Announcements for Monday, 14OCT2024

- Week 6 Homework Assignments available on eLearning
  - Graded and Timed Quiz 6 – “Compounds” due **tonight at 6:00 PM (EDT)**
- Exam 1 is now available for reviewing through ***Gradescope***
- Requests for Exam Question Regrades Now Open
  - Monday, 14OCT2024, 12:01 AM (EDT) – Wednesday, 16OCT2024, 11:59 PM (EDT)
  - MUST be submitted through ***Gradescope*** (do not email instructors)
  - see Canvas announcement from Oct 11 for regrading policies and procedure
  - after the deadline, Exam 1 grades will not be changed

ANY GENERAL QUESTIONS? Feel free to see me after class!

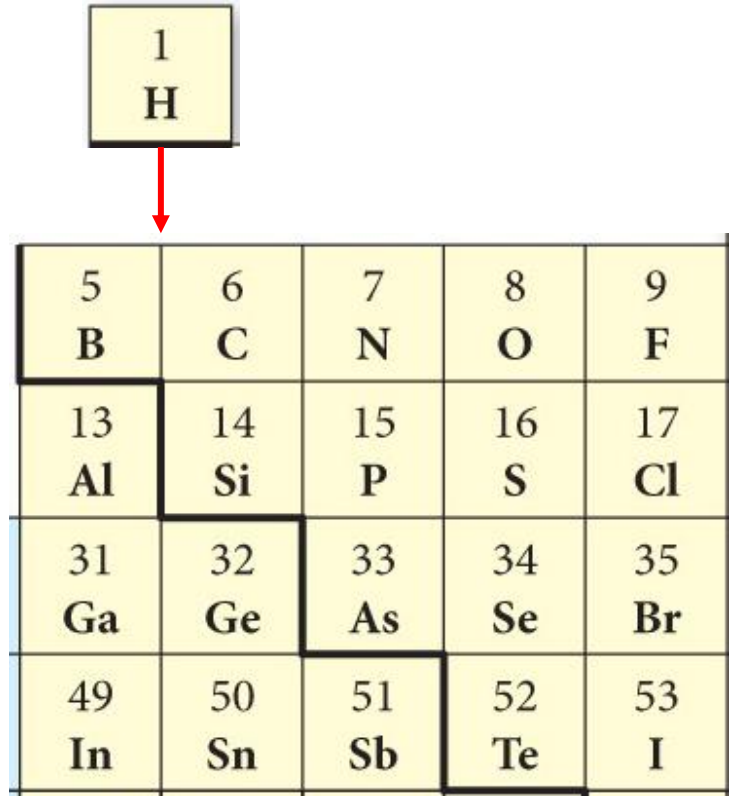
Try This On Your Own

Rank the following bonds in order of increasing polarity and indicate the dipole moment of each bond (if present) with an arrow.

C–F C–O C–H

least polar most polar

C–H < C–O < C–F



Resonance

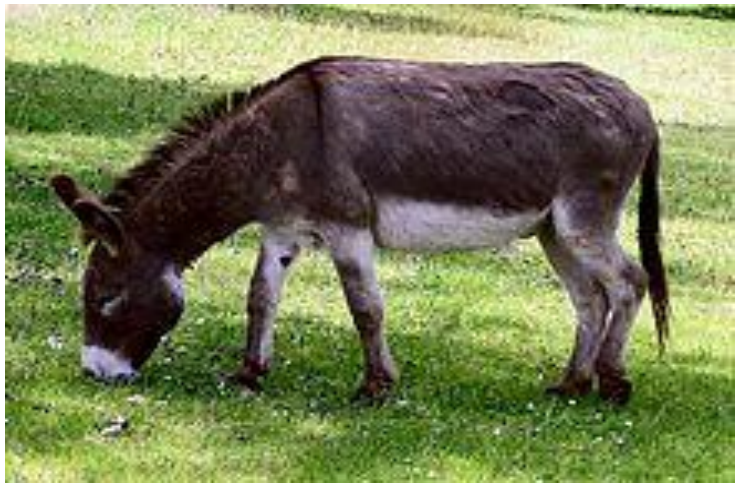
- the structures of some molecules and ions cannot be adequately described by a single valid Lewis structure
  - more than one valid Lewis structure differing in only in the position of electrons/multiple-bonds
- resonance structures **must** have the same order of atom connectivity (i.e., the same skeletal structure)
  - cyanate ion (NCO^-) vs. fulminate ion (CNO^-)
- the true structure of the species is a mixture/hybrid of the different resonance structures
  - the actual structure of the species DOES NOT FLIP-FLOP between the different resonance structures
  - the "better" the resonance structure, the more it contributes to the overall structure of the species

$O_3(g)$

Resonance Hybrid – an analogy

horse

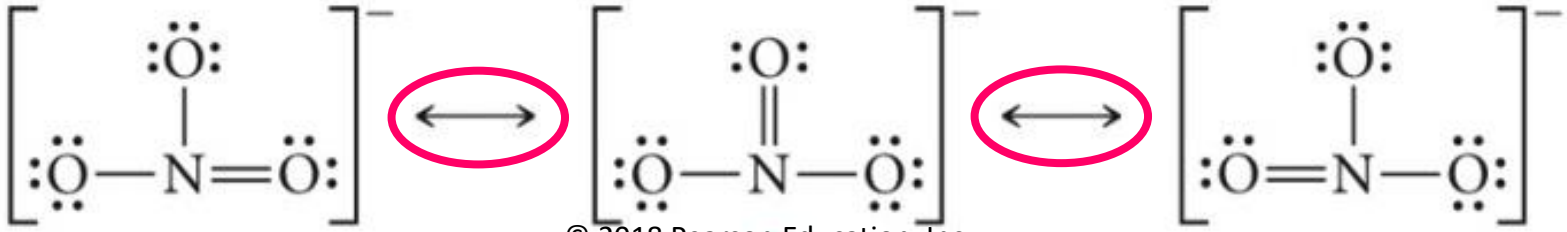
donkey



mule

the mule (the hybrid) does not flip-flop between being a horse and being a donkey

Three Resonance Structures for the Nitrate Ion

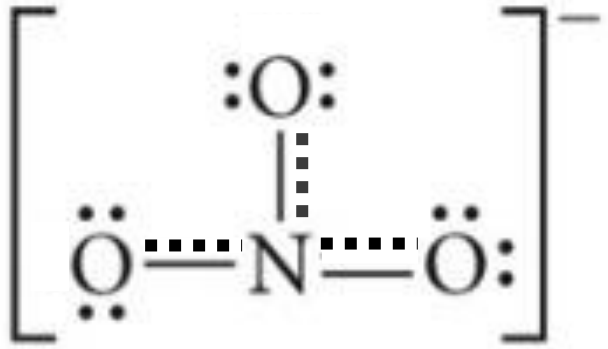


2 single bonds
1 double bond

2 single bonds
1 double bond

2 single bonds
1 double bond

double-headed arrow (↔) used to show resonance



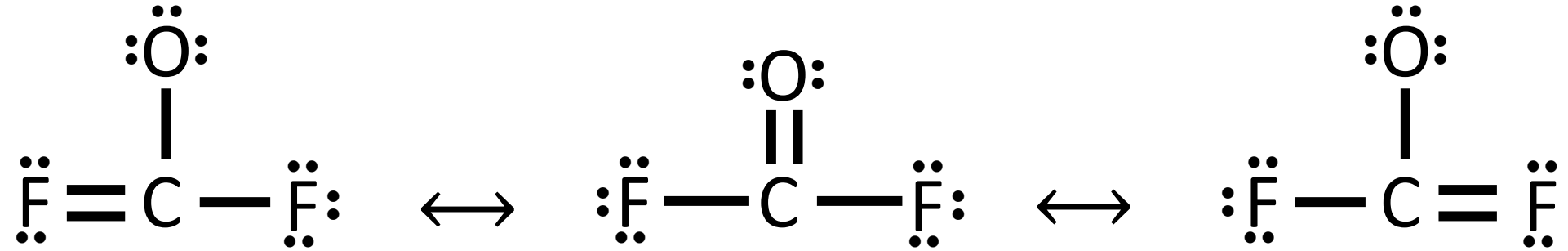
Resonance Hybrid

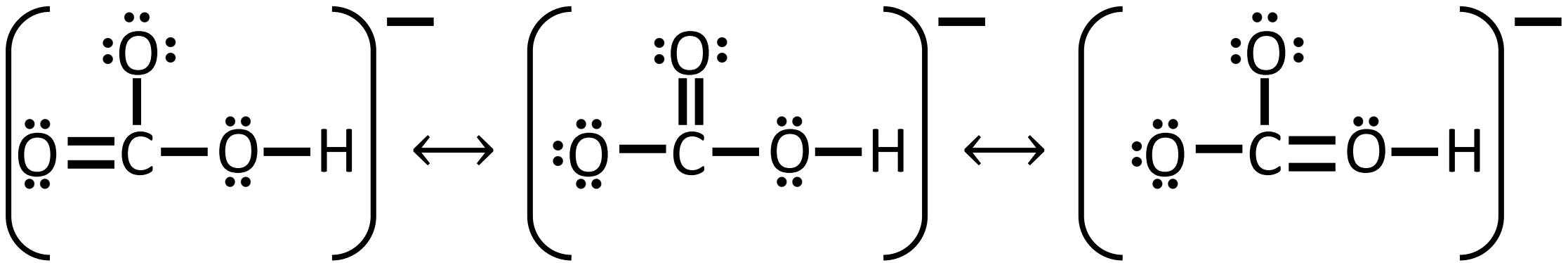
3 identical "1⅓" bonds

- same length and same strength
  2 electrons delocalized over 3 bonds
- here, think of electrons as being charged clouds

- That we must represent the structure of the nitrate ion with three separate structures is a limitation of Lewis model of bonding

Are some Lewis structures better than others?

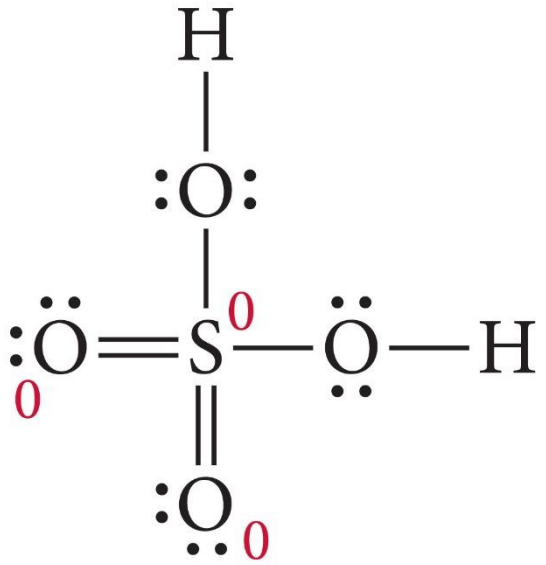




Formal Charge

formal charge = valence of the atom – ½ # bonding e⁻s – # nonbonding e⁻s

- charges assigned to atoms for the purposes of distinguishing and ranking competing Lewis structures
- ***fictitious charges*** used to designate electron ownership of each atom
  - an atom fully "owns" all its nonbonding electrons
  - an atom only "owns" half of each pair of bonding electrons



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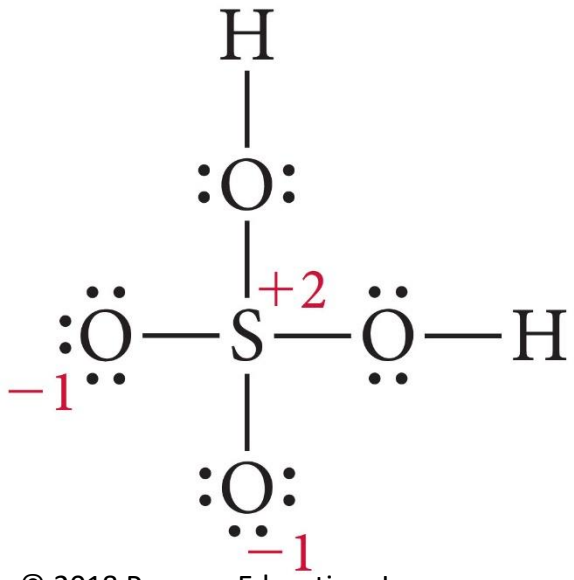

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Some Rules Regarding Formal Charges

1. the sum of all formal charges must equal the overall charge of the species
2. minimal formal charges (+1, –1) are always better than excessive formal charges (±2, ±3…etc.)
3. when unavoidable, negative formal charges should reside on most electronegative atoms (F, O, N…)

Try This On Your Own

Draw the different Lewis structures for the fulminate ion (CNO^-) (nitrogen is central atom) and determine the BEST structure based on formal charges.

Exceptions to the Octet Rule

Exceptions to the Octet Rule – Odd-Numbered Valences

- aka radicals or free radicals
- highly reactive and unstable species
- they occur when there is an odd-number of valence electrons due to the presence of an odd-number of Group 5A and/or 7A elements
- usually place the single electron on the atom that minimizes formal charges
  - examples: NO, ClO

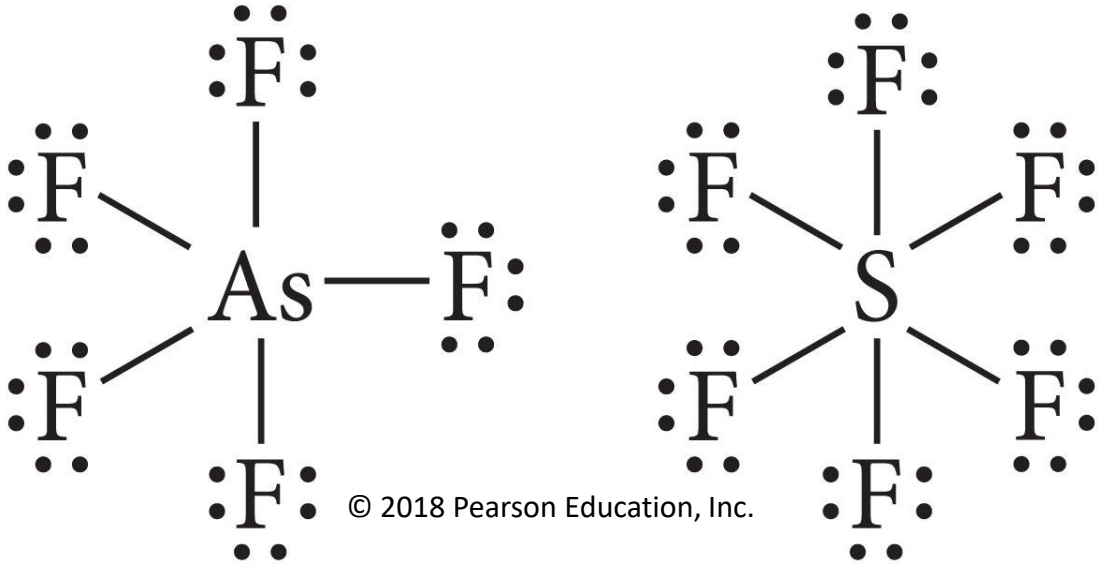
Exceptions to the Octet Rule – Incomplete Octets

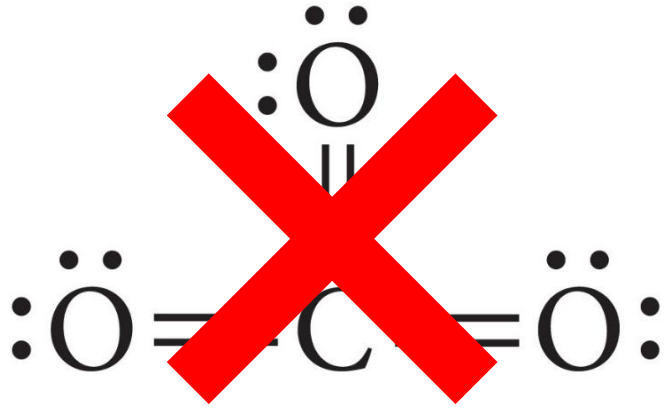
- some atoms are satisfied having less than eight electrons in their outer valence shell

  - beryllium (Be): four electrons in outer shell
  - boron (B): six electrons in outer shell

Exceptions to the Octet Rule – Expanded Octets

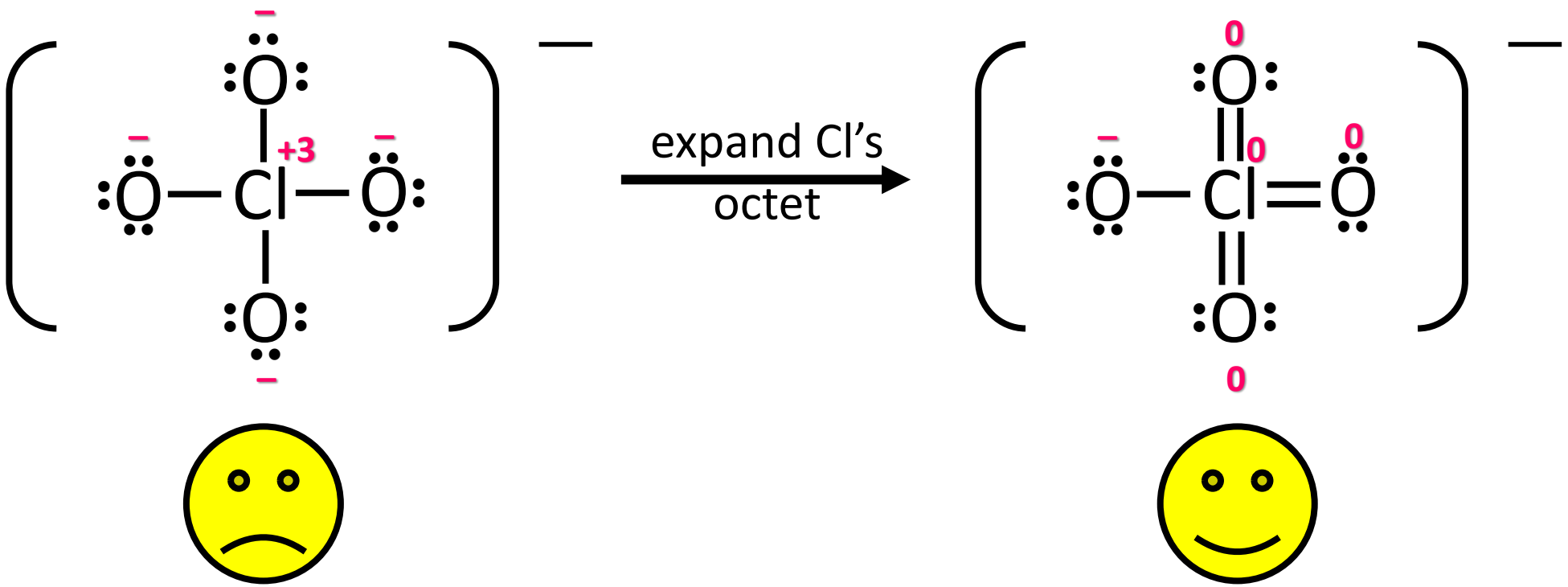
- Period 3 atoms (P, S, Cl…) and beyond (As, Se, Br, Kr, I, Xe…) can expand their octets and accommodate more than eight electrons in their outer shell
  - due to easy access to relatively low energy d-orbitals
- if they can, atoms will expand their octets to reduce formal charges
- PERIOD 2 ATOMS (C, N, O, F) NEVER EXPAND THEIR OCTETS
  - the cardinal sin of Lewis structures!
  - no d-orbitals for Period 2





Try This

- Draw the Lewis structure for ClO_4^- in which the central atom obeys the octet rule and assign formal charges to each atom. Can a better structure be drawn if the central atom expands its octet?



Criteria for the “Best” Lewis Structure – A Summary

1. The structure must have the proper number of electrons as determined by the total valences of the atoms
2. All atoms that can have complete octets (C, O, N, F) DO have complete octets or expand their octets (in the case of Period 3 atoms and beyond in periodic table)
   - NEVER expand the octet of Period 2 elements (C, O, N, F)
   - Remember that Be and B can have incomplete octets
3. Formal charges are minimized
   - zero formal charges are best, formal charges of +1 or –1 are acceptable, formal charges with 2s or 3s are excessive and should be avoided
   - expand the octet of a central atom to reduce formal charges if the atom is in Period 3 and beyond
4. If formal charges are absolutely necessary, negative formal charges should be on the more/most electronegative atom(s)

Try This On Your Own

How many resonance structures can be drawn for the selenate ion (SeO_4^{2-}) in which the central atom has zero formal charge?

Average Bond Energy

- **bond energy =** the amount of energy required to break 1 mole of covalent bonds ***in the gas phase*** into separated atoms ***in the gas phase***
  - always endothermic (energy is absorbed)
  - the reverse process (making bonds) is exothermic (energy released)

★ if you know the energy change of one process, you also know the energy change of the reverse process just by changing the sign

- the stronger the bond, the more stable (less reactive) the bond
  - $N_2(g)$ (946 kJ/mol) vs. $O_2(g)$ (498 kJ/mol)
- ***AVERAGE*** bond energies
- in general for a given pair of atoms the bond energies increase with multiple bonds:
  - triple > double > single
- example: **C–C bonds** and **C–O bonds**

MEMORIZE: X–Y (g) → X(g) + Y(g)

TABLE 5.3 Average Bond Energies

Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)
H—H	436	C—C	347
H—C	414	C═C	611
H—N	389	C≡C	837
H—O	464	C—O	360
H—F	565	C═O	736*
H—Cl	431	C—Cl	339
H—Br	364	N—N	163
H—I	297	N═N	418

*799 in CO_2