Chapter 6: Chemical Periodicity

We just finished discussing the structure of atoms and introduced its relationship to chemical periodicity: the variation in the properties of elements with their positions in the periodic table.

\[ \text{electron as wave-like} \Rightarrow \text{Schrödinger Equation} \Rightarrow \text{quantum numbers: } n, l, m_l, m_s \Rightarrow \text{electron configuration} \Rightarrow \text{predicted properties} \Rightarrow (\text{periodicity}) \text{ according to periodic table} \]

The history of the periodic table is given in Section 5-1. Mendeleev and Meyer (1869) independently arranged the known elements into a pattern based on their properties, thus setting the stage for the...

**Periodic Law**: The properties of the elements are periodic functions of their atomic numbers (the numbers of protons in the nucleus).

**Terms for the Periodic Table**:

- **group or family**: vertical columns
  - The elements have similar chemical and physical properties.

- **period**: horizontal rows
  - The elements have properties that change progressively across the table.

**Group A**: "representative" elements
- show distinct and fairly regular variations in properties with the atomic number
- their last electron is added to an s or p orbital

**Group B**: show less dramatic changes in properties with increasing atomic number
- their last electron is added to an \((n-1)d\) orbital which lies inside the outer ns and np electrons.
The representative elements:

- Group IA (except H): alkali metals
- Group IIA: alkaline earth metals
- Group VIIA: halogens (salt-formers)
- Group 0: noble (rare) gases

d-transition elements:
- In B group (except IIIB): electrons are being added to d-orbitals

(Note: IIIB is excluded since their last e⁻ is added to s orbital. Elements are Zn, Cd, Hg, but their properties are similar to d-transition elements.)

1st transition series: 21Sc → 29Cu
2nd transition series: 39Y → 97Ag
3rd transition series: 57La, 72Hf → 79Au
4th transition series: 89Ac

Inner transition elements:
- Located between IIIB and IVB: electrons are being added to f-orbitals

1st inner transition series: lanthanides 58Ce → 71Lu (Lutetium)
2nd inner transition series: actinides 90Th → 103Lr (Lawrencium)

Lewis Dot Representations of Representative Elements

- Only the electrons shown in the outer s & p orbitals are shown as dots.
  These are called VALENCE electrons.
- Paired and unpaired electrons are shown.

**TABLE 2.3** Lewis Electron Dot Formulas for Representative Elements

- Memoize or deduce from periodic table.
Periodic Properties of Group A Elements

The physical and chemical properties of elements recur periodically. There are 5 properties we will consider in depth:

1) Atomic radii
2) Ionization energy
3) Electron affinity
4) Ionic radii
5) Electronegativity

(1) Atomic Radii (Fig 6-1.)
Values have been determined indirectly (units: angstroms $1\text{Å} = 10^{-10}\text{m}$, nanometers $1\times10^{-9}\text{m}$) as we move from left to right within a particular energy level (e.g., $n=2$), the atomic number increases. Therefore, for a neutral atom, protons are added to the nucleus; electrons are added to the electron cloud in the same major energy level. There is greater and greater attraction; the electron cloud is pulled closer and closer into the nucleus.
Result: the atomic radii decreases. Eg. Li > Be > B > C > N > O > F > Ne
as we move from top ($n=1$) to bottom ($n=7$), electrons are added to higher and higher energy levels which are correspondingly larger and larger. Result: the atomic radii increases. Eg. Be < Mg < Ca < Sr < Ba

Chemical reactions result from the interaction of the outermost electrons of the elements involved. Therefore, it is important to know how tightly the electrons of an element are held and how easily the element gains or loses electrons.

To give us this information, the energy involved in these processes is measured.

Convention: energy is released (exothermic): energy has negative value energy is absorbed (endothermic): energy has positive value
(2) First Ionization Energy: minimum amount of energy required to remove the most loosely bound electron from an isolated gaseous atom to form an ion with a 1+ charge.

\[ \text{e.g. } K(g) \rightarrow K^+(g) + e^- \quad \text{I.E.} = 419 \text{ kJ/mol of K(g) atoms} \]

or \[ K(g) + 419 \text{ kJ/mol} \rightarrow K^+(g) + e^- \]

(process requires energy - is endothermic)

For calcium:
First ionization energy, \(1E_1\): \[ \text{Ca}(g) + 590 \text{ kJ} \rightarrow \text{Ca}^+(g) + e^- \]
Second ionization energy, \(1E_2\): \[ \text{Ca}^+(g) + 1145 \text{ kJ} \rightarrow \text{Ca}^{2+}(g) + e^- \]

\(1E_2 > 1E_1\) since it is more difficult to remove an electron from a positively charged species than a neutral one.

Again, \(1E\) measures how tightly the electrons are bound to the atom.
As \(1E \uparrow\), the difficulty in removing an electron \(\uparrow\)

![Graph showing trend in ionization energy](image)

General trend in \(1E_1\) of A Group Elements with position in periodic table. Exceptions occur at IIIA and VIA. These can be explained by quantum mechanics (see pp 226).

\[ \pm \text{ the outer He electron is more tightly bound than any other (has highest 1E,) the outer Cs electron is the easiest to remove (has lowest 1E,)} \]

(Note: Fr is ignored because it is rare and radioactive)

Knowledge of the relative values of \(1E\) assist in predicting which elements form covalent bonds (by sharing electrons) and which form ionic bonds (electrons are transferred from one atom to another).
(3) **Electron Affinity**: the amount of energy involved in the process in which an electron is added to an isolated gaseous atom to form an ion with a 1- charge.

Examples:

$$\text{Be}(g) + e^- + 241 \text{ kJ} \rightarrow \text{Be}^- (g)$$

E.A. = $+241 \text{ kJ/mol}$

(exothermic)

$$\text{Cl}(g) + e^- \rightarrow \text{Cl}^- (g) + 348 \text{ kJ}$$

E.A. = $-348 \text{ kJ/mol}$

(exothermic)

For $^{35}\text{Cl}^-$:

\[
\begin{align*}
\# p &= 17 \\
\# e &= 18 \quad (\text{charge of -1 means 1 extra electron}) \\
\# n &= 18
\end{align*}
\]

General trend in electron affinities of A group elements with position in periodic table. There are many exceptions.

- It is easier to add an electron going from left to right or bottom to top.
- Halogens gain electrons easily — have more negative electron affinities.

(4) **Ionic Radii**

Most parent atoms will react with other atoms in order to gain a noble gas configuration, by either gaining or losing electrons.

<table>
<thead>
<tr>
<th>LEFT SIDE OF PERIODIC TABLE</th>
<th>Group electronic configuration</th>
<th>IA</th>
<th>II A</th>
<th>III A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>electrons lost</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>final charge on ion</td>
<td>+1</td>
<td>+2</td>
<td>+3</td>
</tr>
</tbody>
</table>

Atoms in these groups will lose electrons to form cations and become positively charged.

In periods 2 and 3, ions from IA, II A and III A are ISOELECTRONIC (have the same total number of electrons).

eg: $^{11}\text{Na}^+$, $^{12}\text{Mg}^{2+}$ and $^{13}\text{Al}^{3+}$ all have 10 electrons and are isoelectronic with the noble gas, $^{10}\text{Ne}$, neon.
In order of decreasing ionic radii: \( Na^+ > Mg^{2+} > Al^{3+} \) since as more electrons are removed, the remaining electrons are held more tightly.

Also, \( Na > Na^+ , \ Mg > Mg^{2+} \)

<table>
<thead>
<tr>
<th>Group electronic config</th>
<th>VA</th>
<th>VIA</th>
<th>VIIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>ns(^2)np(^3)</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>ns(^2)np(^4)</td>
<td>-3</td>
<td>-2</td>
<td>-1</td>
</tr>
</tbody>
</table>

Atoms in these groups will gain electrons to have noble gas configuration - they form anions.

Example: In period 2, \( N^{3-}, O^{2-}, F^- \) all have 10 electrons and are isoelectronic with \( 10\text{Ne}, 11\text{Na}^+, 12\text{Mg}^{2+} \) and \( 13\text{Al}^{3+} \).

In order of decreasing ionic radii: \( N^{3-} > O^{2-} > F^- \). As electrons are added to a neutral atom, the electron cloud is expanded. Therefore \( N^{3-} > N \)

To generalize: eq \( H^- > H > H^+ \)

1. Simple negatively charged ions (anions) are always larger than parent atom.
2. Simple positively charged ions (cations) are always smaller than parent atom.
3. Within an isoelectronic series, atomic radii decrease as atomic no. increases.

General trend in ionic radii of A Group elements with position in periodic table.

(5) Electronegativity: a measure of the relative tendency of an atom to attract electrons to itself when chemically combined with another atom. (These values appear on the periodic table in the exam)

General trend in electronegativity of A Groups with position in periodic table. Range

\[ \begin{align*}
F & \text{ highest EN (4.0)} \\
O & \text{ next highest EN (3.5)} \\
N & \text{ (3.0)} \\
\end{align*} \]

Fr \( \rightarrow \) F
Electronegativity is used to help assign oxidation numbers.

In a simple binary (2 element) compound, the more electronegative element "wants" electrons more and "gets" the negative oxidation number.

Examples:

<table>
<thead>
<tr>
<th>ox. no.</th>
<th>+1 -1</th>
<th>+1 -1</th>
<th>-3 +1</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>NaH</td>
<td>NH₃</td>
<td></td>
</tr>
<tr>
<td>EN 1.0</td>
<td>3.0</td>
<td>1.0</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>3.0</td>
<td>2.1</td>
</tr>
</tbody>
</table>