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Chapter 8 Chemical Bonding I: Basic Concepts

8.1 Lewis Dot Symbols

- Valence electrons determine an element's chemistry.
- Lewis dot symbols represent the valence electrons of an atom as dots arranged around the atomic symbol.
- Most useful for main-group elements

Lewis Dot Symbols of the Main Group Elements



Write Lewis dot symbols for the following:

(a) N

(b) S²⁻

(c) K⁺

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Write Lewis dot symbols for the following:



(c) K⁺ K⁺

8.2 Ionic Bonding

- Ionic bond: electrostatic force that holds oppositely charge particles together
- Formed between cations and anions
- Example Na• + :CI• \longrightarrow Na+ + :CI• $IE_1 + EA_1 = 496 \text{ kJ/mol} - 349 \text{ kJ/mol} = 147 \text{ kJ/mol}$ m.p. = 801°C $\Delta H_f^\circ = -410.9 \text{ kJ/mol}$

Microscopic View of NaCl Formation



 Lattice energy = the energy required to completely separate one mole of a solid ionic compound into gaseous ions



 $NaCl(s) \rightarrow Na^{+}(g) + Cl^{-}(g) \qquad \Delta H_{lattice} = +788 \text{ kJ/mol}$

Because they are defined as an *amount* of energy, lattice energies are always positive.

Coulombic attraction:



• Lattice energy (like a coulombic force) depends on

- Magnitude of charges
- Distance between the charges

Lattice energies of alkali metal iodides



The ionic radii sums for LiF and MgO are 2.01 and 2.06 Å, respectively, yet their lattice energies are 1030 and 3795 kJ/mol. Why is the lattice energy of MgO nearly four times that of LiF?



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• **Born-Haber cycle**: A method to determine lattice energies



Born-Haber cycle for CaO



#1 Heat of sublimation = $\Delta H_{f^{\circ}}[Ca(g)] = +178 \text{ kJ/mol}$

#2 1st & 2nd ionization energies = $I_1(Ca) + I_2(Ca) = +1734.5 \text{ kJ/mol}$

#3 (1/2) Bond enthalpy = (1/2) D(O=O) = $\Delta H_{f^{\circ}}[O(g)]$ = +247.5 kJ/mol

#4 1st & 2nd electron affinities = $EA_1(O) + EA_2(O) = +603 \text{ kJ/mol}$

#5 – (Lattice Energy) = $-\Delta H_{\text{lattice}}[\text{CaO}(s)]$ = (the unknown)

#6 Standard enthalpy of formation = $\Delta H_f^{\circ}[CaO(s)] = -635 \text{ kJ/mol}$

 $+178 + 1734.5 + 247.5 + 603 - \Delta H_{latt} = -635$

8.3 Covalent Bonding

Atoms share electrons to form covalent bonds.

$$H \bullet + \bullet H \longrightarrow H \bullet H \bullet H \to H \bullet H \bullet H$$

• In forming the bond the atoms achieve a more stable electron configuration.

- Octet: Eight is a "magic" number of electrons.
- Octet Rule: Atoms will gain, lose, or share electrons to acquire eight valence electrons
 - Examples:



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Lewis Structures



Shared electrons \Rightarrow Bonds Non-bonding valence electrons \Rightarrow Lone pairs

- Multiple Bonds
 - The number of shared electron pairs is the number of bonds.



 Bond strength and bond length 									
bond stren	bond strength		<	double <	triple				
bond lengt	h	single	>	double >	triple				
	N–N		N	=N	N≡N				
Bond Strength	163 kJ/	mol	41	8 kJ/mol	941 kJ/mol				
Bond Length	1.47 Å		1.	24 Å	1.10 Å				

8.4 Electronegativity and Polarity

- Nonpolar covalent bond = electrons are shared equally by two bonded atoms
- Polar covalent bond = electrons are shared unequally by two bonded atoms

M:X	$M^{\delta +} X^{\delta -}$	M^+X^-
Pure covalent bond	Polar covalent bond	Ionic bond
Neutral atoms held together by <i>equally</i> shared electrons	Partially charged atoms held together by unequally shared electrons	Oppositely charged ions held together by electrostatic attraction

Electron density distributions



red \Rightarrow high electron densitygreen \Rightarrow intermediate electron densityblue \Rightarrow low electron density

 $H \rightarrow F$

δ+ δ-H – F

alternate representations

- Electronegativity: ability of an atom to draw shared electrons to itself.
 - More electronegative elements attract electrons more strongly.
 - relative scale
 - related to *IE* and *EA*
 - unitless
 - smallest electronegativity: Cs 0.7
 - largest electronegativity: F 4.0

Electronegativity: The Pauling Scale

Increasing electronegativity

1A																	8A
1																	18
Н	2A											3A	4A	5A	6A	7A	
2.1	2	I										13	14	15	16	17	
Li 1.0	Be 1.5											B 2.0	С 2.5	N 3.0	O 3.5	F 4.0	
Na 0.9	Mg 1.2	3B 3	4B 4	5B 5	6B 6	7B 7	8	8 B 9	10	1 B 11	2B 12	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	Lu 1.3	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	
Fr 0.7	Ra 0.9																

Increasing electronegativity

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Variation in Electronegativity with Atomic Number



Polar and nonpolar bonds



- Dipole moments and partial charges
 - Polar bonds often result in polar molecules.
 - A polar molecule possesses a *dipole.*
 - **dipole moment (\mu)** = the quantitative measure of a dipole



SI unit: coulomb•meter (C•m) common unit: debye (D)

$$1D = 3.34 \times 10^{-30} \,\mathrm{C} \cdot \mathrm{m}$$

8.5 Drawing Lewis Structures

- 1) Draw skeletal structure with the central atom being the least electronegative element.
- 2) Sum the valence electrons. Add 1 electron for each negative charge and subtract 1 electron for each positive charge.
- 3) Subtract 2 electrons for each bond in the skeletal structure.
- 4) Complete electron octets for atoms bonded to the central atom except for hydrogen.
- 5) Place extra electrons on the central atom.
- 6) Add multiple bonds if atoms lack an octet. Copyright McGraw-Hill 2009

What is the Lewis structure of NO_3^- ?

- Draw skeletal structure with central atom being the least electronegative.
- 2) Sum valence electrons. Add 1 for each negative charge and subtract 1 for each positive charge.

 $NO_3^- \Rightarrow (1 \times 5) + (3 \times 6) + 1 = 24$ valence $e^- 24 e^-$

- 3) Subtract 2 for each bond in the skeletal structure.
- 4) Complete electron octets for atoms bonded to the central atom except for hydrogen.
- 5) Place extra electrons on the central atom.
- 6) Add multiple bonds if atoms lack an octet.

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 $-6e^{-}$

O - N - O

·Ö·

$$\begin{bmatrix} \vdots \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ 0 - N = \vdots \end{bmatrix}^{-} 24 e^{-}_{27}$$

Steps for Drawing Lewis Structures

Step	CH ₄	CCl ₄	H ₂ O	0 ₂	CN ⁻
1	$\substack{\mathbf{H} = \begin{bmatrix} \mathbf{H} \\ \mathbf{H} \\ \mathbf{H} \end{bmatrix} = \mathbf{H}}_{\mathbf{H}}$	Cl - Cl - Cl	Н—О—Н	0-0	C—N
2	8	32	8	12	10
3	8 - 8 = 0	32 - 8 = 24	8 - 4 = 4	12 - 2 = 10	10 - 2 = 8
4	H = H = H	:Ċl: :Ċl-Ċ-Ċl: :Ċl:	Н—О—Н	:Ö—Ö:	:С—ÿ:
5			н−ё́−н		_
6				io=oi	[:C≡N:]

8.6 Lewis Structures and Formal Charge

• The electron surplus or deficit, relative to the free atom, that is assigned to an atom in a Lewis structure.



Example:
$$H_2O = H_2O + H_2O$$

-1/2 bonding $e^- = -1$

formal charge = 0

- H: orig. valence $e^- = 1$ O: orig. valence $e^- = 6$
 - non-bonding $e^- = -0$ non-bonding $e^- = -4$

$$-$$
 1/2 bonding $e^- = -2$

formal charge = 0

Formal charges are not "real" charges.

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Example: Formal charges on the atoms in ozone

0::0:0::

$$O = 6 - 4 - \frac{1}{2}(4)$$

= 0
$$O = 6 - 2 - \frac{1}{2}(6)$$

= +1
$$O = 6 - 6 - \frac{1}{2}(2)$$

= -1

- Formal charge guidelines
 - A Lewis structure with *no* formal charges is generally better than one with formal charges.
 - Small formal charges are generally better than large formal charges.

Н

 Negative formal charges should be on the more electronegative atom(s).

Example:

H C O H or C O ?

Answer:



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Identify the best structure for the isocyanate ion below:

(a)
$$\begin{bmatrix} \vdots \\ \vdots \\ -2 \end{bmatrix}^{-2} = N = \begin{bmatrix} \vdots \\ 0 \end{bmatrix}^{-2}$$

(b)
$$\left[:C \equiv N - \overset{\cdot}{O}_{-1}:\right]^{-1}$$

Identify the best structure for the isocyanate ion below:

(a)
$$\begin{bmatrix} \vdots \ddot{C} = N = \ddot{O} \vdots \\ -2 & +1 & 0 \end{bmatrix}^{-2}$$

(b)
$$\begin{bmatrix} :C \equiv N - \ddot{O} \vdots \\ -1 & +1 & -1 \end{bmatrix}^{-1}$$

(c)
$$\begin{bmatrix} : \ddot{C} - N \equiv O \vdots \\ -3 & +1 & +1 \end{bmatrix}^{-1}$$

8.7 Resonance

• **Resonance** structures are used when two or more equally valid Lewis structures can be written.

Example: NO₂

These two bonds are known to be identical.

[:O - N = O:]

Solution:
$$\begin{bmatrix} \vdots \vdots \\ \vdots \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} \vdots \\ N \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} i \\ N \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} i \\ N \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} i \\ N \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} i \\ N \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} i \\ N \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} i \\ N \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} i \\ N \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} i \\ N \\ \vdots \\ \end{bmatrix} = \begin{bmatrix} i \\ N \\ \end{bmatrix} = \begin{bmatrix} i \\ N$$

Two *resonance structures*, their average or the *resonance hybrid*, best describes the nitrite ion.

The double-headed arrow indicates resonance.

Additional Examples

Carbonate: CO₃²⁻





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8.8 Exceptions to the Octet Rule

- Exceptions to the octet rule fall into three categories:
 - Molecules with an incomplete octet
 - Molecules with an odd number of electrons
 - Molecules with an expanded octet

Incomplete Octets



- Common with Be, B and Al compounds, but they often dimerize or polymerize.



Odd Numbers of Electrons

Example: NO (nitrogen monoxide or nitric oxide)

$$NO \Rightarrow (1 \times 5) + (1 \times 6) = 11 \text{ valence } e^-$$

$$0 \quad 0 \quad -1 \quad +1$$

$$:N = O: \quad \longrightarrow : N = O: \quad \text{Are these both}$$

$$equally good?$$

Example: NO₂ (nitrogen dioxide)



- Expanded Octet
 - Elements of the 3rd period and beyond have *d*-orbitals that allow more than 8 valence electrons.



8.9 Bond Enthalpy

- Bond enthalpy is the energy associated with breaking a particular bond in one mole of gaseous molecules.
 - Bond enthalpy is one measure of molecular stability.
 - Symbol: ΔH^{o}
 - For diatomic molecules these are accurately measured quantities.

 $\begin{array}{ll} \operatorname{Cl}_{\mathbf{2}}(g) \to \operatorname{Cl}(g) + \operatorname{Cl}(g) & \Delta H^{\mathsf{o}} = 243.4 \text{ kJ} \\ \operatorname{HCl}(g) \to \operatorname{H}(g) + \operatorname{Cl}(g) & \Delta H^{\mathsf{o}} = 431.9 \text{ kJ} \end{array} \qquad \text{single bonds} \\ \operatorname{O}_{\mathbf{2}}(g) \to \operatorname{O}(g) + \operatorname{O}(g) & \Delta H^{\mathsf{o}} = 495.0 \text{ kJ} & \text{double bond} \\ \operatorname{N}_{\mathbf{2}}(g) \to \operatorname{N}(g) + \operatorname{N}(g) & \Delta H^{\mathsf{o}} = 945.4 \text{ kJ} & \text{triple bond} \\ \end{array}$

 Bond enthalpies for polyatomic molecules depend upon the bond's environment.

$$\begin{array}{cccc} H & H & H \\ H - C - H \rightarrow H - C & + H \\ H & H \end{array} & \begin{array}{c} \Delta H = 435 \text{ kJ} \\ \Delta H = 435 \text{ kJ} \\ \Delta H = 435 \text{ kJ} \\ \Delta H = 410 \text{ kJ} \\ \Delta H = 410 \text{ kJ} \\ 6\% \text{ less} \end{array}$$

- Average bond enthalpies are used for polyatomic molecules.
 - Provide only estimates

Prediction of bond enthalpy



$\Delta H^{\circ} = \Sigma BE(reactants) - \Sigma BE(products)$

Example: Calculate the enthalpy of reaction for $CH_4(g) + Br_2(g) \rightarrow CH_3Br(g) + HBr(g)$

Solution: Consider ONLY bonds broken or formed.



TABLE 8.6	Bond Enthalpies		
Bond	Bond Enthalpy (kJ/mol)	Bond	Bond Enthalpy (kJ/mol)
H-H*	436.4	C-S	255
H-N	393	C=S	477
Н-О	460	N-N	193
H-S	368	N=N	418
H-P	326	N≡N	941.4
H-F	568.2	N-O	176
H–Cl	431.9	N=O	607
H–Br	366.1	0-0	142
H-I	298.3	0=0	498.7
С-Н	414	O-P	502
С-С	347	O=S	469
C=C	620	P-P	197
C≡C	812	P=P	489
C-N	276	S-S	268
C=N	615	S=S	352
C≡N	891	F-F	156.9
С-О	351	CI-CI	242.7
$C=O^{\dagger}$	745	CI-F	193
C≡O	1070	Br-Br	192.5
С-Р	263	I–I	151.0

*Bond enthalpies shown in red are for diatomic molecules.

[†]The C=O bond enthalpy in CO₂ is 799 kJ/mol.

Key Points

- Lewis dot symbols
- Ionic bonding
- Lattice energy
- Born-Haber cycle
- Covalent bonding
- Octet rule
- Lewis structures
- Bond order
- Bond polarity

Key Points

- Electronegativity
- Dipole moment
- Drawing lewis structures
- Formal charge
- Resonance structures
- Incomplete octets
- Odd numbers of electrons
- Expanded octets
- Bond enthalpy