Bonding and Structure of Metals

• Any successful model for the bonding in metals must be able to explain:
  
  – Good thermal and electrical conductivity
  – Reflectivity

• Molecular orbital theory can be extended to solid materials including metals
Molecules of Metal Atoms

Orbital Energy Levels in Solids

The energy levels of sodium as a function of internuclear distance ($r_0$ = equilibrium distance)

Figure 8-9 Envelopes of energy bands, with shading to indicate filling. (a) an insulator, (b) a metallic conductor, (c) overlapping conduction bands as in Na.
The energy gap (band gap) between the conduction band and the valence band determines, whether a compound is an insulator, semiconductor or metal.
Electrical Conductivity

Solids only conduct electrons when there is a partially filled band available (unpaired electrons)

–> The transition metals with their incomplete sets of d-electrons have partially filled \( d \) bands and have therefore a high conductivity

–> For semiconductors the presence of impurities (dopands) increases the number of electrons that are unpaired

–> Solids with completely filled or empty bands are insulators!

Temperature Dependence

• The conductivity of metals decreases with increasing temperature, whereas semiconductors show better conductivity:
Thermal Conductivity

- Most of the heat transport in metals occurs via the mobile electrons at the top of the band
  -> heating of metals gives these electrons extra kinetic energy. They move to other parts of the metal lattice and release some of the kinetic energy

- Some solids transport heat via vibrations (phonons) in the solids
  -> e.g. diamond has a very high thermal conductivity as a consequence of its vibrations
The Structure of Metals

• The structure of most metals can be described in terms of packing hard spheres (representing the metal atoms)

--> this type of model is also used for ionic solids

• Three different packing arrangements are commonly found:
  - Body centered cubic packing (bcc)
  - Cubic close (cpp) or face centered cubic packing (fcc)
  - Hexagonal close packing (hcp)

• Some rarer types are:
  - Tetragonal, trigonal and orthorhombic packing
Crystal Structures of the Metallic Elements

Simple Cubic Packing

- The most basic crystal structure (also called primitive cubic)
- Atoms are placed at the eight corners
Hexagonal Close and Cubic Close Packing

HCP has ABAB.. repeat

FCC has ABCABC.. repeat

FCC unit cell

And another view of hcp and ccp...

A single close-packed layer, A, with the hexagonal packing outlined.

two close-packed layers, A and B. Octahedral holes can be seen extending through both layers surrounded by three atoms in each layer. Tetrahedral holes are under each atom of the second layer and over each atom of the bottom layer. Each is made up of three atoms from one layer and one from the other.

Cubic close-packed layers, in an ABC pattern. Octahedral holes are offset, so no hole extends through all three layers.

Hexagonal close-packed layers. The third layer is exactly over the first layer in this ABA pattern. Octahedral holes are aligned exactly over each other, one set between the first two layers A and B, the other between the second and third layers, B and A.

Layer 1 (A)  Layer 2 (B)  Layer 3 (A or C)
Packing efficiency

- The various packing types make different use of the available space:

<table>
<thead>
<tr>
<th>Packing type</th>
<th>Coordination number</th>
<th>Occupancy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple cubic (sc)</td>
<td>6</td>
<td>52</td>
</tr>
<tr>
<td>Body-centered cubic (bcc)</td>
<td>8</td>
<td>68</td>
</tr>
<tr>
<td>Hexagonal close-packed (hcp)</td>
<td>12</td>
<td>74</td>
</tr>
<tr>
<td>Cubic close-packed (ccp)</td>
<td>12</td>
<td>74</td>
</tr>
</tbody>
</table>

Body Centered Cubic Packing (bcc)
Ionic Bonding

- Compounds between a metallic element and electronegative nonmetals can be described as collection of ions \((M^{n+}, X^{n-})\) held together electrostatically.

- This idea was developed by Arrhenius by looking at the conductivity of solutions prepared by dissolving “ionic compounds” in water.
  (not believed at first, but got the 1903 Nobel prize)

Properties of Ionic Compounds

- Tend to form hard and brittle crystals

- High melting point: typically several hundred or thousand Kelvin
  However: Salts that are liquid at room temperature have been prepared using organic cations

- Very low electrical conductivity, but conduct electricity quite well when molten

- Most dissolve in high polarity solvents to form conducting solids
The Ionic to Covalent Continuum

- In practice, no compound is truly ionic!

- Compounds containing elements with very different electronegativities tend to be more ionic:

![Graph showing the relationship between electronegativity difference and ionic character.]

Ionic Size

- Cations are always smaller than the parent atom → higher nuclear charge
  (the outermost electrons experience a higher effective charge compared to the neutral atom)

- Anions are always larger than their parent atoms → electron-electron repulsion
  (the outermost electrons experience a lower effective charge compared to the neutral atom)
Ionic Radii

- There are various different ways to determine the ionic radii. 
  -> Each gives slightly different answers (therefore: be consistent 
  with the source of your data when doing calculations!)

- A good way to measure the radii involves measuring electrons density in crystals. 
  The minimum in density between the ions is the boundary between the ions

Effective Ion Charge

- Isoelectronic ions (= ions with identical electron configuration, but 
  different nuclei)

<table>
<thead>
<tr>
<th>Ion:</th>
<th>Radius</th>
<th>Ion:</th>
<th>Radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>116 pm</td>
<td>N³⁻</td>
<td>132 pm</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>86 pm</td>
<td>O²⁻</td>
<td>124 pm</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>68 pm</td>
<td>F⁻</td>
<td>117 pm</td>
</tr>
</tbody>
</table>
Periodic Trends in Size

• Similar to those found for atoms

<table>
<thead>
<tr>
<th>Ion:</th>
<th>Radius</th>
<th>Ion:</th>
<th>Radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>F⁻</td>
<td>117 pm</td>
<td>Mn²⁺</td>
<td>97 pm</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>167 pm</td>
<td>Fe²⁺</td>
<td>92 pm</td>
</tr>
<tr>
<td>Br⁻</td>
<td>182 pm</td>
<td>Co²⁺</td>
<td>88 pm</td>
</tr>
<tr>
<td>I⁻</td>
<td>206 pm</td>
<td>Ni²⁺</td>
<td>83 pm</td>
</tr>
</tbody>
</table>

Trends in Physical Properties

• Decreasing ion size and increasing ion charge favor better binding of the solid (higher lattice energy)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>KF</td>
<td>857 °C</td>
</tr>
<tr>
<td>KCl</td>
<td>772 °C</td>
</tr>
<tr>
<td>KBr</td>
<td>735 °C</td>
</tr>
<tr>
<td>KI</td>
<td>685 °C</td>
</tr>
<tr>
<td>NaF</td>
<td>988 °C</td>
</tr>
<tr>
<td>MgF₂</td>
<td>1266 °C</td>
</tr>
<tr>
<td>AlF₃</td>
<td>1291 (sublimes)</td>
</tr>
</tbody>
</table>
Polarization and Covalency

- “ionic” compounds tend to have a considerable covalent contribution to their bonding when they contain polarizing cations

- *Polarizing cations* = cations capable of distorting the anion’s electron cloud towards the cation:

  ![Polarization effects](image)

  **Fig. 4.19** Polarization effects: (a) idealized ion pair with no polarization, (b) mutually polarized ion pair, (c) polarization sufficient to form covalent bond. Dashed lines represent hypothetical unpolarized ions.

Fajan’s Rules

- Small highly charged cations are more polarizing

- Large highly charged anions are more polarizable

- Polarization is favored for cations that do not have a noble gas electron configuration:

  e.g. Ag⁺, Cu⁺, Zn²⁺, Cd²⁺, Hg²⁺, Tl⁺, etc.
Physical Effect of Covalency

- “Ionic” solids with a significant covalent contribution to bonding show “anomalous” physical properties:
  
  \[ \text{\rightarrow may not be water soluble} \]

Hydration of Ions

- Ionic solids are usually soluble in water because the dipole on water interacts with the ionic charges
  
  \[ \text{\rightarrow negative end of the dipole coordinates to the cation} \]
  \[ \text{\rightarrow strength of interaction increases with decreasing cation size and increasing charge} \]

- Strong coordination may lead to the formation of *hydrates*
Ion Hydration on Dissolution

Hydration Energy
Structure of Ionic Compounds

- It is often convenient to think about the cations lying in holes (interstices) between arrays of anions.

- Typically, assume ions are hard spheres.

- Usually, a compound will adopt a structure that maximizes the number of anions around each cation without causing the anions to touch.

Radius Ratio Rules

- It is possible to predict the type of ion coordination that you will get, if you know the ratio of the cation to anion size:

<table>
<thead>
<tr>
<th>$r^+/r^-$ ratio</th>
<th>Preferred Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 0.732</td>
<td></td>
</tr>
<tr>
<td>0.414–0.732</td>
<td></td>
</tr>
<tr>
<td>0.225–0.414</td>
<td></td>
</tr>
</tbody>
</table>
Calculation of the Limiting Values

**Example 5.1:** Calculate the ideal \( r_m/r_x \) for cation–anion and anion–anion contact for an octahedral arrangement of anions around a cation as sketched in one plane in Figure 5.20a.

**Solution:** The right triangle sketched here has two sides equal to \((r_m + r_x)\) with the hypotenuse equal to \(2r_x\).

\[
(2r_x)^2 = (r_m + r_x)^2 + (r_m + r_x)^2
\]

\[
4r_x^2 = 2(r_m + r_x)^2
\]

\[
\sqrt{3}r_x = r_m + r_x
\]

\[
r_m/r_x = (\sqrt{2} - 1) = 0.414
\]

**Example 5.2:** Show that the ideal \( r_m/r_x \) for the cation–anion and anion–anion contact for a tetrahedral arrangement of anions around a cation is 0.225.

**Solution:** The drawing shows one edge of the tetrahedron with two anions touching and the cation at the center of the tetrahedron. A line perpendicular to the edge bisects the tetrahedral angle. The length of the edge is \(2r_x\). The distance from a tetrahedral vertex to the center is \(r_m + r_x\). The angle \(\theta\) is 109°28'/2, and we have

\[
\sin \theta = \frac{r_x}{r_m + r_x} = \sin 54°44'
\]

0.816 \((r_m + r_x) = r_x\)

0.816\(r_m = 0.184r_x\)

\[
r_m/r_x = 0.225
\]

Structures with Simple Cubic Packing

- A simple cubic array contains holes that are eight coordinate:
Structures with Octahedral Cation Coordination

• Close packed arrays of anions have both, octahedral and tetrahedral interstices

  --> Filling octahedral holes in a cubic close packed array

  --> Filling the holes in a hexagonal close packed array

Holes in Close Packed Arrays

• There are one octahedral and two tetrahedral holes for every atom in a close packed array:
The NaCl Structure

Tetrahedral Coordination

- Structures based on filling tetrahedral holes in close packed anion arrays are commonly found

  → Filling all the tetrahedral sites in a cubic close packed array gives the ZnS **Zinc Blende structure**

  → Filling all the tetrahedral sites in a hexagonal close packed structure gives the ZnS **Wurzite structure**
Violations of the Radius Rules

- The radius rule only works for ~2/3 of all known compounds

Reason:
- Ions are not really hard spheres
- Covalent contribution to bonding can interfere
- Ionic radius varies with coordination number

- There are empirical methods to reliably predict structures
  \(\rightarrow\) *Structure Maps*

Structure Maps

The structure of a compound can be predicted based on the difference in electronegativity between the elements and the average principle quantum number of the valence orbitals.
Inorganic Thermodynamics

- Thermodynamic arguments can be used to predict or explain the outcome of inorganic chemical reactions:
  - The majority of organic chemical reactions are dependent upon kinetic control ($\Delta G^\ddagger$, activation energy)
  - Many inorganic reactions are under thermodynamic control (free energy change, $\Delta G$)
Free Energy

• For a reaction to be spontaneous the free energy change must be negative

• The free energy term consist of a entropic ($\Delta S$) and enthalpic ($\Delta H$) contribution:

Tabulated Enthalpy Data

• A considerable amount of thermodynamic data has been derived from experiments and is readily available

Enthalpies of formation:

\[ C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \]

• Bond energies:
  Measure of the strength of a covalent bond

→ sum of all bond energies in a molecule gives the energy of formation
Lattice Energy

• For an ionic compound the lattice energy is defined as the energy needed to break up the solid into its constituent ions in the gas phase:

\[ \text{MX}_{(s)} \rightarrow \text{M}^+_{(g)} + \text{X}^-_{(g)} \]

• → Determined by a combination of long range electrostatic interactions and short range repulsions

Attractive and Repulsive Interactions

• There are electrostatic interactions between every pair of ions in the solid:

  – Electrostatic energy between an ion pair \((Z_1, Z_2)\) separated by the distance \(r\):

  \[ E = \frac{Ze_0^2}{4\pi\varepsilon_0 r^n} \]

  \(n = \) Born exponent, usually quite large (NaCl: \(n = 8\))

  – Ions are not just point charges, but consist of electron clouds which repel each other at very close distances:
Madelung Constant ($A$)

- The actual value of the electrostatic component of the energy depends upon the crystal structure:

The Madelung constant $A$ is evaluated for a particular lattice by considering geometry and distance of the attracting and repelling forces.

For NaCl:

$$A = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}}...$$

attraction by 6 Cl$^-$ ion "1st shell"
repulsion by 12 Na$^+$ ion "2nd shell"
attraction by 8 Cl$^-$ ion "2nd shell"

Note: The Madelung constant may be obtained mathematically from converging series using computer programs.
Madelung Constants

\[
\text{Table 1.11 Madelung constants for some common ionic lattices}
\]

<table>
<thead>
<tr>
<th>Structure</th>
<th>Madelung constant (A)</th>
<th>A (\nu)</th>
<th>Coordination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caesium chloride</td>
<td>1.763</td>
<td>0.88</td>
<td>8:8</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>1.748</td>
<td>0.87</td>
<td>6:6</td>
</tr>
<tr>
<td>Fluorite</td>
<td>2.519</td>
<td>0.84</td>
<td>8:4</td>
</tr>
<tr>
<td>Zinc blende</td>
<td>1.638</td>
<td>0.82</td>
<td>4:4</td>
</tr>
<tr>
<td>Wurtzite</td>
<td>1.641</td>
<td>0.82</td>
<td>4:4</td>
</tr>
<tr>
<td>Corundum</td>
<td>4.172</td>
<td>0.83</td>
<td>6:4</td>
</tr>
<tr>
<td>Rutile</td>
<td>2.408</td>
<td>0.80</td>
<td>6:3</td>
</tr>
</tbody>
</table>

**Total Lattice Energy**

- The total lattice energy corresponds to the combination of the attracting and repulsing energy terms \(N\): Avogadro’s number:

\[
U = - \frac{N}{4\pi \varepsilon_0} \cdot \frac{AZ_1Z_2e^2}{r} + \frac{NB}{r^n}
\]

- The term \(B\) is calculated using the equation for the equilibrium situation:

\[
\frac{dU}{dr} = 0 = \frac{N}{4\pi \varepsilon_0} \cdot \frac{AZ_1Z_2e^2}{r^2} - \frac{nNB}{r^{n+1}} \quad \quad B = - \frac{1}{4\pi \varepsilon_0} \cdot \frac{AZ_1Z_2e^2r^{n-1}}{n}
\]

\[
U_0 = \frac{N A Z_1 Z_2 e^2}{4\pi \varepsilon_0 \mu_0} \left(1 - \frac{1}{n}\right) \quad \quad \text{Born-Landé Equation}
\]
Born Exponent

- The Born exponent depends upon the type of ions involved - larger ions have a relatively higher electron density, and therefore also larger values of $n$.
- For most calculations the values suggested by Pauling are sufficiently accurate:

<table>
<thead>
<tr>
<th>Ion configuration:</th>
<th>$n$</th>
<th>Example: NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>5</td>
<td>Na$^+$ $\rightarrow$ [Ne] $\rightarrow$ $n = 7$</td>
</tr>
<tr>
<td>Ne</td>
<td>7</td>
<td>Cl$^-$ $\rightarrow$ [Ar] $\rightarrow$ $n = 9$</td>
</tr>
<tr>
<td>Ar, Cu$^+$</td>
<td>9</td>
<td>Average: $n = 8$</td>
</tr>
<tr>
<td>Kr, Ag$^+$</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Xe, Au$^+$</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

Thermodynamic data for alkali metal halides

<table>
<thead>
<tr>
<th>Structure$^*$</th>
<th>$r_0$ ($10^{-8}$ m)</th>
<th>$\Delta U_f$</th>
<th>$\Delta U_{\text{C}}$</th>
<th>$\Delta U_{\text{A}}$</th>
<th>$\Delta U_{\text{L}}$</th>
<th>$\Delta U_{\text{A}}$ $\text{calc.}$</th>
<th>$\Delta U_{\text{A}}$ $\text{expt.}$</th>
<th>$\text{calc/}$ $\text{expt.}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>2.01</td>
<td>-610</td>
<td>-1205</td>
<td>178</td>
<td>-16</td>
<td>-3</td>
<td>-13</td>
<td>-1033</td>
</tr>
<tr>
<td>LiCl</td>
<td>2.57</td>
<td>-402</td>
<td>-944</td>
<td>117</td>
<td>-24</td>
<td>-3</td>
<td>9</td>
<td>-845</td>
</tr>
<tr>
<td>LiBr</td>
<td>2.75</td>
<td>-350</td>
<td>-882</td>
<td>105</td>
<td>-26</td>
<td>-3</td>
<td>8</td>
<td>-798</td>
</tr>
<tr>
<td>LiF</td>
<td>3.03</td>
<td>-270</td>
<td>-809</td>
<td>96</td>
<td>-30</td>
<td>-4</td>
<td>7</td>
<td>-740</td>
</tr>
<tr>
<td>NaF</td>
<td>2.31</td>
<td>-574</td>
<td>-1047</td>
<td>143</td>
<td>-18</td>
<td>-2</td>
<td>9</td>
<td>-915</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.81</td>
<td>-411</td>
<td>-860</td>
<td>100</td>
<td>-21</td>
<td>-3</td>
<td>6</td>
<td>-778</td>
</tr>
<tr>
<td>NaBr</td>
<td>2.98</td>
<td>-360</td>
<td>-812</td>
<td>94</td>
<td>-23</td>
<td>-3</td>
<td>5</td>
<td>-739</td>
</tr>
<tr>
<td>NaF</td>
<td>3.23</td>
<td>-288</td>
<td>-750</td>
<td>82</td>
<td>-25</td>
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<td>4</td>
<td>-692</td>
</tr>
<tr>
<td>KF</td>
<td>2.66</td>
<td>-563</td>
<td>-908</td>
<td>119</td>
<td>-28</td>
<td>-3</td>
<td>7</td>
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<tr>
<td>KCl</td>
<td>3.14</td>
<td>-436</td>
<td>-771</td>
<td>90</td>
<td>-28</td>
<td>-3</td>
<td>4</td>
<td>-709</td>
</tr>
<tr>
<td>KBr</td>
<td>3.29</td>
<td>-392</td>
<td>-735</td>
<td>84</td>
<td>-29</td>
<td>-3</td>
<td>3</td>
<td>-680</td>
</tr>
<tr>
<td>KI</td>
<td>3.53</td>
<td>-328</td>
<td>-686</td>
<td>75</td>
<td>-29</td>
<td>-3</td>
<td>3</td>
<td>-640</td>
</tr>
<tr>
<td>RbF</td>
<td>2.82</td>
<td>-551</td>
<td>-862</td>
<td>116</td>
<td>-33</td>
<td>-5</td>
<td>6</td>
<td>-778</td>
</tr>
<tr>
<td>RbCl</td>
<td>3.29</td>
<td>-433</td>
<td>-737</td>
<td>85</td>
<td>-33</td>
<td>-4</td>
<td>3</td>
<td>-686</td>
</tr>
<tr>
<td>RbBr</td>
<td>3.43</td>
<td>-391</td>
<td>-705</td>
<td>79</td>
<td>-32</td>
<td>-4</td>
<td>3</td>
<td>-659</td>
</tr>
<tr>
<td>RbI</td>
<td>3.66</td>
<td>-330</td>
<td>-661</td>
<td>73</td>
<td>-33</td>
<td>-4</td>
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<td>-622</td>
</tr>
<tr>
<td>CsF</td>
<td>3.01</td>
<td>-545</td>
<td>-808</td>
<td>101</td>
<td>-41</td>
<td>-5</td>
<td>5</td>
<td>-748</td>
</tr>
<tr>
<td>CsCl</td>
<td>3.56</td>
<td>-447</td>
<td>-685</td>
<td>81</td>
<td>-44</td>
<td>-6</td>
<td>2</td>
<td>-652</td>
</tr>
<tr>
<td>CsBr</td>
<td>3.71</td>
<td>-409</td>
<td>-658</td>
<td>77</td>
<td>-47</td>
<td>-6</td>
<td>2</td>
<td>-632</td>
</tr>
<tr>
<td>CsI</td>
<td>3.95</td>
<td>-351</td>
<td>-618</td>
<td>68</td>
<td>-46</td>
<td>-6</td>
<td>1</td>
<td>-601</td>
</tr>
</tbody>
</table>

$^*$a = NaCl; b = CsCl.
Formation of Ionic Compounds

• Energies of Formation can be calculated by considering the process of formation to occur in distinct series of steps

• Consider the formation of \( \text{NaCl}_{(s)} \):

1) atomize the metal
2) dissociate chlorine molecules
3) ionize the sodium
4) form ions from the chlorine atoms
5) bring the ions together to form solid NaCl

Born-Haber Cycles

• This approach is often depicted with a diagram:

1) atomize the metal
2) dissociate chlorine molecules
3) ionize the sodium
4) form ions from the chlorine atoms
5) bring the ions together to form solid NaCl
Stability of Ionic Compounds

- Born-Haber cycles along with lattice energy calculations and experimentally measured quantities such as ionization energies allow the calculation of enthalpies of formation for compounds that have never been made.

- This also allows you to rationalize why some compounds form and others do not.

Magnesium Fluorides

- Why is MgF\(_2\) the only stable magnesium fluoride?

<table>
<thead>
<tr>
<th>Enthalpy contributions (kJmol(^{-1}))</th>
<th>MgF</th>
<th>MgF(_2)</th>
<th>MgF(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg atomization</td>
<td>+150</td>
<td>+150</td>
<td>+150</td>
</tr>
<tr>
<td>F-F bond energy</td>
<td>+80</td>
<td>+160</td>
<td>+240</td>
</tr>
<tr>
<td>Mg ionization</td>
<td>+740</td>
<td>+219</td>
<td>+9930</td>
</tr>
<tr>
<td>F electron affinity</td>
<td>-330</td>
<td>-660</td>
<td>-990</td>
</tr>
<tr>
<td>Lattice energy</td>
<td>-900</td>
<td>-2880</td>
<td>-5900</td>
</tr>
<tr>
<td>(\Delta H_f)</td>
<td>-260</td>
<td>-1040</td>
<td>+3430</td>
</tr>
</tbody>
</table>

\[ 2 \text{MgF}_2(s) \rightarrow \text{MgF}_2(s) + \text{Mg}(s) \]
Dissolution of Ionic Solids

- The process of dissolving an ionic solid can be divided into two stages:

  1) Break up the solid into gas phase ions:
     - Required energy corresponds to the lattice energy:
       - MgO: 393 kJmol\(^{-1}\)
       - NaCl: 915 kJmol\(^{-1}\)
     - Entropically favorable (highly ordered solid is converted into a gas of ions)

  2) Solvate those ions:
     - Energetically favorable for polar solvents (ion-dipole interactions)
     - Interaction orders solvent molecules around the ions, an entropically unfavorable process

Solvated Ions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius [pm]</th>
<th>Hydrated Ion</th>
<th>Radius [pm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>116</td>
<td>Na(OH(<em>2))(</em>{13})^{+}</td>
<td>276</td>
</tr>
<tr>
<td>K(^+)</td>
<td>152</td>
<td>K(OH(<em>2))(</em>{7})^{+}</td>
<td>232</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ion</th>
<th>Hydration Enthalpy [kJmol(^{-1})]</th>
<th>Charge Density [Cmm(^{-3})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>-390</td>
<td>24</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>-1890</td>
<td>120</td>
</tr>
<tr>
<td>Al(^{3+})</td>
<td>-4610</td>
<td>264</td>
</tr>
</tbody>
</table>
The Entropy and Enthalpy Balance

- For NaCl, dissolution in water is favorable at room temperature ($\Delta G = \sim -9 \text{ kJmol}^{-1}$):

  \[
  \begin{align*}
  &\text{NaCl}_{(s)} \quad \rightarrow \quad \text{Na}^+_{(g)} + \text{Cl}^-_{(g)} \\
  &\Delta H = +4 \text{ kJmol}^{-1} \\
  &\Delta H_{\text{NaCl}} = +788 \text{ kJmol}^{-1} \\
  &\Delta H_{\text{Na}^+_{(aq)} + \text{Cl}^-_{(aq)}} = -28 \text{ kJmol}^{-1} \\
  &\Delta H_{\text{TAS}} = +406 \text{ kJmol}^{-1} \\
  \end{align*}
  \]

  -> The reaction is entropically driven

Enthalpies of Solution

- The dissolution of salts in water can be exothermic or endothermic (due to entropic term!)

- -> this concept is applied hot and cold packs:

  \[
  \begin{align*}
  &\text{NH}_4\text{NO}_3_{(s)} \quad \rightarrow \quad \text{NH}_4\text{NO}_3_{(aq)} \\
  &\Delta H^0 = 26 \text{ kJmol}^{-1} \\
  &\text{CaCl}_2_{(s)} \quad \rightarrow \quad \text{CaCl}_2_{(aq)} \\
  &\Delta H^0 = -82 \text{ kJmol}^{-1}
  \end{align*}
  \]
Kinetic vs. Thermodynamic Control

- The outcome of a reaction is not always determined by thermodynamics
  - the rate of formation of two reaction products may differ and will influence the product distribution
  - a catalyst can favor the formation of a particular product by lowering the activation energy
Unstable Molecules

- Kinetic control can be used to make thermodynamically unstable products (e.g. shock sensitive explosives)

\[
\begin{align*}
N_2(g) + \frac{3}{2} Cl_2(g) & \rightarrow NCl_3(l) \quad \Delta G^0 = +250 \text{ kJ mol}^{-1} \\
NH_3(g) + 3 Cl_2(g) & \rightarrow NCl_3(l) + 3 HCl(g) \quad \Delta G^0 < 0
\end{align*}
\]

Intermolecular Forces

- Attractive interactions between molecules allow the formation of molecular liquids and solids

- There are a number of different types of intermolecular forces
  - Dispersion/London/van der Waals forces
  - Dipolar interactions
  - Hydrogen bonds
Dispersion Forces

- All molecular and atomic species are attracted to each other by dispersion forces
- Fluctuations in charge distribution polarize nearby atoms and molecules. This induced dipole interacts with the original uneven charge distribution

Strength of Dispersion Forces

- The strength of the interaction depends on
  - Number of electrons in atom or molecule
  - Spatial extent of atom or molecule
- Increasing electron count tends to increase the strength of the interaction
  → there is more charge to move around
- Increasing spatial extent increase the interaction
  → more extended charge separation possible
Boiling Points of MH₄ Species

- The boiling point reflects the magnitude of intermolecular forces:

![](image.png)

Interactions Between Polar Molecules

- Some molecules have a permanent dipole moment
  --> low symmetry charge distribution

- To get a low symmetry charge distribution the bonds must be polar
  (large electronegativity difference)
  --> uneven distribution of charge between two bonded atoms

  Note: polar bonds do not guarantee a polar molecule!
Dipole-dipole vs. Dispersion Interactions

- Molecular dipoles can give a significant contribution to intermolecular forces

- But: Dispersion forces are generally more important

Hydrogen Bonding

“A hydrogen bond exists when a hydrogen atom is bonded to two or more other atoms”

→ not an ordinary covalent bond, since the hydrogen atom has only one orbital (1s) to engage in covalent bonding

Macroscopic effects of H-bonding:
Anomalous properties such as greatly increased melting and boiling points, examples: HF, H₂O, NH₃

Typical H-bond: Hydrogen is attached to two very electronegative atoms, usually in a linear fashion and not symmetrically:

A–H······B
Effect of Hydrogen Bonding

Thermodynamics of H-Bonds

- Hydrogen bonds to very electronegative atoms can be strong:

  \[
  \begin{align*}
  \text{F}^- + \text{HF} & \rightarrow \text{F} \bullet \bullet \text{HF}^- & \Delta H &= -161 \text{ kJmol}^{-1} \\
  \text{H}_2\text{O} + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O} \bullet \bullet \bullet \text{HOH (ice)} & \Delta H &= -25 \text{ kJmol}^{-1} \\
  \text{HCN} + \text{HCN} & \rightarrow \text{HCN} \bullet \bullet \bullet \bullet \text{HCN} & \Delta H &= -12 \text{ kJmol}^{-1}
  \end{align*}
  \]
Chemical Forces and Interactions

<table>
<thead>
<tr>
<th>Type of interaction</th>
<th>Strength</th>
<th>Energy-distance function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent bond</td>
<td>Very strong</td>
<td>Complex, but long range</td>
</tr>
<tr>
<td>Ionic bond</td>
<td>Very strong</td>
<td>1/r, long range</td>
</tr>
<tr>
<td>Ion-dipole</td>
<td>Strong</td>
<td>1/r^2, short range</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td>Moderately strong</td>
<td>1/r^3, short range</td>
</tr>
<tr>
<td>Ion-induced dipole</td>
<td>Weak</td>
<td>1/r^4, very short range</td>
</tr>
<tr>
<td>Dipole-induced dipole</td>
<td>Very weak</td>
<td>1/r^6, extremely short range</td>
</tr>
<tr>
<td>London dispersion forces</td>
<td>Very weak</td>
<td>1/r^6, extremely short range</td>
</tr>
</tbody>
</table>

Intermolecular Forces in Biology

- Proteins consist of long chains of covalently linked amino acids (up to several hundred linked amino acids!)
- These chains can form two distinct architectural elements, which are both stabilized via H-bonds:
Structure of Proteins

- The tertiary structure (=3-dimensional architecture) is determined by combination of electrostatic, van der Waals and H-bonding interactions between the amino acid chains:

![Alpha-helix and Beta-sheet](image)

H-Bonding in DNA

- The double-helical structure of DNA is also formed by H-bonding interactions:
Virus Capsules

- The capsules of viruses consist of proteins, which are held together by non-covalent interactions: