Chemical Bonding

Bonding Theories: Learning Outcomes

Electrovalent and covalent bonding,	1. Write Lewis dot representations of atoms 2. Predict whether bonding between specified elements will be primarily ionic, covalent or polar covalent 3. Write Lewis dot and dash formulas for molecules and polyatomic ions 4. Recognize exceptions to the octet rule 5. Write formal charges for atoms in covalent structures 6. Describe resonance and know when to write resonance structures and how to do so
hydrogen bonding, Van der Waals force, metallic bonding and conductivity of metal,	7. Explain different types of bonding

molecular geometry	**8. Describe the basic ideas of the valence shell electron pair repulsion (VSEPR) theory** **9. Use the VSEPR theory to predict the electronic geometry and the molecular geometry of polyatomic molecules and ions** **10. Describe the relationships between molecular shapes and polarities** **11. Predict whether a molecule is polar or nonpolar**
valence bond theory	**12. Describe the basic ideas of the valence bond (VB) theory** **13. Analyze the hybrid orbitals used in bonding in polyatomic molecules and ions** **14. Use the the theory of hybrid orbitals to describe the bonding in double and triple bonds**
orbital molecule theory	**15. Describe the basic concepts of molecular orbital theory** **16. Distinguish among bonding, antibonding and nonbonding orbitals** **17. Construct molecular orbital energy level diagram for homonuclear and heteronuclear diatomic molecule of elements** **18. Calculate the bond order and relate it to bond stability**

Lewis Dot Formulas of Atoms

- Lewis dot formulas or Lewis dot representations are a convenient bookkeeping method for tracking **valence electrons.**
  - Valence electrons are those electrons that are transferred or involved in chemical bonding.
    - They are chemically important.

Lewis Symbols and the Octet Rule

- Valence electrons are found in the outermost orbitals or an atom.
- may be represented as dots around the symbol of the element.
- The number of electrons available for bonding are indicated by unpaired dots.

Lewis Symbols and the Octet Rule

These symbols are called Lewis symbols.

We generally place the electrons on four sides of a square around the element symbol.

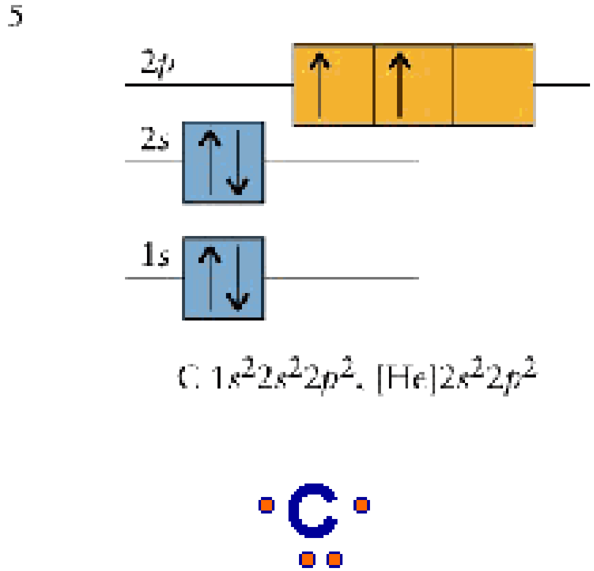
Octet rule: we know that s^2p^6 is a noble gas configuration.

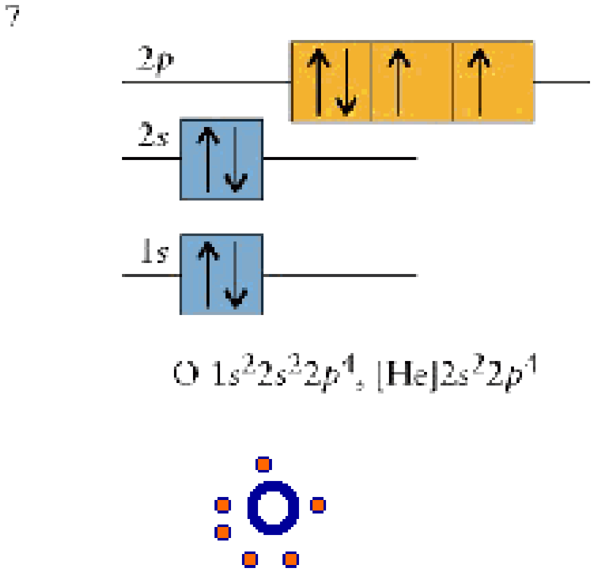
We assume that an atom is stable when surrounded by **8** electrons (4 electron pairs).

TABLE 8.1 Electron-Dot Symbols

Element	Electron Configuration	Electron-Dot Symbol
Li	[He]$2s^1$	Li•
Be	[He]$2s^2$	•Be•
B	[He]$2s^2 2p^1$	•Ḃ•
C	[He]$2s^2 2p^2$	•Ċ•
N	[He]$2s^2 2p^3$	•Ṅ:
O	[He]$2s^2 2p^4$	:Ȯ:
F	[He]$2s^2 2p^5$	•F:
Ne	[He]$2s^2 2p^6$	:Ne:

Examples





Represent **valence electrons** only!

Lewis Electron-Dot Symbols

For main group elements -

→ The A group number gives the number of valence electrons.

→ Place one dot per valence electron on each of the four sides of the element symbol.

→ Pair the dots (electrons) until all of the valence electrons are used.

Example:

Nitrogen, N, is in Group 5A and therefore has 5 valence electrons.

Lewis Electron-Dot Symbols for Elements in Periods 2 & 3

Period	1A(1)	2A(2)	3A(13)	4A(14)	5A(15)	6A(16)	7A(17)	8A(18)
	ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
2	Li	Be	B	C	N	O	F	Ne
3	Na	Mg	Al	Si	P	S	Cl	Ar

Octet Rule

- Transfer or sharing of electrons results in the formation of an octet of electrons
- Electronic configuration of s^2p^6 on each atom
- When main group metal atom forms a cation, it loses its s valence electrons and acquires the electron configuration of the preceding noble gas
- When p-block elements acquire electrons and form anions, they do so until they have reached the electron configuration of the following noble gas

Types of Chemical Bonding

1. **Metal with nonmetal:**

   electron transfer and ionic bonding

2. **Nonmetal with nonmetal:**

   electron sharing and covalent bonding

3. **Metal with metal:**

   electron pooling and metallic bonding

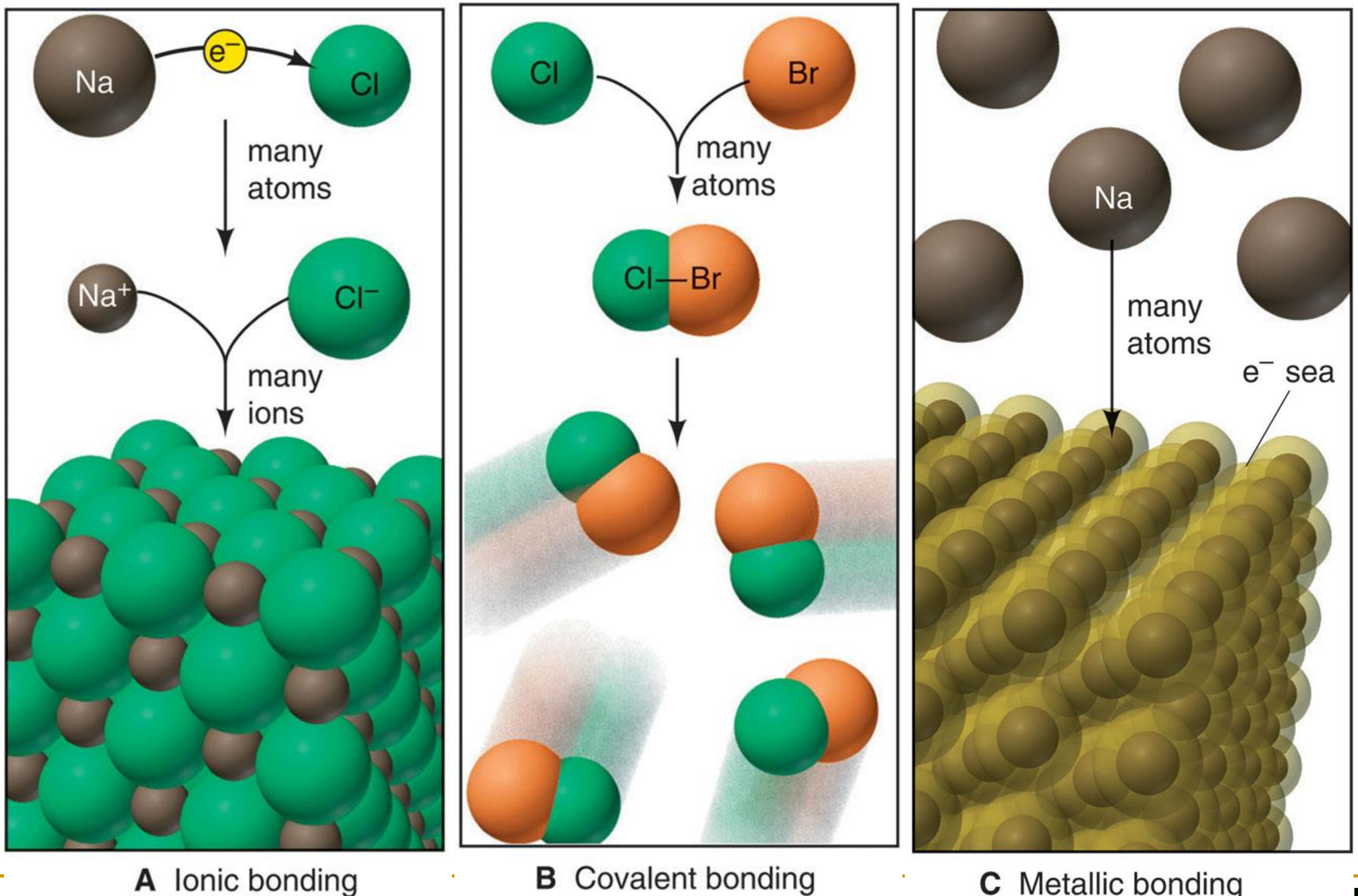
Introduction

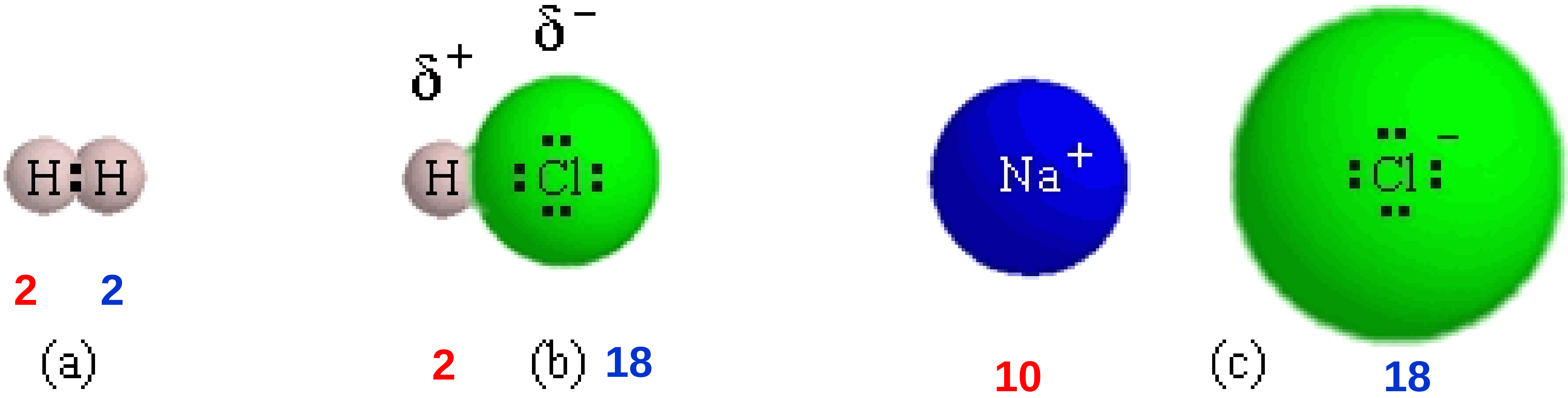
- ***Ionic bonding*** results from electrostatic attractions among ions, which are formed by the transfer of one or more electrons from one atom to another.

- ***Covalent bonding*** results from sharing one or more electron pairs between two atoms.

Figure 9.2

The three models of chemical bonding





Electrons in nonpolar covalent, polar covalent, and ionic bonds:

(a) the electrons are *shared equally*; **(covalent bond)**

(b) the electrons are held *closer to the more-negative* chlorine atom;

(polar covalent bond)

(c) one electron has been *transferred* from sodium to chlorine.

(ionic / electrovalent bond)

Comparison of Ionic and Covalent Compounds

- <u>Melting point comparison</u>
  - Ionic compounds are usually solids with high melting points
    - Typically > $400^{o}C$
  - Covalent compounds are gases, liquids, or solids with low melting points
    - Typically < $300^{o}C$
- <u>Solubility in polar solvents</u>
  - Ionic compounds are generally soluble
  - Covalent compounds are generally insoluble

Comparison of Ionic and Covalent Compounds

- <u>Solubility in nonpolar solvents</u>
  - Ionic compounds are generally insoluble
  - Covalent compounds are generally soluble
- <u>Conductivity in molten solids and liquids</u>
  - Ionic compounds generally conduct electricity
    - They contain mobile ions
  - Covalent compounds generally do not conduct electricity

Comparison of Ionic and Covalent Compounds

- <u>Conductivity in aqueous solutions</u>
  - Ionic compounds generally conduct electricity
    - They contain mobile ions
  - Covalent compounds are poor conductors of electricity
- <u>Formation of Compounds</u>
  - Ionic compounds are formed between elements with large differences in electronegativity
    - Often a metal and a nonmetal
  - Covalent compounds are formed between elements with similar electronegativities
    - Usually two or more nonmetals

Electrovalent / Ionic Bonds

- An ionic bond is the electrostatic forces of attraction between 2 oppositely charged ions formed as a result of the *complete transfer* of one or more electrons from one atom to another.

a) The atom that loses electron (usually a metal) becomes a positive ion or *cation*, while the atom that gains electron (usually non-metal) becomes a negative ion or *anion*.

b) The cation and anion formed usually have the electron *configuration of an inert gas* (octet rules)

Ionic Bonding

Formation of Ionic Compounds

- An **ion** is an atom or a group of atoms possessing a net electrical charge.
- Ions come in two basic types:

1. positive (+) ions or cations
   - These atoms have lost 1 or more electrons.
2. negative (-) ions or anions
   - These atoms have gained 1 or more electrons.

Formation of Ionic Compounds

- An ion will be formed most easily if

a) The electronic structure of the ion is stable.

b) The charge on the ion formed is small *(limit: +4 for cation and -3 for anion).*

c) The cation is formed from a large atom, while the anion is formed from a small atom. *(i.e. low ionisation energy for cation and high electron affinity for anion).*

Formation of Ionic Compounds

- Monatomic ions consist of one atom.
  - Na^+, Ca^{2+}, Al^{3+} - cations
  - Cl^-, O^{2-}, N^{3-} -anions

- Polyatomic ions contain more than one atom.
  - NH_4^+ - cation
  - NO_2^-,CO_3^{2-}, SO_4^{2-} - anions

Formation of Ionic Compounds

- Reaction of Group IA Metals with Group VIIA Nonmetals

IA metal	VIIA nometal	
$2\,Li_{(s)}$ +	$F_{2(g)}$ →	$2\,LiF_{(s)}$
silver	yellow	white solid
solid	gas	with an $842^{o}C$
		melting point

Formation of Ionic Compounds

- The underlying reason for the formation of LiF lies in the electron configurations of Li and F.

	1s	2s	2p
Li	↑↓	↑	
F	↑↓	↑↓	↑↓↑↓↑

These atoms form ions with these configurations.

	1s	2s	2p	
Li^+	↑↓			same configuration as [He]
F^-	↑↓	↑↓	↑↓ ↑↓ ↑↓	same configuration as [Ne]

Formation of Ionic Compounds

- The Li^+ ion contains two electrons, same as the helium atom.
  - Li^+ ions are isoelectronic with helium.
- The F^- ion contains ten electrons, same as the neon atom.
  - F^- ions are isoelectronic with neon.
- *Isoelectronic* species contain the same number of electrons.

Formation of Ionic Compounds

- We can also use Lewis dot formulas to represent the neutral atoms and the ions they form.

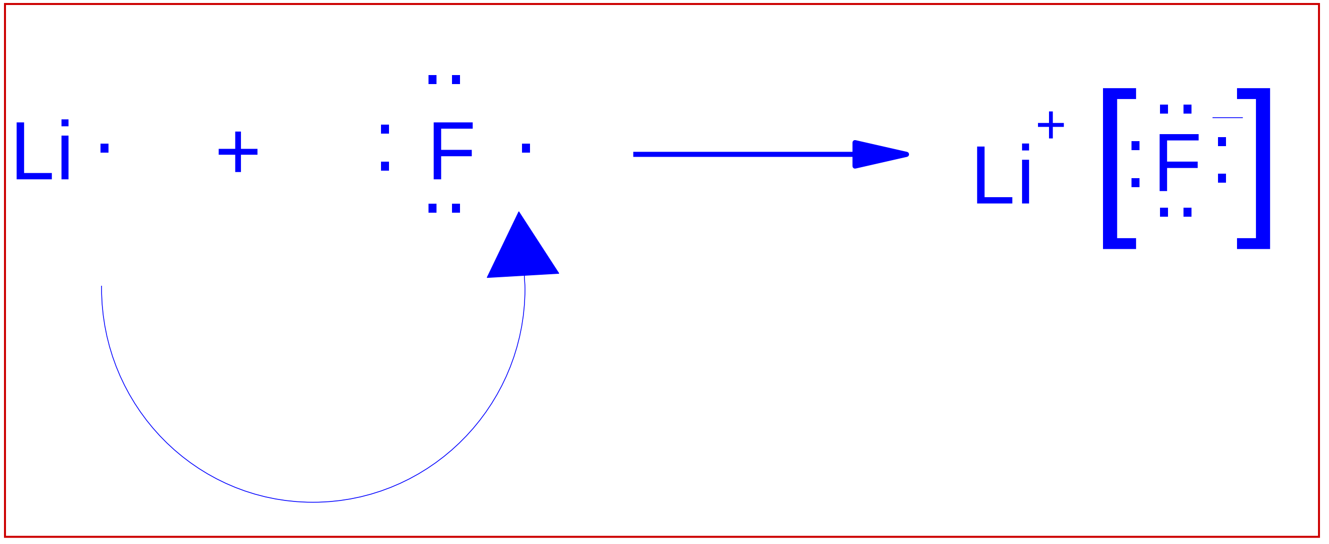


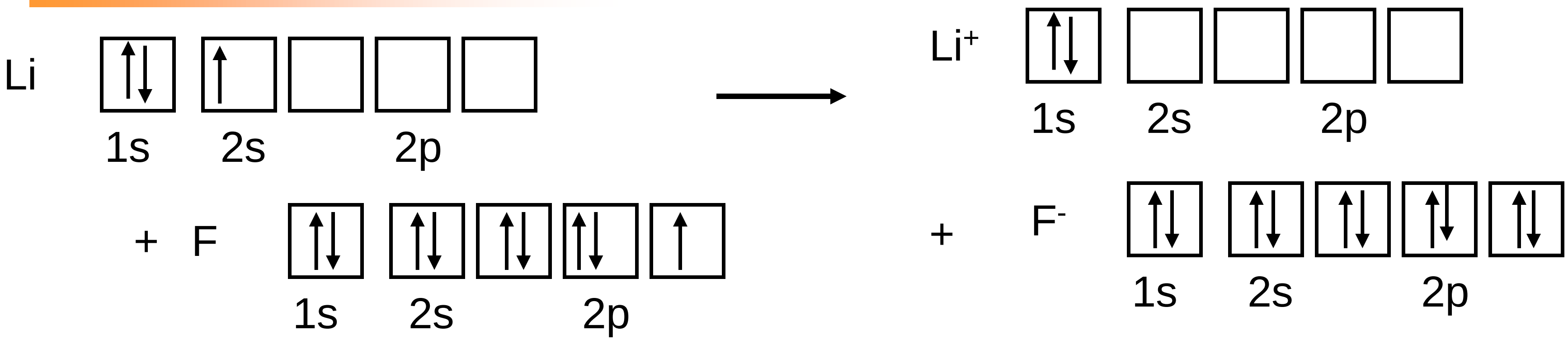
Figure 9.4

Three ways to represent the formation of Li^+ and F^- through electron transfer.

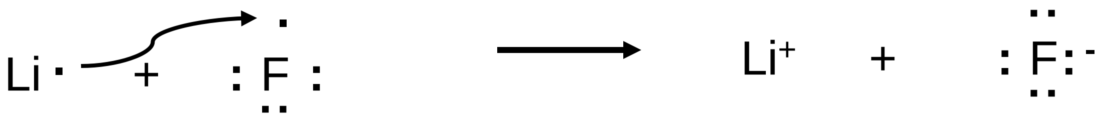
Electron configurations

Li $1s^2 2s^1$ + F $1s^2 2s^2 2p^5$ $\longrightarrow$ Li^+ $1s^2$ + F^- $1s^2 2s^2 2p^6$

Orbital diagrams



Lewis electron-dot symbols

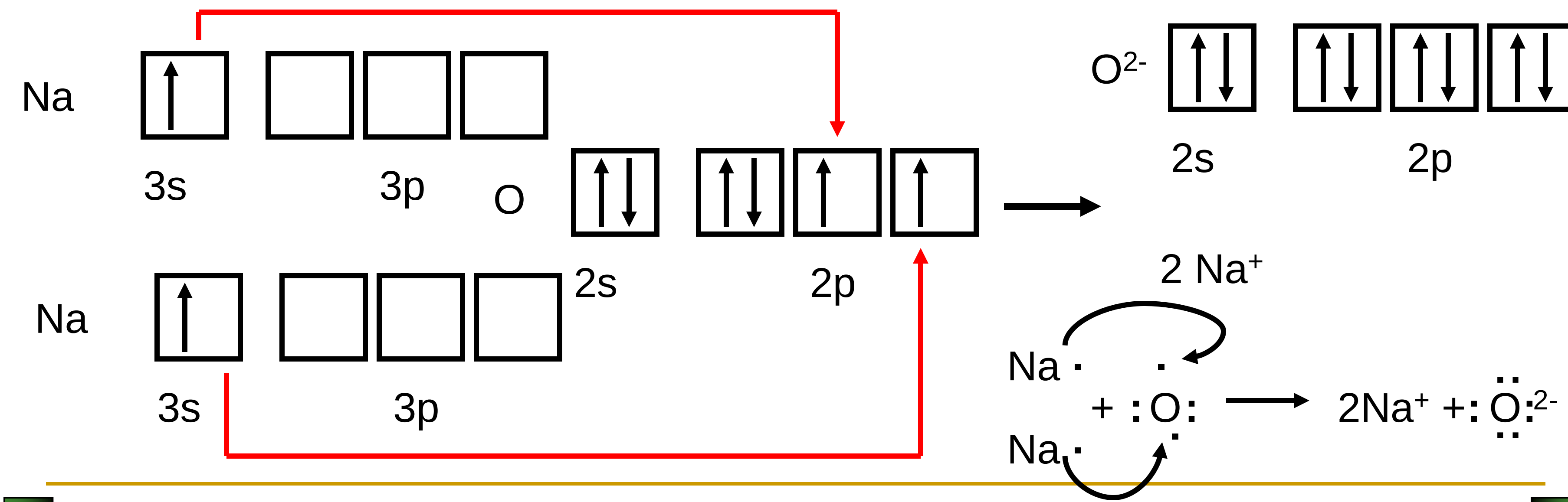


SAMPLE PROBLEM 9.1 SBB — Depicting Ion Formation

PROBLEM: Use partial orbital diagrams and Lewis symbols to depict the formation of Na^{+} and O^{2-} ions from the atoms, and determine the formula of the compound.

PLAN: Draw orbital diagrams for the atoms and then move electrons to make filled outer levels. It can be seen that 2 sodiums are needed for each oxygen.

SOLUTION:



Formation of Ionic Compounds

- Coulomb's Law describes the attraction of positive ions for negative ions due to the opposite charges.

$$F \propto \frac{(q^{+})(q^{-})}{d^{2}}$$

where

$$F = \text{force of attraction between ions}$$

$$q = \text{magnitude of charge on ions}$$

$$d = \text{distance between center of ions}$$

Formation of Ionic Compounds

- Small ions with high ionic charges have large Coulombic forces of attraction.
- Large ions with small ionic charges have small Coulombic forces of attraction.

$$Al_2^{3+}O_3^{2-} > Ca^{2+}O^{2-} > K^{1+}Cl^{-}$$

Formation of Ionic Compounds

- Write the Lewis dot formula representation for the reaction of K and Br.

Try this!

Formation of Ionic Compounds

- In general for the reaction of IA metals and VIIA nonmetals, the reaction equation is:

$$2\ M_{(s)} + X_2 \rightarrow 2\ M^+X^-_{(s)}$$

  - where M is the metals Li to Cs
  - and X is the nonmetals F to I.

Electronically this is occurring.

	ns	np			ns	np
M	↑		→	M^+		
X	↑↓	↑↓ ↑↓ ↑	→	X^-	↑↓	↑↓ ↑↓ ↑↓

Formation of Ionic Compounds

- Next we examine the reaction of IIA metals with VIIA nonmetals.
- This reaction forms mostly ionic compounds.
  - Notable exceptions are $BeCl_2$, $BeBr_2$, and BeI_2 which are covalent compounds.
- One example is the reaction of Be and F_2.

$$Be_{(s)} + F_{2(g)} \rightarrow BeF_{2(g)}$$

Formation of Ionic Compounds

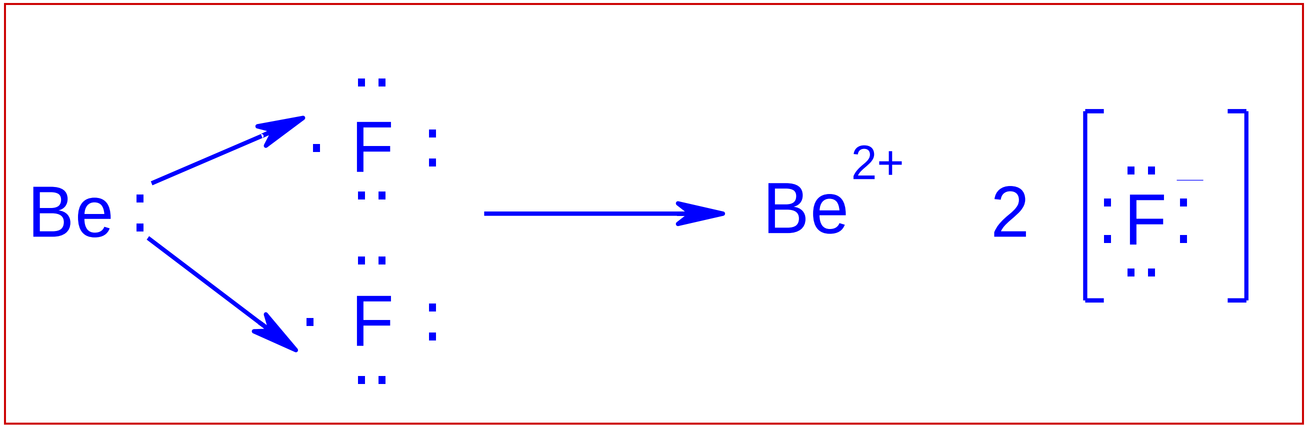
- The valence electrons in these two elements are reacting in this fashion.

	2s	2p				2s	2p		
Be [He]	↑↓				→ Be^{2+}				
F [He]	↑↓	↑↓	↑↓	↑	→ F^{-}	↑↓	↑↓	↑↓	↑↓

Next, draw the Lewis dot formula representation of this reaction.

You do it!

Formation of Ionic Compounds



- The remainder of the IIA metals and VIIA nonmetals react similarly.
- Symbolically this can be represented as:

$$M_{(s)} \;+\; X_2 \rightarrow M^{2+}X_2^{-}$$

M can be any of the metals Be to Ba.

X can be any of the nonmetals F to Cl.

Formation of Ionic Compounds

Simple Binary Ionic Compounds Table

Reacting Groups	Compound General Formula	Example
IA + VIIA	MX	NaF
IIA + VIIA	MX_2	$BaCl_2$
IIIA + VIIA	MX_3	AlF_3
IA + VIA	M_2X	Na_2O
IIA + VIA	MX	BaO
IIIA + VIA	M_2X_3	Al_2S_3

Formation of Ionic Compounds

Reacting Groups	Compound General Formula	Example
IA + VA	M_3X	Na_3N
IIA + VA	M_3X_2	Mg_3P_2
IIIA + VA	MX	AlN

H, a nonmetal, forms ionic compounds with IA and IIA metals for example, LiH, KH, CaH_2, and BaH_2.

Other hydrogen compounds are covalent.

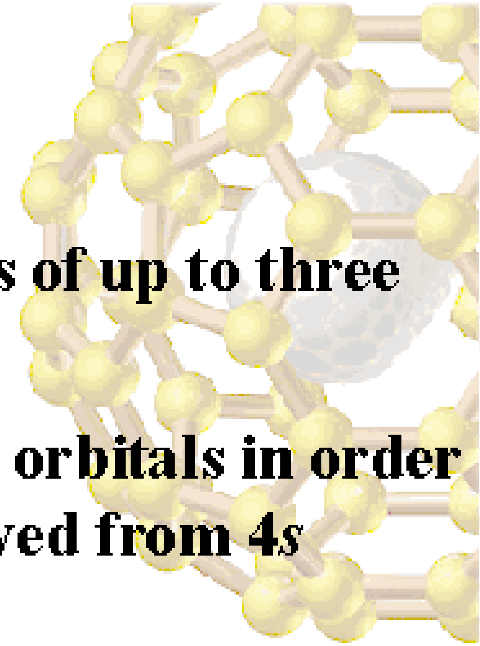
Ionic Bonding

Energetics of Ionic Bond Formation

Lattice Energies for Some Ionic Compounds

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	$MgCl_2$	2326
LiCl	834	$SrCl_2$	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		

Ionic Bonding



Transition-Metal Ions

Lattice energies compensate for the loss of up to three electrons.

In general, electrons are removed from orbitals in order of decreasing *n* (i.e. electrons are removed from 4*s* before the 3*d*).

Polyatomic Ions

Polyatomic ions are formed when there is an overall charge on a compound containing covalent bonds. E.g. SO_4^{2-}, NO_3^{-}.

Sizes of Ions

Ion size is important in predicting lattice energy.

Just as atom size is periodic, ion size is also periodic.

In general:

- **Cations are smaller than their parent ions.**
- **Electrons have been removed from the most spatially extended orbital.**
- **The effective nuclear charge has increased.**
- **Therefore, the cation is smaller than the parent.**

Anions are larger than their parent ions.

- **Electrons have been added to the most spatially extended orbital. This means total e^--e^- repulsion has increased.**
- **The nuclear charge has remained the same, but the number of screening electrons has increased.**
- **Therefore, anions are larger than their parents.**

Sizes of Ions

For ions of the same charge, ion size increases down a group.

All the members of an isoelectronic series have the same number of electrons.

As nuclear charge increases in an isoelectronic series the ions become smaller:

$$O^{2-} > F^{-} > Na^{+} > Mg^{2+} > Al^{3+}$$

TABLE 6.1 Some Common Main-Group Ions and Their Noble Gas Electron Configurations

Group 1A	Group 2A	Group 3A	Group 6A	Group 7A	Electron Configuration
H^+					[None]
H^-					[He]
Li^+	Be^{2+}				[He]
Na^+	Mg^{2+}	Al^{3+}	O^{2-}	F^-	[Ne]
K^+	Ca^{2+}	*Ga^{3+}	S^{2-}	Cl^-	[Ar]
Rb^+	Sr^{2+}	*In^{3+}	Se^{2-}	Br^-	[Kr]
Cs^+	Ba^{2+}	*Tl^{3+}	Te^{2-}	I^-	[Xe]

* These ions do not have a true noble gas electron configuration because they have an additional filled *d* subshell.