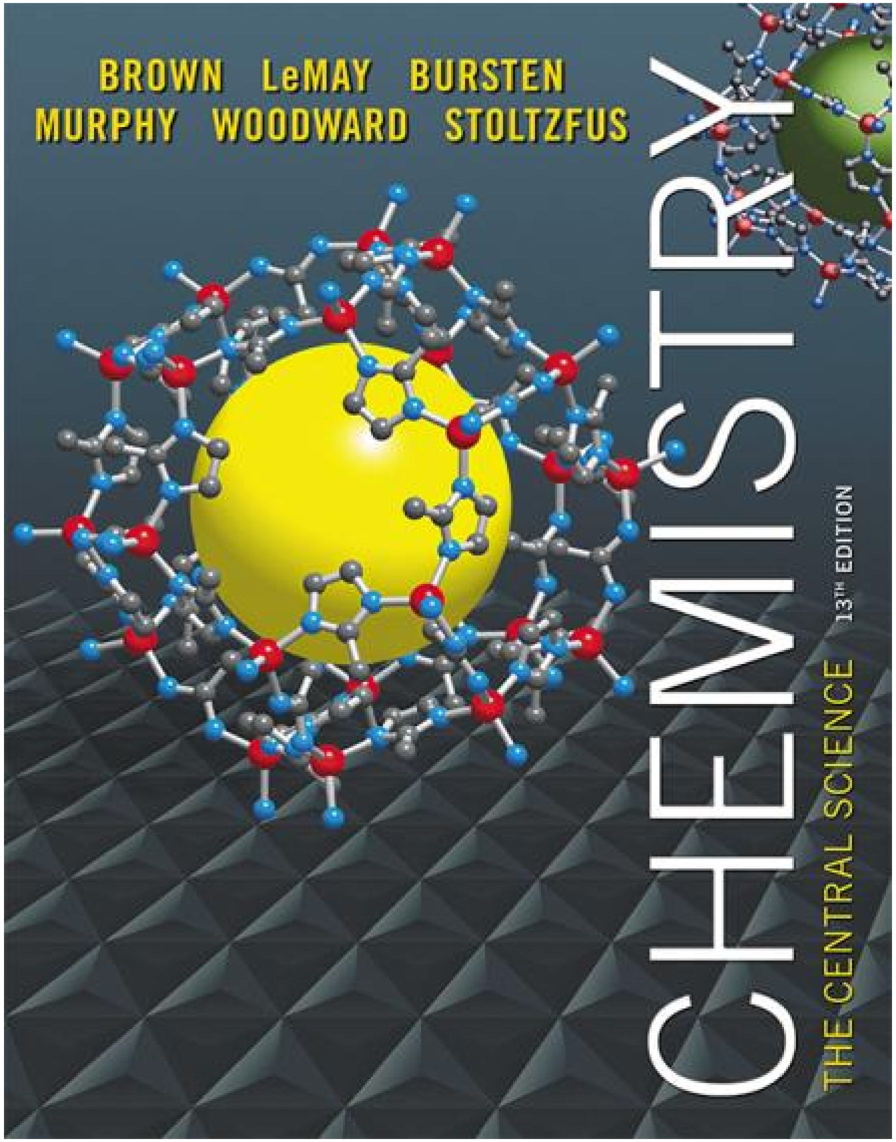


Lecture Presentation

Chapter 18

Chemistry of the Environment

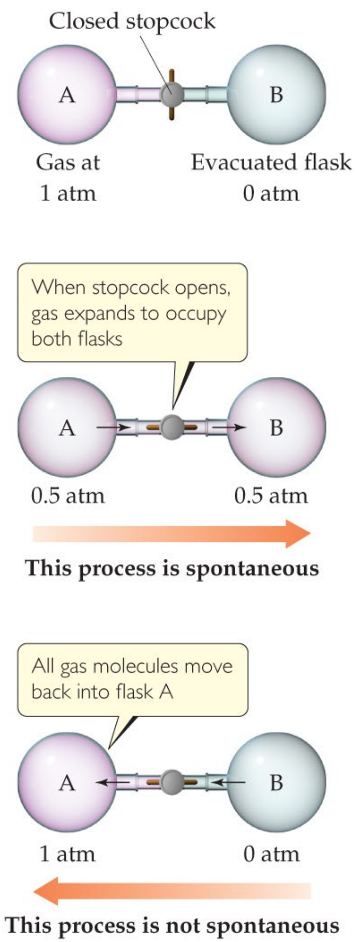
Changes in Internal Energy

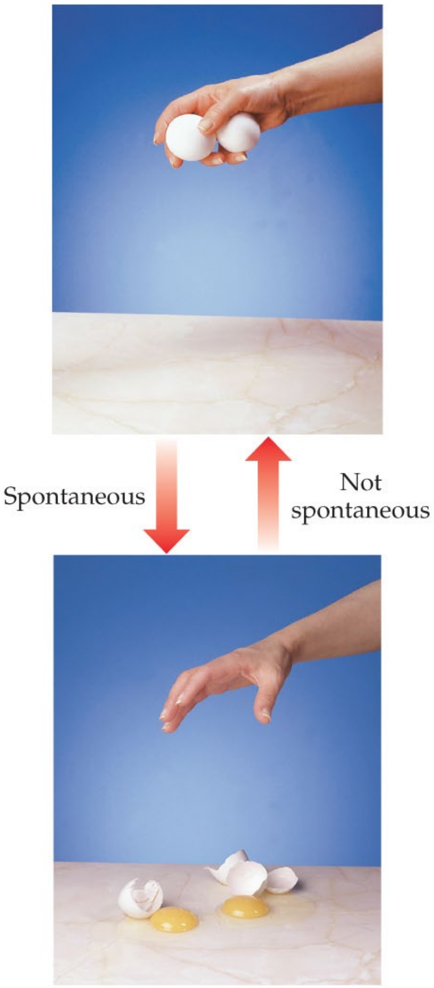
- When energy is exchanged between the system and the surroundings, it is exchanged as either heat (q) or work (w).
- That is, $\Delta E = q + w$.

Exergonic process must be exothermic (right or wrong?)

Spontaneous Processes

- **Spontaneous processes** proceed without any outside assistance.
- The gas in vessel A will spontaneously effuse into vessel B, but it will *not* spontaneously return to vessel A.
- Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.





Entropy

- **Entropy** can be thought of as a measure of the randomness of a system.
- It is a state function:

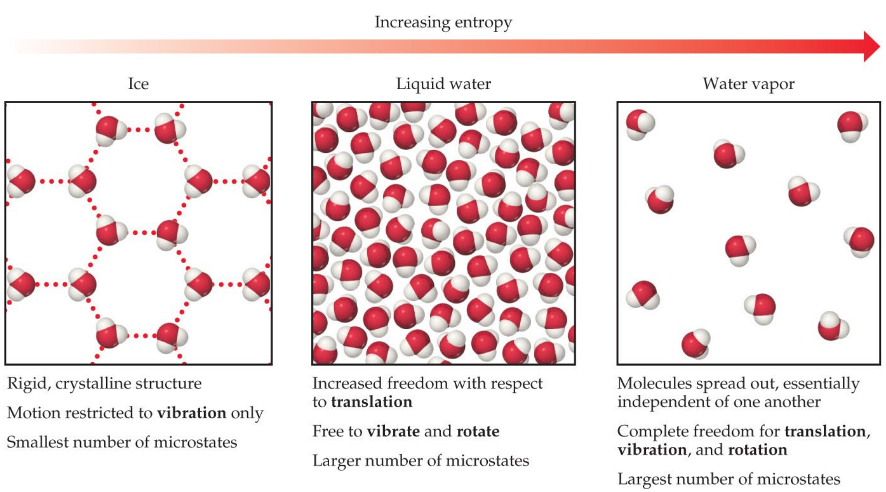
$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

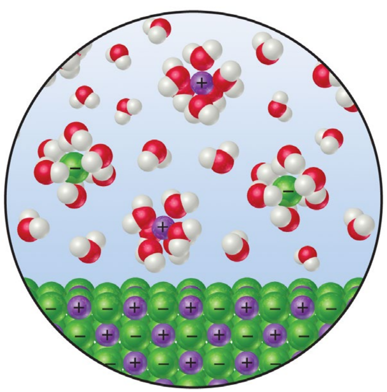
- It can be found by heat transfer from surroundings at a given temperature:

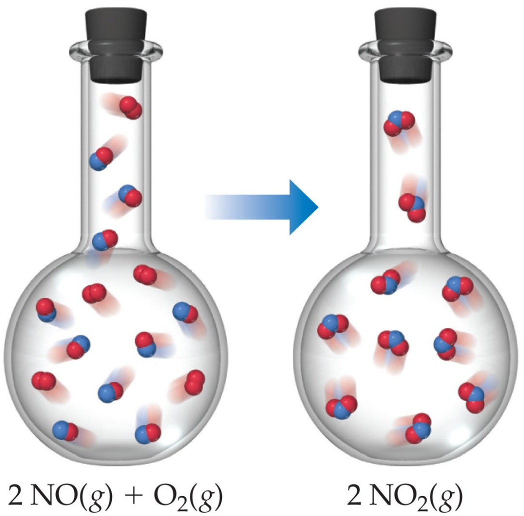
$$\Delta S = \frac{q_{\text{rev}}}{T} \quad (\text{constant } T)$$

Entropy and Physical States

- Entropy increases with the freedom of motion of molecules.
- $S(g) > S(l) > S(s)$
- Entropy of a system increases for processes where
  - gases form from either solids or liquids.
  - liquids or solutions form from solids.
  - the number of gas molecules increases during a chemical reaction.



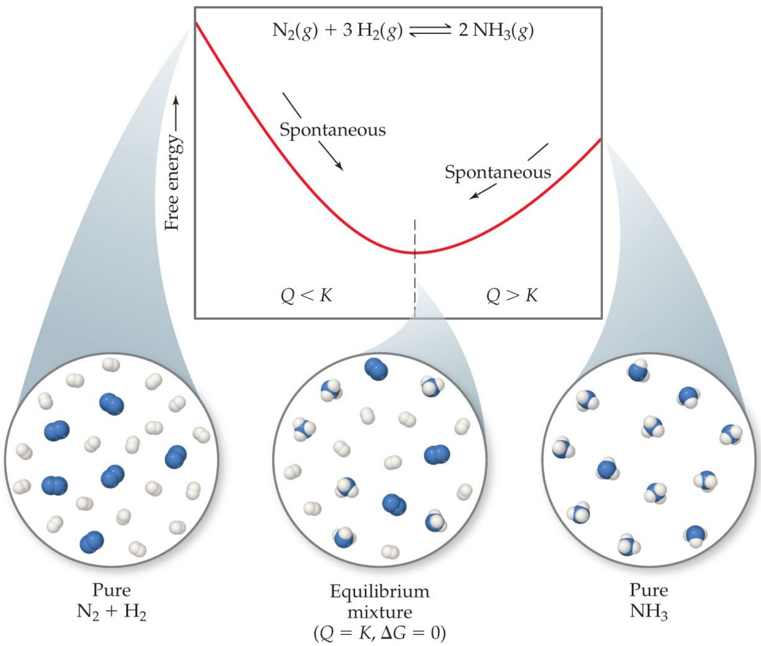




Total Entropy and Spontaneity

- $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$
- Substitute for the entropy of the surroundings:
  - $\Delta S_{\text{universe}} = \Delta S_{\text{system}} - \Delta H_{\text{system}}/T$
- Multiply by $-T$:
  - $-T\Delta S_{\text{universe}} = -T\Delta S_{\text{system}} + \Delta H_{\text{system}}$
- Rearrange:
  - $-T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$
- Call $\boldsymbol{-T\Delta S_{\text{universe}}}$ the **Gibbs Free Energy (ΔG)**:
  - $\boldsymbol{\Delta G = \Delta H - T\Delta S}$

Gibbs Free Energy



1. If ΔG is negative, the forward reaction is spontaneous.
2. If ΔG is 0, the system is at equilibrium.
3. If ΔG is positive, the reaction is spontaneous in the reverse direction.

17) ΔS is positive for the reaction ________.

A) $2H_2 (g) + O_2 (g) \rightarrow 2H_2O (g)$

B) $2NO_2 (g) \rightarrow N_2O_4 (g)$

C) $CO_2 (g) \rightarrow CO_2 (s)$

D) $BaF_2 (s) \rightarrow Ba^{2+} (aq) + 2F^- (aq)$

E) $2Hg (l) + O_2 (g) \rightarrow 2HgO (s)$

30) A reaction that is not spontaneous at low temperature can become spontaneous at high temperature if ΔH is ________ and ΔS is ________.

A) +, +

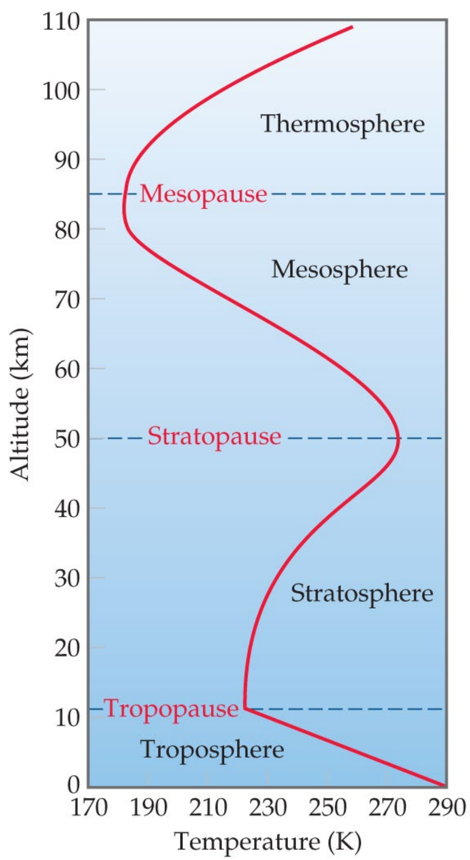
B) -, -

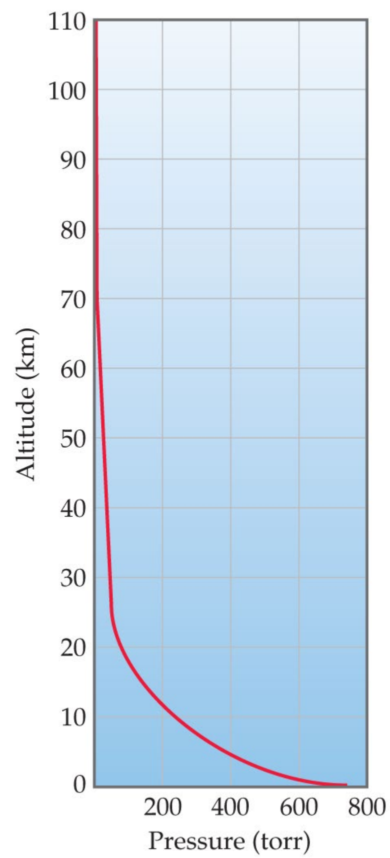
C) +, -

D) -, +

E) +, 0

Atmosphere





- The atmosphere consists of the **troposphere**, **stratosphere** (combined 99.9 mass %), **mesosphere**, and **thermosphere**.
- Temperature varies greatly with altitude. Within the troposphere (where we live), as altitude increases, temperature decreases.
- Pressure decreases with altitude in the atmosphere.

Composition of the Atmosphere

- The composition of gases in the atmosphere is not uniform.
- Heavier gases tend to “sink” in the atmosphere, leaving lighter ones at the top.
- Near sea level, the majority of the atmosphere is nitrogen and oxygen.

Table 18.1 The Major Components of Dry Air near Sea Level

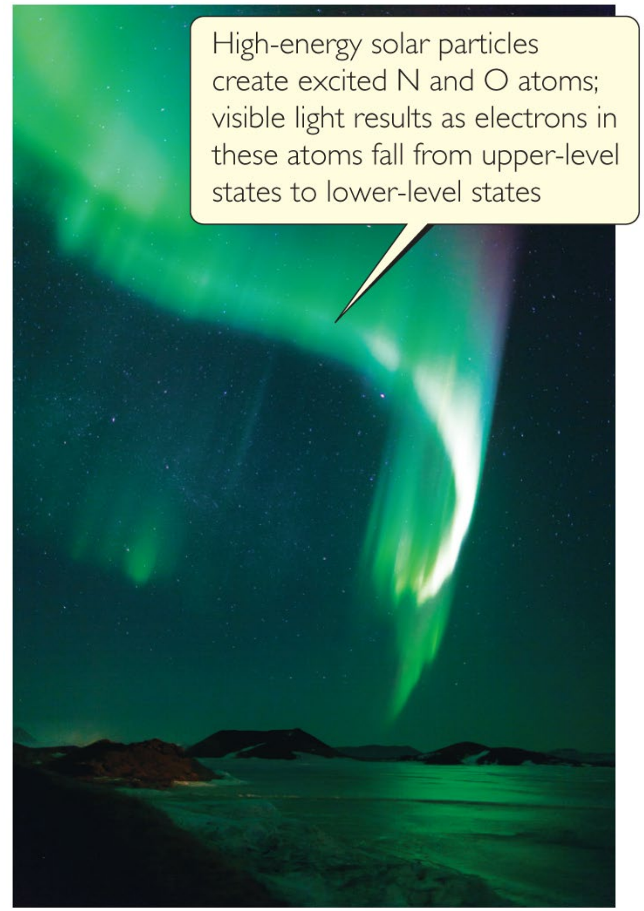
Component*	Content (mole fraction)	Molar Mass (g/mol)
Nitrogen	0.78084	28.013
Oxygen	0.20948	31.998
Argon	0.00934	39.948
Carbon dioxide	0.000400	44.0099
Neon	0.00001818	20.183
Helium	0.00000524	4.003
Methane	0.000002	16.043
Krypton	0.00000114	83.80
Hydrogen	0.0000005	2.0159
Nitrous oxide	0.0000005	44.0128
Xenon	0.000000087	131.30

*Ozone, sulfur dioxide, nitrogen dioxide, ammonia, and carbon monoxide are present as trace gases in variable amounts.

Chemistry of the Environment

Chemistry of Nitrogen and Oxygen

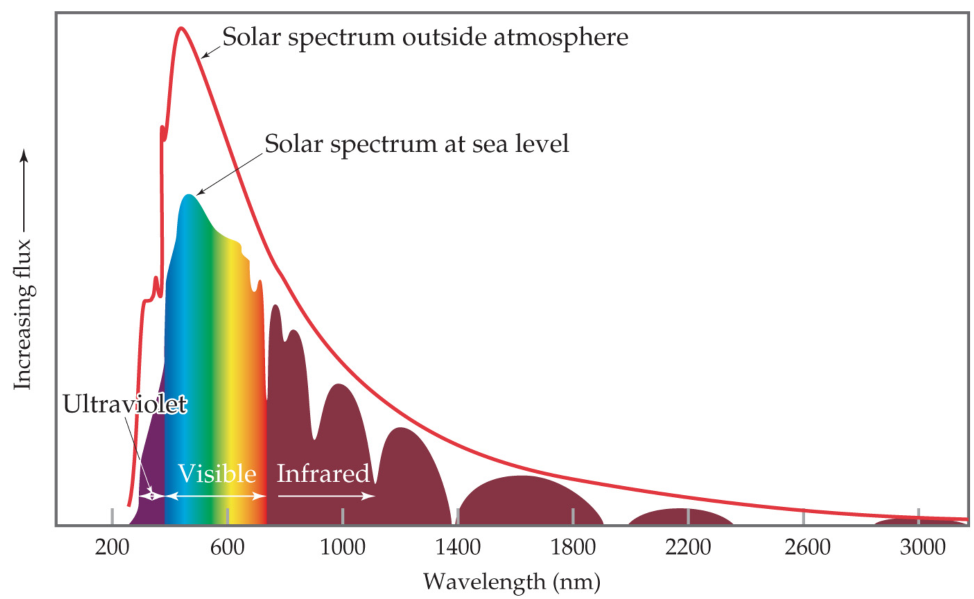
- Nitrogen is largely unreactive due to the bond energy associated with breaking the N≡N.
- Oxygen has a much lower bond enthalpy than nitrogen, and is therefore more reactive.
- Oxides of nonmetals are acidic; oxides of active metals are basic.



Chemistry of the Environment

Photochemical Reactions in the Atmosphere

- Beyond the stratosphere is where the “outer defense” of Earth against radiation and high-energy particles occurs.
- Chemical changes which occur there can be described as *phtotodissociation* or *photoionization*.



Chemistry of the Environment

Photodissociation

- Rupture of a bond due to absorption of a photon
- Ions are *not* formed; radicals (having unpaired electrons) are often formed.
- One of the most important reactions in the upper atmosphere is the photodissociation of oxygen molecules to oxygen atoms:

$$:\!\ddot{O}\!=\!\ddot{O}\!: + h\nu \longrightarrow :\!\ddot{\underset{\cdot\cdot}{O}} + \ddot{\underset{\cdot\cdot}{O}}\!:$$

Photoionization

- Sometimes when molecules in the upper atmosphere absorb solar radiation, they emit electrons; this is **photoionization**.
- The result is formation of a cation.

Table 18.3 Photoionization Reactions for Four Components of the Atmosphere

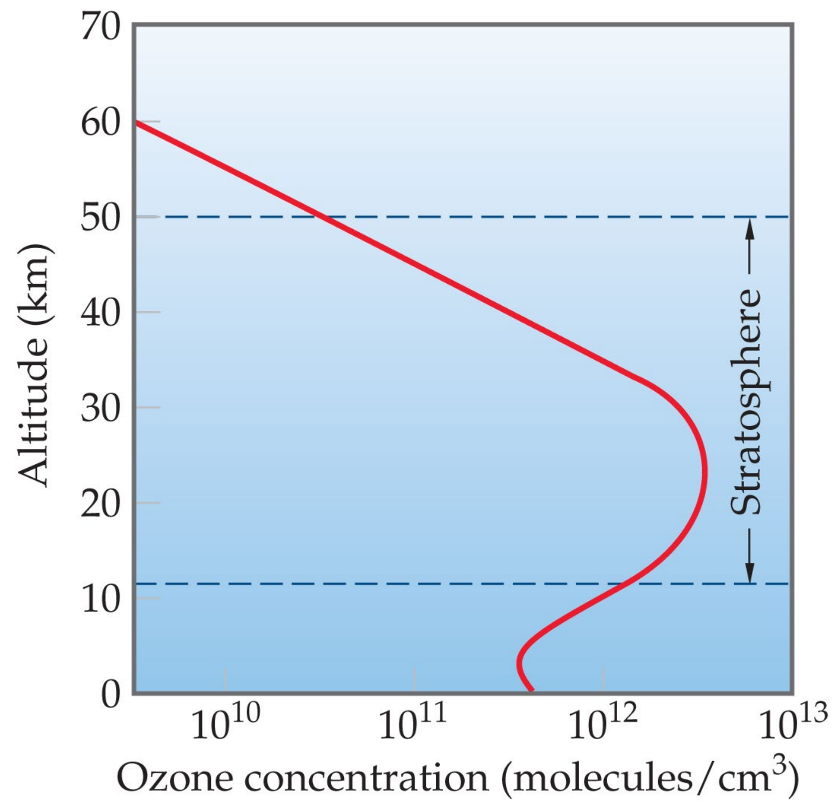
Process	Ionization Energy (kJ/mol)	λ_{max}(nm)
$N_2 + h\nu \longrightarrow N_2^+ + e^-$	1495	80.1
$O_2 + h\nu \longrightarrow O_2^+ + e^-$	1205	99.3
$O + h\nu \longrightarrow O^+ + e^-$	1313	91.2
$NO + h\nu \longrightarrow NO^+ + e^-$	890	134.5

Ozone

- Ozone absorbs much of the radiation between 240 and 310 nm, protecting us from UV radiation.
- It forms from reaction of molecular oxygen with the oxygen atoms produced in the upper atmosphere by photodissociation.

$$O + O_2 \longrightarrow O_3$$

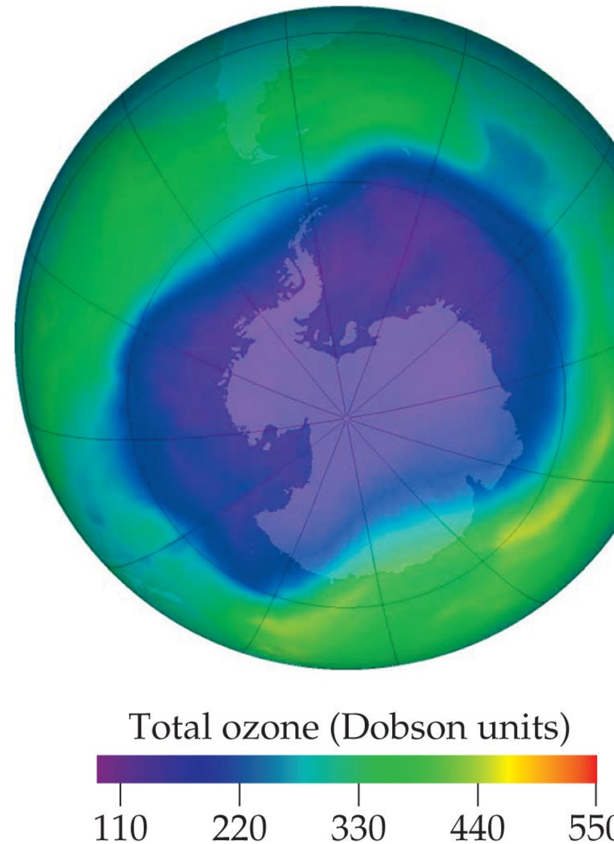
- The ozone layer occurs in the stratosphere, at an altitude of about 25 km.



Chemistry of the Environment

Ozone Depletion

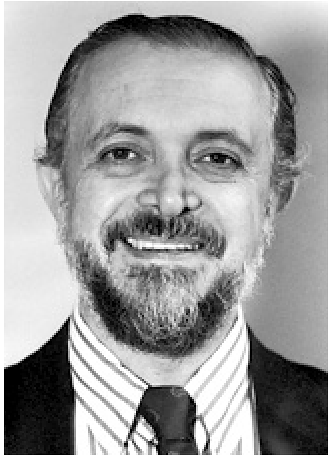
- In 1974 Rowland and Molina discovered that chlorine from chlorofluorocarbons (CFCs) may be depleting the supply of ozone in the upper atmosphere by chemical means.
- Despite a ban on CFCs in over 100 countries, ozone depletion will continue because of the chemical nature of CFCs.



Chemistry of the Environment

The Nobel Prize in Chemistry 1995

"for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone"



Paul J. Crutzen Mario J. Molina F. Sherwood Rowland

Chemistry of the Environment

Chlorofluorocarbons (CFCs)

- CFCs were used for years as aerosol propellants and refrigerants.
- They are not water soluble (do not get washed out of the atmosphere by rain) and are quite unreactive (not degraded naturally).
- The C—Cl bond is easily broken by light with a wavelength between 190 and 225 nm in the stratosphere, where the ozone layer exists.
- The chlorine atoms formed react with ozone:

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

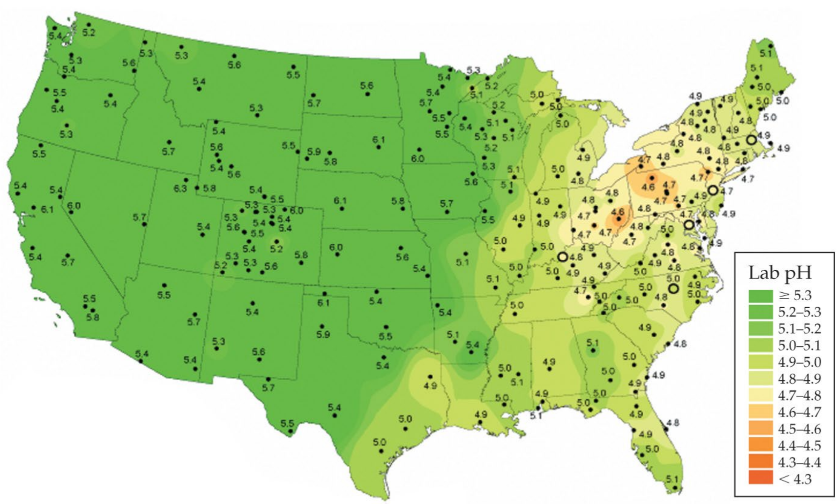
Pollutants in the "Average" City

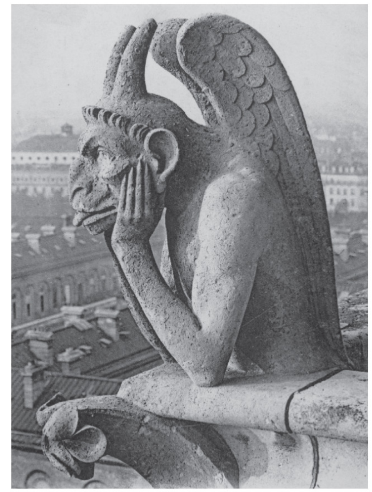
Table 18.4 Median Concentrations of Atmospheric Pollutants in a Typical Urban Atmosphere

Pollutant	Concentration (ppm)
Carbon monoxide	10
Hydrocarbons	3
Sulfur dioxide	0.08
Nitrogen oxides	0.05
Total oxidants (ozone and others)	0.02

- The table lists pollutant gases present in the "typical" urban environment.
- It assumes no major smog problems in the city.
- Although the typical value for SO_2 is low, it is considered the most serious health hazard on the list.

Acid Rain





(a)

(b)

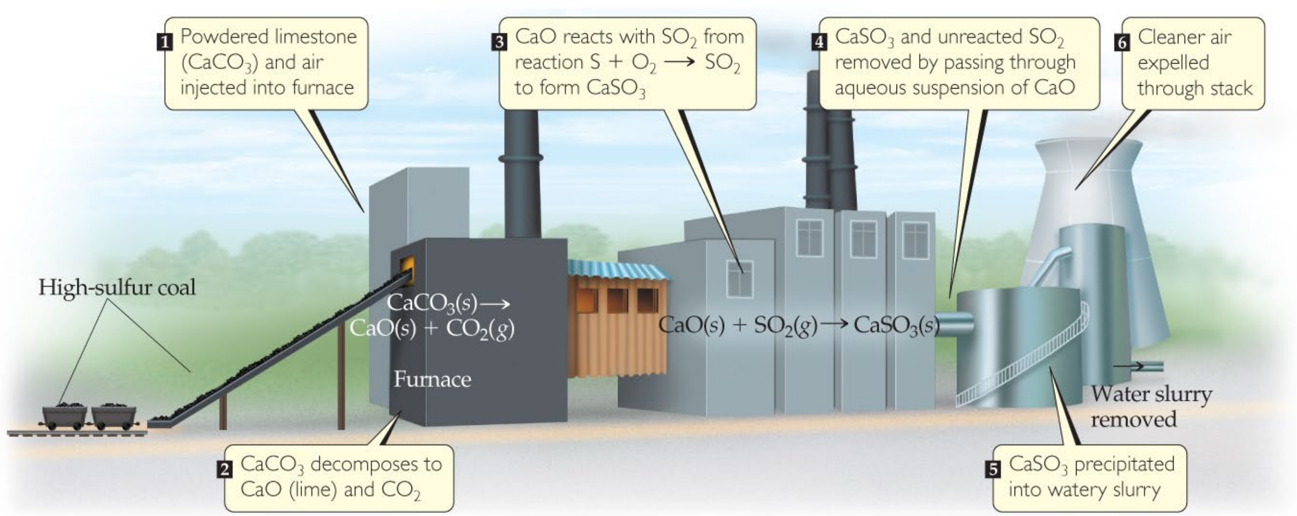
- SO_2 is a by-product of the burning of coal or oil.
- It reacts with moisture in the air to form sulfuric acid.
- It is primarily responsible for acid rain. (Nitrogen oxides also contribute to acid rain.)
- High acidity in rainfall causes corrosion in building materials.

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

Chemistry of the Environment

Chemical Methods to Prevent Emissions from Power Plants

- Powdered limestone ($CaCO_3$) can be added to the furnace of a power plant. It is converted to CaO, which reacts with SO_2 to make $CaSO_3$.
- Gases can pass through a suspension of CaO, with the same result.



Chemistry of the Environment

Nitrogen Oxides & Smog

- Smog, that brownish gas that hangs above large cities, is primarily nitrogen dioxide, NO_2.
- It forms from the oxidation of nitric oxide, NO, a component of car exhaust.
- These nitrogen oxides are just some components of photochemical smog.

- Ozone, carbon monoxide, and hydrocarbons also contribute to air pollution that causes severe respiratory problems in many people.

Chemistry of the Environment

The Greenhouse Effect

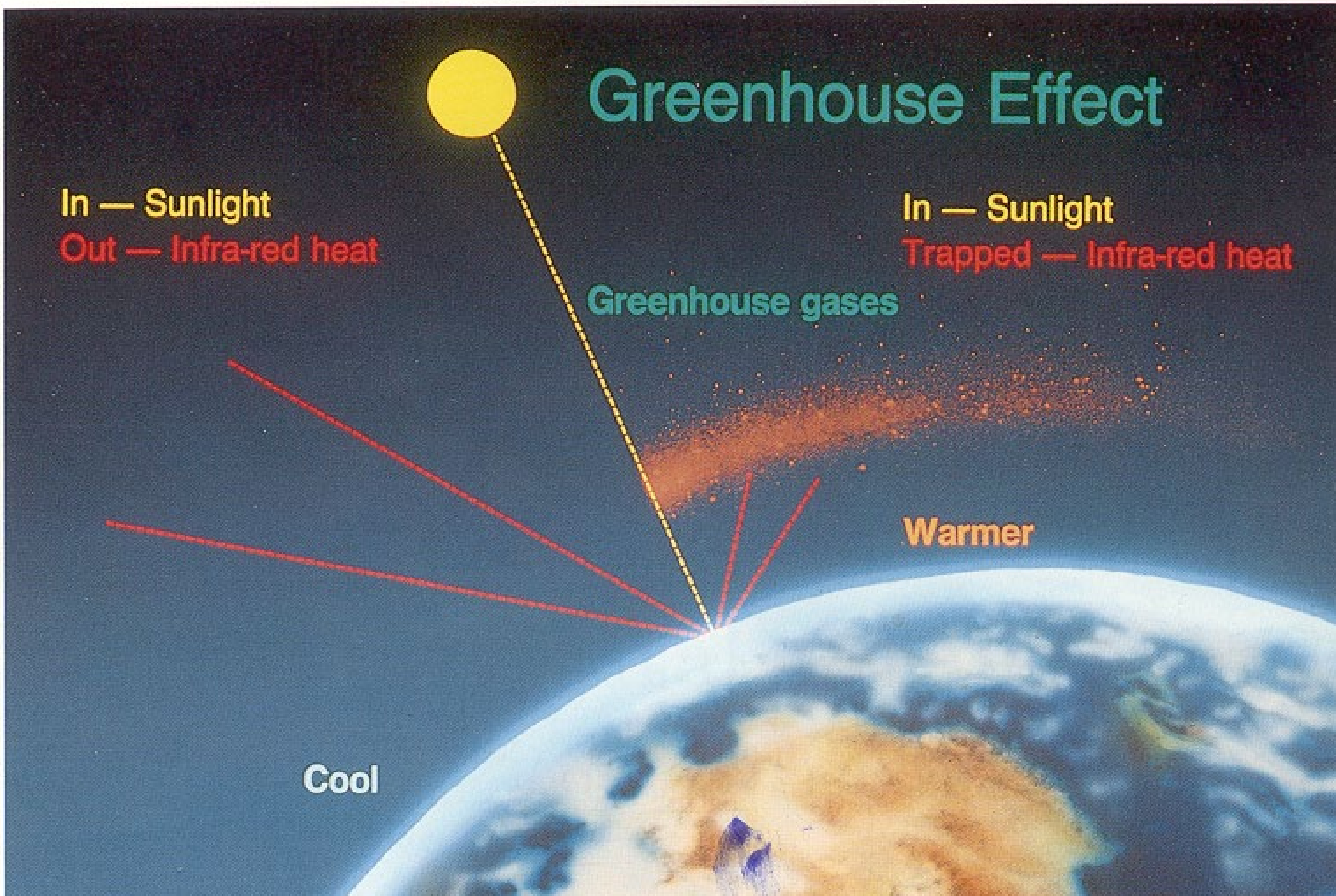


Figure I. *How the Greenhouse Effect works*

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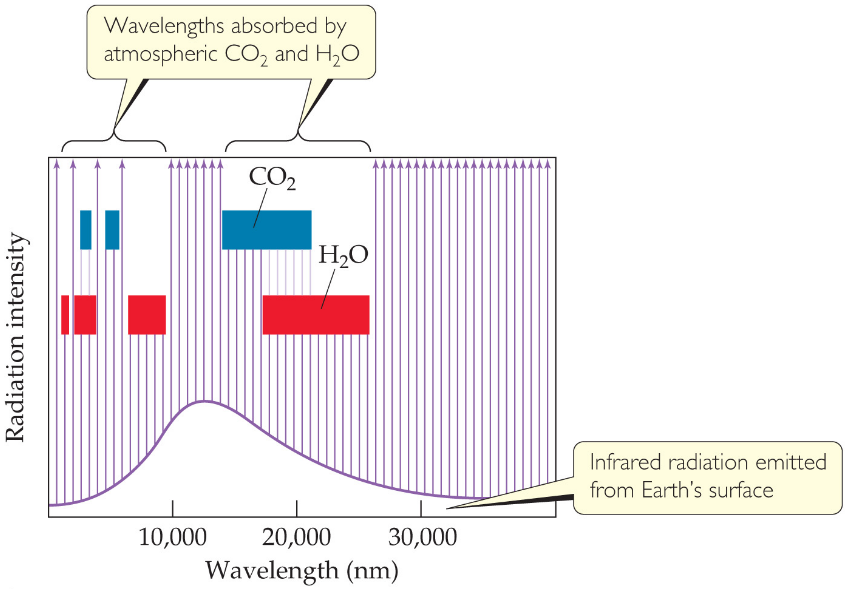
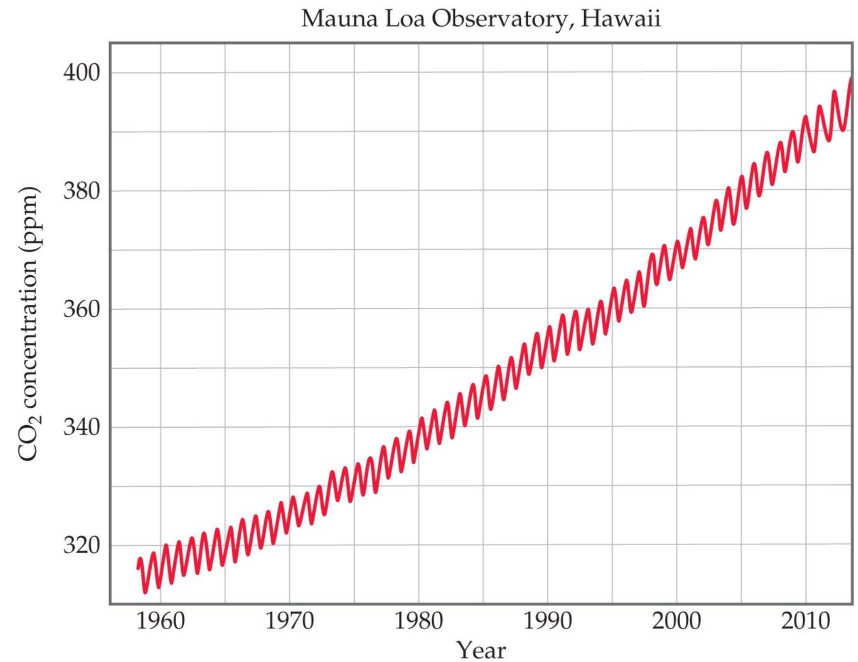
The Greenhouse Effect



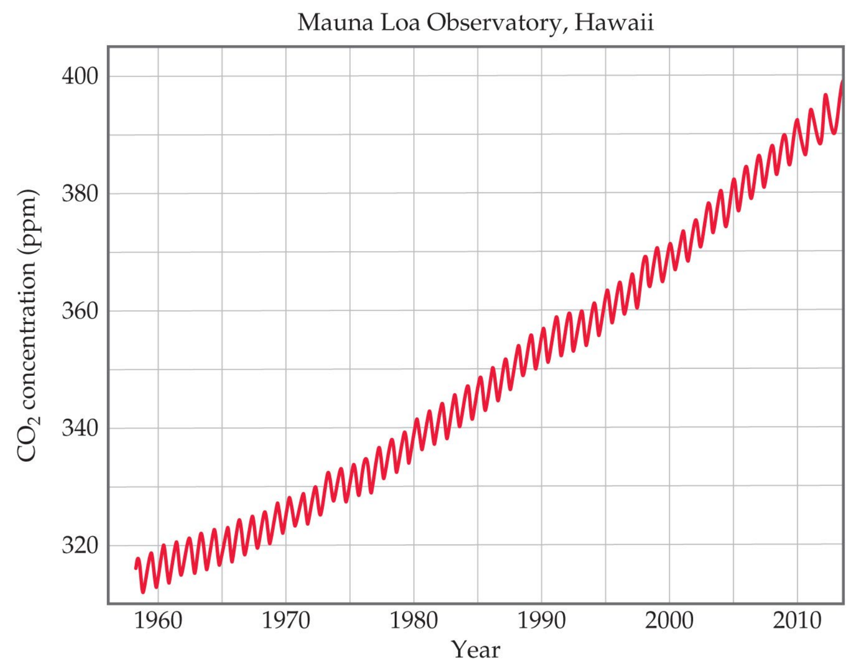


Carbon dioxide and water vapor absorb some radiation from the surface; the ozone layer prevents some radiation from entering; the overall balance keeps the Earth's surface temperature consistent.

Chemistry of the Environment

The Effect of Increasing Amounts of Carbon Dioxide

- Water is the major absorber of radiation; its levels vary by location and time of year
- CO_2 levels from human use of fossil fuels (primarily coal and oil) have increased dramatically over the last century.
- This is likely causing an unnatural increase in atmospheric temperatures.



Chemistry of the Environment

Global Warming

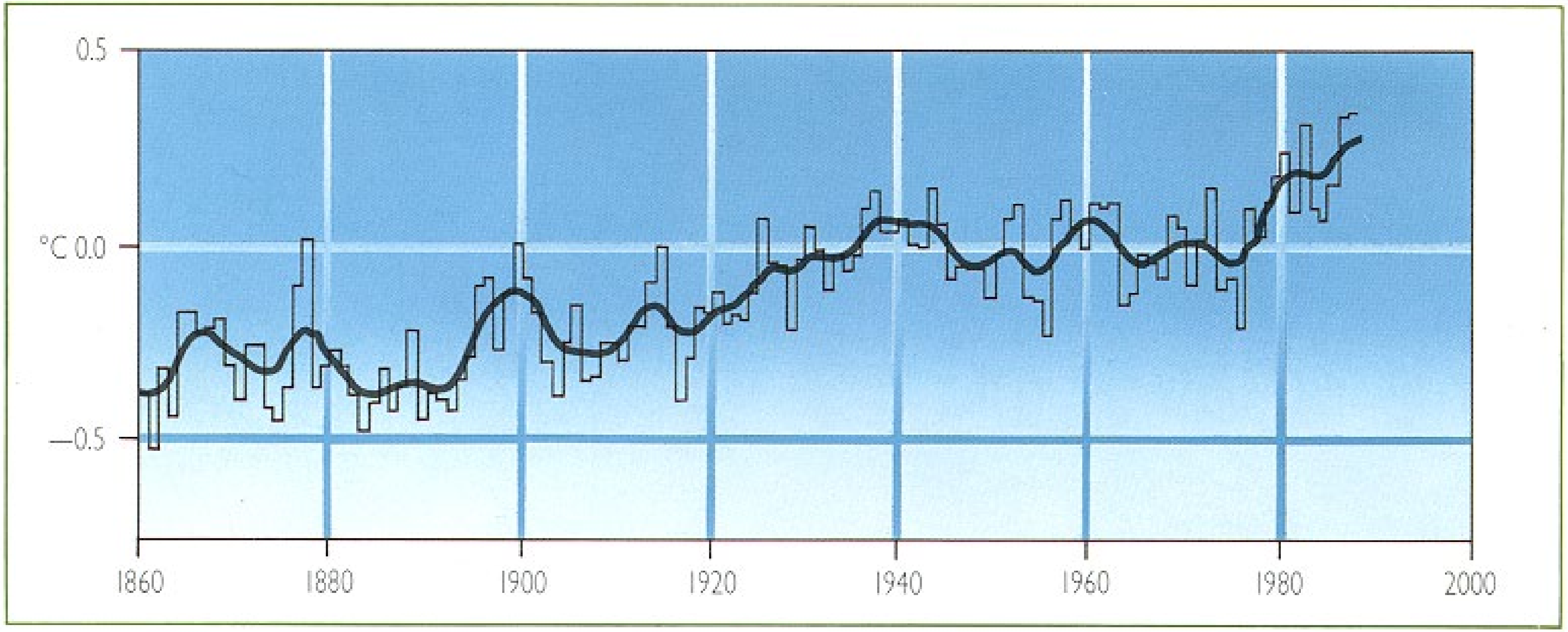
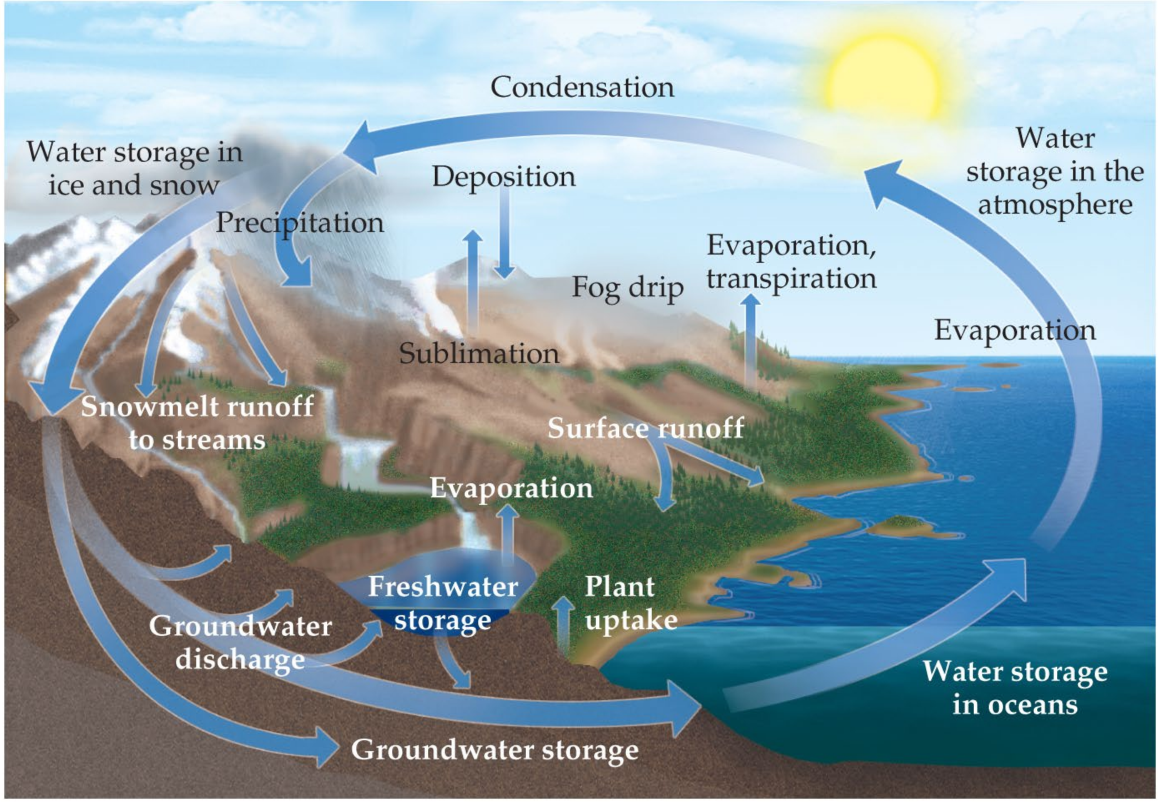


Figure 3. *Global Warming*

Chemistry of the Environment

The Global Water Cycle



Most of the processes depicted here depend on the phase changes of water.

Chemistry of the Environment

The World Ocean

- 97.2% of all water on Earth is in the ocean.
- The vast ocean contains many important compounds and minerals.
- However, the ocean is only a commercial source of sodium chloride, bromine (from bromide salts), and magnesium (from its salts).

Table 18.5 Ionic Constituents of Seawater Present in Concentrations Greater than 0.001 g/kg (1 ppm)

Ionic Constituent	Salinity	Concentration (*M*)
Chloride, Cl^-	19.35	0.55
Sodium, Na^+	10.76	0.47
Sulfate, SO_4^{2-}	2.71	0.028
Magnesium, Mg^{2+}	1.29	0.054
Calcium, Ca^{2+}	0.412	0.010
Potassium, K^+	0.40	0.010
Carbon dioxide*	0.106	2.3×10^{-3}
Bromide, Br^-	0.067	8.3×10^{-4}
Boric acid, H_3BO_3	0.027	4.3×10^{-4}
Strontium, Sr^{2+}	0.0079	9.1×10^{-5}
Fluoride, F^-	0.0013	7.0×10^{-5}

*CO_2 is present in seawater as HCO_3^- and CO_3^{2-}.

- Absorption of CO_2 in oceans plays a major role in the global climate.

Fresh Water

- All fresh water is only about 0.6% of water on the planet.
- U.S. use of fresh water:
  - Agriculture (41%)
  - Hydroelectric power (39%)
  - Industry (6%)
  - Household needs (6%)
  - Drinking water (1%)
- Use of water adds dissolved materials, including human wastes; it will become increasingly expensive to guarantee our water supply.

Groundwater

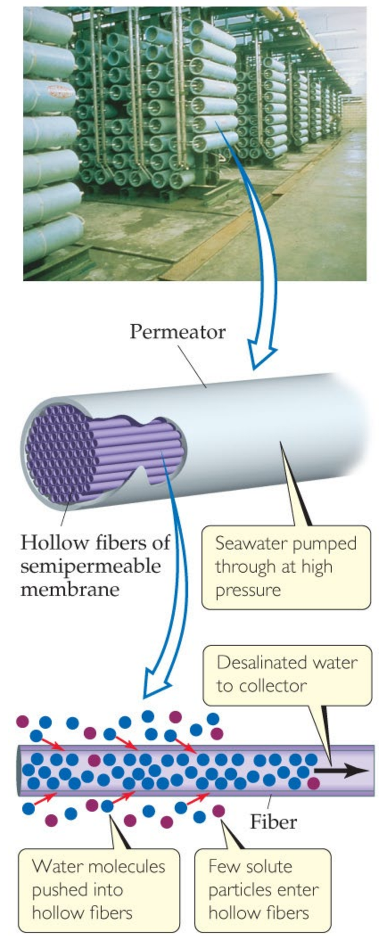
- Groundwater is fresh water under the soil in aquifers.
- Approximately 20% of the world's fresh water is groundwater.
- When used, these sources of water are not readily regenerated. It takes a long time for water to penetrate the rock layers which create an aquifer.
- Not all groundwater is potable. Due to the ions in rock formations, some will contain poisons, like arsenic, in high levels.
- Water contains excessive amount of Ca^{2+} and Mg^{2+} is called hard water.

Dissolved Oxygen and Water Quality

- The amount of O_2 in water is an important indicator of water quality.
- When aerobic bacteria act on biodegradable matter, they use oxygen.
- Excessive amounts of biodegradable matter can result in inability of normal animal life to exist in the water.
- It can also lead to anaerobic oxidation conditions, which give off bad odors.
- Excessive plant nutrients can lead to eutrophication, or excessive dead plant matter in water.

Water Purification—Desalination

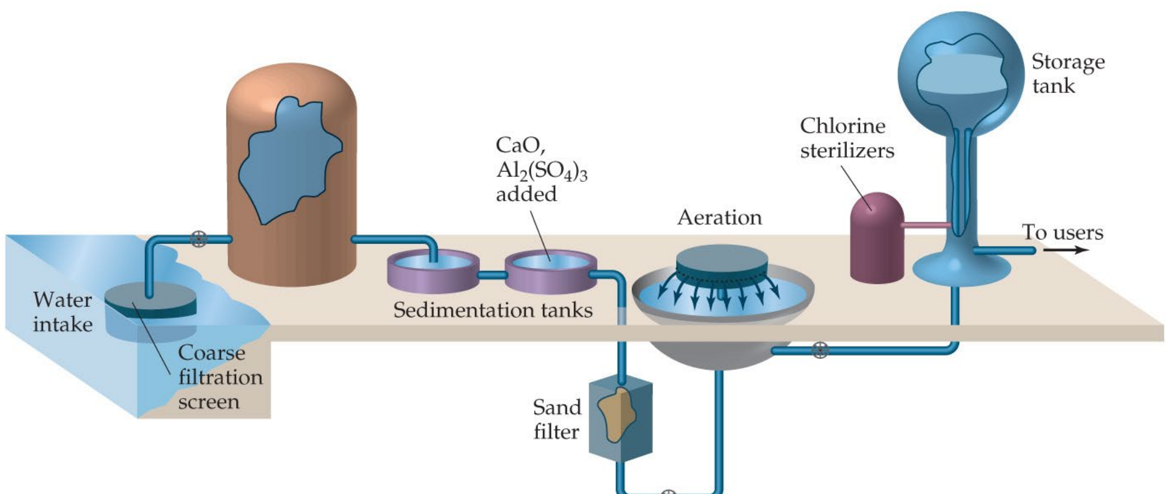
- Seawater has too high a concentration of NaCl for human consumption.
- It can be desalinated through **reverse osmosis**.
- Water naturally flows through a semipermeable membrane from regions of low salt concentration to regions of high salt concentration.
- If pressure is applied, the water can be forced through a membrane in the opposite direction, concentrating the pure water.



Chemistry of the Environment

Water Purification—Municipal Water Treatment

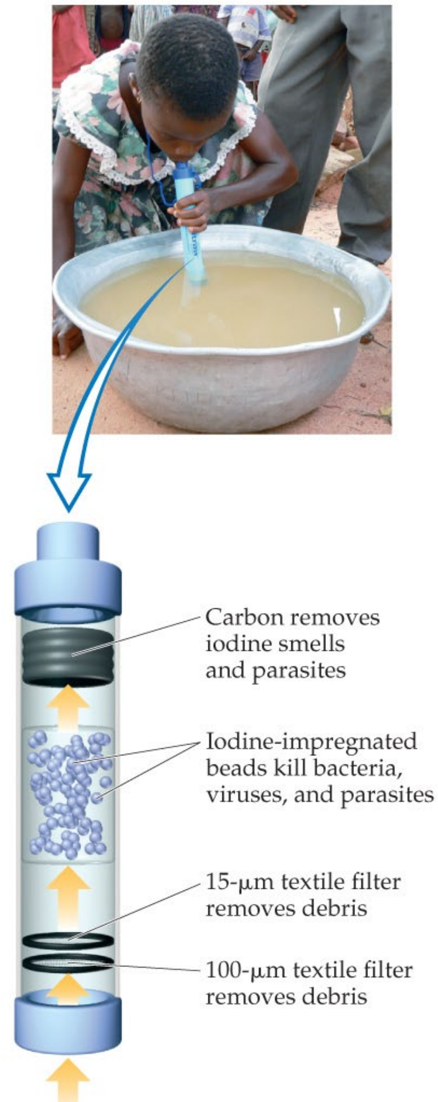
- Steps to purifying water for a municipal supply:
  - ➢ CaO and $Al_2(SO_4)_3$ are added for the removal of very small particles.
  - ➢ Water is aerated to increase amount of dissolved oxygen and for oxidation of organic impurities.
  - ➢ Ozone or chlorine is used to disinfect the water.



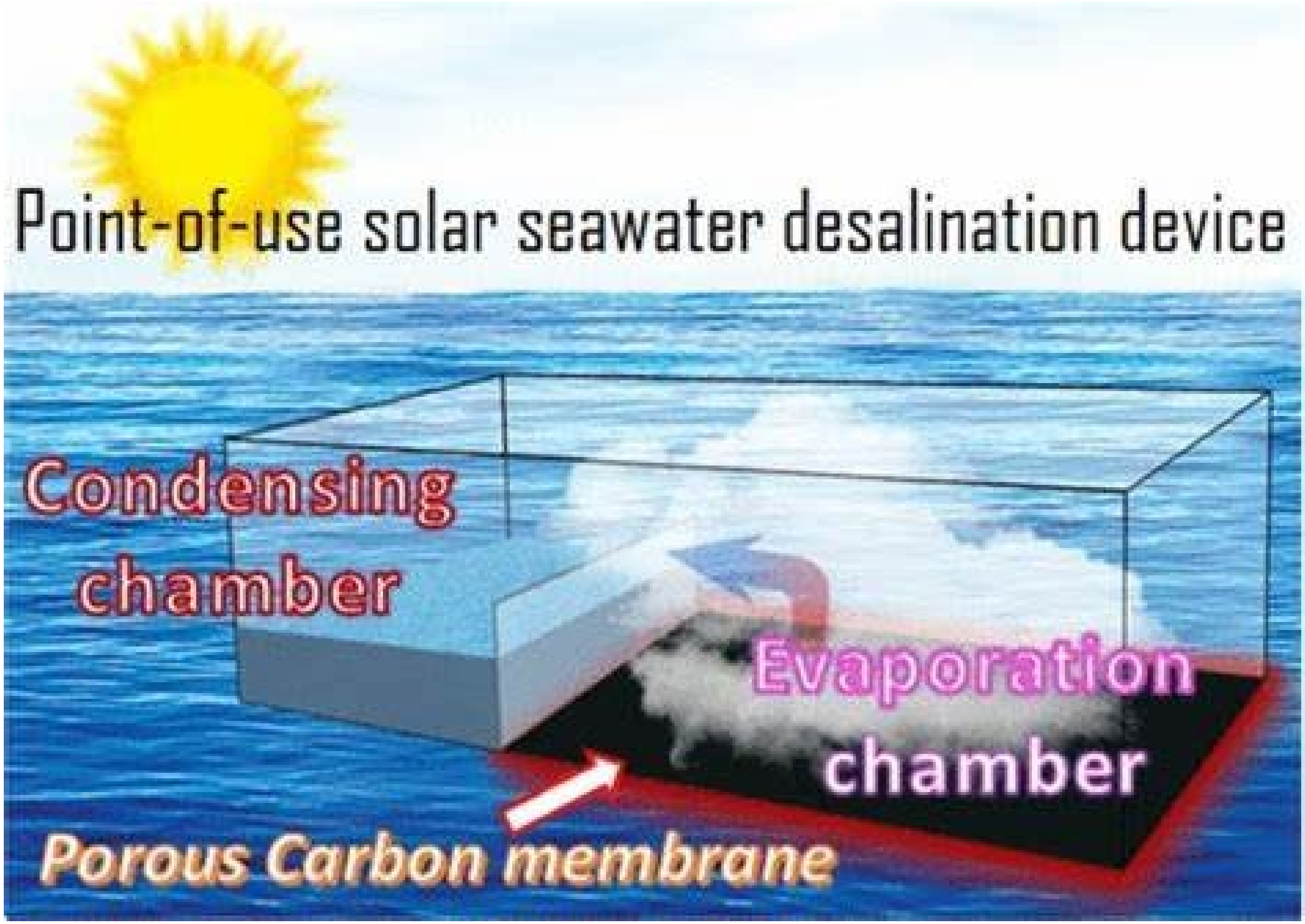
Chemistry of the Environment

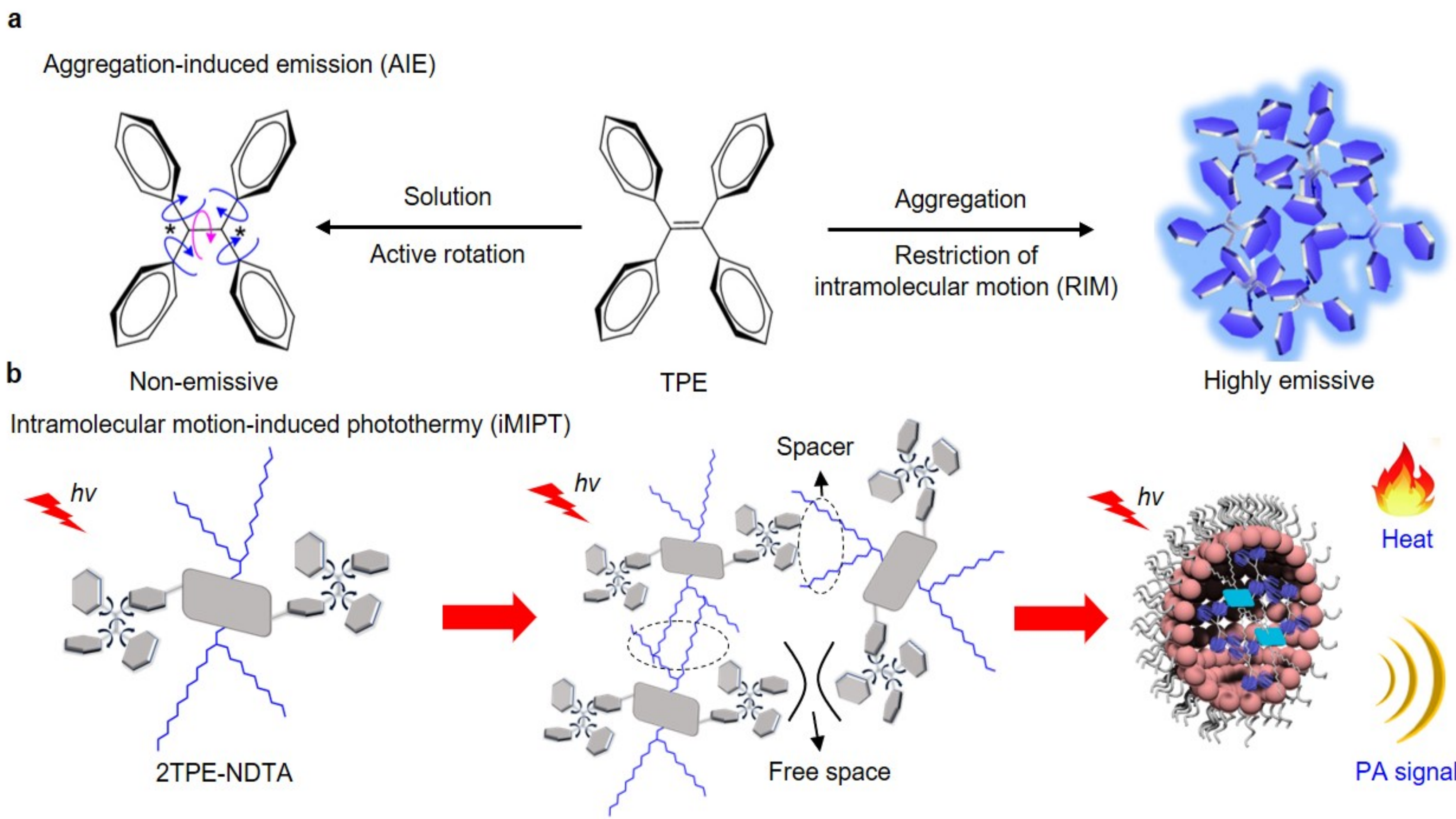
Water Purification—LifeStraw

- As one sucks water through the straw, filters remove most of the sediment and bacteria.
- Iodine-impregnated beads then kill viruses and bacteria.
- Charcoal removes the iodine smell and most remaining parasites.



Chemistry of the Environment


Point-of-use solar seawater desalination device
Condensing chamber
Evaporation chamber
Porous Carbon membrane



Chemistry
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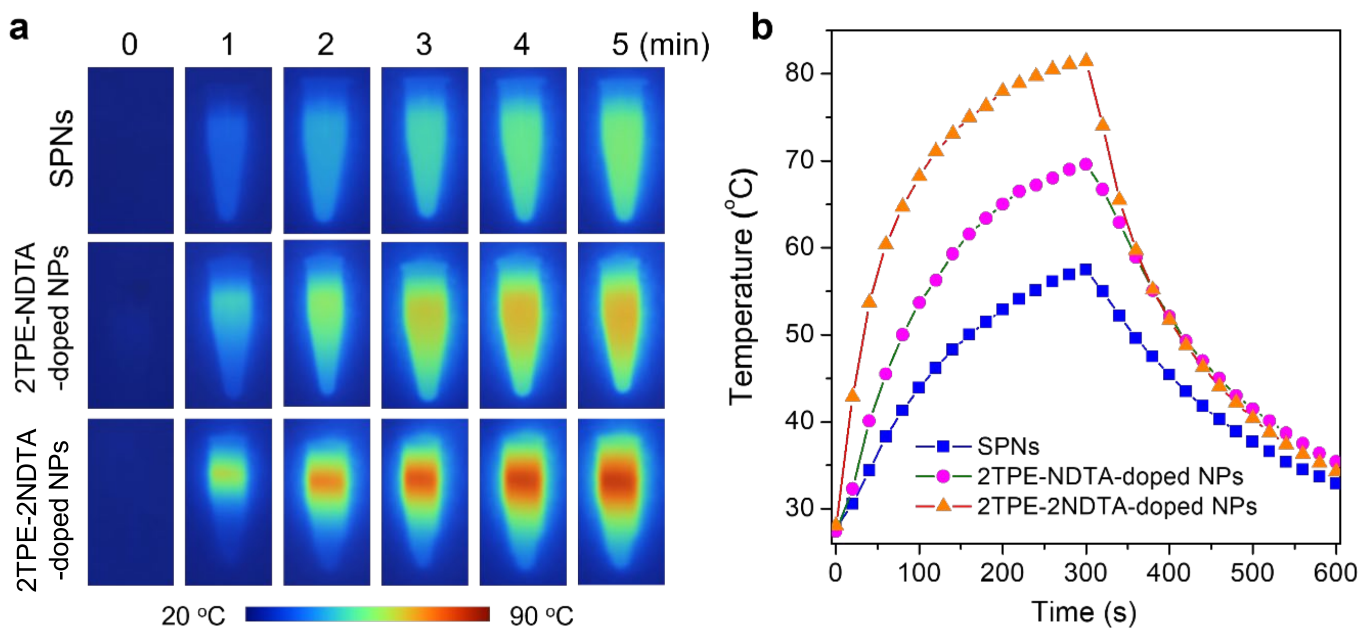

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Chemistry of the Environment

Green Chemistry

- The Earth can largely be considered a closed system, which can exchange energy with the rest of the universe, but energy keeps inside its mass.
- For humanity to thrive, we need to keep our processes in balance with Earth's natural processes.
- This is the basis for Green Chemistry.
- **Green Chemistry** is an initiative that promotes the design and application of chemical products and processes that are compatible with human health and that preserve the environment.

Green Chemistry Principles

1. Prevention: It is better to prevent waste than to clean it up after it has been created.
2. Atom Economy: Methods to make chemical compounds should be designed to maximize the incorporation of all starting atoms into the final product.
3. Less Hazardous Chemical Syntheses: Wherever practical, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

Green Chemistry Principles

4. Design of Safer Chemicals: Chemical products should be designed to minimize toxicity and yet maintain their desired function.
5. Safer Solvents and Auxiliaries: The use of auxiliary substances should be eliminated wherever possible and, if used, should be as nontoxic as possible.
6. Design for Energy Efficiency: Energy requirements should be recognized for their environmental and economic impacts and should be minimized (e.g., carry out reactions at room temperature and pressure).

Green Chemistry Principles

7. Use of Renewable Feedstocks: A raw material should be renewable whenever technically and economically practical.
8. Reduction of Derivatives: Unnecessary derivatization should be minimized or avoided if possible to save reagents and waste.
9. Catalysis: Catalytic reagents improve yields within a given time and with less energy and are, therefore, preferred.

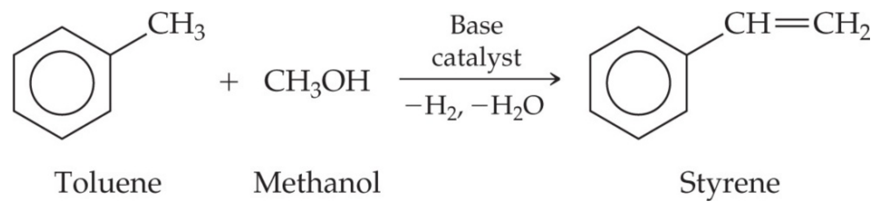
Green Chemistry Principles

10. Design for Degradation: Chemical products should be designed so that at the end of their function they break down into innocuous products and do not persist in the environment.
11. Real-Time Analysis for Pollution Prevention: Analytical methods should be developed to allow for real-time monitoring and control prior to the formation of hazardous substances.
12. Inherently Safer Chemistry for Accident Prevention: Reagents and solvents used in a chemical process should be chosen to minimize the potential for chemical accidents.

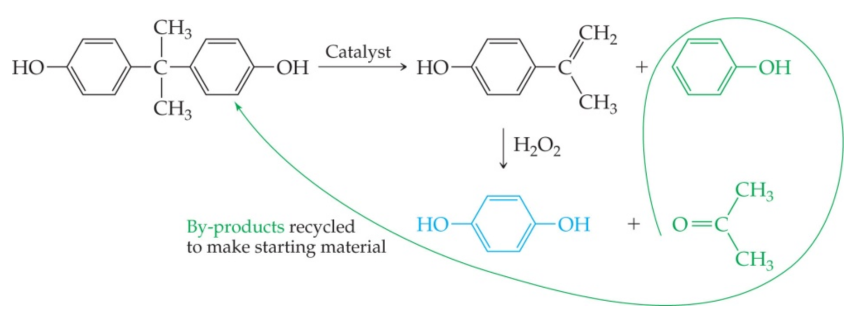
Chemistry of the Environment

Examples of Green Chemistry

- Preparation of styrene using toluene and methanol



- Replacing chlorofluorocarbon solvents with liquid or supercritical CO_2
- Hydroquinone production by a new method that recycles by-products



Examples of Green Chemistry

- Catalytic chemical process –metathesis
- (2005 Nobel Prize) for less energy, less greenhouse gas emission
- Computer chips manufacturing – uses supercritical CO2 fluid
- Medicines with less side effects
- Biodegradable plastics – “Ecoflex”

continued

- Paint – a mixture of soya oil and sugar to replace fossil-fuel-derived paint
- Water-based acrylic paints with low VOC – made from recycled soda bottle plastic (PET), acrylics and soyabean oil