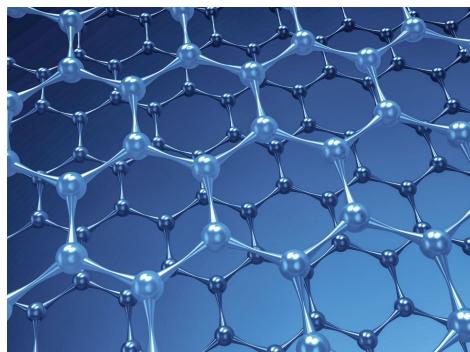




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Chapter 11

Intermolecular Forces and Liquids and Solids

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1

Phases

A **phase** is a homogeneous part of the system in contact with other parts of the system but separated from them by a well-defined boundary.

2 Phases

Solid phase - ice

Liquid phase - water

Table 11.1 Characteristic Properties of Gases, Liquids, and Solids

State of Matter	Volume/Shape	Density	Compressibility	Motion of Molecules
Gas	Assumes the volume and shape of its container	Low	Very compressible	Very free motion
Liquid	Has a definite volume but assumes the shape of its container	High	Only slightly compressible	Slide past one another freely
Solid	Has a definite volume and shape	High	Virtually incompressible	Vibrate about fixed positions

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2

2

Intermolecular Forces ₁

Intermolecular forces are attractive forces **between** molecules.

Intramolecular forces hold atoms together in a molecule.

Intermolecular vs Intramolecular

- 41 kJ to vaporize 1 mole of water (**inter**).
- 930 kJ to break all O – H bonds in 1 mole of water (**intra**).

Generally, **intermolecular** forces are much weaker than **intramolecular** forces.

“Measure” of intermolecular force boiling point melting point.

$$\Delta H_{\text{vap}}$$

$$\Delta H_{\text{fus}}$$

$$\Delta H_{\text{sub}}$$

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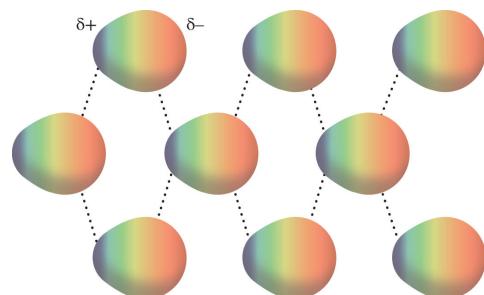
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Intermolecular Forces ₂

Dipole-Dipole Forces

Attractive forces between **polar molecules**.

Orientation of Polar Molecules in a Solid



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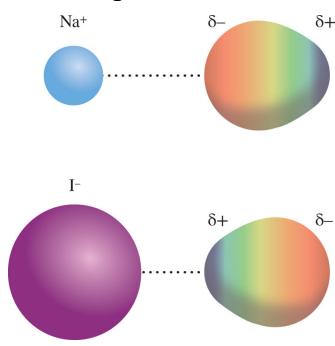
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Intermolecular Forces ₃

Ion-Dipole Forces

Attractive forces between an **ion** and a **polar molecule**.

Ion-Dipole Interaction

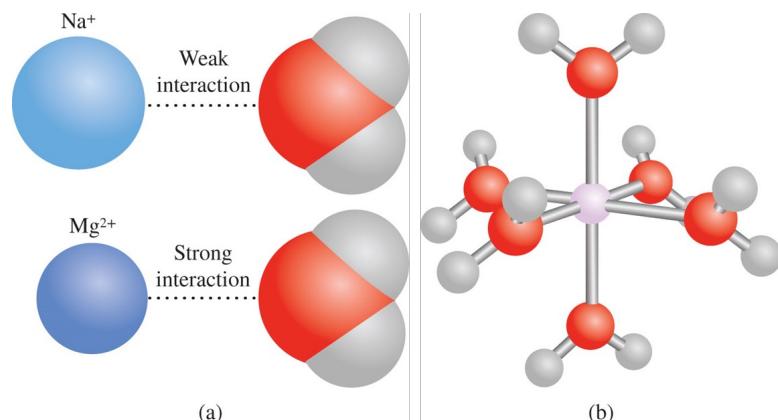


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Interaction Between Water and Cations



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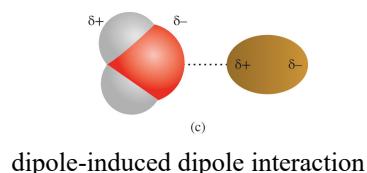
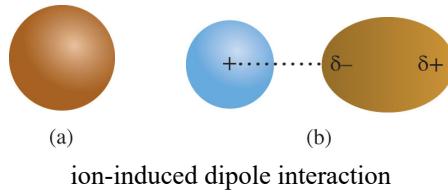
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Intermolecular Forces 4

Dispersion Forces

Attractive forces that arise as a result of **temporary dipoles induced** in atoms or molecules.

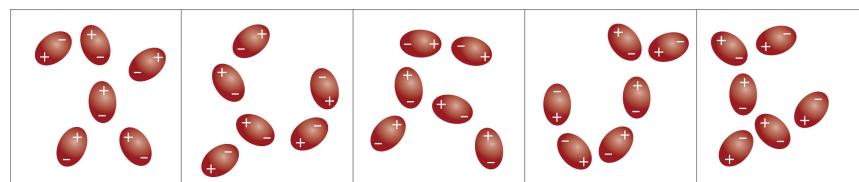


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Induced Dipoles Interacting With Each Other



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8

Intermolecular Forces 5

Dispersion Forces Continued

Polarizability is the ease with which the electron distribution in the atom or molecule can be distorted.

Polarizability increases with:

- greater number of electrons.
- more diffuse electron cloud.

Dispersion forces usually increase with molar mass.

Table 11.2

Melting Points of Similar Nonpolar Compound

Compound	Melting Point (°C)
CH ₄	-182.5
CF ₄ ↓	-150.0 ↓
CCl ₄ ↓	-23.0 ↓
CBr ₄ ↓	90.0 ↓
Cl ₄ ↓	171.0 ↓

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Example 11.1 1

What type(s) of intermolecular forces exist between the following pairs?

(a) HBr and H₂S

(b) Cl₂ and CBr₄

(c) I₂ and NO₃⁻

(d) NH₃ and C₆H₆

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Example 11.1 ₂

Strategy

Classify the species into three categories: ionic, polar (possessing a dipole moment), and nonpolar. Keep in mind that dispersion forces exist between *all* species.

Solution

- Both HBr and H₂S are polar molecules. Therefore, the intermolecular forces present are dipole-dipole forces, as well as dispersion forces.
- Both Cl₂ and CBr₄ are nonpolar, so there are only dispersion forces between these molecules.

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Example 11.1 ₃

- I₂ is a homonuclear diatomic molecule and therefore nonpolar, so the forces between it and the ion NO₃⁻ are ion-induced dipole forces and dispersion forces.
- NH₃ is polar, and C₆H₆ is nonpolar. The forces are dipole-induced dipole forces and dispersion forces.

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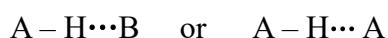
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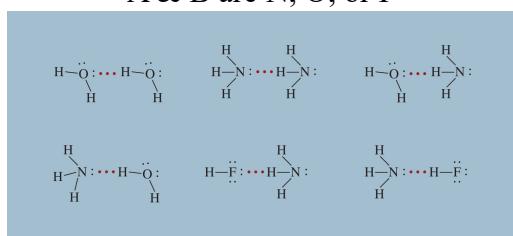
Intermolecular Forces ₆

Hydrogen Bond

The **hydrogen bond** is a special dipole-dipole interaction between the hydrogen atom in a polar N – H, O – H, or F – H bond and an electronegative O, N, or F atom.



A & B are N, O, or F

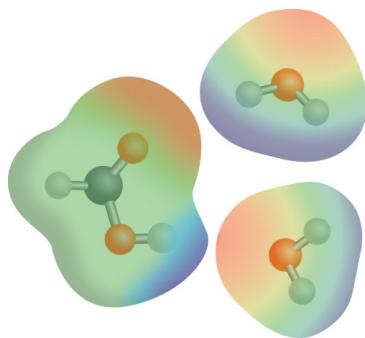


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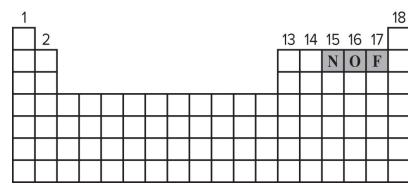
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Hydrogen Bond



HCOOH and water

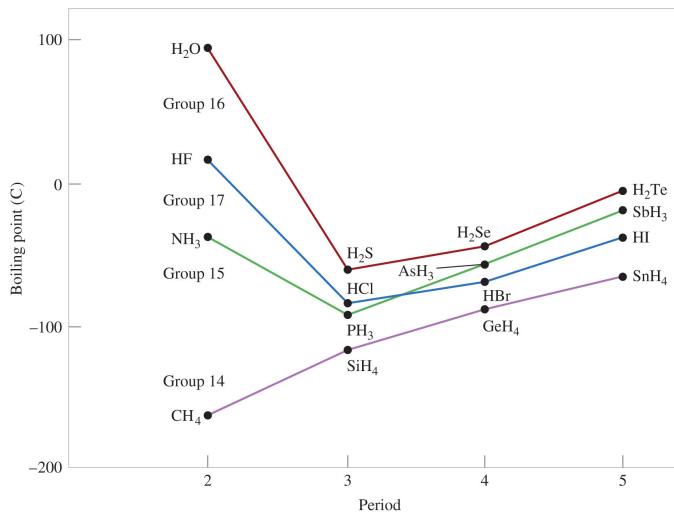


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Why is the hydrogen bond considered a “special” dipole-dipole interaction?



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Example 11.2

Which of the following can form hydrogen bonds with water?



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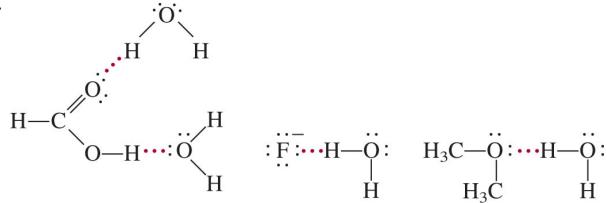
Example 11.2₂

Strategy

A species can form hydrogen bonds with water if it contains one of the three electronegative elements (F, O, or N) or it has a H atom bonded to one of these three elements.

Solution

There are no electronegative elements (F, O, or N) in either CH₄ or Na⁺. Therefore, only CH₃OCH₃, F₂, and HCOOH can form hydrogen bonds with water.



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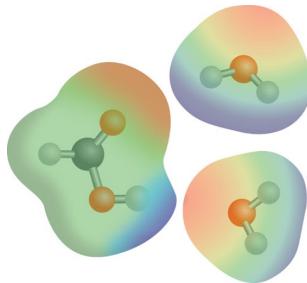
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Example 11.2₃

Check

Note that HCOOH (formic acid) can form hydrogen bonds with water in two different ways.



HCOOH forms hydrogen bonds with two H₂O molecules.

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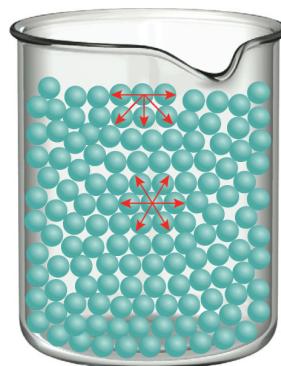
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Properties of Liquids ₁

Surface tension is the amount of energy required to stretch or increase the surface of a liquid by a unit area.

Strong
intermolecular
forces

High surface
tension



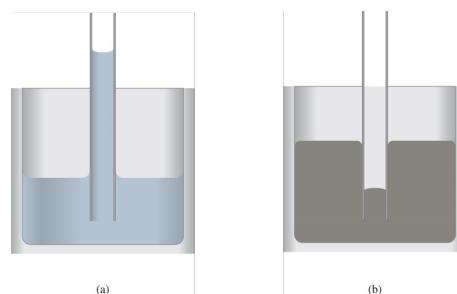
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Properties of Liquids ₂

Cohesion is the intermolecular attraction between like molecules.

Adhesion is an attraction between unlike molecules.



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Properties of Liquids 3

Viscosity is a measure of a fluid's resistance to flow.

Table 11.3 Viscosity of Some Common Liquids at 20°C

Strong
intermolecular
forces

High
viscosity

Liquid	Viscosity (Ns/m^2) [*]
Acetone($\text{C}_3\text{H}_6\text{O}$)	3.16×10^{-4}
Benzene(C_6H_6)	6.24×10^{-4}
Blood	4×10^{-3}
Carbon tetrachloride(CCl_4)	9.69×10^{-4}
Diethylether($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$)	2.33×10^{-4}
Ethanol($\text{C}_2\text{H}_5\text{OH}$)	1.20×10^{-3}
Glycerol($\text{C}_3\text{H}_8\text{OH}$)	1.49
Mercury(Hg)	1.55×10^{-3}
Water(H_2O)	1.01×10^{-3}

*The SI units of viscosity are newton-second per meter squared.

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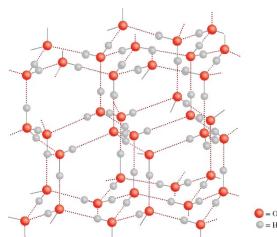
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Water is a Unique Substance

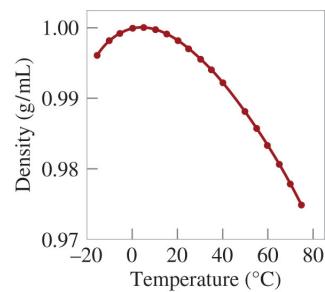
3-D Structure of Water



Ice is less dense than water



Density of Water



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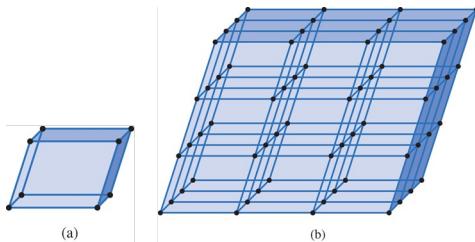
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Solids

A **crystalline solid** possesses rigid and long-range order. In a crystalline solid, atoms, molecules or ions occupy specific (predictable) positions.

An **amorphous solid** does not possess a well-defined arrangement and long-range molecular order.

A **unit cell** is the basic repeating structural unit of a crystalline solid.



At lattice points:

- Atoms
- Molecules
- Ions

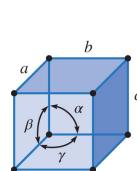
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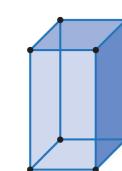
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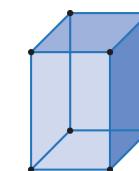
Seven Basic Unit Cells



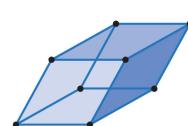
Simple cubic
 $a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$



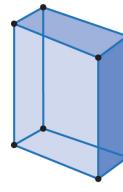
Tetragonal
 $a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



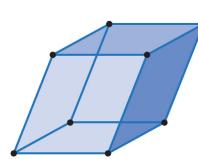
Orthorhombic
 $a \neq b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



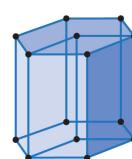
Rhombohedral
 $a = b = c$
 $\alpha = \beta = \gamma \neq 90^\circ$



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



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



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

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Three Types of Cubic Unit Cells

The slide displays three types of cubic unit cells. Each type is shown twice: once as a wireframe cube with spheres at its vertices, and once as a solid cluster of spheres.

- Simple cubic:** A wireframe cube with one sphere at each of its 8 vertices. Below it is a solid cluster of 8 spheres.
- Body-centered cubic:** A wireframe cube with one sphere at its center. Below it is a solid cluster of 9 spheres (1 central + 8 corner).
- Face-centered cubic:** A wireframe cube with one sphere at the center of each of its 6 faces. Below it is a solid cluster of 14 spheres (1 central + 8 face centers + 6 corner).

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Arrangement of Identical Spheres in a Simple Cubic Cell

The slide illustrates the arrangement of identical spheres in a simple cubic cell. It shows three views:

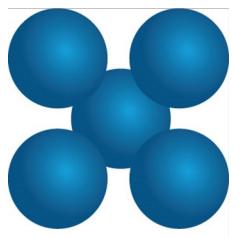
- A top-down view showing a 3x3 grid of 9 spheres. One sphere is labeled with a lowercase 'x'.
- A front-side view showing a 3D perspective of 9 spheres arranged in a 3x3 cube, with a wireframe cube overlaid.
- A perspective view showing a wireframe cube containing 9 spheres, with blue shading highlighting the spheres at the corners and faces.

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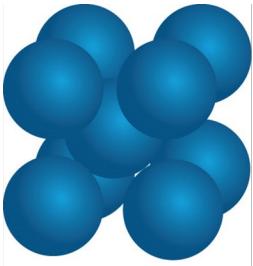
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Arrangement of Identical Spheres in a Body-Centered Cubic Cell



(a)



(b)



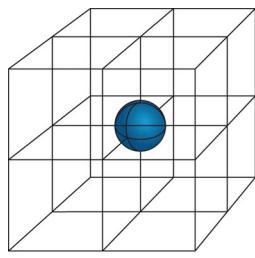
(c)

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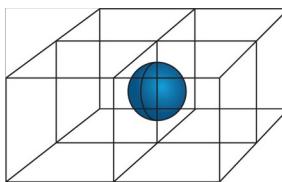
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A Corner Atom, an Edge-Centered Atom, and a Face-Centered Atom



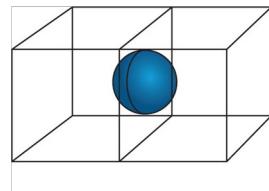
(a)

Shared by 8
unit cells



(b)

Shared by 4
unit cells



(c)

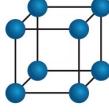
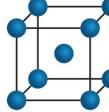
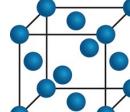
Shared by 2
unit cells

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Number of Atoms Per Unit Cell

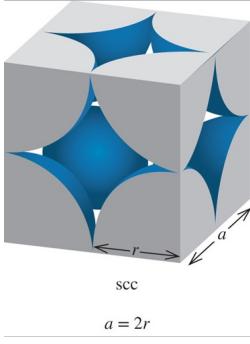
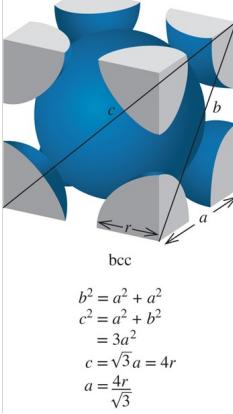
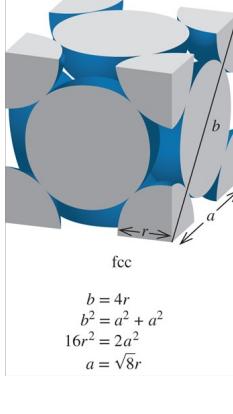
 Simple cubic	 Body-centered cubic	 Face-centered cubic
1 atom/unit cell $(8 \times 1/8 = 1)$	2 atoms/unit cell $(8 \times 1/8 + 1 = 2)$	4 atoms/unit cell $(8 \times 1/8 + 6 \times 1/2 = 2)$

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Relation Between Edge Length and Atomic Radius

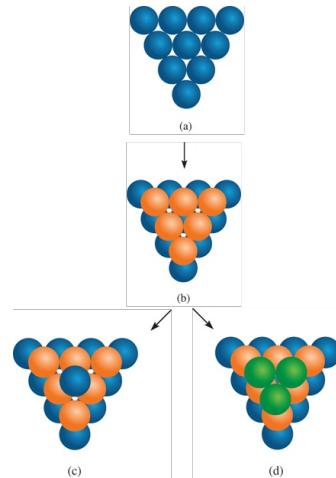
 SCC $a = 2r$	 bcc $\begin{aligned} b^2 &= a^2 + a^2 \\ c^2 &= a^2 + b^2 \\ &= 3a^2 \\ c &= \sqrt{3}a = 4r \\ a &= \frac{4r}{\sqrt{3}} \end{aligned}$	 fcc $\begin{aligned} b &= 4r \\ b^2 &= a^2 + a^2 \\ &= 2a^2 \\ 16r^2 &= 2a^2 \\ a &= \sqrt{8}r \end{aligned}$
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Closest Packing: Hexagonal and Cubic

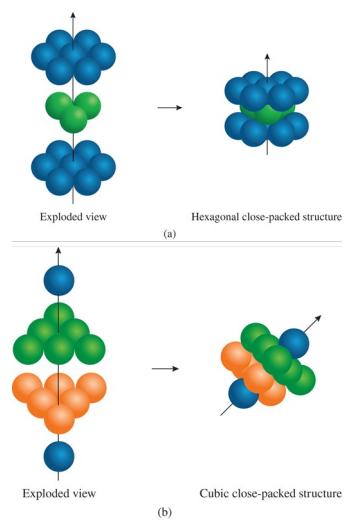


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Exploded Views



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Example 11.3₁

Gold (Au) crystallizes in a cubic close-packed structure (the face-centered cubic unit cell) and has a density of 19.3 g / cm³.

Calculate the atomic radius of gold in picometers.

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Example 11.3₂

Strategy

We want to calculate the radius of a gold atom.

For a face-centered cubic unit cell, the relationship between radius (r) and edge length (a), according to Figure 11.22, is $a = \sqrt{8}r$.

Therefore, to determine r of a Au atom, we need to find a . The volume of a cube is $V = a^3$ or $a = \sqrt[3]{V}$.

Thus, if we can determine the volume of the unit cell, we can calculate a . We are given the density in the problem.

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

need to find
want to calculate
given

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Example 11.3 ₃

The sequence of steps is summarized as follows:

density of unit cell → volume of unit cell → edge length of unit cell → radius of Au atom

Solution

Step 1: We know the density, so in order to determine the volume, we find the mass of the unit cell. Each unit cell has eight corners and six faces. The total number of atoms within such a cell, according to Figure 11.19, is

$$\left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4$$

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Example 11.3 ₄

The mass of a unit cell in grams is

$$\begin{aligned} m &= \frac{4 \text{ atoms}}{1 \text{ unit cell}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{197.0 \text{ g Au}}{1 \text{ mol Au}} \\ &= 1.31 \times 10^{-21} \text{ g/unit cell} \end{aligned}$$

From the definition of density ($d = m/V$), we calculate the volume of the unit cell as follows:

$$V = \frac{m}{d} = \frac{1.31 \times 10^{-21} \text{ g}}{19.3 \text{ g/cm}^3} = 6.79 \times 10^{-23} \text{ cm}^3$$

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Example 11.3 ₅

Step 2: Because volume is length cubed, we take the cubic root of the volume of the unit cell to obtain the edge length (a) of the cell

$$\begin{aligned} a &= \sqrt[3]{V} \\ &= \sqrt[3]{6.79 \times 10^{-23} \text{ cm}^3} \\ &= 4.08 \times 10^{-8} \text{ cm} \end{aligned}$$

Step 3: From Figure 11.22 we see that the radius of an Au sphere (r) is related to the edge length by

$$a = \sqrt{8}r$$

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Example 11.3 ₆

Therefore,

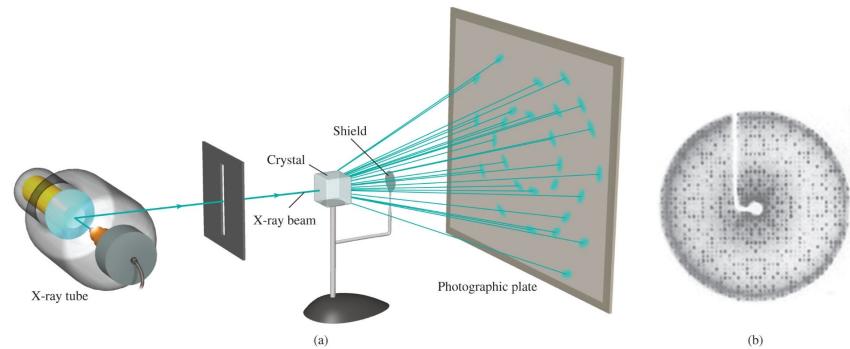
$$\begin{aligned} r &= \frac{a}{\sqrt{8}} = \frac{4.08 \times 10^{-8} \text{ cm}}{\sqrt{8}} \\ &= 1.44 \times 10^{-8} \text{ cm} \\ &= 1.44 \times 10^{-8} \cancel{\text{cm}} \times \frac{1 \times 10^{-2} \cancel{\text{m}}}{1 \cancel{\text{cm}}} \times \frac{1 \text{pm}}{1 \times 10^{-12} \cancel{\text{m}}} \\ &= 144 \text{ pm} \end{aligned}$$

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An Arrangement for Obtaining the X-ray Diffraction Pattern of a Crystal

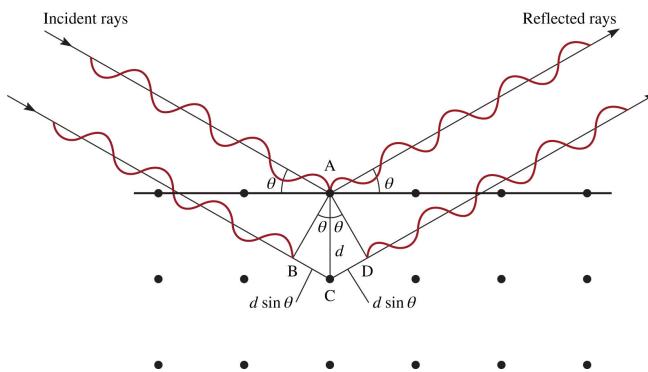


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Reflection of X-rays from Two Layers of Atoms



$$\text{Extra distance} = BC + CD = 2d \sin \theta = n\lambda \quad (\text{Bragg Equation})$$

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Example 11.4₁

X-rays of wavelength 0.154 nm strike an aluminum crystal; the rays are reflected at an angle of 19.3°.

Assuming that $n = 1$, calculate the spacing between the planes of aluminum atoms (in pm) that is responsible for this angle of reflection.

The conversion factor is obtained from 1 nm = 1000 pm.

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Example 11.4₂

Strategy

This is an application of Equation (11.1).

Solution

Converting the wavelength to picometers and using the angle of reflection (19.3°), we write

$$\begin{aligned} d &= \frac{n\lambda}{2\sin\theta} = \frac{\lambda}{2\sin\theta} \\ &= \frac{0.154 \text{ nm} \times \frac{1000 \text{ pm}}{1 \text{ nm}}}{2\sin 19.3^\circ} \\ &= 233 \text{ pm} \end{aligned}$$

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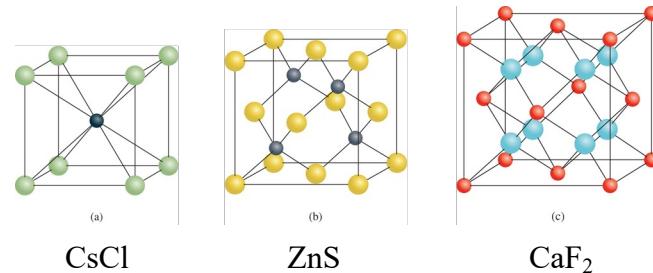
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Types of Crystals

Ionic Crystals

- Lattice points occupied by cations and anions.
- Held together by electrostatic attraction.
- Hard, brittle, high melting point.
- Poor conductor of heat and electricity.



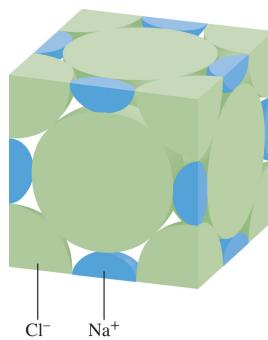
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Example 11.5

How many Na^+ and Cl^- ions are in each NaCl unit cell?



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Example 11.5 2

Solution

NaCl has a structure based on a face-centered cubic lattice. One whole Na^+ ion is at the center of the unit cell, and there are twelve Na^+ ions at the edges. Because each edge Na^+ ion is shared by four unit cells, the total number of Na^+ ions is $1 + (12 \times \frac{1}{4}) = 4$.

Similarly, there are six Cl^- ions at the face centers and eight Cl^- ions at the corners. Each face-centered ion is shared by two unit cells, and each corner ion is shared by eight unit cells, so the total number of Cl^- ions is $(6 \times \frac{1}{2}) + (8 \times \frac{1}{8}) = 4$.

Thus, there are four Na^+ ions and four Cl^- ions in each NaCl unit cell.

Check

This result agrees with sodium chloride's empirical formula.

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Example 11.6 1

The edge length of the NaCl unit cell is 564 pm. What is the density of NaCl in g/cm^3 ?

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Example 11.6₂

Strategy

To calculate the density, we need to know the mass of the unit cell. The volume can be calculated from the given edge length because $V = a^3$. How many Na^+ and Cl^- ions are in a unit cell? What is the total mass in amu? What are the conversion factors between amu and g and between pm and cm?

Solution

From Example 11.5 we see that there are four Na^+ ions and four Cl^- ions in each unit cell. So the total mass (in amu) of a unit cell is

$$\text{mass} = 4(22.99 \text{ amu} + 35.45 \text{ amu}) = 233.8 \text{ amu}$$

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Example 11.6₃

Converting amu to grams, we write

$$233.8 \text{ amu} \times \frac{1 \text{ g}}{6.022 \times 10^{23} \text{ amu}} = 3.882 \times 10^{-22} \text{ g}$$

The volume of the unit cell is $V = a^3 = (564 \text{ pm})^3$. Converting pm^3 to cm^3 , the volume is given by

$$V = (564 \text{ pm})^3 \times \left(\frac{1 \times 10^{-12} \text{ m}}{1 \text{ pm}} \right)^3 \times \left(\frac{1 \text{ cm}}{1 \times 10^{-2} \text{ m}} \right)^3 = 1.794 \times 10^{-22} \text{ cm}^3$$

Finally, from the definition of density

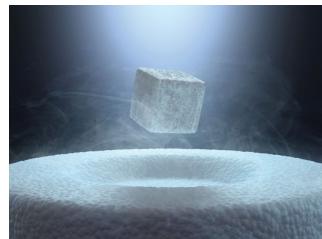
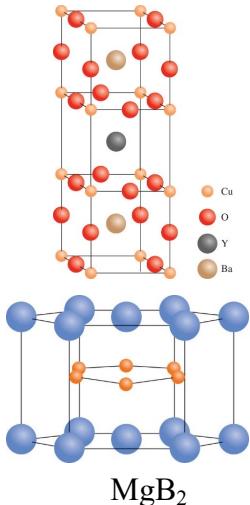
$$\begin{aligned} \text{density} &= \frac{\text{mass}}{\text{volume}} = \frac{3.882 \times 10^{-22} \text{ g}}{1.794 \times 10^{-22} \text{ cm}^3} \\ &= 2.16 \text{ g/cm}^3 \end{aligned}$$

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Chemistry In Action: High-Temperature Superconductors



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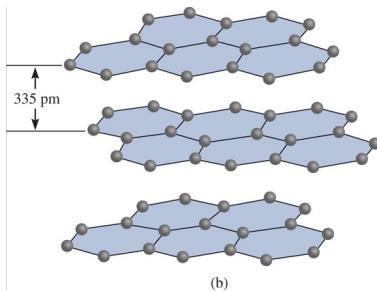
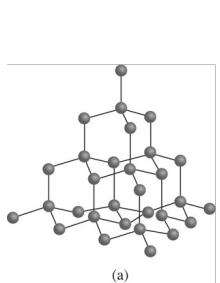
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Types of Crystals 1

Covalent Crystals

- Lattice points occupied by atoms.
- Held together by covalent bonds.
- Hard, high melting point.
- Poor conductor of heat and electricity.



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Types of Crystals ₂

Molecular Crystals

- Lattice points occupied by molecules.
- Held together by intermolecular forces.
- Soft, low melting point.
- Poor conductor of heat and electricity.



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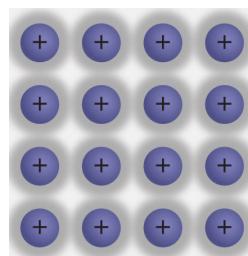
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Types of Crystals ₃

Metallic Crystals

- Lattice points occupied by metal atoms.
- Held together by metallic bonds.
- Soft to hard, low to high melting point.
- Good conductors of heat and electricity.

Cross Section of a Metallic Crystal

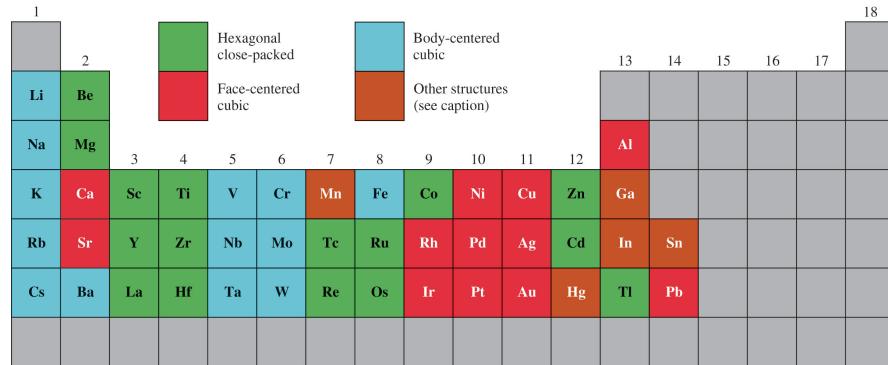


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Crystal Structures of Metals



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Types of Crystals 4

Table 11.4 Types of Crystals and General Properties

Type of Crystal	Force(s) Holding the Units Together	General Properties	Examples
Ionic	Electromagnetic attraction	Hard, brittle, high melting point, poor conductor of heat and electricity	NaCl, LiF, MgO, CaCO ₃
Covalent	Covalent bond	Hard, high melting point, poor conductor of heat and electricity	C (Diamond), SiO ₂ (quartz)
Molecular*	Dispersion forces, dipole-dipole forces, hydrogen bonds	Soft, low melting point, poor conductor of heat and electricity	Ar, CO ₂ , I ₂ , H ₂ O, C ₁₂ H ₂₂ O ₁₁ (sucrose)
Metallic	Metallic bond	Soft to hard, low to high melting point, good conductor of heat and electricity	All metallic element; for example, Na, Mg, Fe, Cu

*Included in this category are crystals made up of individual atoms.

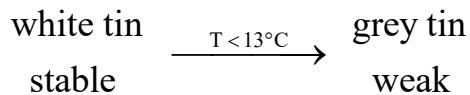
[†]Diamond is a good thermal conductor.

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Chemistry In Action: And All for the Want of a Button



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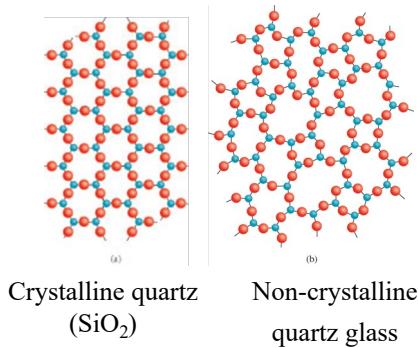
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Types of Solids

An ***amorphous solid*** does not possess a well-defined arrangement and long-range molecular order.

A **glass** is an optically transparent fusion product of inorganic materials that has cooled to a rigid state **without crystallizing**.

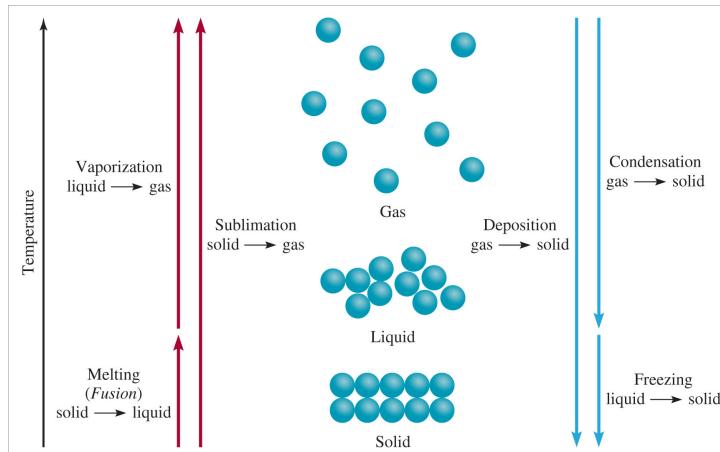


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Phase Changes



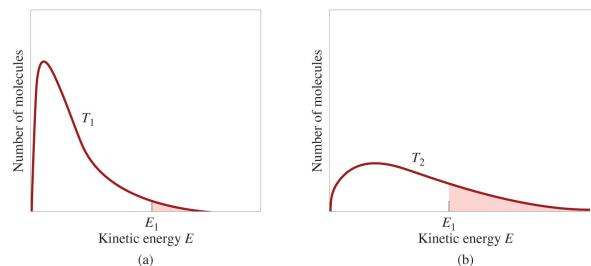
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Effect of Temperature on Kinetic Energy

$$T_2 > T_1$$



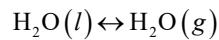
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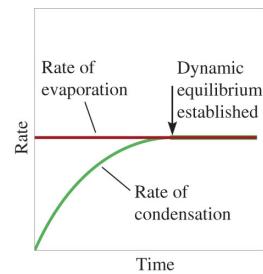
Equilibrium Vapor Pressure

The ***equilibrium vapor pressure*** is the vapor pressure measured when a dynamic equilibrium exists between condensation and evaporation.



Dynamic Equilibrium

$$\begin{array}{c} \text{Rate of} \\ \text{condensation} \end{array} = \begin{array}{c} \text{Rate of} \\ \text{evaporation} \end{array}$$

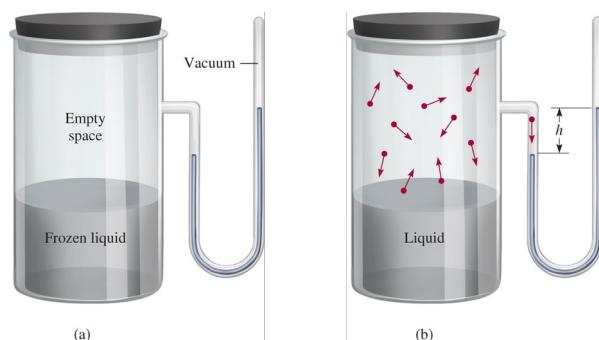


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Measurement of Vapor Pressure



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Molar Heat of Vaporization

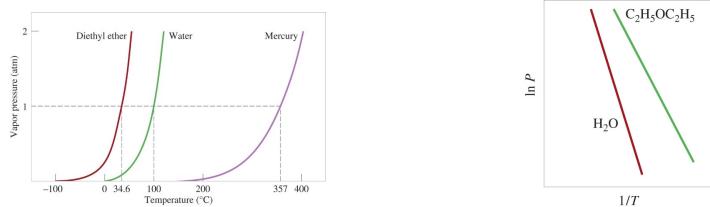
Molar heat of vaporization (ΔH_{vap}) is the energy required to vaporize 1 mole of a liquid at its boiling point.

Clausius-Clapeyron Equation

$$\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + C$$

P = (equilibrium) vapor pressure.
 T = temperature (K).
 R = gas constant (8.314 J/K.mol).

Vapor Pressure Versus Temperature



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Alternate Forms of the Clausius-Clapeyron Equation

At two temperatures

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

or

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

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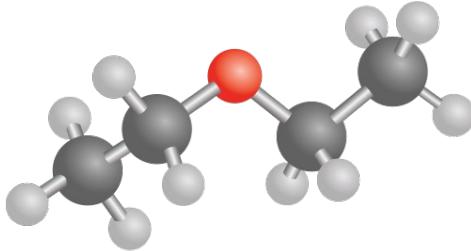
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Example 11.7₁

Diethyl ether is a volatile, highly flammable organic liquid that is used mainly as a solvent.

The vapor pressure of diethyl ether is 401 mmHg at 18°C. Calculate its vapor pressure at 32°C.



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Example 11.7₂

Strategy

We are given the vapor pressure of diethyl ether at one temperature and asked to find the pressure at another temperature. Therefore, we need Equation (11.5).

Solution

Table 11.6 tells us that $\Delta H_{\text{vap}} = 26.0 \text{ kJ/mol}$. The data are

$$\begin{aligned} P_1 &= 401 \text{ mmHg} & P_2 &=? \\ T_1 &= 18^\circ\text{C} = 291 \text{ K} & T_2 &= 32^\circ\text{C} = 305 \text{ K} \end{aligned}$$

From Equation (11.5) we have

$$\begin{aligned} \ln \frac{P_1}{P_2} &= \frac{26,000 \text{ J/mol}}{8.314 \text{ J/K}\cdot\text{mol}} \left[\frac{291\text{K} - 305\text{K}}{(291\text{K})(305\text{K})} \right] \\ &= -0.493 \end{aligned}$$

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Example 11.7 ₃

Taking the antilog of both sides (see Appendix 4), we obtain

$$\frac{401}{P_2} = e^{-0.493} = 0.611$$

Hence

$$P_2 = 656 \text{ mmHg}$$

Check

We expect the vapor pressure to be greater at the higher temperature. Therefore, the answer is reasonable.

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Boiling Point

The **boiling point** is the temperature at which the (equilibrium) vapor pressure of a liquid is equal to the external pressure.

The **normal boiling point** is the temperature at which a liquid boils when the external pressure is 1 atm.

Table 11.6 Molar Heats of Vaporization for Selected Liquids

Substance	Boiling Point * (°C)	ΔH_{vap} (kJ/mol)
Argon (Ar)	-186	6.3
Benzene (C_6H_6)	80.1	31.0
Diethylether ($C_2H_5OC_2H_5$)	34.6	26.0
Ethanol (C_2H_5OH)	78.3	39.3
Mercury (Hg)	357	59.0
Methane (CH_4)	-164	9.2
Water (H_2O)	100	40.79

*Measured at 1 atm.

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Critical Temperature and Pressure

The ***critical temperature*** (T_c) is the temperature above which the gas cannot be made to liquefy, no matter how great the applied pressure.

The ***critical pressure*** (P_c) is the minimum pressure that must be applied to bring about liquefaction at the critical temperature.

Table 11.7 Critical Temperatures and Critical Pressures of Selected Substances

Substance	T_c (°C)	P_c (atm)
Ammonia(NH ₃)	132.4	111.5
Argon(Ar)	-186	6.3
Benzene(C ₆ H ₆)	288.9	47.9
Carbon dioxide(CO ₂)	31.0	73.0
Diethyl ether(C ₂ H ₅ OC ₂ H ₅)	192.6	35.6
Ethanol(C ₂ H ₅ OH)	243	63.0
Mercury(Hg)	1462	1036
Methane(CH ₄)	-83.0	45.6
Molecular hydrogen(H ₂)	-239.9	12.8
Molecular nitrogen(N ₂)	-147.1	33.5
Molecular oxygen(O ₂)	-118.8	49.7
Sulfur hexafluoride(SF ₆)	45.5	37.6
Water(H ₂ O)	374.4	219.5

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The Critical Phenomenon of SF₆



$T < T_c$



$T > T_c$



$T \sim T_c$



$T < T_c$

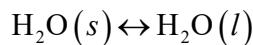
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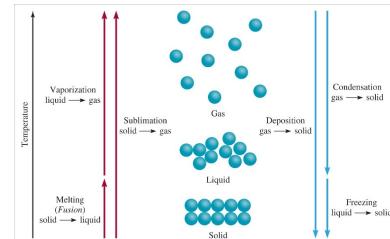
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Solid-Liquid Equilibrium



The **melting point** of a solid or the **freezing point** of a liquid is the temperature at which the solid and liquid phases coexist in equilibrium.



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Molar Heat of Fusion

Molar heat of fusion (ΔH_{fus}) is the energy required to melt 1 mole of a solid substance at its freezing point.

Table 11.8 Molar Heats of Fusion for Selected Substances

Substance	Melting point* (°C)	ΔH_{fus} (kJ/mol)
Argon (Ar)	-190	1.3
Benzene (C ₆ H ₆)	5.5	10.9
Diethyl ether (C ₂ H ₅ OC ₂ H ₅)	-116.2	6.90
Ethanol (C ₂ H ₅ OH)	-117.3	7.61
Mercury (Hg)	-39	23.4
Methane (CH ₄)	-183	0.84
Water (H ₂ O)	0	6.01

*Measured at 1 atm.

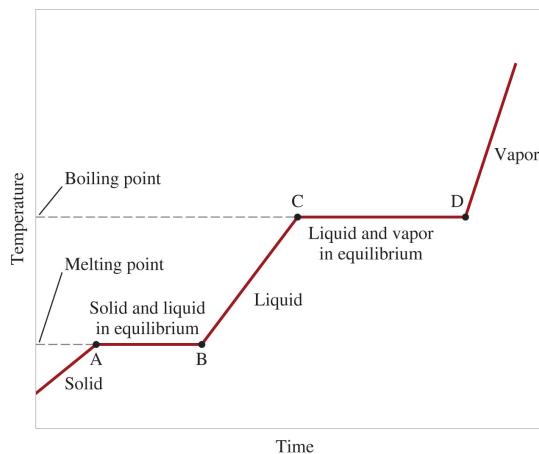
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Heating Curve



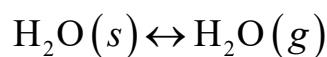
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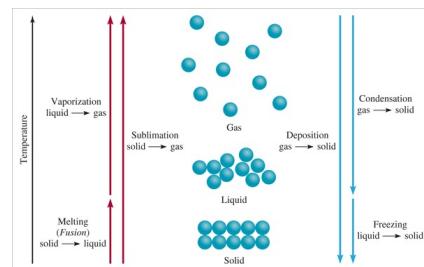
Solid-Gas Equilibrium



Molar heat of sublimation (ΔH_{sub}) is the energy required to sublime 1 mole of a solid.

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

(Hess's law)



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Example 11.8 ₁

Calculate the amount of energy (in kilojoules) needed to heat 346 g of liquid water from 0°C to 182°C.

Assume that the specific heat of water is 4.184 J/g°C over the entire liquid range and that the specific heat of steam is 1.99 J/g°C.

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Example 11.8 ₂

Strategy

The heat change (q) at each stage is given by $q=ms\Delta t$ (see p. 247), where m is the mass of water, s is the specific heat, and Δt is the temperature change.

If there is a phase change, such as vaporization, then q is given by $n \Delta H_{\text{vap}}$, where n is the number of moles of water.

Solution

The calculation can be broken down in three steps.

Step 1: Heating water from 0°C to 100°C

Using Equation (6.12) we write

$$\begin{aligned} q_1 &= ms\Delta t \\ &= (346 \text{ g})(4.184 \text{ J/g}^\circ\text{C})(100^\circ\text{C} - 0^\circ\text{C}) \\ &= 1.45 \times 10^5 \text{ J} \\ &= 145 \text{ kJ} \end{aligned}$$

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Example 11.8 ₃

Step 2: Evaporating 346 g of water at 100°C (a phase change)

In Table 11.7 we see $\Delta H_{vap} = 40.79 \text{ kJ/mol}$ for water, so

$$q_2 = 346 \cancel{\text{g H}_2\text{O}} \times \frac{1 \cancel{\text{mol H}_2\text{O}}}{18.02 \cancel{\text{g H}_2\text{O}}} \times \frac{40.79 \text{ kJ}}{1 \cancel{\text{mol H}_2\text{O}}}$$

$$= 783 \text{ kJ}$$

Step 3: Heating steam from 100° C to 182° C

$$q_3 = ms\Delta t$$

$$= (346 \text{ g})(1.99 \text{ J/g}^\circ\text{C})(182^\circ\text{C} - 100^\circ\text{C})$$

$$= 5.65 \times 10^4 \text{ J}$$

$$= 56.5 \text{ kJ}$$

Example 11.8 ₄

The overall energy required is given by

$$q_{\text{overall}} = q_1 + q_2 + q_3$$

$$= 145 \text{ kJ} + 783 \text{ kJ} + 56.5 \text{ kJ}$$

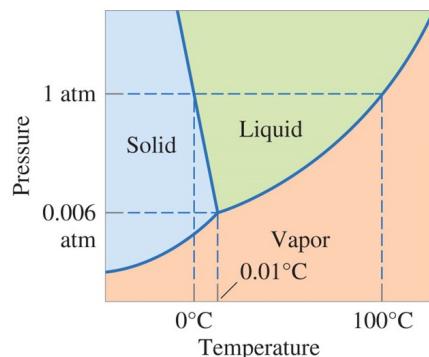
$$= 985 \text{ kJ}$$

Check

All the qs have a positive sign, which is consistent with the fact that heat is absorbed to raise the temperature from 0°C to 182°C. Also, as expected, much more heat is absorbed during the phase transition.

Phase Diagram of Water

A **phase diagram** summarizes the conditions at which a substance exists as a solid, liquid, or gas.



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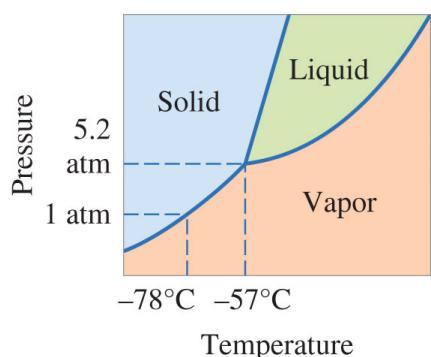
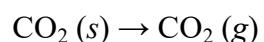
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Phase Diagram of Carbon Dioxide

At 1 atm



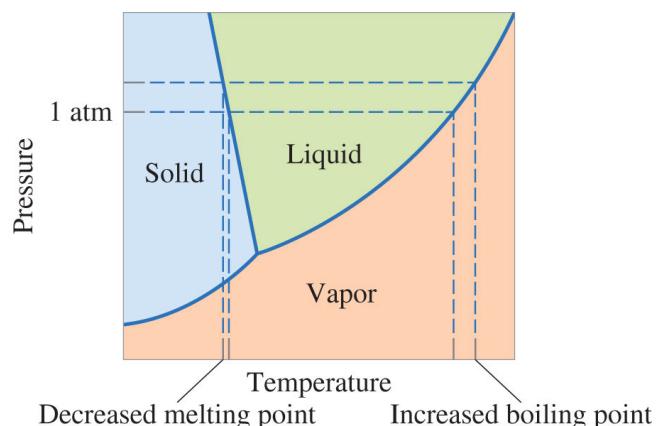
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Effect of Increase in Pressure on the Melting Point of Ice and the Boiling Point of Water



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Chemistry In Action: Ice Skating



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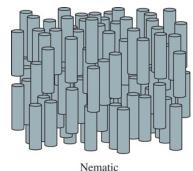
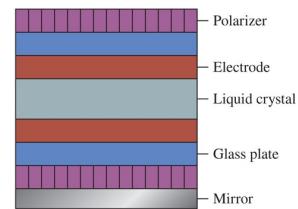
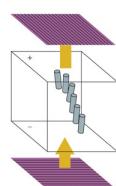
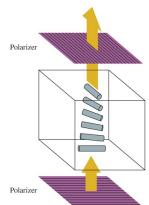
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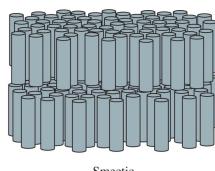
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Chemistry In Action: Liquid Crystals



Nematic



Smectic

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