LECTURE 18/36 OCT/~~18~~ 21/02

COVALENT BOND
IONIC BOND
LEWIS STRUCTURES

BACKGROUND: OXTOBY CH 16

READ TODAY GRAY CH 1-2 - P57-76

NEXT LEC GRAY CH 2 - p77-100

COVALENT BOND

ONE OF THE MOST IMPORTANT PREDICTION OF QM IS RELATED TO MOLECULAR STRUCTURE. IN THE SIMPLEST CASE OF A HOMONUCLEAR DIATOMIC MOLECULE, QM DESCRIBES CORRECTLY H_2 AND PREDICTS THAT NO He_2 MOLECULE WILL BE FOUND. IT ALSO PREDICTS THAT H_2 IS A DIAMAGNETIC MOLECULE WHILE H_2^+ IS PARAMAGNETIC.

BEFORE USING QM TO DESCRIBE MOLECULES WE REVIEW LEWIS STRUCTURES. IN THE LEWIS MODEL WE DESCRIBE H_2 AS

$$H{:}H \quad \text{OR} \quad H-H$$

WHERE THE SINGLE LINE REPRESENTS THE 2 SHARED ELECTRONS.

IN THE CASE OF FLUORINE WE USE THE OCTET RULE

$$:\ddot{\underset{..}{F}}-\ddot{\underset{..}{F}}:$$

THE BOND ENERY (BE) FOR $H_{2(g)}$ IS EQUAL TO 103 Kcal mol^{-1} WHILE FOR $F_{2(g)}$ IS 33 Kcal mol^{-1}.

THE DIFFENCE IN ENERGY IS DUE TO THE REPULSION OF THE UNSHARED ELECTRONS

FOR THE SECOND ROW ELEMENT WE USE THE OCTET RULE WHILE MORE THAN 8e^- MAY BE ASSOCIATED WITH ATOMS IN THE THIRD AND HIGHER ROWS.

IONIC BOND

IN CONTRAST WITH electron SHARING (COVALENT BOND), OTHER ATOMS DO NOT SHARE AT ALL OR PARTIALLY SHARE ELECTRONS. ELECTRON AFFINITIES AND IONIZATION ENERGIES HELP US TO UNDERSTAND THIS PROPERTY. IN THE CASE OF $NaCl_{(s)}$ WE CONSIDER THAT THE 3S e^- IN Na IS TRANSFERRED TO A 3P ORBITAL (Cl).

$$[Na^+][:\ddot{Cl}:^-]$$

OR

$$Na^+Cl^-$$

THE MODEL IS CONSISTENT WITH BOND ENERGIES

STANDARD BOND ENERGY = ENERGY REQUIRED TO DISSOCIATE A MOLECULE INTO ITS COMPONENT ELEMENTS

$$NaCl \longrightarrow Na + Cl$$

FIRST

$$NaCl \longrightarrow Na^+ + Cl^-$$

IN THE SOLID Na^+ AND Cl^- ARE SEPARATED BY A DISTANCE OF 2.36 Å.

$$E_1 = -\frac{q_1 q_2}{4\pi\epsilon_0 r_1} \quad \text{WITH} \quad r_1 = 1\,\text{A}^\circ$$

$$E_1 = 332 \text{ Kcal mol}^{-1}$$

$$1\,eV = 23.069 \text{ kcal mol}^{-1} \text{ (GRAY p 54).}$$

FOR $r_2 = 2.36\,\text{A}^\circ$

$$E_2 = -\frac{q_1 q_2}{4\pi G_0} \frac{1}{r_1} \frac{r_1}{r_2} = 332 \text{ kcal mol}^{-1} \frac{1}{2.36}$$

$$E_2 = 140 \text{ kcal mol}^{-1}$$

<u>IONIZATION ENERGY</u>

$$Na + h\nu_{IE} \longrightarrow Na^+ + e^-$$

$$h\nu_{IE} = 5.14\,eV = 119 \text{ kcal mol}^{-1}$$

<u>ELECTRON AFFINITY</u>

$$Cl^- + h\nu_{EA} \longrightarrow Cl + e^-$$

$$h\nu_{EA} = 3.61\,eV = 83 \text{ kcal mol}^{-1}$$

$$NaCl \longrightarrow Na^+ + Cl^-$$

$$E = 140\ \text{kcal mol}^{-1} - 119\ \text{kcal mol}^{-1} + 83\ \text{kcal mol}^{-1}$$

$$E = 104\ \text{kcal mol}^{-1}$$

EXPERIMENTAL $E_{BE} = 98\ \text{kcal mol}^{-1}$

ERROR $\simeq$ 6% !

COVALENT BOND WITH IONIC CHARACTER

MOLECULES LIKE HCl ARE NEITHER PURELY COVALENT NOR PURELY IONIC. THE LEWIS STRUCTURE FOR HCl

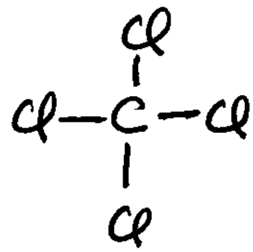
$$\overset{\delta+}{H} - \overset{\delta-}{\ddot{\underset{..}{Cl}}}:$$

ELECTRON PAIR IS PULLED TOWARDS THE CHLORINE ATOM. AS A CONSEQUENCE, H-Cl HAS A PERMANENT DIPOLE MOMENT.

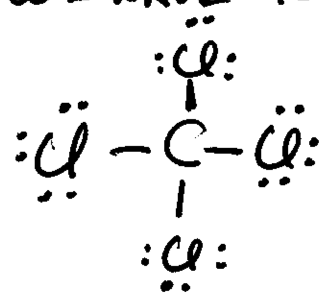
MOLECULES WITH PERMANENT DIPOLE TEND TO ALIGNE IN AN ELECTRIC FIELD.

LEWIS STRUCTURES

CCl_4 CARBON TETRACHLORIDE



BUT WE HAVE TO USE THE OCTET RULE. THUS



OCTET RULE = 8 VALENCE e^- ASSOCIATED WITH EACH ATOM.

VALENCE e^- NOT INVOLVED IN BONDING ARE THE LONE PAIR OR UNSHARED PAIR ELECTRONS.

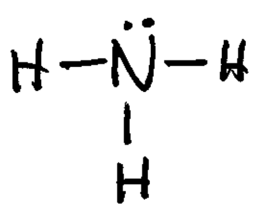
IN THE CASE OF CCl_4 THE C–Cl BOND HAS A PARTIAL IONIC CHARACTER,

$$\overset{\delta+}{C}-\overset{\delta-}{Cl}.$$

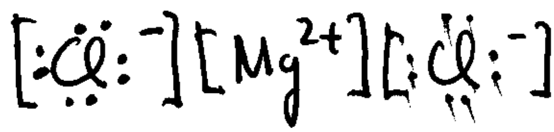
THEREFORE THIS BOND HAS A POLAR CHARACTER BUT CCl_4 DOESNOT HAVE A PERMANENT DIPOLE

THE SUM OF THE 4 DIPOLES IS EQUAL TO ZERO.

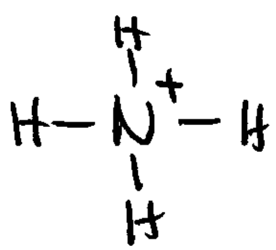
NH_3 AMONIA (COVALENT)



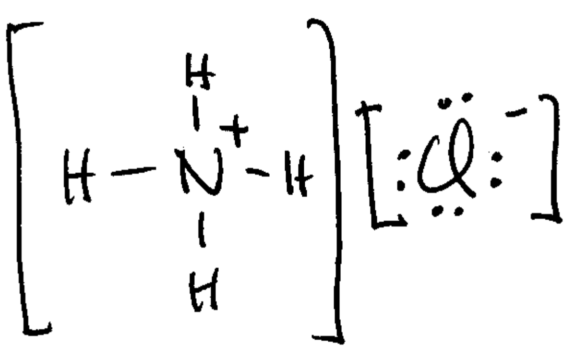
$MgCl_2$ MAGNESIUM CHLORIDE (IONIC)



NH_4Cl AMONIUM CHLORIDE



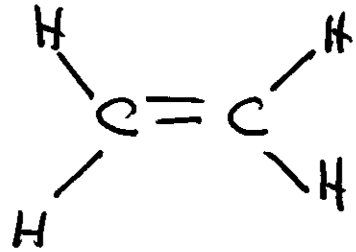
THE CHARGE ON THE NITROGEN IS CALLED A FORMAL CHARGE.

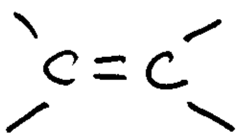


DOUBLE AND TRIPLE BONDS

C_2H_4

ETHYLENE



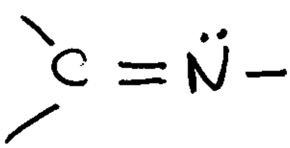


$-\ddot{N}=\ddot{N}-$

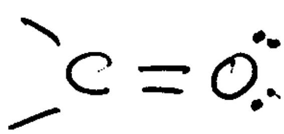
$-C\equiv C-$

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

N_2 $\quad :N\equiv N:$



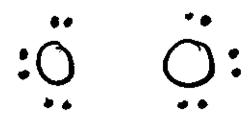
$-C\equiv N:$

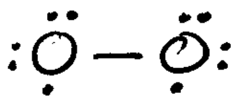


NO NITRIC OXIDE

$:\ddot{N}\cdot \quad \ddot{\underset{..}{O}}: \longrightarrow \quad :\dot{N}=\underset{..}{O}:$

ONE UNPAIRED e^- $\Rightarrow$ PARAMAGNETIC

O_2  MOLECULAR OXYGEN IS PARAMAGNETIC



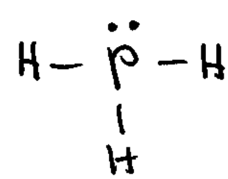
 CONSISTENT WITH BOND LENGTH

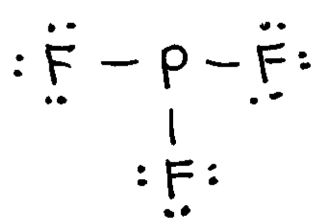
PROBLEM?

OCTET RULE ⟷ SECOND ROW (B, C, N, O, F)
NON METALLIC

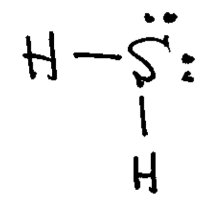
EXCEPTION TO THE RULE VERY RARE

BEYOND THE SECOND ROW THE OCTET RULE IS NOT THAT GENERAL.

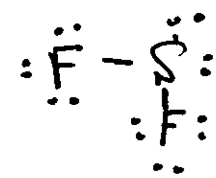
PHOSPHINE PH_3 

PHOSPHOROUS TRIFLUORIDE PF_3 

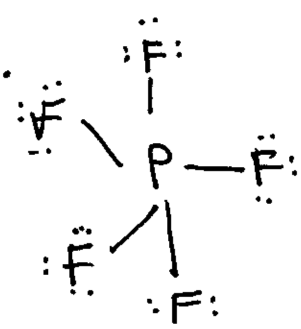
HYDROGEN SULFIDE H_2S

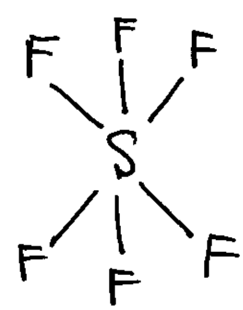


SULFUR DIFLUORIDE SF_2



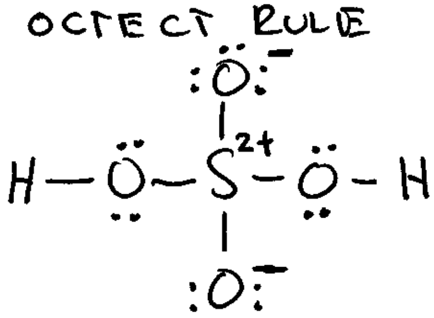
BUT PF_5 AND SF_6 DO NOT FOLLOW THE OCTET RULE. P AND S CAN USE THE 3d ORBITALS.



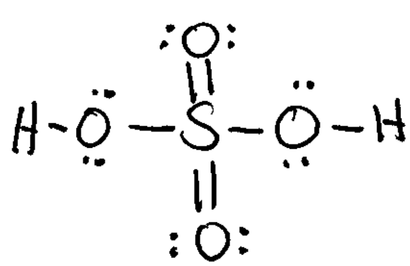


CONSIDER SULFURIC ACID H_2SO_4

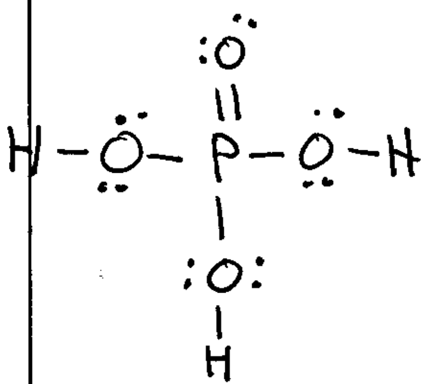
THE OCTECT RULE IMPLIES



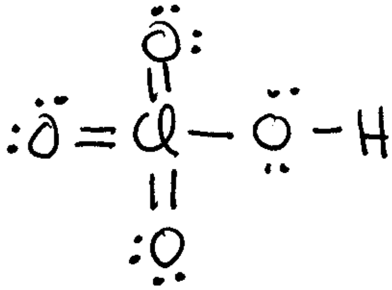
BUT S IS AN ELECTRONEGATIVE NON METAL !



PHOSPHORIC ACID H_3PO_4

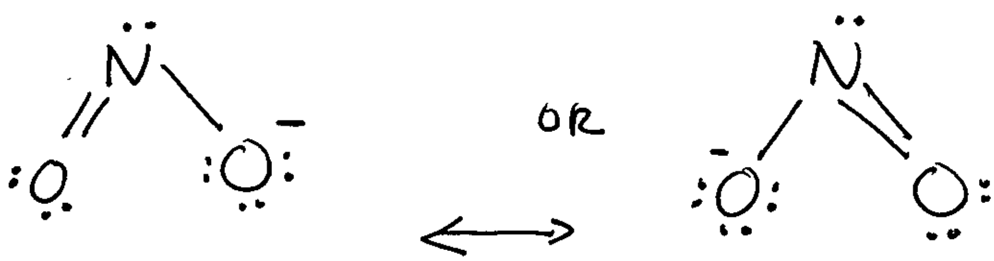


PERCHLORIC ACID $HClO_4$

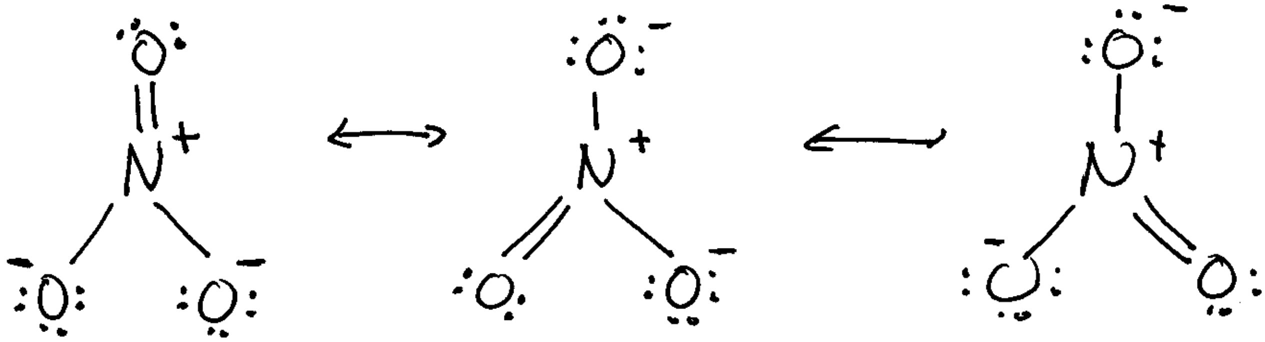


RESONANCE

CONSIDER NO_2^-



NO_3^-



HOW ABOUT SO_4^{2-}