CHEM2100J Chapter 03 RC

Zeng Haoxuan

UM-SJTU Joint Institute
zenghaoxuan@sjtu.edu.cn

September 26, 2023

Table of Contents

Atomic & Ionic Radius

- Atomic Radius
  - Van der Waals radius - half the distance between the centers of neighboring atoms in a sample of solidified gas.
  - Covalent radius - the contribution an atom makes to the length of a covalent bond
  - Metallic radius - half the distance between the centers of neighboring atoms in crystal lattice
  - Trend: Increase down a group; decrease across a period
- Ionic Radius
  - Trend(for the same element): cation $<$ atom $<$ anion

Ionization Energy

- Ionization energy is measure of how difficult it is to remove an electron
- First Ionization Energy
  - The minimum energy needed to remove an electron from a neutral atom in **GAS** phase
  - $J(g) \rightarrow J^+(g) + e^-(g)$, $I = E(J^+) - E(J)$
  - The sign of I is always **POSITIVE**
  - Trend: Period $\uparrow$, first ionization energy $\downarrow$; Group $\uparrow$, first ionization energy $\uparrow$
- N th Ionization Energy
  - Higher than the previous ones
  - Much higher when the electron is to be removed from a closed shell

Electron Affinity

- The electron affinity E_{ea} is the energy released when an election is added to a **GAS** phase atom
  - $X(g) + e^-(g) \rightarrow X^-(g)$, $E_{ea}(X) = E(X) - E(X^-)$
  - $E_{ea} > 0$ - release energy; $E_{ea} < 0$ - absorb energy
- Electron affinities are highest toward the right of the periodic table
- Group 14 $>$ Group 15 - same reason as that for the ionization energy

Exercise

- Who has the highest radius?
  K^+, Cl^-, S, Ca^{2+}, S^{2-}
- Who has the largest and second largest first ionization energy?
  K, Ca, Ga, Ge, As, Se, Br
- Who has the smallest electron affinity?
  Rb, Sr, Cs, K

Ionic Bonds

- Ionic means gaining & losing electrons
  - Metal elements LOSE electrons $\rightarrow$ CATIONS
  - Nonmetal elements GAIN electrons $\rightarrow$ ANIONS
- The entire compound is held together by electrostatic attractions, this attraction is called ionic bond
  - The essence of ionic bond is the electrostatic attraction
  - Ionic bond is non-directional - in any directions
  - Ionic bond is non-saturable - between unlimited number of atoms

Lattice Energy

- Definition: the difference in energy between the ions of a compound widely separated as a **GAS** and packed together in a solid.
- Lattice energy is a **global** characteristic of the entire crystal
- Radius $\downarrow$ charge $\uparrow \Rightarrow$ lattice energy $\uparrow \Rightarrow$ stronger ionic bonds

Exercise

Arrange the following compounds according to lattice energy in descending order: KI, MgO, BaO, CaO

Lattice Energy

- Definition: the difference in energy between the ions of a compound widely separated as a **GAS** and packed together in a solid.
- Lattice energy is a **global** characteristic of the entire crystal
- Radius $\downarrow$ charge $\uparrow \Rightarrow$ lattice energy $\uparrow \Rightarrow$ stronger ionic bonds

Exercise

Arrange the following compounds according to lattice energy in descending order: KI, MgO, BaO, CaO

Answer

$MgO > CaO > BaO > KI$

Coulomb Interactions

- Ionic solid is not held by bonds between specific pairs of ions
  - all cations interact with all anions
  - all cations(anions) repel one another
- Coulomb's potential energy
  - $E_{p,12} = \frac{z_1 z_2 e^2}{4\pi\epsilon_0 d_{12}}$
  - measures the strength of attraction between **individual** ion pairs
- Radius $\downarrow$ charge $\uparrow \Rightarrow$ coulomb's potential energy $\uparrow$
- Coulomb's potential energy $\uparrow \Rightarrow$ melting point$\uparrow$; brittleness$\uparrow$

Covalent Bonds

- Covalent means sharing electrons
  - Electrons are shared until reaching a noble-gas configuration
  - Covalent bonds form between two non-metal elements that do not form ions
- The chemical bonds formed by sharing electrons between atoms are called covalent bonds
  - The essence of covalent bond is the electrical effect of shared electrons on the two atomic nuclei
  - Covalent bond is directional - electron cloud overlaps the most
  - Covalent bond is saturable - must have unpaired electrons

Lewis Structure

- Octet rule - atoms go as far as possible toward completing their octets by sharing electron pairs.
- Concepts
  - Lone pair - a pair of valence electrons that does not participate in bonding
  - Bond type - single; double; triple; (quadruple?)
  - Bond order- number of bonds that link a specific pair of atoms.
- Drawing
  - 1. Determine the number of bonds
  - 2. Arrange atoms and show them by chemical symbol
  - 3. Connect bonds by lines
  - 4. Complete octet with lone pairs

How to Arrange Atoms?

- Determining central atom
  - Electronegativity - atoms with lower electronegativity are in the middle(as central atoms)
  - Symmetry - Eg. SO_2
  - The first to write - Eg. OF_2
  - Use the known structure to predict - Eg. P_4O_{10}
  - C is always the central atom and is tetravalent (four covalent bonds);
- Determining end atom
  - H atoms tend to be terminal atoms (this is not the case in boranes);
  - Halogen atoms are often used as end groups;
  - O atoms are often linked to H to form -OH as an end group

Exception to Octet Rule

- Radical
  - Species having electrons with unpaired spins are called radical
  - Radicals are unstable and highly reactive
  - Odd compound can be considered as radicals - Eg. NO, NO_2
- Expanded valence shell
  - p-block atoms can only accommodate more than 8 electrons in its valence shell in Period 3 or later periods
  - Atoms of these elements have empty d-orbital and the size is adequately large
- Incomplete octets
  - Atom of IIIA elements exist in compounds with an incomplete octet
  - Coordinate covalent bond - both electrons come from one atom
  - Dimmer - linked pair of molecules

Lewis Structure

Exercise

Determine the central atom and number of lone pairs on the central atom of each following molecules. Draw the Lewis structure.

a) IF_5

b) AsF_5

c) H_2SO_3

Resonance Structure

- Molecules with double or triple bonds may be represented by various Lewis structure
- The blending of these structures is called resonance
  - The actual structure is a resonance hybrid of the contributing Lewis structures
  - Electrons shown in different positions are said to be delocalized
- Remarks
  - Keep relative positions of atoms and the number of paired and unpaired electrons
  - Only change the position of electrons(bonds, charges)
  - Low-energy structures contribute more to the resonance mixture

Exercise

How many resonance does NO_3^- have? Draw them all.

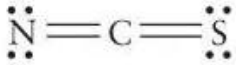
Formal Charge

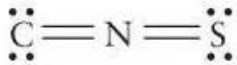
- Formula
  - Formal charge$=V-(L+\frac{1}{2}B)$
  - V - the number of **valence electrons** in free atom
  - L - number of electrons present in bonded atom as **lone pairs**
  - B - number of **bonding electrons** on th atom
- Remark
  - Formal charge is a measure of the **redistribution** of electrons
  - Formal gives an indication of the extent to which atoms gain or lost electrons when forming covalent bonds

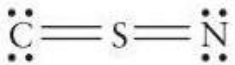
Formal Charge

Exercises

Calculate the formal charge of each atom in the following structures:



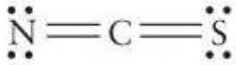
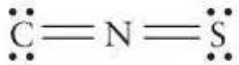
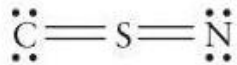




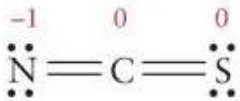
Formal Charge

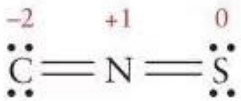
Exercises

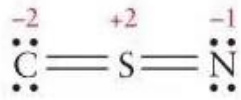
Calculate the formal charge of each atom in the following structures:

Answer







Further questions:

- Are the above three structures resonance structures?
- Which of the three structures is most stable?

Correcting the Covalent Model

- Polar covalent bond
  - there are nonzero partial charges on the atoms
  - electric dipole moment - $\vec{\mu} = q\vec{d}$; in non-SI units debye(D)
- Electronegativity - the electron-pulling power of an atom when it is part of a molecule
- Ionic character - there is no sharp dividing line between ionic and covalent bonding

Correcting the Ionic Bond Model

- Polarizing power
  - The ability of atoms and ions to cause distortions
  - Radius$\downarrow$ Charge$\uparrow$ $\Rightarrow$ Polarizing Power$\uparrow$
- Polarizability
  - The ability of atoms and ions to undergo distortion
  - Radius$\uparrow$ Charge$\downarrow$(algebraically) $\Rightarrow$ Polarizability$\uparrow$
- Compounds composed of highly polarizing cations and highly polarizable anions have significant covalent character

Exercise

The stability of a certain carbonate compound is influenced by its cations. The stronger the polarizing power of the cation is, the less stable the carbonate compound becomes. Based on this information, which of the following is the most stable?

$$MgCO_3,\ FeCO_3,\ Na_2CO_3,\ MnCO_3,\ BeCO_3$$

Bond Strength & Bond Length

- Bond strength
  - Bond order: single bond=1; double bond=2;triple bond=3
  - Bond order$\uparrow \Rightarrow$ bond strength $\uparrow$
- Bond length
  - Bond strength$\uparrow \Rightarrow$ bond length$\downarrow$
  - Atomic radius$\uparrow \Rightarrow$ bond length$\uparrow$

Reference

- Atkins, P. (2016) *Chemical principles: The quest for insight*. New York: W H Freeman.
- Prof. Milias Liu, Lecture Slides. 23FA VC210
- MA Anlin, RC Slides. 22FA VC210
- ZONG Junzhe, RC Slides, 22FA VC210

Thanks!