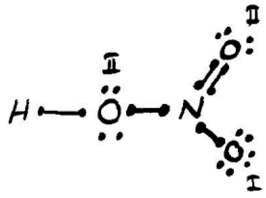
CHEMICAL BONDING

FORMAL CHARGE

Formal charge is the apparent electronic charge of each atom in a molecule based on the electron dot structure. All bonds are considered to have 100% covalent character while determining the formal charge.

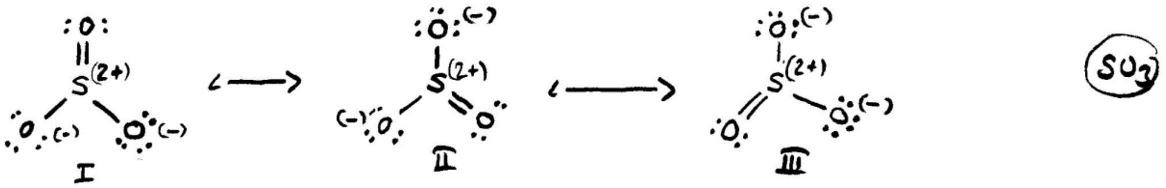
Formal charge = Number of valence electrons (group number)-[number of unpaired electrons + number of covalent bonds]



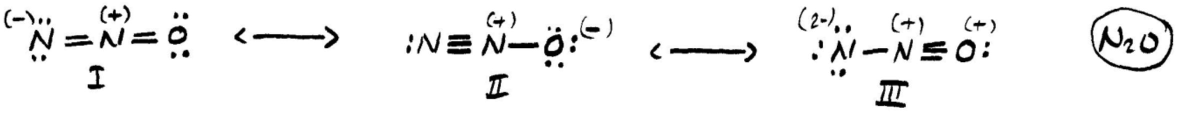
$N: 5-4=1$
$H: 1-1=0$
$O_{I}: 6-7=-1$
$O_{II}: 6-6=0$

RESONANCE

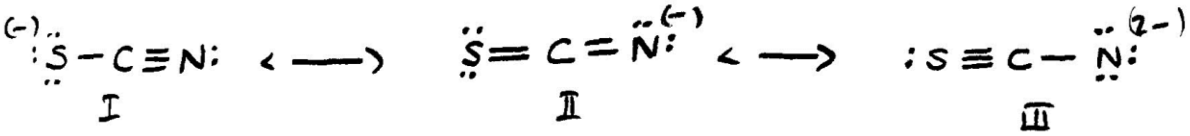
Resonance means that the octet principle and observed experimental properties of a molecule is not explained by a single electronically formula and that a molecule is shown by more than one Lewis point structure.



Experimental data have shown that all S-O bonds in this molecule are equivalent and have a length between the single bond and the double bond. The actual structure of the molecule is a mixture of all resonance structures. The molecule is so stable how many resonance structures are possible.

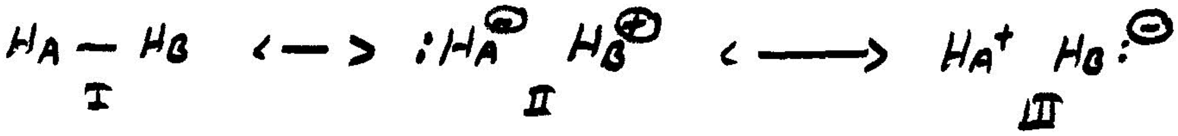


All three structures provide the octet principle. However, structure III is not a resonance structure for N_2O since the N-O bond will break as a result of electrostatic repulsion due to the same kind of formal charges on neighboring atoms. Due to the fact that the negative formal charges are on the electronegative atom, the resonance structure II is preferred over the structure I. Therefore, proton is attached to the N atom in HNCS molecule.

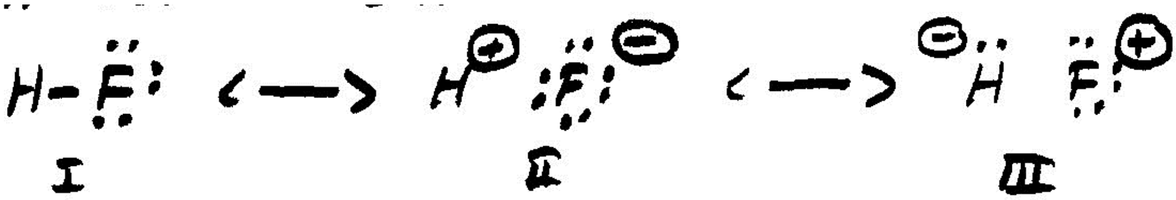


RESONANCE and STABILITY of RESONANCE STRUCTURES

Quantum mechanics proposes the following three structures to explain the charge distribution of a simple molecule such as H_2.



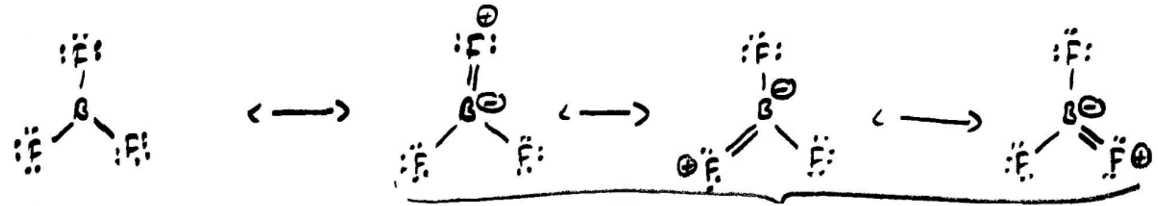
The actual structure for H_2 is a mixture in which these three structures contribute to the stability. Calculations have shown that I is more stable and II and III are equally stable. So the resonance mixture is more characteristic of structure I. Since II and III will contribute equally, the resultant dipole moments of these structures are 0 and therefore the actual structure is the apolar. The resonance which is applied by giving the σ bond electrons to one of the bond atoms is called ionic covalent resonance.



II is more stable than III. Therefore, the resonance contribution of III is negligible and it is considered as a hybrid structure in which the resonance hybrids I and II contribute in proportion to their stability. In addition, due to the high electronegativity of F, it is thought that II contributes more. The contribution of ionic structure in AB type molecules can be predicted from ionic resonance energy values.

In primary resonance structures, the molecules with the following characteristics have secondary or tertiary resonance structures.

1. *The central atom has not completed its octet has not completed and the valence shell of the atoms connected to the central atom is full.*

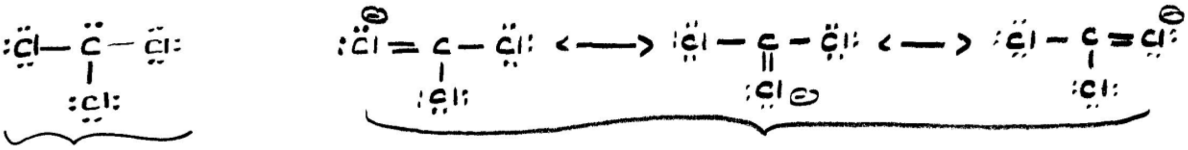


Primary resonance structure

Secondary resonance structures

Acidity order $BF_3 < BCl_3 < BBr_3$

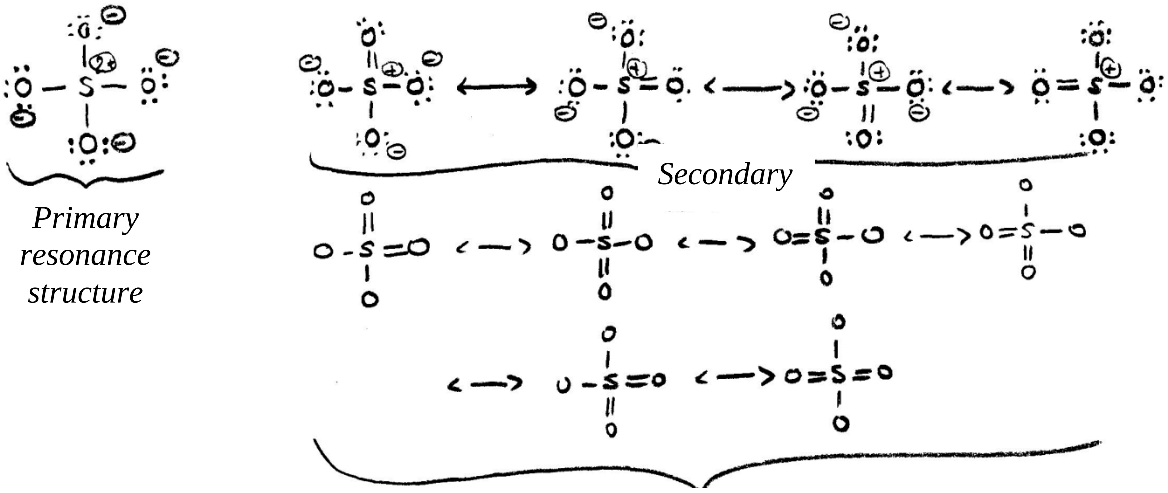
2. *The central atom contains a lone pair of electrons and there is an empty orbital in the bonded atom or atomic groups. Examples:* CCl_3^-, $N(SiH_3)_3$ *and* CH_3OSiH_3.



Primary resonance structure

Secondary resonance structures

3. *The central atom is an element in the 3rd or lower periods and the formal charge is positive. The valence shell of the bound substituents is full. Examples:* ClO_2^-, SO_2, ClO_3^-, SO_3, SO_4^{2-}.



Primary resonance structure

Secondary

Tertiary resonance structures

BOND ORDER, BOND ENERGY and BOND LENGTH

The bond energy is considered as a measure of the chemical bond force. It is the energy required to break chemical bonds. The arithmetic mean of bond-dissociation energies (bond forces) of a particular bond measured in different chemical environments is called the bond energy. That is, the average bond energy is the energy required to break off a particular bond in any chemical environment.

1. *Bond degree and bond energy increases while bonding is shortened.*

$C-C$	347 kJ·mol^{-1}	$N-N$	159 kJ·mol^{-1}
$C=C$	418 kJ·mol^{-1}	$N=N$	418 kJ·mol^{-1}
$C\equiv C$	514 kJ·mol^{-1}	$N\equiv N$	945 kJ·mol^{-1}

2. *In VA group elements, bond order is the highest (3). The highest bond energy and the shorter bond are in the VA group compared to the other group elements.*

3. *In the molecules having the same bond degree, the atomic size and bond energy decreases while the bond lengthens.*

4. *Lone pairs of electrons of adjacent atoms reduce the bond energy. As a group when we go down from the top to bottom, the bond energy decreases. However, the bond energy of F_2 is smaller than expected. This is due to the fact that there are lone pairs of electrons on the F atoms.*

5. *In molecules with the same bond degree in the same period, bond energies depend on both atomic size and electron electron repulsion. C_2 has higher bonding energy than O_2. Because lone pairs of electrons on the O atom push each other more. As the atom grows, the bond energy decreases. Due to the increase in the atomic sizes in the lower periods, the effect of electron electron repulsion decreases.*

$$:C{=}C: \;\; ; \;\; :\ddot{O}{=}\ddot{O}:$$

6. *In CH_4, C makes sp^3 hybridization. In $H_3C\cdot$, C also makes sp^3 hybridization, but, one electron is present in one of the hybrid orbitals. As a result, the s character of the hybrid orbital to be used in the formation of the C-H bond will increase and a more powerful hybrid orbital overlaps with 1s orbital of H and the bond will be stronger.*

Decrease in bond energies of H_2C and HC is due to increased pushing between single electrons.

$$CH_4 \longrightarrow H_3C\cdot + H\cdot \qquad BE_1 = 421{,}1\ kJ.mol^{-1}$$
$$H_3C\cdot \longrightarrow H_2\dot{C}\cdot + H\cdot \qquad BE_2 = 469{,}9\ kJmol^{-1}$$
$$H_2\dot{C}\cdot \longrightarrow H\dot{\underset{\cdot}{C}}\cdot + H\cdot \qquad BE_3 = 415{,}0\ kJmol^{-1}$$
$$H\dot{\underset{\cdot}{C}}\cdot \longrightarrow \cdot\dot{\underset{\cdot}{C}}\cdot + H\cdot \qquad BE_4 = 334{,}7\ kJmol^{-1}$$

$\Delta H_{BE(C\text{-}H)}$=*arithmetic mean of all*

The CONTRIBUTION of σ and π BONDS TO MULTIPLE BONDS

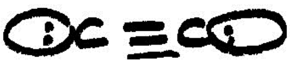
The multiple bond formed between the two atoms usually contains one σ and one or two π bonds. To measure how much of the multiple bond energy is due to the interaction of σ and how much of the multiple bond energy is due to the interaction of π;

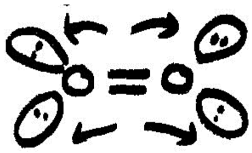
1. *The strength of a bond depends on the chemical environment of the bond. The inductive and steric effect of substituents, hybridization and electron-electron repulsion affect the bond force. The energy of the N-N bond with only the σ interaction is different in the $H_2N\text{-}NH_2$ and $F_2N\text{-}NF_2$ molecules.*
2. *σ and π interactions mutually reinforce each other. A strong σ interaction leads to a strong π interaction or a strong π interaction leads to a strong σ interaction. With this mutual reinforcement (synergistic) effect, the σ interaction in HN=NH is stronger than the σ interaction in $H_2N\text{-}NH_2$.*

$$E_\sigma = E_s\left[\frac{d_s}{d_m}\right]$$

E_σ= σ bond energy
E_S=single bond energy
d_S= single bond length
d_m= multiple bond length

3. *In the O_2, the σ interaction is weaker than the π interaction indicates that electron-electron repulsions weaken the σ interaction.*





4. *In a group, the interaction between σ and π generally weakens from top to bottom.*
5. *In a group, the π interaction decreases more than the σ interaction from top to bottom.*

BOND FORCE and BOND ENERGY

Bond force constants are found from IR or Raman spectroscopic data. Vibration frequencies are measured by these methods. The frequency of a molecule with two atoms as a wavenumber;

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_1 . m_2}{m_1 + m_2} \cdot \frac{1}{N}$$

Hooke law
1mdyn/Å=10^2 Nm^{-1}
μ*=reduced mass*
k*=bond force constant*
c*=the speed of light*

N*=Avagadro number*
m_1 *and* ***m_2****=atomic mass of elements*

Average bond energy of O-H bond in H_2O molecule:

$$H_2O(g) \longrightarrow HO(g) + H(g) \quad \Delta H_1 = D_1 = 499\ kJmol^{-1}$$

$$OH(g) \longrightarrow O(g) + H(g) \quad \Delta H_2 = D_2 = 428\ kJmol^{-1}$$

$$\Sigma_{O-H} = \frac{499+428}{2} = 463{,}5\ kJmol^{-1}$$

Average bond energy of C-O bond in CO_2 molecule:

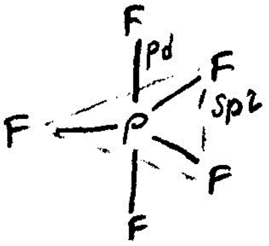
$$CO_2(g) \longrightarrow CO(g) + O(g) \quad \Delta H_1 = D_1 = 531\ kJmol^{-1}$$

$$CO(g) \longrightarrow CO(g) + O(g) \quad \Delta H_2 = D_2 = 1072\ kJmol^{-1}$$

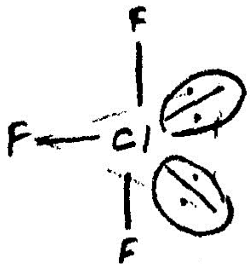
To break the second O-H bond in the H_2O molecule requires less energy, while in the CO_2 molecule this is the exactly opposite. The reason for this is that the bond degree changes due to the changing hybridization of the A atom in the AX_{n-1} structure formed by the separation of X. As the bond energy increases with an increasing bond degree, the second dissociation energy is higher in CO_2 molecule.

BOND ENERGY and BOND LENGTH

The s orbital is the closest orbital to the nucleus. For this reason, the bond participating in a hybrid orbital with a high s character is shorter and thus the bond energy is higher. There are two different bonds in the PF_5 and ClF_3 molecules. Since s character in axial positions is low, axial X-F bonds are longer than equatorial X-F bonds. The difference between axial bonds and equatorial bonds in ClF_3 is larger than that of PF_5. Unpaired electron pairs increase the s character of the hybrid orbital in which it exists, while reducing the s character of the hybrid orbital in the equatorial Cl-F bond.



P-F *(axial)=157.7 pm*
P-F *(equatorial)=153.3 pm*



Cl-F *(axial)=167.8 pm*
Cl-F *(equatorial)=159.8 pm*

In the reactions in the gas phase, if the number of chemical species reacting is equal to the number of chemical species formed after the reaction, ΔS≈0. Therefore, whether the reaction occurs spontaneously depends on the sign of ΔH. In the gas phase reactions, the enthalpy change is equal to the sum of the energies of the bonds broken and formed.

$$\Delta H = \sum E_{\text{broken}} - \sum E_{\text{formed}}$$

$$2HBr(g) + I_2(g) \longrightarrow Br_2(g) + 2HI(g)$$

$$\Delta H = (2E_{H\text{-}Br} + E_{I\text{-}I}) - (E_{Br\text{-}Br} + 2E_{H\text{-}I}) = 95\ kJmol^{-1}$$

This result indicates that the reaction does not occur spontaneously.

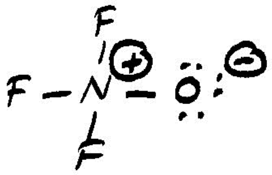
$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g) \qquad \Delta H^\circ_f = \Delta H$$

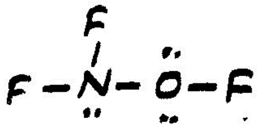
$$\underline{\Delta H^\circ_f = \Delta H = \left(\frac{1}{2}\varepsilon_{N\equiv N} + \frac{3}{2}\varepsilon_{H\text{-}H}\right) - \left(3\varepsilon_{N\text{-}H}\right) = -48\,kJmol^{-1}}$$

THE USE of BOND ENERGIES TO DETERMINE MOLECULAR STRUCTURE and REACTION ENTALPY

The most stable structure or the lowest energy structure for a molecule can be determined using the bond energy

For example, two point structures may be possible for NOF_3.


(I)


(II)

(II) is more stable than (I). Because the formal charges of atoms are 0.

$E_{(I)}=3\varepsilon_{N\text{-}F} + 1\varepsilon_{N\text{-}O}=3\ (283) + 1\ (201)=1050\ kJmol^{-1}$

$E_{(II)}=2\varepsilon_{N\text{-}F} + 1\varepsilon_{N\text{-}O} + 1\varepsilon_{O\text{-}F}=2\ (283) + 1\ (201) + 1\ (184)=951\ kJmol^{-1}$

These results show that the structure (I) has 1050-951=99 $kJmol^{-1}$ *lower energy.*

Structure (I) is more stable according to bond energy

Although the structure (II) seems more stable in terms of formal charges, it is more unstable due to repulsion between electron pairs of neighboring atoms.

DIPOL MOMENT

Bonds between atoms with different electronegativity are polar bonds. Such bonds are partial negative and positive, and have permanent dipole character. The polarity of the dipole molecule $A^{\delta+}-B^{\delta-}$ *can be experimentally measured by measuring the dielectric constant (ε) of the AB molecule. The dielectric constant is the ratio of the capacity of a capacitor filled with the AB molecule to the capacity (Cv) in vacuum.*

$$\frac{C}{C_v} = \frac{\varepsilon}{\varepsilon_v}$$

$A^{\delta+}-B^{\delta-}$ *or* $A\overset{\longrightarrow}{-}B$

The dipole moment is a magnitude giving the dipol property and is equal to the distance between the negative charge and the positive charge multiplied by the load. Measured by the Debay unit. The compounds with high dipole moment have high polarity and high boiling point. The polarity of the bonds is given by the dipole moment. The dipole moment is a vector $(A^{\delta+}\longrightarrow B^{\delta-})$ *directed towards a more electronegative atom.*

.

$$\mu = q.d$$

$$\mu = 1{,}6.10^{-19}\,C.\ 1.10^{-10}\,m = 1{,}6.10^{-29}\,C.m$$

$$1{,}6.10^{-19}\,C = 4{,}8.10^{-10}\,esb \qquad 1.10^{-18}\,esb..cm = 1D$$

$$\mu = 1{,}6.10^{-29}\,C.m.\frac{4{,}8.10^{-10}\,esb}{1{,}6.10^{-19}\,C}.\frac{100\,cm}{1m}$$

$$\mu = 4{,}8.10^{-18}\,esb..cm = 4{,}8\,D$$

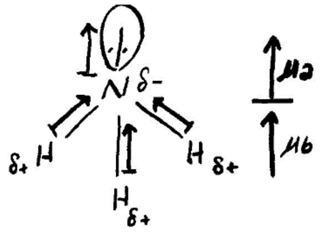
$$\boldsymbol{\mu_{exp.}}$$

$$IC\% = \frac{\mu_{deney}}{\mu_{calc.}} \times 100$$

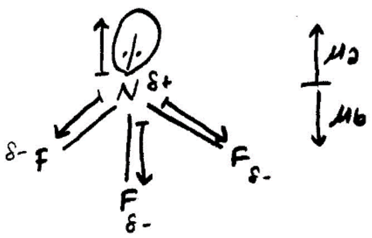
$IC\% > \%50$ ionic

$< \%50$ covalent

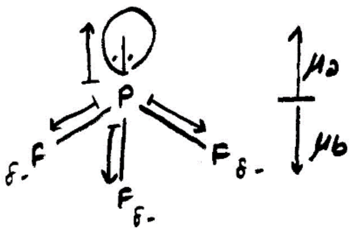
QUESTION: *Compare the dipole moments, polarity and boiling points of NH_3, NF_3 and PF_3.*



$\mu_{molekül} = \mu_a + \mu_b \neq 0$



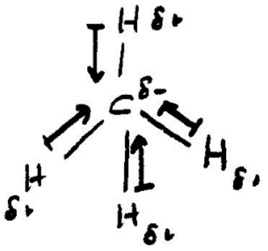
$\mu_{molekül} = \mu_a - \mu_b \neq 0$



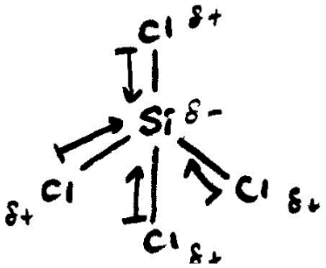
$\mu_{molekül} = \mu_a - \mu_b$

Since the most polar molecul is NH_3, the boiling point of NH_3 is the highest. Since the polarity of the P-F bond is higher than the polarity of the N-F bond, or since the bond dipole moment of the P-F bond is greater than the bond dipol moment of N-F bond, the boiling point of PF_3 is higher than that of NF_3.

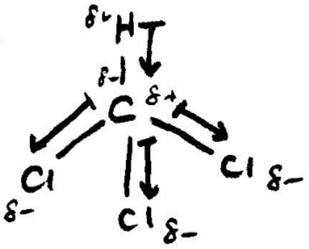
QUESTION: *Compare the dipole moments, polarity and boiling points of CH_4, $SiCl_4$ and $CHCl_3$.*



$\mu_{molecule}=0$
apolar



$\mu_{molecule}=0$
apolar



$\mu_{molecule}\neq 0$
polar

boiling point sequence: $CHCl_3 > SiCl_4 > CH_4$