

# \*Chapter 9: Ionic and Covalent Bonding.

## \*9.1: Describing Ionic Bonds:

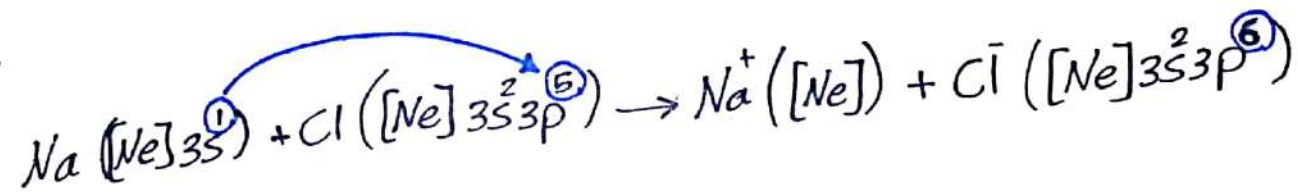
\* Ionic Bond: a chemical bond formed by the electrostatic attraction between positive and negative ions.

\* one or more electrons are transferred from the valence shell of one atom to another.

\* Cation: (+)ive ion, the atom loses electrons.

\* anion: (-)ive ion, the atom gains electrons

example:



→ after an electron transfer, ions are formed, each of which has a noble-gas configuration.

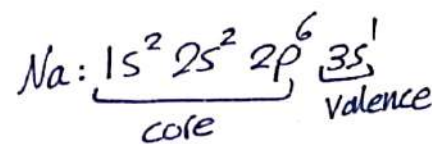
\* Lewis Electron-Dot Symbols: a symbol in which the electrons in the valence shell of an atom or ion are represented by dots placed around the letter symbol of the element.



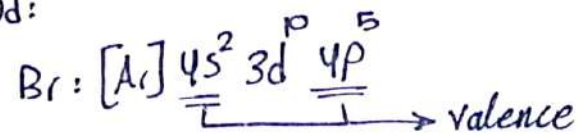
\* Lewis Electron-Dot Symbols for Atoms of second and Third Periods:

Group \ Period	1A $ns^1$	2A $ns^2$	3A $ns^2 np^1$	4A $ns^2 np^2$	5A $ns^2 np^3$	6A $ns^2 np^4$	7A $ns^2 np^5$	8A $ns^2 np^6$
second	Li $\cdot$	$\cdot$ Be $\cdot$	$\cdot$ B $\cdot$	$\cdot$ C $\cdot$	$\cdot$ N $\cdot$	$\cdot$ O $\cdot$	$\cdot$ F $\cdot$	$\cdot$ Ne $\cdot$
Third	Na $\cdot$	$\cdot$ Mg $\cdot$	$\cdot$ Al $\cdot$	$\cdot$ Si $\cdot$	$\cdot$ P $\cdot$	$\cdot$ S $\cdot$	$\cdot$ Cl $\cdot$	$\cdot$ Ar $\cdot$

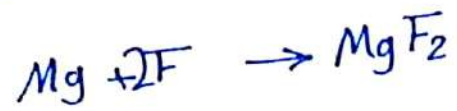
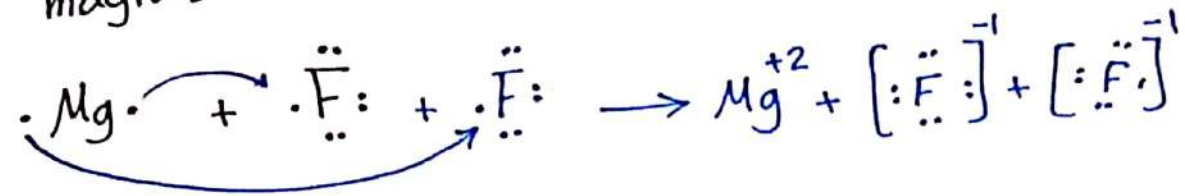
\* core electrons aren't shown:



\* Pseudo: core + (n-1)d:



\* **Example:** Use Lewis electron-dot symbols to represent the transfer of electrons from magnesium to fluorine atoms to form ions with noble-gas configurations.

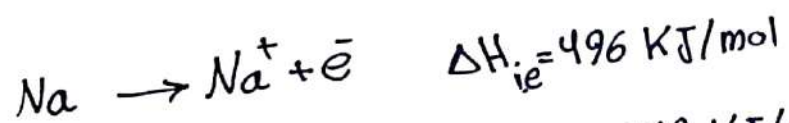


### \* Energy Involved in Ionic Bonding

\* The bond occur in two steps:

1] An electron is transferred between the two separate ~~atoms~~ <sup>ions</sup> atoms to give ions

2] The ions then attracted one another to form an ionic bond.



$$496 - 349 = 147 \text{ KJ/mol}$$

\* 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.

\* when (+)ive and (-)ive ions bond  $\rightarrow$  energy is released.



\* Coulomb's law: the potential energy obtained in bringing two charges  $Q_1$  and  $Q_2$ , 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.

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

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

$$E = -8.18 \times 10^{-19} \text{ J} \rightarrow \text{energy of one ion pair}$$

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

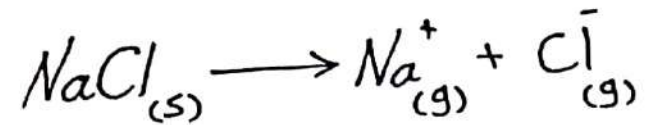
Na charge is  $+e$   
Cl charge is  $-e$  }  $e = 1.602 \times 10^{-19} \text{ C}$

$r$  = distance between  $\text{Na}^+$  and  $\text{Cl}^-$   
 $= 2.82 \times 10^{-10} \text{ m}$

\* The minus sign means energy is released

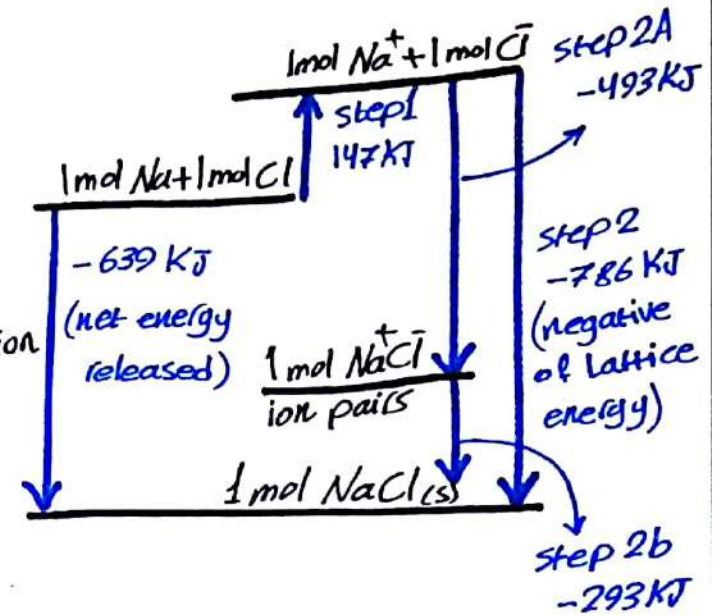
\* Multiply by Avogadro's no.  $= 6.022 \times 10^{23} \rightarrow -493 \text{ kJ/mol}$

\* Lattice Energy: the change in energy that occurs when an ionic solid is separated into isolated ions in the gas phase.



\* 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.



\* The Born-Haber Cycle for NaCl (Energy diagram)

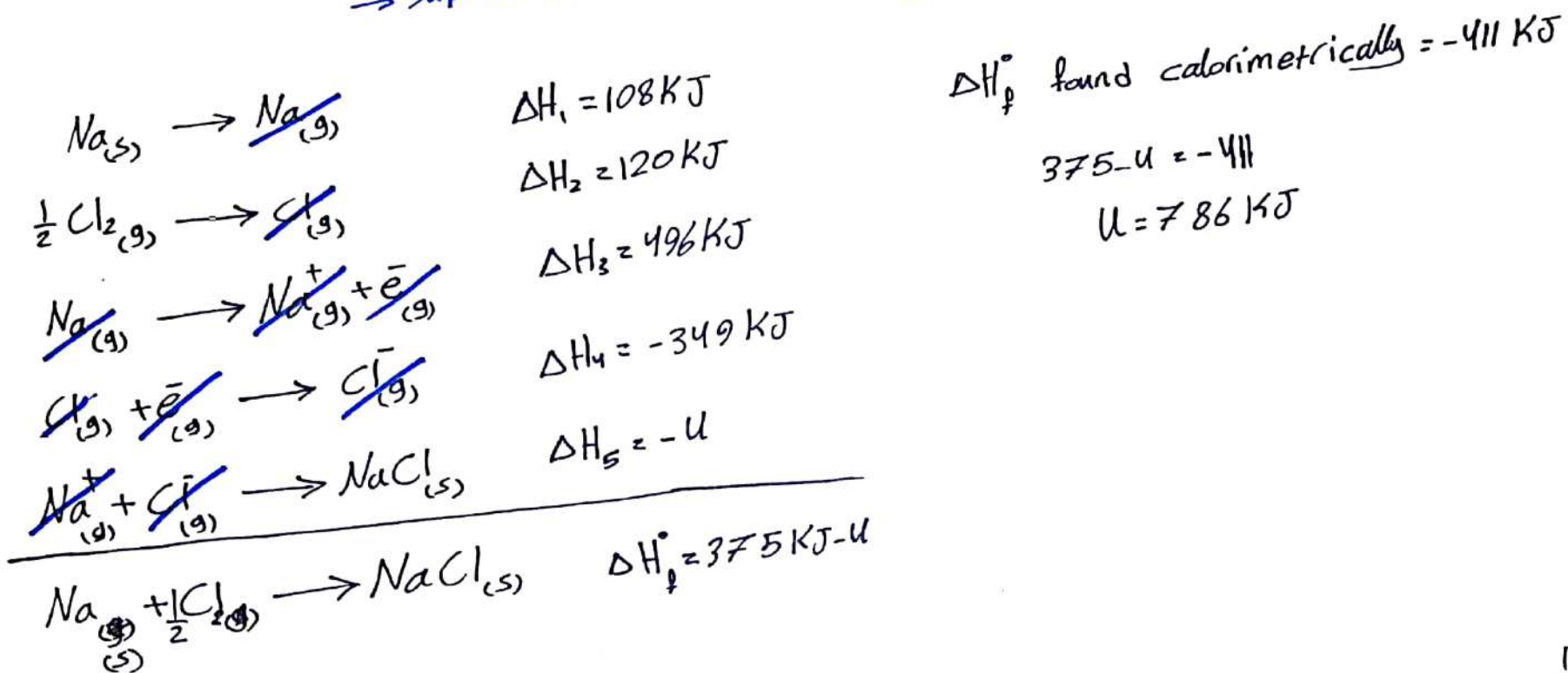
- 1] Sublimation of sodium: Metallic sodium is vaporized to a gas of sodium atoms (s → g) → it is measured to be 108 kJ/mol Na
- 2] Dissociation of chlorine: Chlorine molecules are dissociated to atoms.  $\left(\frac{1}{2} \text{Cl}_{2(g)} \rightarrow \text{Cl}_{(g)}\right)$  → it is measured to be 120 kJ/mol Cl or 240 kJ/mol of bonds.

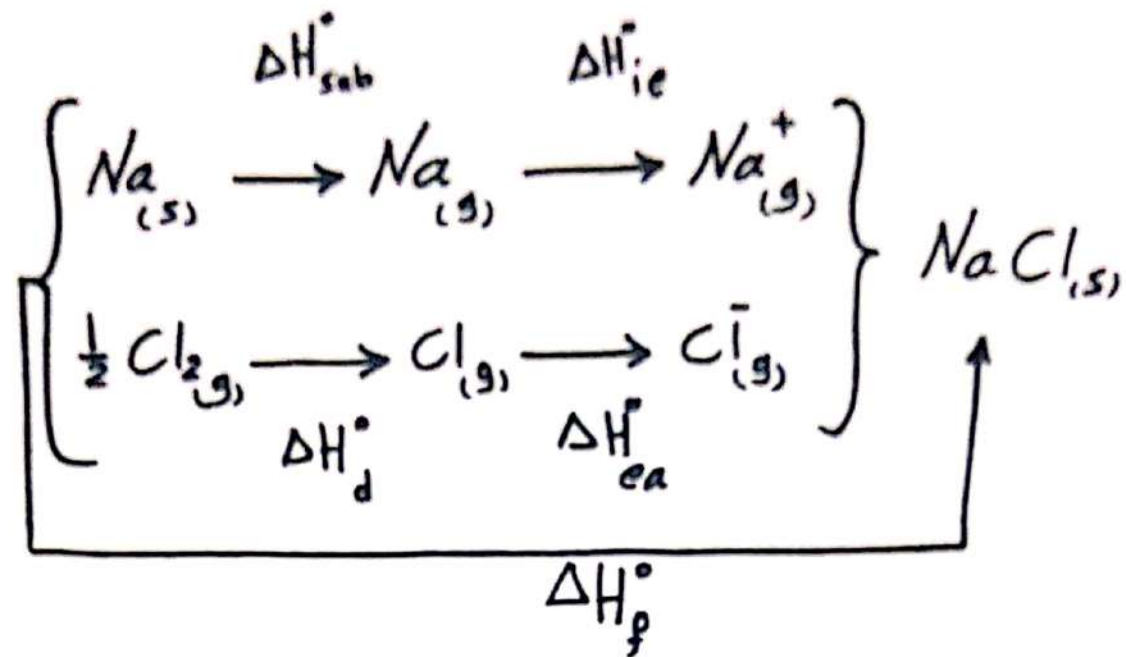


3] Ionization of sodium: Sodium ions are ionized to  $\text{Na}^+$  ions, equals the IE of atomic sodium which equals  $496 \text{ kJ/mol Na}$ .

4] Formation of chlorine ion: the electrons from the ionization of sodium atoms are transferred to chlorine atoms, it equals the negative of the EA of atomic chlorine which equals  $-349 \text{ kJ/mol Cl}$ .

5] Formation of  $\text{NaCl}_{(s)}$  from ions: The ions  $\text{Na}^+$  and  $\text{Cl}^-$  combine to give solid sodium chloride, because it is reverse of the one corresponding to the lattice energy, so it equals the negative of the Lattice Energy.  
 $\rightarrow$  suppose  $U$  is the lattice energy the the formation of  $\text{NaCl}_{(s)} = -U$





$$\Delta H_{\text{f}}^{\circ} = \Delta H_{\text{sub}}^{\circ} + \Delta H_{\text{ie}}^{\circ} + \Delta H_{\text{ea}}^{\circ} + \frac{1}{2} \Delta H_{\text{d}}^{\circ} + U_{\circ} \rightarrow \text{Lattice Energy}$$

$$-411 = 108 + 496 + (-349) + \frac{1}{2}(240) + U_{\circ}$$

$$U_{\circ} = -786 \text{ kJ/mol}$$

## \* Properties of Ionic Substances:

→ Ionic substances are high melting solids.

→ strong ionic bonds (strong electrostatic interaction) → high melting points of ionic solids.

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

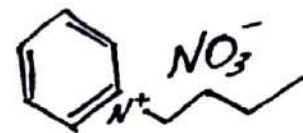
charges  $Mg^{+2}, O^{-2}$

charges  $Na^+, Cl^-$

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

\* The liquid melts from an ionic solid consist from ions, and so the liquid conducts an electric currents. If solid dissolves in a molecular liquid, such as water, the resulting solution consists of ~~ions~~ ions ~~dispersed~~ dispersed among molecules; the solution also conducts an electric current.

\* Ionic liquids have low m.p (RT) because of the cations are large and non-spherical





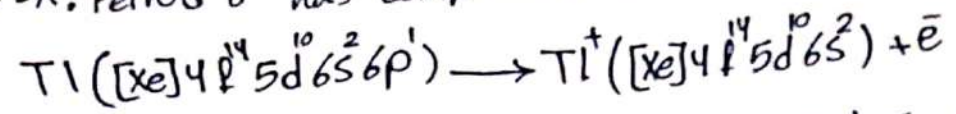
## \*9.2: Electron Configurations of Ions.

\* it is easier to lose valence electrons but it is hard to lose other electrons, in the  
Ions of Main group elements.

→ no compounds are found with ions having charges greater than the group no.

\* Boron in group 3A normally make a covalent bond

\* Thallium in 3A, Period 6 has compounds with +1 ions and compounds with +3 ions



\* in group 4A (C, Si, and Ge) usually form covalent rather than ionic bonds

\* Tin (Sn) and lead (Pb) - group 4A - commonly forms ionic compounds with +2 ions

\* Tin forms  $\text{SnCl}_2 \rightarrow$  ionic compound

$\text{SnCl}_4 \rightarrow$  covalent compound

\* Bi (group 5A) forms ionic  $\text{Bi}^{+3}$  and covalent  $\text{Bi}^{+5}$

\* groups from 5A to 7A gain electrons (high EA)

\* EA of N ( $2s^2 2p^3$ ) = 0

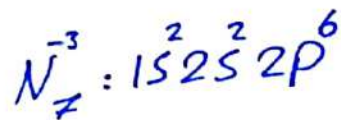
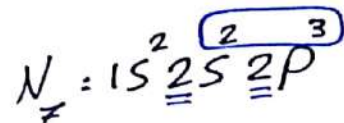
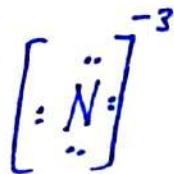
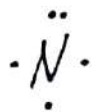
\* Summary:

1] Cations of Group 1A to 3A having noble-gas or pseudo-noble-gas configurations, the ion charge equal the group no.

2] Cations of group 3A to 5A having  $ns^2$  electron configurations, the ion charges equal the group no. minus two. Ex:  $Tl^+$ ,  $Sn^{+2}$ ,  $Pb^{+2}$ , and  $Bi^{+3}$

3] Anions of group 5A to 7A having noble gas or pseudo-noble-gas configurations, the ion charges equal the group no. minus eight.

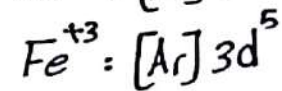
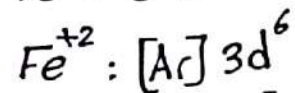
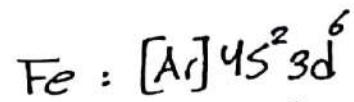
\* Example: write the electron configuration and the Lewis symbol for  $N^{-3}$ .



## \* Transition - Metal Ions:

→ most transition elements form several cations of different charges

For example:

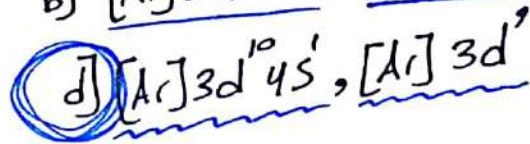
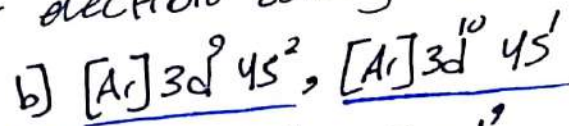
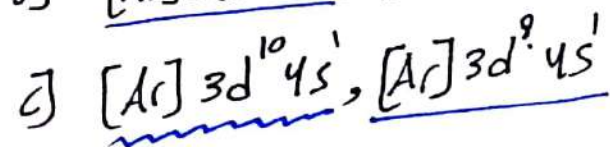
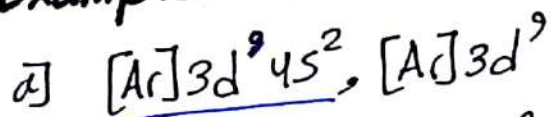


loses 4s electrons first  
then loses 3d electrons

\* losing ns electrons first, then one or more from (n-1)d electrons

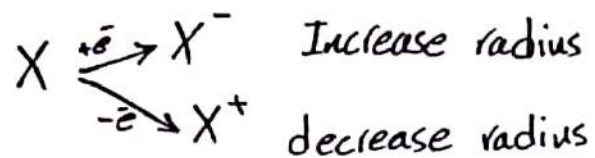
\* The +2 ion is common for the transition metals and are obtained by the loss of the highest-energy s electrons from the atom

\* Example: what are the correct electron configurations for Cu and  $\text{Cu}^{+2}$ ?





## \*9.3: Ionic Radii



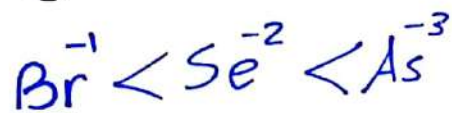
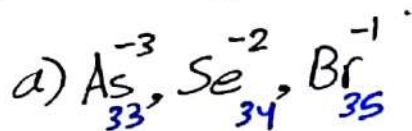
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↓ Periodic Table

\*ionic radius: a measure of the size of the spherical region around the nucleus of an ion within which the electrons are most likely to be found.

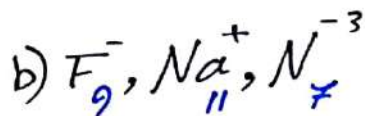
\*Isoelectronic: refers to different species having the same no. and configuration of electrons.

\*within isoelectronic series, the radius increase as the atomic no. decrease.

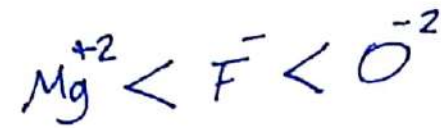
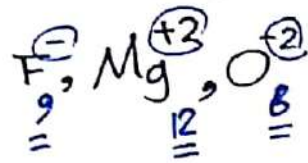
\*Example: Arrange the following in order of increasing ionic radius:



< atomic no.  
< protons (+)



\*Example: arrange the following ions in order of decreasing ionic radius:



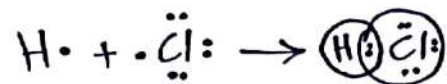
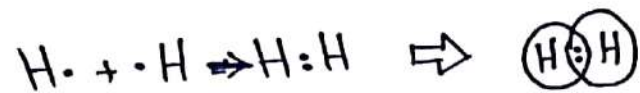
\*Example: which has the larger radius, N<sup>-3</sup> or P<sup>-3</sup>? P<sup>-3</sup>

## \* 9.4: Describing Covalent Bonds

\* Covalent Bond: a chemical bond formed by the sharing of a pair of electrons between atoms.

\* The distance between nuclei at minimum energy is called the bond length of  $H_2$

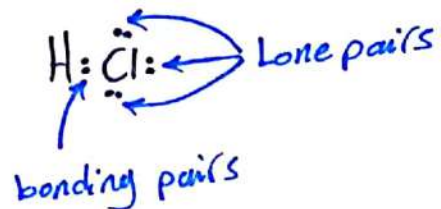
\* Lewis Formulas:



→ Lewis electron-dot formula: a formula using dots to represent valence electrons.

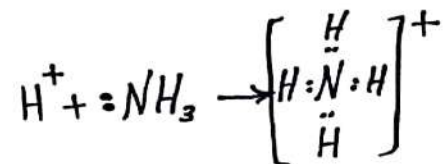
→ bonding pair: an electron pair shared between two atoms.

→ lone or nonbonding pair: an electron pair that remains on one atom and is not shared.





\* Coordinate covalent bonds: a bond formed when both electrons of the bond are donated by one atom



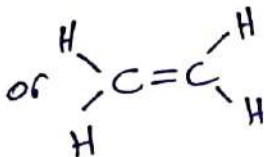
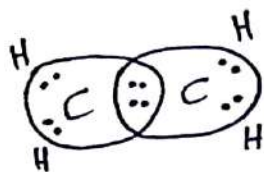
\* Octet Rule: The tendency of atoms in molecules to have eight electrons in their valence shells (two for hydrogen atom)

\* Multiple Bonds:

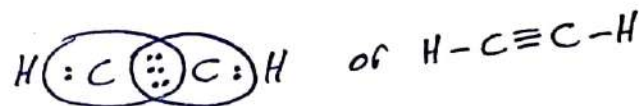
→ single bond: a covalent bond in which a single pair of electrons is shared by two atoms.

→ double bond: a covalent bond in which two pairs of electrons are shared by two atoms.

→ Triple bond: a covalent bond in which three pairs of electrons are shared by two atoms.



Ethylene



Acetylene

## \*9.5: Polar Covalent Bonds; Electronegativity.

\*Polar covalent bond: (Polar bond): covalent bond in which the bonding electrons spend more time near one atom than the other.

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

→ Robert S. Mulliken electronegativity:

$$X = \frac{I.E. + E.A.}{2}$$

increasing  
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↑  
Periodic Table

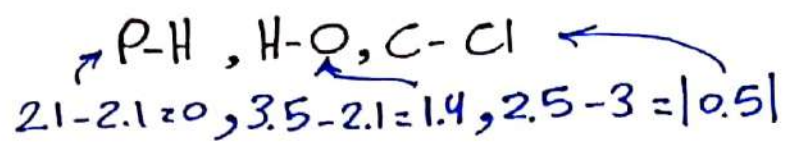
→ Linus Pauling's electronegativity: electronegativity increases from left to right and decreases from top to bottom in the periodic table.

# metals are the least electronegativity elements (they are electropositive) and non-metals the most electronegative.

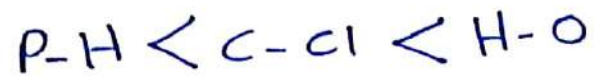
\* The absolute value of the difference in electronegativity of two bonded atoms gives rough measure of the polarity to be expected in a bond.

Cl	N	O	F
3	3	3.5	4

\* Example: arrange the following bonds in order of increasing polarity:



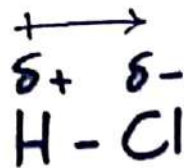
electronegativities: P = 2.1  
H = 2.1  
~~O~~ O = 3.5  
C = 2.5  
Cl = 3



\* The electrons are pulled toward the more electronegative atom.

ex. H-Cl

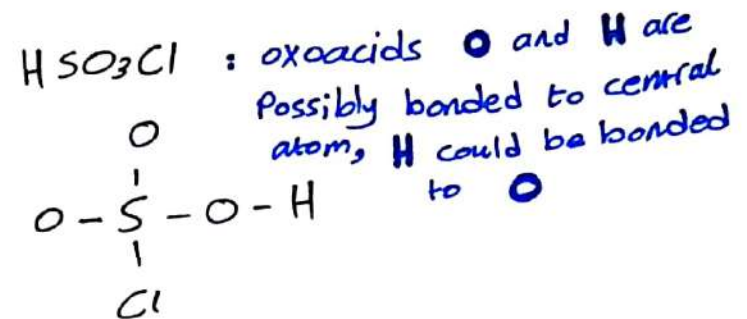
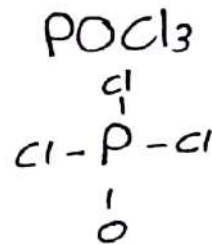
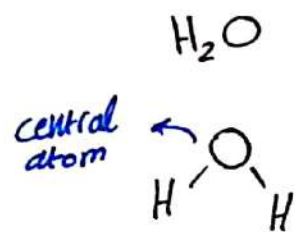
electronegativities: Cl = 3  
H = 2.1





## \*9.6: Writing Lewis Electron-Dot Formulas.

→ skeleton structure: tells which atoms are bonded to one another.



\*steps:

1] calculate the total no. of valence electrons, by summing the no. of valence electrons (group no.)

2] write the skeleton structure of the molecule or ion.

3] distribute electrons to the atoms surrounding the central atom (or atoms).

4] distribute the remaining electrons as pairs to the central atom (or atoms),

if there are fewer than 8 electrons on central atom it may be multiple bond, or triple,

→ atoms often form multiple bonds are  $C, N, O,$  and  $S$

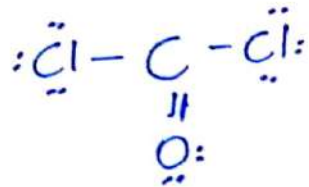
\*Example: sulfur dichloride  $\text{SCl}_2$  is a red molecule, write Lewis formula for it:



\*Example: what is the electron-dot formula of carbonyl chloride, or phosgene

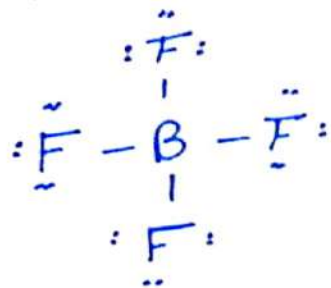


$$4+6+2 \times 7 = 24$$



\*Example: obtain the electron-dot formula of the  $\text{BF}_4^-$  ion?

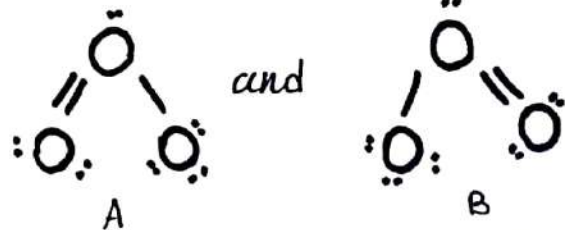
$$3+4 \times 7 + 1 = 32$$



## \*9.7: Delocalized Bonding: Resonance.

\*delocalized bonding: a type of bonding in which a bonding pair of electrons is spread over a number of atoms rather than localized between two.

example: ozone :  $O_3$



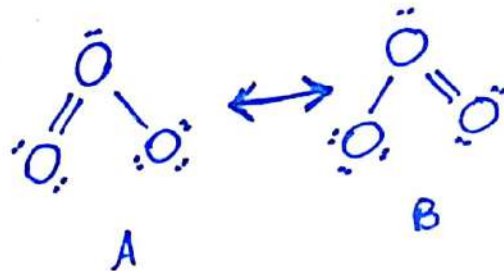
neither of them is correct.



\*not double or triple, intermediate type.

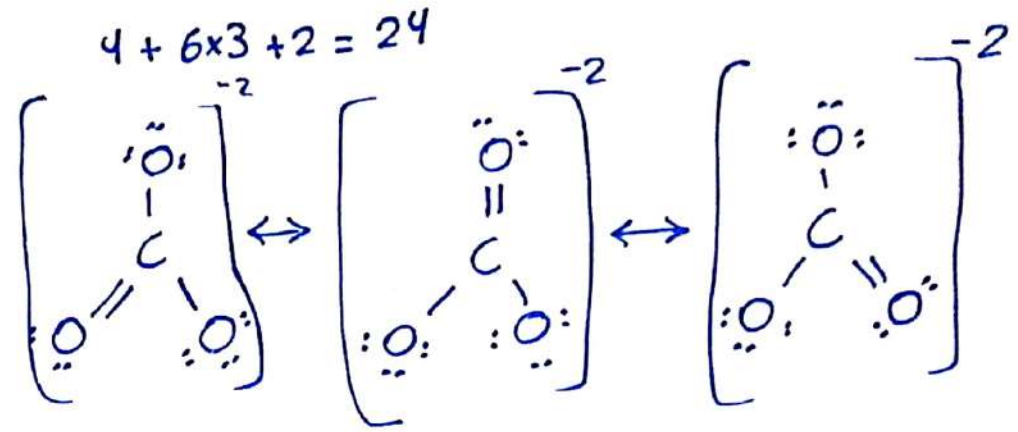
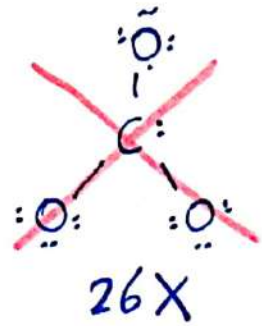
the true one

\*resonance description: you describe the electron structure of a molecule having delocalized bonding by writing all possible electron-dot formula. these are called resonance formulas





**\*Example:** describe the electron structure of the carbonate ion,  $\text{CO}_3^{2-}$ , in terms of electron-dot formulas:



## \*9.8: Exceptions to the Octet Rule

\*a few molecules have an odd no. of electrons and cannot satisfy the octet rule, such as NO.

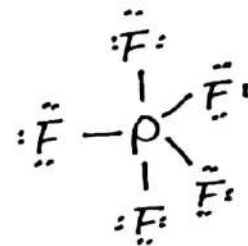
\*other exceptions:

1] group of molecules with an atom having fewer than eight valence electrons around it.

2] group of molecules with an atom having more than eight valence electrons around it.

\* the second group (have more than  $8e^-$ ) have numerous examples.

such as: phosphorus pentafluoride  $PF_5$

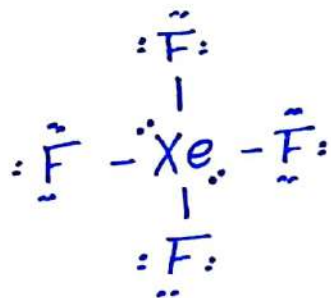


→ The octet rule stems that the main group elements in most cases employ only ns and np valence shell, ( $8e^-$ ), elements of the second period are restricted to these orbitals, but from the third period on, the elements have unfilled nd orbitals, which may be used in bonding.



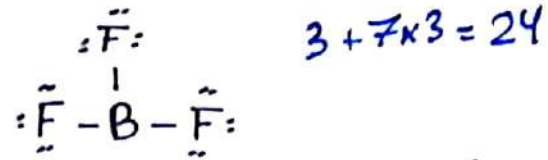
\* **Example:** Xenon, a noble gas, forms a number of compounds. one of them is  $XeF_4$ , what is the electron-dot formula of the  $XeF_4$  molecule?

$$8 + 7 \times 4 = \underline{36e^-} \quad \underline{32}$$

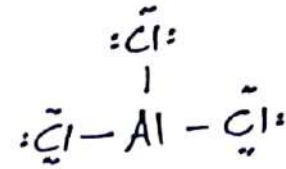
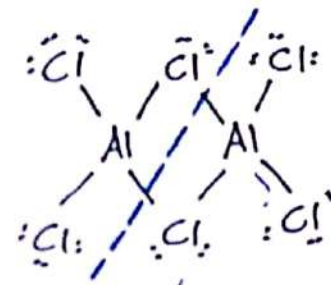


\* For the first group (have fewer than  $8e^-$ ) consist mostly of group 2A or 3A atoms, mainly (B, Be, Al).

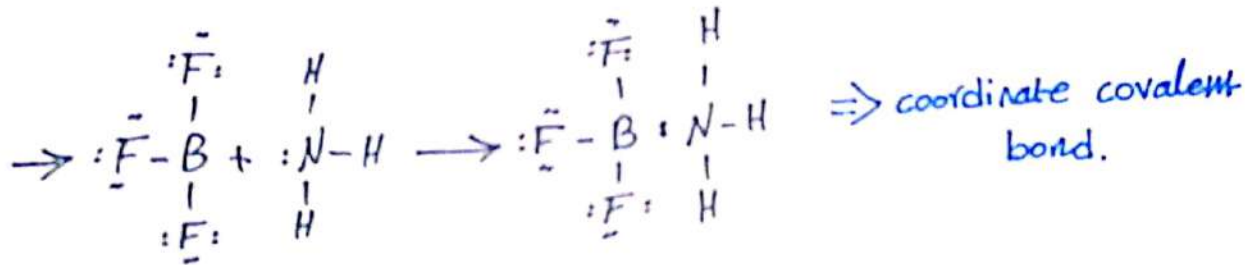
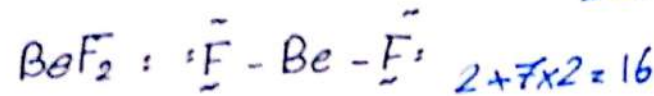
such as: Boron trifluoride  $BF_3$ :



$AlCl_3$  it forms  $Al_2Cl_6$ :



↓  
2 Cl atoms are a bridge positions.





## \*9.9: Formal Charge and Lewis Formulas

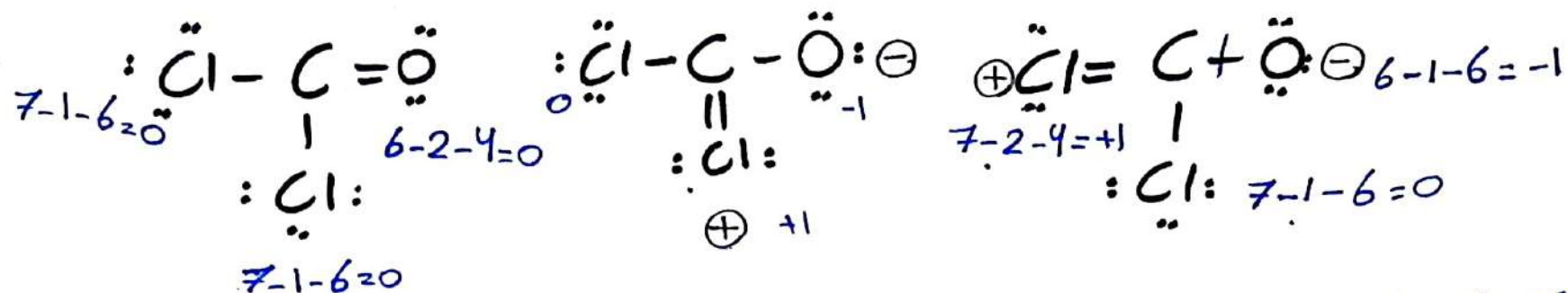
\*Formal charge: the hypothetical charge you obtain for an atom by assuming that bonding electrons are equally shared between bonded atoms and that the electrons of each lone pair belong completely to one atom.

\*rules of formula charge:

- 1] half of the electrons of the bond are assigned to each atom in the bond (counting each dash as two electrons)
- 2] both electrons of a lone pair are assigned to the atom which the lone pair belongs.

$$\text{Formal Charge} = \frac{1}{2} (\text{no. of electrons in a bond}) - (\text{no. of lone pair electrons}) + \text{valence electrons on free atom}$$

example:  $\text{COCl}_2$

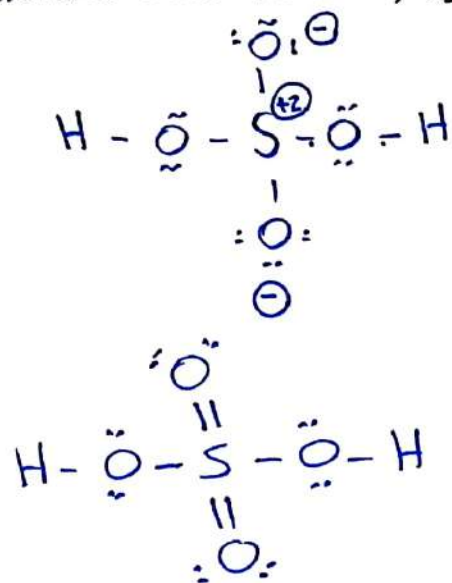


**RULE A:** Whenever you can write several Lewis formulas for a molecule, choose the one having the lowest magnitudes of formal charges.

**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.

\* Example: write the Lewis formula that best describes the charge distribution in the sulfuric acid molecule,  $H_2SO_4$ , according to the rules of formal charge:



$$2 + 6 + 6 \times 4 = 32e^-$$

$$O = 6 - 2 - 4 = 0$$

2 bonds

$$O = 6 - 1 - 6 = -1$$

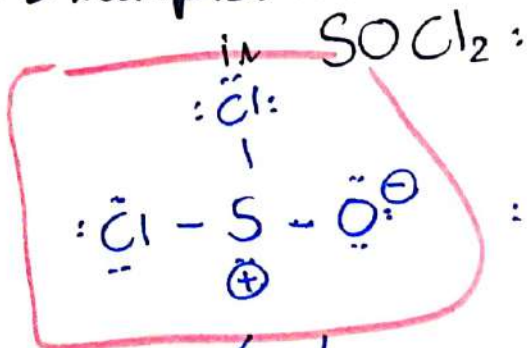
1 bond

$$H = 1 - 1 = 0$$

$$S = 6 - 4 - 0 = +2$$

$$S = 6 - 6 = 0$$

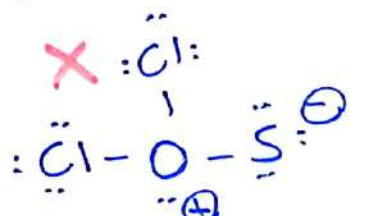
\* Example: write the Lewis formula that best describes the charge distribution in  $SOCl_2$ :



$$O = 6 - 1 - 6 = -1$$

$$Cl = 7 - 1 - 6 = 0$$

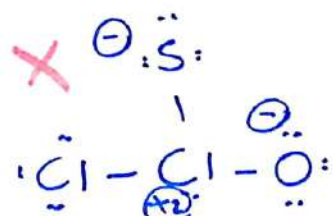
$$S = 6 - 3 - 2 = +1$$



$$O = 6 - 3 - 2 = +1$$

$$Cl = 7 - 1 - 6 = 0$$

$$S = 6 - 1 - 6 = -1$$

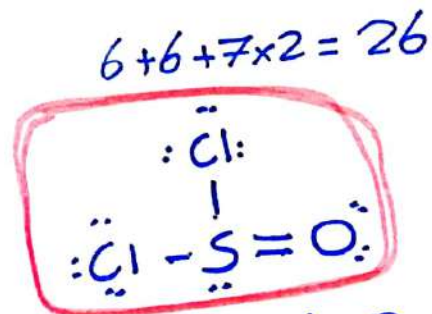


$$O = 6 - 1 - 6 = -1$$

$$Cl_{\text{central}} = 7 - 3 - 2 = +2$$

$$Cl = 7 - 1 - 6 = 0$$

$$S = 6 - 1 - 6 = -1$$



$$Cl = 7 - 1 - 6 = 0$$

$$O = 6 - 2 - 4 = 0$$

$$S = 6 - 4 - 2 = 0$$



## \*9.10: Bond Length and Bond Order.

\* Bond length (bond distance): the distance between the nuclei in a bond.

\* Covalent radius: the value of that atom in a set of covalent radii assigned to atoms in such away that the sum of the covalent radii of atoms A and B predicts the approximate A-B bond length.

\* Covalent radii of atom X = half the covalent bond length of a homonuclear X-X single bond. 

→ covalent radii for (C=76 pm) & (Cl=102 pm) → covalent radius of C-Cl =  $\frac{76+102}{2}$  = 178 pm

→ bond lengths:

Triple bond < double bond < single bond  
3                      2                      1

\* The value of any given set of radii should follow the two major periodic trends for atomic radii:

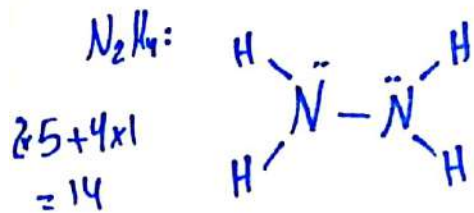
1. within a period, the covalent radius tends to decrease with increasing atomic number.
2. within a group, the covalent radius tends to increase with period number.

\* The bond order: the number of pairs of electrons in a bond.

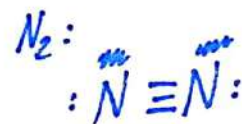
for example in  $:\ddot{\text{C}}:\ddot{\text{C}}:$  the bond order is 1

\* as the bond order increase, the bond strength increase and the nuclei are pulled inward, decreasing the bond length.

\* Example: Consider the molecules  $\underline{\text{N}_2\text{H}_4}$ ,  $\text{N}_2$  and  $\text{N}_2\text{F}_2$ . which molecule has the shortest nitrogen-nitrogen bond? and which has the longest nitrogen-nitrogen?

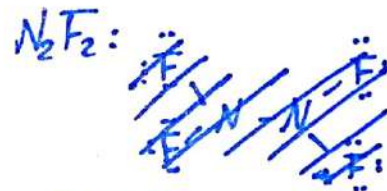


single  
(longest)

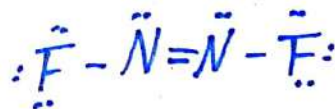


$5 \times 2 = 10$

Triple  
(shortest)



$5 \times 2 + 7 \times 2 = 24$



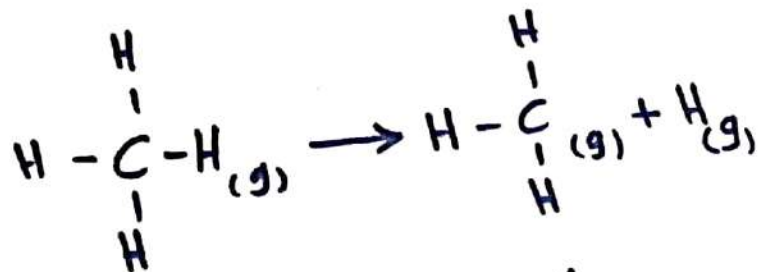
double

increase ←  
الجدول الدوري  
↓ increase  
Periodic Table

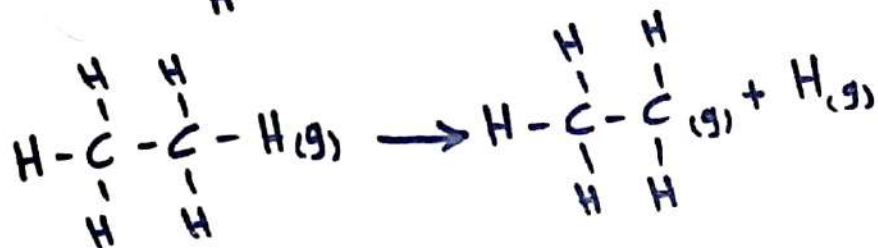
## \* 9.11: Bond Enthalpy:

\* the terms "bond enthalpy" and "bond energy" are often used interchangeably.

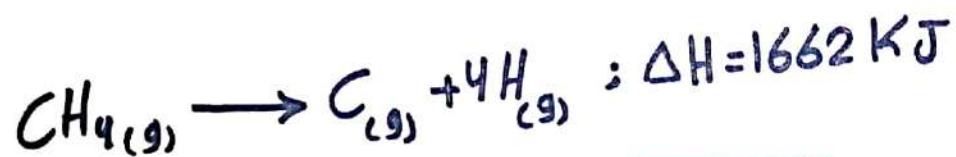
\* bond enthalpy: the average enthalpy change for the breaking of an A-B bond in a molecule in the gas phase.



$$\Delta H = 435 \text{ kJ}$$



$$\Delta H = 410 \text{ kJ}$$



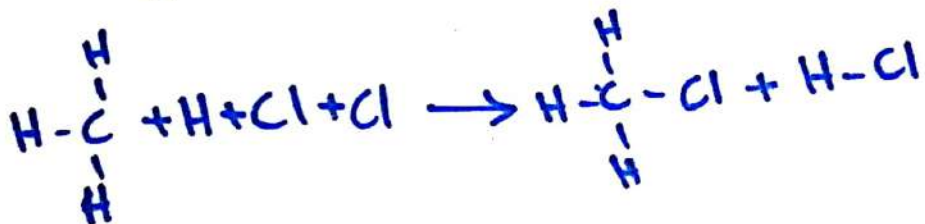
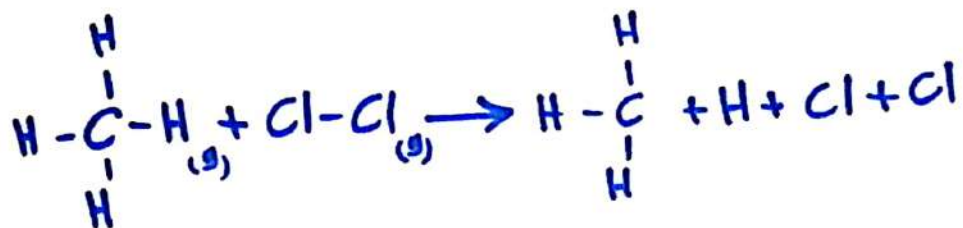
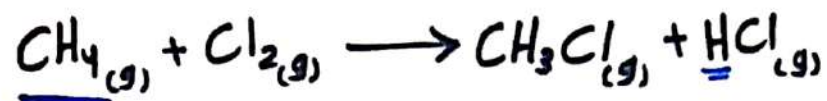
$$\text{BE}(\text{C}-\text{H}) = \frac{1}{4} \times 1662 = \boxed{416 \text{ kJ}}$$

\* bond enthalpies are always positive number.

\* the larger enthalpy, the stronger the bond is.  
↓  
chemical



\* imagine this reaction: and determine  $\Delta H$




$$\Delta H = 413 + 242 - 328 - 431 = -104 \text{ kJ} \rightarrow \text{minus means heat is released.}$$

$$\text{BE: } (\underline{\text{C-H}}) = 413$$

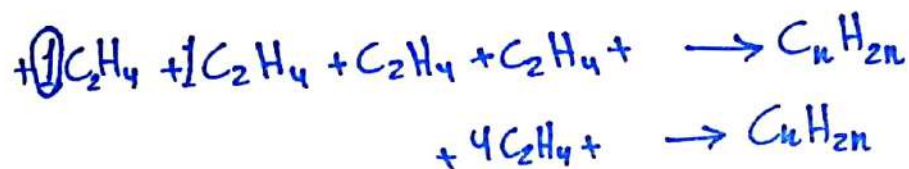
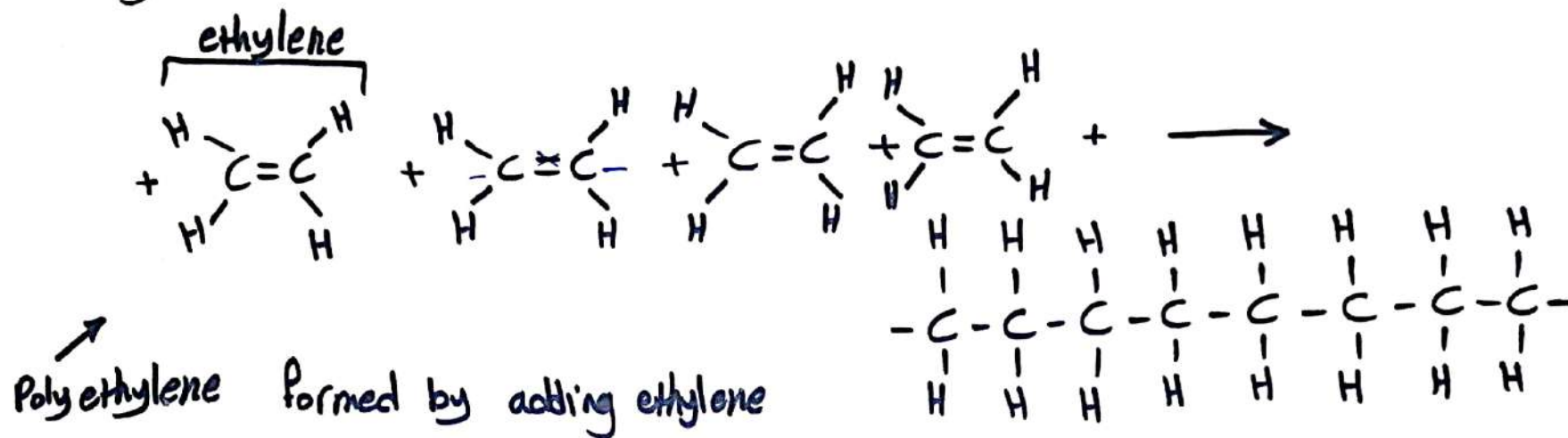
$$(\underline{\text{Cl-Cl}}) = 242$$

$$(\underline{\text{C-Cl}}) = 328$$

$$(\underline{\text{H-Cl}}) = 431$$

 \* 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.

\*Example: Estimate the enthalpy change per mole of ethylene for this reaction using bond enthalpies: BE: (C=C) = 614 (C-C) = 348



$$\Delta H = 614 - (2 \times 348) = \boxed{-82 \text{ KJ}}$$