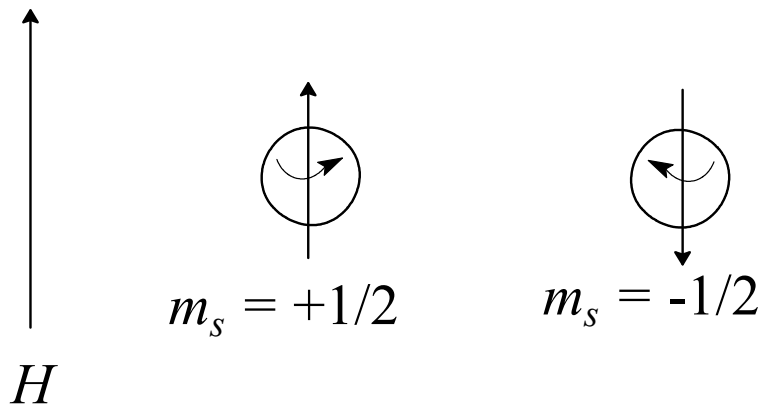
Electron Spin

- ☞ In 1921 Otto Stern and Walter Gerlach showed that a beam of neutral silver atoms ($Z = 47$) passing through a nonhomogeneous magnetic field was split into two divergent beams.
  - ✔ Atoms in each beam had different orientations of a magnetic moment from their one unpaired electron.

- ☞ In 1925 George Uhlenbek and Samuel Goudsmit interpreted the doublet line structure in the emission spectra of multielectron atoms in terms of two magnetic orientations for the electron, which they attributed to *electron spin.*
  - ✔ Electron spin is quantized according to two allowed values of a *spin quantum number,* m_s, with values of +½ or –½, corresponding to alignment of the electron's magnetic moment with or against an applied magnetic field.

Model of Quantized Electron Spin



- ☞ The electron acts as if it were spinning on its axis, where opposite spin directions would create opposite magnetic moments.
  - ✔ In light of wave-particle duality the picture of a spinning electron should not be taken too literally.

- ☞ When two electrons form a pair within the same atom they align their spins in opposition, causing net cancellation of their oppositely oriented magnetic moments.

$$\underline{\uparrow\downarrow}$$

$$M_s = +\tfrac{1}{2} - \tfrac{1}{2} = 0$$

Electronic Configurations of Multielectron Atoms

☞ The arrangement or **configuration** of electrons in various orbitals gives rise to a total **energy state** for the atom.

- There are many possible electronic configurations, so there are many possible corresponding energy states.

☞ The lowest possible overall energy state for an atom is its **ground state**.

- The configuration of electrons in specific orbitals that gives rise to this lowest energy state is called the **ground state configuration.**

- Any other configuration will result in a higher energy state, called an **excited state** for the atom.

The Aufbau Concept

aufbauen (Ger.) = to build up

☞ The ground state configuration of an atom can be predicted by a bookkeeping process in which electrons are added sequentially to orbitals in the order of their increasing energy.

☺ The predicted configurations are always correct for the main-group elements (A groups) and are usually correct (with some notable exceptions) for the first transition series elements (period 4).

☹ Predictions are often slightly or seriously wrong for 5th and 6th period transition elements and the elements of both the lanthanide and actinide series.

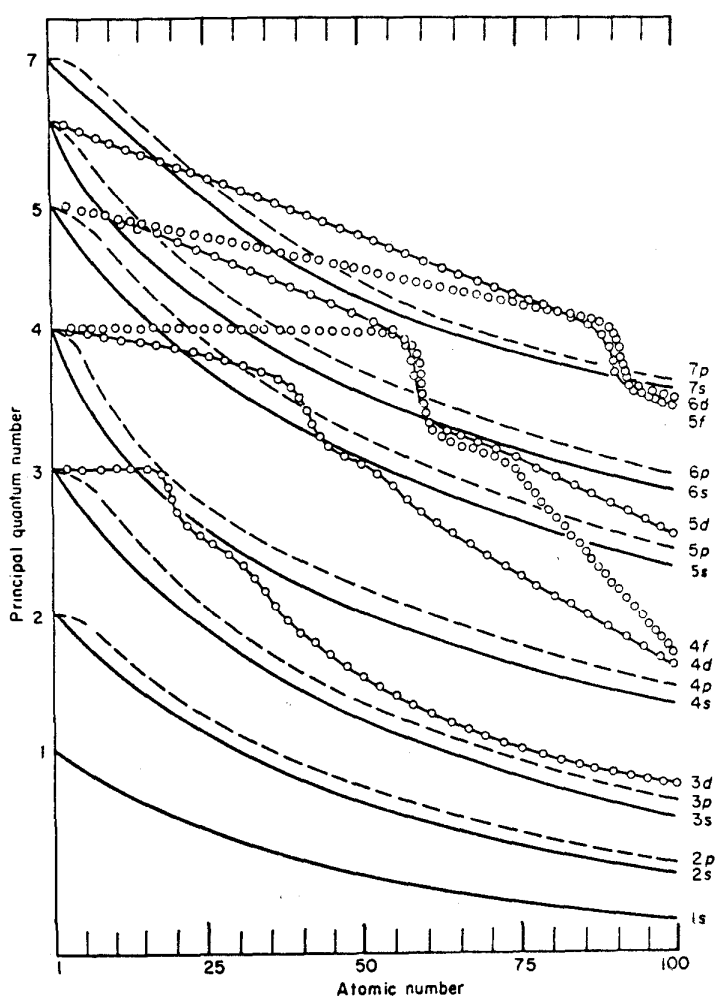
Orbital Energies in Multielectron Atoms

- Orbital energies depend upon both n and l, not just n as in the one-electron atoms.

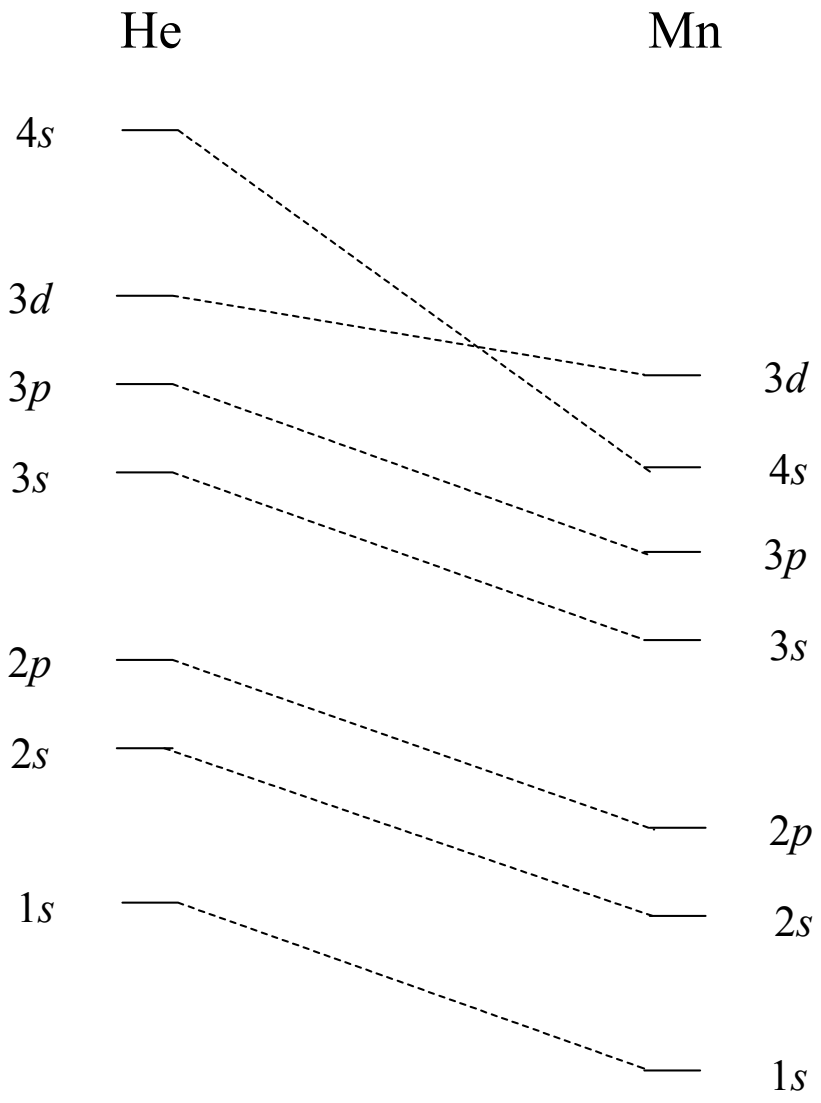
- Within the same shell (same n), subshells vary in energy in the order

$$ns < np < nd < nf$$

- The relative ordering of subshells from different shells varies in a complicated way with changing nuclear charge, Z.



Variation in Subshell Ordering
He (Z = 2) vs. Mn (Z = 25)



Effective Nuclear Charge

☞ Variation in the subshell energies and relative ordering result from the amount of the nuclear charge experienced by each electron in a multielectron atom.

✎ The portion of the nuclear charge that an electron experiences, called the effective nuclear charge, Z^*, is less than the full nuclear charge, Z, because of other electrons between it and the nucleus, expressed by

$$Z^* = Z - S$$

where S is the reduction in the charge experienced by the outermost electrons due to the **screening** or **shielding** by lower-lying electrons.

Screening

☞ The degree of screening depends upon both the shell and subshell of the electron of interest.

- ✎ Electrons with higher n value are further away from the nucleus and are more highly screened from the nuclear charge by lower lying electrons.
  - ☛ Z^* decreases with increasing n.
- ✎ Within the same shell (same n value), subshells with higher value of l are more extensive and lie further from the nucleus.
  - ☛ Z^* decreases with increasing l within the same shell.
- ✎ The effectiveness of lower-lying subshells in screening declines in the order $s > p > d > f$.

Examples:

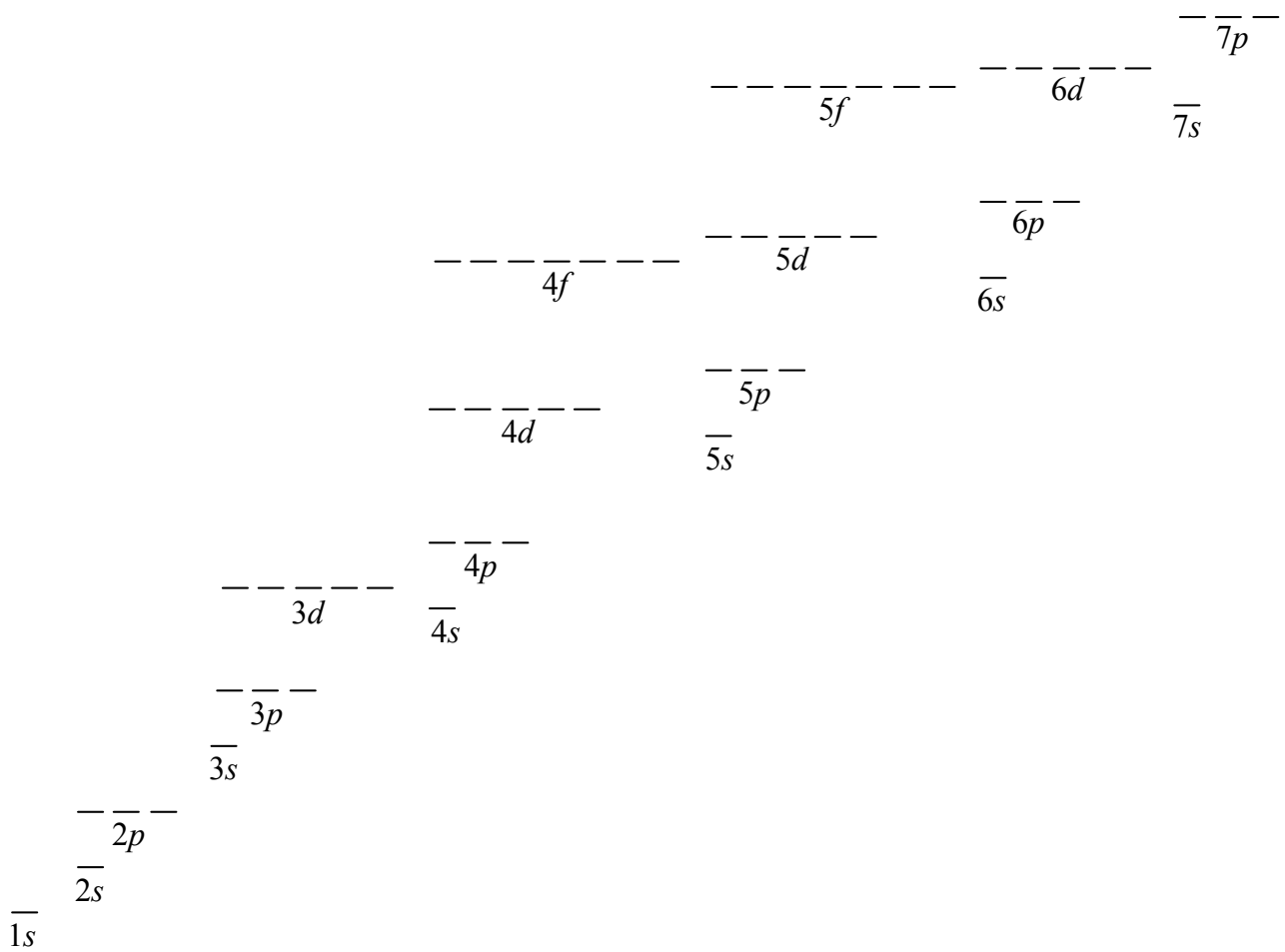
Z^* declines in the order $1s > 2s > 3s > 4s$.
Subshell energies increase in the order $1s < 2s < 3s < 4s$.

Z^* declines in the order $4s > 4p > 4d > 4f$.
Subshell energies increase in the order $4s < 4p < 4d < 4f$.

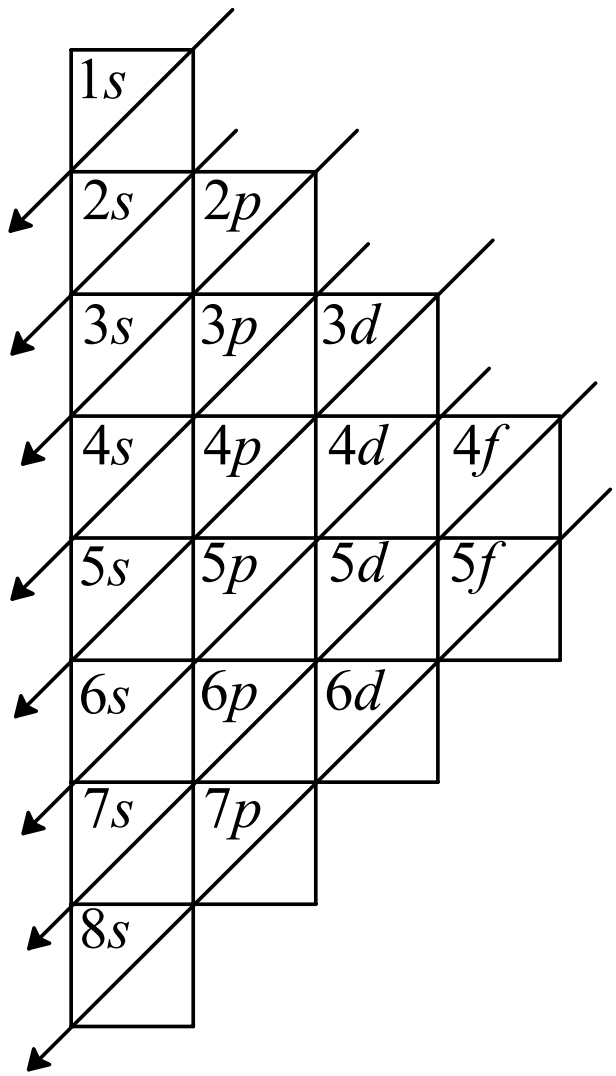
Aufbau Order of Atomic Orbitals

☺ For the purposes of applying aufbau principles to predict ground-state electronic configurations, we only need to know the relative energy order of the subshells when electrons occupy them in the ground-state configuration.

The Aufbau Order of Subshells



Mnemonic for the Aufbau Order



Pauli Exclusion Principle

Wolfgang Pauli - 1925

No two electrons in the same atom can have the same set of all four quantum numbers (n, l, m_l, m_s).

Consequences:

1. If n, l, and m_l are the same for two electrons, then one must have $m_s = +½$ and the other must have $m_s = -½$. The two electrons are said to be *paired* in the same orbital.

   Paired electrons: ↑↓

2. Each orbital can have only two electrons, and the capacities of subshells are thus two times the number of orbitals comprising them.

   Maximum capacities: s^2, p^6, d^{10}, f^{14}

Hund's Rule of Maximum Multiplicity

Frederic Hund - 1925

Electrons in the same subshell will tend to distribute so that they are in different degenerate (same energy) orbitals with their spins parallel (same value of m_s), so long as the Pauli Exclusion Principle allows.

Consequences:

1. Electrons occupy different degenerate orbitals when possible, because this minimizes electron-electron repulsions.

   ↑ ↑ ___ not ↑↓ ___ ___

2. Electrons avoid pairing when possible, because it requires energy to pair (*pairing energy*).

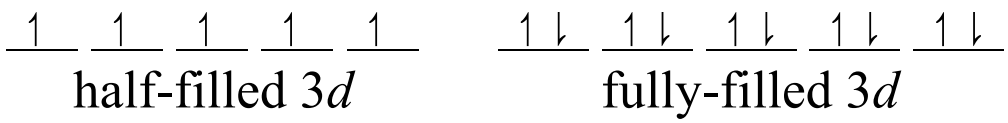
3. Electrons must pair when a subshell is more than half filled (Pauli Exclusion Principle).

   ↑↓ ↑ ↑ not ↑↑ ↑ ↑

☞ Hund's rule applies to the ground-state configuration of an atom, not to its excited states.

Exchange Energy

☞ Configurations in which a subshell is half- or fully-filled have extra stability.



✓ These configurations result in a symmetrical distribution of electronic charge, which minimizes repulsions.

✓ The slight energy advantage of these configurations is called **exchange energy**.

✓ Exchange energy becomes more significant with greater orbital multiplicity (more orbitals per subshell); i.e.,

$$s < p < d < f$$

☛ Exchange energy sometimes results in ground-state configurations that deviate from the aufbau predictions.

Electronic Configurations for the First Ten Elements

Element	1*s*	2*s*	2*p*			Spectroscopic Notation
H	↑					$1s^1$
He	↑↓					$1s^2$
Li	↑↓	↑				$1s^2 2s^1$
Be	↑↓	↑↓				$1s^2 2s^2$
B	↑↓	↑↓	↑			$1s^2 2s^2 2p^1$
C	↑↓	↑↓	↑	↑		$1s^2 2s^2 2p^2$
N	↑↓	↑↓	↑	↑	↑	$1s^2 2s^2 2p^3$
O	↑↓	↑↓	↑↓	↑	↑	$1s^2 2s^2 2p^4$
F	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p^5$
Ne	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2 2s^2 2p^6$

Third Period Configurations

	1A	2A											3A	4A	5A	6A	7A	8A
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar

$_{11}$Na $1s^2 2s^2 2p^6 3s^1$

$_{12}$Mg $1s^2 2s^2 2p^6 3s^2$

$_{13}$Al $1s^2 2s^2 2p^6 3s^2 3p^1$

$_{14}$Si $1s^2 2s^2 2p^6 3s^2 3p^2$

$_{15}$P $1s^2 2s^2 2p^6 3s^2 3p^3$

$_{16}$S $1s^2 2s^2 2p^6 3s^2 3p^4$

$_{17}$Cl $1s^2 2s^2 2p^6 3s^2 3p^5$

$_{18}$Ar $1s^2 2s^2 2p^6 3s^2 3p^6$

Fourth Period Configurations

	1A	2A	3B	4B	5B	6B	7B	┌	8B	┐	1B	2B	3A	4A	5A	6A	7A	8A
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr

$_{19}$K $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
$_{20}$Ca $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

$_{21}$Sc $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
$_{22}$Ti $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
$_{23}$V $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
$_{24}$Cr $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ ⇦Irregular
$_{25}$Mn $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
$_{26}$Fe $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
$_{27}$Co $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
$_{28}$Ni $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
$_{29}$Cu $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ ⇦ Irregular
$_{30}$Zn $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

$_{31}$Ga $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$
$_{32}$Ge $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
$_{33}$As $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$
$_{34}$Se $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$
$_{35}$Br $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
$_{36}$Kr $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

Fifth Period Configurations

	1A	2A	3B	4B	5B	6B	7B	┌	8B	┐	1B	2B	3A	4A	5A	6A	7A	8A
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe

$_{37}$Rb [Kr]$5s^1$
$_{38}$Sr [Kr]$5s^2$

$_{39}$Y [Kr]$4d^1 5s^2$
$_{40}$Zr [Kr]$4d^2 5s^2$
$_{41}$Nb [Kr]$4d^4 5s^1$ ⇦ No easy explanation
$_{42}$Mo [Kr]$4d^5 5s^1$ ⇦ Like Cr
$_{43}$Tc [Kr]$4d^6 5s^1$ ⇦ No easy explanation
$_{44}$Ru [Kr]$4d^7 5s^1$ ⇦ No easy explanation
$_{45}$Rh [Kr]$4d^8 5s^1$ ⇦ No easy explanation
$_{46}$Pd [Kr]$4d^{10} 5s^0$ ⇦ Fully-filled 4*d*
$_{47}$Ag [Kr]$4d^{10} 5s^1$ ⇦ Like Cu
$_{48}$Cd [Kr]$4d^{10} 5s^2$

$_{49}$In [Kr]$4d^{10} 5s^2 5p^1$
$_{50}$Sn [Kr]$4d^{10} 5s^2 5p^2$
$_{51}$Sb [Kr]$4d^{10} 5s^2 5p^3$
$_{52}$Te [Kr]$4d^{10} 5s^2 5p^4$
$_{53}$I [Kr]$4d^{10} 5s^2 5p^5$
$_{54}$Xe [Kr]$4d^{10} 5s^2 5p^6$

Configurations in the Sixth Period

	1A	2A	3B	4B	5B	6B	7B	┌	8B	┐	1B	2B	3A	4A	5A	6A	7A	8A
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

$_{55}$Cs [Xe]$6s^1$
$_{56}$Ba [Xe]$6s^2$

$_{57}$La [Xe]$5d^1 6s^2$

$_{58}$Ce [Xe]$4f^1 5d^1 6s^2$
$_{59}$Pr [Xe]$4f^3 6s^2$
$_{60}$Nd [Xe]$4f^4 6s^2$
$_{61}$Pm [Xe]$4f^5 6s^2$
$_{62}$Sm [Xe]$4f^6 6s^2$
$_{63}$Eu [Xe]$4f^7 6s^2$
$_{64}$Gd [Xe]$4f^7 5d^1 6s^2$
$_{65}$Tb [Xe]$4f^9 6s^2$
$_{66}$Dy [Xe]$4f^{10} 6s^2$
$_{67}$Ho [Xe]$4f^{11} 6s^2$
$_{68}$Er [Xe]$4f^{12} 6s^2$
$_{69}$Tm [Xe]$4f^{13} 6s^2$
$_{70}$Yb [Xe]$4f^{14} 6s^2$
$_{71}$Lu [Xe]$4f^{14} 5d^1 6s^2$

$_{72}$Hf [Xe]$4f^{14} 5d^2 6s^2$
$_{73}$Ta [Xe]$4f^{14} 5d^3 6s^2$
$_{74}$W [Xe]$4f^{14} 5d^4 6s^2$
$_{75}$Re [Xe]$4f^{14} 5d^5 6s^2$
$_{76}$Os [Xe]$4f^{14} 5d^6 6s^2$
$_{77}$Ir [Xe]$4f^{14} 5d^7 6s^2$
$_{78}$Pt [Xe]$4f^{14} 5d^9 6s^1$
$_{79}$Au [Xe]$4f^{14} 5d^{10} 6s^1$
$_{80}$Hg [Xe]$4f^{14} 5d^{10} 6s^2$

$_{81}$Tl [Xe]$4f^{14} 5d^{10} 6s^2 6p^1$
$_{82}$Pb [Xe]$4f^{14} 5d^{10} 6s^2 6p^2$
$_{83}$Bi [Xe]$4f^{14} 5d^{10} 6s^2 6p^3$
$_{84}$Po [Xe]$4f^{14} 5d^{10} 6s^2 6p^4$
$_{85}$At [Xe]$4f^{14} 5d^{10} 6s^2 6p^5$
$_{86}$Rn [Xe]$4f^{14} 5d^{10} 6s^2 6p^6$

Configurations in the Seventh Period

	1A	2A	4B	5B	6B	7B	┌	8B	┐
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

$_{87}$Fr [Rn]$7s^1$
$_{88}$Ra [Rn]$7s^2$
$_{89}$Ac [Rn]$6d^1 7s^2$

$_{90}$Th [Rn]$6d^2 7s^2$
$_{91}$Pa [Rn]$5f^2 6d^1 7s^2$
$_{92}$U [Rn]$5f^3 6d^1 7s^2$
$_{93}$Np [Rn]$5f^4 6d^1 7s^2$
$_{94}$Pu [Rn]$5f^6 7s^2$
$_{95}$Am [Rn]$5f^7 7s^2$
$_{96}$Cm [Rn]$5f^7 6d^1 7s^2$
$_{97}$Bk [Rn]$5f^9 7s^2$
$_{98}$Cf [Rn]$5f^{10} 7s^2$
$_{99}$Es [Rn]$5f^{11} 7s^2$
$_{100}$Fm [Rn]$5f^{12} 7s^2$
$_{101}$Md [Rn]$5f^{13} 7s^2$
$_{102}$No [Rn]$5f^{14} 7s^2$
$_{103}$Lr [Rn]$5f^{14} 6d^1 7s^2$

Predicted Aufbau configurations

$_{104}$Rf [Rn]$5f^{14} 6d^2 7s^2$
$_{105}$Db [Rn]$5f^{14} 6d^3 7s^2$
$_{106}$Sg [Rn]$5f^{14} 6d^4 7s^2$
$_{107}$Bh [Rn]$5f^{14} 6d^5 7s^2$
$_{108}$Hs [Rn]$5f^{14} 6d^6 7s^2$
$_{109}$Mt [Rn]$5f^{14} 6d^7 7s^2$
[110] [Rn]$5f^{14} 6d^8 7s^2$
[111] [Rn]$5f^{14} 6d^9 7s^2$
[112] [Rn]$5f^{14} 6d^{10} 7s^2$

Valence Configurations

☞ The outermost electrons in an atom constitute the valence configuration.

- Electrons are gained, lost, and shared from the subshells of the valence configuration in forming chemical bonds.

- Elements have characteristic valence configurations based on their positions in the periodic table.

Periodic Table Showing Subshells Being Filled

s-block representative elements
p-block representative elements
d-block transition elements
f-block lanthanides and actinides

	1A	2A	3B	4B	5B	6B	7B	┌─	8B	─┐	1B	2B	3A	4A	5A	6A	7A	8A
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Rf	Ha	Sg	Ns	Hs	Mt									

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Valence Configurations
by
Periodic Table Position

Block	Type	Valence Configuration
s	Groups 1A & 2A	ns^x (x = 1, 2)
p	Nonmetals (Groups 3A - 8A)	ns^2np^x (x = 1 - 6)
d	Transition metals	$(n\text{-}1)d^xns^y$ (x = 1 - 10; y = 0 - 2)
f	Lanthanides/Actinides	$(n\text{-}2)f^xns^y$ (x = 1 - 14; y = 0 - 2)

Periodic Table for Practice in Predicting Valence Configurations by Position

	1A	2A											3A	4A	5A	6A	7A	8A
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg	3B	4B	5B	6B	7B	┌	8B	┐	1B	2B	Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Rf	Ha	Sg	Ns	Hs	Mt									

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr