CH-110 Advanced General Chemistry I

Prof. A. Steinauer
angela.steinauer@epfl.ch

Housekeeping notes

Which periodic table at exam?

Indicative feedback: please fill it out.

- **SESSION ID: 090543**

Student questions

1. Why does the 3d and 4f orbitals' energy get lowered when occupied? Do the 3p or 4p orbital energies also get lowered when occupied? Why does the 4p orbital not become lower compared to the 4s orbital when filled, similar to how the 3d orbital energy becomes lowered below the 4s orbital energy when filled?

Answer: Most orbitals become more stable when filled with electrons. The 3d orbitals in particular become lower in energy when filled because the added electrons experience stronger attraction to the nucleus (due to **increased effective nuclear charge**). This makes the 3d orbitals lower in energy than the 4s orbital after filling.

The question is how close in energy are the empty and filled orbitals to the other orbitals. The 3d orbitals are very close in energy to the 4s orbitals and only slightly higher than them when empty. The filling with electrons stabilizes the 3d orbitals and this stabilization happens to make them lower in energy than the 4s orbitals. The same trend can be observed for the 4f orbitals compared with the 6s orbitals.

The p-orbitals have a larger energy gap compared to the s-orbitals and even after filling them, they will not be close in energy to the s-orbitals.

Student questions

2. Exam question: «The difference between two successive energy levels of an electron in a one-dimensional box decreases as n decreases." Why false?

Answer: this statement is **true**, the solution online was incorrect. We fixed this.

3. Comment: There was a typo on last week's problem set solutions.

Answer: Exercise 4.9 mistakenly referred to argon instead of arsenic. We fixed this.

4. Comment: The answer in exercise 3.4 c) was misleading.

Answer: Please disregard this statement from the solution, it is incorrect: "This can lead to the electron moving faster within the atom or potentially being ejected from the atom entirely, a phenomenon known in atomic physics as the photoelectric effect. " We will fix this and upload a new version.

Student questions

5. Example 1D.1, why is the probability calculated by taking the ratio of $\psi(x)^2$ and not the ratio of $\psi(x)^2 \times dV$ because the probability is given by $P(x) = \psi(x)^2 \times dV$?

In Example 1D.1, we calculated the probability of finding an electron at a certain location. The **probability** $P(x,t)$ is the likelihood of finding the particle in a specific **region** of space, not just at a single point. To get the probability, you must integrate the **probability density** over that region.

For example, the probability of finding the particle in a very small volume element dV around point x is given by:

$$P(x) = \psi(x)^2 \times dV$$

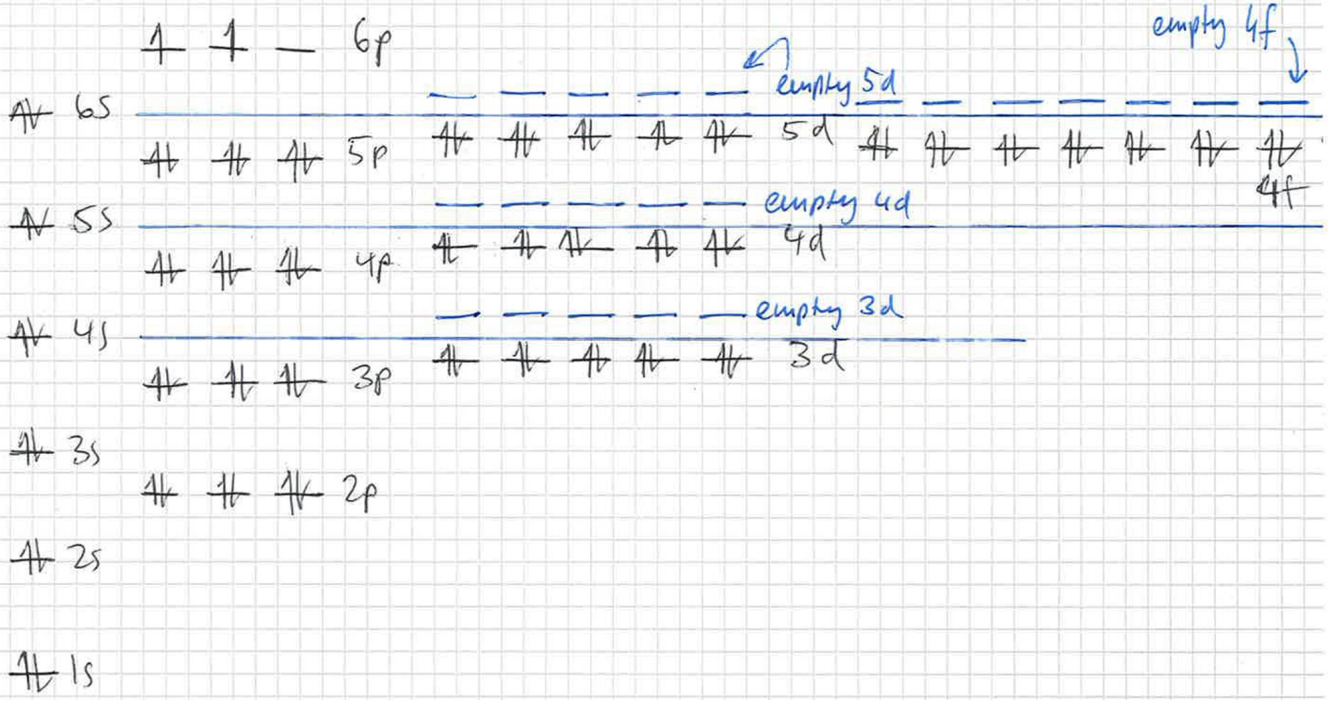
In general, for any region R, the probability is calculated by summing (integrating) the probability density $\psi(x)^2$ over the entire region R:

$$P(R) = \int \psi(R)^2 dV$$

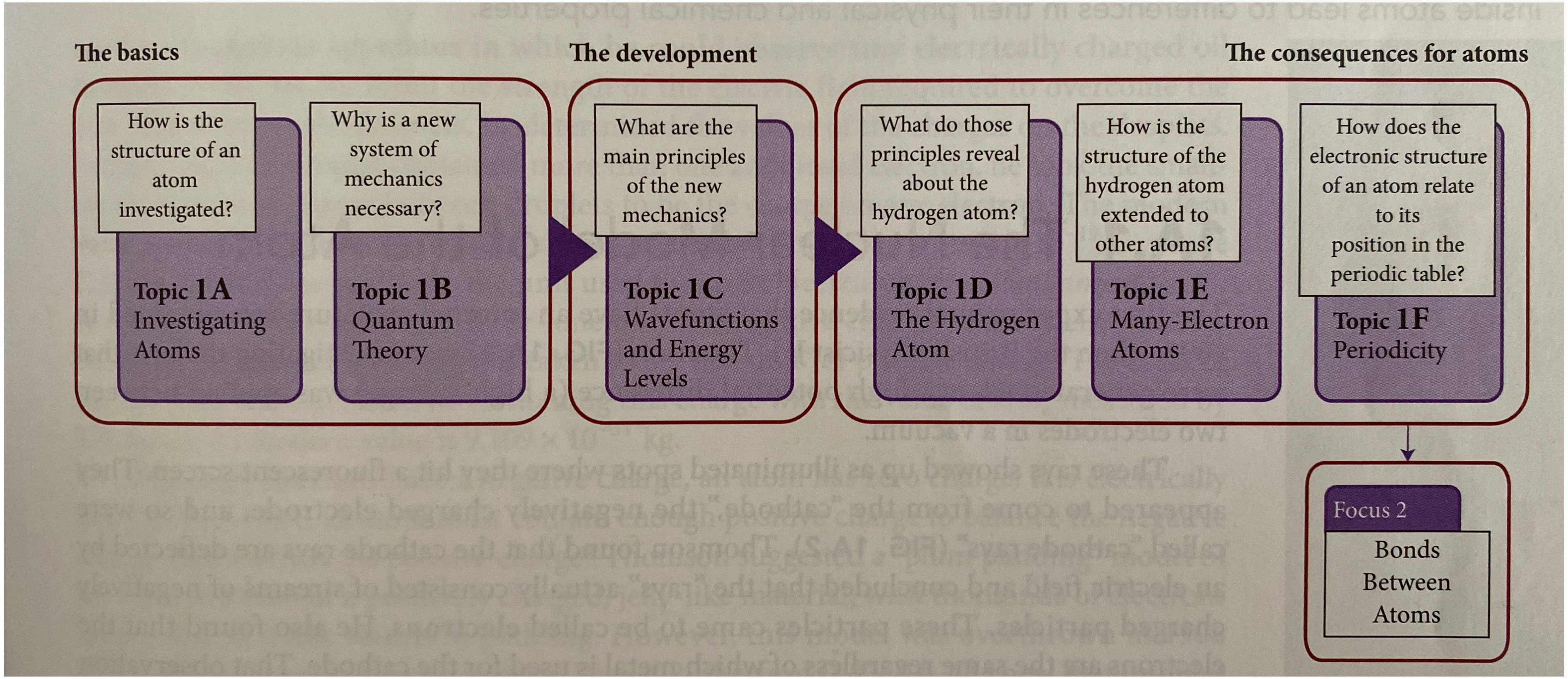
However, you are not expected to solve integrals or derivatives at the exam, thus, this example includes an approximation that does not require solving an integral: We focus on the relative probability of finding an electron in a small region a distance a_0 from the nucleus relative to the probability of finding it **in the same small region** located right at the nucleus. Since the volume element dV is the same in both cases, it cancels out, and the ratio of probabilities is given by:

$$\frac{P(r = a_0)}{P(r = 0)} = \frac{\Psi^2(a_0) \times dV}{\Psi^2(0) \times dV} = \frac{\Psi^2(a_0)}{\Psi^2(0)}$$

Pb : $Z = 82$ $[\mathrm{Xe}]\,4f^{14}5d^{10}6s^{2}6p^{2}$



Overview Chapter 1 (Focus 1: Atoms)



The basics

How is the structure of an atom investigated?

Topic 1A Investigating Atoms

Why is a new system of mechanics necessary?

Topic 1B Quantum Theory

The development

What are the main principles of the new mechanics?

Topic 1C Wavefunctions and Energy Levels

The consequences for atoms

What do those principles reveal about the hydrogen atom?

Topic 1D The Hydrogen Atom

How is the structure of the hydrogen atom extended to other atoms?

Topic 1E Many-Electron Atoms

How does the electronic structure of an atom relate to its position in the periodic table?

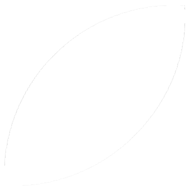
Topic 1F Periodicity

Focus 2

Bonds Between Atoms

Periodicity

Topic 1F



Last week: Topic 1F.1 Atomic radius
Last week: Topic 1F.2 Ionic radius
Topic 1F.3 Ionization energy
Topic 1F.4 Electron affinity
Topic 1F.5 Electronegativity
Topic 1F.6 The general properties of the elements

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- The periodic table summarizes trends in the properties of the elements. The ability to **predict the properties of an element from its location** in the periodic table is a central skill of a chemist.

WHAT DO YOU NEED TO KNOW ALREADY?

- The structure of the **periodic table**, the **building-up principle** (Topic 1E)
- **Oxidation state** (Fundamentals K)
- Definition of **ionization energy** (Topic 1D)

1F.3 Ionization energy

- The formation of an **ionic compound** depends on the **removal of one or more electrons from one atom** (Na to Na^+) and the transfer of those electrons to another atom (Cl to Cl^-).
- The **ionization energy**, I, is the miminum energy needed to remove an electron from an atom in the gas phase:

$$X(g) \rightarrow X^+(g) + e^-(g)$$

$$I = E(X^+) - E(X)$$

- Where $E(X)$ is the energy of species X.
- And $E(X^+) - E(X)$ is the energy difference between the ionized and the neutral atom.
- Reported as molar quantities in kilojoules per mole (kJ/mol) or in electronvols (eV).

1F.3 Ionization energy

- **First ionization energy $\boldsymbol{I_1}$**: minimum energy needed to remove an electron from a neutral atom in the gas phase

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

$$energy\ required = I_1(746\frac{kJ}{mol}, 7.73\ eV)$$

- Ionization energy is a measure of how difficult it is to remove an electron:
- Elements with **low ionization energies** can be expected to form cations readily, conduct electricity (requires movement of free electrons)
- Elements with **high ionization energies** are unlikely to form cations and are unlikely to conduct electricity

1F.3 Ionization energy

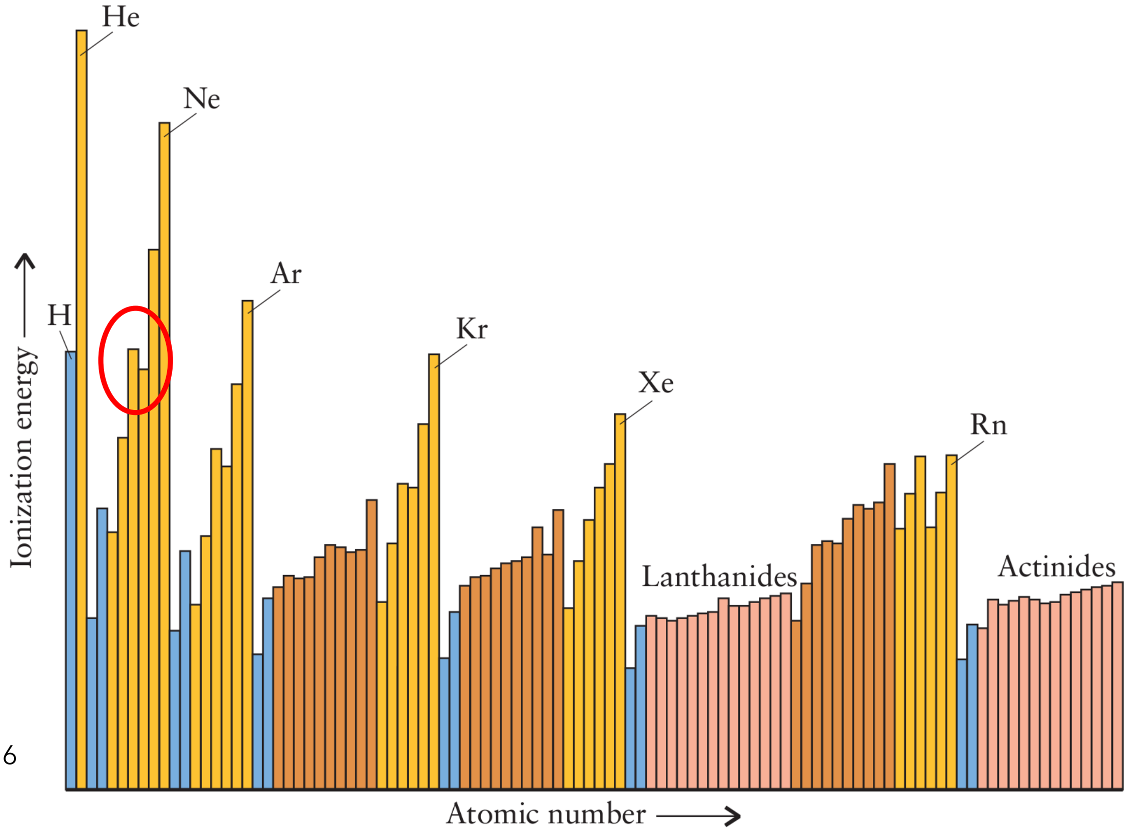


Figure 1F.6

TRENDs: First ionization energies typically decrease down a group.

First ionization energies generally increase across a period.

- First ionization energies **increase across period**: increase in effective nuclear charge across period.
- **Ionization energy of oxygen < nitrogen:** nitrogen has one electron per p-orbital, oxygen is pairing up 8th electron with other p-electrons, energy goes up

1F.3 Ionization energy

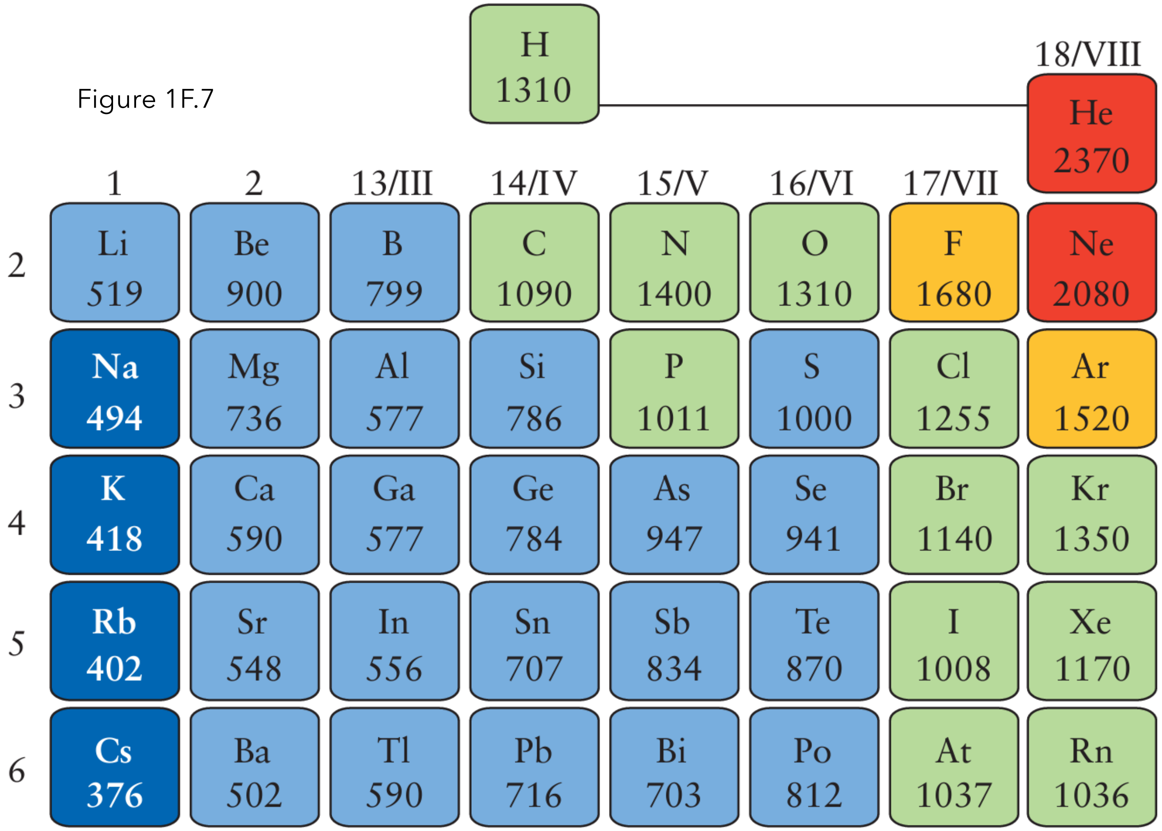


Figure 1F.7

	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
				H 1310				He 2370
2	Li 519	Be 900	B 799	C 1090	N 1400	O 1310	F 1680	Ne 2080
3	Na 494	Mg 736	Al 577	Si 786	P 1011	S 1000	Cl 1255	Ar 1520
4	K 418	Ca 590	Ga 577	Ge 784	As 947	Se 941	Br 1140	Kr 1350
5	Rb 402	Sr 548	In 556	Sn 707	Sb 834	Te 870	I 1008	Xe 1170
6	Cs 376	Ba 502	Tl 590	Pb 716	Bi 703	Po 812	At 1037	Rn 1036

- **Decrease down group:** outermost electrons are farther and farther away from nucleus, experiencing less nuclear charge.

TREND: First ionization energies typically decrease down a group.

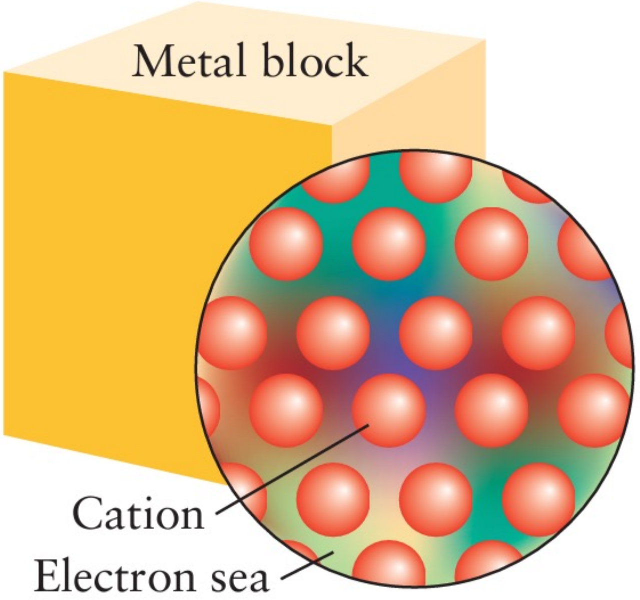
First ionization energies generally increase across a period.

1F.3 Ionization energy

Metallic character

- **Low ionization energies**
- Lower left of periodic table
- A block of metal: **collection of cations of the element surrounded by a sea of valence electrons that the atoms have lost**
- s-block, d-block, f-block, lower left of the p-block can form metallic solids because they can lose electrons easily.
- Elements with high ionization energies are on the upper right of the periodic table

Figure 1F.8



1F.3 Ionization energy

The second ionization energy, I_2

- The minimum energy needed to remove an electron from a singly charged gas-phase cation.

$$Cu^{+}(g) \rightarrow Cu^{2+}(g) + e^{-}(g)$$

$$energy\ required = I_2\left(1958\frac{kJ}{mol}, 20.29\ eV\right)$$

- The second ionization energy is **always higher than the first** → it takes more energy to remove an electron from a positively charged atom than from a neutral one
- Group 1: $I_2 >> I_1$
- Group 2: $I_2 > I_1$

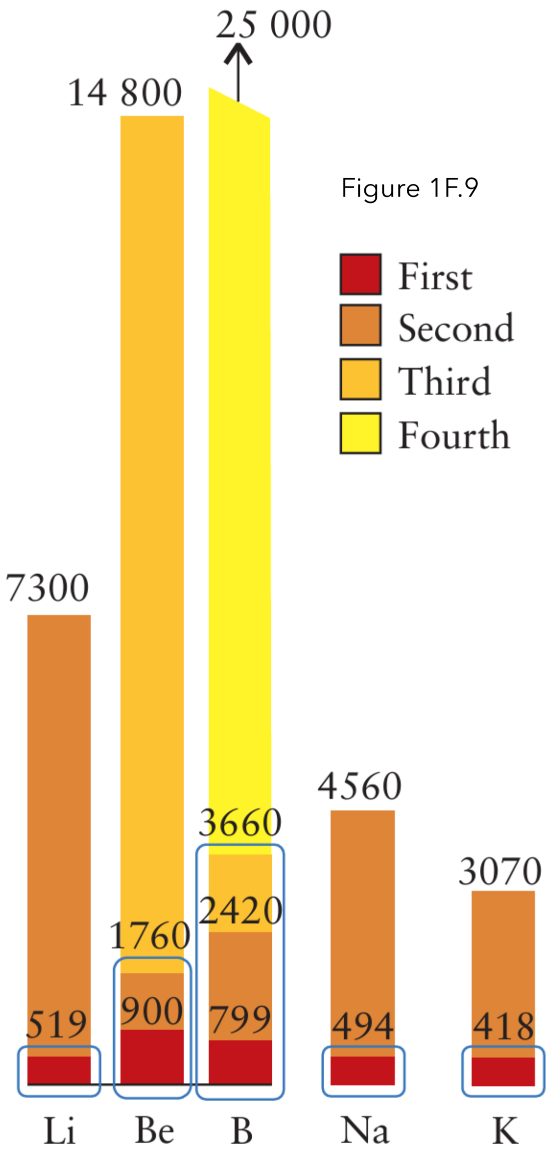
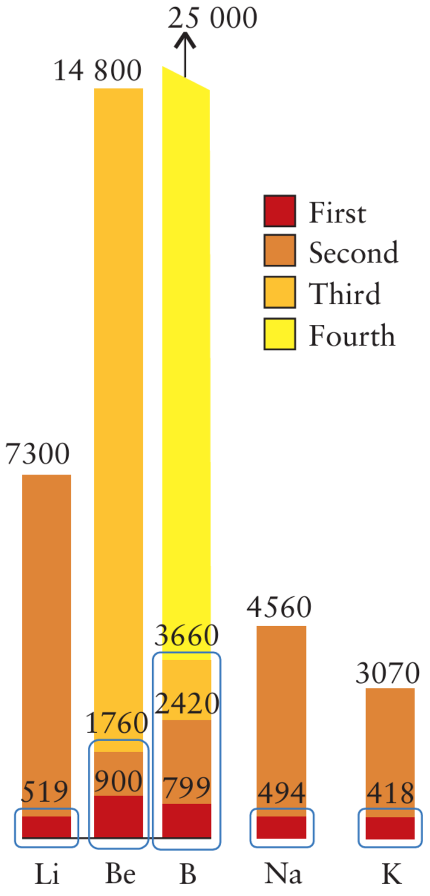


Figure 1F.9

Why is there a large decrease in third ionization energy between beryllium and boron?

Answer: There is a large decrease in third ionization energy between beryllium and boron because, after removing two electrons from beryllium, the third ionization involves removing an electron from a stable, fully-filled noble gas core, which requires significantly more energy, while boron's third electron is from a higher-energy p-orbital, making it easier to remove.



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1F.3 Ionization energy

Summary

TRENDS:

The **first ionization energy** is highest for elements close to helium and is lowest for elements close to cesium.

Second ionization energies are higher than first ionization energies (of the same element) and very much higher if the electron is to be removed from a closed shell.

Metals are found toward the lower left of the periodic table because these elements have low ionization energies and can readily lose their electrons.

Electron Affinity

Topic 1F.4

1F.4 Electron affinity

Ionization energy vs. electron affinity

- Ionization energy indicates how difficult it is to **remove** an electron from an atom.
- How does the energy change when an electron **attaches** to an atom to form a negative ion (Cl to Cl^-)?
- **The electron affinity, E_{ea}, of an element is the energy released when an electron is added to a gas-phase atom.**
- **Pos. E_{ea}:** energy released when an electron attaches to atom
- **Neg. E_{ea}:** energy must be supplied to push an electron onto an atom

1F.4 Electron affinity

Ionization energy vs. electron affinity

The electron affinity of an element X is defined as

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

$$E_{ea}(X) = E(X) - E(X^{-})$$

Where $E(X)$ is the energy of a gas-phase atom X and $E(X^{-})$ is the energy of the gas-phase anion.

For instance, the electron affinity of chlorine is the energy released in the process

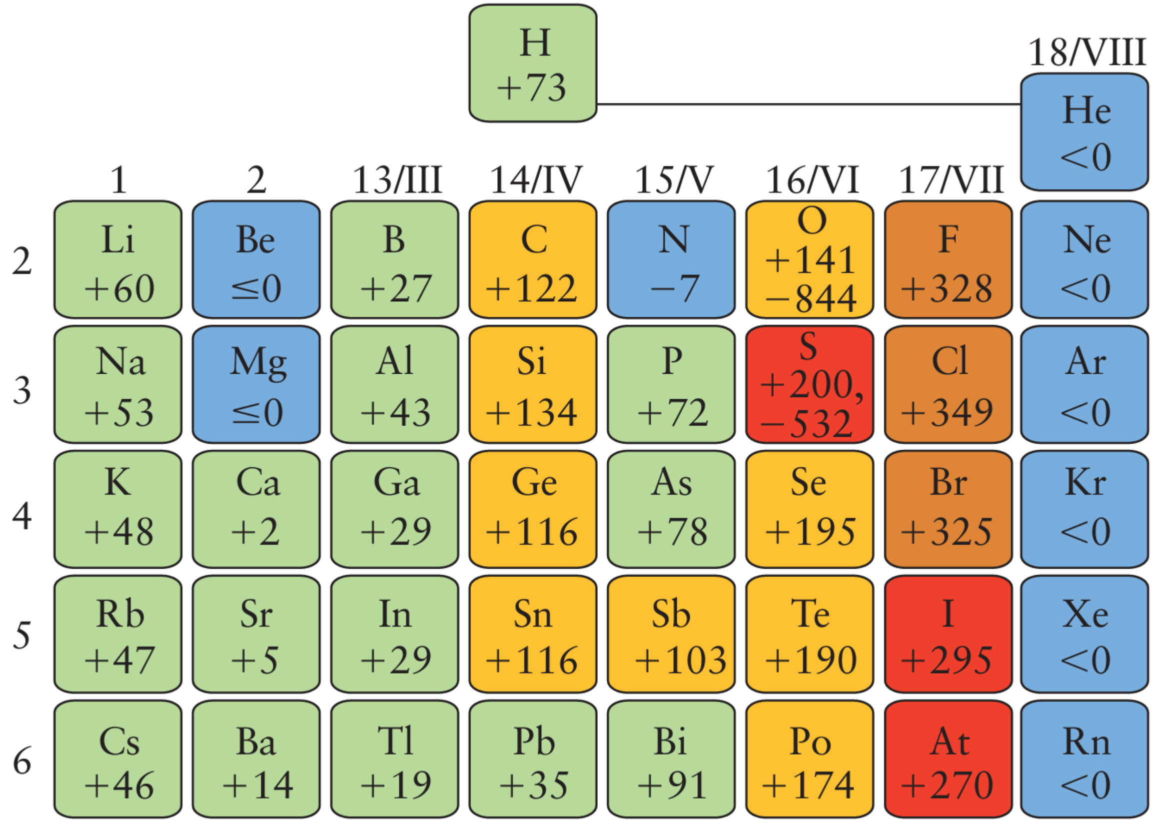
$$Cl(g) + e^{-}(g) \rightarrow Cl^{-}(g)$$

$$energy\ released = E_{ea}\left(349\frac{kJ}{mol}, 3.63\ eV\right)$$

Because the electron has a lower energy when it occupies one of the atom's orbitals, the difference $E(Cl) - E(Cl^{-})$ is positive, and the electron affinity of chlorine is positive.

1F.4 Electron affinity

Variation in electron affinity in kJ/mol of main-group elements



	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
				H +73				He <0
2	Li +60	Be ≤0	B +27	C +122	N −7	O +141 −844	F +328	Ne <0
3	Na +53	Mg ≤0	Al +43	Si +134	P +72	S +200, −532	Cl +349	Ar <0
4	K +48	Ca +2	Ga +29	Ge +116	As +78	Se +195	Br +325	Kr <0
5	Rb +47	Sr +5	In +29	Sn +116	Sb +103	Te +190	I +295	Xe <0
6	Cs +46	Ba +14	Tl +19	Pb +35	Bi +91	Po +174	At +270	Rn <0

Figure 1F.10

TREND: Electron affinities are highest toward the right of the periodic table.

Pos. E_{ea}: energy released when an electron attaches to atom

Neg. E_{ea}: energy must be supplied to push an electron onto an atom

1F.4 Electron affinity

A note about electron affinities IN OUR TEXTBOOK

Convention:

- **Positive energy:** energy released from the system
- **Negative energy:** energy must be supplied or is absorbed by the system

For example:

Electron affinity for sulfur:

- $E_{ea}(1)$ is positive (electron attachment to S to form S^- releases energy)
- $E_{ea}(2)$ is negative (it requires energy to make S^- take up another electron)

1F.4 Electron affinity

TRENDs

- **TREND:** Electron affinities are highest toward the right of the periodic table.
- Particularly true in the upper right of the periodic table: **oxygen, sulfur, halogens**
- In these atoms, an incoming electron occupies a p-orbital close to a nucleus with a high effective charge and can experience its attraction quite strongly
- **Noble gases have negative electron affinities** because any electron added to them must occupy an orbital outside a closed shell and far from the nucleus: this process requires energy, the electron affinity is negative
- **Halide (group 17) plus electron builds a closed shell** (noble-gas configuration). Second electron affinity for halides is strongly negative.
- Group 16 (O or S): two vacancies in its valence shell p-orbitals, can accommodate two additional electrons. First electron affinity positive.

1F.4 Electron affinity

Summary

TREND: Elements with the highest electron affinities are those in Groups 16 and 17.

1F.4 Electron affinity

Example 1F.2 Predicting trends in electron affinity

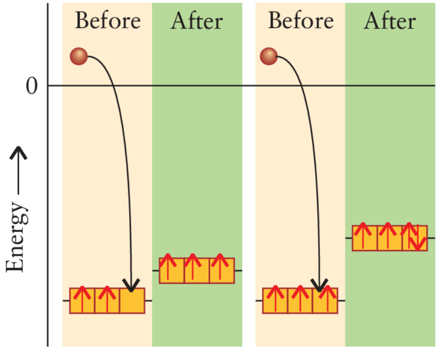
EXAMPLE 1.12 **Predicting trends in electron affinity**

The electron affinity of carbon is greater than that of nitrogen; indeed, the latter is negative. Suggest a reason for this observation.

PLAN When a periodic trend is different from what is expected, we examine the electron configurations of all the species to look for clues to the observed behavior.

SOLVE We expect more energy to be released when an electron enters the N atom, because an N atom is smaller than a C atom and its nucleus is more highly charged: the effective nuclear charges for the outermost electrons *of the neutral atoms* are 3.8 for N and 3.1 for C. However, the opposite is observed, and so we must also consider the effective nuclear charges experienced by the valence electrons in the anions (Fig. 1.55). When C^- forms from C, the additional electron occupies an empty 2p-orbital (see **6**). The incoming electron is well separated from the other p-electrons, and so it experiences an effective nuclear charge close to 3.1. When N^- forms from N, the additional electron must occupy a 2p-orbital that is already half full (see **7**). The effective nuclear charge experienced by this electron is therefore much less than 3.8; so energy is required to form N^-, and the electron affinity of nitrogen is lower than that of carbon.

Self-Test 1.15A Account for the large decrease in electron affinity between lithium and beryllium.



(a) Carbon (b) Nitrogen

Figure 1F.11 The energy changes taking place when an electron is added to a carbon atom and a nitrogen atom. (a) A carbon atom can accommodate an additional electron in an empty p-orbital. (b) When an electron is added to a nitrogen atom it must pair with an electron in a p-orbital. The incoming electron experiences so much repulsion from those already present in the nitrogen atom that the electron affinity of nitrogen is less than that of carbon and is in fact negative.

Why is there a large decrease in electron affinity between fluorine and neon?

Answer: There is a large decrease in electron affinity between fluorine and neon because neon has a complete and stable $2p^6$ electron configuration, making it energetically unfavorable to add an electron, whereas fluorine readily gains an electron to complete its valence shell.

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Electronegativity

Topic 1F.5

1F.5 Electronegativity

A combination of ionization energy and electron affinity

- Introduced by American chemist Robert Mulliken in 1934:
- Electronegativity, X (Greek letter chi)
- **"The power of an atom to attract electrons to itself when part of a compound."** (see Topic 2D)

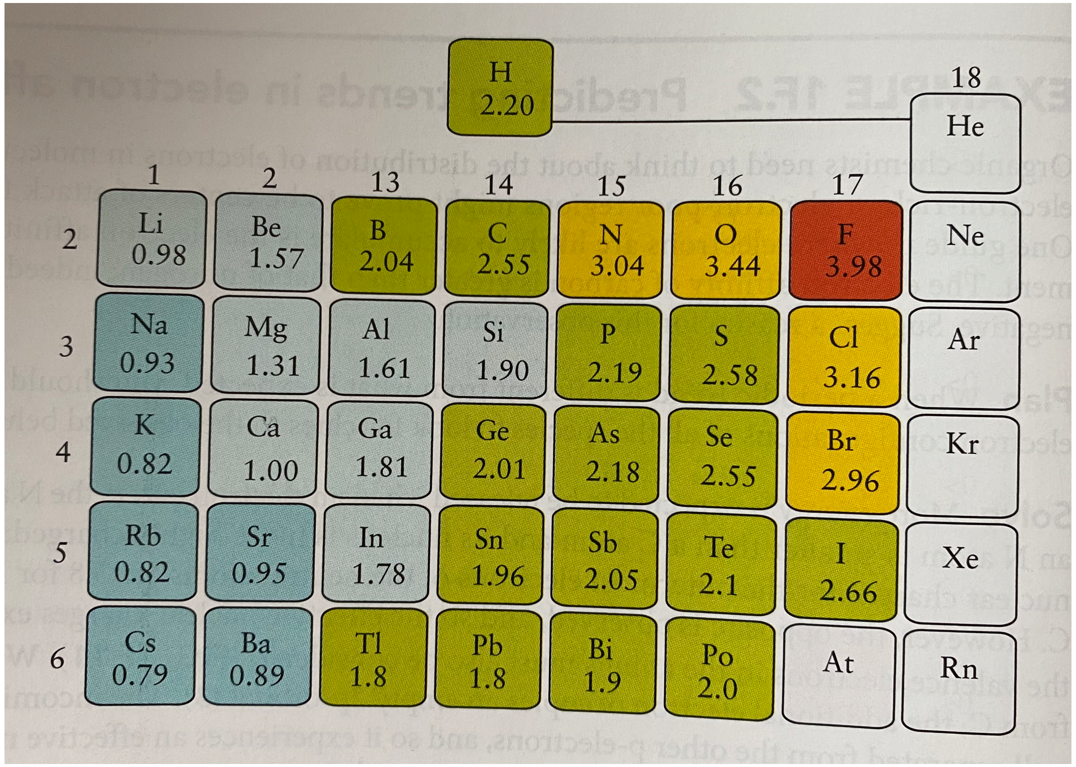
Definition:

$$\mathrm{X} = \frac{1}{2}(I + E_a)/eV$$

With the ionization energy and the electron affinity expressed in electronvolts (so electronegativity is **unitless**).

1F.5 Electronegativity

Variation in the electronegativities of the main-group elements



	1	2	13	14	15	16	17	18
				H 2.20				He
2	Li 0.98	Be 1.57	B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31	Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr
5	Rb 0.82	Sr 0.95	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe
6	Cs 0.79	Ba 0.89	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At	Rn

Figure 1F.12

- Elements with **high ionization energies and high electron affinities**: highly electronegative
- Elements **with low ionization energies and low electron affinities**: low electronegativity.
- Careful: electropositive is used for a different concept and is NOT the opposite of electronegative.

1F.5 Electronegativity

Summary

TREND: The electronegativity of an element, its power of an atom to attract electros to itself when part of a compound, is highest close to the top right of the periodic table.

F > O > Cl > N > Br > I > S > C/Se > H >…

The General Properties of the Elements

Topic 1F.6

1F.6 The general properties of the elements

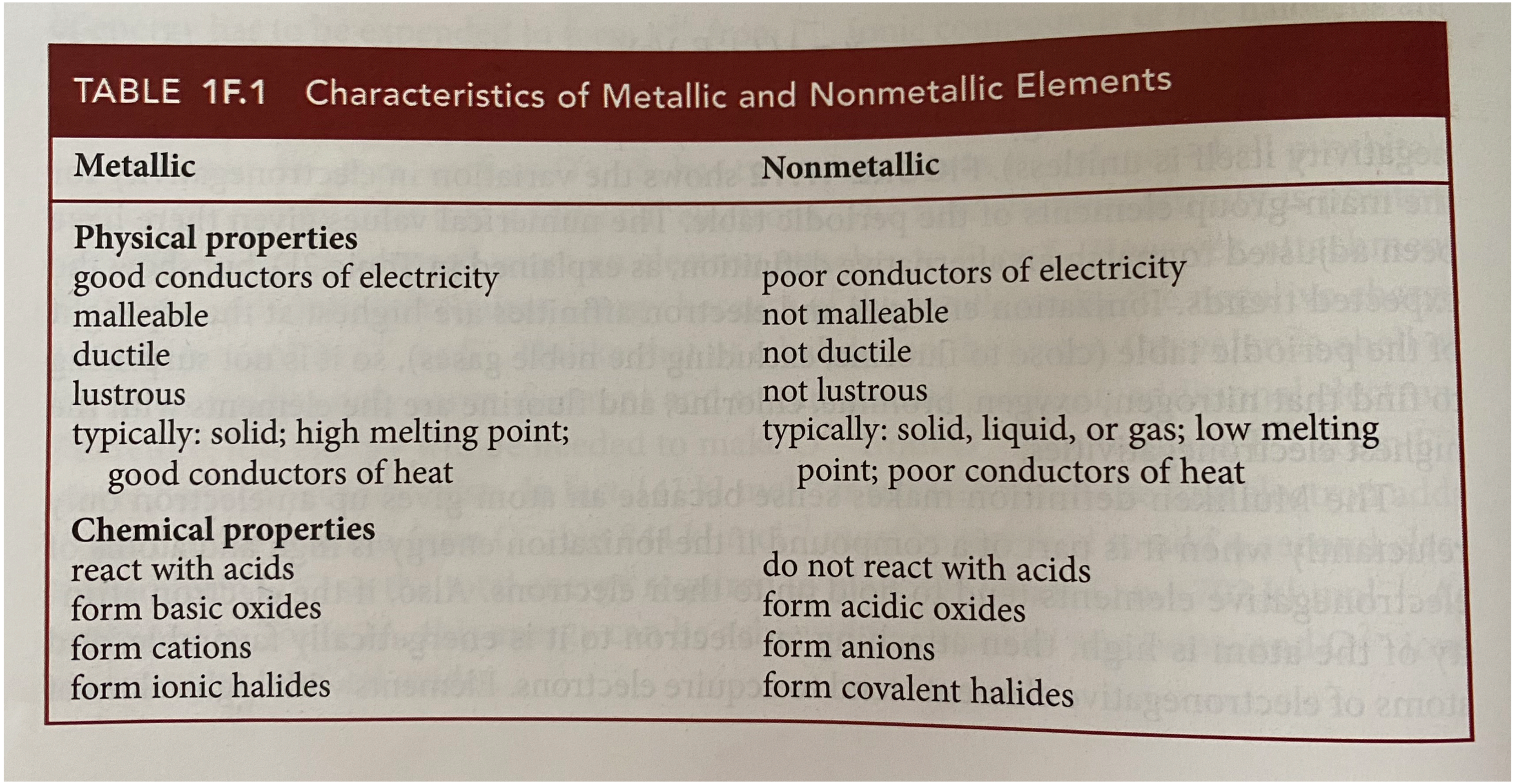


TABLE 1F.1 Characteristics of Metallic and Nonmetallic Elements

Metallic	Nonmetallic
Physical properties	
good conductors of electricity	poor conductors of electricity
malleable	not malleable
ductile	not ductile
lustrous	not lustrous
typically: solid; high melting point; good conductors of heat	typically: solid, liquid, or gas; low melting point; poor conductors of heat
Chemical properties	
react with acids	do not react with acids
form basic oxides	form acidic oxides
form cations	form anions
form ionic halides	form covalent halides

Figure 1F.13- 1F.16

1F.6 The general properties of the elements

Alkali metals (Group 1)

- **s-block** elements
- Low ionization energy: valence electrons easily lost
- Soft, silvery, reactive metals
- Low melting points
- Produce hydrogen when they come in contact with water.
- Sodium is kept under mineral oil to protect it from air (**Fig. 1F.13**)
- A freshly cut surface becomes quickly covered with oxide.

Figure 1F.13

1F.6 The general properties of the elements

Group 14 elements

- Elements on the left of the **p-block**
- As you move down the group, they have low enough ionization energies to have metallic character.
- From left to right (**Fig. 1F.14**): carbon (as graphite), silicon germanium, tin, and lead

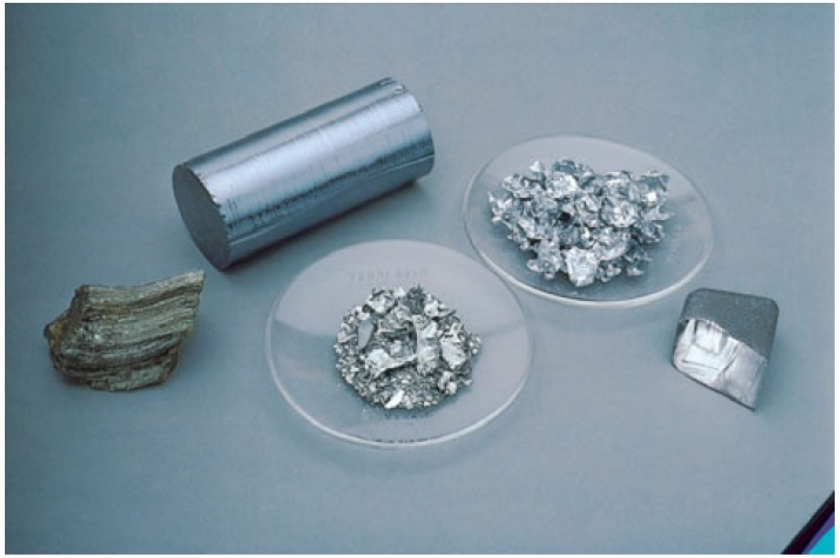


Figure 1F.14

1F.6 The general properties of the elements

Group 16 to 18 elements

- Elements at the right of the **p-block**
- **High electron affinities**: they tend to gain electrons to complete shells.
- Except for the metalloids tellurium and polonium, the members of group 16 and 17 are **non-metals**.
- They typically form molecular **compounds** with one another.
- From left to right (**Fig. 1F.15**): oxygen, sulfur, selenium, and tellurium (Group 16). Note the trend from nonmetal to metalloid moving down the group.
- Group 18: Noble gases, completed shells, unreactive (inert gases).

Figure 1F.15

1F.6 The general properties of the elements

d-block elements

- All **d-block** elements are metals: d-metals or **transition metals**
- Their properties are transitional between the s- and the p-block elements (except group 12)
- **When a d-block element loses electrons to form a cation, it first loses its s-electrons.**
- From left to right (**Fig. 1F.16**). Top row: scandium, titanium, vanadium, chromium, and manganese. Bottom row: iron, cobalt, nickel, copper, and zinc.

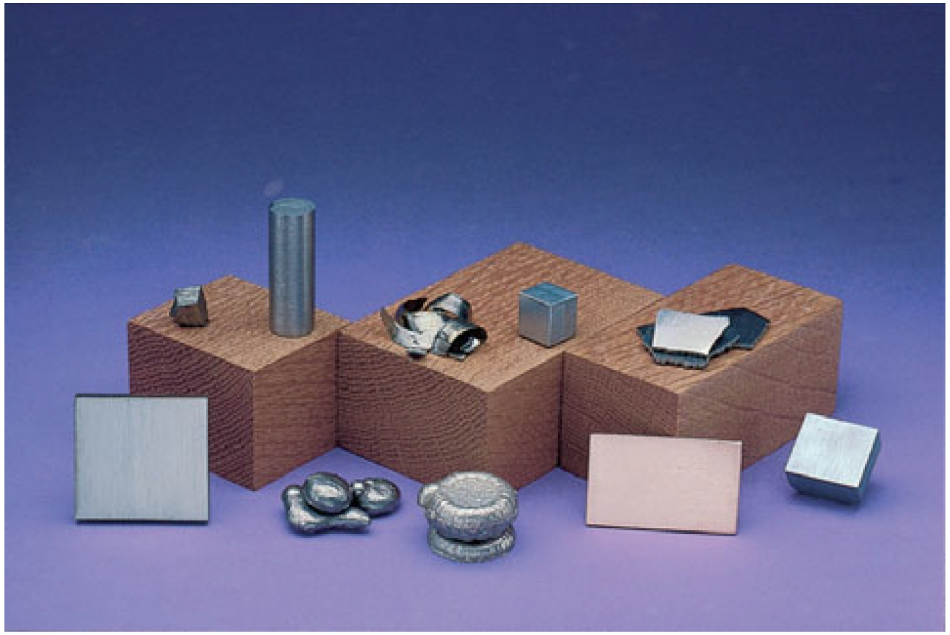


Figure 1F.16

1F.6 The general properties of the elements

d-block elements exist in different oxidation states

Most d-block elements form ions **in different oxidation states** because the d-electrons have similar energies and a variable number of them can be lost when they form compounds.

- For example, iron forms Fe^{2+} or Fe^{3+}, copper forms Cu^{+} and Cu^{2+}.

Copper and potassium both have **a single electron in their outermost s-shell**: $4s^1$. Cu forms Cu^{+} and Cu^{2+}, but K only forms K^{+} and **not** K^{2+}, why?

- To form Cu^{2+}, an electron is removed from the d-subshell of $[Ar]3d^{10}$ (second ionization energy: 1958 kJ/mol)
- To form K^{2+}, an electron would have to be removed from potassium's argon-like core (second ionization energy: 3051 kJ/mol)

1F.6 The general properties of the elements

d-block elements are (bio-)catalysts

- Availability of d-orbitals and the similarity of atomic radii of the d-block elements are important for many areas:
- They can accelerate reactions as **catalysts** in industry.

  Catalyst: a substance that accelerates a reaction but is not itself consumed)
- Ability to form ions with different charges is important **in nature**

1F.6 The general properties of the elements

f-block elements

- f-block elements of same period **have very similar radii** and chemical properties
- Separating and isolating lanthanoids ("lanthanides") delayed their use
- Studied intensely for **superconducting** materials
- Actinoids ("actinides") are radioactive
- None of the elements following plutonium occurs naturally on earth in any significant amount

1F.6 The general properties of the elements

Summary

All elements in the s-block are reactive metals.

The p-block elements tend to gain electrons to complete closed shells; they range from metals through metalloids to nonmetals.

All d-block elements are metals with properties between those of s-block and p-block metals. Many d-block elements are capable of forming cations with several different charges.

The skills you have mastered are the ability to

- ☐ Account for periodic trens in atomic radii, ionization energies, electron affinities, and electronegativities.
- ☐ Summarize in a general way the properties of the elements in relation to their location in the periodic table.

Summary: Many properties of the elements, especially their periodic variation, can be predicted through inspection of the periodic table and by considering the concept of effective nuclear charge.

Bonds Between Atoms

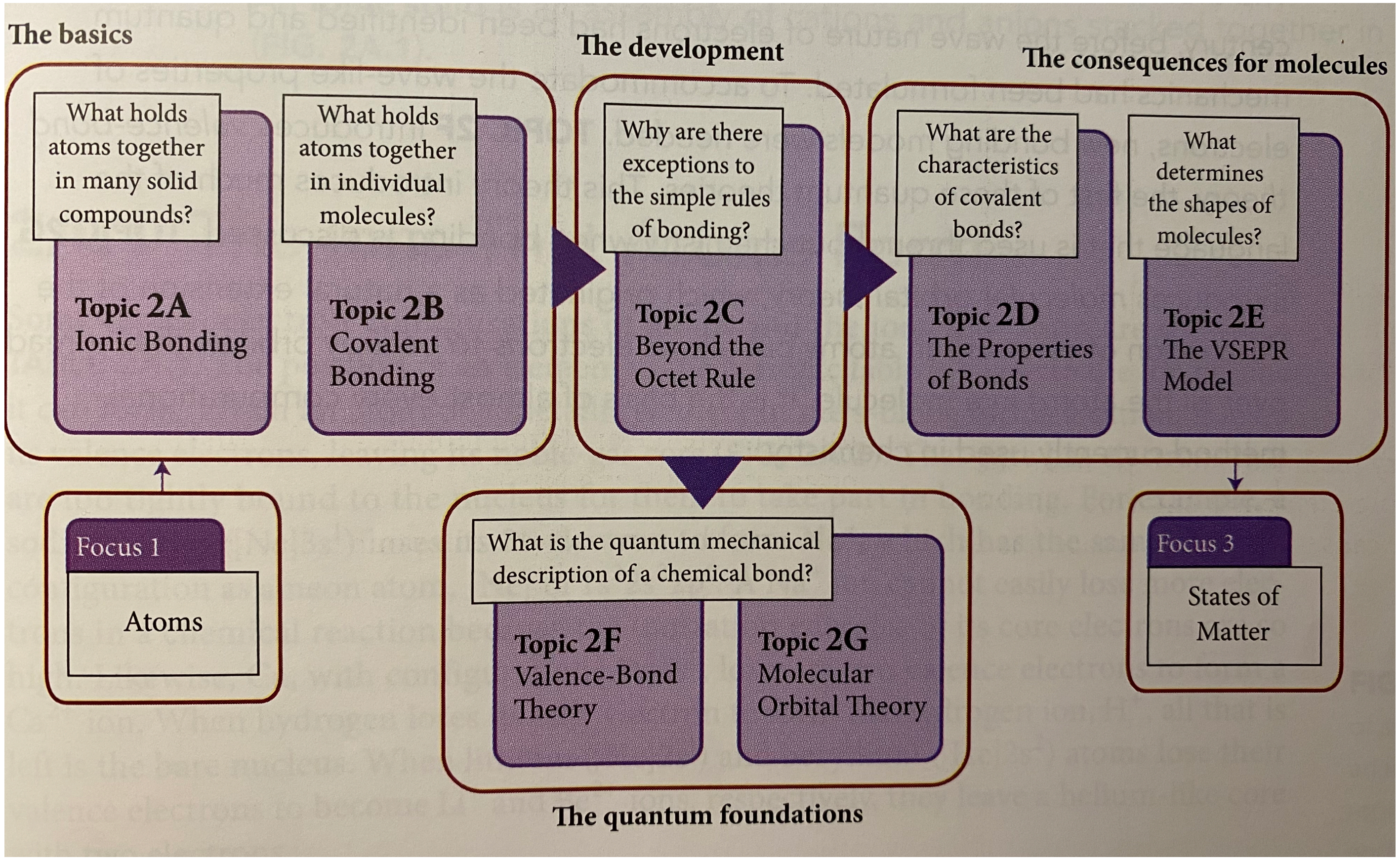
Focus 2

Focus 2: Bonds between atoms

Vale!

- "Vale!" ("Be strong!") was what the Romans said on parting. **Valence is all about strength of links between atoms.**
- A *chemical bond* is the link between atoms that occurs when the valence electrons of two or more atoms move to new locations and settle into lower-energy arrangements.

Overview Chapter 2 (Focus 2: Bonds Between Atoms)



The basics

What holds atoms together in many solid compounds?

Topic 2A
Ionic Bonding

What holds atoms together in individual molecules?

Topic 2B
Covalent Bonding

The development

Why are there exceptions to the simple rules of bonding?

Topic 2C
Beyond the Octet Rule

The consequences for molecules

What are the characteristics of covalent bonds?

Topic 2D
The Properties of Bonds

What determines the shapes of molecules?

Topic 2E
The VSEPR Model

Focus 1
Atoms

What is the quantum mechanical description of a chemical bond?

Topic 2F
Valence-Bond Theory

Topic 2G
Molecular Orbital Theory

The quantum foundations

Focus 3
States of Matter

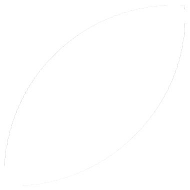
Focus 2: Bonds between atoms

Overview over focus 2

- **Complete transfer of electrons between atoms**: formation of ions and **ionic** compounds (Topic 2A).
- **Incomplete transfer of electrons**: formation of **covalent** bonds (Topic 2B).
- Exceptions to the octet rule (Topic 2C).
- Topic 2D explores how the **properties of bonds can be explained**.
- Topic 2E shows how the **shapes of molecules** can be predicted.
- To accommodate the wave-like properties of electrons, a new bonding model, the **valence-bond theory** was developed (Topic 2F).
- Topic 2G introduces the **molecular orbital theory**, a theory that explains how electrons occupy orbitals in molecules.

Ionic Bonding

Topic 2A



Topic 2A.1 The ions that atoms form
Topic 2A.2 Lewis symbols
Topic 2A.3 The energetics of ionic bond formation
Topic 2A.4 Interactions between ions

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- One of the principal kinds of bonding in compounds.

WHAT DO YOU NEED TO KNOW ALREADY?

- Electron configurations of many-electron atoms (Topic 1E)
- Potential energy, nature of Coulomb interaction between charges (Fundamentals A)
- Ionic radius, ionization energy, and electron affinity (Topic 1F)

The Ions that Atoms Form

Topic 2A.1

2A.1: The ions that atoms form

Ionic solids

- The **ionic model** is a description of chemical bonding in terms of **electrostatic interactions** between ions.
- It is particularly appropriate for describing binary compounds formed between **metallic and nonmetallic** elements, such as sodium chloride (NaCl).
- An **ionic solid** is an assembly of cations and anions stacked together in a regular array (Fig. 2A.1).

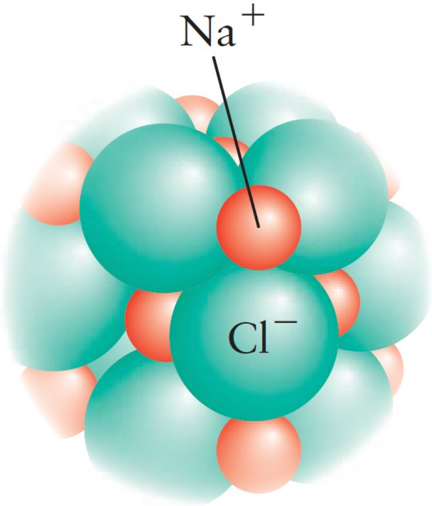


Figure 2A.1

2A.1: The ions that atoms form

Typical electron configurations of atoms and the ions they form

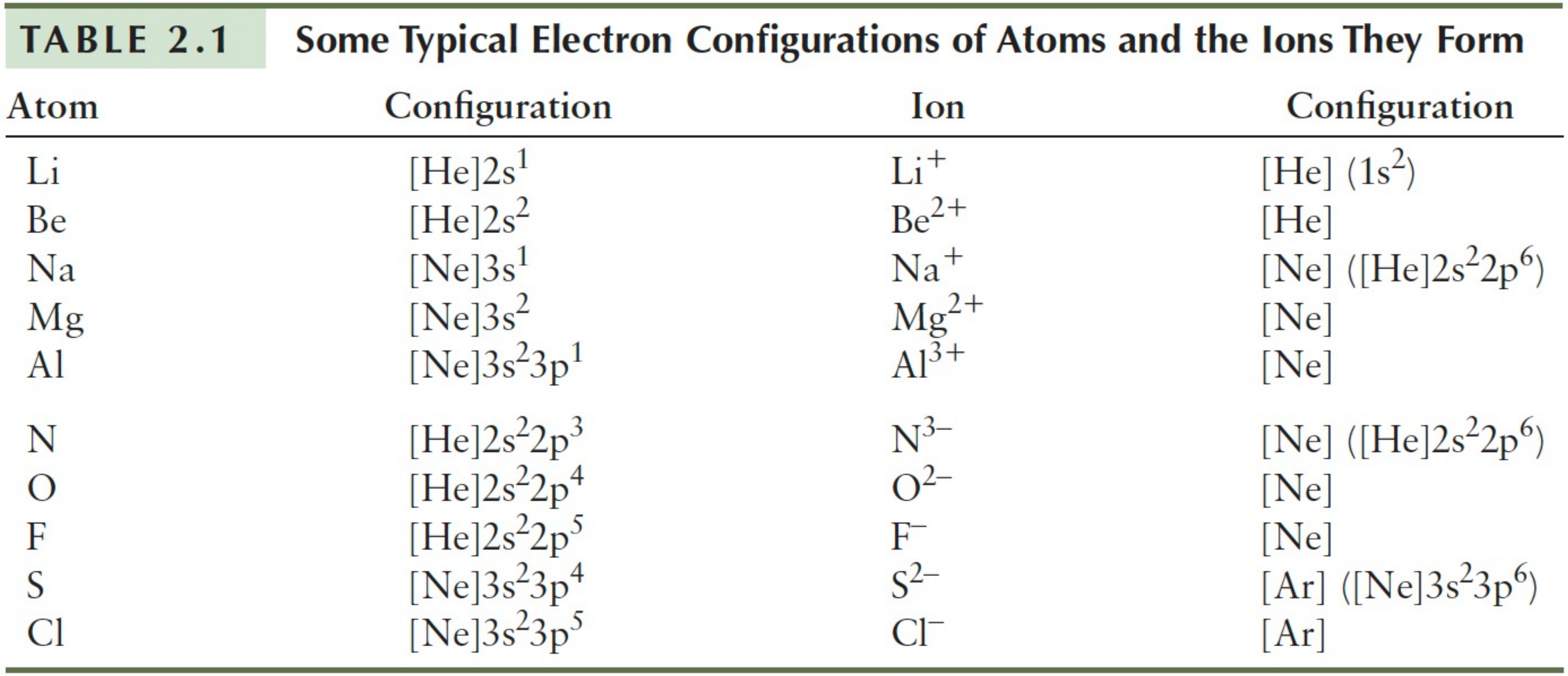


TABLE 2.1 Some Typical Electron Configurations of Atoms and the Ions They Form

Atom	Configuration	Ion	Configuration
Li	$[He]2s^1$	Li^+	$[He]$ $(1s^2)$
Be	$[He]2s^2$	Be^{2+}	$[He]$
Na	$[Ne]3s^1$	Na^+	$[Ne]$ $([He]2s^22p^6)$
Mg	$[Ne]3s^2$	Mg^{2+}	$[Ne]$
Al	$[Ne]3s^23p^1$	Al^{3+}	$[Ne]$
N	$[He]2s^22p^3$	N^{3-}	$[Ne]$ $([He]2s^22p^6)$
O	$[He]2s^22p^4$	O^{2-}	$[Ne]$
F	$[He]2s^22p^5$	F^-	$[Ne]$
S	$[Ne]3s^23p^4$	S^{2-}	$[Ar]$ $([Ne]3s^23p^6)$
Cl	$[Ne]3s^23p^5$	Cl^-	$[Ar]$

2A.1: The ions that atoms form

s-block elements

- s-block elements lose their valence electrons to leave a noble gas core (Fig. 2A.2).
- Core has electrons that are **too tightly bound** to the nucleus for them to take part in bonding.
- Sodium ([Ne]$3s^1$) loses its 3s-electron to form Na^+
- Ca ([Ar]$4s^2$) loses ist two 4s-electrons to form Ca^{2+}
- Hydrogen loses its only 1s-electron to form H^+, a bare nucleus.

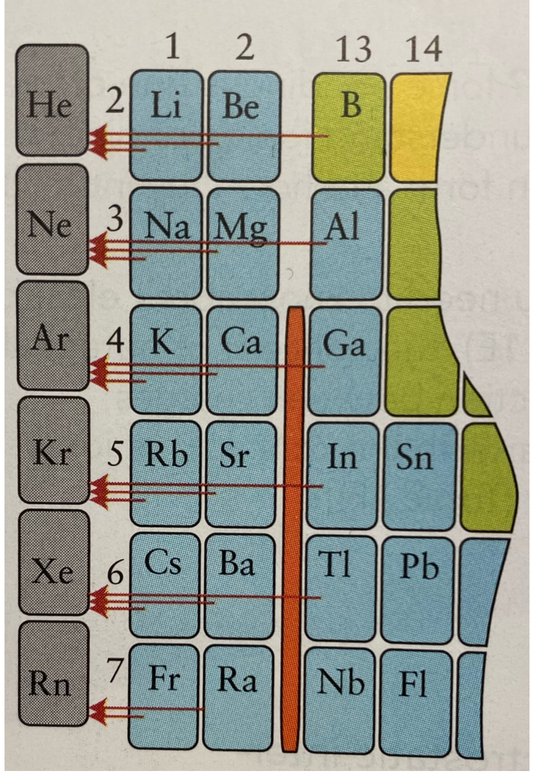


Figure 2A.2

2A.1: The ions that atoms form

p-block elements

Group 13, 14: on the left of p-block

- Period 3: Aluminum ([Ne]$3s^23p^1$) forms Al^{3+}
- Period 4: Gallium ([Ar]$3d^{10}4s^24p^1$) forms Ga^{3+} with configuration [Ar]$3d^{10}$
- A complete d-shell is stabilized and not easy to remove.

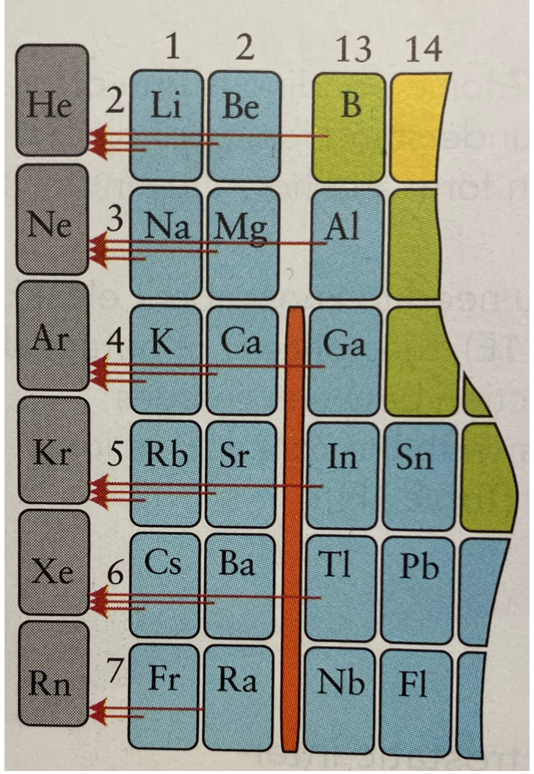


Figure 2A.2

2A.1: The ions that atoms form

d-block elements

- d-block elements can lose a variable number of electrons: **variable valence.**
- When d-block elements form ions, the *n*s-electrons are lost first, followed by a variable number of (*n*-1)d-electrons

E.g. Fe ([Ar]$3d^6 4s^2$) → Fe^{2+} ([Ar]$3d^6$) → Fe^{3+} ([Ar]$3d^5$)

Iron ([Ar]$3d^6 4s^2$) rarely goes beyond losing three electrons to form cation Fe^{4+}

- d-block behavior **not always easy to predict**:

E.g. copper ([Ar]$3d^{10} 4s^1$) forms Cu^+ ([Ar]$3d^{10}$) and Cu^{2+} with configuration [Ar]$3d^9$, but not Cu^{3+} with [Ar]$3d^8$

2A.1: The ions that atoms form

Variable valence in the lower p-block: inert-pair effect

- Group 13: compare aluminum ([Ne]$3s^2p^1$) and indium ([Kr]$4d^{10}5s^25p^1$):
- Aluminum only forms Al^{3+}
- Indium forms In^+ and In^{3+} with [Kr]$4d^{10}5s^2$ and [Kr]$4d^{10}$, respectively.
- The ability of elements to form ions **two units lower in charge than expected** from the group number is called the **inert-pair effect** because the pair of 5s-electrons remains on the ion in the former case and is therefore relatively "inert".

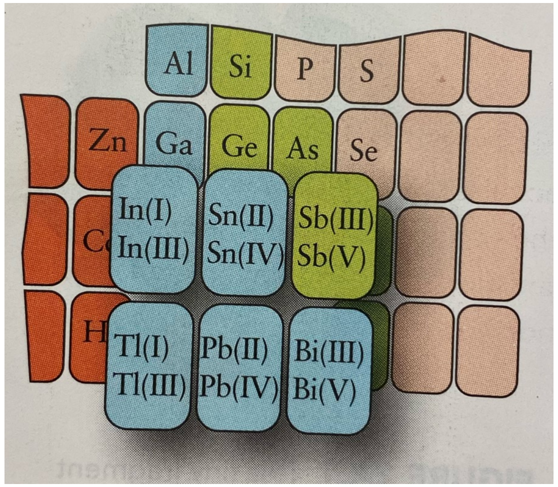


Figure 2A.3

Write the electron configuration of the lead(IV) ion.

Rank	Responses
1	[XE] 4F14 5D10
2	[XE]5D^10
3	XE 4F14 5D10
4	[XE]4F145D10
5	[XE]5D10
6	[XE]6S(2)5D(8)

Keyword:

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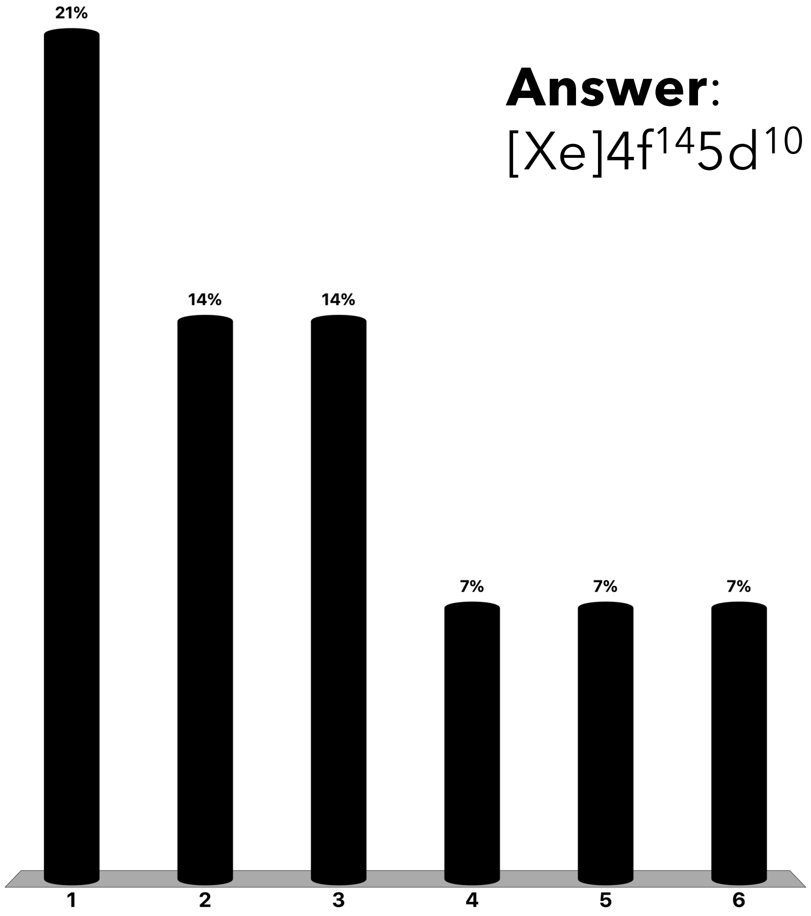
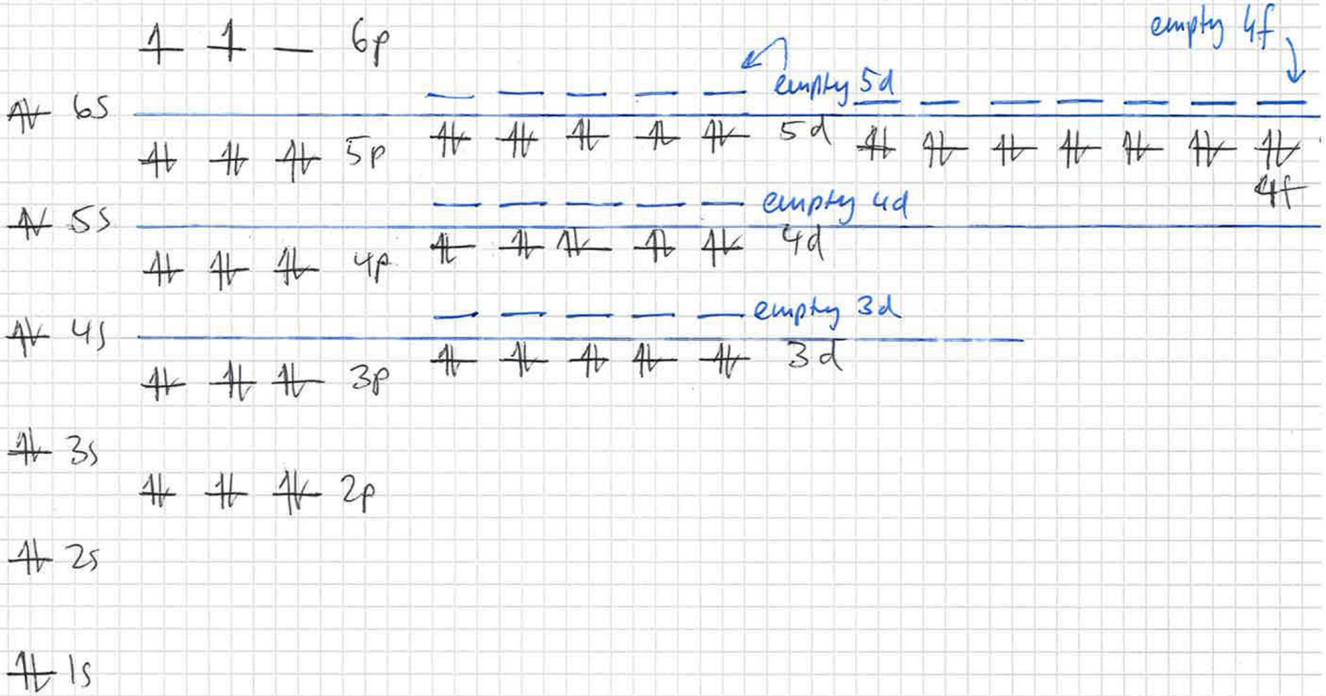


Answer:
$[Xe]4f^{14}5d^{10}$

Pb : $Z = 82$ $[Xe]\,4f^{14}\,5d^{10}\,6s^{2}\,6p^{2}$



2A.1: The ions that atoms form

Nonmetals gain electrons

- Ionization energies too high:
- Nonmetals are likely to **gain electrons** and **form anions**
- Anions with **noble gas configurations: duplet** (helium-like configuration, $1s^2$) or **octet** (eight valence-electron configuration, ns^2np^6)
- E.g. hydrogen becomes the hydride ion, H^-
- Nitrogen becomes the nitride ion, N^{3-} ($[He]2s^22p^6$)

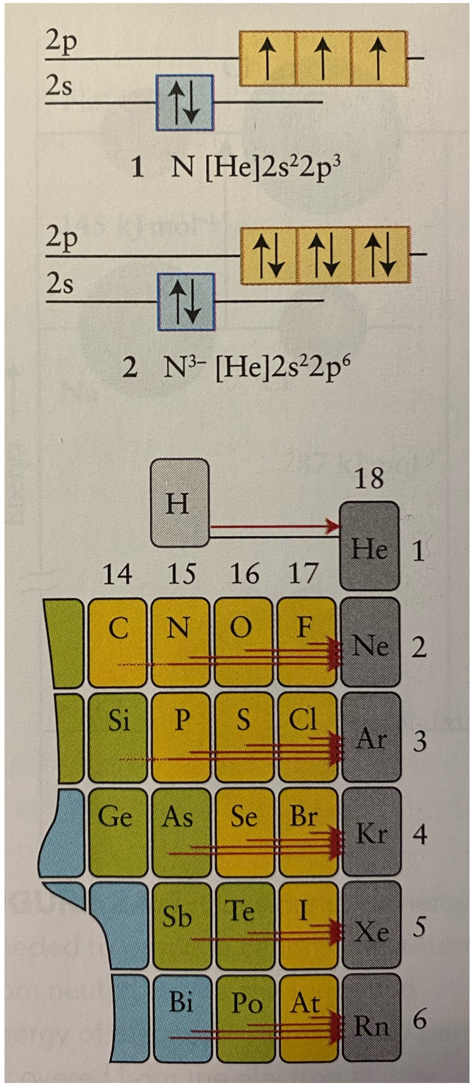


Figure 2A.4

2A.1: The ions that atoms form

Nonmetals gain electrons

- When electron affinity is positive, as for halogens, **energy is released** when an electron is added to the valence shell.
- A chloride ion ([Ne]$3s^2 3p^6$) has a lower energy than a chlorine atom ([Ne]$3s^2 3p^5$) plus a free electron.
- Adding a second electron to chloride to form Cl^{2-} requires energy.
- Add **just enough electrons to complete an octet** in a valence shell, but no more.

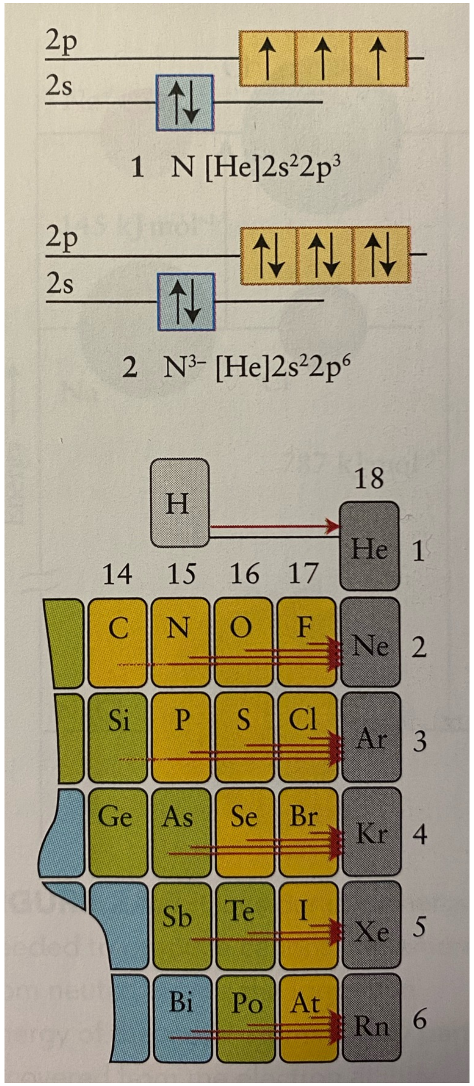


Figure 2A.4

Predict the electron configuration of the iodide ion.

Rank	Responses
1	[XE]
2	[KR] 4D10 5S...
3	[KR]4D10 5S2...
4	I-
5	XE
6	(KR) 4D10 5S...

Keyword:

Keyword Matches: 0

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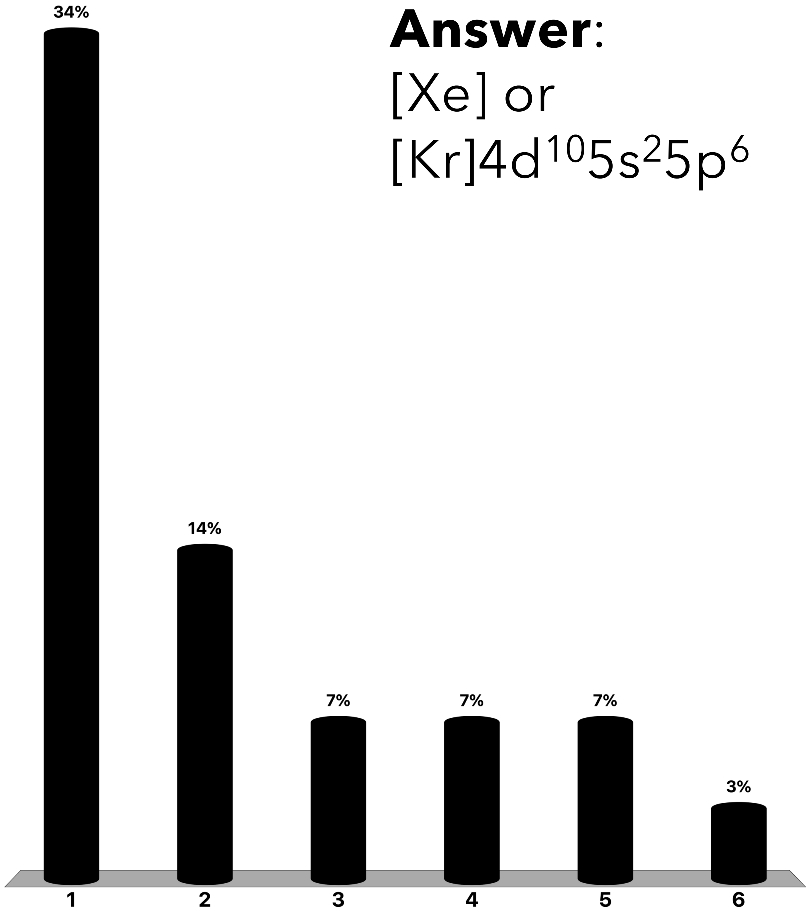


Answer:
[Xe] or
$[Kr]4d^{10}5s^{2}5p^{6}$

2A.1: The ions that atoms form

Summary

To predict the electron configuration of a monatomic **cation**, remove the outermost electrons **in the order *n*p, *n*s and (*n*-1)d.**

d-block elements and elements lower in the p-block often display variable valence.

For a monatomic **anion**, **add electrons** until the next **noble-gas configuration** has been reached.

The transfer of electrons results in the formation of an octet (or duplet) of electrons in the valence shell on each of the ions.

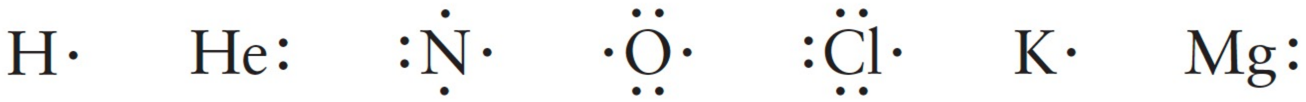
Lewis Symbols

Topic 2A.2

2A.2: Lewis symbols

G. N. Lewis

- G. N. Lewis was among the first to recognize that the recently discovered electron was key to chemical bonding.
- He devised a simple way to keep track of valence electrons when atoms form ions.
- Each valence electron is **represented as a dot**
- Arranged **around the element**
- Modern interpretation: a single dot is an electron in an orbital, **a pair of dots represents two paired electrons sharing an orbital**.



2A.2: Lewis symbols

G. N. Lewis

- Nitrogen: $2s^2 2p_x^1 2p_y^1 2p_z^1$

- An ionic compound consists of charged ions, electrically neutral.
- Electrons removed from atoms of metallic elements must find a home in the orbitals of the nonmetallic elements.

2A.2: Lewis symbols

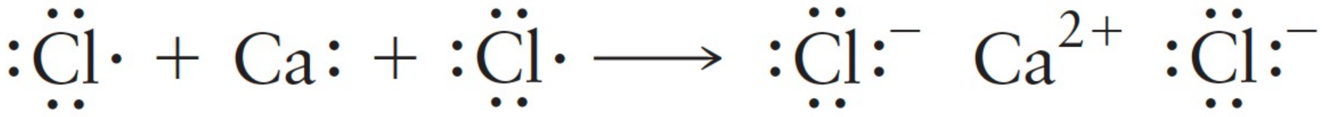
Lewis symbol rules for ionic solids

- Represent the **cation** by **removing the appropriate number of dots** from the symbol from the atom of the metallic element.
- Represent the **anion** by transferring those dots to the Lewis symbol for the atom of the nonmetallic element to **complete its valence shell**.
- If necessary, **adjust the numbers of atoms** of each kind so that all the dots removed from the atoms of the metallic element are accommodated by the atoms of the nonmetallic element.
- Write the **charge** of each ion as a superscript.

2A.2: Lewis symbols

Lewis symbol rules with calcium chloride as an example

- Calcium atom loses two valence electrons: Ca^{2+}
- Chloride gains one electron: Cl^-



- The ratio of two chloride ions for each calcium ion results in the formula $CaCl_2$.
- **Note**: this formula denotes a **formula unit**, not a molecule. There are no individual $CaCl_2$ molecules, a crystal of calcium chloride consissts of a huge number of these ions in 3D arrays, with two Cl^- ions for each Ca^{2+} ion.

2A.2: Lewis symbols

Self-test: Draw the formula unit of magnesium bromide using Lewis symbols.

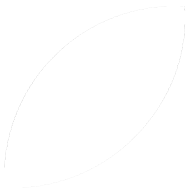
2A.2: Lewis symbols

Summary

Formulas of compounds consisting of the monatomic ions of main-group elements can be predicted by assuming that **cations have lost all their valence electrons** and **anions have gained electrons in their valence shells until each ion has an octet** of electrons, or a duplet in the case of H, Li, and Be.

The Energetics of Ionic Bond Formation

Topic 2A.3



2A.3: The energetics of ionic bond formation

A crystal of NaCl

- A crystal of NaCl has a lower energy compared to separated Na plus Cl atoms
- The formation of the solid is imagined as taking place **in three hypothetical steps**, starting with gaseous sodium and chlorine atoms:

1. Electrons are removed from gaseous sodium atoms.
2. These removed electrons attach to gaseous chlorine atoms.
3. The resulting gaseous cations and anions clump together as a solid crystal.

$Na(g) \rightarrow Na^+(g) + e^-(g)$ Energy required = 494 kJ/mol

$Cl(g) + e^- \rightarrow Cl(g)$ Energy released = 349 kJ/mol

Net change in energy: +145 kJ/mol

A gas of widely separated Na$^+$ and Cl$^-$ ions has a higher energy than a gas of neutral Na and Cl ions.

2A.3: The energetics of ionic bond formation

The lattice energy

- What happens when Na^+ and Cl^- come together to form a crystalline solid:
- Difference in energy between the ions of a compound when they are widely separated and when they are packed together in a solid is called the **lattice energy**, which is **usually very large**.
- "Lattice": orderly arrangement of ions in a crystal

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \qquad \text{Energy released = 787 kJ/mol}$$

- The net change in energy for the overall process is 145 – 787 kJ/mol = **–642 kJ/mol**

$$Na(g) + Cl(g) \rightarrow NaCl(s) \qquad \text{Energy released = 642 kJ/mol}$$

- **Conclusion**: A solid composed of Na^+ and Cl^- ions has a much lower energy than a collection of widely separated Na and Cl atoms.

2A.3: The energetics of ionic bond formation

The lattice energy

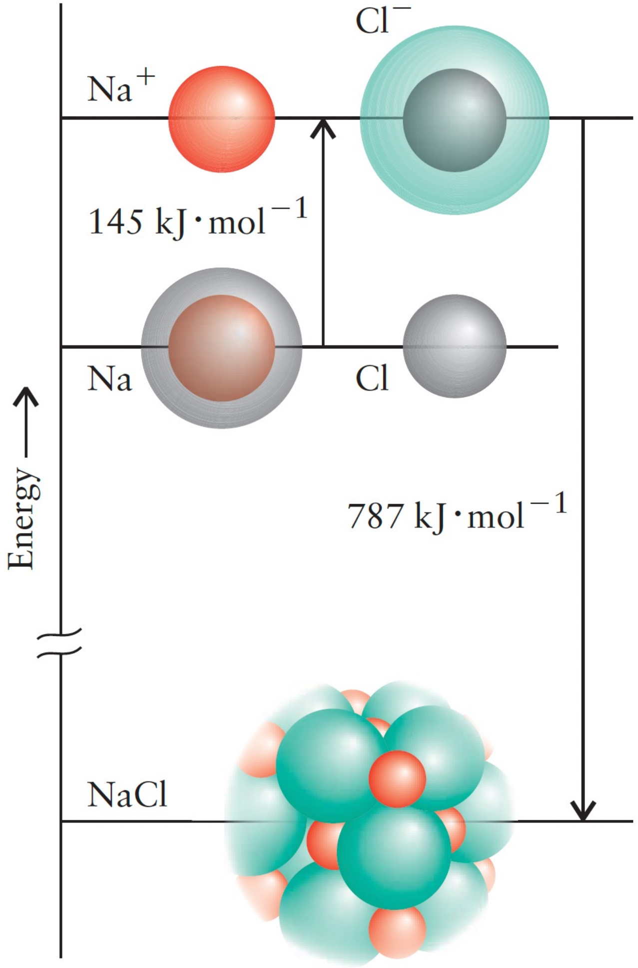


Figure 2A.6

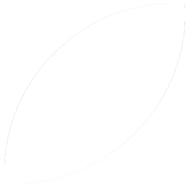
2A.3: The energetics of ionic bond formation

Summary

The decrease in energy that accompanies the formation of an ionic solid is due largely to the attraction between oppositely charged ions.

Interactions Between Ions

Topic 2A.4



2A.4 Interactions between ions

Properties of an ionic solid

- In an ionic solid, there are **no specific bonds.**
- All the cations are attracted to all the anions to some extent.
- All the cations repel one another, all the anions repel one another, to some extent.
- An ionic bond is a **"global" interaction characteristic** of the entire crystal, a net lowering of energy of the entire crystal relative to widely separated neutral atoms
- Ionic solids have a **high melting point**: a high temperature is needed before the ions have enough energy to move past one another and the solid melts to form a liquid.
- **Brittleness**: when an ionic solid is struck by a mechanical force, like a hammer, ions with the same charges come into contact and repel one another, the solid shatters into fragments

2A.4 Interactions between ions

Why ionic solids are brittle

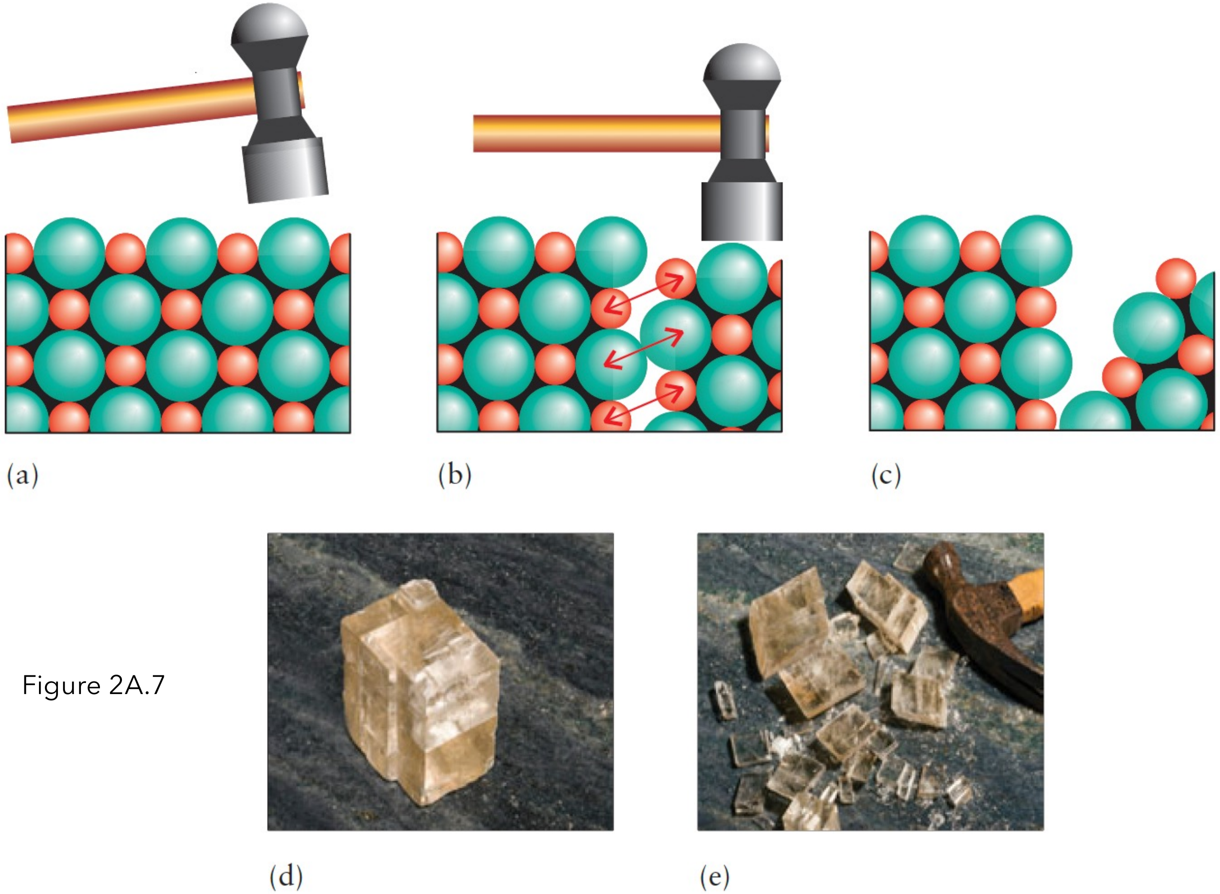


Figure 2A.7

(a) The original solid consists of an orderly arrangement of cations and anions.

(b) A hammer blow can push ions with like charges into adjacent positions; this proximity of like charges results in strong repulsive forces (arrows).

(c) As a result of the repulsive forces, the solid breaks apart.

(d) The smooth faces of this calcite crystal result from the regular arrangement of calcium and carbonate ions.

(e) The blow of a hammer has shattered the crystal, leaving flat, regular surfaces consisting of planes of ions.

2A.4 Interactions between ions

Coulomb potential energy of two individual ions

$$E_{p,12} = \frac{(z_1 e)\times(z_2 e)}{4\pi\varepsilon_0 r_{12}} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_{12}}$$

- $z_1 e$: charge of ion 1 with e, the fundamental charge
- $z_2 e$: charge of ion 2
- r_{12}: distance between the centers of the two ions
- ε_0: the electric constant
- **Note**: The charge number, z, is positive for cations and negative for anions, and the charge of an ion is ze, where e is the fundamental charge. Chemists, however, almost always refer to z itself as the charge and speak of a cahrge of +1, –1, and so on. In other words, chemists typically refer to charge as **multiples of the fundamental charge**.

2A.4 Interactions between ions

Potential energy in a 3D array of ions with different charges

- Every ion in an ionic solid is attracted to all the oppositely charged ions and repelled from all the other ions with like charges.

$$E_p = A \times \frac{N_A z_1 z_2 e^2}{4\pi\varepsilon_0 d}$$

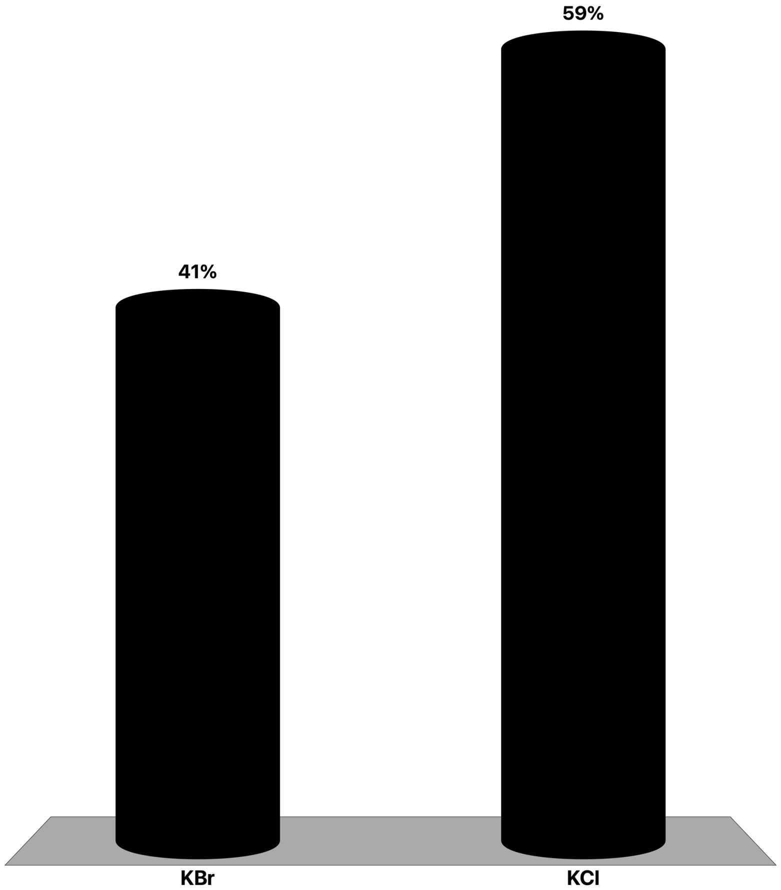
- Note that $z_1 z_2$ is **negative**, as the ions have opposite charges.
- The factor A is a numerical coefficient called the **Madelung constant**, its value depends on how the ions are arranged about one another (see **Topic 3G**)
- The potential energy **is strongly negative** when the ions are highly charged (large values of z) and when the separation between them is small (small values of d)

The ionic solids KBr and KCl crystallize to form structures of the same type. In which compound are the interactions between ions stronger?

A. KBr

B. KCl

Answer: Since both KCl and KBr consist of K^+ ions and either Cl^- or Br^- ions, the charges are the same. The answer is mainly determined by the **ionic radii** of the anions. The **chloride ion (Cl^-)** is **smaller** than the **bromide ion (Br^-)**. According to **Coulomb's law**, the smaller the distance between the ions, the stronger the electrostatic attraction between them, and thus the stronger the lattice energy.



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2A.4 Interactions between ions

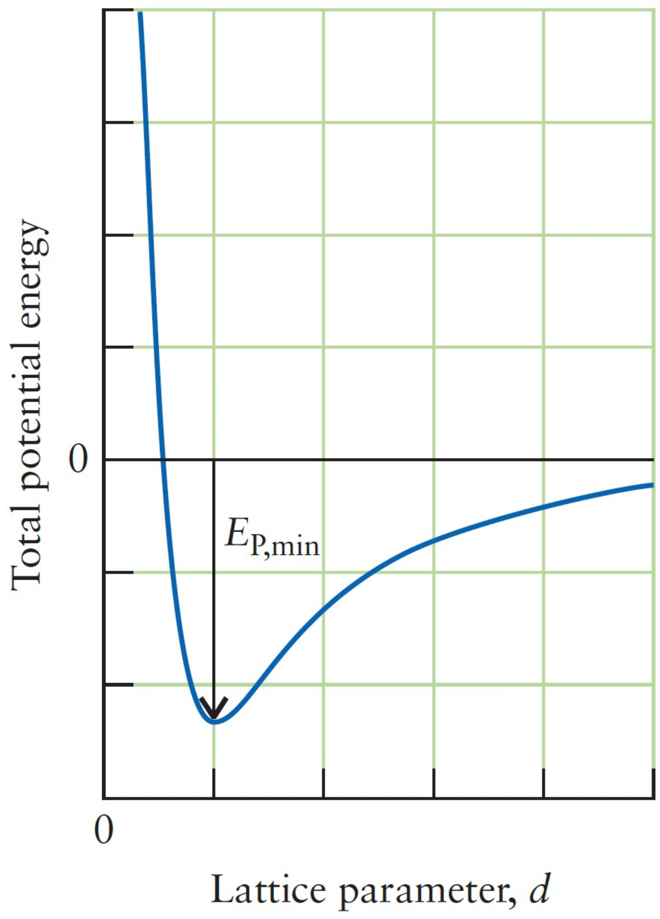
Potential energy of interaction

- Potential energy becomes **more negative** as separation (d) **decreases**
- As soon as the ions come into contact: **repulsive effects** between neighbors become important: energy quickly rises again.
- Repulsive contribution to the potential energy rises rapidly with decreasing separation:

$$E_p^* \propto e^{-\frac{d}{d^*}} \text{ with } d^* \text{ a constant (usually 34.5 pm)}$$

- The total energy is the sum of E_p and E_p^* and passes through a minimum as the ions approach each other, then rises sharply again when they are very lcose (**Fig. 2A.10**).

Figure 2A.10



2A.3: The energetics of ionic bond formation

Summary

Ionic solids typically have high melting points and are brittle. The lattice energy of an ionic solid is large when the ions are small and highly charged.

The skills you have mastered are the ability to

- ☐ Write the electron configuration for an ion.
- ☐ Account for the formation of ions in terms of ionization energy, electron affinity, and the electrostatic interactions between them.
- ☐ Predict the chemical formula of an ionic compound and draw its formula unit by using Lews symbols
- ☐ Account for the origin and magnitude of the lattice energy.

Summary: You have learned that in ionic bonding, electrons are transferred from one atom to another and that the patterns of ionic bond formation can be represented by formula units based on Lewis symbols. You have seen that the greater the charge and the smaller the ion, the greater the energy lowering when an ionic solid forms from widely separated atoms.

Student questions

Is there any easy way to remember the order of orbitals in the building-up principle?

1. Look at the periodic table
2. Follow this trick:

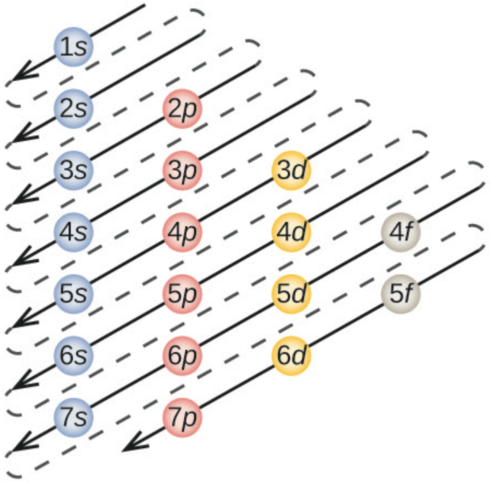


Figure source: https://wisc.pb.unizin.org/minimisgenchem/chapter/electron-configurations-orbital-box-notation-m7q7/

Student questions

Here's another image to show you the relative energies of **empty** orbitals.

Be aware that energies change after orbitals are filled. E.g. the *n*d-orbitals will be lower compared to their (*n*+1)s-orbitals after filling.

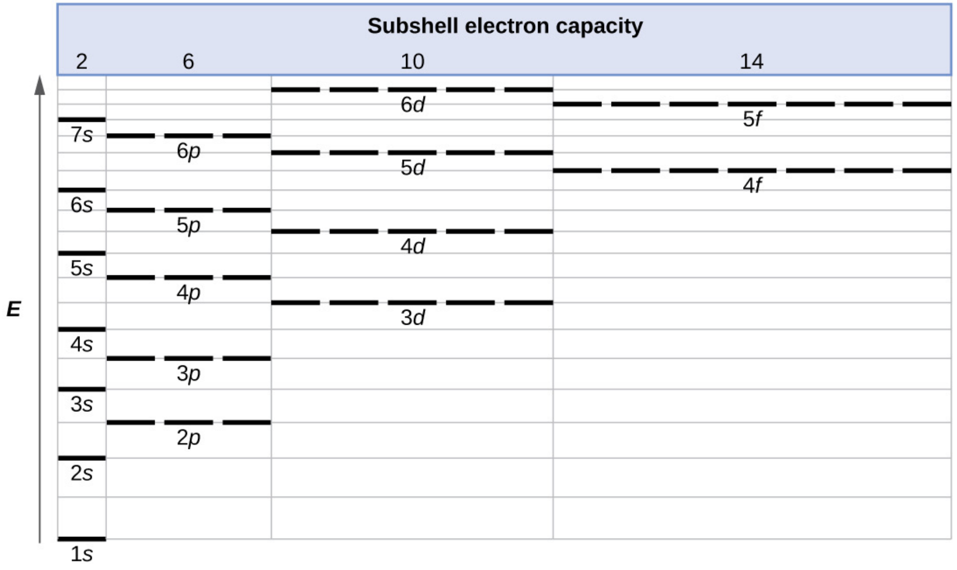


Figure source: https://wisc.pb.unizin.org/minimisgenchem/chapter/electron-configurations-orbital-box-notation-m7q7/

Student questions

What is the definition of "valence electrons"? For example, what are the valence electrons for iodide? Do we include the filled 4d-orbitals in the valence shell?

Definition in our textbook "the electrons in the outermost shell".

A more refined definition:

For the **main group elements**, the valence electrons are defined as those electrons residing in the electronic shell of **highest principal quantum number *n***.

- Iodide, I^-, with electronic configuration $[Kr]4d^{10}5s^25p^6$ has eight valence electrons, the 4d-electrons don't count.

For the **transition metals**, a valence electron is defined as an electron that resides **outside a noble-gas core**. In the transition metal block, the d-orbitals are very close in energy to the s-orbitals and thus, both are important for the reactivity of these metals and are both considered valence electrons.

- For example, manganese, Mn, with electronic configuration $[Ar]4s^23d^5$ has seven valence electrons.