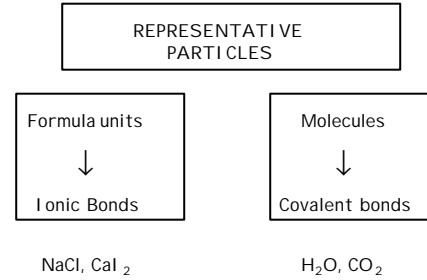


CHEMICAL BONDING

Whenever atoms or ions are strongly attached to one another, we say that there is a chemical bond between them. There are three general types of chemical bonds ionic, covalent, and metallic.

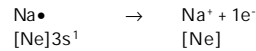
CHEMICAL BONDING



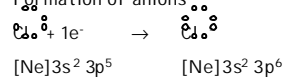
An ionic bond refers to electrostatic forces that exist between ions of opposite charge.

IONIC BONDING

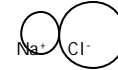
Formation of cations



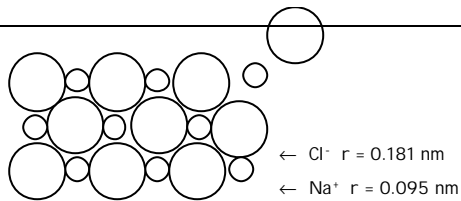
Formation of anions



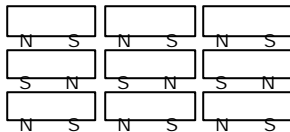
Formula unit of NaCl



The positively charged cation and negatively charged anion are held together by electrostatic attraction.



Crystal of table salt

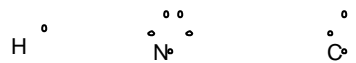


Opposites attract each other.

LEWIS SYMBOLS

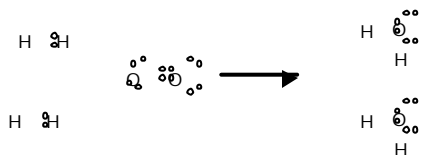
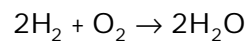
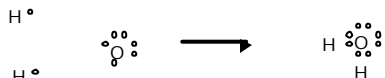
The electrons that are involved in chemical bonding are the valence electrons, those residing in the incomplete outer shell of an atom.

The Lewis symbol for an element consists of the chemical symbol for the element plus a dot for each valence electron.

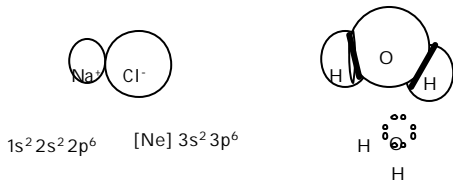


COVALENT BONDS

- A covalent bond results from the sharing of electrons between two nonmetal atoms.
- The electrons belong to both nonmetal atoms.
- Each atom uses the bonding electrons to complete an octet.



The octet rule states that atoms bond in such a way so that each atom acquires eight electrons in its outer shell.

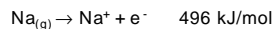


ENERGETICS OF IONIC BOND FORMATION

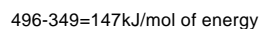
The reaction of sodium with chlorine is very exothermic.

What factors make the formation of ionic compounds so exothermic?

All the ionization energies were endothermic.



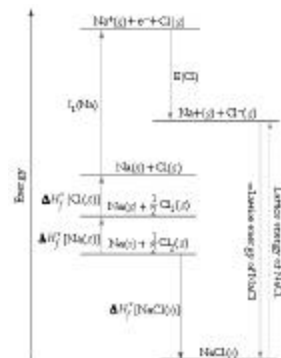
If the transfer of an electron from one atom to another were the only factor in forming an ionic bond, the overall process would rarely be exothermic.



Ionic compounds are stable due to the attraction between ions of unlike charge. This attraction draws the ions together, releasing energy and causing the ions to form a solid array or lattice.

A measure of just how much stabilization results from the arranging of oppositely charged ions in an ionic solid is given by the lattice energy.

The lattice energy is the energy required to completely separate a mole of a solid ionic compound into its gaseous ions.



Group 1A	Group 2A	Group 3A	Group 6A	Group 7A
Li ⁺ 0.68 1.38	Be ²⁺ 0.31 0.80	B ³⁺ 0.25 0.82	O ²⁻ 0.71 1.30	F ⁻ 0.71 1.30
Na ⁺ 0.97 1.58	Mg ²⁺ 0.66 1.30	Al ³⁺ 0.51 1.43	S ²⁻ 1.02 1.88	Cl ⁻ 0.99 1.81
K ⁺ 1.33 1.96	Ca ²⁺ 0.99 1.78	Ga ³⁺ 0.62 1.26	Se ²⁻ 1.16 1.99	Br ⁻ 1.38 1.96
Rb ⁺ 1.47 2.11	Sr ²⁺ 1.13 1.87	In ³⁺ 0.81 1.44	Te ²⁻ 1.25 2.21	I ⁻ 1.50 2.25

Ionic size plays a crucial role in determining structure and stability of ionic solids. Lattice and energies and crystal structure.

TRANSITION-METAL IONS

The lattice energies of ionic compounds are generally large enough to compensate for the lost of up to only three electrons (Co²⁺, Fe³⁺, Zn²⁺).

Because most transition metals have more than three electrons beyond a noble-gas core, attainment of a noble-gas configuration is not feasible.

In forming ions, transition metals lose the valence-shell *s* electrons first, then as many *d* electrons as are required to reach the charge of the ion.

Silver possesses a [Kr] 5s²4d⁹ electron configuration. The Ag⁺ ion has the following electron configuration [Kr]4d¹⁰



Transition metals generally do not form ions with noble-gas configurations.

The octet rule, although useful, is clearly limited in scope.

POLYATOMIC IONS

Many common ions are polyatomic (SO₄²⁻, NH₄⁺).

Polyatomic ion contain two or more atoms that bound together by predominantly covalent bonds. The group of atoms as a whole acts as a charged species when forming ionic compounds with cations.

Ionic substances possess several characteristic properties. They are usually brittle substances with high melting points.

They are usually crystalline, meaning that the solids have flat surfaces that make characteristic angle with one another.

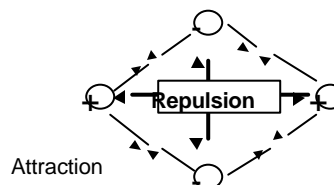
Ionic crystals can often be cleaved; that is, they break apart along smooth, flat surfaces.

The vast majority of chemical substances do not have the characteristics of ionic material.

Covalent substances tend to be liquids, gases, and pliable solids with low melting points.

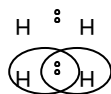
The hydrogen molecule, H_2 , provides the simplest possible example of a covalent bond.

When two hydrogen atoms are close to each other, electrostatic interactions occur between them.



LEWIS STRUCTURES

The formation of covalent bonds can be represented using Lewis symbols.



The sharing of a pair of electrons constitutes a single covalent bond. In many molecules atoms attain complete octets by sharing more than one pair of electrons between them. When two electron pairs are shared two lines are drawn, representing a double bond. A triple bond corresponds to the sharing of three pairs of electrons.

Consider: C_2H_4 , N_2

Guidelines for Drawing Lewis Structures

1. Calculate the total number of valence electrons (should be an even #).
2. Divide the total number of valence electrons by 2 to find the # of electron pairs in the molecule.
3. Surround the central atom with four electron pairs. Then move the other remaining atoms around the central atom. Use the remaining electron pairs to complete an octet around each of the other atoms.
4. If there are not enough electron pairs to provide an octet for each atom, move a nonbonding electron pair between two atoms that already share an electron pair.

FORMAL CHARGE

In some instances we can draw several different Lewis structures that all obey the octet rule. Formal charge helps one decide which is most reasonable.

The formal charge of an atom equals the number of valence electrons in the isolated atom, minus the number of electrons assigned to the atom in the Lewis structure.

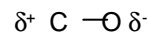
POLAR COVALENT BONDS

In a polar covalent bond one of the atoms exerts a greater attraction for the bonding electrons than the other.

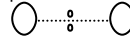
When the electrons are drawn more closely to one of the atoms, the bond is said to be polarized.

If the difference in relative ability to attract electrons is large enough, an ionic bond is formed.

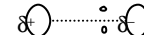
We identify a polar bond using the Greek letter delta (δ).



Non-polar covalent bonding



Polar covalent bonding



The differences in electronegativity between two atoms to gauge the polarity of the bonding between them. Consider these three fluorine-containing compounds:

Compound	F_2	HF	LiF
Electronegativity difference	$4-4=0$	$4-2.1=1.9$	$4-1=3$
Type of bond	Nonpolar covalent	Polar covalent	Ionic

In general, if the difference is <0.5 , the bond is considered nonpolar. If the difference is from 0.5 to 2.0, the bond is considered polar. If the difference is greater than or equal to 2.0, it is considered to be ionic.

Drawing Lewis Structures

1 Sum the valence electrons from all atoms.

- Write the symbols for the atoms and connect them with a single bond.
- Complete the octets of the atoms bonded to the central atom.
- Place and leftover electrons on the central atom, even if doing so results in more than an octet.
- If there are not enough electrons to give the central atom an octet, try multiple bonds.

EXCEPTIONS TO THE OCTET RULE

The term exception does not mean rare.

- Molecules can have an odd number of electrons.
- Molecules can have more than an octet
- Molecules can have less than an octet

ODD NUMBER OF ELECTRONS

A few molecules such as ClO_2 , NO , and NO_2 have an odd number of electrons. Thus, complete pairing is impossible, and an octet around each atom cannot be achieved.

Molecules that have less than an octet is a somewhat rare. And is most often encountered in compounds of boron and beryllium.

Consider BF_3 :

The third and largest class of exceptions consists of molecules or ions in which there are more than eight electrons in the valence shell of an atom

Consider PCl_5

We are forced to expand the valence shell and place 10 electrons around the central atom.

Other examples: SF_6 , AsF_6^- , and ICl_4^-

Expanded valence shells are observed only for elements in period 3 and beyond in the periodic table.

STRENGTHS OF COVALENT BONDS

The stability of a molecule is related to the strengths of the covalent bonds it contains.

We can measure the amount of energy needed to break a chemical bond by relating bond strength to the enthalpy change in reactions in which bonds are broken.

The bond enthalpy is the enthalpy change, ΔH , for the breaking of a bond in a mole of gaseous substance.

TABLE 8.4 Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			C—H	339	Br—Cl	218
C—I	240	H—H	436	C—F	327	Br—Br	193
C—S	259	H—F	567	C—Cl	253		
		H—Cl	431	C—Br	218	I—Cl	208
Si—H	323	H—Br	366	C—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						

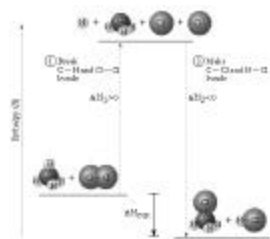
Multiple Bonds

C=C	614	N=N	418	O ₂	495
C≡C	839	N≡N	941		
C=C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

Bond enthalpy is always a positive quantity; energy is always required to break chemical bonds.

One usually uses bond enthalpies to estimate ΔH_{rxn} only if ΔH_f° values are not readily at hand.

$$\Delta H_{\text{rxn}} = \Sigma(\text{bond enthalpies of bond broken}) - \Sigma(\text{bond enthalpies of bonds formed})$$



$$\Delta H_{\text{rxn}} = (413 \text{ kJ} + 242 \text{ kJ}) - (328 \text{ kJ} + 431 \text{ kJ}) = -104 \text{ kJ}$$

OXIDATION NUMBERS

In keeping track of electrons, it is sometimes helpful to assign charges to atoms by assigning shared electrons to the more electronegative atom. Consider HCl:



By giving Cl eight valence-shell electrons, it will have one more than the neutral atom. In effect Cl has a -1 charge. Hydrogen is stripped of its' electron and is assigned a charge of $+1$.

Charges assigned in this fashion are called oxidation numbers or oxidation states.

The oxidation number of an atom is the charge that results when the electrons in a covalent bond are assigned to the more electronegative atom; it is the charge an atom would possess if the bonding were ionic.

Oxidation numbers are useful in a variety of situations, such as in naming compounds, in balancing chemical equations for reactions in which changes in oxidation number occur, and in examining trends in chemical properties.

- The oxidation number of an element in its elemental form is zero.
- The oxidation number of a monoatomic ion is the same as its charge.
- In binary compounds the element with greater electronegativity is assigned a negative oxidation number equal to its charge in simple ionic compounds of the element.
- The sum of the oxidation numbers equals zero for an electrically neutral compound and equals the overall charge for an ionic species.

It is natural to ask what are the differences between oxidation numbers and formal charges, and why do we use them both to keep track of electrons? In calculating formal charges, we assume that all atoms have the same electronegativity (bonds are treated as being nonpolar).

In calculating oxidation numbers, we assume that electrons transfer completely to to the more electronegative atom.

In practice, formal charges generally reflect the actual charges on atoms more accurately than do oxidation numbers.

