NOTES FOR GUIDANCE (CANDIDATES)

1 This leaflet contains an article which is needed in preparation for a question in the externally assessed examination F332.

2 You will need to read the article carefully and also have covered the learning outcomes for Unit F332 (Chemistry of Natural Resources). The examination paper will contain questions on the article. You will be expected to apply your knowledge and understanding of the work covered in Unit F332 to answer these questions. There are 20 marks available on the paper for these questions.

3 You can seek advice from your teacher about the content of the article and you can discuss it with others in your class. You may also investigate the topic yourself using any resources available to you.

4 For the examination on 19 January 2012 you will be given a fresh copy of this article, together with a question paper. You will not be able to bring your copy of the article, or other materials, into the examination.

5 You will not have time to read this article for the first time in the examination if you are to complete the examination paper within the specified time. However, you should refer to the article when answering the questions.

This document consists of 4 pages. Any blank pages are indicated.

INSTRUCTION TO EXAMS OFFICER/INVIGILATOR

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Chlorine dioxide

Adapted from www.lenntech.com/water-disinfection/disinfectants-chlorine-dioxide.htm

Chlorine dioxide is mainly used as a bleach and as a disinfectant. As a disinfectant it is effective even at low concentrations because of its unique qualities.

When was chlorine dioxide discovered?

Chlorine dioxide was discovered in 1814 by Sir Humphrey Davy. In the last few years a reaction similar to his has been used to produce large quantities of chlorine dioxide from sodium chlorate (V).

\[ 2NaClO_3(aq) + 4HCl(aq) \rightarrow 2ClO_2(aq) + Cl_2(aq) + 2NaCl(aq) + 2H_2O(l) \]

What are the characteristics of chlorine dioxide?

Chlorine dioxide (ClO₂) is a green-yellowish gas with a chlorine-like, irritating odour. Chlorine dioxide is a neutral chlorine compound consisting of small, volatile molecules which have a bent structure with the O–Cl–O bond angle of 117°. In aqueous solutions chlorine dioxide is a radical and reacts strongly with reducing agents. Chlorine dioxide is an unstable gas that dissociates into chlorine gas (Cl₂) and oxygen gas (O₂) exothermically. At –59°C, solid chlorine dioxide becomes a reddish liquid. At 11°C chlorine dioxide turns into a gas.

Can chlorine dioxide be dissolved in water?

One of the most important qualities of chlorine dioxide is its high water solubility, especially in cold water. Chlorine dioxide does not hydrolyse when it enters water; it remains a dissolved gas in solution. Chlorine dioxide is approximately 10 times more soluble than chlorine in water. Chlorine dioxide can be removed by aeration or by blowing carbon dioxide through the solution.

What are the applications of chlorine dioxide?

Chlorine dioxide has many applications. It is used in the electronics industry to clean circuit boards, in the oil industry to treat sulfides and to bleach textiles and candles. In World War II, chlorine became scarce and chlorine dioxide was used as a bleach. Nowadays, chlorine dioxide is used most often to bleach paper. It produces a clearer and stronger fibre than chlorine does. Chlorine dioxide has the advantage that it produces less harmful by-products than chlorine. Chlorine dioxide gas is used to sterilise medical and laboratory equipment, surfaces, rooms and tools. Chlorine dioxide can be used as an oxidiser or disinfectant. It is a strong oxidiser and it effectively kills pathogenic micro-organisms such as fungi, bacteria and viruses. It also prevents and removes bio-film. As a disinfectant and pesticide it is mainly used in liquid form. Chlorine dioxide can also be used against anthrax, because it is effective against spore-forming bacteria.
Chlorine dioxide as an oxidiser

Chlorine dioxide can act as an oxidiser. It has this ability due to unique one-electron exchange mechanisms. Chlorine dioxide attacks the electron-rich centres of organic molecules. One electron is transferred to chlorine dioxide from the electron-rich centre of the organic molecule and the chlorine dioxide is reduced to chlorite (ClO$_2^-$). In other applications it is often reduced to chloride.

In comparison to chlorine and ozone, less chlorine dioxide is required to obtain an active residual disinfectant. One way to compare different chlorine-containing chemicals’ oxidising capacities, which shows how many electrons are transferred during an oxidation or reduction reaction, is to calculate their ‘available chlorine’. To do this calculation, the molar mass of the compound must be known, as well as the number of electrons it exchanges during the reaction. For example, sodium hypochlorite, NaClO, has a molar mass of 74.5 and accepts two electrons when it reacts. The calculation is done by dividing the relative atomic mass of chlorine by the molar mass of the sodium hypochlorite, then multiplying by two (because the Cl in NaClO accepts two electrons during reactions, whereas Cl in Cl$_2$ only accepts one electron). The answer is multiplied by 100 to give a percentage. The calculation for sodium hypochlorite would give:

$$\text{Available chlorine} = \left(\frac{35.5}{74.5}\right) \times 2 \times 100\% = 95.3\%$$

The chlorine atom in chlorine dioxide has an oxidation number of +4. For this reason, chlorine dioxide accepts five electrons when it is reduced to chloride. During the reduction, a chlorine radical forms, until finally stable chloride ions are produced. When we look at the molar mass, chlorine dioxide has more than 2.5 times the oxidation capacity of chlorine.

The chlorine atom remains until stable chloride is formed. This explains why no potentially toxic chlorinated substances are formed. When chlorine reacts it not only accepts electrons; it also takes part in addition and substitution reactions.

Does chlorine dioxide produce by-products?

Pure chlorine dioxide gas that is applied to water produces less disinfection by-products than oxidants such as chlorine. Unlike ozone (O$_3$), pure chlorine dioxide does not oxidise bromide (Br$^-$) ions to bromate ions (BrO$_3^-$). Additionally, chlorine dioxide does not produce large amounts of aldehydes, ketones, or other disinfection by-products that originate from the oxidation of organic substances.

What are the disinfection applications of chlorine dioxide?

Drinking water treatment is the main application of disinfection by chlorine dioxide. Thanks to its biocidal abilities, chlorine dioxide is also used in other branches of industry today. Examples are: sewage water disinfection, industrial process water treatment, cooling tower water disinfection, industrial air treatment, mussel control, foodstuffs production and treatment, industrial waste oxidation and gas sterilisation of medical equipment.

END OF ADVANCE NOTICE ARTICLE