Mid-Term Examination for CHMB55
Environmental Chemistry

Date: Feb. 9, 2009, 11 am to 1 pm
Maximum: 50+2 marks

1. What are the three chemicals that make up polar stratospheric clouds? **(1.5)**

   Water (H_2O), sulfuric acid (H_2SO_4), nitric acid (HNO_3)

2. Ozone forms in both stratosphere and troposphere as a result of the reaction:

   $$O + O_2 \rightarrow O_3.$$

   What is the source of mono-atomic oxygen in the stratosphere and in the troposphere, respectively? **(2)**

   In the stratosphere: $O_2 \xrightarrow[\text{(UV-C)}]{} 2\ O\cdot$

   In the troposphere: $NO_2\cdot \xrightarrow[\text{(UV-A)}]{} NO\cdot + O\cdot$

3. What process triggers the sudden onset of the Antarctic ozone hole during spring time? **(2)**

   The reappearance of the sun during polar sunrise causes the photolysis of Cl_2 gas into Cl· radicals, which then act as catalysts in the ozone destruction. Cl_2 is formed from inactive chlorine species (HCl and $ClONO_2$) during the winter as a result of heterogeneous reactions on the surface of polar stratospheric clouds.

4. What non-linear process was responsible for the abruptness of the appearance of the Antarctic ozone hole in the 1980s? **(2)**

   The reaction between two ClO· radicals to from ClOOCl is the rate determining step in the catalytic destruction of ozone in the lower stratosphere. It is a second order reaction with respect to ClO· concentration. Therefore, the rate of ozone destruction has a quadratic, rather than a linear, dependence on the amount of chlorine in the stratosphere. As Cl concentrations steadily increased, eventually the threshold was reached where the reaction of two ClO· radicals proceeds quickly.

5. For a gaseous substance to act as an ozone-depleting substance, the loss of that substance from the troposphere needs to be inefficient, so that it can reach the stratosphere. Which two processes may contribute to the loss of a substance from the troposphere? **(2)**

   A substance may be degraded in the troposphere, e.g. by reaction with photooxidants such as the hydroxyl radical or ozone.

   A substance maybe deposited from the troposphere with precipitation, e.g. by dissolving efficiently in rain droplets.

6. A substance may not be lost from the troposphere by either of the two processes in 5., reach the stratosphere, and still not be an ozone-depleting substance. Explain. **(1)**

   A substance that does not generate chlorine or bromine radicals in the stratosphere will not act as an ozone-depleting substance.

7. How can the answers to question 5. and 6. help in developing strategies for finding substitutes for ozone-depleting substances? **(3)**

   Among the strategies for substituting ozone-depleting substances are:

   - substitute with a substance that more easily undergoes degrading reactions in the troposphere, by for example being susceptible to attack by the OH radical
   - substitute with a substance that is more easily deposited with precipitation, by e.g. having a high water solubility
   - substitute with a substance that contains neither chlorine nor bromine.

8. Name a natural and an anthropogenic source of nitric oxide to the atmosphere. **(2)**

   Natural: Lightning.
   Anthropogenic: Hot flames in combustion engines or power plants.

9. Formulate the most likely reactions that the following species would undergo in the clean troposphere (only the first step)? **(6)**

$CH_3\text{-}O\cdot + O_2 \rightarrow CH_2O + HOO\cdot$

$C_4H_9\cdot + O_2 \rightarrow C_4H_9\text{-}O\text{-}O\cdot$

$C{\equiv}O + \cdot OH \rightarrow HO\text{-}\cdot C{=}O$

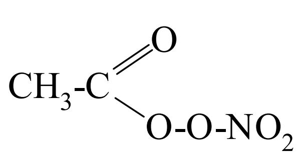
$C_2H_5\text{-}O\text{-}O\cdot + NO\cdot \rightarrow C_2H_5\text{-}O\cdot + NO_2\cdot$

$SO_2 + \cdot OH \rightarrow O_2S\cdot\text{-}OH$

$NH_3 + \cdot OH \rightarrow NH_2\cdot + H_2O$

10. What does PAN stand for? Draw its molecular structure. **(2)**

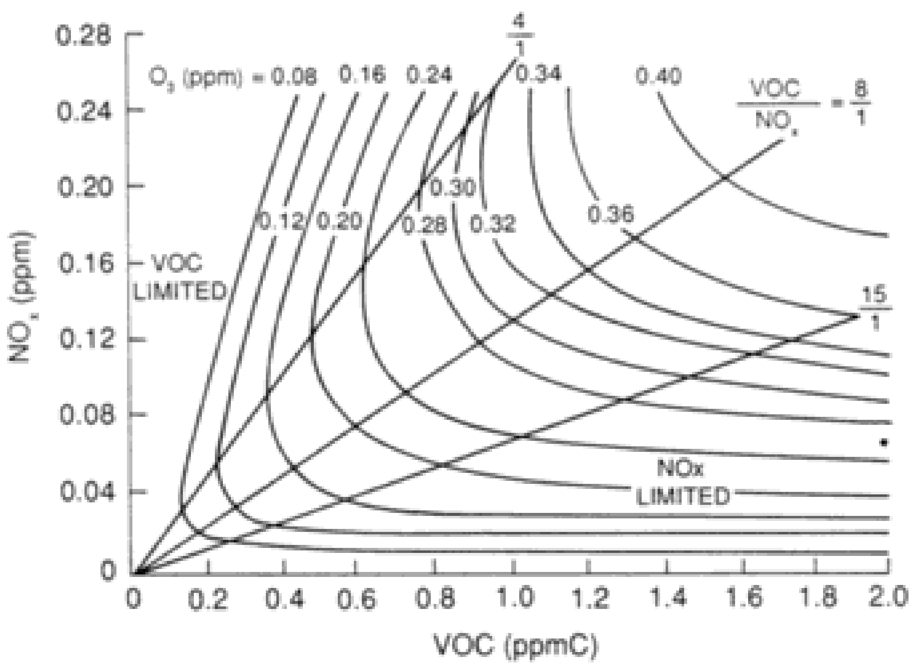
   Peroxyacetylnitrate



11. Name the three non-radical species that are formed during the oxidation of methane? **(1.5)**

formaldehyde (CH_2O), carbon monoxide (CO), carbon dioxide (CO_2)

The following diagram shows ozone isopleths (lines of equal ozone concentration) as a function of the NOx and VOC concentrations.



12. Explain what NOx and VOC stands for? **(2)**

NOx: Nitric oxide (NO·) and Nitrogen dioxide (NO_2·)

VOC: volatile organic compounds

13. What peak ozone concentration would you predict to occur, if the VOC concentration is 1.6 ppm and the NOx concentration is 0.1 ppm? **(1)**

0.31 ppm

14. By how much (reduction in percent) would you have to reduce the concentrations of NOx to half that concentration of ozone? By how much (reduction in percent) would you have to reduce the concentrations of VOC to achieve the same? **(2)**

NOx: From 0.1 ppm to 0.025 ppm, i.e. by a factor of approx. 4 (75 %)

VOC: From 1.6 ppm to 0.35 ppm, i.e. by a factor of approx. 4.5 (78 %)

15. An air mass, that is advected from a highly polluted urban area to suburbs and rural areas downwind, shifts its location in the diagram from the upper left to the lower right. Based on the diagram, suggest what primary pollutant should be targeted for emission reduction within the GTA and within the areas downwind of the GTA in order to reduce the severity of photochemical smog episodes during the Ontario summer. Explain! **(2)**

    Within the GTA, ozone levels are VOC limited, suggesting that VOC reductions would be more effective in reducing ozone formation.

    In the areas East/downwind of the GTA, ozone levels are NOx limited and reductions in NOx would presumably be more effective in reducing photochemical smog.

Bonus Question: Speculate which forests have a greater influence on the occurrence of photochemical smog in an area: those that are located upwind of an urban area or those located downwind? Explain! **(2)**

Since trees are sources of VOCs (such as isoprene and α-pinene) to the atmosphere, a forest would have a stronger influence on the occurrence of photochemical smog in an area where ozone formation is VOC limited, i.e. within the urban areas. Therefore, a forest upwind of an urban area is more likely to contribute to photochemical smog than a downwind forest.

16. The diagram above reveals that situations exist where lowering NOx at constant VOC will result in increased peak ozone concentrations. Give a NOx/VOC concentration pair where this is the case. **(1)**

    For example, if [NOx] = 0.20 ppm and [VOC] = 0.5 ppm.

17. Explain why that is the case. **(2)**

    At relatively high NOx concentrations (high relative to those of the VOC), the OH· radical is more likely to react with NO_2· to form nitric acid HNO_3. Lowering the NOx under such conditions allows more OH· radicals to initiate reactions of VOCs and thus yield higher O_3 concentrations.

18. Explain what it means if a measurement yields a TSP of 40 and a $PM_{2.5}$ of 10. What can you deduce from the difference between the two numbers? **(3)**

    A TSP of 40 means that the concentration of total suspended particulate matter (including all particles with diameters smaller than 100 μm) in the atmosphere is 40 $\mu g/m^3$. A $PM_{2.5}$ of 10 means that the concentration of particulate matter with diameters smaller than 2.5 μm is 10 $\mu g/m^3$. From these two numbers we can deduce that the concentration of atmospheric particles in the size range 2.5 to 100 μm is 30 $\mu g/m^3$.

19. What processes limit the atmospheric residence time of ultrafine, fine and coarse particles, respectively? **(2)**

Ultrafine particles:	coagulation into large particles
Fine particles:	wet deposition
Coarse particles:	gravitational settling

20. Which of these three types of chemicals has the longest atmospheric residence time? **(1)**

Fine particles

21. Name and briefly describe the types of aerosol that are formed by gas-to-particle conversion. **(3)**

"Sulfate aerosol": formed when sulfuric acid H_2SO_4 and nitric acid HNO_3 dissolve in water droplets and combine with ammonium ions NH_4^+. When the water evaporates, salt crystals of $(NH_4)_2SO_4$ and NH_4NO_3 are formed.

"secondary organic aerosol": relatively large hydrocarbons (more than seven carbons) are being oxidized (e.g. to carboxylic acids), whch lowers their vapour pressure to such a degree that they condense into organic particles.

22. Assume that sulfur dioxide is present in the atmosphere at a concentration of 1 ppm. The Henry's law constant of sulfur dioxide is $10^{+0.1}$ M/atm, and the pK_A for sulfurous acid is 1.77. What would be the pH of rain, if sulfur dioxide were the only acidifying trace gas present in the atmosphere? **(5)**

First step is the dissolution of gaseous SO_2 into the water of the raindrop

$SO_2\ (g) + H_20\ (aq) \rightarrow H_2SO_3\ (aq)$

The extent of that dissolution process is controlled by the Henry's law constant $K_{H\ =}\ 10^{+0.1}$ M/atm:

$K_H = [H_2SO_3\ (aq)] / pSO_2$ (1)

Where pSO_2 is the partial pressure of SO_2 in the atmosphere: $P_{SO2} = 1\ ppm = 10^{-6}$ atm

Then the sulfurous acid dissociated in the water:

$H_2SO_3\ (aq) \rightarrow H^+\ (aq) + HSO_3^-\ (aq)$

The extent of that dissociation is determined by the acid's $K_A = 10^{-1.77}$ M:

$K_A = [HSO_3^-(aq)]\cdot[H^+(aq)] / [H_2SO_3\ (aq)]$ (2)

The charge balance stipulates that the number of positive charges equals the number of negative charges:

$[HSO_3^-(aq)] = [H^+(aq)]$ (3)

Combining equations (1), (2) and (3), we obtain:

$[H^+(aq)]^2 = K_A \cdot K_H \cdot pSO_2 = 10^{-1.77}$ M · $10^{+0.1}$ M/atm · 10^{-6} atm = $10^{-7.67}$ M^2

$[H^+(aq)] = 10^{-7.67/2}$ M = $10^{-3.84}$ M

pH = 3.84