

PHYS1001B College Physics IB

Thermodynamics II — Thermal Properties of Matter (Ch. 18)

Introduction



The higher the temperature of a gas, the greater the average kinetic energy of its molecules. How much faster are molecules moving in the air above a frying pan (100°C) than in the surrounding kitchen air (25°C)?

Outline

- ▶ 18-1 Equations of State
- ▶ 18-2 Molecular Properties of Matter
- ▶ 18-3 Kinetic-Molecular Model of an Ideal Gas
- ▶ 18-4 Heat Capacities
- ▶ 18-5 Molecular Speeds
- ▶ 18-6 Phases of Matter

18-1 Equations of State

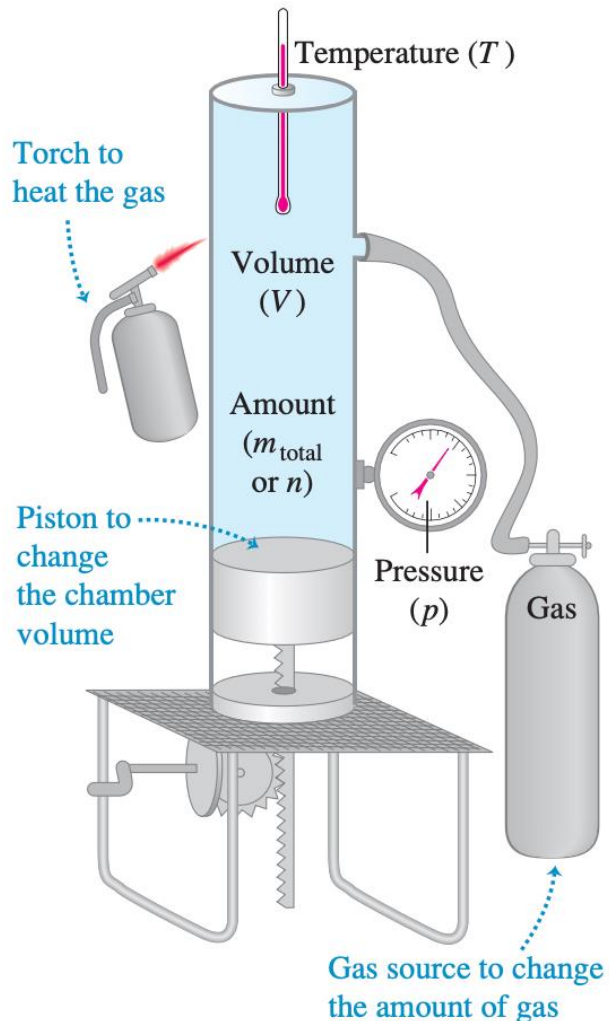
- The conditions in which a particular material exists are described by physical quantities such as pressure, volume, temperature, and amount of substance. These variables describe the *state* of the material and are called **state variables**.
- In a few cases the relationship among p , V , T , and m (or n) is simple enough that we can express it as an equation called the **equation of state**.

Equation of state for a solid material

$$V = V_0[1 + \beta(T - T_0) - k(p - p_0)]$$

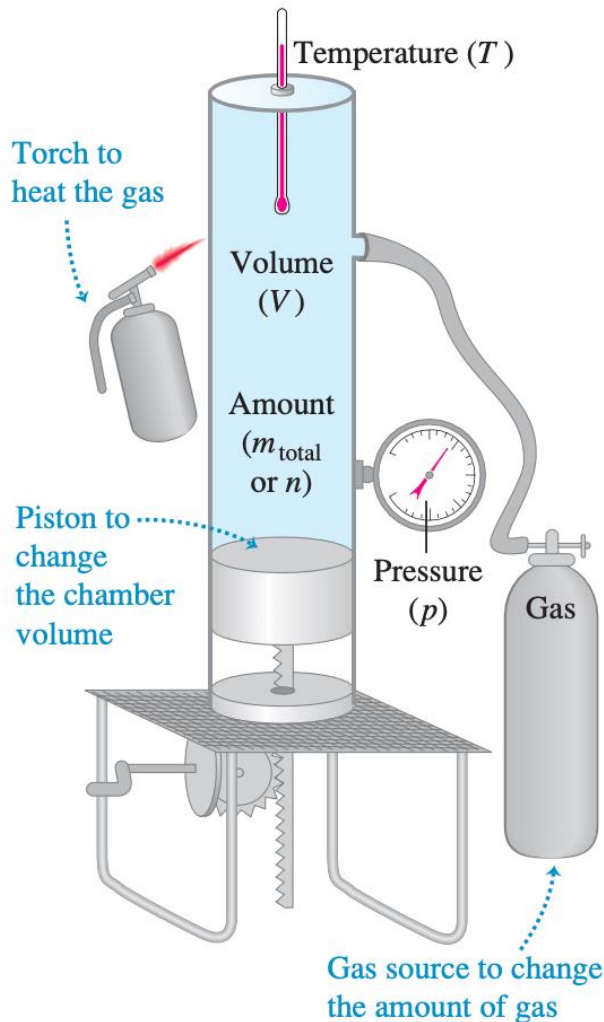
temperature coefficient of volume expansion β
compressibility k

18-1 Equations of State



1. The volume V is proportional to the number of moles n . If we double the number of moles, keeping pressure and temperature constant, the volume doubles.
2. The volume varies *inversely* with the absolute pressure p . If we double the pressure while holding the temperature T and number of moles n constant, the gas compresses to one-half of its initial volume. In other words, $pV = \text{constant}$ when n and T are constant.
3. The pressure is proportional to the *absolute* temperature. If we double the absolute temperature, keeping the volume and number of moles constant, the pressure doubles. In other words, $p = (\text{constant}) T$ when n and V are constant.

18-1 Equations of State



ideal-gas equation

$$pV = nRT$$

gas constant (or *ideal-gas constant*)

$$R = 8.314 \text{ J/mol} \cdot \text{K}$$

Variation -- Density expression

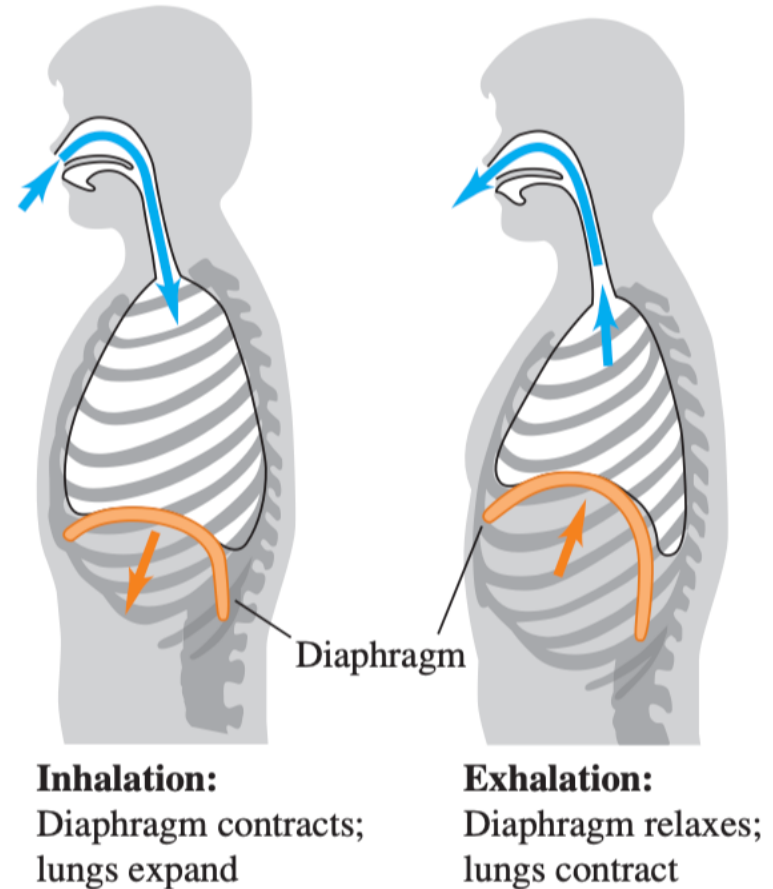
$$pV = \frac{m_{\text{total}}}{M} RT \quad \rho = \frac{pM}{RT}$$

18-1 Equations of State

As the tire warms (T increases), the volume V changes only slightly but the pressure p increases.



Pressure and volume



Sample Problem

Example 18.1 Volume of an ideal gas at STP

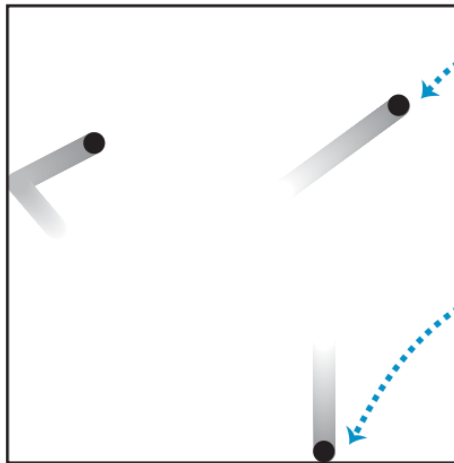
What is the volume of a container that holds exactly 1 mole of an ideal gas at *standard temperature and pressure* (STP), defined as $T = 0^\circ\text{C} = 273.15\text{ K}$ and $p = 1\text{ atm} = 1.013 \times 10^5\text{ Pa}$?

EXECUTE: From Eq. (18.3), using R in $\text{J/mol} \cdot \text{K}$,

$$\begin{aligned} V &= \frac{nRT}{p} = \frac{(1\text{ mol})(8.314\text{ J/mol} \cdot \text{K})(273.15\text{ K})}{1.013 \times 10^5\text{ Pa}} \\ &= 0.0224\text{ m}^3 = 22.4\text{ L} \end{aligned}$$

18-1 Equations of State

(a) An idealized model of a gas

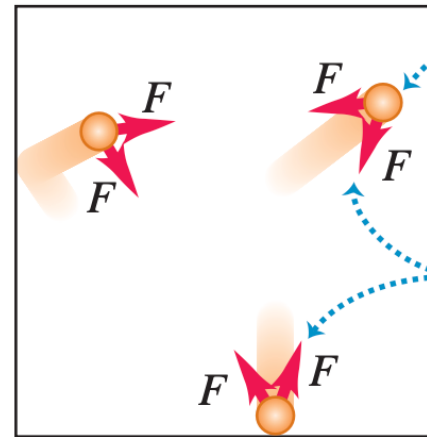


Gas molecules are infinitely small.

They exert forces on the walls of the container but not on each other.

$$pV = nRT$$

(b) A more realistic model of a gas



Gas molecules have volume, which reduces the volume in which they can move.

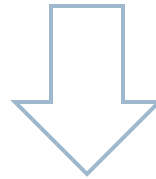
They exert attractive forces on each other, which reduces the pressure ...

... and they exert forces on the container's walls.

18-1 Equations of State

ideal-gas equation

$$pV = nRT$$



- volumes of the molecules
- attractive forces between molecules

Van der Waals equation

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

The constants a and b are empirical constants, different for different gases.

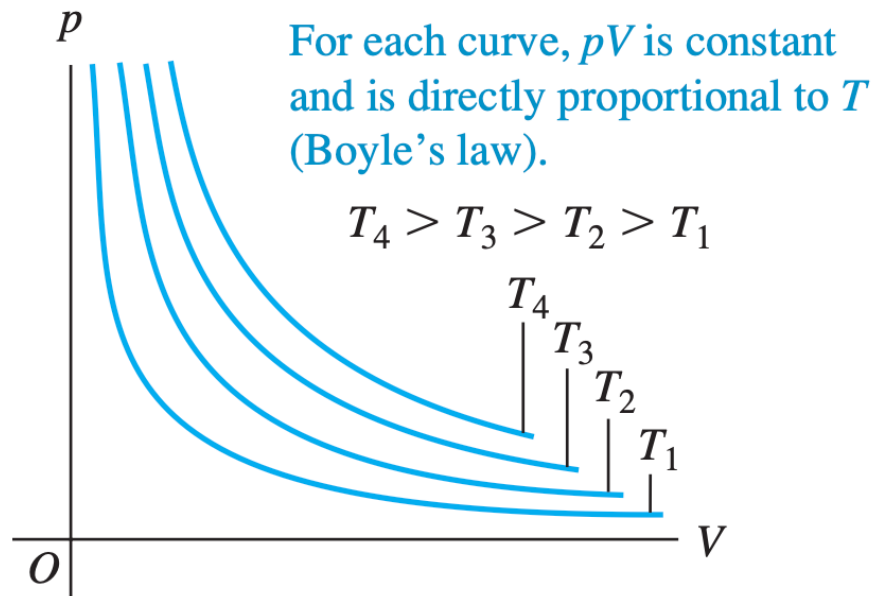
18-1 Equations of State

pV - diagram

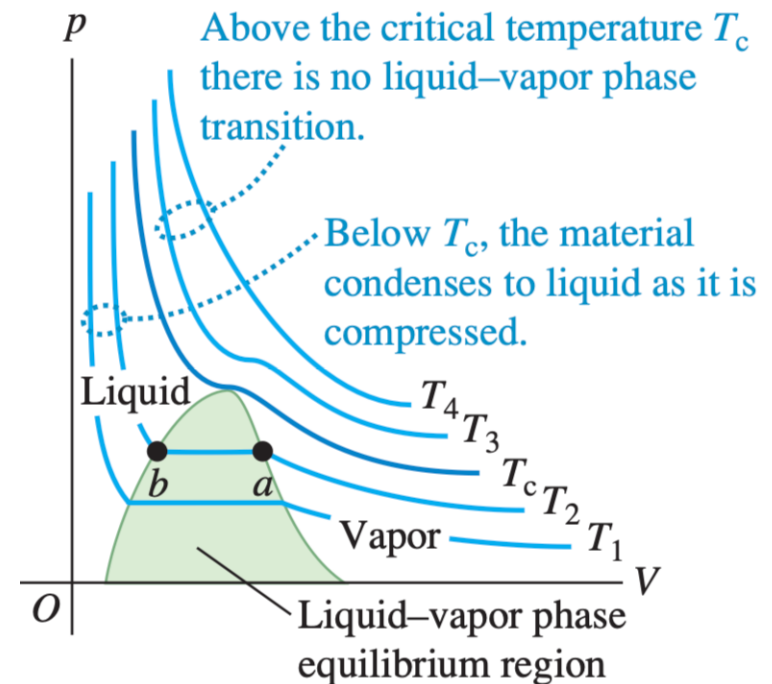
Each curve, representing behavior at a specific temperature, is called an **isotherm**

Ideal gas

Each curve represents pressure as a function of volume for an ideal gas at a single temperature.

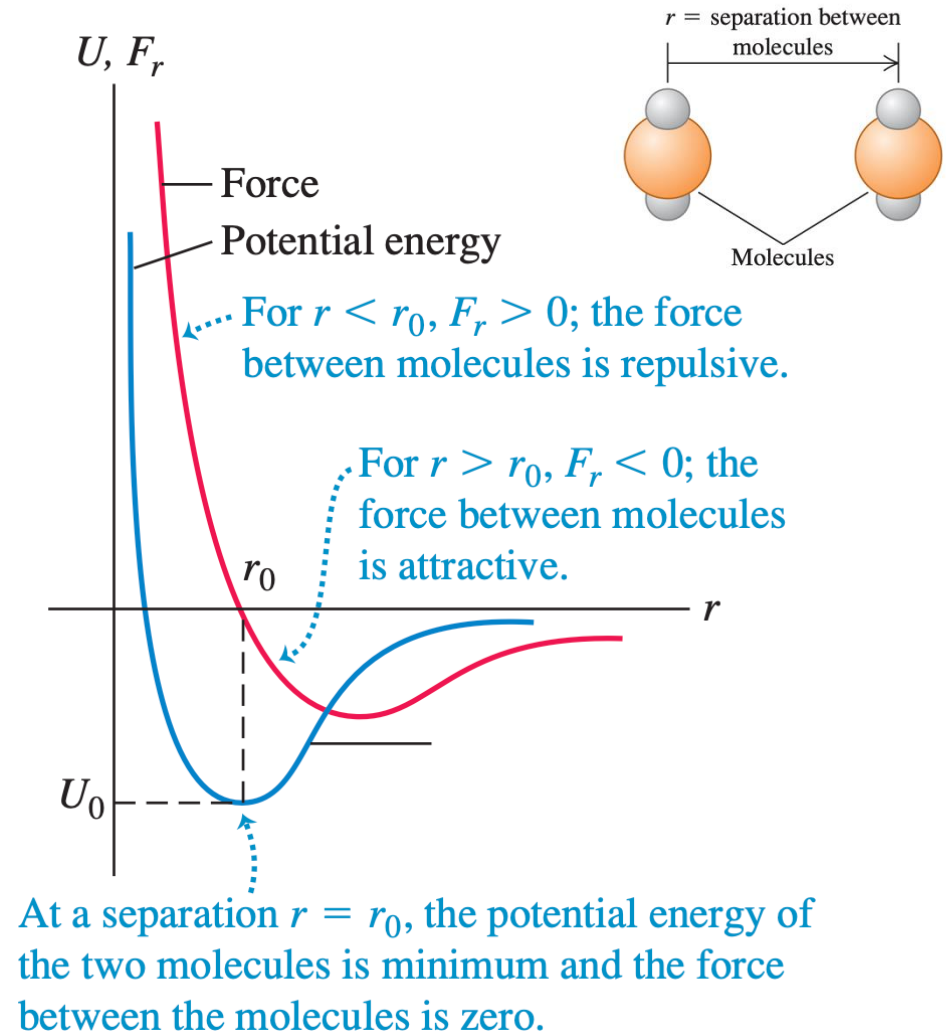


Nonideal gas

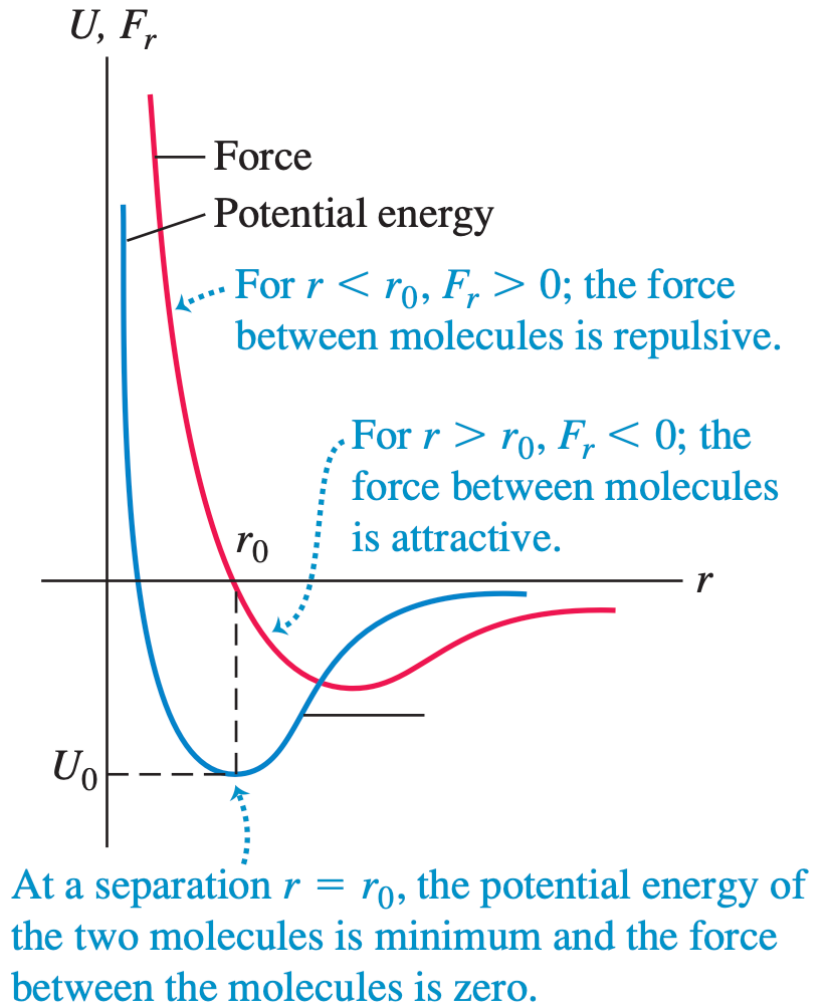


18-2 Molecular Properties of Matter

- At close separations, the electrons around each atom repel each other through electrostatic repulsion.
- At intermediate separations, the electrons and protons of the atoms attract each other through electrostatic (dipole) attraction.
- At far separations, the binding force decreases exponentially.



18-2 Molecular Properties of Matter



In *solids*, molecules vibrate about more or less fixed points. In a crystalline solid these points are arranged in a *crystal lattice*. The vibration of molecules in a solid about their equilibrium positions may be nearly simple harmonic if the potential well is approximately parabolic in shape at distances close to r_0 .

In a *liquid*, the intermolecular distances are usually only slightly greater than in the solid phase of the same substance, but the molecules have much greater freedom of movement.

The molecules of a *gas* are usually widely separated and so have only very small attractive forces. In molecular terms, an *ideal gas* is a gas whose molecules exert *no* attractive forces on each other (see Fig. 18.5a) and therefore have no *potential* energy.

18-2 Molecular Properties of Matter

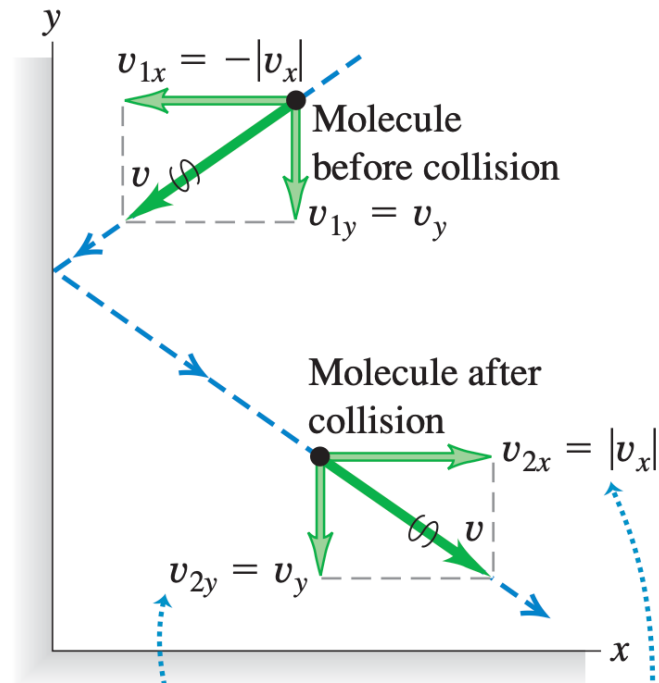
Moles and Avogadro's Number

One mole is the amount of substance that contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12.

$$M = N_A m \quad (\text{molar mass, Avogadro's number, and mass of a molecule})$$

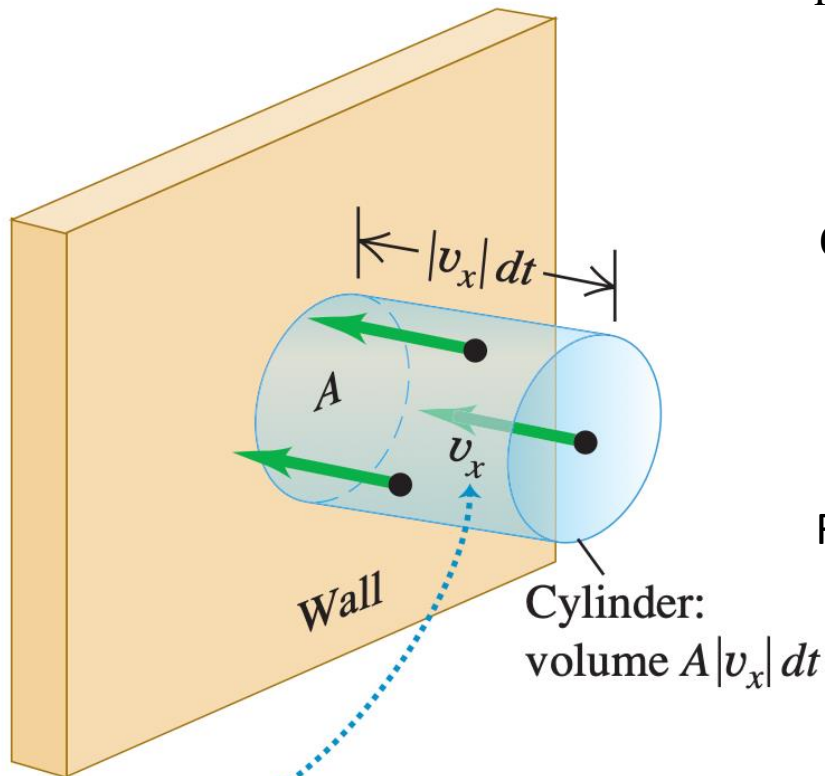
$$N_A = 6.022141791302 \times 10^{23} \text{ molecules/mol (Avogadro's number)}$$

18-3 Kinetic-Molecular Model of an Ideal Gas



- Velocity component parallel to the wall (y-component) does not change.
- Velocity component perpendicular to the wall (x-component) reverses direction.
- Speed v does not change.

18-3 Kinetic-Molecular Model of an Ideal Gas



All molecules are assumed to have the same magnitude $|v_x|$ of x -velocity.

number of collisions with A during dt

$$\frac{1}{2} \left(\frac{N}{V} \right) (A |v_x| dt)$$

Change of momentum

$$dP_x = \frac{1}{2} \left(\frac{N}{V} \right) (A |v_x| dt) (2m |v_x|) = \frac{NAmv_x^2 dt}{V}$$

Rate of change of momentum (Force)

$$\frac{dP_x}{dt} = \frac{NAmv_x^2}{V}$$

$$p = \frac{F}{A} = \frac{Nmv_x^2}{V}$$

18-3 Kinetic-Molecular Model of an Ideal Gas

Pressure and Molecular Kinetic Energies

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$$(v^2)_{\text{av}} = (v_x^2)_{\text{av}} + (v_y^2)_{\text{av}} + (v_z^2)_{\text{av}}$$

$$(v_x^2)_{\text{av}} = \frac{1}{3}(v^2)_{\text{av}}$$

$$pV = \frac{1}{3}Nm(v^2)_{\text{av}}$$

$$pV = \frac{2}{3}K_{\text{tr}} \qquad K_{\text{tr}} = \frac{1}{2}m(v^2)_{\text{av}}$$

18-3 Kinetic-Molecular Model of an Ideal Gas

$$pV = \frac{2}{3}K_{\text{tr}}$$

$$pV = nRT$$

$$K_{\text{tr}} = \frac{3}{2}nRT$$

(average translational kinetic energy of n moles of ideal gas)

Boltzmann constant

$$k = \frac{R}{N_A} = \frac{8.314 \text{ J/mol} \cdot \text{K}}{6.022 \times 10^{23} \text{ molecules/mol}} \\ = 1.381 \times 10^{-23} \text{ J/molecule} \cdot \text{K}$$

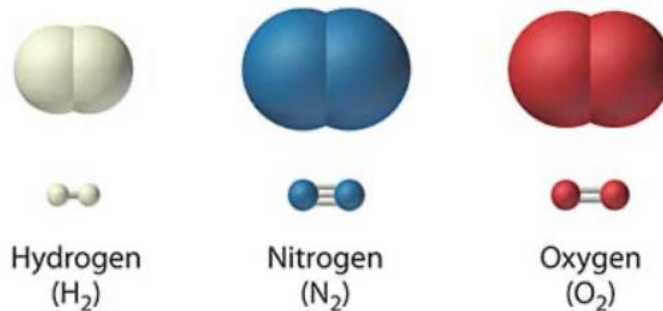
$$\frac{1}{2}m(v^2)_{\text{av}} = \frac{3}{2}kT$$

(average translational kinetic energy of a gas molecule)

18-3 Kinetic-Molecular Model of an Ideal Gas

root-mean-square speed v_{rms}

$$v_{\text{rms}} = \sqrt{(v^2)_{\text{av}}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$



M : 2 g mol⁻¹ 28 g mol⁻¹ 32 g mol⁻¹

Which one can most easily escape from the earth?

Sample Problem

Example 18.6 Molecular kinetic energy and v_{rms}

(a) What is the average translational kinetic energy of an ideal-gas molecule at 27°C? (b) What is the total random translational kinetic energy of the molecules in 1 mole of this gas? (c) What is the root-mean-square speed of oxygen molecules at this temperature?

EXECUTE: (a) From Eq. (18.16),

$$\begin{aligned}\frac{1}{2}m(v^2)_{\text{av}} &= \frac{3}{2}kT = \frac{3}{2}(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K}) \\ &= 6.21 \times 10^{-21} \text{ J}\end{aligned}$$

(b) From Eq. (18.14), the kinetic energy of one mole is

$$K_{\text{tr}} = \frac{3}{2}nRT = \frac{3}{2}(1 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K}) = 3740 \text{ J}$$

(c) We found the mass per molecule m and molar mass M of molecular oxygen in Example 18.5. Using Eq. (18.19), we can calculate v_{rms} in two ways:

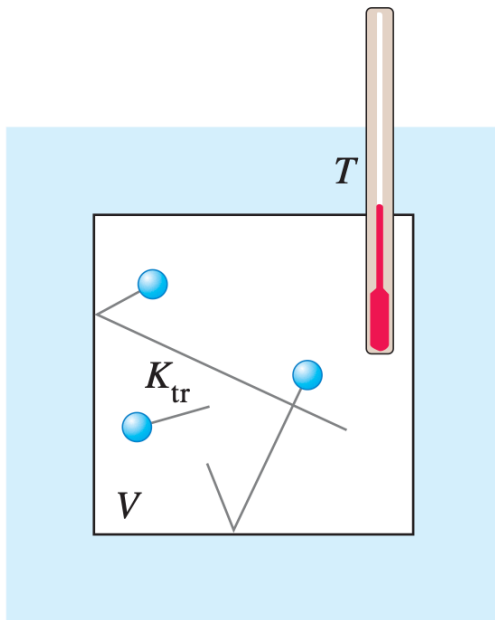
$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{5.31 \times 10^{-26} \text{ kg}}}$$

$$= 484 \text{ m/s} = 1740 \text{ km/h} = 1080 \text{ mi/h}$$

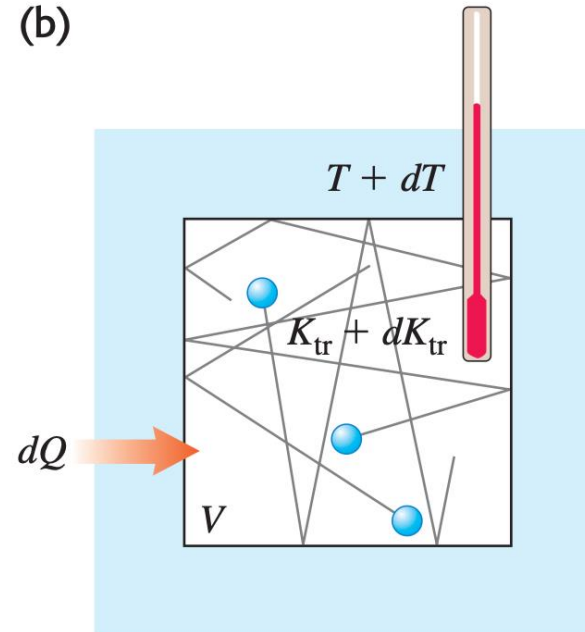
$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{32.0 \times 10^{-3} \text{ kg/mol}}} = 484 \text{ m/s}$$

18-4 Heat Capacities

(a)



(b)



18.17 (a) A fixed volume V of a monatomic ideal gas. (b) When an amount of heat dQ is added to the gas, the total translational kinetic energy increases by $dK_{\text{tr}} = dQ$ and the temperature increases by $dT = dQ/nC_V$.

18-4 Heat Capacities

$$C_V = \frac{3}{2}R \quad (\text{ideal gas of point particles})$$

$$C_V = \frac{3}{2}(8.314 \text{ J/mol} \cdot \text{K}) = 12.47 \text{ J/mol} \cdot \text{K}$$

$$C_V = \frac{5}{2}R \quad (\text{diatomic gas, including rotation})$$

$$C_V = \frac{5}{2}(8.314 \text{ J/mol} \cdot \text{K}) = 20.79 \text{ J/mol} \cdot \text{K}$$

$$C_V = 3R \quad (\text{ideal monatomic solid})$$

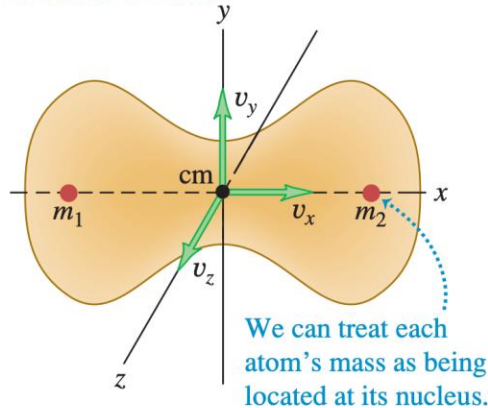
$$C_V = (3)(8.314 \text{ J/mol} \cdot \text{K}) = 24.9 \text{ J/mol} \cdot \text{K}$$

Type of Gas	Gas	C_V (J/mol · K)
Monatomic	He	12.47
	Ar	12.47
Diatomic	H ₂	20.42
	N ₂	20.76
	O ₂	20.85
	CO	20.85
Polyatomic	CO ₂	28.46
	SO ₂	31.39
	H ₂ S	25.95

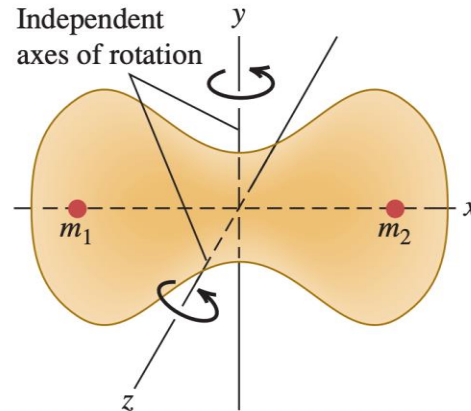
18-4 Heat Capacities

Motions of a diatomic molecule

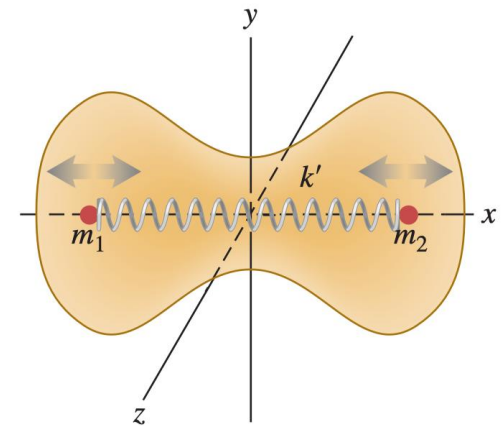
(a) **Translational motion.** The molecule moves as a whole; its velocity may be described as the x -, y -, and z -velocity components of its center of mass.



(b) **Rotational motion.** The molecule rotates about its center of mass. This molecule has two independent axes of rotation.

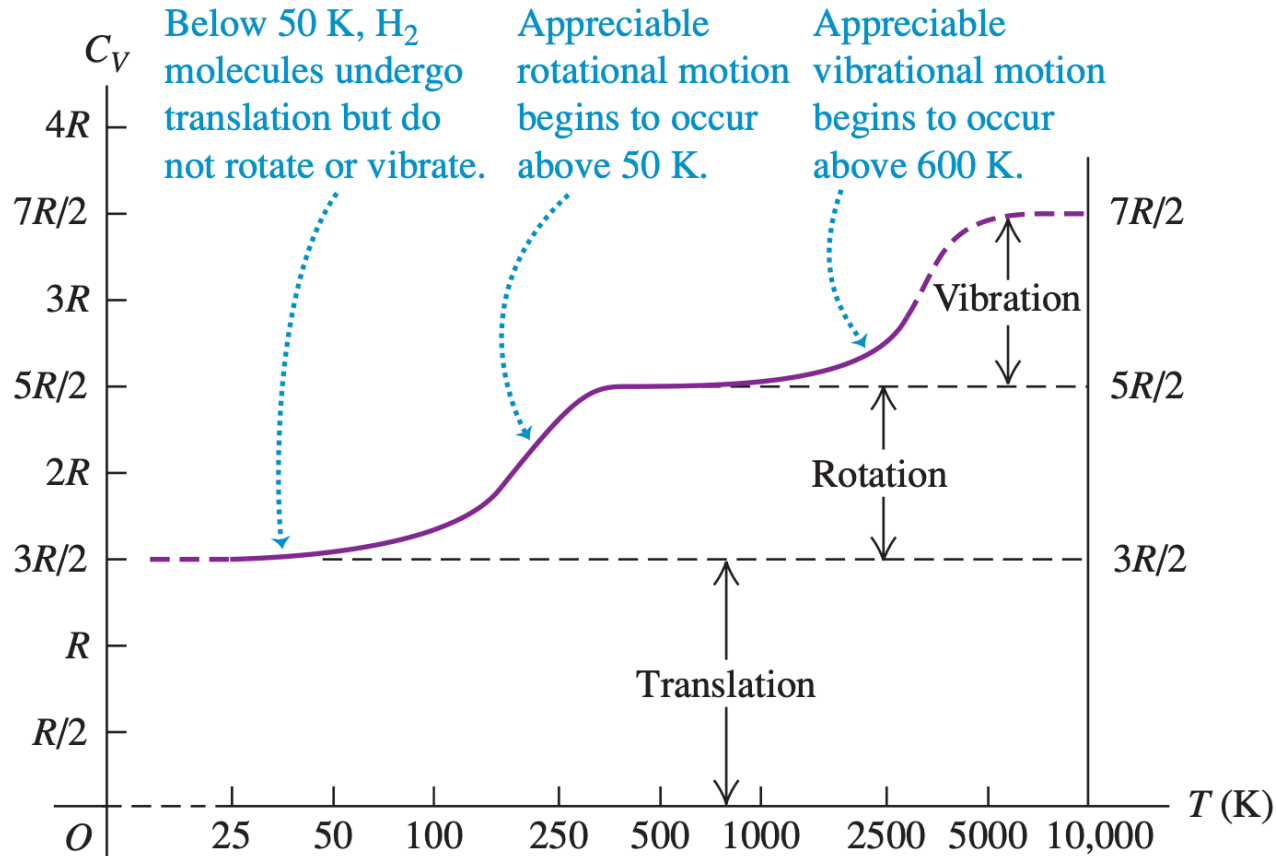


(c) **Vibrational motion.** The molecule oscillates as though the nuclei were connected by a spring.

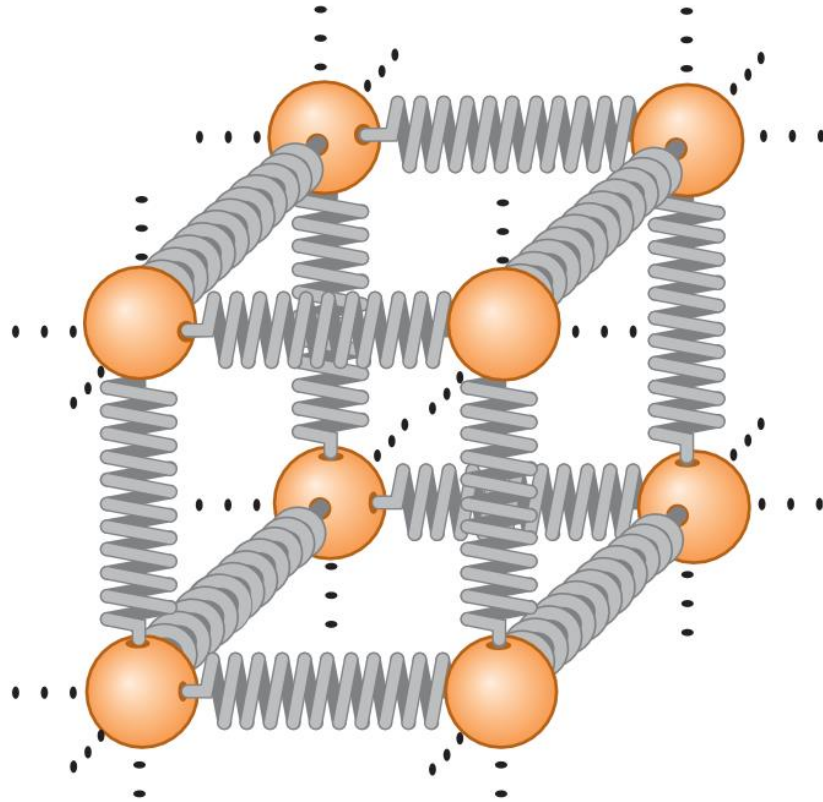


- principle of **equipartition of energy**
- The number of velocity components needed to describe the motion of a molecule completely is called the number of **degrees of freedom**

18-4 Heat Capacities



18-4 Heat Capacities



- 3D harmonic oscillator
- average kinetic energy $\frac{3}{2} kT$
- average potential energy $\frac{3}{2} kT$

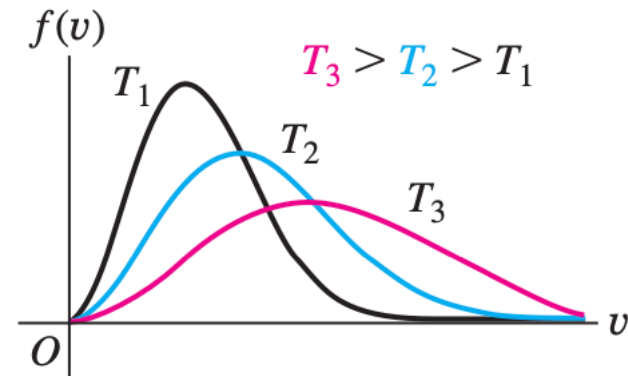
$$E_{\text{total}} = 3NkT = 3nRT$$

$$C_V = 3R$$

18-5 Molecular Speeds

Maxwell–Boltzmann distribution.

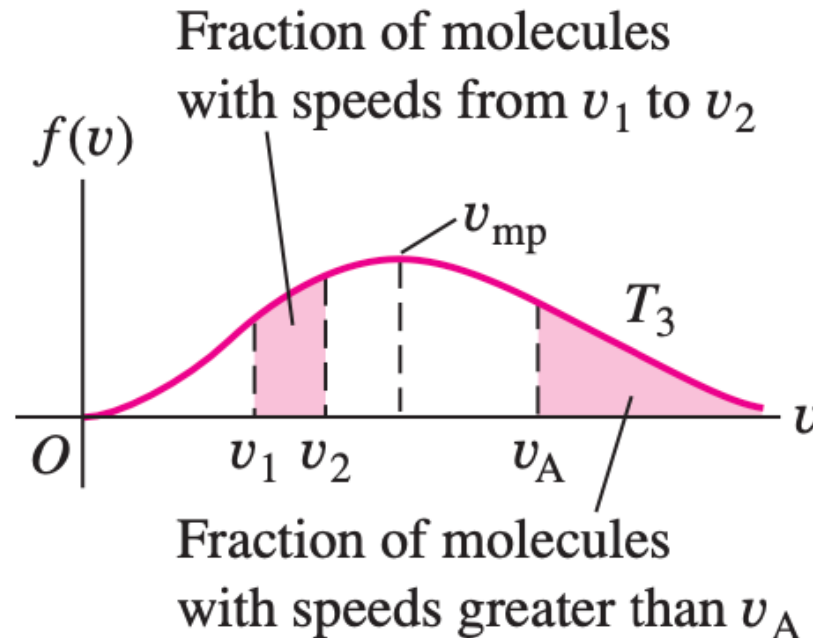
$$f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT}$$



As temperature increases:

- the curve flattens.
- the maximum shifts to higher speeds.

18-5 Molecular Speeds



most probable

$$v_{mp} = \sqrt{\frac{2kT}{m}}$$

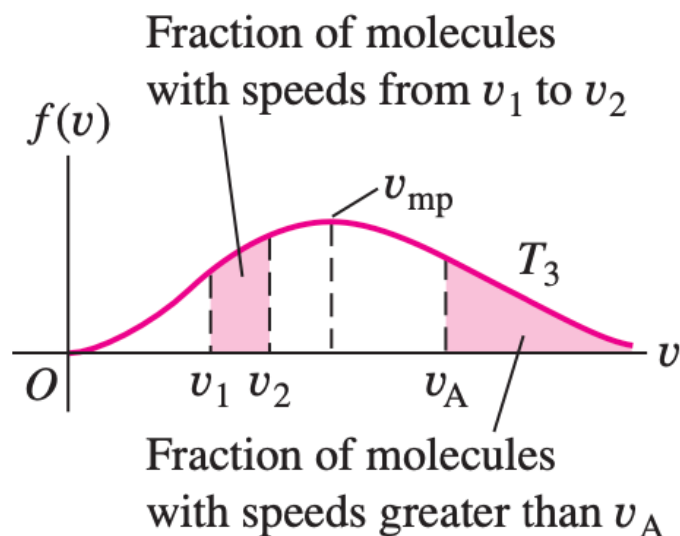
Average

$$v_{av} = \sqrt{\frac{8kT}{\pi m}}$$

Root mean square

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$

18-5 Molecular Speeds



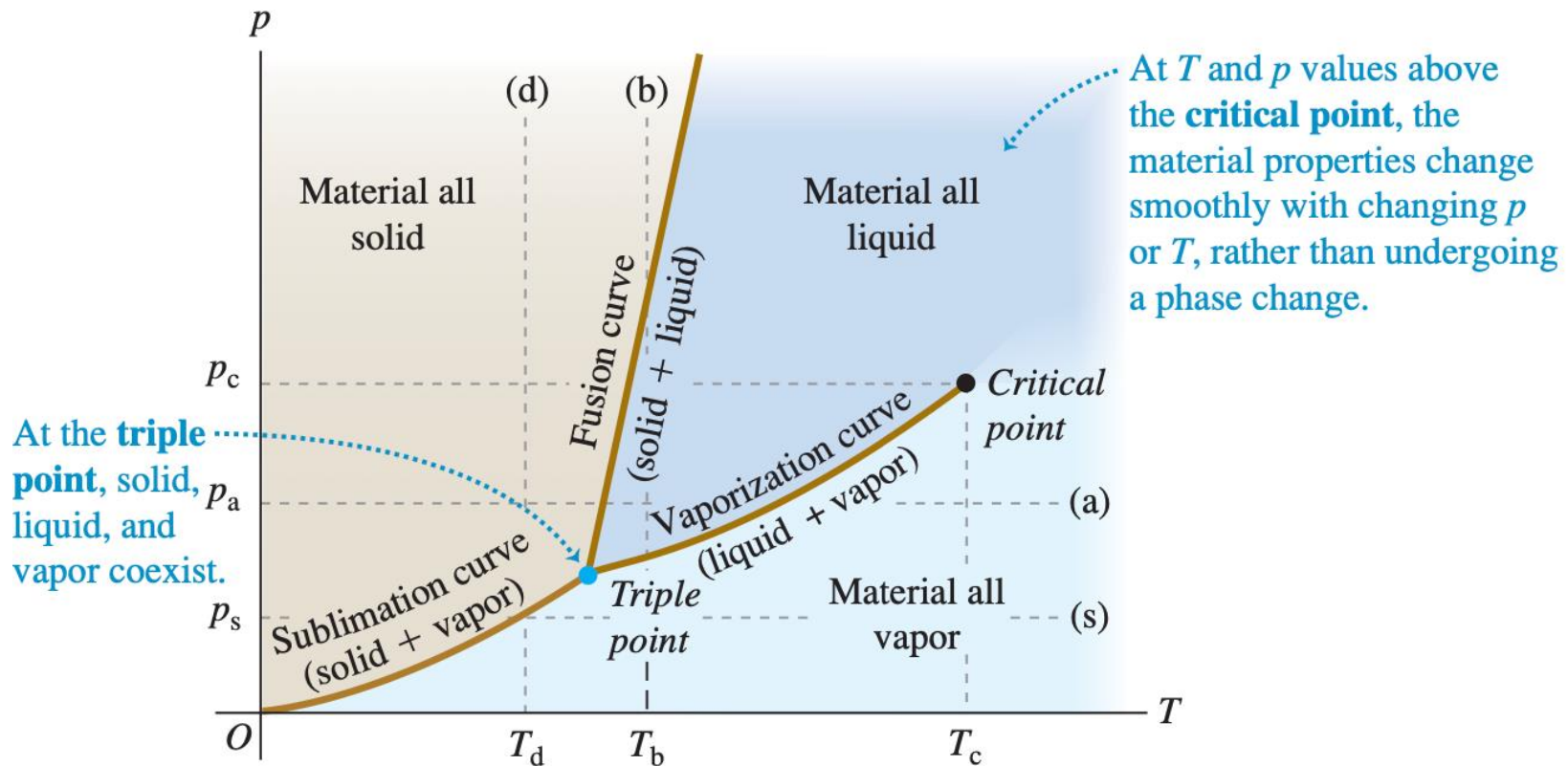
related to cooling of evaporation
activation energy of chemical reaction

Table 18.2 Fractions of Molecules in an Ideal Gas with Speeds Less than Various Multiples of v/v_{rms}

v/v_{rms}	Fraction
0.20	0.011
0.40	0.077
0.60	0.218
0.80	0.411
1.00	0.608
1.20	0.771
1.40	0.882
1.60	0.947
1.80	0.979
2.00	0.993

18-6 Phases of Matter

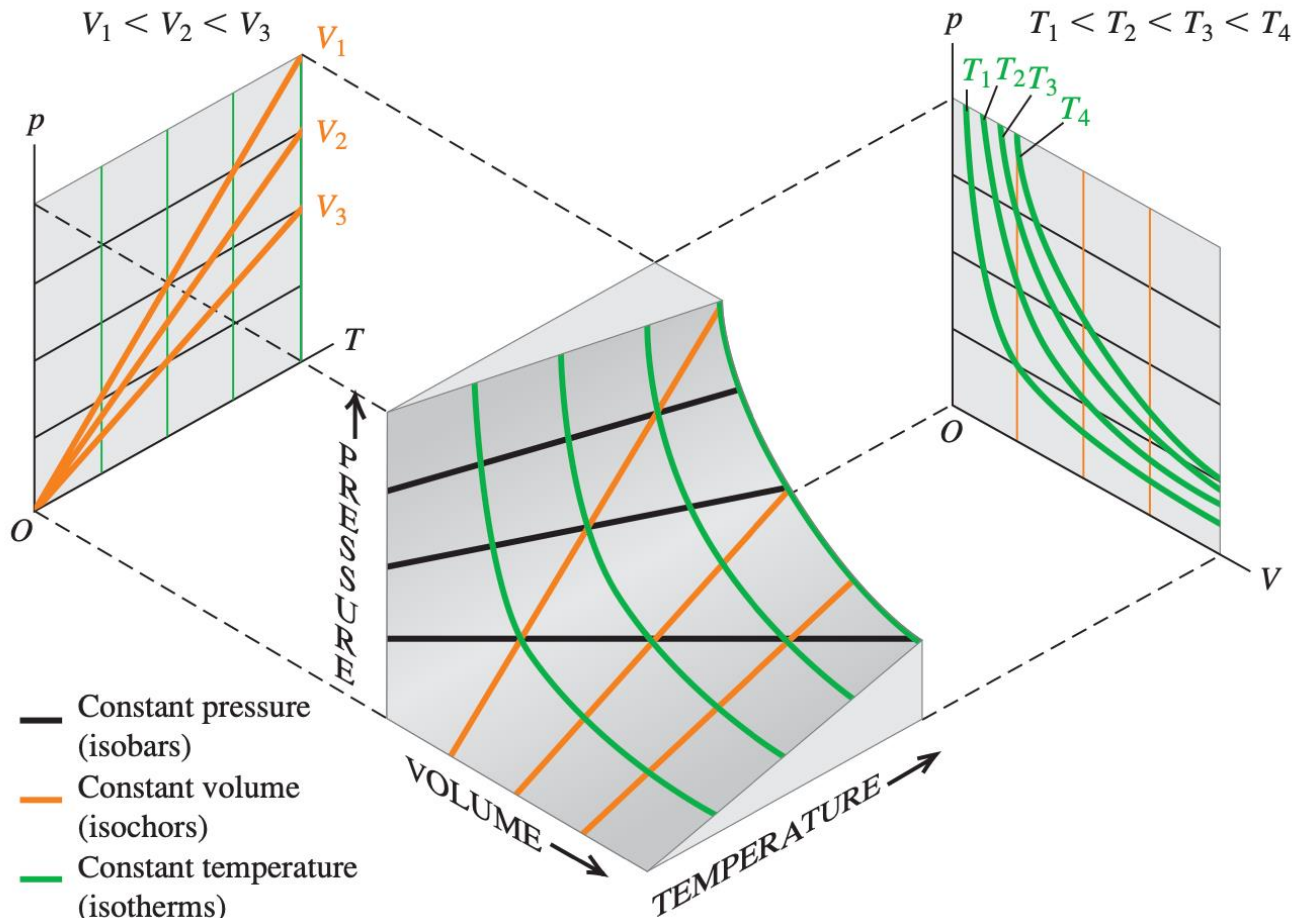
phase diagram



A transition from one phase to another ordinarily requires **phase equilibrium** between the two phases

18-6 Phases of Matter

pVT -surface for an ideal gas



18-6 Phases of Matter

pVT -surface for a substance

