LECTURE NOTES FOR GENERAL CHEMISTRY ©2007 MM

CHAPTER 9 CHEMICAL BONDS

CHEMICAL BONDS ARE ELECTRICAL FORCES

AN ELECTRON IN A CHEMICAL BOND IS ATTRACTED TO BOTH NUCLEI

TWO NUCLEI APPROACH EACH OTHER UNTIL THEIR REPULSIVE FORCES (LIKE CHARGES REPEL) ARE EQUAL TO THEIR ATTRACTIVE FORCES

VALENCE ELECTRONS ARE ELECTRONS IN AN ATOM'S OUTER MOST SHELL

CHEMICAL BONDS ARE MADE WITH VALENCE ELECTRONS

WHEN METALS AND NONMETALS COMBINE, VALENCE ELECTRONS ARE TRANSFERRED TO THE NONMETAL FROM THE METAL. THIS IS IONIC BONDING

EXAMPLE

$Na + F \longrightarrow Na^+ F^-$ BOTH ATOMS NOW HAVE "CLOSED" OR FILLED SHELLS

$[Ne]3s^1$ $[He]2s^2 2p^5$ $[Ne]$ $[Ne]$ THE NOBLE GAS CONFIGURATION

THE "OCTET" RULE

WHEN NONMETALS COMBINE PAIRS OF ELECTRONS ARE SHARED

THIS IS COVALENT BONDING

EXAMPLE

$H\cdot + H\cdot \longrightarrow H_2$ H:H THIS IS A LEWIS SYMBOL

LEWIS SYMBOLS

1A	2A	3A	4A	5A	6A	7A	8A
Li·	·Be·	·B̈·	·C̈·	·N̈:	:Ö:	:F̈:	:N̈e:

USING THE ABOVE IONIC REACTION:

$Na\cdot + :\ddot{F}: \longrightarrow Na^+ + :\ddot{F}:^-$

ANOTHER

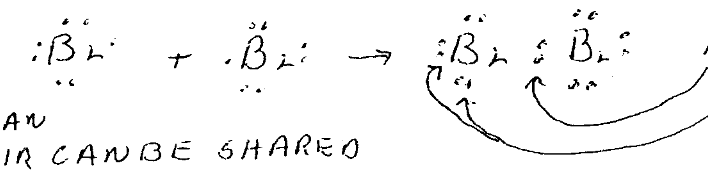
$Ca: + :\ddot{O}: \longrightarrow Ca^{2+} + :\ddot{O}:^{2-}$

IONIC COMPOUNDS FREQUENTLY FORM CRYSTALS - A REGULAR, ALTERNATING ARRANGEMENT OF POSITIVE AND NEGATIVE IONS - A CRYSTAL "LATTICE"

THE BORN-HABER CYCLE IS A THERMOCHEMICAL CALCULATION SUMMING THE ENTHALPY CHANGES INVOLVED IN FORMING AN IONIC COMPOUND FROM THE ELEMENTS. MOST OF THE FAVORABLE ENERGY CHANGE COMES FROM FORMING THE BONDS IN THE CRYSTAL — THE "LATTICE ENERGY"

COVALENT BONDING - ELECTRON PAIRS ARE SHARED

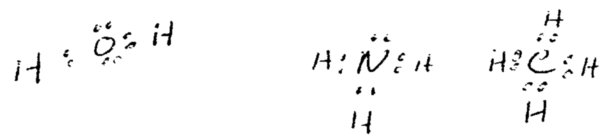
ATOMS TRY TO ATTAIN THE NOBLE GAS STRUCTURE



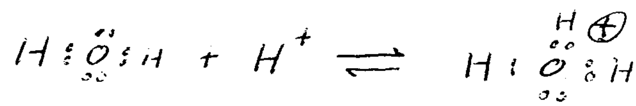
A SHARED PAIR OF ELECTRONS

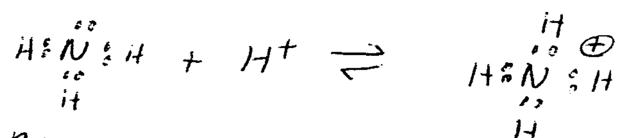
LONE PAIRS

MORE THAN ONE PAIR CAN BE SHARED



IF ONE ATOM CONTRIBUTES BOTH ELECTRONS ITS CALLED A COORDINATE COVALENT BOND





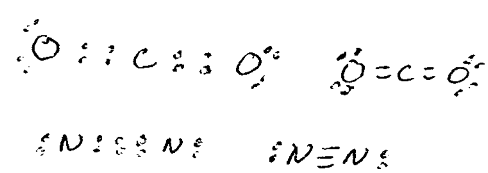
AMMONIA

AMMONIUM

MULTIPLE BONDS ARE POSSIBLE

DOUBLE BOND → 2 PAIRS SHARED

TRIPLE BOND → 3 PAIRS SHARED



A STRAIGHT LINE BETWEEN 2 NUCLEI INDICATES AN ELECTRON-PAIR BOND

POLAR COVALENT BONDS

ELECTRONEGATIVITY IS A ~~A~~ MEASURE OF HOW STRONGLY AN ATOM ATTRACTS ELECTRONS

THE VALUES RANGE FROM ABOUT 1 TO 4

ELECTRONS ARE NOT SHARED EVENLY IN A BOND IF THE BONDED ATOMS DIFFER IN ELECTRONEGATIVITY

WITHIN A PERIOD, ELECTRONEGATIVITY INCREASES FROM LEFT TO RIGHT

WITHIN A GROUP, ELECTRONEGATIVITY INCREASES FROM BOTTOM TO TOP

THE ELECTRONEGATIVITY <u>DIFFERENCE</u> DETERMINES HOW EVENLY ELECTRON PAIRS WILL BE SHARED

NON POLAR

H – H   Cl – Cl   DIFFERENCE = 0

SLIGHTLY POLAR

C – H 0.4   Si – H 0.3

QUITE POLAR

C – F 1.5   C – O 1.0

SO POLAR THAT THEY ARE NO LONGER COVALENT — IONIC

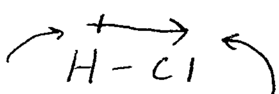
$Na^+ Cl^-$ 2.1   Mg – F 2.8

THERE IS NO DISTINCT BOUNDARY BETWEEN IONIC AND POLAR COVALENT

WE DEPICT POLARITY IN TWO WAYS → δ+, δ−   δ = delta (PARTIAL)

$\overset{\delta^+}{H} - \overset{\delta^-}{Cl}$ INDICATES WHERE THE PARTIAL PLUS AND PARTIAL MINUS IS

OR WITH AN ARROW



POSITIVE END   NEGATIVE END OF THE MOLECULE

WRITING LEWIS STRUCTURES FOR MOLECULES

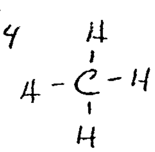
1) WRITE A SKELETAL STRUCTURE

THE CENTRAL ATOM USUALLY HAS THE LOWEST ELECTRONEGATIVITY

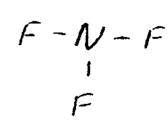
ATTACH ALL ATOMS TO THE CENTRAL ATOM WITH SINGLE DASHES

HYDROGEN ONLY MAKES 1 BOND, SO CANNOT BE THE CENTRAL ATOM

CH_4



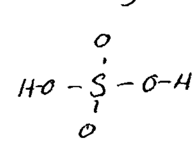
NF_3



TWO MORE USEFUL TIPS

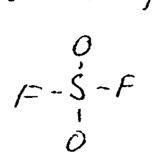
1) IN ACIDS (OXOACIDS) H IS ATTACHED TO O

H_2SO_4



2) MOLECULES AND POLYATOMIC IONS USUALLY HAVE COMPACT, SYMMETRICAL STRUCTURES

SO_2F_2



NOT F – O – S – O – F

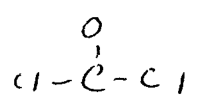
LEWIS STRUCTURES

1) WRITE A SKELETAL STRUCTURE
2) DETERMINE THE TOTAL NUMBER OF VALENCE ELECTRONS

   FOR ANIONS ADD 1 e^- FOR EACH MINUS CHARGE

   FOR CATIONS SUBTRACT 1 e^- FOR EACH PLUS CHARGE
3) PLACE PAIRS OF ELECTRONS AROUND THE TERMINAL ATOMS (NOT H)
4) ASSIGN ANY REMAINING ELECTRONS AS LONE PAIRS AROUND THE CENTRAL ATOM(S)
5) IF NECESSARY, MOVE ONE OR MORE LONE PAIRS FROM A TERMINAL ATOM TO FORM A MULTIPLE BOND TO A CENTRAL ATOM MOST COMMON WITH C=O, N=O OR C≡N N≡N

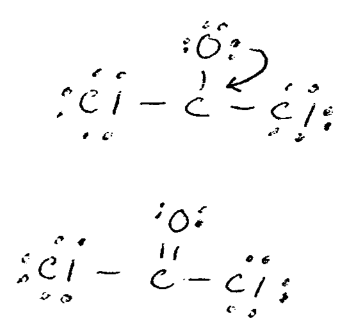
EXAMPLE PHOSGENE $COCl_2$



SKELETAL

TOTAL VALENCE ELECTRONS = C_4 O_6 Cl_7 Cl_7 = 24

PLACE LONE PAIRS ON TERMINAL ATOMS



ALL 24 ASSIGNED

BUT CARBON HAS NO OCTET

SO, MOVE A LONE PAIR INTO A BOND

TO SEE WHY THE NON BONDED LONE PAIR WAS MOVED FROM O RATHER THAN Cl, WE NEED THE CONCEPT OF FORMAL CHARGE

FORMAL CHARGE IS A BOOKKEEPING METHOD FOR ELECTRONS

FORMAL CHARGE IS THE <u>DIFFERENCE</u> BETWEEN THE NUMBER OF ELECTRONS IN THE FREE ATOM AND THE NUMBER OF ELECTRONS IN THE BONDED ATOM

THE NUMBER OF VALENCE ELECTRONS IN THE FREE ATOM EQUAL ITS GROUP NUMBER

FORMAL CHARGE

THE NUMBER OF ELECTRONS IN THE BOUND ATOM IS

1) ALL ITS LONE PAIRS
2) PLUS HALF ITS SHARED PAIRS

IF EACH ATOM IN A LEWIS STRUCTURE CONTRIBUTES HALF OF THE ELECTRONS TO THE BONDS IT FORMS, NONE OF THE ATOMS WILL HAVE A FORMAL CHARGE

THE APPEARANCE OF FORMAL CHARGES INDICATES COORDINATE COVALENT BONDS

USUALLY, FORMAL CHARGES = ZERO

WHERE NECESSARY, SMALL AS POSSIBLE

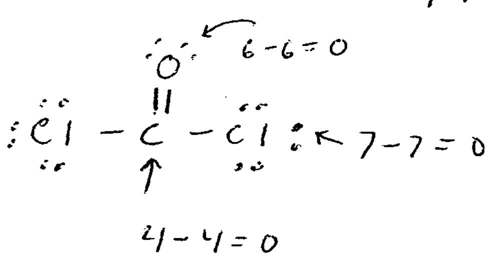
ADJACENT ATOMS DO NOT CARRY FORMAL CHARGES OF THE SAME SIGN

THE TOTAL FORMAL CHARGE ON A NEUTRAL MOLECULE = 0

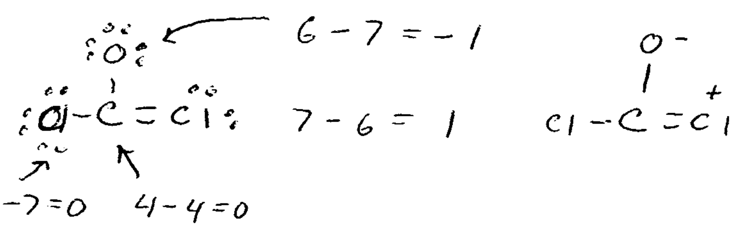
THE TOTAL FORMAL CHARGE ON A POLYATOMIC ION = NET CHARGE FOR THE ION

IN THE $COCl_2$ EXAMPLE

FREE ATOM C = 4
O = 6
Cl = 7



BUT FOR THE ALTERNATIVE STRUCTURE



A MORE SOPHISTICATED CONCEPT

RESONANCE STRUCTURES

ESPECIALLY IN ORGANIC CHEMISTRY

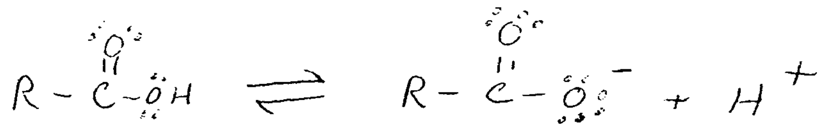
SOMETIMES ELECTRONS MAY NOT BE ASSOCIATED WITH ONE LEWIS STRUCTURE, BUT A COMBINATION OF TWO OR MORE MAY BE NEEDED TO SHOW THE STRUCTURE

A PRIME EXAMPLE IS THE CARBOXYLATE ANION

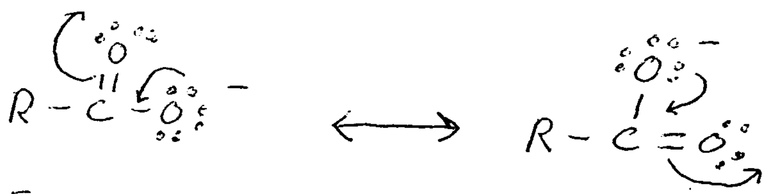
RESONANCE STRUCTURES

WHEN ONE LEWIS STRUCTURE ISN'T ENOUGH

THE CARBOXYLATE ANION IS THE CONJUGATE BASE OF THE CARBOXYLIC ACID

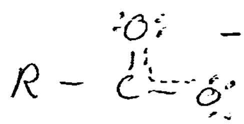


IN MAKING RESONANCE STRUCTURES, MOVE LONE PAIRS TO MAKE DOUBLE BONDS AND DOUBLE BOND ELECTRONS TO MAKE LONE PAIRS



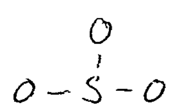
THE ELECTRONS ARE SAID TO BE "DELOCALIZED"

THE ACTUAL STRUCTURE IS NEITHER OF THESE, BUT A RESONANCE HYBRID

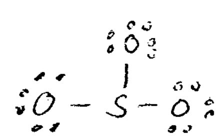


ANOTHER EXAMPLE

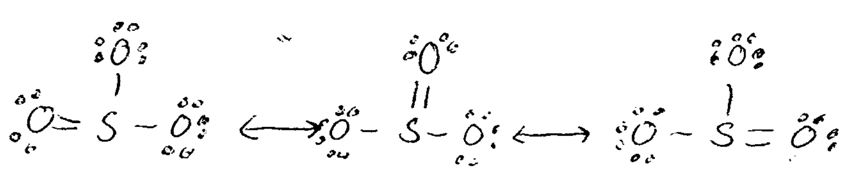
SO_3 EACH ATOM HAS 6 e^- SO $6 \times 4 = 24$



SKELETON

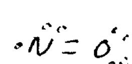


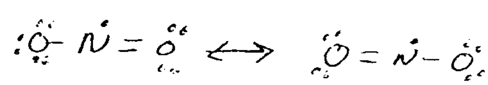
LONE PAIRS ASSIGNED S HAS NO OCTET



MOLECULES THAT DON'T FOLLOW THE OCTET RULE

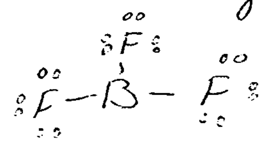
1) ODD NUMBER OF VALENCE ELECTRONS

NO $5 + 6 = 11$ 

NO_2 $5 + 6 + 6 = 17$ 

MOLECULES WITH INCOMPLETE OCTETS

Boron and occaisionally Aluminum

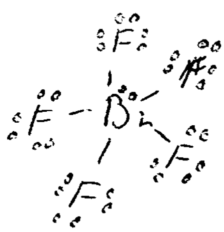


A VALID STRUCTURE

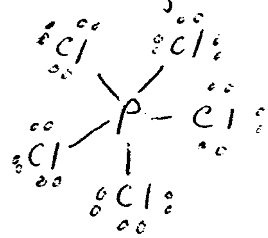
STRUCTURES WITH EXPANDED VALENCE SHELLS

3^{rd} Period AND HIGHER ELEMENTS MAY HAVE EXPANDED VALENCE SHELLS

BrF_5



PCl_5



BOND LENGTHS AND BOND ENERGIES

BOND ORDER → SINGLE, DOUBLE, TRIPLE BONDS

BOND LENGTH → DISTANCE BETWEEN TWO NUCLEI IN A BOND

THE MORE ELECTRONS IN THE BOND, THE SHORTER AND TIGHTER IT IS

FOR UNLIKE ATOMS THE LENGTH OF THE COVALENT BOND IS THE SUM OF THE COVALENT RADII OF THE 2 ATOMS

IF THERE IS A SIGNIFIGANT ELECTRONEGATIVITY DIFFERENCE BETWEEN THE TWO ATOMS, THE BOND WILL BE SOMEWHAT SHORTER

EXAMPLE

C–C BOND IS 154 pm RADIUS = 79 pm

Cl–Cl BOND IS 199 pm RADIUS = 99.5 pm

178.5 pm 178 OBSERVED

BOND ENERGY

ENERGY MUST BE ABSORBED TO BREAK A COVALENT BOND

THE BOND DISSOCIATION ENERGY IS THE AMOUNT OF ENERGY IT TAKES TO BREAK ONE MOLE OF COVALENT BONDS IN THE GAS PHASE

$$Cl_{2(g)} \longrightarrow 2\,Cl_{(g)} \quad \Delta H = B.D.E. = D = +243\ kJ/mol$$

CALCULATIONS WITH BOND ENERGIES

$$\Delta H = \Delta H_{BROKEN} + \Delta H_{MADE}$$

BREAKING BONDS TAKES ENERGY ΔH POSITIVE

MAKING BONDS RELEASES ENERGY ΔH NEGATIVE

EXAMPLE MAKE HCl FROM H_2 AND Cl_2 $H_2 + Cl_2 \rightarrow 2HCl$

BREAK H−H 436
Cl−Cl 243
ΔH_{BREAK} = 679

MAKE 2 X H−Cl
2 X −431 = −862

$$\Delta H_{OVERALL} = 679 + (-862) = -183 \text{ KJ/mol}$$

SKILLS

SKILLS	PROBLEMS
WRITE LEWIS SYMBOLS FOR ATOMS, MOLECULES	EX 1, 2, 6, 7, 8, 11 PROB 8, 9, 33, 41, 57c, 61 35
WORK WITH ELECTRONEGATIVITY AND POLAR BONDS	PROB 43, 45 EX 9.4, 9.5
ASSIGN FORMAL CHARGES	EX 9.9 PROB 47, 49
WRITE RESONANCE STRUCTURES	EX 9.10 PROB 51
WORK WITH BOND LENGTHS	
DO BOND ENERGY CALCULATIONS	EX 9.13 PROB 65, 69, 73, 75