CHEMSTRY Gilbert an atoms-focused approach Foster



Chapter 4 Chemical Bonding Understanding Climate Change

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Chapter Outline

- 4.1 Types of Chemical Bonds
- 4.2 Naming Compounds and Writing Formulas
- 4.3 Lewis Structures
- 4.4 Electronegativity, Unequal Sharing, and Polar Bonds
- 4.5 Vibrating Bonds and the Greenhouse Effect
- 4.6 Resonance
- 4.7 Formal Charge: Choosing among Lewis Structures
- 4.8 Exceptions to the Octet Rule
- 4.9 The Lengths and Strengths of Covalent Bonds





Bond – an attractive force that holds two atoms together.

Atoms bond to obtain a more stable electronic configuration.



Types of Chemical Bonds:

- Ionic bond: Electrostatic attraction between cations and anions. Occurs between metals and non-metals.
- **Covalent bond:** Sharing of outermost electrons 'ties' atoms together. Occurs between non-metals.
- Metallic bond: Outer electrons are 'shared' by all atoms. Occurs between metals.

Molecular Compounds – Covalent Bonding

- Molecular compounds are substances formed when <u>nonmetals</u> combine by <u>sharing</u> electrons to form covalent bonds.
- The atoms combine to form discrete molecules in such a way as each atom attains a noble gas configuration (surrounded by 8 e⁻).
- The distance between the atoms when energy is at a minimum is called the <u>bond length</u>.



Types of Chemical Bonds

Covalent

Ionic

Metallic





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Binary Ionic Compounds

 Binary Compounds – composed of only two elements, though may have more than two atoms:

NaCl, KF, CaCl₂, Fe_2O_3 ...

- Binary ionic compounds consist of cations (usually metals) and anions (usually nonmetals), e.g., MgCl₂
 - Charges must cancel out to give the compound a neutral charge overall

Cation (metal) – name is the same as the element, + 'ion'

•Fixed charge cations – metals that only form one cation (such as Group 1 and 2 metals): $Li^{+1} \rightarrow lithium ion, Ca^{+2} \rightarrow calcium ion$

•Variable charged cations – metals that may form different cations (most transition metals). Use Roman numerals to show the charge: $Fe^{+2} \rightarrow iron (II) ion$ $Fe^{+3} \rightarrow iron (III) ion$

 Anion (non-metal) – use the root of the element name, change the ending to 'ide', + 'ion':

$S \rightarrow S^{\text{-2}}$ sulfur \rightarrow sulfide ion

$N \rightarrow N^{-3}$ nitrogen \rightarrow nitride ion

$O \rightarrow O^{-2}$ oxygen \rightarrow oxide ion

Naming Ionic Compounds

List the cation first, then the anion
Do not include 'ion' in the name
Names must be distinctive, in order to distinguish between similar compounds, such as with variable-charged metals

- NaCl sodium chloride
- CaF_2 calcium fluoride
- Fel_2 iron (II) iodide
- Fel_{3} iron (III) iodide

Naming Ionic Compounds

For ionic compounds with variable charged cations:

- •Basically, all metals are variable charged, except for:
- Group 1, Group 2, Ag⁺¹, Zn⁺², Cd⁺², Al⁺³, Ga⁺³
- •For all other metals, the Stock System (Roman Numerals) must be used:

```
Cu_2O - copper (I) oxide
```

CuO – copper (II) oxide

Group	lon usually formed
1 (1A)	+1 H can form -1 ion
2 (2A)	+2
13 (3A)	+3
14 (4A)	+/-4
15 (5A)	-3
16 (6A)	-2
17 (7A)	-1
18 (8A)	0

Fixed charge cations

To determine the charge on a variable charge cation, treat the formula as an algebraic expression:

To determine the iron charge in Fe_2O_3 •let Fe = x and O = y (x and y are ionic charges) •the charges of the ions must add up to the overall charge, which is 0 in this case, so 2x + 3y = 0

Writing ionic compound formulas

- •The formula shows a ratio of one ion to the other.
- •The ionic charges must cancel out so that the overall charge is neutral
- •Always list the metal first, then the non-metal
- •Select subscripts to balance charges
- •Reduce subscripts if needed to obtain the lowest whole number ratio between ions

Practice: Ionic Compounds

Write the name of the following compounds:

- a) NaBr
- b) CrCl₃

Write the chemical formula of the following compounds:

- c) Zinc nitride
- d) Copper(I) oxide

Common Polyatomic Ions

- Polyatomic Ions
 - Charged group of two or more atoms joined together by covalent bonds
- Oxoanions
 - Polyatomic anions containing oxygen in combination with one or more other elements
 - Examples: acetate (C₂H₃O₂⁻), nitrate (NO₃⁻), carbonate (CO₃²⁻), perchlorate (ClO₄⁻), sulfate (SO₄²⁻) (See Table 4.3)

Polyatomic Ions

These are covalently bonded atoms with an overall charge (an ionic 'molecule'):

 $NO_{3^{-1}}$ – nitrate ion CIO_3^{-1} – chlorate ion $C_2H_3O_2^{-1}$ – acetate ion OH⁻¹ – hydroxide ion SO_{1}^{-2} – sulfate ion CO_{3}^{-2} – carbonate ion $PO_{1^{-3}}$ – phosphate ion H_3O^{+1} – hydronium ion NH_{4}^{+1} – ammonium ion (NH_{3} – ammonia)

Oxyions (oxoanions)

Polyatomic ions containing oxygen and another non-metal

Most common forms end in 'ate'
One less oxygen ends in 'ite'
Two less oxygens, 'hypo' prefix and 'ite' suffix
One more oxygen, 'per' prefix and 'ate' suffix

$$CIO^{-1}$$
 – hypochlorite ion
 CIO_{2}^{-1} – chlorite ion
 CIO_{3}^{-1} – chlorate ion
 CIO_{4}^{-1} – perchlorate ion

Practice: Polyatomic Ions

Write the names of the following compounds: a) Cr(ClO₄)₃ b) NH₄NO₃

Write the chemical formulas for the following compounds:

- a) Lithium bicarbonate
- b) Calcium hypobromite

Naming Molecular Compounds

- Binary Molecular Compounds (e.g., SO₃)
 - Compounds consisting of two nonmetals
 - First element in the formula is named first.
 S = sulfur
 - Second element name is changed by adding suffix -ide.

 $O = oxygen \rightarrow oxide$

• Add prefixes to identify quantity of atoms (see Table 4.4).

 $SO_3 = sulfur trioxide$

Naming Molecular Compounds

- •The formula name must indicate the subscripts
- •use prefixes to show subscripts
- •The prefix 'mono' is not used on the first element listed
- Remember that molecules have fixed numbers of atoms linked together, so DO NOT reduce coefficients to lower ratios

Rules for Using Prefixes

- Do not use the prefix mono- when naming first element: SO₃ monosulfur trioxide
- 2. Prefixes ending with oor a are modified when used with elements beginning with vowels; P_4O_{10} tetraphosphorus decaoxide

TABLE 4.4	Naming Prefixes for Molecular Compounds
one	mono-
two	di-
three	tri-
four	tetra-
five	penta-
six	hexa-
seven	hepta-
eight	octa-
nine	nona-
ten	deca-

TABLE 8.6 Some Binary Molecular Compounds that Have Common Names

Compound Formula	Accepted Common Name
H ₂ O	water
H_2O_2	hydrogen peroxide
NH ₃	ammonia
N_2H_4	hydrazine
CH ₄	methane
C_2H_6	ethane
PH ₃	phosphine
AsH ₃	arsine

- Binary Acids
 - Contain hydrogen and a monoatomic anion (e.g., Cl⁻, S²⁻)
 - Most common binary acids are halogen (e.g., HCl, HBr)
 - Acid names:
 - the prefix "hydro" + the halogen base name
 + the suffix "ic" + the word acid.
 - Example HBr hydrobromic acid

If oxoanion name ends in: -ate -ite

Corresponding acid ends in: -ic -ous

TABLI	4.5 Oxoa Chlo Corr	anions of rine and Their esponding Acids							
lon	Formula	Name							
	ClO-	hypochlorite							
	ClO2-	chlorite							
	ClO3-	chlorate							
	C10 ₄ -	perchlorate							
Acid	Formula	Name							
	HCIO	hypochlorous acid							
	HClO ₂	chlorous acid							
	HClO ₃	chloric acid							
	HCIO.	perchloric acid							

Practice: Naming Compounds and Acids

Identify each of the following as a molecular compound, an ionic compound, or an acid. Name or give formulas for the compounds.

- a) $K_2Cr_2O_7$
- b) Na₃N
- c) NO_2
- d) H₂CrO₄
- e) Sodium carbonate
- f) Sulfurous acid
- g) Iron(II) phosphate

- For elements in standard state, use chem. symbols
 - Except for diatomic elements:
 - H₂, N₂, O₂, F₂, Cl₂, Br₂, and I₂ exist as diatomic molecules in their standard states
 - These seven gases are $H_2 + "7"$

1 1A					Copyright e		onipa	1163, 116. F61	mission requ	ied for repro		spiay.					18 8A
1 H 1.008	2 2A	A Atomic number Cr 52.00 Atomic mass												15 5A	16 6A	17 7A	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 — 8B —	10	11 1B	12 2B	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Te (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (268)	110	111	112	(113)	(114)	(115)	(116)	(117)	(118)
						-		,						-			

Metals	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Metalloids	Ce 140.1	Pr 140.9	Nd 144.2	Pm (145)	Sm 150.4	Eu 152.0	Gd 157.3	Ть 158.9	Dy 162.5	Но 164.9	Er 167.3	Tm 168.9	Үь 173.0	Lu 175.0
Nonmetals	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

The 1-18 group designation has been recommended by the International Union of Pure and Applied Chemistry (IUPAC) but is not yet in wide use. In this text we use the standard U.S. notation for group numbers (1A-8A and 1B-8B). No names have been assigned for elements 110-112. Elements 113-118 have not yet been synthesized. *Source:* Raymond Chang, *General Chemistry: The Essential Concepts*, Third Edition, Copyright 2003 The McGraw-Hill Companies, New York, NY.

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- Gilbert Lewis (1916)
 - Proposed that atoms form chemical bonds by sharing electrons to acquire electron configuration of a noble gas
- Octet Rule
 - Atoms tend to lose, gain, or share electrons to obtain a set of 8 valence electrons (*ns²np⁶*)

- Lewis Symbols (Dot Structures)
 - Chemical symbol for an atom surrounded by one or more dots representing valence electrons
 - "Dots" arranged around elemental symbol
 - First 4 electrons = unpaired (top, sides, bottom)
 - Next 4 added to form pairs
 - Examples: Na· (one valence e⁻), ·Mg· (two e⁻)

Unpaired dots = bonding capacity

Main Group Elements: Members of same family have same # valence electrons, similar bonding capacities

1								18
•н	2		13	14	15	16	17	:He
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55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
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Valence electrons (ve)

- The outer electrons are called "valence electrons" or "bonding electrons"
- Most atoms want to get 8 v.e. (octet rule), which they do by gaining, losing, or sharing electrons.

– Main exception: Hydrogen wants 2 v.e.

 Noble gases already have 8 v.e. (except helium which has 2), which is why they almost never react.
Lewis Structures: Ionic Bonds

- A Nonmetal and a Metal:
 - Metals lose valence electrons to achieve noble gas electron configuration.
 - Nonmetal gain electrons to achieve noble gas electron configuration.

$$Na \cdot + \cdot Cl: \rightarrow Na^{+} \left[:Cl: \right]^{-}$$

e⁻ transfer [Ne] [Ar]

Lewis Structures: Molecular Compounds



- Bonding pair of electrons
 - Shared electrons form covalent bonds, and count as valence electrons for both atoms
- Single bond: Two atoms sharing one pair e⁻.
 - H:H, or H–H
- Lone pair: Pair of e⁻ that is not shared.

•
$$H: \overset{\bullet}{O}: H$$
 or $H = \overset{\bullet}{O} = \overset{\bullet}{H}$ (lone pairs)

Drawing Lewis Structures

- 1. Determine the # of valence electrons:

 Sum valence electrons for all atoms in molecule; add/subtract electrons to account for ionic charges

2. Arrange atoms in pattern that shows how they are bonded:

 Atom with least electronegativity is usually central; other atoms arranged around this atom

– Connect atoms with single bonds

Drawing Lewis Structures

- 3. Complete octets of atoms connected to central atom by adding lone pairs.
- 4. Compare the # of electrons in structure to the # determined in step 1:
 - Place remaining electrons around central atom.
- 5. Complete octet around central atom (if needed) by converting one or more lone pairs on adjacent atom into bonding pairs.

Multiple Bonds



- Double Bond:
 - Two electron pairs shared by two atoms
 - Represented as a double line (=).
 - Example: $O_2 \rightarrow O:: O \rightarrow O=O$
- Triple Bond:
 - Three electron pairs shared by two atoms
 - Represented as triple line (\equiv)
 - Example: $N_2 \rightarrow :N:::N: \rightarrow :N \equiv N:$

Practice: Lewis Structures

Draw the Lewis structure for MgF₂.

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

Practice: Lewis Structures

Draw the Lewis structure for: H_2O , H_2CO , and CH_4 .

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

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Electronegativity

- Electronegativity (EN):
 - Relative ability of an atom to attract electrons in a bond to itself.



Electronegativity Trends

- Electronegativity (EN) attraction for bonding (shared) electrons
- The difference in EN between the bonding atoms determines if the bond is ionic or covalent
- Electronegativity increases moving up, to the right in periodic table (omitting noble gases).

Ionization Energies and Electronegativity



EN: increases across a row;

decreases down a column.

Polar Covalent Bonds

- Polar Covalent Bond:
 - Unequal sharing of bonding pair of electrons between atoms
 - Results in uneven distribution of charge
- Bond Polarity:
 - A measure of the extent to which bonding electrons are unequally shared due to differences in electronegativity of the bonded atoms

•With a large EN difference (such as between metals and non-metals), the more electronegative atom takes the electrons from the other atom and forms ions.

•If the ENs are identical, both have the same attraction, and the bonding electrons are shared equally. (non-polar covalent bonds)

•For small EN differences, the electrons are shared, but not equally (polar covalent bonds)

Bond Polarity

- Polar (covalent) Bond:
 - Partial negative and positive charges (δ +, δ –)
 - Direction of polarity indicated by arrow pointing to more negative end of bond, with + sign at positive end
 - Degree of polarity depends on differences in electronegativity

EN difference	Bond Type
0 – 0.3	Non-polar (covalent)
0.3 – 1.7	Polar (covalent)
1.7 +	Ionic

Electronegativity values for elements are listed in tables

Bond Polarity

 Bond polarity increases as ∆EN increases.





Which of the following bonds in each pair are more polar?

C–S or C–O CI–CI or O=O N–H or C–H

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

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Vibration Modes





Bond Stretching

- Absorption of energy by *atoms*:
 - Absorb radiation if frequency matches ∆E of electron energy levels (Chapter 7)
- Absorption of energy by *molecules*:
 - Absorb infrared radiation if frequency matches vibrational modes of molecular bonds = infrared active
 - Basis of "greenhouse effect"

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•Not all molecules can be accurately represented by a single Lewis Structures

- Sometimes two or more structures may be drawn with identical formal charges
- In this case the actual structure of the molecule is an average of all of the similar structures
- •These are called **Resonance Structures**

Resonance Structures: Ozone

Resonance:

When two or more equivalent Lewis structures can be drawn for one compound

Resonance Structures:

Two or more Lewis structures with the same arrangement of atoms but different arrangement of bonding pairs of electrons



Resonance in Organic Compounds

Benzene: a) alternating single, double bonds

b) circle indicates uniform distribution of electrons, equivalent C–C bonds



Practice: Resonance Structures



Draw all possible resonance structures for SO_2 .

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

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Resonance Structures: N₂O

• Three possible Lewis structures. Which one is best?

$$N \equiv N - O$$
 $N \equiv O$ $N = N = O$

- Formal Charge:
 - Determined by the difference between the number of valence e⁻ in the free atom and the sum of lone pair + ½ bonding e⁻ in a molecule

Calculating Formal Charges

- Formal charge (FC):
- FC = (# valence electrons) [(# unshared e^-) + 1/2(# of e^- in bonding pairs)]

Formal Charge Calculations for the Resonance Structures of $\mathrm{N_2O}$											
Step		:N≡N— <mark>ö</mark> :			N=N=0			: <u>₩</u> —N≡0:			
1	Number of valence electrons	5	5	6	5	5	6	5	5	6	
2	Number of lone pair electrons	2	0	6	4	0	4	6	0	2	
3	Number of shared electrons	6	8	2	4	8	4	2	8	6	
4	$FC = valence - [lone pair + \frac{1}{2} (shared)]$	0	+1	-1	-1	+1	0	-2	+1	+1	

Choosing the Best Structure

- Most Stable Resonance Structures:
 - Formal charges equal or close to zero
 - Negative formal charges on the more electronegative element

Formal Charge Calculations for the Resonance Structures of $\mathrm{N_2O}$											
Step		:N≡N—ö:			N=N=0			: <u>₩</u> —N≡0:			
1	Number of valence electrons	5	5	6	5	5	6	5	5	6	
2	Number of lone pair electrons	2	0	6	4	0	4	6	0	2	
3	Number of shared electrons	6	8	2	4	8	4	2	8	6	
4	$FC = valence - [lone pair + \frac{1}{2} (shared)]$	0	+1	-1	-1	+1	0	-2	+1	+1	

Practice: Formal Charge

Determine the most stable structure for the phosphite ion by calculating formal charge for the atoms in each ion. 3

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:



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Exceptions to the Octet Rule

- Molecules having odd number of electrons = free radicals
 - Example: NO
- Molecules with atoms having more than an octet = expanded valence shell
 - Example: SF₆

Odd-Electron Molecules

- Odd number of valence electrons (11).
- Formal charges: N = [5 (3+2)] = 0
 O = [6 (4+2)] = 0
- Structure is reasonable, except for the lack of octet on N atom
- Free Radical:
 - Odd-electron molecule with an unpaired e⁻ in its Lewis structure. Very reactive!

Expanded Valence Shell

- Expanded shells observed for elements with Z > 12
- Example: SF₆
- Sulfur (S) in SF₆
 - Has Z > 12 (Z = 16)
 - Bonded to strongly electronegative element (F)
 - FC for sulfur = 0; FC for fluorine = 0





Expanded Valence Shell



- Elements with Z > 12 (3rd row):
 - Expand valence shell by using empty d orbitals
- Expanded Valence Shells Occur:
 - In molecules having strongly electronegative elements (F, O, CI)
 - When expanded, shell decreases formal charge on central atom

Practice: Expanded Valence Shell

What is the Lewis dot structure of SO₄²⁻ ion? Does this ion have resonance structures?

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:
Chapter Outline

- 4.1 Types of Chemical Bonds
- 4.2 Naming Compounds and Writing Formulas
- 4.3 Lewis Structures
- 4.4 Electronegativity, Unequal Sharing, and Polar Bonds
- 4.5 Vibrating Bonds and the Greenhouse Effect
- 4.6 Resonance
- 4.7 Formal Charge: Choosing among Lewis Structures
- 4.8 Exceptions to the Octet Rule
- 4.8 The Lengths and Strengths of Covalent Bonds

Bond Lengths



O-to-O Bond Lengths:

- Single bond $(H_2O_2) = 148 \text{ pm}$
- Double bond $(O_2) = 121 \text{ pm}$
- ?? bond (O_3) = 128 pm



Bond Lengths

- Bond Length Depends On:
 - Identity of the atoms
 - # of bonds between them
- Bond Order:
 - The # of bonds between two atoms
 - 1 for a single bond
 - 2 for a double bond
 - 3 for a triple bond



TABLE 4.7	Average Lengths and Energies of Selected Covalent Bonds							
Bond	Bond Length (pm)	Bond Energy (kJ/mol)	Bond	Bond Length (pm)	Bond Energy (kJ/mol)	Bond	Bond Length (pm)	Bond Energy (kJ/mol)
с—с	154	348	N—H	104	391	s—s	204	266
C=C	134	614	N—N	147	163	S—H	134	347
c≡c	120	839	N=N	124	418	н—н	74	436
C—N	147	293	N≡N	110	945	H—F	92	567
C=N	127	615	N—O	136	201	H—Cl	127	431
C≡N	116	891	N=O	122	607	H—Br	141	366
с—о	143	358	N≡O	106	678	н—і	161	299
C=0	123	743ª	0—0	148	146	F—F	143	155
c≡o	113	1072	0=0	121	498	Cl—Cl	200	243
С—Н	110	413	О—Н	96	463	Br—Br	228	193
C—F	133	485	s—o	151	265	I—I	266	151
C—Cl	177	328	s=o	143	523			
The bond energy	ry of the C=O bo	nd in CO. is 799 kI	/mol.					





- Bond Energy:
 - Energy needed to break 1 mole of covalent bonds in the gas phase
 - Breaking bonds consumes energy (+); forming bonds releases energy (-)
 - Using bond energies to estimate ΔH_{rxn}

$$\Delta \clubsuit_{\rm rxn} = \Sigma \Delta \clubsuit_{\rm bond\, breaking} - \Sigma \Delta H_{\rm bond\, forming}$$

Practice: Calculating ΔH_{rxn}

- Calculate the ∆H_{rxn} for the following reaction using bond energies from Table 4.7.
 - $:N \equiv N: + 3 H H \rightarrow 2 H \dot{N} H$
 - Collect and Organize:
 - Analyze:
 - Solve:
 - Think about It:

This concludes the Lecture PowerPoint presentation for Chapter 4



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