

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

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SCHOOL:_____

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

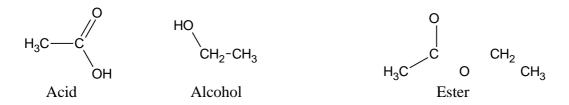
(a) Consider the following compounds and rank them in order of increasing ability to react

QUESTION TWO (6 marks)

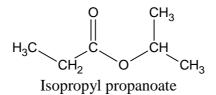
The following colourless liquids are supplied in unlabeled bottles: octan-1-amine, octanoic acid, octane, distilled water, sodium carbonate solution, hydrochloric acid solution. Using just the unlabeled bottles and some empty test tubes, how could you determine which is which?

QUESTION THREE (7 marks)

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



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

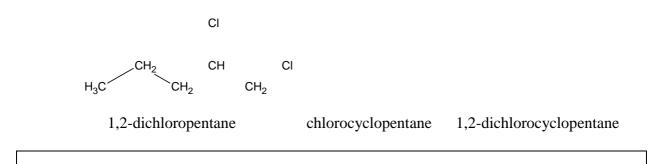




QUESTION FOUR (7 marks)

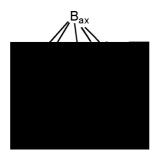
(a) Alkenes are known to form geometric (configurational) isomers. There are two requirements for this type of isomerism. Briefly explain why 1-chloropropene forms geometric isomers while 2-chloropropene does not.

(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

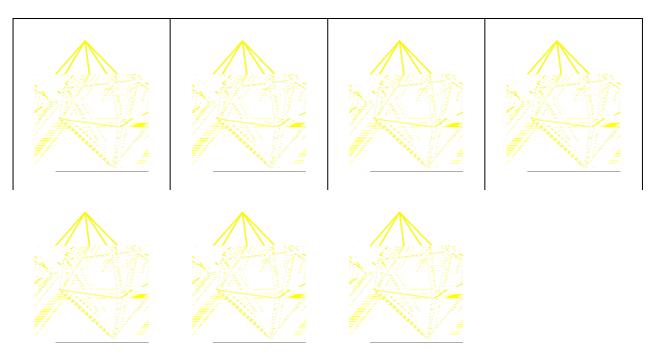


QUESTION FIVE (6 marks)

 $[B_7H_7]^2$ 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 (SO₂);

(iii) Nitrogen dioxide (NO₂).

- (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 , SO₂ and NO₂ in order of increasing bond angle.
- (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)

(ii) What were the changes in concentration?

(iii) What were the equilibrium concentrations?

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

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:

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

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

What was the percentage purity of the sample?

- (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 °C. 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?

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 essure 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 °C. 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.

(iv) Calculate the rate at which propane must leave the cylinder (in cm³ s¹) to produce 15 kW (i.e. 15 kJ s¹).

(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, C₂H

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:

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

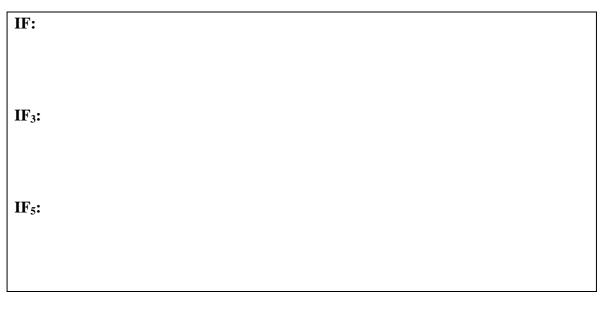
Calculate the mass of iron that would be produced if the overall enthalpy change was 1000 kJ.

(b) Chlorine trifluoride, ClF₃, is one of the most reactive substances known: it

(c) Iodine forms the fluorides IF, IF₃, IF₅ and IF₇.

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 .



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

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

Disproportionation of $IF_3 = 19.8 \text{ kJ mol}^{-1}$

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

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

Only one of IF, IF₃ and IF₅, does NOT in fact disproportionate. Suggest which one and justify your choice.

QUESTION ELEVEN (10 marks)

Nitrite ions can be determined quantitatively by titration with permanganate ions (MnO₄) in acidic solution, according to the equation: $2MnO_4 + 5NO_2 + 6H^+ = 2Mn^{2+} + 3H_2O + 5NO_3$

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

- (b) In a typical experiment to determine the concentration of nitrite ions, 25.0 mL of a 0.0200 mol L¹ solution of potassium permanganate(VII) was acidified, heated to about 40 °C 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?
 - (ii) Calculate the concentration, in mol L^{-1} , of nitrite ions in solution.

- (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+} .
- (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.

PERIODIC TABLE OF THE ELEMENTS