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For issue on or after: 13 March 2013

AS GCE CHEMISTRY B (SALTERS)

F332/01 Chemistry of Natural Resources

ADVANCE NOTICE

Duration: 1 hour 45 minutes

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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 **4 June 2013** 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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Atmospheric Nitrogen: Out of Thin Air

Adapted from an article in Chemistry Review Magazine, Volume 20, Number 2, November 2010 by Tim Harrison and Dudley Shallcross. Published by Philip Allan Updates.

Molecular nitrogen, N_2, is an inert gas (Fig. 1) and makes up nearly 80% of the Earth's atmosphere. It is only in the upper atmosphere (altitudes higher than 100 km) that this gas becomes more reactive, where significant levels of very short wavelength radiation can be found (80–100 nm) that can break the bonds between nitrogen atoms through photolysis.

$$N \equiv N$$

Fig. 1: Structure of molecular nitrogen

Due to its great stability, nitrogen gas accounts for 99.9999% of atmospheric nitrogen, with nitrous oxide (N_2O, see Fig. 2) representing around 99% of the remainder. Therefore you would imagine that the global atmospheric nitrogen cycle is well understood.

$$N \equiv N \rightarrow O$$

Fig. 2: Structure of nitrous oxide (dinitrogen oxide)

However, despite their small and highly variable sources, there are other nitrogen containing species (Fig. 3), which are present in the atmosphere at trace levels, playing a disproportionately large role in determining atmospheric composition. Ammonia (NH_3), for example, is the only alkaline gas in the atmosphere and is important in the neutralisation of acidic aerosols.

NO_2 Nitrogen dioxide	HNO_3 Nitric acid	NO Nitric oxide
NH_3 Ammonia	$(NH_4^+)_2\ SO_4^{2-}$ Ammonium sulfate	

Fig. 3: Formulae of some other nitrogen containing compounds

Nitrogen oxides, NO and NO_2, play a vital role in the production and destruction of low altitude (tropospheric) smog, and so affect the radiative budget (the balance of incoming and outgoing radiation) of the Earth and the oxidising capacity of the atmosphere.

Ammonia has a short lifetime in the atmosphere of approximately 10 days and is removed predominantly by both **wet and dry deposition** processes, with some additional loss via reaction with $HO^\bullet$ radicals. The main sources arise from biological activity, such as the decomposition of urea ($(NH_2)_2CO$) in animal urine by enzymes, the decomposition of excrement and the release from soils and the ocean following mineralisation of organic material. Anthropogenic (man-made) sources centre around its use in fertilisers and as a by-product of waste production. Since deposition processes dominate its loss and sources are diverse, levels of ammonia are highly variable, ranging from 0.1 to 10 ppbv (parts per billion by volume) over continental regions. Ammonia forms ammonium sulfate aerosols that, when deposited, cause a decrease in soil pH, leading to a decline in plant growth.

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+$$

In the atmosphere, NO and NO_2 (collectively known as NO_x) are tightly coupled during sunlit hours and rapidly interconvert with one another in the presence of ozone (see Box 1):

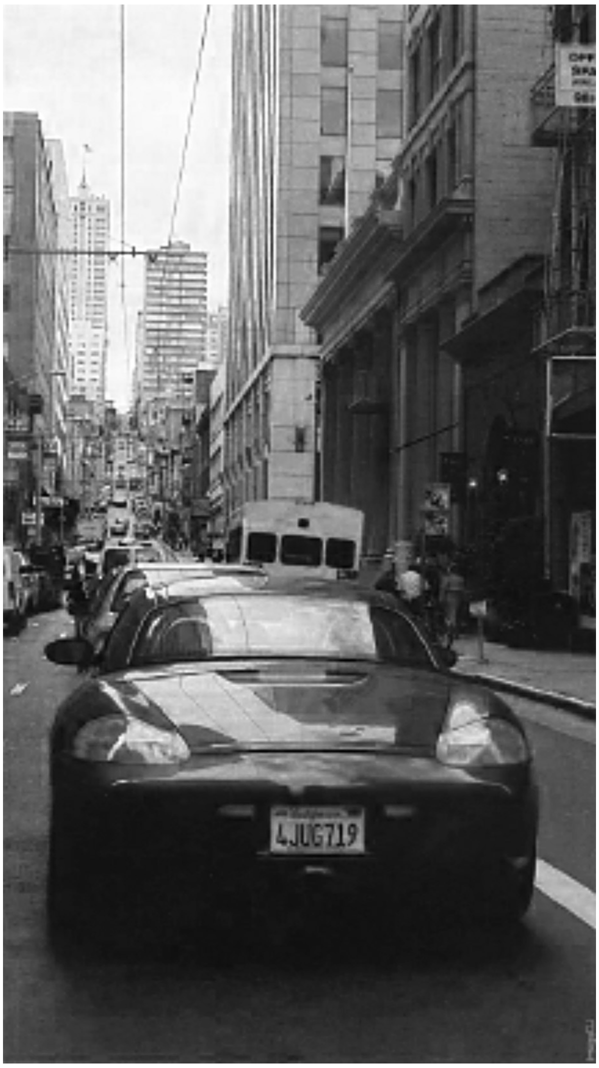
$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 \rightarrow NO + O$$

$$O + O_2 \rightarrow O_3$$

Box 1: Ozone

Ozone, O_3, is a molecule containing three oxygen atoms with a similar shape to a water molecule. It has an important role in the stratosphere, where it absorbs incoming UV radiation from the Sun and prevents it from reaching the Earth's surface.



New cars are equipped with catalytic converters, which convert NO_x to oxygen and nitrogen.

Individually, NO and NO_2 have extremely short lifetimes of the order of seconds, but by considering the two compounds together as NO_x, the lifetime is essentially lengthened to many hours. Hence, NO and NO_2 display strong diurnal (daily) cycles and their concentrations will display a seasonal cycle. In urban areas, NO_x can reach levels of 100 ppbv (parts per billion by volume), and in particularly polluted environments ppmv (parts per million by volume) levels, whereas clean maritime levels are only 5–10 pptv (parts per trillion by volume). The major loss processes for NO_x are conversion to HNO_3 by reacting with an $HO^{\bullet}$ radical or by dry deposition of NO_x.

$$NO_2 + HO^{\bullet} \rightarrow HNO_3$$

HNO_3 can be removed by wet and dry deposition, constituting a loss of NO_x from the atmosphere. In the **troposphere**, in the presence of volatile organic compounds, NO_x can promote the formation of ozone and can also be used to form temporary nitrate reservoirs such as nitroethaneperoxoate or peroxyacetylnitrate (PAN), which is an alkanoyl nitrate ($CH_3C(O)O_2NO_2$). PAN can allow NO_x to be transported away from source regions and influence chemistry on regional and global scales. For most sources, NO_x is emitted in the form of NO. Natural sources of NO are from soil processes and lightning discharge, while an ever-increasing source is that from the high-temperature combustion of fossil fuels.

$$O + N_2 \rightarrow NO + N$$

$$N + O_2 \rightarrow NO + O$$

There are considerable uncertainties within the budget for NO_x, such as the soil and lightning source strength, although the burden from fossil fuels is reasonably well defined and set to increase globally, despite the growing use of **three-way catalysts** in vehicles that reduce nitrogen oxide exhausts to nitrogen and oxygen.

Opportunity NO_x

Nitrous oxide (N_2O) is an important greenhouse gas. Its current atmospheric mixing ratio is about 310 ppbv, compared with an estimated pre-industrial level of around 285 ppbv. N_2O has an extremely long lifetime (~150 years) and is virtually inert in the troposphere, being destroyed in the **stratosphere** by direct photolysis and reaction with excited oxygen atoms.

$$N_2O \rightarrow N_2 + O$$

$$N_2O + O^* \rightarrow 2NO$$

$$N_2O + O^* \rightarrow N_2 + O_2$$

Nitrous oxide is released to the atmosphere from both soils and aquatic systems with undisturbed soils, cultivated soils and oceans making up the bulk of the known sources. Denitrifying bacteria transform nitrate to N_2 and some N_2O under anaerobic conditions (in the absence of oxygen), which can then escape to the ocean surface and enter the atmosphere. There are many uncertainties, including the estimation of the ocean source, since N_2O is both lost to and emitted from the oceans. Since it delivers NO_x to the stratosphere, N_2O plays an important role in controlling the abundance of stratospheric ozone.

Turn over

Glossary

Dry deposition the chemical or physical removal of particles and gases from the atmosphere by impact with the Earth's surface.

Stratosphere the second major layer of Earth's atmosphere, just above the troposphere and below the mesosphere, between 10 and 50 km altitude.

Three-way catalyst a catalytic converter used in vehicle exhausts to decrease the toxicity and levels of harmful engine emissions. A three-way catalyst converts NO_x to oxygen and nitrogen, oxidises carbon monoxide to carbon dioxide and oxidises uncombusted hydrocarbons to carbon dioxide and water.

Troposphere the lowest portion of Earth's atmosphere. It contains approximately 90% of the atmosphere's mass and 99% of its water vapour and aerosols.

Wet deposition the removal of substances from the atmosphere to Earth's surface through incorporation in rain, snow, hail, fog, etc.

Nitrogen is an element essential to life, not only in its building blocks but also in its processes. It is therefore important to understand how nitrogen is transferred through its various compounds from a biological perspective, and also how human activities affect it. With a better understanding of the latter, we can look at how to minimise nitrogenous pollution, so this continues to be a highly active area of research.

END OF ADVANCE NOTICE ARTICLE