_{4\,(aq)} + O_{2\,(g)}$$ 1 point

4. Oxidation of Ag^+ with powerful oxidizing agents in the presence of appropriate ligands can result in the formation of high-valent silver complexes. A complex **Z** is synthesized and analyzed by the following procedures:

An aqueous solution containing 0.500 g of $AgNO_3$ and 2 mL of pyridine (d = 0.982 g/mL) is added to a stirred, ice-cold aqueous solution of 5.000 g of $K_2S_2O_8$. The reaction mixture becomes yellow, then an orange solid (**Z**) is formed which has a mass of 1.719 g when dried.

Elemental analysis of **Z** shows the mass percentages of C, H, N elements are 38.96%, 3.28%, 9.09%, respectively.

A 0.6164 g **Z** is added to aqueous NH_3. The suspension is boiled to form a clear solution during which stage the complex is destroyed completely. The solution is acidified with excess aqueous HCl and the resulting suspension is filtered, washed and dried (in darkness) to obtain 0.1433 g of white solid (**D**). The filtrate is collected and treated with excess $BaCl_2$ solution to obtain 0.4668 g (when dry) of white precipitate (**E**).

4a. **Determine** the empirical formula of **Z** and calculate the percentage yield in the preparation.

Calculations:

- Mole Ag in 0.6164 g of **Z** = mole of AgCl = 0.001 mole
- Mole SO_4^{2-} from 0.6160 g of **Z** = mole $BaSO_4$ = 0.002 mol
- Mass percentage of Ag = 0.001×107.87/0.6164 = 17.50 %
- Mass percentage of SO_4^{2-} = 0.002×96.06/0.6164 = 31.17 %
- From EA:

$$\text{Ratio } Ag^{2+} : SO_4^{2-} : C : H : N = \frac{17.50}{107.87} : \frac{31.17}{192.12} : \frac{38.96}{12.01} : \frac{3.28}{1.01} : \frac{9.09}{14.01} = 1 : 2 : 20 : 20 : 4$$

The empirical formula of **Z** is: $C_{20}H_{20}AgN_4O_8S_2$ **2 points**

$$\text{Yield} = \frac{1.719}{\frac{0.500}{169.87} \times 616.4} \times 100\% = \mathbf{94.7\ \%}$$ **1 point**

4b. Ag (IV) and Ag (V) compounds are extremely unstable and found only in few fluorides. Thus, the formation of their complexes with organic ligands in water can be discounted. To confirm the oxidation number of silver in **Z**, the effective magnetic moment (μ_{eff}) of **Z** was determined and found to be 1.78 BM. Use the spin only formula to **determine** the number of unpaired electrons in Z and the molecular formula of **Z.** (**Z** contains a mononuclear complex with only one species of Ag and only one type of ligand in the ligand sphere.)

- $\sqrt{n(n+2)} = 1.78$ (n is number of unpaired electron of Ag)
- $n = 1$, corresponds to Ag^{II} (d^9)
- Most rational molecular formula of **Z** is **$[Ag^{II}(Py)_4](S_2O_8)$** **3 point**

4c. Write down all chemical equations for the preparation of **Z**, and its analysis.

Formation of **Z**:

$2Ag^+_{(aq)} + 8Py_{(l)} + 3S_2O_8^{2-}{}_{(aq)} \longrightarrow 2[Ag^{II}(Py)_4](S_2O_8)_{(s)} + 2SO_4^{2-}{}_{(aq)}$ 2 pts

Destruction of **Z** with NH_3:

$[Ag^{II}(Py)_4](S_2O_8)_{(s)} + 6NH_{3\,(l)} \longrightarrow [Ag(NH_3)_2]^+_{(aq)} + ½\,N_{2\,(g)} + 2SO_4^{2-}{}_{(aq)} + 3NH_4^+{}_{(aq)} + 4Py_{(l)}$ 2 pts

(All reasonable N –containing products and O_2 are acceptable)

Formation of **D**:

$[Ag(NH_3)_2]^+_{(aq)} + 2H^+_{(aq)} + Cl^-_{(aq)} \longrightarrow AgCl_{(s)} + 2NH_4^+{}_{(aq)}$ 1 pt

Formation of **E**:

$Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow BaSO_{4\,(s)}$ 1pt

Student name **Student code**

Theoretical **Problem 4** **4.0 %** of the total	**Code:**		Question	1a	1b	2	3a	3b	3c	Total
	Examiner		Mark	4	1	10	2	6	4	**27**
			Grade							

Problem 4. Zeise's Salt

1. Zeise's salt, K[$PtCl_3C_2H_4$], was one of the first organometallic compounds to be reported. W. C. Zeise, a professor at the University of Copenhagen, prepared this compound in 1827 by reacting $PtCl_4$ with boiling ethanol and then adding potassium chloride (Method 1). This compound may also be prepared by refluxing a mixture of $K_2[PtCl_6]$ and ethanol (Method 2). The commercially available Zeise's salt is commonly prepared from $K_2[PtCl_4]$ and ethylene (Method 3).

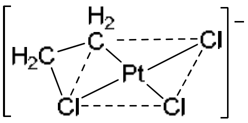
1a. Write balanced equations for each of the above mentioned preparations of Zeise's salt, given that in methods 1 and 2 the formation of 1 mole of Zeise's salt consumes 2 moles of ethanol.

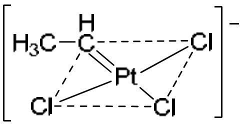
1b. Mass spectrometry of the anion $[PtCl_3C_2H_4]^-$ shows one set of peaks with mass numbers 325-337 and various intensities.

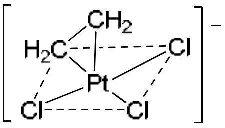
Calculate the mass number of the anion which consists of the largest natural abundance isotopes (using given below data).

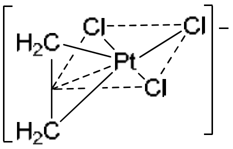
Isotope	$^{192}_{78}Pt$	$^{194}_{78}Pt$	$^{195}_{78}Pt$	$^{196}_{78}Pt$	$^{198}_{78}Pt$	$^{35}_{17}Cl$	$^{37}_{17}Cl$	$^{12}_{6}C$	$^{13}_{6}C$	$^{1}_{1}H$
Natural abundance, %	0.8	32.9	33.8	25.3	7.2	75.8	24.2	98.9	1.1	99.99

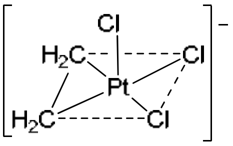
2. Some early structures proposed for Zeise's salt anion were:


(Z1)


(Z2)


(Z3)


(Z4)


(Z5)

In structure **Z1**, **Z2**, and **Z5** both carbons are in the same plane as dashed square. [You should assume that these structures do not undergo any fluxional process by interchanging two or more sites.]

Student name **Student code**

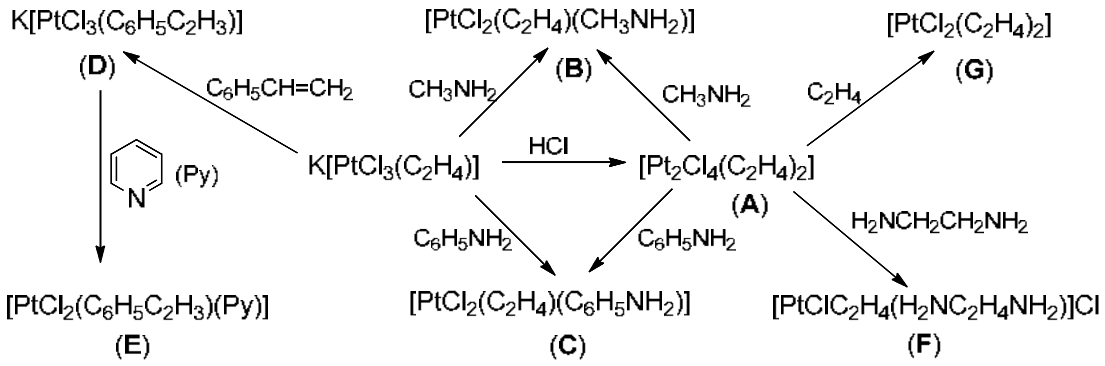
2a. NMR spectroscopy allowed the structure for Zeise's salt to be determined as structure **Z4**. For each structure **Z1-Z5**, **indicate** in the table below how many different environments of hydrogen atoms there are, and how many different environments of carbon atoms there are.

Structure	Number of different environments of hydrogen	Number of different environments of carbon
Z1		
Z2		
Z3		
Z4		
Z5		

3. For substitution reactions of square platinum(II) complexes, ligands may be arranged in order of their tendency to facilitate substitution in the position *trans* to themselves (*the trans effect*). The ordering of ligands is:

$CO , CN^- , C_2H_4 > PR_3 , H^- > CH_3^- , C_6H_5^- , I^- , SCN^- > Br^- > Cl^- > Py > NH_3 > OH^- , H_2O$

In above series a left ligand has stronger *trans effect* than a right ligand.
Some reactions of Zeise's salt and the complex $[Pt_2Cl_4(C_2H_4)_2]$ are given below.



Student name **Student code**

3a. **Draw the structure of A**, given that the molecule of this complex has a centre of symmetry, no Pt-Pt bond, and no bridging alkene.

A

3b. **Draw** the structures of **B**, **C**, **D**, **E**, **F** and **G**.

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

3c. **Suggest** the driving force(s) for the formation of **D** and **F** by choosing one or more of the following statements (for example, i and ii):

i) Formation of gas

ii) Formation of liquid

iii) Trans effect

iv) Chelate effect

Structure	**D**	**F**
Driving force(s)		

Theoretical **Problem 4** **4.0 %** of the total	**Code:**		Question	1a	1b	2a	3a	3b	3c	Total
	Examiner		Mark	4	1	10	2	**6**	**4**	**27**
			Grade							

Problem 4. Zeise's Salt

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1a. Write balanced equations for each of the above mentioned preparations of Zeise's salt, given that in methods 1 and 2 the formation of 1 mole of Zeise's salt consumes 2 moles of ethanol.

$PtCl_4 + 2\ C_2H_5OH \rightarrow H[PtCl_3C_2H_4] + CH_3CH{=}O + HCl + H_2O$

$H[PtCl_3C_2H_4] + KCl \rightarrow K[PtCl_3C_2H_4] + HCl$

$K_2[PtCl_6] + 2\ C_2H_5OH \rightarrow K[PtCl_3C_2H_4] + CH_3CH{=}O + KCl + 2\ HCl + H_2O$

$K_2[PtCl_4] + C_2H_4 \rightarrow K[PtCl_3C_2H_4] + KCl$

1pt for each (2 pts if the first two reactions combined), total of 4 pts

1b. Mass spectrometry of the anion $[PtCl_3C_2H_4]^-$ shows one set of peaks with mass numbers 325-337 *au* and various intensities.

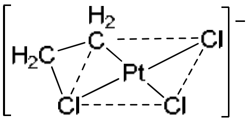
Calculate the mass number of the anion which consists of the largest natural abundance isotopes (using given below data).

Isotope	$^{192}_{78}Pt$	$^{194}_{78}Pt$	$^{195}_{78}Pt$	$^{196}_{78}Pt$	$^{198}_{78}Pt$	$^{35}_{17}Cl$	$^{37}_{17}Cl$	$^{12}_{6}C$	$^{13}_{6}C$	$^{1}_{1}H$
Natural abundance, %	0.8	32.9	33.8	25.3	7.2	75.8	24.2	98.9	1.1	99.99

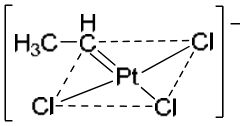
Calculations:

$195 + 3\times35 + 2\times12 + 4\times1 = 328$ 1 pt

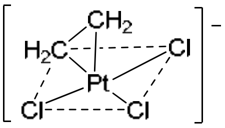
2. Some early structures proposed for Zeise's salt anion were:



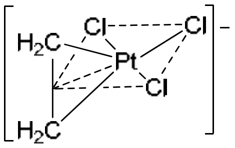
(Z1)



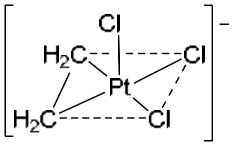
(Z2)



(Z3)



(Z4)



(Z5)

In structure **Z1**, **Z2**, and **Z5** both carbons are in the same plane as dashed square. [You should assume that these structures do not undergo any fluxional process by interchanging two or more sites.]

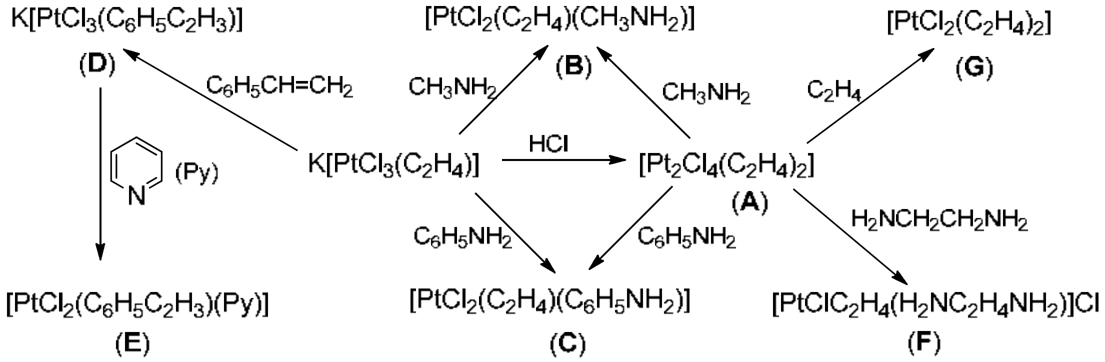
2a. NMR spectroscopy allowed the structure for Zeise's salt to be determined as structure **Z4**. For each structure **Z1-Z5**, **indicate** in the table below how many hydrogen atoms are in different environments, and how many different environments of hydrogen atoms there are, and how many different environments of carbon atoms there are?

Structure	Number of different environments of hydrogen	Number of different environments of carbon
Z1	2 1pt	2 1 pt
Z2	2 1pt	2 1 pt
Z3	2 1pt	2 1 pt
Z4	1 1pt	1 1 pt
Z5	2 1pt	1 1 pt

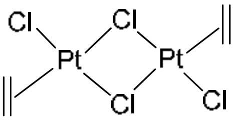
3. For substitution reactions of square platinum(II) complexes, ligands may be arranged in order of their tendency to facilitate substitution in the position *trans* to themselves (*the trans effect*). The ordering of ligands is:

$$CO , CN^- , C_2H_4 > PR_3 , H^- > CH_3^- , C_6H_5^- , I^- , SCN^- > Br^- > Cl^- > Py > NH_3 > OH^- , H_2O$$

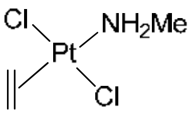
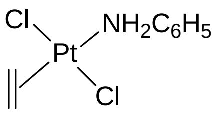
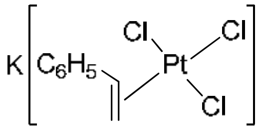
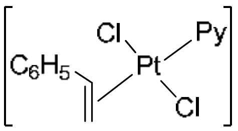
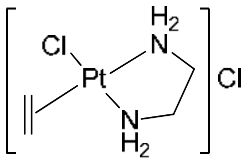
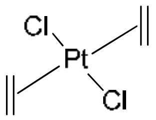
In above series a left ligand has stronger *trans effect* than a right ligand.
Some reactions of Zeise's salt and the complex $[Pt_2Cl_4(C_2H_4)_2]$ are given below.



3a. <u>Draw the structure of A</u>, given that the molecule of this complex has a centre of symmetry, no Pt-Pt bond, and no bridging alkene.

Structure of **A**		2 pt

3b. **Draw** the structures of **B**, **C**, **D**, **E**, **F** and **G**.

B	**C**	**D**
 1 pt	 1 pt	 1 pt
E	**F**	**G**
 1 pt	 1 pt	 1 pt

3c. **Suggest** the driving force(s) for the formation of **D** and **F** by choosing one or more of the following statements (for example, i and ii):

i) Formation of gas

ii) Formation of liquid

iii) Trans effect

iv) Chelate effect

Structure	**D**	**F**
Driving force(s)	i	iii and iv
	2 pts	2 pts

Problem 4. From one yellow powder to another: A simple inorganic riddle
(6 points)

Question	1	2	3	4	Total
Marks	8	8	3	5	24

The yellow binary compound **X_1** was completely dissolved in concentrated nitric acid by heating, the gas evolved is 1.586 times denser than air. Upon adding an excess of barium chloride to the solution formed a white solid **X_2** precipitates. It was filtered. The filtrate reacts with an excess of silver sulfate solution forming a precipitate of two solids **X_2** and **X_3**, also separated from solution by filtration. To the new filtrate the solution of sodium hydroxide was being added drop-wise until the solution became nearly neutral (about pH 7). At this time a yellow powder **X_4** (77.31 wt.% of Ag) crystallized from the solution. The mass of **X_4** is nearly 2.4 times larger than that the mass of the first portion of **X_2**.

1. Determine the chemical formulae of **X_1** – **X_4**.

Calculations:

X_1 = **X_2** = **X_3** = **X_4** =

2. Determine the chemical formula of the gas and provide equations for all reactions in ionic or non-ionic form.

Calculation

Chemical formula of the gas ________

Dissolution of **X_1**

Formation of **X_2**

Formation of $\mathbf{X}_2$ and $\mathbf{X}_3$

Addition of NaOH and formation of $\mathbf{X}_4$

3. In the structural unit of $\mathbf{X}_1$ all atoms of only one element are in equivalent positions. Draw the structure of $\mathbf{X}_1$.

4. Predict the products of $\mathbf{X}_1$ interaction with:
   a) excess oxygen;
   b) excess of hot concentrated sulfuric acid;
   c) solid $KClO_3$ with grinding.

Write down the reaction equations.

a)

b)

c)

Problem 4. From one yellow powder to another: A simple inorganic riddle
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Marks	8	8	3	5	24

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1. Determine the chemical formulae of **X_1 – X_4**.

Calculations:

The precipitate **X_2** formed by addition of barium chloride in acidic medium is barium sulfate $BaSO_4$. **1 pt**

The precipitate **X_3** formed by addition of silver sulfate is silver chloride AgCl **1 pt**

The yellow precipitate **X_4** formed by addition of alkali can be mercury oxide HgO or silver phosphate Ag_3PO_4. The ratio of molar masses **X_4 : X_2** is 0.931 for HgO : $BaSO_4$ which is not valid and 1.798 for Ag_3PO_4 : $BaSO_4$ which gives 2.4 being multiplied by 4/3. So, the molar ratio is $4Ag_3PO_4 : 3BaSO_4$ which corresponds to P : S = 4:3, i.e. to formula of **X_1** P_4S_3.

X_1 = P_4S_3 **X_2** = $BaSO_4$ **X_3** = AgCl **X_4** = Ag_3PO_4

2 pts for Ag_3PO_4

4 pts for P_4S_3 (**0 pts** without calculations)

Total – **8 pts**

2. Determine the chemical formula of the gas and provide equations for all reactions in ionic or non-ionic form.

Calculation

The gas evolved has a molar mass $1.586 \times 29 = 46$ g/mol, that is NO_2. **1 pt**

Chemical formula of the gas _________

Dissolution of **X_1**

$P_4S_3 + 38HNO_3 = 4H_3PO_4 + 3H_2SO_4 + 38NO_2 + 10H_2O$ **2 pt**

Formation of $\mathbf{X_2}$

$H_2SO_4 + BaCl_2 = BaSO_4\downarrow + 2HCl$ **1 pt**

Formation of $\mathbf{X}_2$ and $\mathbf{X_3}$

$Ag_2SO_4 + 2HCl = 2AgCl\downarrow + H_2SO_4$ **1 pt**

$BaCl_2 + Ag_2SO_4 = BaSO_4\downarrow + 2AgCl\downarrow$ **1 pt**

Addition of NaOH and formation of $\mathbf{X_4}$

$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$ **1 pt**

$2H_3PO_4 + 6NaOH + 3Ag_2SO_4 = 2Ag_3PO_4\downarrow + 3Na_2SO_4 + 6H_2O$ **2 pts**

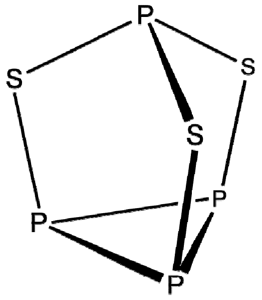
(neutralization of H_3PO_4 and subsequent reaction with Ag_2SO_4 will also be accepted)

(50% of points for non-balanced reactions with correct products)

Total – **8 pts**

3. In the structural unit of $\mathbf{X_1}$ all atoms of only one element are in equivalent positions. Draw the structure of $\mathbf{X}_1$.

Phosphorus sulfide P_4S_3 is a molecular cage



3 pts

(Any reasonable structures with correct valencies of sulfur and phosphorus will also be accepted. **1 pt** for the structure with non-equivalent atoms of both elements)

4. Predict the products of $\mathbf{X_1}$ interaction with:
   - a) excess oxygen;
   - b) excess of hot concentrated sulfuric acid;
   - c) solid $KClO_3$ with grinding.

Write down the reaction equations.

a) $P_4S_3 + 8O_2 = 2P_2O_5 + 3SO_2$ **1 pt**

b) $P_4S_3 + 16H_2SO_4 = 4H_3PO_4 + 19SO_2 + 10H_2O$ **2 pts**

(oxidation of sulfide to S instead of SO_2 is full mark)

c) $3P_4S_3 + 16KClO_3 = 16KCl + 6P_2O_5 + 9SO_2$ **2 pts**

(50% of points for non-balanced reactions with correct products)

Total – **5 pts**

Problem 1 5% of the total

Nitrogen trifluoride is a surprisingly stable compound that was first prepared in the melt electrolysis of a mixture of ammonium fluoride and hydrogen fluoride.

1.1. On which electrode does nitrogen trifluoride form? Write a balanced chemical equation for the electrode half reaction for the formation of NF_3.

Interestingly the related fluoroamine (NH_2F) and difluoroamine (NHF_2) are very unstable materials; decomposition of either pure substance can even be explosive. This is dangerous as they are formed in the electrolysis as side products.

1.2. Which of NF_3, NHF_2 or NH_2F compound is expected to condense at the lowest temperature?

The N-F bond lengths in these molecules were determined to be 136, 140 and 142 pm. The change in the bond lengths can be explained with a simple electrostatic model taking into account the partial charges on the atoms.

1.3. Assign the N-F bond lengths (136, 140, 142 pm) to the molecules.

When NHF_2 is bubbled through a solution of KF in HF, a binary nitrogen – fluorine compound can be obtained as a mixture of two geometric isomers.

1.4. Write a balanced chemical equation for the formation of the binary nitrogen-fluorine compound.

Tetrafluoroammonium ion (NF_4^+) and its corresponding salt can form from NF_3 with elementary fluorine in the presence of an appropriate reagent.

1.5. Propose a suitable reagent and write a balanced chemical equation for the reaction.

NF_4^+ ions form stable salts with a number of anions. These are very sensitive to humidity, because NF_4^+ ion hydrolyzes forming NF_3 and O_2. Interestingly nitrogen trifluoride always forms quantitatively, while the quantity of oxygen is often less than expected due to side reactions.

1.6. Write a balanced chemical equation for the hydrolysis of NF_4^+. Write a balanced chemical equation for a possible side reaction that can decrease the theoretically expected O_2:NF_3 mole ratio.

Tetrafluoroammonium salts were investigated for use as solid rocket fuels, because NF_3 and F_2 are released from them on heating. One of them has a fluorine content of 65.6 m/m%, all of which is converted into NF_3 and F_2 upon decomposition. During the decomposition 2.5 times as many moles of F_2 are formed as of NF_3.

1.7. Determine the formula of the salt in question.

Problem 1 5% of the total

1.1.	1.2.	1.3.	1.4.	1.5.	1.6.	1.7.	Sum
3	1	2	2	2	4	3	17

1.1. On which electrode does nitrogen trifluoride form?

☐ Cathode ☐ Anode

Write a balanced chemical equation for the electrode half reaction for the formation of NF_3.

$NH_4^+ + 3\ F^- \longrightarrow NF_3 + 4\ H^+ + 6\ e^-$ or $NH_4F + 2\ HF \longrightarrow NF_3 + 6\ H^+ + 6\ e^-$ or equ.

3p (1p choosing anode, 1p species, 1p coefficients)

1.2. Which of NF_3, NHF_2 or NH_2F compound is expected to condense at the lowest temperature?

☐ NF_3 ☐ NHF_2 ☐ NH_2F

NF_3

1.3. Assign the N-F bond lengths (136, 140, 142 pm) to the molecules.

Molecule	NH_2F	NHF_2	NF_3
N-F bond length, pm			

The partial positive charge on N increases in this order, so the attraction also increases between the N and F.

1.4. Write a balanced chemical equation for the formation of the binary nitrogen – fluorine compound.

$2\ NHF_2 + 2\ KF \longrightarrow N_2F_2 + 2\ KHF_2$ or $2\ NHF_2 \longrightarrow N_2F_2 + 2\ HF$

2p (1p N_2F_2, 1p equation)

1.5. Propose a suitable reagent for the formation of NF_4^+ and write a balanced chemical equation for the reaction.

$NF_3 + F_2 + SbF_5 \longrightarrow NF_4^+ + SbF_6^-$ any strong fluoride acceptor (AsF_5, BF_3)

2p (1p species, 1p coefficients)

1.6. Write a balanced chemical equation for the hydrolysis of NF_4^+.

$2\ NF_4^+ + 2\ H_2O \longrightarrow 2\ NF_3 + O_2 + 2\ HF + 2\ H^+ \Rightarrow n(O_2):n(NF_3) = 1:2$

2p (1p species, 1p coefficients)

Write a balanced chemical equation for a possible side reaction that can decrease the theoretically expected $O_2:NF_3$ mole ratio.

e.g.: $NF_4^+ + 2\ H_2O \longrightarrow NF_3 + H_2O_2 + HF + H^+$ HOF, O_3, OF_2 also accepted.

2p (1p species, 1p coefficients)

1.7. Determine the formula of the salt in question.

Your work:

From the $NF_3:F_2$ ratio it is clear that the anion also contains fluorine. Moreover, the starting NF_4^+: liberated F_2 ratio is 1:2, and all fluorine content is released. With a $(NF_4)_x\mathbf{A}F_y$ composition, $x:y = 1:4$.

$$\frac{8xM(\mathrm{F})}{8xM(\mathrm{F})+xM(\mathrm{N})+M(\mathbf{A})} = 0.656 \quad \Rightarrow \frac{M(\mathbf{A})}{x} = 65.7\ \mathrm{g/mol}$$

With x=1, the atomic mass of **A** is close to zinc, but not all fluorine would be released with Zn. If x=2, then the element is xenon, and the formula is $(NF_4)_2XeF_8$

3p (1.5p for Zn)

Formula:

Problem 5 8% of the total

5500 years ago in ancient Egypt people learned for the first time how to synthesize a blue pigment. Now we know this pigment as Egyptian blue. About 2000 years later in ancient China another pigment was widely used, which is now referred to as Chinese blue. The two pigments are similar in structure, but have different elemental compositions.

Ushabti figurines from Egyptian pharaoh tomb covered with Egyptian blue and a Chinese blue soap dispenser sold at Alibaba

The ancient method of preparation for these pigments can be easily reproduced in a modern laboratory.

When considering the amounts, assume that all of the compounds in this task are pure, and the yields are quantitative.

To make **Egyptian blue**, one should heat 10.0 g of mineral **A** with 21.7 g of SiO_2 and 9.05 g of mineral **B** at 800–900°C for a prolonged time. 16.7 dm^3 of a mixture of two gaseous products are released (the volume is measured at 850°C and $1.013 \cdot 10^5$ Pa (1.013 bar) pressure. In result, 34.0 g of the pigment was obtained. No other products are formed. As the gas mixture is cooled, one component of the mixture condenses. As the remaining gas is further cooled to 0°C, the gaseous volume reduces to 3.04 dm^3.

5.1.1. Find the mass of the gaseous mixture formed upon heating of **A** with **B** and SiO_2.

5.1.2. Determine the quantitative composition of this gas mixture.

When 10.0 g of mineral **A** is heated with 21.7 g of SiO_2 in the absence of **B**, it forms 8.34 dm^3 of gaseous products (measured at 850°C and $1.013 \cdot 10^5$ Pa = 1.013 bar pressure). Mineral **A** contains only one metal.

5.1.3. Calculate the molar mass and determine the formula of mineral **B**. Hint: it is an ionic solid insoluble in water and containing no water of crystallization.

In order to obtain **Chinese blue**, one should take 17.8 g of mineral **C** instead of mineral **B** (keeping the amounts of mineral **A** and SiO_2 same as for Egyptian blue), and run the reaction at higher temperatures. Besides the pigment, the same gaseous products in the same quantities are formed as in the preparation of Egyptian blue.

5.1.4. Determine the formula of mineral **C**.

5.1.5. Determine the formulae of Egyptian blue and Chinese blue.

5.1.6. Determine the formula of mineral **A**.

Elemental analysis of some samples of Chinese blue shows traces of sulfur. This led to a conclusion that those were synthesized using another common mineral instead of **C**.

5.2.1. Suggest a formula for the mineral used in place of **C**.

5.2.2. Could the temperature of synthesis of Chinese blue be decreased if this mineral is used instead of **C**?

If during the synthesis of Chinese blue we take a smaller amount of silica than in the process above, we will obtain a purple pigment: Chinese violet. It was used, in particular, for coloring the famous Terracotta army soldiers.

Terracotta army from Xian, China and reconstruction of its original coloring

5.3. Write down the formula of a binary compound that forms under the conditions required for Chinese violet and is responsible for the change of the color.

Problem 5 8% of the total

5.1.1.	5.1.2.	5.1.3.	5.1.4.	5.1.5.	5.1.6.	5.2.1.	5.2.2.	5.3.	Sum
1	3	2	2	5	2	1	1	2	19

5.1.1. Find the mass of the gaseous mixture formed upon heating of **A** with **B** and SiO_2.

Your work:

m = 10.0 + 21.7 + 9.05 – 34.0 = 6.75 g

1 p

5.1.2. Determine the quantitative composition of this gas mixture.

Your work:

At 850°C, the number of moles of gaseous products is:

$$n_1 = \frac{pV}{RT} = \frac{101325\ \text{Pa} \cdot 0.0167\ \text{m}^3}{8.314\ \text{Jmol}^{-1}\text{K}^{-1} \cdot (850\text{K} + 273\text{K})} = 0.181\ \text{mol}$$

while at 0°C

$$n_2 = \frac{pV}{RT} = \frac{101325\ \text{Pa} \cdot 0.00304\ \text{m}^3}{8.314\ \text{Jmol}^{-1}\text{K}^{-1} \cdot 273\ \text{K}} = 0.136\ \text{mol}$$

The difference of 0.045 moles is probably water that has condensed. Hence, the mass of the gas at 0°C is m = 6.75–0.045·18 = 5.94 g, and the molar mass is $m/n_2 \approx$ 44 g/mol. Taken into account that we dealt with minerals, and the temperature was high, we can conclude that the rest of the gas is CO_2.

The gas formed at 850°C contains 0.045 mol of H_2O and 0.136 mol of CO_2.

3p (0.5p for finding each compound, 1p for the quantity of each compound)

The gaseous mixture formed at 850°C contains ……… mol of ………. and ……… mol of ………

5.1.3. Calculate the molar mass and determine the formula of mineral **B**. Hint: it is an ionic solid insoluble in water and containing no water of crystallization.

Your work:

Heating of mineral **A** with SiO_2 alone produces half of the gases evolved in the presence of **B**. Thus, **B** should form the rest 0.181/2 = 0.0905 moles of gases and is a carbonate of some metal. If it forms pure CO_2, the molar mass of **B** per carbonate group is 9.05 g / 0.0905 mol = 100 g mol^{-1}. The molar mass of CO_3 group is
60 g mol^{-1}, so the mass of metal per carbonate group is 40 g mol^{-1}.

This corresponds to Ca, **B** – $CaCO_3$

2p

B is:

5.1.4. Determine the formula of mineral **C**.

Your work:

Similar to the previous question, the molar mass of **C** per carbonate group is 17.8 g / 0.0905 mol = 197 g mol^{-1}. The mass of metal per carbonate group is 137 g mol^{-1}.

This corresponds to Ba, **C** – $BaCO_3$.

2p

C is:

5.1.5. Determine the formulae of Egyptian blue and Chinese blue.

Your work:

Taking into account the molar ratios of known compounds, we can write a general equation of formation of Egyptian blue:

A + 2 $CaCO_3$ + 8 SiO_2 = pigment + 3 CO_2 + H_2O

The composition of Egyptian blue can be written as $2CaO{\cdot}8SiO_2{\cdot}nMe_xO_y$. Oxide Me_xO_y forms from mineral **A**. Let us find the molar mass of nMe_xO_y:

$$M(\text{pigment}) = M(2\text{CaO}\cdot 8\text{SiO}_2) + M(n\text{Me}_x\text{O}_y)$$

$$M(\text{pigment}) = 2M(\text{CaCO}_3)\frac{m(\text{pigment})}{m(\text{CaCO}_3)}$$

$$M(n\text{Me}_x\text{O}_y) = 2M(\text{CaCO}_3)\frac{34.0\text{ g}}{9.05\text{ g}} - M(2\text{CaO}\cdot 8\text{SiO}_2) \approx 159\text{ g/mol}$$

Trying different values (at least from 1 to 3) of n, x, and y, we ensure that the only possibility is $n = 2$, $x = y = 1$, Me is Cu. This is supported by a blue color of a pigment.

The formula of Egyptian blue is then $CaCuSi_4O_{10}$.

The formula of Chinese blue is $BaCuSi_4O_{10}$.

3p for proving presence of Cu (1.5 p for correct molar mass of oxide without further advances)

2p for formulas of the pigments

Any correct way of calculation is fully marked

Egyptian blue is: Chinese blue is:

5.1.6. Determine the formula of mineral **A**.

Your work:

Upon heating **A** turns into 2 CuO, 1 CO_2 and 1 H_2O.

It means that **A** is malachite $Cu_2CO_3(OH)_2$.

2p

A is:

5.2.1. Suggest the formula of the mineral used in place of **C**.

$BaSO_4$ (the most stable compound containing Ba and S, mineral barite)

1p (BaS is soluble and reactive, can not be a mineral.)

5.2.2. Could the temperature of synthesis of Chinese blue be decreased if this mineral is used instead of **C**?

☐ Yes ☐ No

No. $BaSO_4$ is more stable than $BaCO_3$.

1p

5.3. Write down a formula of a binary compound that forms under the conditions required for Chinese violet and is responsible for the change of the color.

Cu_2O (mixing red with blue gives purple)

2p

Problem 6

6% of the total

Problem 6	A		B			C		Total
	A1	A2	B1	B2	B3	C1	C2	
Total	3	8	4	3.5	5	2	4	**29.5**
Score								

Problem 6: Iron

Iron (Fe) is the fourth most abundant element in the Earth's crust and has been used for more than 5,000 years.

Part A.

Pure iron is easily oxidized, which limits its utilization. Element **X** is one of the alloying elements that is added to improve the oxidation resistance property of iron.

6-A1) Below is some information about the element **X**:

(1) In first ionization, an electron with quantum numbers $n_1 = 4 - l_1$ is removed.
(2) In second ionization, an electron with quantum numbers $n_2 = 5 - l_2$ is removed.
(3) The atomic mass of **X** is lower than that of Fe.

What is the element **X**?

(Answer by writing the proper symbol according to the periodic table.)

Part B.

Iron in natural water is in the form of $Fe(HCO_3)_2$, which ionizes to Fe^{2+} and HCO_3^-. To remove iron from water, $Fe(HCO_3)_2$ is oxidized to an insoluble complex $Fe(OH)_3$, which can be filtered out of the water.

6-B1) Fe^{2+} can be oxidized by $KMnO_4$ in a basic solution to yield $Fe(OH)_3$ and MnO_2 precipitates. Write the balanced ionic equation for this reaction in a basic solution.

Under this condition, HCO_3^- ions are converted to CO_3^{2-}. Write the balanced ionic equation for this reaction in a basic solution.

6-B2) A covalent compound **A** which contains more than 2 atoms and, a potential oxidizing agent, can be prepared by the reaction between diatomic halogen molecule (**Q**$_2$) and Na**Q**O$_2$.

$$1\mathbf{Q}_2 + x\mathrm{Na}\mathbf{Q}\mathrm{O}_2 \rightarrow y\mathbf{A} + z\mathrm{Na}\mathbf{Q} \qquad \text{where } x+y+z \le 7$$

where x, y and z are the coefficients for the balanced equation. Among the binary compounds between hydrogen and halogen, H**Q** has the lowest boiling point. Identify **Q** and if **A** has an unpaired electron, draw a Lewis structure of compound **A** with zero formal charge on all atoms. **(Answer by writing the proper symbol according to the periodic table.)**

Q = …………….......

Lewis structure of compound **A**

What is the molecular geometry of compound **A**? (Mark ✓ in an appropriate box.)

☐ linear ☐ bent ☐ cyclic ☐ tetrahedral ☐ trigonal planar ☐ other

6-B3) Compound **D** is an unstable oxidizing agent that can be used to remove $Fe(HCO_3)_2$ from natural water. It consists of elements **G**, **Z** and hydrogen and the oxidation number of **Z** is +1. In this compound, hydrogen is connected to the element having the higher electronegativity among them. Below is some information about the elements **G** and **Z**:

(1) **G** exists in its normal state as a diatomic molecule, $\mathbf{G}_2$.
(2) **Z** has one proton fewer than that of element **E**. **E** exists as a gas under standard conditions. $\mathbf{Z}_2$ is a volatile solid.
(3) The compound $\mathbf{EG}_3$ has a pyramidal shape.

Identify the elements **G** and **Z** and draw a molecular structure of compound **D**.
(Answer by writing the proper symbol according to the periodic table.)

G = ……….……………..……   **Z** = …………………….…..

Molecular structure of compound **D**

Problem 6

6% of the total

Problem 6	A		B			C		Total
	A1	**A2**	**B1**	**B2**	**B3**	**C1**	**C2**	
Total	3	8	4	3.5	5	2	4	**29.5**
Score								

Problem 6: Iron

Iron (Fe) is the fourth most abundant element in the Earth's crust and has been used for more than 5,000 years.

Part A.

Pure iron is easily oxidized, which limits its utilization. Element **X** is one of the alloying elements that is added to improve the oxidation resistance property of iron.

6-A1) Below is some information about the element **X**:

(1) In first ionization, an electron with quantum numbers $n_1 = 4 - l_1$ is removed.
(2) In second ionization, an electron with quantum numbers $n_2 = 5 - l_2$ is removed.
(3) The atomic mass of **X** is lower than that of Fe.

What is the element **X**? (3 points)

(Answer by writing the proper symbol according to the periodic table.)

Answer Cr *(3 points)* *(1 point for Cu)*

Part B.

Iron in natural water is in the form of $Fe(HCO_3)_2$, which ionizes to Fe^{2+} and HCO_3^-. To remove iron from water, $Fe(HCO_3)_2$ is oxidized to an insoluble complex $Fe(OH)_3$, which can be filtered out of the water. (4 points)

6-B1) Fe^{2+} can be oxidized by $KMnO_4$ in a basic solution to yield $Fe(OH)_3$ and MnO_2 precipitates. Write the balanced ionic equation for this reaction in a basic solution.

$3Fe^{2+} + MnO_4^- + 5OH^- + 2H_2O \rightarrow 3Fe(OH)_3 + MnO_2$ *(3 points)*

Under this condition, HCO_3^- ions are converted to CO_3^{2-}. Write the balanced ionic equation for this reaction in a basic solution.

$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$ *(1 point)*

6-B2) A covalent compound **A** which contains more than 2 atoms and, a potential oxidizing agent, can be prepared by the reaction between diatomic halogen molecule (**Q**$_2$) and Na**Q**O$_2$.

$$1\mathbf{Q}_2 + x\mathrm{Na}\mathbf{Q}\mathrm{O}_2 \rightarrow y\mathbf{A} + z\mathrm{Na}\mathbf{Q} \qquad \text{where } x+y+z \leq 7$$

where x, y and z are the coefficients for the balanced equation. Among the binary compounds between hydrogen and halogen, H**Q** has the lowest boiling point. Identify **Q** and if **A** has an unpaired electron, draw a Lewis structure of compound **A** with zero formal charge on all atoms. **(Answer by writing the proper symbol according to the periodic table.)**

Q = ……..Cl…………. (1.5 points)

Lewis structure of compound **A** (1.3 points)

(All are correct answers. Student draws only one structure.)

What is the molecular geometry of compound A? (Mark ✓ in the appropriate boxes.) (0.7 point)

☐ linear ☑ bent ☐ cyclic ☐ tetrahedral ☐ trigonal planar ☐ other

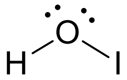
6-B3) Compound **D** is an unstable oxidizing agent that can be used to remove $Fe(HCO_3)_2$ from natural water. It consists of elements **G**, **Z** and hydrogen and the oxidation number of **Z** is +1. In this compound, hydrogen is connected to the element having the higher electronegativity among them. Below is some information about the elements **G** and **Z**:

(1) **G** exists in its normal state as a diatomic molecule, G_2.
(2) **Z** has one proton fewer than that of element **E**. **E** exists as a gas under standard conditions. Z_2 is a volatile solid.
(3) The compound EG_3 has a pyramidal shape.

Identify the elements **G** and **Z** and draw a molecular structure of compound **D**.
(Answer by writing the proper symbol according to the periodic table.)

G = …….O……… **Z** = ……...I…….. (2 points for each)

Molecular structure of compound **D** (1 points)



hydrogen is connected to the element having the highest electronegativity (0.5 points)
the oxidation of Z in compound D is +1 (0.5 point)

Part C.

^{59}Fe is a radiopharmaceutical isotope which is used in the study of iron metabolism in the spleen. This isotope decays to ^{59}Co as follows:

$$^{59}_{26}Fe \rightarrow ^{59}_{27}Co + \mathbf{a} + \mathbf{b} \qquad (1)$$

6-C1) What are **a** and **b** in equation (1)? (Mark ✓ in the appropriate boxes.)

proton	neutron	beta	positron	alpha	gamma
		✓			✓

(total = 2 points, 1 for each correct answer)

Problem 7

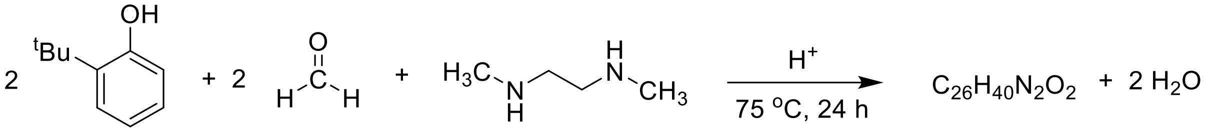
6% of the total

Problem 7	A					Total
	A1	**A2**	**A3**	**A4**	**A5**	
Total	4.5	1.5	6	6	2	20
Score						

Problem 7: Chemical Structure Puzzles

Titanium complexes have been investigated for their antitumor activity. Many factors including isomerism and sizes have shown to affect the potency of the complexes. This question deals with the synthesis and characterization of some titanium complexes.

7-A1) A reaction of 2 equivalents of 2-*tert*-butylphenol, 2 equivalents of formaldehyde, and *N*,*N'*-dimethylethylene-1,2-diamine under acidic conditions at 75 °C affords three major products with the same chemical formula of $C_{26}H_{40}N_2O_2$, as shown in the equation below. Draw the structure of each product.



Product 1:
Product 2:

Product 3:

7-A2) If 2,4-di-*tert*-butylphenol is used as a substrate instead of 2-*tert*-butylphenol using the same stoichiometry as that in **7-A1)**, only one product **X** was obtained. Draw the structure of **X**.

A reaction between **X** from **7-A2)** and $Ti(O^iPr)_4$ [^iPr = isopropyl] in diethyl ether under an inert atmosphere resulted in the six-coordinate Ti complex **Y**, as a yellow crystalline solid and isopropanol at room temperature.

$$a\,\mathbf{X} + b\,Ti(O^iPr)_4 \xrightarrow{Et_2O} d\,\mathbf{Y} + c\,{}^iPrOH \qquad \textbf{(equation 1)}$$

UV-Vis spectra of **X**, $Ti(O^iPr)_4$, and **Y** reveal that only the product **Y** has an absorption at λ = 370 nm. By varying the volumes of **X** and $Ti(O^iPr)_4$, each with the concentration of 0.50 mol dm^{-3}, and using benzene as the solvent, the absorbance data at λ = 370 nm are given below:

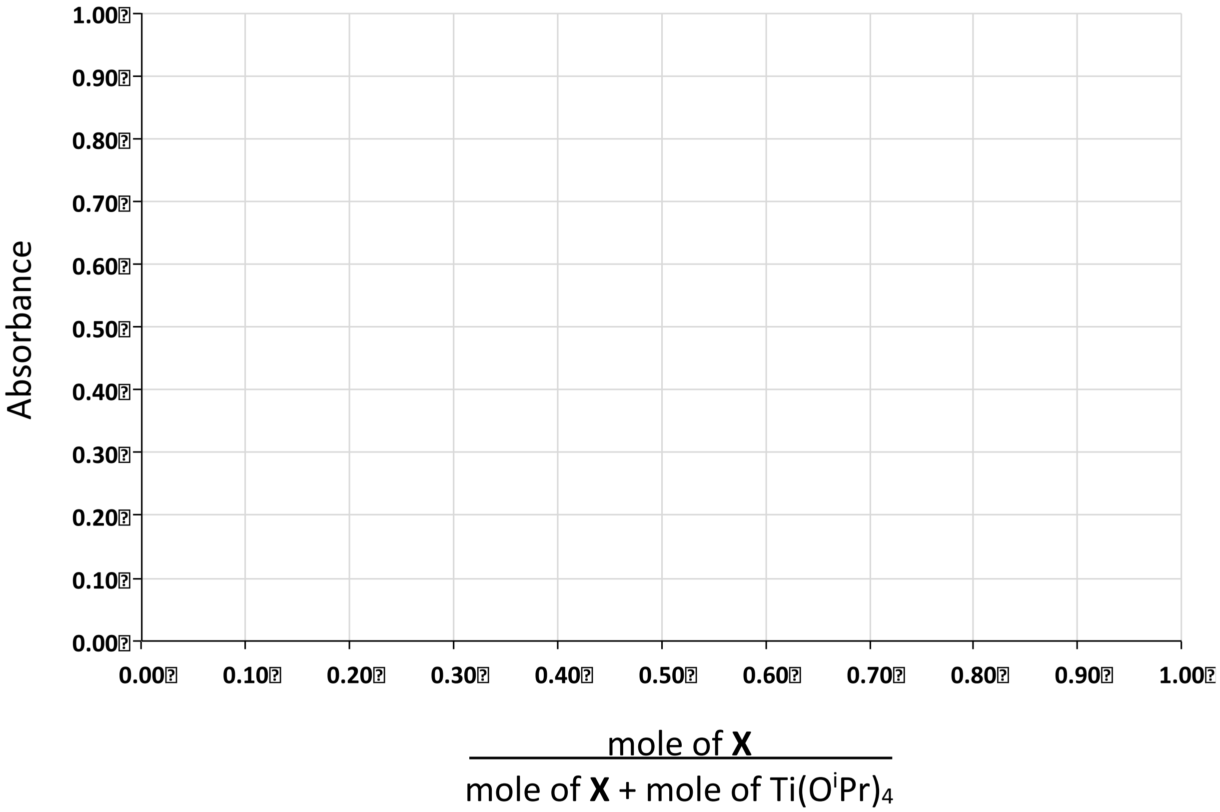
Volume of X (cm^3)	**Volume of $Ti(O^iPr)_4$ (cm^3)**	**Volume of benzene (cm^3)**	**Absorbance**
0	1.20	1.80	0.05
0.20	1.00	1.80	0.25
0.30	0.90	1.80	0.38
0.50	0.70	1.80	0.59
0.78	0.42	1.80	0.48
0.90	0.30	1.80	0.38
1.10	0.10	1.80	0.17
1.20	0	1.80	0.02

7-A3) Fill in appropriate values in the table provided below.

$\dfrac{\text{mole of } \mathbf{X}}{\text{mole of } \mathbf{X} + \text{mole of } Ti(O^iPr)_4}$	Absorbance
	0.05
	0.25
	0.38
	0.59
	0.48
	0.38
	0.17
	0.02

(2 digits after the decimal)

Plot a graph showing a relationship between $\dfrac{\text{mole of }\mathbf{X}}{\text{mole of }\mathbf{X}+\text{mole of Ti(O}^{i}\text{ Pr)}_4}$ and absorbance in the space provided below.



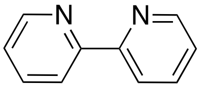
The value of $\dfrac{\text{mole of }\mathbf{X}}{\text{mole of }\mathbf{X}+\text{mole of Ti(O}^{i}\text{ Pr)}_4}$ which maximizes the amount of the product **Y** represents the stoichiometry of **X** in the chemical formula of **Y**. Based on the graph above, what is the molar ratio between Ti:**X** in the complex **Y**?

The molar ratio between Ti:**X** in the complex **Y** is ....

7-A4) The Ti complex **Y** is six-coordinated. The IR spectrum of **Y** does not contain a broad absorption band in the range of 3200–3600 cm^{-1}. **Y** exists as three diastereomers. Ignoring stereochemistry at N atoms, draw clearly the structures of all three diastereomers.

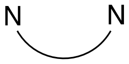
Note that you do not need to draw the complete structure of the ligand. Only identify donor atoms that involve in coordination with titanium and the ligand framework between the donor atoms can be drawn as follows:

For example:

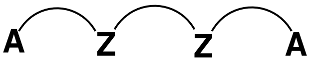


(2,2'-bipyridine)

can be drawn as:



If you did not get a structure of **X from **7-A2)**, use the following ligand symbol to represent **X** (**A** and **Z** are donor atoms):



Diastereomer 1:
Diastereomer 2:

Diastereomer 3:

7-A5) Under certain conditions, the reaction shown in **equation 1** affords only one diastereomer of **Y**. Given that structures of **Y** are "fixed" (no intramolecular movement), the ^{1}H NMR spectrum of **Y** in $CDCl_3$ shows four singlet resonances at δ 1.25, 1.30, 1.66, and 1.72 corresponding to the *tert*-butyl groups. Draw a structure of the only possible diastereomer of **Y**.

(You do not need to draw the complete structure of the ligand. Only identify donor atoms that involve in coordination and the ligand framework between the donor atoms can be drawn as shown in **7-A4)**)

Problem 7

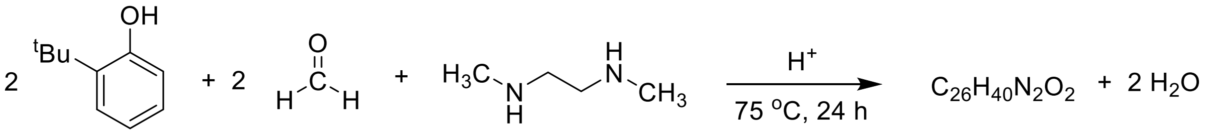
6% of the total

Problem 7	A					Total
	A1	**A2**	**A3**	**A4**	**A5**	
Total	4.5	1.5	6	6	2	20
Score						

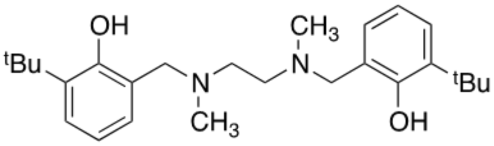
Problem 7: Chemical Structure Puzzles

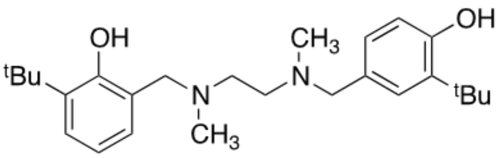
Titanium complexes have been investigated for their antitumor activity. Many factors including isomerism and sizes have shown to affect the potency of the complexes. This question deals with the synthesis and characterization of some titanium complexes.

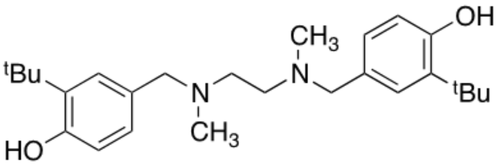
7-A1) A reaction of 2 equivalents of 2-*tert*-butylphenol, 2 equivalents of formaldehyde, and *N*,*N'*-dimethylethylene-1,2-diamine under acidic conditions at 75 °C affords three major products with the same chemical formula of $C_{26}H_{40}N_2O_2$, as shown in the equation below. Draw the structure of each product.



Ans


(*o*,*o*-substituted)


(*o*,*p*-substituted)


(*p*,*p*-substituted)

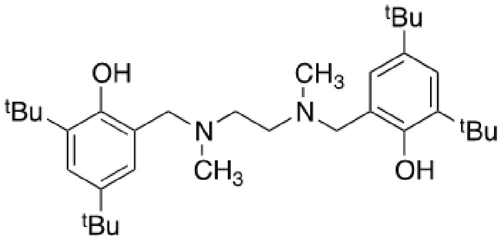
(4.5 points)

Score distribution: +1.5 points for each product

If phenolic OH is used as a nucleophile for the iminium ion, get 0.5 point.
Reasonable structures with missing Cs results in 0.25 deduction

7-A2) If 2,4-di-*tert*-butylphenol is used as a substrate instead of 2-*tert*-butylphenol using the same stoichiometry as that in **7-A1)**, only one product **X** was obtained. Draw the structure of **X**.

Ans



(1.5 points)

0 point for other isomers (meta-substitutions, etc.)

If 2,6-di-tert-butylphenol is drawn (with correct substitution), 0.25 deduction.

A reaction between **X** from **7-A2)** and $\mathrm{Ti(O^iPr)_4}$ [^{i}Pr = isopropyl] in diethyl ether under an inert atmosphere resulted in the six-coordinate Ti complex **Y**, as a yellow crystalline solid and isopropanol at room temperature.

$$a\,\mathbf{X} + b\,\mathrm{Ti(O^iPr)_4} \xrightarrow{\mathrm{Et_2O}} d\,\mathbf{Y} + c\,{}^{i}\mathrm{PrOH} \qquad \textbf{(equation 1)}$$

UV-Vis spectra of **X**, $\mathrm{Ti(O^iPr)_4}$, and **Y** reveal that only the product **Y** has an absorption at λ = 370 nm. By varying the volumes of **X** and $\mathrm{Ti(O^iPr)_4}$, each with the concentration of 0.50 mol $\mathrm{dm^{-3}}$, and using benzene as the solvent, the absorbance data at λ = 370 nm are given below:

Volume of X ($\mathrm{cm^3}$)	**Volume of $\mathrm{Ti(O^iPr)_4}$ ($\mathrm{cm^3}$)**	**Volume of benzene ($\mathrm{cm^3}$)**	**Absorbance**
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0.20	1.00	1.80	0.25
0.30	0.90	1.80	0.38
0.50	0.70	1.80	0.59
0.78	0.42	1.80	0.48
0.90	0.30	1.80	0.38
1.10	0.10	1.80	0.17
1.20	0	1.80	0.02

7-A3) Fill in appropriate values in the table provided below.

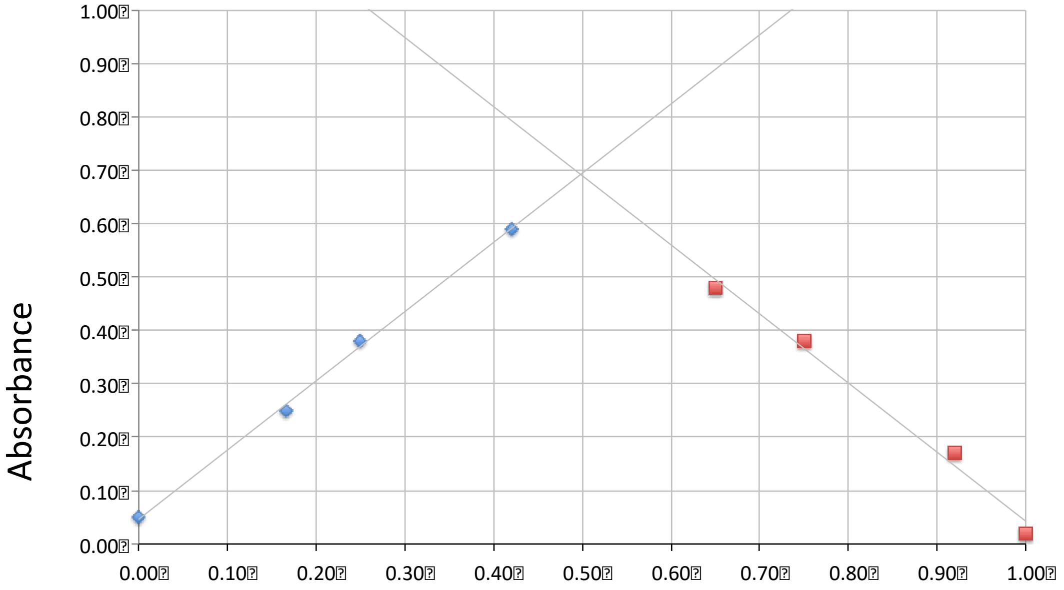
$\dfrac{\text{mole of }\mathbf{X}}{\text{mole of }\mathbf{X} + \text{mole of Ti(O}^{i}\,\text{Pr)}_4}$	Absorbance
0	0.05
0.17	0.25
0.25	0.38
0.42	0.59
0.65	0.48
0.75	0.38
0.92	0.17
1.00	0.02

(2 digits after the decimal)

(0.25 points for each correct value in the left column)

Plot a graph showing a relationship between $\dfrac{\text{mole of }\mathbf{X}}{\text{mole of }\mathbf{X} + \text{mole of Ti(O}^{i}\,\text{Pr)}_4}$ and absorbance in the space provided below.

Ans



$$\frac{\text{mole of } \mathbf{X}}{\text{mole of } \mathbf{X} + \text{mole of Ti(O}^{i}\text{Pr)}_4}$$

(0.25 point for each data)

The trendlines are not considered for scoring.

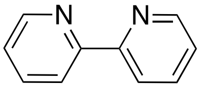
The value of $\frac{\text{mole of } \mathbf{X}}{\text{mole of } \mathbf{X} + \text{mole of Ti(O}^{i}\text{Pr)}_4}$ which maximizes the amount of the product **Y** represents the stoichiometry of **X** in the chemical formula of **Y**. Based on the graph above, what is the molar ratio between Ti:**X** in the complex **Y**?

*The molar ratio between Ti:**X** in the complex **Y** is ....1:1........or 1............................*
(2 points for the ratio)
1 point for the correct answer without the graph
If the ratio is >1.2 or <0.8 (0 point)
***Note:** Based on the given data, the turning point in Job's plot occurs at mole fraction of **X** ~ 0.5. As a result, we conclude that the product has the ratio of Ti:**X** = 1:1.*

7-A4) The Ti complex **Y** is six-coordinated. The IR spectrum of **Y** does not contain a broad absorption band in the range of 3200–3600 cm^{-1}. **Y** exists as three diastereomers. Ignoring stereochemistry at N atoms, draw clearly the structures of all three diastereomers.

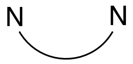
Note that you do not need to draw the complete structure of the ligand. Only identify donor atoms that involve in coordination with titanium and the ligand framework between the donor atoms can be drawn as follows:

For example:

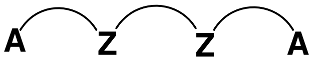


(2,2'-bipyridine)

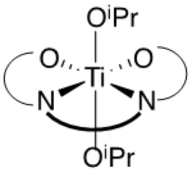
can be drawn as:



If you did not get a structure of **X from **7-A2)**, use the following ligand symbol to represent **X** (**A** and **Z** are donor atoms):

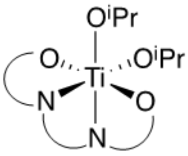


Ans



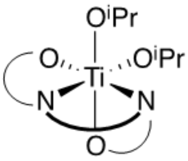
trans(O^{i}Pr,O^{i}Pr)

A



cis(O^{i}Pr,O^{i}Pr)
trans(O,O)

B



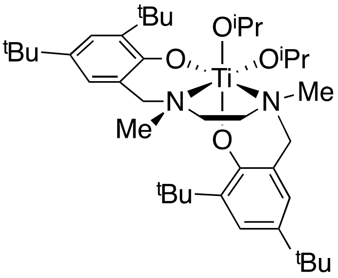
cis(O^{i}Pr,O^{i}Pr)
cis(O,O)

C

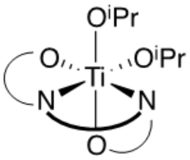
(6 points)
Score distribution: 1.5 points for each isomer
1.5 points if the proposed structures do have three possible diastereomers.
Bidentate ligands will not be considered for partial credits.
Any O-H functional groups in the structure will get 0.25 point deduction.
Without any reasonable monodentate ligands, 0.25 point deduction.

7-A5) Under certain conditions, the reaction shown in **equation 1** affords only one diastereomer of **Y**. Given that structures of **Y** are "fixed" (no intramolecular movement), the ^{1}H NMR spectrum of **Y** in $CDCl_3$ shows four singlet resonances at δ 1.25, 1.30, 1.66, and 1.72 corresponding to the *tert*-butyl groups. Draw a structure of the only possible diastereomer of **Y**.

(You do not need to draw the complete structure of the ligand. Only identify donor atoms that involve in coordination and the ligand framework between the donor atoms can be drawn as shown in **7-A4)**)



or



cis(OiPr,OiPr)
cis(O,O)

(2 points)
Only six-coordinated structures featuring tert-butyl groups in the chelate ligand structure will be considered for any credits.

Note for mentors: *The ^{1}H NMR spectra of isomers **A** and **B** contain two resonances assignable to the tert-butyl groups.*

Problem 8

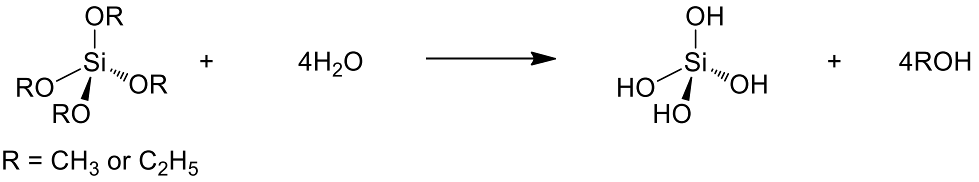
5% of the total

Problem 8	A					Total
	A1	A2	A3	A4	A5	
Total	6	5.5	3	4	1.5	20
Score						

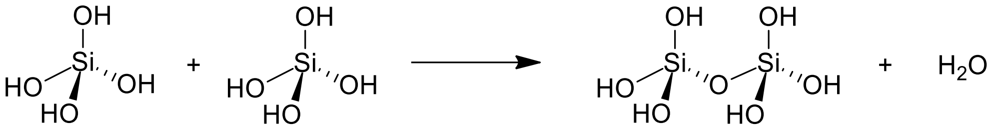
Problem 8: Silica Surface

Silica exists in various forms like amorphous and crystalline. Silica can be synthesized *via* sol-gel process by using silicon alkoxides like tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) as the details below:

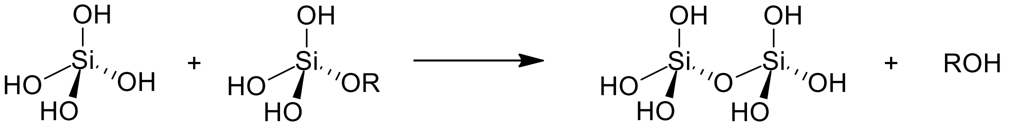
a. Hydrolysis

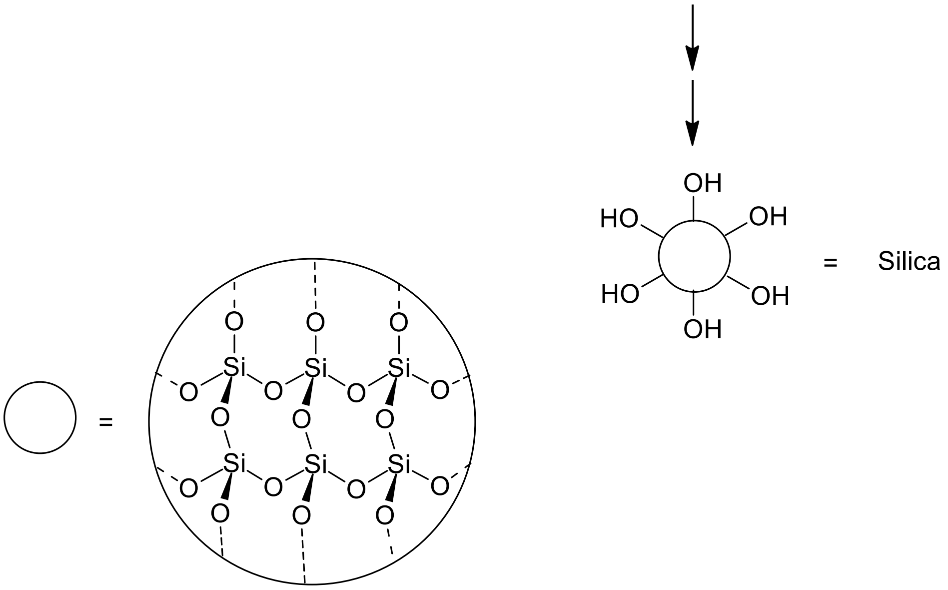


b. Water condensation

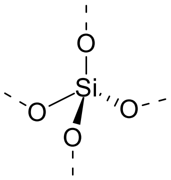


c. Alcohol condensation



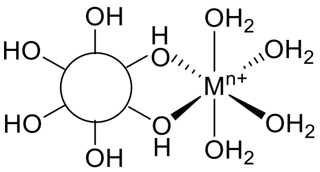


In bulk silica, all silicon atoms are tetrahedrally bonded to four oxygen atoms giving three-dimensional solid network. The silicon environments found inside silica is presented below:

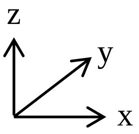


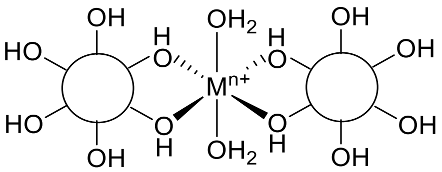
8-A1) Three silicon atom environments (similar to the example above) are commonly observed at the silica **surface**. The three structures of the silicon environments must be **drawn** in the provided boxes.

Silica can be used as an effective metal ion adsorbent in water. The proposed structure for metal-silica complex is as follows:



I





II

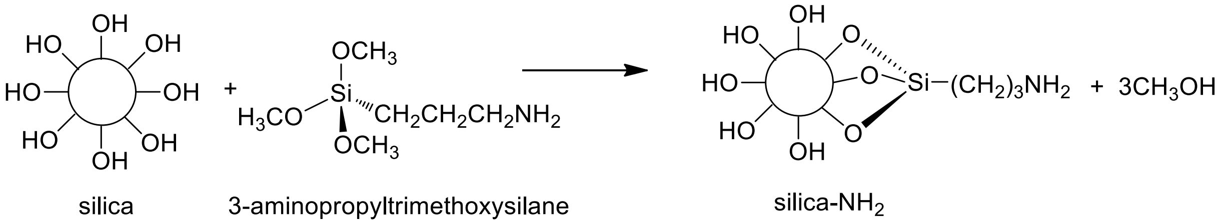
8-A2) After Cu^{2+} is being adsorbed, the color of silica changes from white to pale blue. The visible spectrum shows a broad absorption band (with a shoulder) at $\lambda_{max} = 550$ nm. If Cu^{2+} can bind with silica and adopt the structure similar to **II**, draw the splitting diagram of the *d*-orbitals of Cu^{2+} ion including the label of the *d* orbitals in the complex and **specify** the corresponding electronic transition(s) for the visible absorption.

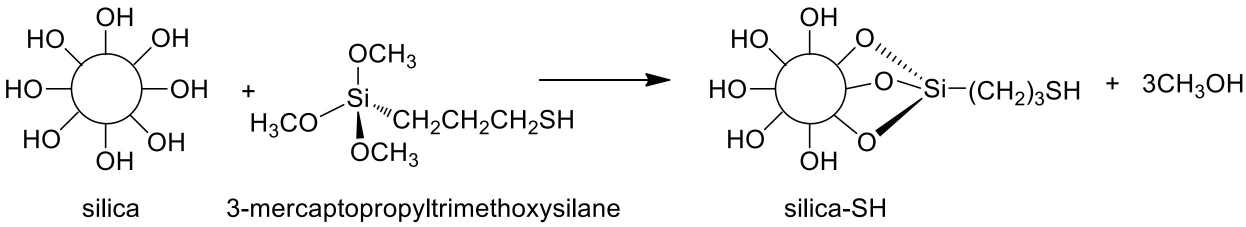
The splitting diagram:

The corresponding electronic transition(s) (indicate the lower energy *d*-orbital and higher energy *d*-orbital)

8-A3) If the first row transition metal ions form complexes with silica analogous to Cu^{2+}, which metal ion(s) do(es) have the analogous to electronic transition(s) to Cu^{2+}? The metal ion(s) must be in +2 or +3 oxidation state. Please note that the silanol groups (Si-OH) and water are weak field ligands.

However, silica is randomly bonded to various types of metal ion. To increase the selectivity, modification of silica surface has been performed by grafting with various organic molecules like 3-aminopropyltrimethoxysilane and 3-mercaptopropyltrimethoxysilane.





8-A4) If Hg^{2+} is only bonding to sulfur binding sites in silica-SH, the **symmetric** complex of $[Hg(silica\text{-}SH)_2]^{2+}$ is formed. Draw the structure of $[Hg(silica\text{-}SH)_2]^{2+}$, specify the direction of the bond axes, and draw the corresponding *d*-orbital splitting. (You may use R-SH instead of drawing the whole structure of silica-SH.)

The structure:

d-orbital splitting diagram :

8-A5) Specify true or false for the following statements:

a) *d-d* transition is found in $[(Hg(silica\text{-}SH)_x)]^{2+}$

☐ True ☐ False

b) The $[Cu(silica\text{-}NH_2)_x]^{2+}$ in a similar geometry, is expected to have a color similar to other copper(II) amine complexes.

☐ True ☐ False

c) In the visible absorption spectra, λ_{max} of $[Cu(silica\text{-}NH_2)_x]^{2+}$ is greater than that of $[Cu(silica\text{-}OH)_x]^{2+}$.

☐ True ☐ False

Problem 8

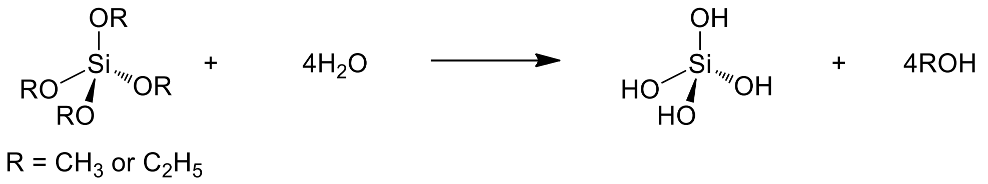
5% of the total

Problem 8	A					Total
	A1	A2	A3	A4	A5	
Total	6	5.5	3	4	1.5	20
Score						

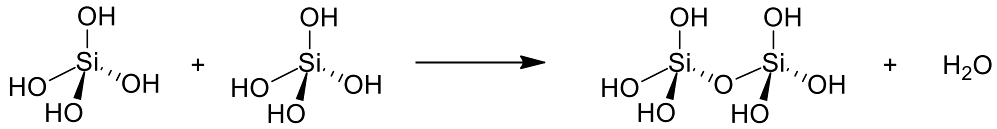
Problem 8: Silica Surface

Silica exists in various forms like amorphous and crystalline. Silica can be synthesized *via* sol-gel process by using silicon alkoxides like tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) as the details below:

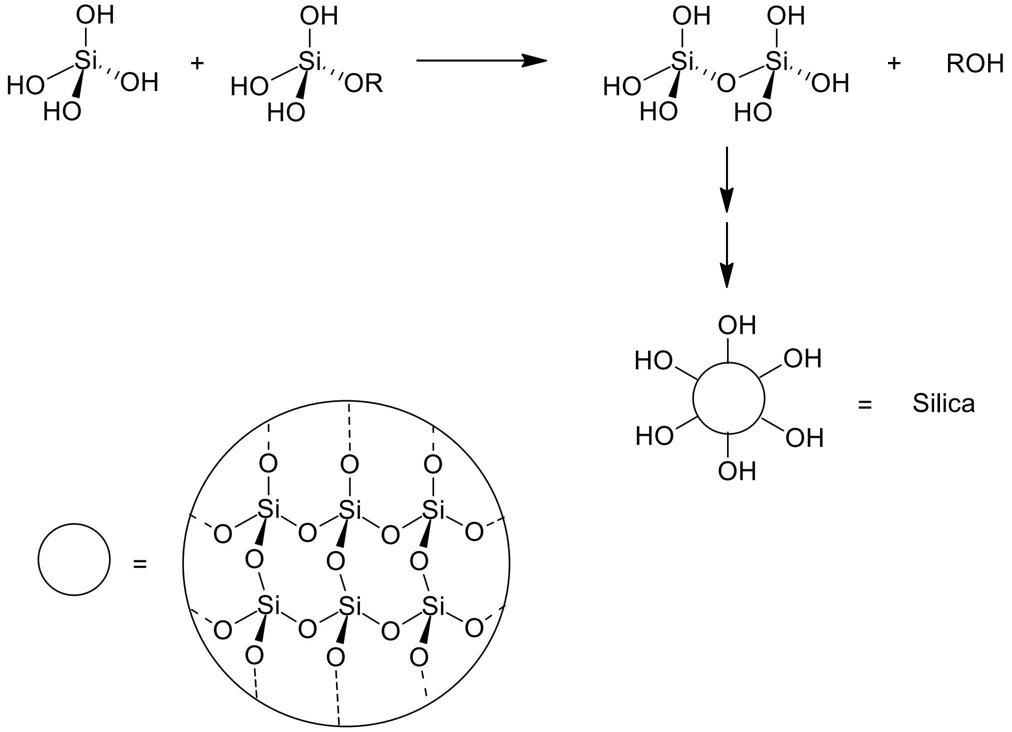
a. Hydrolysis



b. Water condensation



c. Alcohol condensation



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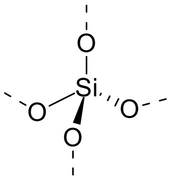
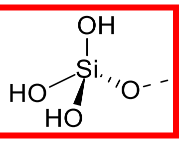


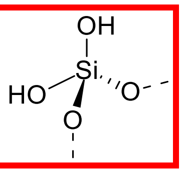
8-A1) Three silicon atom environments (similar to the example above) are commonly observed at the silica **surface**. The three structures of the silicon environments must be **drawn** in the provided boxes.

Answer *(total = 6 points)*

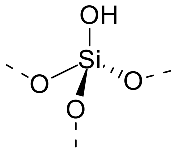
Q1 =



Q2 =



Q3 =



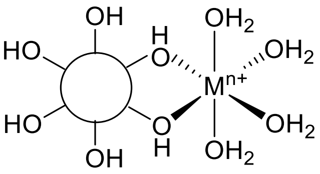
Marking scheme

Draw 1 structure => 2 points

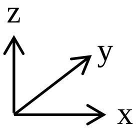
Draw 2 structures => 4 points

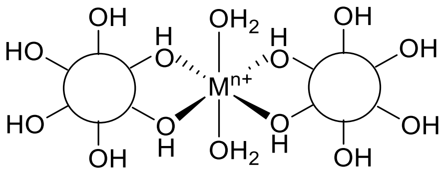
Draw 3 structures => 6 points

Silica can be used as an effective metal ion adsorbent in water. The proposed structure for metal-silica complex is as follows:



I





II

8-A2) After Cu^{2+} is being adsorbed, the color of silica changes from white to pale blue. The visible spectrum shows a broad absorption band (with a shoulder) at λ_{max} = 550 nm. If Cu^{2+} can bind with silica and adopt the structure similar to **II**, draw the splitting diagram of the *d*-orbitals of Cu^{2+} ion including the label of the *d* orbitals in the complex and **specify** the corresponding electronic transition(s) for the visible absorption.

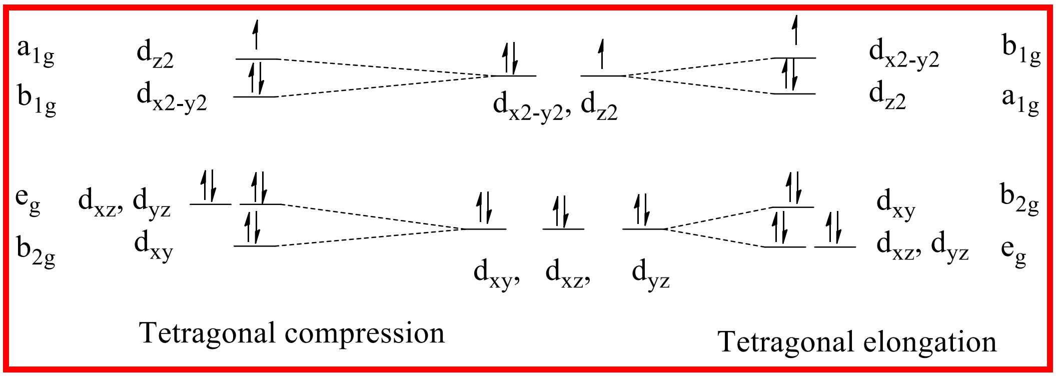
The splitting diagram:

The corresponding electronic transition(s) (indicate the lower energy *d*-orbital and higher energy *d*-orbital)

Answer (total = 5.5 points)

Cu^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

Cu^{2+}-complex → tetragonal distortion → Tetragonal elongation or tetragonal compression



Electronic Transition:

1. Tetragonal compression: d_{xy} → d_{z2} and d_{xz} , d_{yz} → d_{z2}
2. Tetragonal elongation: d_{xz} , d_{yz} → d_{x2-y2} and d_{xy} → d_{x2-y2}

Marking scheme

Draw one splitting diagram with d-orbital label; tetragonal compression or tetragonal elongation => 3.5 points

Specify the correct electronic transitions according to the drawn diagram => 2 points

For partial credits:

- The label of certain d-orbital is missing => 0.5 point is deleted for each missing d-orbital label

- Draw a regular octahedral field splitting with d-orbital label => 1.5 points and specify the corresponding electronic transition => 0.5 point

- *Only the splitting diagram without d-orbital label => 0 point*
- *Write the third electronic transition => -0.5 point*

8-A3) If the first row transition metal ions form complexes with silica analogous to Cu^{2+}, which metal ion(s) do(es) have the analogous to electronic transition(s) to Cu^{2+}? The metal ion(s) must be in +2 or +3 oxidation state. Please note that the silanol groups (Si-OH) and water are weak field ligands.

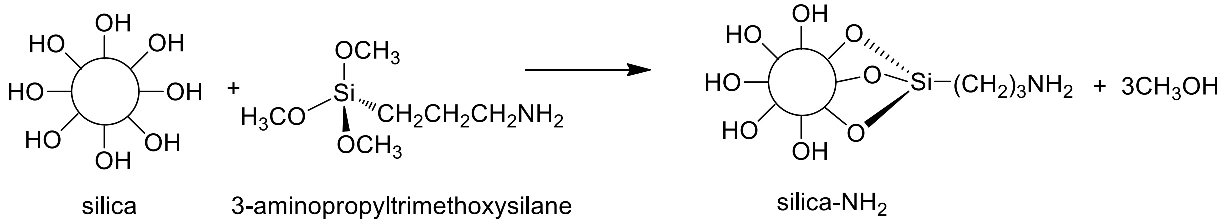
Answer (total = 3 points)

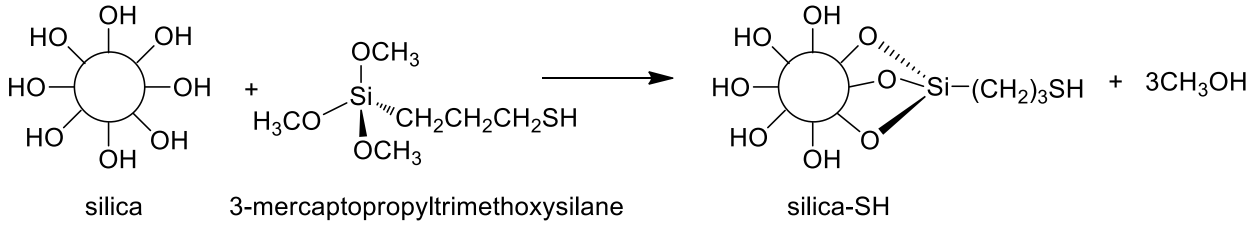
Cr^{2+}, Mn^{3+}

(1.5 point for each metal ion)

(the extra incorrect metal ion => -0.5 each)

However, silica is randomly bonded to various types of metal ion. To increase the selectivity, modification of silica surface has been performed by grafting with various organic molecules like 3-aminopropyltrimethoxysilane and 3-mercaptopropyltrimethoxysilane.





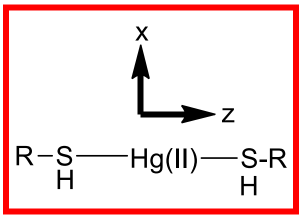
8-A4) If Hg^{2+} is only bonding to sulfur binding sites in silica-SH, the **symmetric** complex of $[Hg(\text{silica-SH})_2]^{2+}$ is formed. Draw the structure of $[Hg(\text{silica-SH})_2]^{2+}$, specify the direction of the bond axes, and draw the corresponding *d*-orbital splitting. (You may use R-SH instead of drawing the whole structure of silica-SH.)

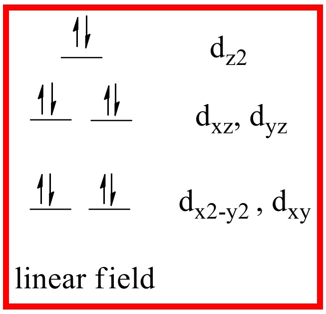
The structure:

d-orbital splitting diagram :

Answer (total = 4 points)

Linear structure:





Marking scheme

Draw the correct structure => 1 point

Draw the correct d-orbital splitting diagram (no need to fill in the electrons)- corresponding to the specified axes =>0.5 point for the axes

=>2.5 points for the diagram

For partial credits:

- Draw the correct structure without axes but possible splitting diagram => 1+2 points

- Draw the correct structure with wrong axes but possible splitting diagram => 1+2 points

8-A5) Specify true or false for the following statements:

a) *d-d* transition is found in $[(Hg(silica\text{-}SH)_x)]^{2+}$

☐ True ☐ False

b) The $[Cu(silica\text{-}NH_2)_x]^{2+}$ in a similar geometry, is expected to have a color similar to other copper(II) amine complexes.

☐ True ☐ False

c) In the visible absorption spectra, λ_{max} of $[Cu(silica\text{-}NH_2)_x]^{2+}$ is greater than that of $[Cu(silica\text{-}OH)_x]^{2+}$.

☐ True ☐ False

Answer (total = 1.5 points)

a) *d-d* transition is found in silica-SH-Hg^{2+}.

☐ True ☑ False

Explanation : Hg^{2+} is a d^{10}- metal ion in which *d-d* transition is **not** found.

b) The $[(Cu(silica\text{-}NH_2)_x]^{2+}$ is expected to have a color similar to other copper(II) amine complexes.

☑ True ☐ False

Explanation : Various copper amine complexes like $[Cu(en)(H_2O)_4]^{2+}$, $[Cu(en)_2(H_2O)_2]^{2+}$ and $[Cu(en)_3]^{2+}$ have deep blue color. $[(Cu(silica\text{-}NH_2)_x]^{2+}$ containing similar ligands to these copper complexes is expected to have a similar color.

c) In the visible absorption spectra, λ_{max} of $[(Cu(silica\text{-}NH_2)_x]^{2+}$ is greater than that of $[(Cu(silica\text{-}OH)_x]^{2+}$.

☐ True ☑ False

Explanation : R-NH_2 is **a stronger** field ligand as compared to R-OH. This results in a larger energy gap or a smaller λ_{max} of $[(Cu(silica\text{-}NH_2)_x]^{2+}$ as compared to that of $[(Cu(silica\text{-}OH)_x]^{2+}$.

Marking scheme

0.5 point for each correct answer

Theoretical Problem 5 8% of the total	Question	5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	5.9
	Points	3	3	1	5	3	2	4	1	2
	Score									
	Question	5.10	5.11	5.12	5.13	5.14	5.15	5.16	5.17	**Total**
	Points	5	7	3	2	6	1	1	1	**50**
	Score									

Problem 5. Bohemian garnet

Bohemian garnet (pyrope) is a famous Czech blood-coloured semi-precious stone. The chemical composition of natural garnets is expressed by the general stoichiometric formula of $A_3B_2(SiO_4)_3$, where A^{II} is a divalent cation and B^{III} is a trivalent cation. Garnets have a cubic unit cell that contains 8 formula units. The structure comprises 3 types of polyhedra: the A^{II} cation occupies a dodecahedral position (it is surrounded by eight O atoms), the B^{III} cation occupies an octahedral position (it is surrounded by six O atoms) and Si^{IV} is surrounded by four O atoms arranged into a tetrahedron.

The most common garnet mineral is almandine with the formula of $Fe_3Al_2(SiO_4)_3$. Its unit cell parameter is a = 11.50 Å.

5.1 Calculate the theoretical density of almandine.

ρ = g cm^{-3}

The Bohemian garnet has the composition of $Mg_3Al_2(SiO_4)_3$. The pure compound is colourless and the colour of natural garnets comes from chromophores – transition metal cations that substitute the host material cations. The red colour of the Bohemian garnet comes from trace amounts of Cr^{III} ions in the octahedral sites and Fe^{II} ions in the dodecahedral sites.

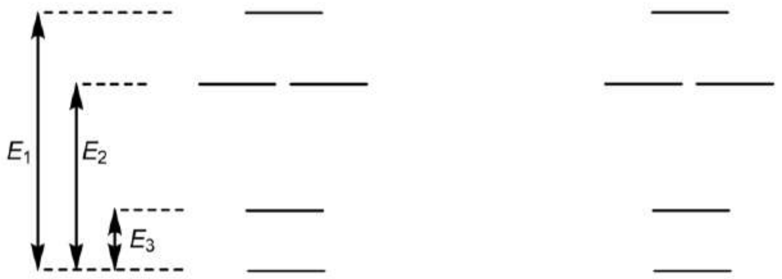
5.2 Draw the splitting diagram for the $[Cr^{III}O_6]^{oct}$ d-orbitals and fill it with electrons.

5.3 Identify the 1st transition row element(s) whose trivalent cation(s) M^{III} placed in an **octahedral** position is/are diamagnetic in the low-spin arrangement and paramagnetic in the high-spin arrangement.

5.4 The figure below shows d-orbital splitting in a dodecahedral crystal field. Fill in the electrons for the $[Fe^{II}O_8]^{dod}$ chromophore for both existing arrangements.

a) high-spin arrangement

b) low-spin arrangement



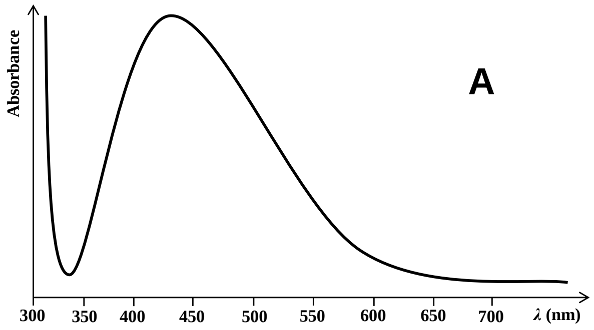
5.5 Derive inequalities (e.g. $P < E_1 + E_2 + E_3$) for the pairing energy (P) magnitude in relation to energies E_1, E_2 and E_3 for both arrangements.

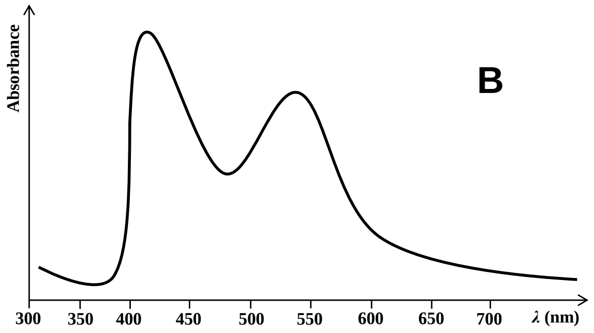
a) high-spin arrangement: P

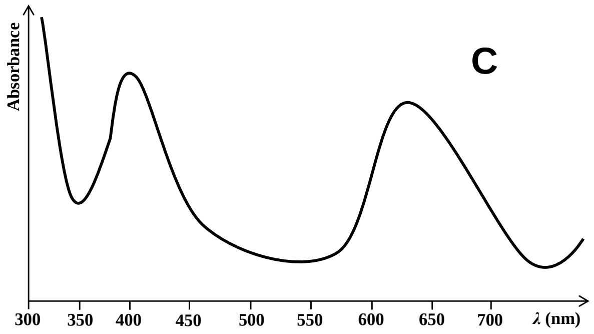
b) low-spin arrangement: P

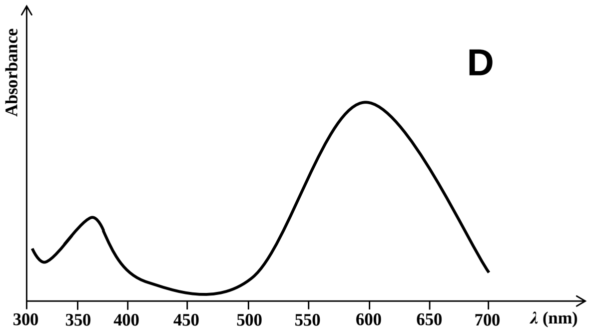
5.6 Assuming that $P > E_3$, identify the 1st transition row element(s) whose divalent cation M^{II} placed in dodecahedral position is diamagnetic in the low-spin arrangement and paramagnetic in the high-spin arrangement.

The figures below show simplified absorption spectra of four coloured minerals – blood-coloured Bohemian garnet, green uvarovite, blue sapphire and yellow-orange citrine.









5.7 Match the spectra with the minerals.

Bohemian garnet:	Sapphire:
Uvarovite:	Citrine:

5.8 If illuminated with monochromatic blue-green light, how will the Bohemian garnet appear?

☐ Red
☐ Yellow
☐ Blue
☐ Blue-green
☐ Yellow-orange
☐ Violet
☐ Black
☐ White

Andradite is another garnet mineral; its chemical composition is $Ca_3Fe_2(SiO_4)_3$. A double cation substitution – Ti^{IV} for Fe^{III} in the octahedral position and Fe^{III} for Si^{IV} in the tetrahedral position – gives rise to black schorlomite. Its chemical composition can be expressed as $Ca_3[Fe,Ti]_2^{oct}([Si,Fe]^{tet}O_4)_3$.

5.9 Calculate the percentage of Si^{IV} ions in a sample of schorlomite that must be substituted with Fe^{III}, if we know that 5% of Fe^{III} ions in octahedral position are substituted with Ti^{IV}.

p = %

The colour of the mineral is caused by two chromophores: $[Fe^{III}O_6]^{oct}$ and $[Fe^{III}O_4]^{tet}$. The central ions of both chromophores have equal number of unpaired electrons.

5.10 Draw the d-orbital splitting diagrams for both chromophores and fill in the electrons.

$[Fe^{III}O_6]^{oct}$: $[Fe^{III}O_4]^{tet}$:

A tetrahedral field causes a smaller splitting than the octahedral field ($\Delta_{tet} = \frac{4}{9}\,\Delta_{oct}$). Surprisingly for the Fe^{III} ion, the energy of the first d–d transition (although very weak) for the octahedral chromophore is smaller (11 000 cm^{-1}) than for the tetrahedral one (22 000 cm^{-1}).

5.11 Calculate the size of pairing energy (*P*) and the sizes of Δ_{oct} and Δ_{tet} splitting. Assume that the pairing energy is equal in both chromophores.

$P =$ cm^{-1}

$\Delta_{oct} =$ cm^{-1}

$\Delta_{tet} =$ cm^{-1}

Synthetic garnet YAG (Yttrium-Aluminium-Garnet), used in optoelectronics, has the composition $Y_3Al_5O_{12}$. Its structure is derived from the general garnet structure $A_3B_2(SiO_4)_3$ by placing the ions Y^{III} and Al^{III} to the A, B and Si positions.

5.12 Based on your knowledge of the relative ion radii, determine which cation occupies which position.

A: B: Si:

5.13 For the use in LED technology, YAG is doped with Ce^{III}. Determine the values of x and y in the formula of YAG in which 5% of yttrium atoms are substituted with cerium.

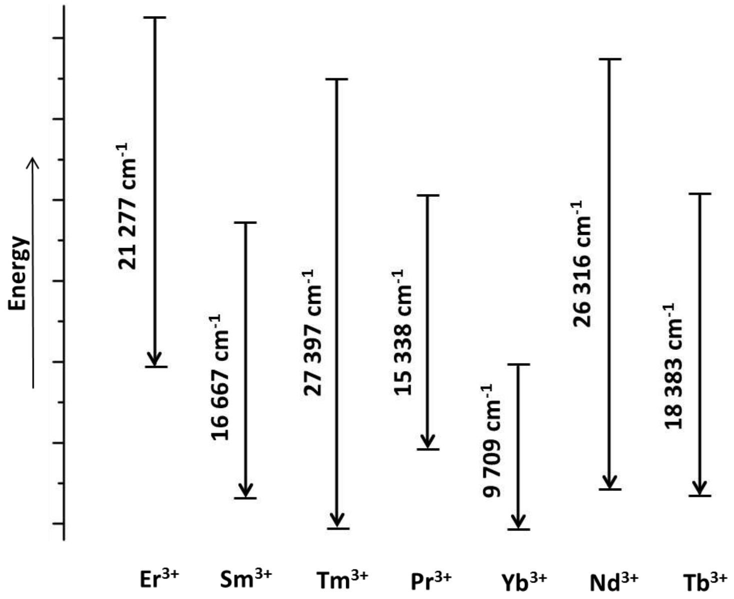
$Y_xCe_yAl_5O_{12}$

x = y =

If you are unable to determine x and y, use $x = 2.25$ and $y = 0.75$ in further calculations.

5.14 The Ce^{III}-doped YAG is prepared by annealing the mixture of Y_2O_3, Al_2O_3 and CeO_2 in an H_2 atmosphere. Use the formula from 5.13, write down a balanced equation for this reaction with the smallest whole-number stoichiometric coefficients.

Doping the YAG structure with rare-earth ions enables the production of lasers with emission wavelengths ranging from the UV to the mid-IR region. In the scheme below, simplified f–f energy transitions of selected rare-earth ions are shown.



5.15 Which cation has a transition which corresponds to blue light emission.

☐ Er^{3+}
☐ Yb^{3+}
☐ Sm^{3+}
☐ Nd^{3+}
☐ Tm^{3+}
☐ Tb^{3+}
☐ Pr^{3+}

5.16 Calculate the emission wavelength of this light.

λ = nm

5.17 According to a legend, Noah used a stick with a garnet stone for illumination during his voyage. Assuming only the photoluminescence effect, determine the colour of the laser light emitted from his stick if the stone were the blood-coloured Bohemian garnet.

☐ Red
☐ Yellow
☐ Blue
☐ Blue-green
☐ Yellow-orange
☐ Violet
☐ Black
☐ White

Theoretical Problem 5 8% of the total	Question	5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	5.9
	Points	3	3	1	5	3	2	4	1	2
	Score									
	Question	5.10	5.11	5.12	5.13	5.14	5.15	5.16	5.17	**Total**
	Points	5	7	3	2	6	1	1	1	**50**
	Score									

Problem 5. Bohemian garnet

Bohemian garnet (pyrope) is a famous Czech blood coloured semi-precious stone. The chemical composition of natural garnets is expressed by the general stoichiometric formula of $A_3B_2(SiO_4)_3$, where A^{II} is a divalent cation and B^{III} is a trivalent cation. Garnets have a cubic unit cell that contains 8 formula units. The structure comprises 3 types of polyhedra: the A^{II} cation occupies a dodecahedral position (it is surrounded with eight O atoms), the B^{III} cation occupies an octahedral position (it is surrounded with six O atoms) and Si^{IV} is surrounded with four O atoms arranged into a tetrahedron.

The most common garnet mineral is almandine with the formula of $Fe_3Al_2(SiO_4)_3$. Its unit cell parameter is a = 11.50 Å.

5.1 Calculate the theoretical density of almandine.

$M(\text{almandine}) = 497.75\ \text{g mol}^{-1}$

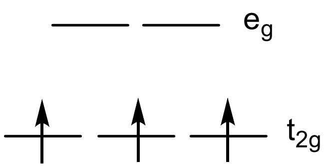
$\rho = m / V = (8 \times M) / (N_A \times a^3) = (8 \times 497.75) / [6.022 \times 10^{23} \times (11.50 \times 10^{-8})^3] = 4.35\ \text{g cm}^{-3}$

3 points in total
correct molar mass 1 point, correct equation 1 point, correct numerical calculation starting from correct equation 1 point

The Bohemian garnet has the composition of $Mg_3Al_2(SiO_4)_3$. Pure compound is colourless and the colour of natural garnets comes from chromophores – transition metal cations that substitute the host material cations. The red colour of the Bohemian garnet comes from trace amounts of Cr^{III} ions in the octahedral sites and Fe^{II} ions in the dodecahedral sites.

5.2 Draw the splitting diagram for the $[Cr^{III}O_6]^{oct}$ d-orbitals and fill it with electrons.

Splitting diagram – configuration d^3:



3 points in total
correct orbital splitting 1 point, correct number of electrons 1 point, correct configuration according

to Hund's rule 1 point, −1 point if only a line not indicating the electron spin is used (deducted only once per Problem); orbital marking is not evaluated

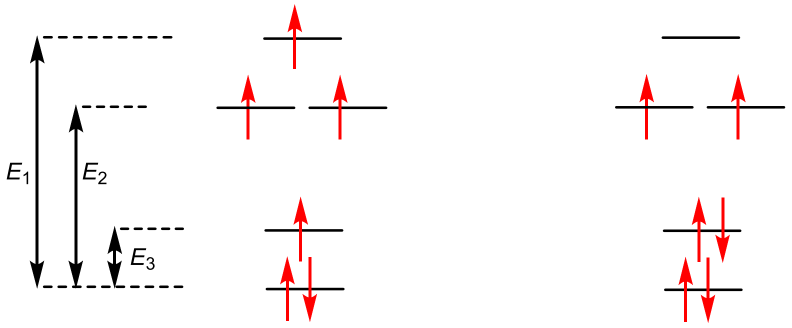
5.3 Identify the 1st transition row element(s) whose trivalent cation(s) M^{III} placed in an **octahedral** position is/are diamagnetic in the low-spin arrangement and paramagnetic in the high-spin arrangement.

Co

1 point
correct answer 1 point, incorrect answer −1 point, minimum 0 points (the score may not be negative)

5.4 The figure below shows d-orbitals splitting in the dodecahedral crystal field. Fill in the electrons for the $[Fe^{II}O_8]^{dod}$ chromophore for both existing arrangements.

a) high-spin arrangement b) low-spin arrangement



5 points in total
correct number of electrons 1 point, correct high-spin configuration 2 points, correct low-spin configuration 2 points (any other configuration 0 points: high spin and low spin configurations differ in total spin. Any other configurations do not fulfil this condition.)
If incorrect number of electrons is considered, then the correctness of such a configuration is taken into account.

5.5 Derive the inequalities (e.g. $P < E_1 + E_2 + E_3$) for the pairing energy (P) magnitude in relation to energies E_1, E_2 and E_3 for both arrangements.

a) high-spin arrangement: $P > E_1 - E_3$
b) low-spin arrangement: $P < E_1 - E_3$

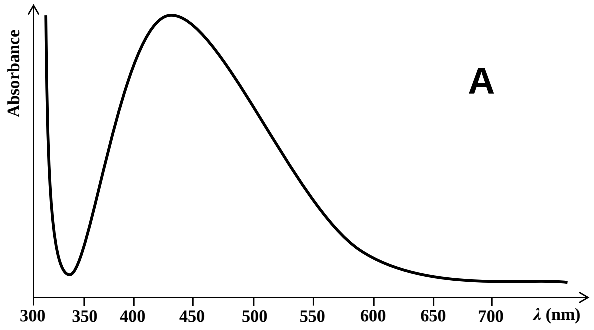
3 points in total
correct BOTH inequality signs 1 point (half-points are not allowed), correct right-side terms (according to the answer in 5.4) 1 + 1 points

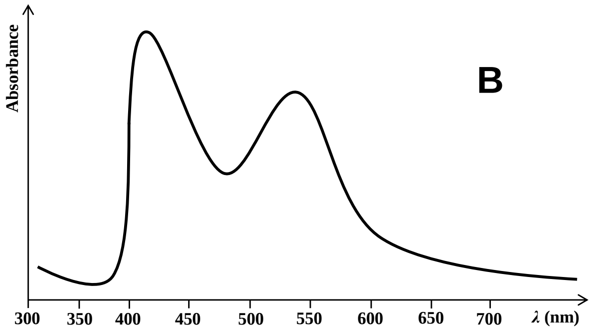
5.6 Assuming that $P > E_3$, identify the 1st transition row element(s) whose divalent cation M^{II} placed in dodecahedral position is diamagnetic in the low-spin arrangement and paramagnetic in the high-spin arrangement.

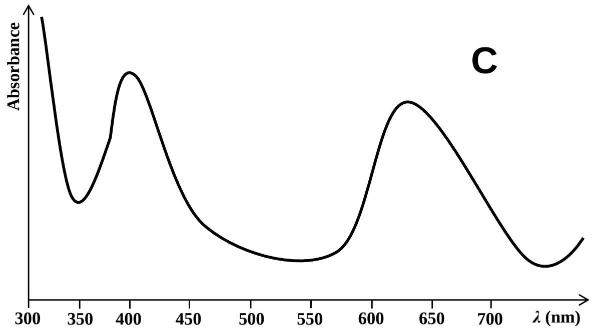
Cr, Ni

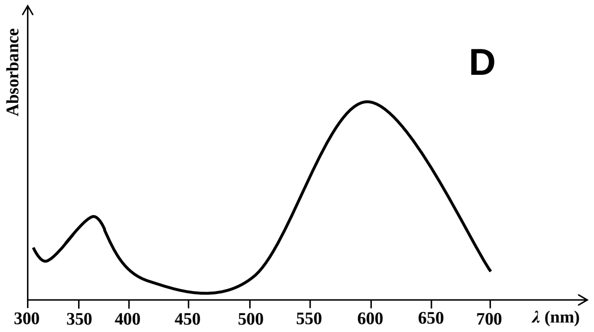
2 points
each correct metal 1 point, each incorrect metal −1 point, minimum 0 points (the score may not be negative)

The figures below show simplified absorption spectra of four coloured minerals – blood-coloured Bohemian garnet, green uvarovite, blue sapphire and yellow-orange citrine.









5.7 Match the spectra with the minerals.

Bohemian garnet: **B**
Uvarovite: **C**
Sapphire: **D**
Citrine: **A**

4 points in total, each correct assignment 1 point

5.8 If illuminated with monochromatic blue-green light, how will the Bohemian garnet look?

☐ Red
☐ Yellow
☐ Blue
☐ Blue-green
☐ Yellow-orange
☐ Violet
☒ Black
☐ White

1 point

Andradite is another garnet mineral; its chemical composition is $Ca_3Fe_2(SiO_4)_3$. A double cation substitution – Ti^{IV} for Fe^{III} in the octahedral position and Fe^{III} for Si^{IV} in the tetrahedral position – gives rise to black schorlomite. Its chemical composition can be expressed as $Ca_3[Fe,Ti]_2^{oct}([Si,Fe]^{tet}O_4)_3$.

5.9 Calculate the percentage of Si^{IV} ions in a sample of schorlomite that must be substituted with Fe^{III}, if we know that 5% of Fe^{III} ions in octahedral position are substituted with Ti^{IV}.

Both substitutions change the charge by 1 unit per ion. Taking total number of ions in formula into consideration we get:

$5\% \times 2 = p \times 3$

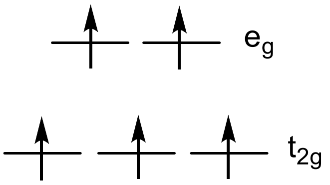
$p = 3.33\ \%$

2 points
correct starting consideration in the form of an equation 1 point, correct numerical calculation 1 point

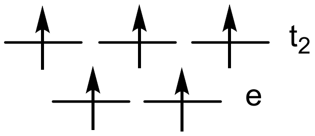
The colour of the mineral is caused by two chromophores: $[Fe^{III}O_6]^{oct}$ and $[Fe^{III}O_4]^{tet}$. The central ions of both chromophores have equal number of unpaired electrons.

5.10 Draw the d-orbitals splitting diagrams for both chromophores and fill in the electrons.

$[Fe^{III}O_6]^{oct}$:



$[Fe^{III}O_4]^{tet}$:



5 points in total
correct octahedral splitting 1 point, correct tetrahedral splitting 1 point, correct number of electrons 1 point, correct high-spin configurations 1 + 1 points; orbital marking is not evaluated.

Tetrahedral field causes a smaller splitting than the octahedral field ($\Delta_{tet} = \frac{4}{9}\Delta_{oct}$). Surprisingly for the Fe^{III} ion, the energy of the first d–d transition (although very weak) for the octahedral chromophore is smaller ($11\,000\ cm^{-1}$) than for the tetrahedral one ($22\,000\ cm^{-1}$).

5.11 Calculate the size of pairing energy (P) and the sizes of Δ_{oct} and Δ_{tet} splitting. Assume that the pairing energy is equal in both chromophores.

Because $\Delta_{oct} < P$ (high-spin configuration in tetrahedral as well as in octahedral field), the wavenumber corresponds to electron transition from the upper to the lower level in both cases and thus:

$11\,000\ cm^{-1} = P - \Delta_{oct}$

$22\,000\ \text{cm}^{-1} = P - \Delta_{\text{tet}} = P - \frac{4}{9}\Delta_{\text{oct}}$

By solving the system of these equations we get:

$P = 30\,800\ \text{cm}^{-1}$

$\Delta_{\text{oct}} = 19\,800\ \text{cm}^{-1}$

$\Delta_{\text{tet}} = 8\,800\ \text{cm}^{-1}$

Alternative solution comes from the assumption (independent of the result of 5.10) of the low-spin arrangement in octahedral field and high-spin arrangement in tetrahedral field:

$11\,000\ \text{cm}^{-1} = \Delta_{\text{oct}} - P$

$22\,000\ \text{cm}^{-1} = P - \Delta_{\text{tet}} = P - \frac{4}{9}\Delta_{\text{oct}}$

By solving the system of these equations we get:

$P = 48\,400\ \text{cm}^{-1}$

$\Delta_{\text{oct}} = 59\,400\ \text{cm}^{-1}$

$\Delta_{\text{tet}} = 26\,400\ \text{cm}^{-1}$

7 points in total
formulation of equations 2 + 2 points, correct energy values (i.e. correct numerical calculation starting from correct assumption) 1 + 1 + 1 points

Synthetic garnet YAG (Yttrium Aluminium Garnet), used in optoelectronics, has the composition of $Y_3Al_5O_{12}$. Its structure is derived from the general garnet structure $A_3B_2(SiO_4)_3$ by placing the ions Y^{III} and Al^{III} to the A, B and Si positions.

5.12 Based on your knowledge of the relative ion radii, determine which cation occupies which position.

A: Y^{III} B: Al^{III} Si: Al^{III}

3 points in total, each correct assignment 1 point

5.13 For the use in LED technology, YAG is doped with Ce^{III}. Determine the values of x and y in the formula of YAG in which 5% of yttrium atoms are substituted with cerium.

$Y_xCe_yAl_5O_{12}$ $x = 2.85$ $y = 0.15$

2 points in total, each value 1 point

If you don't get result, use $x = 2.25$ and $y = 0.75$.

5.14 The Ce^{III}-doped YAG is prepared by annealing the mixture of Y_2O_3, Al_2O_3 and CeO_2 in H_2 atmosphere. Use the formula from 5.13, write down a balanced equation for this reaction with the smallest whole-number stoichiometric coefficients.

$$57\ Y_2O_3 + 6\ CeO_2 + 100\ Al_2O_3 + 3\ H_2 \longrightarrow 40\ Y_{2.85}Ce_{0.15}Al_5O_{12} + 3\ H_2O$$

$$(\text{or } 2\ Y_{57}Ce_3Al_{100}O_{240} + 3\ H_2O)$$

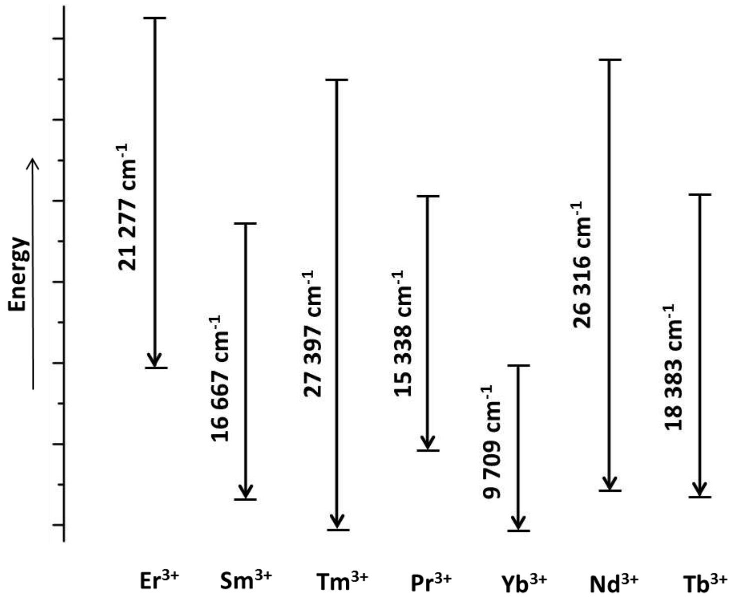
for $x = 2.25$ and $y = 0.75$:

$$9\ Y_2O_3 + 6\ CeO_2 + 20\ Al_2O_3 + 3\ H_2 \longrightarrow 8\ Y_{2.25}Ce_{0.75}Al_5O_{12} + 3\ H_2O$$

$$(\text{or } 2\ Y_9Ce_3Al_{20}O_{48} + 3\ H_2O)$$

complete set of correct coefficients 6 points
−1 point if correct stoichiometric coefficients are only on one side of the equation
−1 point if stoichiometric coefficients are correct and whole-number but not the smallest
−2 points if stoichiometric coefficients are correct but not whole-numbers
if hydrogen+water are omitted from the equation or when redox change was incorrect, then penalty −3 point is applied
if incorrect formula in 5.13 is given, the answer is judged with respect to the incorrect formula

Doping the YAG structure with rare-earths ions enables the production of lasers with emission wavelengths ranging from the UV to the mid-IR region. In the scheme below, simplified f–f energy transitions of selected rare-earths ions are shown.



5.15 Which cation has a transition which corresponds to blue light emission.

☒ Er^{3+} ☐ Sm^{3+} ☐ Tm^{3+} ☐ Pr^{3+}
☐ Yb^{3+} ☐ Nd^{3+} ☐ Tb^{3+}

1 point

5.16 Calculate the emission wavelength of this light.

$\lambda = \frac{1}{2\,127\,700}$ m = 4.70×10^{-7} m = 470 nm

1 point. The result of 5.16 is evaluated with respect to the answer in 5.15

5.17 According to a legend, Noah used a stick with a garnet stone for illumination during his voyage. Assuming only the photoluminescence effect, determine the colour of the laser light emitted from his stick if the stone were the blood-coloured Bohemian garnet.

☐ Red
☐ Yellow
☐ Blue
☒ Blue-green
☐ Yellow-orange
☐ Violet
☐ Black
☐ White

1 point

Sommario