

Survey of Elements



- very small atom

All noble gases have very high first I.E.'s which is in line with their chemical inertness

First short period of elements

Li, Be, B, C, N, O, F, Ne



- like H, facile loss of one electron dominates the chemistry

- Li^+ is found in solids and solution Li reacts with O_2 , N_2 , H_2O and many more...

Increase in nuclear charge as we add electrons to the same shell. I.E.'s reflect trends in shielding as we discussed at the beginning of the semester.

First Ionization Energies:

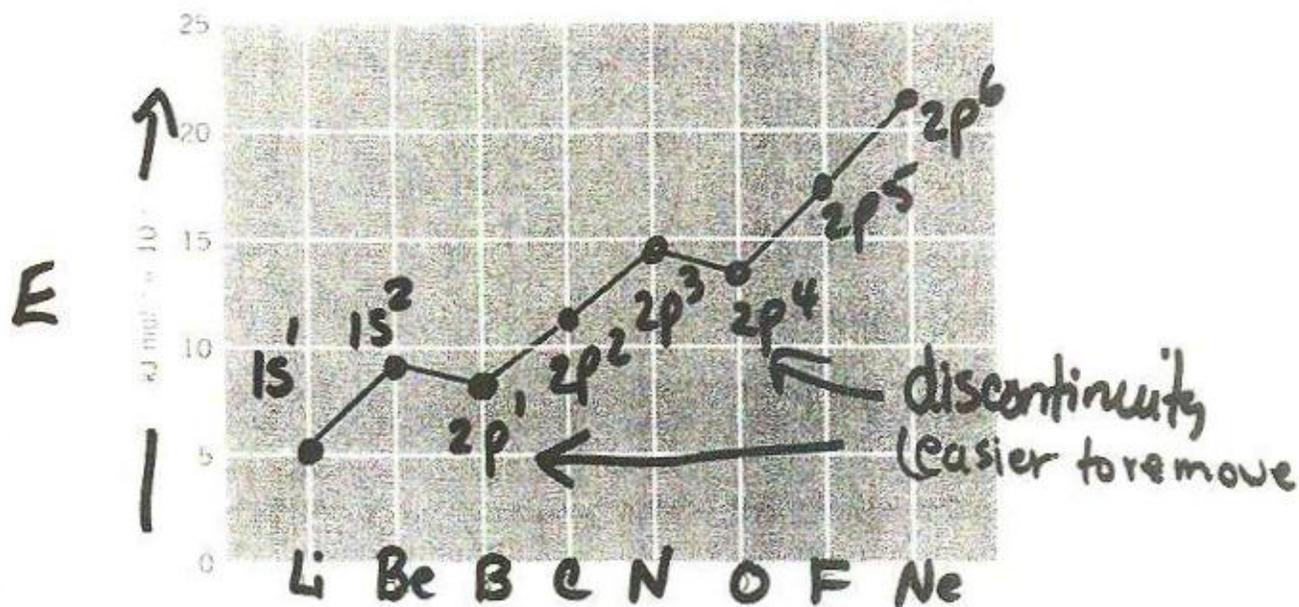
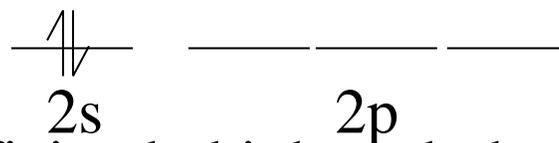


Figure 8-11 First ionization enthalpies of the elements Li to Ne. See also Fig. 2-11.

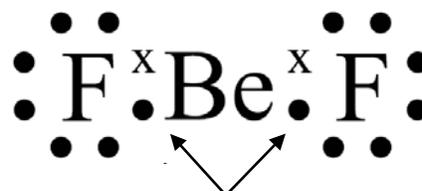
p electrons are better shielded than s electrons

Be has a high I.E. $2s^2$



The first and second I.E. are sufficiently high such that loss of both electrons to give Be^{2+} does not occur with even the most electronegative elements!

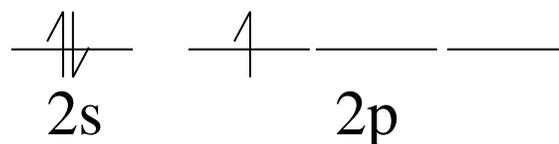
e.g. in BeF_2 , the ox. state is not really Be^{2+} (we assign formal charges as if they are ox. states but the reality is that this is not often true)



In reality these bonds are quite covalent

The elements after Be have even higher I.E.'s so there are no simple cations of B, C, N, O, F or Ne

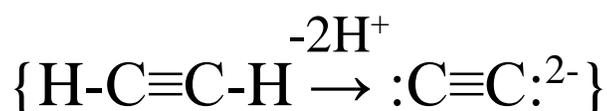
Boron



No simple B^{n+} chemistry – B forms covalent bonds



- first element to be stable as an anion (e.g. C_2^{2-} exists)



- True “non-metal”

Found with single, double, triple bonds to itself and to N and O mainly

- Ability to bind to itself (catenate) is unparalleled among the elements - responsible for polymer chain formation!



- Forms anions like N^{3-} that are stable with electropositive metals, M^{n+} .
- N_2 is relatively unreactive

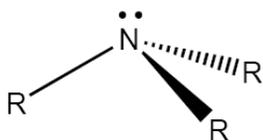
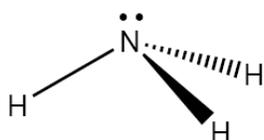
Why?

(a) $N\equiv N$ bond strength

(b) Electronic structure

(The lone pairs on the ends are not accessible – M.O. theory)

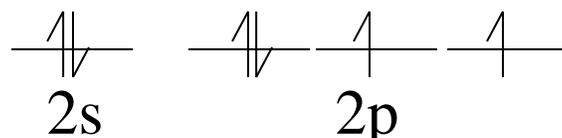
- compounds of N are covalent and usually involve three single bonds to other elements



e.g. amines

but can involve triple bonds: $C\equiv N$, $N\equiv N$, etc.

Oxygen $2s^2 2p^4$



- two unpaired electrons in O atom according to Aufbau filling
- *two unpaired electrons on O_2 molecule M.O. theory predicted that the HOMO is a double – degenerate π orbital: $\sigma_1^2 \sigma_2^2 \sigma_3^2 \pi_1^4 \pi_2^2$
(12 electrons in the O_2 valence shell; the last two are parallel due to Hund's Rule)

(p. 109 Chapter 3 on M.O. theory)

- O_2 is very reactive with these two unpaired electrons in the HOMO.
- Anions O^{2-} , O_2^- , O_2^{2-} exist in solid
- Covalent bonds exist in molecules CO , SO_3 , etc.,
- OH^- exists in solids and solution



- one unpaired electron on the F atom
 - extremely reactive due to low bond energy in F_2
→ Why is the F-F bond not so stable?
 - Ionic compounds containing F^- and covalent compounds with $X^+ - F^-$ are well-known
(the bonds, however, are quite polar)
-

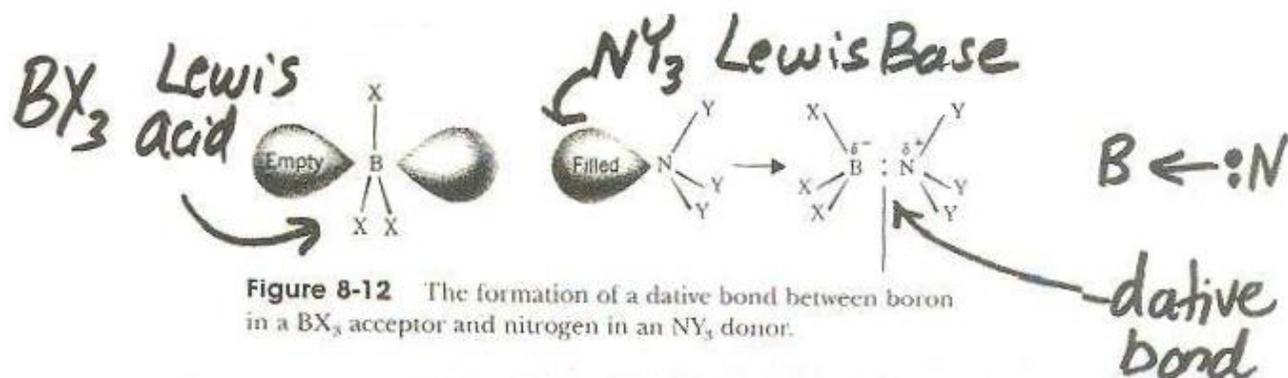
Covalent Bonds

Three main points:

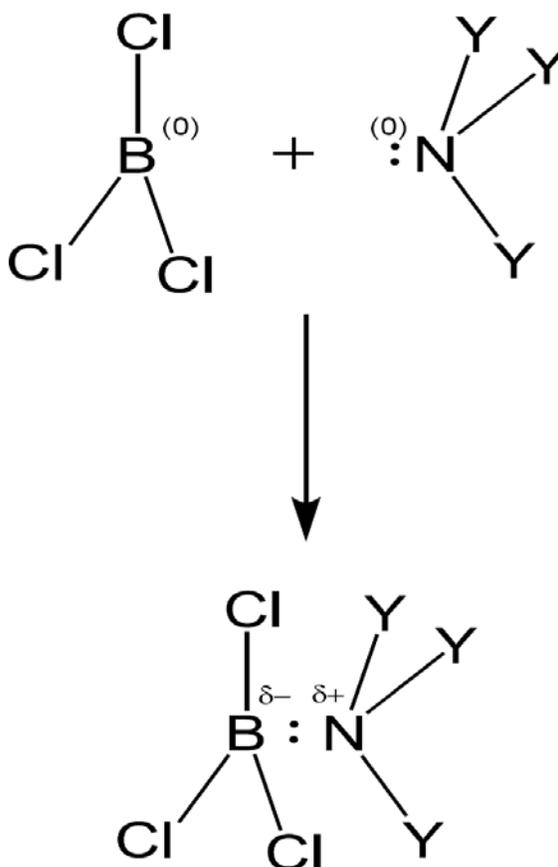
1. Be, B, C have fewer unpaired electrons than the number of bonds they typically form. e.g. C $2s^2 2p^2$ has only two unpaired electrons
(recall promotion to hybrid orbitals with 4 u.e.'s is proposed)

2. The elements of the first period Li→F obey the octet rule ($2s^2 2p^6$ is most stable electronic configuration after all) elements attempt to achieve an octet of electrons around them (octet rule doesn't apply strictly to elements after F)

3. In electron deficient systems such as Boron with only 3 valence electrons (BCl_3 , *etc.*,) (too few electrons) there is a tendency for these molecules to accept electrons into their empty orbitals:

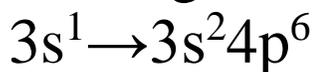


Note: $\text{B}:\text{N}$ would mean complete sharing
 $\text{B}^{\delta-}:\text{N}^{\delta+}$ means a significant polarity exists from the original free states.



Second Short Period

Na, Mg, Al, Si, P, S, Cl, Ar



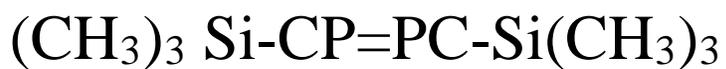
Valence electron structures are similar to Li, Be, B, C, N, O, F, Ne, but their chemistry differs considerably (especially Si, P, S, Cl)

These elements are more like the rest of the heavier elements in their respective groups (columns)

Why? Five Main Reasons

1. First of all, it is not favorable to form $p\pi$ - $p\pi$ multiple bonds such as $\text{Si}=\text{Si}$, $\text{Si}=\text{O}$, $\text{P}=\text{P}$ etc.,

This can be rationalized by considering that, in order to achieve good π - π overlap; atoms have to get close together. More repulsion is encountered due to filled 2s, 2p. The only way to stabilize such bonds as $\text{Si}=\text{Si}$, $\text{Si}=\text{P}$, $\text{Ge}=\text{Ge}$, $\text{Ge}=\text{C}$, $\text{P}=\text{P}$ is to put bulky substituents on the atoms to make them have fewer bonds to other groups which makes them engage in a second bond to each other.



C-SiMe₃ is very bulky

This doubly – bond phosphorus compound is kinetically stable.

2. When multiple bonding (σ/π combined) is exhibited for this period, the orbitals involved are the low-lying d orbitals. $p\pi - d\pi$ bonding occurs as in $\text{O}=\text{PR}_3$ (We don't have to expect the octet rule to be strictly obeyed for elements like P)

3. The possibility of using 3d orbitals leads to more bonds than four in many cases
 PCl_5 , SF_6 , SiF_6^{2-} etc.,

4. The shapes of molecules and the nature of the bonds differ in compounds of $\text{Li} \rightarrow \text{Ne}$ versus $\text{Na} \rightarrow \text{Ar}$.
 See VSEPR again in Chap. 3.

5. The compounds of cations and anions differ in these two periods



Al^{3+} is very different from B^{3+} , very electropositive – not very covalent. (Cl-Cl bond is actually stronger than F-F, so free Cl^- is not as prevalent. Cl_2 is much less reactive.

Rest of the Non-Transition Elements

As already stated, the first row of elements at the top of the periodic table does not serve as a reliable guide for the chemistry of the elements in those groups. The second short row $\text{Na} \rightarrow \text{Ar}$ is much more representative.

Two main points need to be clarified for chemistry of non-transition elements.

1. What are the differences in the row Li, Be, B, C, N, O, F, Ne and the remaining elements in the elements below each one (in the same group).
2. What are the regular variations after this?
For example, how do things change from the row $\text{Li} \rightarrow \text{Ne}$ for each group (column)?

The regular variations that occur as you descend a group:

- (1) Metallic character of the elements
- (2) Properties of the oxide compounds
 - (a) Ionic vs. covalent
Which ties in with:
 - (b) Acidic vs. basic
- (3) Properties of the halide compounds
 - (a) Molecular vs. ionic
 - (b) Ease of hydrolysis of the compound
- (4) Trends in covalency
- (5) Trends in structure
Molecular vs. extended structures etc.,
- (6) Properties of the hydride compounds
- (7) Tendency for catenation (elements binding to another one itself)
- (8) Importance of $p\pi$ - $p\pi$ versus $p\pi$ - $d\pi$ bonding (or even $d\pi$ - $d\pi$)
- (9) The general strength of the covalent bonds to particular elements
- (10) The relative importance of low-valent versus high-valent oxidation states of the elements

The rest of the Chapter 8 is an introduction to what is covered in Chapters 9 – 22

Sec. 8-12

The Transition Elements of d and f blocks

Strict definition is:

“elements **that have** partly filled d or f sub-shells”

Broader definition is:

Elements **that form** compounds with partly filled d or f sub-shells

(includes Cu, Ag, Au which are d^{10})

Note:

Most of the community refer only to the “d-block” elements as “transition” elements. It is not really common to call the f block elements, transition elements.

f-block elements

- More commonly called “rare earth” elements
- two rows:
 - Lanthanides
 - Actinides

Lanthanides

La (Z=57) → Lu (Z=71)

Comprise a row of 15 elements

→lanthanides

Although La (Lanthanum) is: [Xe] 5d¹6s²

And Lu (Lutetium) is: [Xe] 4f¹⁴5d¹6s²,

They are not considered to be d-block elements because of their chemical and physical properties

Actinides

Ac (Z=89) → Lu (Z=103)

(actinium) (Lawrencium)

When you get to Sc (Scandium) (Z=21) [Ar]4d¹5s²

and Y (Yttrium) (Z=39) [Kr]4d¹5s²

the d orbitals become lower than s orbitals upon filling **but** as you continue to add electrons, **the 4f level drops below both the d & s levels.**

So why is not the electronic configuration of scandium $[\text{Ar}] 3d^3$ rather than $[\text{Ar}] 3d^1 4s^2$?

SOLUTION

Making Sc^{3+}

Imagine you are building a scandium atom from boxes of protons, neutrons and electrons. You have built the nucleus from 21 protons and 24 neutrons, and are now adding electrons around the outside. So far you have added 18 electrons to fill all the levels up as far as 3p. Essentially you have made the ion Sc^{3+} .

Making Sc^{2+}

Now you are going to add the next electron to make Sc^{2+} . Where will the electron go? The 3d orbitals at scandium have a lower energy than the 4s, and so the next electron will go into a 3d orbital. The structure is $[\text{Ar}] 3d^1$.

Making Sc^+

You might expect the next electron to go into a lower energy 3d orbital as well, to give $[\text{Ar}] 3d^2$. But it doesn't. You have something else to think about here as well. If you add another electron to any atom, you are bound to increase the amount of repulsion. Repulsion raises the energy of the system, making it less energetically stable. It obviously helps if this effect can be kept to a minimum.

The 3d orbitals are quite compactly arranged around the nucleus. Introducing a second electron into a 3d orbital produces more repulsion than if the next electron went into the 4s orbital. There is not a very big gap between the energies of the 3d and 4s orbitals. The reduction in repulsion more than compensates for the energy needed to do this.

The energetically most stable structure for Sc^+ is therefore $[\text{Ar}] 3d^1 4s^1$.

Making Sc:

Putting the final electron in, to make a neutral scandium atom, needs the same sort of discussion. In this case, the lowest energy solution is the one where the last electron also goes into the 4s level, to give the familiar $[\text{Ar}] 3d^1 4s^2$ structure.

Summary

In each of these cases we have looked at, the 3d orbitals have the lowest energy, but as we add electrons, repulsion can push some of them out into the higher energy 4s level.

- If you build up the scandium atom from scratch, the last electrons to go in are the two 4s electrons. These are the electrons in the highest energy level, and so it is logical that they will be removed first when the scandium forms ions. And that's what happens.
- The 4s electrons are also clearly the outermost electrons, and so will largely define the radius of the atom. The lower energy 3d orbitals are inside them, and will contribute to the screening. There is no longer any conflict between these properties and the order of orbital filling.

f orbitals < d < s in lanthanides & actinides

Table 26-1 Some Properties of Scandium, Yttrium, and the Lanthanides

Z	Name	Symbol	Electron Configuration	Valences	M ³⁺ Radius (Å)	M ³⁺ Color
21	Scandium	Sc	[Ar]3d ¹ 4s ²	3	0.68	Colorless
39	Yttrium	Y	[Kr]4d ¹ 5s ²	3	0.88	Colorless
57	Lanthanum	La	[Xe]5d ¹ 6s ²	3	1.06	Colorless
58	Cerium	Ce	[Xe]4f ¹ 5d ¹ 6s ²	3, 4	1.03	Colorless
59	Praseodymium	Pr	[Xe]4f ³ 6s ²	3, 4	1.01	Green
60	Neodymium	Nd	[Xe]4f ⁴ 6s ²	3	0.99	Lilac
61	Promethium	Pm	[Xe]4f ⁵ 6s ²	3	0.98	Pink
62	Samarium	Sm	[Xe]4f ⁶ 6s ²	2, 3	0.96	Yellow
63	Europium	Eu	[Xe]4f ⁷ 6s ²	2, 3	0.95	Pale pink
64	Gadolinium	Gd	[Xe]4f ⁷ 5d ¹ 6s ²	3	0.94	Colorless
65	Terbium	Tb	[Xe]4f ⁹ 6s ²	3, 4	0.92	Pale pink
66	Dysprosium	Dy	[Xe]4f ¹⁰ 6s ²	3	0.91	Yellow
67	Holmium	Ho	[Xe]4f ¹¹ 6s ²	3	0.89	Yellow
68	Erbium	Er	[Xe]4f ¹² 6s ²	3	0.88	Lilac
69	Thulium	Tm	[Xe]4f ¹³ 6s ²	3	0.87	Green
70	Ytterbium	Yb	[Xe]4f ¹⁴ 6s ²	2, 3	0.86	Colorless
71	Lutetium	Lu	[Xe]4f ¹⁴ 5d ¹ 6s ²	3	0.85	Colorless

Actinides

Table 27-1 The Actinide Elements and Some of Their Properties

Z	Name	Symbol	Electronic Structure ^a of Atom	Radii (Å)	
				M ³⁺	M ⁴⁺
89	Actinium	Ac	6d7s ²	1.11	
90	Thorium	Th	6d ² 7s ²		0.90
91	Protactinium	Pa	5f ² 6d7s ² or 5f ¹ 6d ² 7s ²		0.96
92	Uranium	U	5f ³ 6d7s ²	1.03	0.93
93	Neptunium	Np	5f ⁵ 7s ²	1.01	0.92
94	Plutonium	Pu	5f ⁶ 7s ²	1.00	0.90
95	Americium	Am	5f ⁷ 7s ²	0.99	0.89
96	Curium	Cm	5f ⁷ 6d7s ²	0.985	0.88
97	Berkelium	Bk	5f ⁸ 6d7s ² or 5f ⁹ 7s ²	0.98	
98	Californium	Cf	5f ¹⁰ 7s ²	0.977	
99	Einsteinium	Es	5f ¹¹ 7s ²		
100	Fermium	Fm	5f ¹² 7s ²		
101	Mendelevium	Md	5f ¹³ 7s ²		
102	Nobelium	No	5f ¹⁴ 7s ²		
103	Lawrencium	Lr	5f ¹⁴ 6d7s ²		
104	Rutherfordium	Rf			

^aOutside Rn structure.

The f orbitals have shapes that do not allow the electrons to shield each other very well from the effects of the increased nuclear charge. A $4f^{1-14}$ filling involves a level $n = 4$ that is fairly close to the nucleus.

As a result, there is a big shrinkage in the radii of the atoms and ions of the lanthanides La→Lu. The accumulation of successive shrinkage is called the lanthanide contraction.

Review: Shielding effect In multi-electron atoms, the electrons in the outermost shell do not experience the complete nuclear charge because of interaction with the inner electrons. Thus, the outermost electrons are “shielded” or “screened” from the nucleus by the inner electrons. The d and f orbitals show poor shielding effect. Poor shielding means poor screening of nuclear charge. The shielding effect of different orbitals is as follows: s orbitals > p orbitals > d orbitals > f orbitals.

Electrons closer to the nucleus experience greater nuclear attraction and effectively shield other electrons from nuclear attraction. The electrons in the s-orbital have maximum probability of being found near the nucleus and this probability decreases in the order $p > d > f$ orbitals. As the distance of electrons from nucleus increases its shielding effect decreases.

Effect of shielding on d-block elements: In the periodic table,

atomic radii of representative elements decrease as we move from left to right. In contrast, the atomic radii of transition metals decrease only slightly from left to right. The outermost 4s electrons are shielded by inner 3d electrons. Since 3d electrons show poor shielding effects therefore effective nuclear charge felt by the 4s electrons of the elements from left to right show only gradual decrease in atomic radii.

Moreover, the atomic sizes of the elements in the third transition series are virtually the same as those of the corresponding members in the second transition series. This is due to lanthanide contraction.

Shielding effect in f-block elements:

The lanthanide and actinide contraction in f-block elements is due to the poor shielding of 4f and 5f orbitals.

Ramifications of Lanthanide Contraction

→Second and third row d-block transition elements have nearly the same size!

Zr	Nb	Mo	Tc	Ru	Rh	Pd
Hf	Ta	W	Re	Os	Ir	Pt

The atoms in each pair are not as different in size as one would expect.

And size of atoms/ions helps determine chemical & physical properties!

Q. Why?

A. Valence electrons are involved in the processes that are what we call “chemistry”. Their I.E.’s *etc.*, are somewhat determined by distance from the nucleus.

Properties of Transition-metals (elements)

- (1) All are metals
- (2) Practically all are hard, high melting, high boiling elements that are good conductors
- (3) They form alloys with each other
- (4) Many are highly electropositive such that they dissolve in mineral acids (oxidized)
- (5) They exhibit variable valence
- (6) They form paramagnetic compounds