CHAPTER 3

Crystallography
Atomic Structure

- Atoms are made of
  - Protons: mass 1.00728 amu, +1 positive charge
  - Neutrons: mass of 1.00867 amu, neutral
  - Electrons: mass of 0.00055 amu, -1 negative charge
  - (1 amu = 1/12$^{\text{th}}$ the weight of a $^{12}\text{C}$ atom)
- $\# \text{ of proton} = \# \text{ of electron} = \text{atomic number (z)}$: controls the chemical property of an element.
- $\# \text{ of proton} + \# \text{ of neutron} = \text{Mass number (m)}$
- Atoms with same z but different m are called isotopes:
  - E.g., $^{39}\text{K}$, $^{40}\text{K}$, $^{41}\text{K}$
- Atomic Mass = Mass of an atom divided by 1/12$^{\text{th}}$ the mass of a $^{12}\text{C}$ atom
  - So atomic mass are slightly different from mass number
- Atomic weight = weighted average of atomic masses of the isotopes
## Atomic Weight of Potassium (K)

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Atomic Mass</th>
<th>Abundance</th>
<th>Weighted Average</th>
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<tbody>
<tr>
<td>$^{39}\text{K}$</td>
<td>38.964</td>
<td>93.26%</td>
<td>39.098</td>
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<tr>
<td>$^{40}\text{K}$</td>
<td>39.964</td>
<td>0.01%</td>
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<tr>
<td>$^{41}\text{K}$</td>
<td>40.963</td>
<td>6.73%</td>
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</tbody>
</table>
Electrons

• In classical model: electrons orbit around the nucleus in “concentric” shells or orbitals which are consecutively numbered (n=1, 2, 3…)
• # of electron that can be accommodated in any orbital = \(2n^2\)
• According to the Quantum Theory, electrons are organized in discrete energy levels identified with four different quantum numbers: \(n\), \(l\), \(m_1\), and \(m_2\)
• **Pauli’s exclusion principle**: No two electrons in an atom can have same four quantum numbers
  – The four numbers are like an address: city, street, building and room: no two electrons can occupy the same room
The Four Quantum Numbers

- **Distance**: Principal Quantum Number: \( n \)
  - K shell \((n=1)\), L shell \((n=2)\), M shell \((n=3)\), N shell \((n=4)\) and so on

- **Shapes**: Angular Momentum Quantum Number: \( l \)
  - Value between 0 and \((n-1)\)
  - Sub shells: s, p, d, f

- **Orientation**: Magnetic Quantum Number: \( m_1 \)
  - Value between \(-l\) and \(+l\)

- **Spin**: Spin Quantum Number: \( m_2 \)
  - Value +1/2 or -1/2
Figure 3.1 Geometry of orbitals in the $s$, $p$, and $d$ subshells. Orbitals represent the volume of space around a nucleus in which an electron is most probably located.
Electrons

- Principle Quantum number $n$ denotes distance from the nucleus
- Greater distance = higher energy
- Distance increases in discrete steps
- $n$ is correlated with shells: Don’t confuse $n$ with $N$

<table>
<thead>
<tr>
<th>$n$</th>
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<tr>
<td>shell</td>
<td>K</td>
<td>L</td>
<td>M</td>
<td>N</td>
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</table>
Angular Quantum Number ($l$) and Magnetic Quantum Number ($m_l$)

- Within each shell are subshells and the angular quantum number distinguishes different subshells with different shapes (spherical, dumbbell shaped, quadralobate etc).
- The subshells are identified with letters s,p,d,f.

<table>
<thead>
<tr>
<th>$l$</th>
<th>0</th>
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<tr>
<td>subshells</td>
<td>s</td>
<td>p</td>
<td>d</td>
<td>f</td>
</tr>
</tbody>
</table>

- The value of $l$ can be from 0 to $n$-1.
  - Thus K shell ($n=1$) can only have $l=0$ – which is a spherical subshell;
  - L shell ($n=2$) can have $l=0$, and 1 so has only s and p subshells
  - p subshell in L shell ($n=2$) is 2p subshell

- The magnetic quantum number ($m_l$) identifies the orientation of the subshells and can have values between integers –$l$ to +$l$ (this is “el”).
  - So for p subshell ($l=1$), $m_l$ can be -1,0,+1
  - The number of possible orbital in a subshell is $2l+1$.
Figure 3.1 Geometry of orbitals in the $s$, $p$, and $d$ subshells. Orbitals represent the volume of space around a nucleus in which an electron is most probably located.
Spin Quantum Number (m₂)

• Spin Quantum number (m₂) = identifies right hand or left hand spins of electrons in a subshell and can have values +1/2 and -1/2
• The electron spins generate magnetic field
• Usually the number of left handed and right handed spins are same hence no net magnetism
• In magnetic minerals the spins are not balanced hence a net magnetic moment
• Range in energy levels of different subshells: 4s has lower energy than 3d
• Electrons systematically fill orbitals in order of energy levels: so 4s will get filled before 3d
• The general progression of increasing energy levels is:
  • 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 6d 5f

• Atoms with all subshells filled are the noble gases
• Non-noble gas atoms have a “noble gas” core in which all the subshells are filled + some extra electrons which occupy subshells within shells which are not totally filled
• These additional electrons are called Valence electrons.
• Na has a Ne noble gas core + 3s valence electrons

Figure 3.2 Relative energy level of electron subshells. Electrons fill subshells in order of increasing energy level (compare Table 3.3).
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<td>70</td>
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</tr>
</tbody>
</table>

Introduction to Mineralogy, Second edition

William D. Nesse

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Neon (Ne) atom: all the subshells filled

Sodium (Na) atom Ne core + 1 additional electron: Valence electron

- **Pseudo-noble gas core**: A noble gas core + an entirely filled d or f subshell. Example: As (Arsenic) (z=33) has a pseudo Ar (Argon) Core

<table>
<thead>
<tr>
<th>Shell/subshell</th>
<th>K</th>
<th>L</th>
<th>M</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1s</td>
<td>2s</td>
<td>2p</td>
<td>3s</td>
</tr>
<tr>
<td>As</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>Ar</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
</tr>
</tbody>
</table>
Atoms have a tendency to fill the outermost shell.

This they do either

- By gaining or losing electrons:
  - Atoms become negatively charged when they gain an electron: **Anion**
  - Atoms become positively charged when they lose an electron: **Cation**
  - Bond formed by electrostatic attraction between anion and cation: **Ionic Bond**
- By sharing electrons: **Covalent Bond**
• Anions have net –ve charge, cations have net +ve charge

• The charge of an ion is known as it’s **valence or oxidation state**

• Some elements can form ions of different valence states: e.g.: Fe$^{2+}$ (Ferrous) and Fe$^{3+}$ (Ferric) ions

• Metals typically form cations and non-metals form anions (why?) (Hint: check at the number of valence electrons in metals)
Figure 3.3 Common oxidation states of elements 1 through 38.
Electronegativity

- Was defined by Linus Pauling in 1932
- Electronegativity is a measure of the propensity of an element to gain or lose electrons
- Pauling used an arbitrary scale where Li had an electronegativity of 1, Carbon 2.5 and F had an electronegativity = 4.
- Atoms with low electronegativity readily loses electrons, those with high electronegativity readily gains electrons
- Electronegativity values can be used to estimate the nature of chemical bonds
Chemical Bonding

• Bonds that involve valence electrons: ionic, covalent, and metallic bonds
  – Helps elements to acquire noble gas (or pseudo noble gas) configuration
• Bonds that do not involve valence electrons: van der Waal’s and hydrogen bonds
Ionic Bonding

- Forms by electrostatic attraction ($F_A$) between an anion and a cation
- The strength of the attraction between ions of charge $q^+$ and $q^-$ at a distance $d$ is given by Coulomb’s law:
  $$F_A \propto (q^+)(q^-)/d^2$$
- The attraction between charges is opposed by Born repulsion when electrons of anions and cations overlap
  $$F_R \propto -n/d^{1+n}$$
  where $n$ is an integer dependent on the number of filled electron shells
- The net force is the sum of the attraction and repulsion:
  $$F = F_A + F_R$$
- The equilibrium distance is given where $F = 0$; For Na+ and Cl- = 2.8 Å
**Figure 3.4** Ionic bonding between Na$^+$ and Cl$^-$: (a) The attractive $F_A$ and repulsive $F_R$ forces between Na$^+$ and Cl$^-$ ions.
Ionic bonds

- Net positive and net negative charges must be equal: \( \text{Na}^+\text{Cl}^- \), but \( \text{Ca}^{2+}\text{Cl}^-_2 \)
- Ions pack together in systematic and symmetric manner – positive and negative ions alternate to form electrically neutral crystalline solid
- Bonds are fairly strong
- Tend to be brittle – strong resistance to sliding because sliding brings cations against cations and anions against anions
- Orderly structures ensure failure along cleavage planes
Covalent Bonding

- Occurs when orbitals of two atoms overlap and
- Overlapping orbitals have no more than two electrons combined
- The electrons in the overlapping orbitals move around both the atoms
- Because the electrons are attracted to the nucleus of both the atoms— a bond is established
- The strength of the bond depends on the degree of overlap – the greater the overlap, the stronger the bond
- In diamond high degree of overlap produces very strong bond – as evident in diamonds extreme hardness.

Figure 3.5 Formation of covalent sigma (σ) bonds with carbon in diamond.
Covalent Bonding in Diamond

- Diamonds: $1s^22s^22p^2$: to share 4 electrons, 4 unpaired bonds are needed
- Diamond does that by promoting one of the 2s electron to vacant p orbital – this provides four unpaired orbitals (with one electron each)
- Since all the bonds between adjacent carbon atoms need to be identical -- orbitals of 2s and 2p subshells are hybridized to form four identical sp$^3$ orbitals
- The hybrid orbital is made of one large lobe pointing away from nucleus and a small lobe positioned around nucleus: the large lobes define the corners of a tetrahedron
- Electrons are shared between overlapping sp$^3$ orbitals: sigma ($\sigma$) bonding
• In graphite $2p_z$ orbital is not hybridized.
• The three $sp^2$ hybrid orbitals share electrons to form strong sheets
• The $P_z$ orbitals share electron side by side rather than end to end: $\pi$ bonding
• Electrons are free to move along $\pi$ bonding making graphite a good conductor

Figure 3.6 Formation of covalent $\sigma$ and $\pi$ bonds with carbon in graphite.
Figure 3.7 Hybrid orbitals. Each consists of a large and small lobe (Figure 3.5d); only the large lobe is shown.
Metallic Bond

• Valence electrons are free to move between atoms forming a “glue of electrons holding the atoms together
  1. Valence electrons are weakly held
  2. Forms when the number of electrons that must be shared to form a noble-gas configuration is large (e.g., Na needs 7 electrons)

  3. Availability of vacant energy levels where valence electrons can move in
  4. When atoms are brought into close proximity, the energy levels of subshells spread out in a band
  5. When energy level of unfilled bands overlap filled bands, the electrons are free to migrate from filled bands (valence bands) into unfilled bands (conduction band)

![Energy bands form when atoms are brought into close proximity. (a) Magnesium. Energy levels of the 3s and 3p subshells spread into bands that overlap.](image)

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• Because bonds are weak, metals are soft and malleable
• Because valence requirement are met by sea of electrons, one metal can easily substitute for other making alloys
• Bands spread and overlap when the atoms are at close proximity
• Hence at high pressure all materials tend to behave like metals
• Ionic, covalent and metallic bonds are valence dependent, i.e., dependent on acquiring a stable electron configuration
• Many bonds have characteristics intermediate between these three
• Ionic Bond: High difference in electronegativity between anion and cation
• Covalent and metallic: low or zero difference in electronegativity
• Pauling (1960): empirical mathematical relationship

\[
\% \text{ ionic character} = 1 - e^{-0.25(x_a - x_c)^2} \times 100 \\
(x_a - x_c) = \text{difference in electronegativity}
\]

• Of the eight most abundant elements in the crust: O: electronegativity = 3.5 always from anion, the other seven: (Si, Al, Fe, Ca, Na, K, Mg) all form cations when bonding with O and have electronegativity differences from 1.7 (Si) = 50% ionic to 2.7 (K) = 80% ionic
• Native elements C, S, Au, Ag, have zero electronegativity difference: either covalent or metallic bonds
• Elements with relatively low electronegativity (1.8-2.4): more metallic
• Non-metals (S,C) with higher electronegativity favor covalent bonding
• Ionic and covalent bond: low conductivity because valence electrons are tightly held in specific orbitals
• Metallic bonding: high conductivity; higher temperature causes thermal vibration which impedes free flow of electrons – hence lower conductivity.
Bonds……………(contd)

• Van der Waals Bond:
  – Weak, electrostatic bond, easily formed and broken

• Hydrogen Bond
  – Charges on a molecule are polarized, positive charges on one end and negative charges on the other end
  – The negative side of the molecule attracts positive side of the next molecule and so on
  – Best example: Water molecule (H\textsubscript{2}O)
Water Molecule

- Two hydrogen ions bond to Oxygen ion forming 104° angle
- Therefore, the two positive charges are on the same side of the water molecule. This gives the molecule an electrical polarity. Although the molecule as a whole is electrically neutral, one side has a negative polarity and the other side (with the hydrogen ions) has a positive polarity
Water molecules are attracted to each other forming chains of molecules known as polymers.
Water is known as the Universal Solvent

• it can dissolve more substances than anything else. Ions are attracted to either side of the water molecule. This attraction is stronger than many bonds - for example it is stronger than the ionic bond holding sodium to chlorine. This is why NaCl dissolves in water.
• pure water can withstand electrical fields.
Hydrogen Bonds in Liquid Water

The Crystal Lattice Structure of Ice

A Water Molecule

Hydrogen bonds

Water molecules

104° 31' (bond angle in water)

109° 28' (bond angle in ice)

cr. 2 Å
Water and Ice

• When water freezes, ice forms six sided open ring like hexagonal structure: the openness gives ice a lower density (0.92) than water (1).

• Salts dissolved in water cannot easily be accommodated in the ice structure, therefore areas of very salty brine is left out when seawater freezes.

• Liquid water consists of both structured (hydrogen bonded polymers – less dense) and unstructured water (denser).
Hydrogen bonding

Figure 3.11 Hydrogen bonding in ice.
Van der Waal’s bonding:

- Like Hydrogen bond, Van der Waals’s bond also depends on asymmetrical charge distribution
- Consider Graphite structure: sheets formed by covalent sigma and pi bonds.
- Charges on both sides of the sheet are same when the electron position in one of the sheets is averaged over time
- At any given instance, more electrons can be in one side of the sheet giving the sheets a polarized character
- The +ve charge side on one side attracts more electrons from the neighboring sheets – making those polarized too.
- This result is weak electrostatic bond between sheets
- Soft minerals, greasy feel: graphite, talc

Figure 3.12 Van der Waals bonding. Sheets of carbon are bonded internally by \( \pi \) and \( \sigma \) covalent bonds (Figure 3.6).
Size of Atoms and Ions

- It is difficult to determine the size of an atom or ion:
  - Fuzzy cloud of electron which need not be spherical
  - Overlapping orbitals in covalent bonding
- Effective Radius assuming atoms or ions are packed as little spheres: based on distance between the centers of adjacent atoms or ions
  - Atomic radius (of uncharged atom)
  - Ionic radius (of anion or cation)
- For covalent or metallic bonded single element crystalline solid: Bond Length \( L = 2R \)
- For ionic bonded solids: \( L = R_a + R_c \)
- The Effective ionic radius depends on the valence of the ion (oxidation state) and how many anions are packed around the cation (coordination number) – more densely packed → smaller radius.
  - Anions > uncharged atoms > cations
  - Higher + charge → smaller cation

Figure 3.13 Bond length and effective radius.
Figure 3.14 Effective atomic radii for the elements.
Figure 3.15 Effective radii as a function of oxidation state (charge) for oxygen (O), sulfur (S), phosphorus (P), manganese (Mn), and iron (Fe), elements that occur in different oxidation states.
Figure 3.16 Effective ionic radii of the common cations as a function of coordination number.
Figure 3.17 Spin configuration in Fe$^{3+}$. (a) Low spin. Electrons are paired in the $d_{xy}$ orbital even though the $3d_{x^2-y^2}$ orbital is vacant. (b) High spin. No electrons are paired in the orbitals.