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Fig. 1.13 The modern periodic table in which the elements are arranged in numerical order according to the number of protons (and electrons) they possess.

• Syllabus for Introduction to Inorganic Chemistry (Chemistry 222) Summer 2011
• Instructor: Dr. Aislinn Sirk
• Office: Elliot 246
• Email: asirk@uvic.ca
• Lectures: Tuesday, Wednesday & Friday; 9:30 – 10:20 pm; Elliot 060
• Office Hours: Wednesday 11:00-12:30 or by appt
• Webpage: http://web.uvic.ca/~asirk/chem222.htm
• Recommended Text: Housecroft & Sharpe “Inorganic Chemistry” (3rd Ed., Pearson, 2008). Most of the lecture material can be found in this text (or earlier editions), but the lectures will be the ultimate authority.
• Other Useful Texts:
  • Rayner-Canham & Overton “Descriptive Inorganic Chemistry” (3rd Ed., 2002)
  • Rodgers “Descriptive Inorganic, Coordination and Solid-State Chemistry” (2nd Ed, 2002)
  • Messerer & Tai “Inorganic Chemistry” (3rd Ed., 2004)
  • Shriver & Atkins “Inorganic Chemistry” (3rd Ed., 1999)
• Course Content: a survey of the s-, p-, and d-block elements and their compounds
• Periodic trends in physical and chemical properties
• Solid state structures: ionic, covalent, metallic systems
• Molecular orbital diagrams for simple molecules
• Coordination chemistry, including colours and magnetism of transition metal complexes
• 222 Lecture Grading:
  • Periodic Table Quiz (May 13) 3%
  • Online Quiz/iclicker 7%
  • Term tests (10% each)
  • Final Exam (3 hours) 60%
• Final Grade: Lecture 67% Lab 33%
• You must pass BOTH the lab and lecture sections in order to pass the course
• NOTES:
  • I will periodically (!) hand out problem sets and then post solutions via the course web page. These problem sets will not be graded.
  • The lecture material and the laboratory material are NOT intended to correspond directly. Dave Berry can answer any questions you have about the laboratory.

Course objectives

• survey elements and compounds from across the periodic table

• learn about the tools and models chemists use to understand structure & bonding

• become familiar with periodic trends in physical & chemical properties
Recognize these elements?

Known elements
~2400 years ago
Known elements (1776)

John Dalton 1803

Other Possible Classifications
“triads” 1829 Dobereiner (Jena) in Germany ie: F,Cl,Br all behaved similarly
“octaves” 1864 Newlands (London)
Comparison of eka-silicon with germanium

**eka-silicon**

- 72 g/mol
- 5.5 g/cm³
- “high” m.p.

Es forms EsO₂ which has high m.p. and ρ = 4.7 g/cm³

EsCl₄ volatile liquid with b.p. < 100°C and ρ = 1.9 g/cm³

**germanium**

- 72.59 g/mol
- 5.36 g/cm³
- m.p. = 958 °C

Ge forms GeO₂ m.p. = 1100 °C and ρ = 4.70 g/cm³

GeCl₄ volatile liquid with b.p. 83°C and ρ = 1.88 g/cm³

---

**Fig. 1.13** The modern periodic table in which the elements are arranged in numerical order according to the number of protons (and electrons) they possess.
The modern periodic table in which the elements are arranged in numerical order according to the number of protons (and electrons) they possess.

Fig. 1.13

Two concepts that will guide our survey of the periodic table:

1. The relative size of atoms (or ions) of the elements.
Two concepts that will guide our survey of the periodic table:

(2) the relative **electronegativity** of the elements

“the power of an atom in a molecule to attract electrons to itself”  Linus Pauling ~1930

---

![Electronegativities of the elements](image_url)

**Fig. 9-8** The electronegativities of the elements. Rodgers, 3rd Ed., p. 227

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(1) the relative **size** of atoms (or ions) of the elements

Atomic orbitals are defined by three quantum numbers:

- **n**: the principal quantum number “size” 1,2,3…
- **l**: orbital angular momentum quantum number “shape” 0,1,2…n-1 and named s, p, d, f
- **m**: magnetic quantum number “orientation” -l… 0… +l
11

Why and how do atomic radii vary?

Dalton’s atomic model

Bohr’s model (1913)

Bohr’s model predicts:

Electron escapes the nucleus - ionization

Allowed energy states

Ground state
Bohr’s model predicts:

The amount of energy absorbed or emitted by moving between states is given by

$$\Delta E = E_f - E_i = h\nu = \frac{hc}{\lambda} = -2.18 \times 10^{-18} J \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$
The wave behavior of matter: De Broglie

\[ \lambda = \frac{h}{mv} \]

\( \lambda \) = wavelength (m)
\( h \) = Plank’s constant (s\(^{-1}\))
\( m \) = mass (kg)
\( v \) = velocity (m/s)

Heisenberg’s uncertainty principle

\[ \Delta x \cdot \Delta (mv) \geq \frac{h}{4\pi} \]

\( \Delta x \) = uncertainty in position (m)
\( \Delta (mv) \) = uncertainty in momentum (kgm\(^{-1}\)s\(^{-1}\))
\( h \) = Plank’s constant (s\(^{-1}\))
\[ 4\pi = 4\pi \]
Erwin Schrödinger proposed an equation containing both wave and particle terms. The solution of the equation is known as a wave function, $\Psi$ (psi).

Quantum Mechanics and Atomic Orbitals

Can the cat be alive and dead at the same time?

Quantum Mechanics and Atomic Orbitals

Schrödinger's Comic

The last panel of this comic is both funny and not funny at the same time.

Until you read it, there's no way to tell which it will end up being.

http://xkcd.com/45/
Wavefunctions ($\Psi$): 

$$ -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t) \Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t} $$

(a) $L = \frac{\lambda}{2}$
(b) $L = 2\frac{\lambda}{2}$
(c) $L = 3\frac{\lambda}{2}$

The wave functions

$$ \psi_n(x) = \frac{2}{\sqrt{L}} \sin \frac{n\pi x}{L} $$

Energy

- $n = 1$
- $n = 2$
- $n = 3$

The Schrödinger Equation

$$ -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t) \Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t} $$

Wave Functions for One-Electron Atoms

- $\psi(1s) = \left(\frac{1}{\pi}\right)^{1/2} \left(\frac{Z}{a_0}\right)^{1/2} e^{-Zr/a_0}$
- $\psi(2s) = \frac{1}{\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/a_0}$
- $\psi(2p_x) = \frac{1}{\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \sin \theta \cos \phi$
- $\psi(2p_y) = \frac{1}{\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \sin \theta \sin \phi$
- $\psi(2p_z) = \frac{1}{\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \cos \theta$

$$ a_0 = \frac{\hbar^2}{4\pi^2 m_e c^2} = 0.529 \times 10^{-8} \text{ cm} $$
$\psi^2$ is the probability of finding an electron in a given volume of space, and thus is more relevant to our need to gauge the size of an orbital and can be represented in Cartesian coordinates.

Easier to visualize shape of the space in which an electron can (probably) be found, and the distance it is likely to be from the nucleus, by splitting $\psi$ into a combination of angular and radial parts.

Radial distribution functions describe the probability of finding an electron at a given distance from the nucleus.

---

For interest only: do not need to memorise

**The Schrödinger Equation**

\[-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t) \Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t}\]

**Wave Functions for One-Electron Atoms**

- $\psi(1s) = \left(\frac{1}{r}\right)^{1/2} \left(\frac{Z}{a_0}\right)^{1/2} e^{-Zr/a_0}$
- $\psi(2s) = \frac{1}{\sqrt{2}} \left(\frac{Z}{a_0}\right)^{1/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \sin \theta \cos \phi$
- $\psi(2p_x) = \frac{1}{\sqrt{2}} \left(\frac{Z}{a_0}\right)^{1/2} \left(\frac{Zr}{a_0}\right)^{3/2} e^{-Zr/2a_0} \sin \phi$
- $\psi(2p_y) = \frac{1}{\sqrt{2}} \left(\frac{Z}{a_0}\right)^{1/2} \left(\frac{Zr}{a_0}\right)^{3/2} e^{-Zr/2a_0} \sin \theta \sin \phi$
- $\psi(2p_z) = \frac{1}{\sqrt{2}} \left(\frac{Z}{a_0}\right)^{1/2} \left(\frac{Zr}{a_0}\right)^{3/2} e^{-Zr/2a_0} \cos \theta$

\[a_0 = \frac{\hbar^2}{4\pi^2 m \rho^2} = 0.529 \times 10^{-8} \text{ cm}\]
(1) the relative **size** of atoms (or ions) of the elements

**Readings**
- H and S chapter 1 (all)
- Box 1.3, Particle in a box
- Box 1.6 and try the self study exercises

**Fig. 1.4** Definition of the polar coordinates \((r, \theta, \phi)\) for a point shown here in pink; \(r\) is the radial coordinate and \(\theta\) and \(\phi\) are angular coordinates. \(\theta\) and \(\phi\) are measured in radians (rad). Cartesian axes \((x, y, z)\) are also shown.

**Fig. 1.7** Radial distribution functions, \(4\pi r^2 R(r)^2\), for the 1s, 2s and 3s atomic orbitals of the hydrogen atom.
To memorise

Fig. 1.8 Radial distribution functions, $4\pi r^2 R(r)^2$, for the 3$s$, 3$p$ and 3$d$ atomic orbitals of the hydrogen atom.

Fig. 1.10 Representations of an $s$ and a set of three degenerate $p$ atomic orbitals. The lobes of the $p_x$ orbital are elongated like those of the $p_y$ and $p_z$ but are directed along the axis that passes through the plane of the paper.
To memorise

Fig. 1.11 Representations of a set of five degenerate $d$ atomic orbitals.


f orbitals (Lanthanoids and Actinoids: for interest only)
The $s$ orbitals (to memorize) ($l = 0$)

- All $s$ orbitals are spherical
- As $n$ increases, the $s$ orbitals get larger
- As $n$ increases, the number of nodes increases

For an $s$ orbital, the number of nodes is given by $n - 1$
The $p$ orbitals: ($l=1$) to memorize

- $p$ orbitals are dumbbell-shaped
- 3 values of $m_l$
  - two lobes and a node at the nucleus
  - 3 different orientations ($x,y,z$)

Atomic radii: multi-electron atoms & electron configuration (cont’d)

- We have discussed an atomic model for which a series of wavefunctions describe the behaviour of an electron in well-defined volumes of space around the nucleus (orbitals).
- Recall: Orbitals are defined by three quantum numbers:
  - $n$: the principal quantum number
  - $l$: orbital angular momentum quantum number
  - $m_l$: magnetic quantum number
  - when filling orbitals with electrons, there is a fourth quantum number
    - $m_s$: magnetic spin quantum number
• the electron tends to be further from the nucleus as n increases

• best to compare like “l” values between different “shells” or n-values - e.g. 1s, 2s, 3s

• Difficult to visualize probability at specific instants & locations. Easier to imagine many locations of an electron over an extended period of time.

Multi-electron atoms & electron configuration
• Ground state electronic configurations of the elements are governed by the Aufbau principal, in conjunction with Hund’s first rule & the Pauli exclusion principal:

  (note language: actually the electron’s energy varies depending on which orbital it is in)

(1) **Aufbau principal** Orbitals are filled in the order of energy (lowest E orbital is filled first)

(2) **Hund’s rule**: for a set of degenerate orbitals, electrons will not spin-pair until each orbital in the set contains one electron, and electrons singly occupying this degenerate set will have parallel spins.

(3) **Pauli exclusion principal**: no two electrons in the same atom may have the same set of n, l, m\(l\), and m\(s\) quantum numbers.
Single electron atoms vs. many electron atoms

Atomic radii: multi-electron atoms & electron configuration (cont’d)

- Picture emerges of relative ordering of orbital energies for atomic elements:
  - Energy gaps narrow and “shells” start to overlap (n = 3, 4, …) Why?
Two ways to remember the orbital filling order

Electron Configurations and the Periodic Table

The periodic table can be used as a guide for electron configurations.

- The period number is the value of \( n \)
- \( s \)-block: alkali and alkaline earth metals
- \( d \)-block: transition metals
- \( p \)-block: main group elements
- \( f \)-block: lanthanoids and actinoids
Electron Configurations and the Periodic Table

1.13

The modern periodic table in which the elements are arranged in numerical order according to the number of protons (and electrons) they possess.
**Atomic orbitals: my expectations**

- Be able to draw s, p, and d-orbitals, showing them correctly placed on the Cartesian axes, with the appropriate number and orientation(s) of any nodal planes, and indicating clearly the phases, or signs, of the lobes.

- Be aware that these pictures are actually showing “boundary surfaces”, inside which there is (overall) a (typically) 95-99% probability of finding an electron.

- Recall that within an “n” level, orbitals with the same “l” are degenerate, while those with differing “l” are not. (E.g. electrons in different 3p orbitals have the same energy for any given atom, but they have different energies from those in the 3s orbital.)

- Recognize the periodic trend in the size of atoms (they get bigger as the period numbers (n) increase down the periodic table) correlates with the increasing probability of finding an electron far from the nucleus.

- Recognize that all these familiar orbital shapes and sizes are based on the solution of the Schrödinger wave equation for the hydrogen atom.

- Our ability to know accurately electron energies and orbital shapes diminishes drastically as we move from a one-e- atom to multi-electron atoms.

---

**Two concepts that will guide our survey of the periodic table:**

1. The relative **size** of atoms (or ions) of the elements

   ![Periodic Table Diagram](image)

   **Fig. 9-5** The variation in atomic radii in [some] representative elements.

   Rodgers, 3rd Ed., p. 224
Two concepts that will guide our survey of the periodic table:

1. The relative size of atoms (or ions) of the elements.

Change in atomic radii (n=6 and higher):
- Relativistic effects: a decrease in radius, compared to that predicted by the Schrödinger wave equation, for the elements with n=6 (6th period) and higher.
- "Lanthanoid contraction": steady decrease in size along the series of elements La-Lu (before Hf).
Quantifying $Z_{\text{eff}}$: Slater’s Rules

- Effective nuclear charge, $Z_{\text{eff}}$, felt by electrons as they are “placed” in the atomic orbitals *increases* as successive electrons are added across a period.
- Effective nuclear charge, $Z_{\text{eff}}$, *decreases* as successive periods are filled.

Ionic radii relative to metallic (or covalent) radii (in Å)

Brown, LeMay, Bursten & Murphy “Chemistry The Central Science” 11th Ed., Pearson 2009, Fig. 7.8, p. 263
Two concepts that will guide our survey of the periodic table:

(2) the relative *electronegativity* of the elements

"the power of an atom in a molecule to attract electrons to itself" Linus Pauling ~1930

Electronegativity

Bond dissociation energies for heteronuclear diatomic molecules (e.g. HCl) are often not simply the geometric mean of those for the corresponding homonuclear diatomics (e.g. H-H and Cl-Cl)

\[ \text{BDE (kJ/mol):} \]

(i) Pauling electronegativity values, \( \chi^P \)

(ii) Allred-Rochow electronegativity values, \( \chi^{AR} \)

(iii) Mulliken (-Jaffé) electronegativity values, \( \chi^M \)

- The three scales are not directly comparable, but periodic trends are similar
Electron configuration and periodic trends

- Other phenomena that correlate with shielding and $Z_{\text{eff}}$ arguments:

  (ii) 1st electron affinity: $-\Delta U$ (internal energy) at 0K for $X(g) + e^- \rightarrow X^-(g)$

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Electron configuration and periodic trends

- Other phenomena that correlate with shielding and $Z_{\text{eff}}$ arguments:
  
  (i) 1st ionization energy: $\Delta U$ (internal energy) at 0K for $X(g) \rightarrow X^+(g) + e^-$

Other Trends in the Periodic Table

Boiling Point
Other Trends in the Periodic Table
Electrical Conductivity/Resistivity