WHY?

• Why is water usually a liquid and not a gas?
• Why does liquid water boil at such a high temperature for such a small molecule?
• Why does ice float on water?
• Why do snowflakes have 6 sides?
• Why is I$_2$ a solid whereas Cl$_2$ is a gas?
• Why are NaCl crystals little cubes?
Liquids, Solids
& Intermolecular Forces
Chap. 13
Have studied **INTRA**molecular forces—the forces holding atoms together to form molecules.

**Now turn to forces between molecules — INTER**molecular forces.

Forces between molecules, between ions, or between molecules and ions.
**Ion-Ion Forces for comparison of magnitude**

Na\(^+\)–Cl\(^-\) in salt

These are the strongest forces.

Lead to solids with high melting temperatures.

**NaCl**, mp = 800 °C

**MgO**, mp = 2800 °C
Water is highly polar and can interact with positive ions to give hydrated ions in water.
Water is highly polar and can interact with positive ions to give hydrated ions in water.
Attraction Between Ions and Permanent Dipoles

- Many metal ions are hydrated. This is the reason metal salts dissolve in water.

- Fe(H₂O)₆³⁺
- Ni(H₂O)₆²⁺
- Co(H₂O)₆²⁺
- Cu(H₂O)₆²⁺

Octahedral

[\text{M(H₂O)₆}^{n⁺}]
Attraction between ions and permanent dipoles depends on ion charge and ion-dipole distance. Measured by $\Delta H$ for $M^{n+} + H_2O \rightarrow [M(H_2O)_x]^{n+}$
Dipole–Dipole Forces

Such forces bind molecules having permanent dipoles to one another.
Influence of dipole-dipole forces is seen in the boiling points of simple molecules.

<table>
<thead>
<tr>
<th>Compd</th>
<th>Mol. Wt.</th>
<th>Boil Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)</td>
<td>28</td>
<td>-196 °C</td>
</tr>
<tr>
<td>CO</td>
<td>28</td>
<td>-192 °C</td>
</tr>
<tr>
<td>Br(_2)</td>
<td>160</td>
<td>59 °C</td>
</tr>
<tr>
<td>ICl</td>
<td>162</td>
<td>97 °C</td>
</tr>
</tbody>
</table>
A special form of dipole-dipole attraction, which enhances dipole-dipole attractions.

H-bonding is strongest when X and Y are N, O, or F.

<table>
<thead>
<tr>
<th>Types of Hydrogen Bonds [X—H···:Y]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N—H···:N</td>
</tr>
<tr>
<td>N—H···:O</td>
</tr>
<tr>
<td>N—H···:F</td>
</tr>
</tbody>
</table>
H-Bonding Between Methanol and Water
H-Bonding Between Two Methanol Molecules
H-Bonding Between Ammonia and Water

This H-bond leads to the formation of NH$_4^+$ and OH$^-$. 
Hydrogen Bonding in $\text{H}_2\text{O}$

H-bonding is especially strong in water because

- the O—H bond is very polar
- there are 2 lone pairs on the O atom

Accounts for many of water’s unique properties.
Ice has open lattice-like structure.

Ice density is < liquid.

And so solid floats on water.

Snow flake: http://www.its.caltech.edu/~atomic/snowcrystals/snow3x.jpg
Ice has open lattice-like structure. Ice density is $< 1$ liquid and so solid floats on water.
Hydrogen Bonding in $\text{H}_2\text{O}$

H bonds $\rightarrow$ abnormally high specific heat capacity of water (4.184 g/K•mol).

This is the reason water is used to put out fires, it is the reason lakes/oceans control climate, and is the reason thunderstorms release huge energy.
Hydrogen Bonding

H bonds leads to abnormally high boiling point of water.

See Screen 13.7
Boiling Points of Simple Hydrocarbon Compounds
H-bonding is especially strong in biological systems — such as DNA.

DNA — helical chains of phosphate groups and sugar molecules. Chains are helical because of tetrahedral geometry of P, C, and O.

Chains bind to one another by specific hydrogen bonding between pairs of Lewis bases.

— adenine with thymine
— guanine with cytosine
Portion of a DNA chain

Double helix of DNA

Pairing between bases on two chains leads to the double helix of DNA. In humans, there are about 3 billion base pairs in all of our DNA.
Base-Pairing through H-Bonds
Double Helix of DNA
Hydrogen Bonding in Biology

Hydrogen bonding and base pairing in DNA.

See Screen 13.6
How can non-polar molecules such as O\textsubscript{2} and I\textsubscript{2} dissolve in water?

The water dipole **INDUCES** a dipole in the O\textsubscript{2} electric cloud.

Dipole-induced dipole
FORCES INVOLVING
INDUCED DIPOLES

Solubility increases with mass the gas

Table 13.2  •  The Solubility of Some Gases in Water*

<table>
<thead>
<tr>
<th>Gas</th>
<th>Molar Mass (g/mol)</th>
<th>Solubility at 20 °C (g gas/100 g water)†</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>2.01</td>
<td>0.000160</td>
</tr>
<tr>
<td>N₂</td>
<td>28.0</td>
<td>0.000190</td>
</tr>
<tr>
<td>O₂</td>
<td>32.0</td>
<td>0.000434</td>
</tr>
</tbody>
</table>

The dipole of water induces a dipole in O₂ by distorting the O₂ electron cloud.
FORCES INVOLVING INDUCED DIPOLES

- Consider I\(_2\) dissolving in alcohol, CH\(_3\)CH\(_2\)OH.

The alcohol temporarily creates or INDUCES a dipole in I\(_2\).
FORCES INVOLVING INDUCED DIPOLES

Formation of a dipole in two nonpolar I₂ molecules.

<table>
<thead>
<tr>
<th>I – I</th>
<th>I – I</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Dipole</td>
<td>No Dipole</td>
</tr>
</tbody>
</table>

Induced dipole-induced dipole

Two nonpolar atoms or molecules (Time-averaged shape is spherical)

Momentary attractions and repulsions between nuclei and electrons in neighboring molecules lead to induced dipoles.

Correlation of the electron motions between the two atoms or molecules (which are now dipolar) leads to a lower energy and stabilizes the system.
The induced forces between I$_2$ molecules are very weak, so solid I$_2$ sublimes (goes from a solid to gaseous molecules).
The magnitude of the induced dipole depends on the tendency to be distorted.

Higher molec. weight --> larger induced dipoles.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ (methane)</td>
<td>-161.5</td>
</tr>
<tr>
<td>C₂H₆ (ethane)</td>
<td>-88.6</td>
</tr>
<tr>
<td>C₃H₈ (propane)</td>
<td>-42.1</td>
</tr>
<tr>
<td>C₄H₁₀ (butane)</td>
<td>-0.5</td>
</tr>
</tbody>
</table>
Boiling Points of Hydrocarbons

Note linear relation between bp and molar mass.
# Intermolecular Forces Summary

<table>
<thead>
<tr>
<th>Type of Interaction</th>
<th>Factors Responsible for Interaction</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipole–dipole</td>
<td>Dipole moment (depends on atom electronegativities and molecular structure)</td>
<td>H₂O, HCl</td>
</tr>
<tr>
<td>Hydrogen bonding, X — H … :Y</td>
<td>Very polar X — H bond (where X = F, N, O) and atom Y with lone pair of electrons</td>
<td>H₂O … H₂O</td>
</tr>
<tr>
<td></td>
<td>An extreme form of dipole–dipole interaction</td>
<td></td>
</tr>
<tr>
<td>Dipole/induced dipole</td>
<td>Dipole moment of polar molecule and polarizability of nonpolar molecule</td>
<td>H₂O … I₂</td>
</tr>
<tr>
<td>Induced dipole/induced dipole (London dispersion forces)</td>
<td>Polarizability</td>
<td>I₂ … I₂</td>
</tr>
</tbody>
</table>
Methane Hydrate

http://www.gsj.go.jp/dMG/hydrate/MH.burn.gif
In a liquid

- molecules are in constant motion
- there are appreciable intermolec. forces
- molecules close together
- Liquids are almost incompressible
- Liquids do not fill the container
The two key properties we need to describe are **EVAPORATION** and its opposite—**CONDENSATION**.

In **evaporation**, energy is added, breaking intermolecular bonds, and moving from liquid to vapor. Conversely, in **condensation**, energy is removed, making intermolecular bonds, and moving from vapor to liquid.
To evaporate, molecules must have sufficient energy to break IM forces.

Breaking IM forces requires energy. The process of evaporation is endothermic.
Liquids—
Distribution of Energies

Distribution of molecular energies in a liquid.
KE is proportional to T.

Minimum energy req’d to break IM forces and evaporate.

See Figure 13.12
Distribution of Energy in a Liquid

Figure 13.12
At higher T a much larger number of molecules has high enough energy to break IM forces and move from liquid to vapor state.

High E molecules carry away E. You cool down when sweating or after swimming.
When molecules of liquid are in the vapor state, they exert a **VAPOR PRESSURE**.

**EQUILIBRIUM VAPOR PRESSURE** is the pressure exerted by a vapor over a liquid in a closed container when the **rate of evaporation** = the **rate of condensation**.
Equilibrium Vapor Pressure

Liquid in flask evaporates and exerts pressure on manometer.

See Fig. 13.15
Vapor Pressure

CD, Screen 13.9
Equilibrium Vapor Pressure

Figure 13.16
FIGURE 13.16: VP as a function of T.

1. The curves show all conditions of P and T where LIQ and VAP are in EQUILIBRIUM.
2. The VP rises with T.
3. When VP = external P, the liquid boils.
   This means that BP’s of liquids change with altitude.
Boiling Liquids

Liquid boils when its vapor pressure equals atmospheric pressure.
Boiling Point at Lower Pressure

When pressure is lowered, the vapor pressure can equal the external pressure at a lower temperature.
Consequences of Vapor Pressure Changes

When can cools, vp of water drops. Pressure in the can is less than that of atmosphere, so can is crushed.
Liquids

Figure 13.16: VP versus T

4. If external $P = 760$ mm Hg, $T$ of boiling is the NORMAL BOILING POINT.

5. VP of a given molecule at a given $T$ depends on IM forces. Here the VP’s are in the order of increasing strength of IM interactions:

```
ether: \( \text{H}_5\text{C}_2\text{O} \), dipole-dipole
alcohol: \( \text{H}_5\text{C}_2\text{O} \), H-bonds
water: \( \text{H}_2\text{O} \), extensive H-bonds
```

increasing strength of IM interactions
Liquids

**HEAT OF VAPORIZATION** is the heat req’d (at constant P) to vaporize the liquid.

\[
\text{LIQ} + \text{heat} \quad \rightarrow \quad \text{VAP}
\]

<table>
<thead>
<tr>
<th>Compd.</th>
<th>(\Delta H_{\text{vap}}) (kJ/mol)</th>
<th>IM Force</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>40.7 (100 °C)</td>
<td>H-bonds</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>26.8 (-47 °C)</td>
<td>dipole</td>
</tr>
<tr>
<td>Xe</td>
<td>12.6 (-107 °C)</td>
<td>induced dipole</td>
</tr>
</tbody>
</table>
Molecules at surface behave differently than those in the interior.

Molecules at surface experience net INWARD force of attraction.

This leads to **SURFACE TENSION** — the energy req’d to break the surface.
Surface Tension

SURFACE TENSION also leads to spherical liquid droplets.
Intermolec. forces also lead to **CAPILLARY** action and to the existence of a concave meniscus for a water column.

- **ADHESIVE FORCES** between water and glass
- **COHESIVE FORCES** between water molecules
Capillary Action

Movement of water up a piece of paper depends on H-bonds between H\textsubscript{2}O and the OH groups of the cellulose in the paper.
Finding the Lattice Type

**PROBLEM**
Al has density $= 2.699 \text{ g/cm}^3$ and Al radius $= 143 \text{ pm}$.
Verify that Al is FCC.

**SOLUTION**
1. Calc. unit cell volume
$V = (\text{cell edge})^3$
Edge distance comes from face diagonal.
Diagonal distance $= \sqrt{2} \cdot \text{edge}$
Finding the Lattice Type

**PROBLEM**  Al has density = 2.699 g/cm³ and Al radius = 143 pm. Verify that Al is FCC.

**SOLUTION**

\[ V = (\text{cell edge})^3 \text{ and face diagonal} = \sqrt{2} \cdot \text{edge} \]

\[(\text{Diagonal})^2 = 2(\text{edge})^2\]

Therefore,

\[ \text{Diag} = \sqrt{2} \cdot (\text{edge}) \]
PROBLEM  Al has density = 2.699 g/cm$^3$ and Al radius = 143 pm. Verify that Al is FCC.

SOLUTION

Here diagonal = 4 • radius of Al = 572 pm
Therefore, edge = 572 pm / $\sqrt{2} = 404$ pm
In centimeters, edge = 4.04 x 10^{-8} cm
So, V of unit cell = (4.04 x 10^{-8} cm$^3$

V = 6.62 x 10^{-23} cm$^3$
PROBLEM  Al has density = 2.699 g/cm\(^3\) and Al radius = 143 pm. Verify that Al is FCC.

SOLUTION

2. Use V and density to calc. mass of unit cell from

\[ \text{DENS} = \frac{\text{MASS}}{\text{VOL}} \]

Mass = density \( \cdot \) volume

\[ = (6.62 \times 10^{-23} \text{ cm}^3)(2.699 \text{ g/cm}^3) \]

\[ = 1.79 \times 10^{-22} \text{ g/unit cell} \]
Finding the Lattice Type

**PROBLEM**  Al has density = 2.699 g/cm$^3$ and Al radius = 143 pm. Verify that Al is FCC.

**SOLUTION**

3. Calculate number of Al per unit cell from mass of unit cell.

\[
\text{Mass 1 Al atom} = \frac{26.98 \text{ g}}{\text{mol}} \cdot \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}}
\]

\[
1 \text{ atom} = 4.480 \times 10^{-23} \text{ g}, \text{ so}
\]

\[
\frac{1.79 \times 10^{-22} \text{ g}}{\text{unit cell}} \cdot \frac{1 \text{ atom}}{4.480 \times 10^{-23} \text{ g}} = 3.99 \text{ Al atoms/unit cell}
\]
Number of Atoms per Unit Cell

How can there be 4 atoms in a unit cell?

1. Each corner Al is 1/8 inside the unit cell.
   
   8 corners (1/8 Al per corner) = 1 net Al

2. Each face Al is 1/2 inside the cell
   
   6 faces (1/2 per face) = 3 net Al’s