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

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

Figure 10.25: Graphite consists of layers of carbon atoms.

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

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

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

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

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\textsubscript{8} molecules. (b) White phosphorus (containing P\textsubscript{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.

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\textsuperscript{2-} ions (yellow) are closest packed with the Zn\textsuperscript{2+} ions (red) in alternating tetrahedral holes.

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.

**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).

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

<table>
<thead>
<tr>
<th>Solid</th>
<th>Distance Between Atoms in Molecule*</th>
<th>Closest Distance Between Molecules in the Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>P\textsubscript{4}</td>
<td>220 pm</td>
<td>380 pm</td>
</tr>
<tr>
<td>S\textsubscript{8}</td>
<td>76 pm</td>
<td>170 pm</td>
</tr>
<tr>
<td>Cl\textsubscript{2}</td>
<td>199 pm</td>
<td>362 pm</td>
</tr>
</tbody>
</table>
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.

Table 10.17: Types and Properties of Solids

<table>
<thead>
<tr>
<th>Type of Solid</th>
<th>Description</th>
<th>Molecular Motion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Network</td>
<td>Atoms</td>
<td>Limited mobility</td>
</tr>
<tr>
<td>Molecule</td>
<td>Atoms</td>
<td>Complete mobility</td>
</tr>
<tr>
<td>Crystal</td>
<td>Ions</td>
<td>Limited mobility</td>
</tr>
</tbody>
</table>

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

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

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 \((\text{C}_2\text{H}_5\text{OH})\), and diethyl ether \((\text{C}_2\text{H}_5\text{O})_2\) have quite different vapor pressures.

Figure 10.41: Diagram showing the reason vapor pressure depends on temperature.
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:
\[
\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{RT_1} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

A Problem to Consider

• Carbon disulfide, CS$_2$, has a normal boiling point of 46°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°C?

Substituting into the Clausius-Clapeyron equation, we obtain:
\[
\ln \frac{P_2}{P_1} = \frac{26.8 \times 10^3 \text{ J/mol}}{8.31 \text{ J/(mol·K)}} \left( \frac{1}{319 \text{ K}} - \frac{1}{308 \text{ K}} \right)
\]
\[
= (3225 \text{ K}) \times (-1.12 \times 10^4 \text{ K}^{-1}) = -0.361
\]

A Problem to Consider

• Carbon disulfide, CS$_2$, has a normal boiling point of 46°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°C?

• Taking the antiln we obtain:
\[
\frac{P_2}{(760 \text{ mm Hg})} = \text{antiln}(-0.361)
\]
\[
P_2 = \text{antiln}(-0.361) \times 760 \text{ mm Hg}
\]
\[
P_2 = 530 \text{ mm Hg}
\]
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.

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.

$$\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l); \quad \Delta H_{\text{fus}} = 6.01 \text{ kJ}$$

### Table 10.9 Melting Points and Enthalpies of Fusion for Several Representative Solids

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point ($^\circ$C)</th>
<th>Enthalpy of Fusion (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_4$</td>
<td>256</td>
<td>0.45</td>
</tr>
<tr>
<td>$\text{HCl}$</td>
<td>-115</td>
<td>1.99</td>
</tr>
<tr>
<td>$\text{HF}$</td>
<td>18</td>
<td>1.97</td>
</tr>
<tr>
<td>$\text{CCl}_4$</td>
<td>54</td>
<td>3.11</td>
</tr>
<tr>
<td>$\text{CH}_3\text{Cl}$</td>
<td>64</td>
<td>3.70</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>0</td>
<td>6.17</td>
</tr>
<tr>
<td>$\text{NaCl}$</td>
<td>900</td>
<td>59.3</td>
</tr>
<tr>
<td>$\text{NaNO}_3$</td>
<td>301</td>
<td>106</td>
</tr>
</tbody>
</table>

Melting Point

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

$$\text{vapor pressure of solid} = \text{vapor pressure of liquid}$$

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

Boiling Point

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

\[
\text{vapor pressure of liquid} = \text{pressure of surrounding atmosphere}
\]

### Table 10.10: Boiling Point of Water at Various Locations

<table>
<thead>
<tr>
<th>Location</th>
<th>Sea Level (mm)</th>
<th>h (ft)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top of Mt. Everest, Tibet</td>
<td>26,628</td>
<td>210</td>
<td>79</td>
</tr>
<tr>
<td>Top of Mt. McKinley, Alaska</td>
<td>20,300</td>
<td>667</td>
<td>79</td>
</tr>
<tr>
<td>Top of Mt. Whitney, Calif.</td>
<td>44,494</td>
<td>1450</td>
<td>76</td>
</tr>
<tr>
<td>Leadville, Colo.</td>
<td>3,658</td>
<td>120</td>
<td>80</td>
</tr>
<tr>
<td>Top of Mt. Washington, N.Y.</td>
<td>2,034</td>
<td>667</td>
<td>98</td>
</tr>
<tr>
<td>Hudson Falls, N.Y.</td>
<td>0</td>
<td>0</td>
<td>98</td>
</tr>
<tr>
<td>Midway, Wisc.</td>
<td>881</td>
<td>290</td>
<td>98</td>
</tr>
<tr>
<td>New York City, N.Y.</td>
<td>211</td>
<td>701</td>
<td>100</td>
</tr>
<tr>
<td>Death Valley, Calif.</td>
<td>–282</td>
<td>771</td>
<td>100.3</td>
</tr>
</tbody>
</table>
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.
  $$58.8 \text{ mol NH}_3 \times 23.4 \text{ kJ/mol} = 1.38 \times 10^3 \text{ kJ}$$

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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

Represent 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.

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

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

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

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

*Figure 11.13: Observing the critical phenomenon.*
Figure 10.49: The phase diagram for water.

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.

Figure 10.52: The phase diagram for carbon dioxide.