Chemistry 1901/1903 - 2007

Lecture 4: Biological effects of Radiation. Medical Imaging.

Lecture 5: The Periodic Table - Chemistry’s Next Big Idea
  • The periodic table in its historical context
  • The periodic table and periodic trends today.

Lecture 6: Quantum Theory
1803 - Dalton’s Big Idea – Atomic Theory

- Elements are made of tiny particles called atoms
- All atoms of a given element are identical
- The atoms of a given element are different from those of any other element
- Atoms of one element can combine with atoms of other elements to form compounds. A given compound always has the same relative numbers of types of atoms.
- Atoms cannot be created, divided into smaller particles, nor destroyed in the chemical process. A chemical reaction simply changes the way atoms are grouped together.
- When atoms combine in only one ratio, "...it must be presumed to be a binary one, unless some cause appear to the contrary" Based on this assumption, Dalton concluded that water was OH.
1869 - Mendeleev’s First Draft

The periodic table is a great piece of organization or system for understanding chemistry. To understand its significance, try to imagine what it was like for the people in the 19th century who were trying to make sense out of chemistry.

How many atoms were known? 62, many of which had the wrong atomic mass.

What was known about the structure of the atom?

It would be almost 30 years (1897) before electrons were identified, and 40 years (1909) before Rutherford put forward the now standard model of the atom as a nucleus surrounded by electrons.
How did Mendeleev do it?

He grouped elements by common properties. But what properties were known?

E.g. Stoichiometry of oxides, hydrides...

- Atomic volumes
- Melting points of elements and compounds

What properties were not known or understood?

- Atomic Number, Nuclear structure
- Multiple oxidation states e.g. SnO and SnO₂; CO and CO₂
- Ionization energies, Electronegativities
- Noble Gases not yet discovered
Periodic Trends

Meyer (a contemporary and rival of Mendeleev) plotted the atomic volume as a function of atomic weight, showing periodicity. (Remember, some atomic weights were incorrect at this time.)
1869 - Mendeleev’s First Periodic Table

The Periodic Table was developed in a number of steps, gradually identifying and correcting errors. In this version elements with similar properties are grouped in rows, with atomic mass increasing down columns and left to right.

<table>
<thead>
<tr>
<th>H</th>
<th>Be 9.4</th>
<th>Mg 24</th>
<th>Zn 65.2</th>
<th>Cd 112</th>
<th>Au 197?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li 7</td>
<td>B 11</td>
<td>Al 27.4</td>
<td>? 68</td>
<td>? 70</td>
<td>Sn 118</td>
</tr>
<tr>
<td></td>
<td>C 12</td>
<td>Si 28</td>
<td>As 75</td>
<td>Sb 122</td>
<td>Bi 210</td>
</tr>
<tr>
<td></td>
<td>N 14</td>
<td>P 31</td>
<td>Se 79.4</td>
<td>Te 128.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O 16</td>
<td>S 32</td>
<td>Br 80</td>
<td>J 127</td>
<td></td>
</tr>
<tr>
<td></td>
<td>F 19</td>
<td>Cl 35.5</td>
<td>Rb 85.4</td>
<td>Cs 133</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na 23</td>
<td>K 39</td>
<td>Sr 87.6</td>
<td>Ba 137</td>
<td>Pb 207</td>
</tr>
<tr>
<td></td>
<td>Ca 40</td>
<td>? 45</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>?Er 56</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Not an element

Wrong mass in 1869
Corrected by Mendeleev
Constructing groups

This 1871 version of Mendeleev’s periodic table shows explicitly how the oxides and hydrides were used to create groups, which are shown vertically here.

Notice the “-” marks, indicating where Mendeleev expected an element to be, but none was known at the time.
Mendeleev used his table to predict the properties of some of these undiscovered elements, as well as their masses, notably scandium, gallium, and germanium.
Predictions Based on Periodic Trends

Given the state of chemical knowledge at the time, the development of the periodic table was a triumph of organization by Mendeleev, and others who contributed.

It was a powerful *empirical* organizer and predictor of atomic masses, missing atoms, and many chemical properties.

E.g. *ekal-silicon* (Germanium)  
<table>
<thead>
<tr>
<th>Property</th>
<th>Predicted</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic weight</td>
<td>72</td>
<td>72.32</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>5.5</td>
<td>5.47</td>
</tr>
<tr>
<td>Atomic volume</td>
<td>13</td>
<td>13.22</td>
</tr>
<tr>
<td>Valence</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>0.073</td>
<td>0.076</td>
</tr>
<tr>
<td>Specific Gravity of GeO₂</td>
<td>4.7</td>
<td>4.703</td>
</tr>
<tr>
<td>Boiling pt of GeCl₄</td>
<td>&lt;100°C</td>
<td>86°C</td>
</tr>
</tbody>
</table>

However, without a microscopic theory we cannot understand the reason why the Periodic Table has this structure. The development of atomic structure and quantum mechanics in fact make the structure of the Periodic Table obvious, as we shall see.
A Timeline of Atomic Structure Development

1803  J Dalton provided evidence for fundamental indivisible particles - atoms.

1897  JJ Thomson discovered electrons.

1909  RA Millikan measured the charge of an electron.

1909  E Rutherford proposed an atom be composed of a small positive nucleus (1912) surrounded by a lot of space occupied by electrons.

1913  HG-J Moseley determined the charge on the nucleus.

Rutherford & others regard the atomic weight as being the number of protons and the nuclear charge as being the number of protons minus the number of electrons in the nucleus.

1913  N Bohr applied quantum theory to electrons in atoms.

1920  J Aston found isotopes by mass spectrometry

1932  J Chadwick discovered the neutron.

This gives a fairly complete picture of the nucleus as composed of charged protons and uncharged neutrons, and of isotopes as atoms with the same number of protons but different numbers of neutrons.
Atomic Number

Measurement of nuclear charge and discovery of the neutron allowed the definition of the atomic number, and the proper ordering of the elements in the periodic table.

How? In 1913 Moseley measured the x-ray wavelengths generated by various metals in discharge tubes, showing that they varied systematically with the order of the element in the periodic table. Specifically, he plotted the square root of the x-ray frequency, $\nu$, against the order or atomic number, $Z$, to (empirically) obtain a straight line (of slope $k$).

$$Z \propto \sqrt{\nu} = k \sqrt{\nu} \propto 1/\sqrt{\lambda}$$

We will understand this result only after we have a quantum mechanical picture of electronic structure (in about 3 lectures), which determines x-ray wavelengths. In fact the emitted x-rays are related to those observed in electron capture processes.
This showed that order in the periodic table was a fundamental property of atoms, and demonstrated some gaps and anomalies like:

- $^{27}\text{Co}$ (mass = 58.93) comes before $^{28}\text{Ni}$ (mass = 58.7)
- $^{18}\text{Ar}$ (mass = 39.95) comes between $^{17}\text{Cl}$ (35.45) and $^{19}\text{K}$ (39.10)
- Predicted missing elements $^{61}\text{Pm}$ - others later predicted $^{43}\text{Tc}$ & $^{75}\text{Re}$

Predicted Elements from X-ray Spectroscopy

<table>
<thead>
<tr>
<th>Period</th>
<th>1A</th>
<th></th>
<th>2A</th>
<th></th>
<th>3A</th>
<th>4A</th>
<th>5A</th>
<th>6A</th>
<th>7A</th>
<th>8A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H 1.008</td>
<td></td>
<td>Li 6.941</td>
<td></td>
<td>Be 9.012</td>
<td></td>
<td>B 10.81</td>
<td></td>
<td>C 12.01</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>K 39.10</td>
<td></td>
<td>Ca 40.08</td>
<td></td>
<td>Sc 44.96</td>
<td></td>
<td>Ti 47.90</td>
<td></td>
<td>V 50.94</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Rb 65.39</td>
<td></td>
<td>Sr 87.62</td>
<td></td>
<td>Y 88.91</td>
<td></td>
<td>Zr 91.22</td>
<td></td>
<td>Nb 92.90</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Cs 132.9</td>
<td></td>
<td>Ba 137.3</td>
<td></td>
<td>La 138.9</td>
<td></td>
<td>Hf 178.5</td>
<td></td>
<td>Ta 180.9</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Eu 152.0</td>
<td></td>
<td>Ac 227</td>
<td></td>
<td>4f 144.2</td>
<td></td>
<td>5f 154</td>
<td></td>
<td>6f 186.9</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Sm 150.4</td>
<td></td>
<td>Eu 152</td>
<td></td>
<td>Gd 157.3</td>
<td></td>
<td>Tb 159.2</td>
<td></td>
<td>Dy 162.5</td>
<td></td>
</tr>
</tbody>
</table>

1917: Predicted Elements

1925: Predicted Elements

1939: Predicted Elements
Ionization Energy - The energy required to remove one electron from a neutral atom in the gas phase - is one of the properties that most clearly shows periodic trends. Remember that this property, like x-ray wavelength, was not known to Mendeleev in the 1860’s.

Eliminating the transition and rare earth elements so that all periods are equal length makes the trends even more apparent.
Periodic Electronic Properties

Ionization Energy - The energy required to remove one electron from a neutral atom in the gas phase.

This plot shows the overall behaviour of all known elements, with trends along rows and down groups.

- Ionization energy decreases down the main groups (not transition elements).
- Ionization energy increases (approximately) left to right across a row.

He = 2400 kJ mol$^{-1}$
Atomic volume was one of the key properties first used to show periodic trends. We now know that most of the volume of an atom is due to the electron “cloud” surrounding the nucleus. Like Moseley’s x-ray spectroscopy, these reflect both nuclear charge and electronic structure.

Modern correlations refer to atomic radius, rather than volume. This needs to be defined carefully, as atomic radii depend on

- the nature of the bonding - so they vary from one compound to another,
- and on the state of matter - so they differ between solid, liquid, and gas phases.

We define the metallic radius as one-half of the nearest-neighbour distance in a metallic crystal.

For non-metals we define the covalent radius as one-half of the distance between bonded atoms in a diatomic molecule of the element, e.g. N₂, F₂.
Periodic Trends in Atomic Size

2. Atomic radii thus calculated increase down groups, and decrease left to right across rows from the alkali metals to the Noble gases. The largest atoms are at the bottom left corner of the periodic table (Fr - 0.270 nm), and the smallest is at top right (He - 0.031 nm).

The trend is roughly opposite to ionization energies. This makes reasonable sense as atoms whose electrons are held closest to the nucleus should be hardest to ionise.

Meyer’s Atomic volume plot, re-scaled to the atomic number on the x-axis, matches the modern radius representation well.
Summary

You should now be able to

- Name some of the periodic trends and chemical properties used to construct the periodic table.
- Assign atoms to appropriate groups in the periodic table on the basis of their relevant properties.
- Explain the historic significance of key events in the development of modern atomic structure theory such as
  - nuclear charge, atomic mass, discovery of the neutron
- Define Ionization Energy and Atomic Radius and know their trends in the Periodic Table.

Next Lecture

Quantum theory
- Historical context and key experimental results.
- Postulates of quantum theory.
- Allowed energies for electrons in “hydrogen-like” atoms.