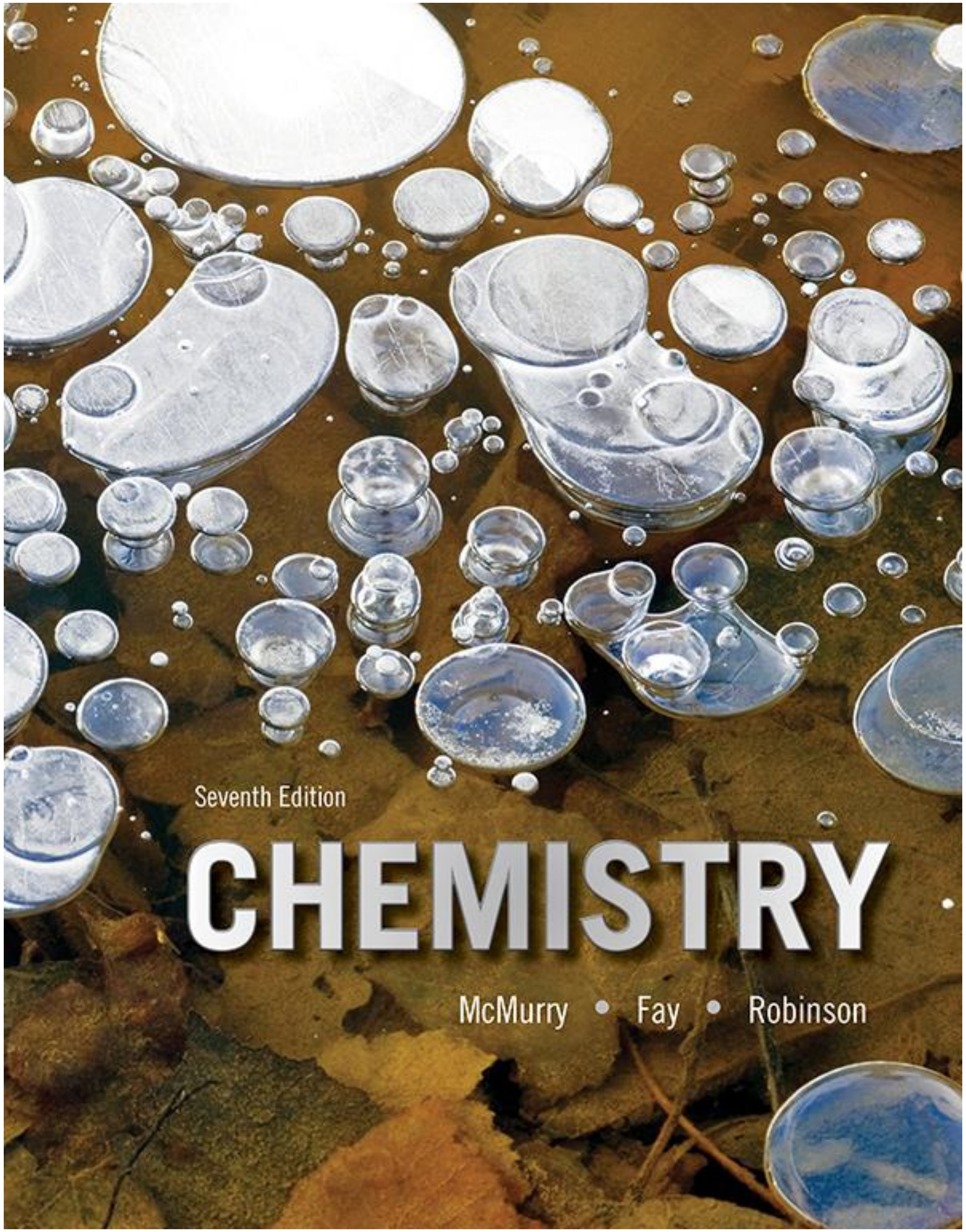

Lecture Presentation

Chapter 11

Liquids, Solids, and Phase Changes

John E. McMurry
Robert C. Fay

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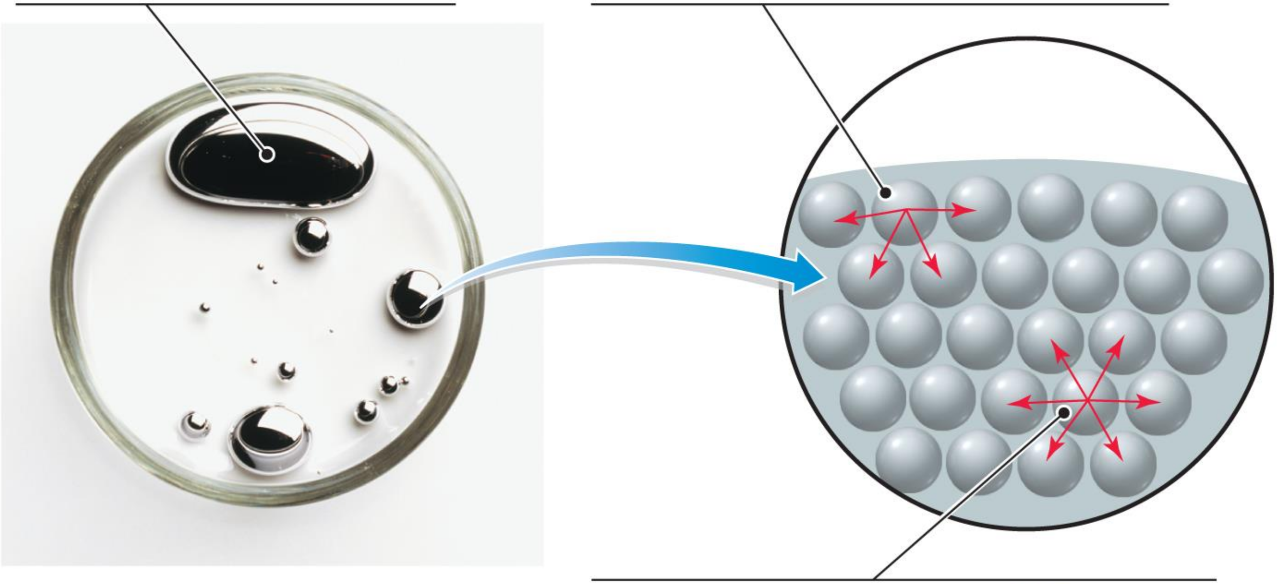
John E. McMurry, Robert C. Fay, Jill Robinson

Properties of Liquids

Viscosity: The measure of a liquid’s resistance to flow

Surface Tension: The resistance of a liquid to spread out and increase its surface area



Surface tension causes these drops of liquid mercury to form beads.

Molecules or atoms on the **surface** feel attractive forces on only one side and are thus drawn in toward the liquid.

Molecules or atoms in the **middle** of a liquid are attracted equally in all directions.

Properties of Liquids

Viscosity: The measure of a liquid’s resistance to flow

Surface Tension: The resistance of a liquid to spread out and increase its surface area

Properties of Liquids

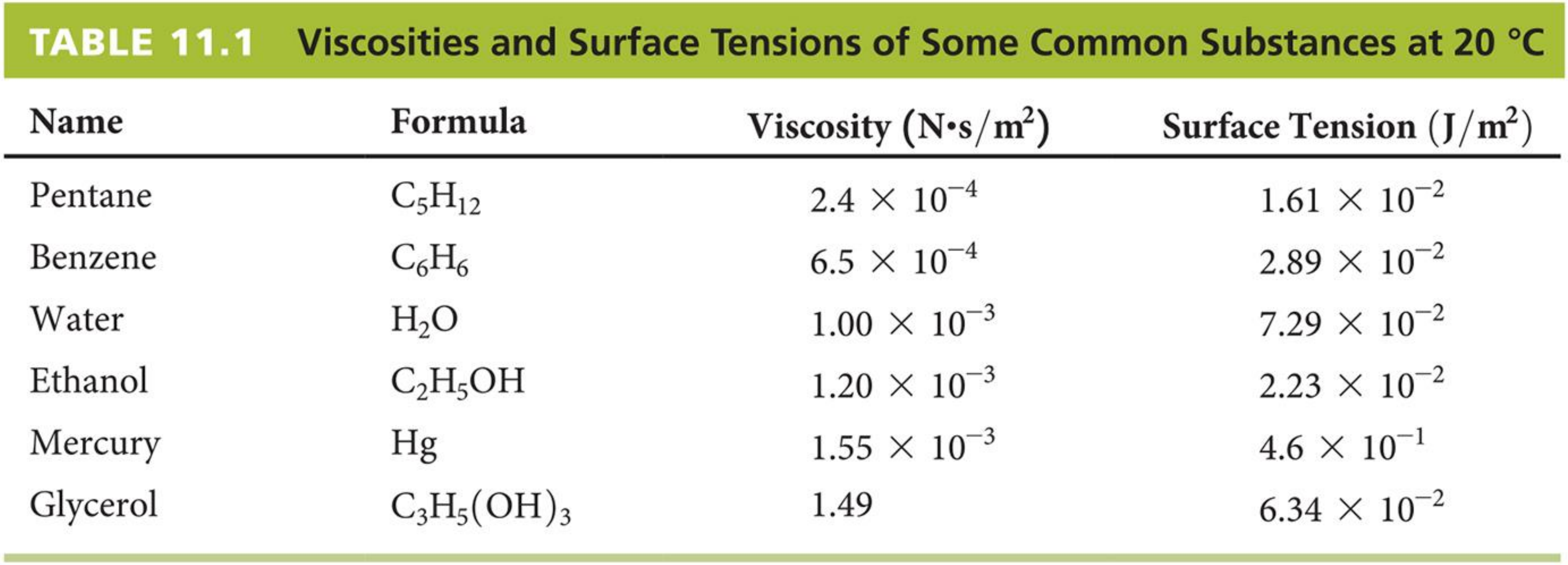


TABLE 11.1 Viscosities and Surface Tensions of Some Common Substances at 20 °C

Name	Formula	Viscosity ($N \cdot s/m^2$)	Surface Tension (J/m^2)
Pentane	C_5H_{12}	2.4×10^{-4}	1.61×10^{-2}
Benzene	C_6H_6	6.5×10^{-4}	2.89×10^{-2}
Water	H_2O	1.00×10^{-3}	7.29×10^{-2}
Ethanol	C_2H_5OH	1.20×10^{-3}	2.23×10^{-2}
Mercury	Hg	1.55×10^{-3}	4.6×10^{-1}
Glycerol	$C_3H_5(OH)_3$	1.49	6.34×10^{-2}

Phase Changes between Solids, Liquids, and Gases

Phase Change (State Change): A change in the physical form but not the chemical identity of a substance

Fusion (melting): Solid to liquid

Freezing: Liquid to solid

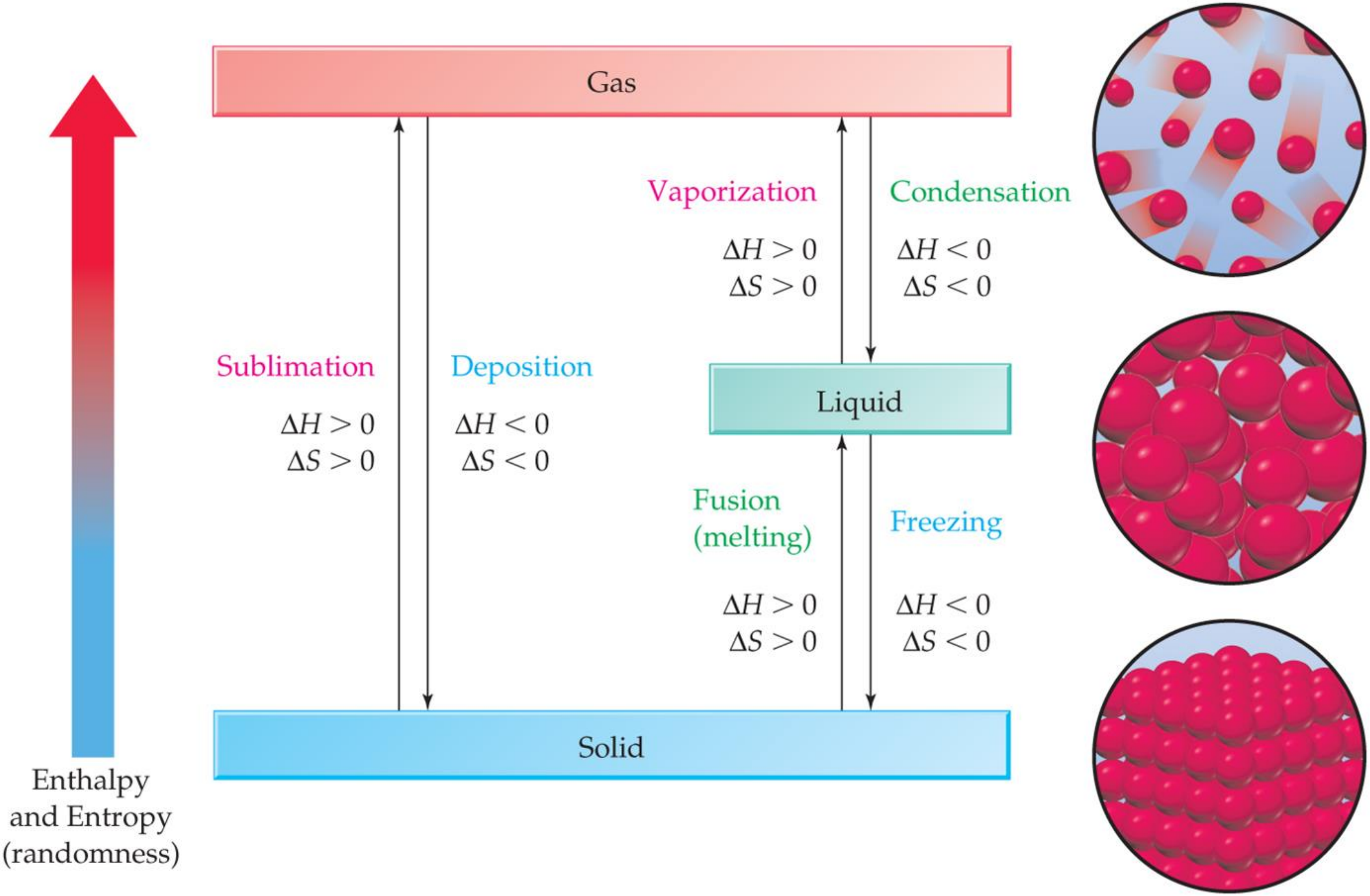
Vaporization: Liquid to gas

Condensation: Gas to liquid

Sublimation: Solid to gas

Deposition: Gas to solid

Phase Changes between Solids, Liquids, and Gases



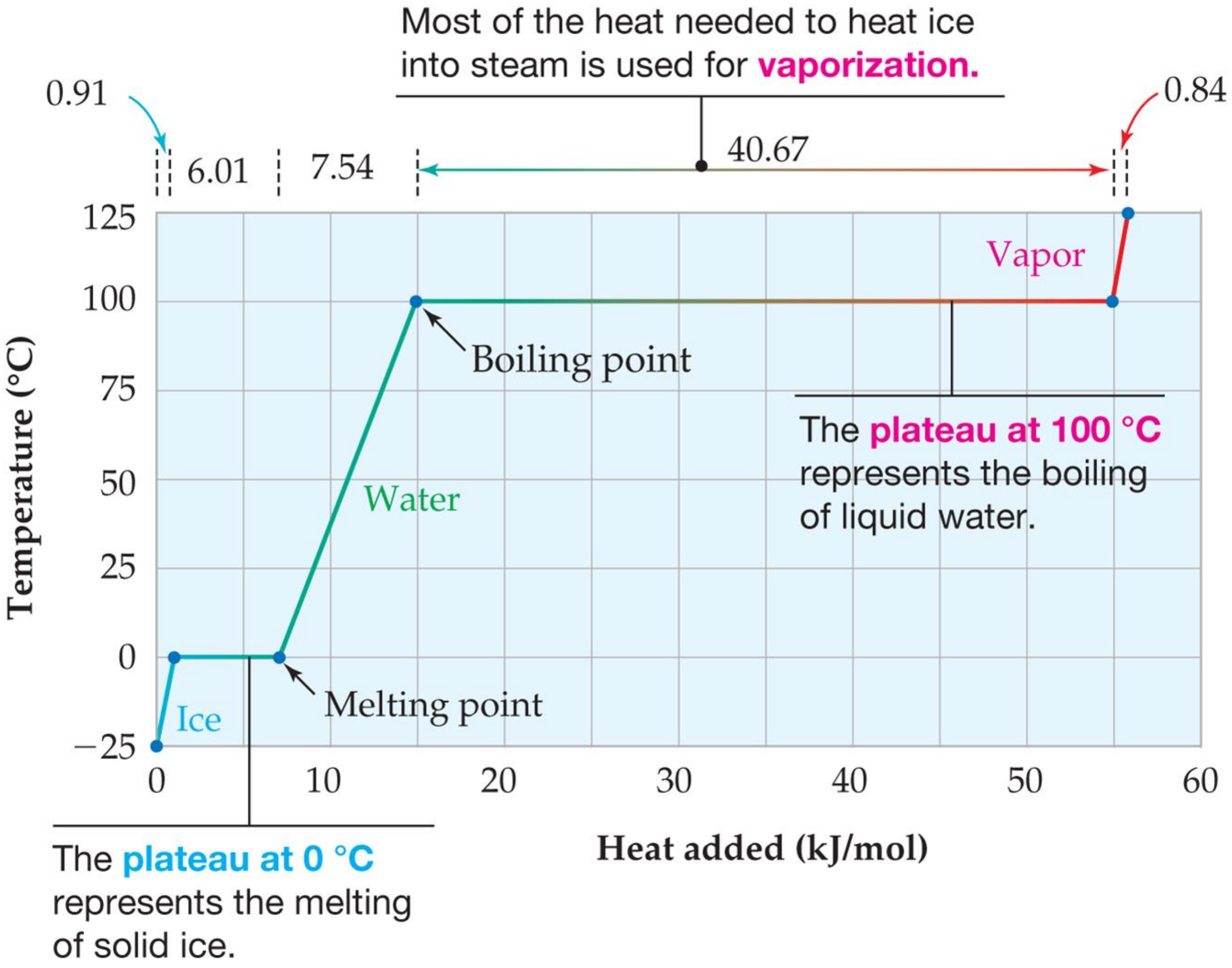
Phase Changes between Solids, Liquids, and Gases

Heat (Enthalpy) of Fusion (ΔH_{fusion}): The amount of energy required to overcome enough intermolecular forces to convert a solid to a liquid

Heat (Enthalpy) of Vaporization (ΔH_{vap}): The amount of energy required to overcome enough intermolecular forces to convert a liquid to a gas

Phase Changes between Solids, Liquids, and Gases

Heating Curve for Water


Most of the heat needed to heat ice into steam is used for **vaporization.**

The **plateau at 100 °C** represents the boiling of liquid water.

The **plateau at 0 °C** represents the melting of solid ice.

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Phase Changes between Solids, Liquids, and Gases

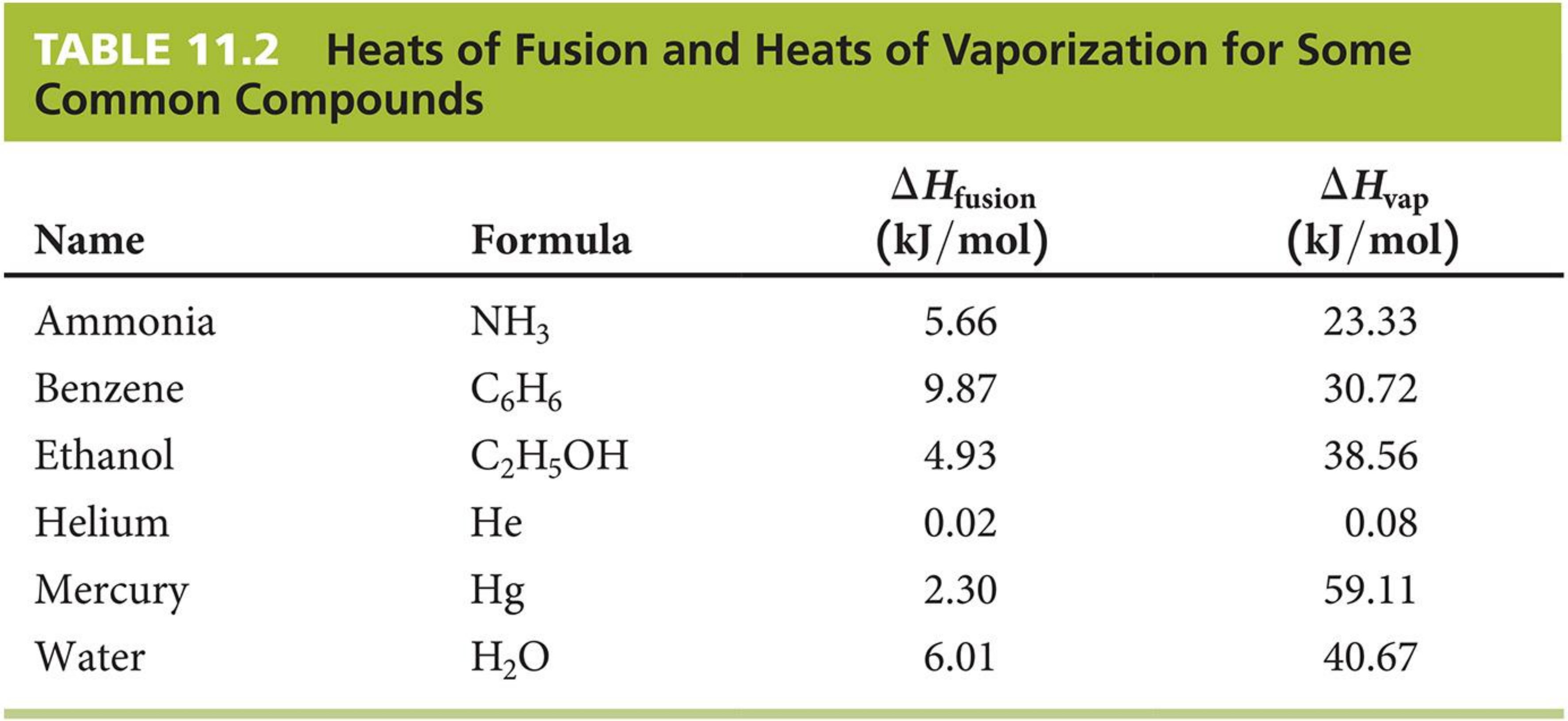
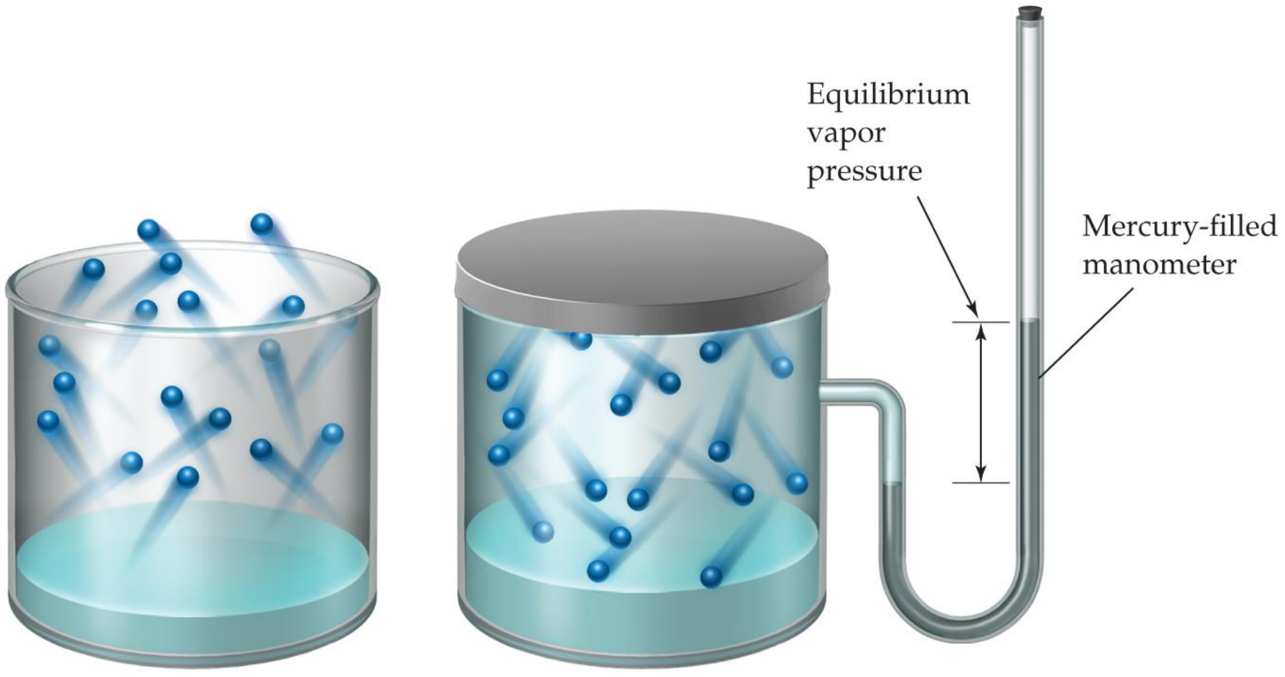


TABLE 11.2 Heats of Fusion and Heats of Vaporization for Some Common Compounds

Name	Formula	ΔH_{fusion} (kJ/mol)	ΔH_{vap} (kJ/mol)
Ammonia	NH_3	5.66	23.33
Benzene	C_6H_6	9.87	30.72
Ethanol	C_2H_5OH	4.93	38.56
Helium	He	0.02	0.08
Mercury	Hg	2.30	59.11
Water	H_2O	6.01	40.67

Evaporation, Vapor Pressure, and Boiling Point

Vapor Pressure: The partial pressure of a gas in equilibrium with a liquid at a constant temperature



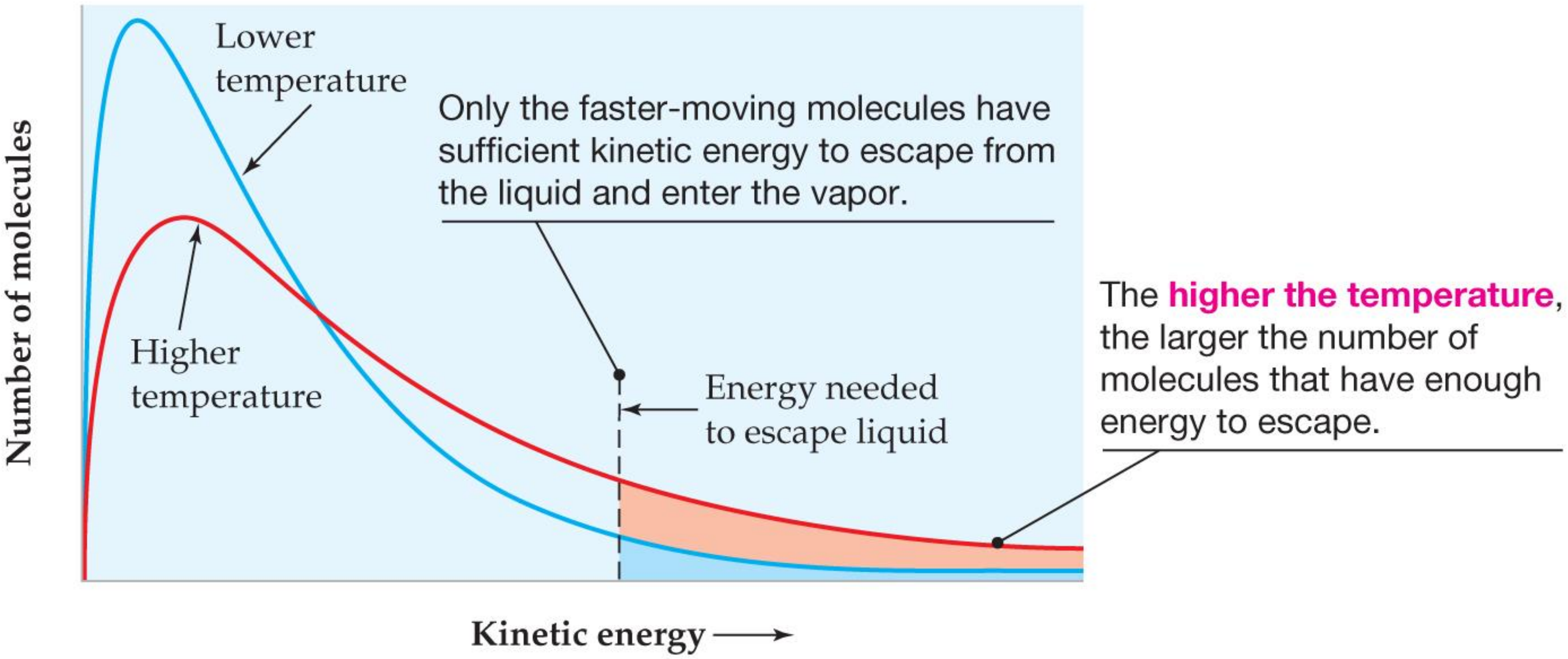
A liquid sitting for a length of time in an open container evaporates, but …

… a liquid sitting in a closed container causes a rise in pressure.

Evaporation, Vapor Pressure, and Boiling Point

Vapor Pressure: The partial pressure of a gas in equilibrium with a liquid at a constant temperature

Evaporation, Vapor Pressure, and Boiling Point



Only the faster-moving molecules have sufficient kinetic energy to escape from the liquid and enter the vapor.

The **higher the temperature**, the larger the number of molecules that have enough energy to escape.

Evaporation, Vapor Pressure, and Boiling Point

Clausius–Clapeyron Equation

$$\ln P_{\text{vap}} = \left(-\frac{\Delta H_{\text{vap}}}{R}\right)\frac{1}{T} + C$$

$$y \quad = \qquad m \qquad x + b$$

Evaporation, Vapor Pressure, and Boiling Point

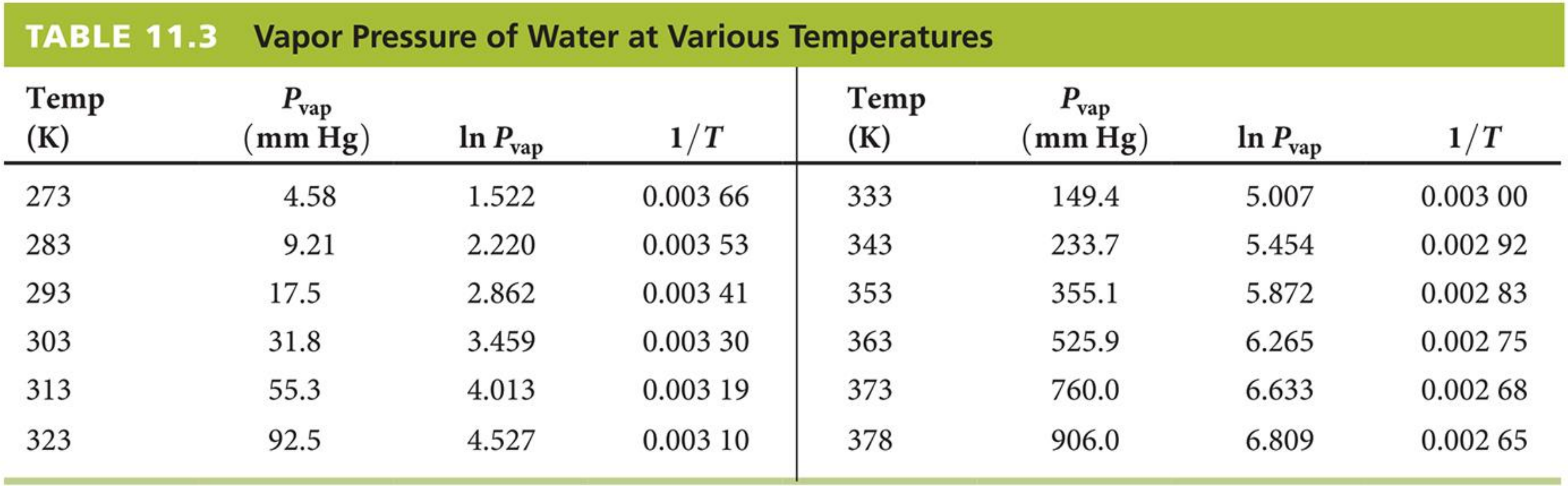
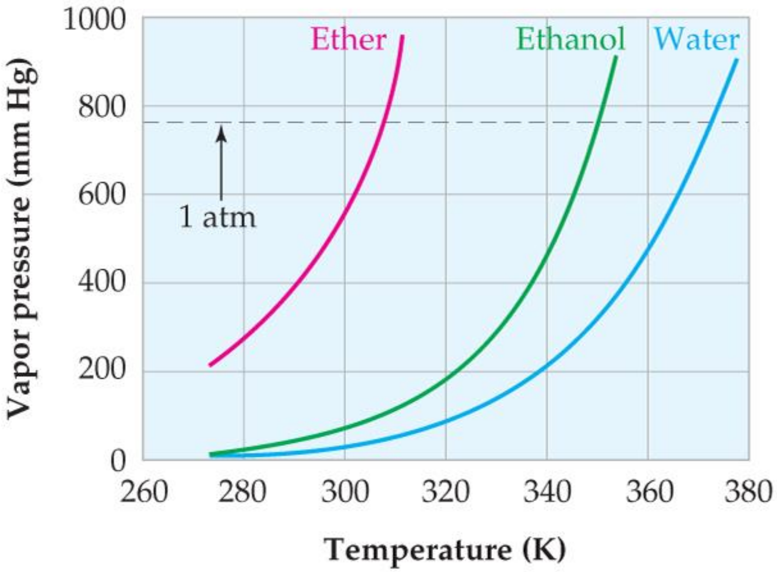


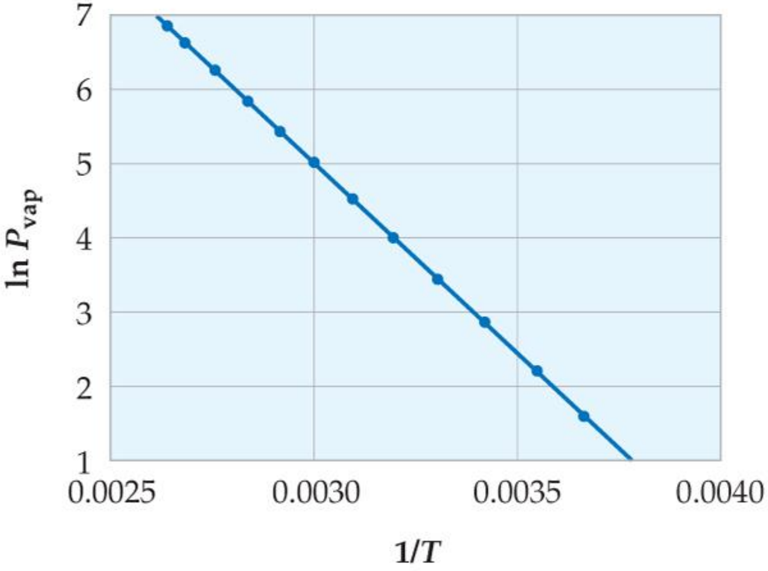
TABLE 11.3 Vapor Pressure of Water at Various Temperatures

Temp (K)	P_{vap} (mm Hg)	ln P_{vap}	$1/T$	Temp (K)	P_{vap} (mm Hg)	ln P_{vap}	$1/T$
273	4.58	1.522	0.003 66	333	149.4	5.007	0.003 00
283	9.21	2.220	0.003 53	343	233.7	5.454	0.002 92
293	17.5	2.862	0.003 41	353	355.1	5.872	0.002 83
303	31.8	3.459	0.003 30	363	525.9	6.265	0.002 75
313	55.3	4.013	0.003 19	373	760.0	6.633	0.002 68
323	92.5	4.527	0.003 10	378	906.0	6.809	0.002 65

Evaporation, Vapor Pressure, and Boiling Point



The vapor pressures of **ether**, **ethanol**, and **water** show a nonlinear rise when plotted as a function of temperature.



A plot of ln P_{vap} versus $1/T$ (kelvin) for water, prepared from the data in Table 11.3, shows a linear relationship.

Kinds of Solids

Amorphous Solids: Particles are randomly arranged and have no ordered long-range structure. An example is rubber.

Crystalline Solids: Particles have an ordered arrangement extending over a long range.

- Ionic solids
- Molecular solids
- Covalent network solids
- Metallic solids

Kinds of Solids

(a) A crystalline solid, such as this amethyst, has flat faces and distinct angles. These regular macroscopic features reflect a similarly ordered arrangement of particles at the atomic level.

(b) An amorphous solid like rubber has a disordered arrangement of its constituent particles.

Kinds of Solids

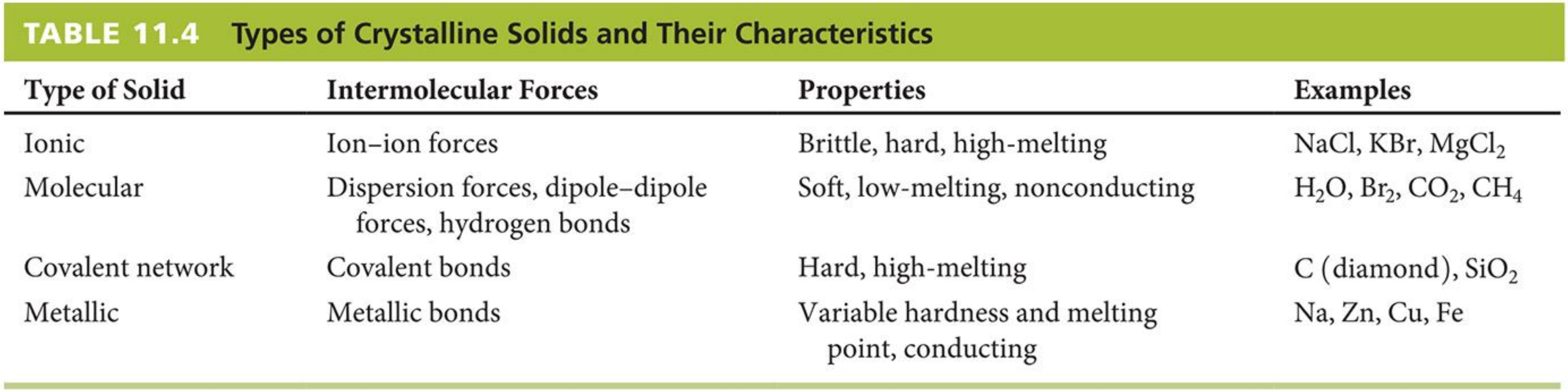
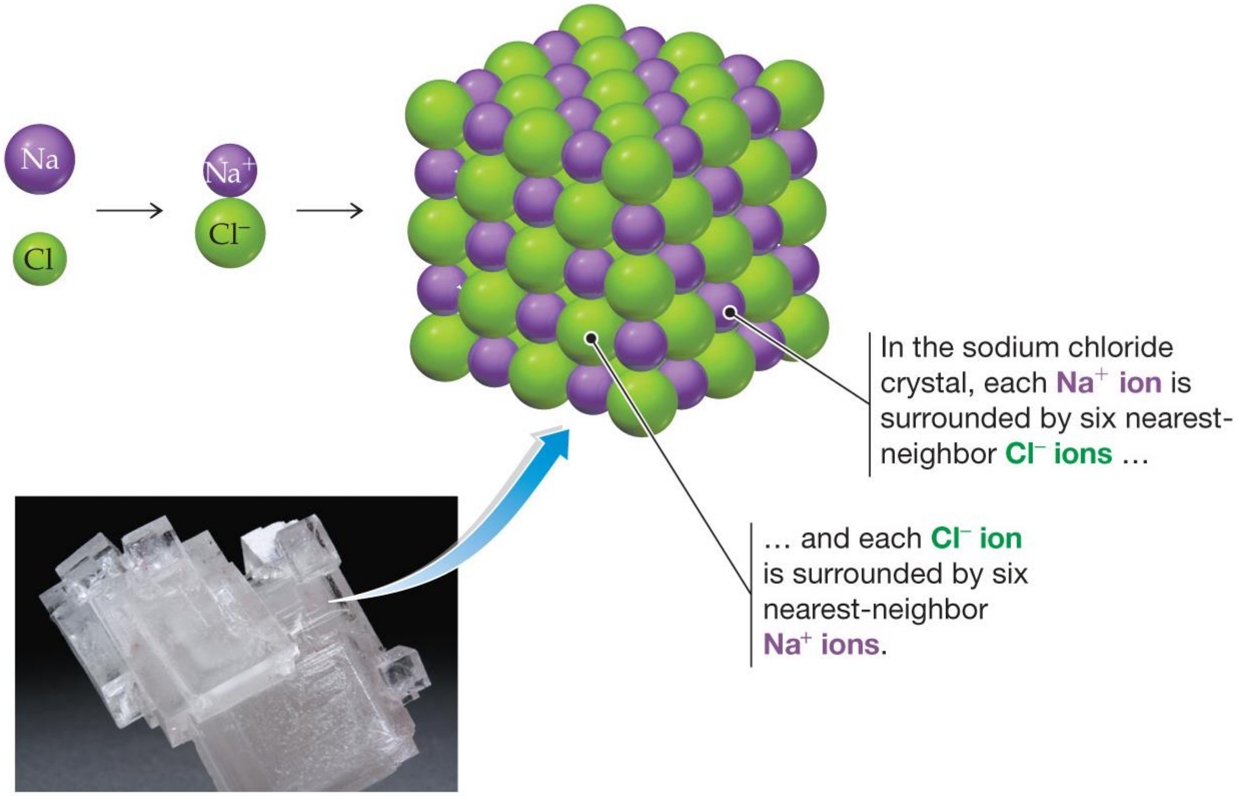


TABLE 11.4 Types of Crystalline Solids and Their Characteristics

Type of Solid	Intermolecular Forces	Properties	Examples
Ionic	Ion–ion forces	Brittle, hard, high-melting	NaCl, KBr, $MgCl_2$
Molecular	Dispersion forces, dipole–dipole forces, hydrogen bonds	Soft, low-melting, nonconducting	H_2O, Br_2, CO_2, CH_4
Covalent network	Covalent bonds	Hard, high-melting	C (diamond), SiO_2
Metallic	Metallic bonds	Variable hardness and melting point, conducting	Na, Zn, Cu, Fe

Kinds of Solids

Ionic Solids: Particles are ions ordered in a regular, three-dimensional arrangement and held together by ionic bonds. An example is sodium chloride.



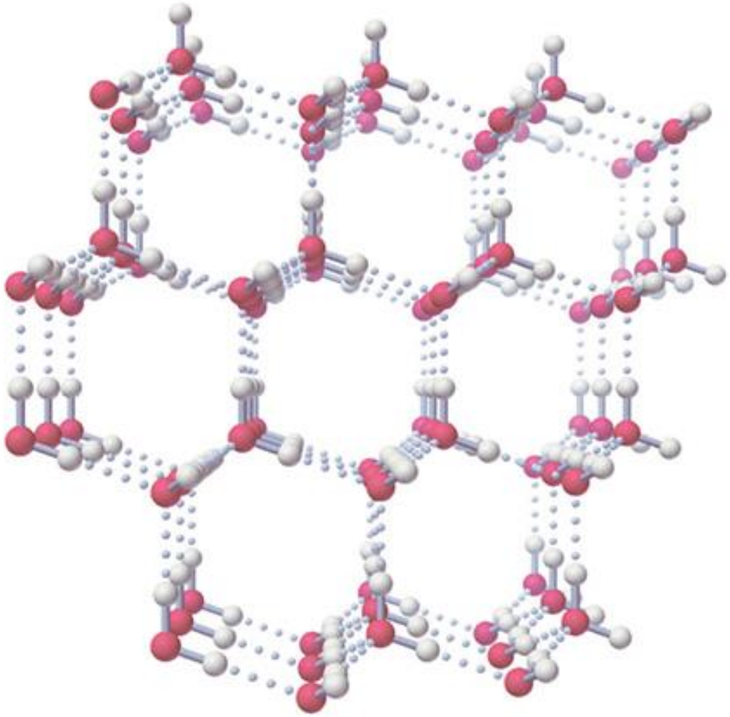
In the sodium chloride crystal, each **Na^+ ion** is surrounded by six nearest-neighbor **Cl^- ions** …

… and each **Cl^- ion** is surrounded by six nearest-neighbor **Na^+ ions**.

Kinds of Solids

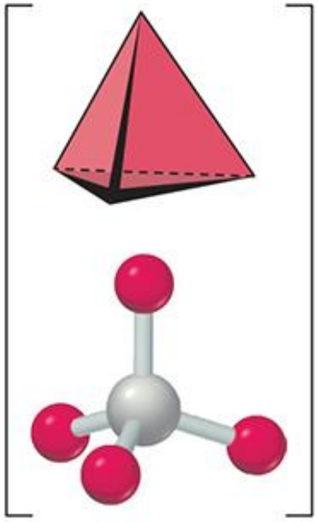
Molecular Solids: Particles are molecules held together by intermolecular forces. An example is ice.

(a) Ice consists of individual H_2O molecules held together in a regular manner by hydrogen bonds.

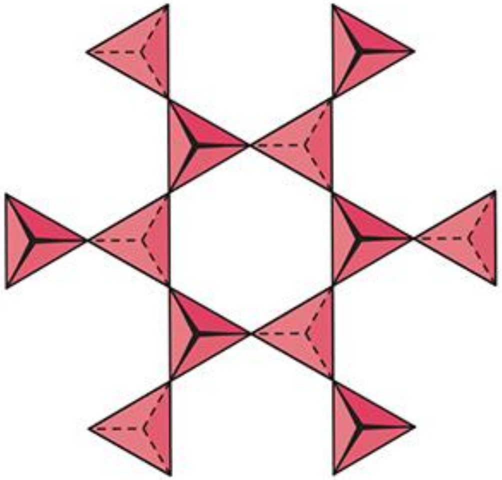


Kinds of Solids

Covalent Network Solids: Particles are atoms linked together by covalent bonds into a giant, three-dimensional array. An example is quartz.



(b) Quartz (SiO_2) is essentially one very large molecule with Si–O covalent bonds. Each silicon atom has tetrahedral geometry and is bonded to four oxygens; each oxygen has approximately linear geometry and is bonded to two silicons.

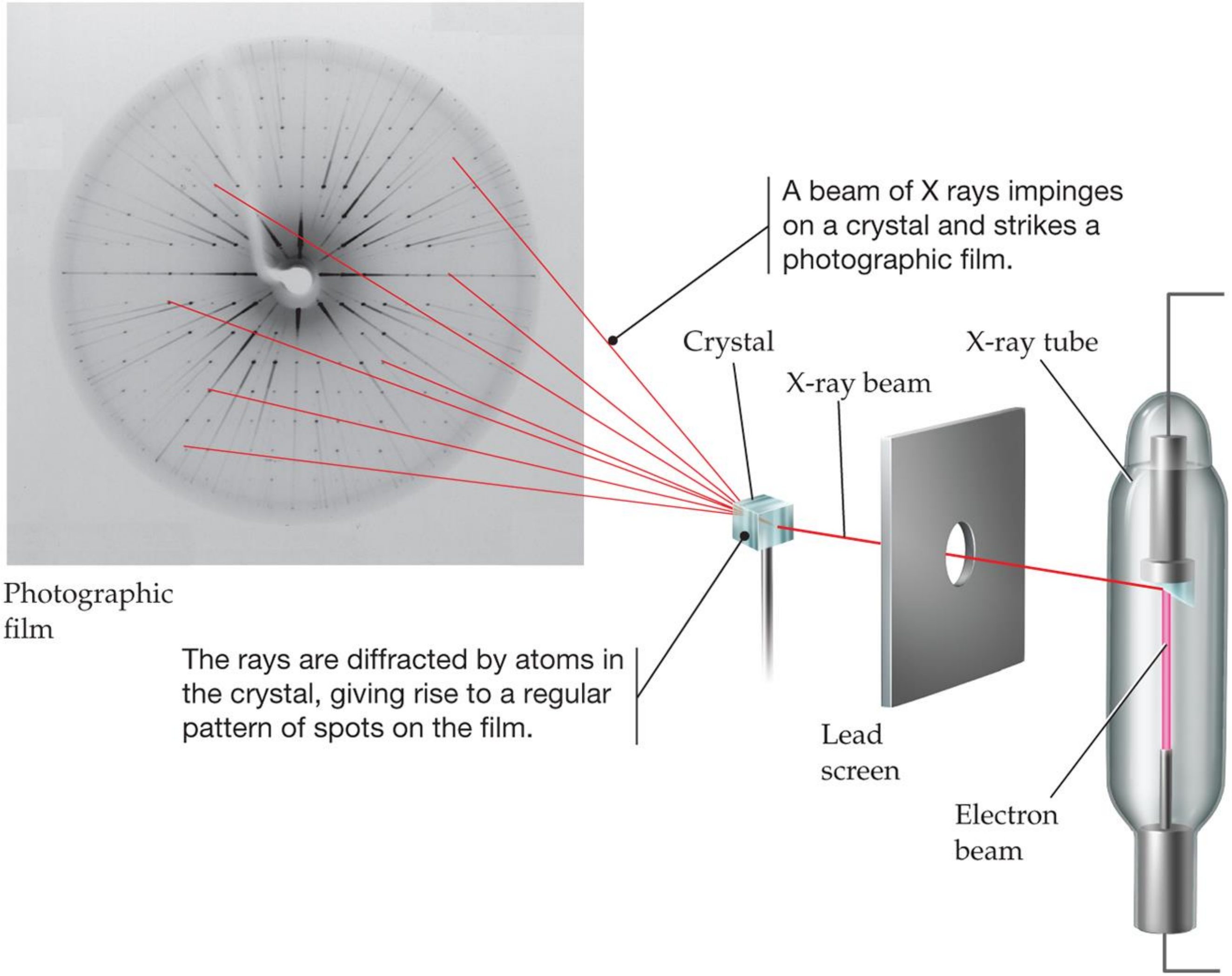


(c) This shorthand representation shows how SiO_4 tetrahedra join at their corners to share oxygen atoms.

Kinds of Solids

Metallic Solids: Particles are metal atoms whose crystals have metallic properties such as electrical conductivity. An example is iron.

Probing the Structure of Solids: X-Ray Crystallography

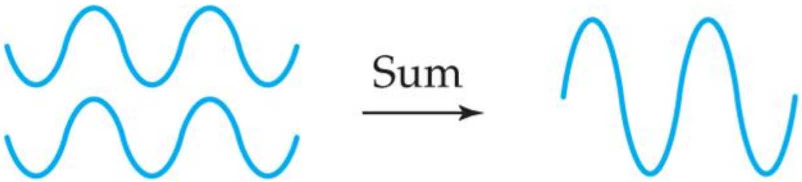


A beam of X rays impinges on a crystal and strikes a photographic film.

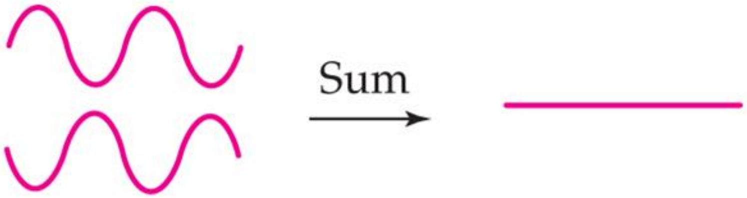
The rays are diffracted by atoms in the crystal, giving rise to a regular pattern of spots on the film.

Probing the Structure of Solids: X-Ray Crystallography

Interference occurs when two waves pass through the same region of space.



Constructive interference occurs if the waves are in-phase, producing a wave with increased intensity.

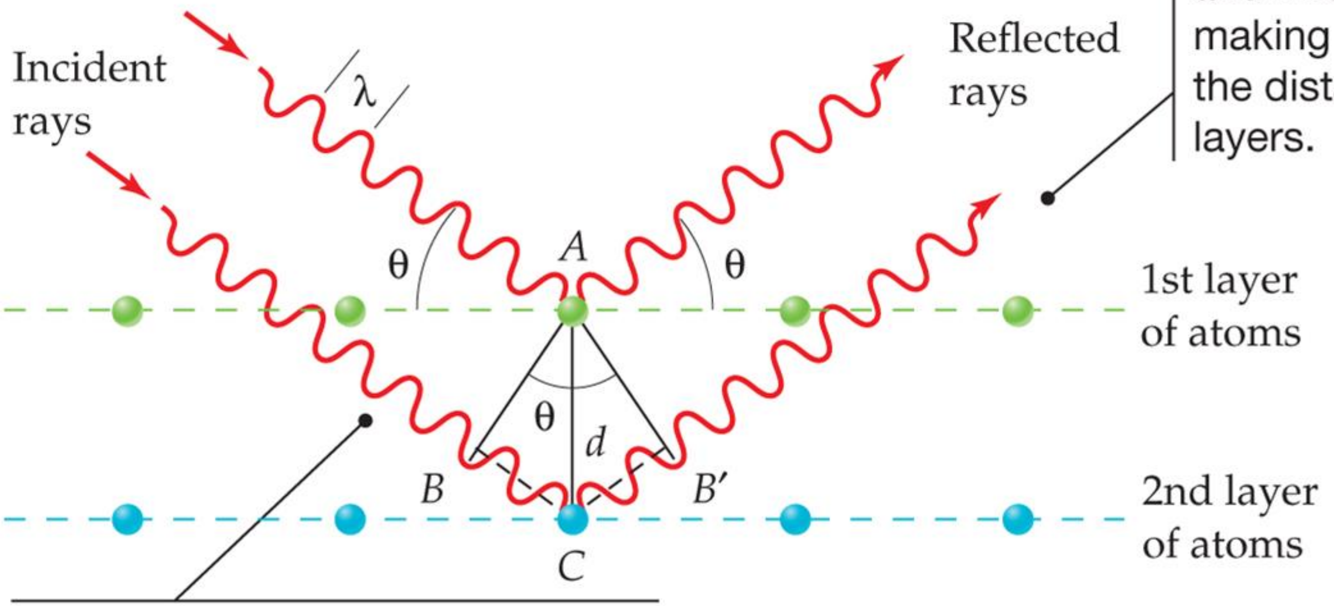


Destructive interference occurs if the waves are out-of-phase, resulting in cancellation.

Probing the Structure of Solids: X-Ray Crystallography

Diffraction occurs when electromagnetic radiation is scattered by an object containing regularly spaced lines (such as a diffraction grating) or points (such as the atoms in a crystal).

Probing the Structure of Solids: X-Ray Crystallography



If the extra distance is a whole number of wavelengths, the reflected rays are in-phase and interfere constructively, making it possible to calculate the distance *d* between the layers.

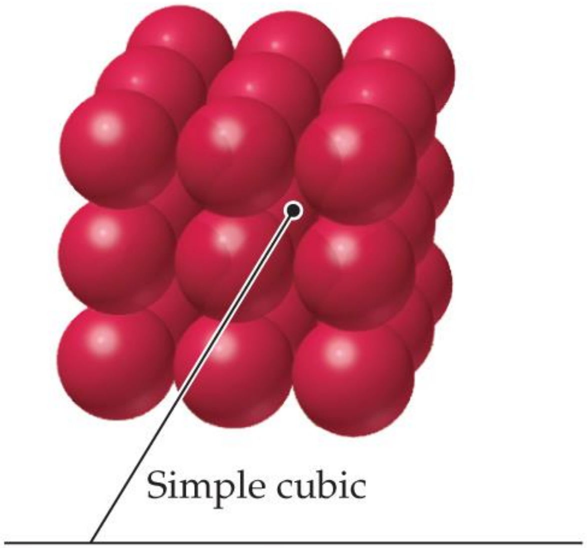
Rays striking atoms in the **second layer** travel a distance equal to *BC* + *CB′* farther than rays striking atoms in the **first layer**.

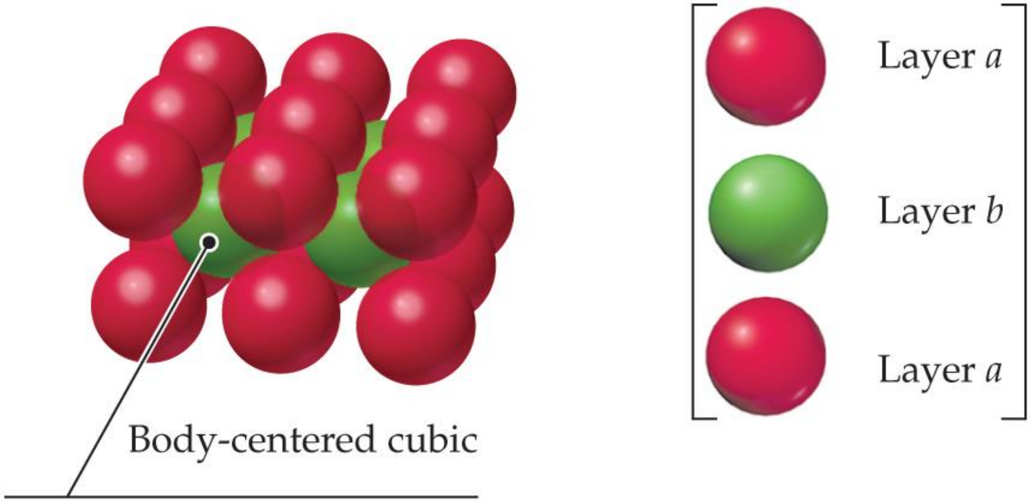
Bragg Equation: $d = \dfrac{n\lambda}{2 \sin \theta}$

The Packing of Spheres in Crystalline Solids: Unit Cells

(a) Simple Cubic Packing:
All **layers are identical**, and all atoms are lined up in stacks and rows.

(b) Body-Centered Cubic Packing:
The spheres in **layer *a*** are separated slightly and the spheres in **layer *b*** are offset so that they fit into the depressions between atoms in layer *a*. The third layer is a repeat of the first.



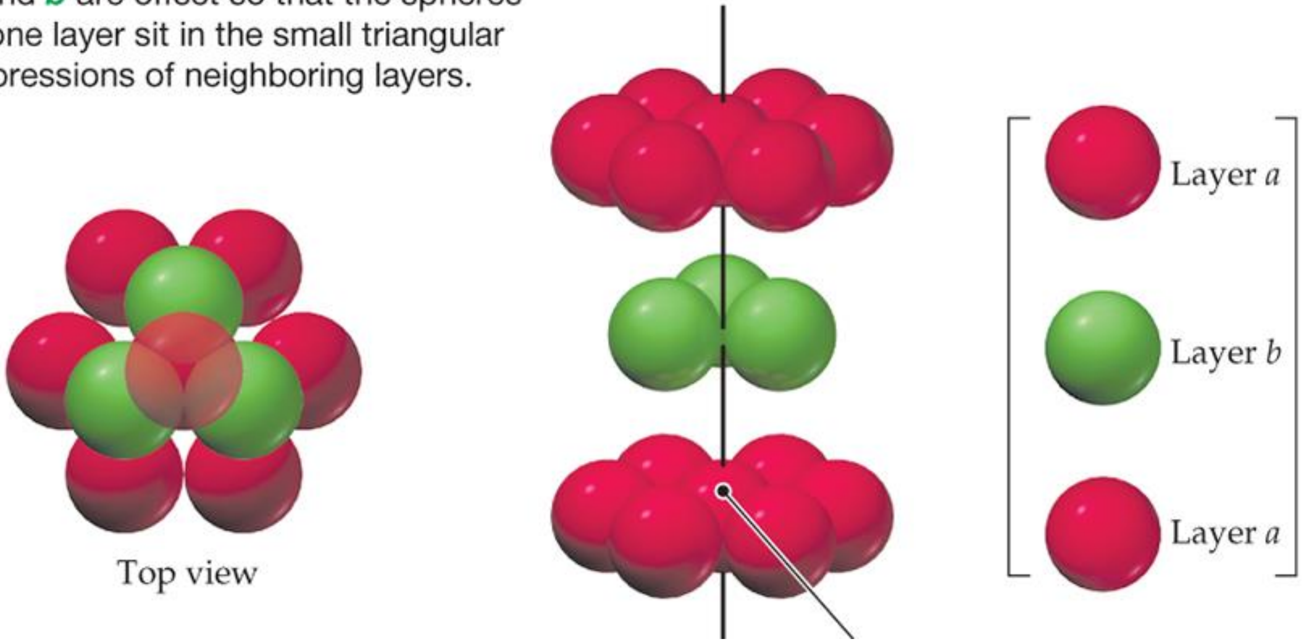


Coordination Number 6:
Each sphere is touched by six neighbors, four in the same layer, one directly above, and one directly below.

Coordination Number 8:
Each sphere is touched by eight neighbors, four in the layer below, and four in the layer above.

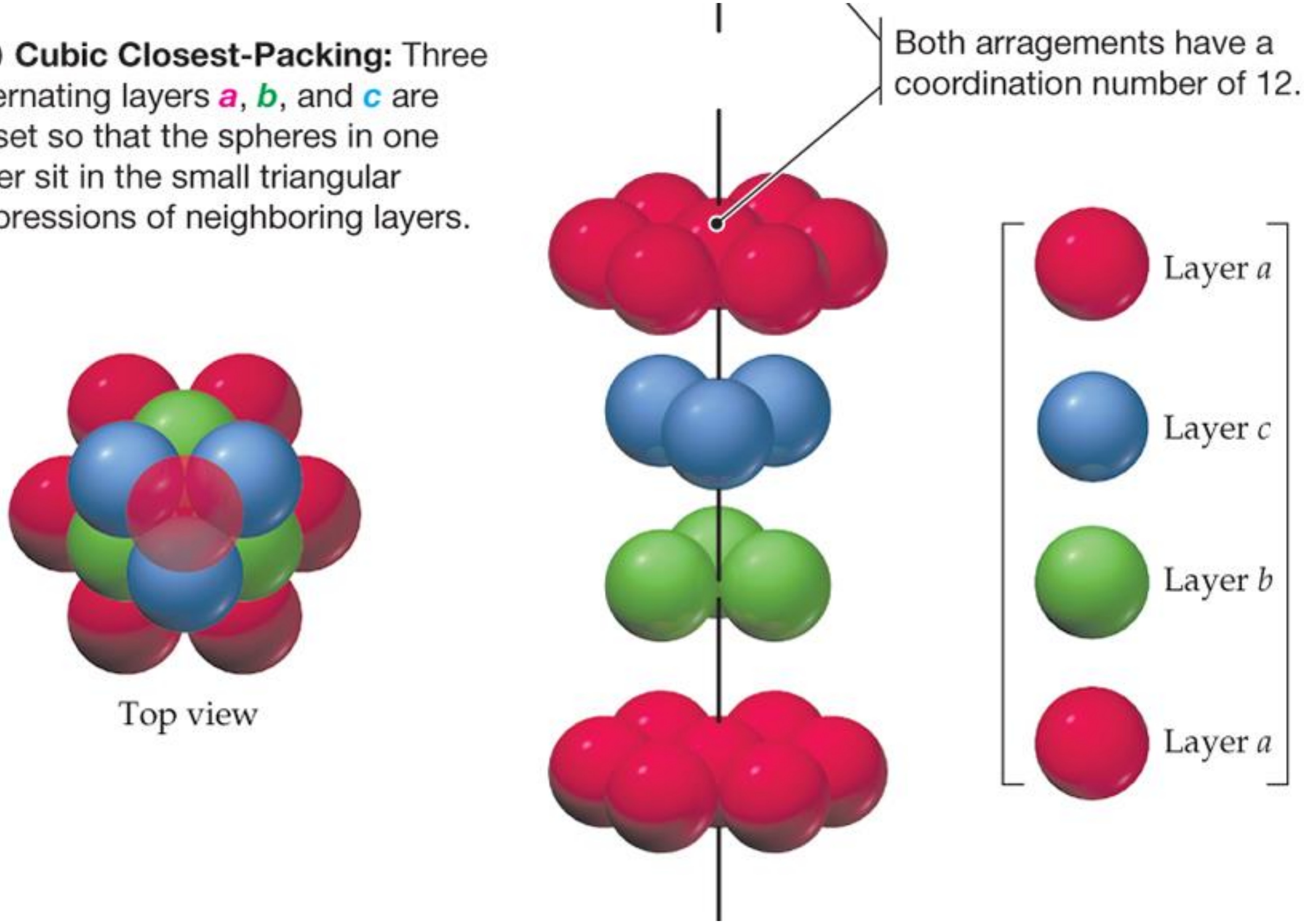
The Packing of Spheres in Crystalline Solids: Unit Cells

(a) Hexagonal Closest-Packing: Two alternating hexagonal layers *a* and *b* are offset so that the spheres in one layer sit in the small triangular depressions of neighboring layers.



The Packing of Spheres in Crystalline Solids: Unit Cells

(b) Cubic Closest-Packing: Three alternating layers ***a***, ***b***, and ***c*** are offset so that the spheres in one layer sit in the small triangular depressions of neighboring layers.



Both arragements have a coordination number of 12.

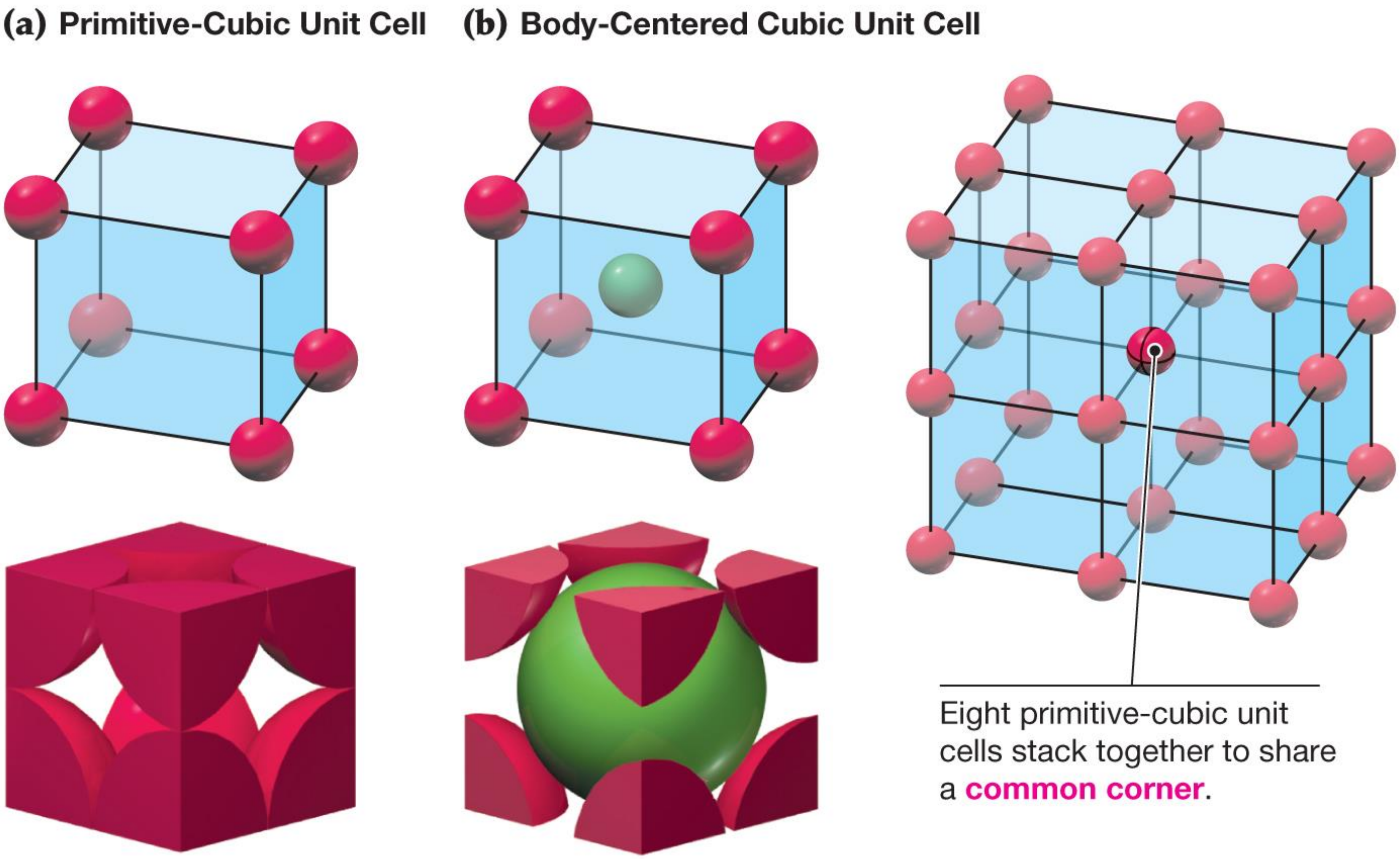
The Packing of Spheres in Crystalline Solids: Unit Cells

Unit Cell: A small, repeating unit that makes up a crystal

The Packing of Spheres in Crystalline Solids: Unit Cells

Primitive Cubic

Body-Centered Cubic



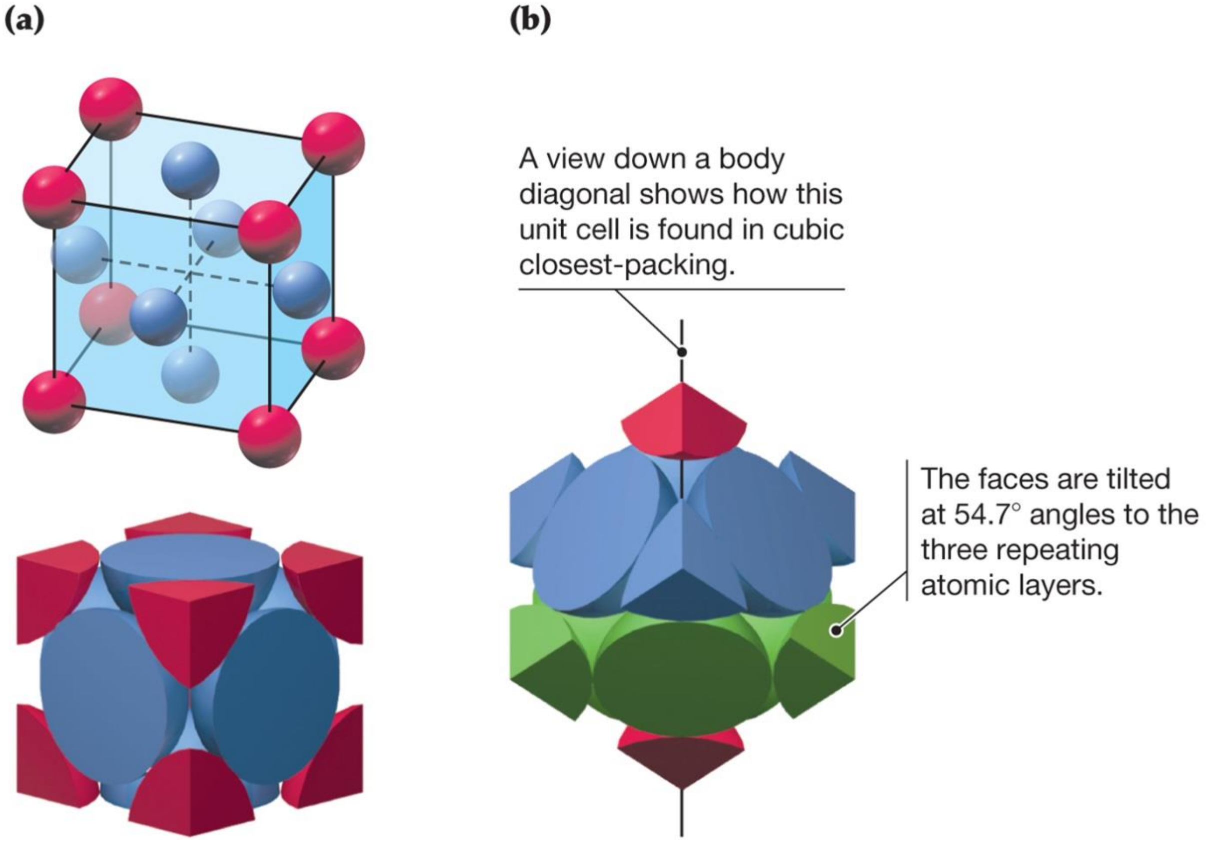
(a) Primitive-Cubic Unit Cell

(b) Body-Centered Cubic Unit Cell

Eight primitive-cubic unit cells stack together to share a **common corner**.

The Packing of Spheres in Crystalline Solids: Unit Cells

Face-Centered Cubic



A view down a body diagonal shows how this unit cell is found in cubic closest-packing.

The faces are tilted at 54.7° angles to the three repeating atomic layers.

The Packing of Spheres in Crystalline Solids: Unit Cells

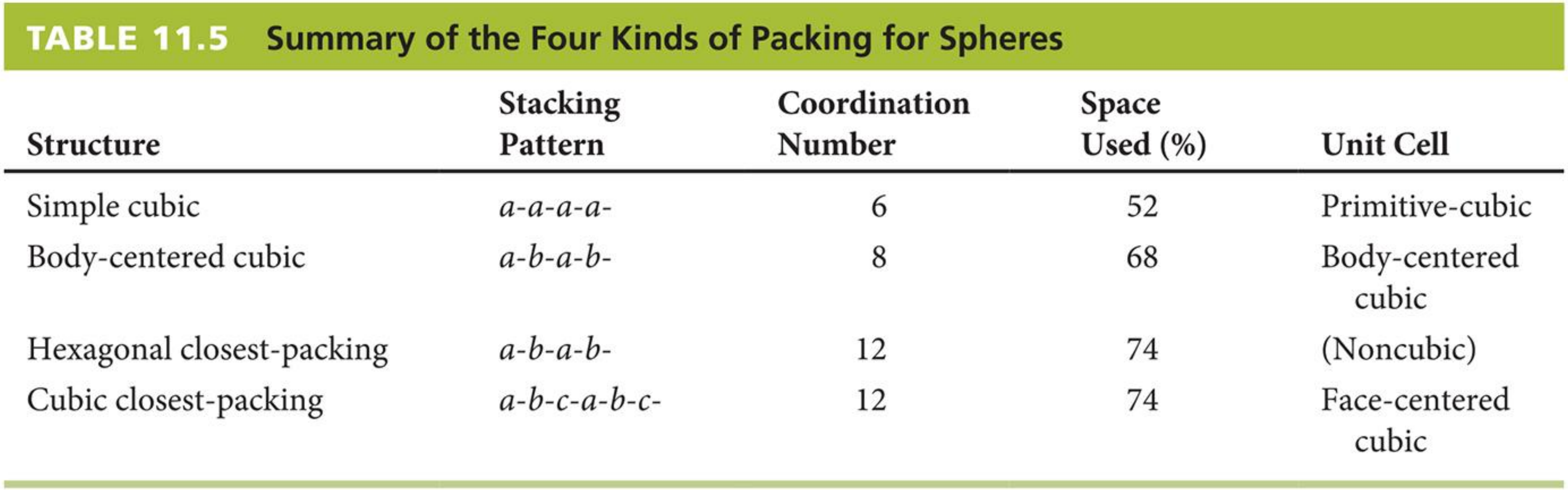
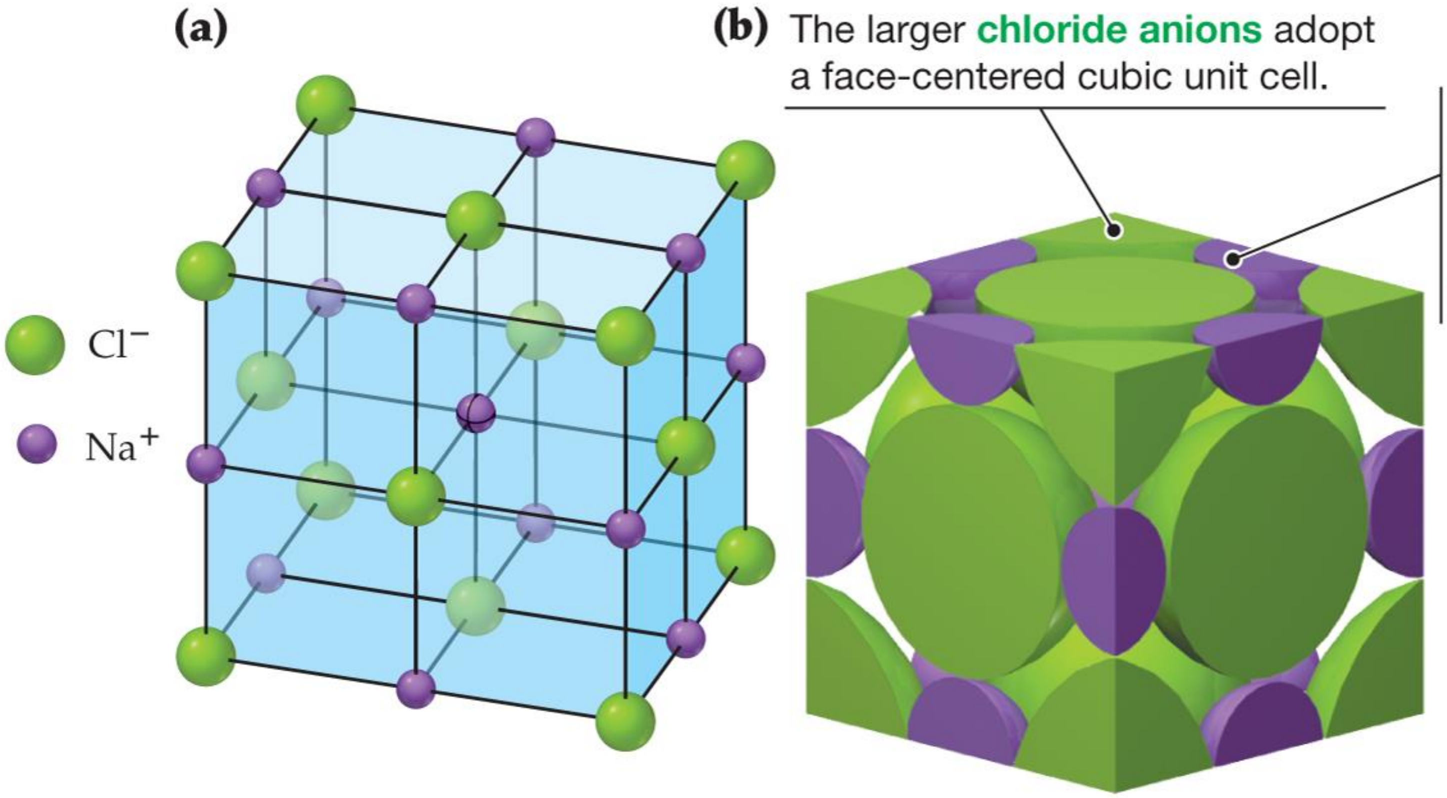


TABLE 11.5 Summary of the Four Kinds of Packing for Spheres

Structure	Stacking Pattern	Coordination Number	Space Used (%)	Unit Cell
Simple cubic	*a-a-a-a-*	6	52	Primitive-cubic
Body-centered cubic	*a-b-a-b-*	8	68	Body-centered cubic
Hexagonal closest-packing	*a-b-a-b-*	12	74	(Noncubic)
Cubic closest-packing	*a-b-c-a-b-c-*	12	74	Face-centered cubic

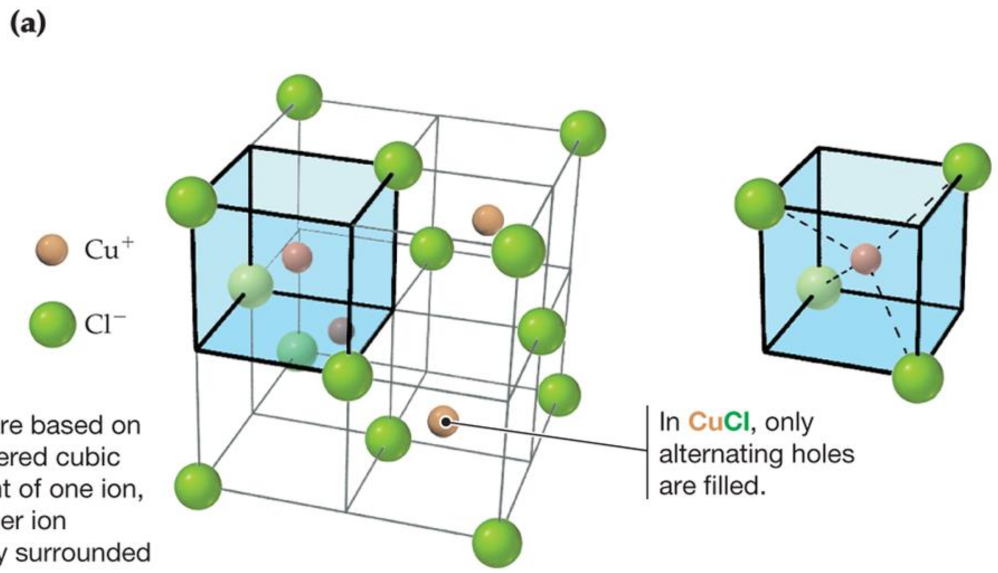
Structures of Some Ionic Solids



The larger **chloride anions** adopt a face-centered cubic unit cell.

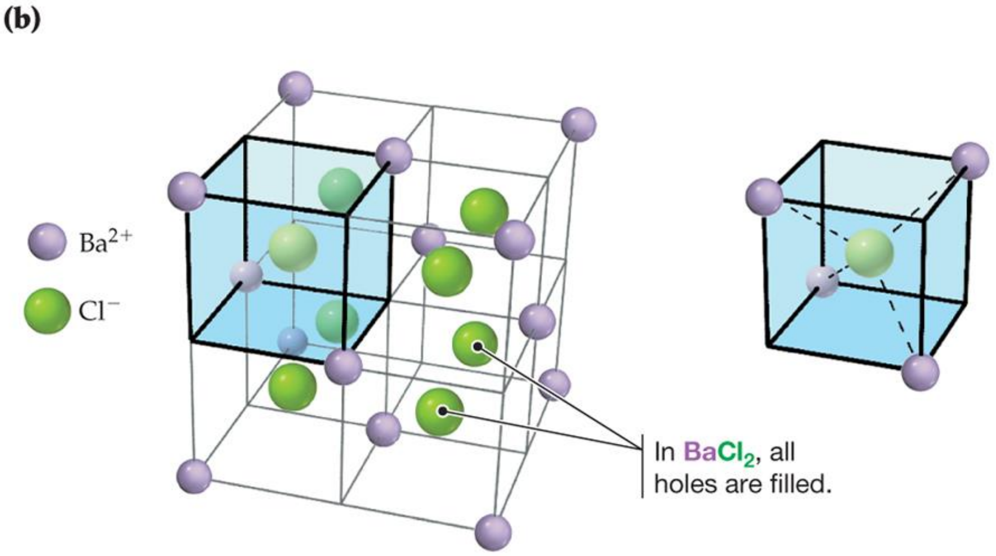
The smaller **sodium cations** fit into the holes between adjacent **anions.**

Structures of Some Ionic Solids



Both cells are based on a face-centered cubic arrangement of one ion, with the other ion tetrahedrally surrounded in holes.

In **CuCl**, only alternating holes are filled.



In **$BaCl_2$**, all holes are filled.

Structures of Some Covalent Network Solids

Carbon Allotropes

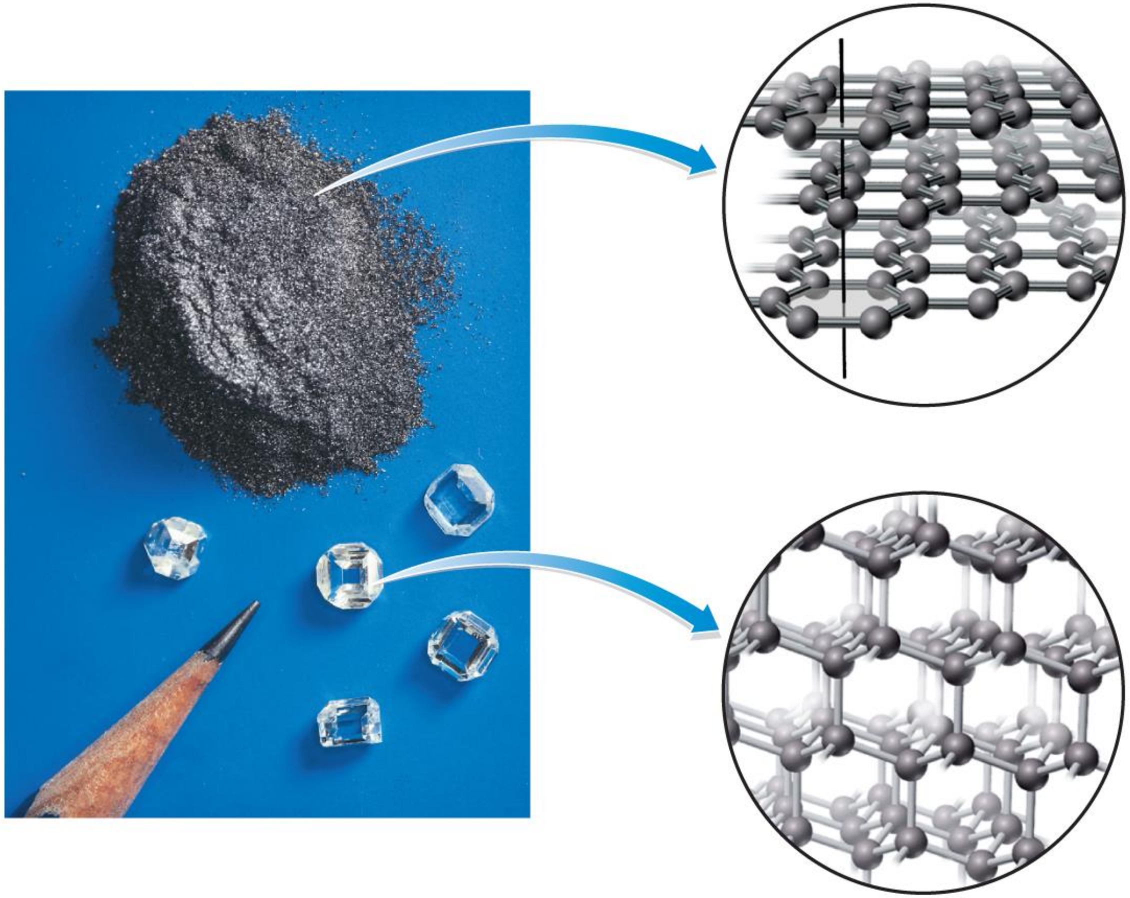
Allotropes: Different structural forms of an element

Carbon

- Graphite
- Diamond
- Fullerene
- Nanotubes

Structures of Some Covalent Network Solids

Carbon Allotropes



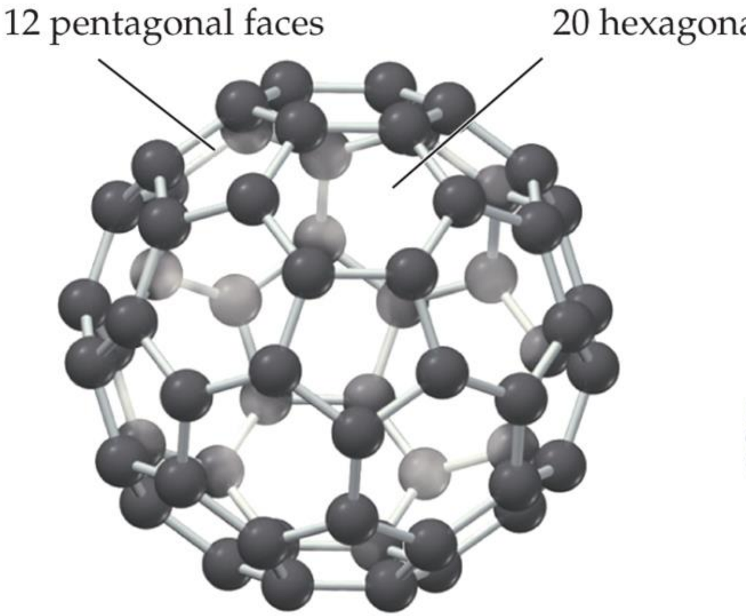
(a) Graphite is a covalent network solid consisting of two-dimensional sheets of sp^2-hybridized carbon atoms organized into six-membered rings.

The atoms in each sheet are offset slightly from the atoms in neighboring sheets.

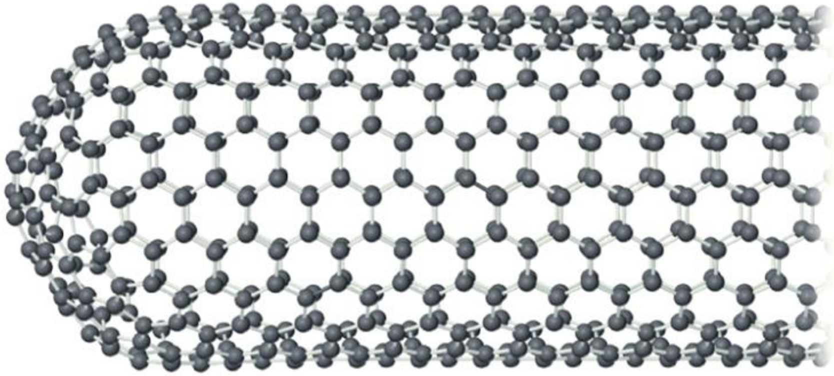
(b) Diamond is a vast, three-dimensional array of sp^3-hybridized carbon atoms, each of which is bonded with tetrahedral geometry to four other carbons.

Structures of Some Covalent Network Solids

Carbon Allotropes



(a) Fullerene is a molecular solid whose molecules have the shape of a soccer ball. The ball has 12 pentagonal and 20 hexagonal faces, and each carbon atom is sp^2-hybridized.

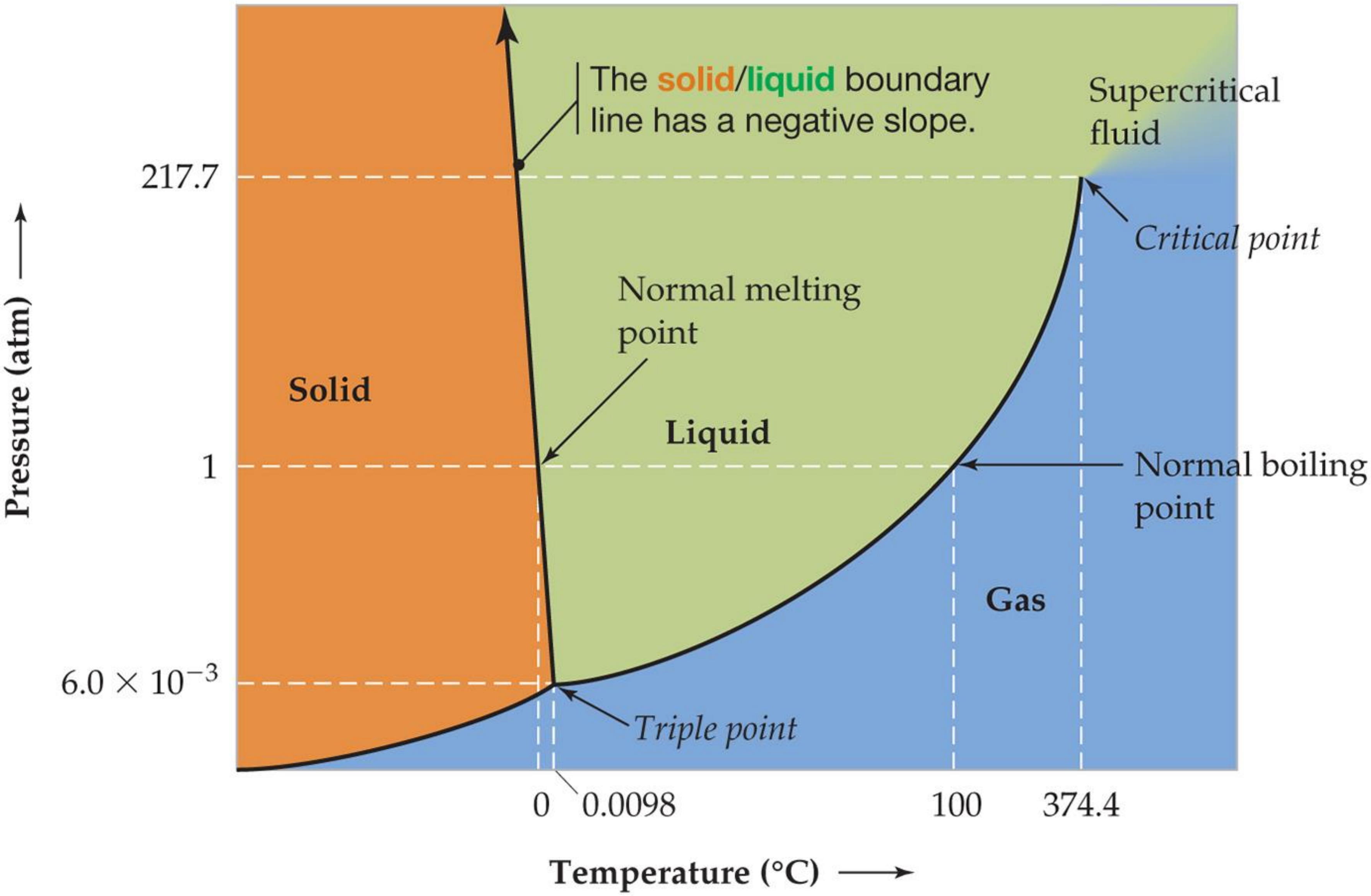


(b) Carbon nanotubes consist of sheets of graphite rolled into tubes of 2–30 nm diameter.

Structures of Some Covalent Network Solids

Silica (SiO_2)

- Quartz
- Sand
- Quartz glass



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Phase Diagrams

Normal Boiling Point: The temperature at which boiling occurs when there is exactly 1 atm of external pressure

Normal Melting Point: The temperature at which melting occurs when there is exactly 1 atm of external pressure

Triple Point: A point at which three phases coexist in equilibrium

Phase Diagrams

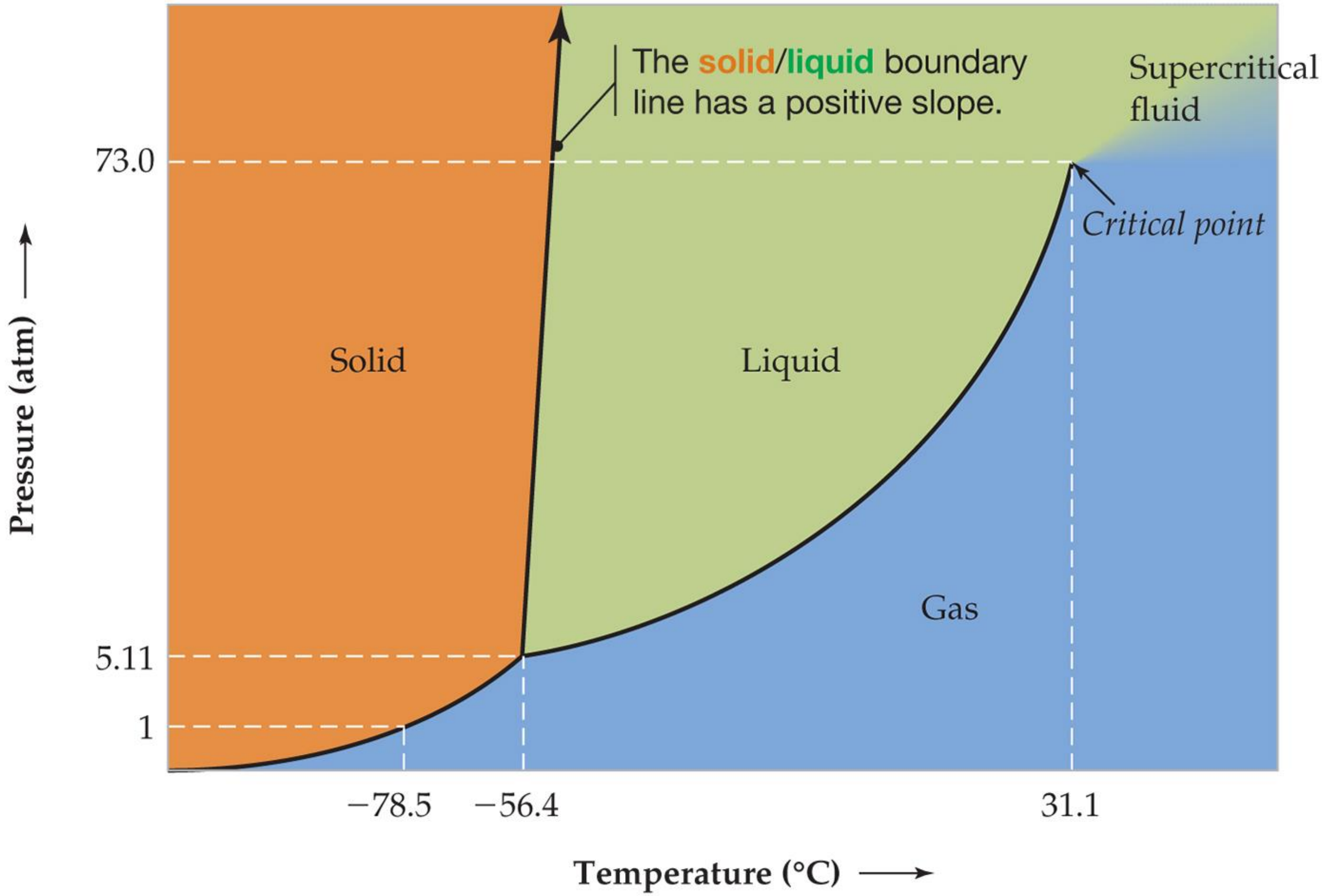
Critical Point: A combination of temperature and pressure beyond which a gas cannot be liquified

- **Critical Temperature**: The temperature beyond which a gas cannot be liquified regardless of the pressure
- **Critical Pressure**: The pressure beyond which a liquid cannot be vaporized regardless of the temperature

Supercritical Fluid: A state of matter beyond the critical point that is neither liquid nor gas

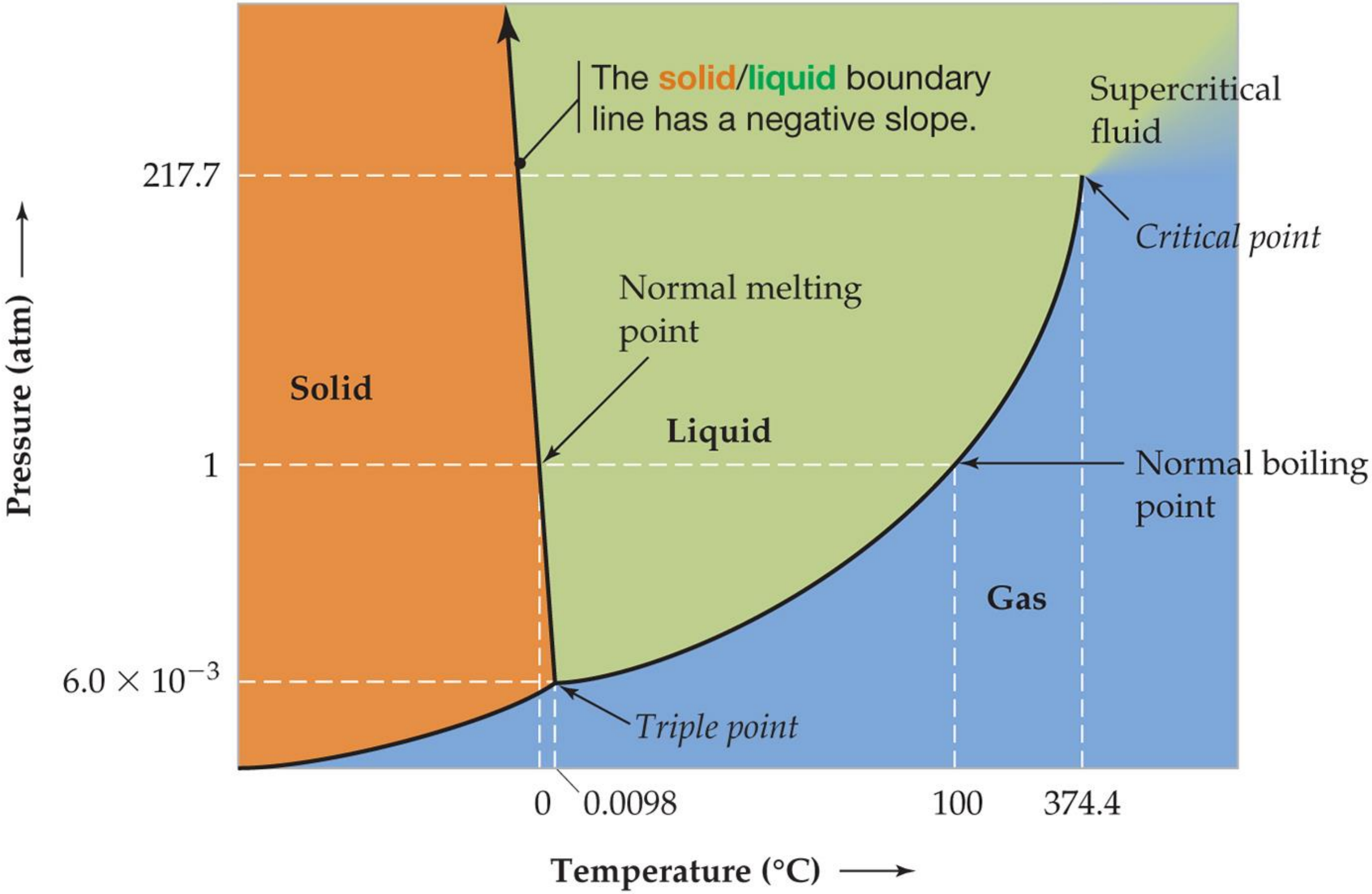
Phase Diagrams

Carbon Dioxide



Phase Diagrams

Water



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Phase Diagrams

Water

Phase Diagrams

Water