Chapter 18
Kinetic Theory of Gases

Units of Chapter 18

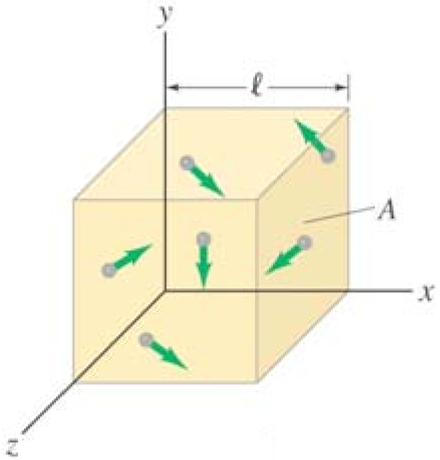
- The Ideal Gas Law and the Molecular Interpretation of Temperature
- Distribution of Molecular Speeds
- Real Gases and Changes of Phase
- Vapor Pressure and Humidity
- Van der Waals Equation of State
- Mean Free Path
- Diffusion

18-1 The Ideal Gas Law and the Molecular Interpretation of Temperature

Assumptions of kinetic theory:

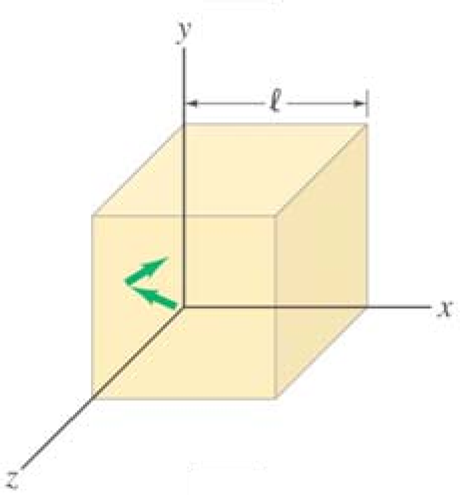
- large number of molecules, moving in random directions with a variety of speeds
- molecules are far apart, on average
- molecules obey laws of classical mechanics and interact only when colliding
- collisions are perfectly elastic

18-1 The Ideal Gas Law and the Molecular Interpretation of Temperature



The **force** exerted on the wall by the collision of one molecule is

$$F = \frac{\Delta(mv)}{\Delta t} = \frac{2mv_x}{2\ell/v_x} = \frac{mv_x^2}{\ell}.$$



Then the force due to **all** molecules colliding with that wall is

$$F = \frac{m}{\ell} N\overline{v_x^2}.$$

18-1 The Ideal Gas Law and the Molecular Interpretation of Temperature

The **averages of the squares** of the speeds in all three directions are equal:

$$F = \frac{m}{\ell} N \frac{\overline{v^2}}{3}.$$

So the **pressure** is:

$$P = \frac{1}{3} \frac{N m \overline{v^2}}{V}.$$

18-1 The Ideal Gas Law and the Molecular Interpretation of Temperature

Rewriting, $PV = \frac{2}{3}N\left(\frac{1}{2}m\overline{v^2}\right),$

so

$$\overline{K} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT.$$

The average translational kinetic energy of the molecules in an ideal gas is directly proportional to the temperature of the gas.

18-1 The Ideal Gas Law and the Molecular Interpretation of Temperature

Example 18-1: Molecular kinetic energy.

What is the average translational kinetic energy of molecules in an ideal gas at 37°C?

18-1 The Ideal Gas Law and the Molecular Interpretation of Temperature

We can now calculate the average **speed** of molecules in a gas as a function of **temperature**:

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}.$$

18-1 The Ideal Gas Law and the Molecular Interpretation of Temperature

Example 18-2: Speeds of air molecules.

What is the rms speed of air molecules (O_2 and N_2) at room temperature (20°C)?

18-1 The Ideal Gas Law and the Molecular Interpretation of Temperature

Conceptual Example 18-3: Less gas in the tank.

A tank of helium is used to fill balloons. As each balloon is filled, the number of helium atoms remaining in the tank decreases. How does this affect the rms speed of molecules remaining in the tank?

18-1 The Ideal Gas Law and the Molecular Interpretation of Temperature

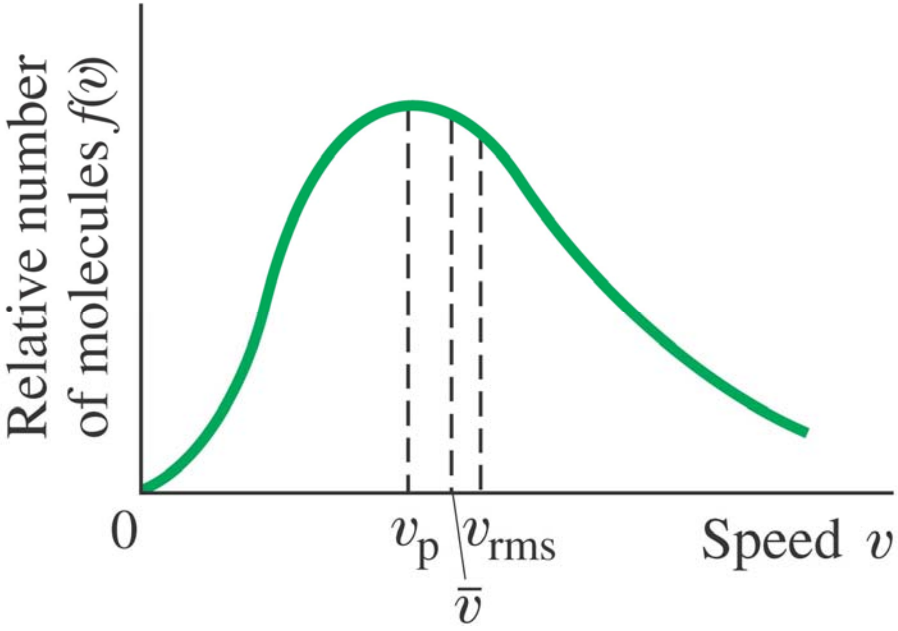
Example 18-4: Average speed and rms speed.

Eight particles have the following speeds, given in m/s: 1.0, 6.0, 4.0, 2.0, 6.0, 3.0, 2.0, 5.0. Calculate (a) the average speed and (b) the rms speed.

18-2 Distribution of Molecular Speeds

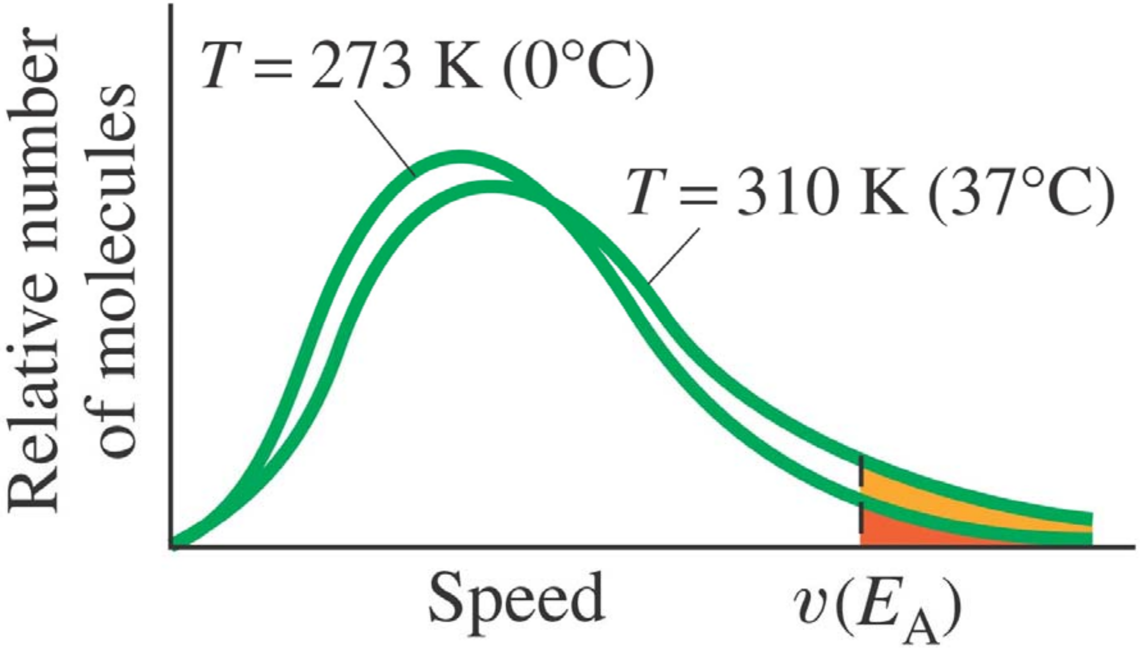
The molecules in a gas will not all have the same speed; their distribution of speeds is called the Maxwell distribution:

$$f(v) = 4\pi N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{1}{2}\frac{mv^2}{kT}}.$$



18-2 Distribution of Molecular Speeds

The Maxwell distribution depends only on the absolute temperature. This figure shows distributions for two different temperatures; at the higher temperature, the whole curve is shifted to the right.



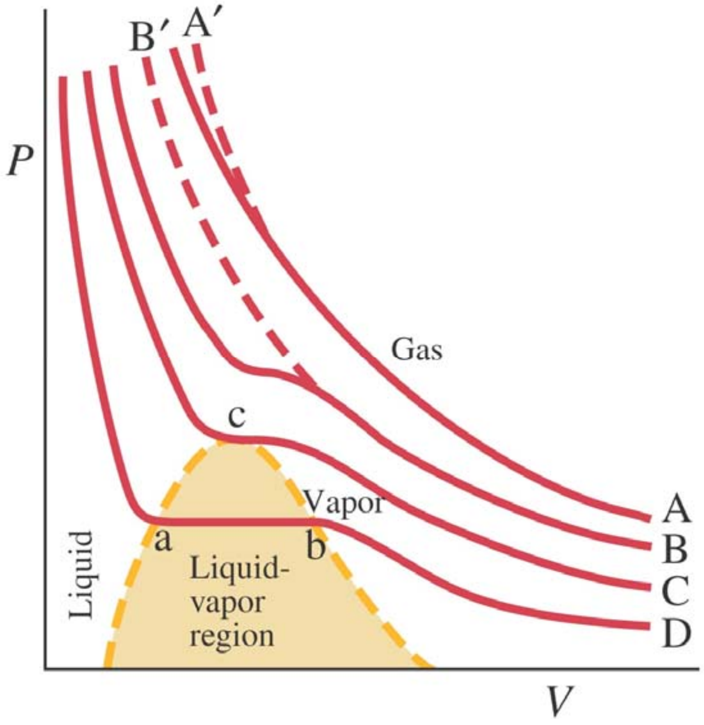
18-2 Distribution of Molecular Speeds

Example 18-5: Determining $\bar{v}$ and v_p.

Determine formulas for (a) the average speed, $\bar{v}$, and (b) the most probable speed, v_p, of molecules in an ideal gas at temperature T.

18-3 Real Gases and Changes of Phase

The curves here represent the behavior of the gas at different **temperatures**. The **cooler** it gets, the **further** the gas is from ideal.



In curve D, the gas becomes **liquid**; it begins condensing at (b) and is entirely liquid at (a). The point (c) is called the **critical point**.

18-3 Real Gases and Changes of Phase

Below the **critical temperature**, the gas can **liquefy** if the pressure is sufficient; above it, no amount of **pressure** will suffice.

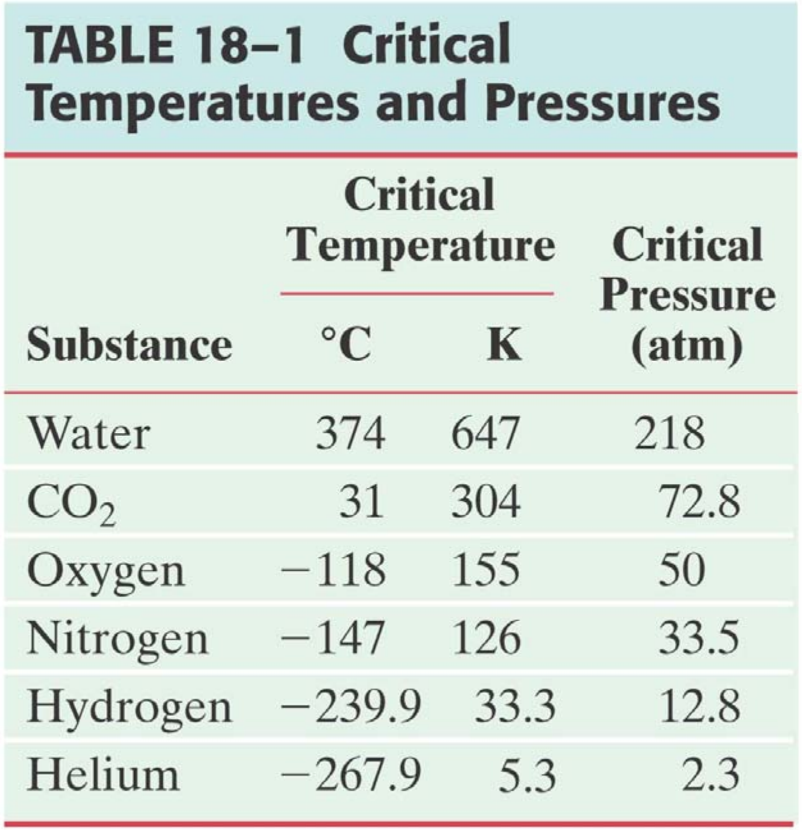
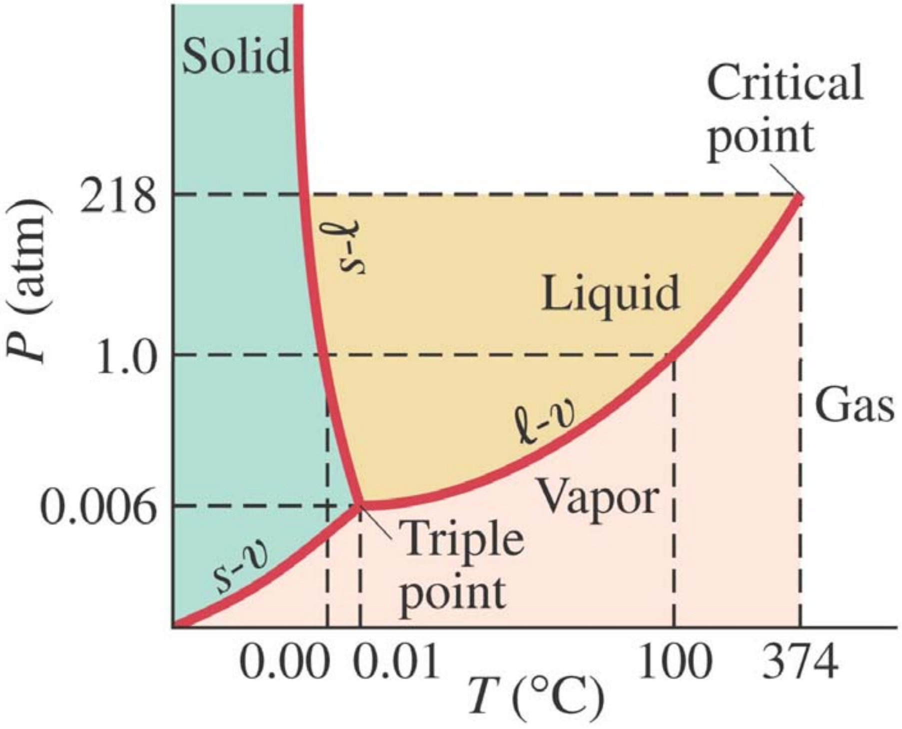


TABLE 18–1 Critical Temperatures and Pressures

Substance	Critical Temperature °C	Critical Temperature K	Critical Pressure (atm)
Water	374	647	218
CO_2	31	304	72.8
Oxygen	−118	155	50
Nitrogen	−147	126	33.5
Hydrogen	−239.9	33.3	12.8
Helium	−267.9	5.3	2.3

18-3 Real Gases and Changes of Phase

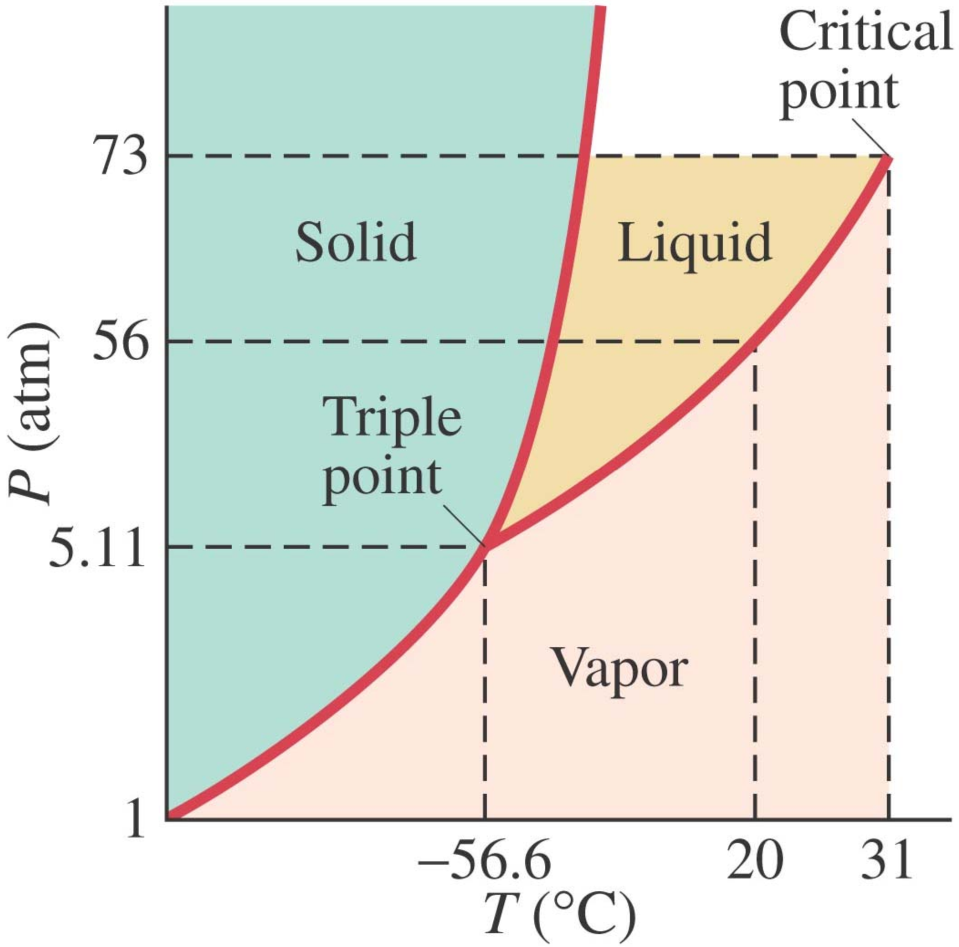
A *PT* diagram is called a **phase diagram**; it shows all three phases of matter. The solid-liquid transition is **melting** or **freezing**; the liquid-vapor one is **boiling** or **condensing**; and the solid-vapor one is **sublimation**.



Phase diagram of water.

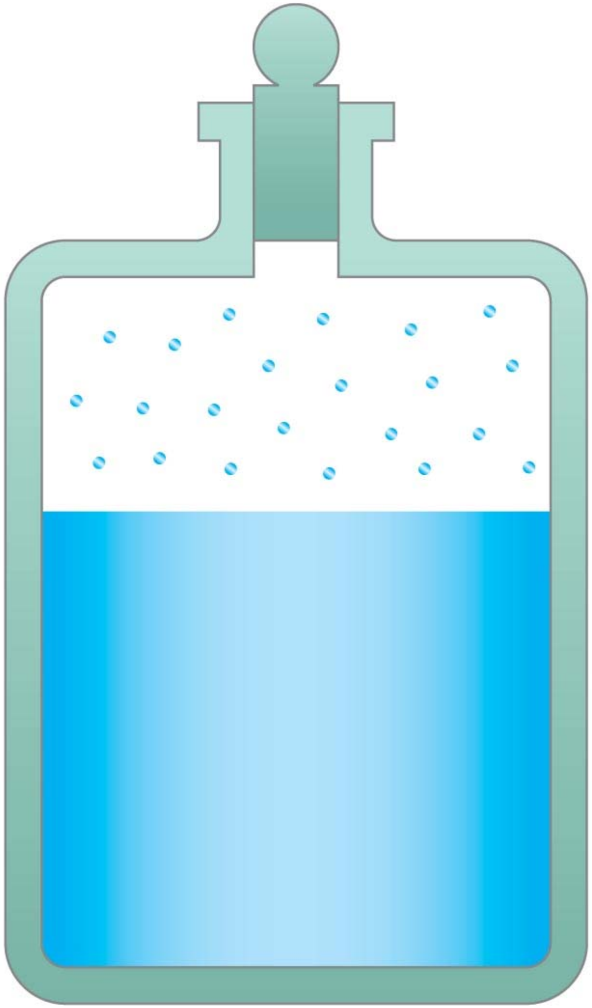
18-3 Real Gases and Changes of Phase

The triple point is the only point where all three phases can coexist in equilibrium.



Phase diagram of carbon dioxide.

18-4 Vapor Pressure and Humidity



An open container of water can **evaporate**, rather than boil, away. The **fastest** molecules are escaping from the water's surface, so evaporation is a **cooling** process as well.

The inverse process is called **condensation**.

When the evaporation and condensation processes are in **equilibrium**, the vapor just above the liquid is said to be **saturated**, and its pressure is the **saturated vapor pressure**.

18-4 Vapor Pressure and Humidity

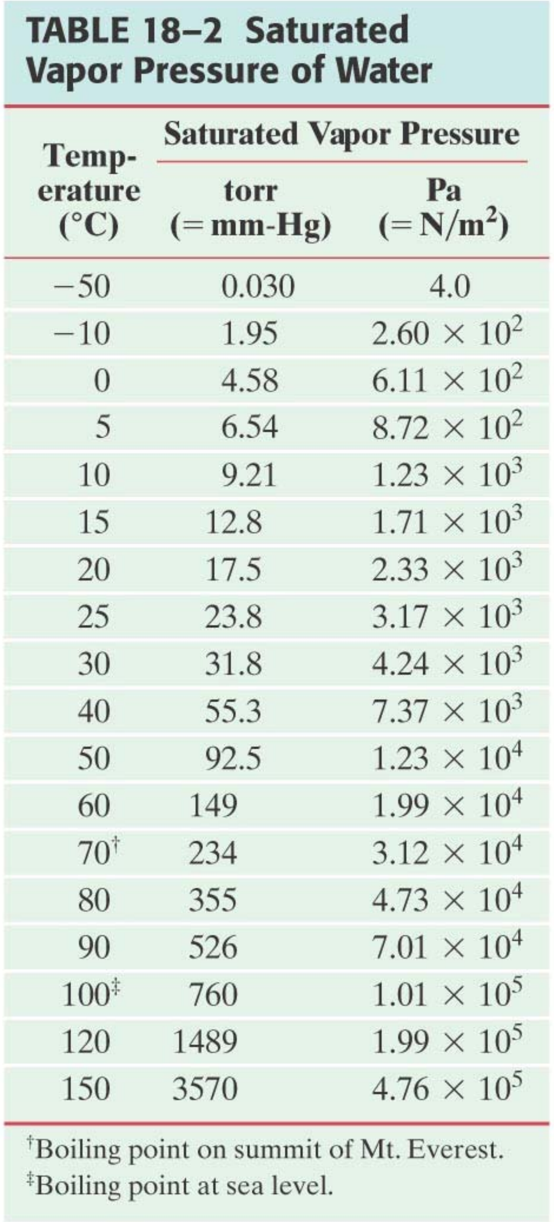


TABLE 18–2 Saturated Vapor Pressure of Water

Temperature (°C)	Saturated Vapor Pressure torr (= mm-Hg)	Saturated Vapor Pressure Pa (= N/m^2)
−50	0.030	4.0
−10	1.95	2.60×10^2
0	4.58	6.11×10^2
5	6.54	8.72×10^2
10	9.21	1.23×10^3
15	12.8	1.71×10^3
20	17.5	2.33×10^3
25	23.8	3.17×10^3
30	31.8	4.24×10^3
40	55.3	7.37×10^3
50	92.5	1.23×10^4
60	149	1.99×10^4
70†	234	3.12×10^4
80	355	4.73×10^4
90	526	7.01×10^4
100‡	760	1.01×10^5
120	1489	1.99×10^5
150	3570	4.76×10^5

†Boiling point on summit of Mt. Everest.
‡Boiling point at sea level.

The saturated vapor pressure increases with temperature.

18-4 Vapor Pressure and Humidity

A liquid **boils** when its saturated vapor pressure equals the **external** pressure.

18-4 Vapor Pressure and Humidity

Partial pressure is the pressure each component of a mixture of gases would exert if it were the only gas present. The partial pressure of water in the air can be as low as zero, and as high as the saturated vapor pressure at that temperature.

Relative humidity is a measure of the saturation of the air.

$$\text{Relative humidity} = \frac{\text{partial pressure of } H_2O}{\text{saturated vapor pressure of } H_2O} \times 100\%.$$

18-4 Vapor Pressure and Humidity

Example 18-6: Relative humidity.

On a particular hot day, the temperature is 30°C and the partial pressure of water vapor in the air is 21.0 torr. What is the relative humidity?

18-4 Vapor Pressure and Humidity

When the humidity is **high**, it feels **muggy**; it is hard for any more water to evaporate.

The **dew point** is the temperature at which the air would be saturated with water.

If the temperature goes below the dew point, **dew**, **fog**, or even **rain** may occur.

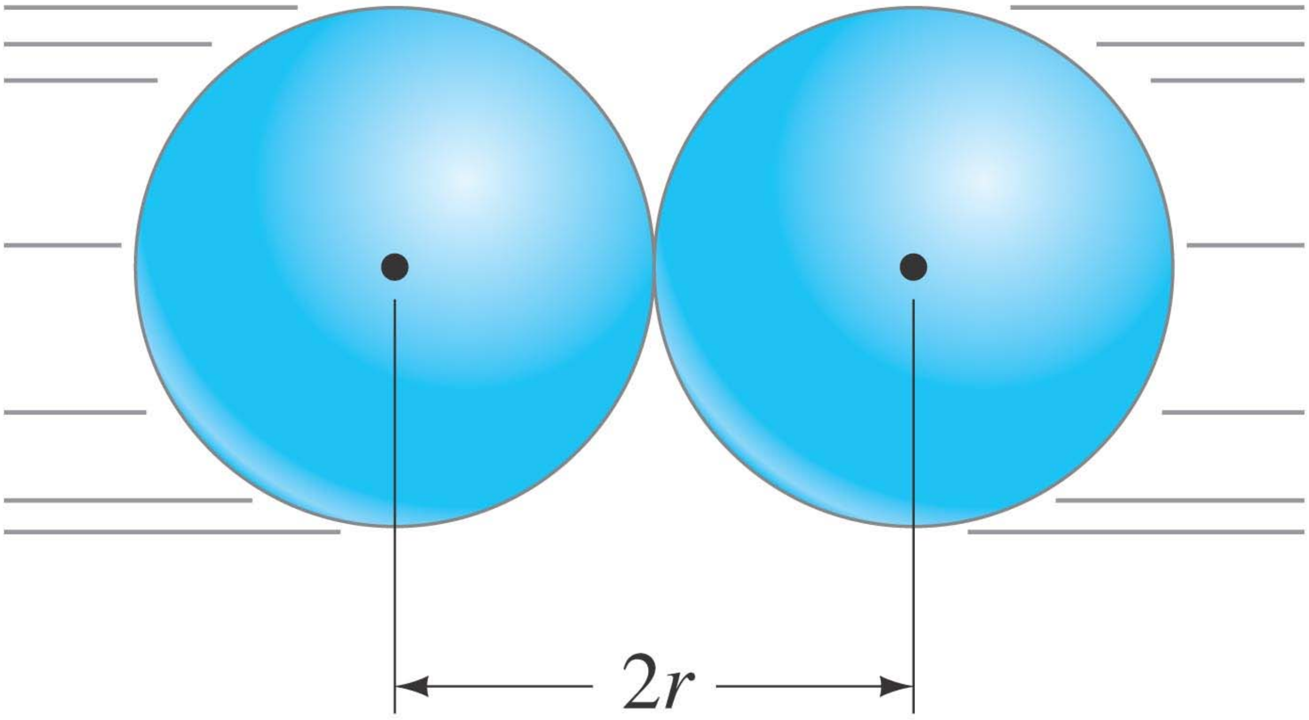
18-4 Vapor Pressure and Humidity

Conceptual Example 18-7: Dryness in winter.

Why does the air inside heated buildings seem very dry on a cold winter day?

18-5 Van der Waals Equation of State

To get a more realistic model of a gas, we include the finite size of the molecules and the range of the intermolecular force beyond the size of the molecule.



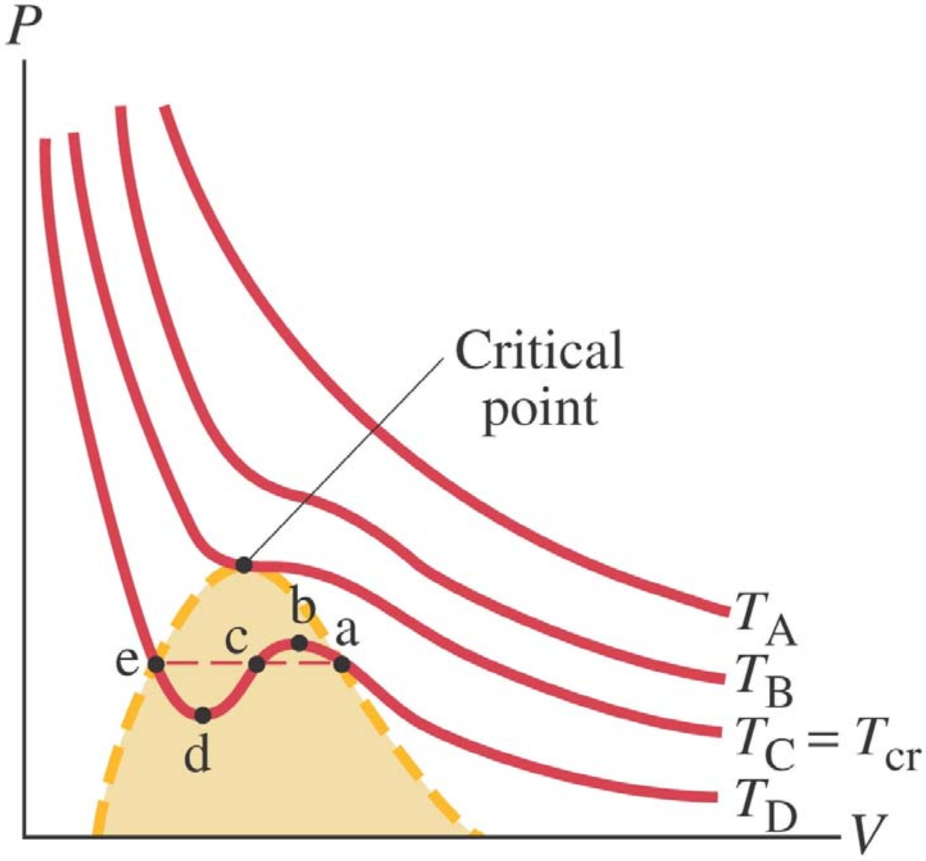
18-5 Van der Waals Equation of State

We assume that some fraction *b* of the volume is unavailable due to the finite size of the molecules. We also expect that the pressure will be reduced by a factor proportional to the square of the density, due to interactions near the walls. This gives the Van der Waals equation of state; the constants *a* and *b* are found experimentally for each gas:

$$\left(P + \frac{a}{(V/n)^2}\right)\left(\frac{V}{n} - b\right) = RT.$$

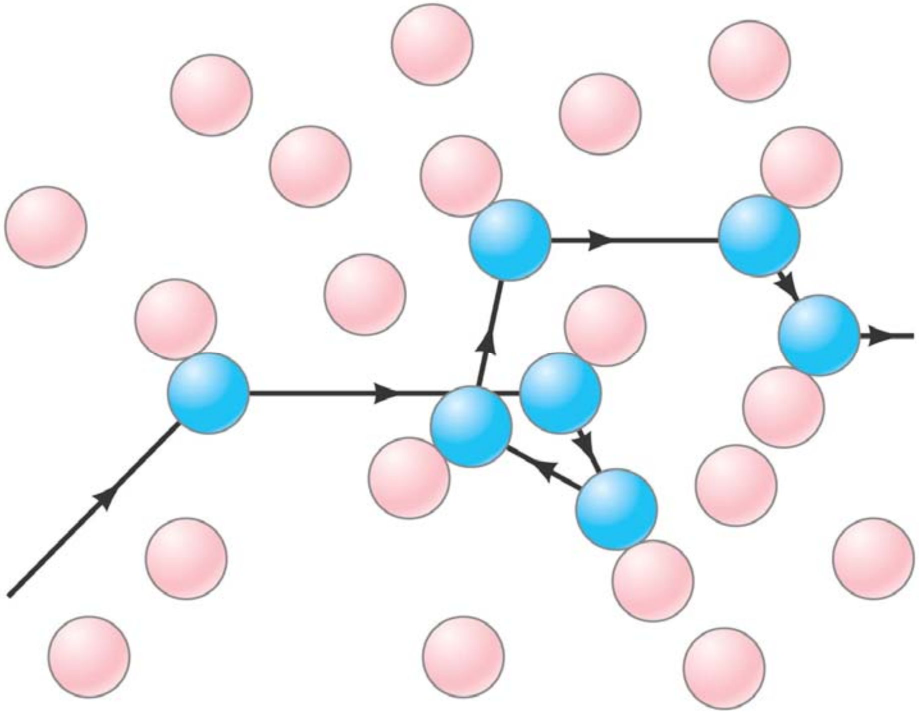
18-5 Van der Waals Equation of State

The PV diagram for a Van der Waals gas fits most experimental data quite well.



18-6 Mean Free Path

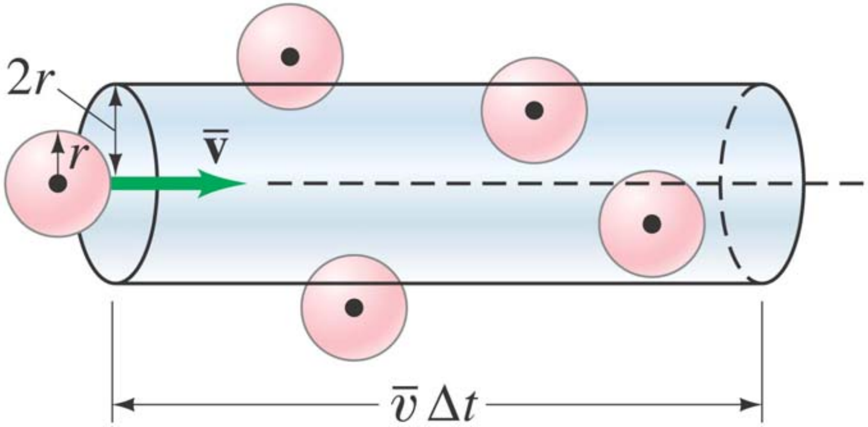
Because of their finite size, molecules in a gas undergo frequent collisions. The average distance a molecule travels between collisions is called the mean free path.



18-6 Mean Free Path

The mean free path can be calculated, given the average speed, the density of the gas, the size of the molecules, and the relative speed of the colliding molecules. The result:

$$\ell_M = \frac{1}{4\pi\sqrt{2}r^2(N/V)}.$$



18-6 Mean Free Path

Example 18-8: Mean free path of air molecules at STP.

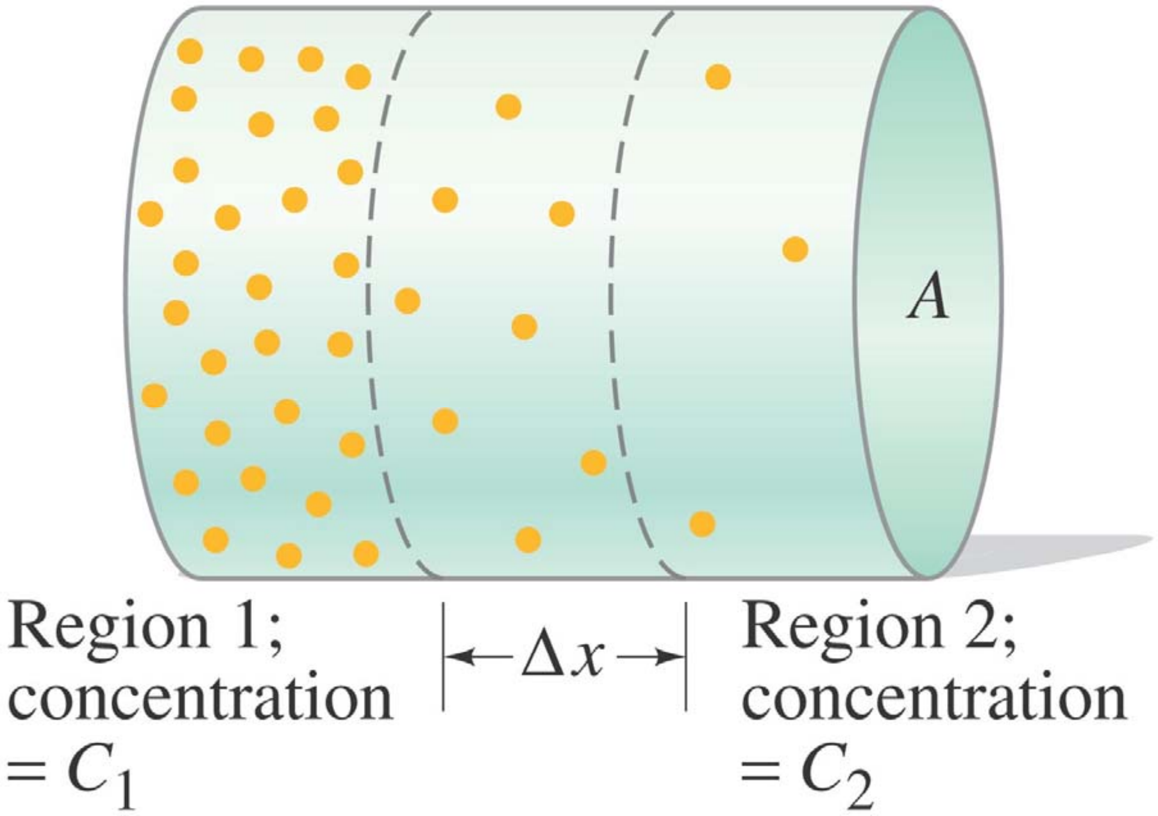
Estimate the mean free path of air molecules at STP, standard temperature and pressure (0°C, 1 atm). The diameter of O_2 and N_2 molecules is about 3×10^{-10} m.

18-7 Diffusion

Even without stirring, a few drops of dye in water will gradually **spread** throughout. This process is called **diffusion**.

18-7 Diffusion

Diffusion occurs from a region of **high** concentration to a region of **lower** concentration.



18-7 Diffusion

The **rate** of diffusion is given by:

$$J = DA\frac{dC}{dx}.$$

In this equation, *D* is the **diffusion constant**.

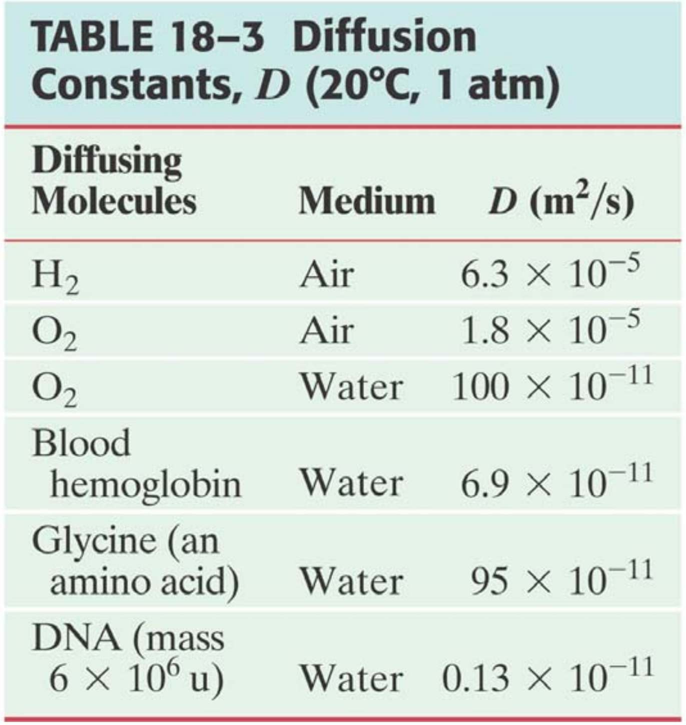


TABLE 18–3 Diffusion Constants, *D* (20°C, 1 atm)

Diffusing Molecules	Medium	D ($\mathrm{m^2/s}$)
H_2	Air	6.3×10^{-5}
O_2	Air	1.8×10^{-5}
O_2	Water	100×10^{-11}
Blood hemoglobin	Water	6.9×10^{-11}
Glycine (an amino acid)	Water	95×10^{-11}
DNA (mass 6×10^6 u)	Water	0.13×10^{-11}

18-7 Diffusion

Example 18-9: Diffusion of ammonia in air.

To get an idea of the time required for diffusion, estimate how long it might take for ammonia (NH_3) to be detected 10 cm from a bottle after it is opened, assuming only diffusion is occurring.

18-7 Diffusion

Conceptual Example 18-10: Colored rings on a paper towel.

A child colors a small spot on a wet paper towel with a brown marker. Later, she discovers that instead of a brown spot, there are concentric colored rings around the marked spot. What happened?

Summary of Chapter 18

- The average kinetic energy of molecules in a gas is proportional to the temperature.
- Below the critical temperature, a gas can liquefy if the pressure is high enough.
- At the triple point, all three phases are in equilibrium.
- Evaporation occurs when the fastest moving molecules escape from the surface of a liquid.
- Saturated vapor pressure occurs when the two phases are in equilibrium.

Summary of Chapter 18

- Relative humidity is the ratio of the actual vapor pressure to the saturated vapor pressure.
- The Van der Waals equation of state takes into account the finite size of molecules.
- The mean free path is the average distance a molecule travels between collisions.
- Diffusion is the process whereby the concentration of a substance becomes uniform.