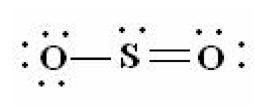
DELOCALIZED BONDING: RESONANCE

- When writing Lewis structure for SO_2, the following structure can be obtained:

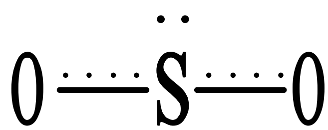
Total number of electrons: = 18 electrons



- This implies that the **O — S** should be longer than the **S = O** bond
  (single bond) (double bond)

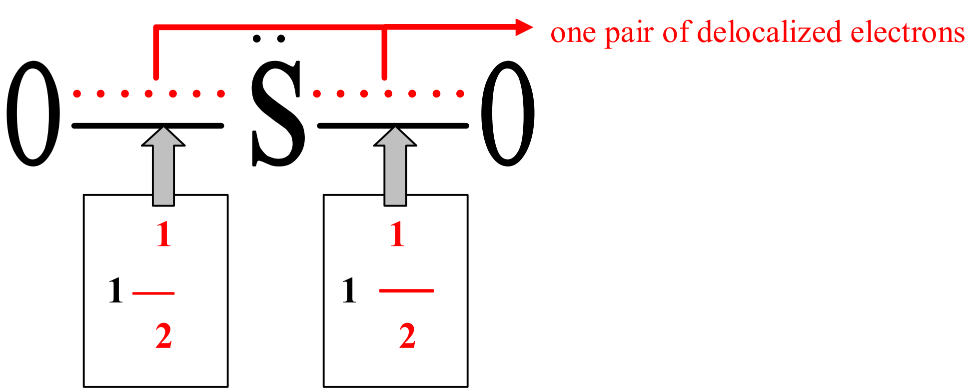
- However, experimental data indicates that the two Sulfur - Oxygen bonds:
  - have the same Bond Length, and
  - have the same Bond Energies

- Explanation: One of the bonding electron pairs is spread over a region of all three atoms:

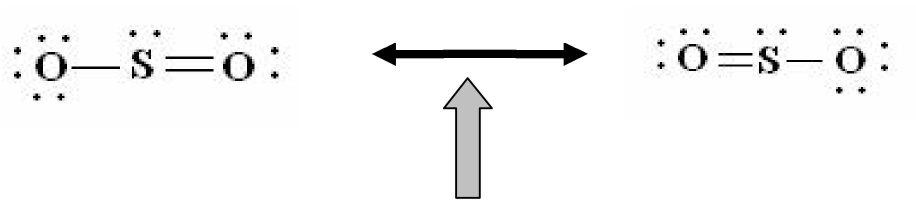


- This phenomenon is called "**Delocalized Bonding**" or "**Resonance**"

Bond Order:



- To describe a molecule such as SO_2 by Lewis structures, all possible electron-dot formulas must be written:



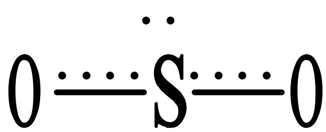
indicates **resonance**

- The two formulas are referred to as **"resonance formulas"** or **"contributing structures"**

Conclusions:

1. The molecule does not flip back and forth between different resonance formulas.

2. The **actual structure** referred to as **"the resonance hybrid"** is in between the extremes given by the resonance formulas or contributing structures.



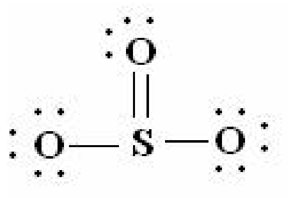
3. Delocalized bonding (resonance) exists for molecules that differ only in the allocation of single and double bonds to the same kind of atoms.

Examples:

1. Write resonance descriptions for **SO_3**

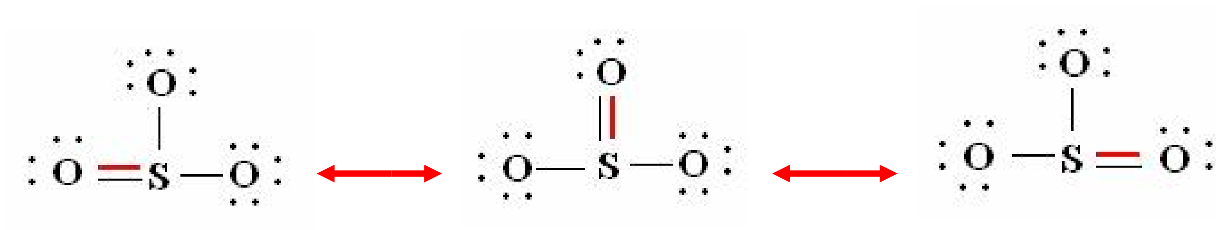
Total number of electrons:	1 S = 1 x 6 electrons =	6 electrons
	3 O = 3 x 6 electrons =	18 electrons
	Total:	= 24 electrons

- One possible electron-dot formula for SO_3 is:



- Because the Sulfur – Oxygen bonds are expected to be equivalent, the structure must be described in resonance terms.

- One electron pair is delocalized over the region of all three Sulfur – Oxygen bonds:



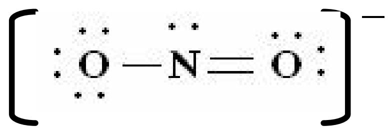
$$\text{Bond Order} = \frac{\text{Number of Bonds in one structure}}{\text{Number of contributing structures}} = \frac{4}{3} = 1\frac{1}{3}$$

2. Write resonance descriptions for the nitrite ion (NO_2^-)

Total number of electrons:
1 N = 1 x 5 electrons = 5 electrons
2 O = 2 x 6 electrons = 12 electrons
Negative charge (- 1) = 1 electron

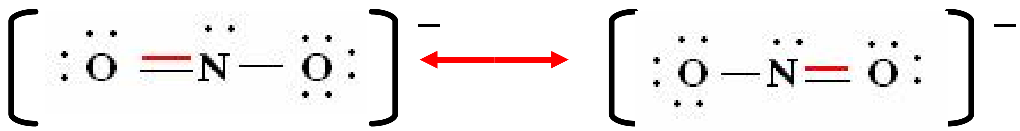
Total: = **18 electrons**

- One possible electron-dot formula for SO_3 is:



- Because the Nitrogen – Oxygen bonds are expected to be equivalent, the structure must be described in resonance terms.

- One electron pair is delocalized over the region of both Nitrogen – Oxygen bonds:



$$\text{Bond Order} = \frac{\text{Number of Bonds in one structure}}{\text{Number of contributing structures}} =$$

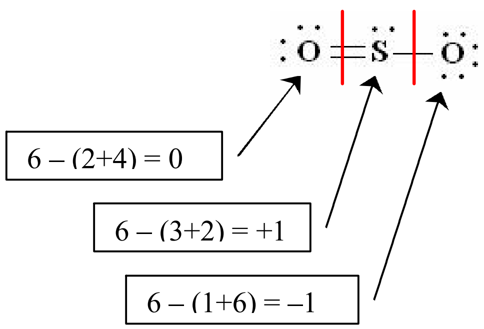
FORMAL CHARGES

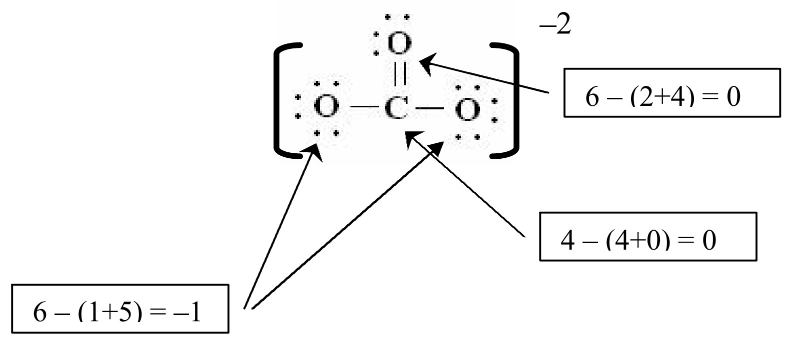
- Chemists use **formal charges** to determine which Lewis structure is correct or more plausible.
- Formal charges are hypothetical charges assigned to each element based on the number of valence electrons and the number of electrons used in bonding.
- Formal charges for each atom in a molecule is calculated as shown below:

Formal charge = valence electrons – (½ bonding electrons + non-bonding electrons)

Examples:

Assign formal charges to each atom in the structures shown below:





- The sum of all formal charges in a structure must equal the total charge on that structure.
- When evaluating structures based on formal charges, two rules must be considered:

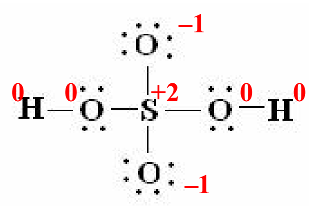
Rule A: • Whenever more than one Lewis structure can be written for a molecule, choose the one with the lowest magnitude of formal charges.

Rule B: • When two proposed structures for a molecule have the same magnitude of formal charges, choose the one having the negative formal charge on the more electronegative atom.

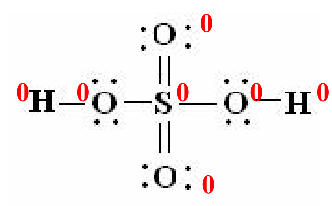
Example:

Two possible Lewis structures for H_2SO_4 are shown below. Based on formal charges, determine which structure is more plausible:

(A)

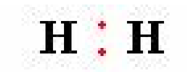


(B)

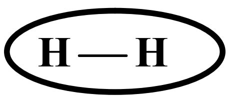


Structure B is favored due to **lower magnitude** formal charges

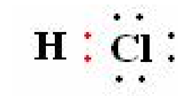
ELECTRONEGATIVITY



- Both H atoms **attract bonding electrons equally.**
- The bonding electrons are **equally shared.**
- They belong equally to both H atoms.

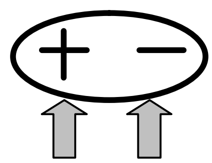


No Poles



- Cl atom attracts bonding electrons stronger than the H atom.
- The bonding electrons are **unequally shared.**
- They belong more to the Cl atom than to the H atom.
- The Cl side of the molecule acquires a partial negative charge (δ–).
- The H side of the molecule acquires a partial positive charge (δ+).

δ+ δ-
H — Cl



Positive Pole **Negative Pole**

H — H

Non-polar Covalent Bond

Forms between like atoms

No partial charges

δ+ δ– → **(less than full charges)**

H — Cl **(less than 1+ or 1–)**

Polar Covalent Bond

Forms between unlike atoms

Partial charges present

The atom that has a stronger attraction for the bonding electrons; Cl carries a partial negative charge.

- **Terminology: Cl is more electronegative than H**
- **ELECTRONEGATIVITY (E.N.) is the ability of an atom involved in a covalent bond to attract the bonding electrons to itself.**

ELECTRONEGATIVITY SCALE

- **Linus Pauling** derived a relative electronegativity scale based on bond energies:

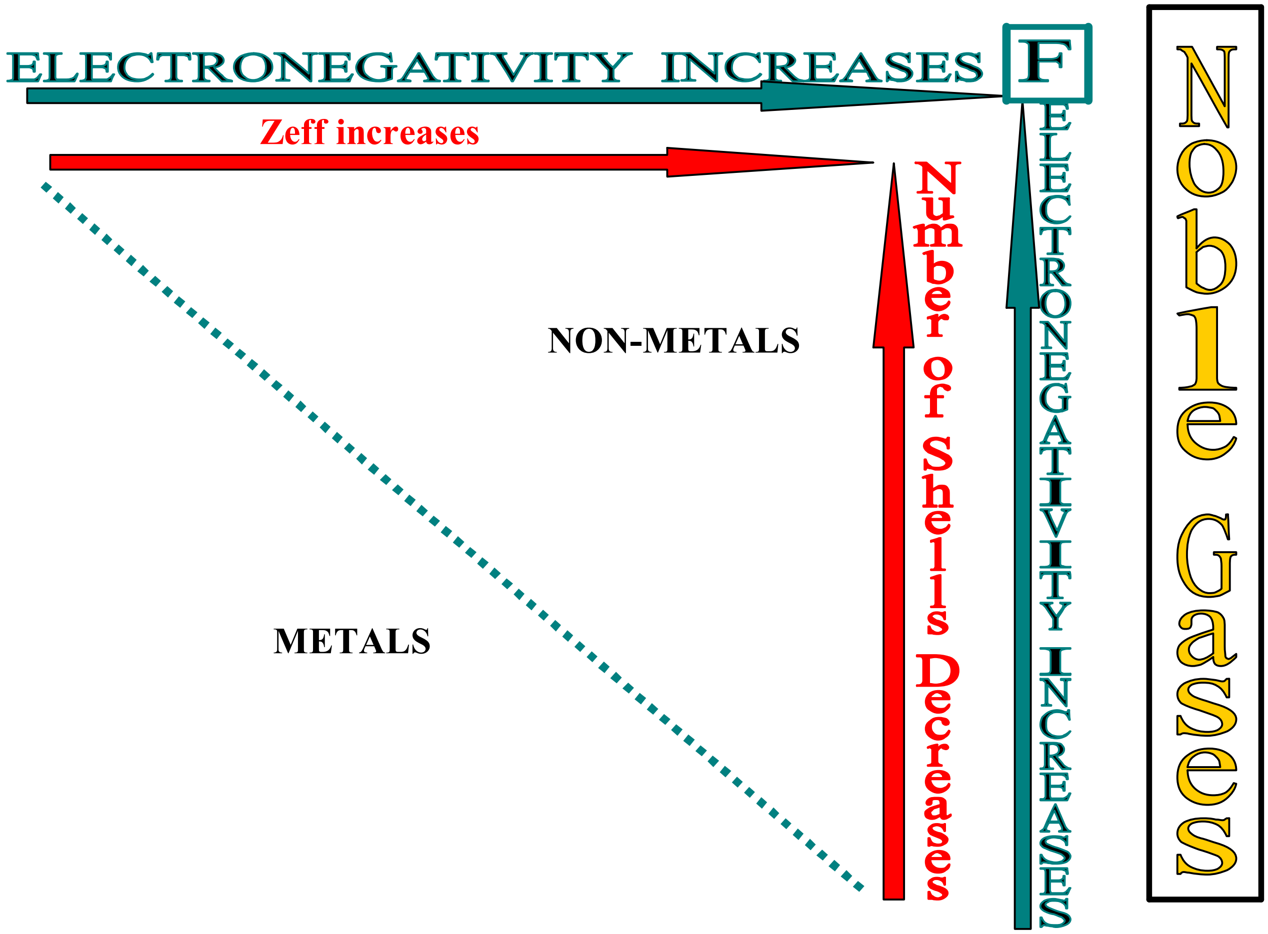
Cs → **F**

Electronegativity: **0.7** (**Least Electronegative Element**) — **Electronegativity increases** → **4.0** (**Most Electronegative Element**)

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB	VIIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA
								H 2.1								
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.5	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac-No 1.1-1.7														

NOTE:

- The trend of the **ELECTRONEGATIVITY** values parallels that of **ELECTRON AFFINITY**
- The same **2 factors** affect both these trends: **Zeff** and **Number of Shells**)



The more different the electronegativity of the elements involved in a bond → **The larger the electronegativity difference (ΔEN)** → The more unequal the electron sharing → **The more polar the bond**

Example: Which bond is more polar , H — Cl or H — F ?

H — Cl	**H — F**
EN(H) = 2.1 EN(Cl) = 3.0	EN(H) = 2.1 EN (F) = 4.0
ΔEN = EN(Cl) – EN(H) **ΔEN = 3.0 – 2.1 = 0.9**	ΔEN = EN(F) – EN(H) **ΔEN = 4.0 – 2.1 = 1.9**
Less polar bond	**More polar bond**
Partial charges not so well separated	**Partial charges better separated**

BOND POLARITY

- **Bond Polarity is a measure of the inequality in the sharing of bonding electrons**

- Most chemical bonds are neither 100 % covalent (equal sharing of bonding electrons), nor 100 % ionic (no sharing); instead, they fall somewhere in between (unequal sharing).

In Summary:

1. **<u>Nonpolar Covalent Bond</u>** (forms between identical atoms)
   There is no difference in electronegativity between the bonded atoms

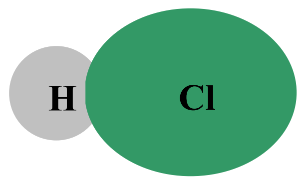
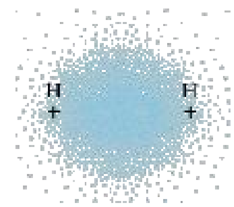
2. **<u>Polar Covalent Bond</u>** (forms between moderately different atoms)
   The electronegativity difference between the bonded atoms is greater than zero, but less than 1.7

3. **<u>Ionic Bond</u>** (forms between very different atoms)
   The electronegativity difference between the bonded atoms is 1.7 or greater.

	BOND TYPE
$\Delta EN = 0$	**Non-polar Covalent**
$0 < \Delta EN < 1.7$	**Polar Covalent**
$\Delta EN > 1.7$	**Ionic**

Degree of Ionic Character Increases ↓

SUMMARY OF BONDS

IONIC BOND	POLAR COVALENT BOND	NON-POLAR COVALENT BOND
$Na^+ Cl^-$ 	$\delta+$ $\delta-$ H — Cl 	H — H 
charges distinctly separated	**partial separation of charges**	**no separation of charges**
Forms by electron transfer	**Forms by unequal sharing of electrons**	**Forms by equal sharing of electrons**
Forms between very different atoms	**Forms between somewhat different atoms**	**Forms between identical atoms**
$\Delta EN > 1.7$	**$1.7 > \Delta EN > 0$**	**$\Delta EN = 0$**

Percentage Ionic Character Increases

←

(gradual transition

PERCENT IONIC CHARACTER

- The primary factor that determines the nature of the bond between two atoms is the Electronegativity Difference (Δ EN) between the atoms:
  - Large Δ EN (Δ EN > 1.7) ⟶ Ionic Bond
  - Moderate Δ EN (0 < Δ EN < 1.7) ⟶ Polar Covalent Bond
  - No Δ EN (Δ EN = 0) ⟶ Non-polar Covalent Bond
- The degree of ionic character of the bond can vary from zero (ΔEN = 0) to over 90% (ΔEN = 3.05) , depending on the electronegativities of the bonded atoms.
- There is no sharp dividing line between ionic and covalent bonds.
- As a very rough guide, bonds become more than 50 % ionic when Δ EN > 1.7
- A bond is considered:

  Ionic: If the % Ionic Character > 50% (Δ EN > 1.7)
  Covalent: If the % Ionic Character < 50% (Δ EN < 1.7)

- Electronegativity Values for each element and the relationship between the **Δ EN** and % Ionic Character of bonds is usually provided on tables such as shown below:

Percent Ionic Character of a Single Chemical Bond

ΔEN	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**	**0.6**	**0.8**	**0.9**	**1.0**	**1.1**	**1.2**	**1.3**	**1.4**	**1.5**	**1.6**	**1.7**
% Ionic Character	**0.5**	**1**	**2**	**4**	**6**	**9**	**15**	**19**	**22**	**26**	**30**	**34**	**39**	**43**	**47**	**51**

ΔEN	**1.8**	**1.8**	**2.0**	**2.1**	**2.2**	**2.3**	**2.4**	**2.5**	**2.6**	**2.7**	**2.8**	**2.9**	**3.0**	**3.1**	**3.2**
% Ionic Character	**55**	**59**	**63**	**67**	**70**	**74**	**76**	**79**	**82**	**84**	**86**	**88**	**89**	**91**	**92**

Examples:

1. What is the % Ionic Character of the bond in MgS ? Is the bond in MgS Ionic or Covalent ?

   EN(S) = 2.58 EN(Mg) = 1.31 Δ EN = 2.58 – 1.31 = **1.27**
   Δ EN = 1.27 **% Ionic Character ≈ 33 %** (less than 50%)
   This bond is Mostly Covalent (Even though Mg is a metal and S is a nonmetal)

2. What is the % Ionic Character of the bond in MgO ?Is the bond in MgO Ionic or Covalent ?

   EN(O) = 3.44 EN(Mg) = 1.31 Δ EN = 3.44 – 1.31 = **2.13**
   Δ EN = 2.13 **% Ionic Character ≈ 68 %** (more than 50%)
   This bond is Mostly Ionic