

Chapter 18

Thermal Properties of Matter

PowerPoint® Lectures for
University Physics, 14th Edition
– Hugh D. Young and Roger A. Freedman

Learning Goals for Chapter 18

Looking forward at ...

- how to relate the pressure, volume, and temperature of a gas.
- how the pressure and temperature of a gas are related to the kinetic energy of its molecules.
- how the heat capacities of a gas reveal whether its molecules are rotating or vibrating.
- how the speeds of molecules are distributed in a gas.
- what determines whether a substance is a gas, a liquid, or a solid.

Introduction

- How does the speed of the molecules in the air above the frying pan compare with that of the ones in the rest of the kitchen?
- How do the atoms of a gas determine its temperature and pressure?
- We'll see how the microscopic properties of matter determine its macroscopic properties.



Equations of state and the ideal-gas law

- Quantities such as pressure, volume, temperature, and the amount of a substance are **state variables** because they describe the state of the substance.
- The **equation of state** relates the state variables.
- The ideal-gas equation is an equation of state for an ideal gas:

Ideal-gas
equation:

$$pV = nRT$$

Gas pressure
Gas volume

Number of moles of gas
Absolute temperature of gas
Gas constant

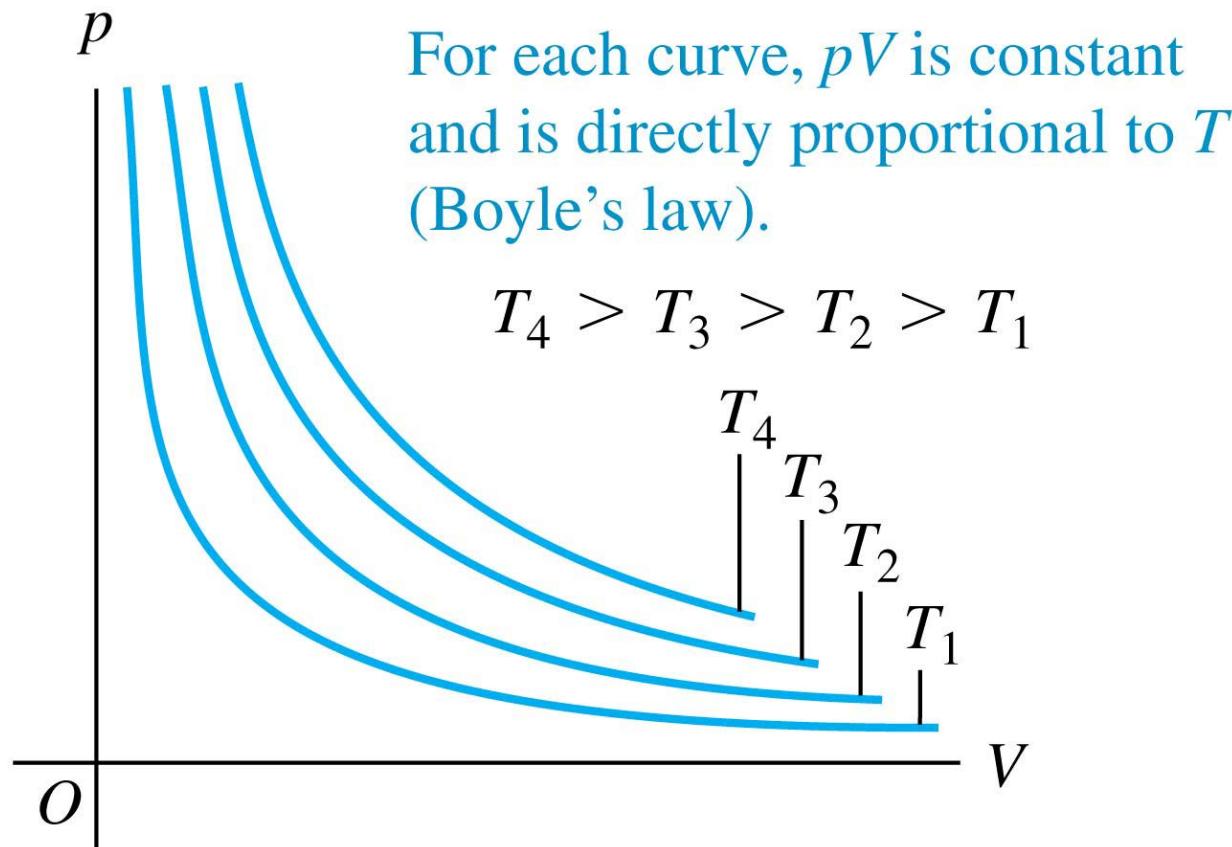
Detailed description: This diagram illustrates the ideal-gas equation. It features the equation $pV = nRT$ in the center. Surrounding the equation are five labels: 'Gas pressure' pointing to p , 'Gas volume' pointing to V , 'Number of moles of gas' pointing to n , 'Absolute temperature of gas' pointing to T , and 'Gas constant' pointing to R . Dotted arrows connect each label to its corresponding variable in the equation.

- Gas constant $R = 8.31 \text{ J/mol}\cdot\text{K}$.
- The **molar mass M (molecular weight)** is the mass per mole. The total mass of n moles is $m_{\text{total}} = nM$.

pV-diagrams

- These show isotherms, or constant-temperature curves, for a constant amount of an ideal gas.

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



Q18.1

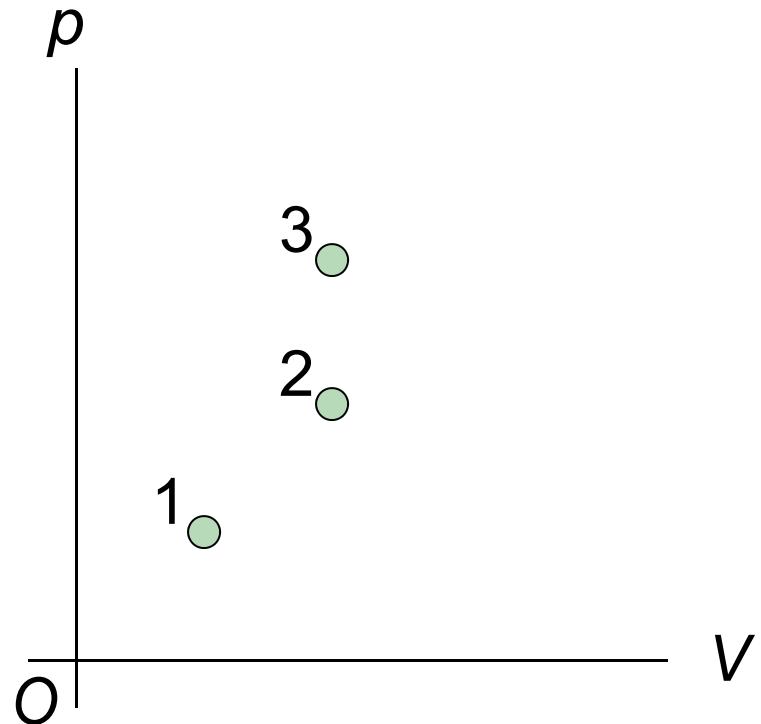
A quantity of an ideal gas is contained in a balloon. Initially the gas temperature is 27° C . You double the pressure on the balloon and change the temperature so that the balloon shrinks to one-quarter of its original volume. What is the new temperature of the gas?

- A. 54° C
- B. 27° C
- C. 13.5° C
- D. -123° C
- E. -198° C

Q18.2

This p - V diagram shows three possible states of a certain amount of an ideal gas. Which state is at the *highest* temperature?

- A. state #1
- B. state #2
- C. state #3
- D. Two of these are tied for highest temperature.
- E. All three of these are at the same temperature.



Q18.3

If you increase the temperature of a given amount of an ideal gas, what happens to the gas pressure p and the volume V of the gas?

- A. p increases.
- B. V increases.
- C. p and V both increase.
- D. Either p increases and V decreases, or p decreases and V increases.
- E. Not enough information is given to decide.

Q-RT18.1

Rank the following ideal gases in order from greatest to least number of moles (p = pressure, V = volume, T = temperature).

- A. $p = 1.00 \text{ atm}$, $V = 1.00 \text{ L}$, $T = 27.0^\circ \text{ C}$
- B. $p = 1.00 \text{ atm}$, $V = 1.00 \text{ L}$, $T = 327.0^\circ \text{ C}$
- C. $p = 1.00 \text{ atm}$, $V = 2.00 \text{ L}$, $T = 27.0^\circ \text{ C}$
- D. $p = 2.00 \text{ atm}$, $V = 2.00 \text{ L}$, $T = 27.0^\circ \text{ C}$
- E. $p = 3.00 \text{ atm}$, $V = 1.00 \text{ L}$, $T = 327.0^\circ \text{ C}$

Application

- The ideal-gas equation $pV = nRT$ gives a good description of the air inside an inflated vehicle tire, where the pressure is about 3 atmospheres and the temperature is much too high for nitrogen or oxygen to liquefy.
- As the tire warms (T increases), the volume V changes only slightly but the pressure p increases.

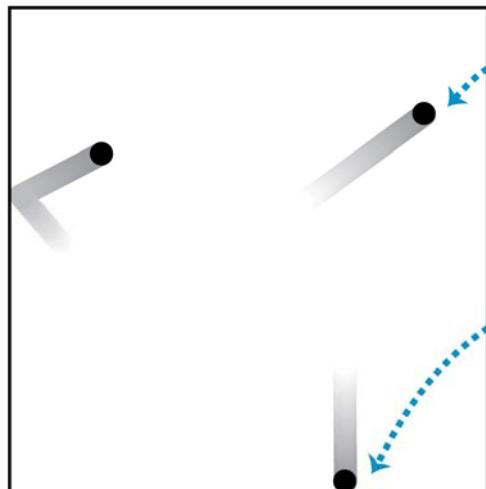


The van der Waals equation

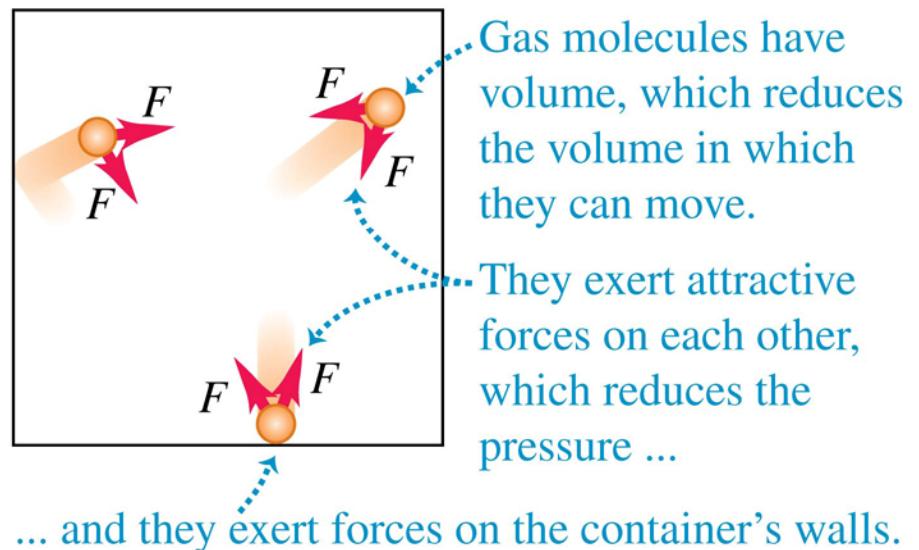
- The model used for the ideal-gas equation ignores the volumes of molecules and the attractive forces between them.
- The *van der Waals equation* is a more realistic model:

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

(a) An idealized model of a gas



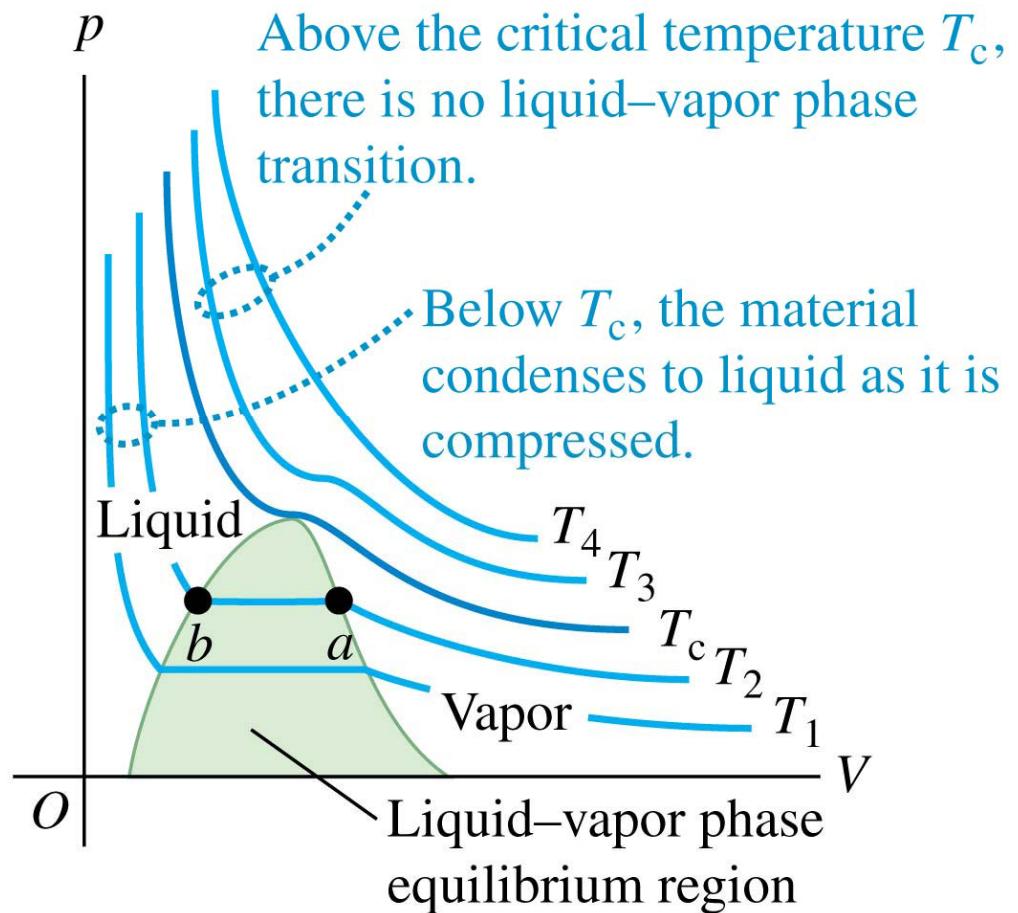
(b) A more realistic model of a gas



pV-diagrams

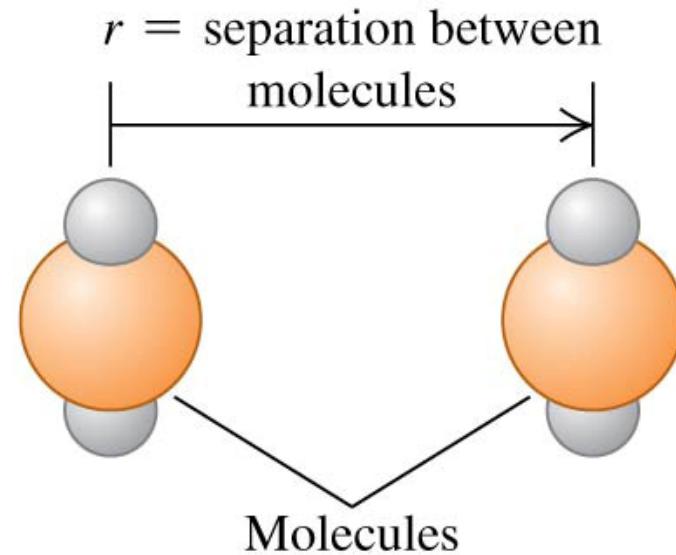
- A *pV*-diagram for a nonideal gas shows isotherms for temperatures above and below the critical temperature T_c .
- At still lower temperatures the material might undergo phase transitions from liquid to solid or from gas to solid.

$$T_4 > T_3 > T_c > T_2 > T_1$$



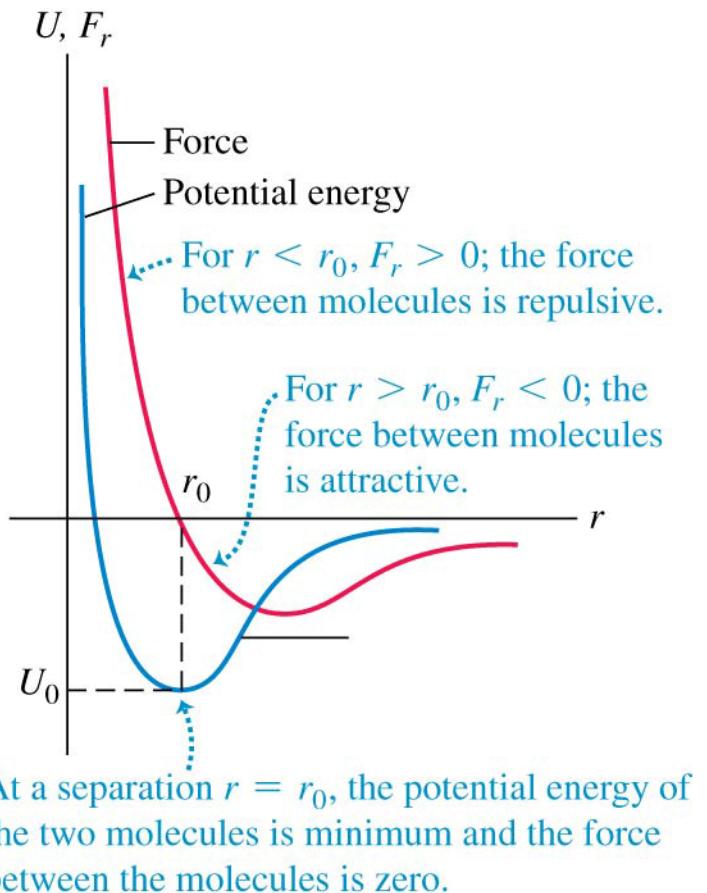
Molecules and intermolecular forces

- Any specific chemical compound is made up of identical molecules.
- In gases the molecules move nearly independently.
- The force between molecules in a gas varies with the distance r between molecules.
- When molecules are far apart, the intermolecular forces are very small and usually attractive.



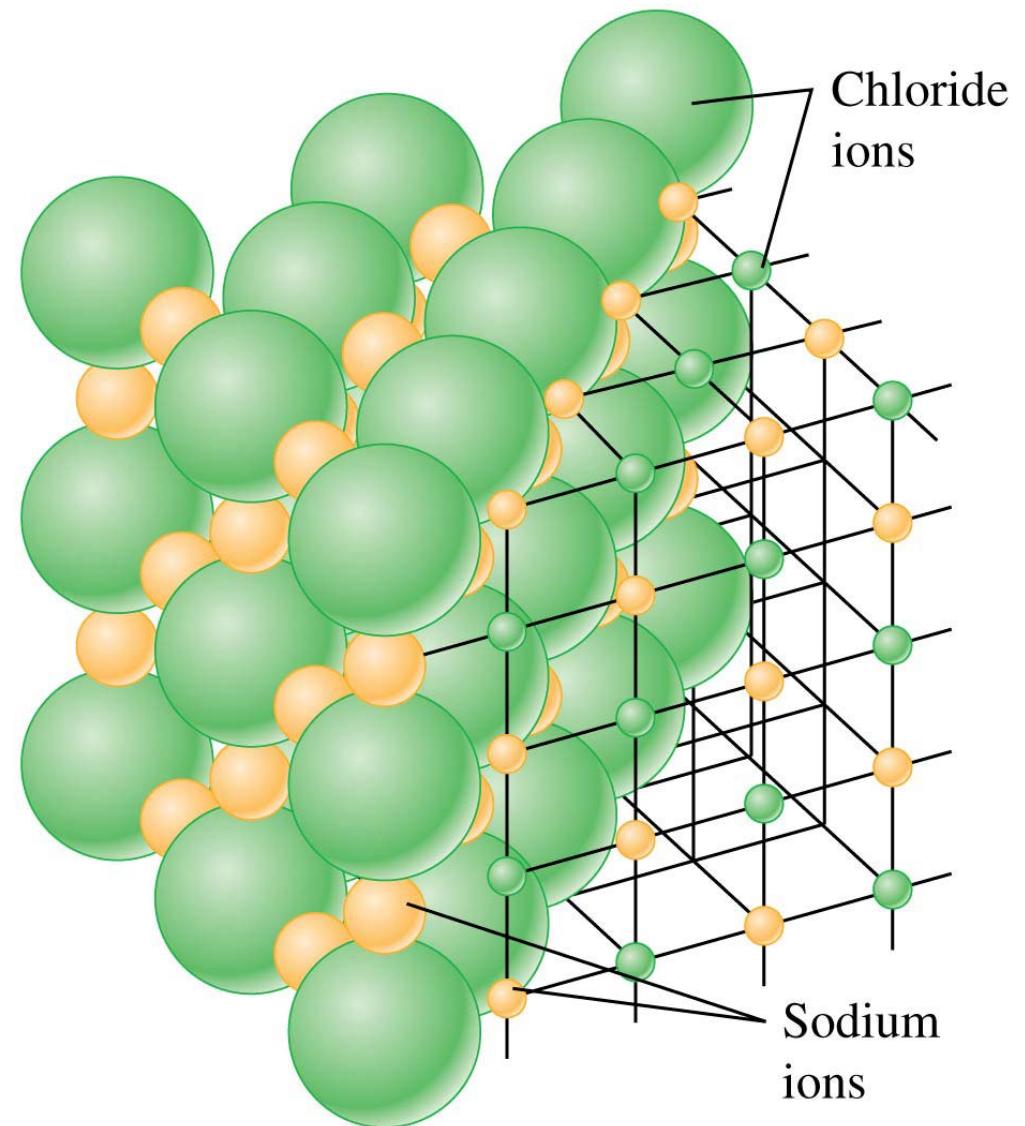
Molecular properties of matter

- Figure 18.8 at the right shows how the force between molecules and their interaction potential energy depend on their separation r .
- Molecules in solids are essentially fixed in place, while those in liquids and gases have much more freedom to move.



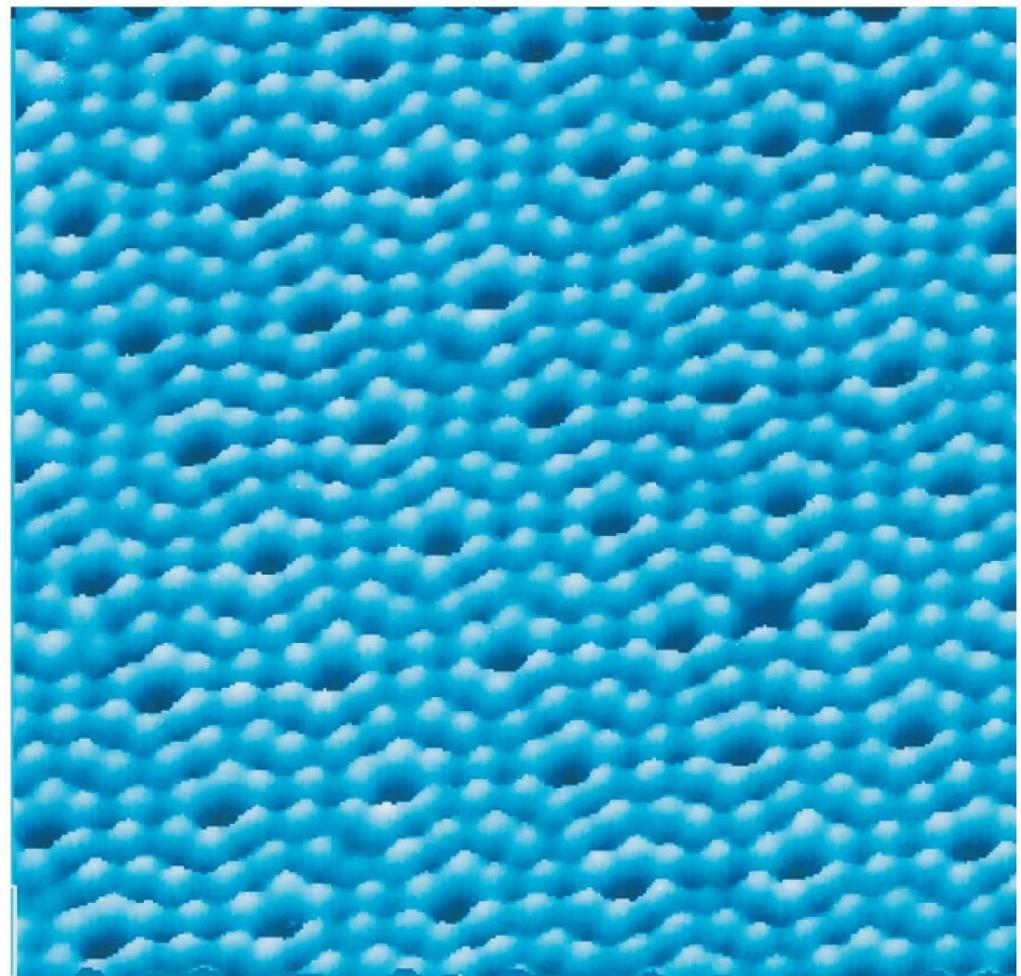
Molecular properties of matter

- This is the schematic representation of the cubic crystal structure of sodium chloride (ordinary salt).



Molecular properties of matter

- This is a scanning tunneling microscope image of the surface of a silicon crystal.
- The area shown is only $9.0 \text{ nm} (9.0 \times 10^{-9} \text{ m})$ across.
- Each blue “bead” is one silicon atom; these atoms are arranged in a (nearly) perfect array of hexagons.



Moles and Avogadro's number

- One *mole* of a substance contains as many elementary entities (atoms or molecules) as there are atoms in 0.012 kg of carbon-12.
- One mole of a substance contains *Avogadro's number* N_A of molecules.
- $N_A = 6.022 \times 10^{23}$ molecules/mol
- The **molar mass** M is the mass of one mole.

$$M = N_A m$$

Molar mass of a substance Avogadro's number
of a molecule of substance

- When the molecule consists of a single atom, the term **atomic mass** is often used instead of molar mass.

Exercises

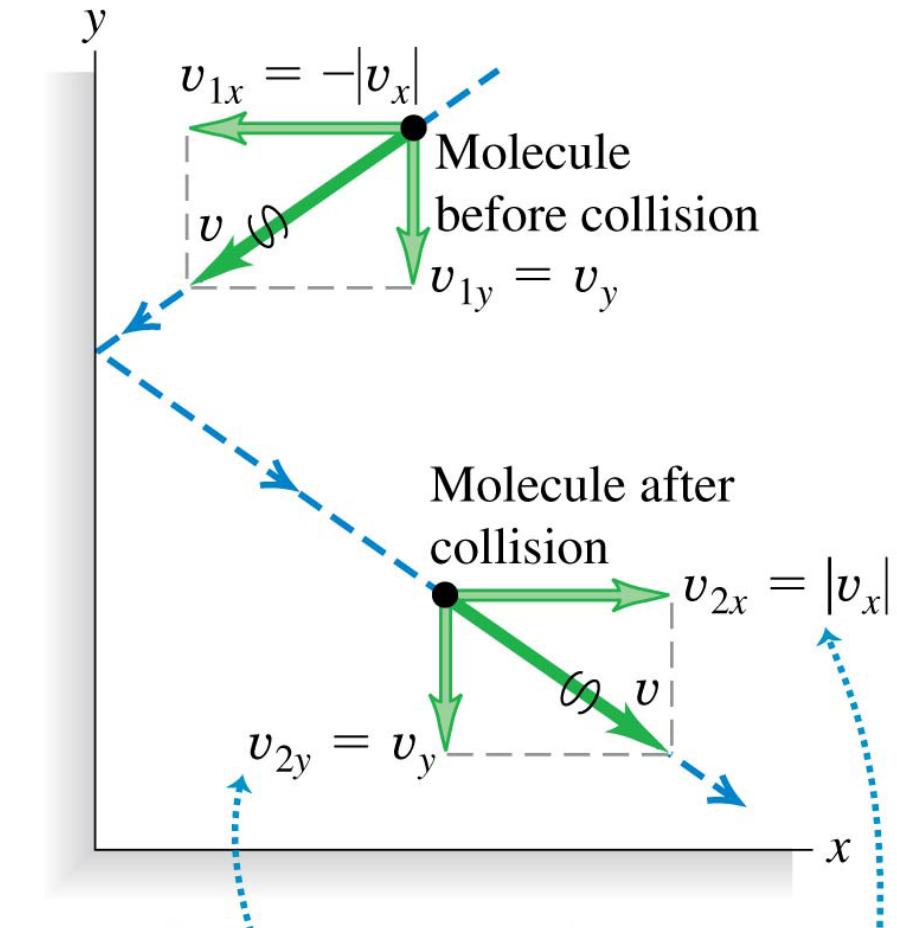
- A 20.0-L tank contains 4.86×10^{-4} kg of helium at 18.0°C. The molar mass of helium is 4.00 g/mol. (a) how many moles of helium are in the tank? (b) what is the pressure in the tank, in Pascal's and in atmospheres? (Assume it's ideal gas and note $1\text{atm} = 1.013 \times 10^5\text{Pa}$)

Kinetic-molecular model of an ideal gas

- The assumptions of the *kinetic-molecular model* are:
 1. A container contains a very large number of identical molecules.
 2. The molecules behave like point particles that are small compared to the size of the container and the average distance between molecules.
 3. The molecules are in constant motion and undergo perfectly elastic collisions.
 4. The container walls are perfectly rigid and do not move.

Collisions and gas pressure

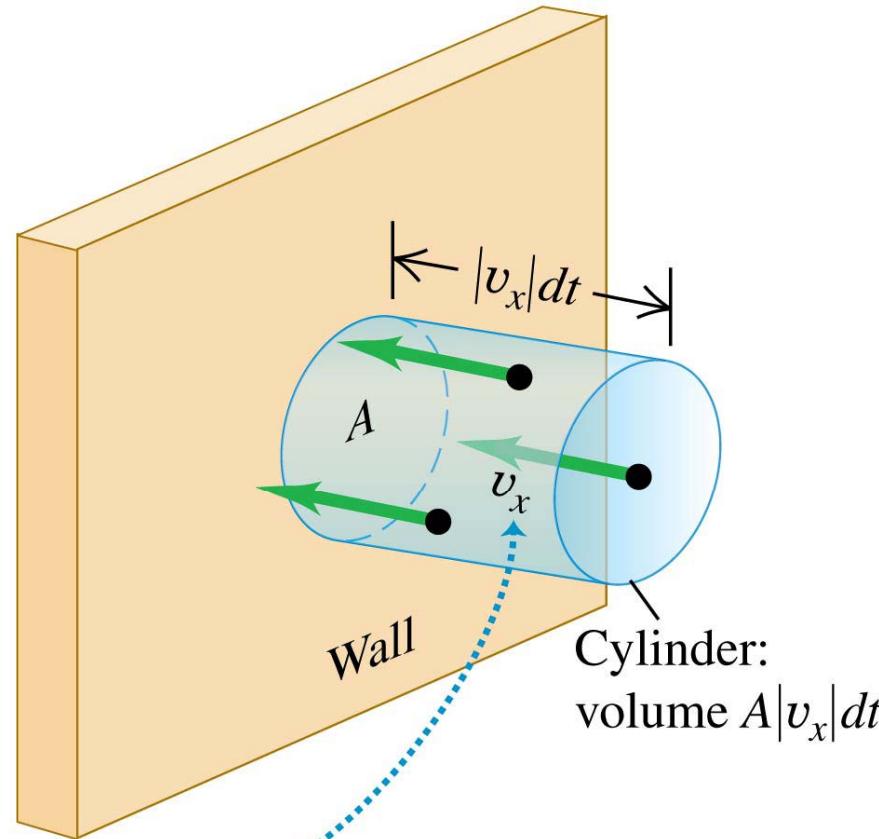
- During collisions the molecules exert *forces* on the walls of the container; this is the origin of the *pressure* that the gas exerts.
- In a typical collision (shown) the velocity component parallel to the wall is unchanged, and the component perpendicular to the wall reverses direction but does not change in magnitude.



- 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.

Collisions and gas pressure

- If a molecule is going to collide with a given wall area A during a small time interval dt , it must be within a distance $|v_x|dt$ from the wall (shown) and it must be headed toward the wall.
- So the number of molecules that collide with A during dt is equal to the number of molecules within the cylinder that have their x -velocity aimed toward the wall.



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

Collisions and gas pressure

- The number of molecules in this cylinder is $(\frac{N}{V})(A |v_x| dt)$.

On average, half of those molecules collide the wall.

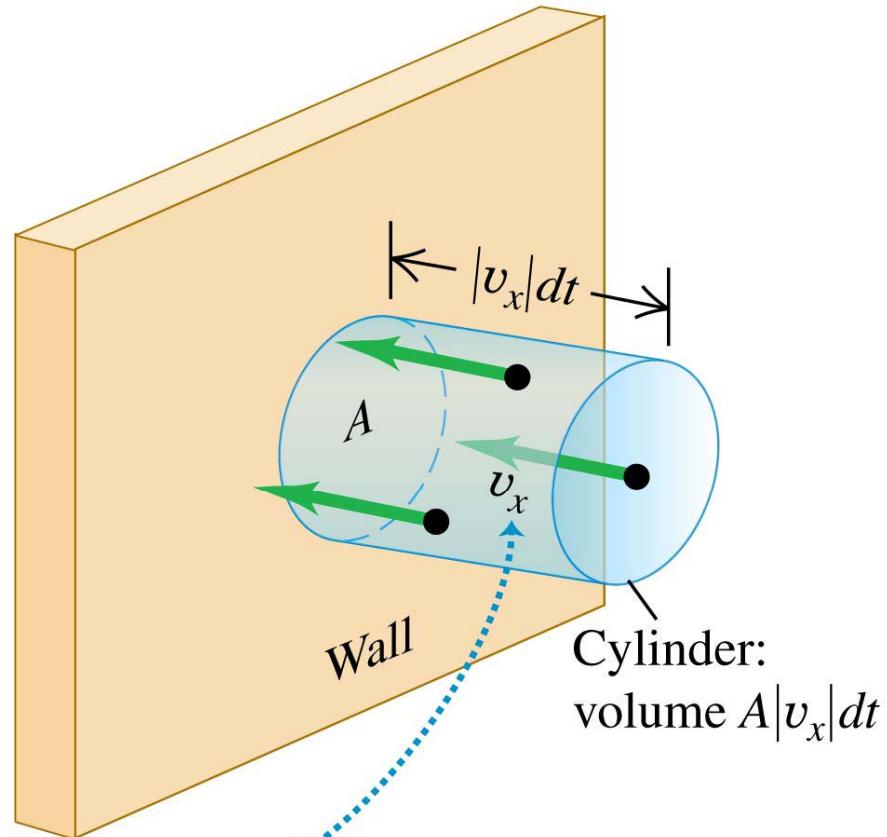
The total momentum change during dt is

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

- Thus, the force on the wall is

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

- The pressure is $p = \frac{F}{A} = \frac{Nm v_x^2}{V} \Rightarrow PV = Nm v_x^2$



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

Pressure and molecular kinetic energies

- Since $v^2 = v_x^2 + v_y^2 + v_z^2$, $(v_x^2)_{av} = \frac{1}{3}(v^2)_{av}$
 $\Rightarrow PV = \frac{1}{3}Nm(v^2)_{av} = \frac{2}{3}N[\frac{1}{2}m(v^2)_{av}] = \frac{2}{3}K_{tr}$, note that $PV = nRT$

where $\frac{1}{2}m(v^2)_{av}$ is the average translational kinetic energy of a single molecule

- The total random kinetic energy K_{tr} of translational motion of all the molecules in a gas is directly proportional to the absolute temperature T :

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

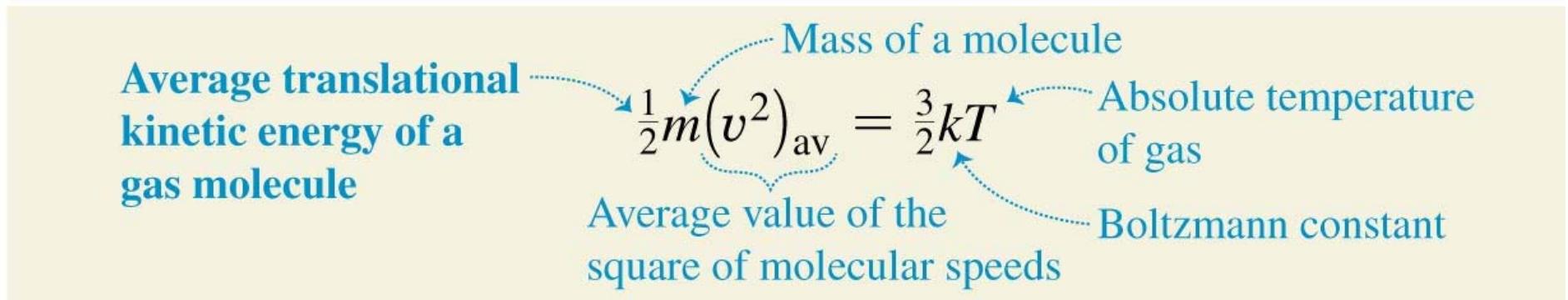
Average translational kinetic energy of an ideal gas Number of moles of gas
Absolute temperature of gas Gas constant

- This means that the average translational kinetic energy *per molecule* depends only on the temperature, not on the pressure, volume, or kind of molecule.

Pressure and molecular kinetic energies

$$K_{tr} = \frac{3}{2}nRT \Rightarrow \frac{K_{tr}}{N} = \frac{1}{2}m(v^2)_{av} = \frac{3}{2}\left(\frac{R}{N_A}\right)T = \frac{3}{2}kT$$

- Boltzmann constant $k = 1.381 \times 10^{-23} \text{ J/molecule} \cdot \text{K}$



Molecular speeds

- The root-mean-square speed of the molecules in a gas is:

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

Root-mean-square speed of a gas molecule **Boltzmann constant** **Absolute temperature of gas**
Average value of the square of molecular speeds **Mass of a molecule** **Gas constant** **Molar mass**

- To compute the rms speed, we square each molecular speed, add, divide by the number of molecules, and take the square root; v_{rms} is the *root* of the *mean* of the *squares*.

Q18.4

Consider two specimens of ideal gas at the same temperature. The molecules in specimen #1 have greater molar mass than the molecules in specimen #2. How do the rms speed of molecules (v_{rms}) and the average translational kinetic energy per molecule (KE) compare in the two specimens?

- A. v_{rms} and KE are both greater in specimen #2.
- B. v_{rms} is greater in specimen #2; KE is the same in both specimens.
- C. v_{rms} is greater in specimen #2; KE is greater in specimen #1.
- D. v_{rms} and KE are the same in both specimens.
- E. None of the above is correct.

Q18.5

Consider two specimens of ideal gas at the same temperature. Specimen #1 has the same total mass as specimen #2, but the molecules in specimen #1 have greater molar mass than the molecules in specimen #2. In which specimen is the *total translational kinetic energy of the entire gas* greater?

- A. specimen #1
- B. specimen #2
- C. The answer depends on the particular mass of gas.
- D. The answer depends on the particular molar masses.
- E. Both C and D are correct.

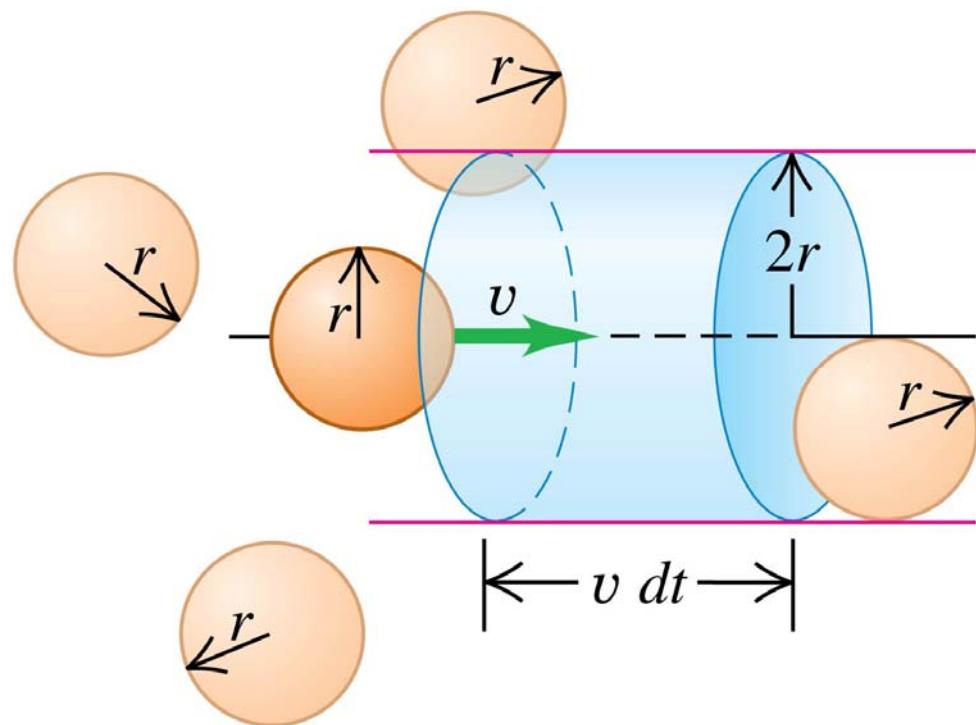
Q18.6

You have a quantity of ideal gas in a cylinder with rigid walls that prevent the gas from expanding or contracting. If you double the rms speed of molecules in the gas, the gas pressure

- A. increases by a factor of 16.
- B. increases by a factor of 8.
- C. increases by a factor of 4.
- D. increases by a factor of 2.
- E. increases by a factor of $2^{1/2}$.

Collisions between molecules

- We model molecules as rigid spheres of radius r as shown at the right.
- The **mean free path** of a molecule is the average distance it travels between collisions.
- The average time between collisions is the **mean free time**.
- In a time dt a molecule with radius r will collide with any other molecule within a cylindrical volume of radius $2r$ and length $v dt$.



Collisions between molecules

- The volume of the cylinder is $4\pi r^2 v dt$, so the total number with centers in this cylinder is $dN = (N/V)4\pi r^2 v dt$. Thus the number of collisions per unit time is $\frac{dN}{dt} = \frac{4\pi r^2 v N}{V}$ (assuming only one molecule is moving).
- Consider all the molecules move at once in reality, the above equation becomes

$$\frac{dN}{dt} = \frac{4\pi \sqrt{2} r^2 v N}{V}$$

- The average time between collisions (called the **mean free time**) is the reciprocal of this expression:

$$t_{mean} = \frac{V}{4\pi \sqrt{2} r^2 v N}$$

Collisions between molecules

- The average distance traveled between collisions is called the **mean free path**.
- In our model, this is just the molecule's speed v multiplied by mean free time:

$$\lambda = vt_{\text{mean}} = \frac{V}{4\pi\sqrt{2}r^2N}$$

Mean free path of a gas molecule

Speed of molecule

Volume of gas

Mean free time between collisions

Radius of a molecule

Number of molecules in gas

$$\lambda = vt_{\text{mean}} = \frac{V}{4\pi\sqrt{2}r^2N} = \frac{nRT / p}{4\pi\sqrt{2}r^2N} = \frac{nRT}{4\pi\sqrt{2}r^2Np} = \frac{nRT}{4\pi\sqrt{2}r^2(nN_A)p} = \frac{kT}{4\pi\sqrt{2}r^2p}$$

- The more molecules there are and the larger the molecule, the shorter the mean distance between collisions.

Exercises

- A container with volume 1.64 L is initially evacuated. Then it is filled with 0.226 g of N₂. Assume that the pressure of the gas is low enough for the gas to obey the ideal-gas law to a high degree of accuracy. If the root-mean-square speed of the gas molecule is 182 m/s, what is the pressure of the gas? (For N₂ gas, $M = 28.014 \times 10^{-3}$ kg/mole.)
- Calculate the mean free path of air molecules at 3.50×10^{-13} atm and 300 K. (Model the air molecules as spheres of radius 2.0×10^{-10} m.)

$$\lambda = \frac{kT}{4\pi\sqrt{2}r^2 p}$$

Heat capacities of gases

- Recall specific heat and molar heat capacity in Chapter 17. What's the theoretical grounds for their values?
- The *degrees of freedom* are the number of velocity components needed to describe a molecule completely.
- A monatomic gas has three degrees of freedom and a diatomic gas has five; the **equipartition of energy principle** states that each degree of freedom has $1/2 kT$ of kinetic energy associated with it.
- For an ideal monatomic gas:

Molar heat capacity at constant volume, ideal gas of point particles

$$C_V = \frac{3}{2}R$$

Gas constant

- For an ideal diatomic gas:

Molar heat capacity at constant volume, ideal diatomic gas

$$C_V = \frac{5}{2}R$$

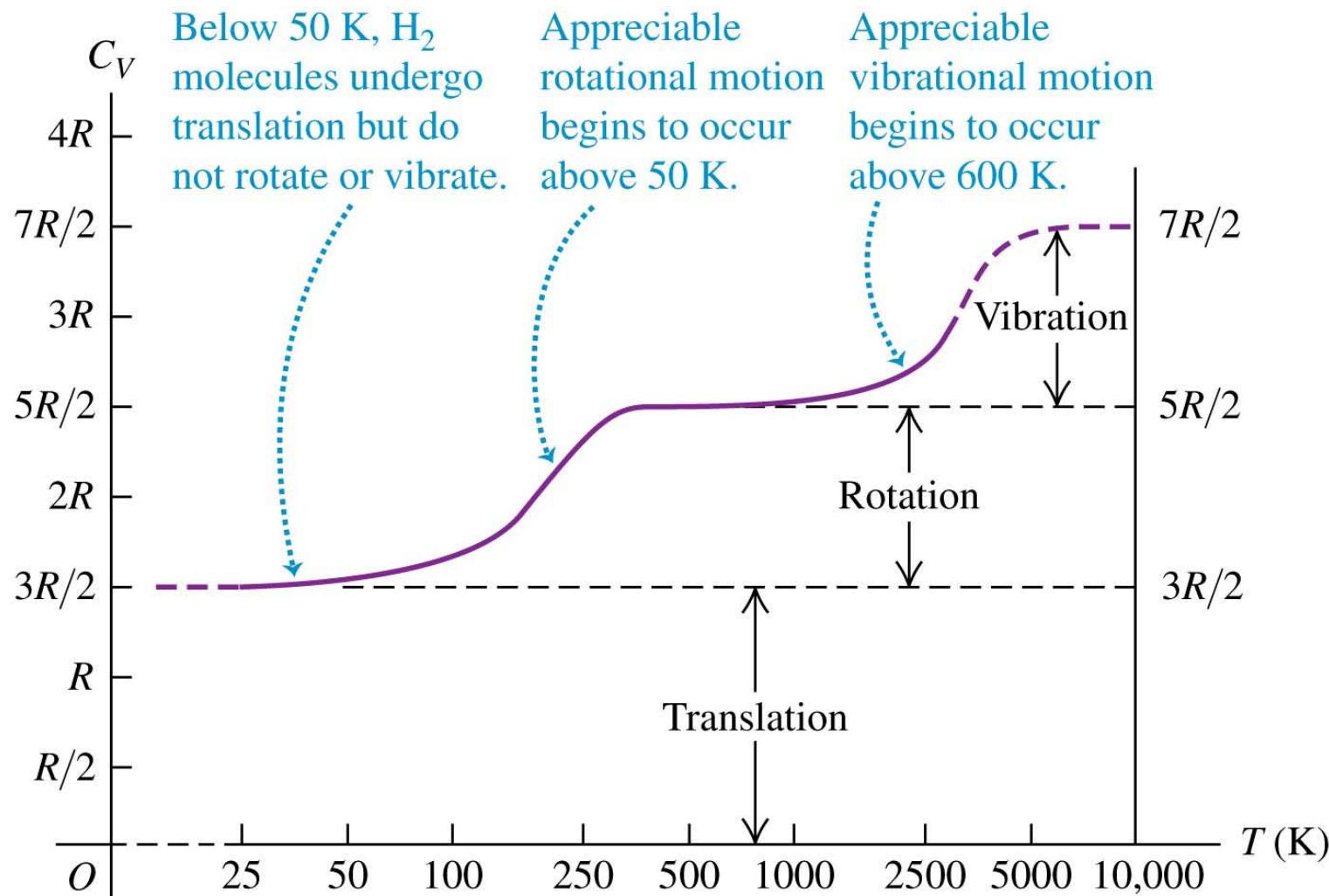
Gas constant

Compare theory with experiment

- Table 18.1 shows that the calculated values for C_V for monatomic gases and diatomic gases agree quite well with the measured values.

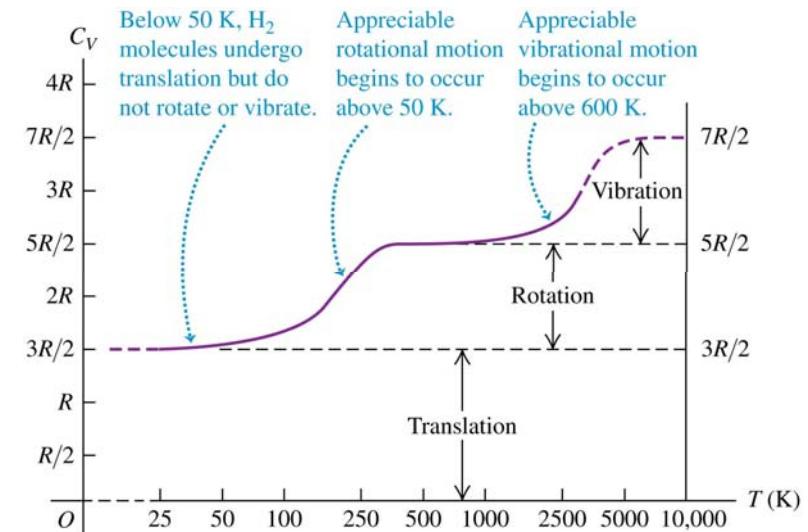
Type of Gas	Gas	C_V (J/mol · K)
Monatomic	He	12.47
	Ar	12.47
Diatomeric	H ₂	20.42
	N ₂	20.76
	O ₂	20.85
Polyatomic	CO	20.85
	CO ₂	28.46
	SO ₂	31.39
	H ₂ S	25.95

Experimental values of C_V for hydrogen gas (H_2)



Heat capacities of solids

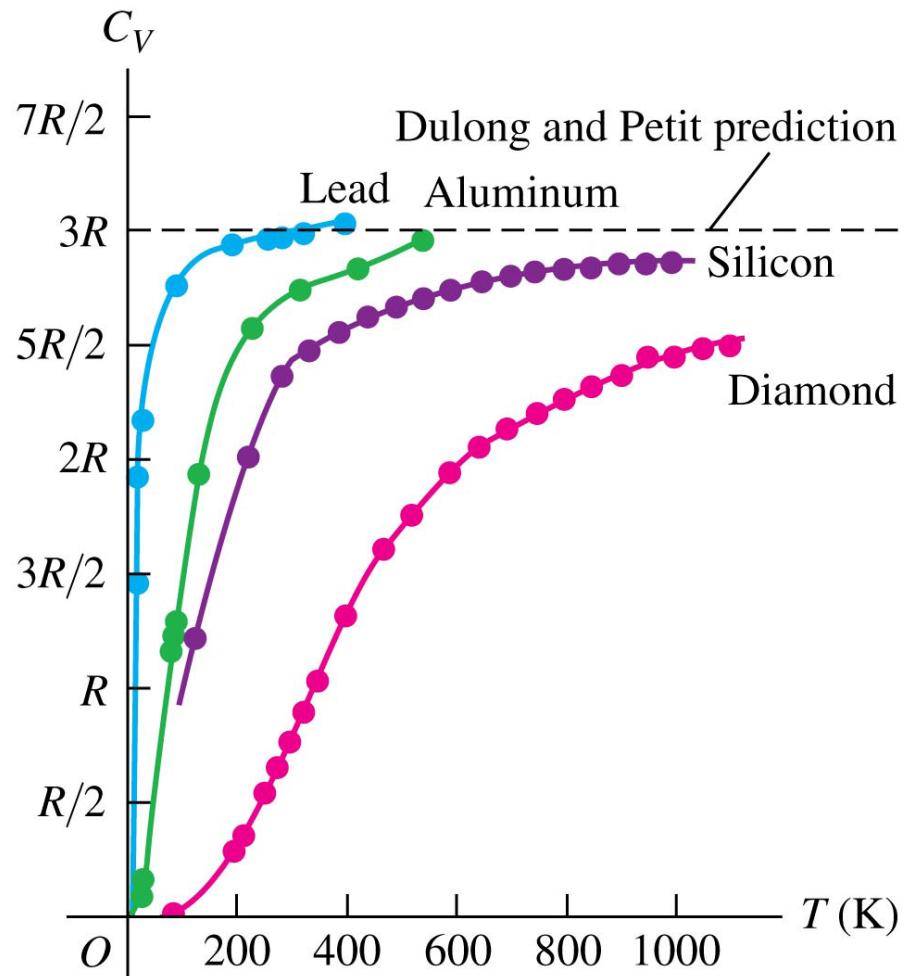
- Consider a crystal consisting of N identical atoms (*a monatomic solid*).
- Each atom is bound to an equilibrium position by interatomic forces.
- We can think of a crystal as an array of atoms connected by little springs.
- Each atom has an average kinetic energy $3/2 kT$ and an average potential energy $3/2 kT$, or an average total energy $3 kT$ per atom.
- The molar heat capacity of a crystal is:



Molar heat capacity of an ideal monatomic solid (rule of Dulong and Petit) $\rightarrow C_V = 3R \leftarrow$ Gas constant

Compare theory with experiment

- Experimental values of C_V for lead, aluminum, silicon, and diamond are given in the figure.
- At high temperatures, C_V for each solid approaches about $3R$, in agreement with the rule of Dulong and Petit.
- At low temperatures, C_V is much less than $3R$.



Q18.7

You have 1.00 mol of an ideal monatomic gas and 1.00 mol of an ideal diatomic gas whose molecules can rotate. Initially both gases are at room temperature. If the same amount of heat flows into each gas, which gas will undergo the greatest increase in temperature?

- A. the monatomic gas
- B. the diatomic gas
- C. Both will undergo the same temperature change.
- D. The answer depends on the molar masses of the gases.
- E. The answer depends on whether or not the diatomic molecules can also vibrate.

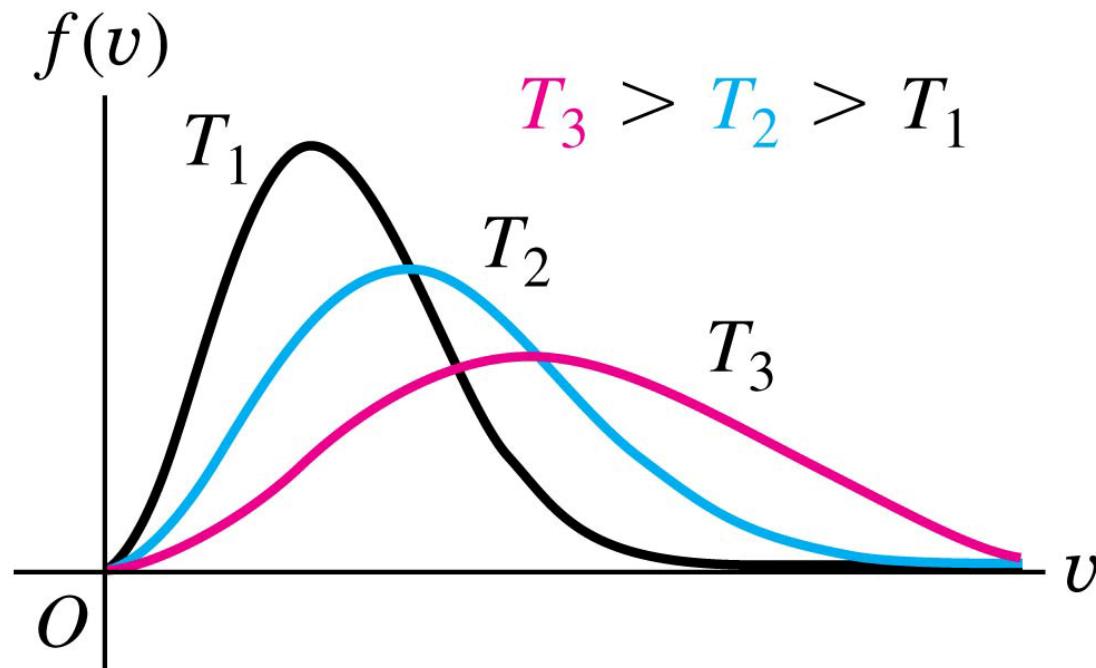
Q18.8

The molar heat capacity at constant volume of diatomic hydrogen gas (H_2) is $5R/2$ at 500 K but only $3R/2$ at 50 K. Why is this?

- A. At 500 K the molecules can vibrate, while at 50 K they cannot.
- B. At 500 K the molecules cannot vibrate, while at 50 K they can.
- C. At 500 K the molecules can rotate, while at 50 K they cannot.
- D. At 500 K the molecules cannot rotate, while at 50 K they can.
- E. At 500 K the molecules can both vibrate and rotate, while at 50 K they cannot.

Molecular speeds

- The *Maxwell-Boltzmann distribution* $f(v)$ gives the distribution of molecular speeds.



As temperature increases:

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

Molecular speeds

- The function $f(v)$ (**Maxwell–Boltzmann distribution**) describes the actual distribution of molecular speeds. It can be derived from statistical mechanics considerations, but that derivation is beyond our scope.

The diagram shows the Maxwell-Boltzmann distribution function:

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

Annotations explain the components:

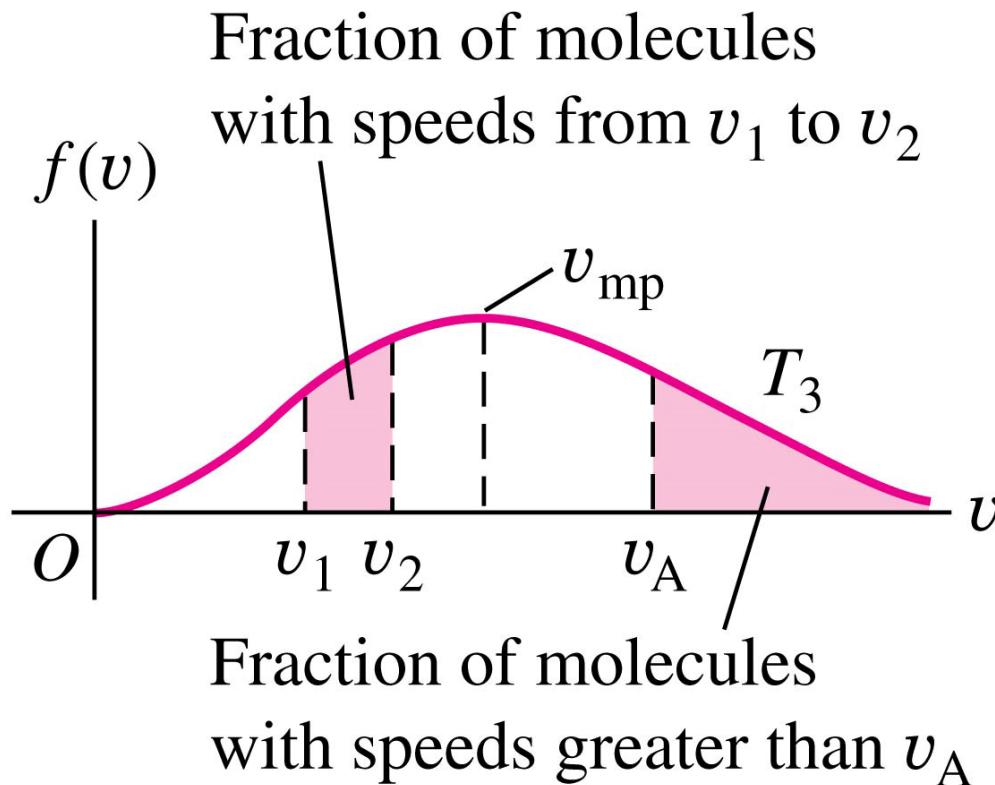
- Maxwell–Boltzmann distribution function** points to the leftmost part of the equation.
- Mass of a gas molecule** points to the term m .
- Molecular speed** points to the term v^2 .
- Boltzmann constant** points to the term kT .
- Absolute temperature of gas** points to the term T .
- Mass of a gas molecule** points to the term m again.
- Molecular speed** points to the term v^2 again.
- Boltzmann constant** points to the term kT again.

- It can also be expressed in terms of the translational kinetic energy of a molecule $\varepsilon = 1/2mv^2$

$$f(\varepsilon) = \frac{8\pi}{m} \left(\frac{m}{2\pi kT} \right)^{3/2} \varepsilon \cdot e^{-\varepsilon/kT}$$

Molecular speeds

- The most probable speed for a given temperature is at the peak of the curve.



$$v_{mp} = \sqrt{\frac{2kT}{m}}; v_{av} = \sqrt{\frac{8kT}{\pi m}}; v_{rms} = \sqrt{\frac{3kT}{m}}$$

Q18.9

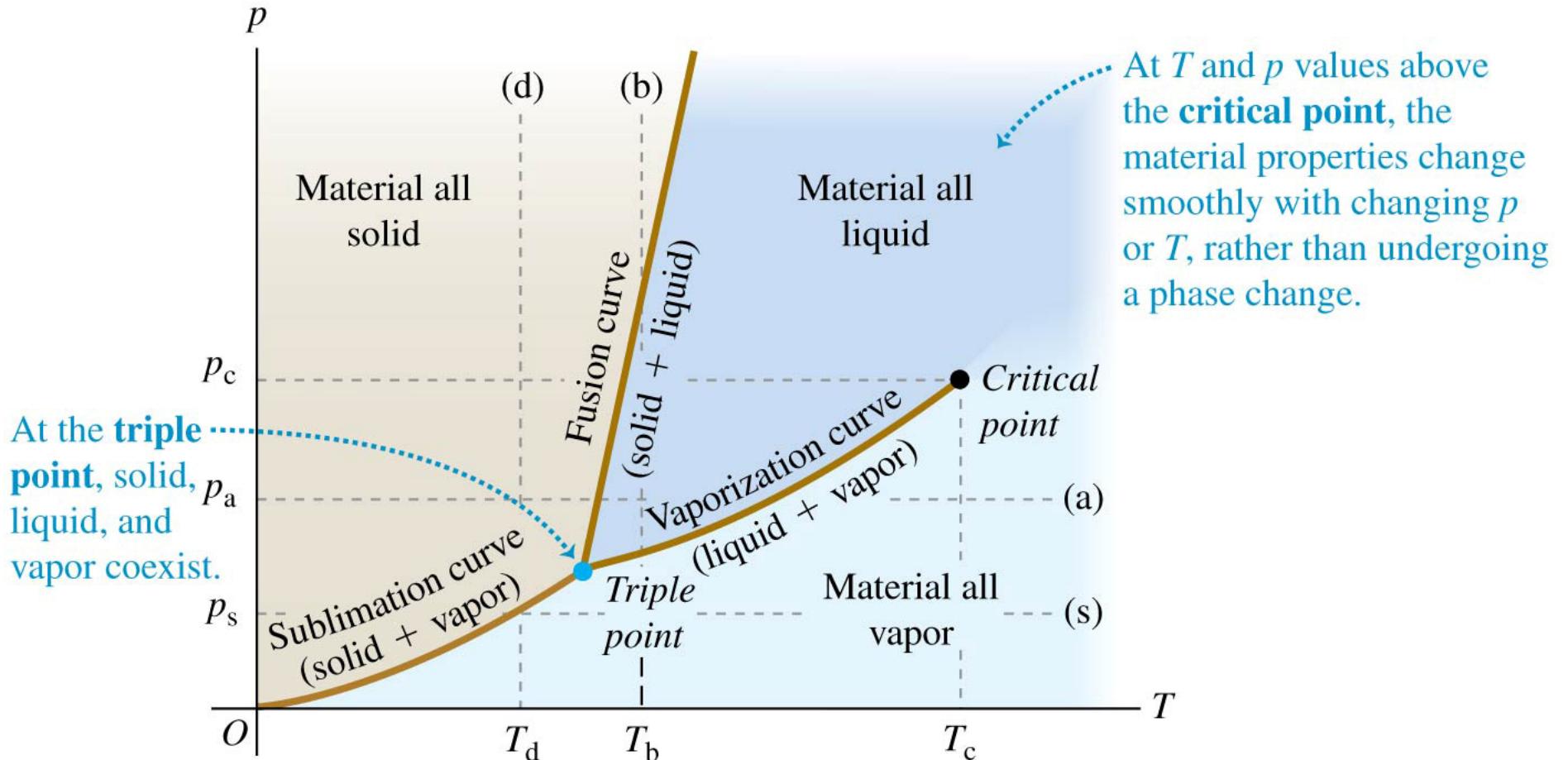
A quantity of gas containing N molecules has a speed distribution function $f(v)$. How many molecules of this gas have speeds between v_1 and $v_2 > v_1$?

- A. $\int_0^{v_1} f(v)dv - \int_0^{v_2} f(v)dv$
- B. $N \left[\int_0^{v_1} f(v)dv - \int_0^{v_2} f(v)dv \right]$
- C. $\int_0^{v_2} f(v)dv - \int_0^{v_1} f(v)dv$
- D. $N \left[\int_0^{v_2} f(v)dv - \int_0^{v_1} f(v)dv \right]$
- E. none of these

Phases of matter

- For an ideal gas we ignore the interactions between molecules.
- But those interactions are what makes matter condense into the liquid and solid phases under some conditions.
- Each phase is stable in only certain ranges of temperature and pressure.
- A transition from one phase to another ordinarily requires **phase equilibrium** between the two phases, and for a given pressure this occurs at only one specific temperature.
- We can represent these conditions on a graph with axes p and T , called a **phase diagram**. (See next slide.)
- Each point on the diagram represents a pair of values of p and T .

A typical pT phase diagram



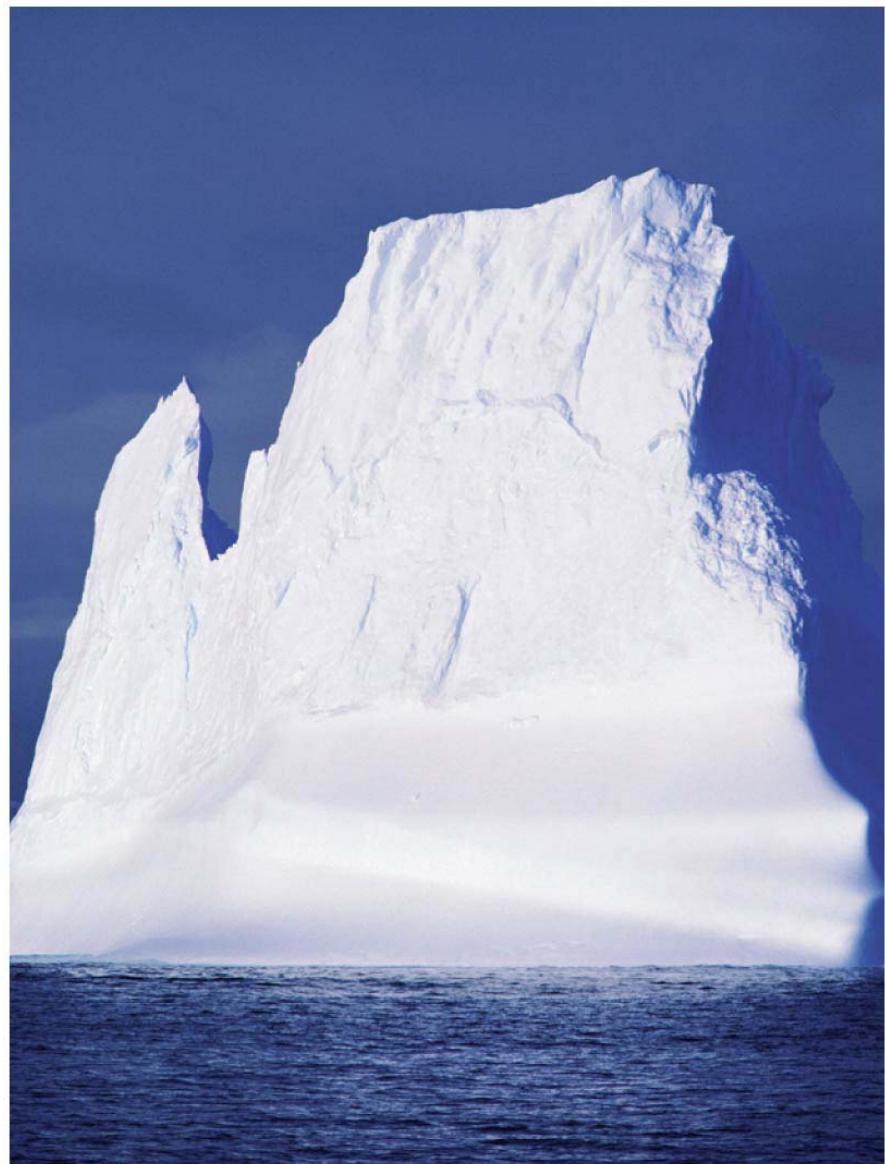
Triple-point data for several substances

TABLE 18.3**Triple-Point Data**

Substance	Temperature (K)	Pressure (Pa)
Hydrogen	13.80	0.0704×10^5
Deuterium	18.63	0.171×10^5
Neon	24.56	0.432×10^5
Nitrogen	63.18	0.125×10^5
Oxygen	54.36	0.00152×10^5
Ammonia	195.40	0.0607×10^5
Carbon dioxide	216.55	5.17×10^5
Sulfur dioxide	197.68	0.00167×10^5
Water	273.16	0.00610×10^5

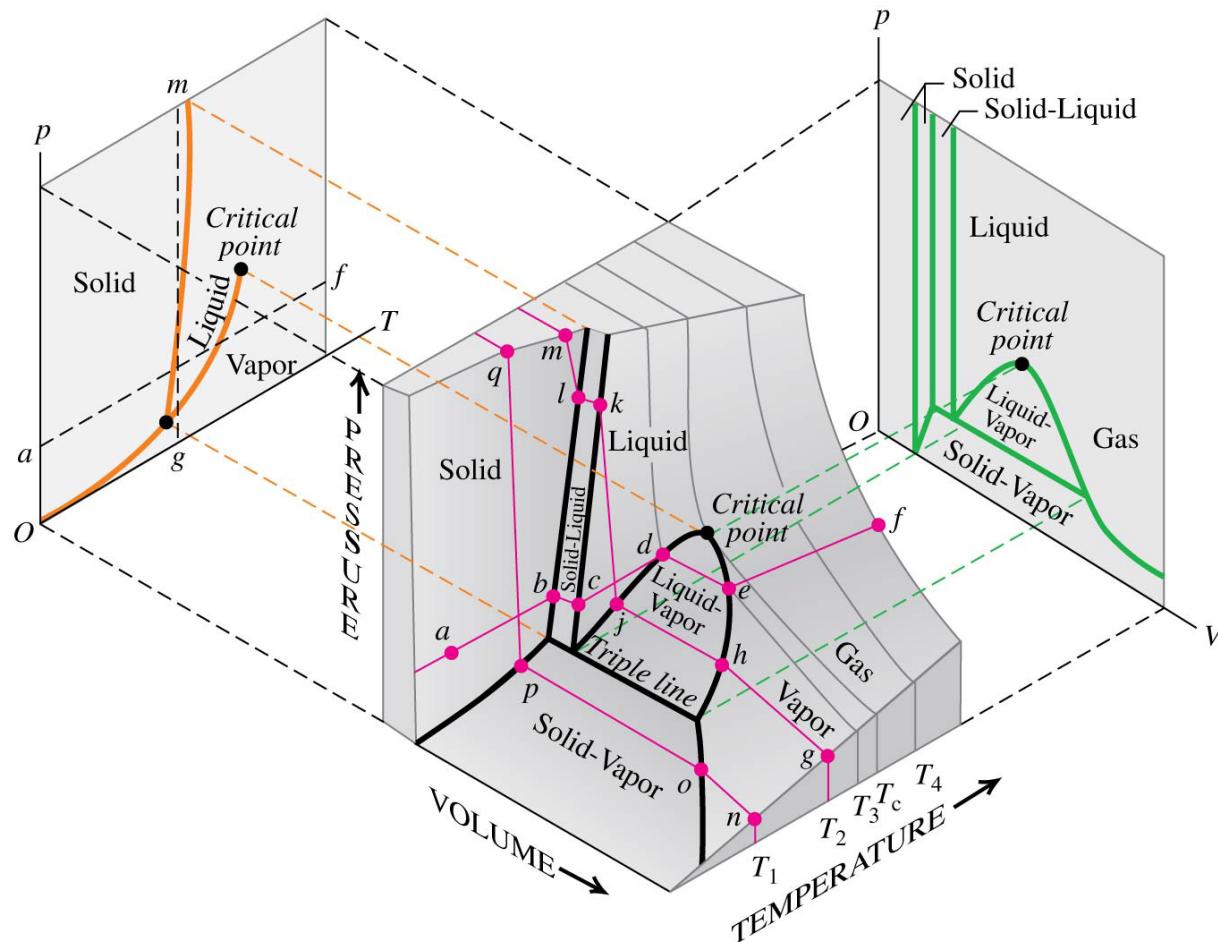
Phases of matter

- Atmospheric pressure on earth is higher than the triple-point pressure of water.
- Depending on the temperature, water can exist as a vapor (in the atmosphere), as a liquid (in the ocean), or as a solid (like the iceberg shown here).



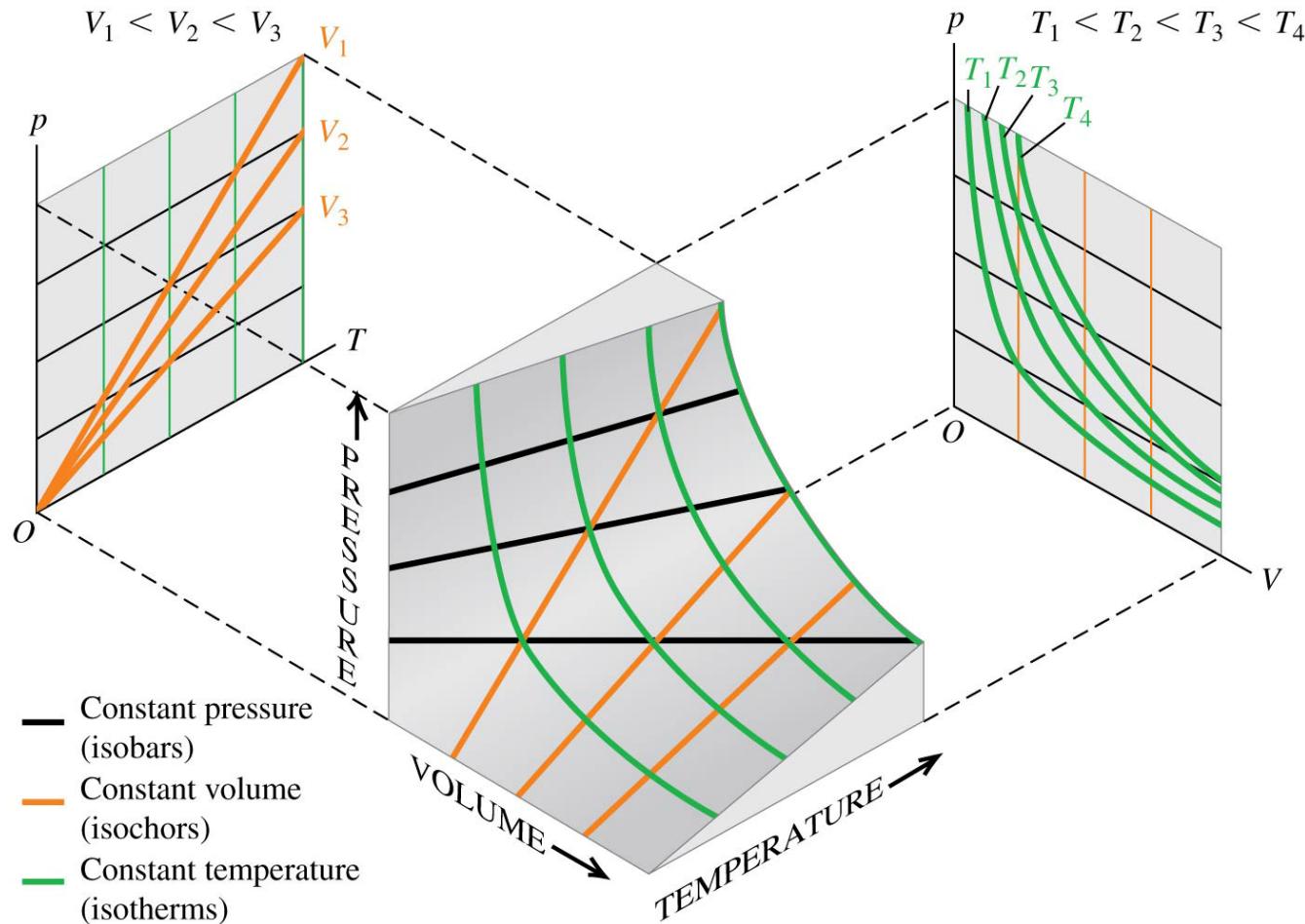
pVT -surface for a substance that expands on melting

- A pVT -surface graphically represents the equation of state. Projections onto the pT - and pV -planes are shown.



pVT-surface for an ideal gas

- The *pVT*-surface for an ideal gas is much simpler than the *pVT*-surface for a real substance, as seen in the previous slide.



Q18.10

If the pressure of the atmosphere is below the triple-point pressure of a certain substance, that substance can exist (depending on the temperature)

- A. as a liquid or as a vapor, but not as a solid.
- B. as a liquid or as a solid, but not as a vapor.
- C. as a solid or as a vapor, but not as a liquid.
- D. as a solid, a liquid, or a vapor.
- E. Not enough information is given to decide.

Exercises

- (a) Compute the specific heat at constant volume of N_2 gas, and compare it with the specific heat of liquid water. The molar mass of N_2 is 28.0 g/mol. (b) You warm 1.00 kg of water at constant volume of 1.00 L from 20.0 °C to 30.0 °C in a kettle. For the same amount of heat, how many kilograms of 20.0 °C air would you be able to warm to 30.0 °C ? What volume (in liters) would this air occupy at 20.0 °C and a pressure of 1.00 atm? Make this simplifying assumption that air is 100% N_2 .
- For N_2 gas, what must the temperature be if 94.7% of all the molecules have speeds less than (a) 1500 m/s; (b) 1000 m/s: (c) 500 m/s? Use table 18.2.

Table 18.2

**Fractions of Molecules
in an Ideal Gas with
Speeds Less Than
Various Multiples of v_{rms}**

TABLE 18.2

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