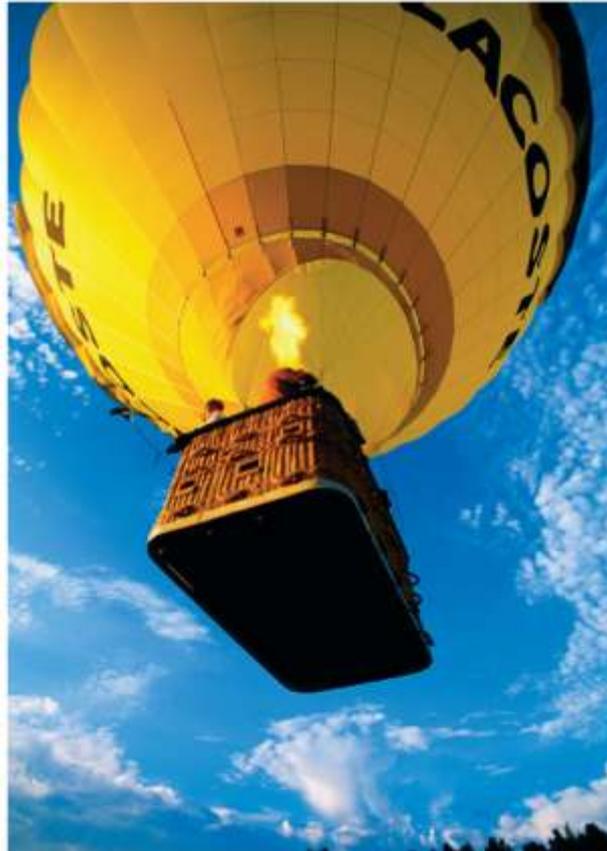


# Chapter 13

## Temperature and Kinetic Theory



# Units of Chapter 13

- **Atomic Theory of Matter**
- **Temperature and Thermometers**
- **Thermal Equilibrium and the Zeroth Law of Thermodynamics**
- **Thermal Expansion**
- **Thermal Stress**
- **The Gas Laws and Absolute Temperature**
- **The Ideal Gas Law**

# Units of Chapter 13

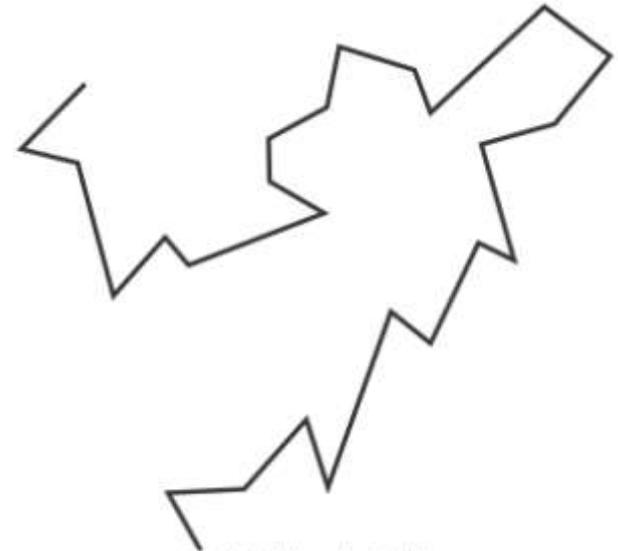
- **Problem Solving with the Ideal Gas Law**
- **Ideal Gas Law in Terms of Molecules:  
Avogadro's Number**
- **Kinetic Theory and the Molecular Interpretation  
of Temperature**
- **Distribution of Molecular Speeds**
- **Real Gases and Changes of Phase**
- **Vapor Pressure and Humidity**
- **Diffusion**

# 13-1 Atomic Theory of Matter

**Atomic and molecular masses are measured in unified atomic mass units (u). This unit is defined so that the carbon-12 atom has a mass of exactly 12.0000 u. Expressed in kilograms:**

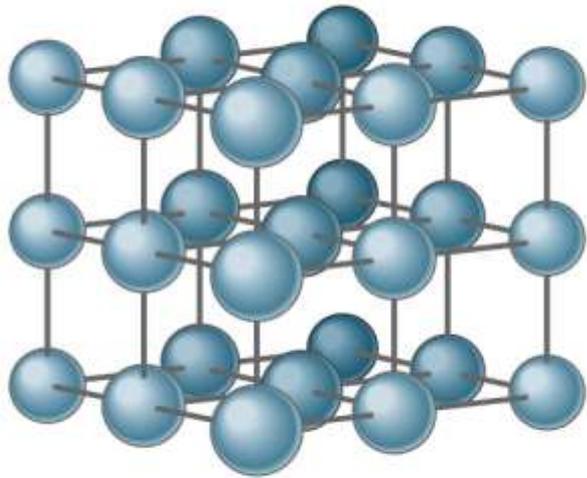
$$1 \text{ u} = 1.6605 \times 10^{-27} \text{ kg}$$

**Brownian motion is the jittery motion of tiny flecks in water; these are the result of collisions with individual water molecules.**

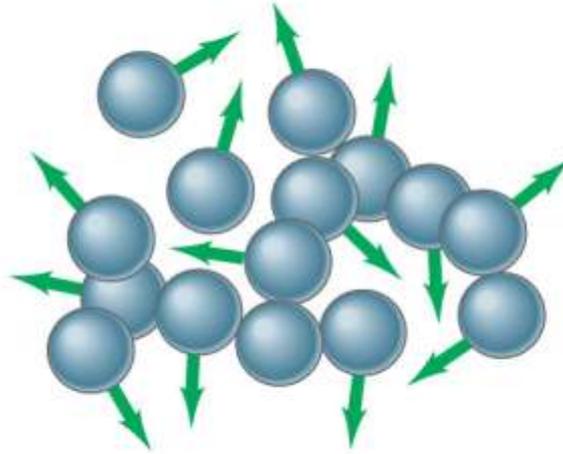


# 13-1 Atomic Theory of Matter

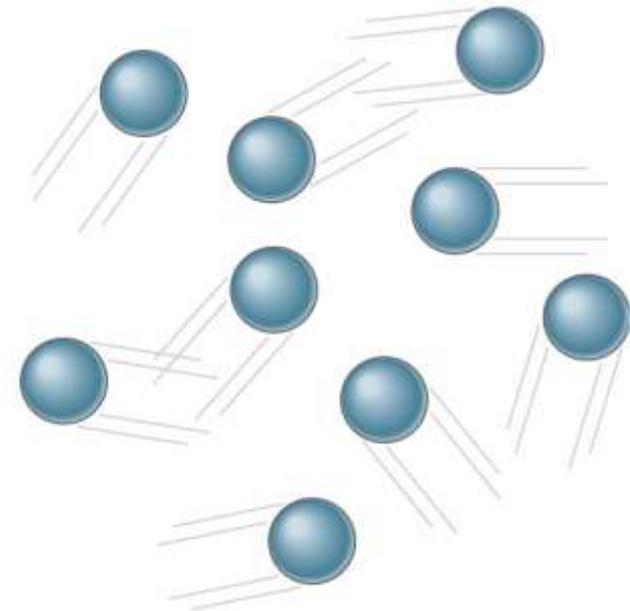
On a microscopic scale, the arrangements of molecules in solids (a), liquids (b), and gases (c) are quite different.



(a)



(b)



(c)

# 13-2 Temperature and Thermometers

**Temperature is a measure of how hot or cold something is.**

**Most materials expand when heated.**



# 13-2 Temperature and Thermometers

**Thermometers are instruments designed to measure temperature. In order to do this, they take advantage of some property of matter that changes with temperature.**

**Early thermometers:**



(a)



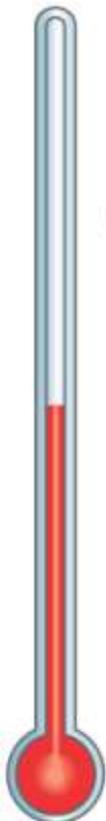
(b)



(c)

# 13-2 Temperature and Thermometers

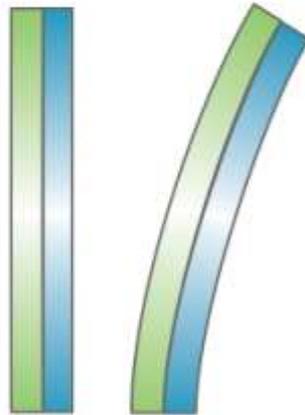
Common thermometers used today include the **liquid-in-glass type** and the **bimetallic strip**.



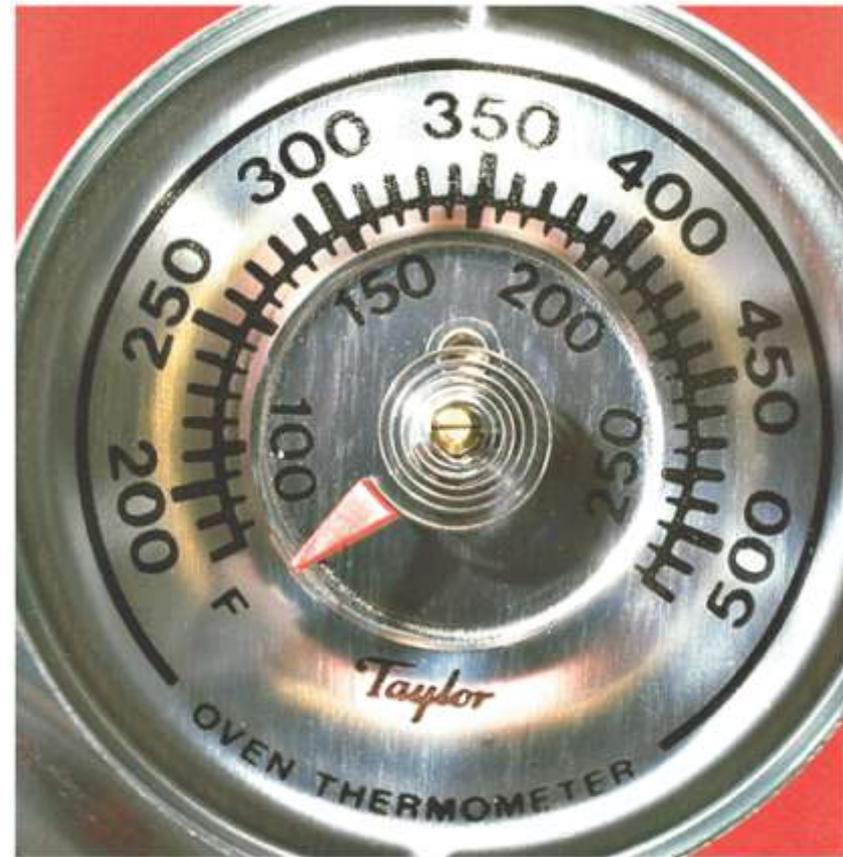
Tube

Bulb (acts as a reservoir)

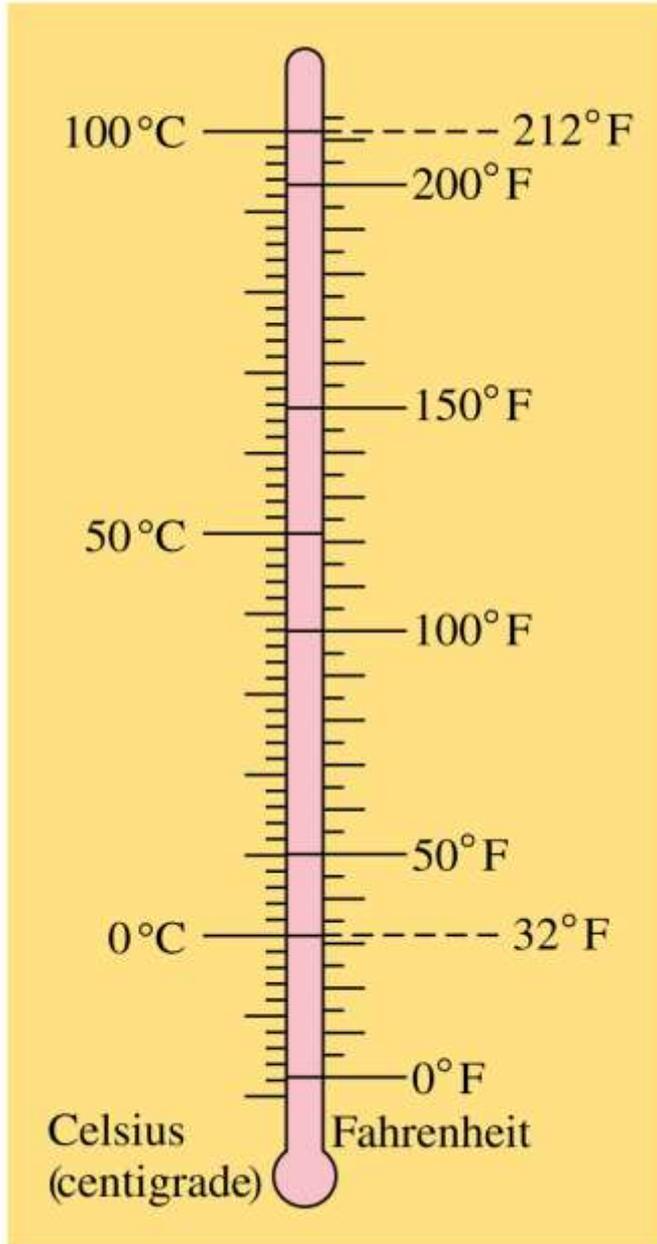
(a)



(b)



# 13-2 Temperature and Thermometers



Temperature is generally measured using either the **Fahrenheit** or the **Celsius** scale.

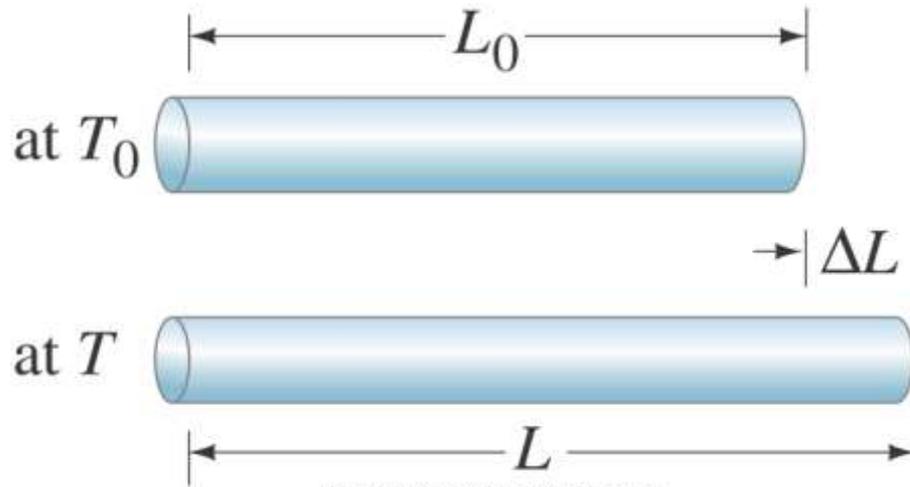
The freezing point of water is **0°C**, or **32°F**; the boiling point of water is **100°C**, or **212°F**.

# 13-3 Thermal Equilibrium and the Zeroth Law of Thermodynamics

**Two objects placed in thermal contact will eventually come to the same temperature. When they do, we say they are in thermal equilibrium.**

**The zeroth law of thermodynamics says that if two objects are each in equilibrium with a third object, they are also in thermal equilibrium with each other.**

# 13-4 Thermal Expansion



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**Linear expansion occurs when an object is heated.**

$$L = L_0(1 + \alpha \Delta T) \quad (13-1b)$$

**Here,  $\alpha$  is the coefficient of linear expansion.**

# 13-4 Thermal Expansion

**Volume expansion is similar, except that it is relevant for liquids and gases as well as solids:**

$$\Delta V = \beta V_0 \Delta T \quad (13-2)$$

**Here,  $\beta$  is the coefficient of volume expansion.**

**For uniform solids,  $\beta \approx 3\alpha$**

# 13-4 Thermal Expansion

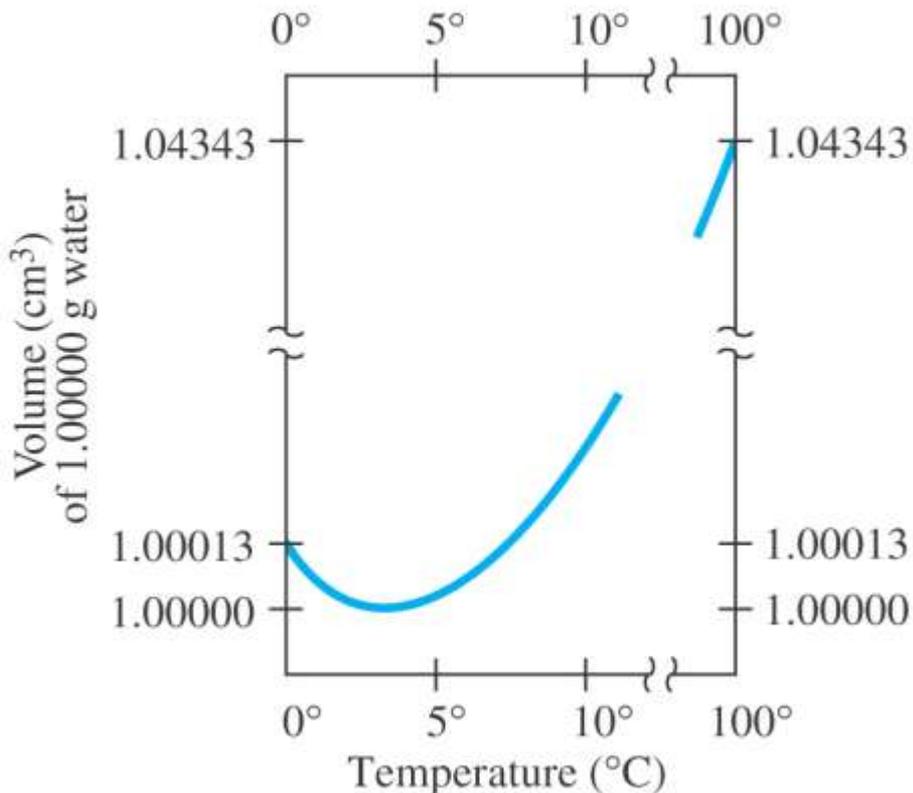
**TABLE 13–1** Coefficients of Expansion, near 20°C

<b>Material</b>	<b>Coefficient of Linear Expansion, <math>\alpha</math> (C°)<sup>-1</sup></b>	<b>Coefficient of Volume Expansion, <math>\beta</math> (C°)<sup>-1</sup></b>
<i>Solids</i>		
Aluminum	$25 \times 10^{-6}$	$75 \times 10^{-6}$
Brass	$19 \times 10^{-6}$	$56 \times 10^{-6}$
Copper	$17 \times 10^{-6}$	$50 \times 10^{-6}$
Gold	$14 \times 10^{-6}$	$42 \times 10^{-6}$
Iron or steel	$12 \times 10^{-6}$	$35 \times 10^{-6}$
Lead	$29 \times 10^{-6}$	$87 \times 10^{-6}$
Glass (Pyrex®)	$3 \times 10^{-6}$	$9 \times 10^{-6}$
Glass (ordinary)	$9 \times 10^{-6}$	$27 \times 10^{-6}$
Quartz	$0.4 \times 10^{-6}$	$1 \times 10^{-6}$
Concrete and brick	$\approx 12 \times 10^{-6}$	$\approx 36 \times 10^{-6}$
Marble	$1.4\text{--}3.5 \times 10^{-6}$	$4\text{--}10 \times 10^{-6}$
<i>Liquids</i>		
Gasoline		$950 \times 10^{-6}$
Mercury		$180 \times 10^{-6}$
Ethyl alcohol		$1100 \times 10^{-6}$
Glycerin		$500 \times 10^{-6}$
Water		$210 \times 10^{-6}$
<i>Gases</i>		
Air (and most other gases at atmospheric pressure)		$3400 \times 10^{-6}$

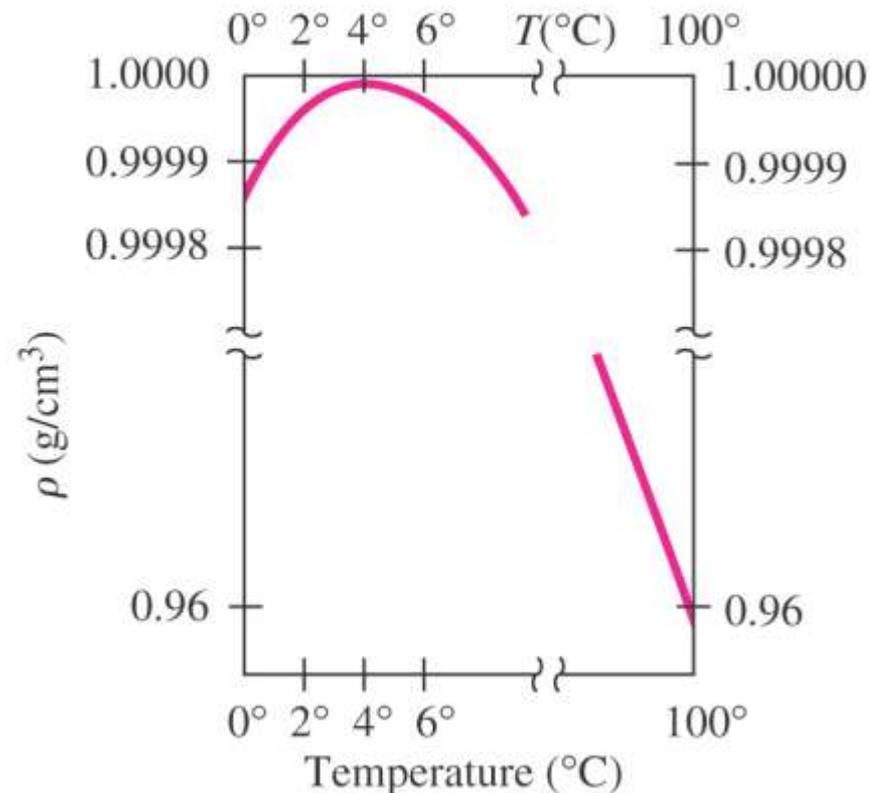
# 13-4 Thermal Expansion

Water behaves differently from most other solids – its **minimum volume** occurs when its temperature is  $4^{\circ}\text{C}$ . As it **cools further, it expands**, as anyone who has left a bottle in the freezer to cool and then forgets about it can testify.

(a)



(b)



## 13-5 Thermal Stresses

A material may be **fixed** at its ends and therefore be unable to expand when the temperature changes. It will then experience large **compressive or tensile stress – thermal stress –** when its temperature changes.

The **force** required to keep the material from expanding is given by:

$$\Delta L = \frac{1}{E} \frac{F}{A} L_0$$

where  $E$  is the Young's modulus of the material.

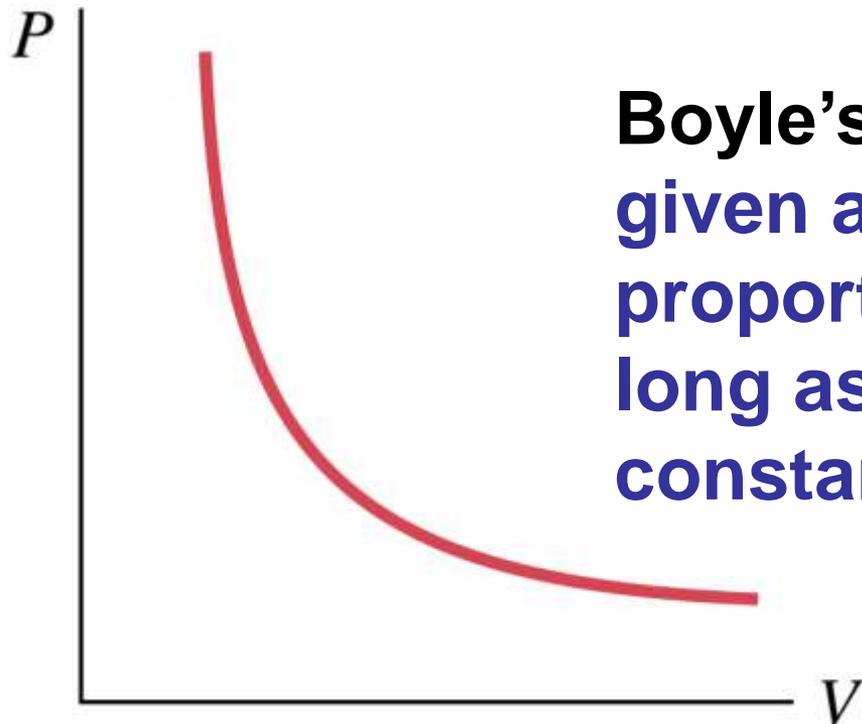
Therefore, the **stress** is:

$$\frac{F}{A} = \alpha E \Delta T$$

# 13-6 The Gas Laws and Absolute Temperature

The relationship between the volume, pressure, temperature, and mass of a gas is called an **equation of state**.

We will deal here with gases that are not too dense.



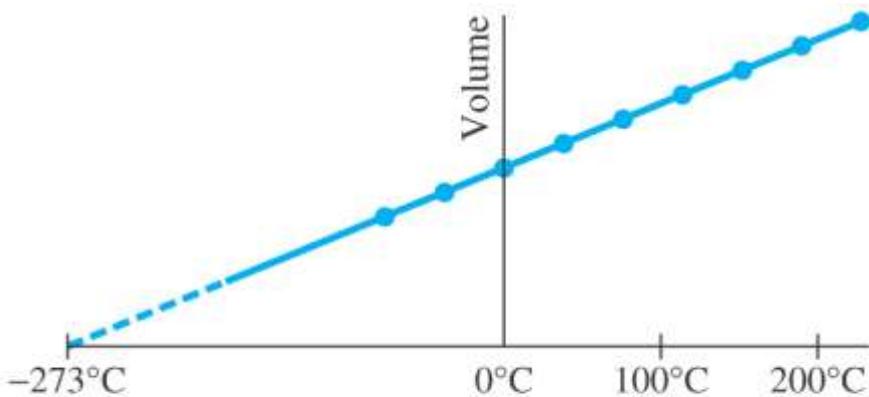
**Boyle's Law: the volume of a given amount of gas is inversely proportional to the pressure as long as the temperature is constant.**

$$V \propto \frac{1}{P}$$

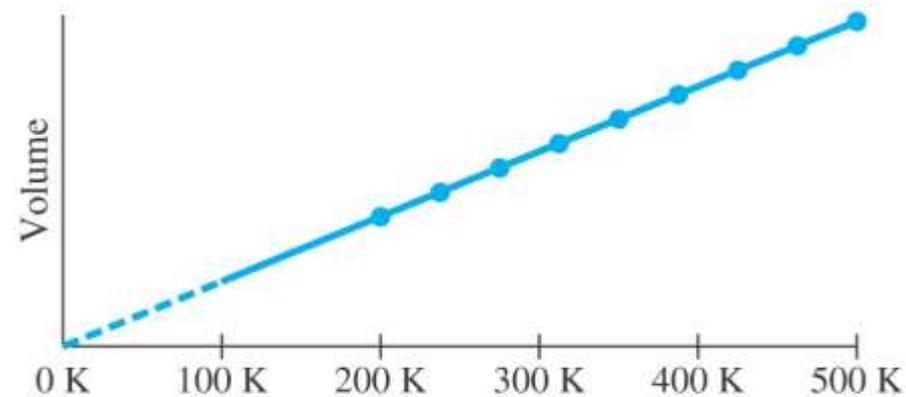
# 13-6 The Gas Laws and Absolute Temperature

The volume is linearly proportional to the temperature, as long as the temperature is somewhat above the condensation point and the pressure is constant:  $V \propto T$

Extrapolating, the volume becomes zero at  $-273.15^{\circ}\text{C}$ ; this temperature is called **absolute zero**.



(a) Temperature ( $^{\circ}\text{C}$ )



(b) Temperature (kelvins, or K)

# 13-6 The Gas Laws and Absolute Temperature

The concept of absolute zero allows us to define a third temperature scale – the absolute, or **Kelvin, scale.**

This scale starts with **0 K at absolute zero**, but otherwise is the same as the Celsius scale.

Therefore, the **freezing point of water is 273.15 K**, and the **boiling point is 373.15 K.**

Finally, when the **volume is constant**, the **pressure is directly proportional to the temperature:**  $P \propto T$

# 13-7 The Ideal Gas Law

We can combine the three relations just derived into a **single relation**:

$$PV \propto T$$

What about the amount of gas present? If the temperature and pressure are constant, the volume is proportional to the amount of gas:

$$PV \propto mT$$



## 13-7 The Ideal Gas Law

**A mole (mol) is defined as the number of grams of a substance that is numerically equal to the molecular mass of the substance:**

**1 mol H<sub>2</sub> has a mass of 2 g**

**1 mol Ne has a mass of 20 g**

**1 mol CO<sub>2</sub> has a mass of 44 g**

**The number of moles in a certain mass of material:**

$$n \text{ (mol)} = \frac{\text{mass (grams)}}{\text{molecular mass (g/mol)}}$$

# 13-7 The Ideal Gas Law

We can now write the ideal gas law:

$$PV = nRT \quad (13-3)$$

where  $n$  is the number of moles and  $R$  is the universal gas constant.

$$\begin{aligned} R &= 8.315 \text{ J}/(\text{mol} \cdot \text{K}) \\ &= 0.0821 \text{ (L} \cdot \text{atm)} / (\text{mol} \cdot \text{K}) \\ &= 1.99 \text{ calories}/(\text{mol} \cdot \text{K}) \end{aligned}$$

# 13-8 Problem Solving with the Ideal Gas Law

Useful facts and definitions:

- **Standard temperature and pressure (STP)**

$$T = 273 \text{ K } (0^\circ\text{C})$$

$$P = 1.00 \text{ atm} = 1.013 \times 10^5 \text{ N/m}^2 = 101.3 \text{ kPa}$$

- **Volume of 1 mol of an ideal gas is 22.4 L**
- **If the amount of gas does not change:**

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

- **Always measure  $T$  in kelvins**
- **$P$  must be the absolute pressure**

# 13-9 Ideal Gas Law in Terms of Molecules: Avogadro's Number

Since the gas constant is **universal**, the **number of molecules in one mole is the same for all gases**. That number is called **Avogadro's number**:

$$N_A = 6.02 \times 10^{23}$$

The number of molecules in a gas is the **number of moles times Avogadro's number**:

$$N = nN_A$$

# 13-9 Ideal Gas Law in Terms of Molecules: Avogadro's Number

Therefore we can write:  $PV = NkT$  (13-4)

where  $k$  is called Boltzmann's constant.

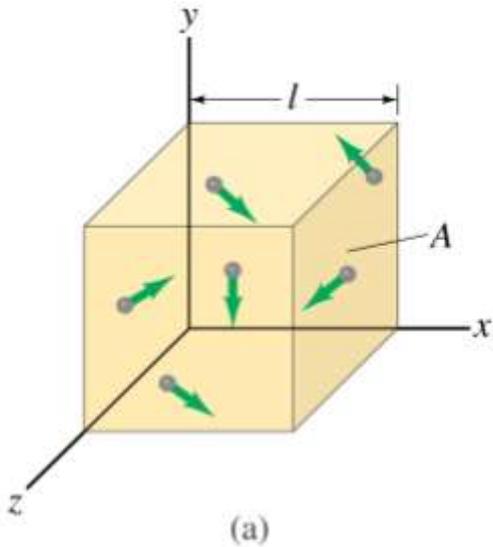
$$k = \frac{R}{N_A} = \frac{8.315 \text{ J/mol} \cdot \text{K}}{6.02 \times 10^{23} / \text{mol}} = 1.38 \times 10^{-23} \text{ J/K}$$

# 13-10 Kinetic Theory 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**

# 13-10 Kinetic Theory and the Molecular Interpretation of Temperature

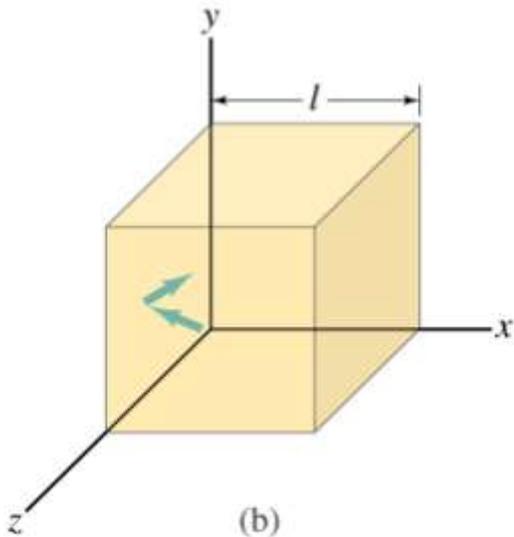


The **force** exerted on the wall by the collision of one molecule is

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

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

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



# 13-10 Kinetic Theory and the Molecular Interpretation of Temperature

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

$$F = \frac{m}{l} N \overline{v^2}$$

So the pressure is:

$$P = \frac{F}{A} = \frac{1}{3} \frac{Nm \overline{v^2}}{Al} = \frac{1}{3} \frac{Nm \overline{v^2}}{V} \quad (13-6)$$

# 13-10 Kinetic Theory and the Molecular Interpretation of Temperature

Rewriting,  $PV = \frac{2}{3} N \left( \frac{1}{2} m \overline{v^2} \right)$  (13-7)

so  $\frac{2}{3} \left( \frac{1}{2} m \overline{v^2} \right) = kT$

$$\overline{\text{KE}} = \frac{1}{2} m \overline{v^2} = \frac{3}{2} kT \quad (13-8)$$

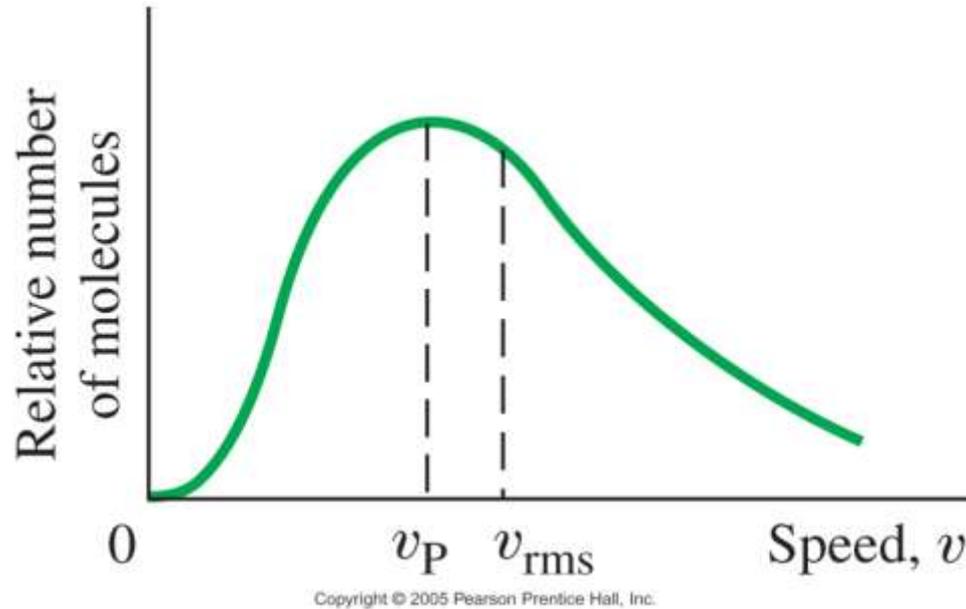
**The average translational kinetic energy of the molecules in an ideal gas is directly proportional to the temperature of the gas.**

# 13-10 Kinetic Theory and the Molecular Interpretation of Temperature

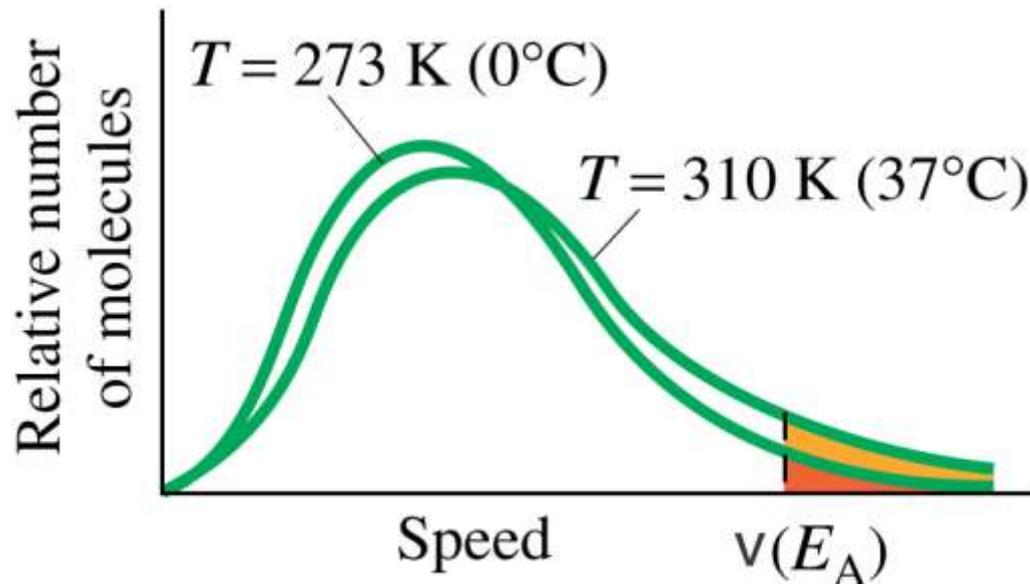
We can invert this to find the average speed of molecules in a gas as a function of temperature:

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}} \quad (13-9)$$

# 13-11 Distribution of Molecular Speeds

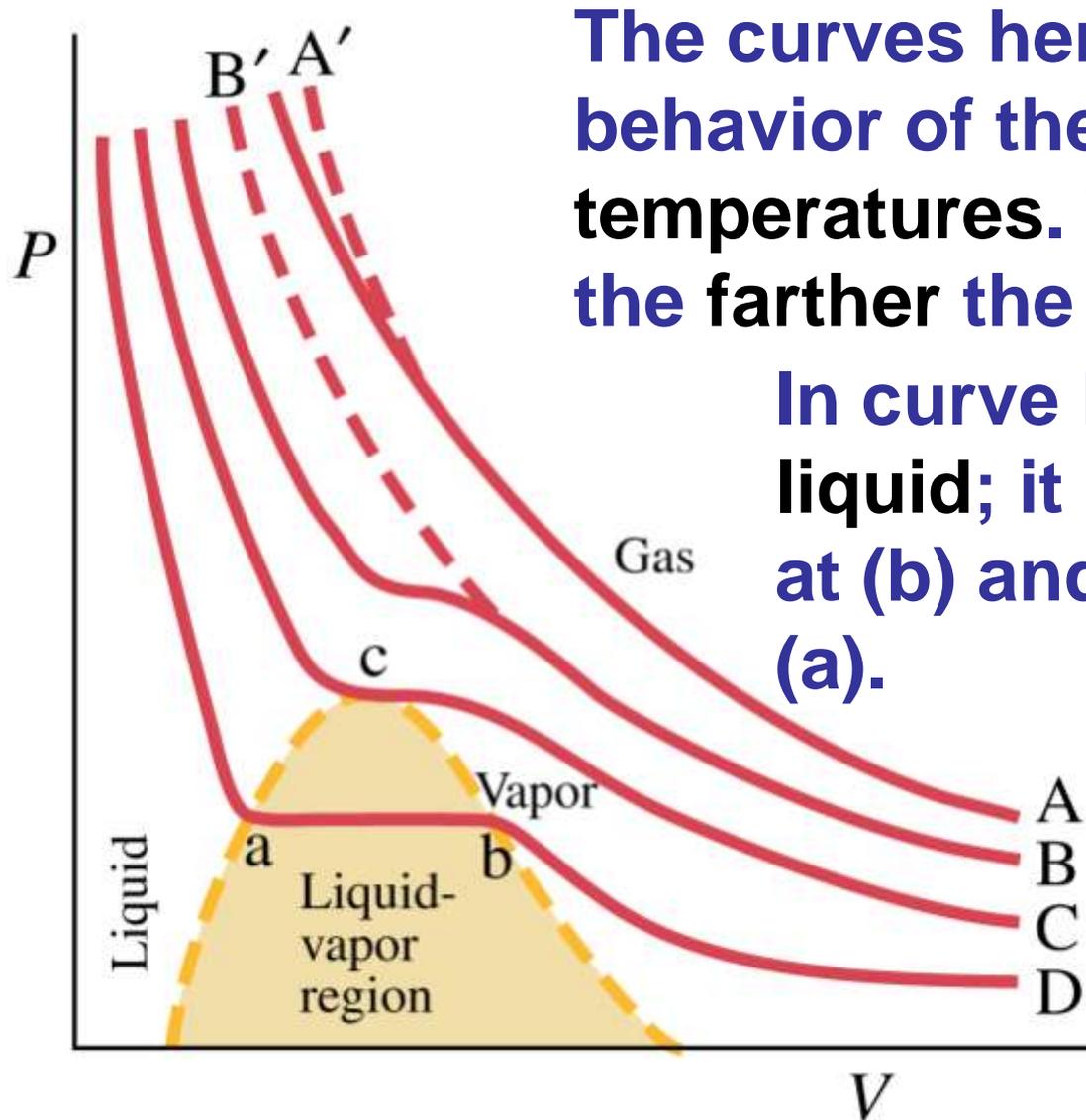


These two graphs show the **distribution** of speeds of molecules in a gas, as derived by **Maxwell**. The most probable speed,  $v_P$ , is not quite the same as the **rms** speed.



As expected, the curves shift to the **right** with temperature.

# 13-12 Real Gases and Changes of Phase



The curves here represent the behavior of the gas at different temperatures. The cooler it gets, the farther 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**.

# 13-12 Real Gases and Changes of Phase

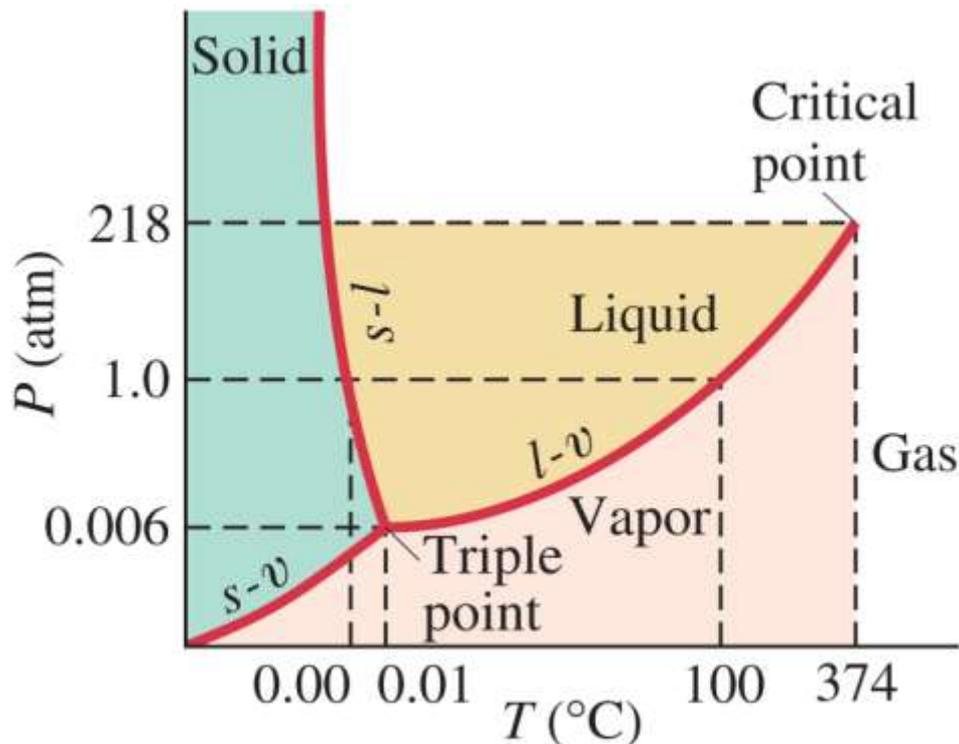
**Below the critical temperature, the gas can liquefy if the pressure is sufficient; above it, no amount of pressure will suffice.**

**TABLE 13–2 Critical Temperatures and Pressures**

Substance	Critical Temperature		Critical Pressure (atm)
	°C	K	
Water	374	647	218
CO <sub>2</sub>	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

# 13-12 Real Gases and Changes of Phase

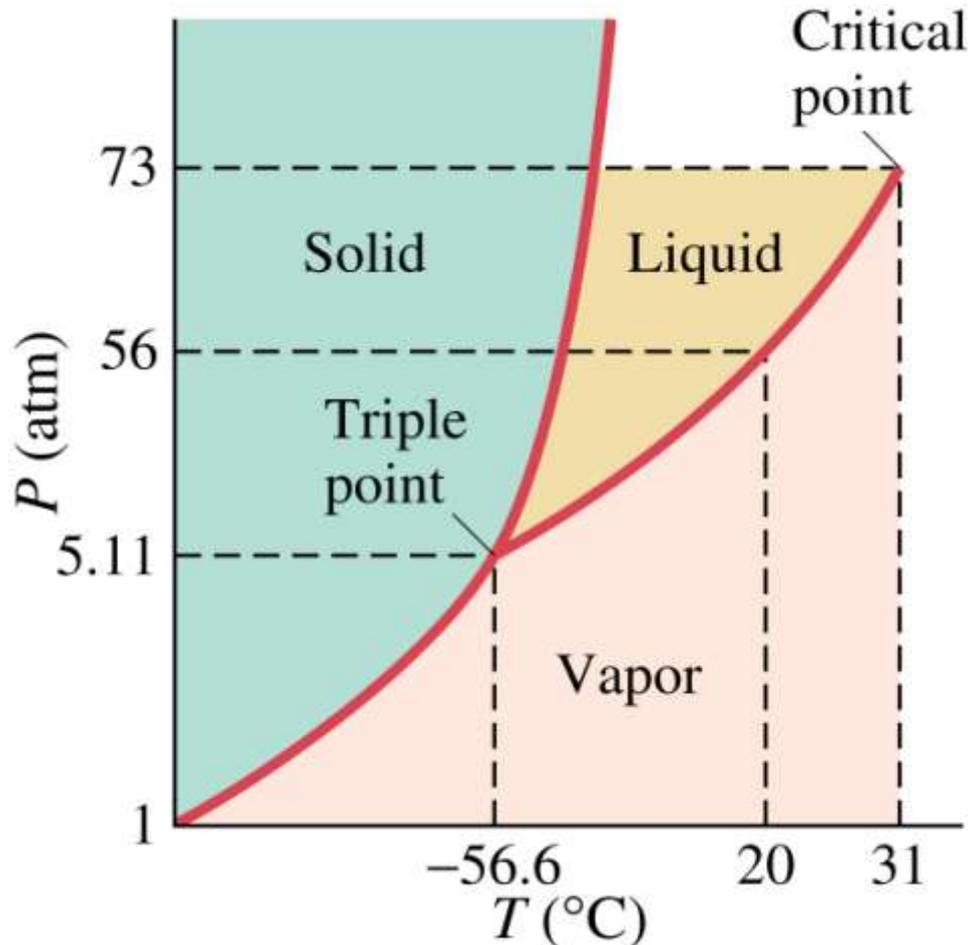
A  $PT$  diagram is called a phase diagram; it shows all three phases of matter. The solid-liquid transition is melting or freezing; the liquid-vapor one is boiling or condensing; and the solid-vapor one is sublimation.



Phase diagram of water

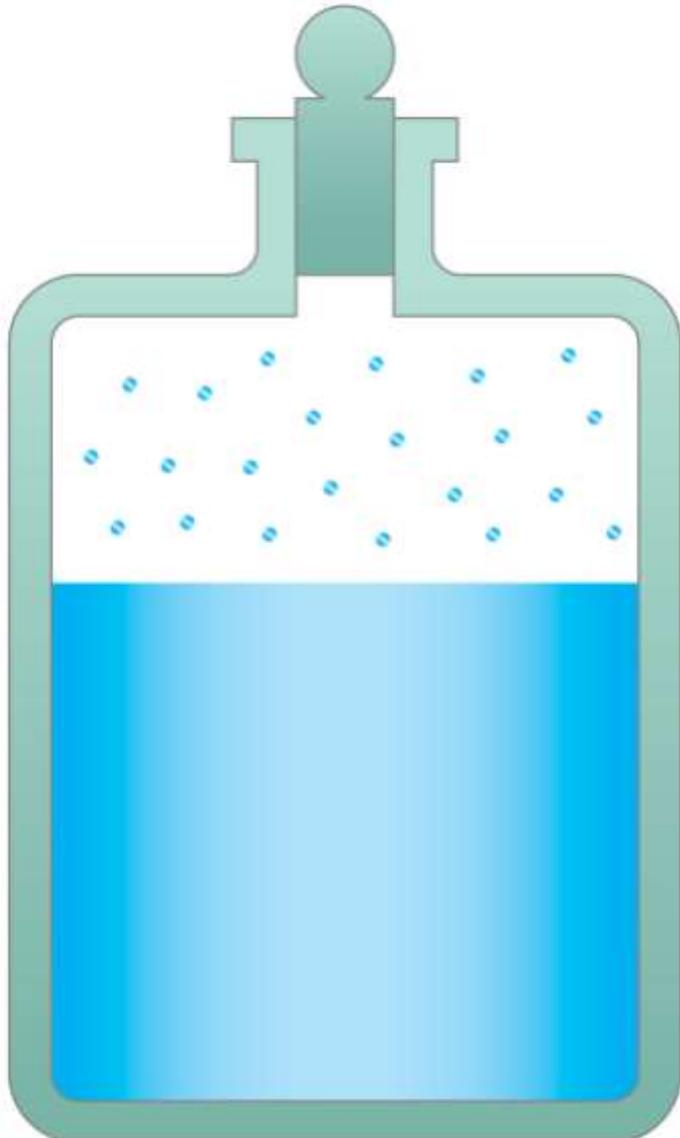
# 13-12 Real Gases and Changes of Phase

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



**Phase diagram of carbon dioxide**

# 13-13 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**.

# 3-13 Vapor Pressure and Humidity

**TABLE 13–3 Saturated Vapor Pressure of Water**

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

<sup>†</sup> Boiling point on summit of Mt. Everest.

<sup>‡</sup> Boiling point at sea level.

**The saturated vapor pressure increases with temperature.**

# 13-13 Vapor Pressure and Humidity



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

# 13-13 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.

$$\text{Relative humidity} = \frac{\text{partial pressure of H}_2\text{O}}{\text{saturated vapor pressure of H}_2\text{O}} \times 100\%$$

# 13-13 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.**

# 13-14 Diffusion

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



(a)



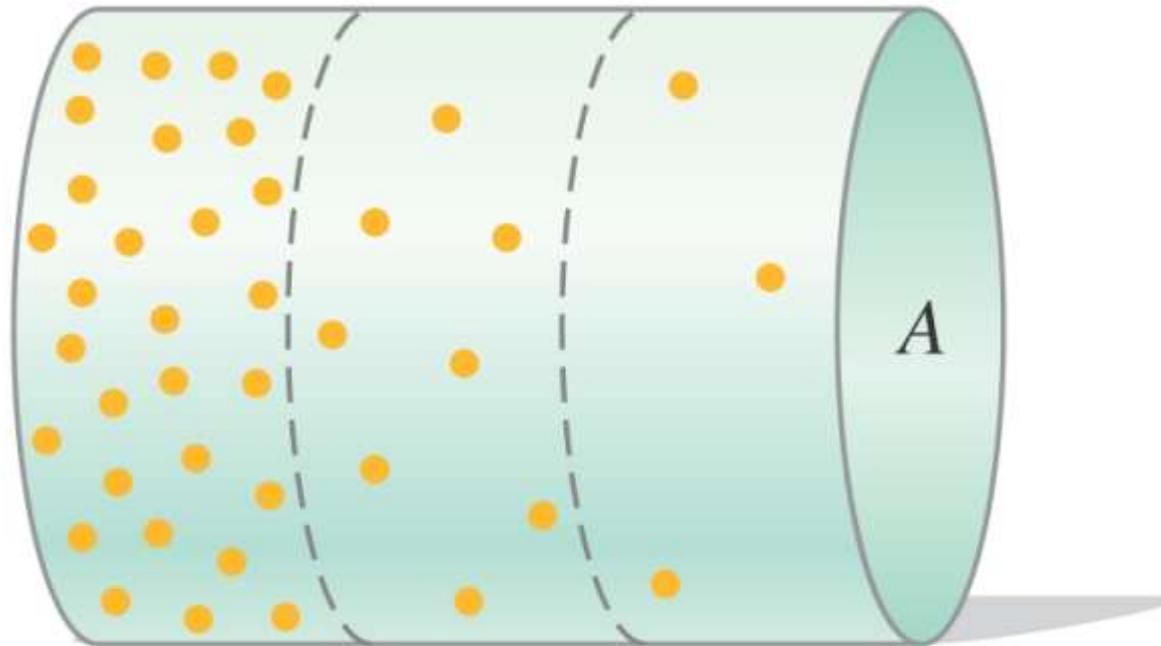
(b)



(c)

# 13-14 Diffusion

Diffusion occurs from a region of high concentration towards a region of lower concentration.



Region 1;  
concentration  
 $= C_1$

$\Delta x$

Region 2;  
concentration  
 $= C_2$

# 13-14 Diffusion

The rate of diffusion is given by:

$$J = DA \frac{C_1 - C_2}{\Delta x} \quad (13-10)$$

**TABLE 13-4 Diffusion Constants,  $D$  (20°C, 1 atm)**

Diffusing Molecules	Medium	$D$ (m <sup>2</sup> /s)
H <sub>2</sub>	Air	$6.3 \times 10^{-5}$
O <sub>2</sub>	Air	$1.8 \times 10^{-5}$
O <sub>2</sub>	Water	$100 \times 10^{-11}$
Blood hemoglobin	Water	$6.9 \times 10^{-11}$
Glycine (an amino acid)	Water	$95 \times 10^{-11}$
DNA (mass $6 \times 10^6$ u)	Water	$0.13 \times 10^{-11}$

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

# Summary of Chapter 13

- **All matter is made of atoms.**
- **Atomic and molecular masses are measured in atomic mass units, u.**
- **Temperature is a measure of how hot or cold something is, and is measured by thermometers.**
- **There are three temperature scales in use: Celsius, Fahrenheit, and Kelvin.**
- **When heated, a solid will get longer by a fraction given by the coefficient of linear expansion.**

# Summary of Chapter 13

- The fractional change in volume of gases, liquids, and solids is given by the coefficient of volume expansion.

- Ideal gas law:  $PV = nRT$

- One mole of a substance is the number of grams equal to the atomic or molecular mass.

- Each mole contains Avogadro's number of atoms or molecules.

- The average kinetic energy of molecules in a gas is proportional to the temperature:

$$\overline{\text{KE}} = \frac{1}{2} m \overline{v^2} = \frac{3}{2} kT$$

# Summary of Chapter 13

- **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.**
- **Relative humidity is the ratio of the actual vapor pressure to the saturated vapor pressure.**
- **Diffusion is the process whereby the concentration of a substance becomes uniform.**