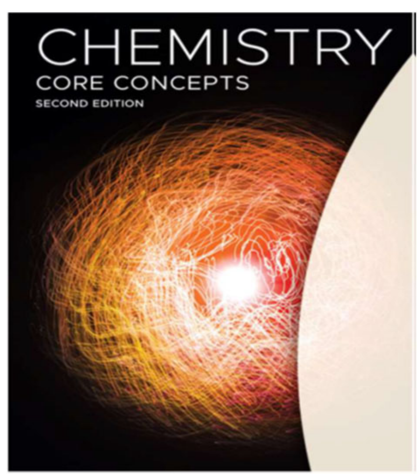
## SLE155 Chemistry for the Professional Sciences

**Burwood and Geelong**


## Class 2
## Chemical Bonding and Molecular Structure

**Bonding, Lewis structures**
**and**
**shapes of molecules**

Chapter 6



# Learning objectives Chapter 6

**Atoms bond together to form molecules by sharing their electrons.**

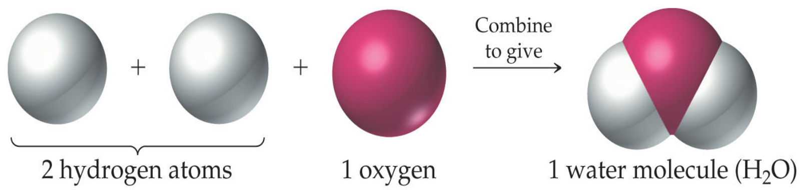
**How are electrons shared between atoms?**
**Can we predict geometry of molecules or their reactivities?**

**Valence shell electron pair repulsion theory (VSEPR) and valence bond theory will be explored to answer these questions.**

# Fundamentals of Bonding

# Covalent Bonds

**Covalent bond—A bond formed by sharing electrons between atoms**
**Molecule—A group of atoms held together by covalent bonds**

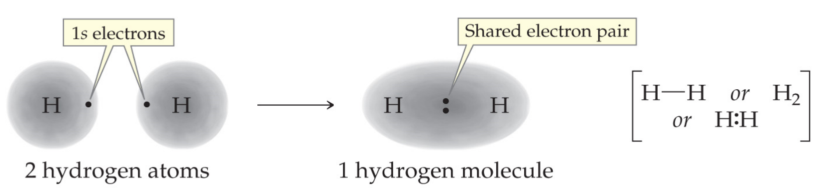





# Covalent Bonds

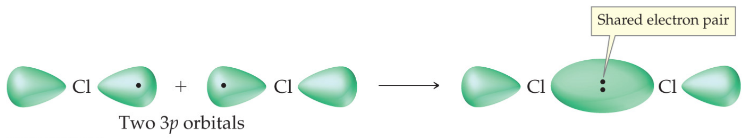
## Covalent bonding in hydrogen ($H_2$):

- **Spherical 1*s* orbitals overlap to give an egg-shaped region.**
- **There are two electrons between the nuclei, providing $1s^2$ configuration of helium.**
- **H-H, H:H and $H_2$ all represent a hydrogen molecule.**



# Covalent Bonds

- Chlorine also exists as a **diatomic molecule** due to the **end-on overlap** of **3*p*** orbitals.

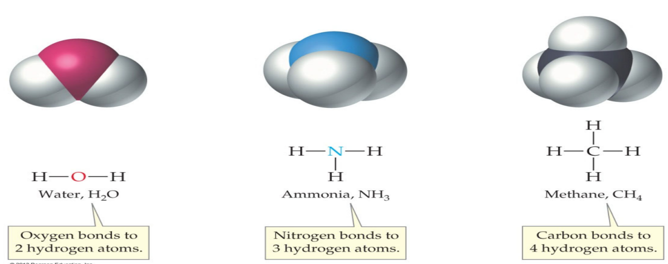




**There are seven elements which exist naturally as diatomic molecules: nitrogen, oxygen, hydrogen, fluorine, chlorine, bromine, and iodine. Learn them!**

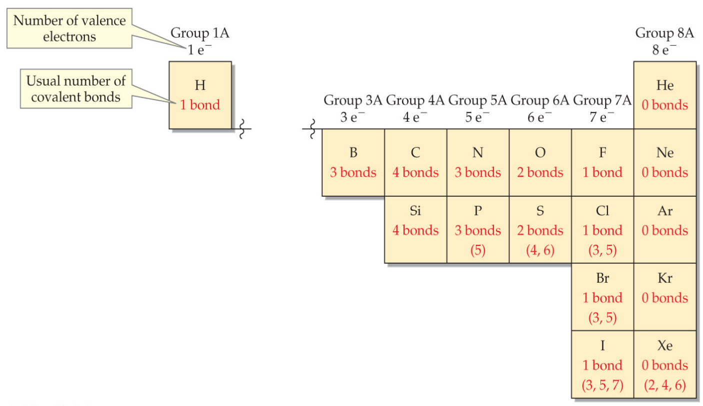
# Covalent Bonds and the Periodic Table

- A **molecular compound** is a compound that consists of molecules rather than ions.



# Covalent Bonds and the Periodic Table

- **Numbers of covalent bonds typically formed by main group elements to achieve octet configurations.**





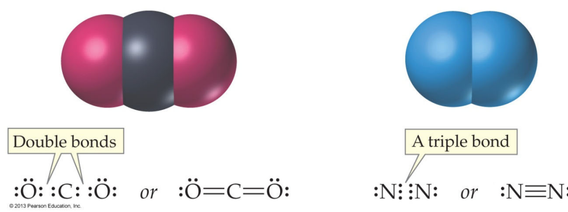

# Covalent Bonds and the Periodic Table

## Exceptions to the Octet Rule:

**Boron has only three electrons to share, so will form compounds with six shared electrons instead of the usual eight.**

**Elements in the third row and below in the periodic table have vacant *d* orbitals that can be used for bonding.**

## Multiple Covalent Bonds




**The only way these molecules' atoms can have outer-shell electron octets is by sharing *more* than two electrons between pairs of atoms, resulting in the formation of *multiple* covalent bonds.**

## Multiple Covalent Bonds

**Single bond—A covalent bond formed by sharing one electron pair (2 electrons).**

**Represented by a single line: H–H**

**Double bond—A covalent bond formed by sharing two electron pairs (4 electrons).**

**Represented by a double line: O=O**

**Triple bond—A covalent bond formed by sharing three electron pairs (6 electrons).**

**Represented by a triple line: N≡N**

## Multiple Covalent Bonds

**Carbon, nitrogen, and oxygen are the elements most often present in multiple bonds.**

**Carbon and nitrogen can form double and triple bonds.**

**Oxygen forms only double bonds.**

**Multiple covalent bonding is particularly common in *organic* molecules, which consist mainly of the element carbon.**

**Note that in compounds containing multiple bonds,**

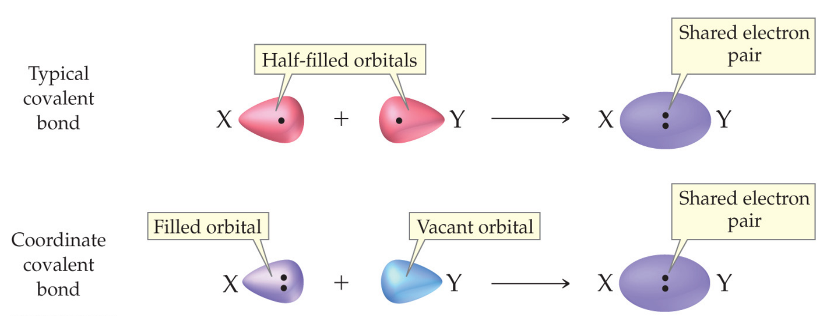
**carbon still forms a total of four covalent bonds,**

**nitrogen still forms a total of three covalent bonds,**

**and oxygen still forms a total of two covalent bonds.**

## Coordinate Covalent Bonds

- **A coordinate covalent bond is the covalent bond that forms when both electrons are donated by the same atom.**



## Characteristics of Molecular Compounds

**Ionic compounds have high melting and boiling points because the attractive forces between oppositely charged ions are so strong.**

***Molecules*** **are neutral, so there is no strong attraction to hold them together.**

**There are weaker forces between molecules, called *intermolecular forces*.**

## Characteristics of Molecular Compounds

**Very weak intermolecular forces = gas.**

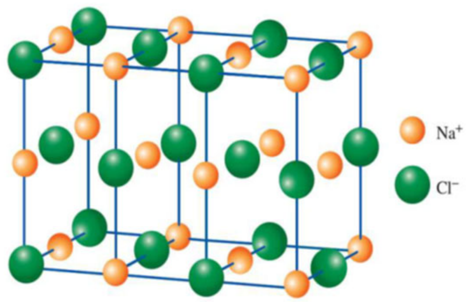
**Somewhat stronger intermolecular forces = liquid.**

**Strongest intermolecular forces = molecular solid.**

**Molecular solids have lower melting and boiling points than ionic compounds, are often insoluble in water, and do not conduct electricity when melted.**

# Ionic Bonding

- Compounds formed between elements of very different
- electronegativities are ionic
- Most ionic compounds are solids with high melting points
- They are held together by the attractive forces between oppositely charged ions




Ionic solids shatter if struck sharply.
Ionic compounds dissolve in water if the attraction between water and the ions overcomes the attraction of the ions for one another. Not all ionic compounds are water soluble.

DEAKIN COLLEGE DEAKIN UNIVERSITY

# Lattice Energy

- Lattice energy is the amount of energy required (in kJ $mol^{-1}$) to break an ionic lattice apart. This depends on the charge and size of the ions:

- Increasing cation size results in a decrease in lattice energy.
- Increasing anion size results in a decrease in lattice energy.

DEAKIN COLLEGE DEAKIN UNIVERSITY

## Lewis structures - summary

**The conventions**

**Each atom is represented by its elemental symbol**
**Only the valence electrons appear in a Lewis structure**

**A line represents one pair of electrons that is shared between two atoms**

**Dots represent the nonbonding electrons on that atom**

## Lewis structures - summary

| | | |
|---|---|---|
| 1. Elemental symbols represent atoms | H | F |
| 2. Only valence electrons appear | 1*s* ↑ | 2*s* ↑↓ ↑↓ ↑↓ ↑ 2*p* |
| 3. Lines represent bonds | H—F | |
| 4. Dots represent nonbonding electrons | H—F: (with three lone pairs on F) | |

# Lewis structures - summary

**Procedure for drawing Lewis structures:**

1. Count the valence electrons
2. Assemble the bonding framework using single bonds
3. Place three nonbonding pairs of electrons on each outer atom except H
4. Assign the remaining valence electrons to inner atoms
5. Minimise formal charges on all atoms.

Note: If the species is an ion, add or subtract one electron for each negative or positive charge respectively.

# Lewis structures - summary

Building Lewis structures

Lewis structures by themselves do not imply any particular geometry for a molecule or ion

A set of eight electrons associated with an atom is often called an octet

Larger atoms can accommodate more than eight electrons, e.g., sulfur atom

The nonbonding pairs of electrons are called lone pairs

## Lewis structure example

**Let's apply this procedure to produce a Lewis structure for $SO_2$.**

**Step 1: Count the valence electrons**

**S = 6, O = 6**

**$SO_2$= [6+(2×6)] = 18 valence electrons**

**It is very important to keep a note of the valence electrons as you work through the steps**

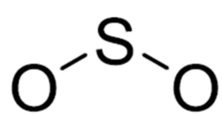
## Lewis structure example

**Step 2: Assemble the bonding framework using single bonds**

**Outer atoms are usually the more electronegative.**

**Usually, one inner atom is attached to two or more other atoms.**

**Oxygen is more electronegative than sulfur, so the oxygen atoms will be on the outside.**



**4 electrons bonding:**

**14 valence electrons leftover**

## Lewis structure example

Step 3: Place three nonbonding electron pairs on each outer atom except H

Each outer atom (except H) is associated with eight electrons (four pairs of electrons), i.e. the octet rule.

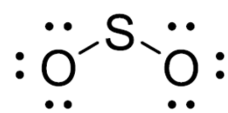
These nonbonding electrons are lone pairs.

4 electrons bonding:

12 electrons in lone pairs:

(18 - 4 - 12 = 2):

2 valence electrons leftover



## Lewis structure example

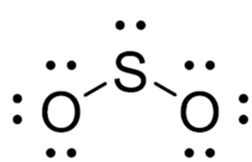
Step 4: Assign the remaining valence electrons to inner atoms

We have assigned 16 electrons in steps 2–3, and $SO_2$ has 18 valence electrons (step 1). Therefore 2 electrons are left.

4 electrons bonding:

14 electrons in lone pairs:

0 valence electrons leftover



# Lewis structure example

**Step 5: Minimise formal charges on all atoms**

**Formal charge = (valence electrons of free atoms) – (electrons assigned to atoms in Lewis structure).**

**Lone pair electrons are assigned to the atom.**

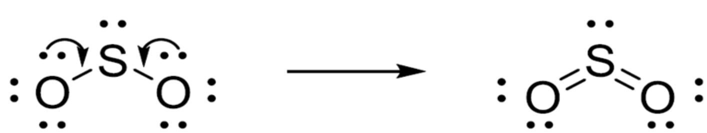
**Electrons in bonds are shared between the atoms (so we divide them by two when calculating the formal charge for each atom).**

**For the Lewis structure above:**

| | |
|---|---|
| Valence electrons of S: 6 | Valence electrons of O: 6 |
| Lone pair electrons: 2 | Lone pair electrons: 6 |
| Shared electrons: 4 | Shared electrons: 2 |
| Formal charge for S: 6 – 2 – 1/2(4) = +2 | Formal charge for O: 6 – 6 – 1/2(2) = –1 |

# Lewis structure example

**We can minimise these formal charges to give a better structure by converting one lone pair from each O into a bond, producing two double bonds:**



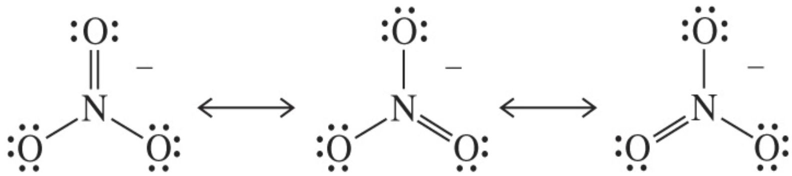
| | |
|---|---|
| Valence electrons of S: 6 | Valence electrons of O: 6 |
| Lone pair electrons: 2 | Lone pair electrons: 4 |
| Shared electrons: 8 | Shared electrons: 4 |
| Formal charge for S: 6 – 2 – 1/2(8) = 0 | Formal charge for O: 6 – 4 – 1/2(4) = 0 |

# Lewis structures

## Resonance structures

Made up of several equivalent Lewis structures.

They are connected by double-headed arrows to emphasise that a complete depiction requires all of them.



# Lewis structures

Resonance structures differ only in the position of the electrons, not the atoms.

Resonance structures are not always equivalent.

Resonance structures that are not equivalent occur when electrons are shifted between atoms of different elements.

## Valence shell electron pair repulsion (VSEPR) theory

The **V**alence **S**hell **E**lectron **P**air **R**epulsion theory considers that molecular shape is determined by repulsions between pairs of electrons.

To minimise these repulsions, electron pairs around a central atom within a molecule will be situated as far apart as possible.

DEAKIN COLLEGE DEAKIN UNIVERSITY

## VSEPR theory

Draw the Lewis structure of the molecule.

Count the number of sets of bonding pairs (BP) and lone pairs (LP) of electrons around the central atom.

LP-LP repulsions are the most important, BP-BP repulsions are the least important.

| Number of sets of electron pairs | Geometry of sets of electron pairs |
|---|---|
| 2 | linear |
| 3 | trigonal planar |
| 4 | tetrahedral |
| 5 | trigonal bipyramidal |
| 6 | octahedral |

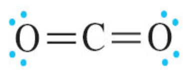
DEAKIN COLLEGE DEAKIN UNIVERSITY

# VSEPR theory

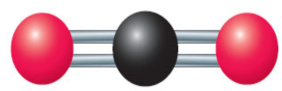
**Two sets of electron pairs around the central atom leads to linear geometry.**

**The two sets of electron pairs need to be as far apart as possible.**

**Example: $CO_2$**



two sets of electron pairs around the C atom



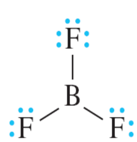
linear shape
bond angle = 180°

DEAKIN COLLEGE DEAKIN UNIVERSITY

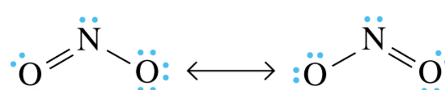
# VSEPR theory

**Three sets of electron pairs around the central atom leads to trigonal planar geometry. Angle is 120°, atoms are in the same plane.**

**The three sets of electron pairs need to be as far apart as possible. We must distinguish between electron pair geometry and the shape of the molecule (where the atoms are).**



**$BF_3$ is trigonal planar**



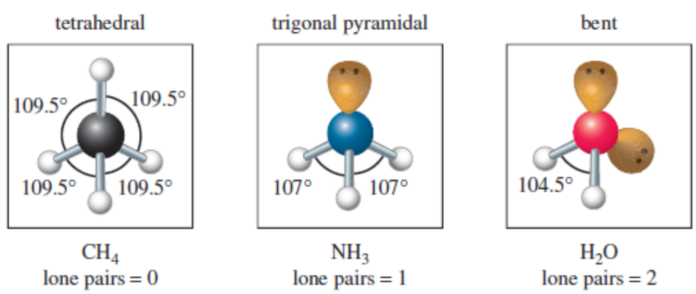
**$NO_2^-$ is bent or V-shaped**

DEAKIN COLLEGE DEAKIN UNIVERSITY

## VSEPR theory

**Four sets of electron pairs around the central atom lead to tetrahedral geometry.**

4 BP   3BP+1LP   2BP+2LP

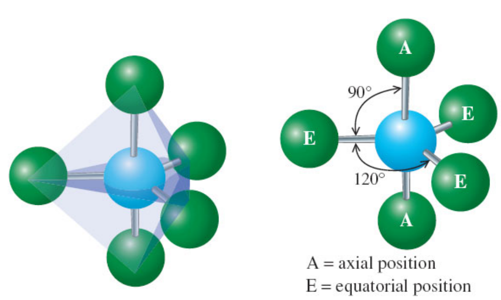



## VSEPR theory

**Five sets of electron pairs around the central atom leads to trigonal bipyramidal geometry.**

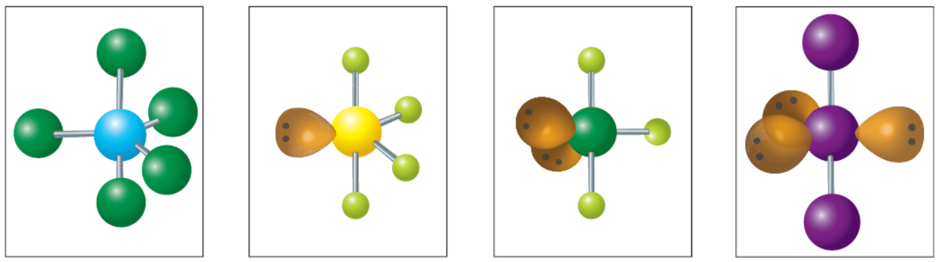
**Example: $PCl_5$**

**Five sets of equivalent electron pairs**




(a)   (b)

# VSEPR theory




$PCl_5$
lone pairs = 0

$SF_4$
lone pairs = 1

$ClF_3$
lone pairs = 2

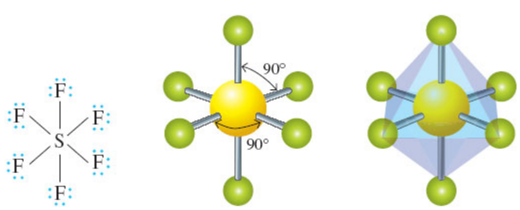
$I_3^-$
lone pairs = 3

# VSEPR theory

Six sets of electron pairs around the central atom leads to octahedral geometry.

Example: $SF_6$

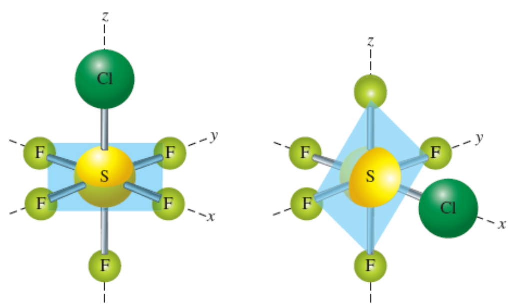
Six sets of electron pairs around the S atom are as far apart as possible.




(a) (b) (c)

## VSEPR theory

**All six positions around an octahedron are equivalent**




## VSEPR theory

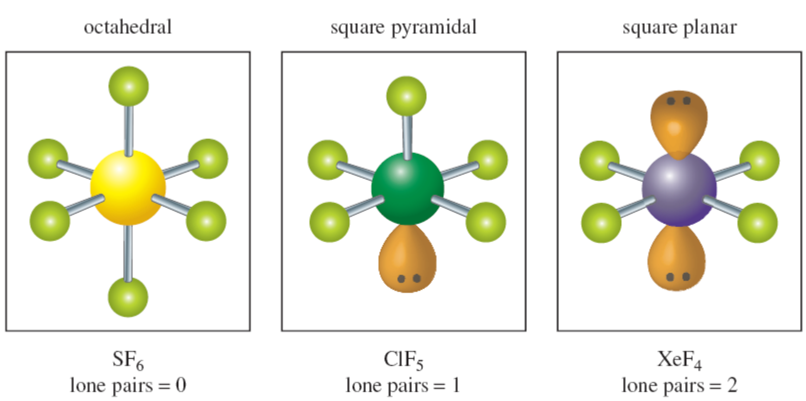


TABLE 5.4 Features of molecular geometries.

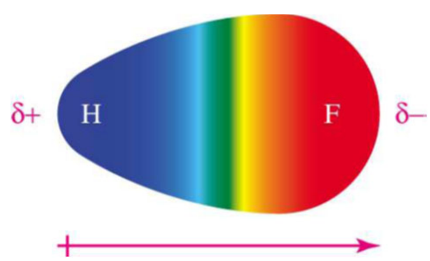
| Number of sets of electron pairs | Number of outer atoms | Lone pairs | Geometry of sets of electron pairs | Molecular shape | Bond angles | Dipole moment[a] | Example |
|---|---|---|---|---|---|---|---|
| 2 | 2 | 0 | linear | linear | 180° | no | $CO_2$ |
| 3 | 3 | 0 | trigonal planar | trigonal planar | 120° | no | $BF_3$ |
| | 2 | 1 | trigonal planar | bent | <120° | yes | $NO_2^-$ (plus other resonance structures) |
| 4 | 4 | 0 | tetrahedral | tetrahedral | 109.5° | no | $CH_4$ |
| | 3 | 1 | tetrahedral | trigonal pyramidal | <109.5° | yes | $NH_3$ |
| | 2 | 2 | tetrahedral | bent | <109.5° | yes | $H_2O$ |
| 5 | 5 | 0 | trigonal bipyramidal | trigonal bipyramidal | 90°, 120° | no | $PCl_5$ |
| | 4 | 1 | trigonal bipyramidal | seesaw | <90°, <120° | yes | $SF_4$ |
| | 3 | 2 | trigonal bipyramidal | T shaped | <90°, <120° | yes | $ClF_3$ |
| | 2 | 3 | trigonal bipyramidal | linear | 180° | no | $I_3^-$ |
| 6 | 6 | 0 | octahedral | octahedral | 90° | no | $SF_6$ |
| | 5 | 1 | octahedral | square pyramidal | <90° | yes | $ClF_5$ |
| | 4 | 2 | octahedral | square planar | 90° | no | $XeF_4$ |

(a) Applies only to molecules with identical outer atoms.

# Polar Bonds and Electronegativity

**When atoms are not identical, bonding electrons may be shared unequally.**

**A polar covalent bond is one in which the electrons are attracted more strongly by one atom than by the other.**




DEAKIN COLLEGE DEAKIN UNIVERSITY

## Polar Bonds and Electronegativity

The ability of an atom to attract electrons when <u>in a compound</u> is called electronegativity.

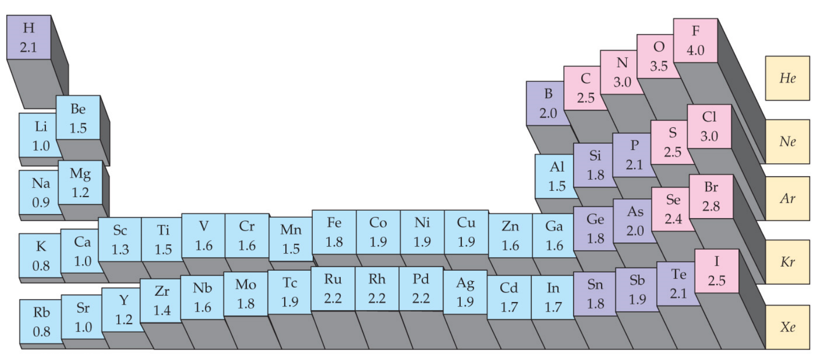
Fluorine, the most electronegative element, is assigned a value of 4, and less electronegative atoms are assigned lower values.

Metallic elements have low electronegativities.

Halogens and reactive nonmetal elements have higher electronegativities.

Electronegativity generally decreases going down the periodic table within the same group.

## Polar Bonds and Electronegativity




Electronegativities of several main-group and transition-metal elements.

You do not need to remember these numbers, just the trends.

## Polar Bonds and Electronegativity

Electronegativity differences of less than about 0.5 result in **nonpolar covalent bonds**.

Differences up to about 1.9 indicate increasingly **polar covalent bonds**.

Differences of about 2 or more indicate substantially **ionic bonds**.

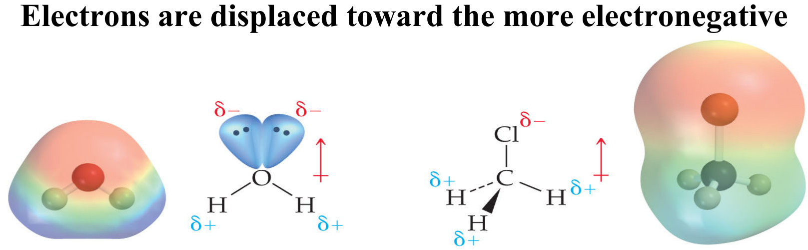
There is **no** dividing line between covalent and ionic bonds; most bonds fall between these categories.

Ionic bonding can be considered as an extreme case of polar covalent bonding.

## Polar Molecules

Molecular polarity is due to individual bond polarities and shape of molecule from lone-pair contributions.

Electrons are displaced toward the more electronegative

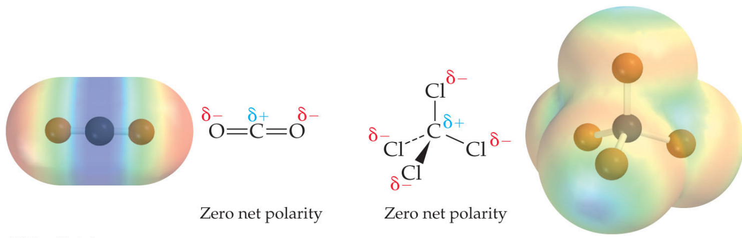





Water, $H_2O$ Chloromethane, $CH_3Cl$

## Polar Molecules

**Molecular polarity depends on the shape of the molecule.**
**Symmetrical molecules can have polar bonds but be non-polar overall.**






DEAKIN COLLEGE in association with DEAKIN UNIVERSITY

## Polar Molecules

- **Polarity has a dramatic effect on the physical properties of molecules particularly on melting points, boiling points, and solubilities.**

**Polar molecules will have stronger intermolecular forces so will melt and boil at higher temperatures.**

DEAKIN COLLEGE in association with DEAKIN UNIVERSITY

# Properties of covalent bonds

## Dipole moment

Most chemical bonds are polar (one end slightly positive, the other slightly negative).

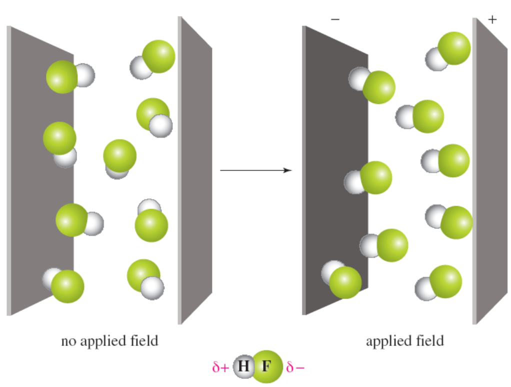
Bond polarities can lead to molecules with dipole moment.

Dipole moment depend on bond polarities ($\Delta\chi$) and on molecular shape.

# Properties of covalent bonds

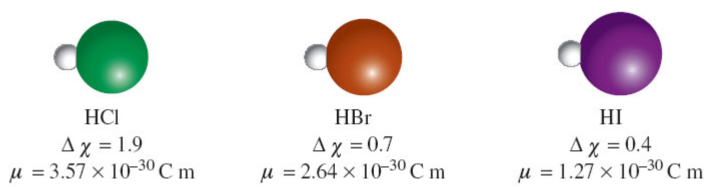
## Dipole moments

A molecule with an asymmetrical distribution of electron density has a dipole moment ($\mu$)

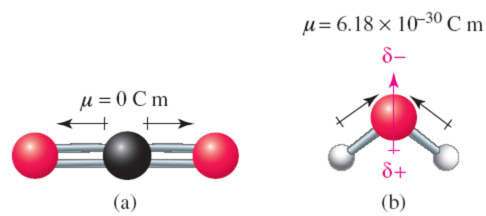


# Properties of covalent bonds

**Dipole moments depend on bond polarities**




**and on molecular shape**

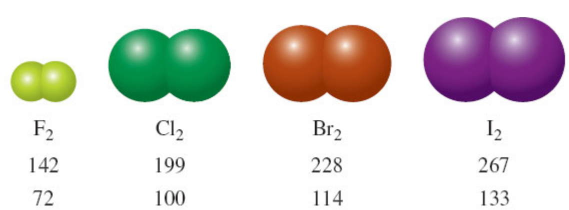



# Properties of covalent bonds

## Bond length

**Bond length of a covalent bond is the nuclear separation distance at which the molecule is most stable.**

**At this distance, attractive interactions are maximised relative to repulsive interactions.**



## Properties of covalent bonds

**The following factors influence bond length:**

**The smaller the atoms, the shorter the bond.**

**The more electrons in a bond, the shorter the bond.**

**The larger the electronegativity difference between the bonded atoms, the shorter the bond.**

## Properties of covalent bonds

### Bond energy

**Is the amount of energy that must be supplied to break a chemical bond.**

**There are three consistent trends:**

**Bond energies increase as more electrons are shared between the atoms,**

**Bond energies increase at the electronegativity difference between bonded atoms increases, and**

**Bond energies decrease as bonds become larger.**

# Chapter 6 – summary

**Fundamentals of bonding**

**Covalent bonds are formed as a result of the sharing of electrons between nuclei.**

**Unequal sharing of electrons between atoms of different electronegativity gives a polar covalent bond.**

**Ionic bonding**

**Ionic compounds are formed between elements with very different electronegativities.**

# Chapter 6 – summary

**Lewis structures**

**Lewis structures show the distribution of valence electrons within a molecule and can be built following a 5 step procedure.**

**VSEPR theory**

**To determine the geometry of a molecule, electron-pair repulsions are minimised by placing the electron pairs as far apart as possible.**