"A" students work (without solutions manual) ~ 10 problems/night.

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Module #12
Intermolecular Forces

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Reference State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>m</td>
<td>size of earth</td>
</tr>
<tr>
<td>Volume</td>
<td>cm³</td>
<td>m</td>
</tr>
<tr>
<td>Weight</td>
<td>gram</td>
<td>mass of 1 cm³ water at specified Temp (and Pressure)</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C, K</td>
<td>boiling, freezing of water (specified Pressure)</td>
</tr>
<tr>
<td>1.66053873x10⁻²⁴kg</td>
<td>amu</td>
<td>(mass of 1C-12 atom)/12</td>
</tr>
<tr>
<td>quantity</td>
<td>mole</td>
<td>atomic mass of an element in grams</td>
</tr>
<tr>
<td>Pressure</td>
<td>atm, mm Hg</td>
<td>earth’s atmosphere at sea level</td>
</tr>
<tr>
<td>Energy, General</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Animal</td>
<td>hp</td>
<td>horse on treadmill</td>
</tr>
<tr>
<td>heat</td>
<td>BTU</td>
<td>1 lb water 1 °F</td>
</tr>
<tr>
<td>Kinetic</td>
<td>J</td>
<td>m, kg, s</td>
</tr>
<tr>
<td>Electrostatic</td>
<td></td>
<td>1 electrical charge against 1 V</td>
</tr>
<tr>
<td>electronic states in atom</td>
<td></td>
<td>Energy of electron in vacuum</td>
</tr>
<tr>
<td>Electronegativity</td>
<td>F</td>
<td></td>
</tr>
</tbody>
</table>

Heat flow measurements  constant pressure, define system vs surroundings per mole basis (intensive)

FITCH Rules

- **G1: Suzuki is Success**
- **G2: Slow me down**
- **G3: Scientific Knowledge is Referential**
- **G4: Watch out for Red Herrings**
- **G5: Chemists are Lazy**

- **C1: It’s all about charge**
- **C2: Everybody wants to “be like Mike”**
- **C3: Size Matters**
- **C4: Still Waters Run Deep**
- **C5: Alpha Dogs eat first**

Intermolecular Forces

1. **Evidence for Intermolecular Forces**
2. Phase Diagrams (briefly)
3. Liquid-Vapor Equilibrium
   1. Kinetic theory
   2. Gas escape as a way to measure liquid intermolecular forces
4. Boiling points related liquid Intermolecular Forces
   1. Dipole-dipole
   2. Dispersion
   3. H-bonding
   4. example application – heat capacity of lakes
5. Solid Intermolecular Forces
   1. Molecular Solids (Dispersion/ H-bonding)
   2. Network Covalent (Covalent) – example glass
   3. Ionic solids (Ion/ion)
   4. Metallic solids (metal bonding)
6. Structures of Crystals
   1. Unit Cells
   2. Common Metal Unit cells
      1. Calculate density of lead
   3. Common Ionic Solid Unit cells
      1. Calculate density of ionic solid
We learned about
“Ideal” behavior of gases - do not notice each other
Violate Rules #C1 (charge) & C3 (size)

But - we have accumulated evidence that molecules
a) Real gases “notice” each other
b) Condensed phase (liquids, solids) notice each other

What evidence have we accumulated?

Robert Boyle, 1660; Boyle’s Law

\[
\frac{V}{n} = V_{\text{molar volume}} = \frac{1}{P} [RT]
\]

Real gases volume are “smaller” than expected - suggesting that they see each other and move to each other

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</tr>
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<td>0.382</td>
</tr>
<tr>
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<td>0.446</td>
</tr>
<tr>
<td>Cl₂(g)</td>
<td>0.478</td>
</tr>
<tr>
<td>C(s)</td>
<td>0.71</td>
</tr>
<tr>
<td>CO₂(g)</td>
<td>0.843</td>
</tr>
<tr>
<td>NaCl(s)</td>
<td>0.866</td>
</tr>
<tr>
<td>Al(s)</td>
<td>0.89</td>
</tr>
<tr>
<td>C₆H₆(l)</td>
<td>1.72</td>
</tr>
<tr>
<td>H₂O(g)</td>
<td>1.87</td>
</tr>
<tr>
<td>C₆H₅OH(l)</td>
<td>2.43</td>
</tr>
<tr>
<td>H₂O(l)</td>
<td>4.18</td>
</tr>
</tbody>
</table>

Specific heat of Water increases to A dramatically large Value from gas To liquid (more Condensed – see each Other more) phase

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PHASE CHANGES – related to Intermolecular Forces

Some NEW vocabulary

- fusion
- Vaporization
- Condensation
- Sublimation

- Melting point
- Boiling point
- Heat
- cool
- Heat of fusion
- Heat of vaporization

<table>
<thead>
<tr>
<th>Substance</th>
<th>mp (°C)</th>
<th>bp (°C)</th>
<th>ΔH fusion (kJ/mol)</th>
<th>ΔH vaporization (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromine Br₂</td>
<td>-7</td>
<td>59</td>
<td>29.6</td>
<td></td>
</tr>
<tr>
<td>Benzene C₆H₆</td>
<td>5</td>
<td>80</td>
<td>30.8</td>
<td></td>
</tr>
<tr>
<td>Water H₂O</td>
<td>0</td>
<td>100</td>
<td>40.7</td>
<td></td>
</tr>
<tr>
<td>Naphthalene C₁₀H₈</td>
<td>80</td>
<td>218</td>
<td>43.3</td>
<td></td>
</tr>
<tr>
<td>Mercury Hg</td>
<td>-39</td>
<td>357</td>
<td>59.4</td>
<td></td>
</tr>
</tbody>
</table>

The heats of fusion and vaporization are a way of describing the energy required to break intermolecular forces sufficient to melt or vaporize the material; trends differ because solid, liquid structures of same substance can be very different.

Energy required to move molecules
Further apart (solid to liquid)
### FITCH Rules

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**G5**: Chemists are Lazy  

**C1**: It’s all about charge

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---

### Chemistry

- **Ek**: Electrical energy of interaction
- **K**: Constant, 8.99x10⁻⁹ J·m/C²
- **Q**: Charge on ion, 1.602x10⁻¹⁹ C
- **r**: Ionic radius

**Coulomb’s Law**

\[
E = \frac{kQ_1Q_2}{d}
\]

\[
d = r_{cation} + r_{anion}
\]

Reference state is some very far distance  
Where they don’t see each other, 0 E of interaction

-400 kJ/mol final  
-1400 kJ/mol —  
+1000 kJ/mol initial

Costs energy to move apart

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**PHASE CHANGES** – related to Intermolecular Forces

- Represents increase in **kinetic energy** of Molecules moving
  \[
  E_k = \frac{1}{2}mv^2
  \]
  And increasing distance (electrostatic energy)

- Represents **kinetic energy** needed To escape solution
Example Problem: What energy is required to take 100.0 g of water at 57 °C into the gas phase? The heat of vaporization of water at 100 °C is 40.67 kJ/mol, and the specific heat capacity of water is 4.184 J/g-K.

\[
q = \frac{4.184 \text{ J/g-K}}{100 \text{ g}} \left[ (100 + 273) \text{ K} - (57 + 273) \text{ K} \right]
\]

\[
q = 17,991 \text{ J}
\]

What was the most “costly” part of the process?

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PHASE CHANGES – related to Intermolecular Forces

How does Pressure affect What is Going on?

For a bubble to break

\[ P_{\text{bubble}} \geq P_{\text{vapor}} + \Delta P \]
How do we get the heat of vaporization
And
What is it related to (what “picture” should we have?)

Only 1 of 2 times water “hits” the Surface does it actually have Enough energy to leave.

From earlier chapter we learned of kinetic energy:

\[ E_k = \frac{1}{2} m v^2 \]

\[ u_{rms} = \sqrt{\frac{3kT}{\text{g}_{\text{molecule}}}} \]

\[ E_k = \frac{1}{2} m_{\text{mass of molecule}} \sqrt{\frac{3kT}{\text{mass of molecule}}} \]

\[ E_k = \left( \frac{3kT}{2} \right) \]

\[ f(x) = e^{-\frac{(x-\mu)^2}{2\sigma^2}} \]

\[ f(x) = e^{-\frac{E_{\text{molecule}}}{kT}} = e^{-\frac{E_{\text{vapor}}}{RT}} \]

Fraction of collisions in which the energy is sufficient to allow water to leave the liquid state

\[ \text{fraction} = f \]

\[ f = e^{-\frac{E_a}{RT}} \]

\[ \ln f = \frac{1}{T} \left( -\frac{E_a}{R} \right) \]

Only 1 of 2 times water “hits” the Surface does it actually have Enough energy to leave.
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### Check data – should be able to get Heat of vaporization for water = 40.7kJ/mol

The intercept “b” is annoying. Get rid of it.

**Rule G5: Chemists are Lazy:**

Which value of “R” do We use?

\[ R = \frac{L}{\text{atm}} \, \frac{\text{mol}}{\text{K}} \]

\[ R = 0.0821 \, \frac{\text{J}}{\text{mol} \cdot \text{K}} \]

\[ R = 8.31 \, \frac{\text{J}}{\text{mol} \cdot \text{K}} \]

\[ R = 8.31 \times 10^2 \, \frac{\text{g} \cdot \text{m}^2}{\text{s}^2 \cdot \text{mol} \cdot \text{K}} \]

---

The intercept “b” is annoying. Get rid of it.
\[
\ln \left[ \frac{P_2}{P_1} \right] = \left[ -\frac{\Delta H_{\text{vaporization}}}{R} \right] \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]
\]

Clausius-Clapeyron equation 1834

Example, Calculate the heat of vaporization for lead knowing that the vapor pressure of elemental lead is 1 mm Hg at 987°C and 10 mm Hg at 1167°C.

\[
\ln \left[ \frac{P_2}{P_1} \right] = \left[ -\frac{\Delta H_{\text{vaporization}}}{R} \right] \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]
\]

\[\begin{align*}
\frac{1\text{mm}}{10\text{mm}} & = \left[ -\frac{\Delta H_{\text{vaporization}}}{8.34\text{J/mol K}} \right] \left[\frac{1}{(1253 \times 987)\text{K}} - \frac{1}{(1253 \times 1167)\text{K}} \right] \\
-2.302 & = \left[ -\frac{\Delta H_{\text{vaporization}}}{8.34\text{J/mol K}} \right] \left[\frac{1}{(1260)\text{K}} - \frac{1}{(1440)\text{K}} \right]
\end{align*}\]

\[\begin{align*}
-2.302 & = \left[ -\frac{\Delta H_{\text{vaporization}}}{8.34\text{J/mol K}} \right] \left[\frac{7.936 \times 10^{-4} \text{J}}{6.944 \times 10^{-4} \text{J}} \right] \\
-2.302 & = \left[ -\frac{\Delta H_{\text{vaporization}}}{8.34\text{J/mol K}} \right] \left[\frac{9.9205 \times 10^{-4} \text{J}}{6.944 \times 10^{-4} \text{J}} \right]
\end{align*}\]

\[\begin{align*}
-192\,875\,579 \times \frac{\text{J}}{\text{mol}} & = -\Delta H_{\text{vaporization}} \\
\Delta H_{\text{vaporization}} & = 192.9 \times \frac{\text{kJ}}{\text{mol}}
\end{align*}\]

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      1. Calculate density of ionic solid
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\[\begin{align*}
\text{Rudolph Clausius} & \quad \text{Polish born German} \\
\text{1822-1888} & \quad \text{Mathematical Physics}
\end{align*}\]

\[\begin{align*}
\text{Benoit Paul Emile Clapeyron} & \quad \text{1799-1864, French} \\
\text{Engineer} & \quad \text{Mathematical physicist(dveloped concept of entropy)}
\end{align*}\]
Molecular Substances, Liquids: Intermolecular Forces

1. Uncharged = non conductors of electricity when pure (I₂)
2. Uncharged = nonsoluble in water
   soluble in nonpolar solvents such as CCl₄
3. Uncharged = low interactions holding them in liquid = low boiling points
4. Uncharged = low interactions holding them in solid = low melting points

Both have same electron-Negativity so equally
Share electrons in the bonds = non polar

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>g/mol</th>
<th>bp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>28</td>
<td>-196</td>
<td></td>
</tr>
<tr>
<td>SiH₄</td>
<td>32</td>
<td>-112</td>
<td></td>
</tr>
<tr>
<td>GeH₄</td>
<td>77</td>
<td>-90</td>
<td></td>
</tr>
<tr>
<td>Br₂</td>
<td>160</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>28</td>
<td>-192</td>
<td></td>
</tr>
<tr>
<td>PH₃</td>
<td>34</td>
<td>-88</td>
<td></td>
</tr>
<tr>
<td>AsH₃</td>
<td>78</td>
<td>-62</td>
<td></td>
</tr>
<tr>
<td>ICl</td>
<td>162</td>
<td>97</td>
<td></td>
</tr>
</tbody>
</table>

Non polar molecules Boil at lower temperature

Who pulls electrons Best?

Holding mass approximately constant:

Boiling point can Increase if the Molar mass goes up

Why?
Dispersion (London) Forces

Largest possible wave crests at each end of bathtub
Place two bathtubs end to end with a rubber divider:
As one wave piles up the water in the Bathtub responds creating a sympathetic Wave

Two bath tubs with sloshing Water separated by rubber
Oscillations of electrons
Set up temporary and Oppositely charged Dipoles which attract Each other
London dispersion
Also referred to as Van der Waals forces

\[ E = \frac{k(Q_1 Q_2)}{d} \]
\[ d = r_{cation} + r_{anion} \]

Dispersion forces arise from induced or temporary dipoles

Effect depends upon
1. number of electrons in the molecule
2. ease of creating a bathtub wave
   (less rigidity or spatial fixedness of electron)
3. distance from nucleus (depth in periodic chart)

<table>
<thead>
<tr>
<th>g/mol</th>
<th>bp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>4</td>
</tr>
<tr>
<td>Ne</td>
<td>20</td>
</tr>
<tr>
<td>Ar</td>
<td>40</td>
</tr>
<tr>
<td>Kr</td>
<td>84</td>
</tr>
</tbody>
</table>

What explains This trend?
As the molar mass goes up, boiling point goes up due to dispersion forces. Different slopes say something about induced dipole moments.

Something unusual happens here. What do these guys have in common? Think of the Lewis dot structures. Think of Whom H is bonded to.

Group 16

Group 15

Group 17

Electronegativity

Hydrogen is bonded with three highly electronegative species. Also having unpaired electrons N, O, F.

Hydrogen loses control of most of its shared electron and is an unhappy camper – needs more electrons.

Electronegativity

Why not HCl also, similar in electronegativity to oxygen and nitrogen?.

Do you see anything here?

Need to be able to get close to the other molecule, - small size matters.

Hydrogen bonds are formed in each case.

$E = \frac{k(Q_a)(Q_b)}{d}$

$d = r_{cation} + r_{anion}$
Example: Would you expect to find hydrogen bonds in hydrazine? (Rocket fuel), \( \text{N}_2\text{H}_4 \)

Valence shell electrons: 
\[
\begin{array}{c|c|c}
\text{N} & 2(5) & 10 \\
\text{H} & 4(1) & 4 \\
\hline
\text{Total} & 14 \\
\end{array}
\]

Skeleton structure: \( \text{H}_2\text{N-NH}_2 \)

Single bonds: 5

Remaining electrons: 4

\[
\begin{align*}
\text{H} & \quad \text{N} \quad \text{N} \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

Example: Would you expect to find hydrogen bonds in Dimethyl ether vs ethyl alcohol?

Both have lone pair (unbonded) electrons on one of the three elements we are interested in (N, O, F).

But hydrogen is not bonded to the atom in dimethyl ether – expect no hydrogen bonding

In Ethyl alcohol hydrogen is bonded to oxygen. Expect hydrogen bonding

Hydrogen Bonding explains much of what we have learned about water.

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</tr>
<tr>
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</tr>
<tr>
<td>C(( l ))</td>
<td>1.87</td>
</tr>
<tr>
<td>C(( H_2 ))</td>
<td>2.24</td>
</tr>
<tr>
<td>C(( O_2 ))</td>
<td>4.18</td>
</tr>
</tbody>
</table>

Hydrogen bonding gives a low density structure in ice

\[
\begin{align*}
\text{d}_{\text{liquid}\text{H}_2\text{O}} &= 1.000 \frac{g}{cm^3}, 0^\circ C \\
\text{d}_{\text{solid}\text{H}_2\text{O}} &= 0.917 \frac{g}{cm^3}, 0^\circ C
\end{align*}
\]

Hydrogen bonded ice structure
Nutrient Cycling in Lake Michigan

Surface temperature rises, ice melts, becomes more dense, falls to bottom
pushing up nutrient
Rich particulate matter which feeds
The spring algae

Particulate matter as
Measured by satellite
Reflection measurements

A late spring phenomena

Summary of Intermolecular Forces in Liquids

Dipole/dipole
Dispersion (bathtubs)
Hydrogen bonding

Effect Observed as:
boiling points
melting points
heat capacity
vapor pressure of liquid
Heat of fusion
Heat of vaporization

Water and it’s density!

Effects also observed for molecular solids

“Α” students work
(without solutions manual)
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Network Covalent, Ionic, and Metallic Solids

Forces between molecules:
- dispersion
- dipole/dipole
- H-bonding

Tendency towards:
- softness, low mp

H bonds (kJ/mol)
- 17-40
- Van der Waals

Graphite (pencil lead)
- Is a molecular solid

Covalent Bond Energies for bonds **inside** a molecule that we have already examined

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length pm</th>
<th>Enthalpy Single Bond kJ/mol (Average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C−C</td>
<td>154</td>
<td>348</td>
</tr>
<tr>
<td>C−N</td>
<td>147</td>
<td>308</td>
</tr>
<tr>
<td>C−O</td>
<td>143</td>
<td>360</td>
</tr>
<tr>
<td>C−S</td>
<td>182</td>
<td>272</td>
</tr>
<tr>
<td>C−F</td>
<td>135</td>
<td>488</td>
</tr>
<tr>
<td>C−Cl</td>
<td>177</td>
<td>330</td>
</tr>
<tr>
<td>C−Br</td>
<td>194</td>
<td>288</td>
</tr>
<tr>
<td>C−I</td>
<td>214</td>
<td>216</td>
</tr>
</tbody>
</table>

Glass making from 2000 B.C. Egypt
- Could not get temperatures > 1000°C

Glass formers have intermediate bond energies with Oxygen

Maximum value of glass formers is: 498 kJ/mol for Boron

Covalent bonds in solids
- These are all Covalent bonds!

Crystal structure of quartz
- Si-O-Si-......

Covalent bonds in the network imply:
1. high melting points (~1000°C)
2. insoluble in all common solvents (solvents can't break the bonds)
3. poor electrical conductors (like molecular solids)
Glass formers have intermediate bond energies with Oxygen, also have the ability to create three or more bonds.

Rule: Size Matters!

Also have a particular small radius with respect to oxygen. Need to form tetrahedra.

How did the Egyptians do it? – a topic to explore

Why is mp so high when enthalpy of fusion is not? Hint: naphthalene a large (multimolar) solid?

How did the Egyptians do it? – a topic to explore

Typical fire temp 500-600°C
Typical chimney fire temp 1000°C
E = \frac{k(Q_1)(Q_2)}{d}

\text{Coulomb's law}

d = r_{cation} + r_{anion}

E = \text{electrical energy of interaction}
K = \text{constant}
Q = \text{charge on ion}
r = \text{ionic radius}

Explain this difference in melting points?

| NaCl | 801 |
| KBr | 734 |

No Clean Socks

| 1. strong electrostatic interaction |
| 2. Strong electrostatic interaction |
| 3. Most (not all) soluble in water (polar water organizes around the ions and satisfies their charges) |

| What Rule(s) Do We Invoke Here? |

What do you observe?

How do you explain it?

| CuSO_4(s) \rightarrow Cu^{2+}_{(aq)} + SO^{2-}_{(aq)} |
| H_2SO_4(l) \rightarrow H^+_{(aq)} + HSO^{3-}_{(aq)} |

| CuS(s) \rightarrow Cu^{2+}_{(aq)} + S^{2-}_{(aq)} |
| H_3PO_4(l) \rightarrow H^+_{(aq)} + H_2PO_{4-}_{(aq)} |

\Delta H^\circ = -66.15 \text{ kJ/mol}
\Delta H^\circ = -73.33 \text{ kJ/mol}
\Delta H^\circ = -14.5 \text{ kJ/mol}
\Delta H^\circ = -20.1 \text{ kJ/mol}
Fluid electron sea explains
1. high electrical conductivity
2. high thermal conductivity: heat is carried by electron collisions
3. Ductile, malleable, electrons are a flexible glue
4. Luster, electrons not restricted to specific bonds
5. Insoluble – electrons are not soluble

A lead “came” factory
Came is used to bend
Around pieces of cut
Glass for stained glass windows

Low Melting Point
High Melting Point
(~1000 °C)
Variable Melting Point
Nonconducting
Conductor
Nonconducting of
electricity
Conductor of
Electricity
Nonconducting in Water
Most are soluble in
water
Insoluble
Insoluble in all
common solvents

Low Boiling Point
High Thermal Conductivity
Ductile/Malleable
Luster

Intermolecular Forces
1. Evidence for Intermolecular Forces
2. Phase Diagrams (briefly)
3. Liquid-Vapor Equilibrium
   1. Kinetic theory
   2. Gas escape as a way to measure liquid intermolecular forces
4. Boiling points related liquid Intermolecular Forces
   1. Dipole-dipole
   2. Dispersion
   3. H-bonding
   4. example application – heat capacity of lakes
5. Solid Intermolecular Forces
   1. Molecular Solids (Dispersion/ H-bonding)
   2. Network Covalent (Covalent) – example glass
   3. Ionic solids (Ion/ion)
   4. Metallic solids (metal bonding)

6. Structures of Crystals
1. Unit Cells
2. Common Metal Unit cells
   1. Calculate density of lead
3. Common Ionic Solid Unit cells
   1. Calculate density of ionic solid
Macroscopic Minerals

CRYSTAL STRUCTURES

Macroscopic Minerals

Crystal Descriptions

- Cube: $a = b = c$
- Tetragonal: $a = b < c$
- Orthorhombic: $a \neq b \neq c$
- Monoclinic: $90^\circ$
- Hexagonal: $a = b \neq c$

Macroscopic Structures of Minerals

Macroscopic Crystal Form

- Isometric
- Hexagonal
- Tetragonal

Macroscopic Structures are often driven by three-dimensional microscopic organization of atoms or ions.

There are 14 kinds of basic microscopic organizational structures (unit cells).

- Simplest unit cell is cubic
- Each of 8 corner atoms is shared by eight cells = 1 atom/cell
- Each of 6 face atoms are shared by two cells

Total atoms = $6 \text{ face} / 2 + 8 \text{ corner} / 8 = 4$

Total atoms = $1 \text{ body} + 8 \text{ corner} / 8 = 2$

Common Metal Crystal Structures

Metal Crystal Structures

Macroscopic Structures are often driven by three-dimensional microscopic organization of atoms or ions.

- Atoms/unit cell: 1, 2, 4
- Follow the corner atom
- Each of 8 corner atoms is shared by eight cells = 1 atom/cell
- Each of 6 face atoms are shared by two cells

Total atoms = $6 \text{ face} / 2 + 8 \text{ corner} / 8 = 4$

Total atoms = $1 \text{ body} + 8 \text{ corner} / 8 = 2$
Example: Calculate the density of lead from its molar mass and the fact that it has a face centered cubic structure and bond length for elemental lead (center of one atom to another) 349.9 pm for elemental lead.

Complicated example from some textbook.

What do we know?

What do we need to know?
Example: Calculate the density of lead from its molar mass and the fact that it has a face centered cubic structure and bond length for elemental lead (center of one atom to another) 349.9 pm for elemental lead.

\[d_{\text{density}} = \frac{g}{cm^3}\]

1. Need volume
   a) fcc determines
   b) side, s, of cube
   c) \(s^3\) is volume
2. Need radius
   a) fcc determines bond length
   b) bond length represents sum of 2 radii
3. Need mass
   a) fcc determines \(4\) atoms/volume
   b) number of atoms
   c) convert atoms to moles to grams

\[4r = s\sqrt{2}\]  
Bond length = 2r

\[4(174.95 \times 10^{-10}\text{ cm}) = s\]
\[s = 494.8 \times 10^{-10}\text{ cm}\]

\[s^3 = V = \left(494.8 \times 10^{-10}\text{ cm}\right)^3 = 1.21 \times 10^{-22}\text{ cm}^3\]

Atoms in a face centered cubic cell: 8 corners/8 + 6 faces/2 = 4

We now know atoms/cm³; what next?

Example: Calculate the density of lead from its molar mass and the fact that it has a face centered cubic structure and bond length of 349.9 pm for elemental lead.

\[2r = 349.9 \text{ pm}\]

\[r = \left[\frac{349.9 \text{ pm}}{2}\right] = \left[\frac{1\text{ m}}{1 \times 10^{12}\text{ pm}}\right] = 174.95 \times 10^{-10}\text{ cm}\]

\[4r = s\sqrt{2}\]

\[4(174.95 \times 10^{-10}\text{ cm}) = s\]
\[s = 494.8 \times 10^{-10}\text{ cm}\]

\[s^3 = V = \left(494.8 \times 10^{-10}\text{ cm}\right)^3 = 1.21 \times 10^{-22}\text{ cm}^3\]

This calculated value is consistent with the reported value of 11.34 g/cm³
~4,000 deaths of mute swans in England/year from fishing sinkers
O'Halloran, 1988

“muck” grazing birds, pick up solid lead as a “pebble” to grind in their gizzards.

Material Specific Heats c. (J/g°C)

<table>
<thead>
<tr>
<th>Substance</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(s)</td>
<td>0.12803</td>
</tr>
<tr>
<td>Pb(l)</td>
<td>0.16317</td>
</tr>
<tr>
<td>Cu(s)</td>
<td>0.382</td>
</tr>
<tr>
<td>Fe(s)</td>
<td>0.446</td>
</tr>
<tr>
<td>Cl₂(g)</td>
<td>0.478</td>
</tr>
<tr>
<td>C(s)</td>
<td>0.71</td>
</tr>
<tr>
<td>CO₂(g)</td>
<td>0.843</td>
</tr>
<tr>
<td>NaCl(s)</td>
<td>0.866</td>
</tr>
<tr>
<td>Al(s)</td>
<td>0.89</td>
</tr>
<tr>
<td>C₂H₆(l)</td>
<td>1.72</td>
</tr>
<tr>
<td>H₂O(g)</td>
<td>1.87</td>
</tr>
<tr>
<td>C₂H₅OH(l)</td>
<td>2.43</td>
</tr>
<tr>
<td>H₂O(l)</td>
<td>4.18</td>
</tr>
</tbody>
</table>

To create spherical lead shot:
Want the material to solidify before it hits the ground so it does not deform.

Uses of lead: summary to date:
- Useful material for environmental transport studies (isotopes)
- Lead acetate – used to “sweeten” wines; easily made from lead and wine
- Lead – used in firing ranges
- Lead – soldering (radiators, cars, electronics)
- Lead – malleable metal (roofs, downspouts, stained glass)
- Lead – glasses and glazes (pottery)
- Lead – Solvent for other metals: purifying silver
- Lead – Density of solid = good X-ray shield

Toxicity of lead: summary to date:
- Similar ionic size to Ca²⁺
- Covalent and ionic bonding
- Same charge as Ca²⁺
- Electrostatic attraction of lead to calcium binding sites will be similar
- Difference: has s² electron – distorts binding in biomolecule
What is the learning point of harping on lead examples?

Ionic crystals somewhat similar to metallic crystals

One ion forms, for example, a uniform cell
The second ion fits in between the first ion

Is this lithium or chloride? How did you know?

What happens when the cation size is increased?

Face Centered Cubic Cl Structure

Body Centered Cubic Cl Structure

Chloride adopts a uniform structure and the smaller Li$^+$ fits in between to satisfy the charge.

Chloride adopts the same structure as for Lithium chloride but the cell is larger because of movement to accommodate the larger Sodium cation.

Cesium is so large that the same structure can not be adopted by chloride.
Ionic Bonds: Collection of Interactions (kJ/mol)

<table>
<thead>
<tr>
<th>Ion</th>
<th>LiF</th>
<th>NaF</th>
<th>KF</th>
<th>CsCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>1017</td>
<td>910</td>
<td>808</td>
<td>657</td>
</tr>
<tr>
<td>LiBr</td>
<td>787</td>
<td>682</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

What “rules” apply here?

Example: Determine the net number of Li+ and F- ions in the LiF unit cell, given that the structure is fcc (for both ions). Calculate its density given that s is 4.02Å on a side.

Fcc = 4 for Li+  
Fcc = 4 for F-  
Total = 8 ions

Necessary? No

\[ d = \frac{N}{\text{vol}} = \frac{4(\text{molecules LiF}) \times \left( \frac{1 \text{mole LiF}}{6.02 \times 10^{23} \text{ atoms LiF}} \right) \times \left( \frac{4(6.04) + 4(19.0)}{4(6.02) + 4(19.0)} \right)}{4.02 \times 10^{-14} \text{ cm}^3} \]

\[ d = \frac{N}{\text{vol}} = \frac{4 \times 10^{-4} \text{ cm}^3}{4.02 \times 10^{-14} \text{ cm}^3} \]

A warning: have to account for all the atoms and their individual Unit cells

I whole
In center

Cl- fcc

4 ⅙ atoms at top
4 ⅔ atoms at the “waist”
4 ⅜ atoms at bottom

Total atoms= 12 ½ atoms

Cl- Cl Cl
Cl-

How about for Na+?

Na+ fcc

1 whole

4 ¼ atoms at the “waist”

Total atoms= 4 Fcc

“A” students work (without solutions manual)
~ 10 problems/night.

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Module #12
Intermolecular Forces

I WANT YOU TO PRACTICE EVERY DAY!
Intermolecular Forces

1. Evidence for Intermolecular Forces
2. Phase Diagrams (briefly)
3. Liquid-Vapor Equilibrium
   1. Kinetic theory
   2. Gas escape as a way to measure liquid intermolecular forces
4. Boiling points related liquid Intermolecular Forces
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Summary Slide

Vapor pressure over a solution is related to the energy required to escape the solution: this ideal leads to the following equation

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

Summary Slide

The boiling point
melting point
vapor pressure over a solid
are affected by intermolecular forces acting in liquids

Forces are:
- dipole/dipole
- dispersion (induced dipole/induced dipole)
- hydrogen bonding: hydrogen bonding occurs with H-F; H-O; and H-N where FON have unbonded electrons

Intermolecular forces operating in solids are:
- the above
- covalent bonding
- ionic bonding
- metallic bonding

Because the type of bond is different the trends change when a material goes from solid to liquid to gas
Relative interaction for ionic bonding can be calculated from Coulomb’s law

$$E = \frac{k(Q_1 Q_2)}{d}$$
$$d = r_{cation} + d_{anion}$$

Organization of molecules (or atoms) within a solid follow 14 different structural types:

- **3 are most common for metals**: simple cubic, face centered cubic, and body-centered cubic.
  - The structure of the cell affects empty volume and therefore, the melting point, density, and stability of the material.

Ionic crystal structures are similar except cations occupy the space that was “empty” in metals.