General Chemistry

Chapter 8

Chap 8 Bonding : General Concepts

- What are chemical bonds ?
- Bond polarity and dipole moments
- Covalent bonds
- VSEPR model

§ 8-1 Types of Chemical Bonds

Bond energy : the energy required to break the bond

Ionic Bonding : an atom that loses electrons react w/ an atom that has high affinity to e^-

Covalent Bonding : electrons are shared by nuclei

(1) Ionic Bonding : 主要靠 Coulombic Interaction or Force

$$\underset{\uparrow \text{energy}}{V} = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r} = 2.31 \times 10^{-19} (\text{J nm}) \left(\frac{Q_1 Q_2}{r}\right)$$

e.x. Na^+ Cl^- 核間距 0.276 nm

$$V(\text{Joule}) = 2.31 \times 10^{-19}\ \text{J}\cdot\text{nm} \times \left(\frac{(+1)(-1)}{0.276\ \text{nm}}\right) = \ominus 8.37 \times 10^{-19}\ \text{J}$$

means that " the ion pair has low energy than separated

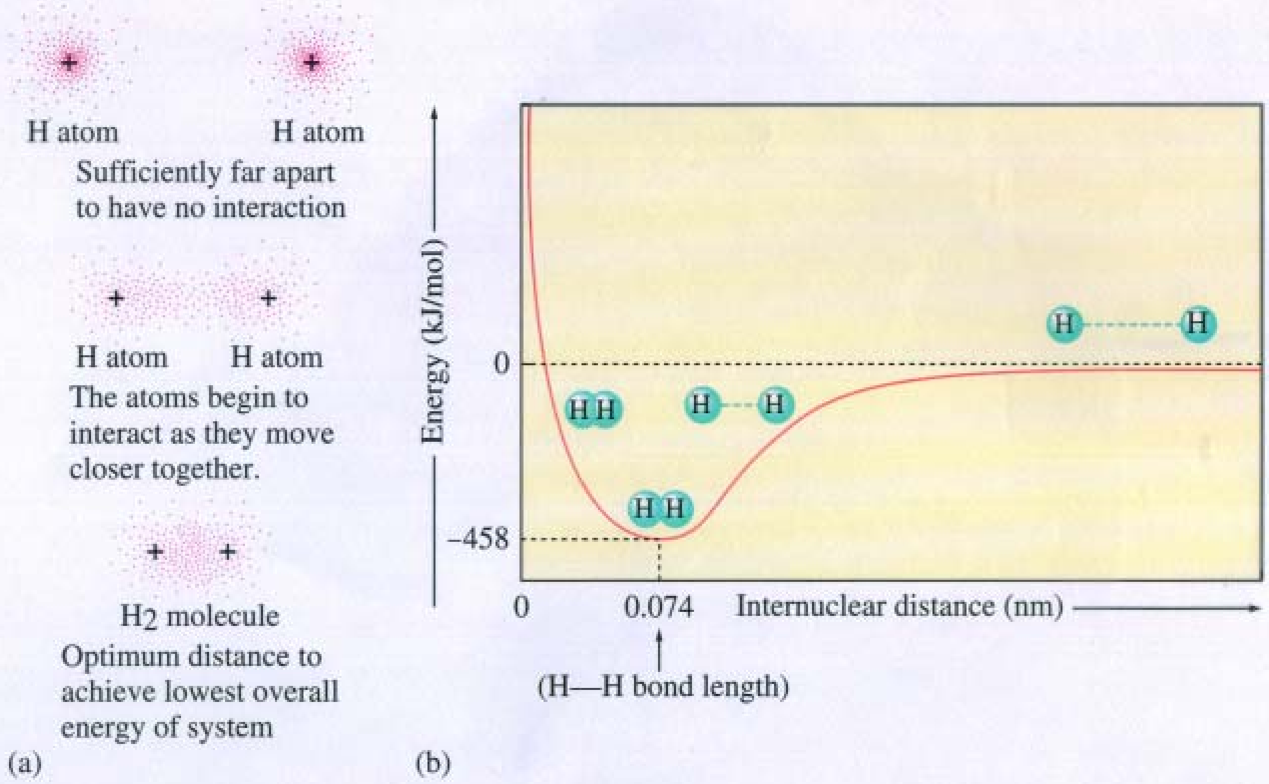

Figure 8.1

Interaction of two H atoms and the energy profile

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$$V = -8.37 \times 10^{-19} \, \mathrm{J/ion\ pair} \times 6.022 \times 10^{23} \, \frac{\mathrm{ion\ pair}}{\mathrm{mole}}$$

$$= \underbrace{-504 \, \mathrm{KJ/mol}}$$

$$Na^{+}_{(g)} + Cl^{-}_{(g)} \rightarrow NaCl_{(g)} \qquad \sim -504 \, \mathrm{KJ/mol}$$

如在 $NaCl_{(s)}$ 結晶格內, energy 會更低

(II) Covalent bonding

$$H_{(g)} + H_{(g)} \longrightarrow H_{2(g)} \qquad -458 \, \mathrm{KJ/mol}$$

See Fig. 8.1

1. The energy terms involved:
   attractions and repulsions among the charged particles
   kinetic energy caused by the motions of the electrons
2. zero reference point of energy:
   atoms at infinite separation
3. bond length is the distance at which the system has minimum energy
4. At very short distances E ↑
   ∵ repulsive forces of nuclei and nuclei
   e^- and e^-

II. Covalent Bonding: electrons are shared by nuclei

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polar covalent bonds :

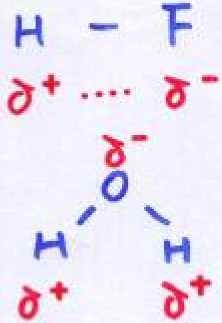

Fig 8-2

§ 8-2 Electronegativity: the ability of an atom in a molecule to attract shared electrons to itself.

Linus Pauling's model: a hypothetical molecule

H X
δ^+ δ^-

Expected H-X bond energy:

$$\sqrt{(\text{H-H bond energy}) \times (\text{X-X bond energy})}$$

(為一假設值) or = $\dfrac{\text{H-H bond energy} + \text{X-X bond energy}}{2}$

The energy difference (Δ):

$$\Delta = (H-X)_{actual} - (H-X)_{expected}$$

$$\text{Net Electronegativity} = EN(X) - EN(H)$$
$$= 0.102\sqrt{\Delta}$$

EN(F) = 4.0 (assigned)

Range : 4.0 (F) ≥ 0.7 (Cs)

Fig 8.3 & 8.2 0.7 (Fr)

Ex. 8.1

	H-H	OH	Cl-H	S-H	F-H
	2.1 2.1	3.5 2.1	3.0 2.1	2.5 2.1	4.0 2.1
$\Delta EN =$	0	1.4	0.9	0.4	1.9

§8.3 Bond Polarity and dipole moment

dipole moment = $\mu = QR$ (SI unit : C m)

Ex. $\overset{\delta+}{H} - \overset{\delta-}{F}$

If HF is totally ionic $H^{+1}\ F^{-1}$

$$\underbrace{\dot{H}\quad \dot{F}}_{R = 9.17 \times 10^{-11} m}$$

$$\mu = (\underline{1.60 \times 10^{-19}\ C})(9.19 \times 10^{-11}\ m)$$
$$= 1.47 \times 10^{-29}\ C \cdot m = 4.40\ \text{Debye}$$

$$1.83\ D = (\delta)(9.17 \times 10^{-11}\ m) \times \frac{1\ D}{3.336 \times 10^{-30}\ Cm}$$

measured

$$(\delta) = 6.66 \times 10^{-20}\ C \quad (\sim 42\%\ \text{ionic bond})$$

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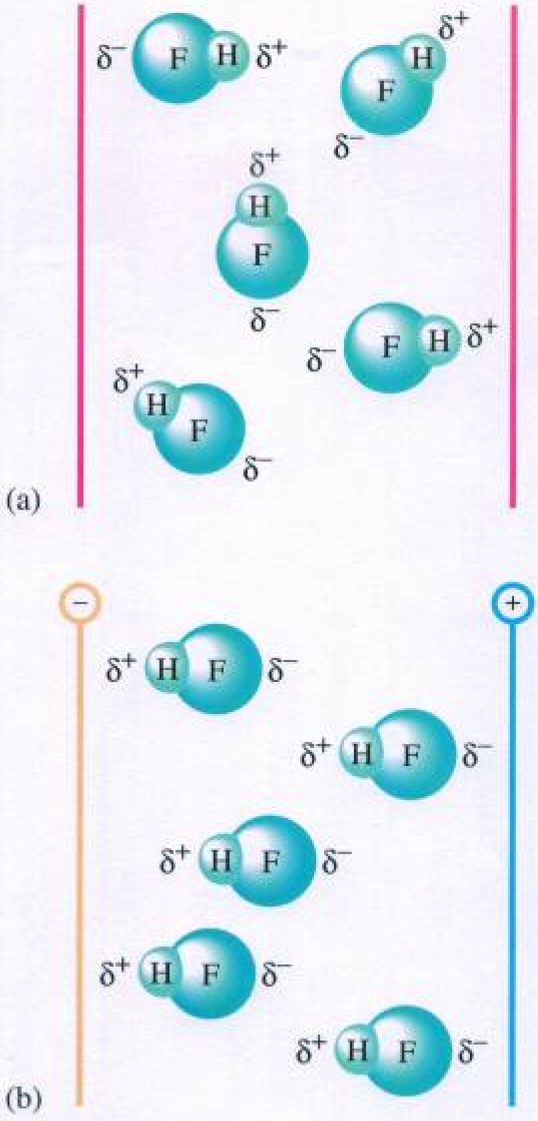

when electric fiel
is "on"
↓
会排列

Figure 8.2

Effect of electric field on HF molecules

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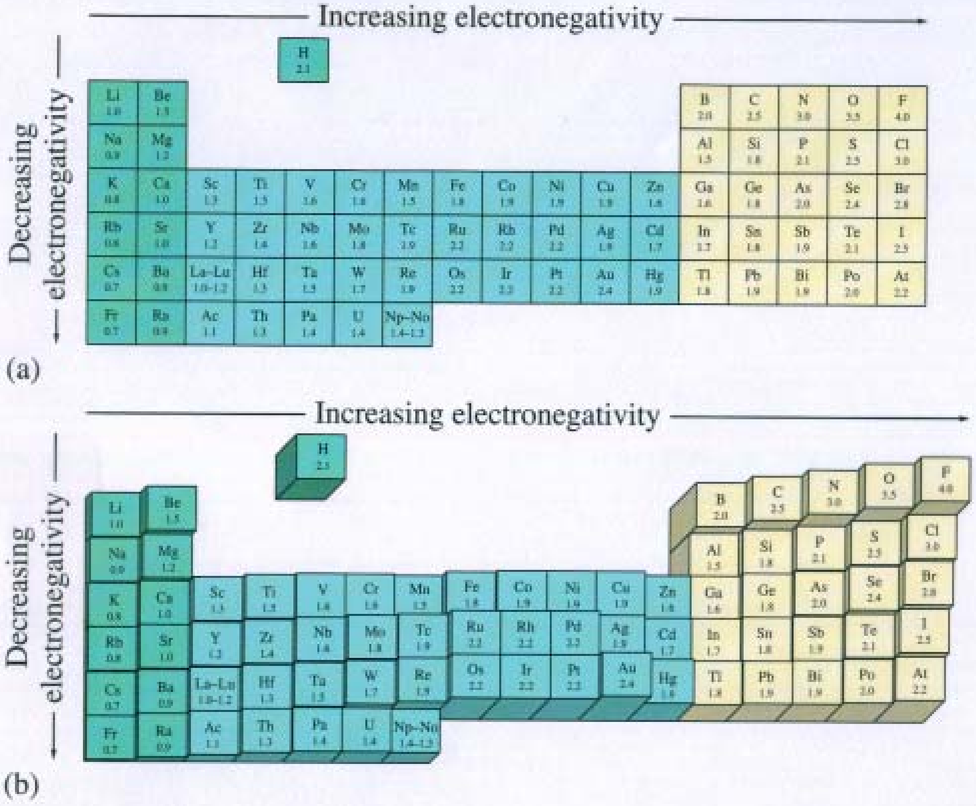

				H 2.1													
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	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 1.0–1.2	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 1.9	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac 1.1	Th 1.3	Pa 1.4	U 1.4	Np–No 1.4–1.3										

Figure 8.3

Pauling electronegativity values

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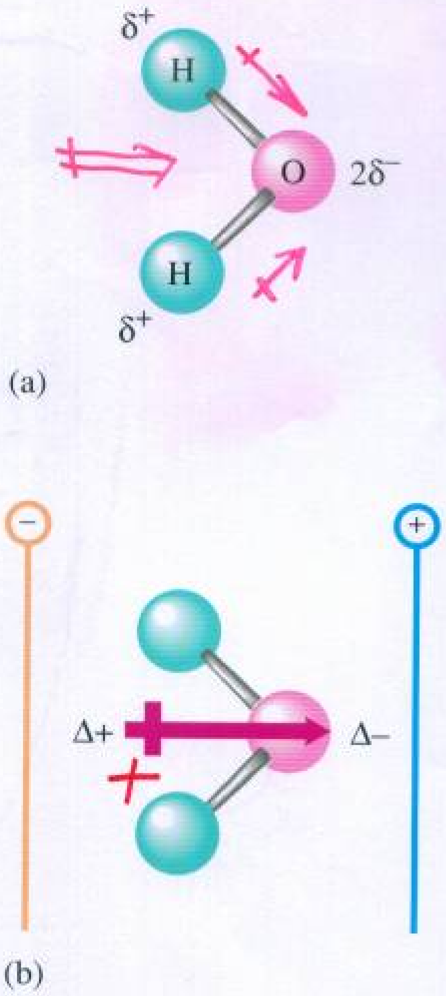
8-8



(a)

(b)

Figure 8.4

Dipole moment for H_2O

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8-~~8~~
9

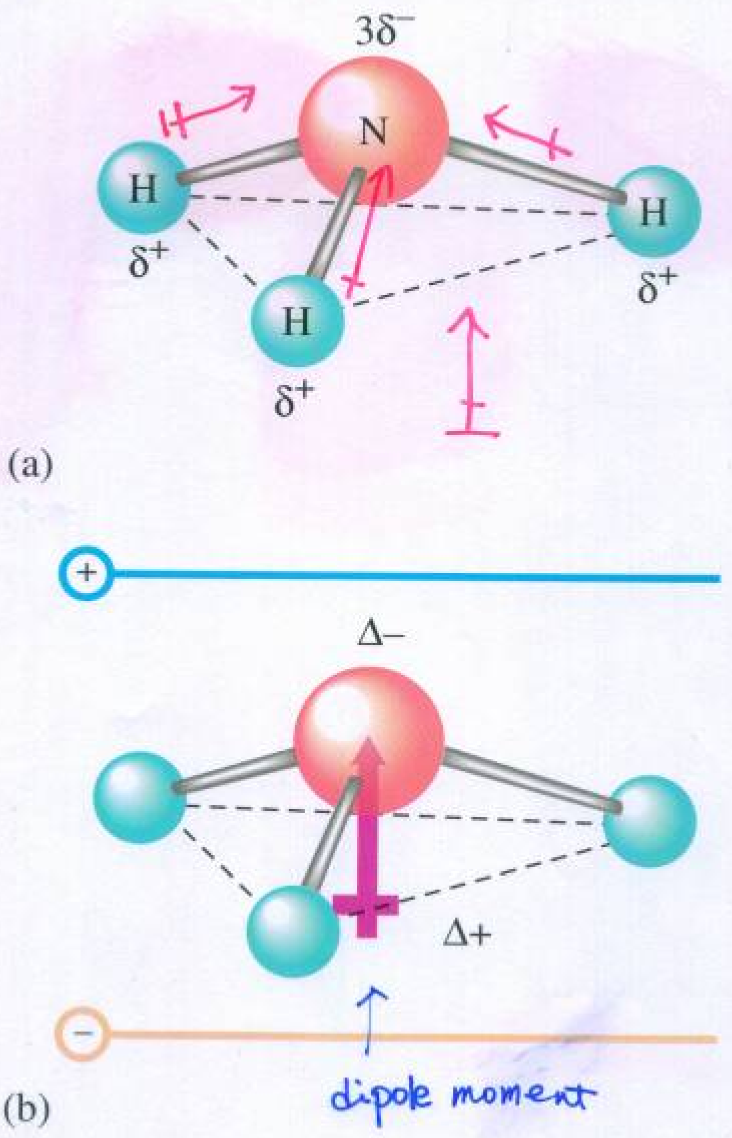


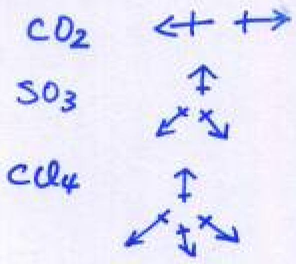
Figure 8.5

Dipole moment for NH_3

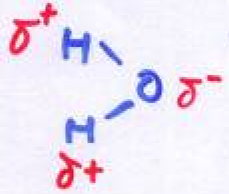
Table 8-2

	dipole moment
CO	0.112
HF	1.83
NaCl	9.00
KBr	10.41

Types of molecules w/ polar bonds w/o Net dipole moment: 8-10



Polyatomic molecules:



is polar molecule

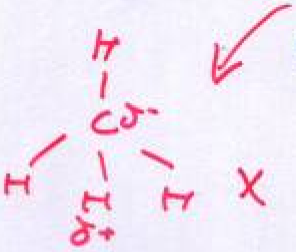
Fig. 8-5 Fig 8-6

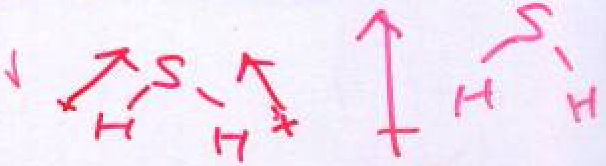
Table. 8-2 (page 356)

Ex. 8-2 $\overset{\delta+\ \delta-}{HCl}$ $\overset{Cl-Cl}{Cl_2}$ SO_3 (planar)

CH_4 (tetrahedral)

H_2S (V-shapes)





§ 8.4 Ions: sizes and their electron configurations

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1. when two nonmetals (非金屬) react to form a covalent bond → share electrons that completes the valence electron configurations of both atoms.

2. nonmetal + 主族 metal → binary ionic compound

Predicting formulas of ionic compounds

valence electron

$\text{Ca} : [\text{Ar}]\boxed{4s^2}$

$\text{O} : [\text{He}]\,2s^2\,2p^4$

↓

$\text{Ca} + \text{O} \rightarrow \text{Ca}^{2+} + \text{O}^{2-}$

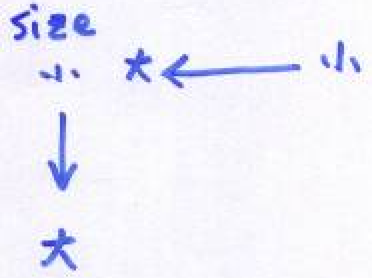
$2e^-$

Table 8-3 (page 360)

Sizes of ions :

ion size plays an important role in determining the structure and stability of ionic solids, the properties of ions in aqueous solution, and the biological effects of ions.

Fig 8.7



isoelectronic ions : ions containing the same number of electrons

		# of e^-
Ex	${}^{8}O^{2-}$	10
	${}^{9}F^{-}$	10
	${}^{11}Na^{+}$	10
	${}^{12}Mg^{2+}$	10
	${}^{13}Al^{3+}$	10
	${}^{10}Ne$	10

${}^{13}Al^{3+}$ ${}^{12}Mg^{2+}$ ${}^{11}Na^{+}$ ${}^{9}F^{-}$ ${}^{8}O^{2-}$

$50 < 65 < 95 < 1{,}36 < 1{,}40$

(pm)

The size decreases as the nuclear charge (Z increases for a series of isoelectronic ions

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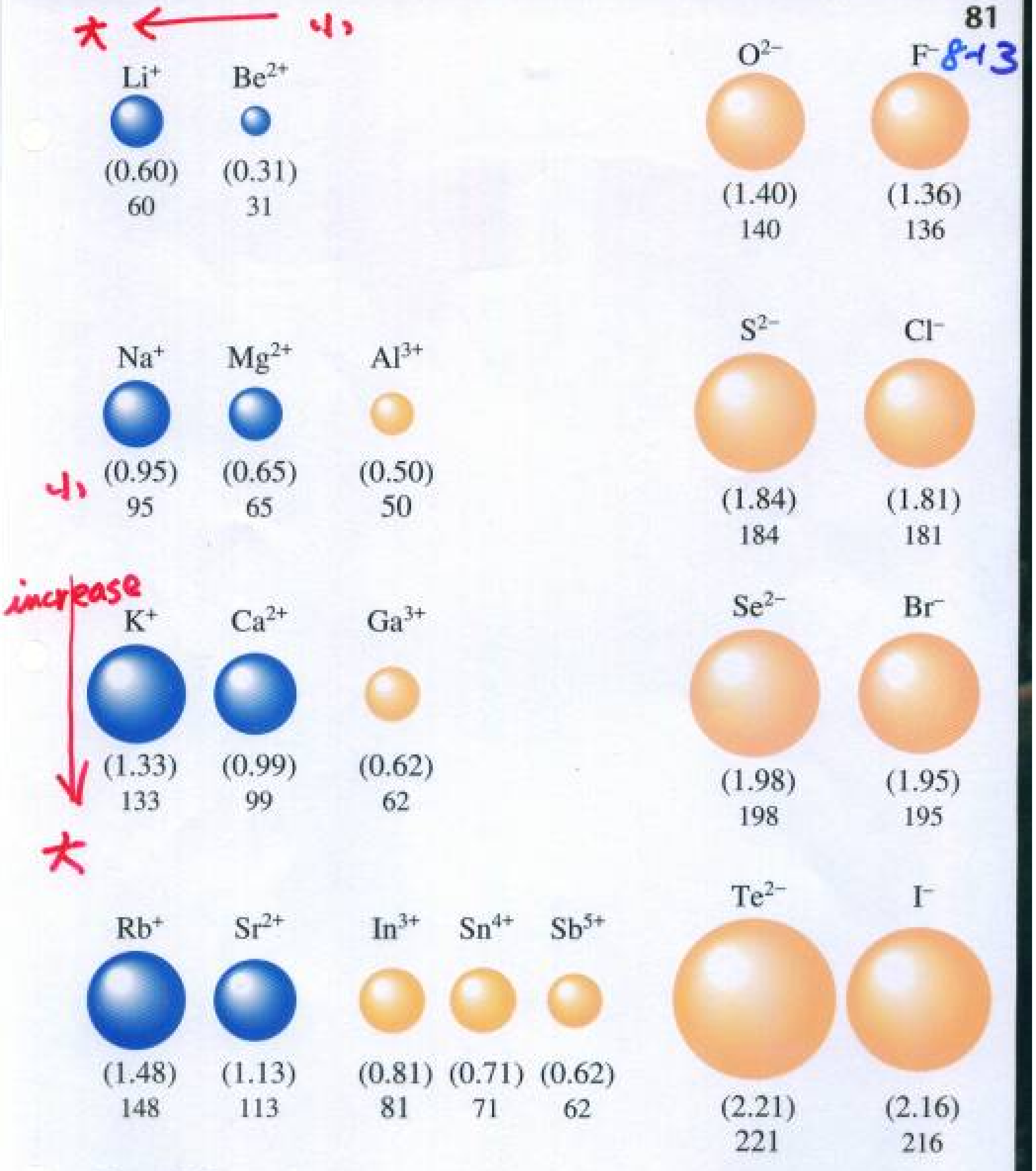


Figure 8.7
Sizes of ions related to position in periodic table

Ex. 8-3

Arrange the ions Se^{2-} Br^{-} Rb^{+} Sr^{2+} in order of decreasing size.

	Se^{2-}	>	Br^{-}	>	Rb^{+}	>	Sr^{2+}
#e	36		36		36		36
Z	34		35		37		38

Ex. 8.4

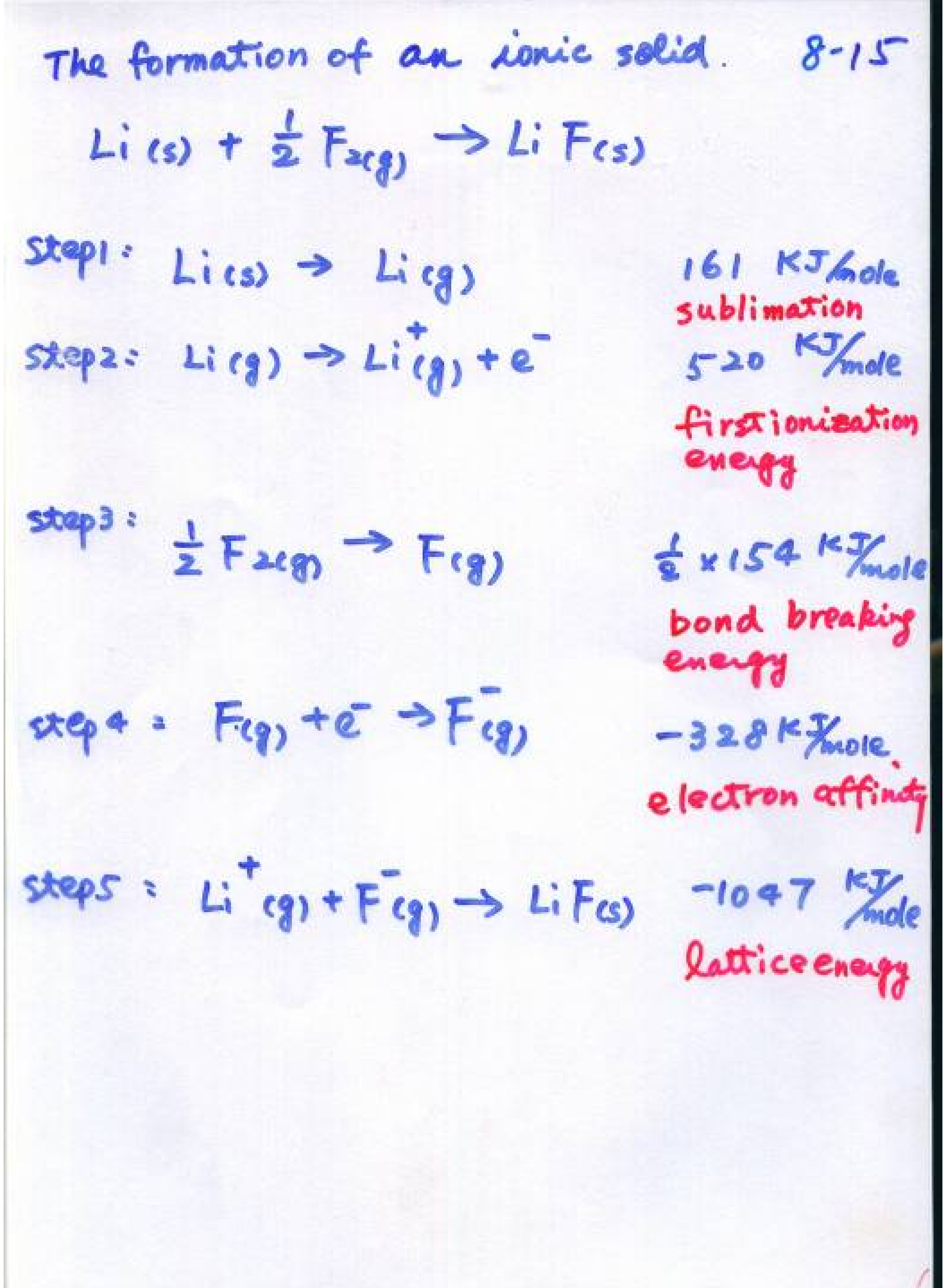
a. 同一族

b. isoelectronic ions

§ 8.5 Formation of binary ionic compounds

$$M^{+}(g) + X^{-}(g) \rightarrow MX(s)$$

lattice energy: the change in energy that takes place when separated gaseous ions are packed together to form an ionic solid.



The formation of an ionic solid. 8-15

$Li_{(s)} + \frac{1}{2} F_{2(g)} \rightarrow LiF_{(s)}$

step1: $Li_{(s)} \rightarrow Li_{(g)}$ 161 KJ/mole

sublimation

step2: $Li_{(g)} \rightarrow Li^{+}_{(g)} + e^{-}$ 520 KJ/mole

first ionization energy

step3: $\frac{1}{2} F_{2(g)} \rightarrow F_{(g)}$ $\frac{1}{2} \times 154$ KJ/mole

bond breaking energy

step4: $F_{(g)} + e^{-} \rightarrow F^{-}_{(g)}$ -328 KJ/mole

electron affinity

step5: $Li^{+}_{(g)} + F^{-}_{(g)} \rightarrow LiF_{(s)}$ -1047 KJ/mole

lattice energy

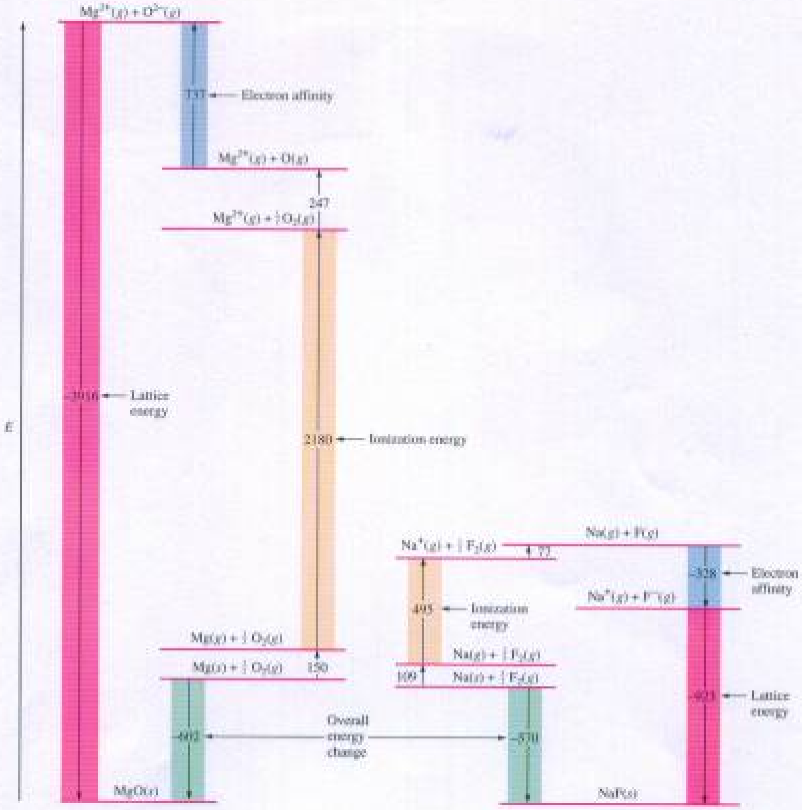


Figure 8.10

Energy of formation of MgO(*s*) versus NaF(*s*)

Lattice Energy Calculations

8-17

$$\text{Lattice energy} = k\left(\frac{Q_1 Q_2}{r}\right)$$

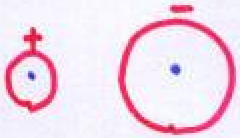
k : a proportionality constant that depends on the structure of the solid & electron configurations of the ions

see page 364"注字" MgO 的 lattice energy ≈ 4倍 NaF

§ 8-6 Partial Ionic Character

covalent (electron shared)

polar covalent bond



ionic (no electron sharing)
(但沒有 100% ionic bond)

Percent ionic character of a bond

$$= \left(\frac{\text{measured dipole moment of X-Y}}{\text{calculated dipole moment of } X^+-Y^-}\right) \times 100\%$$

electronegativity difference v.s. percent ionic character 8-18

↓ 作圖

No " perfect" ionic bond !

Fig 8.12

Ex. NaCl ~ 70% ionic

LiF ~ 85% ionic

Ionic compounds : any compound that conducts an electric current when melted will be classified as ionic

§ 8.7 The covalent chemical Bond

What is a chemical bond ?

↓

forces that cause a group of atoms to behave as a unit

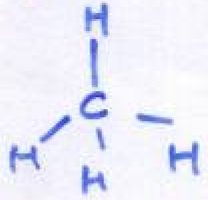
Why do chemical bond occur ?

↓

Bonds occur when collections of atoms are more stable (lower in energy) than the separate atoms

CH_4 (methane 甲烷) 8-19

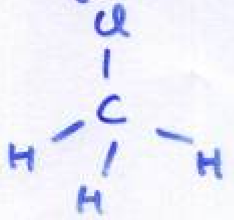
$C_{(g)} + 4H_{(g)} \rightarrow CH_4$ -1652 KJ/mole



4 bonds are formed

$\frac{1652}{4} = 413 kJ$

$C_{(g)} + 3H_{(g)} + Cl_{(g)} \rightarrow CH_3Cl_{(g)}$ -1578 KJ/mole



3 C−H bonds energy $3 \times (413)$

+ 1 C−Cl bond energy x

total 1578

∴ C−Cl bond energy = 339 KJ/mole

A bond represents a quantity of energy

(Lewis & Pauling's idea)

chemical bonds : modern concept.

see page 370

Fundamental Properties of Models

§ 8-8 Covalent Bond Energies and Chemical Reactions

	Energy Required (KJ/mol)
$CH_{4(g)} \rightarrow CH_{3(g)} + H_{(g)}$	435
$CH_{3(g)} \rightarrow CH_{2(g)} + H_{(g)}$	453
$CH_{2(g)} \rightarrow CH_{(g)} + H_{(g)}$	425
$CH_{(g)} \rightarrow C_{(g)} + H_{(g)}$	339
Total	1652

Ave : $\frac{1652}{4} = \underline{\underline{413}}$

C–H bond energy is somewhat sensitive to its environment

e.g.

$HCBr_3$	380
$HCCl_3$	380
HCF_3	430
C_2H_6	410

however, still close to 413 KJ/mole (calculated from CH_4 molecule)

Table 8-4 Average Bond Energies

Single bond : one pair of electrons
double bond : two pairs of " are shared
triple bond : three pairs of "

Table 8-5 Bond Length for Selected Bonds 8-21

Bond type Bond length, Bond energy

有意地阅读！

Bond energy and Enthalpy

$H_{2(g)} + F_{2(g)} \rightarrow 2HF_{(g)}$

$\left.\begin{array}{l} H-H \\ F-F \end{array}\right\}$ breaking

$2\times$ H−F forming

ΔH = sum of the energies required to break old bonds − the energy released in the formation of new bonds

$= \sum D(\text{bonds broken}) - \sum D(\text{bonds form}$

$\Delta H = \underset{D_{H-H}}{\underbrace{1 \times 432\,KJ/mole}} + \underset{D_{F-F}}{\underbrace{1 \times 154\,KJ/mole}} \underset{-2D_{H-F}}{\underbrace{-2\times565\,KJ/}}$

$= -542\,KJ/_{2\,mol\ of\ HF} = -271\,KJ/mol.$

Ex. 8-5 (use Table 8-4)

Calculate ΔH of the reaction

$$CH_{4(g)} + 2Cl_{2(g)} + 2F_{2(g)} \rightarrow CF_2Cl_{2(g)} + 2HF_{(g)} + 2HCl_{(g)}$$

$$\text{Reactants} \xrightarrow{\text{energy required}} \text{atoms} \xrightarrow{\text{Energy released}} \text{products}$$

Reactant bonds broken :

CH_4	4 mol	C–H
$2Cl_2$	2 mol	Cl–Cl
$2F_2$	2 mol	F–F

product bonds formed :

CF_2Cl_2	2 mol	C–F
	2 mol	C–Cl
2HF	2 mol	H–F
2HCl	2 mol	H–Cl

ΔH = energy required to break bonds − energy released to form bonds

§ 8-9 The localized electron bonding model

8-23

localized electron (LE) model: a molecule is composed of atoms that are bound together by using atomic orbitals to share electron pairs.

lone pairs: electron pairs localized on an atom

bonding pairs: electron pairs found in the space between atoms

§ 8.10 Lewis Structure

Lewis structure of a molecule represents the arrangement of valence electrons among the atoms in the molecule (only valence electrons are includ

∵ In most stable compounds the atoms achieve noble gas electron configurations

Ex. K Br

$\overset{+1}{\text{K}}$ $\overset{-1}{:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{Br}}}:}$

$\text{H}\cdot$ $\cdot\text{H}$

$\text{H} : \text{H}$

$\text{He}:$

duet rule ($2e^-$ shared) why?

octet rule $(8e^-)$

8-24

one shared pair of electrons : bonding pair

three pairs of electrons not involved in bonding : lone pair

See Summary on page 376

Ex. H_2O

step 1 : sum of the valence electrons for H_2O:

$1+1+6=8$ valence electrons

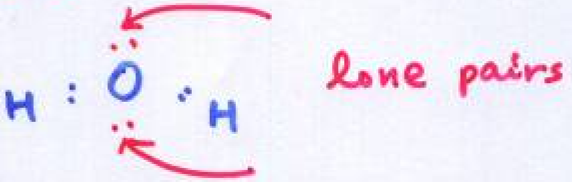
step 2 : use one pair of e^- per bond.

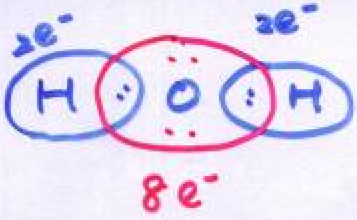
H ÷ O ÷ H (use — or :)

step 3 the remaining electrons → lone pairs

→ distribute lone pairs to achieve a noble gas electron configuration

$8-4=4$

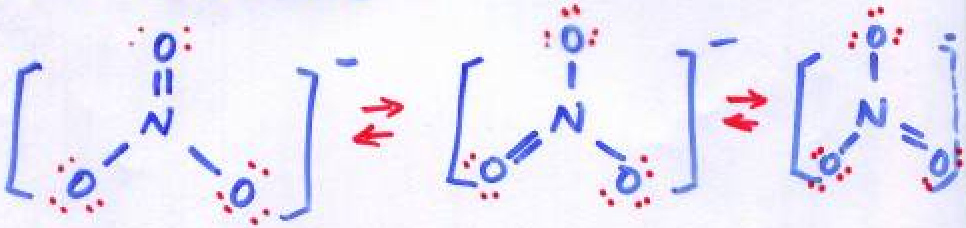




Ex. 8.6 Draw the Lewis structure.

a. HF b. N_2 c. NH_3 d. CH_4

§ 8.13 Resonance



actual structure is an average of three resonance structures

Ex. 8.9 NO_2^-

$5+(6\times2)+1=18$

O – N – O single bond $\begin{array}{r} -4 \\ \hline 14 \end{array}$

N 不符 octet rule

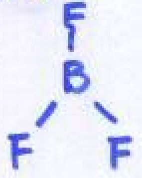
double bond $\begin{array}{r} -18 \\ \hline 12 \end{array}$ better

§ 8-12 Exceptions to the Octet Rule

(1) BF_3

$3 + 7\times 3 = 24$ valence e^-

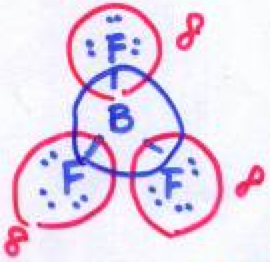
step 1:



$$24 - \underset{\substack{\uparrow \\ \text{\# of Bonds}}}{3\times 2} = 18$$

If 18 均分給 3 F, $\frac{18}{3} = 6/_{\text{each F}}$

step 2:



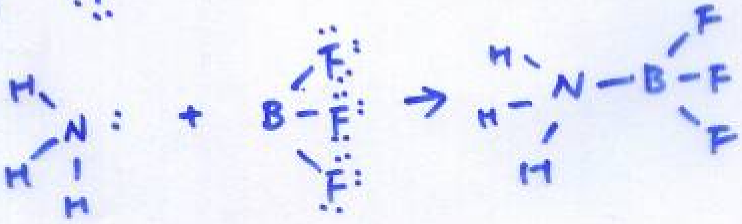
B: only 6 e^- (not 8)

F: 8e^-

$4 + \frac{4}{2} = 6$

B: 8e^-

real structure ?



(2) SF_6 8-27

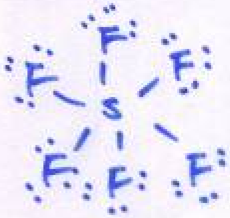
$6 + 6 \times 7 = 48$ valence e^-

step 1 :

$48 - 6 \times 2 = 36$

$36/6 = 6\ e^-$ (lone pair e for F)

step 2 :



S : $2 \times 6 = 12$ (超过 $8e^-$)

∵ Sulfur 是第三週期元素

3s 3p 3d.

S can have 12 e^- by using the 3s, 3p to hold 8 e^-, 4 e^- in 3d orbitals

Page 384 Summary : Lewis structures and the Octet Rule

Ex 8.7 PCl_5

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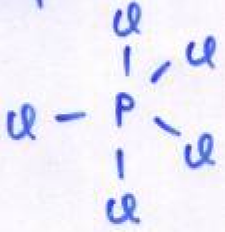
$5 + 5 \times 7 = 40$ valence e^-

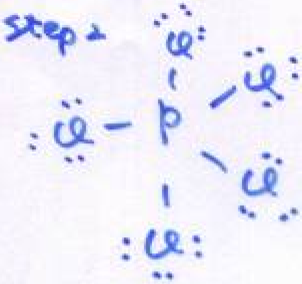
step1



$40 - 2 \times 5 = 30$

$30/5 = 6$

step2



P: $2 \times 5 = 10$

(use 3s 3p 3d orbitals)

I_3^-

$10e^-$ 多的 lone pair 放在中间

只是一个规定

Ex. 8.8 Write the Lewis structure : 8-29

(a) ClF_3 (b) XeO_3 (c) $RnCl_2$ (d) $BeCl_2$

(e) ICl_4^-

Sol: (a)

Cl atom (third row) accepts the extra electrons

Cl : 7 $\quad 7 + 3 \times 7 = 28$ valence e^-

F : 7

steps :

$28 - 3 \times 2 = 22$

$6 \times 3 = 18$

$22 - 18 = 4$

(b)

§ 8.12 Resonance

see page 8-25

Odd-Electron Molecules

NO & NO_2 odd-electron molecules

L.E. Model 處理得不好. 需用 M.O. model
(chapter 9)

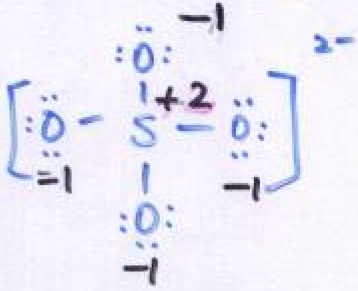
Formal Charge

Formal charge = number of valence electrons on a free atom − number of valence e^- assigned to the atom in the molecule

↑
# of valence e^- of free neutral atom

1. lone pair e^-s belong entirely to the atom
2. shared e^- are divided equally between the two sharing atoms

Ex.

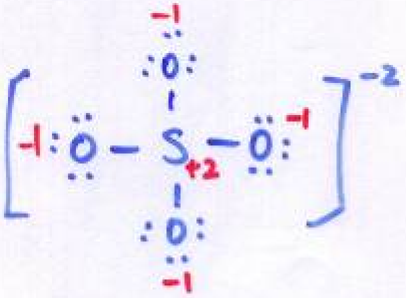


O : 6 + $\frac{1}{2}$ (2) = 7

↑
lone pair e

neutral O : 6 e^-

∴ Formal charge = 6 − 7 = −1



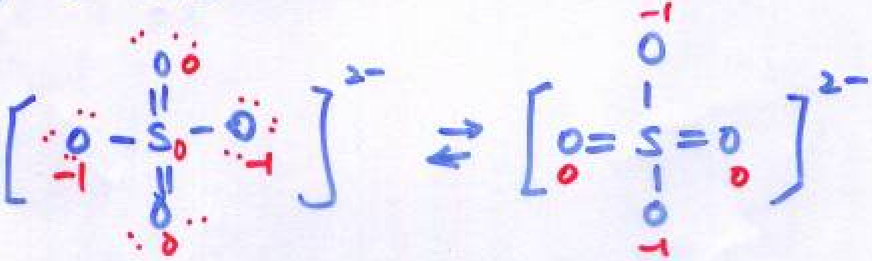
S: $\frac{1}{2} \times (8) = 4$

neutral S : 6

Formal charge $6-4=+2$

Total formal charge : $(-1) \times 4 + (+2) = -2$

另一個 可能的 structure



page 388 "best" Lewis structure

Summary

Ex. 8.10. XeO_3

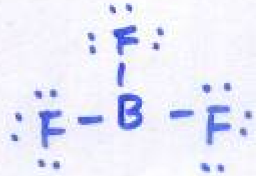
$8+3 \times 6 = 26$ valence e^-

§ 8.13 Molecular Structure : The VSEPR model 332

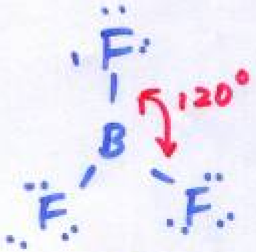
Valence Shell Electron Pair Repulsion Model (VSEPR model)

the structure around a given atom is determined principally by minimizing electron pair repulsions

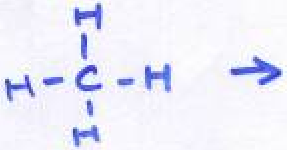
Ex.



? 角度



Trigonal planar



tetrahedral arrangement

Summary : page 391

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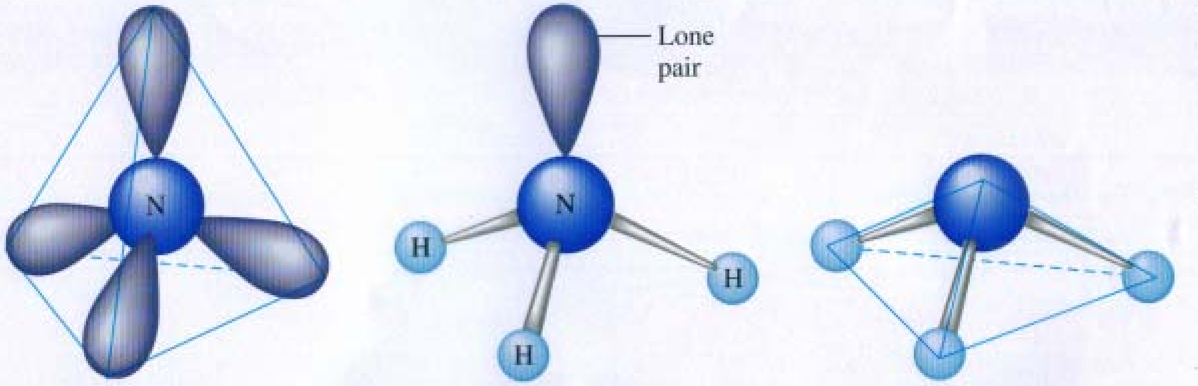
82 8.15 Molecular structure of NH_3



(a) (b) (c)

8-33

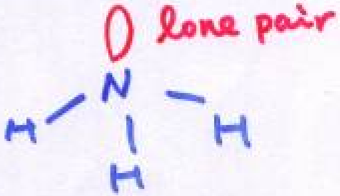
1. Draw the Lewis structure

2. Count the pairs of electrons and arrange them to minimize repulsions

NH_3 4 pairs of electron :

(3 pairs bonding
1 pair nonbonding)

3. determine the positions of the atoms



4. Name the molecular structure

trigonal pyramid

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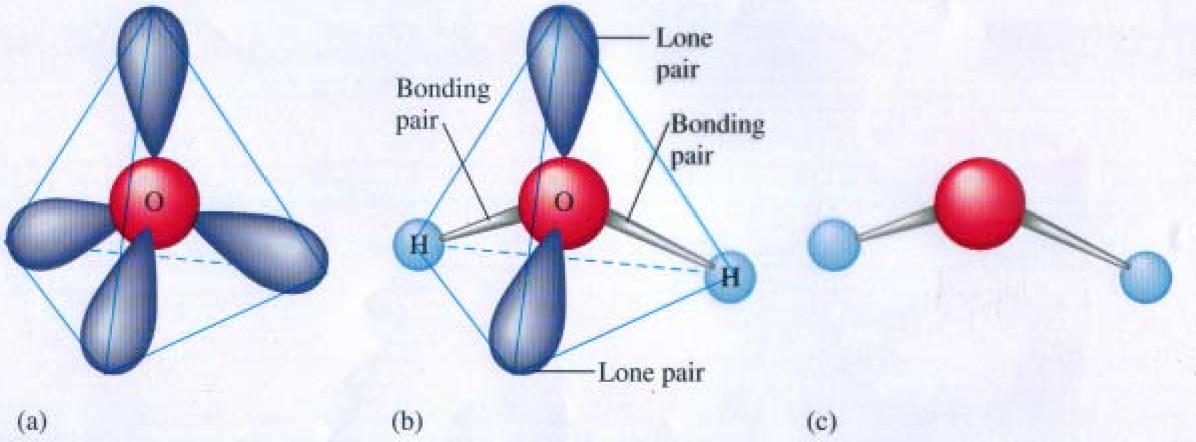
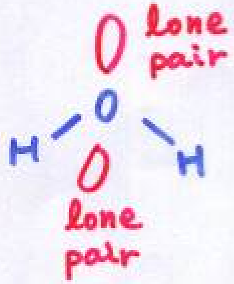
83 8.16 Molecular structure of H_2O



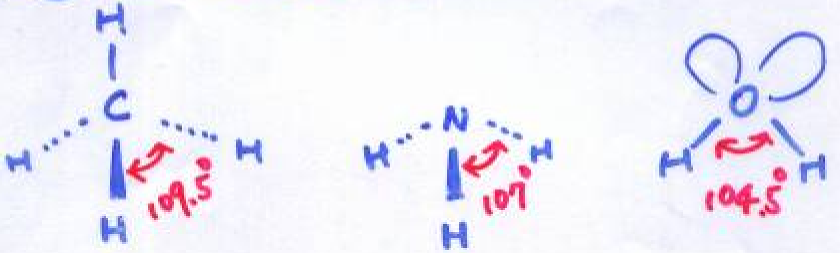
8-35

Ex.8.11 H_2O.

4 pairs:
- 2 bonding pairs
- 2 nonbonding pairs

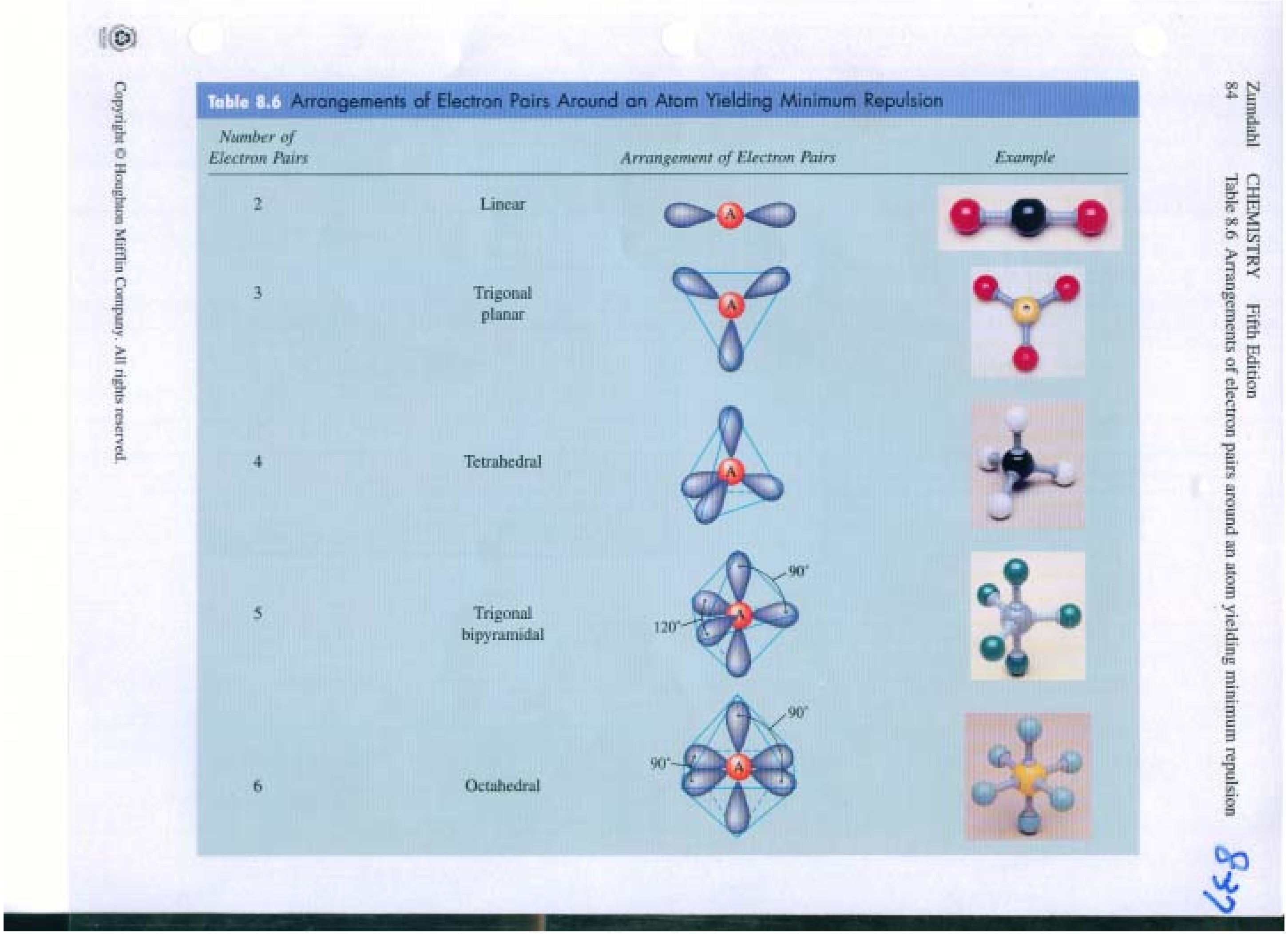


∴ H_2O molecule : a V-shape molecule



	CH_4	NH_3	H_2O
Number of lone pairs	0	1	2
Bond angle	109.5°	107°	104.5°

lone pairs require more space than bonding pair and tend to compress the angles between the bonding pairs



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84
Table 8.6 Arrangements of electron pairs around an atom yielding minimum repulsion

8-37

Table 8.6 Arrangements of Electron Pairs Around an Atom Yielding Minimum Repulsion

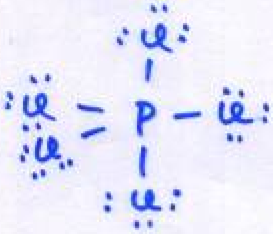
Number of Electron Pairs		*Arrangement of Electron Pairs*	*Example*
2	Linear		
3	Trigonal planar		
4	Tetrahedral		
5	Trigonal bipyramidal		
6	Octahedral		

Ex. 8.12

Compare PCl_5, PCl_4^+, and PCl_6^-

(a) PCl_5

Total valence e^- = $5 + 7 \times 5 = 40$



-5×2 ← 5 single bonds

30

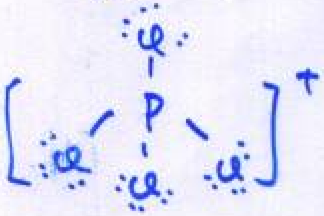
each Cl to have 6 more lone pair electrons to form "octet"

center atom P

有 5 对 电子 → trigonal bipyramid

(b) PCl_4^+

Total valence e^- = $5 + 7 \times 4 - 1 = 32$



4 single bonds → -4×2

24

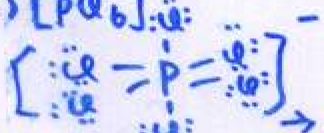
each Cl : 6 more

center atom P

有 4 对 e^- → tetrahedral

(c) $[PCl_6]^-$

$5 + 7 \times 6 + 1 = 48$



6 single bonds -6×2

36

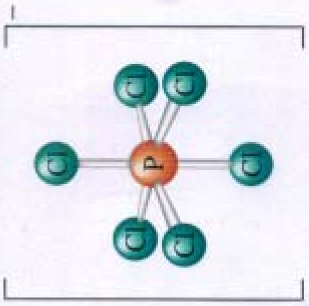
→ octahedral

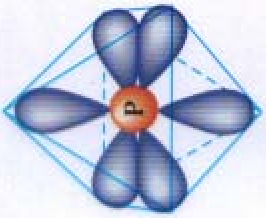
each Cl : 6 more

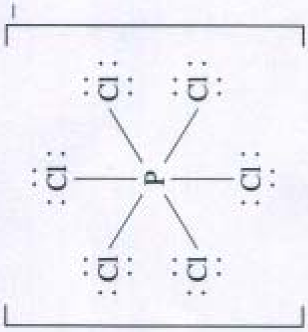
Molecular structure of PCl_6^-

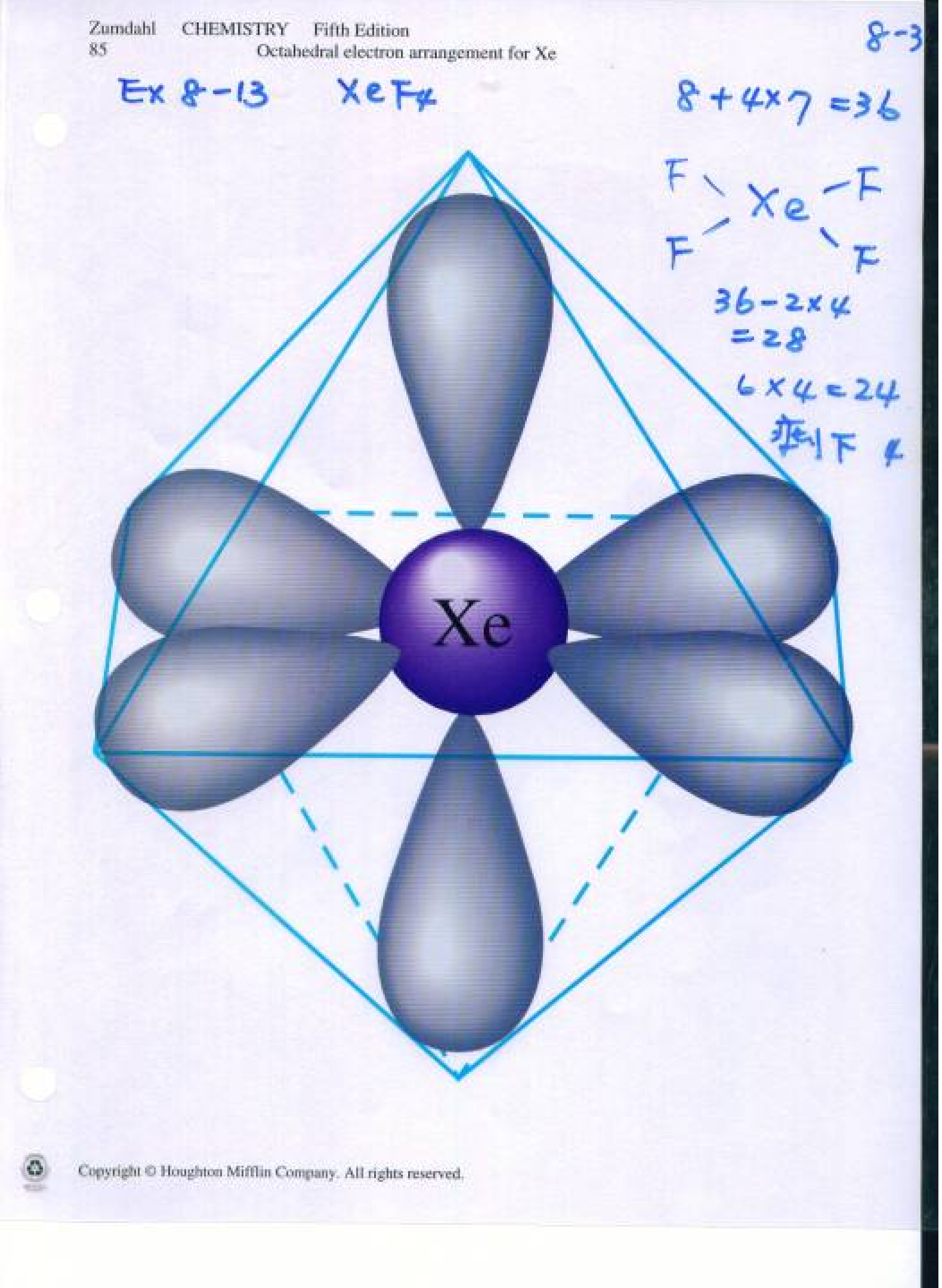
Ex 8-12

8-3









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85 Octahedral electron arrangement for Xe

8-3

Ex 8-13 XeF_4

8+4×7=36

36−2×4
=28

6×4=24
剩下 4

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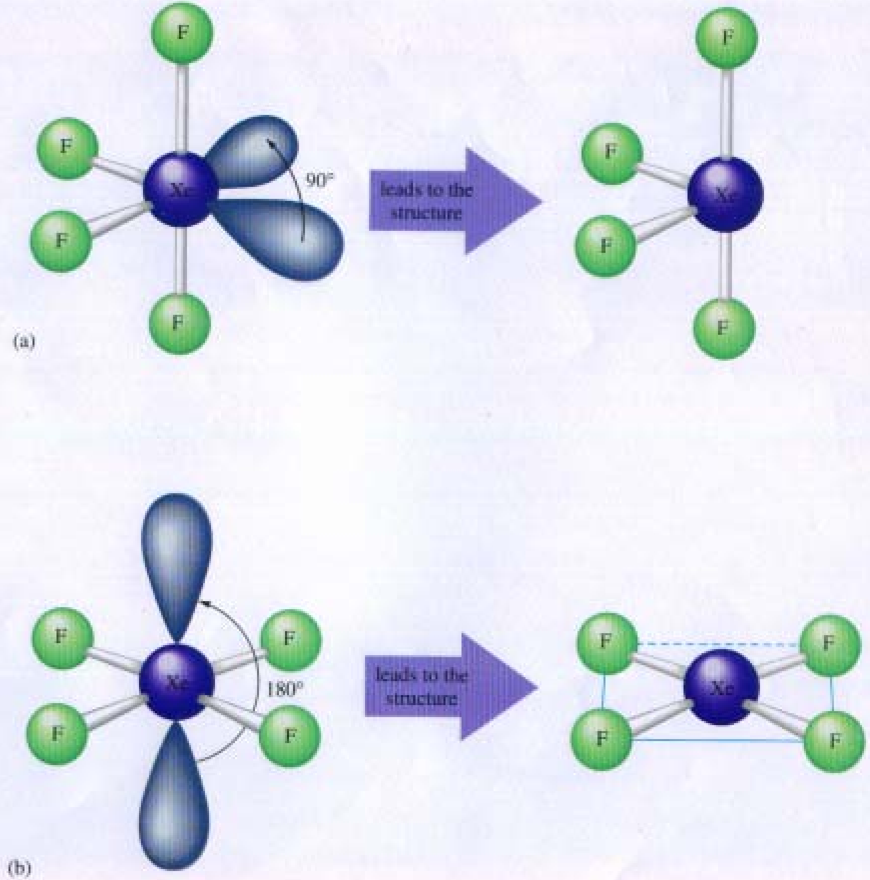
87 8.19 Possible structures for XeF_4

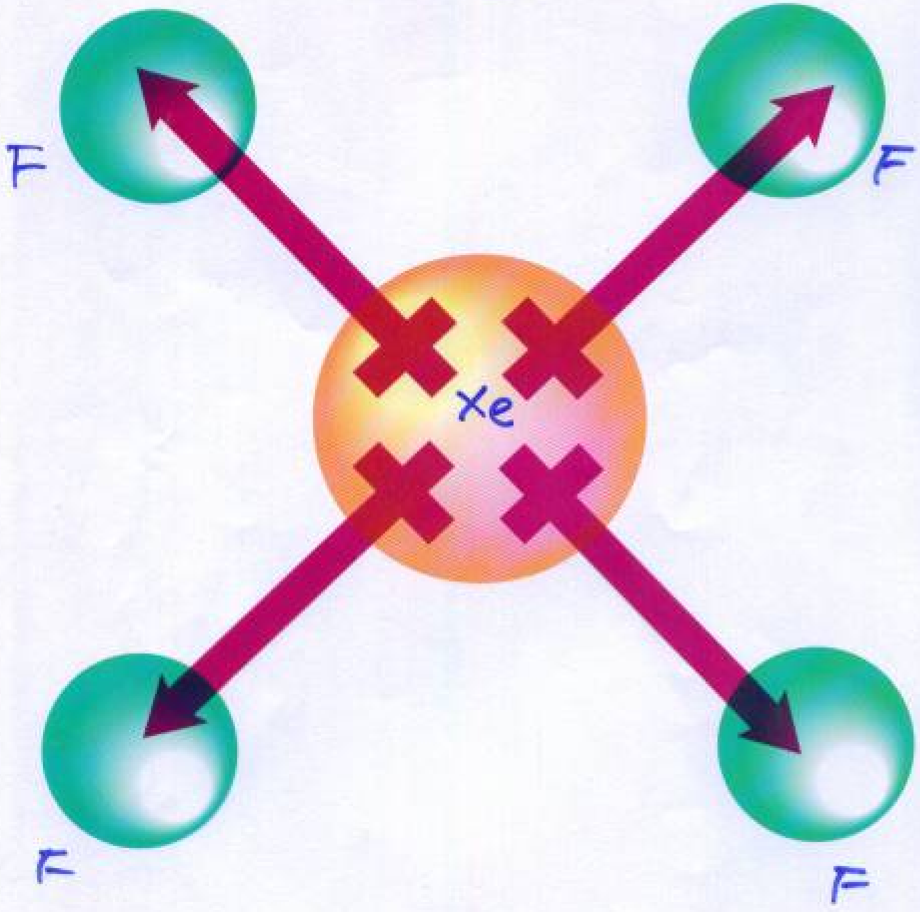


Which is more favorable
?

8-40

8-41

XeF4



Canceling bond dipoles for XeF_4

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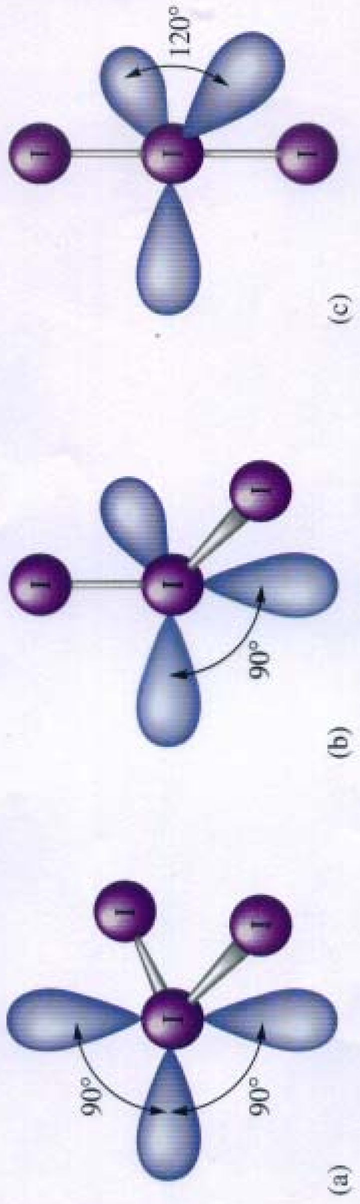
88 8.20 Possible electron arrangements for I_3^- ion

8-4L

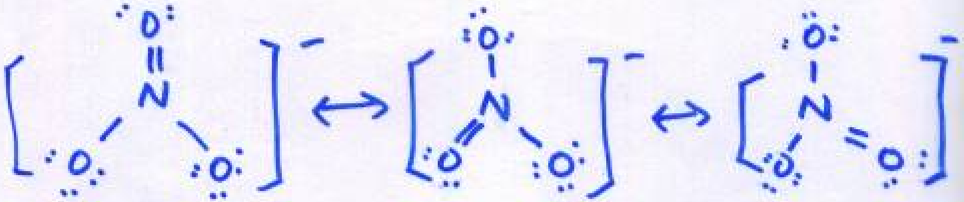


(c)

(b)

(a)

The VSEPR model on Multiple Bonds



已由实驗証明 NO_3^- 為 planar

w/ 120° bond angles

↓

" VESPR "
使用前將 = double bond should be counted as one effective pair

↓

另一种描述法

For the VSEPR model, multiple bonds count as one "effective" electron pair.

如有 resonance 發生

any one of the resonance structures can be used to predict the molecular structure using VSEPR model

8.1k sulfur dioxide SO_2

Lewis structure :

total valence e^- : $6 + 6 \times 2 = 18$

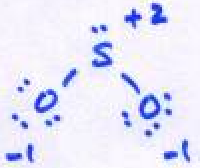
(2 single bonds) $-\ 2 \times 2$

14

O : $-\ 6 \times 2$

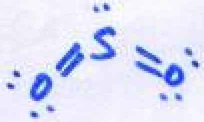
2

S :



better

S 外圍
3 e^- pairs
∴ trigonal planar



better

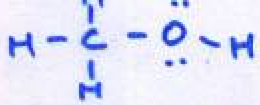
↓

都有 "dipole moment"

page 399 說明

Molecules Containing No Single Central Atom

CH_3OH



$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{..}{\underset{..}{O}}-H}$

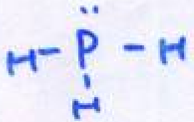
Lewis structure

C : 4 e^- pairs ∴ tetrahedral

O : 4 e^- pairs ∴ tetrahedral

page 400 summary.

The VSEPR model - How Well Does It work?



$\mathrm{H-\overset{..}{\underset{H}{P}}-H}$

94°

$\mathrm{H-\overset{..}{\underset{H}{N}}-H}$

107°

VSEPR model 預測 tetrahedral
< 109.5°

對 PH_3 較不準