Atmospheric Chemistry and Catalysis

The study of catalysis would not be complete without studying the catalytic effects of manmade chemical compounds on the atmosphere, specifically the depletion of the ozone layer.

Ozone Layer

Ozone is produced in the stratosphere (from 16 to 50 km above sea level) by action of sunlight on molecular oxygen:

$$\begin{array}{c} \text{UV} \\ \text{O}_2(g) \xrightarrow{} \text{O}(g) + \text{O}(g) \\ \text{O}(g) + \text{O}_2(g) \xrightarrow{} \text{O}_3(g) \text{ Ozone} \\ \text{O}(g) + \text{O}_2(g) \xrightarrow{} \text{O}_3(g) \end{array}$$

This thin layer of ozone protects us from harmful ultra-violet radiation that contributes to:

- Skin cancer (1% loss of O_3 (g) = 5% increase in cancer rate)
- Eye cancer
- Genetic mutation
- Species extinction (plankton)

Ozone protects us by decomposing into molecular oxygen and singlet oxygen via ultraviolet radiation absorption:

$$O_3(g) \xrightarrow{UV} O_2(g) + O(g)$$

Photochemical Smog

This is a type of pollution occurring in cities due to pollutants emitted from automobile exhaust. Here again, UV radiation is used to start a self-catalyzed process. The first step occurs in a car engine (at high T and P):

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

Then, in the air:

$$\mathrm{NO}(g) + \mathrm{O}_2\left(g\right) \to \ \mathrm{NO}_2(g) + \mathrm{O}(g)$$

$$NO_{2}(g) \rightarrow NO_{2}(g) + O(g)$$

$$O(g) + O_{2}(g) \rightarrow O_{3}(g)$$

$$O(g) + O_{2}(g) \rightarrow O_{3}(g)$$

Solutions to this problem include:

- Changing to cleaner burning fuels
- Using a catalytic converter in the exhaust system (Rh/Al₂O₃)
- Changing the exhaust to a useful material
- Changing the engine design (introduction of fuel injection)
- Increasing the use of public transportation

Depletion of Ozone by CFC's

Chlorofluorocarbons (CFC's, also known as Freons® or Halons) contributed dramatically to ozone depletion when they were in heavy use.

Some typical CFC's are:

CCl₃F (Freon-11) - used as an aerosol propellant

CCl₂F₂ (Freon-12) - used as a propellant and as a refrigerant

CH₃CCl₃ (Freon-140) - used to clean circuit boards

C2Cl4 (perchloroethylene) - used as a solvent in dry cleaning

CCl4 (carbon tetrachloride) - used as a solvent and as a reactant to produce plastics

CFC's produce a catalyst that speed up ozone depletion as follows:

$$CCl_3F(g) \xrightarrow{UV} CCl_2F(g) + Cl(g)$$

Then:

$$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$$

 $ClO(g) + O(g) \rightarrow O_2(g) + Cl(g)$

Net:

$$\frac{\text{Cl}(g)}{\text{Cl}(g)} + O_3(g) + O(g) \rightarrow 2 O_2(g) + \frac{\text{Cl}(g)}{\text{Cl}(g)}$$

Cl acts as a catalyst, with a single atom catalyzing the disintegration of 10⁵ ozone molecules.

Depletion by Nitrous Oxide (NO)

The threat to the ozone layer from vehicles traveling in the stratosphere lead to the cancellation of the U.S.A.'s SST (supersonic transport) plane in the 1970's. It is also the major argument against HST (hypersonic transport) plane development.

In an engine:

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

Then, in the stratosphere:

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

 $NO_2(g) + O(g) \rightarrow O_2(g) + NO(g)$

Net:

$$\frac{NO(g)}{O(g)} + O_3(g) + O(g) \rightarrow 2O_2(g) + \frac{NO(g)}{O(g)}$$

Therefore, NO(g) acts as a catalyst to destroy ozone!