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Chapter 7

CHEMISTRY & CHEMICAL REACTIVITY

Eighth Edition

The Structure of Atoms and Periodic Trends

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Arrangement of Electrons in Atoms

Electrons in atoms are arranged as



Electrons in Atoms



When n = 1, then l = 0

This shell has a single orbital (1s) to which 2 electrons can be assigned.

When
$$n = 2$$
, then $l = 0, 1$

2s orbital three 2p orbitals TOTAL =

2 electrons <u>6 electrons</u> 8 electrons

Electrons in Shells

The number of shells increases with the shell value (n).

Therefore each higher shell holds more electrons. (more orbitals)

Electron Shell (n)	Subshells Available	Orbitals Available (2ℓ + 1)	Number of Electrons Possible in Subshell $[2(2\ell + 1)]$	Maximum Electrons Possible for <i>n</i> th Shell (2 <i>n</i> ²)
1	5	1	2	2
2	5	1	2	8
	p	3	6	
3	5	1	2	18
	p	3	6	
	d	5	10	· Substantiation for the feature of the
4	5	1	2	32
	p	3	6	
	d	5	10	
	<i>f</i>	7	14	
5	5	1	2	50
	p	3	6	
	d	5	10	
	f	7	14	
	g *	9	18	· consumption of
6	5	1	2	72
	p	3	6	
	d	5	10	
	<i>f</i> *	7	14	
	g *	9	18	
	h*	11	22	

*These orbitals are not occupied in the ground state of any known element.

Pauli Exclusion Principle

- To make the quantum theory consistent with experiment, the Austrian physicist Wolfgang Pauli (1900–1958) stated in 1925 his exclusion principle:

"No more than two electrons can occupy the same orbital, and, if there are two electrons in the same orbital, they must have opposite spins."

 This leads to the general statement that no two electrons in an atom can have the same set of four quantum numbers (n, *I*, m_{*I*}, and m_s).

Quantum Numbers



Electrons in an atom are arranged by: (quantum number)

Principle energy levels (shells) n

angular energy levels (sub-shells)

oriented energy levels (orbitals) m₁

Within an individual orbital, there may only be two electrons differentiated by their spin.

m。

Atomic Subshell Energies & Electron Assignments



Based on theoretical and experimental studies of electron distributions in atoms, chemists have found there are two general rules that help predict these arrangements:

- 1. Electrons are assigned to subshells in order of increasing "n + *l*" value.
- 2. For two subshells with the same value of "n + *l*" electrons are assigned first to the subshell of lower n.

Single-Electron Atom Energy Levels



Multi-Electron Atom Energy Levels



3d 4s Зр 3s) + U 2p 11 2s Ш VS.

Screening results in the 4sorbital having a lower energy that that of the 3d-orbital.

> 4s: n + l = 4 + 0 = 43d: n + l = 3 + 2 = 5

Effective Nuclear Charge, Z*



- Z* is the net charge experienced by a particular electron in a multi-electron atom resulting from a balance of the attractive force of the nucleus and the repulsive forces of other electrons.
- Z* increases across a period owing to incomplete screening by inner electrons

Be

- This explains why E(4s electron) < E(3p electron)
- $Z^* \approx [Z (no. inner electrons)]$

Charge felt by 2s electron in: Li $Z^* = 3 - 2 = 1$

$$Z^* = 4 - 2 = 2$$

B $Z^* = 5 - 2 = 3$ and so on!

Effective Nuclear Charge



Z* is the nuclear charge experienced by the outermost electrons.

Effective Nuclear Charge



The value of Z^* for the highest occupied orbital is given by (Z - S), where Z is the atomic number and S is the screening constant. Notice that S increases greatly on going from Ne in the second period to Na in the third period.



Orbital Filling of Electrons



Electrons fill orbitals from the bottom up: Aufbau Principle

Electron Filling Order





Assigning Electrons to Subshells

n = 3

n=2

n=1

2s - 2p-

1s -

Energy





- In a multi-electron atom:
- subshells increase in energy as value of n + / increases.
- 2. for subshells of same n + *I*, the subshell with lower n is lower in energy.

Orbital Filling: The Aufbau Principle & Hund's Rule



Aufbau Principle: Lower energy orbitals fill first.

Hund's Rule:

Degenerate orbitals (those of the same energy) are filled with electrons until all are half filled before pairing up of electrons can occur.

Pauli exclusion principle:

Individual orbitals only hold two electrons, and each should have different spin.

"s" orbitals can hold 2 electrons "p" orbitals hold up to 6 electrons "d" orbitals can hold up to 10 electrons



Hund's Rule.

Degenerate orbitals are filled with electrons until all are half-filled before pairing up of electrons can occur.

Consider a set of 2p orbitals:







Electron Configuration: Orbital Box Notation



Electrons fill the orbitals from lowest to highest energy.

The electron configuration of an atom is the total sum of the electrons from lowest to highest shell.

Example:

Nitrogen: N has an atomic number of 7, therefore 7 electrons

Orbitals



Electron Configuration (*spdf*) notation: 1s²2s²2p³

Atomic Electron Configurations

Atomic Electron Configurations



Electron Configurations & the Periodic Table



Lithium





Group 1A Atomic number = 3 3 total electrons $1s^22s^1$







1s



Group 2A Atomic number = 4 4 total electrons 1s²2s²







2p























Neon





Electron Configuration in the 3rd Period





Electron Configuration in the 3rd Period





Core of Noble Gas Notation



The electron configuration of an element can be represented as a function of the core electrons in terms of a noble gas and the valence electrons.

Full electron configuration *spdf* notation 1s²2s²2p⁶3s²3p²

Orbital Box Notation



Core or Noble Gas Notation

- The innermost electrons (core) can be represented by the full shell of noble gas electron configuration:

 $1s^{2}2s^{2} = [He], 1s^{2}2s^{2}2p^{6} = [Ne], 1s^{2}2s^{2}2p^{6}3s^{2}3p^{6} = [Ar]...$

- ElementFull Electron Config.Core NotationMg1s² 2s² 2p6 3s²[Ne] 3s²
- The outermost electrons are referred to as the "Valence" electrons.

Electron Configuration & the Periodic Table



Transition Metal



All 4th period and beyond d-block elements have the electron configuration [Ar] ns^{x} (n - 1)d^y Where n is the period and x, y are particular to the element.



Transition Element Configurations

Atomic Electron Configurations


Table 7.4	Orbital Box Diagrams for the El	ements Ca Through Zn	
		3 <i>d</i>	45
Ca	[Ar]4 <i>s</i> ²		$\uparrow \downarrow$
Sc	$[Ar]3d^{1}4s^{2}$	$[\uparrow]$	
Ti	$[Ar]3d^{2}4s^{2}$	$\uparrow \uparrow \downarrow$	$\uparrow \downarrow$
V	$[Ar]3d^{3}4s^{2}$	$\uparrow \uparrow \uparrow$	$\uparrow \downarrow$
Cr*	[Ar]3d ⁵ 4s ¹	$[\uparrow]\uparrow[\uparrow]\uparrow]\uparrow]\uparrow$	$[\uparrow]$
Mn	$[Ar]3d^{5}4s^{2}$	$[\uparrow]\uparrow[\uparrow]\uparrow]\uparrow]\uparrow$	$\uparrow\downarrow$
Fe	$[Ar]3d^{6}4s^{2}$	$[\uparrow\downarrow]\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$	
Со	[Ar]3d ⁷ 4s ²	$[\uparrow\downarrow]\uparrow\downarrow]\uparrow]\uparrow[\uparrow]$	$\uparrow \downarrow$
Ni	$[Ar]3d^{8}4s^{2}$	$[\uparrow\downarrow]\uparrow\downarrow[\uparrow\downarrow]\uparrow\uparrow]\uparrow$	$\uparrow \downarrow$
Cu*	[Ar]3d ¹⁰ 4s ¹	$[\uparrow\downarrow]\uparrow\downarrow[\uparrow\downarrow]\uparrow\downarrow[\uparrow\downarrow]\uparrow\downarrow$	\uparrow
Zn	[Ar]3 <i>d</i> ¹⁰ 4 <i>s</i> ²	$[\uparrow\downarrow]\uparrow\downarrow]\uparrow\downarrow]\uparrow\downarrow]\uparrow\downarrow]$	

*See A Closer Look: Questions About Transition Element Electron Configurations, page 314.

Transition Elements

Electron Configurations are written by shell even though the electrons fill by the periodic table:

Ni: last electron to fill: 3d⁸

Lanthanides & Actinides



f-block elements: These elements have the configuration [core] ns^{x} (n - 1)d^y (n - 2)f^z Where n is the period and x, y & z are particular to the element.



Cerium: [Xe] 6s² 5d¹ 4f¹ Uranium: [Rn] 7s² 6d¹ 5f³



Lanthanide Element Configuration

Atomic Electron Configurations





.3 Ground State Electron Configurations	Table 7.3	Ground State Electron Configurations
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Z	Element	Configuration	Z	Element	Configuration	Z	Element	Configuration
1	н	15 ¹	37	Rb	[Kr]5s ¹	74	W	[Xe]4f ¹⁴ 5d ⁴ 6s ²
2	He	15 ²	38	Sr	[Kr]55²	75	Re	[Xe]4f ¹⁴ 5d ⁵ 6s ²
3	Li	[He]2s ¹	39	Y	[Kr]4d ¹ 5s ²	76	Os	[Xe]4f ¹⁴ 5d ⁶ 6s ²
4	Be	[He]2s ²	40	Zr	[Kr]4d ² 5s ²	77	Ir	[Xe]4f ¹⁴ 5d ⁷ 6s ²
5	В	[He]2s ² 2p ¹	41	Nb	[Kr]4d ⁴ 5s ¹	78	Pt	[Xe]4f ¹⁴ 5d ⁹ 6s ¹
6	с	[He]2s ² 2p ²	42	Мо	[Kr]4d ⁵ 5s ¹	79	Au	[Xe]4f ¹⁴ 5d ¹⁰ 6s ¹
7	N	[He]2s ² 2p ³	43	Tc	[Kr]4d ⁵ 5s ²	80	Hg	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²
8	0	[He]2s ² 2p ⁴	44	Ru	$[Kr]4d^75s^1$	81	Tl	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p
9	F	[He]2s ² 2p ⁵	45	Rh	[Kr]4d ⁸ 5s1	82	Pb	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p
10	Ne	[He]2s ² 2p ⁶	46	Pd	[Kr]4d ¹⁰	83	Bi	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p
11	Na	[Ne]3s ¹	47	Ag	[Kr]4d ¹⁰ 5s ¹	84	Po	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p
12	Mg	[Ne]3s ²	48	Cd	[Kr]4d ¹⁰ 5s ²	85	At	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p
13	AL	[Ne]3s ² 3p ¹	49	In	[Kr]4d ¹⁰ 5s ² 5p ¹	86	Rn	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p
14	Si	[Ne]3s ² 3p ²	50	Sn	[Kr]4d ¹⁰ 5s ² 5p ²	87	Fr	[Rn]7s ¹
15	Р	[Ne]3s ² 3p ³	51	Sb	[Kr]4d ¹⁰ 5s ² 5p ³	88	Ra	[Rn]7s ²
16	s	[Ne]3s ² 3p ⁴	52	Te	[Kr]4d ¹⁰ 5s ² 5p ⁴	89	Ac	[Rn]6d ¹ 7s ²
17	CL	[Ne]3s ² 3p ⁵	53	I	[Kr]4d ¹⁰ 5s ² 5p ⁵	90	Th	[Rn]6d ² 7s ²
18	Ar	[Ne]3s ² 3p ⁶	54	Xe	[Kr]4d ¹⁰ 5s ² 5p ⁶	91	Pa	[Rn]5f ² 6d ¹ 7s ²
19	K	[Ar]4s ¹	55	Cs	[Xe]6s ¹	92	U	[Rn]5f ³ 6d ¹ 7s ²
20	Ca	[Ar]4s ²	56	Ba	[Xe]6s²	93	Np	[Rn]5f ⁴ 6d ¹ 7s ²
21	Sc	[Ar]3d ¹ 4s ²	57	La	[Xe]5d ¹ 6s ²	94	Pu	[Rn]5f ⁶ 7s ²
22	ті	[Ar]3d ² 45 ²	58	Ce	[Xe]4f ¹ 5d ¹ 6s ²	95	Am	[Rn]5f ⁷ 7s ²
23	V	[Ar]3d ³ 4s ²	59	Pr	[Xe]4f ⁴ 6s ²	96	Cm	[Rn]5f ⁷ 6d ¹ 7s ²
24	Cr	[Ar]3d ⁶ 4s ¹	60	Nd	[Xe]4f ⁴ 6s ²	97	Bk	[Rn]5f ⁹ 7s ²
25	Mn	[Ar]3d ⁵ 4s ²	61	Pm	[Xe]4f ⁵ 6s ²	98	Ct	[Rn]5f ¹⁰ 7s ²
26	Fe	[Ar]3d ⁶ 4s ²	62	Sm	[Xe]4f ⁶ 6s ²	99	Es	[Rn]5f ¹¹ 7s ²
27	Со	[Ar]3d ⁷ 45 ²	63	Eu	[Xe]4f ² 6s ²	100	Fm	[Rn]5f ¹² 7s ²
28	Ni	[Ar]3d ⁸ 4s ²	64	Gd	[Xe]4f ² 5d ¹ 6s ²	101	Md	[Rn]5f ¹³ 7s ²
29	Cu	[Ar]3d ¹⁰ 4s ¹	65	ть	[Xe]4f ⁹ 6s ²	102	No	[Rn]5f ¹⁴ /s ²
30	Zn	[Ar]3d10452	66	Dy	[Xe]4f ¹⁰ 6s ²	103	Lr	[Rn]5f ¹⁴ 6d ¹ 7s ²
31	Ga	[Ar]3d ¹⁰ 4s ² 4p ¹	67	Ho	[Xe]4f ¹¹ 6s ²	104	Rf	[Rn]5f ¹⁴ 6d ² 7s ²
32	Ge	[Ar]3d ¹⁰ 4s ² 4p ²	68	Er	[Xe]4f ¹² 6s ²	105	Db	[Rn]5f ¹⁴ 6d ³ 7s ²
33	As	[Ar]3d ¹⁰ 4s ² 4p ³	69	Tm	[Xe]4f ¹³ 6s ²	106	Sg	[Rn]5f ¹⁴ 6d ⁴ /s ²
34	Se	[Ar]3d104s24p4	70	Yb	[Xe]4f ¹⁴ 6s ²	107	Bh	[Rn]5f ¹⁴ 6d ⁵ 7s ²
35	Br	[Ar]3d ¹⁰ 4s ² 4p ⁵	71	Lu	[Xe]4f ¹⁴ 5d ¹ 6s ²	108	Hs	[Rn]5f ¹⁴ 6d ⁶ 7s ²
36	Kr	[Ar]3d ¹⁰ 4s ² 4p ⁶	72	Hf	[Xe]4f ¹⁴ 5d ² 6s ²	109	Mt	[Rn]5f ¹⁴ 6d ⁹ 7s ²
			73	Та	[Xe]4f ¹⁴ 5d ³ 6s ²			

*This table follows the general convention of writing the orbitals in order of increasing n when writing electron configurations. For a given n, the subshells are listed in order of increasing ℓ .

Electron Configuration Practice



- What is the complete electron configuration for phosphorous?
- What is the orbital box notation for fluorine?
- What is the noble gas electron configuration arsenic?







Exceptions: Promotion of a 4s electron to a 3d orbital



It is observed that a half-filled or full orbital is more stable that a partially filled orbital.

Since the energies of the 3d and 4s orbitals are quite close, it is possible for a 4s electron to jump up to the empty 3d orbital.

This also occurs for *nd*⁹ elements. It dose not happen between *s* and *p* orbitals.

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Cation Formation:

4s

To form cations one removes electrons from the *outermost shell* inward.

Cr: [Ar] 3d⁵ 4s¹





How do we know the configurations of ions?



By the magnetic properties of ions.



Ions with UNPAIRED ELECTRONS are PARAMAGNETIC (attracted to a magnetic field). Ions without UNPAIRED ELECTRONS are DIAMAGNETIC (not attracted to a magnetic field).



Fe³⁺ ions in Fe₂O₃ have 5 unpaired electrons. This makes the sample paramagnetic.

General Periodic Trends



- Atomic and ionic size
- Ionization energy
- Electron affinity

Higher effective nuclear charge Electrons held more tightly

Larger orbitals. Electrons held less tightly.



Effective Nuclear Charge, Z*



The 2s electron PENETRATES the region occupied by the 1s electron.

2s electron experiences a higher positive charge than expected.



Effective Nuclear Charge, Z*



- Atom Z* Experienced by Electrons in Valence Orbitals
- Li +1.28
- Be
- B +2.58
- C +3.22
- N +3.85
- O +4.49
- F +5.13

Increase in Z* across a period

[Values calculated using Slater's Rules]



Orbital energies "drop" as Z* increases

Consider a simple diatomic molecule.

The distance between the two nuclei is called the bond distance.

If the two atoms which make up the molecule are the same, then half the bond distance is called the covalent radius of the atom.

The covalent radius of chlorine is: (198 pm/2) = 99 pm.

If one knows the bond distance in a heteronuclear bond, then the radius of another atom can be estimated.

$$r_{Carbon} = 176 \text{ pm} - 99 \text{ pm} = 77 \text{ pm}$$

Atomic Radii of Elements

- Par

Atomic Radii of 1 A Elements

Atomic Radii in 3rd Period

Moving across the 3rd period we see the atomic radii of the elements decrease.

Atomic Size

- Size goes UP on going down a group, because electrons are added further from the nucleus, there is less attraction.
- Size goes DOWN on going across a period as the effective nuclear charge of the elements incrcrease.

Atomic Size

Size **decreases** across a period owing to increase in Z*. Each added electron feels a greater and greater + charge.

Trends in Atomic Size

Trends in Atomic Size

Ionization Energy

IE = energy required to remove an electron from an atom in the gas phase.

Mg (g) + 738 kJ \rightarrow Mg⁺ (g) + e-

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Mg⁺(g) + 1451 kJ → Mg²⁺(g) + e-Mg⁺ has 12 protons and only 11 electrons. Therefore, IE for Mg⁺ > Mg.

Ionization Energy

The *ionization energy of an atom* is the energy needed to remove an electron from an atom in the gas phase.

$N_{I}(n-1)(\alpha)$	М n+ (а) т о-	• • • n th ionization energy (L)
$M^+(g) \rightarrow$	M ²⁺ (g) + e ⁻	2 nd ionization energy (I ₂)
$M(g) \rightarrow$	M+ (g) + e-	1^{st} ionization energy (I_1)

In general, the closer to the nucleus an electron is, the higher the ionization energy.

 $I_1 (Na) = 495.8 \text{ kJmol}^{-1}$ $I_2 (Na) = 4562 \text{ kJmol}^{-1}$ Across the periodic table from left-to-right, the 1st ionization energies increase as the atomic radius decreases. This follows the trend seen with Z*.

$$IE = Rhc \times \frac{Z^{*^{2}}}{n^{2}}$$

n		Atomic Radius, pm	Ionization Energy (I ₁), kJ/mol
2	Li	152	520.2
3	Na	186	495.8
4	Κ	227	418.8
5	Rb	248	403.0
6	Cs	265	375.7

The trend down a group on the periodic table also follows **Z*** as increased screening reduces the attractions of valence electrons.

Removing More Than 1 Electron

The general trend: $I_1 < I_2 < I_3 < I_4$...

2nd Period	Li	Be	В	С	N	0	F	Ne
1st	513	899	801	1086	<mark>140</mark> 2	1314	1681	2080
2nd	729 <mark>8</mark>	1757	2427	2352	2856	3388	3374	3952
3rd	11815	14848	3660	4620	4578	5300	6050	6122

Notice that the jump from I_1 to I_2 for Be is not as great as that for Li.

Why?

Answer: The gained stability of a Noble gas electron configuration.

As Z* increases, orbital energies "drop" and IE increases.

Electron Affinity

EA (Δ U) is the energy released when an electron is attached to a gas-phase atom to form an anion.

 $CI(g) + e^{-}(g) \rightarrow CI^{-}(g)$ exothermic

 $\Delta U = -349 \text{ kJ mol}^{-1}$ (a negative sign means energy released)

A large negative EA results if a low energy half-filled or vacant orbital is available.

If EA is positive, energy must be supplied to attach the electron:

 $Ne(g) + e^{-}(g) \rightarrow Ne^{-}(g)$

 $\Delta U = + 116 \text{ kJ mol}^{-1}$ endothermic

Trends in Electron Affinity

Electron Affinity generally increases (becomes more negative) going across a period from Group 1A to Group 7A. (with exceptions)

EA follows of Z* across a period.

General trends:

- Metals have smaller EA's than nonmetals.
- EA is most negative for Groups 6A and 7A.
- Group 8A has positive EA's. (Low electron affinity)

Ionic Radii

The radii of cations are smaller than radii of the corresponding neutral atoms. (same Z, less electrons)

The radii of anions are larger than radii of the corresponding neutral atoms. (same Z, more electrons)

Trends in Ion Sizes

Problem:

Rank the following ions in order of decreasing size? Na⁺, N³⁻, Mg²⁺, F⁻ O²⁻

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lon	# of protons	# of electrons	ratio of e/p
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N ³⁻			
Mg ²⁺			
F-			
O ^{2–}			

Problem:

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Problem:

Rank the following ions in order of decreasing size? Na⁺, N³⁻, Mg²⁺, F⁻ O²⁻

lon	# of protons	# of electrons	ratio of e/p
Na+	11	10	0.909
N ³⁻	7	10	1.43
Mg ²⁺	12	10	0.833
F-	9	10	1.11
O ^{2–}	8	10	1.25

<u>lon</u>	<u>e/p ratio</u>	Since N ³⁻ has the highest ratio of
Na⁺	0.909	electrons to protons, it must have the largest radius.
N ³⁻	1.43	
Mg ²⁺	0.833	
F⁻	1.11	
O ^{2–}	1.25	

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Mg ²⁺	0.833	The rest can be ranked by ratio.		
F⁻	1.11	$N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+}$		
O ^{2–}	1.25	— Decreasing size →		

Notice that they all have 10 electrons: They are *isoelectronic* (same electron configuration) as Ne.

Summary of Periodic Trends



Moving through the periodic table:	Atomic radii	Ionization Energy	Electron Affinity
Down a group	Increase	Decrease	Becomes less exothermic
Across a Period	Decrease	Increase	Becomes more exothermic

Periodic Trends



Each metal reacts to form a noble gas electron configuration:

$$ns^1 \rightarrow (n-1)p^6$$

Reactivity (and exothermicity) increase down the periodic table as ionization energy decreases.

