Chapter 8

Electron Configuration and Chemical Periodicity

Electron Configuration and Chemical Periodicity

8.1 Characteristics of Many-Electron Atoms

8.2 The Quantum-Mechanical Model and the Periodic Table

8.3 Trends in Three Atomic Properties

8.4 Atomic Properties and Chemical Reactivity

Figure 8.1 The effect of electron spin.

Schrodinger Wave Equation

(n, l, m_l, m_s)

spin quantum number m_s

$m_s = +½$ **or** $-½$

$m_s = +½$ $m_s = -½$

Schrodinger Wave Equation

quantum numbers: (n, l, m_l, m_s)

Existence (and energy) of electron in atom is described by its ***unique*** wave function ψ.

Pauli exclusion principle - no two electrons in an atom can have the same four quantum numbers.

Each seat is uniquely identified (E, R12, S8)
Each seat can hold only one individual at a time

TABLE 7.2 Relation Between Quantum Numbers and Atomic Orbitals

n	ℓ	m_ℓ	Number of Orbitals	Atomic Orbital Designations
1	0	0	1	$1s$
2	0	0	1	$2s$
	1	$-1, 0, 1$	3	$2p_x, 2p_y, 2p_z$
3	0	0	1	$3s$
	1	$-1, 0, 1$	3	$3p_x, 3p_y, 3p_z$
	2	$-2, -1, 0, 1, 2$	5	$3d_{xy}, 3d_{yz}, 3d_{xz}, 3d_{x^2-y^2}, 3d_{z^2}$
⋮	⋮	⋮	⋮	⋮

Schrodinger Wave Equation

quantum numbers: (n, l, m_l, m_s)

Shell – electrons with the same value of *n*

Subshell – electrons with the same values of *n* **and** *l*

Orbital – electrons with the same values of *n, l*, **and** m_l

How many electrons can an orbital hold?

If *n, l,* and m_l are fixed, then m_s = ½ or - ½

$\psi = (n, l, m_l, ½)$ or $\psi = (n, l, m_l, -½)$

An orbital can hold 2 electrons

Electron addresses

- #1 Shell number, n — Average distance from nucleus
- #2 Subshell type, l — Region shape
- #3 Orbital, m — Region orientation
- #4 Spin, s — Direction of e^- rotation

These four address components (n, l, m, and s) are called quantum numbers in more formal treatments

#1 - Electron Shells

- Electrons are arranged in shells according to how far out, on average, they are from the nucleus
- These can be visualized as similar to the space occupied by the layers of an onion

Table 8.1 Summary of Quantum Numbers of Electrons in Atoms

Name	Symbol	Permitted Values	Property
principal	n	positive integers (1, 2, 3, …)	orbital energy (size)
angular momentum	l	integers from 0 to n – 1	orbital shape (The l values 0, 1, 2, and 3 correspond to *s*, *p*, *d*, and *f* orbitals, respectively.)
magnetic	m_l	integers from $-l$ to 0 to $+l$	orbital orientation
spin	m_s	+½ or –½	direction of e– spin

Shell Populations

- The innermost shell can hold 2 e^-'s
- The second shell can hold 8 e^-'s
- The third shell can hold 18 e^-'s
- The fourth shell can hold 32 e^-'s
- See the pattern?

Quantum Numbers and The Exclusion Principle

Each electron in any atom is described completely by a set of ***four*** quantum numbers.

The first three quantum numbers describe the orbital, while the fourth quantum number describes electron spin.

Pauli's **exclusion principle** states that *no two electrons in the same atom can have the same four quantum numbers*.

An atomic orbital can hold a ***maximum of two electrons*** and they must have ***opposing spins***.

#1 - Electron shells

Population given by $2n^2$

E.g., 3rd shell has $2\ (3^2) = 2\ (9) = 18\ e^-$

Subshell (sublevel) shapes

s (1 lobe)

p (2 lobes)

d (4 lobes)

f (6 or 8 lobes)

Inside a sodium atom

In a tiny nucleus, we'll find 11 protons and 12 neutrons (assuming this is an atom of Na-23, the only common isotope)

Inside a sodium atom

The nucleus is at the exact center of the 1s orbital

Inside a sodium atom

Finally, the n=3 shell has a single 3s electron in it. The n=3 shell is the biggest yet!

Inside a sodium atom

Finally, the n=3 shell has a single 3s electron in it. It has a single, unpaired e^-.

Inside a sodium atom

The n = 3 shell is also centered about the nucleus...

Inside a sodium atom

The n = 3 shell is also centered about the nucleus...

Inside a sodium atom

The 3s e^- is the most accessible e^- for interacting with another atom

#3 - Subshell Orientations

- Subshells (sublevels) have a number of orientations associated with their type

s subshell	1 orientation
p subshell	3 orientations
d subshell	5 orientations
f subshell	7 orientations

Available subshells (sublevels)

• 1st shell	1s			
• 2nd shell	2s	2p		
• 3rd shell	3s	3p	3d	
• 4th shell		4s	4p	4d	4f

- This completes the first two parts of the electron address

Why is $E_{2s} < E_{2p}$ and $E_{3s} < E_{3p} < E_{3d}$?

Why is $E_{2s} < E_{2p}$ and $E_{3s} < E_{3p} < E_{3d}$?

For a given n state (shell):

Electrons in orbitals with lower values of l penetrate closer to the nucleus (even though r_{mp} decreases with increasing l).

p-electrons are less shielded than d-electrons.
Thus $E_{3p} < E_{3d}$.

p-electrons are less shielded than d-electrons.
Thus $E_{3p} < E_{3d}$.

In a multi-electron atom:

s < p < d < f

Electron Energies and the Periodic Table

- Periodic properties of elements determined by electron configurations
- First two parts of electron address can be easily seen in the periodic table's shape
- Color and label designate the last electron added

The Periodic Table

The Periodic Table

The Periodic Table

The Periodic Table

The Periodic Table

The Periodic Table

The Periodic Table

The Periodic Table

The Periodic Table

Which is the last electron added in an atom of gold?

1. 4f
2. 2p
3. 4s
4. 5d

What is the last electron added in an atom of gold?

Electron Configurations

Electron Configurations

- Notational shorthand to show exact distribution of electrons in a given element
- Assume atom is in its lowest energy state, the ground state

  That is, no vacancies from bottom up
- Just count and list the number of each type of square you cross in arriving at the element of interest

Example 1: Carbon

Carbon

Carbon

Carbon

1s
2s
3s
4s
5s
6s
7s
3d
4d
5d
6d
4f
5f
1s
^{6}C
2p
3p
4p
5p
6p
7p
$1s^2\ 2s^2\ 2p^2$

Carbon

1s
2s
3s
4s
5s
6s
7s
$1s^2\ 2s^2\ 2p^2$
1s
^{6}C
2p
3p
4p
5p
6p
7p
3d
4d
5d
6d
4f
5f

Carbon

1s
2s
3s
4s
5s
6s
7s
$1s^2\ 2s^2\ 2p^2$
Your text calls this the condensed notation
1s
^{6}C
2p
3p
4p
5p
6p
7p
5d
6d
4f
5f

Factors Affecting Atomic Orbital Energies

- The energies of atomic orbitals are affected by
  - nuclear charge (Z) and
  - shielding by other electrons.
- A **higher nuclear charge** increases nucleus-electron interactions and lowers sublevel energy.
- **Shielding** by other electrons reduces the full nuclear charge to an ***effective nuclear charge*** ($\boldsymbol{Z_{eff}}$).
  - Z_{eff} is the nuclear charge an electron actually experiences.
- **Orbital shape** also affects sublevel energy.

Figure 8.2 The effect of nuclear charge on sublevel energy.

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Greater nuclear charge lowers sublevel energy.

It takes *more energy* to remove the 1*s* electron from He^+ than from H.

Shielding and Orbital Energy

- Electrons in the ***same*** energy level shield each other to some extent.
- Electrons in ***inner*** energy levels shield the outer electrons very effectively.
  - The farther from the nucleus an electron is, the lower the Z_{eff} for that particular electron.

Figure 8.3 Shielding and energy levels.

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Figure 8.4 Penetration and sublevel energy.

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Orbital shape causes electrons in some orbitals to “penetrate” close to the nucleus.

Penetration increases nuclear attraction and decreases shielding.

Extreme case A $Z_{eff} = 1$, $IE_{He} = 2.18 \times 10^{-18}$ J

total shielding

Extreme case B $Z_{eff} = 2$, $IE_{He} = 8.72 \times 10^{-18}$ J

no shielding

Experimentally determined $IE_{He} = 3.94 \times 10^{-18}$ J

In between

Slater's rules

Slater's rules are a set of guidelines to estimate the effective nuclear charge (Z_{eff}) experienced by an electron in an atom, accounting for shielding by other electrons.

Here's a breakdown of the process:

1. Write the Electron Configuration:

- First, determine the electron configuration of the atom or ion.
- For example, for oxygen (O), the configuration is $1s^2\ 2s^2\ 2p^4$.

2. Identify the Electron of Interest:

- Choose the electron for which you want to calculate the effective nuclear charge.

3. Calculate the Screening Constant (S)

Slater's rules

Slater's rules provide specific values for the contribution of each electron to the screening constant:

- **For s and p electrons:**
  - **Within the same group:** 0.35 for each other electron in the same group as the electron of interest.
  - **In the next inner shell (n-1):** 0.85 for each electron in the n-1 shell.
  - **In shells two or more lower (n-2, n-3, etc.):** 1.00 for each electron.
- **For d and f electrons:**
  - **Within the same group:** 0.35 for each other electron in the same group.
  - **In lower groups:** 1.00 for each electron in groups to the left.

1. Use slater's rule to estimate the effective nuclear charge of a 2s electron in Beryllium.

$1s^2 \; \boxed{2s^2}$

$\downarrow \qquad \downarrow$

$2 \times 0.85 + 1 \times 0.35$

$S = 2.05$

$Z_{eff} = Z - S$

$= 4 - 2.05$

$= \boxed{1.95}$

S	
n-1 →	0.85
n →	0.35
n-2 →	1.00

Be → 1.912

2. Use slater's rule to estimate the effective nuclear charge of a 2p electron in Fluorine.

$1s^2 \quad 2s^2 \quad 2p^5$

$\rightarrow 5.1$

$2 \times 0.85 + 6 \times 0.35$

$S = 3.8$

$Z_{eff} = Z - S$

$= 9 - 3.8$

$= \boxed{5.2}$

S & p

$n \rightarrow 0.35$

$n-1 \rightarrow 0.85$

$n-2 \rightarrow 1.00$

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Table 8.2 Values of Z_{eff} for the Sublevels in Potassium ($Z = 19$)

Sublevel	Z_{eff}
1*s*	18.49
2*s*	13.01
2*p*	15.03
3*s*	8.68
3*p*	7.73
4*s*	3.50

Splitting of Levels into Sublevels

Each energy level is split into ***sublevels*** of differing energy.

Splitting is caused by penetration and its effect on shielding.

For a given *n* value, a lower *l* value indicates a lower energy sublevel.

Order of sublevel energies: *s* < *p* < *d* < *f*

Figure 8.5

Order for filling energy sublevels with electrons.

In general, energies of sublevels increase as *n* increases (1 < 2 < 3, etc.) and as *l* increases (*s* < *p* < *d* < *f*).

As *n* increases, some sublevels overlap.

Aufbau (building up) principle

Fill energy states (which depend on n and *l*) one electron at a time, starting with the **lowest energy state** and heeding:

1. **Pauli Exclusion Principle**

2. **Hund's rule**: when electrons are added to states of the same E:

A single e^- enters each state before a second e^- enters any state.

Spins remain **parallel** prior to adding a second e^- to any state.

And Hund's Rule, which is one of my favorite rules in chemistry,

Electron Configurations and Orbital Diagrams

Electron configuration is indicated by a shorthand notation:

$n\,l^{\#}$

$\#$ ← # of electrons in the sublevel

l ← as *s*, *p*, *d*, *f*

Orbital diagrams make use of a box, circle, or line for each orbital in the energy level. An arrow is used to represent an electron *and* its spin.

Figure 8.6 **A vertical orbital diagram for the Li ground state.**

Building Orbital Diagrams

The **aufbau principle** is applied – electrons are always placed in the lowest energy sublevel available.

H (Z = 1) $1s^1$ $\boxed{\uparrow}$

1*s*

The **exclusion principle** states that each orbital may contain a maximum of 2 electrons, which must have opposite spins.

He (Z = 2) $1s^2$ $\boxed{\uparrow\downarrow}$

1*s*

Building Orbital Diagrams

Hund's rule specifies that when orbitals of equal energy are available, the lowest energy electron configuration has the maximum number of unpaired electrons with parallel spins.

N (Z = 7) $1s^2 2s^2 2p^3$

Sample Problem 8.1

Correlating Quantum Numbers and Orbital Diagrams

PROBLEM: Write a set of quantum numbers for the third electron and a set for the eighth electron of the F atom.

PLAN: Identify the electron of interest and note its level (n), sublevel, (l), orbital (m_l) and spin (m_s). Count the electrons in the order in which they are placed in the diagram.

SOLUTION:

F (Z = 9) $1s^2 2s^2 2p^5$

For the 3rd electron: n = 2, l = 0, m_l = 0, m_s = +½

For the 8th electron: n = 2, l = 1, m_l = –1, m_s = –½

Figure 8.7 Depicting orbital occupancy for the first 10 elements.

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Template for e^- Configurations

1s	2s	2p	3s	3p
—	—	— — —	—	— — —

4s	3d	4p
—	— — — — —	— — —

Each dash represents an orbital

Carbon Example

6 electrons needed

6 electrons added

$1s^2 2s^2 2p^2$ C

Outermost shells...

- Note that carbon and silicon have similar outer shells

$1s^2 \boxed{2s^2 2p^2}$
carbon

$1s^2 2s^2 2p^6 3s^2 3p^2$
silicon

Iron

1s
2s
3s
4s
5s
6s
7s
$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
3d
^{26}Fe
4d
5d
6d
1s
^{6}C
2p
^{14}Si
3p
4p
5p
6p
7p
4f
5f

Iron Example

26 electrons needed

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

19 electrons added

K

Iron Example

26 electrons needed

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

20 electrons added

Ca

Iron Example

26 electrons needed

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$

21 electrons added

Sc

Iron Example

26 electrons needed

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$

22 electrons added

Ti

Iron Example

26 electrons needed

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

23 electrons added

V

Iron Example

26 electrons needed

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

24 electrons added

Cr (exception)

Iron Example

26 electrons needed

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

25 electrons added

Mn

Iron Example

26 electrons needed

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

26 electrons added

Fe

Noble gas notation

- Eventually, electron configurations get too long!
- Noble gas notation shortens it by using a noble gas core

Fe $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Noble gas notation

Find previous noble gas

Noble gas notation

- Eventually, electron configurations get too long!
- Noble gas notation shortens it by using a noble gas core

Fe $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Noble gas notation

- Eventually, electron configurations get too long!
- Noble gas notation shortens it by using a noble gas core

Fe $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Noble gas notation

- Eventually, electron configurations get too long!
- Noble gas notation shortens it by using a noble gas core

Fe $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Fe $[Ar]4s^2 3d^6$

What's the electron configuration for a neutral bromine atom?

1. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$
2. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
3. $[Ar] 4s^2 3d^{10} 4p^5$
4. $[Ar]\ 3d^{10} 4s^2 4p^5$

They're ALL correct
just different variations!

What's the electron configuration for a neutral bromine atom?

1. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$ (handout order)
2. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$ (layer order)
3. $[Ar] 4s^2 3d^{10} 4p^5$ (noble gas + handout order)
4. $[Ar]\ 3d^{10} 4s^2 4p^5$ (noble gas + layer order)

They're ALL correct
just different variations!

Electron Removal Order

- When forming cations, you remove electrons from the outermost layer first
- Sometimes requires you to regroup notation in layer order

Forming Fe^{2+} cation

Fe neutral atom: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Forming Fe^{2+} cation

Fe neutral atom: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

regrouped: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Forming Fe^{2+} cation

Fe neutral atom: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

regrouped: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Forming Fe^{2+} cation

Fe neutral atom: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

regrouped: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 \boxed{4s^2}$

Fe^{2+} cation: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

(2 outermost e^-'s removed)

Forming Fe^{2+} cation

Fe neutral atom: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

regrouped: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Fe^{2+} cation: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

(2 outermost e^-'s removed)

Electron configuration of ions

Once a **d orbital** is filled, the orbital energy **drops** to below the corresponding s orbital.

Figure 8.26 The crossover of sublevel energies in Period 4.

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Electron Removal Order

- When forming cations, you remove electrons from the outermost layer first
- Sometimes requires you to regroup notation in layer order

What is the electron configuration for a Co^{3+} cation?

1. $[Ar]4s^2 3d^7$
2. $[Ar]4s^2 3d^{10}$
3. $[Ar]4s^2 3d^4$
4. $[Ar]3d^6$

What is the electron configuration for a Co^{3+} cation?

1. $[Ar]4s^2 3d^7$ — nope, neutral Co atom
2. $[Ar]4s^2 3d^{10}$ — nope, it gained 3 e^-'s
3. $[Ar]4s^2 3d^4$ — nope, it lost inner e^-'s
4. $[Ar]3d^6$ — yep, it lost $4s^2$ first

Periodic Trends

- Many periodic properties of atoms are due to their electron configurations
- Members of the same group have similar valence shells

Li	[He]$2s^1$
Na	[Ne]$3s^1$
K	[Ar]$4s^1$
Rb	[Kr]$5s^1$
Cs	[Xe]$6s^1$

Alkali metals all have a valence shell holding one s-electron

Lewis Structures of Atoms

Atomic symbols represent the nucleus plus inner shell e^-'s
Dots are added to indicate valence shell electrons

Note that the number of valence electrons is equal to the element's group number for main group elements

Lewis Structures of Atoms

Atomic symbols represent the nucleus plus inner shell e^-'s
Dots are added to indicate valence shell electrons

Members of Group 4A each have four valence electrons!

How many valence electrons does oxygen have?

1. 1
2. 2
3. 6
4. 8

How many valence electrons does oxygen have?

1. 1
2. 2
3. 6
4. 8

Periodic Trends

Many periodic properties of atoms are due to their electron configurations

- Effective nuclear Charge
- Atomic radius
- Ionization energy
  - energy to remove an electron
- Electronegativity
  - tendency to attract an electron

Metallic Character

Hydrogen ($1s^1$)

- No suitable position for hydrogen in the periodic table, it really could be a class by itself
- Like alkali metals, has a single *s* electron and forms H^+ ion, which is hydrated in solution (H_3O^+)
- Also forms hydride ion H^- in ionic compounds, NaH, CaH_2
- Hydrides reacts with water:

$$2NaH(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

$$CaH_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + 2H_2(g)$$

- Most important compound of hydrogen is water,

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

Effective Nuclear Charge (Z_{eff})

Effective Nuclear Charge (Z_{eff})

$Z_{eff} = Z_{actual}$ – No. of Core Electrons **or** Electron shielding

Figure 5-16 Chemistry, 5/e

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Effective Nuclear Charge (Z_{eff})

Effective nuclear charge (Z_{eff}) is the "positive charge" felt by an electron.

$Z_{eff} = Z - \sigma$ $\quad 0 < \sigma < Z$ (σ = shielding constant)

$Z_{eff} \approx Z$ – number of inner or core electrons

	Z	Core	Z_{eff}	Radius (pm)
Na	11	10	1	186
Mg	12	10	2	160
Al	13	10	3	143
Si	14	10	4	132

metals

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

as expected and now we have all the metals, metalloids and nonmetals

Figure 8.10 A periodic table of partial ground-state electron configurations.

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Main-Group Elements (*s* block)

Main-Group Elements (*p* block)

Transition Elements (*d* block)

Period number: highest occupied energy level

	1A (1) ns^1	2A (2) ns^2	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8)	8B (9)	8B (10)	1B (11)	2B (12)	3A (13) ns^2np^1	4A (14) ns^2np^2	5A (15) ns^2np^3	6A (16) ns^2np^4	7A (17) ns^2np^5	8A (18) ns^2np^6
1	1 **H** $1s^1$																	2 **He** $1s^2$
2	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^2 2p^1$	6 **C** $2s^2 2p^2$	7 **N** $2s^2 2p^3$	8 **O** $2s^2 2p^4$	9 **F** $2s^2 2p^5$	10 **Ne** $2s^2 2p^6$
3	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^2 3p^1$	14 **Si** $3s^2 3p^2$	15 **P** $3s^2 3p^3$	16 **S** $3s^2 3p^4$	17 **Cl** $3s^2 3p^5$	18 **Ar** $3s^2 3p^6$
4	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $4s^2 3d^1$	22 **Ti** $4s^2 3d^2$	23 **V** $4s^2 3d^3$	24 **Cr** $4s^1 3d^5$	25 **Mn** $4s^2 3d^5$	26 **Fe** $4s^2 3d^6$	27 **Co** $4s^2 3d^7$	28 **Ni** $4s^2 3d^8$	29 **Cu** $4s^1 3d^{10}$	30 **Zn** $4s^2 3d^{10}$	31 **Ga** $4s^2 4p^1$	32 **Ge** $4s^2 4p^2$	33 **As** $4s^2 4p^3$	34 **Se** $4s^2 4p^4$	35 **Br** $4s^2 4p^5$	36 **Kr** $4s^2 4p^6$
5	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $5s^2 4d^1$	40 **Zr** $5s^2 4d^2$	41 **Nb** $5s^1 4d^4$	42 **Mo** $5s^1 4d^5$	43 **Tc** $5s^2 4d^5$	44 **Ru** $5s^1 4d^7$	45 **Rh** $5s^1 4d^8$	46 **Pd** $4d^{10}$	47 **Ag** $5s^1 4d^{10}$	48 **Cd** $5s^2 4d^{10}$	49 **In** $5s^2 5p^1$	50 **Sn** $5s^2 5p^2$	51 **Sb** $5s^2 5p^3$	52 **Te** $5s^2 5p^4$	53 **I** $5s^2 5p^5$	54 **Xe** $5s^2 5p^6$
6	55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La*** $6s^2 5d^1$	72 **Hf** $6s^2 5d^2$	73 **Ta** $6s^2 5d^3$	74 **W** $6s^2 5d^4$	75 **Re** $6s^2 5d^5$	76 **Os** $6s^2 5d^6$	77 **Ir** $6s^2 5d^7$	78 **Pt** $6s^1 5d^9$	79 **Au** $6s^1 5d^{10}$	80 **Hg** $6s^2 5d^{10}$	81 **Tl** $6s^2 6p^1$	82 **Pb** $6s^2 6p^2$	83 **Bi** $6s^2 6p^3$	84 **Po** $6s^2 6p^4$	85 **At** $6s^2 6p^5$	86 **Rn** $6s^2 6p^6$
7	87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac**** $7s^2 6d^1$	104 **Rf** $7s^2 6d^2$	105 **Db** $7s^2 6d^3$	106 **Sg** $7s^2 6d^4$	107 **Bh** $7s^2 6d^5$	108 **Hs** $7s^2 6d^6$	109 **Mt** $7s^2 6d^7$	110 **Ds** $7s^2 6d^8$	111 **Rg** $7s^2 6d^9$	112 **Cn** $7s^2 6d^{10}$	113 $7s^2 7p^1$	114 **Fl** $7s^2 7p^2$	115 $7s^2 7p^3$	116 **Lv** $7s^2 7p^4$	117 $7s^2 7p^5$	118 $7s^2 7p^6$

Inner Transition Elements (*f* block)

6	*Lanthanides	58 **Ce** $6s^2 4f^1 5d^1$	59 **Pr** $6s^2 4f^3$	60 **Nd** $6s^2 4f^4$	61 **Pm** $6s^2 4f^5$	62 **Sm** $6s^2 4f^6$	63 **Eu** $6s^2 4f^7$	64 **Gd** $6s^2 4f^7 5d^1$	65 **Tb** $6s^2 4f^9$	66 **Dy** $6s^2 4f^{10}$	67 **Ho** $6s^2 4f^{11}$	68 **Er** $6s^2 4f^{12}$	69 **Tm** $6s^2 4f^{13}$	70 **Yb** $6s^2 4f^{14}$	71 **Lu** $6s^2 4f^{14} 5d^1$
7	**Actinides	90 **Th** $7s^2 6d^2$	91 **Pa** $7s^2 5f^2 6d^1$	92 **U** $7s^2 5f^3 6d^1$	93 **Np** $7s^2 5f^4 6d^1$	94 **Pu** $7s^2 5f^6$	95 **Am** $7s^2 5f^7$	96 **Cm** $7s^2 5f^7 6d^1$	97 **Bk** $7s^2 5f^9$	98 **Cf** $7s^2 5f^{10}$	99 **Es** $7s^2 5f^{11}$	100 **Fm** $7s^2 5f^{12}$	101 **Md** $7s^2 5f^{13}$	102 **No** $7s^2 5f^{14}$	103 **Lr** $7s^2 5f^{14} 6d^1$

Figure 8.11 Orbital filling and the periodic table.

The order in which the orbitals are filled can be obtained directly from the periodic table.

Trends in Metallic Character

Effective Nuclear Charge (Z_{eff})

increasing Z_{eff}

Atomic Radii

metallic radius

covalent radius

Figure 8.12 Defining atomic size.

A. The metallic radius of aluminum.

B. The covalent radius of chlorine.

C. Known covalent radii and distances between nuclei can be used to find unknown radii.

Trends in Atomic Size

Atomic size ***increases*** as the principal quantum number *n* ***increases***.

- As *n* increases, the probability that the outer electrons will be farther from the nucleus increases.

Atomic size ***decreases*** as the effective nuclear charge Z_{eff} ***increases***.

- As Z_{eff} increases, the outer electrons are pulled closer to the nucleus.

For ***main group elements***:

- atomic size ***increases*** down a group in the periodic table and ***decreases*** across a period.

Increasing atomic radius
1A
2A
3A
4A
5A
6A
7A
8A
H
37
He
31
B
C
N
O
F
Ne
Li
152
Be
112
85
77
75
73
72
70
Na
186
Mg
160
Al
143
Si
118
P
110
S
103
Cl
99
Ar
98
K
227
Ca
197
Ga
135
Ge
123
As
120
Se
117
Br
114
Kr
112
Rb
248
Sr
215
In
166
Sn
140
Sb
141
Te
143
I
133
Xe
131
Cs
265
Ba
222
Tl
171
Pb
175
Bi
155
Po
164
At
142
Rn
140
Increasing atomic radius

Atomic Radii Decreases Across the Period

Period 2

Li	Be	B	C	N	O

Li ($3p^+$ & $3e^-$)

Be ($4p^+$ & $4e^-$)

B ($5p^+$ & $5e^-$)

C ($6p^+$ & $6e^-$)

O ($8p^+$ & $8e^-$)

Ne ($10p^+$ & $10e^-$)

Atomic Radii Increases Down the Group

Group IIA

Be
Mg
Ca
Sr
Ba
Ra

Be ($4p^+$ & $4e^-$)

Mg ($12p^+$ & $12e^-$)

Ca ($20p^+$ & $20e^-$)

Trends in Atomic Radii

Ionization Energy

Ionization Energy

Ionization energy is the minimum energy (kJ/mol) required to remove an electron from a gaseous atom in its ground state.

$I_1 + X_{(g)} \longrightarrow X^+_{(g)} + e^-$ $\quad$ I_1 first ionization energy

$I_2 + X^+_{(g)} \longrightarrow X^{2+}_{(g)} + e^-$ $\quad$ I_2 second ionization energy

$I_3 + X^{2+}_{(g)} \longrightarrow X^{3+}_{(g)} + e^-$ $\quad$ I_3 third ionization energy

$$\boxed{I_1 < I_2 < I_3}$$

1st Ionization Energy

1st Ionization Energy

1st Ionization Energy

1st Ionization Energy

1st Ionization Energy

General Trends in First Ionization Energies

TABLE 8.2 The Ionization Energies (kJ/mol) of the First 20 Elements

Z	Element	First	Second	Third	Fourth	Fifth	Sixth
1	H	1,312					
2	He	2,373	5,251				
3	Li	520	7,300	11,815			
4	Be	899	1,757	14,850	21,005		
5	B	801	2,430	3,660	25,000	32,820	
6	C	1,086	2,350	4,620	6,220	38,000	47,261
7	N	1,400	2,860	4,580	7,500	9,400	53,000
8	O	1,314	3,390	5,300	7,470	11,000	13,000
9	F	1,680	3,370	6,050	8,400	11,000	15,200
10	Ne	2,080	3,950	6,120	9,370	12,200	15,000
11	Na	495.9	4,560	6,900	9,540	13,400	16,600
12	Mg	738.1	1,450	7,730	10,500	13,600	18,000
13	Al	577.9	1,820	2,750	11,600	14,800	18,400
14	Si	786.3	1,580	3,230	4,360	16,000	20,000
15	P	1,012	1,904	2,910	4,960	6,240	21,000
16	S	999.5	2,250	3,360	4,660	6,990	8,500
17	Cl	1,251	2,297	3,820	5,160	6,540	9,300
18	Ar	1,521	2,666	3,900	5,770	7,240	8,800
19	K	418.7	3,052	4,410	5,900	8,000	9,600
20	Ca	589.5	1,145	4,900	6,500	8,100	11,000

Ionic Radius

Cation is always **smaller** than atom from which it is formed.

Anion is always **larger** than atom from which it is formed.

Atomic Radii & Ionic Radii

Cation is always **smaller** than atom from which it is formed.

Anion is always **larger** than atom from which it is formed.

Comparison of Atomic Radii with Ionic Radii

Radii for Isoelectronic atoms or ions

Atom or Ion	Radius (nm)	Electron config.
C^{4-}	0.260	$1s^2 2s^2 2p^6$
N^{3-}	0.171	$1s^2 2s^2 2p^6$
O^{-2}	0.140	$1s^2 2s^2 2p^6$
F^{-}	0.136	$1s^2 2s^2 2p^6$
Ne	0.112	$1s^2 2s^2 2p^6$
Na^{+}	0.095	$1s^2 2s^2 2p^6$
Mg^{2+}	0.065	$1s^2 2s^2 2p^6$
Al^{3+}	0.050	$1s^2 2s^2 2p^6$

The Radii (in pm) of Ions of Familiar Elements

Electron Affinity

Electron Affinity

Electron affinity is the negative of the energy change that occurs when an electron is accepted by an atom in the gaseous state to form an anion.

$$X_{(g)} + e^- \longrightarrow X^-_{(g)}$$

$F_{(g)} + e^- \longrightarrow F^-_{(g)}$ $\Delta H = -328$ kJ/mol EA = +328 kJ/mol

$O_{(g)} + e^- \longrightarrow O^-_{(g)}$ $\Delta H = -141$ kJ/mol EA = +141 kJ/mol

$O^-_{(g)} + e^- \longrightarrow O^{2-}_{(g)}$ $\Delta H = +780$ kJ/mol EA = −780 kJ/mol ?

- EA of O^- is highly –ve; *i.e.* O^{2-} formation is unfavorable,
- electron-electron repulsion (*g*) > stability from noble gas configuration;
- O^{2-} ion stabilized by neighboring cation, *e.g.* Li_2O, Mg_2O

TABLE 8.3 Electron Affinities (kJ/mol) of Some Representative Elements and the Noble Gases*

1A	2A	3A	4A	5A	6A	7A	8A
H							He
73							< 0
Li	Be	B	C	N	O	F	Ne
60	≤ 0	27	122	0	141	328	< 0
Na	Mg	Al	Si	P	S	Cl	Ar
53	≤ 0	44	134	72	200	349	< 0
K	Ca	Ga	Ge	As	Se	Br	Kr
48	2.4	29	118	77	195	325	< 0
Rb	Sr	In	Sn	Sb	Te	I	Xe
47	4.7	29	121	101	190	295	< 0
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
45	14	30	110	110	?	?	< 0

*The electron affinities of the noble gases, Be, and Mg have not been determined experimentally, but are believed to be close to zero or negative.

Variation of Electron Affinity With Atomic Number (H – Ba)

Trends in Electron Affinity

Electron Affinity (EA) is the energy change that occurs when 1 mol of electrons is ***added*** to 1 mol of gaseous atoms or ions.

Atoms with a ***low EA*** tend to form ***cations***.
Atoms with a ***high EA*** tend to form ***anions***.

The trends in electron affinity are not as regular as those for atomic size or IE.

Variation in Chemical Properties of the Representative Elements

Ionization energy (IE) and electron affinity (EA) help us to understand:

- the **types** of reactions an element undergo
- the **nature** of the elements' compounds formed

IE measures the attraction of an atom for its **own** electrons

EA expresses the attraction of an atom for **additional** electrons

- IE and EA together gives the insight into the **general attraction** of an atom for electron

With these concepts we can survey the chemical behavior of the elements systematically.

Variation in Chemical Properties of the Representative Elements

The metallic character of the elements

- **decreases** from left to right across a period, and
- **increases** from top to bottom within a group

Metals usually have **low** ionization energies, and Nonmetals usually have **high** electron affinity

On the basis of these trends we can predict the outcome of a reaction involving some of these elements

Periodic Properties of the Elements

General Trends in Chemical Properties

Diagonal Relationships on the Periodic Table

1A	2A	3A	4A
Li	Be	B	C
Na	Mg	Al	Si

Properties of Oxides Across a Period

TABLE 8.4 Some Properties of Oxides of the Third-Period Elements

	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
Type of compound	←	Ionic	→	←	Molecular		→
Structure	←	Extensive three-dimensional	→	←	Discrete molecular units		→
Melting point (°C)	1275	2800	2045	1610	580	16.8	−91.5
Boiling point (°C)	?	3600	2980	2230	?	44.8	82
Acid-base nature	Basic	Basic	Amphoteric	←	Acidic		→

Properties of Oxides Across a Period

- **Basic oxides:**

Na_2O and MgO are **basic** oxides,

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$$

$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$$

- **Amphoteric oxide:**

Al_2O_3 is an **amphoteric** oxide,

$$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$$

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq)$$

Other amphoteric oxides are, ZnO, BeO, and Bi_2O_3

Properties of Oxides Across a Period

- **Acidic oxides:**

  SiO_2, P_4O_{10}, SO_3 and Cl_2O_7 are **acidic** oxides,

  $$SiO_2(s) + 2NaOH(aq) \rightarrow Na_2SiO_3(aq) + H_2O(l)$$

  $$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

  $$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

  $$Cl_2O_7(l) + H_2O(l) \rightarrow 2HClO_4(aq)$$

- **Neutral oxides:**

  Some oxides are **neutral**, CO and NO,
  Do **not** react with water to produce acidic or basic solution

Sample Problem 8.3 Ranking Elements by Atomic Size

PROBLEM: Using only the periodic table (not Figure 8.15), rank each set of main-group elements in order of *decreasing* atomic size:

(a) Ca, Mg, Sr **(b)** K, Ga, Ca

(c) Br, Rb, Kr **(d)** Sr, Ca, Rb

PLAN: Locate each element on the periodic table. Main-group elements increase in size down a group and decrease in size across the period.

Sample Problem 8.3

SOLUTION:

(a) Sr > Ca > Mg
Ca, Mg, and Sr are in Group 2A. Size increases down the group.

(b) K > Ca > Ga
K, Ga, and Ca are all in Period 4. Size decreases across the period.

(c) Rb > Br > Kr
Rb is the largest because it has one more energy level than the other elements. Kr is smaller than Br because Kr is farther to the right in the same period.

(d) Rb > Sr > Ca
Ca is the smallest because it has one fewer energy level. Sr is smaller than Rb because it is farther to the right in the same period; atomic size decreases from left to right along a period.

Behavior Patterns for IE and EA

Reactive nonmetals have high IEs and highly negative EAs.

- These elements attract electrons strongly and tend to form negative ions in ionic compounds.

Reactive metals have low IEs and slightly negative EAs.

- These elements lose electrons easily and tend to form positive ions in ionic compounds.

Noble gases have very high IEs and slightly positive EAs.

- These elements tend to neither lose nor gain electrons.

Magnetic Properties of Transition Metal ions

A species with one or more unpaired electrons exhibits ***paramagnetism*** – it is attracted by a magnetic field.

Ag (Z = 47)

5*s*	4*d*					5*p*		
↑	↑↓	↑↓	↑↓	↑↓	↑↓			

A species with all its electrons paired exhibits ***diamagnetism*** – it is not attracted (and is slightly repelled) by a magnetic field.

Figure 8.27 Measuring the magnetic behavior of a sample.

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The apparent mass of a diamagnetic substance is unaffected by the magnetic field.

The apparent mass of a paramagnetic substance increases as it is attracted by the magnetic field.

Magnetic Properties of Transition Metal Ions

Magnetic behavior can provide evidence for the electron configuration of a given ion.

Ti^{2+} has 2 unpaired electrons and is paramagnetic, providing evidence that the 4*s* electrons are lost before the 3*d* electrons.

Sample Problem 8.7

Writing Electron Configurations and Predicting Magnetic Behavior of Transition Metal Ions

PROBLEM: Use condensed electron configurations to write the reaction for the formation of each transition metal ion, and predict whether the ion is paramagnetic or diamagnetic.

(a) Mn^{2+}(Z = 25) **(b)** Cr^{3+}(Z = 24) **(c)** Hg^{2+}(Z = 80)

PLAN: Write the condensed electron configuration for each atom, recalling the irregularity for Cr. Remove electrons, beginning with the *ns* electrons, and determine if there are any unpaired electrons.

Sample Problem 8.7

SOLUTION:

(a) Mn^{2+}(Z = 25) Mn ([Ar] $4s^2 3d^5$) $\longrightarrow$ Mn^{2+} ([Ar] $3d^5$) + $2e^-$

There are 5 3*d* electrons and they are all unpaired; Mn^{2+} is **paramagnetic**.

(b) Cr^{3+}(Z = 24) Cr ([Ar] $4s^1 3d^5$) $\longrightarrow$ Cr^{3+} ([Ar] $3d^3$) + $3e^-$

There are 3 3*d* electrons and they are all unpaired; Cr^{3+} is **paramagnetic.**

(c) Hg^{2+}(Z = 80) Hg ([Xe] $6s^2 4f^{14} 5d^{10}$) $\longrightarrow$ Hg^{2+} ([Xe] $4f^{14} 5d^{10}$) + $2e^-$

The 4*f* and the 5*s* sublevels are filled, so there are no unpaired electrons. Hg^{2+} is **diamagnetic**.