New Zealand Chemistry Olympiad Trust

Training Group Selection Examination

Monday 2 November 2015

TIME ALLOWED: 120 minutes

Answer **ALL** questions on this examination booklet

Calculators may be used

The marks for the **eleven** (11) questions sum to **100**

A periodic table with atomic masses is also provided

STUDENT'S NAME:_______________________________________

STUDENT'S EMAIL:____

SCHOOL:____

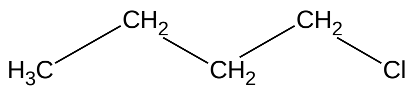
Question	**1** **/5**	**2** **/6**	**3** **/7**	**4** **/7**	**5** **/6**	**6** **/12**	**7** **/12**	**8** **/10**	**9** **/11**	**10** **14**	**11** **/10**	**Total** **/100**
Mark												

QUESTION ONE (5 marks)

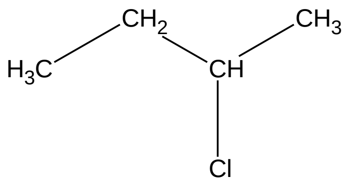
Collision theory requires collisions to have sufficient energy and the correct orientation. Anything (such as part of a molecule) that gets in the way of a collision reduces the likelihood of colliding with the correct orientation.

Chloroalkanes can substitute the chloro group for an OH group, typically using aqueous hydroxide. There are two ways this can happen; SN1 and SN2. In the SN2 pathway, the OH^{-} ion must collide with the carbon with the chloro group directly behind (180°) where the chlorine atom is bonded.

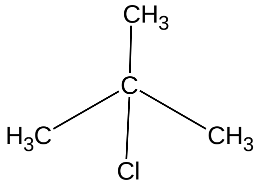
(a) Consider the following compounds and rank them in order of increasing ability to react via 'SN2'. Briefly justify your answer.



(i)



(ii)



(iii)

iii) then (ii) then (i). the larger (in terms of electron cloud) groups blocks collisions with the chloro carbon the most, (i) has two small H and a larger carbon chain, while (ii) has one H and two Carbon groups and finally (iii) is virtually blocked off with three carbon based groups and no small H's.

3 marks

(b) Alternatively, hydroxide could eliminate the chloro group, typically using an alcoholic solvent, in a similar process. This time the collision occurs with a hydrogen on an adjacent carbon to the carbon with the chloro group, to produce water, a Cl^{-} ion and the resulting alkene.

Elimination of the chloro group is often described as the removal of HCl, discuss why this is both an accurate and a misleading description of this elimination process.

The description is accurate as an H and a Cl is lost from the chloroalkanes therefore "HCl" is removed, it is misleading as HCl the compound is not made instead water and Cl^{-} ions are produced.

2 marks

QUESTION TWO (6 marks)

The following colourless liquids are supplied in unlabeled bottles: octan-1-amine, octanoic acid, octane, distilled water, sodium carbonate solution, hydrochloric acid solution. Using just the unlabeled bottles and some empty test tubes, how could you determine which is which?

Systematically select each of the unknowns and mix a small sample with each of the other unknowns. Let's call them A, B, C, D, E and F.

One of the unknowns (let's call it A) will form bubbles with two other unknowns, this is sodium carbonate solution. The two other unknowns (let's call them B and C) are either hydrochloric acid or octanoic acid.

The sodium carbonate (A) will form two layers with octane and octan-1-amine (let's call them D and E) but will form one layer with the last unknown water (call it F).

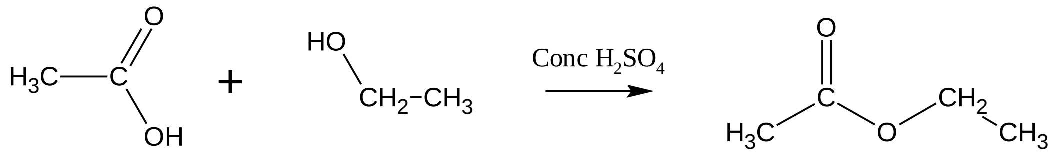
Now look at the water sample (F) with B and C, the one the mixes is hydrochloric acid (let's call that B) while the one that forms two layers is octanoic acid (let's call it C).

Finally take two samples of HCl (B) and add a few drops of D and E and shake, the one that dissolves is octan-1-amine while the other should form droplets that float on top making it octane. (Allow one layer forms with HCl and octan-1-amine while two layers between octane and HCl)

(Note variations of the above are possible)
(1 mark for each unknown clearly identified)

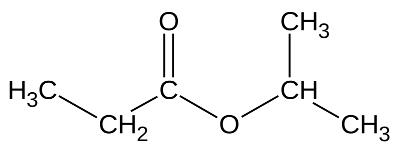
QUESTION THREE (7 marks)

Esters can be generated by the reaction of an alcohol and a carboxylic acid; an example is shown below:

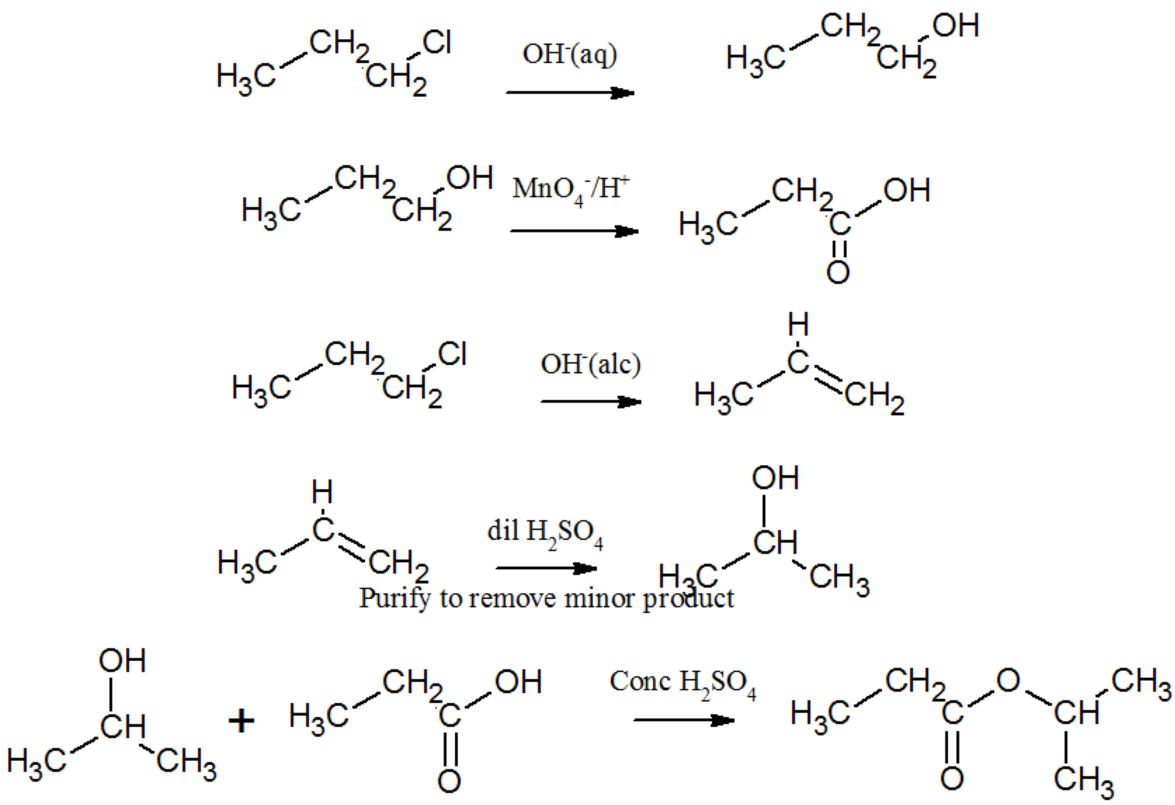


Acid Alcohol Ester

Devise a sequence of reactions that could make isopropyl propanoate (shown below) from 1-chloropropane. Indicate any step(s) that requires purification to remove unwanted organic product(s).



Isopropyl propanoate



Note: other valid approaches possible, including using $Cr_2O_7^{2-}/H^+$ for oxidation.

Marks based on correct steps, 3 marks for alcohol correctly made (with purification), 3 marks for carboxylic acid correctly made, 1 mark for overall esterfication.

QUESTION FOUR (7 marks)

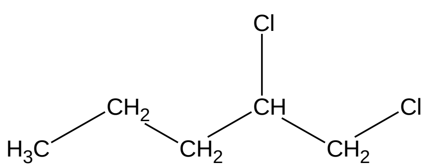
(a) Alkenes are known to form geometric (configurational) isomers. There are two requirements for this type of isomerism. Briefly explain why 1-chloropropene forms geometric isomers while 2-chloropropene does not.

(Requirements: Restricted rotation and differing groups at multiple positions locked by restricted rotation)

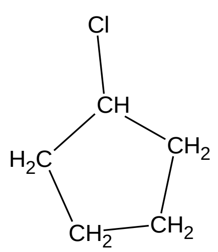
Both alkenes have restricted rotation from their C=C. 2-chloropropene has 2 H's on one of the C=C carbon atoms and so does not having different geometric isomers whereas 1-chloropropene has differing groups on each C of the C=C, they are Cl and H, and CH_3 and H.

2 marks

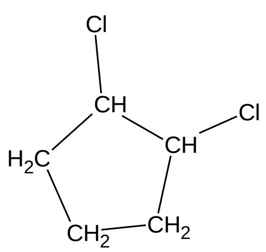
(b) Other classes of compounds also meet the requirements for geometric isomers. One such class of compounds are the cycloalkanes. Discuss how the following compounds do (or do not) meet the requirements for geometric isomers. Draw structures to represent the pair of geometric isomers for any structure that meets the requirements labelling one as 'cis' and the other as 'trans'.



1,2-dichloropentane



chlorocyclopentane



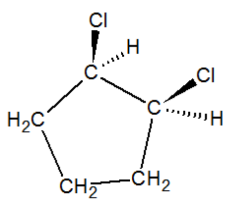
1,2-dichlorocyclopentane

1,2-dichloropentane does have restricted rotation so cannot form geometric isomers. (1 mark)

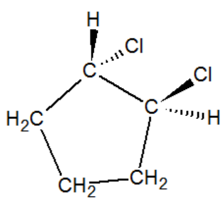
Chlorocyclopentane has restricted rotation due to the ring not able to rotate groups through the middle, but there is only one position with differing groups so no differing geometric isomers. (1 mark)

1,2-dichlorocyclopentane also has restricted rotation due to the ring not able to rotate groups through the middle, and two of these restricted carbons have differing groups (Cl and H) making it possible for geometric isomers. (1 mark)

Structures (2 marks):



cis

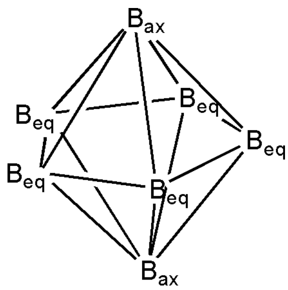


trans

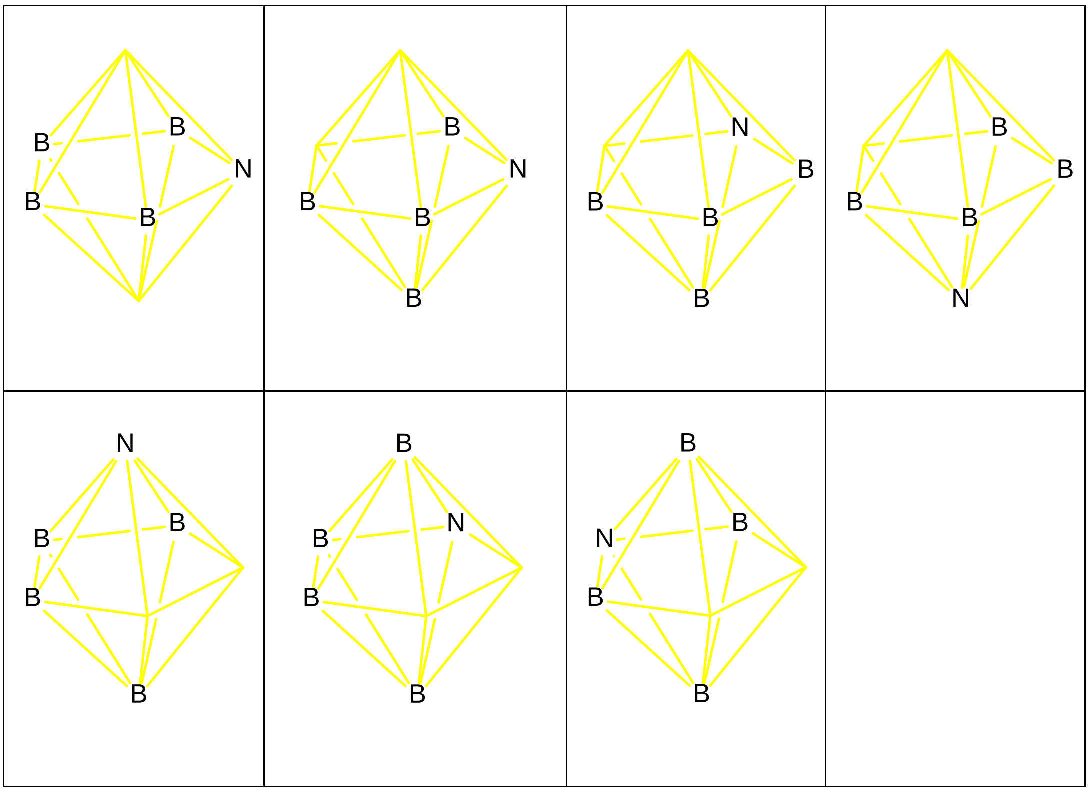
(note any valid way of drawing cis and trans will suffice)

QUESTION FIVE (6 marks)

$[B_7H_7]^{2-}$ is a **pentagonal bipyramid** (shown below without the H atoms) with ten triangular faces. It has two types of B atoms; two axial (ax) and five equatorial (eq). An ***arachno*-pentagonal bipyramid** is missing **two** of these vertices/atoms.



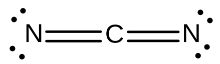
The cluster $[B_4NH_5]^{4-}$, in which one of the B atoms has been replaced by an N atom, is predicted to be an *arachno*-pentagonal bipyramid. Sketch the possible isomers for this ion by writing B or N over the appropriate vertices in the polyhedra given below. If both missing vertices are equatorial, they must be next to each other. You may not need to use all of the polyhedra to show all of the isomers.



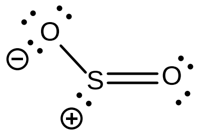
QUESTION SIX (12 marks)

(a) Draw ONE Lewis structure and the 3-dimensional molecular shape for each of the following triatomic species:

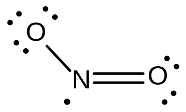
(i) Cyanamide (NCN^{2-});



(ii) Sulfur dioxide (SO_2);



(iii) Nitrogen dioxide (NO_2).

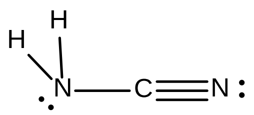


(iv) The "formal charge" is the number of valence electrons in the atom, minus the number of lone-pair electrons at that atom in the Lewis structure, minus the number of bonds to the atom in the Lewis structure. Formal charge can be used to help explain where electrons are likely to be found on atoms in a molecule. Write the formal charge on the atoms of SO_2 in your diagram in part (ii).

(b) List NCN^{2-}, SO_2 and NO_2 in order of increasing bond angle.

$SO_2 < NO_2 < NCN^{2-}$

(c) Addition of two equivalents of acid (2 protons) to cyanamide, NCN^{2-}, gives a product in which the two N atoms are different. Draw a Lewis structure for your proposed product.



QUESTION SEVEN (12 marks)

(a) Discuss the meaning of the term "electrochemical series". Arrange the elements calcium, copper, magnesium, potassium and zinc in an order which illustrates the series. Justify the order you give by considering the behaviour of these elements towards water (or steam).

The electrochemical series is a measure of the ease of oxidation of the metal when it reacts with water.
Decreasing ease of oxidation: potassium > calcium > magnesium > zinc > copper

- Potassium has only one valence electron which is further from the nucleus than in the other metals, so most easily oxidised.
- Calcium has the same valence shell as potassium but as a Group II element, with two valence electrons, which would therefore be less easily oxidised.
- Magnesium is also from Group II, but the two valence electrons are closer to the nucleus, so it is oxidised less easily than calcium.
- Zinc is less reactive towards water than magnesium
- Copper is a stable metal that is unreactive towards water, so will be least easily oxidised.

1 mark for order
3 marks for potassium, calcium and magnesium
1 mark zinc/copper, since the students will not be conversant with transition metals, but will have the knowledge that copper is stable in water (water pipes, kettles)

5 marks

(b) What spontaneous reaction will occur if Cl_2 and Br_2 are added to a solution containing Cl^- and Br^- ions?

Chlorine and bromine both need to gain an electron to form the corresponding ions.
Since chlorine has a higher electronegativity than bromine, it will be reduced more easily.
Therefore chlorine will be reduced to chloride, while the bromide ion will be oxidised to bromine in the counter reaction.
Chlorine + bromide ion → bromine + chloride ion

2 marks

(c) A student placed 0.20 mol of PCl_3(g) and 0.10 mol of Cl_2(g) into a 1.00 L flask at 250 ºC. The reaction $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$ was allowed to come to equilibrium, at which time it was found that the flask contained 0.12 mol of PCl_3.

(i) What were the initial concentrations of the reactants and product?

Since the total volume is 1.00 L, the concentrations will be numerically equal to the number of moles of the reactants and products.
$[PCl_3]$ = 0.20 mol L^{-1}
$[Cl_2]$ = 0.10 mol L^{-1}

(ii) What were the changes in concentration?

Since 0.12 moles of PCl_3 remained, the change in the number of moles will be 0.08 moles.
Since the stoichiometry is 1:1
The concentrations of the reactants will be reduced by 0.08 mol L^{-1} while the concetration of the product will increase by 0.08 mol L-1.
$[PCl_3]$ and $[Cl_2]$ will be **reduced by 0.08 mol L^{-1}** **½ mark**
$[PCl_5]$ will **increase by 0.08 mol L^{-1}** **½ mark**
1 mark

(iii) What were the equilibrium concentrations?

$[PCl_3]$ = 0.12 mol L^{-1}

$[Cl_2]$ = 0.02 mol L^{-1}

$[PCl_5]$ = 0.08 mol L^{-1}

1 ½ marks (½ mark each)

(iv) What is the value for K_c for this reaction?

$K_c = [PCl_5] / [PCl_3][Cl_2] = (0.08) / (0.12)(0.02) = 33.3 \text{ L mol}^{-1} = 33 \text{ l mol}^{-1}$ (2 S.F.)

1 mark

QUESTION EIGHT (10 marks)

(a) A 0.321 g sample of impure sodium carbonate, contaminated by sodium chloride, was dissolved in water. It required 35.4 mL of 0.144 mol L^{-1} HCl to react completely with the sodium carbonate as follows:

$$2HCl(aq) + Na_2CO_3 \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

(The impurity in the sample does not interfere with this analysis.) How much Na_2CO_3 was present in the sample in grams?

No. of moles of HCl used = 35.4/1000 L x 0.144 mol L^{-1} = **5.10 x 10^{-3} mol**
No. of moles of Na_2CO_3 present = 0.5 x 5.10 x 10^{-3} mol = **2.55 x 10^{-3} mol**
Molar mass of Na_2CO_3 = 2 x 23.0 + 12.01 + 16.00 x 3 = 106.01 g mol^{-1}
Mass of Na_2CO_3 present in sample = 2.55 x 10^{-3} mol x 106.01 g mol^{-1} = **0.270 g**

What was the percentage purity of the sample?

Percentage purity of the sample = 100 x 0.270 / 0.321 % = **84.1%**

(b) A sample of an unknown gas having a mass of 3.620 g was allowed to decompose, producing 2.172 g of oxygen and 1.448 g of sulfur. Prior to the decomposition, the sample occupied a volume of 1120 mL when its pressure was 100 kPa and the temperature 25 ºC. The volume of 1 mole of an ideal gas under these conditions is 24.0 L.

(i) What is the percentage composition of the elements in the gas?

40.00% S, 60.00% O

(ii) What is the empirical formula of the gas?

Empirical formula is SO_3

(iii) Assuming the gas behaves as an ideal gas, what is its molecular formula?

Molar mass = 80.1; Molecular formula SO_3

QUESTION NINE (11 marks)

(a) Outdoor flames, such as patio heaters and the Olympic flame, may contribute to global climate change due to the carbon dioxide produced from the combustion of hydrocarbons. Most patio heaters are powered by small cylinders of propane gas. A typical patio heater designed to produce 15 kW of energy runs from a cylinder containing 13 kg of propane. A 'completely full' cylinder at a pressure of 140 psi (9.52 atmospheres) is in fact only filled to about 87% capacity with liquid propane, the remaining volume being taken up by propane vapour. The standard enthalpy change of combustion is defined as the energy change when one mole of a substance is totally combusted in oxygen under standard conditions of 100.0 kPa pressure and 25 ºC. The standard enthalpy change for the complete combustion of propane is –2220 kJ mol^{-1}.
Assume 1 mole of a gas occupies 24 .0 L under the conditions of this question.

(i) Calculate the number of moles of propane contained in the cylinder used for the patio heater.

Moles = 13000/44.1 = 295

(ii) Calculate the mass of carbon dioxide produced when all of the propane in the cylinder is burnt completely.

Mass = 3 x 295 x 44.0 = 38900 g = 38.9 kg (accept 39 kg)

(iii) Calculate the total amount of heat energy released by combustion of all the propane in a cylinder.

Heat energy = 2220 x 295 = 655000 kJ = 655 MJ

(iv) Calculate the rate at which propane must leave the cylinder (in $cm^3\ s^{-1}$) to produce 15 kW (i.e. 15 kJ s^{-1}).

1 mol s^{-1} = 2220 kJ s^{-1} = 2220 kW, so 15 kW = 15/2220 mole s^{-1}

(b) Because pure propane gas is odourless, small amounts of another compound are usually added so that gas leaks can be detected. An example of such an odorant is ethyl mercaptan (ethanethiol, C_2H_5SH). This is chosen since the human nose can detect its presence at levels of only about 0.02 ppb (parts per billion).

(i) Draw a diagram to show how the atoms are bonded together in ethyl mercaptan and predict the bond angle around the sulfur atom.

Sensible bonding diagram with all single covalent bonds. Accept a bond angle anything between 100° - 107°

(ii) Calculate the mass of ethyl mercaptan which must be added to 13 kg of propane to produce 0.02 molecules of ethyl mercaptan per billion (10^9) molecules of propane.

Mass = 295 x 0.02 x 10^{-9} x 62.1 = 3.66 x 10^{-7} g (accept 3.7 or 4.0 x 10^{-7} g)

QUESTION TEN (14 marks)

(a) One of the reactions that occurs when an iron oxide found in iron ore is changed to pure iron is:

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g) \qquad \Delta_r H^o = -26.5 \text{ kJ mol}^{-1}$$

Calculate the mass of iron that would be produced if the overall enthalpy change was –1000 kJ.

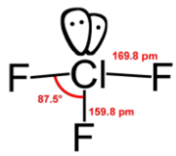
No of moles of iron produced for –26.5 kJ = 2

No of moles of iron produced for –1000 kJ = 2 x (1000/26.5) = **75.5 moles**

Mass of iron = moles x relative atomic mass = 75.5 x 55.9 = **4219 g**

2 marks

(b) Chlorine trifluoride, ClF_3, is one of the most reactive substances known: it causes sand and asbestos to explode and it even reacts with xenon. It has been investigated as a rocket fuel; its reactions with every known fuel are so fast that no ignition delay has ever been measured.



(i) ClF_3 is used to turn uranium into uranium hexafluoride, UF_6, which is used to separate the isotopes of uranium. Chlorine monofluoride, ClF, is a side-product in this reaction. Write a balanced equation for the reaction between uranium and chlorine trifluoride.

$U + 3ClF_3 \rightarrow UF_6 + 3ClF$

2 marks

(ii) ClF_3 is a powerful oxidising agent. Circle each atom / ion on the left hand side of the equation below that is oxidised in the reaction between chlorine trifluoride and silver chloride.

$2AgCl(s) + 2ClF_3(l) \rightarrow 2AgF_2(s) + Cl_2(g) + 2ClF(g)$

2 marks

(c) Iodine forms the fluorides IF, IF_3, IF_5 and IF_7.

In these compounds the oxidation number of iodine is between 0 and +7. This means there is a possibility that a disproportionation reaction will occur to form the compound with iodine in its next highest oxidation number, and elemental iodine. For example, IF_3 might disproportionate to give IF_5 and I_2.

(i) Give balanced equations for the theoretical disproportionation reactions of IF, IF_3 and IF_5.

IF:

$3IF \rightarrow I_2 + IF_3$

IF_3:

$5IF_3 \rightarrow I_2 + 3IF_5$

IF_5:

$7IF_5 \rightarrow I_2 + 5IF_7$

6 marks

(ii) The standard enthalpy change for each of these reactions is given below

Disproportionation of IF = –66.7 kJ mol^{-1}

Disproportionation of IF_3 = –19.8 kJ mol^{-1}

Disproportionation of IF_5 = 156 kJ mol^{-1}

A negative sign indicates that energy is liberated, whereas a positive sign indicates that energy is absorbed.

Only one of IF, IF_3 and IF_5, does NOT in fact disproportionate. Suggest which one and justify your choice.

IF_5 does not disproportionate, because while the other two disproportionations liberate energy, IF_5 REQUIRES energy to disproportionate

2 marks

QUESTION ELEVEN (10 marks)

Nitrite ions can be determined quantitatively by titration with permanganate ions (MnO_4^-) in acidic solution, according to the equation: $2MnO_4^- + 5NO_2^- + 6H^+ \rightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$

(a) Write the two half equations for the overall reaction between permanganate ions and nitrite ions in acidic solution.

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ 1 mark

$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$ 1 mark

$2MnO_4^- + 6H^+ + 5NO_2^- \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

(b) In a typical experiment to determine the concentration of nitrite ions, 25.0 mL of a 0.0200 mol L^{-1} solution of potassium permanganate(VII) was acidified, heated to about 40 ºC and then titrated with a solution of sodium nitrite, of which 26.0 mL was required to reach the end-point.

(i) What colour change would be observed at the end-point of the titration?

The first pale pink colour of excess permanganate in the solution 1 mark

(ii) Calculate the concentration, in mol L^{-1}, of nitrite ions in solution.

$[NO_2^-] = 5/2 \times [MnO_4^-] \times V(MnO_4^-) / V(NO_2^-)$ 2 marks

$= 5/2 \times 0.0200 \times 25.0 / 26.0 \text{ mol } L^{-1} = 0.048 \text{ mol } L^{-1}$

(c) The aqueous Mn^{3+} ion is as powerful an oxidising agent as MnO_4^-, but it is rarely used because it readily disproportionates into solid MnO_2 and Mn^{2+} ions. Write a balanced equation for the disproportionation of the Mn^{3+} ion into MnO_2 and Mn^{2+}.

$2Mn^{3+}(aq) + 2H_2O(l) \rightarrow MnO_2(s) + Mn^{2+}(aq) + 4H^+(aq)$ 3 marks

(d) State and explain how the tendency of Mn^{3+} ion to disproportionate would be affected by changes in the pH of the reaction mixture.

Increasing the pH increases the tendency of Mn^{3+} to disproportionate, 1 mark

Because the position of the above equilibrium would be displaced to the product side in an attempt to restore the hydrogen ion concentration 1 mark

PERIODIC TABLE OF THE ELEMENTS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
					Atomic Number	1 **H** 1.0	Molar Mass / g mol^{-1}										2 **He** 4.0
3 **Li** 6.9	4 **Be** 9.0											5 **B** 10.8	6 **C** 12.0	7 **N** 14.0	8 **O** 16.0	9 **F** 19.0	10 **Ne** 20.2
11 **Na** 23.0	12 **Mg** 24.3											13 **Al** 27.0	14 **Si** 28.1	15 **P** 31.0	16 **S** 32.1	17 **Cl** 35.5	18 **Ar** 40.0
19 **K** 39.1	20 **Ca** 40.1	21 **Sc** 45.0	22 **Ti** 47.9	23 **V** 50.9	24 **Cr** 52.0	25 **Mn** 54.9	26 **Fe** 55.9	27 **Co** 58.9	28 **Ni** 58.7	29 **Cu** 63.5	30 **Zn** 65.4	31 **Ga** 69.	32 **Ge** 72.6	33 **As** 74.9	34 **Se** 79.0	35 **Br** 79.9	36 **Kr** 83.8
37 **Rb** 85.5	38 **Sr** 87.6	39 **Y** 88.9	40 **Zr** 91.2	41 **Nb** 92.9	42 **Mo** 95.9	43 **Tc** 98.9	44 **Ru** 101	45 **Rh** 103	46 **Pd** 106	47 **Ag** 108	48 **Cd** 112	49 **In** 115	50 **Sn** 119	51 **Sb** 122	52 **Te** 128	53 **I** 127	54 **Xe** 131
55 **Cs** 133	56 **Ba** 137	57−71 Lanthanide Series	72 **Hf** 179	73 **Ta** 181	74 **W** 184	75 **Re** 186	76 **Os** 190	77 **Ir** 192	78 **Pt** 195	79 **Au** 197	80 **Hg** 201	81 **Tl** 204	82 **Pb** 207	83 **Bi** 209	84 **Po** 210	85 **At** 210	86 **Rn** 222
87 **Fr** 223	88 **Ra** 226	89−103 Actinide Series	104 **Rf** 261	105 **Db** 262	106 **Sg** 263	107 **Bh** 262	108 **Hs** 265	109 **Mt** 266									

Lanthanide Series	57 **La** 139	58 **Ce** 140	59 **Pr** 141	60 **Nd** 144	61 **Pm** 145	62 **Sm** 150	63 **Eu** 152	64 **Gd** 157	65 **Tb** 159	66 **Dy** 163	67 **Ho** 165	68 **Er** 167	69 **Tm** 169	70 **Yb** 173	71 **Lu** 175
Actinide Series	89 **Ac** 227	90 **Th** 232	91 **Pa** 231	92 **U** 238	93 **Np** 237	94 **Pu** 244	95 **Am** 243	96 **Cm** 247	97 **Bk** 247	98 **Cf** 251	99 **Es** 252	100 **Fm** 257	101 **Md** 258	102 **No** 255	103 **Lr** 262