CONTENTS OF CHAPTER 13

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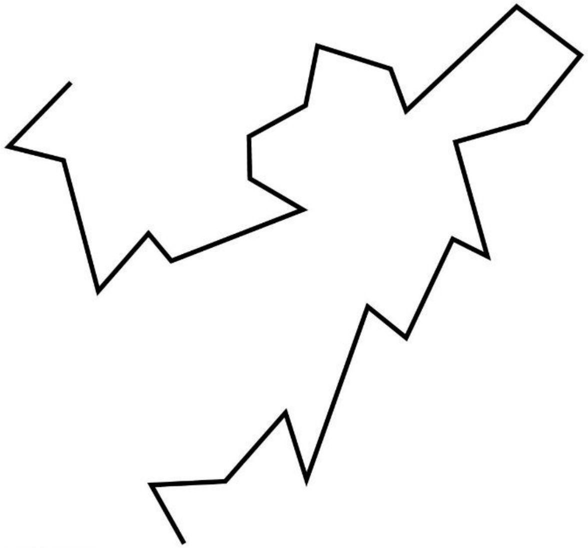
- Ideal Gas Law in Terms of Molecules: Avogadro's Number
- Kinetic Theory and the Molecular Interpretation of Temperature
- Distribution of Molecular Speeds
- Real Gases and Changes of Phase
- Vapor Pressure and Humidity

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:

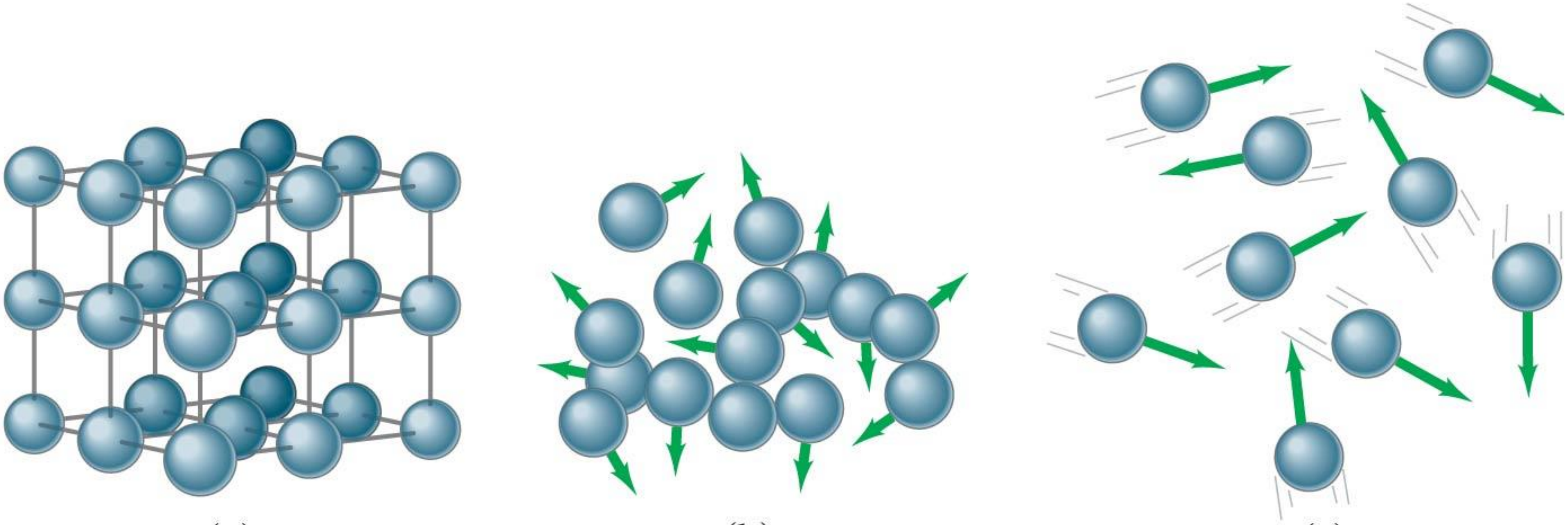
$$1\ \text{u} = 1.6605 \times 10^{-27}\ \text{kg}$$

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



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)

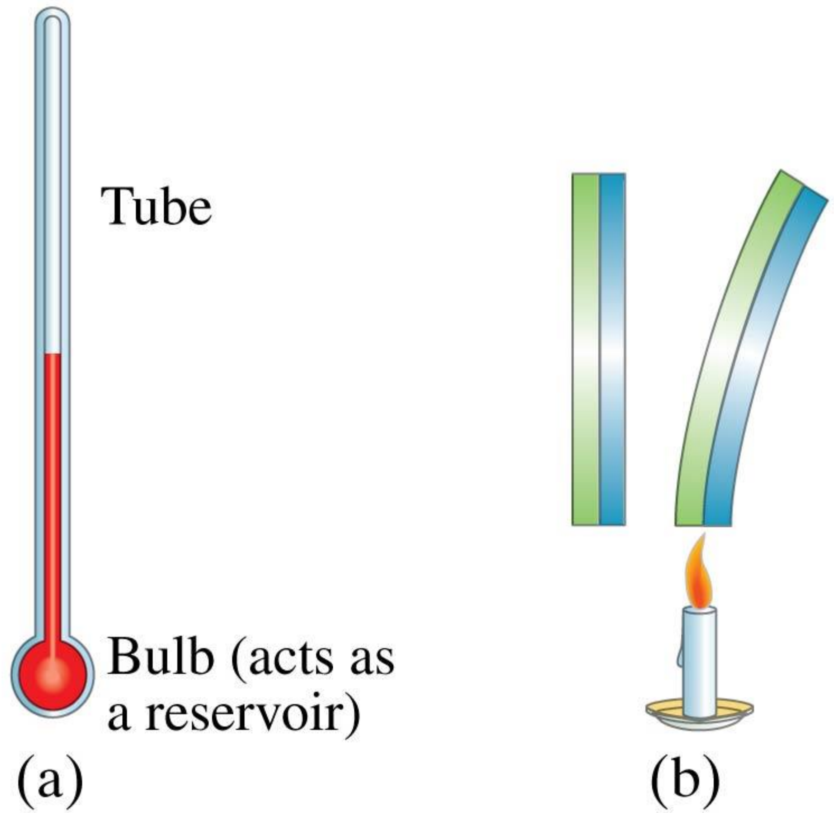
TEMPERATURE AND THERMOMETERS

Temperature is a measure of how hot or cold something is.
Most materials expand when heated.

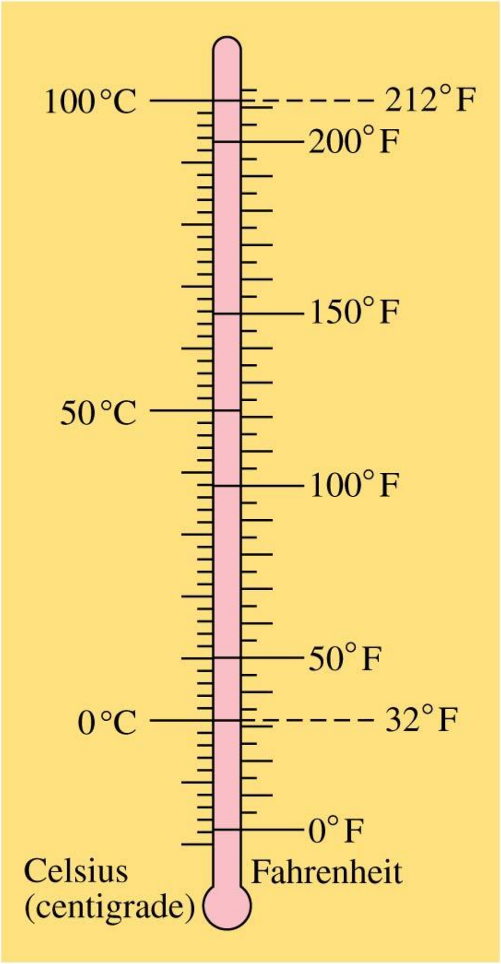
TEMPERATURE AND THERMOMETERS

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

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



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.

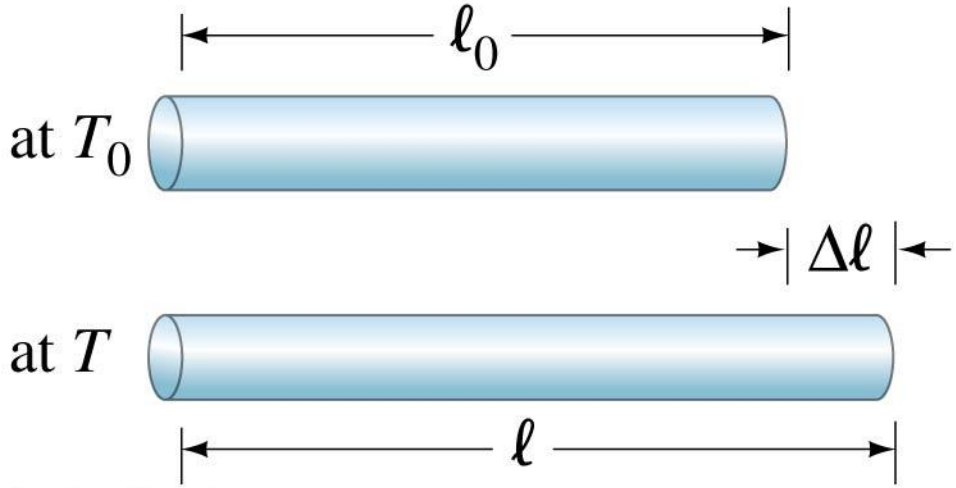
THERMAL EQUILIBRIUM AND THE ZEROTH LAW OF THERMODYNAMICS

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.

THERMAL EXPANSION

Linear expansion occurs when an object is heated.



$$\ell = \ell_0(1 + \alpha\,\Delta T),$$

Here, α is the coefficient of linear expansion.

THERMAL EXPANSION

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

$$\Delta V = \beta V_0 \, \Delta T,$$

Here, β is the coefficient of volume expansion. For uniform solids, $\beta \approx 3a$.

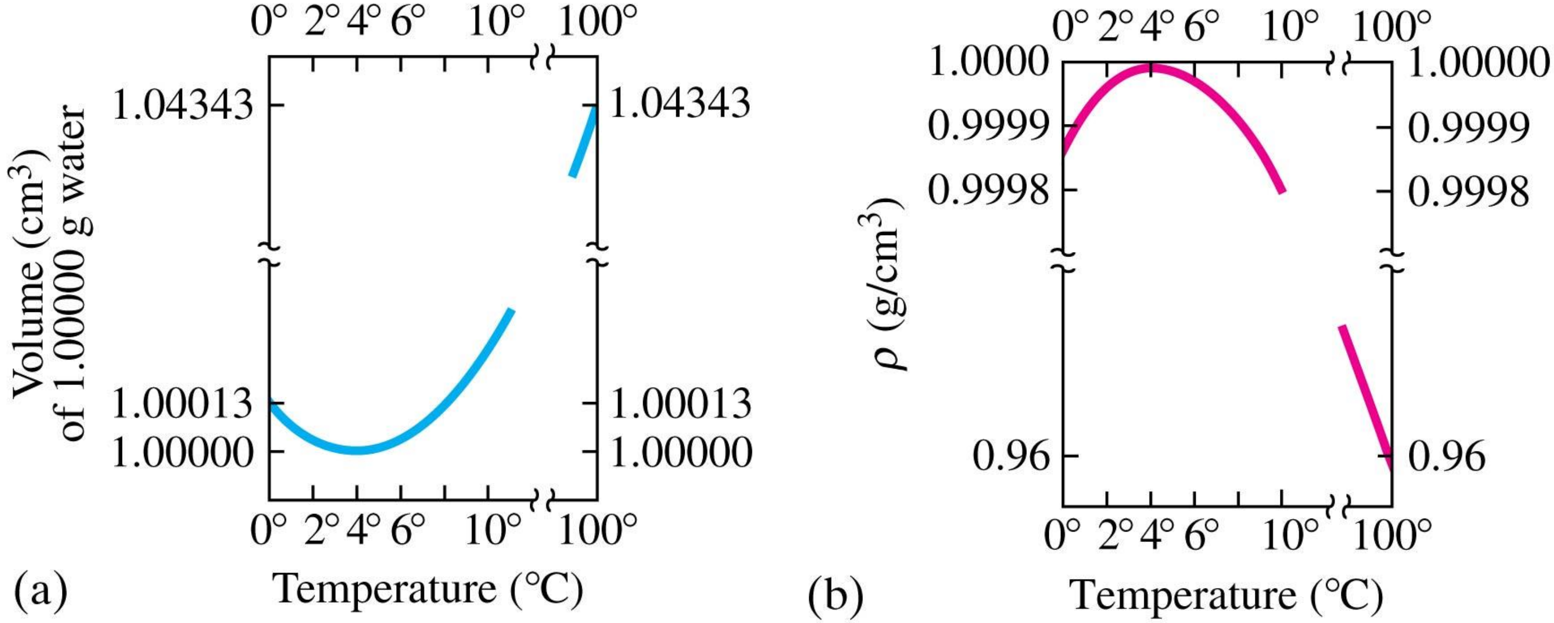
THERMAL EXPANSION

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

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

THERMAL EXPANSION

Water behaves differently from most other solids—its minimum volume occurs when its temperature is 4°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.



THERMAL EXPANSION

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:

$$\Delta\ell = \frac{1}{E}\frac{F}{A}\ell_0,$$

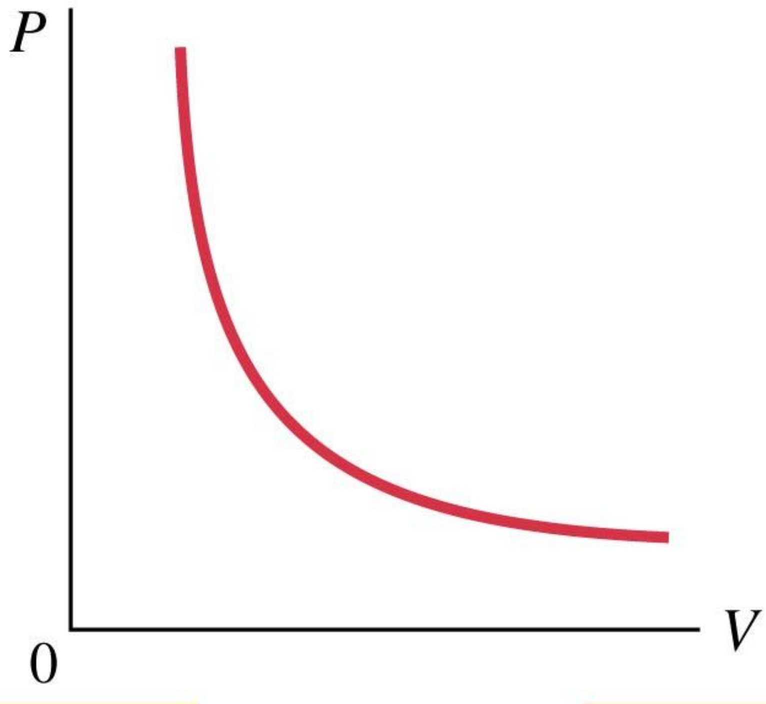
where E is the Young's modulus of the material. Therefore, the stress is:

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

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.

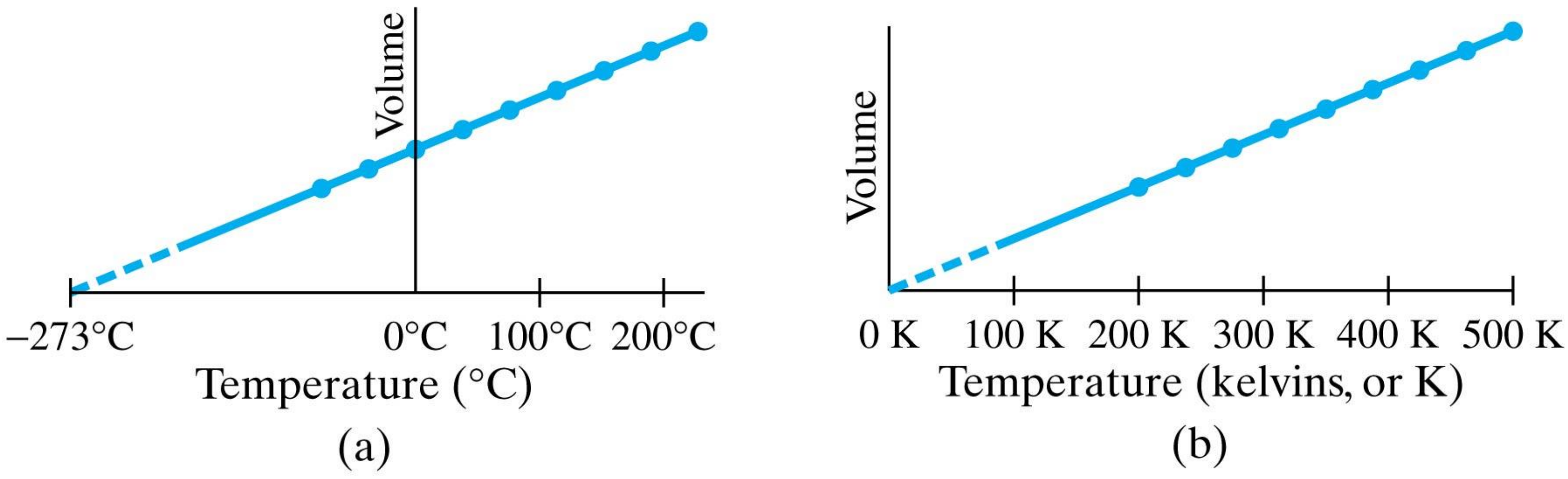
Boyle's Law: the volume of a given amount of gas is inversely proportional to the pressure as long as the temperature is constant. $V \propto 1/P$



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°C; this temperature is called absolute zero.



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: $P \propto T$.

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:

$PV \propto mT$

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_2 has a mass of 2 g

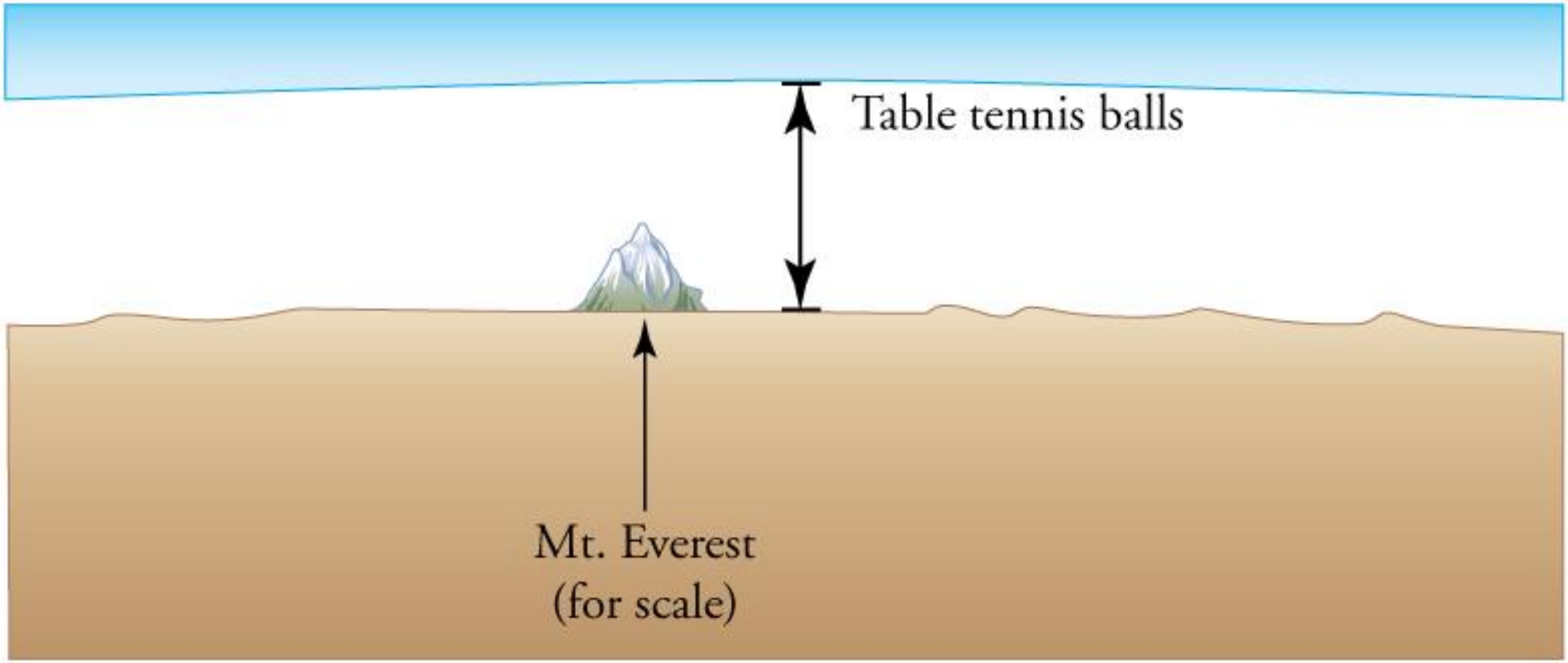
1 mol Ne has a mass of 20 g

1 mol CO_2 has a mass of 44 g

The number of moles in a certain mass of material:

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

FIGURE 13.19



How big is a mole? On a macroscopic level, one mole of table tennis balls would cover the Earth to a depth of about 40 km.

THE IDEAL GAS LAW

We can now write the ideal gas law:

$$PV = nRT$$

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

$$\begin{aligned} R &= 8.314\ \mathrm{J/(mol \cdot K)} && \text{[SI units]} \\ &= 0.0821\ \mathrm{(L \cdot atm)/(mol \cdot K)} \\ &= 1.99\ \mathrm{calories/(mol \cdot K)}. \end{aligned}$$

PROBLEM SOLVING WITH THE IDEAL GAS LAW

Useful facts and definitions:

- Standard temperature and pressure (STP)

$$T = 273\ \text{K}\ (0°\text{C})$$

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

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

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}. \qquad [\text{fixed } n]$$

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

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:

$$N = nN_A$$

IDEAL GAS LAW IN TERMS OF MOLECULES: AVOGADRO'S NUMBER

Therefore we can write:

$$PV = nRT = \frac{N}{N_A}RT,$$

or

$$\boxed{PV = NkT,}$$

where k is called Boltzmann's constant.

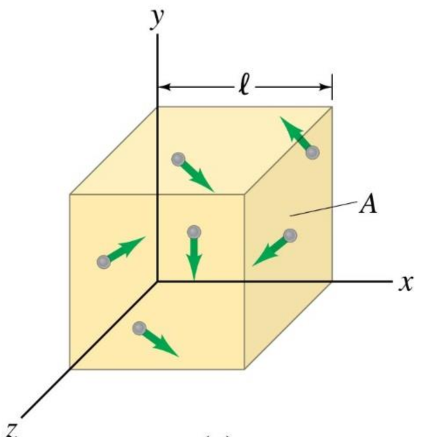
$$k = \frac{R}{N_A} = \frac{8.314\ \mathrm{J/mol \cdot K}}{6.02 \times 10^{23}/\mathrm{mol}} = 1.38 \times 10^{-23}\ \mathrm{J/K}.$$

KINETIC THEORY AND THE MOLECULAR INTERPRETATION OF TEMPERATURE

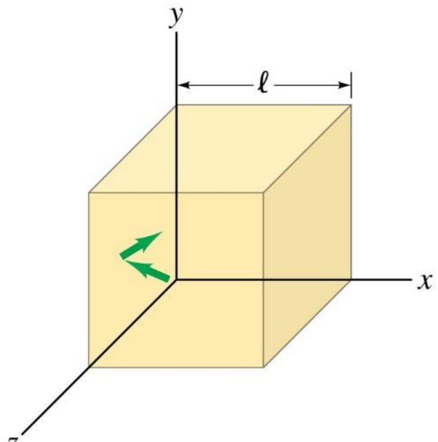
Assumptions of kinetic theory:

- 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

KINETIC THEORY AND THE MOLECULAR INTERPRETATION OF TEMPERATURE



(a)



(b)

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

$$F = \frac{\Delta(mv)}{\Delta t} = \frac{2mv_x}{2\ell/v_x} = \frac{mv_x^2}{\ell}. \qquad \text{[due to one molecule]}$$

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

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

KINETIC THEORY AND THE MOLECULAR INTERPRETATION OF TEMPERATURE

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

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

So the pressure is:

$$P = \frac{F}{A} = \frac{1}{3}\frac{Nm\overline{v^2}}{A\ell}$$

or

$$P = \frac{1}{3}\frac{Nm\overline{v^2}}{V}, \qquad \left[\begin{array}{l}\text{pressure in an}\\ \text{ideal gas}\end{array}\right]$$

KINETIC THEORY AND THE MOLECULAR INTERPRETATION OF TEMPERATURE

Rewriting,

$$PV = \tfrac{2}{3} N\left(\tfrac{1}{2} m\overline{v^2}\right).$$

so

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

or

$$\overline{\mathrm{KE}} = \tfrac{1}{2} m\overline{v^2} = \tfrac{3}{2} kT. \qquad \text{[ideal gas]}$$

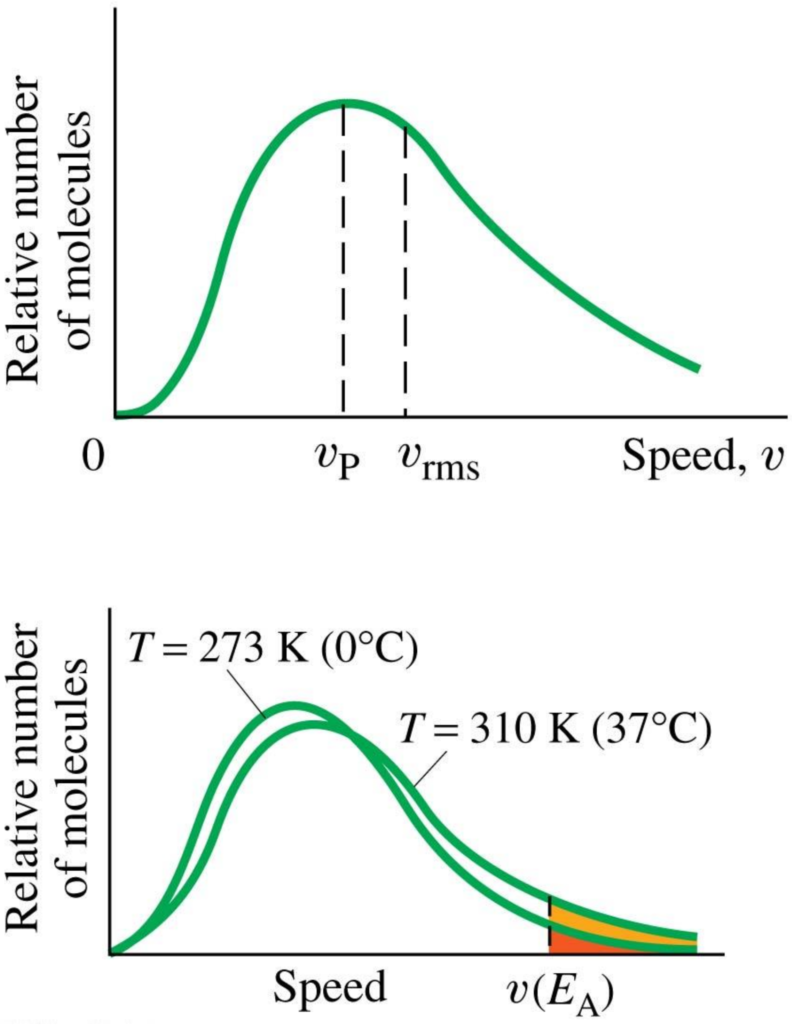
The average translational kinetic energy of the molecules in an ideal gas is directly proportional to the temperature of the gas.

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:

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

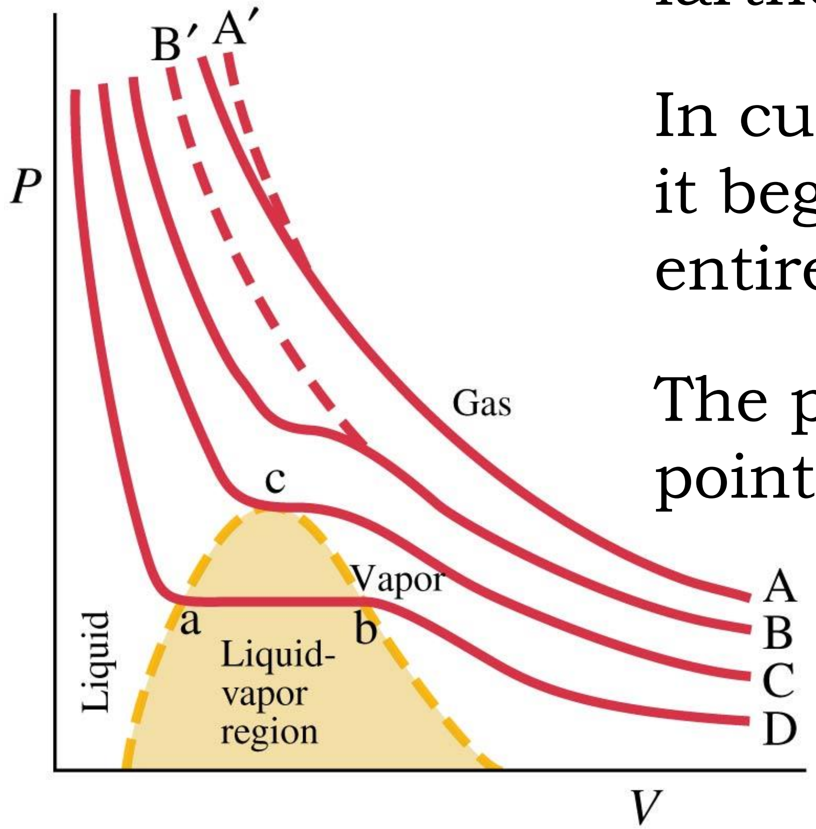
DISTRIBUTION OF MOLECULAR SPEEDS



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.

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.

REAL GASES AND CHANGES OF PHASE

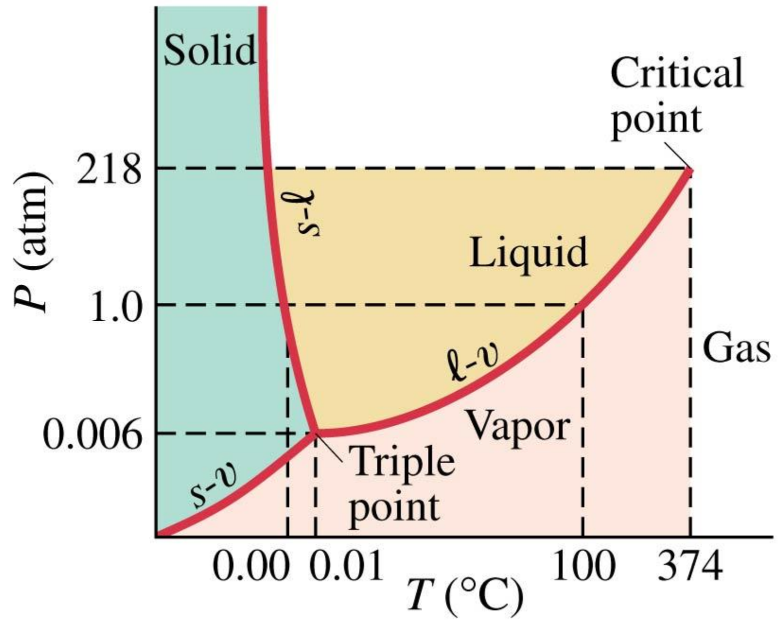
Below the critical temperature, the gas can liquefy if the pressure is sufficient; above it, no amount of pressure will suffice.

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

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.

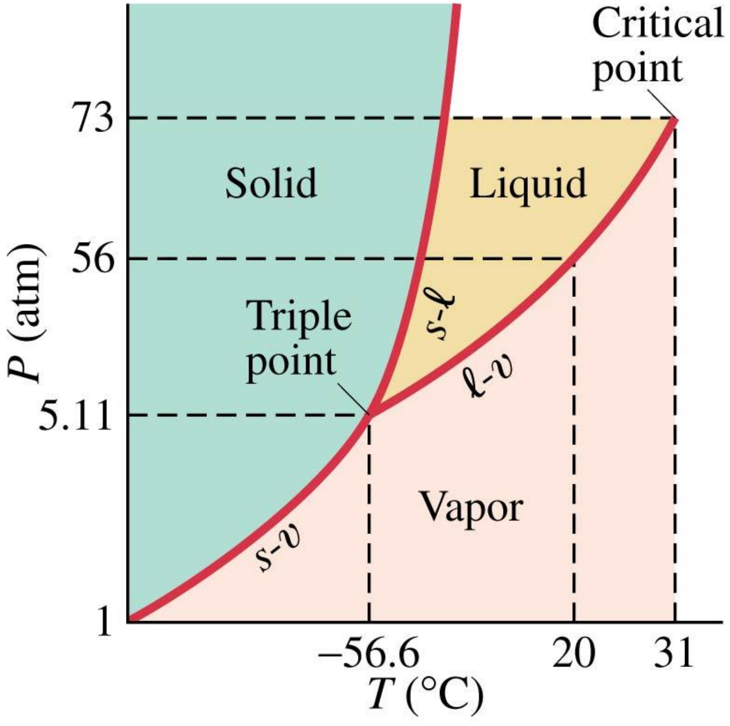
Phase diagram of water



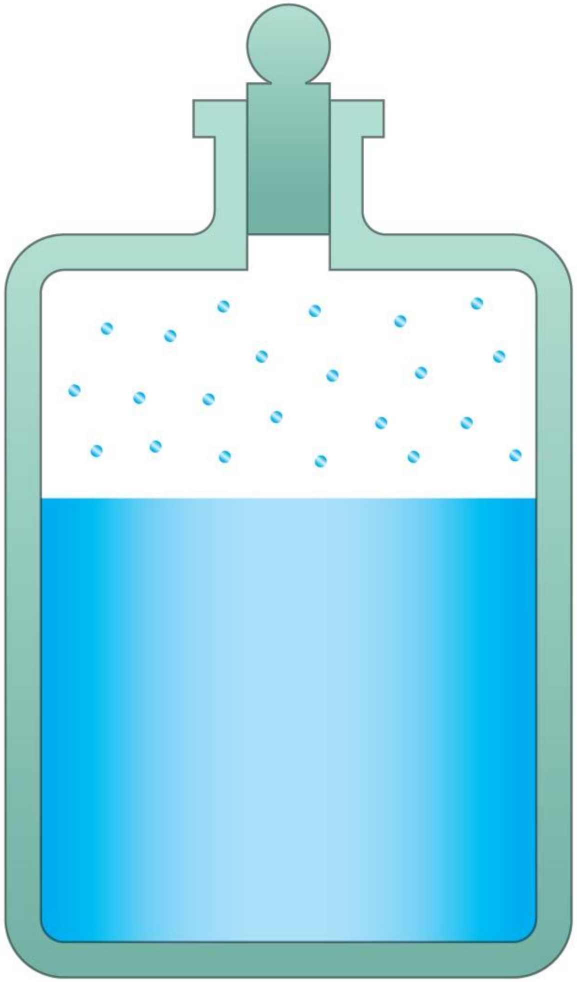
REAL GASES AND CHANGES OF PHASE

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

Phase diagram of carbon dioxide



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.

VAPOR PRESSURE AND HUMIDITY

TABLE 13–3 Saturated Vapor Pressure of Water

Temp-erature (°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.

VAPOR PRESSURE AND HUMIDITY

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

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.

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

VAPOR PRESSURE AND HUMIDITY

(a) (b) (c)

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

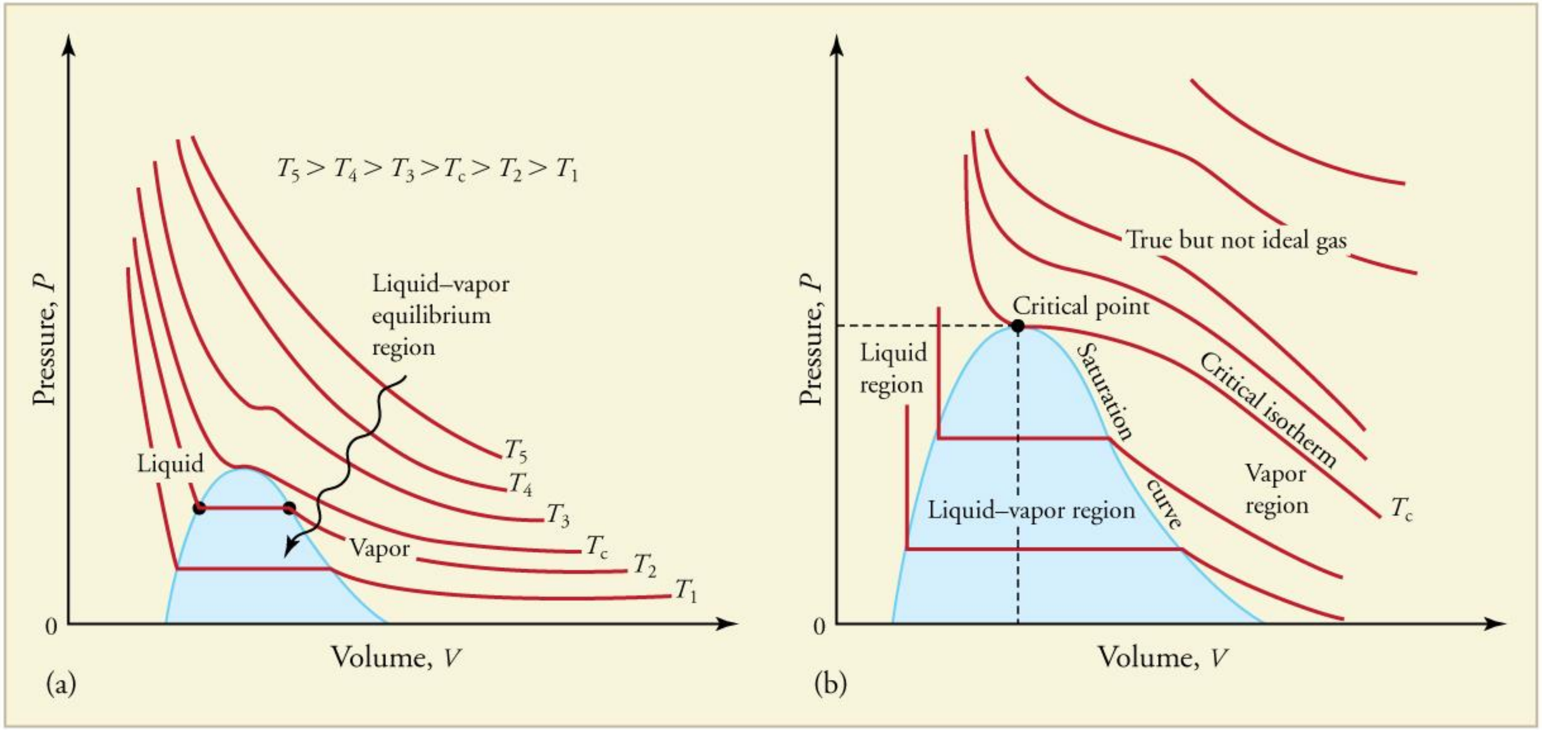
The dew point is the temperature at which the air would be saturated with water.

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

FIGURE 13.16

The air inside this hot air balloon flying over Putrajaya, Malaysia, is hotter than the ambient air. As a result, the balloon experiences a buoyant force pushing it upward.

FIGURE 13.27

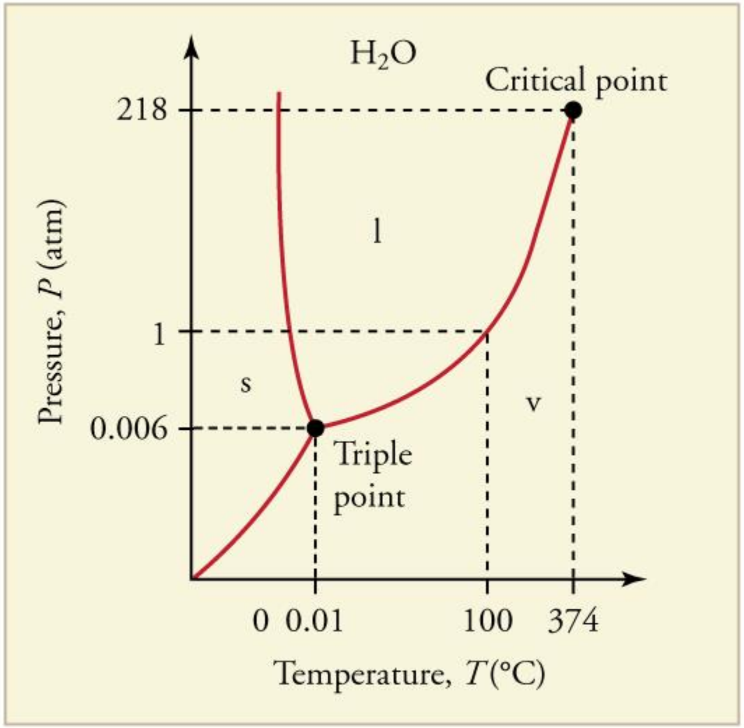


PV diagrams.

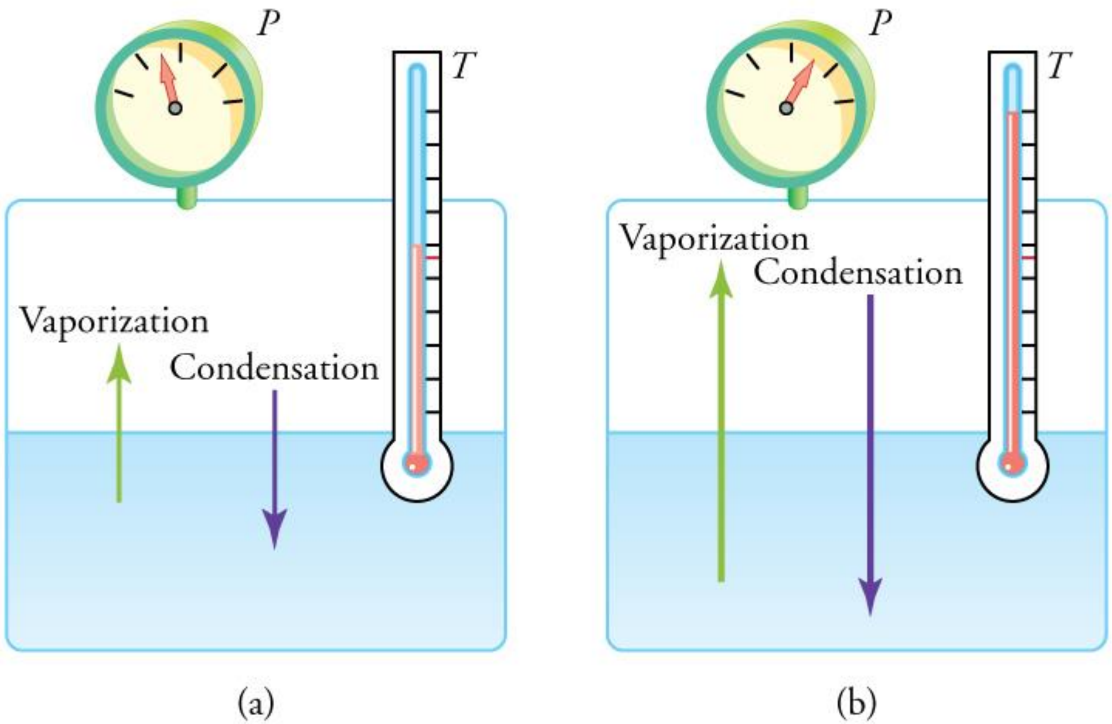
(a) Each curve (isotherm) represents the relationship between *P* and *V* at a fixed temperature; the upper curves are at higher temperatures. The lower curves are not hyperbolas, because the gas is no longer an ideal gas.

(b) An expanded portion of the *PV* diagram for low temperatures, where the phase can change from a gas to a liquid. The term “vapor” refers to the gas phase when it exists at a temperature below the boiling temperature.

FIGURE 13.28



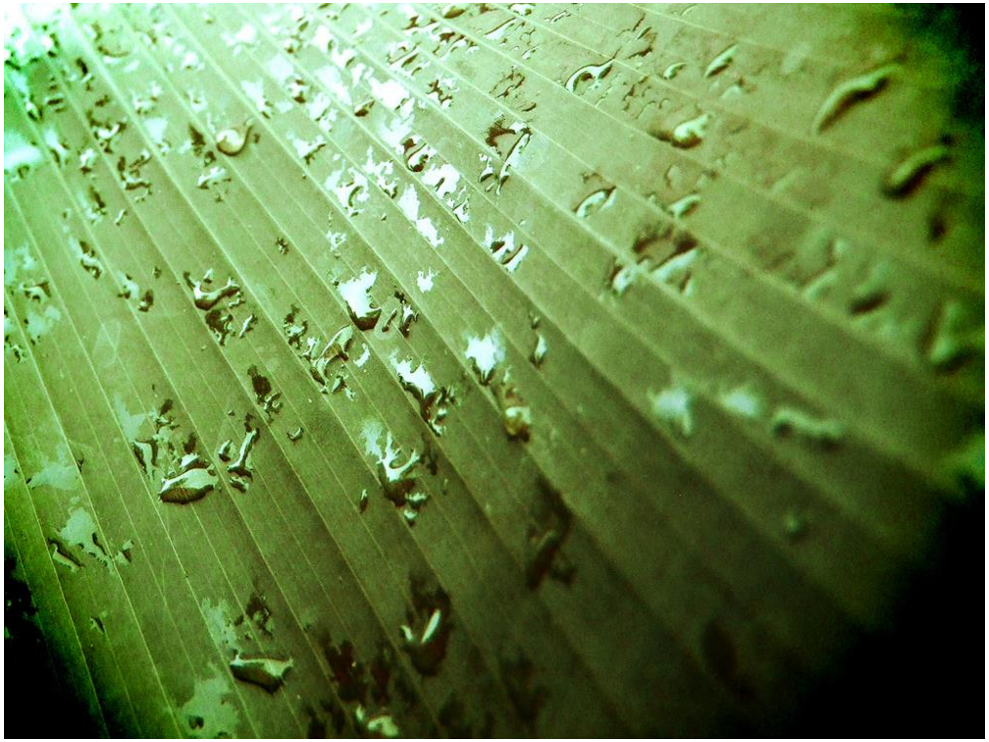
The phase diagram (*PT* graph) for water. Note that the axes are nonlinear and the graph is not to scale. This graph is simplified—there are several other exotic phases of ice at higher pressures.



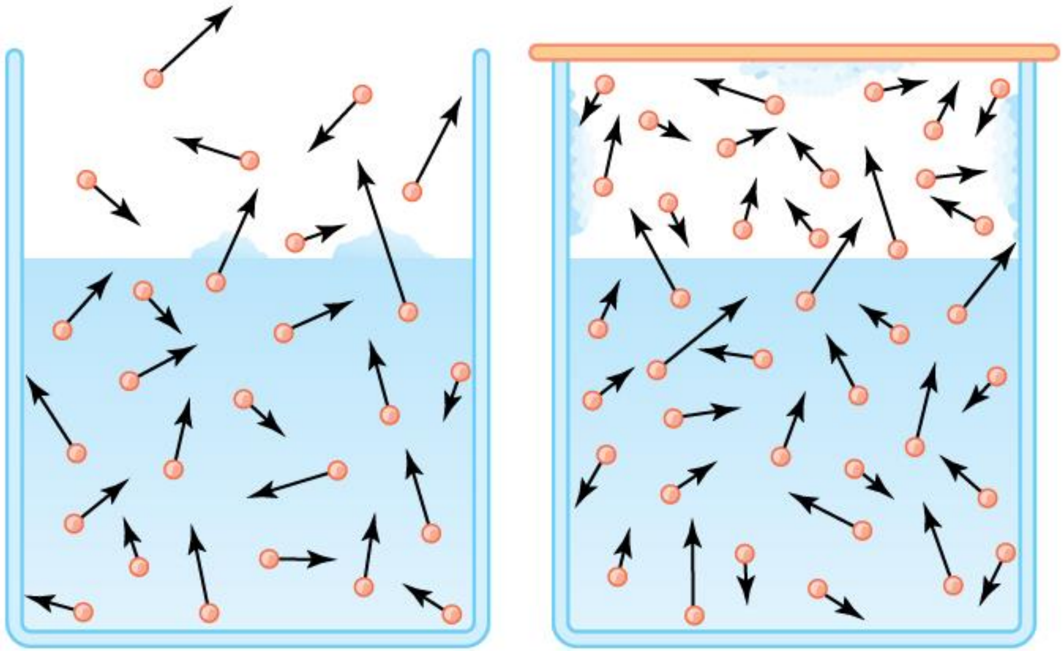
Equilibrium between liquid and gas at two different boiling points inside a closed container.

(a) The rates of boiling and condensation are equal at this combination of temperature and pressure, so the liquid and gas phases are in equilibrium.

(b) At a higher temperature, the boiling rate is faster and the rates at which molecules leave the liquid and enter the gas are also faster. Because there are more molecules in the gas, the gas pressure is higher and the rate at which gas molecules condense and enter the liquid is faster. As a result the gas and liquid are in equilibrium at this higher temperature.



Dew drops like these, on a banana leaf photographed just after sunrise, form when the air temperature drops to or below the dew point. At the dew point, the air can no longer hold all of the water vapor it held at higher temperatures, and some of the water condenses to form droplets.

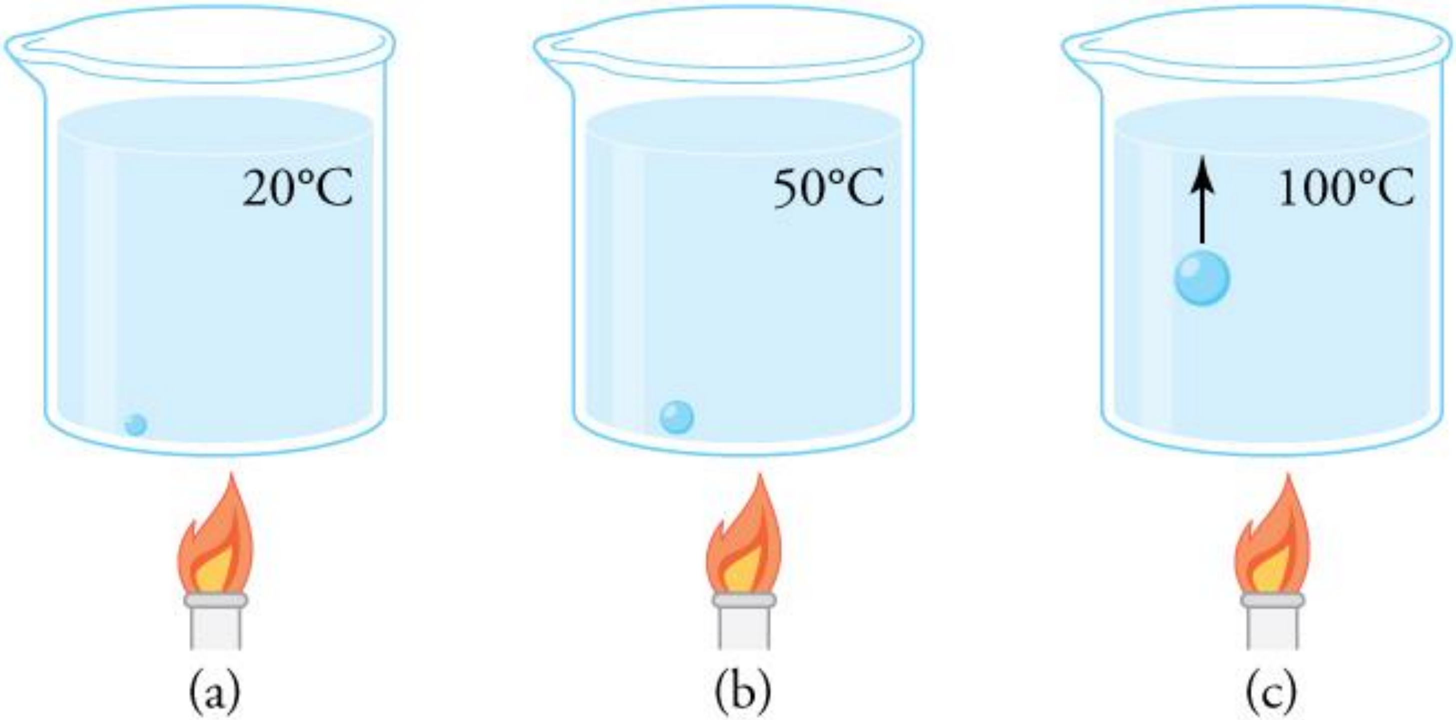


(a) (b)

(a)Because of the distribution of speeds and kinetic energies, some water molecules can break away to the vapor phase even at temperatures below the ordinary boiling point.

(b)If the container is sealed, evaporation will continue until there is enough vapor density for the condensation rate to equal the evaporation rate. This vapor density and the partial pressure it creates are the saturation values. They increase with temperature and are independent of the presence of other gases, such as air. They depend only on the vapor pressure of water. Relative humidity is related to the partial pressure.

FIGURE 13.33

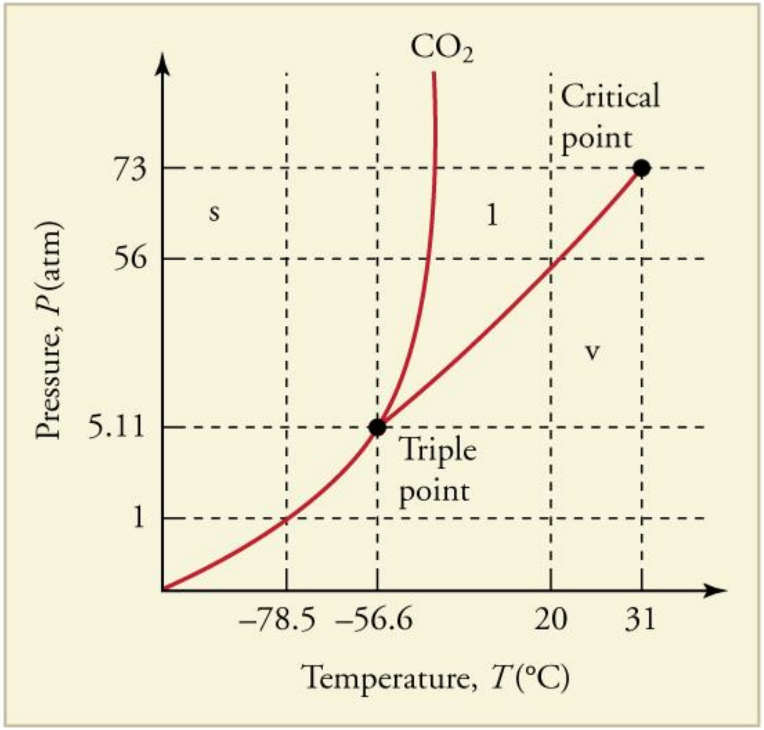


(a) An air bubble in water starts out saturated with water vapor at 20ºC .

(b) As the temperature rises, water vapor enters the bubble because its vapor pressure increases. The bubble expands to keep its pressure at 1.00 atm.

(c) At 100ºC , water vapor enters the bubble continuously because water’s vapor pressure exceeds its partial pressure in the bubble, which must be less than 1.00 atm. The bubble grows and rises to the surface.

FIGURE 13.35



The phase diagram for carbon dioxide. The axes are nonlinear, and the graph is not to scale. Dry ice is solid carbon dioxide and has a sublimation temperature of – 78.5ºC.

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.

SUMMARY OF CHAPTER 13

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

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

or

$$\overline{\mathrm{KE}} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT. \qquad \text{[ideal gas]}$$

- 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.

SUMMARY OF CHAPTER 13

- 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.