

Figure 10.23: Partial representation of the molecular orbital energies in (a) diamond and (b) a typical metal.

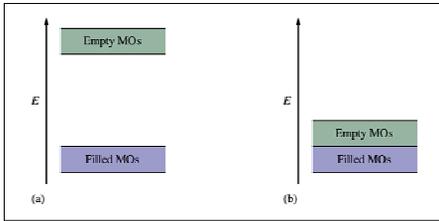


Figure 10.26: (top) The structure of quartz (empirical formula  $\text{SiO}_2$ ). Quartz contains chains of  $\text{SiO}_4$  tetrahedra (bottom) that share oxygen atoms.

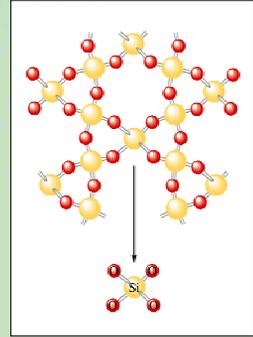


Figure 10.24: The  $p$  orbitals (a) perpendicular to the plane of the carbon ring system in graphite can combine to form (b) an extensive  $\pi$ -bonding network.

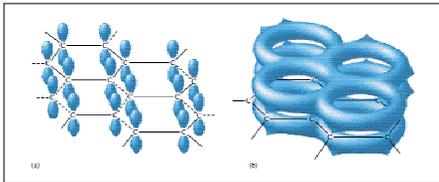


Figure 10.27: Examples of silicate anions, all of which are based on  $\text{SiO}_4^{4-}$  tetrahedra.

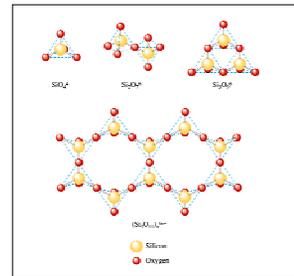


Figure 10.25: Graphite consists of layers of carbon atoms.

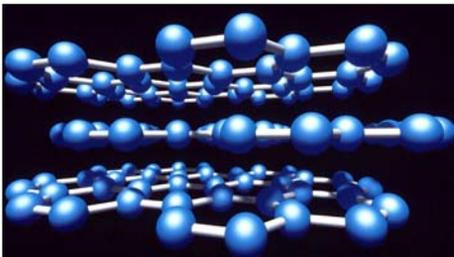


Figure 10.28: Two-dimensional representations of (a) a quartz crystal and (b) a quartz glass.

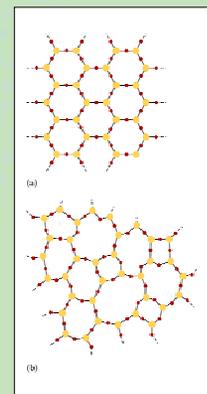
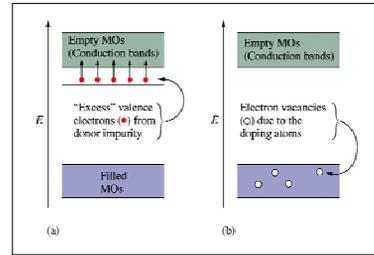


TABLE 10.5 Compositions of Some Common Types of Glass

Type of Glass	Percentages of Various Components					
	SiO <sub>2</sub>	CaO	Na <sub>2</sub> O	PbO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O
Window (soda-lime glass)	72	11	13	—	0.3	3.8
Cookware (aluminosilicate glass)	55	15	—	—	20	—
Heat-resistant (borosilicate glass)	76	3	5	13	2	0.5
Optical	69	12	6	0.3	—	12

Figure 10.30: Energy-level diagrams for (a) an n-type semiconductor and (b) a p-type semiconductor.



## Semiconductors

A substance in which some electrons can cross the band gap.

- Conductivity is enhanced by doping with group 3a or group 5a elements.

Figure 10.31: The p-n junction involves the contact of a p-type and an n-type semiconductor.

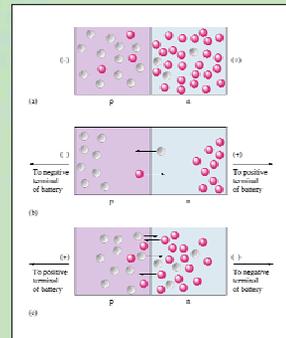
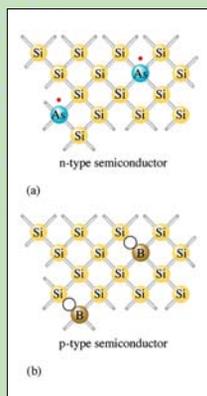


Figure 10.29:

(a) A silicon crystal doped with arsenic, which has one more valence electron than silicon.

(b) A silicon crystal doped with boron, which has one less electron than silicon.



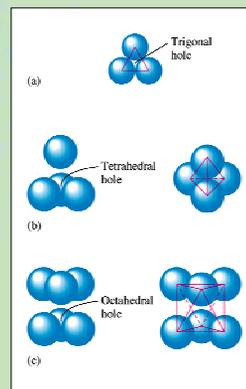
## Types of Solids

- A **molecular solid** is a solid that consists of molecules held together by intermolecular forces.
  - Many solids are of this type.
  - Examples include solid sulfur, solid water (ice), and solid carbon dioxide (dry ice).

Figure 10.34: (a) Sulfur crystals (yellow) contain  $S_8$  molecules. (b) White phosphorus (containing  $P_4$  molecules) is so reactive with the oxygen in air that it must be stored under water.



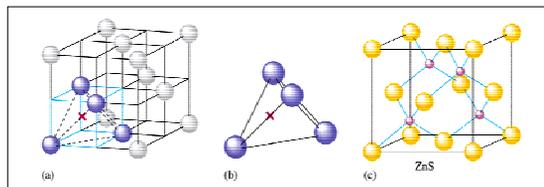
Figure 10.35: The holes that exist among closest packed uniform spheres. (a) The trigonal hole formed by three spheres in a given plane. (b) The tetrahedral hole formed when a sphere occupies a dimple formed by three spheres in an adjacent layer. (c) The octahedral hole formed by six spheres in two adjacent layers.



**TABLE 10.6** Comparison of Atomic Separations Within Molecules (Covalent Bonds) and Between Molecules (Intermolecular Interactions)

Solid	Distance Between Atoms in Molecule*	Closest Distance Between Molecules in the Solid
$P_4$	220 pm	380 pm
$S_8$	206 pm	370 pm
$Cl_2$	199 pm	360 pm

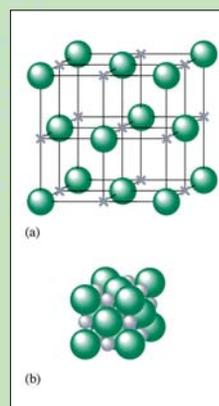
Figure 10.36: (a) The location (X) of a tetrahedral hole in the face-centered cubic unit cell. (b) One of the tetrahedral holes. (c) The unit cell for ZnS where the  $S^{2-}$  ions (yellow) are closest packed with the  $Zn^{2+}$  ions (red) in alternating tetrahedral holes.



## Types of Solids

- An **ionic solid** is a solid that consists of cations and anions held together by electrical attraction of opposite charges (ionic bond).
  - Examples include cesium chloride, sodium chloride, and zinc sulfide (but ZnS has considerable covalent character).

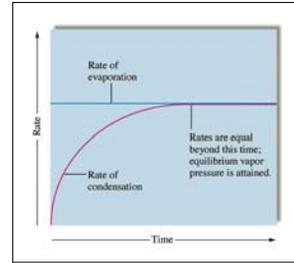
Figure 10.37: (a) The locations (gray X) of the octahedral holes in the face-centered cubic unit cell. (b) Representation of the unit cell for solid NaCl.



**TABLE 10.7** Types and Properties of Solids

Type of Solid:	Atomic		Molecular		Ionic
	Network	Metallic	Group IVA	Molecule	Ion
Structural Unit:	Atom	Atom	Atom	Molecule	Ion
Type of Bonding:	Directional covalent bonds	Nondirectional covalent bonds involving electrons that are delocalized throughout the crystal	London dispersion forces	Polar molecules: dipole-dipole interactions Nonpolar molecules: London dispersion forces	Ionic
Typical Properties:	Hard	Wide range of hardness	Very low melting point	Soft	Hard
	High melting point	Wide range of melting points		Low melting point	High melting point
Examples:	Insulator Diamond	Conductor Silver Iron Brass	Insulator Argon(s)	Insulator Ice (solid H <sub>2</sub> O) Dry ice (solid CO <sub>2</sub> )	Insulator Sodium chloride Calcium fluoride

Figure 10.39: The rates of condensation and evaporation over time for a liquid sealed in a closed container.



## Vapor Pressure

- ... is the pressure of the vapor present at equilibrium.
- ... is determined principally by the size of the intermolecular forces in the liquid.
- ... increases significantly with temperature.
- Volatile liquids have high vapor pressures.

Figure 10.40: (a) The vapor pressure of a liquid can be measured easily using a simple barometer of the type shown here. (b) The three liquids, water, ethanol (C<sub>2</sub>H<sub>5</sub>OH), and diethyl ether [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O], have quite different vapor pressures.

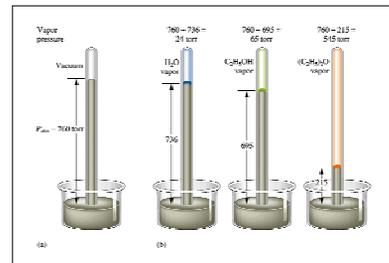


Figure 10.38: Behavior of a liquid in a closed container.

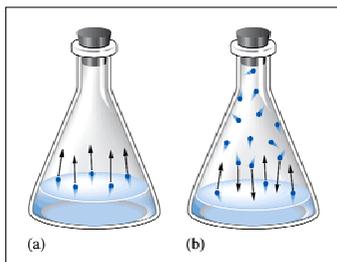
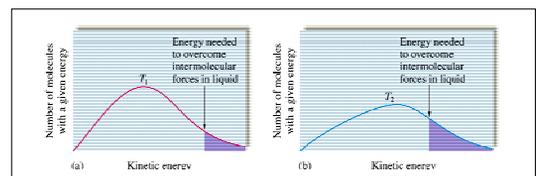


Figure 10.41: Diagram showing the reason vapor pressure depends on temperature.



**TABLE 10.8**  
The Vapor Pressure of Water  
as a Function of Temperature

T (°C)	P (torr)
0.0	4.579
10.0	9.209
20.0	17.535
25.0	23.756
30.0	31.824
40.0	55.324
60.0	149.4
70.0	233.7
90.0	525.8

If we know the vapor pressure,  $P_1$ , of a pure substance at temperature,  $T_1$ , and want to determine the vapor pressure,  $P_2$ , of the substance at a new temperature,  $T_2$ , we can use the Clausius-Clapeyron equation.

Since for a pure substance:

$$\ln P_1 = -\Delta H_{\text{vap}}/RT_1 \quad (1),$$

$$\text{and } \ln P_2 = -\Delta H_{\text{vap}}/RT_2, \quad (2)$$

we can subtract equation (1) from (2) to get:

$$\ln P_2 - \ln P_1 = -\Delta H_{\text{vap}}/RT_2 - (-\Delta H_{\text{vap}}/RT_1).$$

And, collecting terms

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

## Clausius-Clapeyron Equation

- We noted earlier that vapor pressure was a function of temperature.
- It has been demonstrated that the **logarithm of the vapor pressure** of a liquid varies linearly with **absolute temperature, at equilibrium**.
- Consequently, the vapor pressure of a liquid at two different temperatures is described by:

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

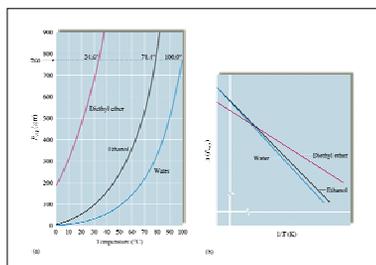
## A Problem to Consider

- Carbon disulfide,  $\text{CS}_2$ , has a normal boiling point of  $46^\circ\text{C}$  (vapor pressure = 760 mmHg) and a heat of vaporization of 26.8 kJ/mol. What is the vapor pressure of carbon disulfide at  $35^\circ\text{C}$ ?
  - Substituting into the Clausius-Clapeyron equation, we obtain:

$$\ln \frac{P_2}{(760 \text{ mm Hg})} = \frac{26.8 \times 10^3 \text{ J/mol}}{8.31 \text{ J/(mol} \cdot \text{K)}} \left( \frac{1}{319 \text{ K}} - \frac{1}{308 \text{ K}} \right)$$

$$= (3225 \text{ K}) \times (-1.12 \times 10^{-4} \text{ K}^{-1}) = -0.361$$

Figure 10.42: (a) The vapor pressure of water, ethanol, and diethyl ether as a function of temperature. (b) Plots of  $\ln(P_{\text{vap}})$  versus  $1/T$  (Kelvin temperature) for water, ethanol, and diethyl ether.



## A Problem to Consider

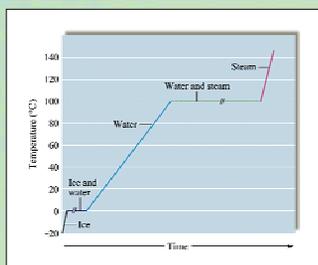
- Carbon disulfide,  $\text{CS}_2$ , has a normal boiling point of  $46^\circ\text{C}$  (vapor pressure = 760 mmHg) and a heat of vaporization of 26.8 kJ/mol. What is the vapor pressure of carbon disulfide at  $35^\circ\text{C}$ ?
  - Taking the antilog we obtain:

$$\frac{P_2}{(760 \text{ mm Hg})} = \text{antilog}(-0.361)$$

$$P_2 = \text{antilog}(-0.361) \times 760 \text{ mm Hg}$$

$$P_2 = 530 \text{ mm Hg}$$

Figure 10.44: The heating curve (not drawn to scale) for a given quantity of water where energy is added at a constant rate.



## Heat of Phase Transition

- To melt a pure substance at its melting point requires an extra boost of energy to overcome **lattice energies**.
  - The heat needed to melt 1 mol of a pure substance is called the **heat of fusion** and denoted  $\Delta H_{\text{fus}}$ .
  - For ice, the heat of fusion is 6.01 kJ/mol.



## Freezing Point

- The temperature at which a pure liquid changes to a crystalline solid, or **freezes**, is called the **freezing point**.
  - The **melting point** is identical to the freezing point and is defined as the temperature at which a solid becomes a liquid.
  - Unlike boiling points, melting points are affected significantly by only large pressure changes.

**TABLE 10.9** Melting Points and Enthalpies of Fusion for Several Representative Solids

Compound	Melting Point (°C)	Enthalpy of Fusion (kJ/mol)
O <sub>2</sub>	-218	0.45
HCl	-114	1.99
HI	-51	2.87
CCl <sub>4</sub>	-23	2.51
CHCl <sub>3</sub>	-64	9.20
H <sub>2</sub> O	0	6.02
NaF	992	29.3
NaCl	801	30.2

## Melting Point

Molecules break loose from lattice points and solid changes to liquid. (Temperature is constant as melting occurs.)

vapor pressure of solid = vapor pressure of liquid

Figure 10.46: Solid and liquid phases in equilibrium with the vapor pressure.

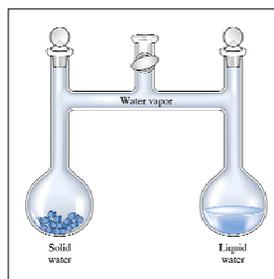
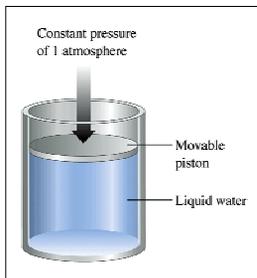


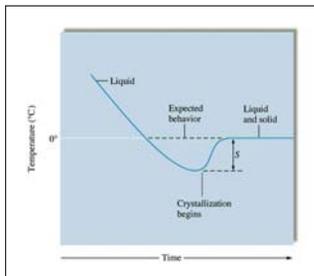
Figure 10.47: Water in a closed system with a pressure of 1 atm exerted on the piston. No bubbles can form within the liquid as long as the vapor pressure is less than 1 atm.



## Boiling Point

- The temperature at which the vapor pressure of a liquid equals the pressure exerted on the liquid is called the **boiling point**.
  - As the temperature of a liquid increases, the vapor pressure increases until it reaches atmospheric pressure.
  - At this point, stable bubbles of vapor form within the liquid. This is called **boiling**.
  - The **normal boiling point** is the boiling point at 1 atm.

Figure 10.48: The supercooling of water. The extent of supercooling is given by  $S$ .



Boiling chip releasing air bubbles acts as a nucleating agent for the bubbles that form when water boils.



## Boiling Point

Constant temperature when added energy is used to vaporize the liquid.

vapor pressure of liquid = pressure of surrounding atmosphere

TABLE 10.10 Boiling Point of Water at Various Locations

Location	Feet Above Sea Level	$P_{\text{atm}}$ (torr)	Boiling Point (°C)
Top of Mt. Everest, Tibet	29,028	240	70
Top of Mt. McKinley, Alaska	20,320	340	79
Top of Mt. Whitney, Calif.	14,494	430	85
Leadville, Colo.	10,150	510	89
Top of Mt. Washington, N.H.	6,293	590	93
Boulder, Colo.	5,430	610	94
Madison, Wis.	900	730	99
New York City, N.Y.	10	760	100
Death Valley, Calif.	-282	770	100.3

Problem 77, p. 504

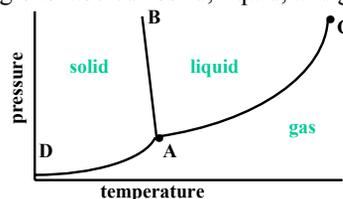
## A Problem to Consider

- The heat of vaporization of ammonia is 23.4 kJ/mol. How much heat is required to vaporize 1.00 kg of ammonia?
  - First, we must determine the number of moles of ammonia in 1.00 kg (1000 g).

$$1.00 \times 10^3 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.0 \text{ g NH}_3} = 58.8 \text{ mol NH}_3$$

## Phase Diagrams

- Below is a typical phase diagram. It consists of three curves that divide the diagram into regions labeled “solid, liquid, and gas”.



## A Problem to Consider

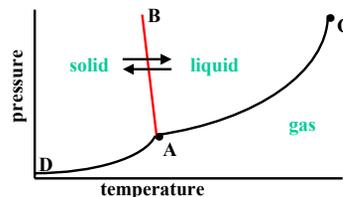
- The heat of vaporization of ammonia is 23.4 kJ/mol. How much heat is required to vaporize 1.00 kg of ammonia?
  - Then we can determine the heat required for vaporization.

$$58.8 \text{ mol NH}_3 \times 23.4 \text{ kJ/mol} = 1.38 \times 10^3 \text{ kJ}$$

Problem 83, p. 504

## Phase Diagrams

- Curve **AB**, dividing the solid region from the liquid region, represents the conditions under which the solid and liquid are in equilibrium.



## Phase Diagram

Represents phases as a function of temperature and pressure.

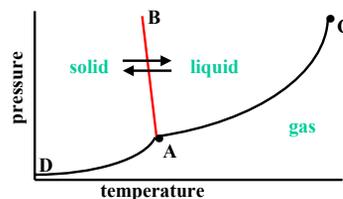
critical temperature: temperature above which the vapor can not be liquefied.

critical pressure: pressure required to liquefy AT the critical temperature.

critical point: critical temperature and pressure (for water,  $T_c = 374^\circ\text{C}$  and 218 atm).

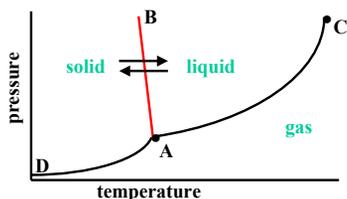
## Phase Diagrams

- Usually, the melting point is only slightly affected by pressure. For this reason, the melting point curve, AB, is nearly vertical.



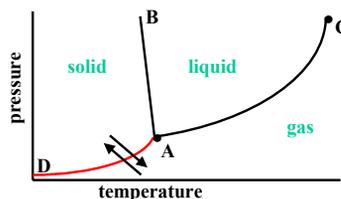
## Phase Diagrams

- If a liquid is **more dense** than its solid, the curve leans slightly to the **left**, causing the melting point to **decrease** with pressure.



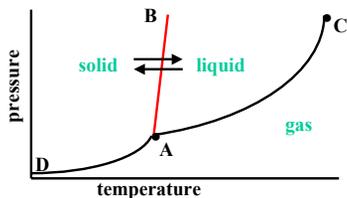
## Phase Diagrams

- Curve **AD**, which divides the solid region from the gaseous region, represents the vapor pressures of the solid at various temperatures.



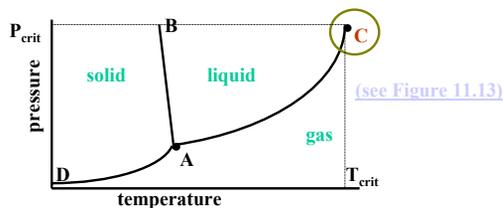
## Phase Diagrams

- If a liquid is **less dense** than its solid, the curve leans slightly to the **right**, causing the melting point to **increase** with pressure.



## Phase Diagrams

- The vapor pressure at the critical temperature is called the **critical pressure**. Note that curve AC ends at the **critical point, C**.



## Phase Diagrams

- Curve **AC**, which divides the liquid region from the gaseous region, represents the boiling points of the liquid for various pressures.

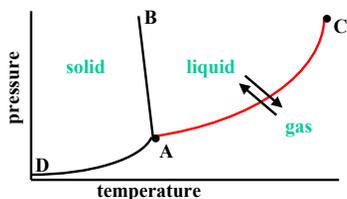


Figure 11.13: Observing the critical phenomenon.

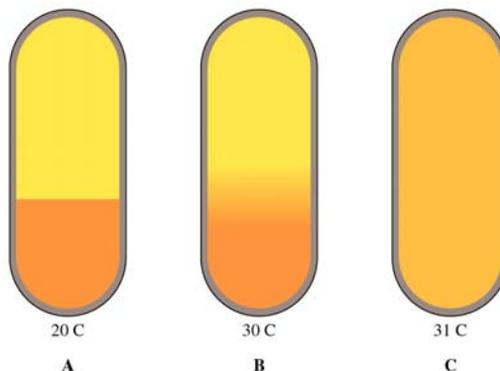


Figure 10.49: The phase diagram for water.

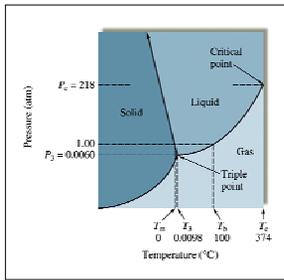


Figure 10.52: The phase diagram for carbon dioxide.

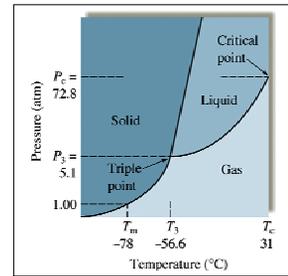


Figure 10.50: Diagrams of various heating experiments on samples of water in a closed system.

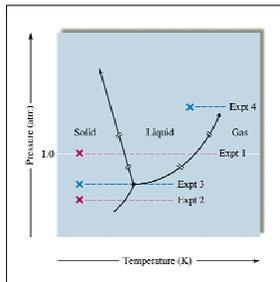


Figure 10.51: The phase diagram for water. At point X on the phase diagram, water is a solid.

