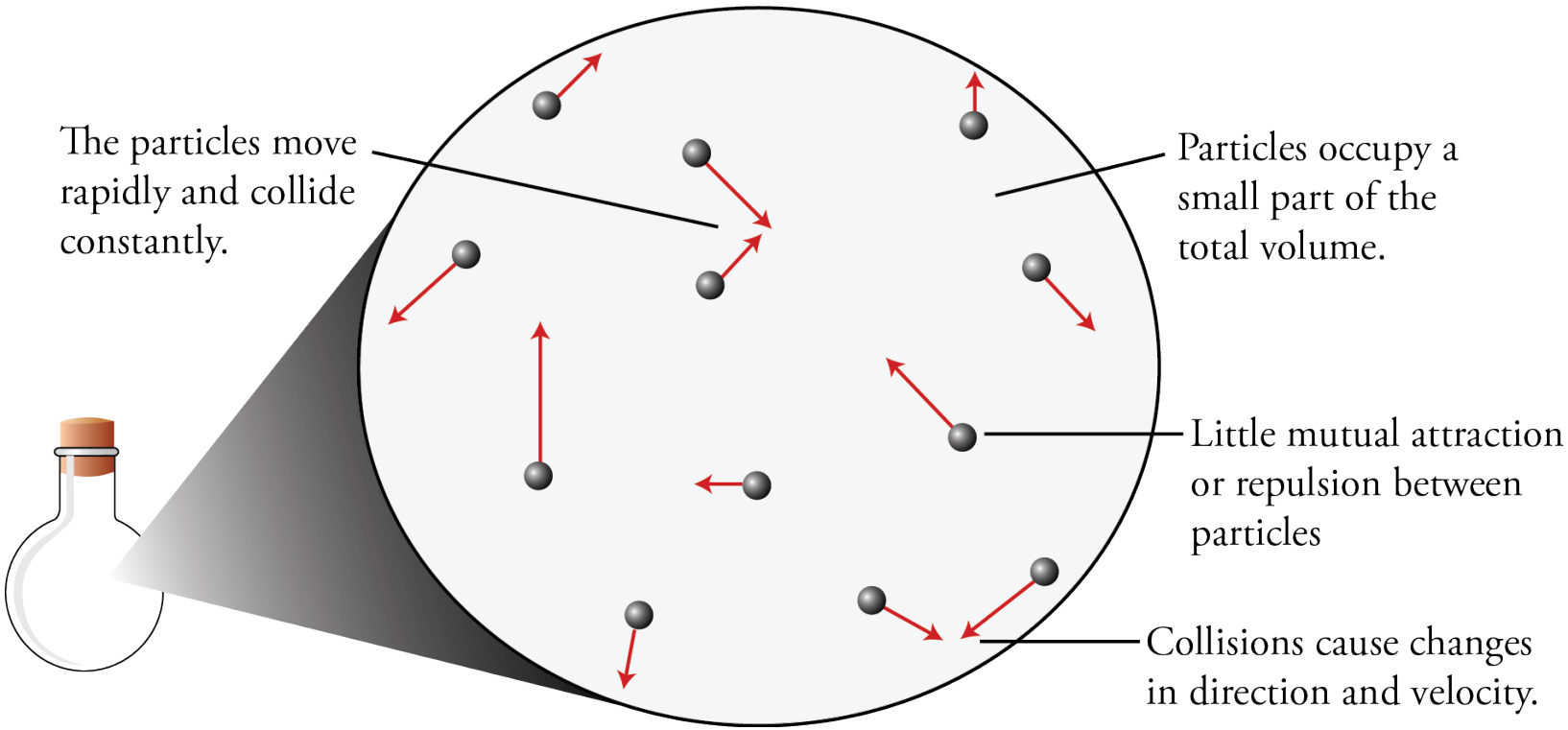
Gases, ozone, and CFCs

An Introduction to Chemistry

by Mark Bishop

Gas


The particles move rapidly and collide constantly.
Particles occupy a small part of the total volume.
Little mutual attraction or repulsion between particles
Collisions cause changes in direction and velocity.

Gas Model

- Gases are composed of tiny, widely-spaced particles.
  - For a typical gas, the average distance between particles is about ten times their diameter.

Gas Model (cont.)

- Because of the large distance between the particles, the volume occupied by the particles themselves is negligible (approximately zero).
  - For a typical gas at room temperature and pressure, the gas particles themselves occupy about 0.1% of the total volume. The other 99.9% of the total volume is empty space. This is very different than for a liquid for which about 70% of the volume is occupied by particles.

Gas Model (cont.)

- The particles have rapid and continuous motion.
  - For example, the average velocity of a helium atom, He, at room temperature is over 1000 m/s (or over 2000 mi/hr). The average velocity of the more massive nitrogen molecules, N_2, at room temperature is about 500 m/s.
  - Increased temperature means increased average velocity of the particles.

Gas Model (cont.)

- The particles are constantly colliding with the walls of the container and with each other.
  - Because of these collisions, the gas particles are constantly changing their direction of motion and their velocity. In a typical situation, a gas particle moves a very short distance between collisions. Oxygen, O_2, molecules at normal temperatures and pressures move an average of 10^{-7} m between collisions.

Gas Model (cont.)

- There is no net loss of energy in the collisions. A collision between two particles may lead to each particle changing its velocity and thus its energy, but the increase in energy by one particle is balanced by an equal decrease in energy by the other particle.

Ideal Gas

- The particles are assumed to be point-masses, that is, particles that have a mass but occupy no volume.
- There are no attractive or repulsive forces at all between the particles.

Ozone, O_3, as Oxidizing Agent

- Used to sanitize hot tubs
- Used in industry to bleach waxes, oils, and textiles.
- Strong respiratory irritant that can lead to shortness of breath, chest pain when inhaling, wheezing, and coughing
- Damages rubber and plastics, leading to premature deterioration of products made with these materials.
- Ozone damages plants.

Ozone as Pollutant

- Highest concentrations found in large industrial cities with lots of cars and lots of sun.

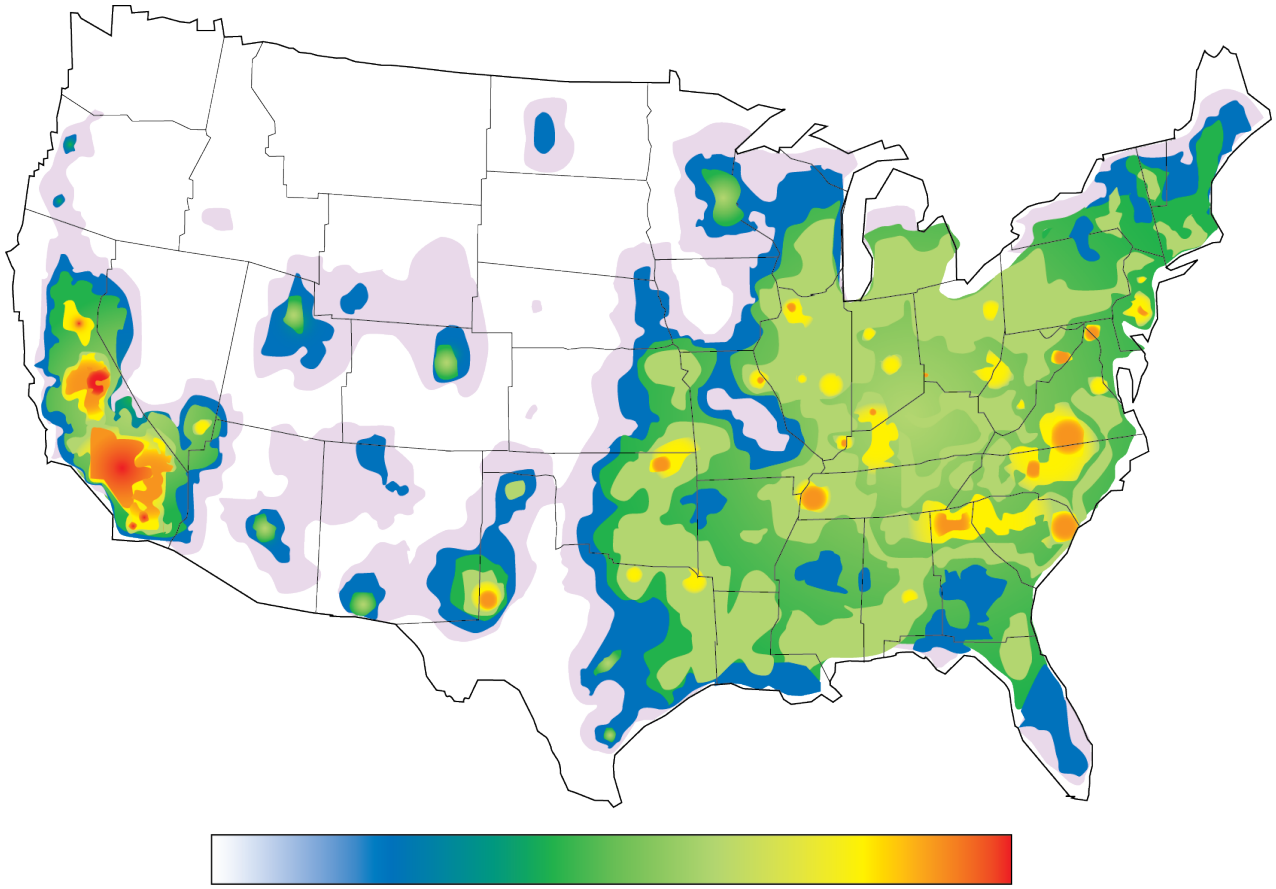
$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

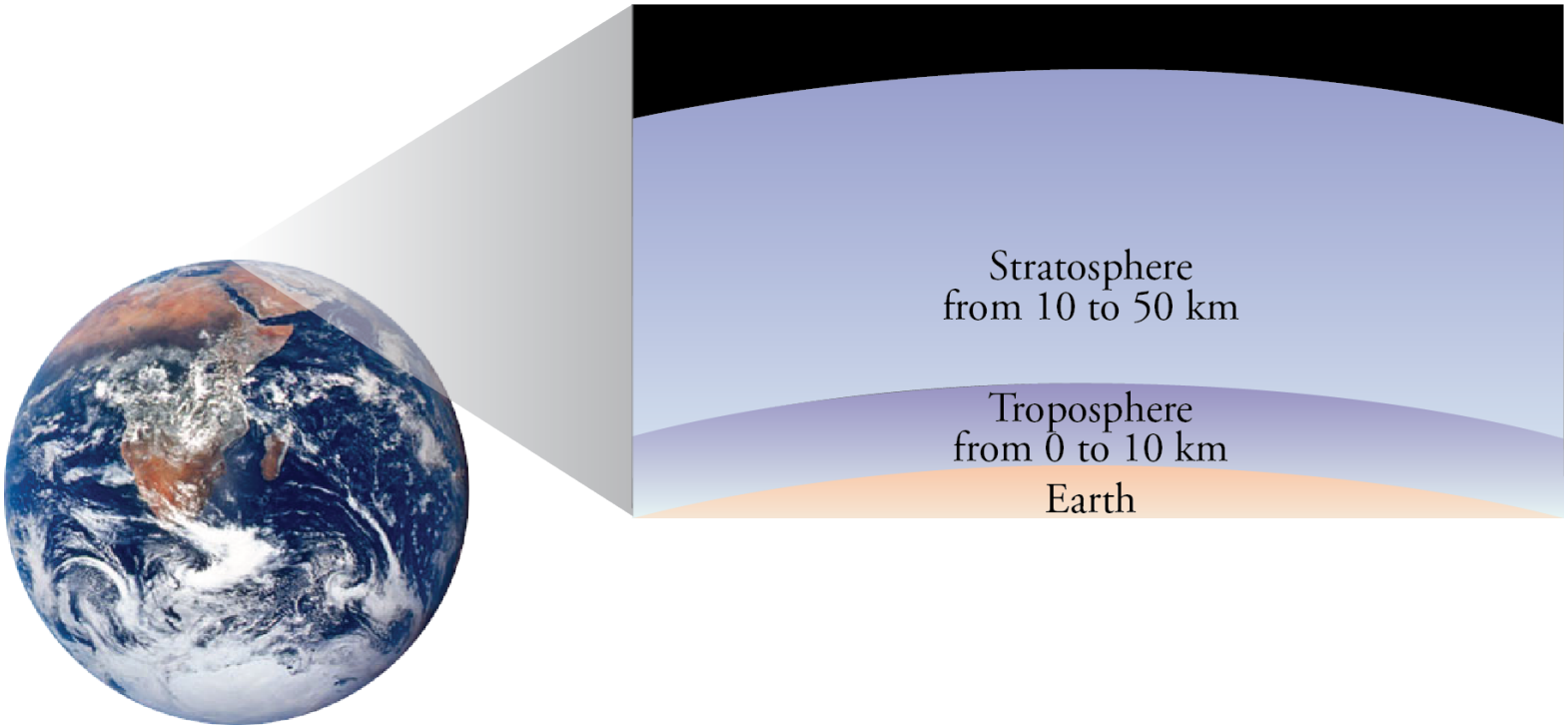
$$NO_2(g) \xrightarrow{\lambda < 400\ \text{nm}} NO(g) + O(g)$$

$$O(g) + O_2(g) \rightarrow O_3(g)$$

National Ozone Concentrations



The Earth's Atmosphere



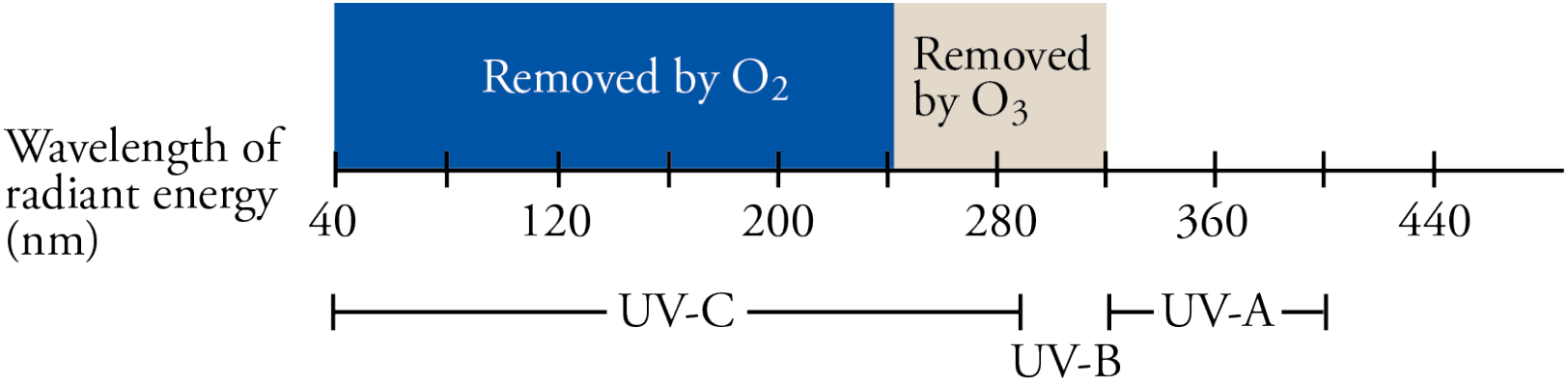
Ultraviolet Radiation

- **UV-A** 320-400 nm
  - reaches the surface of the Earth
  - helps create Vitamin D
- **UV-B** 290-320 nm
  - some reaches the surface of the Earth
  - leads to sunburn, skin aging, and skin cancer
- **UV-C** 40-290 nm
  - mostly removed in upper atmosphere
  - alters DNA (≈260 nm) and protein (≈280 nm)

Removal of UV in Stratosphere

$$O_2(g) \xrightarrow{\text{UV with } \lambda < 242 \text{ nm}} 2O(g)$$

$$O_3(g) \xrightarrow{\text{UV with } \lambda \text{ from 240 to 320 nm}} O(g) + O_2(g)$$



Ozone Destruction

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

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

net reaction

$$O_3(g) + O(g) \xrightarrow{\text{NO catalyst}} 2O_2(g)$$

NASA and Supersonic Planes

- 29 February 2016 - *NASA has given the go-ahead for preliminary design of a "low-boom" supersonic passenger plane that could one day fill the gap left by the retirement of the Concorde jet.*

https://www.theguardian.com/science/2016/mar/01/next-concorde-nasa-kickstarts-quesst-for-new-supersonic-passenger-jet

Ozone Destruction

- 1969 - Paul Crutzen discovered NO_x catalytic cycle.

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

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

net reaction

$$O_3(g) + O(g) \xrightarrow{\text{NO catalyst}} 2O_2(g)$$

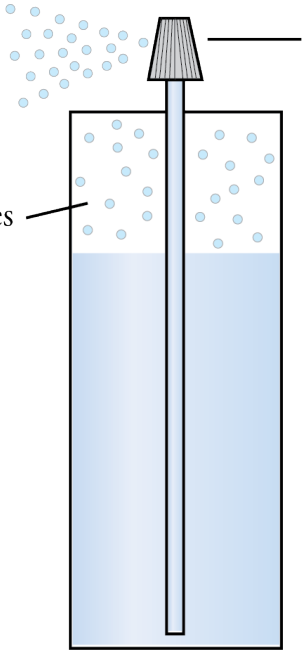
- 1971 – Harold Johnston calculates that NO_x from SST's could double the rate of depletion of the ozone layer.

http://science.sciencemag.org/content/173/3996/517.short

Chlorofluorocarbons (CFCs)

- CFC-11 $CFCl_3$
  - average lifetime in atmosphere is ≈ 50 years
- CFC-12 CF_2Cl_2
  - average lifetime in atmosphere is ≈ 102 years
- used as propellants in aerosol cans, solvents, blowing agents for foams, coolant in refrigerators, and other uses
- very stable, nontoxic, and can be liquefied with minimal pressure

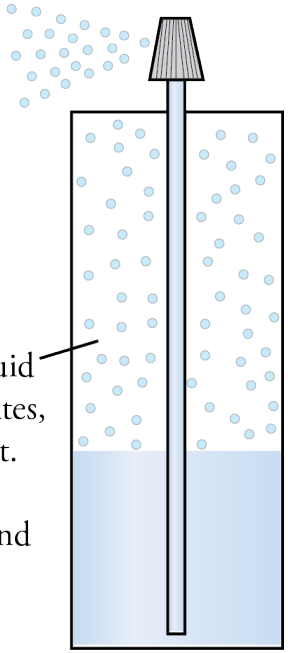
Aerosol Can Propellants



When the valve is pushed, it opens a passageway through which the liquid in the can moves. Because the pressure above the liquid in the can is greater than the external pressure, liquid is pushed out of the can.

The propellant evaporates into the space above the liquid and gives an internal pressure that is slightly greater than the external pressure.

As the volume occupied by the gas above liquid in the can increases, more propellant evaporates, keepingthe pressure above the liquid constant. Therefore, the liquid is expelled from the can with the same pressure when the can is full and when it is almost empty.



Refrigeration

- The refrigerant is a substance that is a gas at normal pressures but one that can be converted into a liquid at slightly greater than normal pressures.
- Outside the refrigerator, gas is compressed to liquid. Increased attractions leads to increased stability, lower PE, and the release of energy into the room.
- Inside the refrigerator, the liquid is allowed to form a gas. Decreased attractions leads to decreased stability, higher PE, and energy is absorbed. This decreases the temperature inside the refrigerator.

CFC Threat to Ozone (1974)
Mario Molina and
F. Sherwood Rowland

$$CF_2Cl_2(g) \xrightarrow{\lambda < 215\ \text{nm}} CF_2Cl(g) + Cl(g)$$

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

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

net reaction

$$O_3(g) + O(g) \xrightarrow{\text{Cl catalyst}} 2O_2(g)$$

Another Possible Mechanism for the CFC Threat to Ozone

$$CF_2Cl_2(g) \xrightarrow{\lambda < 215\ \text{nm}} CF_2Cl(g) + Cl(g)$$

$$2Cl(g) + 2O_3(g) \rightarrow 2ClO(g) + 2O_2(g)$$

$$2ClO(g) \rightarrow ClOOCl(g)$$

$$ClOOCl(g) \rightarrow ClOO(g) + Cl(g)$$

$$ClOO(g) \rightarrow Cl(g) + O_2(g)$$

net reaction

$$2O_3(g) \xrightarrow{\text{Cl catalyst}} 3O_2(g)$$

Inactive Chlorine

$$CH_4(g) + Cl(g) \rightarrow CH_3(g) + HCl(g)$$

$$ClO(g) + NO_2(g) \rightarrow ClONO_2(g)$$

Ozone Hole - Reactions on the surface of ice crystals

$$ClONO_2(g) + HCl(s) \rightarrow Cl_2(g) + HNO_3(s)$$

$$ClONO_2(g) + H_2O(s) \rightarrow HOCl(g) + HNO_3(s)$$

$$HOCl(g) + HCl(s) \rightarrow Cl_2(g) + H_2O(s)$$

$$HOCl(g) \xrightarrow{\text{radiant energy}} Cl(g) + OH(g)$$

$$Cl_2(g) \xrightarrow{\text{radiant energy}} 2Cl(g)$$