

Covalent Bonding

Electron sharing -
Chemical socialism

Learning objectives

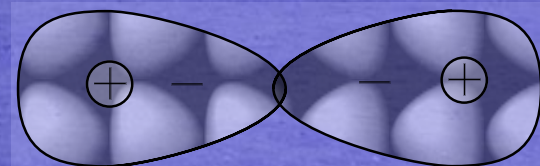
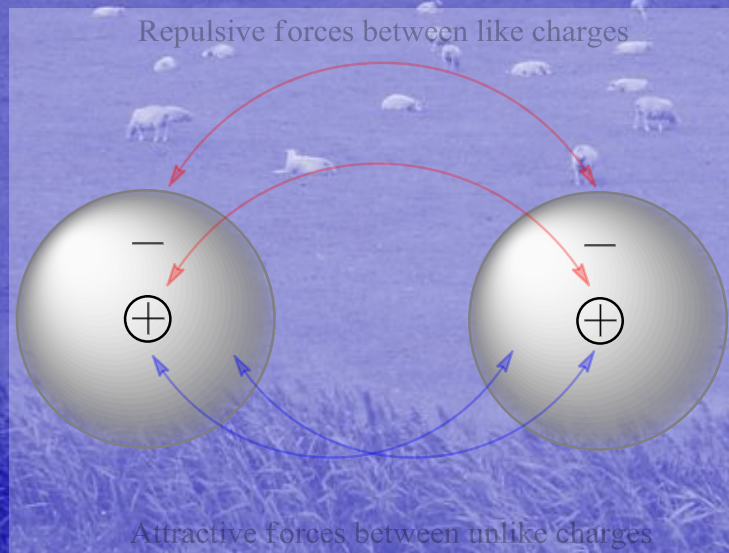
- Describe the covalent bond
- Compare and contrast properties of ionic and covalent compounds
- Apply electronegativity to determination of bond polarity
- Write Lewis dot diagrams for ions and molecules
- Explain physical basis for violation of the octet rule
- Identify and write resonance dot structures for ions and molecules
- Calculate formal charges on atoms in molecules and use formal charges to discriminate between likely and unlikely resonance structures

The ionic model works well for metals and non-metals

- What about compounds between non-metals CO, PCl₃ and diatomic elements like H₂, N₂, O₂, F₂
- Formation of negative ion is favourable
- Formation of a positive ion will be very unfavourable (remember Lewis dot structure)
- Ionic model won't work

Covalent bond: still electrostatics

- Balancing forces:
 - Attractive forces between nucleus and electrons of different atoms
 - Repulsive forces between nuclei and between electrons
- As the atoms approach, electrons shift from approximate spherical distribution to being localized between the atoms

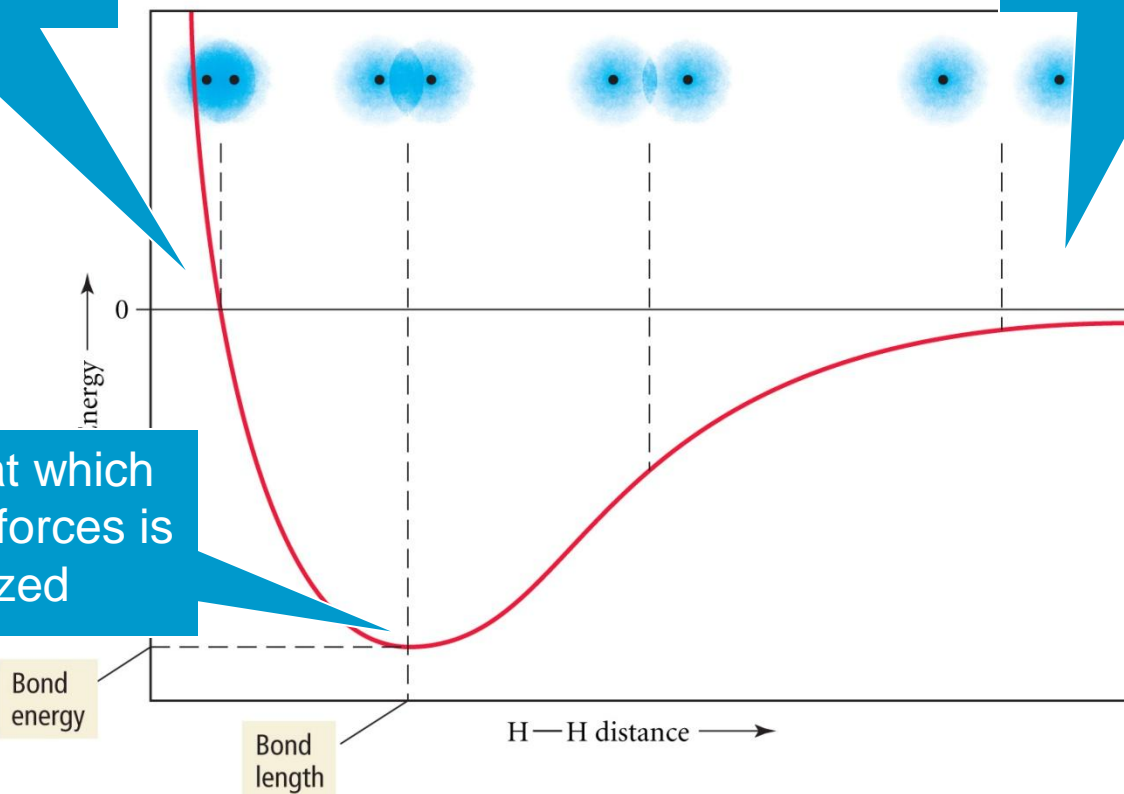


Bond formation is result of net attraction

Internuclear repulsion dominates

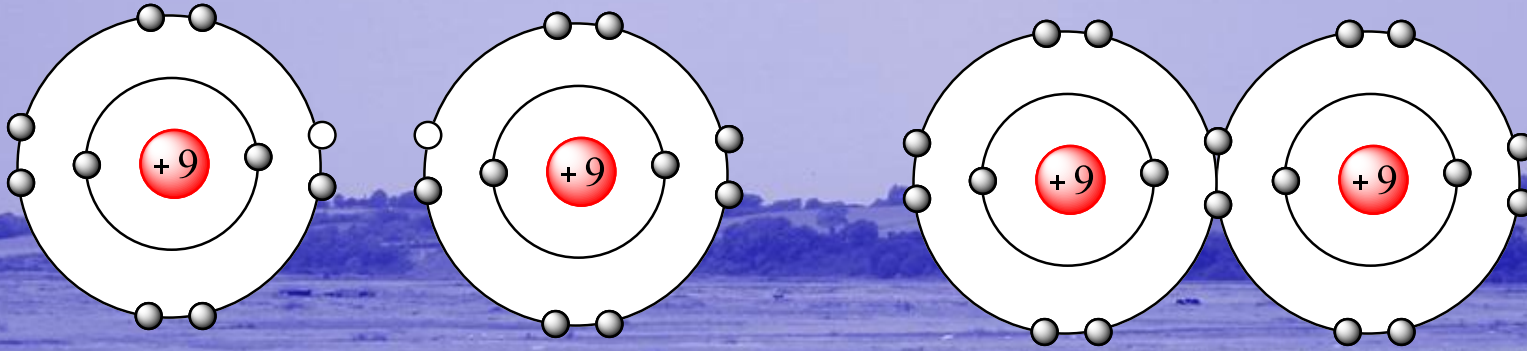
Coulombic force falls off with distance ($1/r^2$)

Interaction Energy of Two Hydrogen Atoms



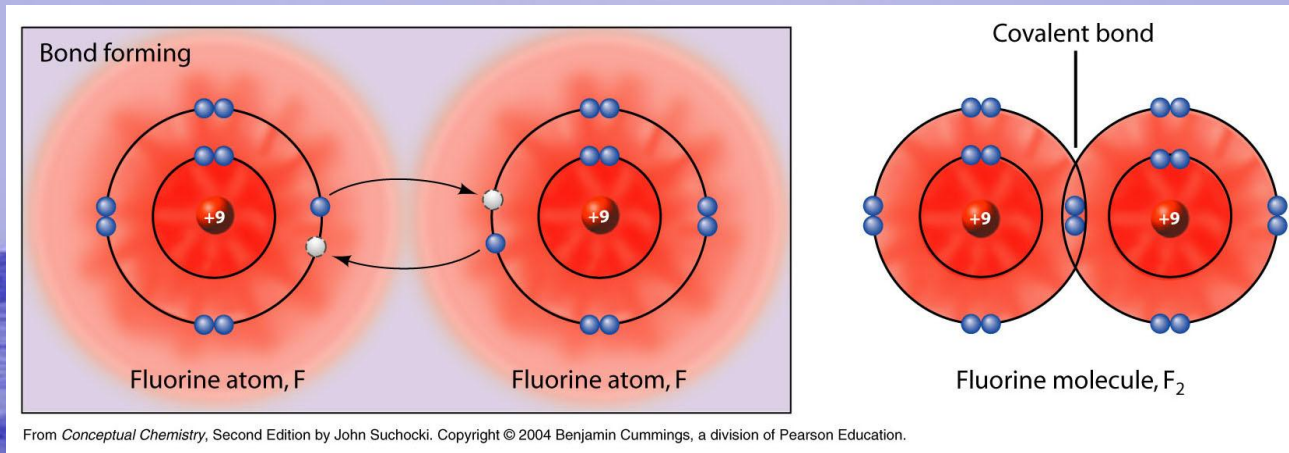
Distance at which balance of forces is optimized

Creative accounting in covalent bond: Sharing two electrons effectively doubles the count in F_2



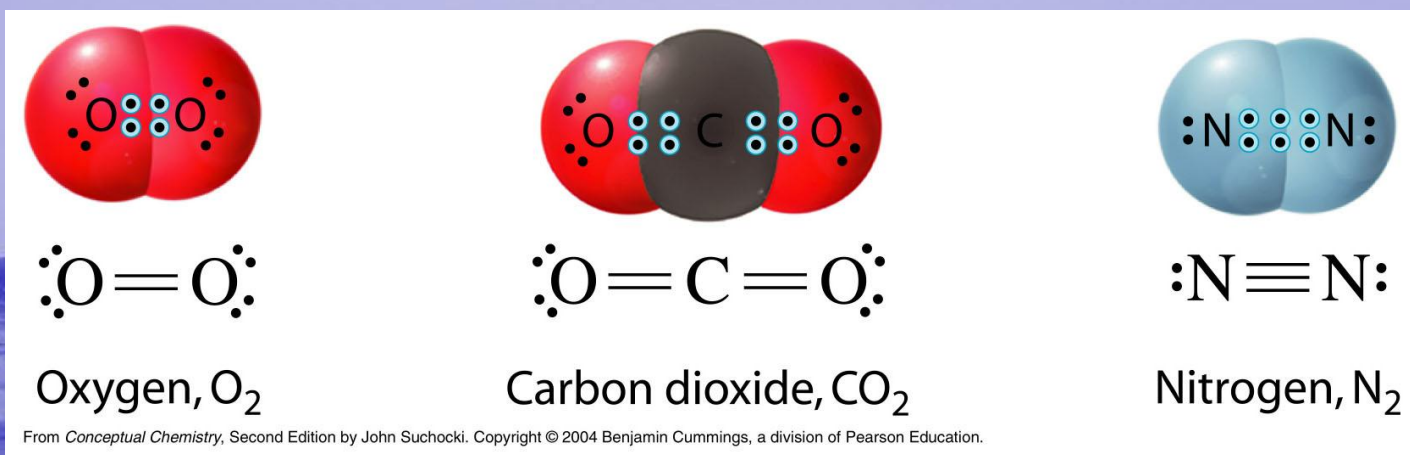
- Each F atom wants 8 electrons in valence shell
- Alone each has seven (one vacancy)
- Sharing 2 electrons each one has 8 – or so it seems
- 14 electrons *appear* to become 16
- Single covalent bond

Sharing two electrons effectively doubles the count



- Each atom wants 8 (octet rule)
- Each F atom alone has seven
- Together they have eight each
- Two shared electrons = single covalent bond

Multiple bonds accommodate more extreme electron deficiency



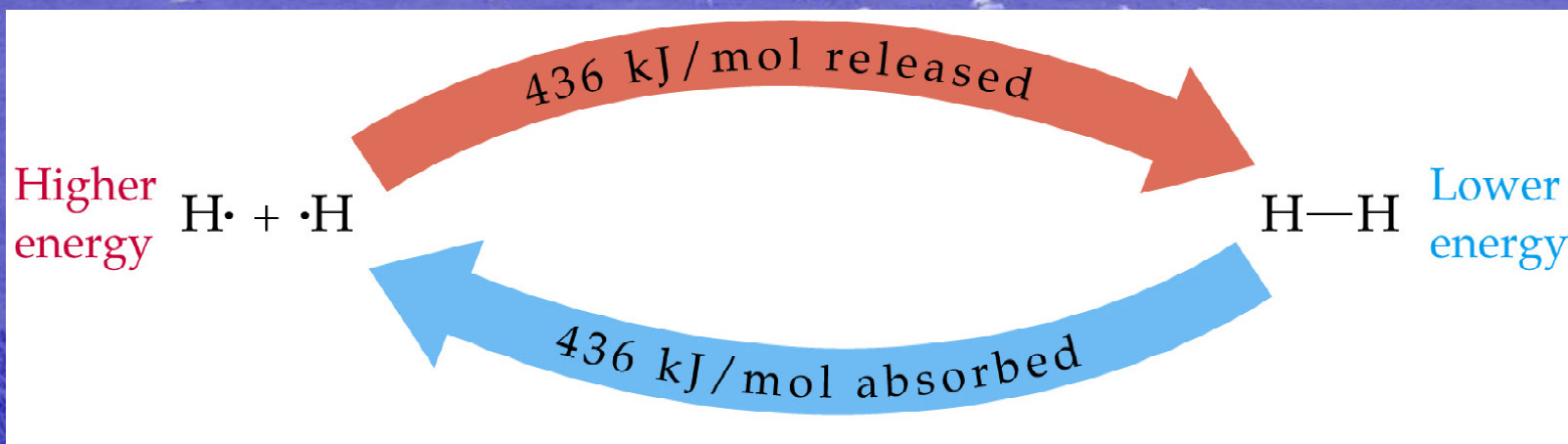
- O₂ and N₂ do not achieve octets by sharing two
- Must share more electrons
- O₂ has double bond
- N₂ has triple bond – one of the strongest in chemistry
 - N₂ is very stable and unreactive – also the major product from explosives

Bond order increases as electron total decreases

Molecule	Group number	Total number of electrons	Bond order
F-F	7	14	1
O=O	6	12	2
$\text{N}\equiv\text{N}$	5	10	3

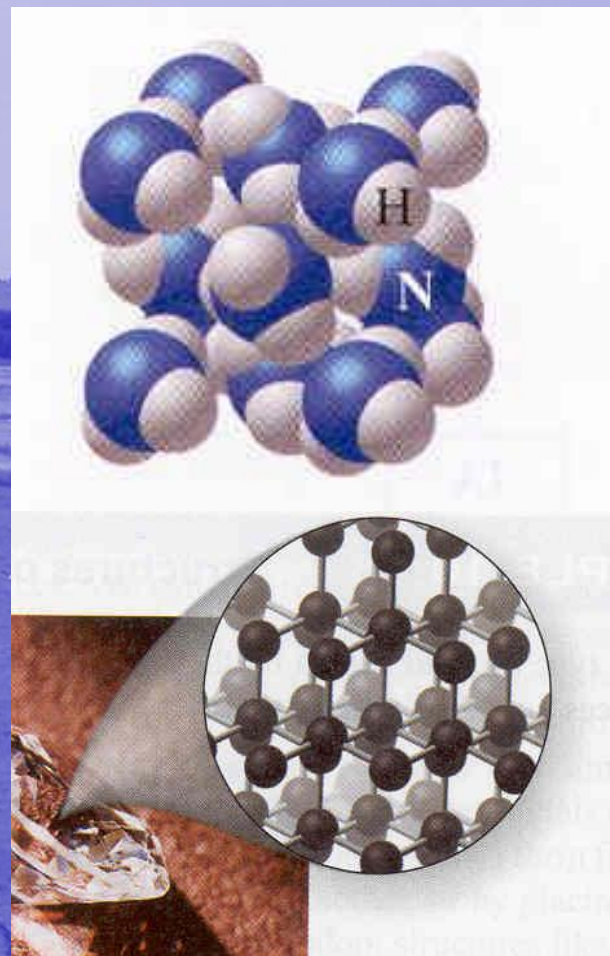
Bond dissociation energy

- Energy needed to break a bond into its component atoms
- Same as energy released in forming bond between atoms



Strength of covalent bonds

- Covalent bonds are strong
- Forces *between* molecules in covalent molecular compounds are weak:
 - CO_2 , CH_4 , HCl , NH_3 are gases
- Where covalent bonding is found in infinite lattices (diamond, silicon etc.) melting points can be very high (m.p. carbon 3500°C)



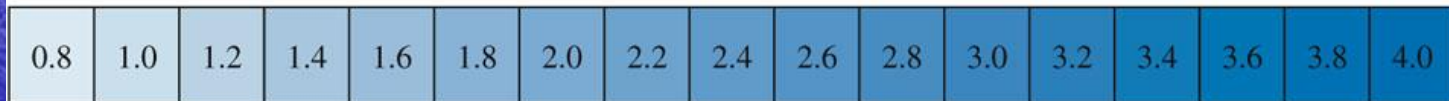
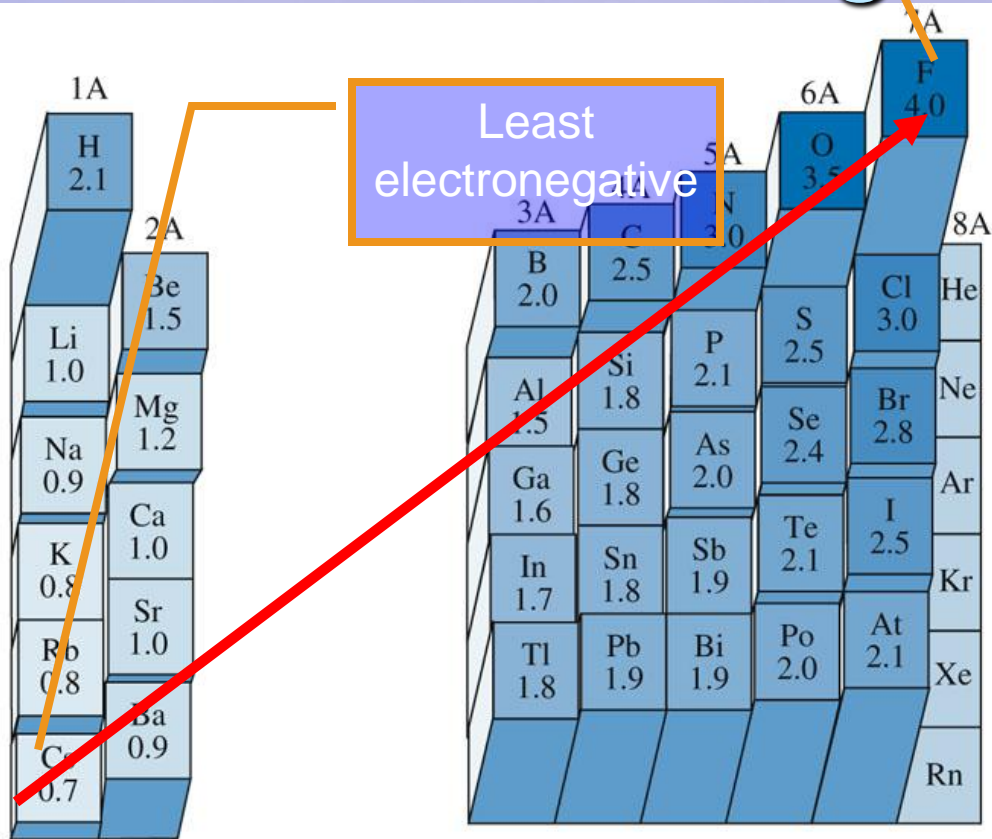
Properties of covalent compounds

- Gases, liquids and solids at room temperature
- May be hard or soft (diamond is a covalent solid)
- Dissolve in *polar* and *non-polar* solvents, depending on molecule's *polarity*
- Solutions and melts do not conduct electricity
- Most covalent compounds are molecular

Polarity

- Unequal sharing of electrons
- Only in homonuclear bonds are electrons perfectly evenly shared
- In heteronuclear bonds electrons are drawn more towards one atom than the other
- The result is separation of charge = polarity

Table of Most electronegative



Weak

Electronegativity

Strong

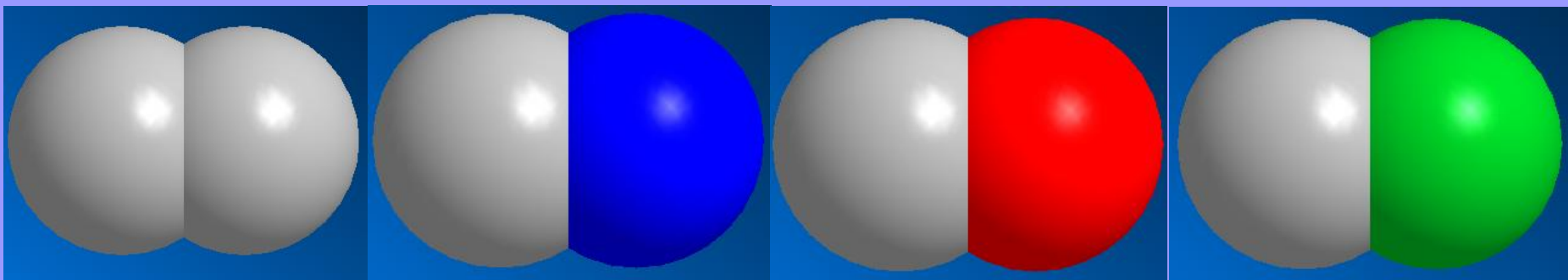
Polar or non-polar?

- The following are loose definitions for polar/non-polar bonds:
- If difference in electronegativity < 0.4 ,
 - Non-polar
- If difference in electronegativity ≥ 0.4 ,
 - Polar
- If difference in electronegativity ≥ 2 ,
 - Ionic

Polarity reflects electronegativity difference

Nonpolar

Polar



0.00

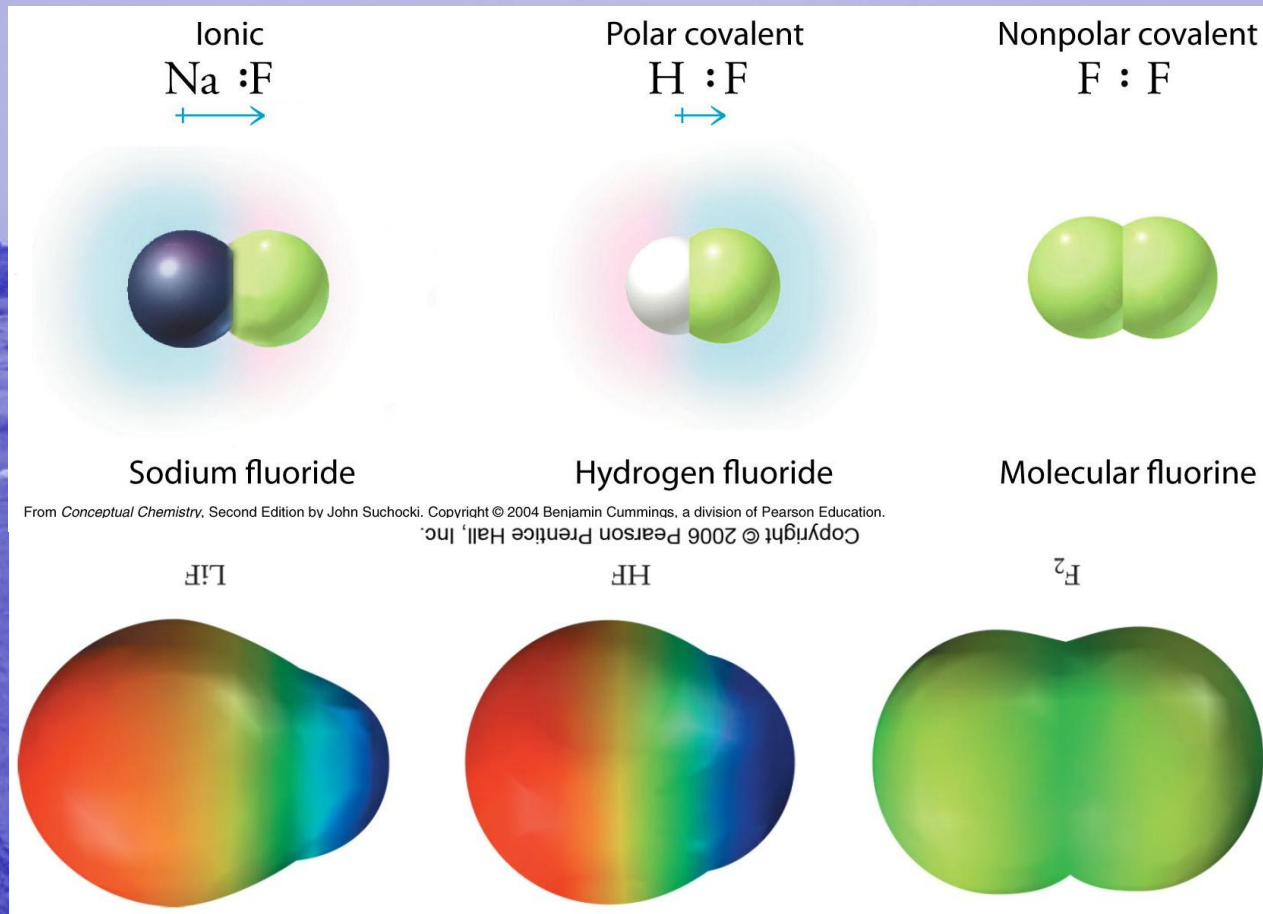
0.49

0.89

1.43

Electronegativity difference

Ionic and covalent: two extremes of possibilities



Wait a (dipole) moment

- Charge separated over a distance r creates a dipole moment

$$\mu = Qr$$

- Units of dipole moment are *debyes* (D)

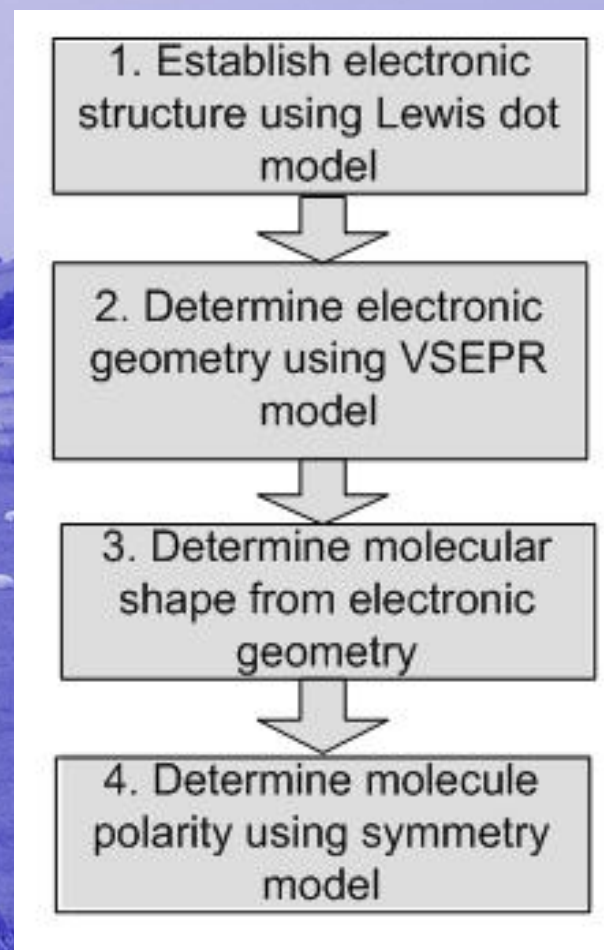
$$1 D = 3.34 \times 10^{-30} \text{ Cm}$$

- Consider charges of +1 and -1 separated by 1 angstrom

$$\mu = Qr = (1.6 \times 10^{-19} \text{ C})(1 \text{ \AA}) \left(\frac{10^{-10} \text{ m}}{1 \text{ \AA}} \right) \left(\frac{1 D}{3.34 \times 10^{-30} \text{ Cm}} \right) = 4.79 D$$

Determining polarity in molecules

- Polarity is a vitally important property of molecules
 - special properties of water are a consequence of polarity
- Prediction of polarity in molecules requires knowledge of molecular structure



Pathways to structure:

Lewis dot diagrams - doing the dots

- Convenient 2D representation of covalent bonding in molecules:
- Starting point for understanding molecular structure
- Indicates nothing about shape
- Show only valence electrons
 - Electrons are either in:
 - bonds
 - lone pairs (stable molecules do not contain unpaired electrons, with a few exceptions)
- Octet rule is guiding principle for distribution of electrons in the molecule

Rules for Lewis dot structures

- Start with the skeleton
- Guidelines for building a skeleton
 1. *Least* electronegative element is the central atom (HOCl not HClO)
 2. Oxygen atoms do not bond with each other except in peroxides or superoxides
 3. In ternary oxoacids (e.g. H_2SO_4), H is not bonded to the central atom but to O.

$$\blacksquare \quad S = N - A$$

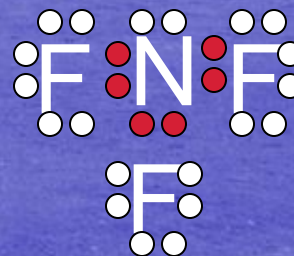
- N = number of electrons required to fill octet for each atom (8 for each element, except 2 for H and 6 for B)
- A = number of valence electrons
- S = number of electrons in bonds

Applying the rules to NF_3

1. Draw the skeleton
2. Calculate N for the molecule
3. Calculate A (all the dots), including charges where appropriate (add one for each $-ve$ charge and subtract one for each $+ve$ charge)
4. Determine S from $S = N - A$
5. Satisfy all octets and create number of bonds dictated by S (may be multiples)



- $N = 8(\text{N}) + 3 \times 8(\text{F}) = 32$
- $A = 5(\text{N}) + 3 \times 7(\text{F}) = 26$
- $S = 32 - 26 = 6$

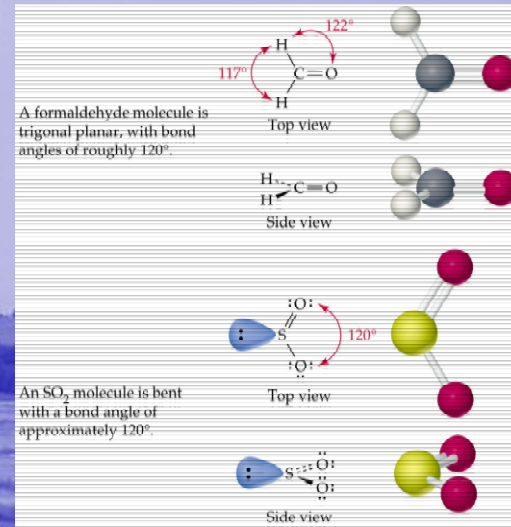


Quality control: two tests for dot structures

- Are the number of dots in the molecule equal to the number of valence electrons?
- Are all the octets satisfied?
- If both yes structure is valid
 - There may be situations where some chemical intelligence is required to distinguish among more than one apparently correct structures
- If either no then back to the drawing board
- If molecule violates the octet rule the second test does not apply, but the first one will

Example of sulphur dioxide

- $N = 24$ (3 atoms @ 8)
- $A = 18$ ($S = 6$, $O = 2 \times 6 = 12$ valence electrons)
- $S = 6$ (3 two-electron bonds)
- 12 non-bonded electrons (6 pairs)



One more example

A large white rectangular area with horizontal blue lines, resembling a sheet of lined paper. The lines are evenly spaced and extend across the width of the rectangle. The background of the slide is a blue-tinted landscape with grass and trees.

Expansion of the octet

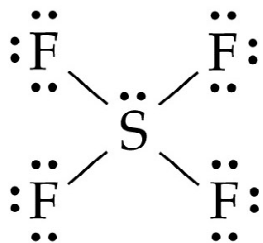
- Elements in second row invariably obey the octet rule
- The heavy congeners regularly disobey it
 - OF_2 but SF_6
 - NCl_3 but PCl_5
- Octet expansion is a consequence of the availability of vacant $3d$ orbitals to third row elements
- No $2d$ orbitals in the second row; $3d$ orbitals are too high in energy

Identifying violators using the $S = N$ – A machine

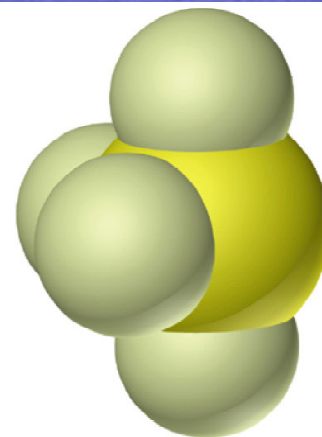
- Proceed with same $S = N$ – A strategy
- Octet expansion is indicated by the inability to obtain a reasonable solution using the formula
- Proceed to plan B: use chemical intuition (or phone a friend)

Consider SF₄

- N = 40, A = 28 + 6 = 34
- S = 6
- 6 bonding electrons and 4 bonds!
- Too many electrons
- Solution:
 - Make all bonds single
 - Complete octets on peripheral atoms
 - Add any excess to the central atom

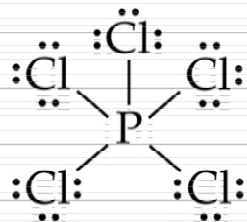


34 electrons distributed

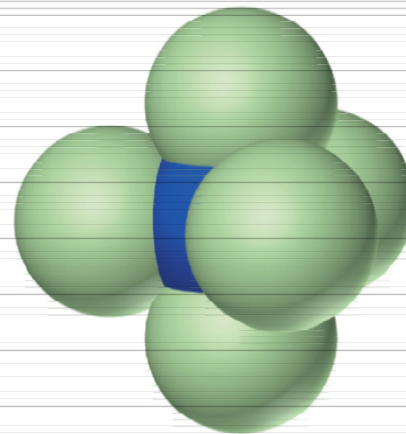


PCl₅

- $N = 48, A = 5 \times 7 + 5 = 40$
- $S = 8$
- Implies 8 bonding electrons but 5 bonds
- Expanded octet
- Solution as before
 - In this case the octet expansion involves an extra bonded atom rather than an extra lone pair on the central atom



Phosphorus pentachloride, PCl₅



Resonance: short-comings of the dot model

- Dot structure of O₃ (or SO₂) can be drawn in two equivalent ways
- Each passes the test
- Neither is realistic by itself (Both S-O bonds are equal in length)
- “True” structure is an average of two “resonance hybrids”
- Explanation in physical terms: resonance hybrids are not real things:
 - Lewis model considers bonds as being between two atoms
 - In many molecules bonding can involve 3 or more atoms
 - This phenomenon is called *delocalization*
 - In O₃ bonding electrons are delocalized over all three O atoms

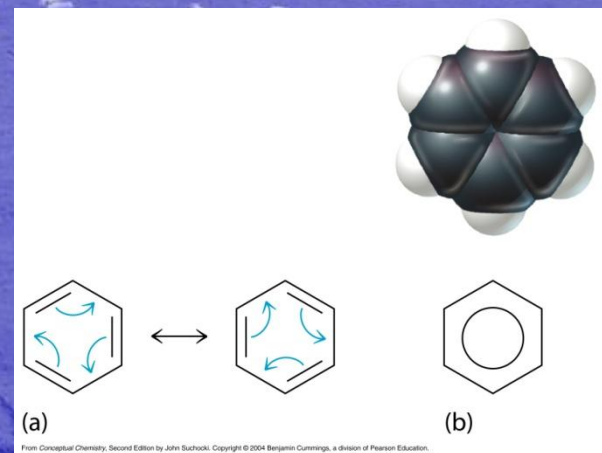
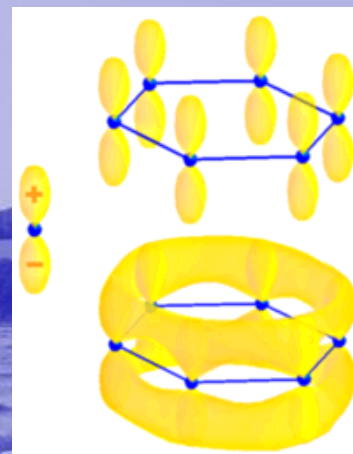


This double-headed arrow means that the structures on either side are contributors to a resonance hybrid.



Benzene: a classic example of delocalization

- The top figure shows the six orbitals on the carbon atoms fused together into a ring of circulating charge
- The lower figure shows the Lewis representation of two “resonance” structures, and the conventional ring within a hexagon



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Biggles, read the (Formal) charges

- *Formal charge* measures degree to which atom gains or loses electrons in formation of covalent bonds
- Formal charge = No. valence electrons in free atom – No. of valence electrons in bonded atom
 - If bonded atom has fewer valence electrons it becomes +ve (formal charge > 0)
- Distinguishes between reasonable and unreasonable resonance structures – most likely structure has lowest formal charges
- Formal charge is on individual atom not on molecule/ion
 - Sum of the formal charges = ion charge
 - Sum of formal charges on neutral molecule = zero

Formal charges: Counting the electrons

- Each electron in a bond counts half
- Each non-bonded electron counts one
- Formal charge = total valence electrons - $\frac{1}{2}(\sum \text{bonding electrons}) - \sum(\text{nonbonding electrons})$

Worked example with COCl_2

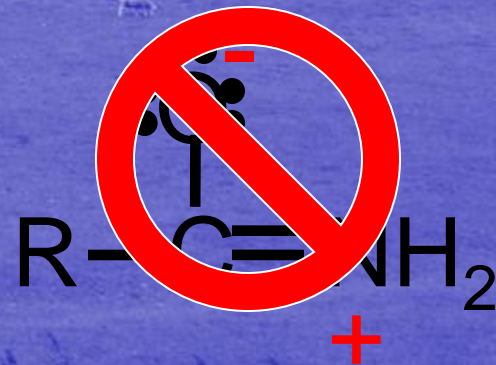
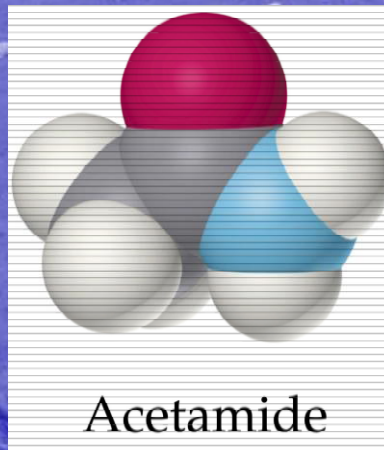
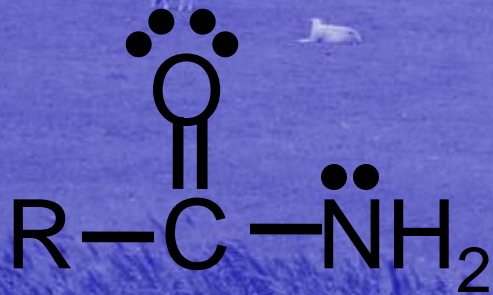
Atom	# valence electrons (=group number)	# bonding electrons	# lone pair electrons	Formal charge
Carbon	4	8	0	$4 - (8 \times 0.5 + 0) = 0$
Oxygen	6	4	4	$6 - (4 \times 0.5 + 4) = 0$
Chlorine	7	2	6	$7 - (2 \times 0.5 + 6) = 0$

Formal charges: worked example in class

A large white rectangular area with horizontal lines, resembling a sheet of lined paper, intended for a worked example.

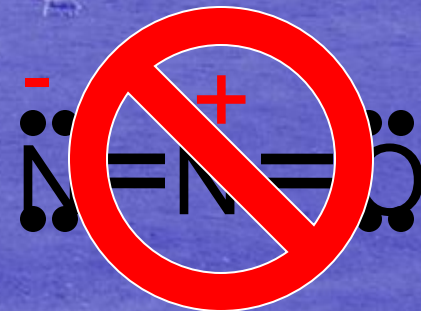
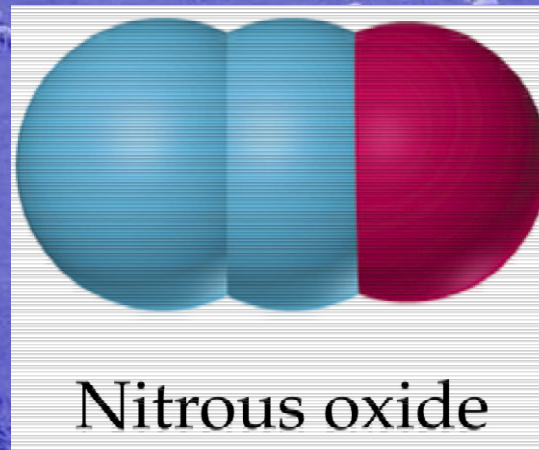
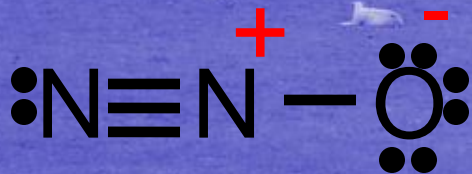
Formal charges and preferred resonance structures: least charge separation

- There are two possible resonance structures for an amide which both satisfy octet requirements
 - Both pass dots test (18) and complete octets
 - Left one has no formal charges - favourable
 - Right one has formal charges - unfavourable



Both resonance structures have formal charges:
electrons prefer more electronegative atom

- In nitrous oxide (N_2O), both resonance structures have formal charges
 - On left, negative charge is on O and on right on N
 - Lower energy structure has negative charge on *more* electronegative atom



Distinguishing possible bonding arrangements

- If skeleton is unknown, formal charges can distinguish more likely arrangements
 - (a) HCIO or (b) HOCl ?
- Draw Lewis structures and compute formal charges:
 - In (a), formal charge on Cl is +1 and on O is -1
 - In (b), formal charges on O and Cl are both 0

