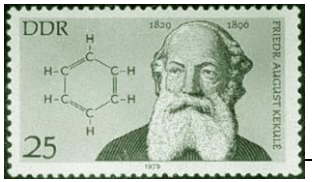
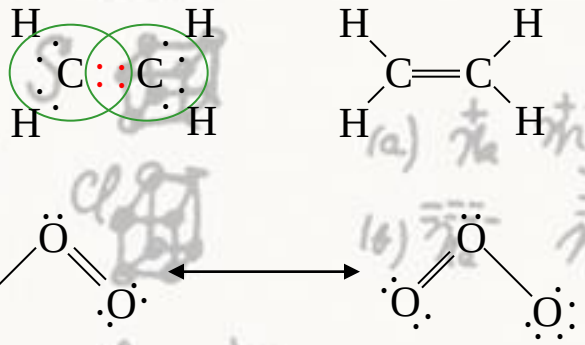


9. 화학결합 I: 공유결합

< Essential Concept >

- Lewis 기호 (•, dot) 
- 이온결합, 격자 에너지
- 공유결합
- 전기음성도, 산화수
- Lewis 구조 쓰기(그리기)
- 형식전하와 Lewis 구조
- 공명의 개념
- 8전자계규칙 및 예외
- 결합에너지 ↔ 열화학



MgO

$K_2Cr_2O_7$ NiO

S_8

Br_2 $C_{12}H_{22}O_{11}$

Mg

Au Cu

Yakko, Wakko, and Dot

"화학결합"
(화학반응)

⇕

dot symbol

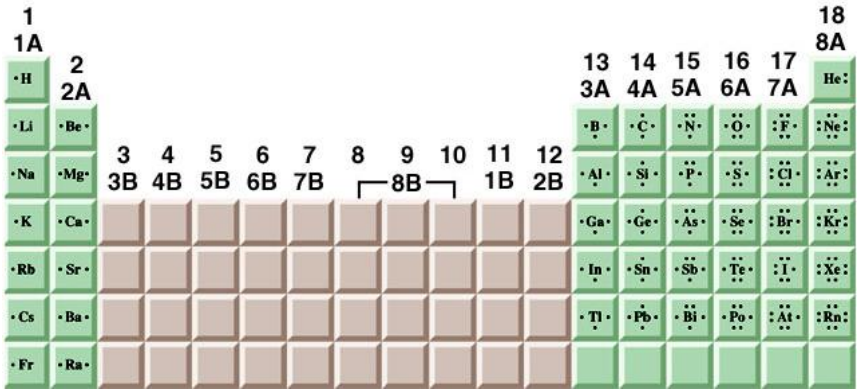
Lewis 점 기호 ← { 전체 전자의 수는 변하지 않음 / 원잣가전자가 중요한 역할

원잣가전자 ↔ •

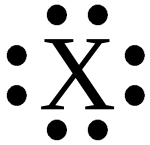
[예] 황(S): $[Ne]3s^2 3p^4$ ⟶ 

- **팔전자계 규칙** (The Octet rule) → 많은 예외 존재

원자들은 원잣가전자가 8개가 될 때까지 전자를 얻거나, 잃거나 공유하려 한다



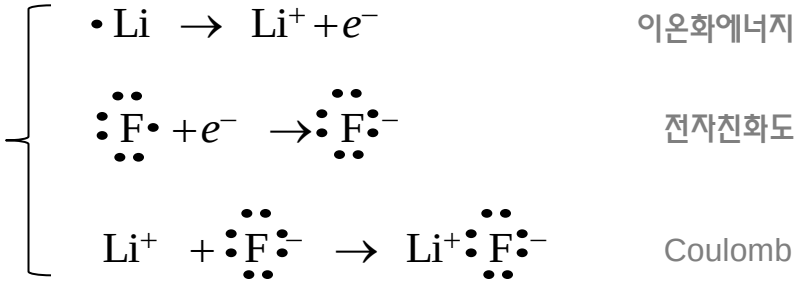
"영족기체"



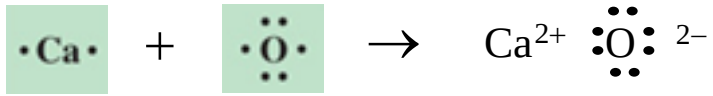
- 8개의 원잣가전자
- 이온화에너지 ↑
- 전자친화도, 반응성 ↓
- ……

이온결합 (금속 ↔ 비금속: 1A / 2A ↔ O / 7A)

$1s^2 2s^1$ $1s^2 2s^2 2p^5$ $1s^2$ $1s^2 2s^2 2p^6$

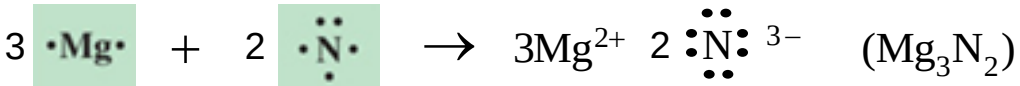


(ex) $2Ca(s) + O_2(g) \rightarrow 2CaO(s)$



[Ar]$4s^2$ $1s^2 2s^2 2p^4$ [Ar] [Ne]

(ex) $3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$



[Ne]$3s^2$ $1s^2 2s^2 2p^3$ [Ne] [Ne]

(이온결합 화합물의) 격자에너지 ← 이온결합화합물의 안정성 ~ 이온화에너지, 전자친화도, Coulomb 등...

lattice energy

- Coulomb의 법칙 $E = k\frac{q_+ q_-}{r} < 0$ ⟷ $F = k\frac{q_+ q_-}{r^2} < 0$

- Born-Haber cycle (← Hess의 법칙)

(ex) LiF

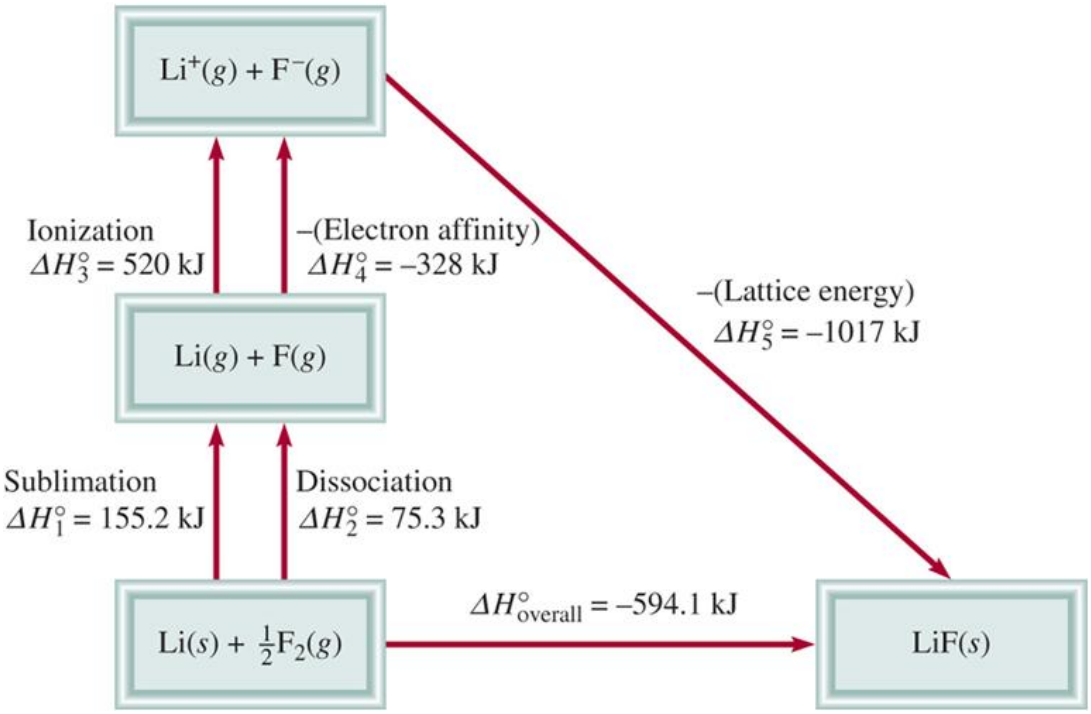


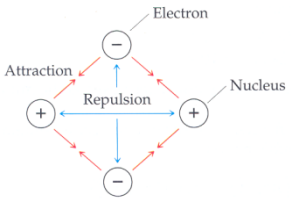
Table 9.1

Lattice Energies and Melting Points of Some Ionic Compounds

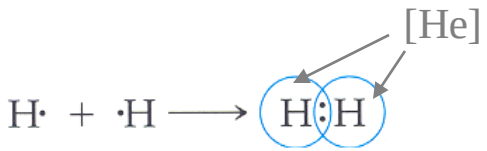
	Lattice Energy (kJ/mol)	Melting Point (°C)
LiF	1017	845
LiCl	828	610
NaCl	788	801
NaBr	736	750
$MgCl_2$	2527	714
MgO	3890	2800
CaO	3414	2580

공유결합 ↔ 비금속간의 화학결합 모델 (G.N.Lewis)

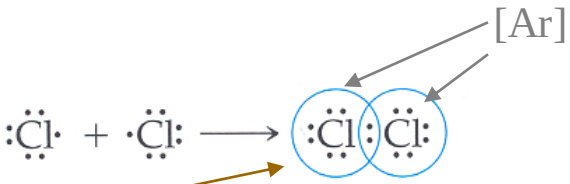
[예] H_2



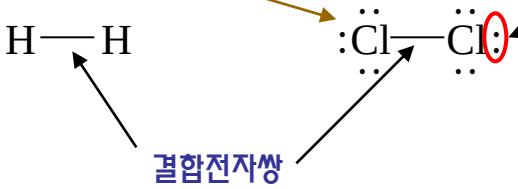
Lewis 기호



Cl_2



"Lewis 구조"



비결합전자쌍 Nonbonding Electron
고립전자쌍 Lone pair

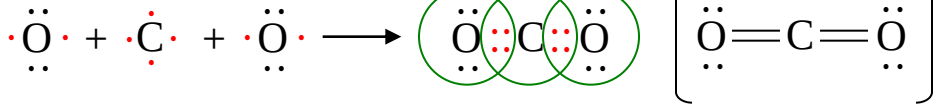
결합전자쌍

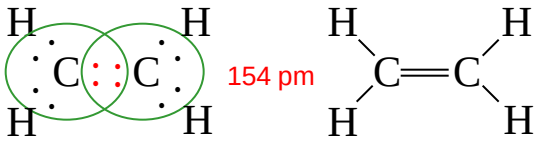
7A	6A	5A	4A
·F:	·O:	·N·	·C· ·C·
H—F:	H—O: (H)	H—N—H (H)	H (H—C—H) H
단일결합			

- 다중결합

CO_2

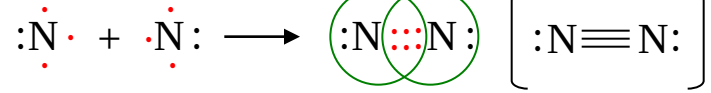
이중결합





삼중결합

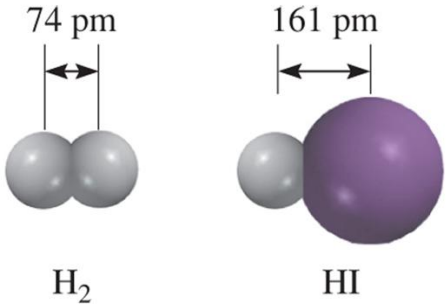
N_2



(반응성 ↓)

N—N 1.47 Å N=N 1.24 Å N≡N 1.10 Å

평균 결합길이



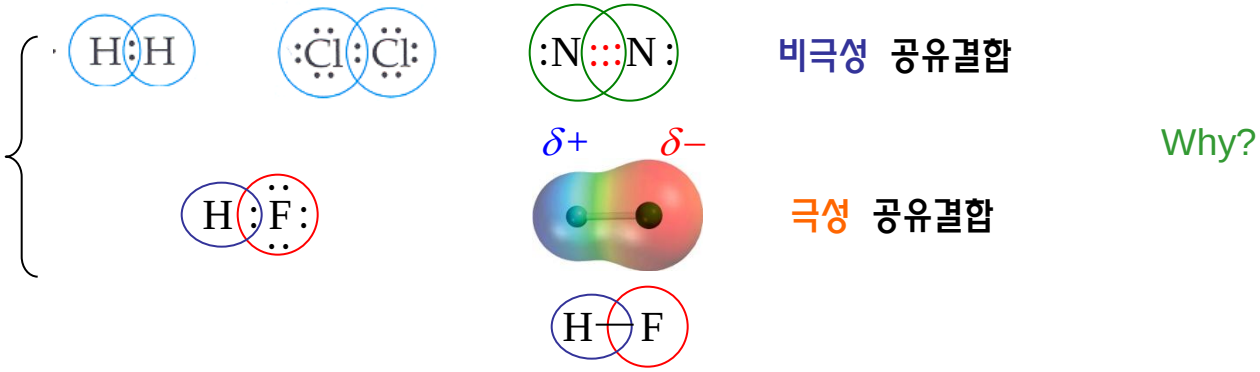
단일결합 > 이중결합 > 삼중결합

Table 9.2

Average Bond Lengths of Some Common Single, Double, and Triple Bonds

Bond Type	Bond Length (pm)
C—H	107
C—O	143
C=O	121
C—C	154
C=C	133
C≡C	120
C—N	143
C=N	138
C≡N	116
N—O	136
N=O	122
O—H	96

전기음성도

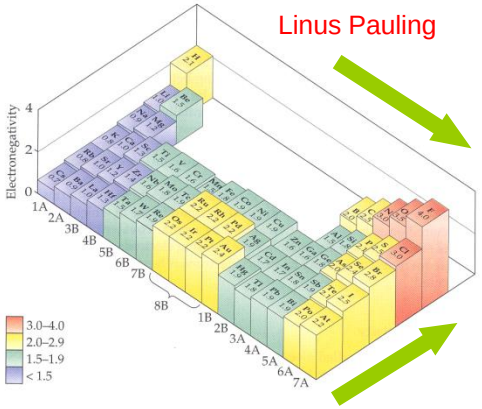


- 전기음성도 ⟶ 원자가 분자 내에서 전자를 끌어당기는 (상대적) 능력

  (~ 이온화에너지, 전자친화도, …)

$A \ll 0,\quad I \gg 0$ ⟶ 전기음성도 ↑

$$F > O > N > Cl > Br > \cdots > Cs$$
4.0 0.7

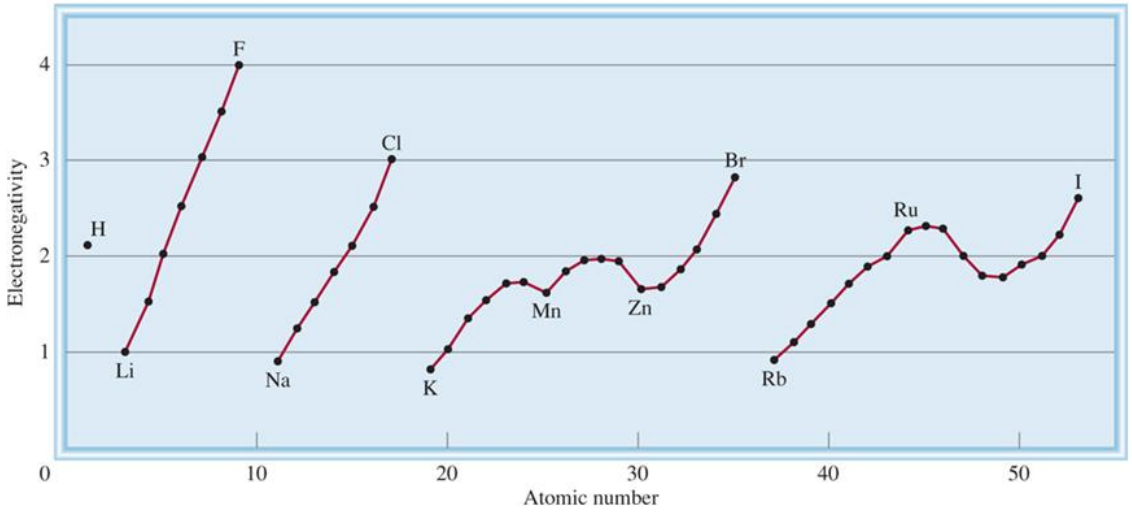


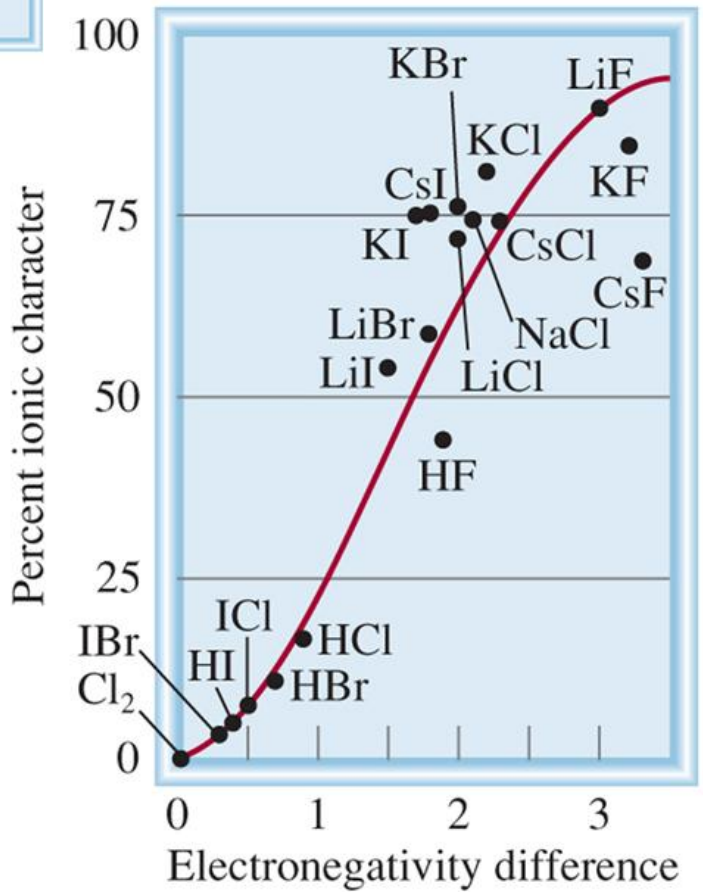
- 결합의 극성 ← '전기음성도 차'

F_2	HF	LiF
$4.0-4.0=0$	$4.0-2.1=1.9$	$4.0-1.0=3.0$
비극성 공유결합	극성 공유결합	이온결합
	$\left(H^{\delta+}F^{\delta-}\right)$	$\left(Li^{+}F^{-}\right)$

< 2.0

- 전기음성도~전자친화도, 전기음성도~산화수





• 전기음성도 ~ 결합의 극성 ~ 산화수, 형식전하

Lewis구조 그리기(쓰기) ← 화합물의 구조/성질을 이해하는데 도움

① 원잣가전자의 수 결정 (이온전하 고려)

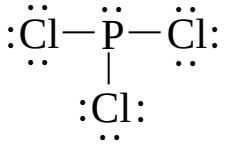
② 각 원자를 단일결합으로 연결

③ 중심원자에 결합된 원자들부터 팔전자계 완성

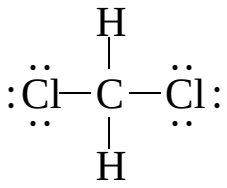
④ 남은 전자를 중심원자에 배정

⑤ 전자가 부족하면 다중결합 시도

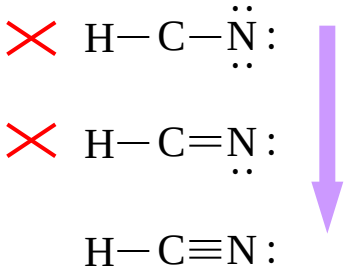
PCl_3 $5+3\times7=26$



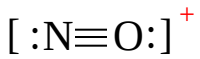
CH_2Cl_2 $2\times1+7\times2+4=20$



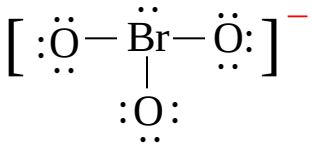
HCN $1+4+5=10$



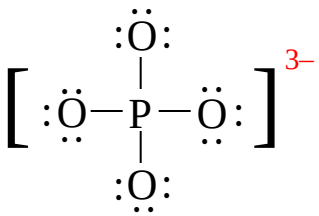
NO^+ $5+6-1=10$



BrO_3^- $7+3\times6+1=26$



PO_4^{3-} $5+4\times6+3=32$



- 일반적으로 전기음성도가 작은 원자가 중심에 위치
- 보통 H와 F는 말단에 위치.

형식전하(formal charge)

(cf. 산화수)

→ 원자의 가전자의 수 – 원자에 할당된 전자수

비공유전자 + 공유전자/2

[예1] 시안화 이온: CN^-

$[:C\equiv N:]^-$

$-1 \quad 0$

$C:\ 4-\left(2+\frac{6}{2}\right)=-1$

$N:\ 5-\left(2+\frac{6}{2}\right)=0$

[예2] CO_2

$\ddot{O}=C=\ddot{O}$ ① ② ③

① $O:\ 6-\left(4+\frac{4}{2}\right)=0$

② $C:\ 4-\left(\frac{8}{2}\right)=0$

③ $O:\ 6-\left(4+\frac{4}{2}\right)=0$

"안정"

$:\ddot{O}-C\equiv O:$ ① ② ③

① $O:\ 6-\left(6+\frac{2}{2}\right)=-1$

② $C:\ 4-\left(\frac{8}{2}\right)=0$

③ $O:\ 6-\left(2+\frac{6}{2}\right)=+1$

[예3] 사이오시안화이온: NCS^-

③ $[:\ddot{N}-C\equiv S:]^-$

$-2 \quad 0 \quad +1$

① $[\ddot{N}=C=\ddot{S}\ ]^-$

$-1 \quad 0 \quad 0$

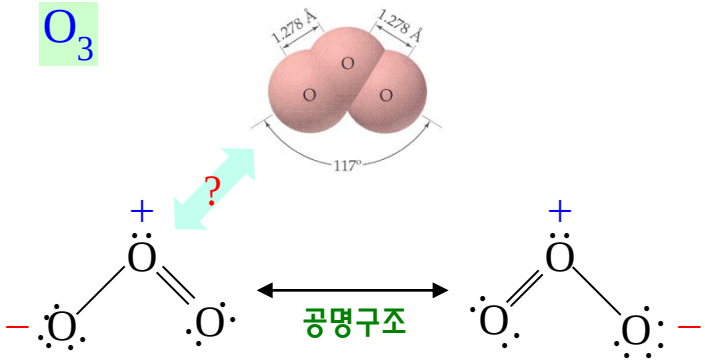
② $[:N\equiv C-\ddot{S}:]^-$

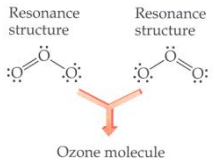
$0 \quad 0 \quad -1$

형식전하 ⇎ 실제전하 (∵전기음성도)

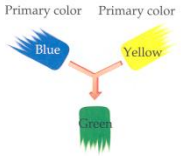
공명구조 ← 2가지 이상의 Lewis 구조가 필요한 경우

O_3

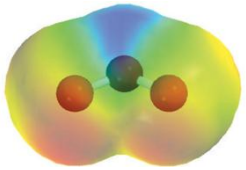




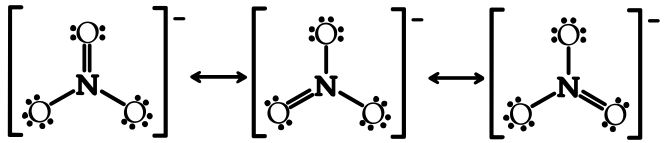
"실제분자는 공명구조의 평균"



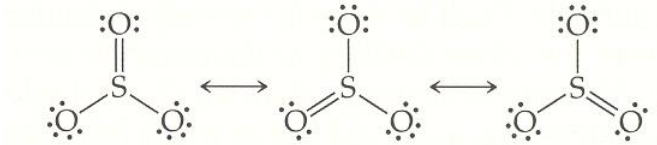
오존 분자의 두 결합길이는 항상 같으며, 그 값은 단일결합 길이보다는 짧고 이중결합 길이보다는 길다



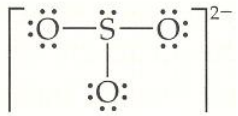
[예] NO_3^-



[예] SO_3 & SO_3^{2-}



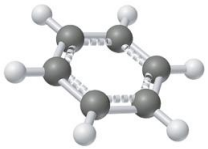
$1\frac{1}{3}$ ↔ 1.42 Å

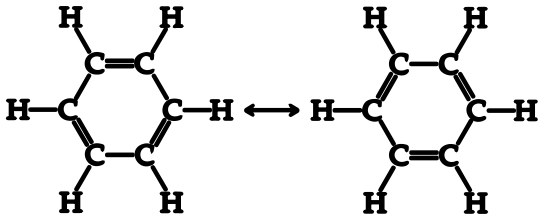


1 ↔ 1.51 Å

- 벤젠의 공명구조 ↔ "방향족" 화합물(aromatic compounds)

C_6H_6

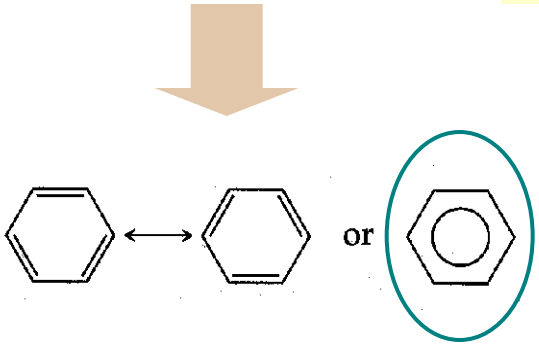


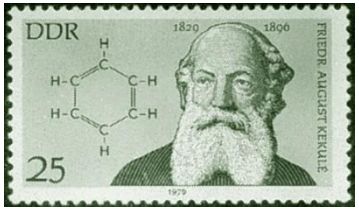


[실험결과] C–C → 1.40 Å

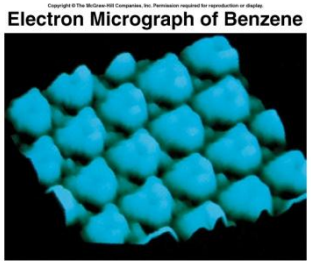
C--C: 1.54 Å

C=C: 1.34 Å



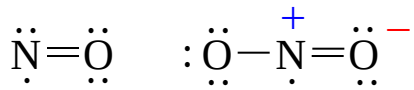


August Kekulé



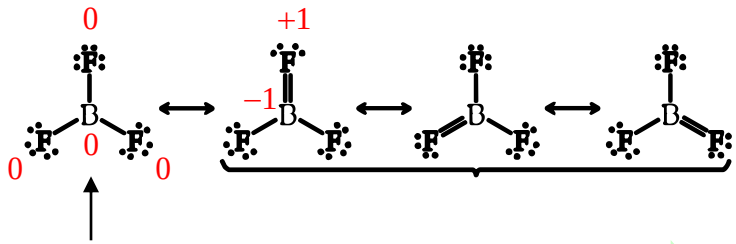
팔전자계 규칙(Octet rule)의 예외

- 홀수의 전자를 가지는 경우 $ClO_2, NO, NO_2, \cdots$



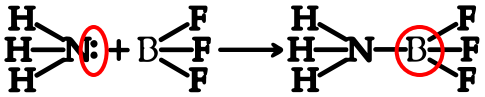
- 8개 미만의 원잣가전자를 가지는 경우 ← $\cdot\dot{B}\cdot$나 $\cdot Be\cdot$화합물

BF_3



"더 적절한 구조"

근거

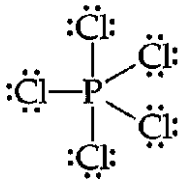


배위(공유)결합

$$NH_3 + BF_3 \rightarrow NH_3BF_3$$

- 8개 이상의 원잣가전자를 가지는 경우 (확장된 팔전자계)

PCl_5



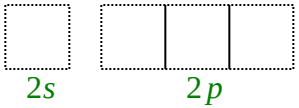
"확장 원잣가 껍질"
(expanded valence shell)

[예] $\underline{SF_4}$, $\underline{AsF_6^-}$, $\underline{ICl_4^-}$

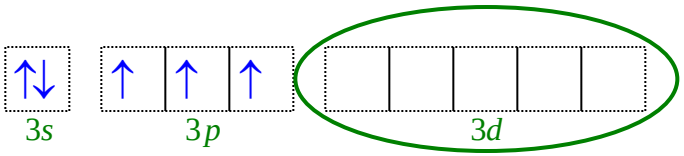
5A 6A 7A

"3주기↓ 원자" 의 경우만 가능
(∵8개 이상의 원잣가전자 가지므로)

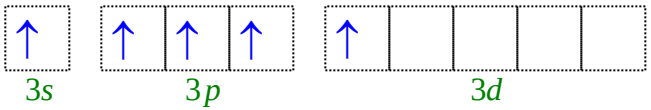
2주기 원소



3주기 원소



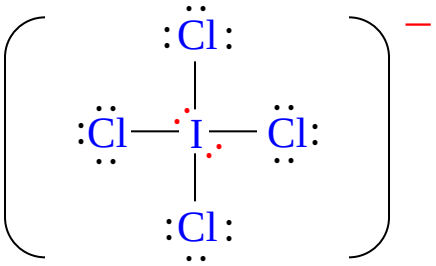
P



중심원자의 크기↑

주변원자의 크기↓, 전기음성도↑ (F, C, O)

[예] ICl_4^- $7+(4\times7)+1=36$

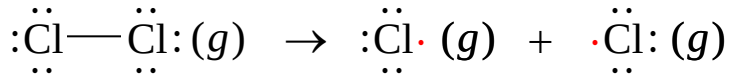


결합에너지(엔탈피) ↔ 분자의 안정성

기체분자 1몰에서 특정 결합을 끊는데 필요한 에너지 (>0)

"dissociation"

$$Cl_2(g) \rightarrow 2\cdot Cl(g), \quad \Delta H = D(Cl-Cl) = 242.7 \text{ kJ/mol}$$



$$H_2(g) \rightarrow H(g) + H(g) \qquad \Delta H = 436.4 \text{ kJ/mol}$$

$$HCl(g) \rightarrow H(g) + Cl(g) \qquad \Delta H = 431.9 \text{ kJ/mol}$$

$$O_2(g) \rightarrow O(g) + O(g) \qquad \Delta H = 498.7 \text{ kJ/mol}$$

$$N_2(g) \rightarrow N(g) + N(g) \qquad \Delta H = 941.4 \text{ kJ/mol}$$

- 평균결합에너지 ↔ 다원자분자

$$H_2O(g) \rightarrow H(g) + OH(g) \qquad \Delta H = 502 \text{ kJ/mol}$$

$$OH(g) \rightarrow H(g) + O(g) \qquad \Delta H = 427 \text{ kJ/mol}$$

$$D(O-H) = \frac{502+427}{2} = 464 \text{ kJ/mol}$$

(분자 내의 나머지 부분에 따라 약간 차이)

<평균결합엔탈피>

TABLE 8.4 Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						

Multiple Bonds

C=C	614	N=N	418	O_2	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

- 결합엔탈피 ↑ ➡ 센 화학결합 ➡ 분자 안정 (반응성 ↓)

[예] Si - O: 368 kJ/mol ← Si 의 결합 중 가장 센 결합

→ 지구 암석의 90% 이상이 SiO_2 와 규산염(Si-O)으로 이루어짐

- 결합엔탈피와 (평균)결합길이

C–C		C=C	C≡C
1.54 Å	(1.40 Å)	1.34 Å	1.20 Å
348 kJ/mol		614 kJ/mol	839 kJ/mol

결합 수 ↑ (결합전자쌍) 결합의 세기 ↑ 결합거리 ↓

- 결합엔탈피와 반응엔탈피

화학반응 ← 기존의 결합 절단 + 새로운 결합 생성

반응엔탈피 ← 결합엔탈피

~~(생성엔탈피)~~

$$\Delta H_{rxn} = \sum (\text{절단될 결합의 결합엔탈피}) - \sum (\text{생성될 결합의 결합엔탈피})$$

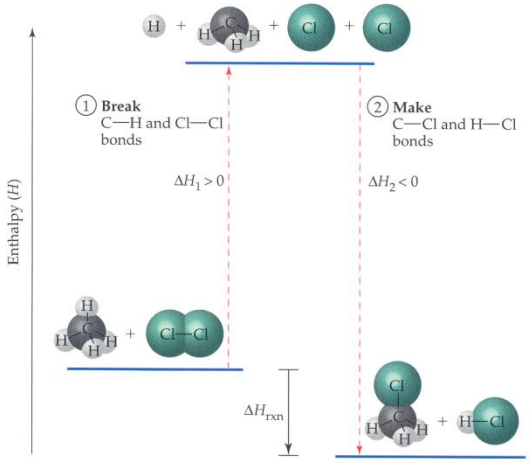
[예] $CH_4(g)+Cl_2(g)\rightarrow CH_3Cl(g)+HCl(g)$

$$H-CH_3(g)+Cl-Cl(g)\rightarrow Cl-CH_3(g)+H-Cl$$

"절단" "생성"

$$\Delta H_{rxn}=[D(C-H)+D(Cl-Cl)]-[D(C-Cl)+D(H-Cl)]$$

$$=[(413+242)-(328+431)]\ \text{kJ} = -104\ \text{kJ} < 0\ !$$



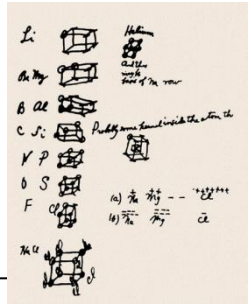
실제 값: -99.8 kJ/mol

평균결합엔탈피

기체상 반응의 반응엔탈피를 생성엔탈피 자료 없이 계산 가능!

[예제] $H-\underset{H}{\overset{|}{N}}-\underset{H}{\overset{|}{N}}-H\ (g) \rightarrow N\equiv N\ (g) + 2\ H-H\ (g)$

9. 화학결합 I: 공유결합 — 연습문제



16 / 20 / 26 / 36 / 42 / 44 / 50 / 52 / 62 / 70 / 76

/ 84 / 86 / 90 / 94 / 100 / 108