Methods of pollution control and waste management

Lecture 9

Volatile organic compounds (VOCs)

Stratospheric ozone depletion

Volatile Organic Compounds (VOCs)

Large group of organic chemicals that have high vapour pressure (<133 Pa at room temperature) results from a low boiling point (< 250 ^{0}C measured at standard atmospheric pressure) most of them with less than about 12 carbon atoms.

- Hydrocarbons
- Halogenated hydrocarbons
- Monomers
- Alkohols
- Aldehydes

Volatile Organic Compounds (VOCs)

VOCs are recognized as major contributors to air pollution, due to their toxic nature and as precursors of ozone and photochemical smog. Some VOCs (e.g., benzene) are toxic and carcinogenic, and are regulated individually as hazardous pollutants.

Sources of emission of VOCs

- **Outdoor**

Chemical plants
Petroleum refineries
Pharmaceutical plants
Automobile and airplane manufactures
Food industries
Textile manufactures
Electronic component plants

- **Indoor**

Office supplies
Printers
Insulating materials
Solvents and cleaning products
Painting facilities
Restaurant and domestic cooking
Wood stoves

VOCs treatment methods

- Adsorption
- Condensation
- Thermal combustion
- Catalytic combustion
- Biological treatment
- Membrane methods

Most VOCs are valuable fuels or solvents. For large VOC-containing gas streams recovery is often economical, but not for small streams.

VOCs treatment methods- adsorption

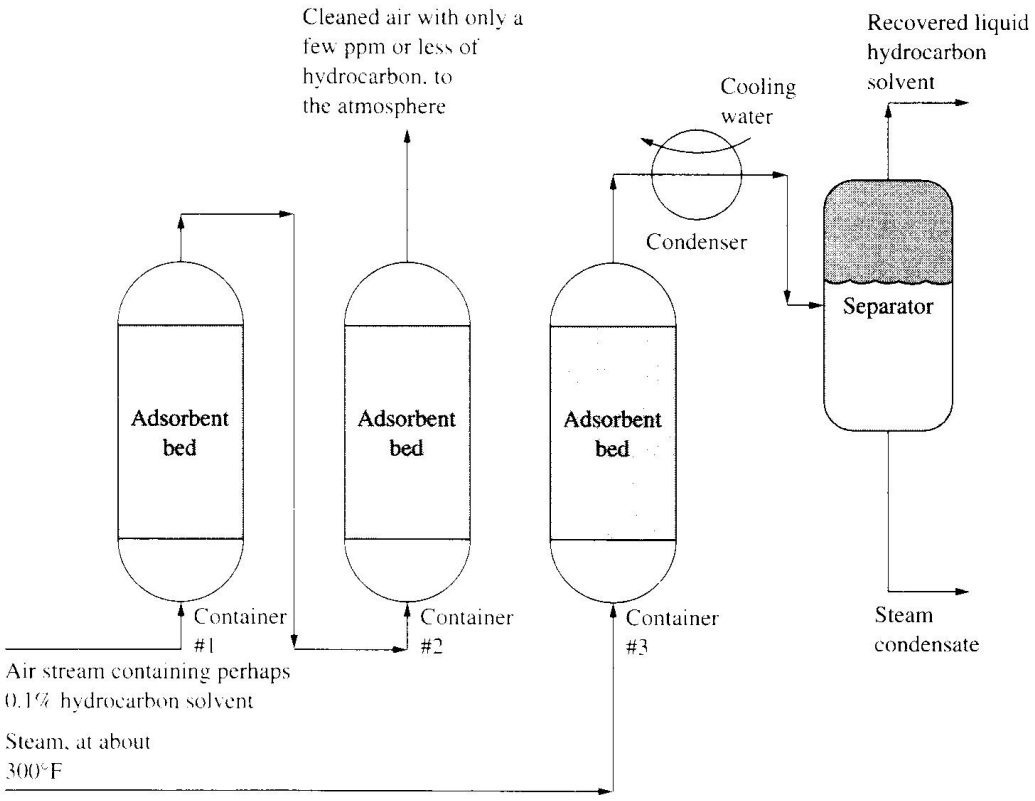


FIGURE 10.10
The typical arrangement for adsorption of a VOC from a gas stream, using three adsorbent beds; automatic switching valves; and steam desorption, condensation, and gravity separation.

Adsorbents:
activated carbon
silica gel
aluminosilicate

Adsorption rate is limited by slowest stage - diffusion (gas stream turbulence and adsorbent surface enlargement to increase rate of adsorption)

VOCs treatment methods- absorption

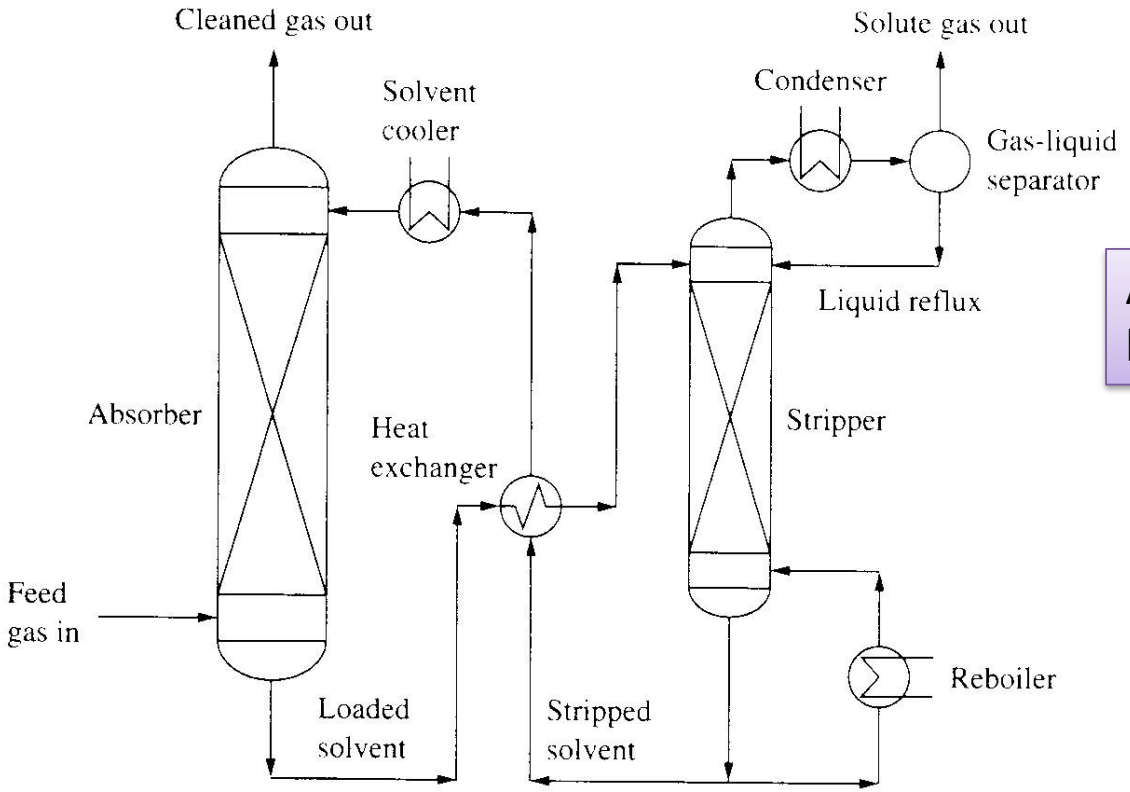


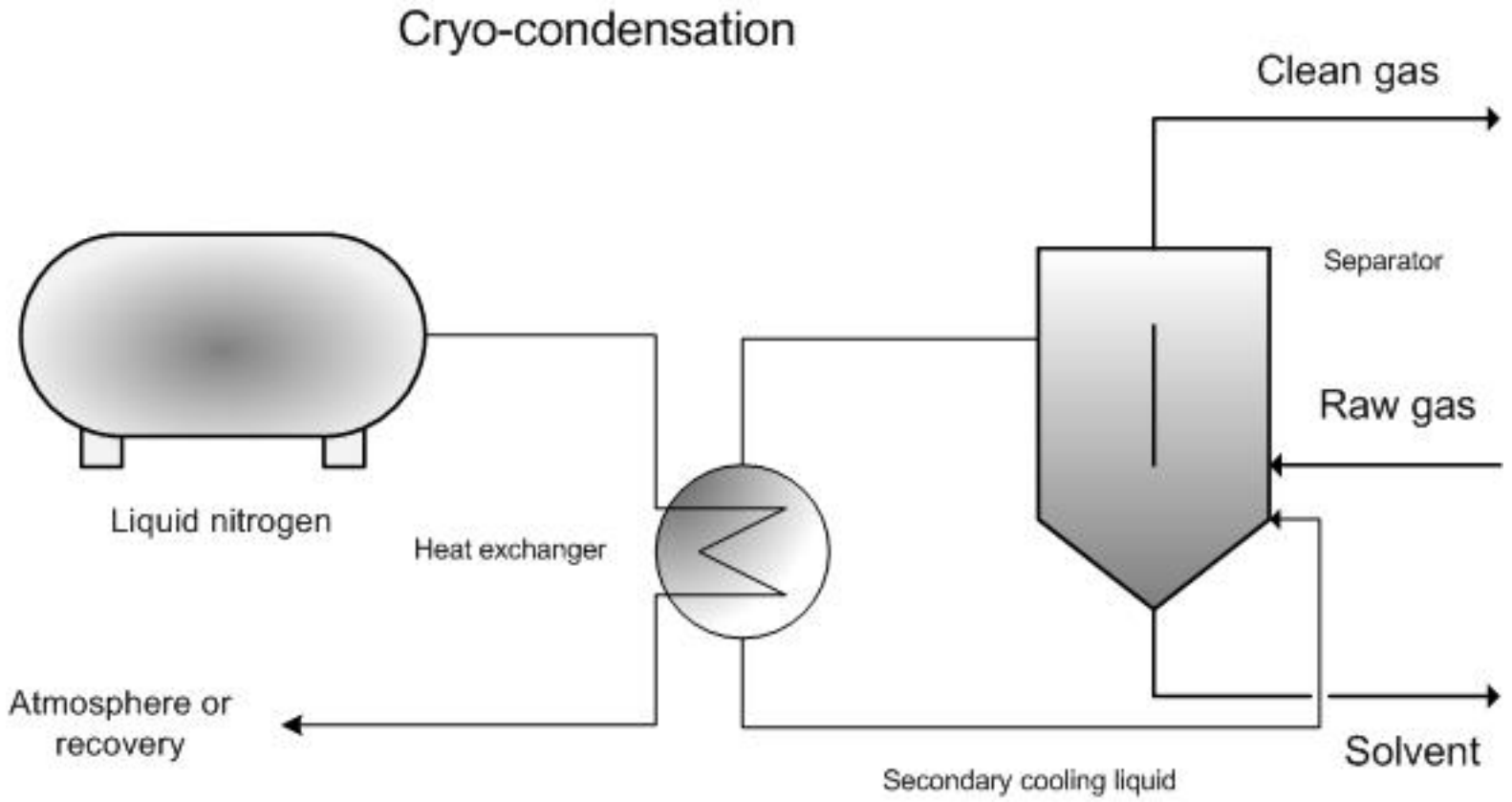
FIGURE 10.15
The flow diagram for the most common method for removing one component from a gas stream.

Absorption in the high boiling organic solvents.

Absorption rate increases with increasing the **interfacial surface and the diffusion rate.**

VOCs treatment methods- condensation

- Condensation is the process of removal of compounds by lowering the temperature of the gas stream containing them.

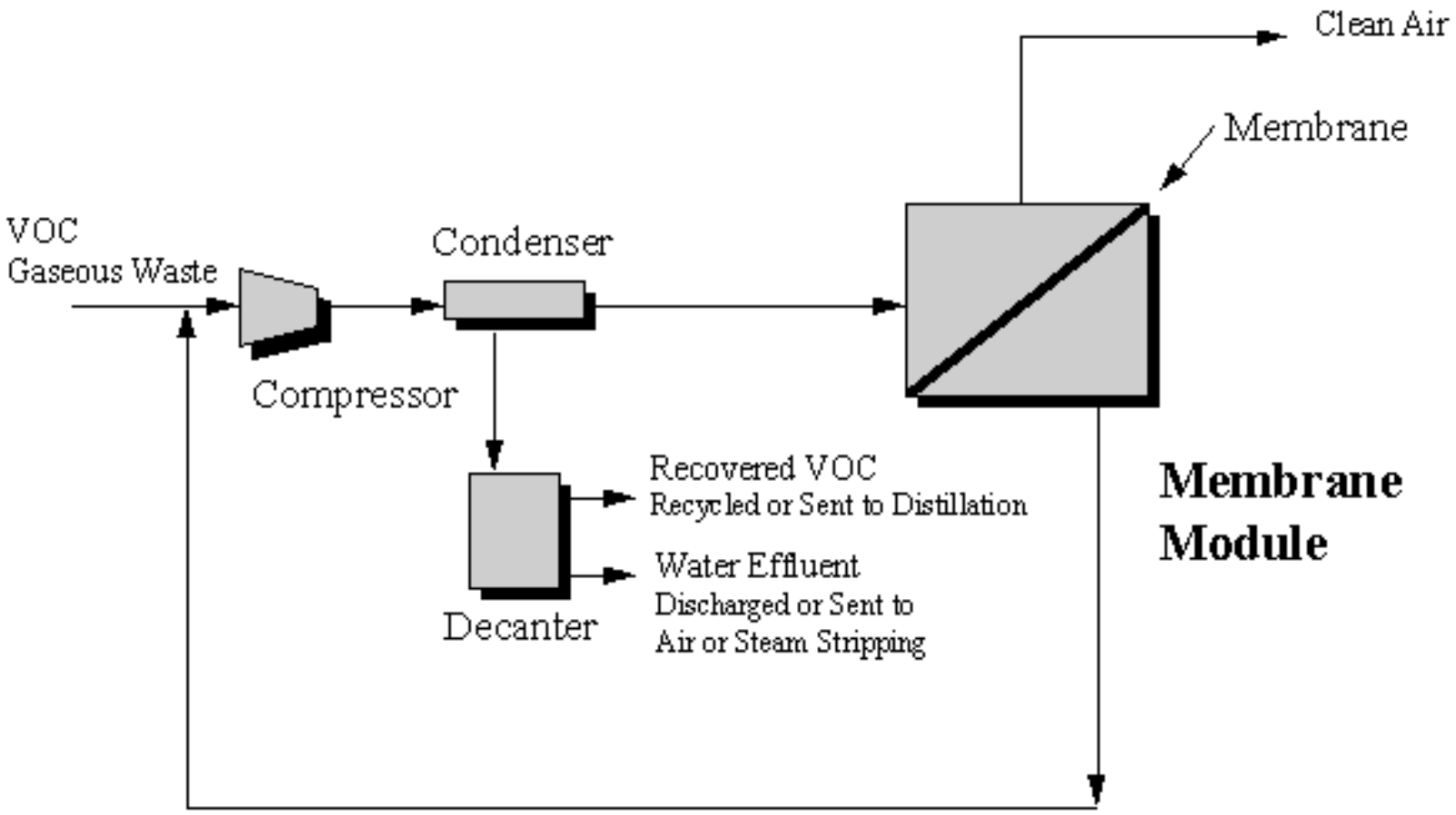


VOCs treatment methods- condensation

Cryogenic condensers are used for:

- Process gases from reactors
- Gases derived from storage tanks (particularly during filling)
- Small gas flows with high VOC concentrations

VOCs treatment methods- membrane and condensation hybrid process



VOCs treatment methods
Direct flame incineration

Direct flame incineration is used when waste gases are combustible and does not need additional fuel or air (temperature > 1200^0C)

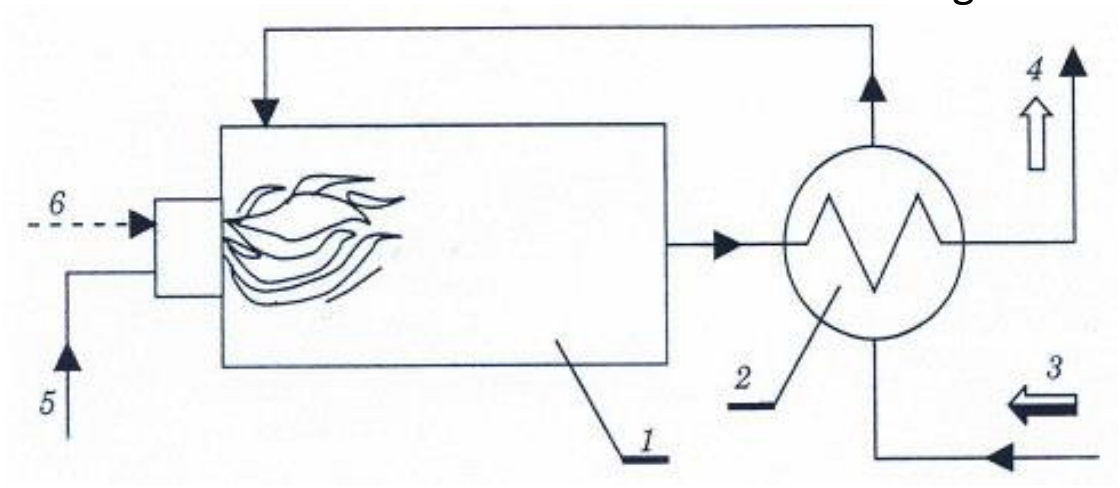
The outlet of a refinery's relief valves are piped to a flare, which is an elevated pipe with pilot lights to ignite any released VOCs.

VOCs treatment methods
Direct flame incineration

Many flares have steam jets running constantly to mix air into the gas being released.

Large, bright orange, smoky flame from the flare indicates a significant release of unburned or partly burned VOCs.

VOCs treatment methods - thermal incineration

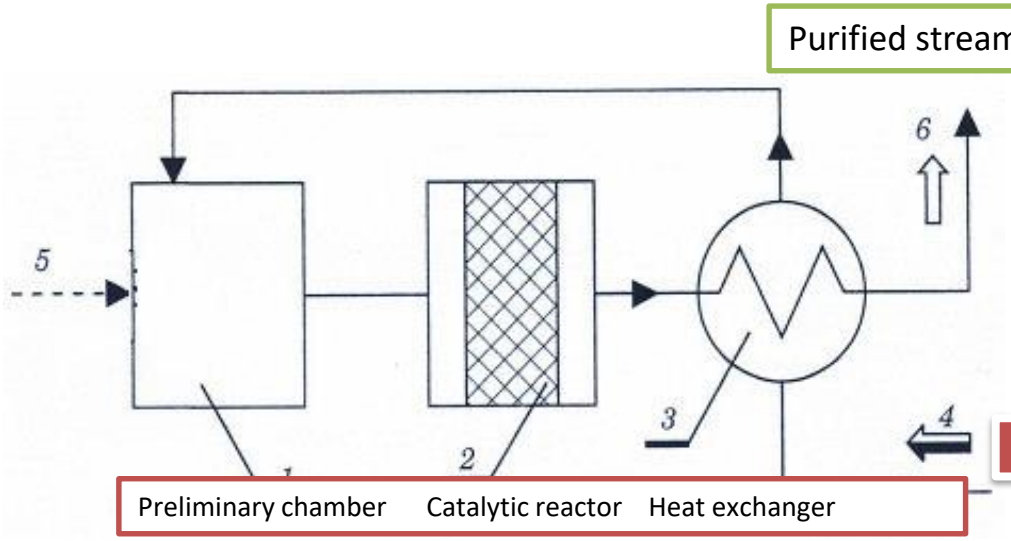


Temperature
600 – 1100^0 C

The contaminated air preheated by fumes in the heat exchanger is introduced to the oxidizing chamber.

In the chamber the contaminants undergo the oxidation to CO_2 and water.

Catalytic combustion



More versatile and economically favorable for low concentrations of organic emissions (< 5000 ppm)

This method operates at relatively low-temperatures (150-350 ^{0}C) with consequent limited emissions of dioxins and NOx

Catalytic combustion

- **Halogenated VOCs**

  Catalytic oxidation of chlorinated HC involves production of HCl and requires the addition of corrosion-resistant materials such as Cr_2O_3, V_2O_5, WO_3 to overcome the activity loss.

$$C_xH_yCl + (2x+z)\,O_2 \longrightarrow x \cdot CO_2 + z\,H_2O + HCl$$

Biological methods in VOCs removal

- Biodegradation by microorganisms (aerobic bacteria). The bacteria oxidize volatile organic compounds to carbon dioxide and water.

$$[CH_2O] + O_2 \longrightarrow CO_2 + H_2O + \Delta H$$

- The typical biofilter (better called a highly porous biochemical reactor) consists of the equivalent of a swimming pool, with a set of gas distributor pipes at the bottom, covered with several feet of soil or compost or loam in which the microorganisms live.

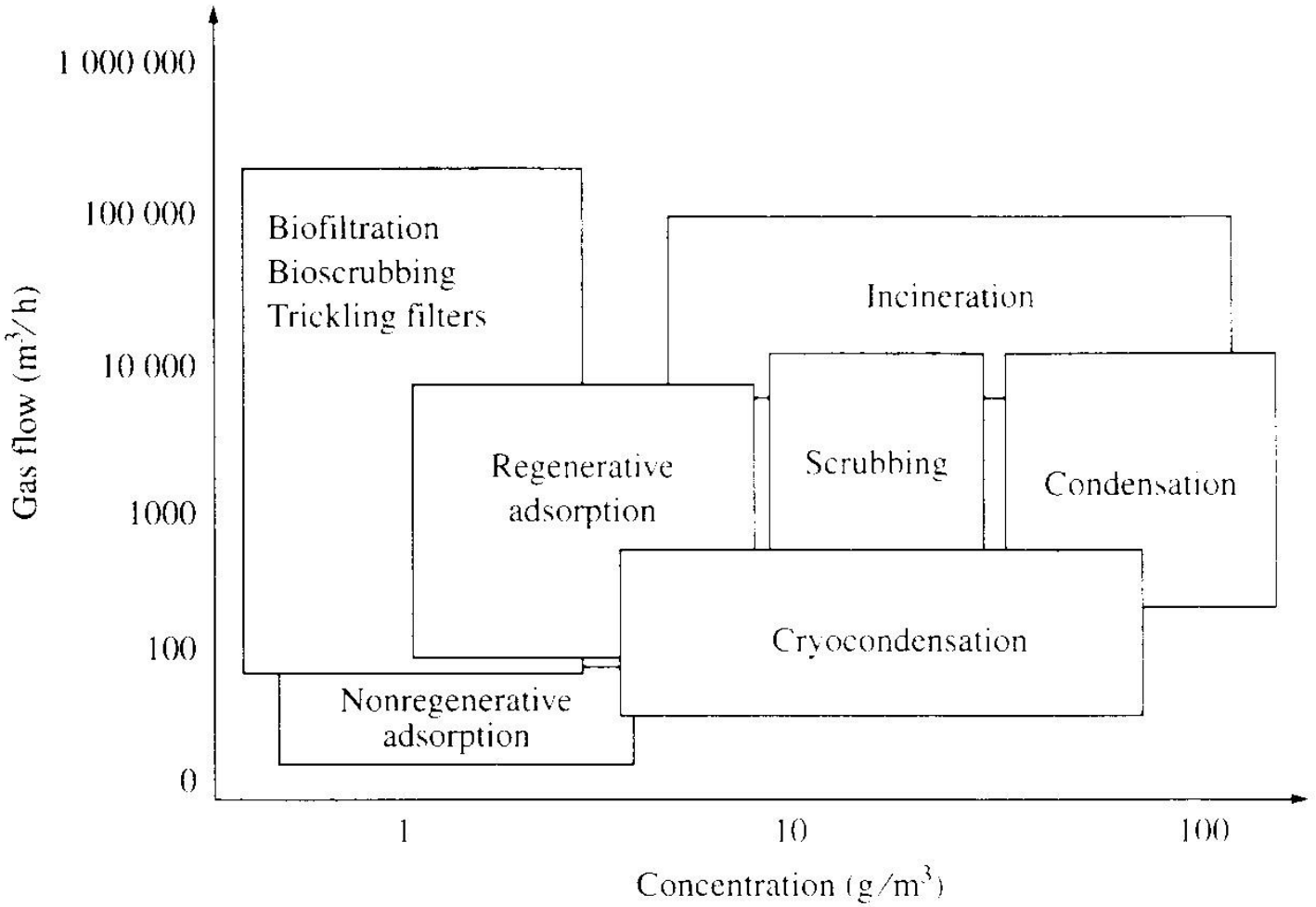


FIGURE 10.19

A guide to choosing VOC control technologies, based on flow rate and concentration only [29]. (With permission of KPMG Management Consultants, Ottawa, Ontario.) Cryocondensation is discussed in Problem 10.21. Nonregenerative adsorbers are placed in a landfill or incinerated, instead of being regenerated as shown in Fig. 10.10.

Chlorofluorocarbons CFCs

Class of compounds initially developed in the 1930s and since the early 1990s their production has been discontinued, but unfortunately their legacy will remain with us for years to come.

- Low viscosity
- Low surface tension
- Low boiling point
- Chemical and biological inertness
- Non-toxic
- Non-flammable

Du Pont trade name **Freons**

When compressed at room temperature, the gases become liquids; when the pressure is released, they revert to gaseous form taking up large amount of heat in the process.

Chlorofluorocarbons CFCs

- Refrigerants for refrigerators and air-conditioners
- Cleaning agents for semi-conductors and precision parts
- Foaming agents for insulating materials and packaging cushions
- Propellants for aerosol sprays

Chlorofluorocarbons CFCs

- 1974, the mechanism of the ozone layer depleted by CFCs was identified
- In 1985, the observation of an ozone hole in the Antarctic Pole provided proof that the ozone layer was depleting
- 1987, The Montreal Protocol on Substances that Deplete the Ozone Layer was adopted

Stratospheric chemistry

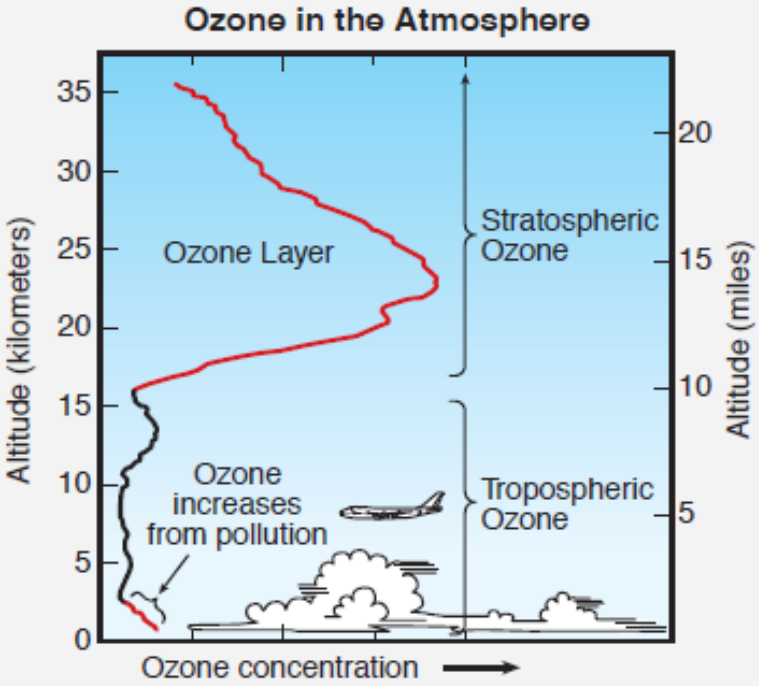
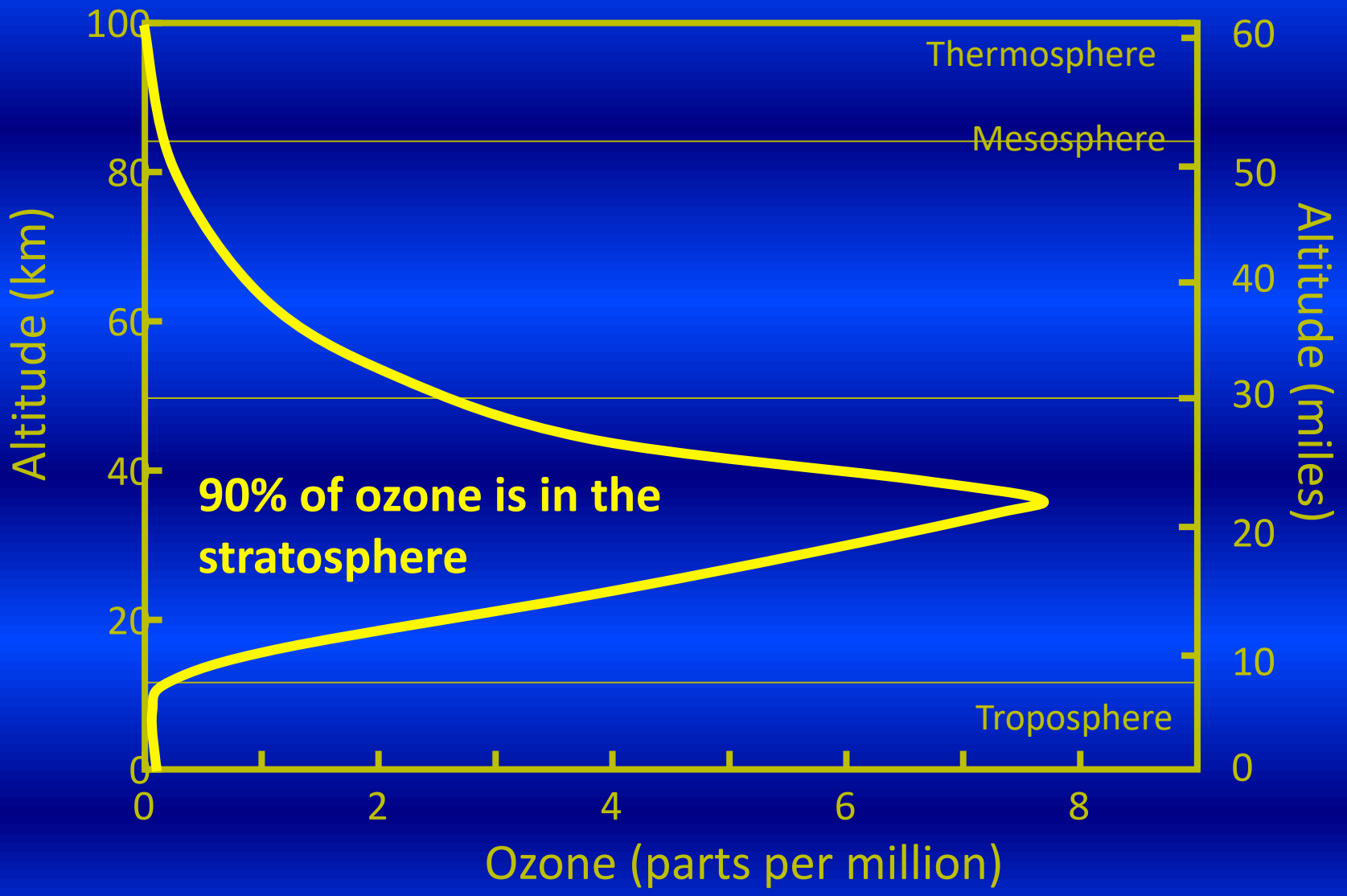


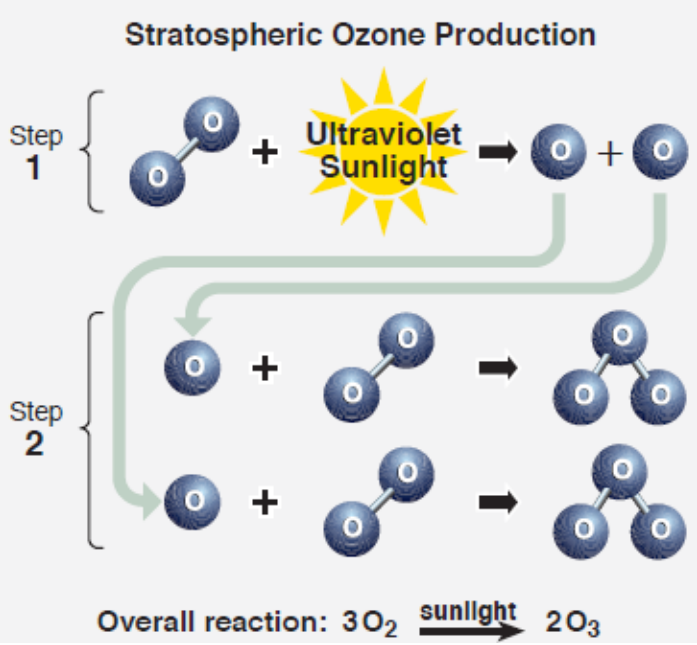
Figure Q1-2. Atmospheric ozone. Ozone is present throughout the lower atmosphere. Most ozone resides in the stratospheric "ozone layer" above Earth's surface. Increases in ozone occur near the surface as a result of pollution from human activities.

The stratospher is located above a troposphere and below a mesosphere (between 15 – 50 km). With cooler heavier air below convection is minimized creating a stable atmosphere with minimal mixing. This region is frequently called the ozone layer. In the stratosphere, ozone is an effective filter capable of absorbing ultraviolet radiation with wavelength 200 – 315 nm.

D.W. Fahey, TWENTY QUESTIONS AND ANSWERS ABOUT THE OZONE LAYER, Panel Review Meeting for the 2002 ozone assessment (Les Diablerets, Switzerland, 24-28 June 2002).


Thermosphere
Mesosphere
Troposphere
90% of ozone is in the stratosphere
Altitude (km)
Altitude (miles)
Ozone (parts per million)
100
80
60
40
20
0
60
50
40
30
20
10
0
0
2
4
6
8

The Chapman reaction sequence



$O_2 + h\nu\ (\lambda<240\ nm) \longrightarrow O + O$ (slow)

$O + O_2 + M \longrightarrow O_3 + M$ (fast)

$O_3\ h\nu\ (\lambda\sim200\text{-}315\ nm) \longrightarrow O_2^* + O$ (fast)

$O + O_3 \longrightarrow O_2 + O_2$ (slow)

At 50 km the lifetime of dioxygen is approximately 1h, at 20 km is about 5 years, in the intermediate range there are both dioxygen and intense high energy radiation, the maximum ozone number density at an altitude of approximately 20 km.

Measuring ozone in the stratosphere

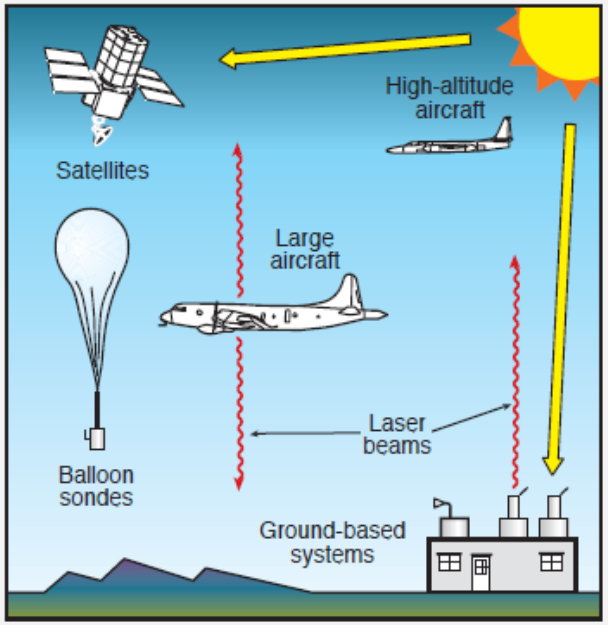


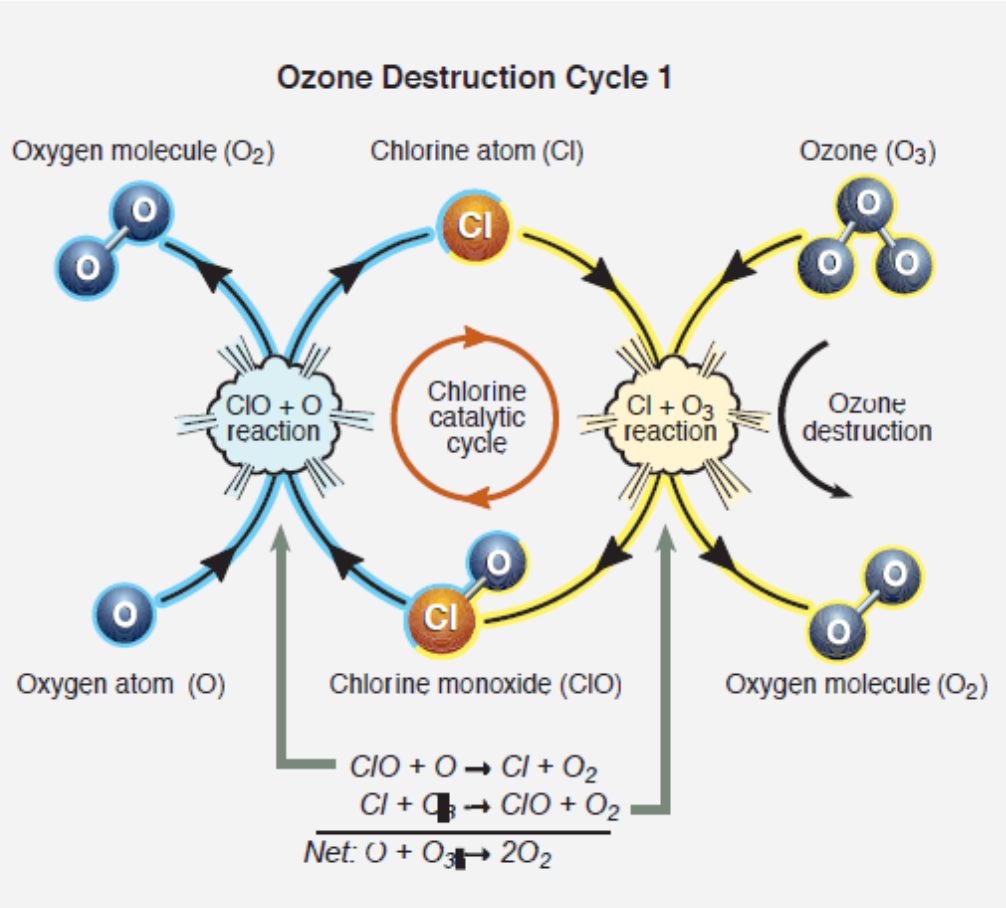
Figure Q5-1. Ozone measurements. Ozone is measured throughout the atmosphere with instruments on the ground and on board aircraft, high-altitude balloons, and satellites. Some instruments measure ozone directly in sampled air and others measure ozone remotely some distance away from the instrument. Instruments use optical techniques with the Sun and lasers as light sources or use chemical reactions that are unique to ozone. Measurements at many locations over the globe are made weekly to monitor total ozone amounts.

Dobson unit is defined in terms of an equivalent thickness of pure ozone. An air column with a Dobson **300 DU** (close to global average) contains as much ozone as in a **3mm thick layer of pure ozone at 0°C and P_o with cross-sectional area of 1 m^2** ($V = 0.003\ m^3$).

Stratospheric concentration of ozone shows variability both in position on the Earth and in the time.

D.W. Fahey, TWENTY QUESTIONS AND ANSWERS ABOUT THE OZONE LAYER, Panel Review Meeting for the 2002 ozone assessment (Les Diablerets, Switzerland, 24-28 June 2002).

Processes for catalytic decomposition of ozone



$$Cl_2CF_2 + h\nu \rightarrow Cl\cdot + ClCF_2$$

$$\cdot Cl + O_3 \rightarrow \cdot ClO + O_2$$

$$\cdot ClO + O \rightarrow \cdot Cl + O_2$$

D.W. Fahey, TWENTY QUESTIONS AND ANSWERS ABOUT THE OZONE LAYER, Panel Review Meeting for the 2002 ozone assessment (Les Diablerets, Switzerland, 24-28 June 2002).

Antarctic and Arctic ozone hole formation

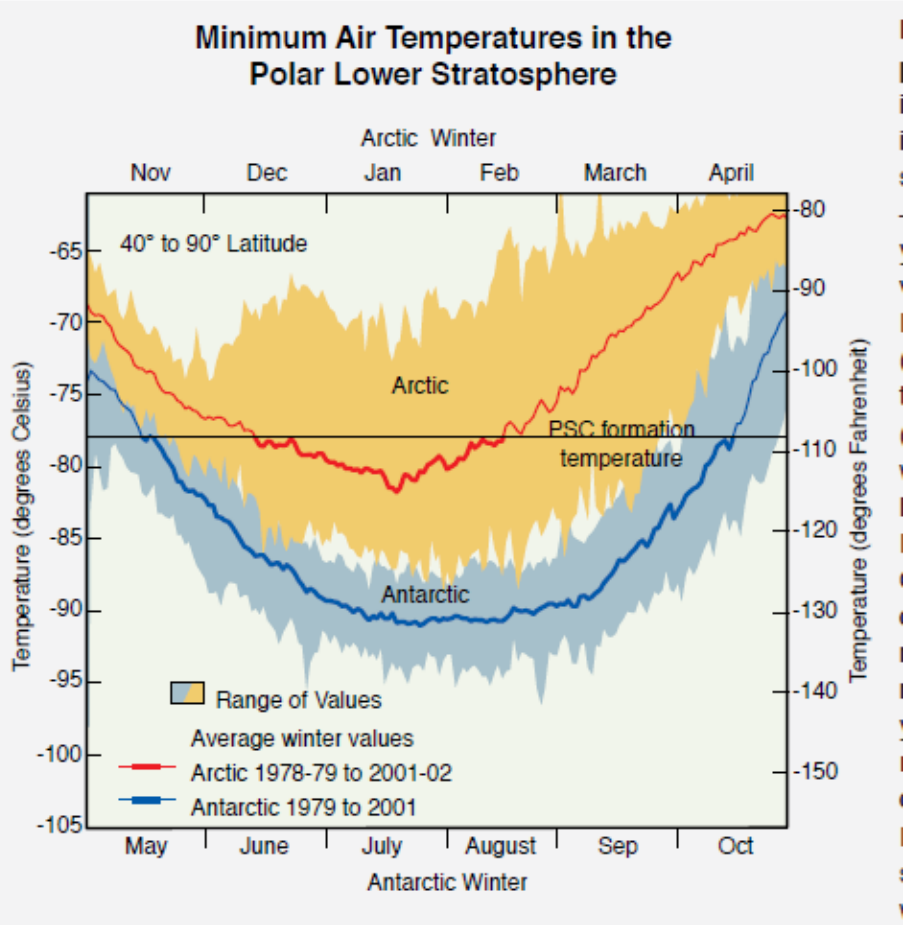
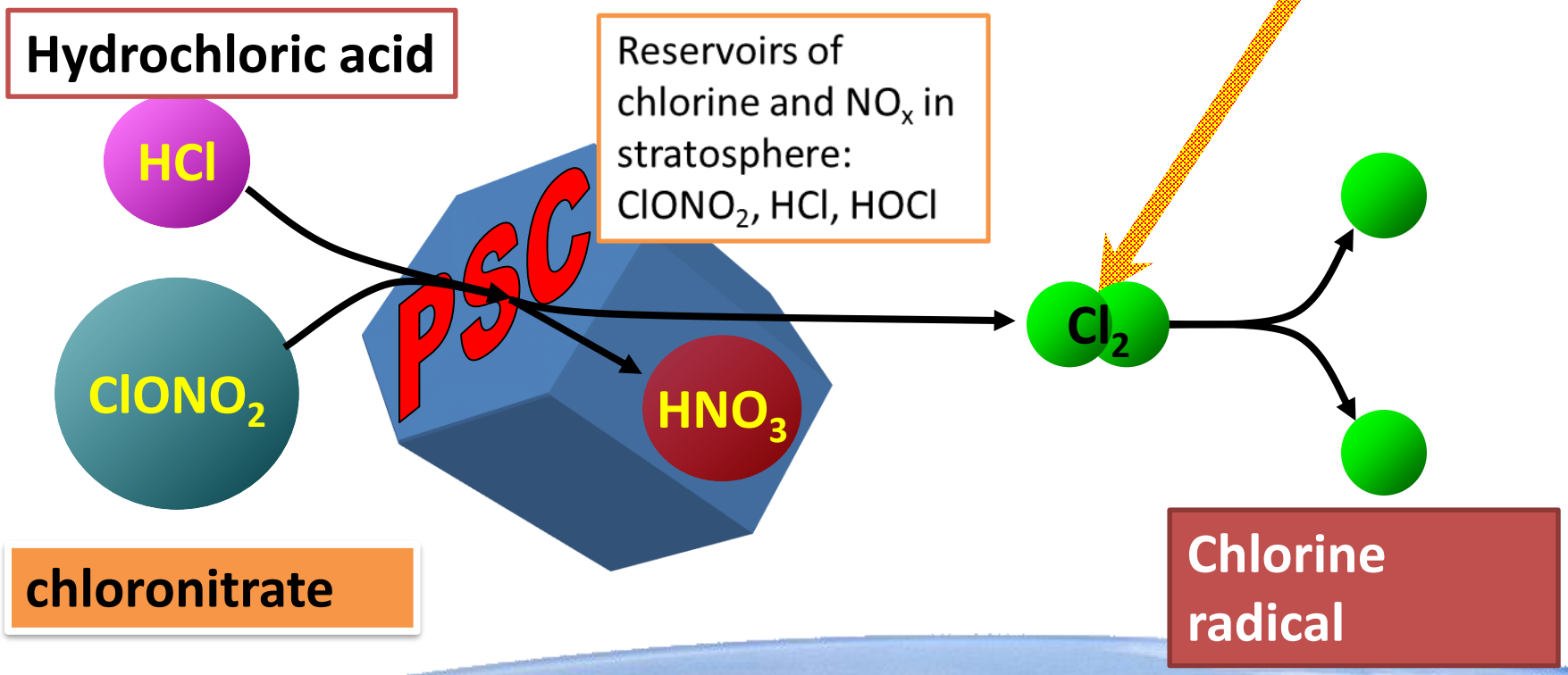


Figure Q10-2. Polar stratospheric clouds. This photograph of an Arctic polar stratospheric cloud (PSC) was taken from the ground at Kiruna, Sweden (67°N), on 27 January 2000. PSCs form during winters in the Arctic and Antarctic stratospheres. The particles grow from the condensation of water along with nitrogen and sulfur gases. Because the particles are large and numerous, the clouds often can be seen with the human eye when the Sun is near the horizon. Reactions on PSCs cause the highly reactive chlorine gas ClO to be formed, which is very effective in the chemical destruction of ozone.

D.W. Fahey, TWENTY QUESTIONS AND ANSWERS ABOUT THE OZONE LAYER, Panel Review Meeting for the 2002 ozone assessment (Les Diablerets, Switzerland, 24-28 June 2002).

Polar ozone hole theory

Solomon et al. (1986), Wofsy and McElroy (1986), and Crutzen and Arnold (1986) suggest reactions on cloud particle surfaces as mechanism for activating chlorine



Cl_2 is easily photolyzed by UV & blue/green light

HNO_3 is sequestered on PSC

Antarctic and Arctic ozone hole formation

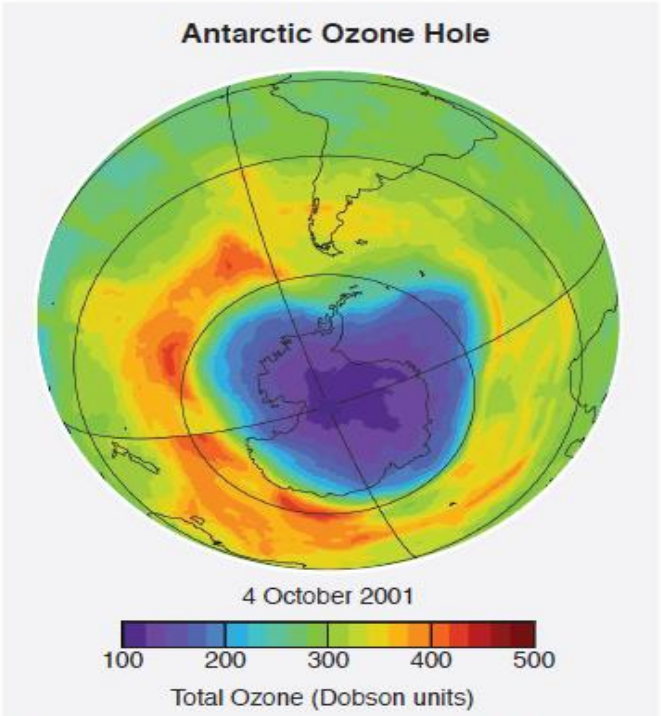
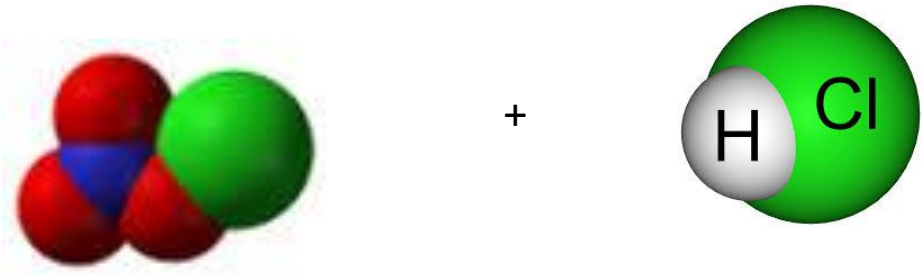


Figure Q11-1. Antarctic "ozone hole." Total ozone values are shown for high southern latitudes as measured by a satellite instrument. The dark regions over the Antarctic continent show the severe ozone depletion now found in every spring. Minimum values of total ozone inside the ozone hole are close to 100 Dobson units (DU) compared with normal springtime values of about 300 DU (see *Q4*). In late spring or early summer (November-December) the ozone hole disappears as ozone-depleted air is displaced and diluted by ozone-rich air from outside the ozone hole.



On the Polar Stratopheric Clouds (PSCs)

$$HCl + ClONO_2 \longrightarrow Cl_2 + HNO_3$$

$$H_2O + ClONO_2 \longrightarrow HOCl + HNO_3$$

$$Cl_2 + h\nu \longrightarrow 2\ Cl\cdot$$

$$HOCl + h\nu \longrightarrow \cdot Cl + \cdot OH$$

D.W. Fahey, TWENTY QUESTIONS AND ANSWERS ABOUT THE OZONE LAYER, Panel Review Meeting for the 2002 ozone assessment (Les Diablerets, Switzerland, 24-28 June 2002).

Replacements for CFCs

- **HCFC substitute gases**

  The Montreal Protocol provides for the transitional use of hydrochlorofluorocarbons, differ chemically from most other halogen source gases in that they contain hydrogen (H) atoms in addition to chlorine and fluorine atoms.

- **HFC substitute gases**

  Hydrofluorocarbons contain only hydrogen, fluorine, and carbon atoms. Because HFCs contain no chlorine or bromine, they do not contribute to ozone depletion. As a consequence, the HFCs are not regulated by the Montreal Protocol. However, HFCs (as well as all halogen source gases) are included to GHGs.

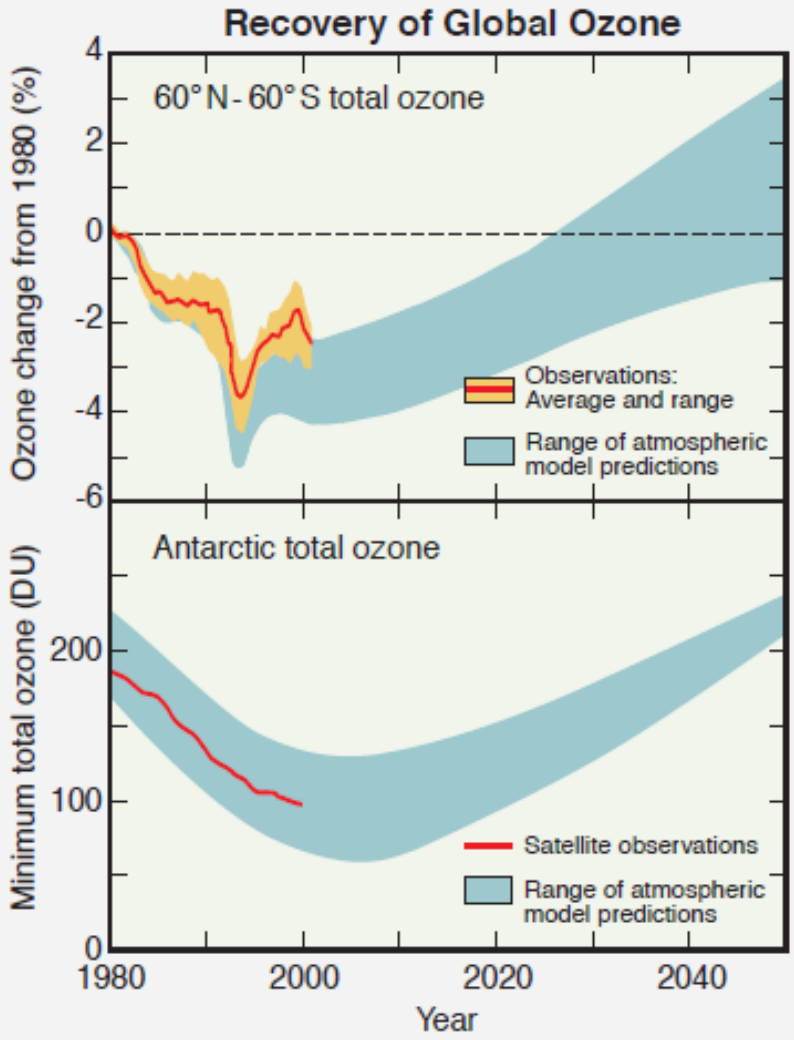


Figure Q20-1. Global ozone recovery predictions. Observed values of global total ozone (top panel) and minimum total ozone over Antarctica (bottom panel) have decreased beginning in the early 1980s. As halogen source gas emissions decrease in the early 21st century, ozone values are expected to increase and recover toward pre-1980 values. Atmospheric computer models that account for changes in halogen gases and other atmospheric parameters can be used to predict how ozone amounts will increase. These model results show that recovery is expected to be significant by 2050, or perhaps earlier. The range of model predictions comes from the use of several different models that have different assumptions about the future climate and composition of the atmosphere. These assumptions are an attempt to account for estimated differences in atmospheric composition and other parameters between 1980, before the "ozone hole" began, and 2050.

D.W. Fahey, TWENTY QUESTIONS AND ANSWERS ABOUT THE OZONE LAYER, Panel Review Meeting for the 2002 ozone assessment (Les Diablerets, Switzerland, 24-28 June 2002).