

Lecture Presentation

Chapter 10

Gases

Characteristics of Gases

- Physical properties of gases are all similar.
- Composed mainly of nonmetallic elements with simple formulas and low molar masses.
- Unlike liquids and solids, gases
 - expand to fill their containers.
 - are highly compressible.
 - have extremely low densities.
- Two or more gases form a homogeneous mixture.



Properties Which Define the State of a Gas Sample

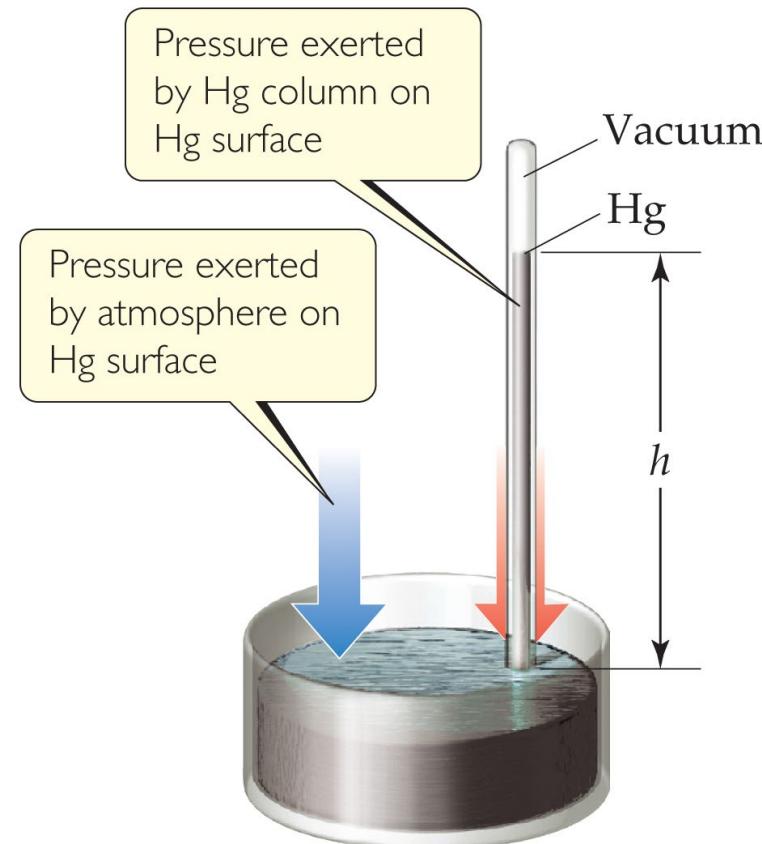
- 1) Temperature
 - 2) Pressure
 - 3) Volume
 - 4) Amount of gas, usually expressed as number of moles
- Having already discussed three of these, we need to define pressure.



Units of Pressure

- **Pascals:** $1 \text{ Pa} = 1 \text{ N/m}^2$ (SI unit of pressure)
- **Bar:** $1 \text{ bar} = 10^5 \text{ Pa} = 100 \text{ kPa}$
- **mm Hg or torr:** These units are literally the difference in the heights measured in mm of two connected columns of mercury, as in the **barometer** in the figure.
- **Atmosphere:**

$$1.00 \text{ atm} = 760 \text{ torr} = 760 \text{ mm Hg} \\ = 101.325 \text{ kPa}$$



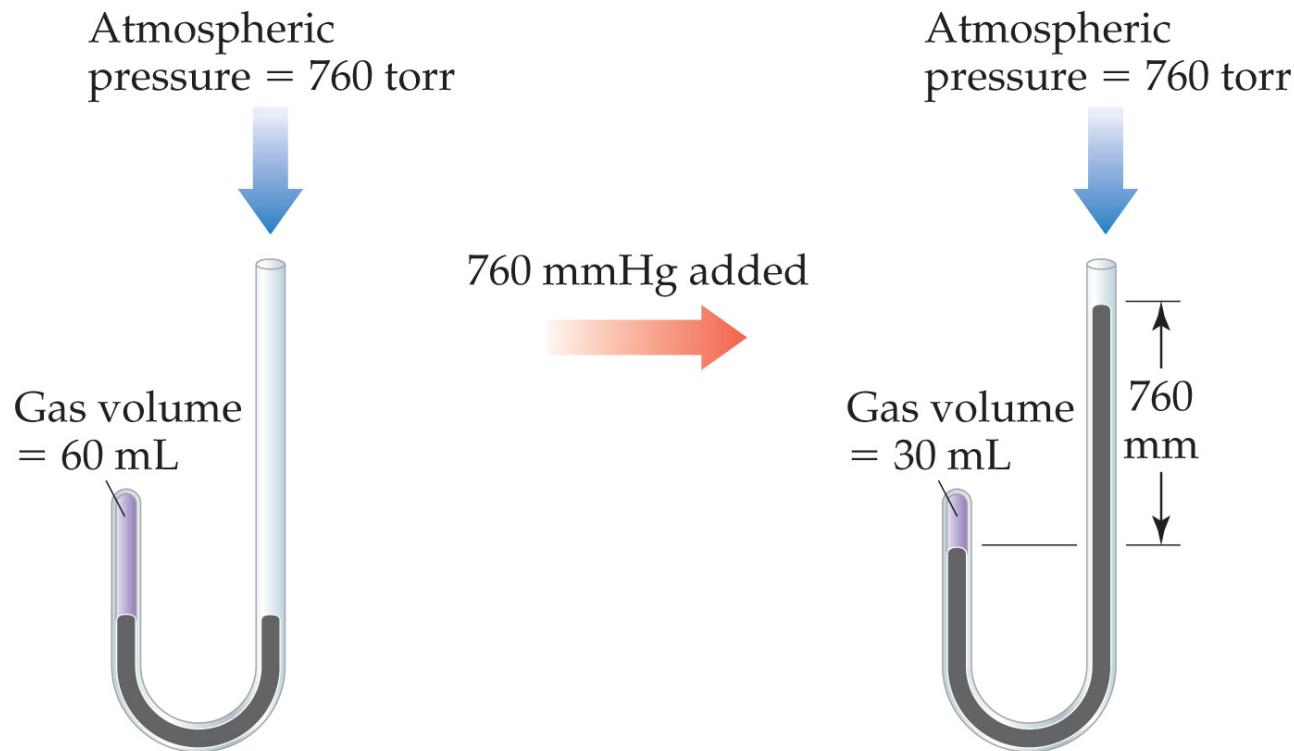
Standard Pressure

- Normal atmospheric pressure at sea level is referred to as **standard atmospheric pressure**.
- It is equal to
 - 1.00 atm.
 - 760 torr (760 mmHg).
 - 101.325 kPa.



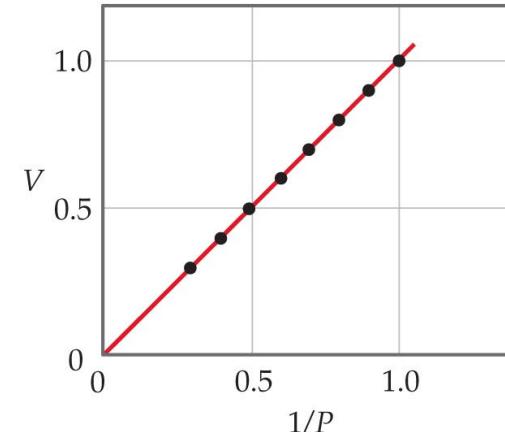
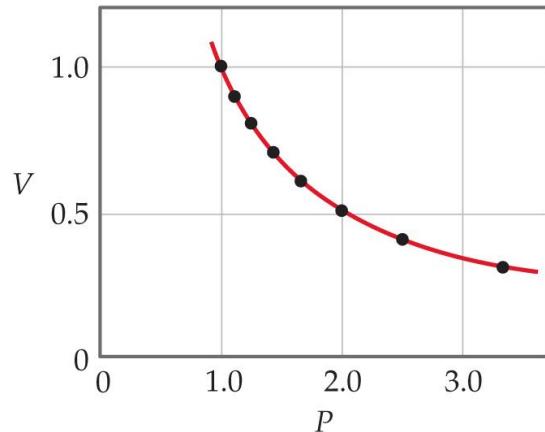
Boyle's Law

The volume of a fixed quantity of gas at constant temperature is inversely proportional to the pressure.



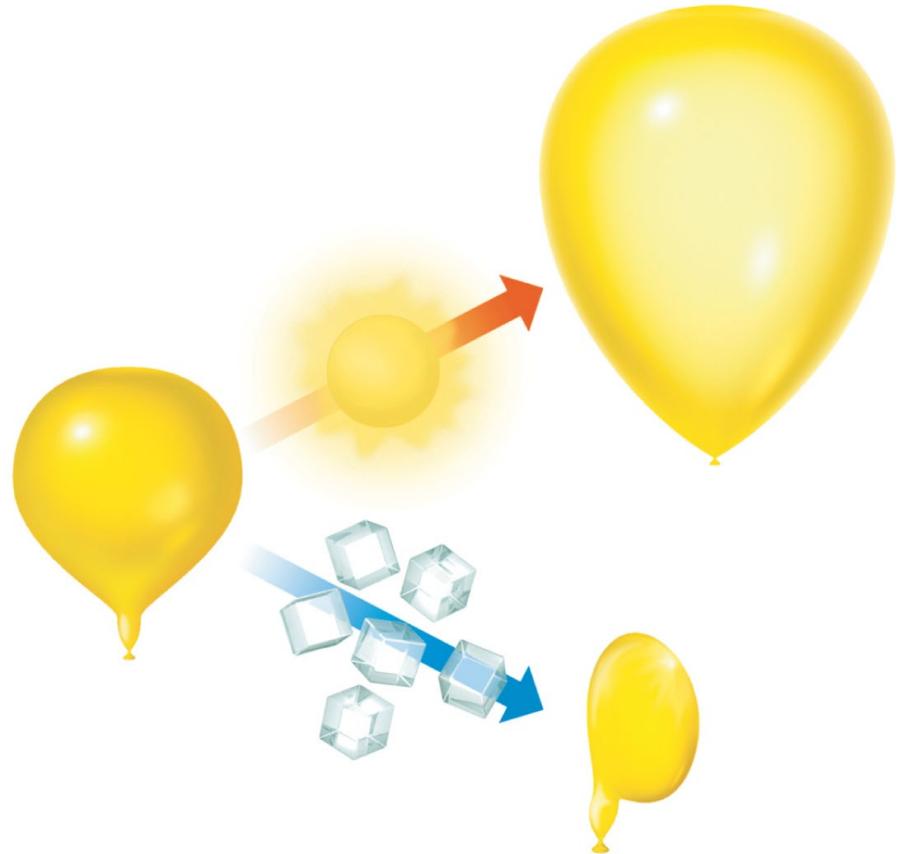
Mathematical Relationships of Boyle's Law

- $PV = \text{a constant}$
- This means, if we compare two conditions:
 $P_1 V_1 = P_2 V_2$.
- Also, if we make a graph of V vs. P , it will *not* be linear. However, a graph of V vs. $1/P$ *will* result in a linear relationship!



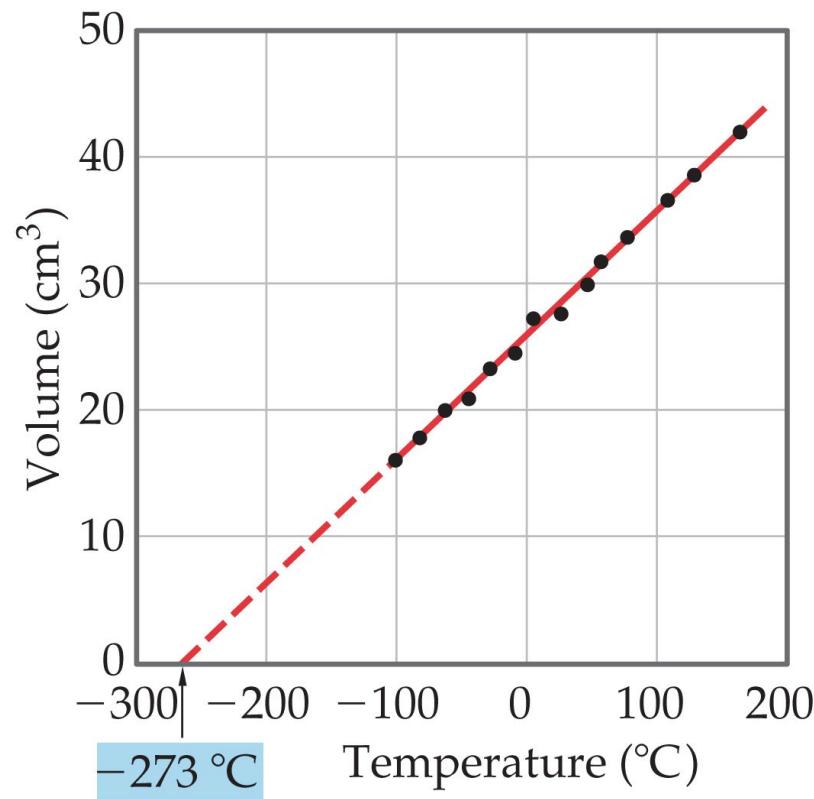
Charles's Law

- The volume of a fixed amount of gas at constant pressure is directly proportional to its absolute temperature.



Mathematical Relationships of Charles's Law

- $V = \text{constant} \times T$
- This means, if we compare two conditions:
 $V_1/T_1 = V_2/T_2$.
- Also, if we make a graph of V vs. T , it will be linear.



Avogadro's Law

- The volume of a gas at constant temperature and pressure is directly proportional to the number of moles of the gas.
- Also, at **STP**, one mole of gas occupies 22.4 L.
- Mathematically: $V = \text{constant} \times n$, or $V_1/n_1 = V_2/n_2$



Volume	22.4 L	22.4 L	22.4 L
Pressure	1 atm	1 atm	1 atm
Temperature	0 °C	0 °C	0 °C
Mass of gas	4.00 g	28.0 g	16.0 g
Number of gas molecules	6.02×10^{23}	6.02×10^{23}	6.02×10^{23}



| Which one of the following is a valid statement of Avogadro's law?

A) $\frac{P}{T} = \text{constant}$

B) $\frac{V}{T} = \text{constant}$

C) $PV = \text{constant}$

D) $\underline{V} = \text{constant} \times n$

E) $V = \text{constant} \times P$

| Of the following, only _____ is impossible for an ideal gas.

A) $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

B) $V_1 T_1 = V_2 T_2$

C) $\frac{V_1}{V_2} = \frac{T_1}{T_2}$

D) $V_2 = \frac{T_2}{T_1} V_1$

E) $\frac{V_1}{V_2} = \frac{T_1}{T_2} = 0$



Ideal-Gas Equation

- So far we've seen that

$V \propto 1/P$ (Boyle's law).

$V \propto T$ (Charles's law).

$V \propto n$ (Avogadro's law).

- Combining these, we get

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

- Finally, to make it an equality, we use a constant of proportionality (R) and reorganize; this gives the Ideal-Gas Equation: $PV = nRT$.



Density of Gases

If we divide both sides of the ideal-gas equation by V and by RT , we get

$$n/V = P/RT.$$

Also: moles \times molecular mass = mass

$$n \times M = m.$$

If we multiply both sides by M , we get

$$m/V = MP/RT$$

and m/V is density, d ; the result is:

$$d = MP/RT.$$



Density & Molar Mass of a Gas

- To recap:
- One needs to know only the molecular mass, the pressure, and the temperature to calculate the density of a gas.
- $d = MP/RT$
- Also, if we know the mass, volume, and temperature of a gas, we can find its molar mass.
- $M = mRT/PV$



- | The volume of a sample of gas (2.49 g) was 752 mL at 1.98 atm and 62 °C. The gas is _____.
- A) SO₂
 B) SO₃
 C) NH₃
 D) NO₂
 E) Ne

$$M = mRT/PV$$

Table 10.2 Numerical Values of the Gas Constant R in Various Units

Units	Numerical Value
L-atm/mol-K	0.08206
J/mol-K*	8.314
cal/mol-K	1.987
m ³ -Pa/mol-K*	8.314
L-torr/mol-K	62.36

*SI unit

R= 0.08206 L-atm/mol-K



Volume and Chemical Reactions

- The balanced equation tells us relative amounts of moles in a reaction, whether the compared materials are products or reactants.
- $PV = nRT$
- So, we can relate volume for gases, as well.
- For example: use ($PV = nRT$) for substance A to get moles A; use the mole ratio from the balanced equation to get moles B; and ($PV = nRT$) for substance B to get volume of B.



7) Sodium bicarbonate is reacted with concentrated hydrochloric acid at 37.0 °C and 1.00 atm. The reaction of 6.00 kg of bicarbonate with excess hydrochloric acid under these conditions will produce _____ L of CO₂.

A) 1.09×10^2

B) 2.85×10^4

C) 1.82×10^4

D) 8.70×10^2

E) 1.82×10^3

$$V = nRT/P$$



Dalton's Law of Partial Pressures

- If two gases that *don't* react are combined in a container, they act as if they are alone in the container.
- The total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone.
- In other words,

$$P_{\text{total}} = p_1 + p_2 + p_3 + \dots$$



Mole Fraction

- Because each gas in a mixture acts as if it is alone, we can relate amount in a mixture to partial pressures:

$$\frac{P_1}{P_t} = \frac{n_1 RT/V}{n_t RT/V} = \frac{n_1}{n_t}$$

- That ratio of moles of a substance to total moles is called the **mole fraction**, χ .

$$X_1 = \frac{\text{Moles of compound 1}}{\text{Total moles}} = \frac{n_1}{n_t}$$



Pressure and Mole Fraction

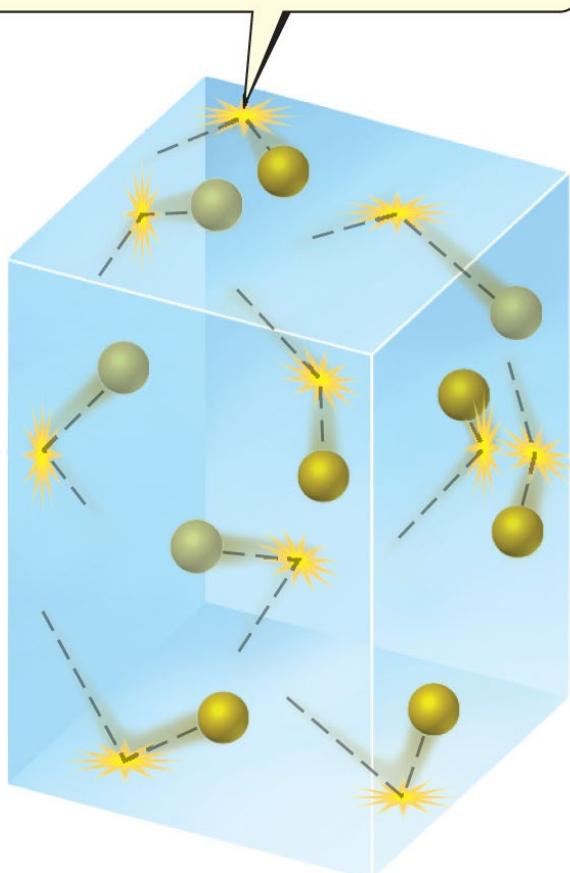
- The end result is

$$P_1 = \left(\frac{n_1}{n_t} \right) P_t = X_1 P_t$$



Kinetic-Molecular Theory

Pressure inside container comes from collisions of gas molecules with container walls



- Laws tell us *what* happens in nature. Each of the gas laws we have discussed tell us what is observed under certain conditions.
- *Why* are these laws observed? We will discuss a *theory* to explain our observations.

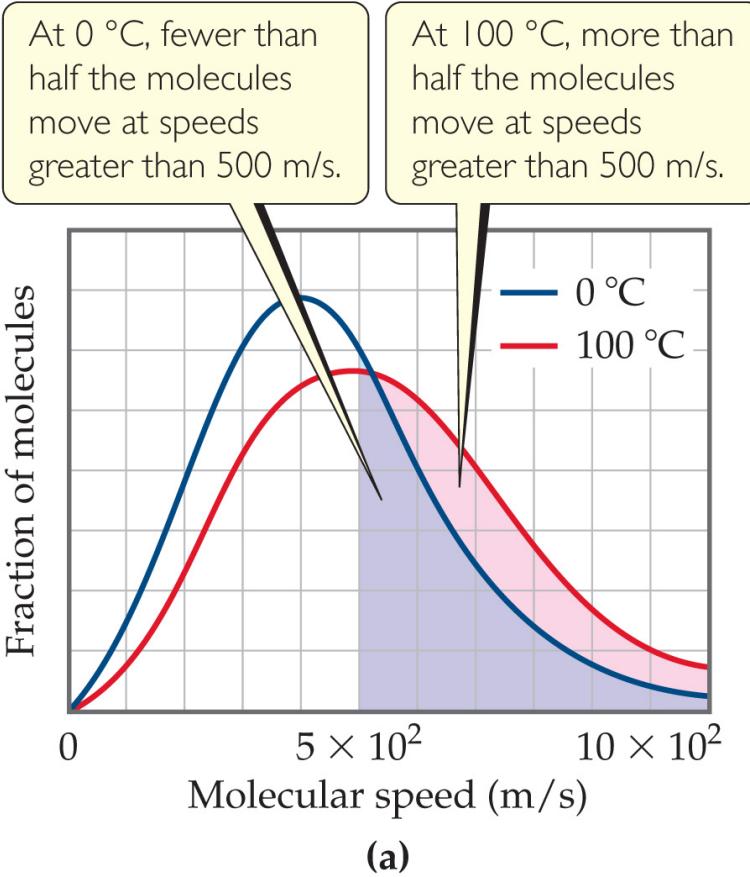


Main Tenets of Kinetic-Molecular Theory

- 1) Gases consist of large numbers of molecules that are in continuous, random motion.
- 2) The combined volume of all the molecules of the gas is negligible relative to the total volume in which the gas is contained.
- 3) Attractive and repulsive forces between gas molecules are negligible.



Main Tenets of Kinetic-Molecular Theory



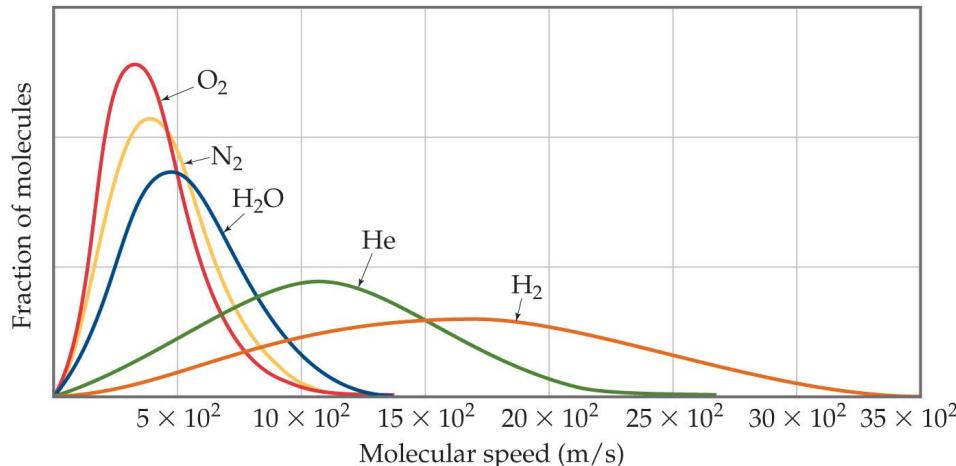
- 4) Energy can be transferred between molecules during collisions, but the *average* kinetic energy of the molecules does not change with time, as long as the temperature of the gas remains constant.
- 5) The average kinetic energy of the molecules is proportional to the absolute temperature.



u_{rms} and Molecular Mass

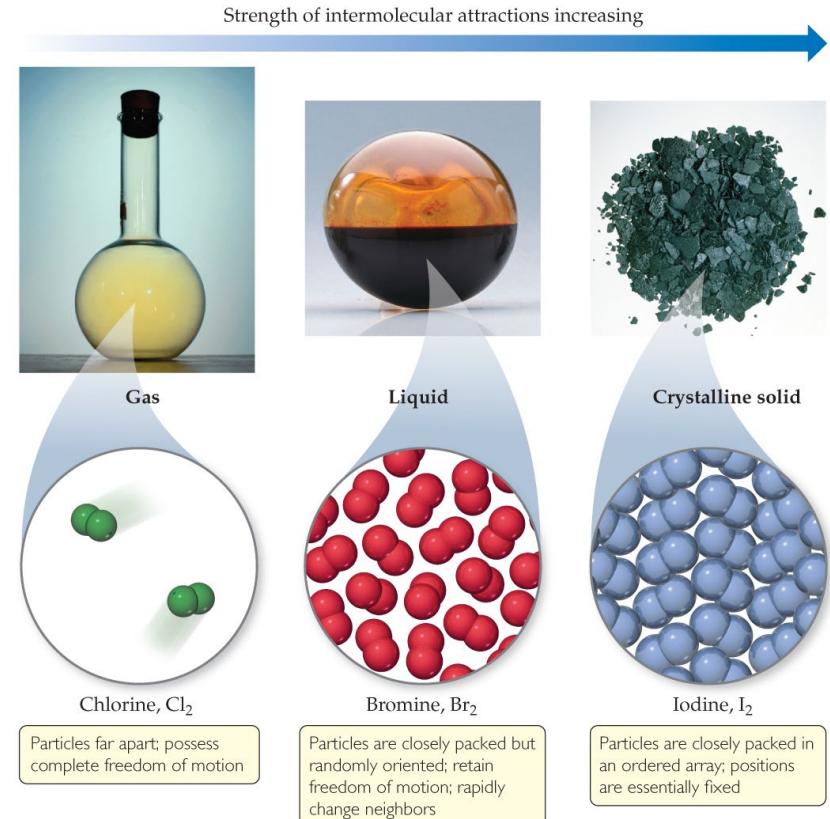
$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

- At any given temperature, the average kinetic energy of molecules is the same.
- So, $\frac{1}{2} m (u_{\text{rms}})^2$ is the same for two gases at the same temperature.
- If a gas has a low mass, its speed will be greater than for a heavier molecule.



States of Matter

- The fundamental difference between states of matter is the strength of the intermolecular forces of attraction.
- Stronger forces bring molecules closer together.
- Solids and liquids are referred to as the *condensed phases*.



Differences in the States of Matter

Table 11.1 Some Characteristic Properties of the States of Matter

Gas	Assumes both volume and shape of its container Expands to fill its container Is compressible Flows readily Diffusion within a gas occurs rapidly
Liquid	Assumes shape of portion of container it occupies Does not expand to fill its container Is virtually incompressible Flows readily Diffusion within a liquid occurs slowly
Solid	Retains own shape and volume Does not expand to fill its container Is virtually incompressible Does not flow Diffusion within a solid occurs extremely slowly

*The atoms in a solid are able to vibrate in place. As the temperature of the solid increases, the vibrational motion increases.



Which State of Matter?

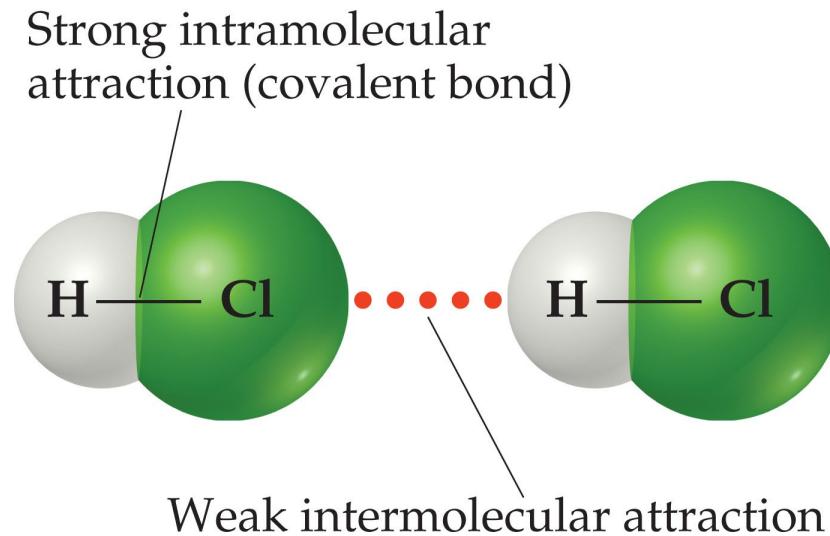
- The answer to this question largely relies on the
 - balance between the kinetic energies of the particles.
 - interparticle energies of attraction.

Table 11.2 Comparing Kinetic Energies and Energies of Attractions for States of Matter

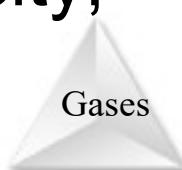
Gas	Kinetic energies >> energies of attraction
Liquid	Comparable kinetic energies and energies of attraction
Solid	Energies of attraction >> kinetic energies



Intermolecular Forces



- The attractions between molecules are not nearly as strong as the intramolecular attractions (bonds) that hold compounds together.
- Many physical properties reflect intermolecular forces, like boiling points, melting points, viscosity, surface tension, and capillary action.



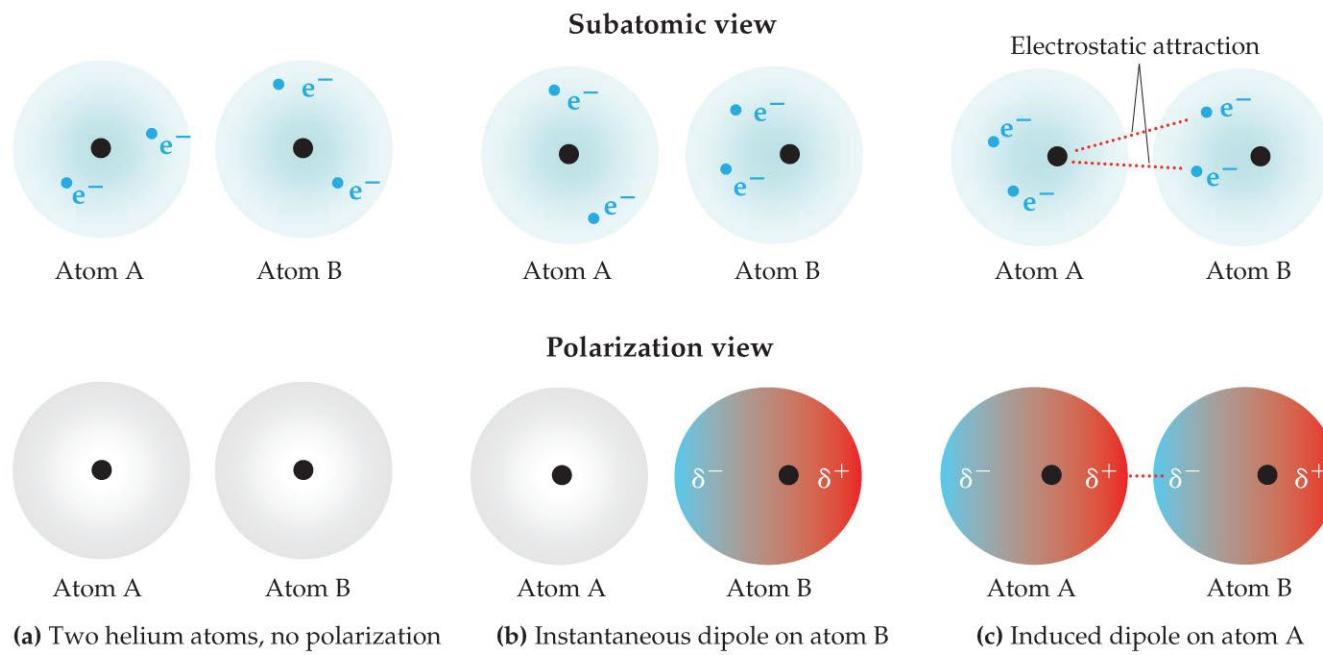
Types of Intermolecular Force

- Weakest to strongest forces:
 - dispersion forces (or London dispersion forces)
 - dipole–dipole forces
 - hydrogen bonding (a special dipole–dipole force)
 - ion–dipole forces
- Note: The first two types are also referred to collectively as *van der Waals forces*.



Dispersion Forces

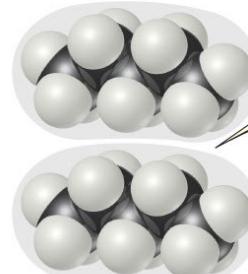
- The figure below shows how a nonpolar particle (in this case a helium atom) can be temporarily polarized to allow dispersion force to form.
- The tendency of an electron cloud to distort is called its **polarizability**.



Factors Which Affect Amount of Dispersion Force in a Molecule

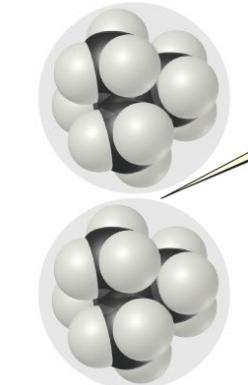
- number of electrons in an atom (**more electrons, more dispersion force**)
- **size of atom or molecule/molecular weight**
- shape of molecules with similar masses (more contact, larger dispersion force)

Linear molecule—larger surface area enhances intermolecular contact and increases dispersion force



n -Pentane (C_5H_{12})
bp = 309.4 K

Spherical molecule—smaller surface area diminishes intermolecular contact and decreases dispersion force

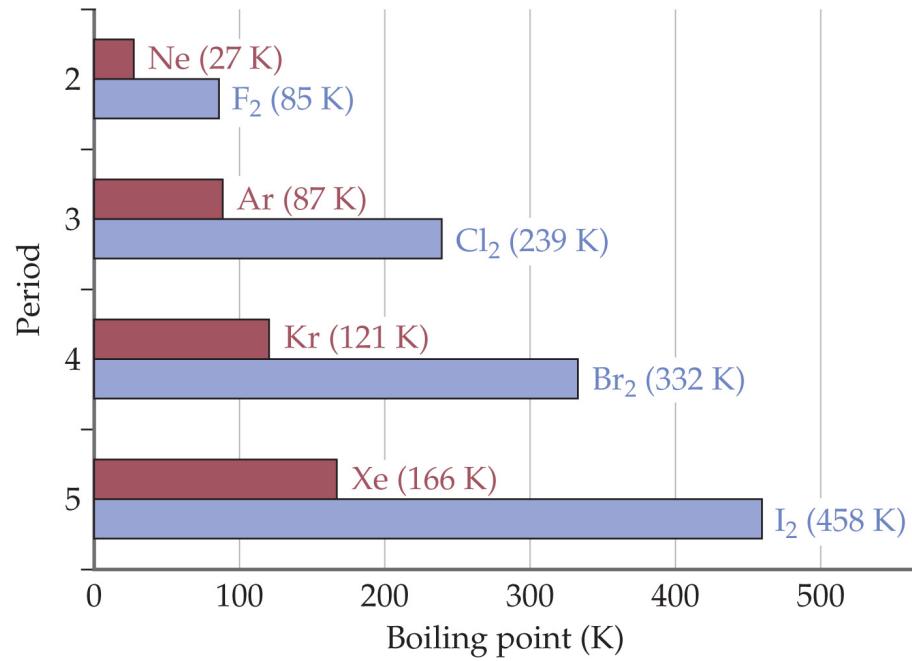


Neopentane (C_5H_{12})
bp = 282.7 K



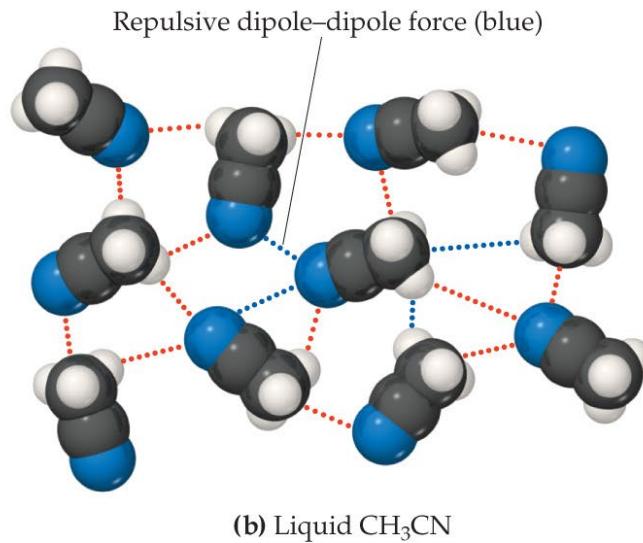
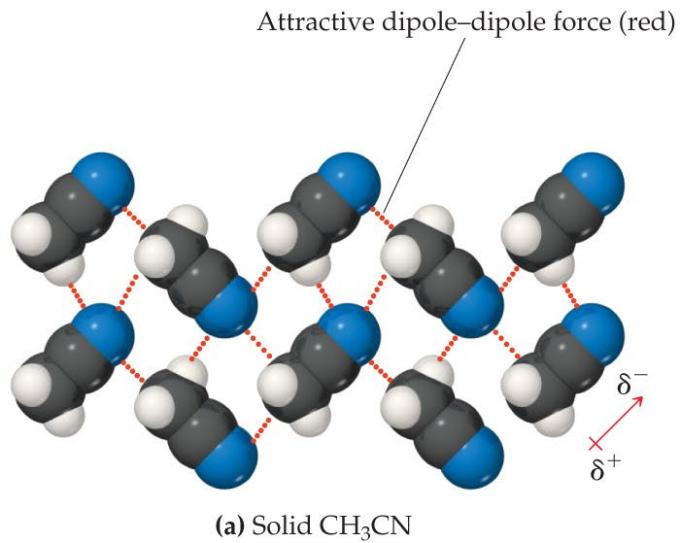
Polarizability & Boiling Point

- If something is **more difficult** to polarize, it has a *lower* boiling point.
- Remember: This means *less* intermolecular force (smaller molecule: lower molecular weight, fewer electrons).

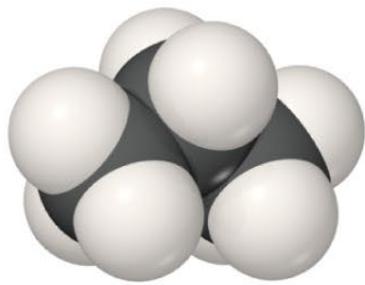


Dipole–Dipole Interactions

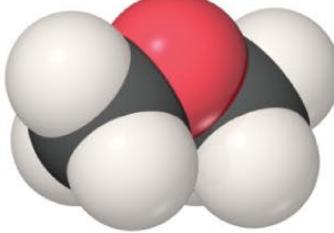
- Polar molecules have a more positive and a more negative end—a dipole (two poles, δ^+ and δ^-).
- The oppositely charged ends attract each other.



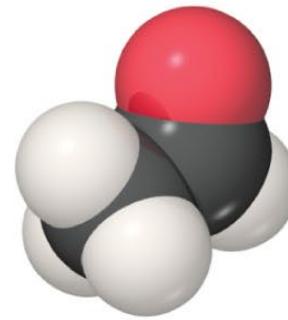
Dipole–Dipole Interactions



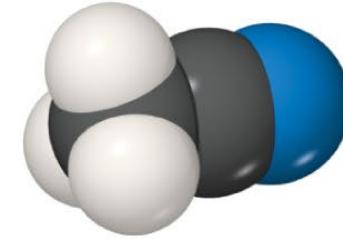
Propane
 $\text{CH}_3\text{CH}_2\text{CH}_3$
MW = 44 amu
 $\mu = 0.1 \text{ D}$
bp = 231 K



Dimethyl ether
 CH_3OCH_3
MW = 46 amu
 $\mu = 1.3 \text{ D}$
bp = 248 K



Acetaldehyde
 CH_3CHO
MW = 44 amu
 $\mu = 2.7 \text{ D}$
bp = 294 K



Acetonitrile
 CH_3CN
MW = 41 amu
 $\mu = 3.9 \text{ D}$
bp = 355 K

Increasing polarity
Increasing strength of dipole–dipole forces

For molecules of approximately equal mass and size, the more polar the molecule, the higher its boiling point.



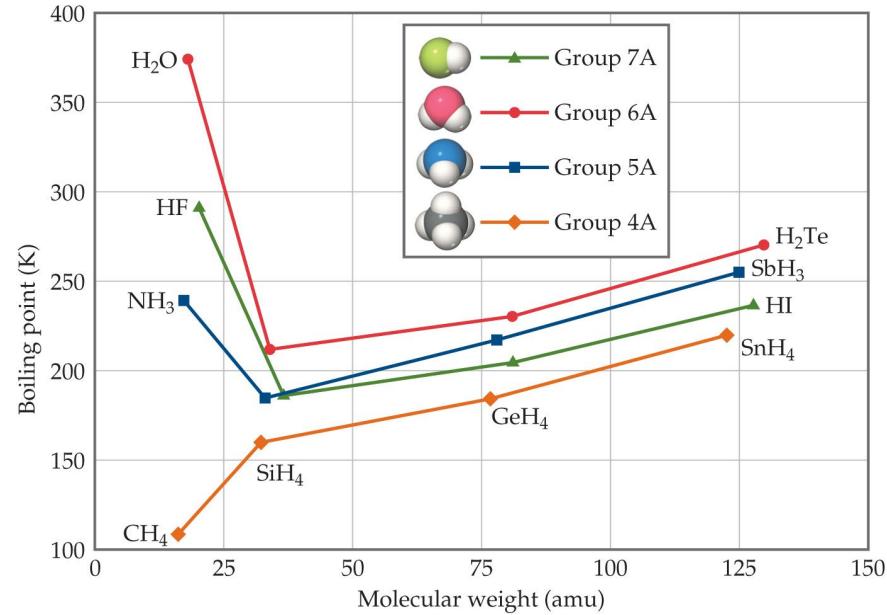
Which Have a Greater Effect: Dipole–Dipole Interactions or Dispersion Forces?

- If two molecules are of comparable size and shape, dipole–dipole interactions will likely be the dominating force.
- If one molecule is much larger than another, dispersion forces will likely determine its physical properties.



What Does This Graph Show Us?

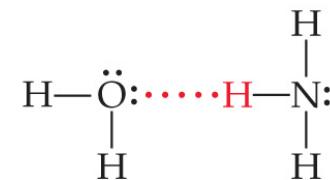
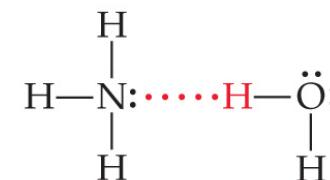
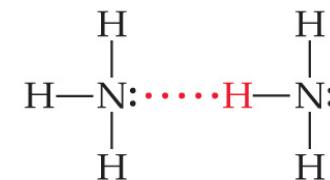
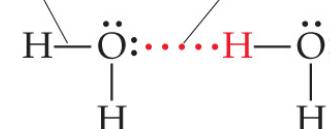
- In a group, the period 3/4/5 elements have higher boiling points as the group member gets larger.
- What happens with the period 2 elements? For group 4A, the trend is continued. What about for the other groups?



Hydrogen Bonding

- The dipole–dipole interactions experienced when H is bonded to N, O, or F are unusually strong.
- We call these interactions **hydrogen bonds**.
- A hydrogen bond is an attraction between a **hydrogen atom** attached to a highly **electronegative atom** and a nearby small electronegative atom in another molecule or chemical group.

Covalent bond,
intramolecular Hydrogen bond,
intermolecular



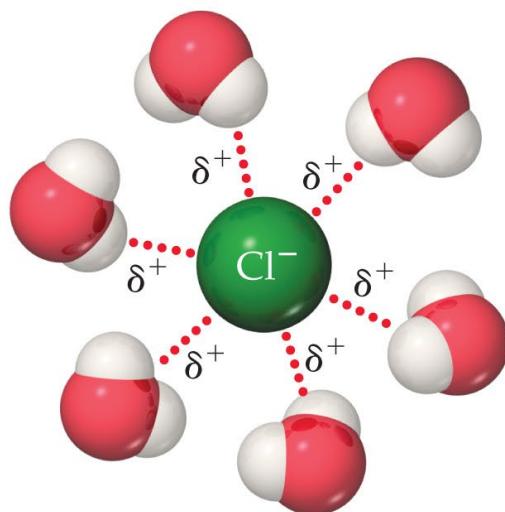
What Forms Hydrogen Bonds?

- Hydrogen bonding arises in part from the high electronegativity of nitrogen, oxygen, and fluorine.
- These atoms interact with a nearly bare nucleus (which contains one proton).

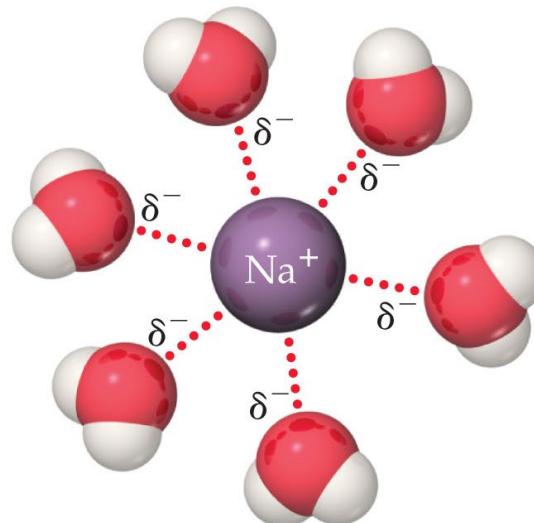


Ion–Dipole Interactions

- Ion–dipole interactions are found in solutions of ions.
- The strength of these forces is what makes it possible for ionic substances to dissolve in polar solvents.



Positive ends of polar molecules are oriented toward negatively charged anion



Negative ends of polar molecules are oriented toward positively charged cation

19) What type(s) of intermolecular forces exist between PH_3 and CO_3^{2-} ?

- A) dispersion forces
- B) dispersion forces and ion-dipole
- C) dispersion forces, ion-dipole, and dipole-dipole
- D) dispersion forces and dipole-dipole
- E) dispersion forces, ion-dipole, dipole-dipole, and hydrogen bonds

Summarizing Intermolecular Forces

Go Figure

Can the energies of multiple dispersion forces between two molecules be larger than the energy of hydrogen bonding between the two molecules?

Type of intermolecular interaction	Atoms Examples: Ne, Ar	Nonpolar molecules Examples: BF ₃ , CH ₄	Polar molecules without OH, NH, or HF groups Examples: HCl, CH ₃ CN	Polar molecules containing OH, NH, or HF groups Examples: H ₂ O, NH ₃	Ionic solids dissolved in polar liquids Examples: NaCl in H ₂ O
Dispersion forces (0.1–30 kJ/mol)	✓	✓	✓	✓	✓
Dipole–dipole interactions (2–15 kJ/mol)			✓	✓	
Hydrogen bonding (10–40 kJ/mol)				✓	
Ion–dipole interactions (>50 kJ/mol)					✓

Figure 11.14 Checklist for determining intermolecular forces. Multiple types of intermolecular forces can be operating in a given substance or mixture. Note that dispersion forces occur in all substances.

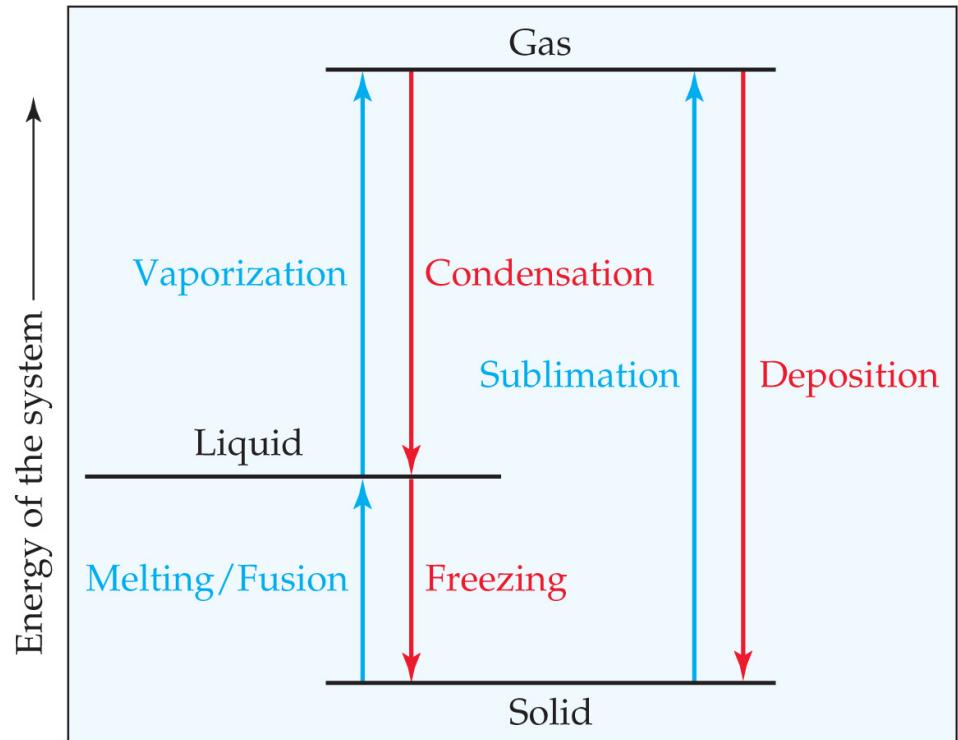
Liquid Properties Affected by Intermolecular Forces

- boiling point (previously discussed) and melting point
- viscosity
- surface tension
- capillary action



Phase Changes

- Conversion from one state of matter to another is called a **phase change**.
- Energy is either added or released in a phase change.
- Phase changes: melting/freezing, vaporizing/condensing, subliming/depositing.

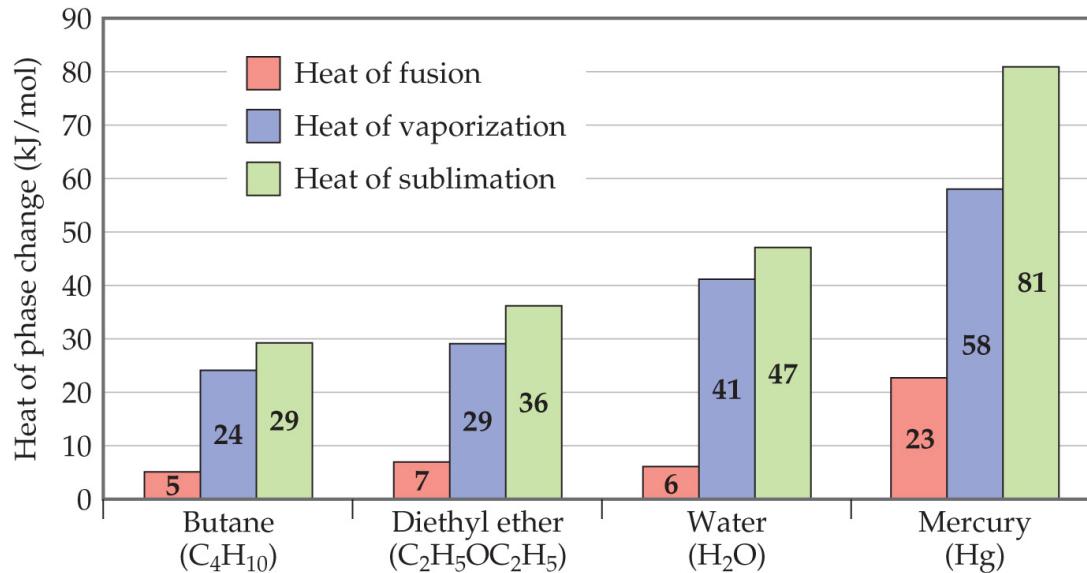


— Endothermic process (energy added to substance)
— Exothermic process (energy released from substance)

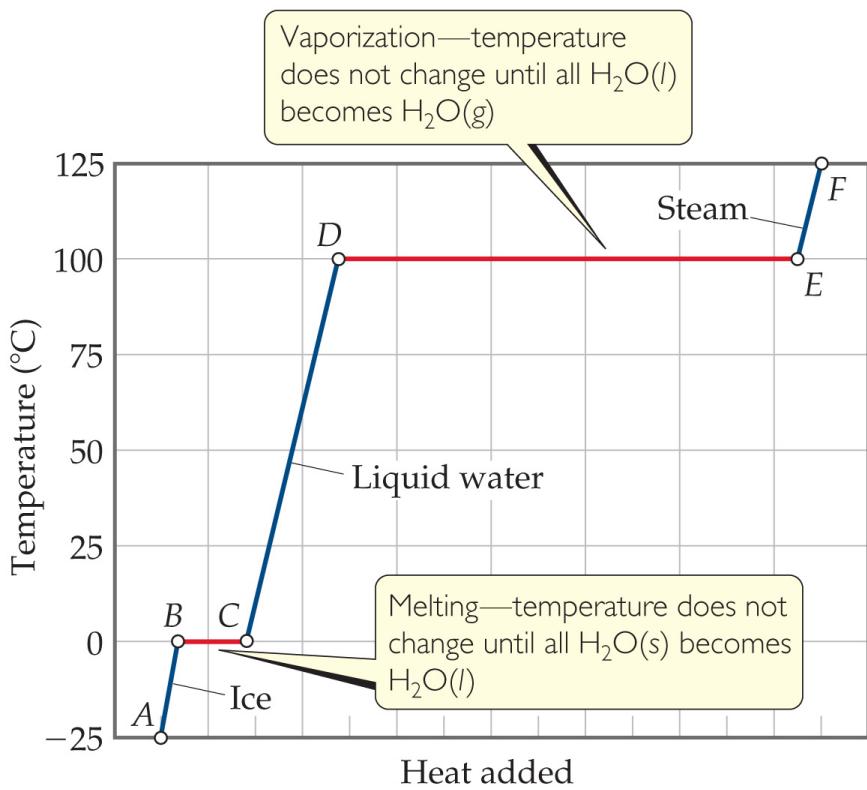


Energy Change & Change of State

- The **heat of fusion** is the energy required to change a solid at its melting point to a liquid.
- The **heat of vaporization** is the energy required to change a liquid at its boiling point to a gas.
- The **heat of sublimation** is the energy required to change a solid directly to a gas.



Heating Curves



- A plot of temperature vs. heat added is called a **heating curve**.
- Within a phase, heat is the product of specific heat, sample mass, and temperature change.
- The temperature of the substance does not rise during a phase change.
- For the phase changes, the product of mass and the heat of fusion or of vaporization is heat.



Supercritical Fluids

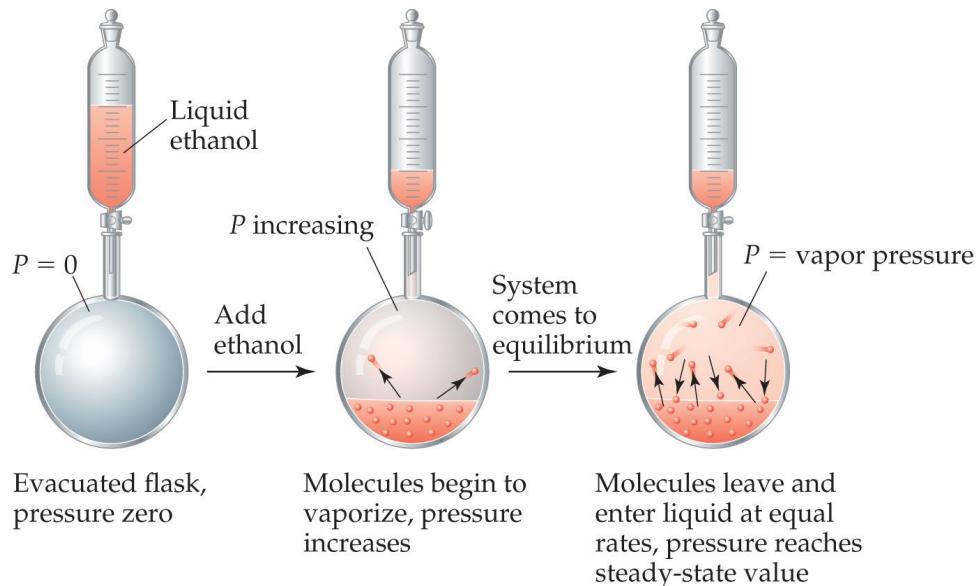
- Gases liquefies when pressure is applied.
- The temperature beyond which a gas *cannot* be compressed is called its **critical temperature**.
The pressure needed to compress the liquid at critical temperature is called **critical pressure**.
- The state beyond this temperature is called a **supercritical fluid**.

Table 11.6 Critical Temperatures and Pressures of Selected Substances

Substance	Critical Temperature (K)	Critical Pressure (atm)
Nitrogen, N ₂	126.1	33.5
Argon, Ar	150.9	48.0
Oxygen, O ₂	154.4	49.7
Methane, CH ₄	190.0	45.4
Carbon dioxide, CO ₂	304.3	73.0
Phosphine, PH ₃	324.4	64.5
Propane, CH ₃ CH ₂ CH ₃	370.0	42.0
Hydrogen sulfide, H ₂ S	373.5	88.9
Ammonia, NH ₃	405.6	111.5
Water, H ₂ O	647.6	217.7



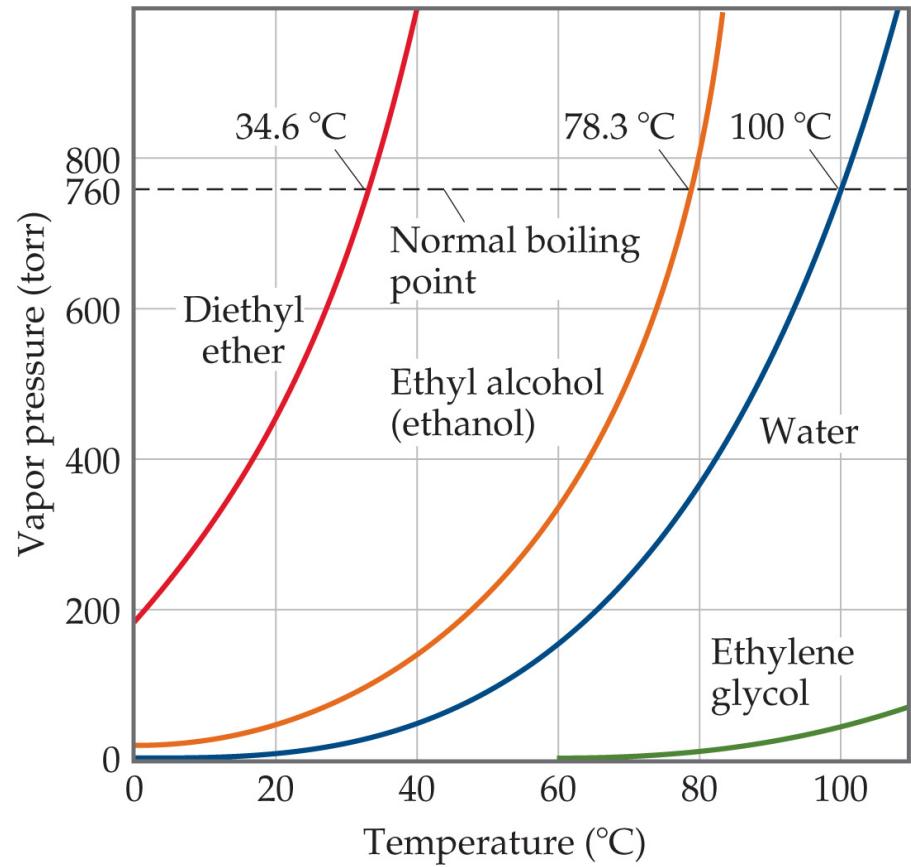
Vapor Pressure



- As more molecules escape the liquid, the pressure they exert increases.
- The liquid and vapor reach a state of **dynamic equilibrium**: liquid molecules evaporate and vapor molecules condense *at the same rate*.

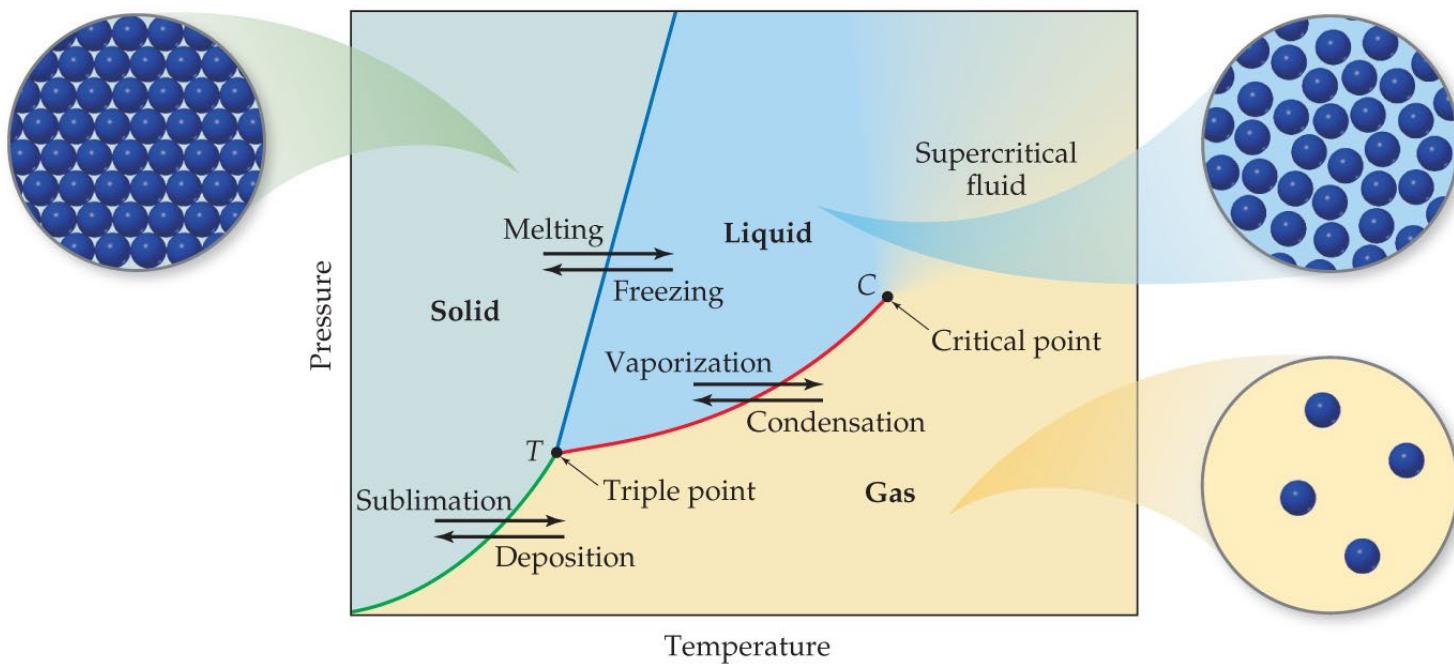
Vapor Pressure

- The **boiling point** of a liquid is the temperature at which its vapor pressure equals atmospheric pressure.
- The **normal boiling point** is the temperature at which its vapor pressure is 760 torr.



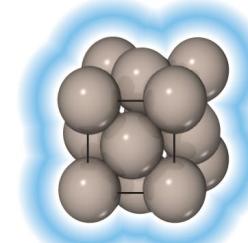
Phase Diagram

- A **phase diagram** is a graph of pressure vs. temperature for a substance. It shows
 - melting, boiling, and sublimation points at different pressures.
 - the triple point and critical point.



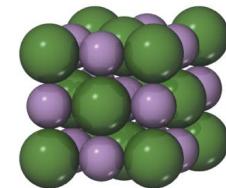
Classifying Solids Based on Bonds

- **Metallic solids** are held together by a “sea” of collectively shared electrons.
- **Ionic solids** are sets of cations and anions mutually attracted to one another.
- **Covalent-network solids** are joined by an extensive network of covalent bonds.
- **Molecular solids** are discrete molecules held together by weak forces.



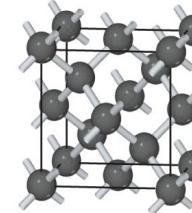
Metallic solids

Extended networks of atoms held together by metallic bonding (Cu, Fe)



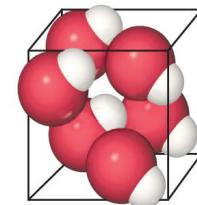
Ionic solids

Extended networks of ions held together by ion-ion interactions (NaCl, MgO)



Covalent-network solids

Extended networks of atoms held together by covalent bonds (C, Si)



Molecular solids

Discrete molecules held together by intermolecular forces (HBr, H₂O)



Gases

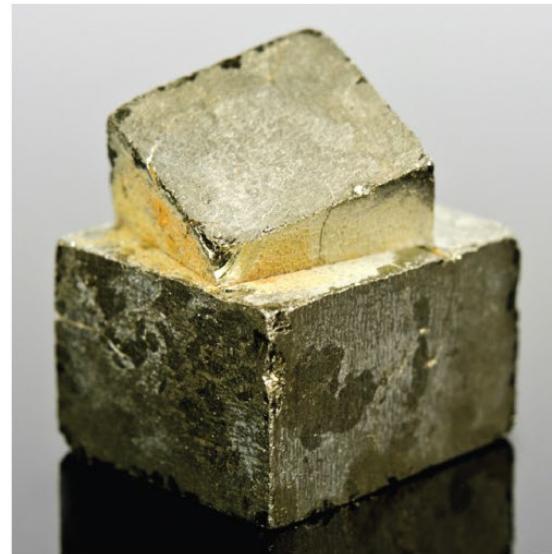
Two Other Types of Solids

- **Polymers** contain long chains of atoms connected by covalent bonds; the chains can be connected to other chains by weak forces. These molecules have different properties than small molecules or metallic or ionic compounds.
- **Nanomaterials** are crystalline compounds with the crystals on the order of 1–100 nm; this gives them very different properties than larger crystalline materials.



One Organization of Solids

- Solids with a regular repeating pattern of atoms are **crystalline**.
- **Amorphous** solids are characterized by a distinct lack of order in the arrangement of atoms.
- Since crystalline solids have a regular pattern, they are of more interest to most chemists.



Iron pyrite (FeS₂), a crystalline solid



Obsidian (typically KAlSi₃O₈), an amorphous solid



Unit Cell

- The basis of a repeating pattern is the unit cell.
- The structure of a crystalline solid is defined by
 - the size and shape of the unit cell.
 - the locations of atoms within the unit cell.

Crystal (晶体结构) = lattice(点阵) +motif (基元)

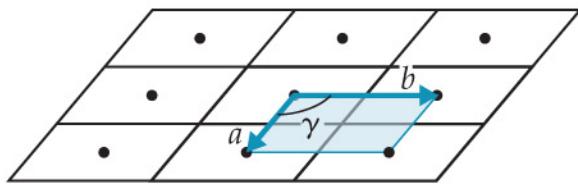


Lattice Points

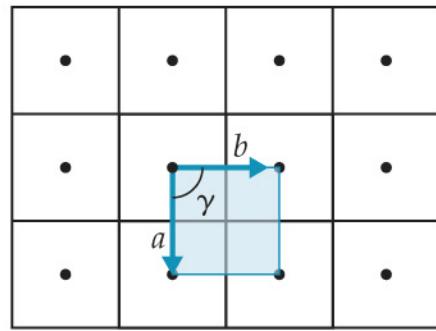
- Positions that define the overall structure of the crystalline compound are called **lattice points**.
- Each lattice point has an identical environment.
- **Lattice vectors** connect the points and define the unit cell.
- The next slide shows how this works for five different two-dimensional lattices.



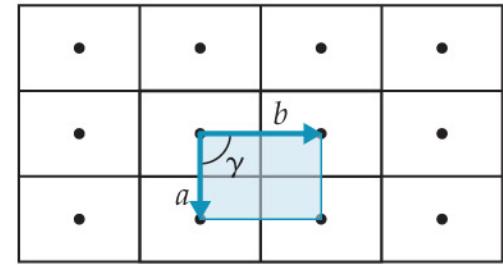
2-D Lattices



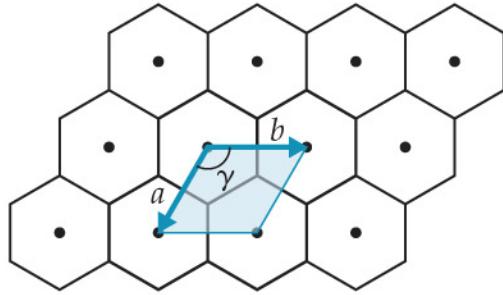
Oblique lattice ($a \neq b, \gamma = \text{arbitrary}$)



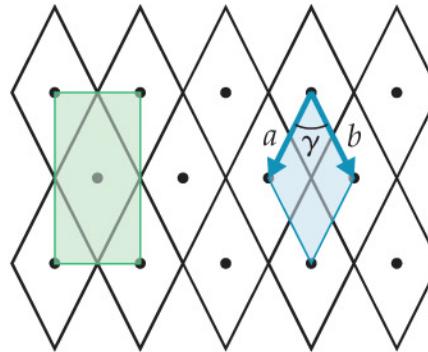
Square lattice ($a = b, \gamma = 90^\circ$)



Rectangular lattice ($a \neq b, \gamma = 90^\circ$)



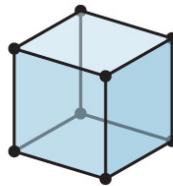
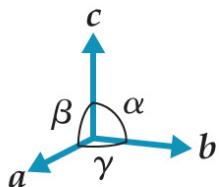
Hexagonal lattice ($a = b, \gamma = 120^\circ$)



Rhombic lattice ($a = b, \gamma = \text{arbitrary}$)
Centered rectangular lattice

3-D Crystal Lattices

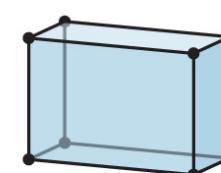
- There are seven basic three-dimensional lattices: cubic, tetragonal, orthorhombic, rhombohedral, hexagonal, monoclinic, and triclinic.



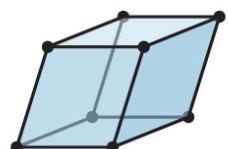
Cubic
 $a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$



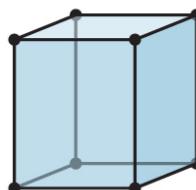
Tetragonal
 $a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



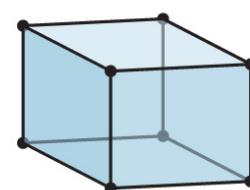
Orthorhombic
 $a \neq b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



Rhombohedral
 $a = b = c$
 $\alpha = \beta = \gamma \neq 90^\circ$



Hexagonal
 $a = b \neq c$
 $\alpha = \beta = 90^\circ, \gamma = 120^\circ$



Monoclinic
 $a \neq b \neq c$
 $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$

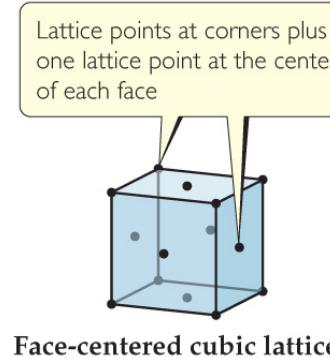
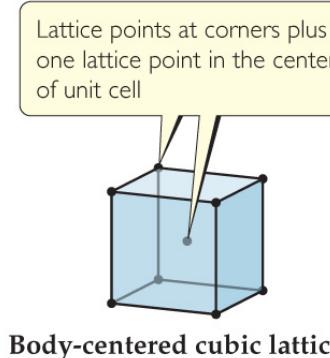
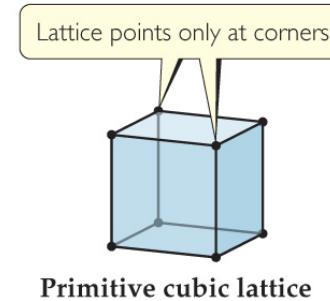


Triclinic
 $a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma$



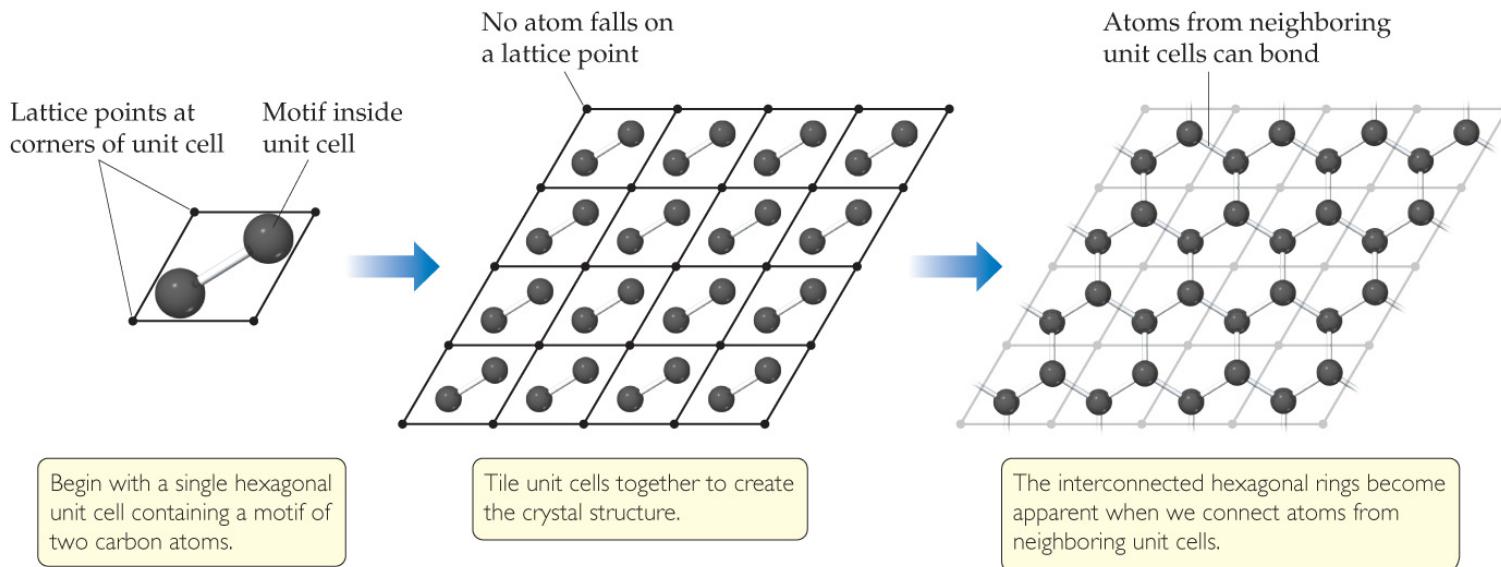
Primitive vs. Centered Lattices

- **Primitive lattices**
lattice points at each corner.
- **Centered lattices**
has one lattice point at the center (**body-center**), or has one lattice point at each face (**face-center**).



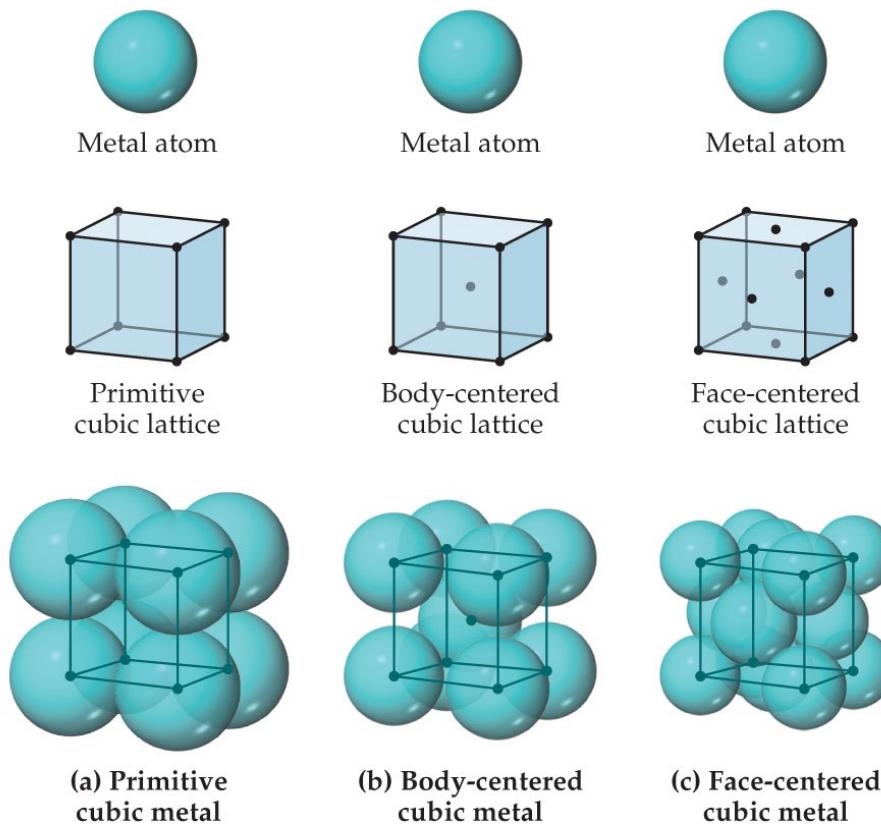
Motifs

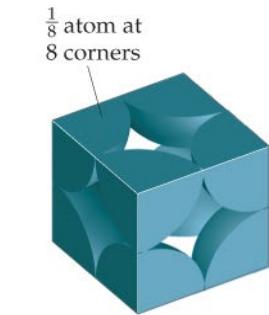
Sometimes, the atoms are *not* on the lattice points, but the overall structure follows a particular unit cell. The groups of atoms that define the overall structure is called a **motif**.



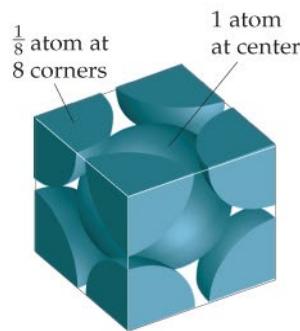
Metallic Structure

- The structures of many metals conform to one of the cubic unit cells: simple cubic, body-centered cubic, or face-centered cubic.

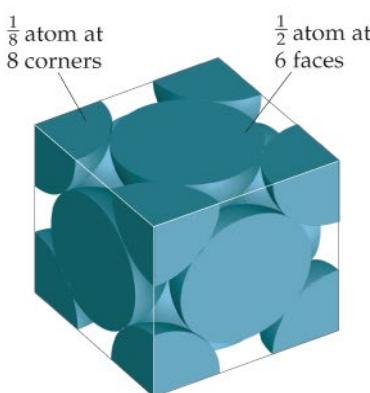




(a) Primitive cubic metal
1 atom per unit cell



(b) Body-centered cubic metal
2 atoms per unit cell



(c) Face-centered cubic metal
4 atoms per unit cell

Cubic Structures

- Not every part of an atom on a lattice point is completely within that unit cell. One can determine how many atoms are within each unit cell.
- Eight cubes meet at a corner, therefore only $1/8$ of that corner atom is within any one unit cell meeting there.
- Two cubes meet at a face, therefore only $1/2$ of that face atom is within any one unit cell meeting there.
- A body-centered atom is entirely within the unit cell.



Alloys

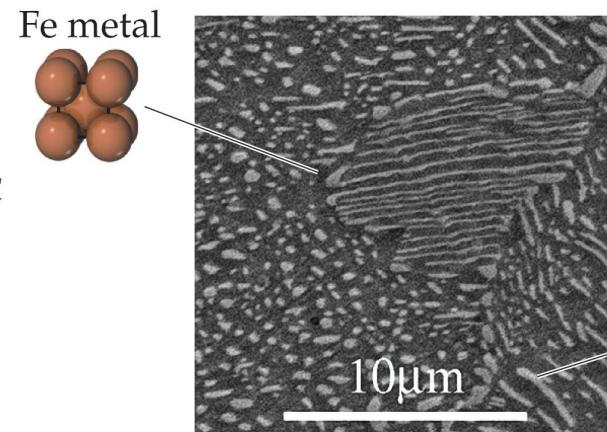
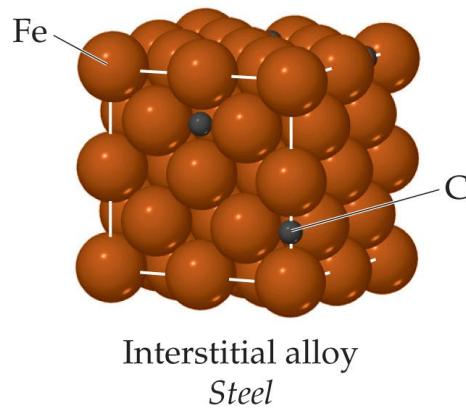
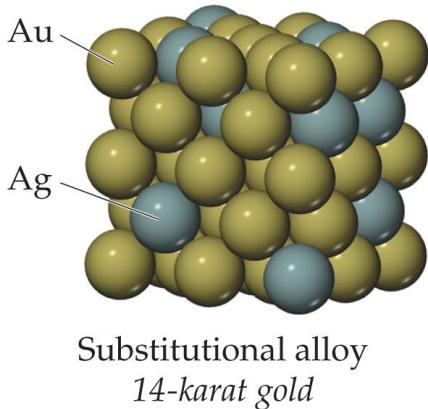
- **Alloys** are materials that contain more than one element and have the characteristic properties of metals.
- It is an important means employed to change the properties of certain metals.

Table 12.2 Some Common Alloys

Name	Primary Element	Typical Composition (by Mass)	Properties	Uses
Wood's metal	Bismuth	50% Bi, 25% Pb, 12.5% Sn, 12.5% Cd	Low melting point (70 °C)	Fuse plugs, automatic sprinklers
Yellow brass	Copper	67% Cu, 33% Zn	Ductile, takes polish	Hardware items
Bronze	Copper	88% Cu, 12% Sn	Tough and chemically stable in dry air	Important alloy for early civilizations
Stainless steel	Iron	80.6% Fe, 0.4% C, 18% Cr, 1% Ni	Resists corrosion	Cookware, surgical instruments
Plumber's solder	Lead	67% Pb, 33% Sn	Low melting point (275 °C)	Soldering joints
Sterling silver	Silver	92.5% Ag, 7.5% Cu	Bright surface	Tableware
Dental amalgam	Silver	70% Ag, 18% Sn, 10% Cu, 2% Hg	Easily worked	Dental fillings
Pewter	Tin	92% Sn, 6% Sb, 2% Cu	Low melting point (230 °C)	Dishes, jewelry

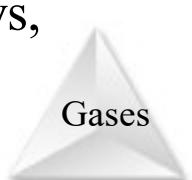


Types of Alloys



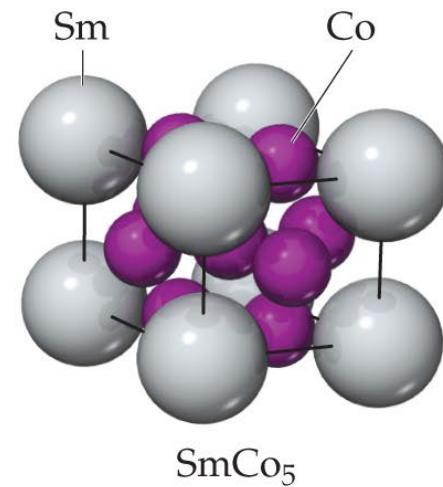
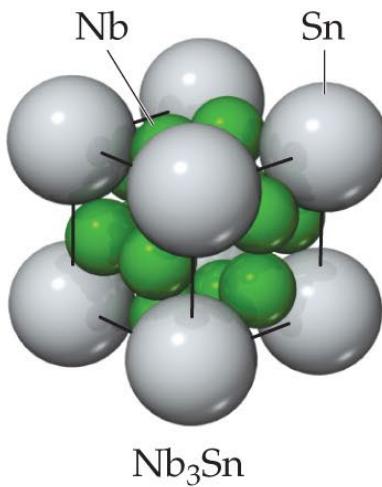
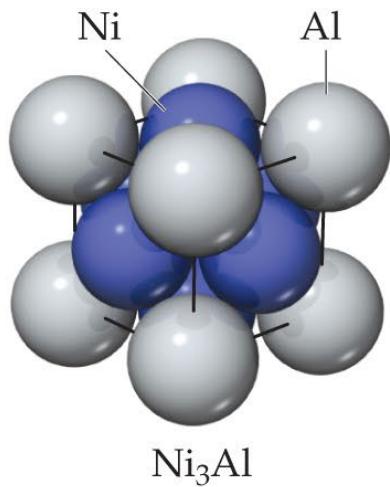
- **Substitutional alloys:** A second element takes the place of a metal atom.
- **Interstitial alloys:** A second element fills a space in the lattice of metal atoms.
- **Heterogeneous alloys:** components not dispersed uniformly

Alloys types: Substitutional alloys, Interstitial alloys, Heterogeneous alloys, Intermetallic Compounds



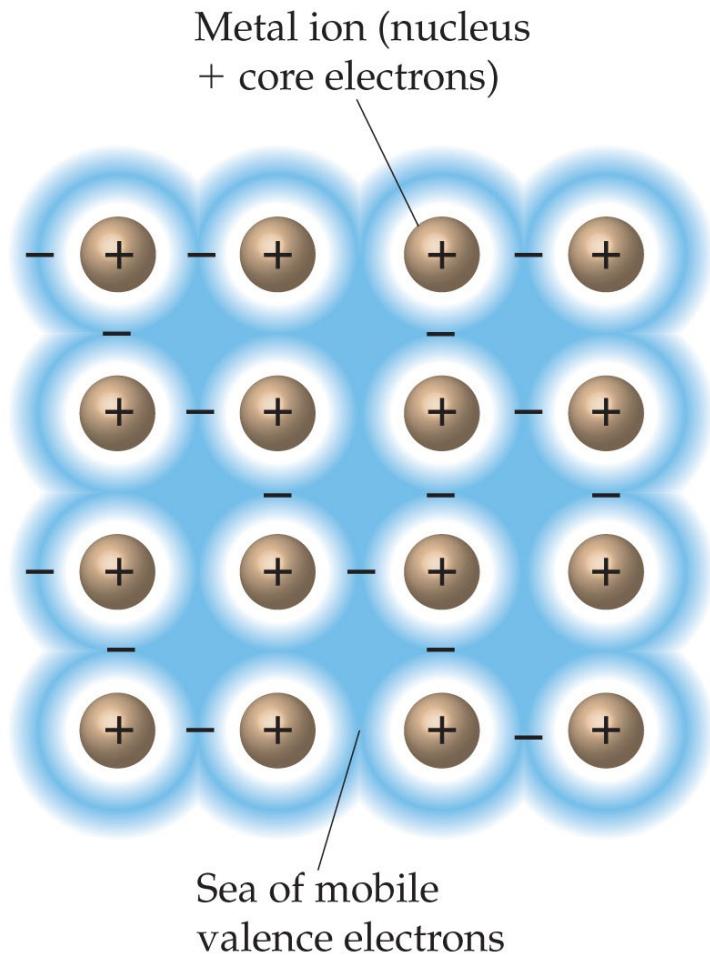
Intermetallic Compounds

- compounds, *not* mixtures
- distinct properties, definite composition (since they are compounds)
- ordered, rather than randomly distributed



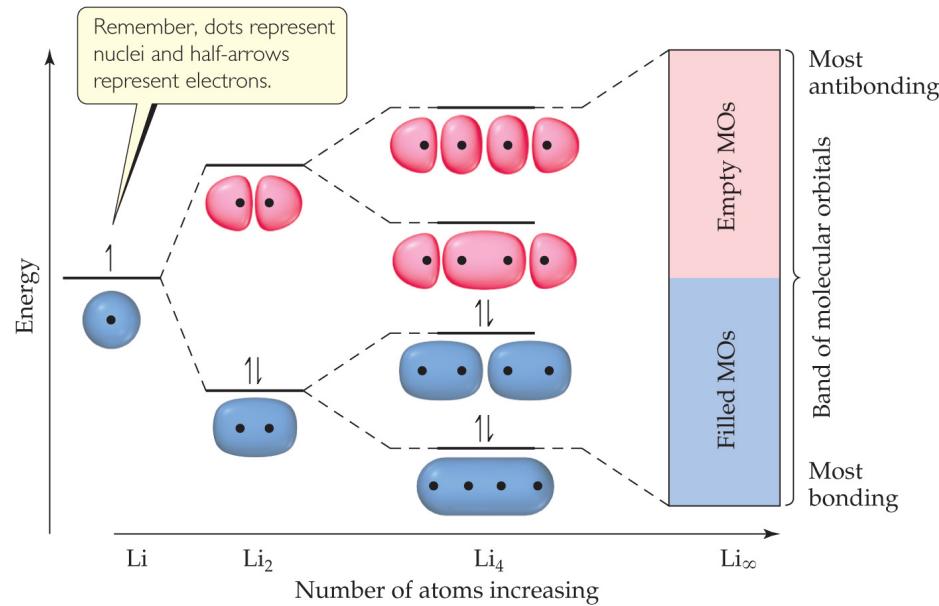
Metallic Bonding

- One can think of a metal as a group of cations suspended in a sea of electrons.
- The electrical and thermal conductivity, ductility, and malleability of metals is explained by this model.



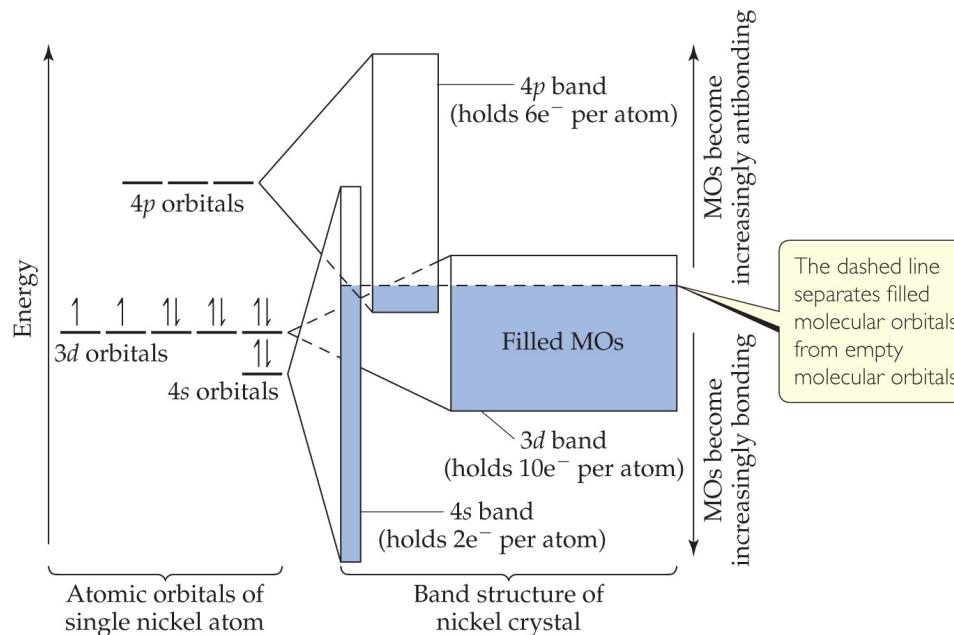
A Molecular-Orbital Approach

As the number of atoms in a chain increases, the energy gap between the bonding orbitals and between the antibonding orbitals disappears, resulting in a continuous band of energy. The approach seen here only takes into account s-orbital population.



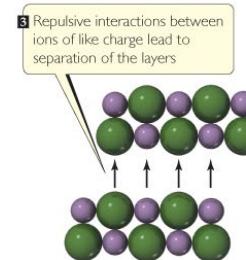
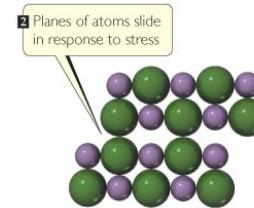
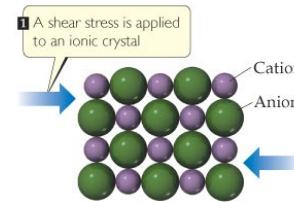
MO Approach with More Orbitals

- Most metals have d and p orbitals to consider.
- Their MO diagrams lead to more bands that better explain conductivity and other properties of metals.



Ionic Solids

- In ionic solids, the lattice comprises alternately charged ions.
- Ionic solids have very high melting and boiling points and are quintessential crystals.



(a)

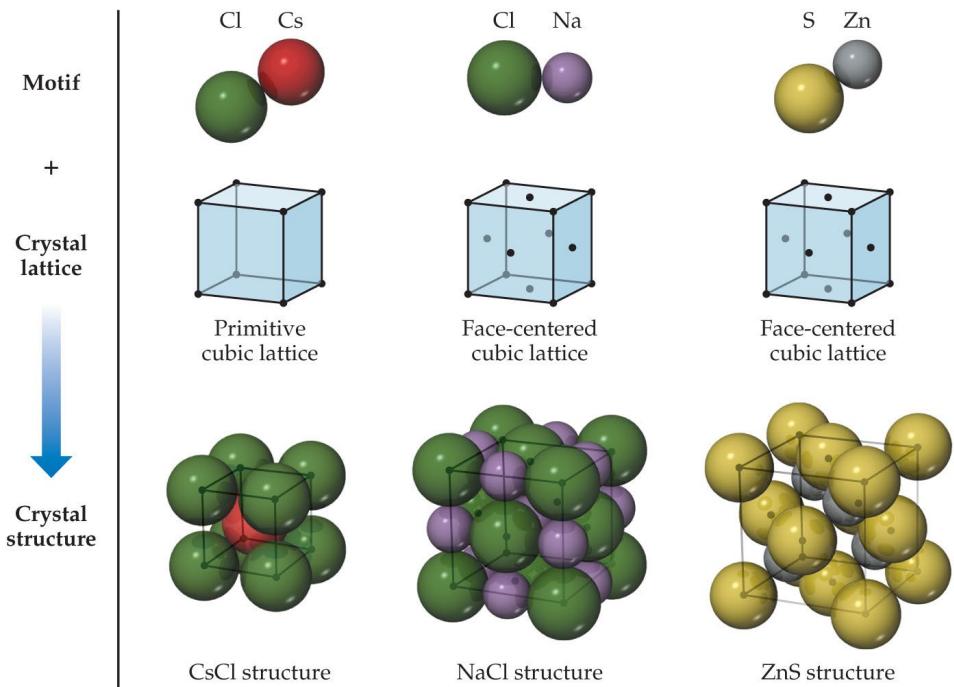


(b)



- Most favorable structures have cation–anion distances as close as possible, but the anion–anion and cation–cation distances are maximized.
- Three common structures for 1:1 salts:
 - CsCl structure
 - NaCl (rock salt) structure
 - zinc blende (ZnS) structure

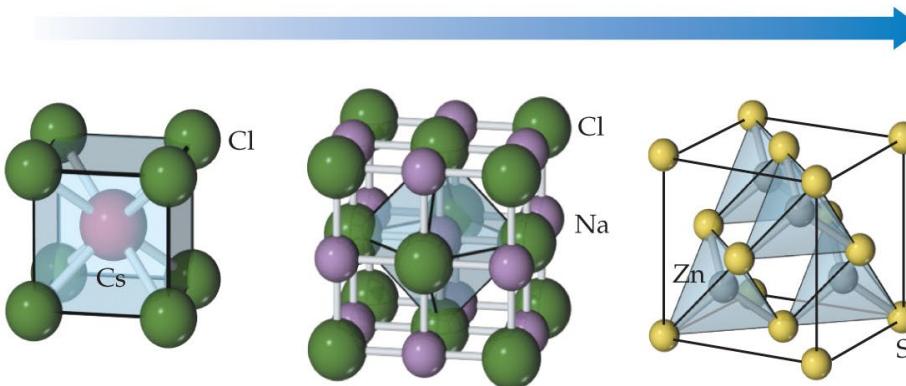
Ionic Solids



Effect of Ion Size on Structure

- The size of the cation compared to the anion (radius ratio) is the major factor in which structure is seen for ionic compounds.

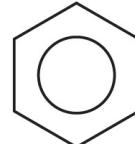
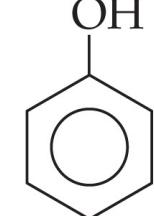
Decreasing r_+/r_-



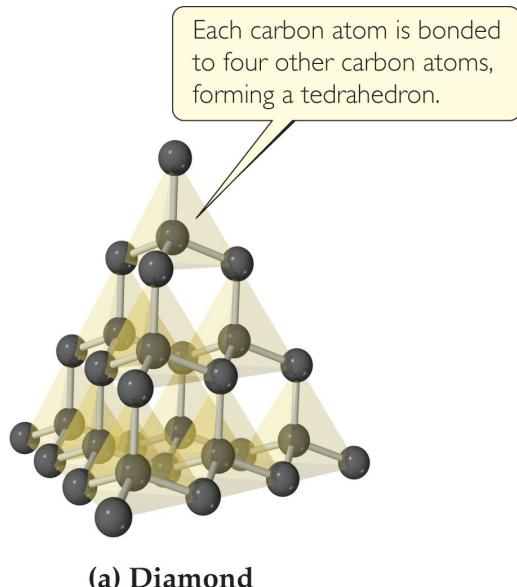
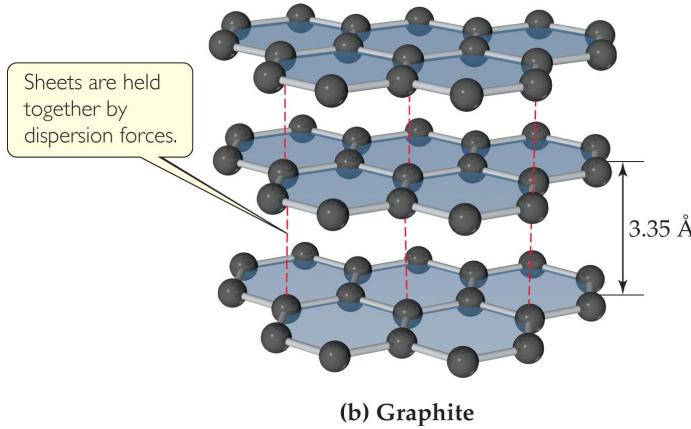
	CsCl	NaCl	ZnS
Cation radius, r_+ (Å)	1.81	1.16	0.88
Anion radius, r_- (Å)	1.67	1.67	1.70
r_+/r_-	1.08	0.69	0.52
Cation coordination number	8	6	4
Anion coordination number	8	6	4

Molecular Solids

- Consist of atoms or molecules held together by weaker forces (dispersion, dipole–dipole, or hydrogen bonds).
- Shape (ability to stack) matters for some physical properties, like boiling point.

		
Benzene	Toluene	Phenol
Melting point (°C)	5	–95
Boiling point (°C)	80	111

Covalent-Network Solids

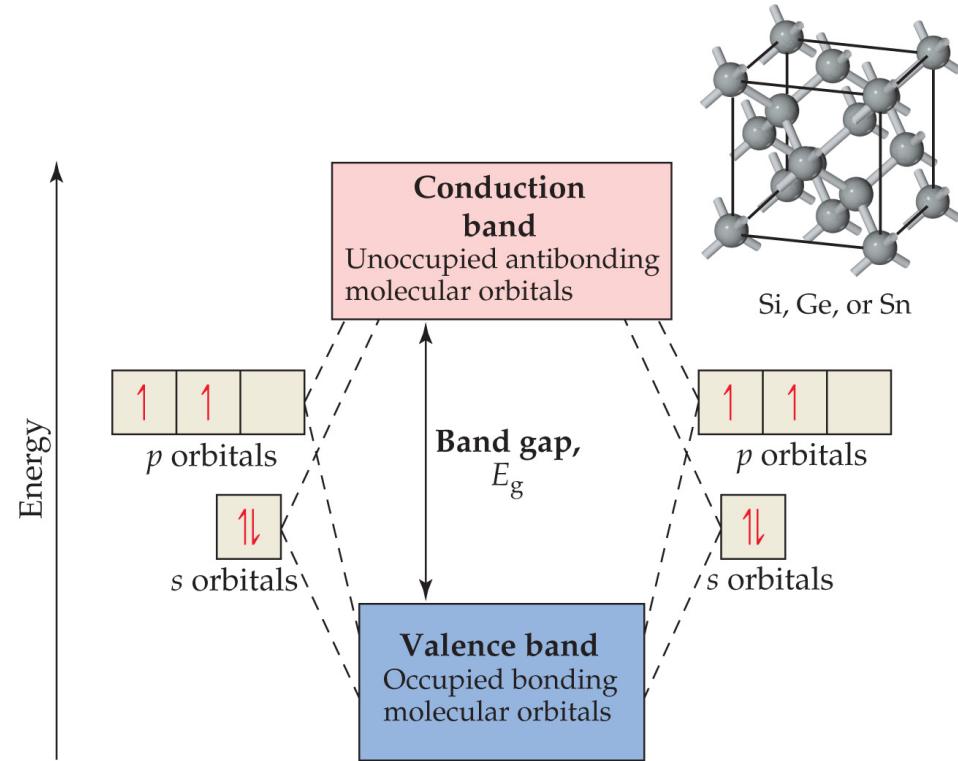


- Atoms are covalently bonded over large network distances with regular patterns of atoms.
- Tend to have higher melting and boiling points.
- Diamond is an example.



Semiconductors

- They have a gap between the occupied MOs (valence band) and the unoccupied ones (conduction band).
- Electrons must enter the conduction band for electron transfer.
- Group IVA elements have gaps between the bands of 0.08 to 3.05 eV (7 to 300 kJ/mol).



Note: Band gaps over 3.5 eV lead to the material being an insulator.



What Forms a Semiconductor?

- Among elements, only Group IVA, **all of which have 4 valence electrons**, are semiconductors.
- Inorganic semiconductors (like GaAs) tend to have an average of 4 valence electrons (3 for Ga, 5 for As).

Table 12.4 Band Gaps of Select Elemental and Compound Semiconductors

Material	Structure Type	E_g , eV [†]						
Si	Diamond	1.11						
AlP	Zinc blende	2.43		13 Al	14 Si	15 P		
Ge	Diamond	0.67	30 Zn	31 Ga	32 Ge	33 As	34 Se	
GaAs	Zinc blende	1.43						
ZnSe	Zinc blende	2.58	48 Cd	49 In	50 Sn	51 Sb	52 Te	
CuBr	Zinc blende	3.05						
Sn [‡]	Diamond	0.08						
InSb	Zinc blende	0.18						
CdTe	Zinc blende	1.50						

[†] Band gap energies are room temperature values, $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$.

[‡] These data are for gray tin, the semiconducting allotrope of tin. The other allotrope, white tin, is a metal.



30) The class of semiconductors, known as elemental, has special features. These are _____.

- A) band gap and individual element valence electrons
- B) periodical table grouping and diamond crystal structure
- C) tetrahedral coordination geometry and sp^2 hybrid orbitals
- D) overlapping hybrid orbitals and filled conduction bands
- E) none of the above

