Partial Charge

(Are Electrons Shared Equally?)

WARM-UP

Model 1: Partial Charge on an Atom.

In a bond between two atoms, electrons are rarely shared equally. Unless the two atoms are identical, one of the atoms typically has more electron-attracting power, or pull, than the other. As a result of "holding on to" more than its half of the two electrons, one of the atoms has a residual negative charge; the other atom ends up with a residual positive charge. This residual charge (or **partial charge**) on an atom can be determined experimentally; an estimate of the partial charge can also be calculated. One simple method is given by equation 1:

$$\text{partial charge on atom "a"} = \delta_a = V_a - N_a - p_a B_a \,, \qquad (1)$$

where

- V_a is the number of valence electrons in atom "a";
- N_a is the number of nonbonding electrons on atom "a" in the Lewis structure;
- B_a is the number of bonding electrons on atom "a" in the Lewis structure;
- p_a is a measure of the electron pull of atom "a" relative to the pull of the atom to which it is bonded. The other atom is referred to as atom "b".

The value of p_a must be between zero and one.

We have seen that an atom's electronegativity is a measure of how strongly an atom attracts its valence electrons in a bond. Consider the HF molecule. The bonding pair of electrons can be thought of as being in the valence shell of *both* the H atom and the F atom. We would expect that the fluorine atom in HF would attract the bonding pair of electrons more strongly than the hydrogen atom (EN of F = 4.19 and EN of H = 2.30). We can estimate p_a, the electron pull of atom "a" relative to atom "b", as follows:

$$p_a = \frac{EN_a}{EN_a + EN_b}. \qquad (2)$$

For H–F, the electron pull of F relative to H, p_F, is

$$p_F = \frac{4.19}{4.19 + 2.30} = 0.646. \qquad (3)$$

The electron pull of H relative to F, p_H, is:

$$p_H = \frac{2.30}{4.19 + 2.30} = 0.354. \qquad (4)$$

Thus, the calculated **partial charges** on the F atom, δ_F, and on the hydrogen atom, δ_H, are:

$$\delta_F = 7 - 6 - 0.646 \times 2 = 7 - 6 - 1.29 = -0.29 \ , \tag{5}$$

$$\delta_H = 1 - 0 - 0.354 \times 2 = 1 - 0 - 0.71 = +0.29 \ . \tag{6}$$

Critical Thinking Questions

1. Equation 5 provides a calculation of the partial charge on the F atom in HF.
   a) Why is there a "7" in equation 5?

   b) Why is there a "6" in equation 5?

   c) Why is there a "2" in equation 5?

2. When two different atoms share electrons, which atom (in terms of electronegativities) has the partial negative charge?

3. For HF, why is the partial negative charge on the fluorine atom, and why is the magnitude of the partial charge on fluorine equal to the magnitude of the partial charge on hydrogen?

4. For any diatomic molecule A–B, what is the following sum: $\delta_A + \delta_B$?

END OF WARM-UP

Model 2: The Relationship Between EN and Partial Charge.

Equation 1 provides a very simple calculational model for obtaining partial charges. The calculated values for δ_H and δ_F using equation 1 are consistent with experimental results for the HF molecule. More sophisticated calculations can be used to provide even better estimates of the partial charges on atoms in molecules.

Table 1. Partial charges on atoms in selected molecules.[1]

Molecule	Partial Charge H	Partial Charge Halogen
HF	+0.29	–0.29
HCl	+0.17	–0.17
HBr	+0.09	–0.09
HI	–0.01	+0.01

Table 2. Electronegativities for several elements.

Element	Electronegativity
H	2.30
C	2.54
N	3.07
O	3.61
S	2.59
F	4.19
Cl	2.87
Br	2.69
I	2.36

Critical Thinking Questions

5. Note the EN values for H and Cl in Table 2. Why is it reasonable that, as shown in Table 1, the hydrogen atom has a positive partial charge and the chlorine atom has a negative partial charge in the HCl molecule?

6. Note the EN values for H, F, and Cl in Table 2, and the partial charges in HF and HCl in Table 1. Why is it reasonable that the hydrogen atom has a more positive partial charge in HF than in HCl?

[1] Excellent estimates of partial charges can be calculated with sophisticated molecular modeling software such as Gaussian and Spartan.

Table 3. Calculated partial charges on atoms within a molecule or ion.

Molecule	Partial Charge Central Atom	Partial Charge Each Terminal Atom
methane, CH_4	−0.266	0.066
tetrafluoromethane, CF_4	0.577	−0.144
ammonia, NH_3	−0.396	0.132
nitrogen trifluoride, NF_3	0.295	−0.098
water, H_2O	−0.383	0.192
dihydrogen sulfide, H_2S	−0.097	0.048
ammonium ion, NH_4^+	−0.094	0.274
carbonate ion, CO_3^{2-}	0.401	−0.800
nitrate ion, NO_3^-	0.704	−0.568

Critical Thinking Questions

7. Compare the values of the partial charges on the carbon atom in methane and on the carbon atom in tetrafluoromethane. Rationalize the positive and negative aspects of these charges. (Hint: use Table 2.)

8. Compare the values of the partial charges on the nitrogen atom in ammonia and on the nitrogen atom in nitrogen trifluoride. Rationalize the positive and negative aspects of these charges.

9. a) Why does the oxygen atom in water have a negative partial charge?

   b) Why does the sulfur atom in dihydrogen sulfide have a negative partial charge?

   c) Why is the oxygen atom in H_2O more negatively charged than the sulfur atom in H_2S?

10. A student says "I have looked at the data in Table 1 and conclude that when comparing two molecules, whichever molecule has the atom with the highest electronegativity will be the one with the largest magnitude partial charges."

Provide an example of a pair of molecules in Table 3 that shows that this student is *not correct*. Explain how your example demonstrates that the student is wrong.

11. A student says "For molecules containing two different atoms, the magnitude of the partial charges is related to the difference in EN of those two atoms."

a) Is the data in Table 1 consistent with this statement? Provide your answer using one or more grammatically correct sentences and include specific examples from Table 1 in your response.

b) Does the data for H_2O and H_2S in Table 3 support this statement? Provide your answer using one or more grammatically correct sentences and specifically address the data in Table 3.

12. Use the data in Table 3 to calculate the sum of the partial charges on *all* of the atoms in each of the following:

a) methane

b) water

c) ammonium ion

d) carbonate ion

13. Comment on the relationship (if any) between the charge on a molecule or ion and the sum of the partial charges on all the atoms in the species.

Exercises

1. The EN of Br is 2.69. Use equation 1 to calculate the partial charge on Br in HBr. What is the partial charge on H in HBr? Compare the values to those in Table 1.
2. The EN of Br is 2.69. Calculate the partial charge on Br in Br_2. Does your answer make sense? Explain.
3. What is the charge on any atom in a homonuclear diatomic molecule?
4. If in the AB molecule $\delta_A = 0.13$, what is δ_B?
5. a) Write the Lewis structure for CO_3^{2-}.

   b) Explain why the partial charge on the oxygen atoms is negative.

   c) Explain why your Lewis structure is consistent with the experimental observation that all three oxygen atoms have the same partial charge.
6. The partial charge on the carbon atom in CI_4 is –0.853. What is the partial charge on each iodine atom?
7. The partial charge on the phosphorus atom in the PO_4^{3-} ion is +2.52. What is the partial charge on each oxygen atom?
8. In the chloromethane molecule, $CHCl_3$, the partial charge on the H atom is +0.16 and the partial charge on each Cl atom is –0.04. What is the partial charge on the C atom?
9. The ENs of atoms A, B and C are: A = 3.0; B = 1.0; C = 2.5. Estimate (without calculation) the partial charges on A, B, and C in each of the following molecules. After estimating the partial charges for all of them, calculate the partial charges assuming that neutral atoms A, B, and C have seven valence electrons each.

   a) A–A b) C–C c) A–B d) A–C

Problem

1. Given the partial charges for H_2O given in Table 3, which of the following is the best estimate of the partial charge on O in OF_2? Explain your reasoning *without* calculating the actual partial charge.

   i) -0.32 ii) -0.44 iii) +0.32 iv) +0.44

ChemActivity 21

Covalent Bonds and Dipole Moments

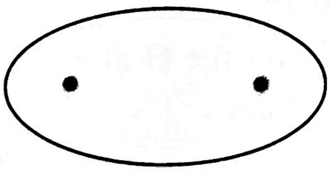
(Do Polar Bonds Make Polar Molecules?)

Model 1: Electronegativities and covalent bonds.

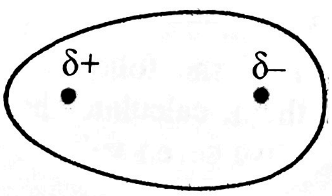
Table 1. Electronegativities for selected elements.

H 2.30								He 4.16
Li 0.91	Be 1.58		B 2.05	C 2.54	N 3.07	O 3.61	F 4.19	Ne 4.79
Na 0.87	Mg 1.29		Al 1.61	Si 1.92	P 2.25	S 2.59	Cl 2.87	Ar 3.24
K 0.73	Ca 1.03	Sc 1.2	Ga 1.76	Ge 1.99	As 2.21	Se 2.42	Br 2.69	Kr 2.97
Rb 0.71	Sr 0.96	Y 1.0	In 1.66	Sn 1.82	Sb 1.98	Te 2.16	I 2.36	Xe 2.58

Figure 1. Types of covalent bonds.



A nonpolar covalent bond forms between identical atoms.



A polar covalent bond forms when there is an electronegativity difference between the atoms.

When comparing two covalent bonds, the one that results in partial charges with larger magnitude is considered to be the **more polar** bond.

Critical Thinking Questions

1. Why do homonuclear molecules (H_2, Cl_2, N_2, etc.) have nonpolar bonds?

2. For HF and HBr, $\delta_H = 0.29$ and 0.09, respectively.

   a) Use electronegativities to explain why the partial charge on H in HF is more positive than the partial charge on H in HBr.

   b) Which bond is more polar, the bond in HF or the bond in HBr? Explain your reasoning.

3. For each pair of molecules below, indicate which contains the more polar bond(s) and explain your reasoning.

   a) O_2 and CO

   b) CO and CCl_4

   c) HBr and PCl_3

Model 2: The Dipole Moment.

The polarity of a bond (or an entire molecule) manifests itself in a measurable physical quantity called the **dipole moment**. A dipole moment, **μ**, is a vector quantity that has both magnitude and direction (bold letters are used for vector quantities).

$$\boldsymbol{\mu} = q \times \boldsymbol{d} \qquad (1)$$

Here, q is the magnitude of the two charges (one positive and one negative) and $\boldsymbol{d}$ is the distance (vector) between the two charges. For a single bond (as in a diatomic molecule), q is the magnitude of the partial charges on the two atoms and $\boldsymbol{d}$ is the bond length. The measured dipole moment for HCl is 1.03 D and for HF it is 1.82 D. (D = debye, after the chemist Peter Debye; 1 D = 3.34×10^{-30} C m). For molecules with more than two atoms, the magnitude and orientation of the molecule's dipole moment results from considering the overall distribution of partial charges in the molecule.

In general, the dipole moment is represented by a vector; a plus sign is used to represent the center of positive charge and the arrow tip represents the center of negative charge. Bond dipoles and dipole moments for HF, HCl, and H_2O are shown in Figures 2 and 3.

Figure 2. Bond dipoles and dipole moments for HF and HCl.

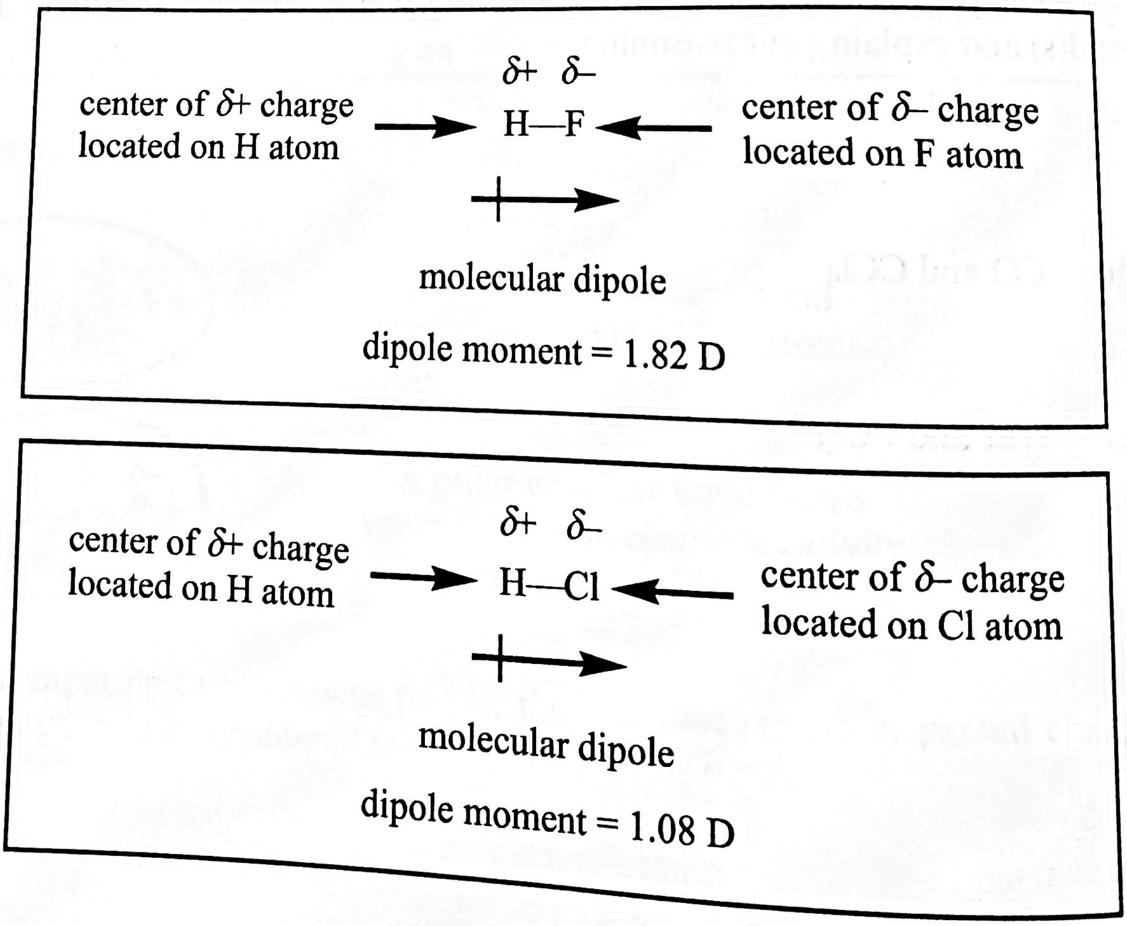


Figure 3. **Bond dipoles and dipole moment for H_2O.**

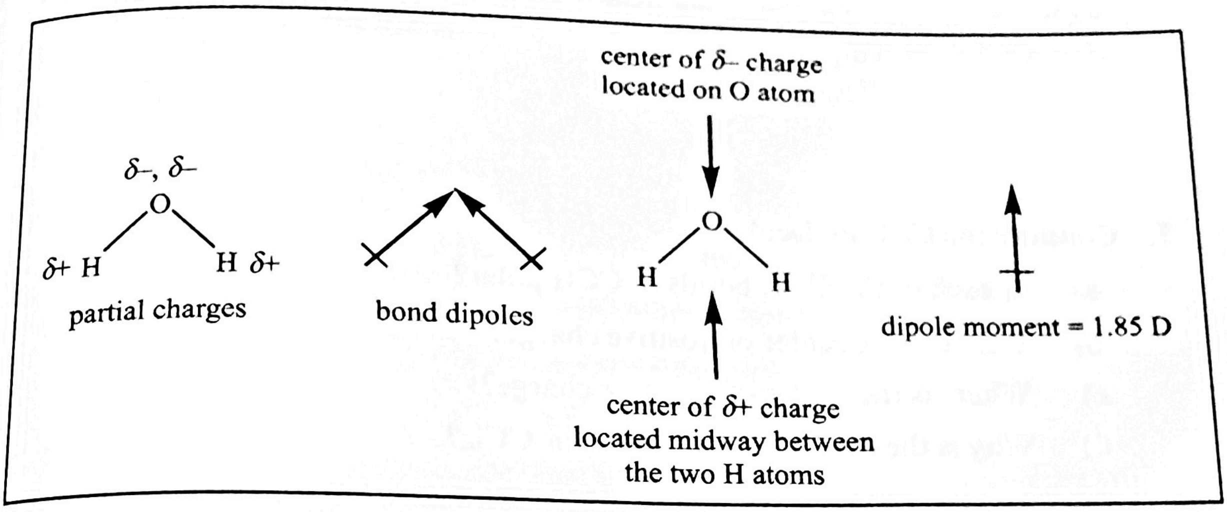


Table 2. Experimental dipole moments for selected molecules.

Molecule	Geometry	Polar Bonds	Dipole Moment (D)
H_2	linear	No	0
HF	linear	Yes	1.82
HCl	linear	Yes	1.08
HBr	linear	Yes	0.83
HI	linear	Yes	0.45
CO_2	linear	Yes	0
OCS	linear	Yes	0.715
CH_4	tetrahedral	Yes	0
CH_3Cl	tetrahedral	Yes	1.892
CH_3Br	tetrahedral	Yes	1.822
CH_3I	tetrahedral	Yes	1.62
CF_4	tetrahedral	Yes	0

Critical Thinking Questions

4. How was the center of positive charge for the H_2O molecule, Figure 3, determined?

5. The CO_2 molecule is linear (OCO) and has polar bonds.
   a) Where is the center of positive charge?
   b) Where is the center of negative charge?
   c) Why is the dipole moment for this molecule equal to zero?

6. The CO_2 (OCO) and OCS molecules are both linear. Both have polar bonds. CO_2 does not have a dipole moment (that is, the dipole moment is zero). Why does OCS have a dipole moment?

7. Consider the CCl_4 molecule.

   a) Is each of the C–Cl bonds in CCl_4 polar?

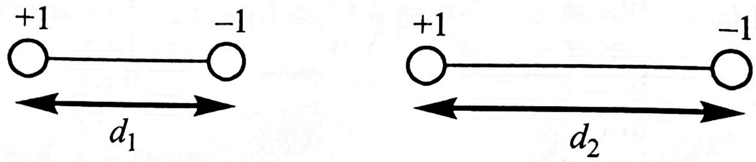
   b) Where is the center of positive charge?

   c) Where is the center of negative charge?

   d) Why is the dipole moment zero for CCl_4?

8. Referring to equation 1, which has the larger dipole moment in each of the following cases?

   a)



   b)

9. Consider HF and HCl:

   a) Which is the bigger atom, F or Cl?

   b) Which has the longer bond length, d, HF or HCl?

   c) Which has the greater partial charge—F in HF or Cl in HCl? (Hint: which is more electronegative—F or Cl?)

   d) Why is the dipole moment of HF larger than the dipole moment of HCl? That is, which appears to be the more important factor in determining the dipole moment: the bond length or the partial charge?

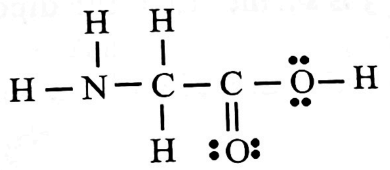
10. Based on the dipole moments for HF, HCl, HBr, and HI in Table 2, which is more important in the determination of a dipole moment—the bond length (distance) or the electronegativity difference? Explain your reasoning.

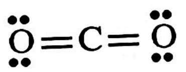
Exercises

1. Classify each of the following bonds as nonpolar or polar.

   C–H in CH_4 ; O–H in H_2O ; Si–Cl in $SiCl_4$; C–H in benzene (C_6H_6);

   N–O in NO_3^- ; H–S in H_2S

   C–O in 

   C–O in 

2. Provide an example of a molecule having polar covalent bonds that are more polar than the bonds in NH_3.

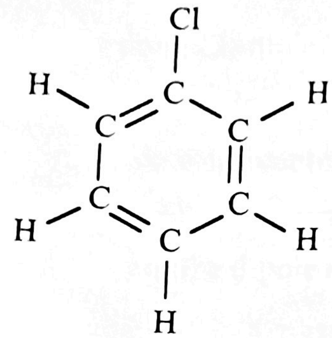
3. Use the vector notation (see Figure 2 above) to designate the dipole moments of: CO ; HI ; ClF .

4. Write the Lewis structure for NO_3^-. Explain why the dipole moment is zero. (Hint: where does the center of negative charge have to be such that the dipole moment is zero?)

5. Classify each of the following molecules (or ions) as nonpolar (dipole moment = 0) or polar (dipole moment ≠ 0).

Hint: it is generally a good idea to determine the shape of the molecule.

O_2 ; I_2; CO ; H_2O ; CO_3^{2-}



6. Which molecule (or ion) of each pair has a dipole moment of zero?

a) N_2 or NO b) CH_4 or CH_3Cl c) SO_2 or SO_3

d) NO_3^- or NO_2^- e) SO_4^{2-} or SO_2 f) CO_2 or OCS

7. Indicate whether the following statement is true or false and explain your reasoning.

The dipole moment of NH_3 is smaller than the dipole moment of CCl_4.

8. Which molecule of each pair has the greater dipole moment?

a) CCl_4 or CH_3Cl

b) CH_3Br or CH_3Cl

c) H_2O or H_2S

9. Based on the data in Table 2, predict the dipole moment of CH_3F.

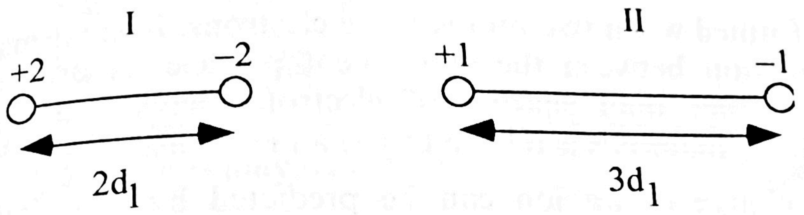
10. For each of the following species: provide the best Lewis structure; sketch the shape of the species including an indication of bond angles; give the hybridization of the central atom; indicate whether or not the molecule is polar (has a nonzero dipole moment).

a) SCN^- b) PBr_3 c) NO_3^- d) NH_3

e) CS_2 f) SO_3 g) $CHCl_3$ h) CH_2Cl_2

Problems

1. For each of the following, which has bonds that are the most polar?
   a) CF_4, NF_3, OF_2
   b) OF_2, SF_2, SeF_2
2. Which has the larger dipole moment, I or II? Clearly explain.



3. For each of the following, which species has the largest dipole moment?
   a) CH_3Cl, CH_3Br, CCl_4, CBr_4, CF_4
   b) CO_2, SO_2, NH_4^+, F_2, O_2^{2-}
4. For each molecule (or ion) indicate whether the dipole moment is equal to zero or not: CN^-; CH_3Br .