

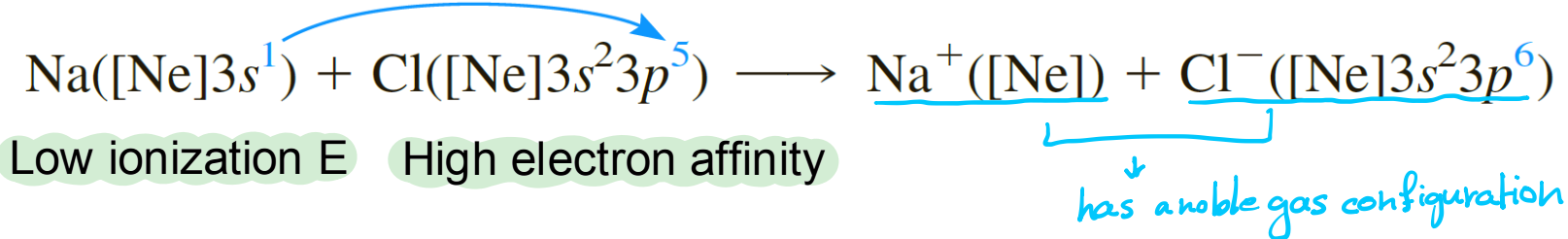
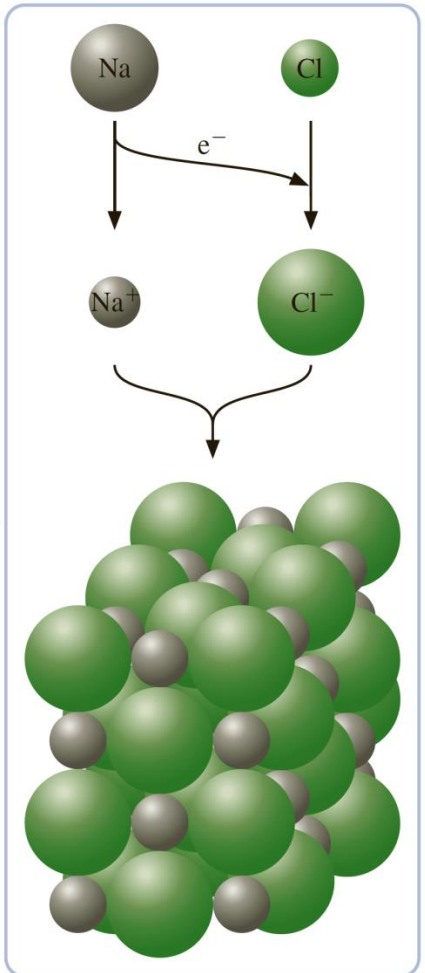
EBBING - GAMMON

General
Chemistry
ELEVENTH EDITION

Ionic and Covalent Bonding

➤ Ionic Bonds 9.1 Describing Ionic Bonds

- ✓ An **ionic bond** is a chemical bond formed by the electrostatic attraction between positive and negative ions.
- ✓ The bond forms between two atoms when one or more electrons are transferred from the valence shell of one atom to the valence shell of the other.
- ✓ The atom that loses electrons becomes a cation (positive ion), and the atom that gains electrons becomes an anion (negative ion).
- ✓ As a result of the electron transfer, ions are formed, each of which has a noble-gas configuration.



➤ Lewis Electron-Dot Symbols

✓ is a symbol in which the electrons in the valence shell of an atom or ion are represented by dots placed around the letter symbol of the element

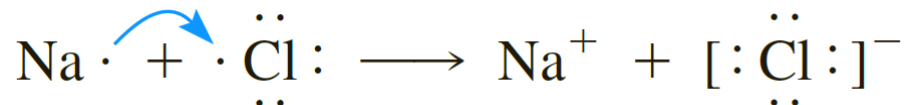
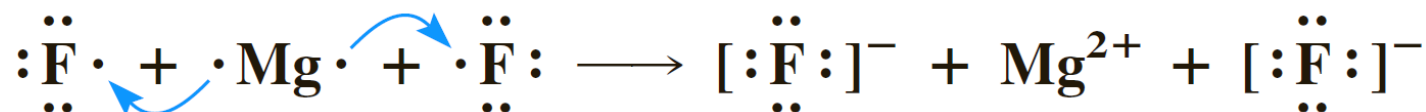


Table 9.1 Lewis Electron-Dot Symbols for Atoms of the Second and Third Periods

Period	1A ns^1	2A ns^2	3A ns^2np^1	4A ns^2np^2	5A ns^2np^3	6A ns^2np^4	7A ns^2np^5	8A ns^2np^6
Second	Li·	·Be·	·B·	·C·	:N·	:O·	:F·	:Ne:
Third	Na·	·Mg·	·Al·	·Si·	:P·	:S·	:Cl·	:Ar:

(Q) Use Lewis electron-dot symbols to represent the transfer of electrons from magnesium to fluorine atoms to form ions with noble-gas configurations



➤ Energy Involved in Ionic Bonding

✓ Formation of an ionic bond between a sodium atom and a chlorine atom:



ionic bond
↳ metal + non-metal



✓ The overall energy is $(496 - 349) = + 147 \text{ kJ/mol}$

→ the process requires more energy to remove an electron from the sodium atom than is gained when the electron is added to the chlorine atom.

→ formation of ions from the atoms is not in itself energetically favorable.

BUT When positive and negative ions bond → energy is released to make the overall process favorable.

Coulomb's law

$$E = \frac{kQ_1Q_2}{r} \quad \text{r} \rightarrow \text{distance between } Q_1 \text{ and } Q_2$$

Coulomb's law states that the potential energy obtained in bringing two charges Q1 and Q2, initially far apart, up to a distance r apart is directly proportional to the product of the charges and inversely proportional to the distance between them.

$$E = \frac{kQ_1Q_2}{r}$$

→ used to calculate the electrostatic attraction
→ formation of ion pair energy

$$k = 8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2$$

The charge on Na^+ is +e and that on Cl^- is -e.

$$e = 1.602 \times 10^{-19} \text{ C}$$

r = distance between Na^+ and Cl^- = 282 pm, or $2.82 \times 10^{-10} \text{ m}$.

$$E = \frac{-(8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2) \times (1.602 \times 10^{-19} \text{ C})^2}{2.82 \times 10^{-10} \text{ m}} = -8.18 \times 10^{-19} \text{ J}$$

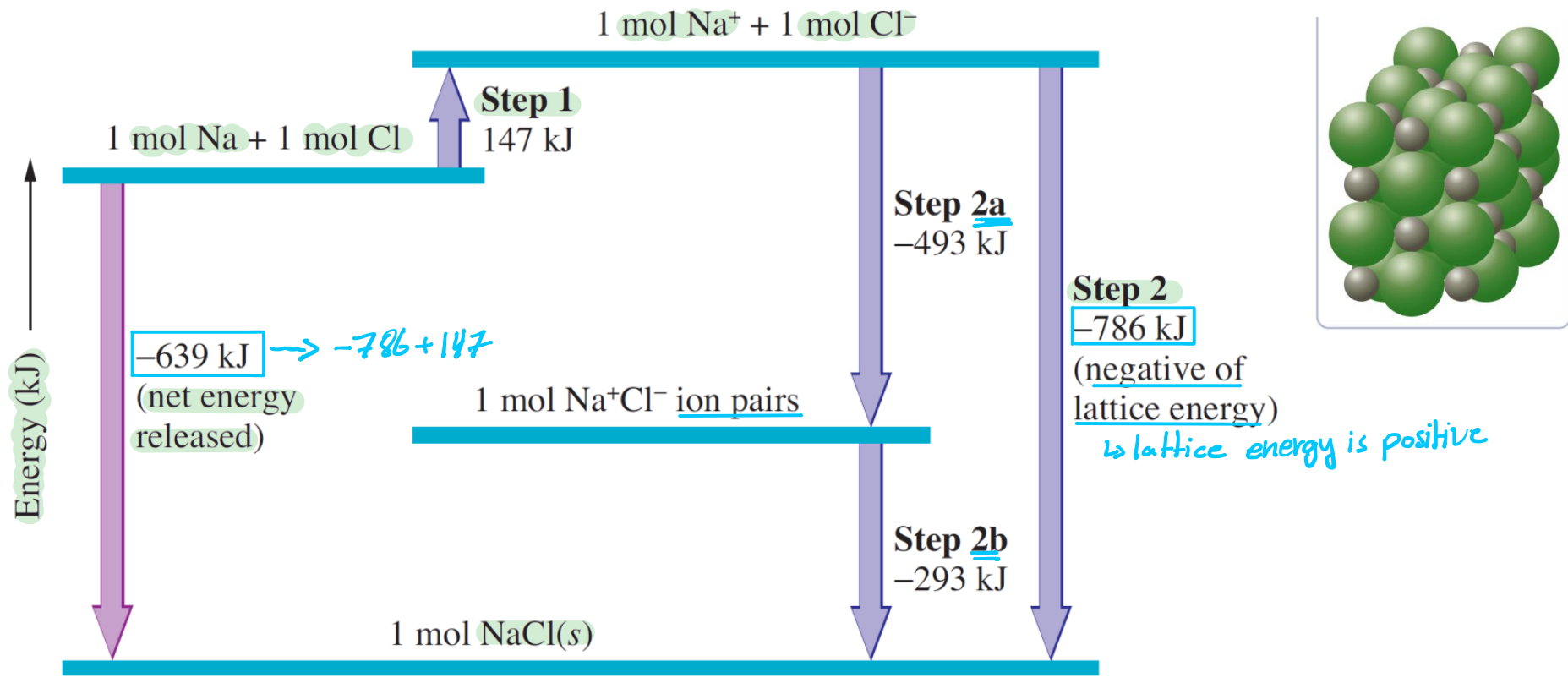
$$1 \rightarrow \frac{-8.18 \times 10^{-19} \text{ J}}{10^3} \text{ kJ}$$

$$6.022 \times 10^{23} \rightarrow \times$$

- ✓ The minus sign means energy is released
- ✓ This energy is for the formation of one ion pair
- ✓ Multiplying by Avogadro's number, 6.02×10^{23} → -493 kJ/mol
↳ for 1 mol of ionpair

✓ The **lattice energy** is the change in energy that occurs (required) when an ionic solid is separated into isolated ions in the gas phase.

✓ For sodium chloride, the process is: $\text{NaCl}(s) \longrightarrow \text{Na}^+(g) + \text{Cl}^-(g)$



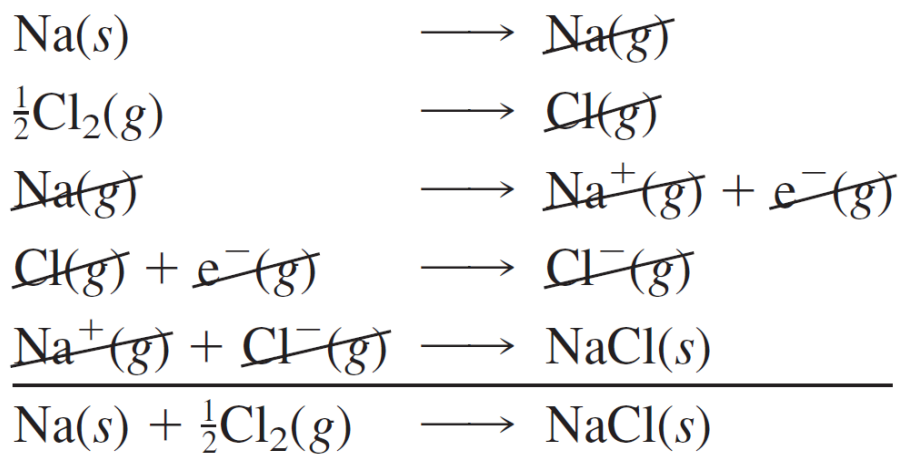
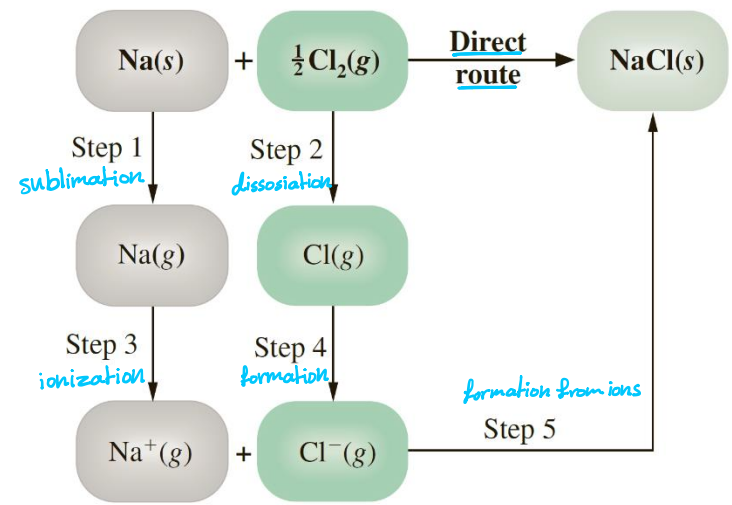
✓ The negative sign shows that there has been a net decrease in energy, which you expect when stable bonding has occurred.

✓ **Ionic bond forms between elements if the ionization energy of one is sufficiently small and the electron affinity of the other is sufficiently large**

important → doctor said

➤ The Born-Haber Cycle for NaCl (Energy diagram)

- 1- Sublimation of sodium
2. Dissociation of chlorine $\frac{1}{2}Cl_2 \rightarrow Cl$
3. Ionization of sodium
4. Formation of chloride ion (E.A.)
5. Formation of NaCl(s) from ions



$$\begin{array}{lcl}
 \Delta H_1 = & 108 \text{ kJ} & \rightarrow \text{sublimation} \\
 \Delta H_2 = & 120 \text{ kJ} & \Rightarrow \frac{240}{2} \rightarrow \text{for } Cl_2 \rightarrow \text{dissociation} \\
 \Delta H_3 = & 496 \text{ kJ} & \rightarrow \text{ionization} \\
 \Delta H_4 = & -349 \text{ kJ} & \rightarrow \text{formation of ion (EA)} \\
 \Delta H_5 = & -U & \rightarrow \text{negative of lattice energy} \\
 \hline
 \Delta H_f^\circ = & 375 \text{ kJ} - U
 \end{array}$$

$$\Delta H_f^\circ = \Delta H_{sub}^\circ + \Delta H_{ie}^\circ + \cancel{1/2} \Delta H_d^\circ + \Delta H_{ea}^\circ - U_o$$

enthalpy of formation determined calorimetrically → -411 kJ ⇒ ΔH_f°

$$375 \text{ kJ} - U = -411 \text{ kJ} \rightarrow U = (375 + 411) \text{ kJ} = 786 \text{ kJ}$$

➤ Properties of Ionic Substances

✓ Strong ionic bonds (strong electrostatic interaction)

→ high-melting points of ionic solids. *⇒ charge 1 → melting point 1
→ E 1*

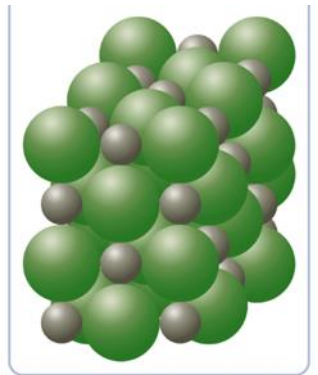
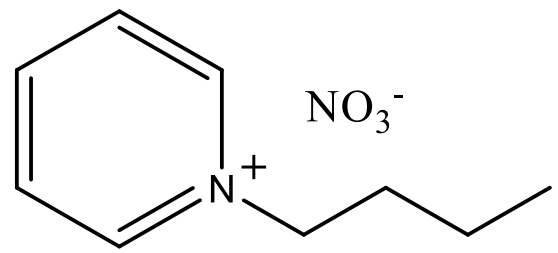
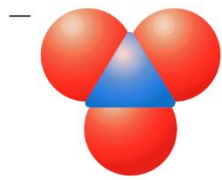
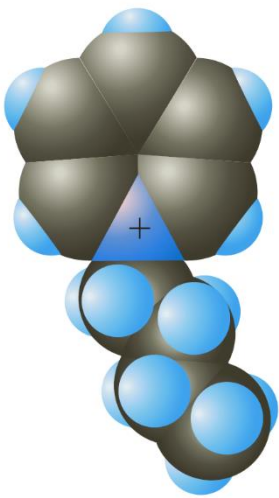
m.p of MgO (2800 °C) > m.p NaCl (801 °C)

charges (Mg²⁺ and O²⁻), *⇒ E = $\frac{k 4Q_e^2}{r}$* charges (Na⁺ and Cl⁻), *⇒ E = $\frac{k 2Q_e^2}{r}$*

$$E = \frac{k Q_1 Q_2}{r}$$

✓ The liquid melt from an ionic solid consists of ions, and so the liquid melts conducts an electric current.

✓ Ionic liquids have low m.p (RT) because the cations are large and non-spherical → weak ionic bonding



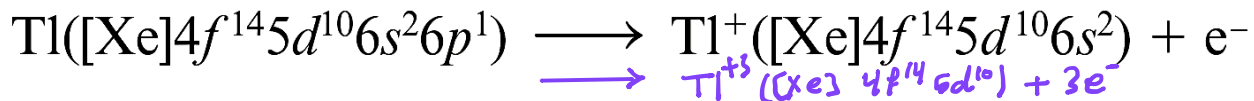
9.2 Electron Configurations of Ions

➤ Ions of the Main-Group Elements

Table 9.2 Ionization Energies of Na, Mg, and Al (in kJ/mol)*

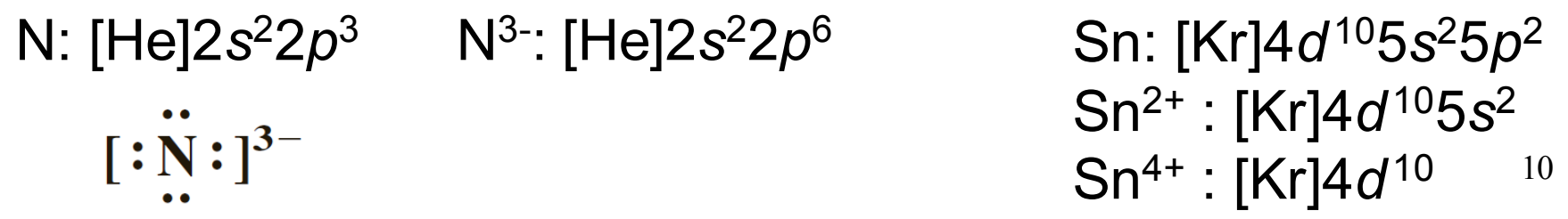
Element	Successive Ionization Energies			
	First	Second	Third	Fourth
Na	496	4,562	6,910	9,543
Mg	738	1,451	7,733	10,542
Al	578	1,817	2,745	11,577

- ✓ Valence electrons are easily removed
- ✓ Much higher energy is needed to remove further electrons.
- No compounds are found with ions having charges greater than the group number. e.g : **Na²⁺, Mg³⁺, Al⁴⁺ (Doesn't exist)**
- ✓ Boron (Group 3A) doesn't form ionic compounds with B³⁺ ions, the bonding is normally covalent.
- ✓ The remaining elements of Group 3A do form compounds containing 3⁺ ions because of decreasing ionization energy.
- ✓ Thallium in 3A, Period 6, has compounds with 1⁺ ions and compounds with 3⁺ ions



- ✓ The first three elements of Group 4A (C, Si, and Ge) are metalloids and usually form covalent rather than ionic bonds.
- ✓ Tin (Sn) and lead (Pb) (group 4A) commonly form ionic compounds with 2^+ ions. $\text{Sn}^{+2} \rightarrow \text{ionic}$ $\text{Sn}^{+4} \rightarrow \text{covalent}$ || $\text{Pb}^{+2} \rightarrow \text{ionic}$ $\text{Pb}^{+4} \rightarrow \text{covalent}$
- ✓ Tin forms tin(II) chloride, SnCl_2 , which is an ionic compound and tin(IV) chloride SnCl_4 which is a covalent compound.
- ✓ Bi (group 5A) forms ionic Bi^{3+} cpds and covalent Bi^{5+} cpds.
- ✓ Anions of Groups 5A to 7A gain electrons (large EA) to form noble-gas or pseudo-noble-gas configurations.
- ✓ Hydrogen forms compounds of the 1^- ion, H^- (hydride ion).
- ✓ Although the electron affinity of nitrogen ($2s^2 2p^3$) = 0 N^{3-} ion ($2s^2 2p^6$) is stable in the presence of Li^+ (Li_3N) and other alkaline earth elements ions (Mg_3N_2). $\text{N}^{3-} \rightarrow \text{with } \text{Li}^+ \text{ and } \text{Mg}^{+2}$

(Q) Write the electron configuration and the Lewis symbol for N^{3-} .



➤ Transition-Metal Ions

✓ M^{2+} is a common oxidation state as two electrons are removed from the outer *ns* shell. Fe: $[Ar] 4s^2 3d^6$

$Fe^{2+} : [Ar] 3d^6$ loses 4s electrons first

$Fe^{3+} : [Ar] 3d^5$ then loses 3d electrons

(Q) What are the correct electron configurations for Cu & Cu^{2+} ?

- A. $[Ar] 4s^2 3d^9, [Ar] 3d^9$
- B. $[Ar] 3d^{10} 4s^1, [Ar] 4s^1 3d^8$
- C. $[Ar] 3d^{10} 4s^1, [Ar] 3d^9$ ✓
- D. $[Ar] 4s^2 3d^9, [Ar] 3d^{10} 4s^1$
- E. $[K] 4s^2 3d^9, [Ar] 3d^9$

*Cu: $[Ar] 3d^{10} 4s^1$
 $Cu^{2+}: [Ar] 3d^9$*

exception

(Q) What are the correct electron configurations for zirconium(II) and zirconium(IV) ions?

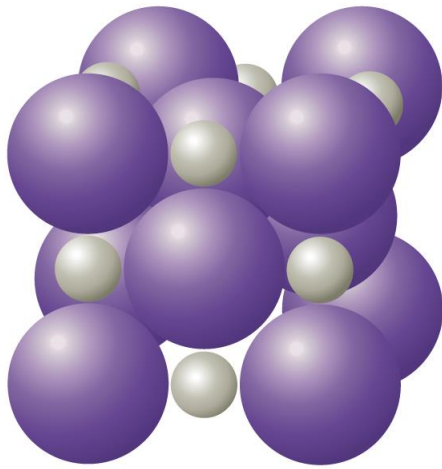
- A. $[Kr] 5d^2$ $[Kr] 4d^1$
- B. $[Ar] 4d^2$ $[Ar] 5s^2$
- C. $[Kr] 5s^2 4d^2$ $[Kr]$
- D. $[Kr] 5s^2 4d^6$ $[Kr] 4d^6$
- E. $[Kr] 4d^2$ $[Kr]$ ✓

*Zr: $[Kr] 5s^2 4d^2$
 $Zr^{2+}: [Kr] 4d^2$
 $Zr^{4+}: [Kr]$*

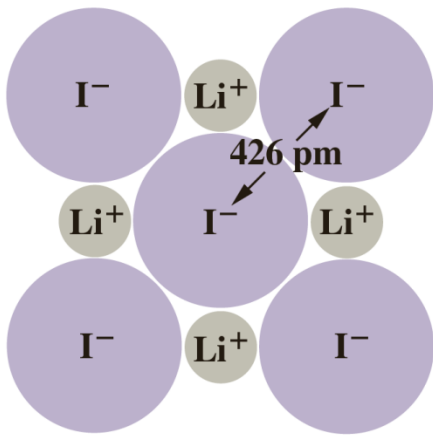
1 IA										18 VIIIA																
1 H Hydrogen 1.008											2 He Helium 4.002602															
3 Li Lithium 6.94	4 Be Beryllium 9.0121831											5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998403163	10 Ne Neon 20.1797									
11 Na Sodium 22.98976928	12 Mg Magnesium 24.305											13 Al Aluminium 26.9815385	14 Si Silicon 28.085	15 P Phosphorus 30.973761998	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948									
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955908	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938044	26 Fe Iron 55.845	27 Co Cobalt 58.933194	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.921595	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798									
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90584	40 Zr Zirconium 91.224	41 Nb Niobium 92.90637	42 Mo Molybdenum 95.95	43 Tc Technetium (98)	44 Ru Ruthenium 98.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90547	54 Xe Xenon 131.29									
55 Cs Caesium 132.90545196	56 Ba Barium 137.327	57 - 71 Lanthanoids										72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.222	78 Pt Platinum 195.084	79 Au Gold 196.966569	80 Hg Mercury 200.592	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)

➤ 9.3 Ionic Radii

Determining the iodide ion radius in the lithium iodide (LiI) crystal



a A three-dimensional view of the crystal.







Ionic radius of I^-
 $= 426 / 2 = 213 \text{ pm}$

Exercise 9.6

arrange the following ions in order of increasing ionic radius: Sr^{2+} , Mg^{2+} , Ca^{2+} .

$$Mg^{2+} < Ca^{2+} < Sr^{2+}$$

→
 ↑
 decrease
 in radius
 (size)

 Na $[He] 2s^2 2p^6 3s^1$	 Na⁺ $[He] 2s^2 2p^6$
 Cl $[Ne] 3s^2 3p^5$	 Cl⁻ $[Ne] 3s^2 3p^6$

✓ Ionic radii increase down any column because of the addition of electron shells.

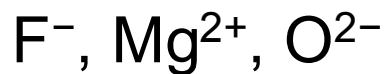
Table 9.3 Ionic Radii (in pm) of Some Main-Group Elements

Period	1A	2A	3A	6A	7A
2	Li ⁺	Be ²⁺		O ²⁻	F ⁻
	60	31		140	136
3	Na ⁺	Mg ²⁺	Al ³⁺	S ²⁻	Cl ⁻
	95	65	50	184	181
4	K ⁺	Ca ²⁺	Ga ³⁺	Se ²⁻	Br ⁻
	133	99	62	198	195
5	Rb ⁺	Sr ²⁺	In ³⁺	Te ²⁻	I ⁻
	148	113	81	221	216
6	Cs ⁺	Ba ²⁺	Tl ³⁺		
	169	135	95		

- radius > + radius

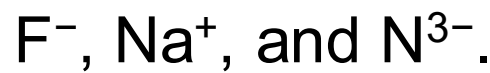
1 IA																				18 VIIIA															
1	2 IIA												5	6	7	8	9	10	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	2											
H Hydrogen 1.008	Li Lithium 6.94	Be Beryllium 9.0121831											B Boron 10.81	C Carbon 12.011	N Nitrogen 14.007	O Oxygen 15.999	F Fluorine 18.998403163	Ne Neon 20.1797	Al Aluminium 26.9815385	Si Silicon 28.085	P Phosphorus 30.973761998	S Sulfur 32.06	Cl Chlorine 35.45	Ar Argon 39.948	He Helium 4.002602										
11 Na Sodium 22.98976928	12 Mg Magnesium 24.305	3 Sc Scandium 44.955908	4 Ti Titanium 47.867	5 V Vanadium 50.9415	6 Cr Chromium 51.9961	7 Mn Manganese 54.938044	8 Fe Iron 55.845	9 Co Cobalt 58.933194	10 Ni Nickel 58.6934	11 Cu Copper 63.546	12 Zn Zinc 65.38	13 Ga Gallium 69.723	14 Ge Germanium 72.630	15 As Arsenic 74.921595	16 Se Selenium 78.971	17 Br Bromine 79.904	18 Kr Krypton 83.798	19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Y Yttrium 88.90584	22 Zr Zirconium 91.224	23 Nb Niobium 92.90637	24 Mo Molybdenum 95.95	25 Tc Technetium (98)	26 Ru Ruthenium 101.07	27 Rh Rhodium 102.90550	28 Pd Palladium 106.42	29 Ag Silver 107.8682	30 Cd Cadmium 112.414	31 In Indium 114.818	32 Sn Tin 118.710	33 Sb Antimony 121.760	34 Se Selenium 127.60	35 Br Bromine 126.90447	36 Kr Krypton 131.293

(Q) arrange the following ions in order of decreasing ionic radius:



isoelectronic series $\rightarrow Mg^{2+}$ (z=12) $\leftarrow F^-$ (z=9) $\leftarrow O^{2-}$ (z=8)

9.49 Arrange the following in order of increasing ionic radius:



*least z
highest r*

isoelectronic series $\rightarrow Na^+$ (z=11) $\leftarrow F^-$ (z=9) $\leftarrow N^{3-}$ (z=7)

9.48 Which has the larger radius, N^{3-} or P^{3-} ? **P^{3-}**

NOT isoelectronic

1 IA												13 IIIA					14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA	
1 H Hydrogen 1.008				2 Be Beryllium 9.0121831											5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998403163	10 Ne Neon 20.1797		
3 Li Lithium 6.94	4 Be Beryllium 9.0121831											13 Al Aluminium 26.9815385	14 Si Silicon 28.085	15 P Phosphorus 30.973761998	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948					
11 Na Sodium 22.98976928	12 Mg Magnesium 24.305	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.921595	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798					
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955908	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938044	26 Fe Iron 55.845	27 Co Cobalt 58.933194	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293					
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➤ Covalent Bonds

✓ a chemical bond formed by the sharing of a pair of electrons between atoms.

9.4 Describing Covalent Bonds

✓ The distance between nuclei at minimum energy is called the bond length of H_2 .

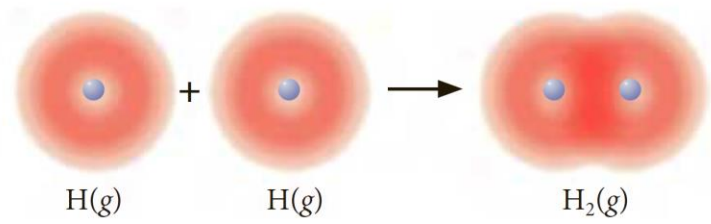


Figure 9.10 ▲
The electron probability distribution for the H₂ molecule
The electron density (shown in red) occupies the space around both atoms.

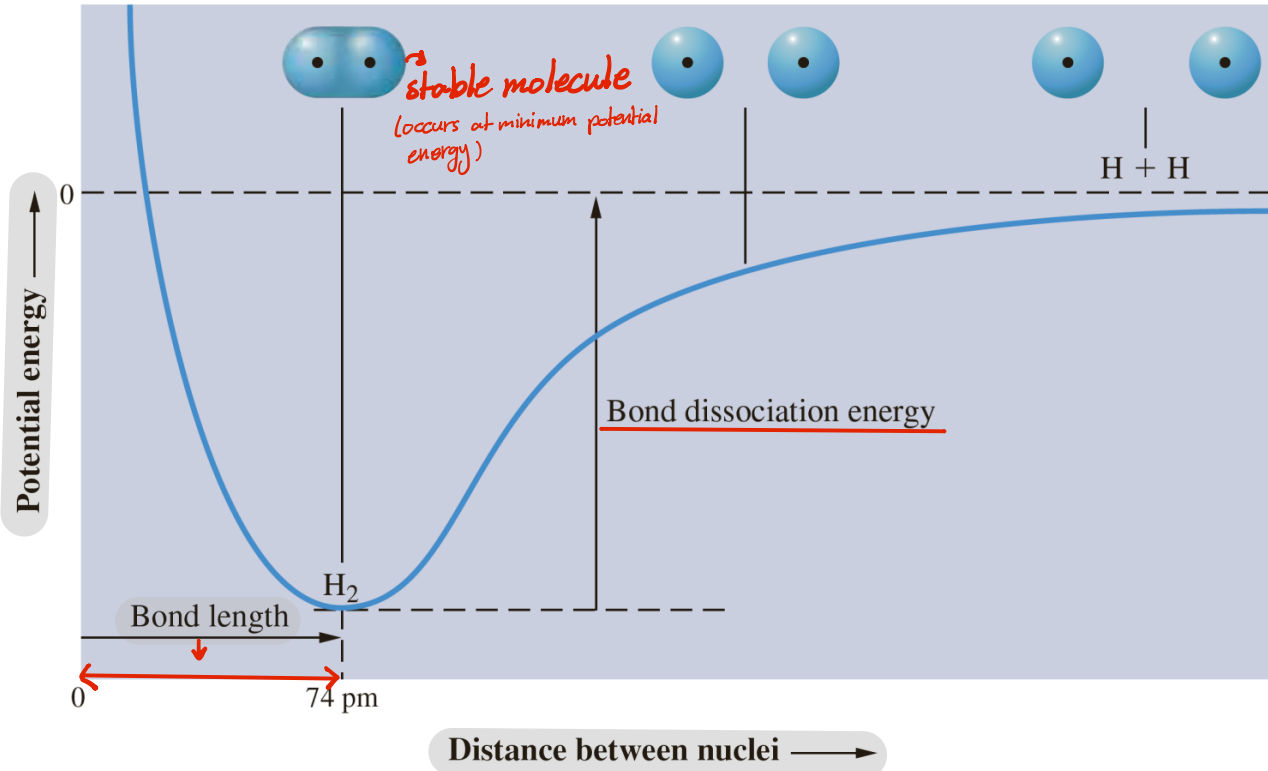
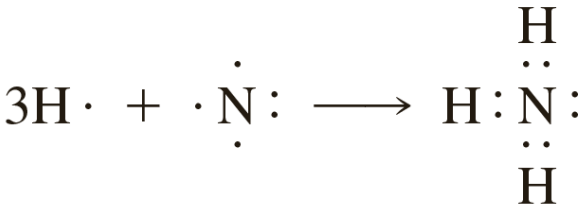
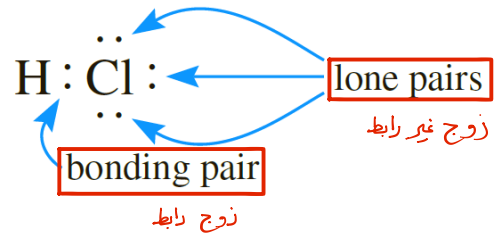
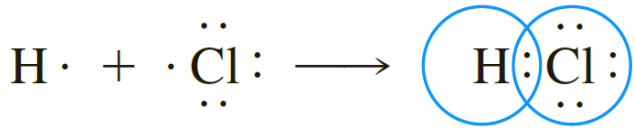
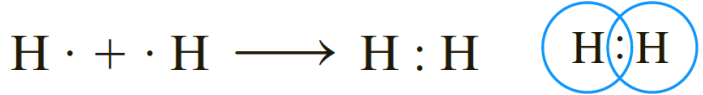


Figure 9.11 ◀
Potential-energy curve for H₂ The stable molecule occurs at the bond distance corresponding to the minimum in the potential-energy curve.

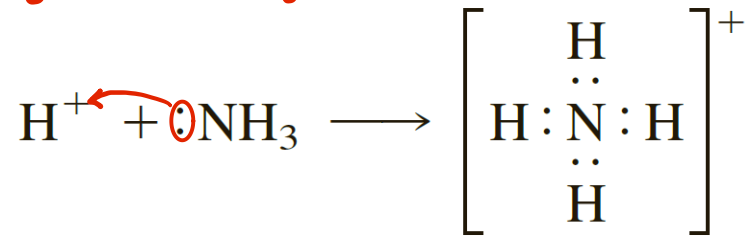
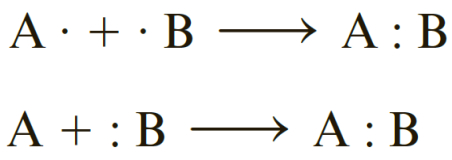
➤ Lewis Formulas



➤ Coordinate Covalent Bonds

رابطة تناسعية تناسعية

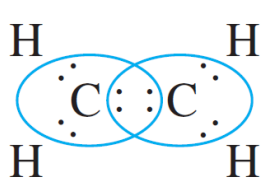
✓ is a bond formed when both electrons of the bond are donated by one atom and the other atom gives an empty orbital



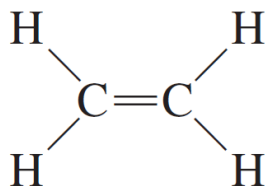
➤ Octet Rule

- ✓ The tendency of atoms in molecules to have eight electrons in their valence shells (two for hydrogen atoms)

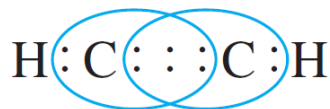
➤ Multiple Bonds



or



Ethylene



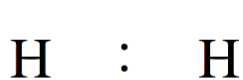
or



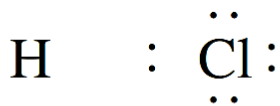
Acetylene

9.5 Polar Covalent Bonds (Polar Bonds)

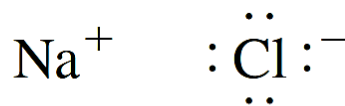
- ✓ is a covalent bond in which the bonding electrons spend more time near one atom than the other.



Nonpolar covalent



Polar covalent



Ionic

*difference in electronegativity \Rightarrow polar bond
no difference in electronegativity \Rightarrow non-polar bond*

➤ **Electronegativity** is a measure of the ability of an atom in a molecule to draw bonding electrons to itself.

✓ Mulliken electronegativity (χ):
$$\chi = \frac{I.E. + E.A.}{2}$$

✓ F has large $E.A.$ and large $I.E.$ → large electronegativity

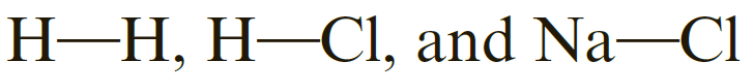
✓ Li has small $E.A.$ and small $I.E.$ → small electronegativity

✓ Pauling's electronegativity (χ): depends on bond enthalpies

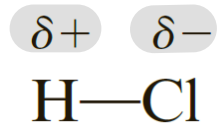
✓ Electronegativity increases from left to right and decreases from top to bottom in the periodic table. ↑ increase in electronegativity (in periodic table)

✓ Metals are the least electronegative elements (they are electropositive) and nonmetals the most electronegative.

✓ The absolute value of the difference in electronegativity of two bonded atoms gives a rough measure of the polarity of a bond



$\Delta\chi$:	0.0	0.9	2.1
	<i>non-polar</i>	<i>polar</i>	<i>ionic</i>



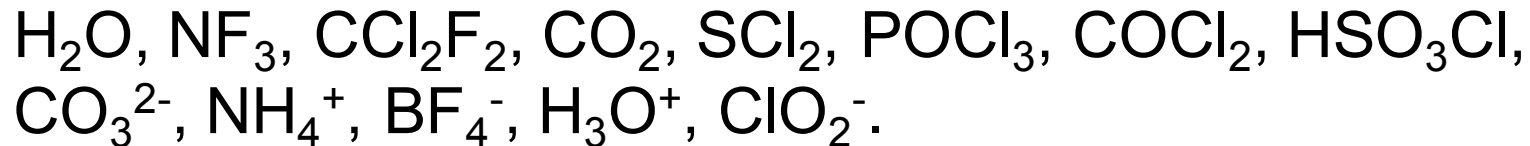
Polar molecule

➤ Writing Lewis Electron-Dot Formulas

↳ first → check the octet rule

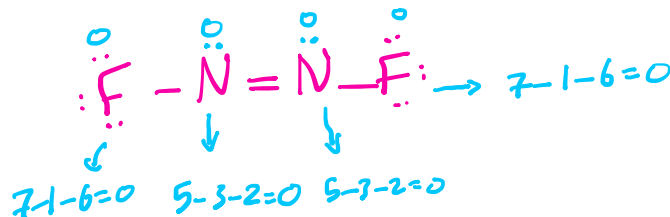
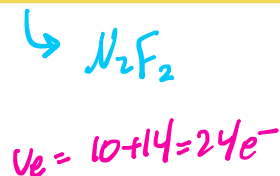
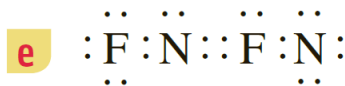
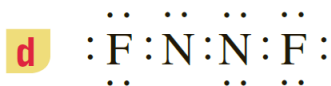
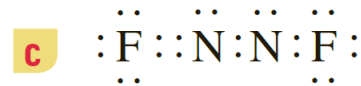
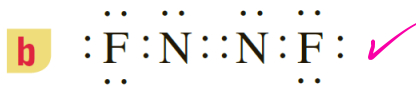
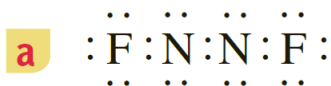
↳ second → check the formal charge

These will be done in class:



CONCEPT CHECK 9.2

Each of the following may seem, at first glance, to be plausible electron-dot formulas for the molecule N_2F_2 . Most, however, are incorrect for some reason. What concepts or rules apply to each, either to cast it aside or to keep it as the correct formula?



writing Lewis e^- dot Formula

1. find the valence electrons for all atoms in the formula.

↳ add one for each negative charge and subtract one for each positive charge



2. draw skeletal for the structure. put the "least electronegativity" atom in the center (with exception for H) → always on the surroundings. "the one that form more bonds"

3. draw single bond between the center and the surrounding atoms

4. complete octet for each atom starting from the surroundings (except H for $2e^-$)

5. draw double or triple bond if needed (when valence electrons finish and the center atom hasn't reached the octet yet!)
→ atoms that often form multiple bond $\Rightarrow C, N, O, S$

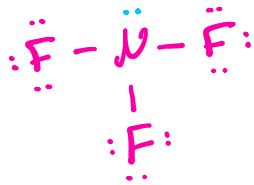
* formal charge for the atom:

$$\text{valence } e^- - \frac{1}{2}(\text{bonding electrons}) - \text{non-bonding electrons} \quad \longrightarrow \text{computed for each atom on it's own.}$$

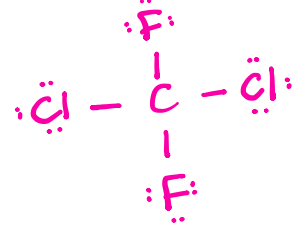
1. H_2O $V_e = (2 \times 1) + 6 = 8e^-$



2. NF_3 $V_e = 5 + (3 \times 7) = 26e^-$



3. CCl_2F_2 $V_e = 4 + (2 \times 7) + (2 \times 7) = 32e^-$



4. CO_2 $V_e = 4 + (2 \times 6) = 16e^-$

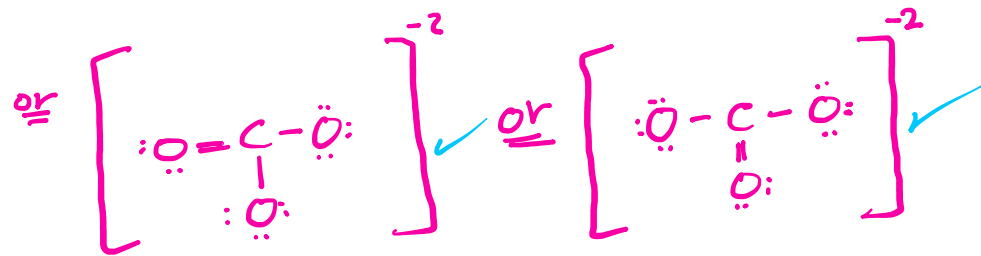
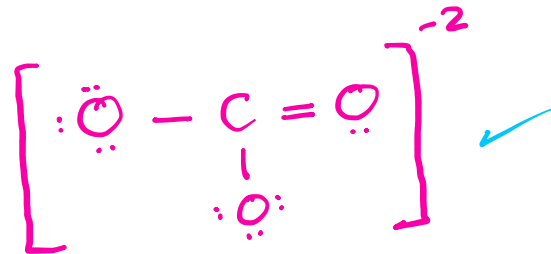


no e^- remained
and C didn't
reach octet
rule so---

5. SCl_2 $V_e = 6 + (2 \times 7) = 20e^-$

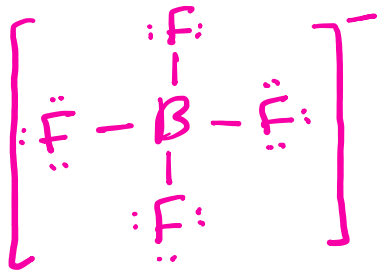


6. CO_3^{2-} $V_e = 4 + (3 \times 6) + 2 = 24e^-$

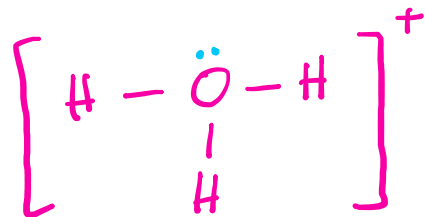


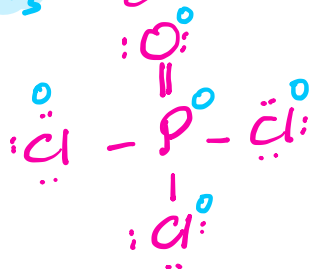
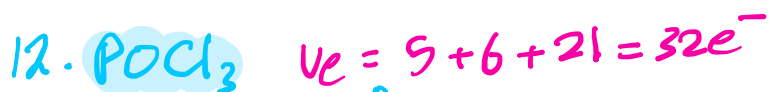
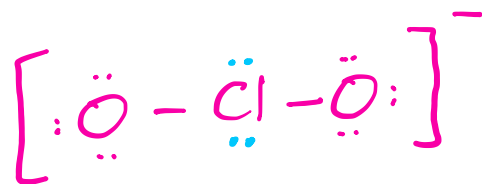
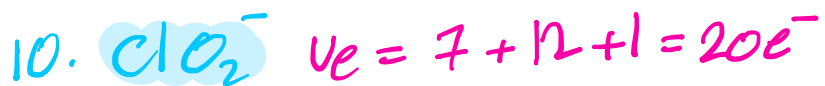
this is called resonance

8. BF_4^- $V_e = 3 + (4 \times 7) + 1 = 32e^-$



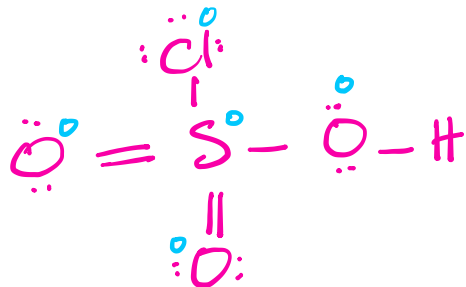
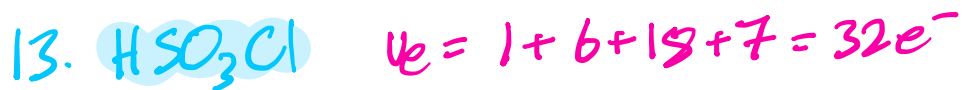
9. H_3O^+ $V_e = 3 + 6 - 1 = 8e^-$



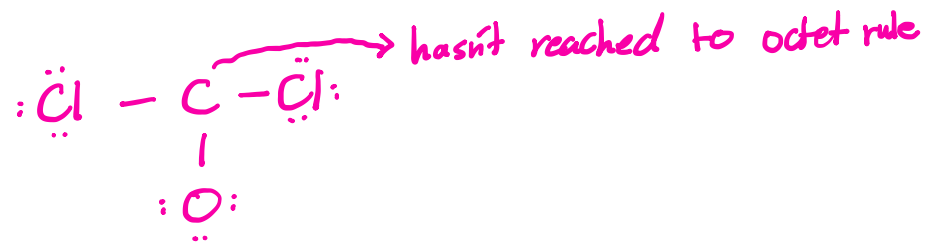
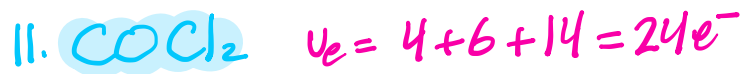


this is an exception for P \rightarrow doesn't follow the octet rule.
(expand octet)

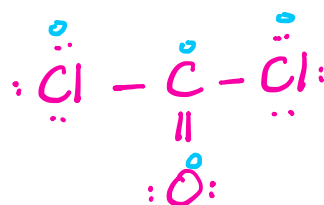
\hookrightarrow to reach a zero formal charge



\rightarrow exception for octet rule
(expand octet)



\downarrow



\Rightarrow from formal charge:

$$\text{C} \Rightarrow 4 - 4 = 0 \checkmark$$

$$\text{Cl} \Rightarrow 7 - 1 - 6 = 0 \checkmark$$

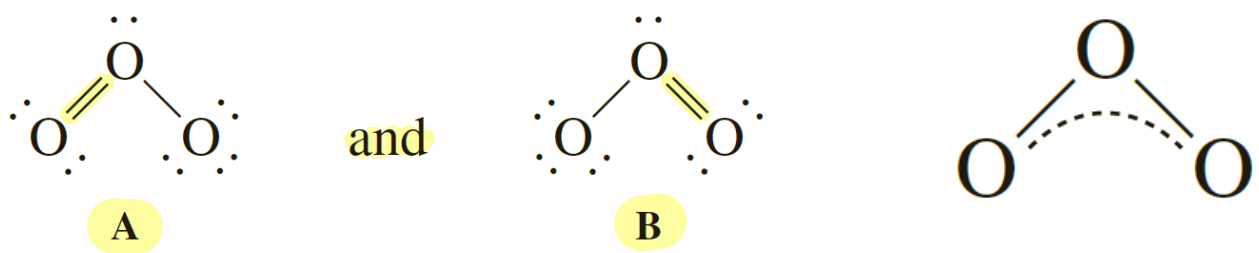
$$\text{Cl} \Rightarrow 7 - 1 - 6 = 0 \checkmark$$

$$\text{O} \Rightarrow 6 - 2 - 4 = 0 \checkmark$$

if C formed double bond
with other atom than O
 \Rightarrow the formal charge won't be
zero X

9.7 Delocalized Bonding: Resonance

Ozone (O₃)

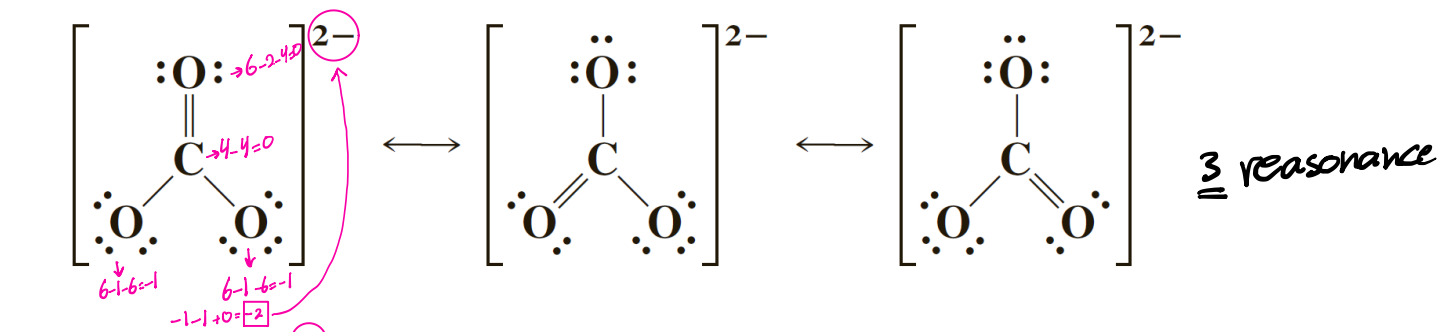


✓ The lengths of the two oxygen–oxygen bonds (that is, the distances between the atomic nuclei) are both 128 pm.

✓ delocalized bonding

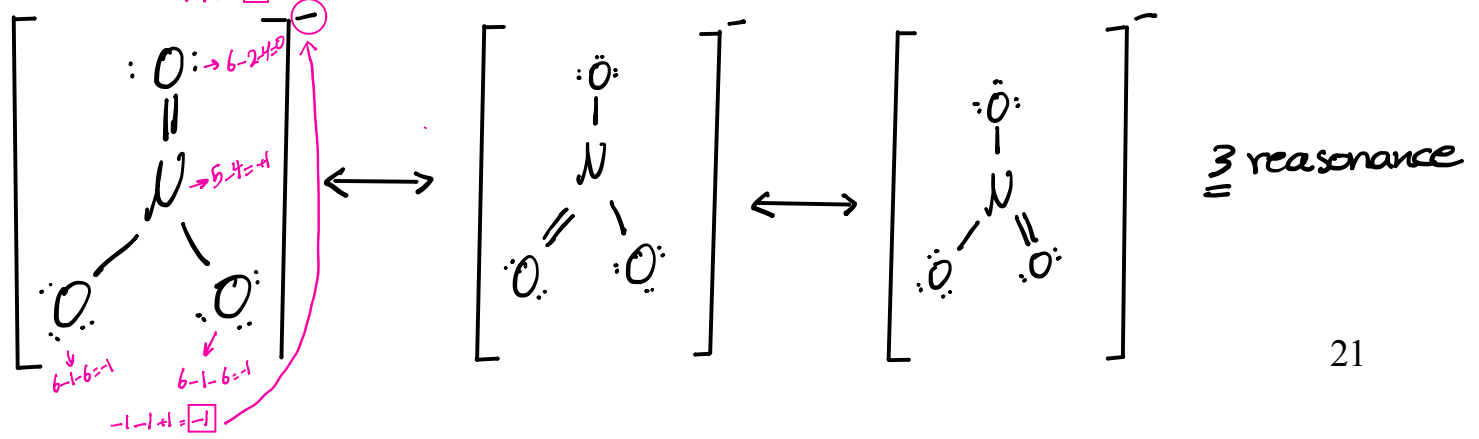
CO₃²⁻

$4 + 18 + 2 = 24e^-$



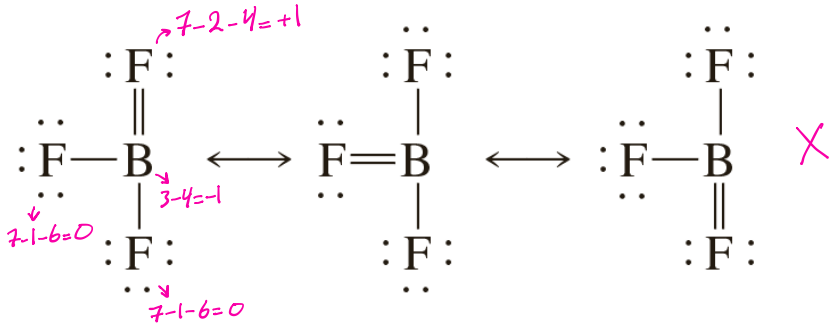
NO₃⁻

$5 + 18 + 1 = 24e^-$



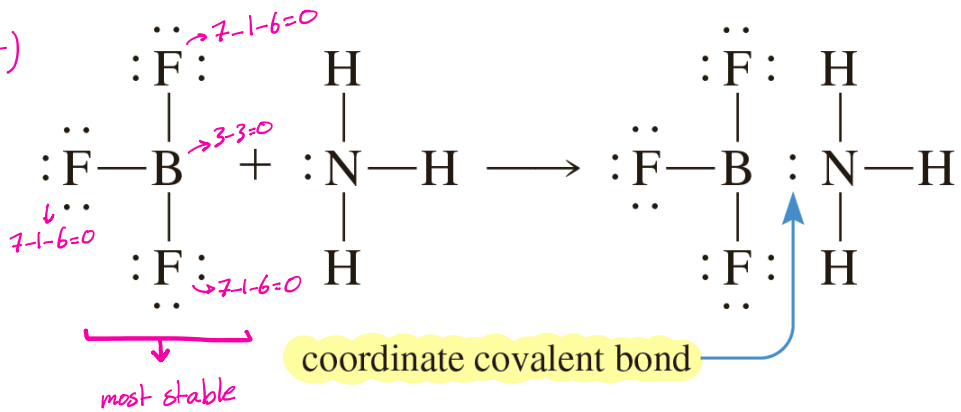
9.8 Exceptions to the Octet Rule

These will be done in class:

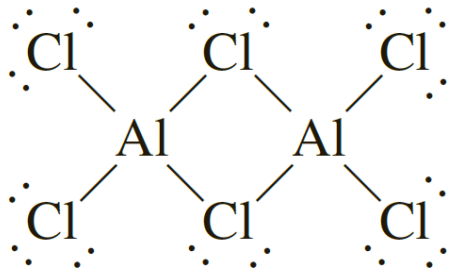


$P, S, Xe \rightarrow$ expand octet (more than $8e^-$)

$B, Be \rightarrow$ incomplete octet (less than $8e^-$)



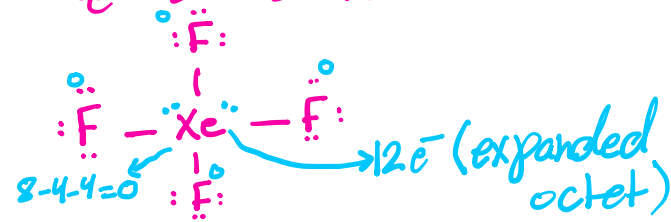
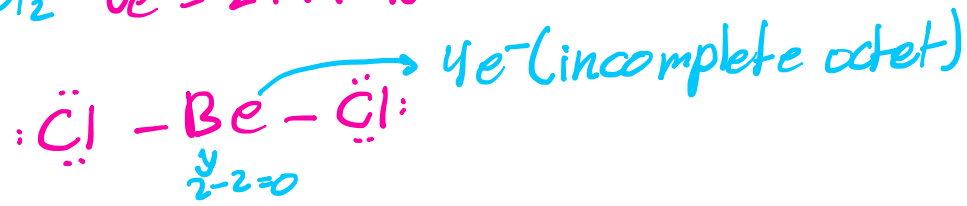
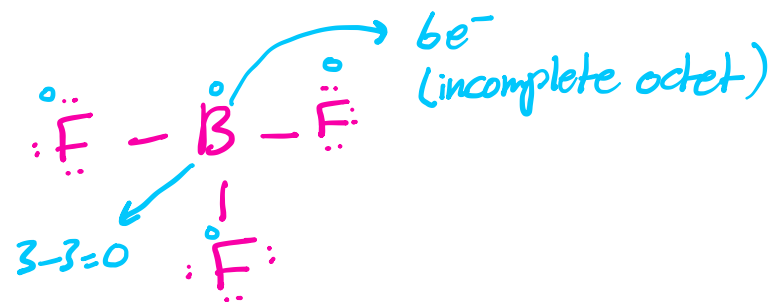
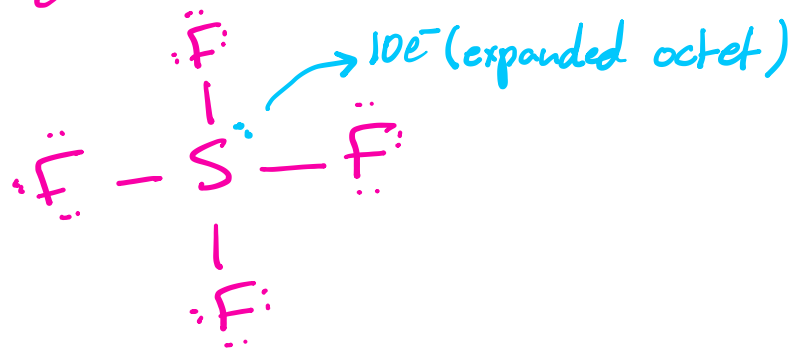
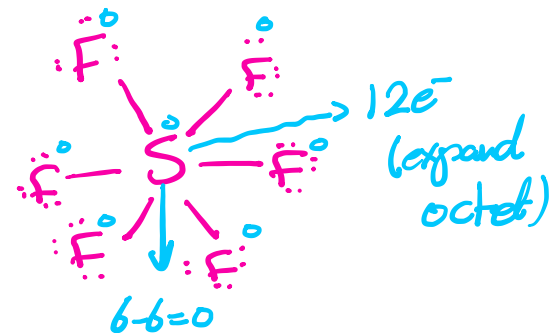
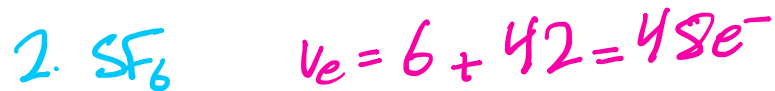
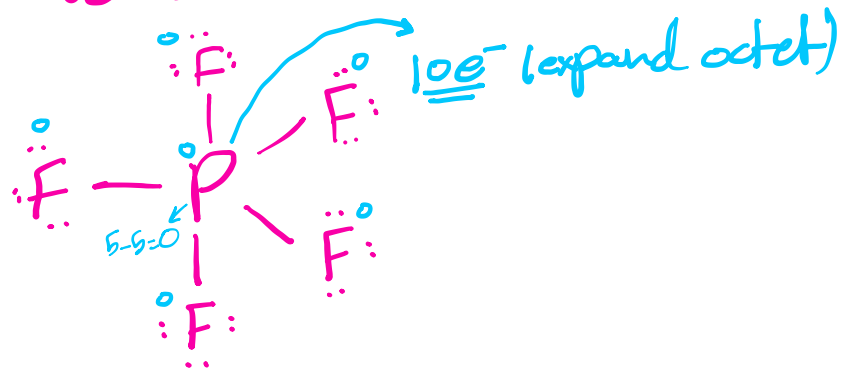
$AlCl_3$ @ RT & at melting point (very low $192^\circ C$)



two of the Cl atoms are in **bridge positions**

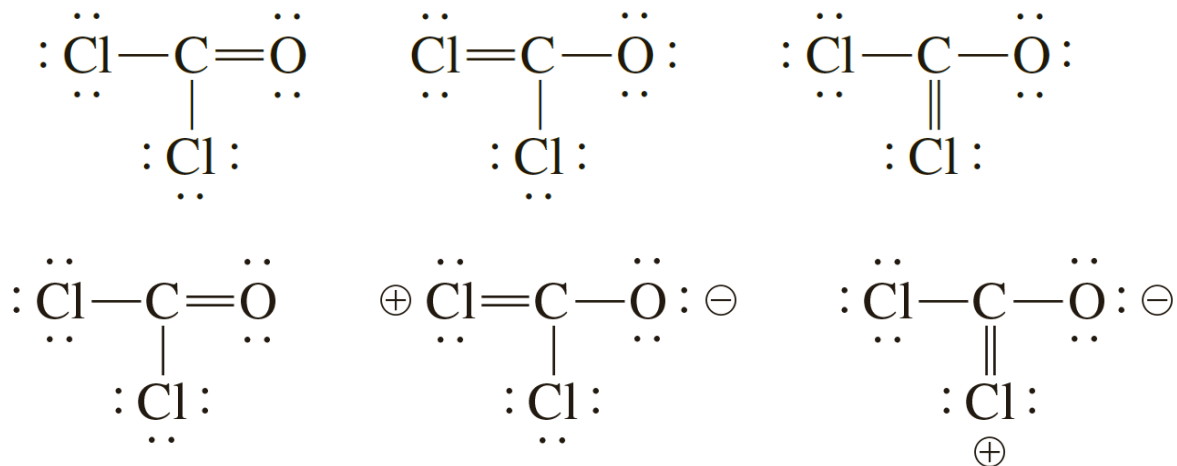
\downarrow
Promotes the stability for the structure.

The octet exceptions:



9.9 Formal Charge and Lewis Formulas

COCl₂

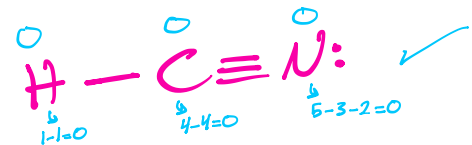
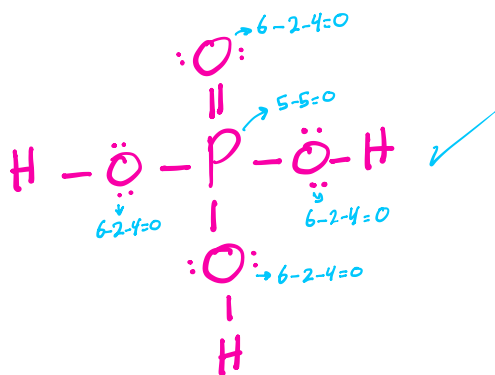
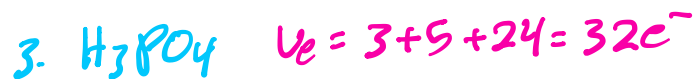
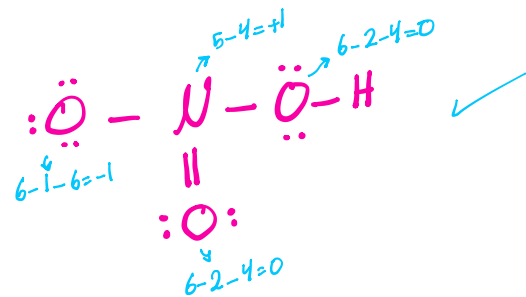
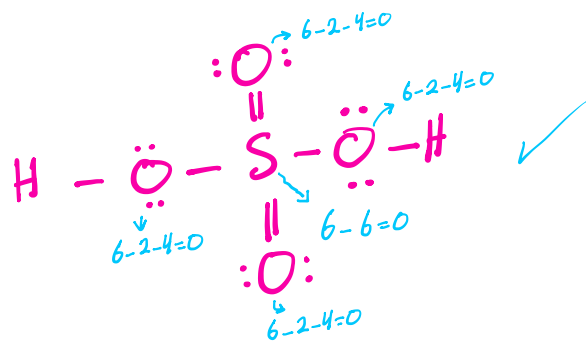


RULE A Whenever you can write several Lewis formulas for a molecule, choose the one having the lowest magnitudes of formal charges.

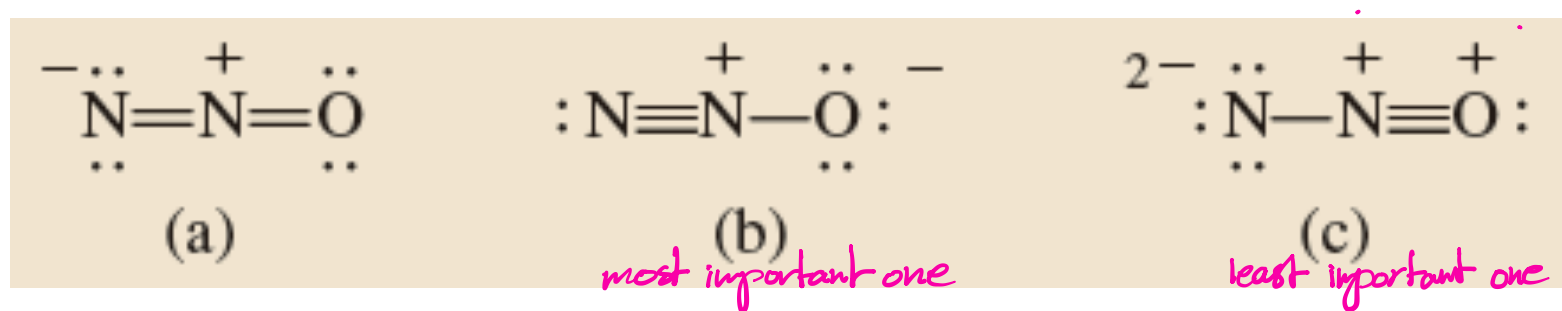
RULE B When two proposed Lewis formulas for a molecule have the same magnitudes of formal charges, choose the one having the negative formal charge on the more electronegative atom.

RULE C When possible, choose Lewis formulas that do not have like charges on adjacent atoms.

(Q) Write the Lewis formula that best describes the charge distribution in the sulfuric acid molecule, H₂SO₄, according to the rules of formal charge. (HNO₃, H₃PO₄, HCN)



(Q) Draw three resonance structures for the molecule nitrous oxide, N_2O (the atomic arrangement is NNO)



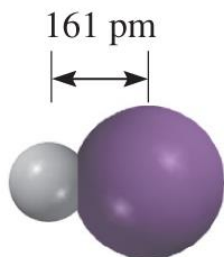
Structure (b) is the most important one because the negative charge is on the more electronegative oxygen atom.

Structure (c) is the least important one because it has a larger separation of formal charges. Also, the positive charge is on the more electronegative oxygen atom.

➤ 9.10 Bond Length and Bond Order



H₂



HI

bond length:

the sum of the covalent radii of atoms A and B predicts the A-B bond length.

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

covalent radius:

Covalent radius of an atom X = half of the covalent bond length of a homonuclear X-X single bond.

If covalent radius of (C = 76 pm) & (Cl = 102 pm) → bond length of C-Cl = (76 + 102) = 178 pm

chloromethane, CH₃Cl, 178.4 pm;

tetrachloromethane, CCl₄, 176.6 pm;

Bond lengths:

the shortest & the strongest

Triple bond < Double Bond < Single Bond

the longest & the weakest

3

2

1

➤ Trends for atomic radii

1. Within a period, the covalent radius tends to decrease with increasing atomic number.

→ From left to right →

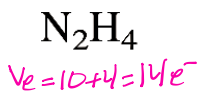
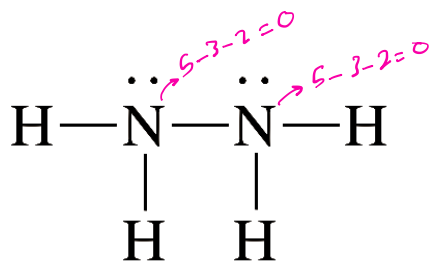
2. Within a group, the covalent radius tends to increase with period number.

↳ From top to bottom ↓

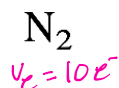
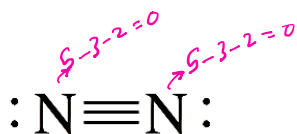
(Q) Consider the molecules N_2H_4 , N_2 , and N_2F_2 . → should draw lewis structure

Which molecule has the shortest nitrogen–nitrogen bond?

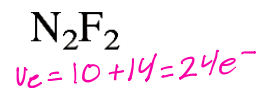
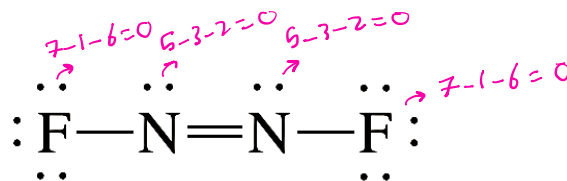
Which has the longest nitrogen–nitrogen bond?



longest



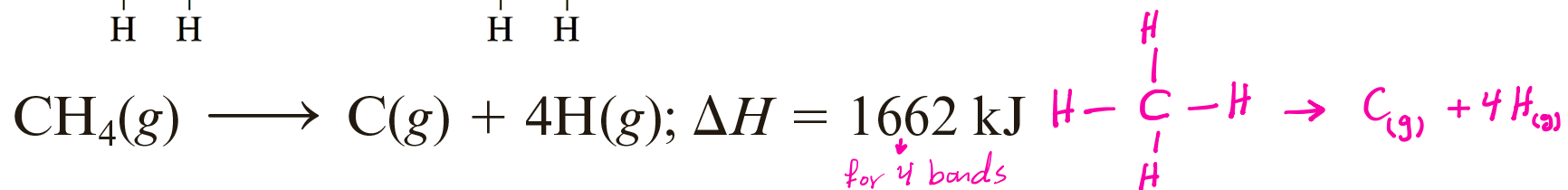
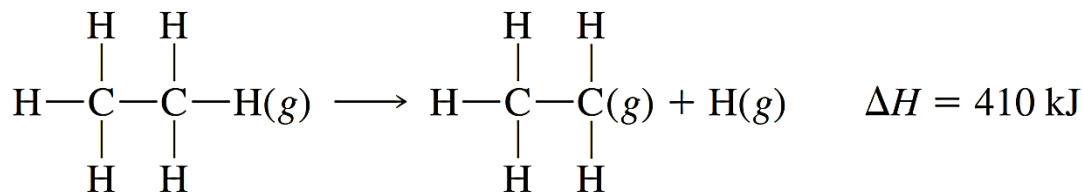
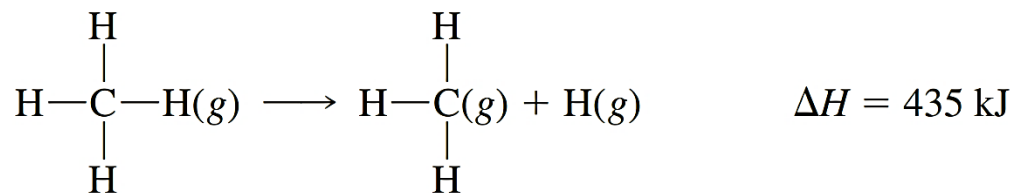
shortest



bond length $\Rightarrow N_2H_4 > N_2F_2 > N_2$

9.11 Bond Enthalpy (BE) → important

“bond enthalpy” and “bond energy” are often used interchangeably



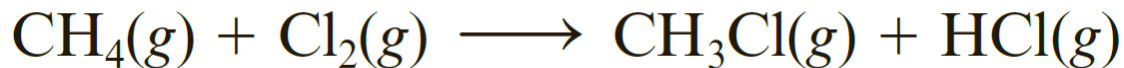
$$\rightarrow BE(\text{C}-\text{H}) = \frac{1}{4} \times 1662 \text{ kJ} = 416 \text{ kJ}$$

for 1 bond

- ✓ Because it takes energy to break a bond, bond enthalpies are always positive numbers.
- ✓ Bond enthalpy is a measure of the strength of a bond:
the larger the bond enthalpy, the stronger the chemical bond

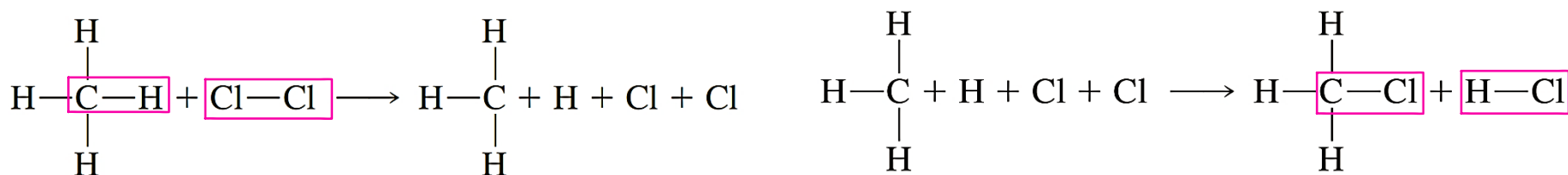
(Q) Use bond enthalpies to estimate the enthalpy change for the following reaction:

⇒ dr said this is imp question ~



Given that bond enthalpies (kJ/mol) for:

(C-H) = 413, (Cl-Cl) = 242, (C-Cl) = 328, (H-Cl) = 431,



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$$\begin{aligned}
 \Delta H &\approx BE(\text{C}-\text{H}) + BE(\text{Cl}-\text{Cl}) - BE(\text{C}-\text{Cl}) - BE(\text{H}-\text{Cl}) \\
 &= (413 + 242 - 328 - 431) \text{ kJ} \\
 &= -104 \text{ kJ}
 \end{aligned}$$

In general, the enthalpy of reaction is (approximately) equal to the sum of the bond enthalpies for bonds broken minus the sum of the bond enthalpies for bonds formed.

$\Delta H =$ *sum of broken bonds enthalpies - sum of formed bonds enthalpies*
↳ enthalpy of reaction

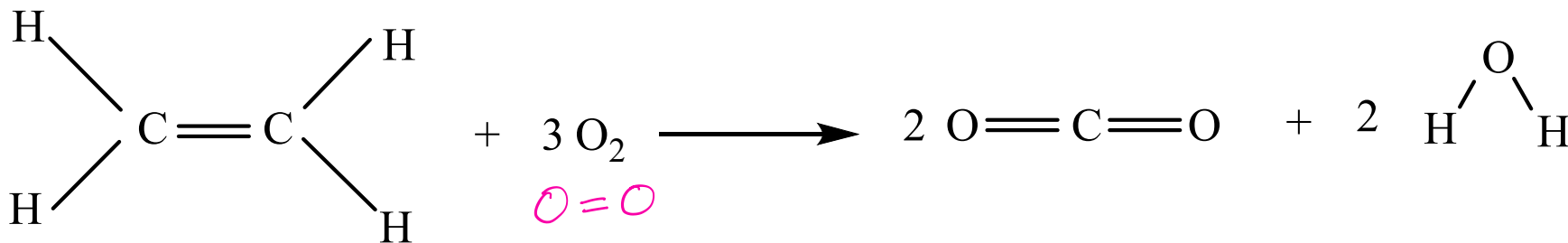
Exercise 9.18 Use bond enthalpies to estimate the enthalpy change for the combustion of ethylene, C_2H_4 , according to the equation



⇒ the eq will be given and we should draw the structure ↓

Given that bond enthalpies (kJ/mol) for:

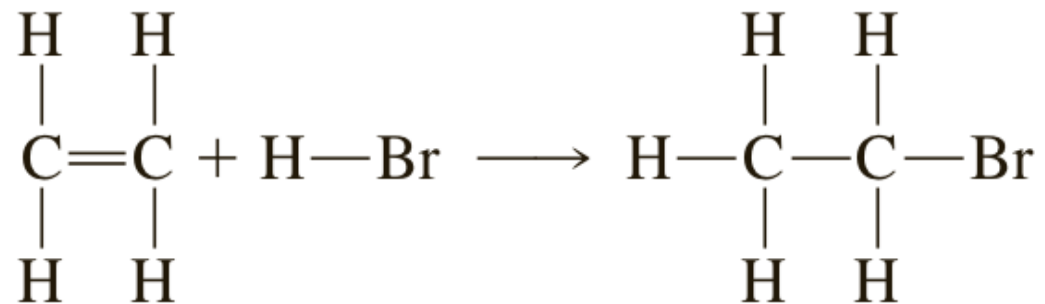
(C=C) = 614, (C-H) = 413, (O=O) = 498, (C=O) = 804, (O-H) = 463



$$\Delta H = \{[614 + (4 \times 413) + (3 \times 498)] - [(4 \times 804) + (4 \times 463)]\} \text{ kJ}$$

$$= -1308 \text{ kJ}$$

9.85 Use bond enthalpies (Table 9.5) to estimate ΔH for the following gas-phase reaction.



$$\begin{aligned} \Delta H &\cong BE(\text{C}=\text{C}) + BE(\text{H}-\text{Br}) - BE(\text{C}-\text{C}) - BE(\text{C}-\text{H}) - BE(\text{C}-\text{Br}) \\ &= (614 + 366 - 348 - 413 - 276) \text{ kJ} = -57 \text{ kJ} \end{aligned}$$