Chapter 8
Concepts of Chemical Bonding
Chemical Bonds

•Three basic types of bonds:
➢Ionic
•Electrostatic attraction between ions
➢Covalent
•Sharing of electrons
➢Metallic
•Metal atoms bonded to several other atoms

Ionic Bonding

Energetics of Ionic Bonding

As we saw in the last chapter, it takes 495 kJ/mol to remove electrons from sodium.

Energetics of Ionic Bonding

We get 349 kJ/mol back by giving electrons to chlorine.

Energetics of Ionic Bonding

•But these numbers don't explain why the reaction of sodium metal and chlorine gas to form sodium chloride is so exothermic!

Energetics of Ionic Bonding

•There must be a third piece to the puzzle.

•What is as yet unaccounted for is the electrostatic attraction between the newly formed sodium cation and chloride anion.

Lattice Energy

•This third piece of the puzzle is the lattice energy:
The energy required to completely separate a mole of a solid ionic compound into its gaseous ions.

•The energy associated with electrostatic interactions is governed by Coulomb's law:

Lattice Energy

•Lattice energy, then, increases with the charge on the ions.

•Which substance would have the largest lattice energy-

Energetics of Ionic Bonding

By accounting for all three energies (ionization energy, electron affinity, and lattice energy), we can get a good idea of the energetics involved in such a process.

Energetics of Ionic Bonding

•These phenomena also helps explain the "octet rule."

Transition Metal ions

•In forming ions the transition metals lose their valence electrons first, then as many d electrons as required to reach the charge of the ion.

•Let us consider Fe

Covalent Bonding

•In these bonds atoms share electrons.

•There are several electrostatic interactions in these bonds:

➢Attractions between electrons and nuclei

➢Repulsions between electrons

➢Repulsions between nuclei

•The atoms in H_2 are held together because the two nuclei are electro- statically attracted to the concentration of negative charge between them.

•The shared pair of electron acts as a glue to bind the atoms together.

Polar Covalent Bonds

•Although atoms often form compounds by sharing electrons, the electrons are not always shared equally.

Electronegativity:

•The ability of atoms in a molecule to attract electrons to itself.

•On the periodic chart, electronegativity increases as you go…

➢…from left to right across a row.

➢…from the bottom to the top of a column.

Polar Covalent Bonds

•When two atoms share electrons unequally, a bond dipole results.

•The dipole moment, μ, produced by two equal but opposite charges separated by a distance, r, is calculated:

$\mu = Qr$

•It is measured in debyes (D).

Polar Covalent Bonds

The greater the difference in electronegativity, the more polar is the bond.

Lewis Structures

Lewis structures are representations of molecules showing all electrons, bonding and nonbonding.

Writing Lewis Structures

PCl_3

•Find the sum of valence electrons of all atoms in the polyatomic ion or molecule.

➢If it is an anion, add one electron for each negative charge.

➢If it is a cation, subtract one electron for each positive charge.

Writing Lewis Structures

•The central atom is the *least* electronegative element that isn't hydrogen. Connect the outer atoms to it by single bonds.

Writing Lewis Structures

•Fill the octets of the outer atoms.

Writing Lewis Structures

•Fill the octet of the central atom.

Writing Lewis Structures

•If you run out of electrons before the central atom has an octet…

…form multiple bonds until it does.

Writing Lewis Structures

•Then assign formal charges.

➢For each atom, count the electrons in lone pairs and half the electrons it shares with other atoms.

➢Subtract that from the number of valence electrons for that atom: The difference is its formal charge.

Writing Lewis Structures

•The best Lewis structure…

➢…is the one with the atoms bear formal charges close to zero.

➢…puts a negative formal charge on the most electronegative atom.

•The formal charges are written below the element and the oxidation numbers are listed below the structures.

Resonance

This is the Lewis structure we would draw for ozone, O_3.

Resonance

•But this is at odds with the true, observed structure of ozone, in which…

➢…both O—O bonds are the same length.

➢…both outer oxygens have a charge of −1/2.

Resonance

•One Lewis structure cannot accurately depict a molecule such as ozone.

•We use multiple structures, resonance structures, to describe the molecule.

Resonance

Just as green is a synthesis of blue and yellow…

…ozone is a synthesis of these two resonance structures.

Resonance

•In truth, the electrons that form the second C—O bond in the double bonds below do not always sit between that C and that O, but rather can move among the two oxygens and the carbon.

•They are not localized, but rather are delocalized.

Resonance

•The organic compound benzene, C_6H_6, has two resonance structures.

•It is commonly depicted as a hexagon with a circle inside to signify the delocalized electrons in the ring.

Exceptions to the Octet Rule

•There are three types of ions or molecules that do not follow the octet rule:

➢Ions or molecules with an odd number of electrons.

➢Ions or molecules with less than an octet.

➢Ions or molecules with more than eight valence electrons (an expanded octet).

Odd Number of Electrons

Though relatively rare and usually quite unstable and reactive, there are ions and molecules with an odd number of electrons.

Fewer Than Eight Electrons

•Consider BF_3:

➢Giving boron a filled octet places a *negative* charge on the boron and a *positive* charge on fluorine.

➢This would not be an accurate picture of the distribution of electrons in BF_3.

Fewer Than Eight Electrons

Therefore, structures that put a double bond between boron and fluorine are much less important than the one that leaves boron with only 6 valence electrons.

Fewer Than Eight Electrons

The lesson is: If filling the octet of the central atom results in a negative charge on the central atom and a positive charge on the more electronegative outer atom, don't fill the octet of the central atom.

More Than Eight Electrons

•The only way PCl_5 can exist is if phosphorus has 10 electrons around it.

•It is allowed to expand the octet of atoms on the 3rd row or below.

➢Presumably *d* orbitals in these atoms participate in bonding.

More Than Eight Electrons

Even though we can draw a Lewis structure for the phosphate ion that has only 8 electrons around the central phosphorus, the better structure puts a double bond between the phosphorus and one of the oxygens.

More Than Eight Electrons

•This eliminates the charge on the phosphorus and the charge on one of the oxygens.

•The lesson is: When the central atom is on the 3rd row or below and expanding its octet eliminates some formal charges, do so.

Covalent Bond Strength

•Most simply, the strength of a bond is measured by determining how much energy is required to break the bond.

•This is the bond enthalpy.

•The bond enthalpy for a Cl—Cl bond,

D(Cl—Cl), is measured to be 242 kJ/mol.

Average Bond Enthalpies

•This table lists the average bond enthalpies for many different types of bonds.

•Average bond enthalpies are positive, because bond breaking is an endothermic process.

Average Bond Enthalpies

NOTE: These are *average* bond enthalpies, not absolute bond enthalpies; the C—H bonds in methane, CH_4, will be a bit different than the

C—H bond in chloroform, $CHCl_3$.

Enthalpies of Reaction

•Yet another way to estimate ΔH for a reaction is to compare the bond enthalpies of bonds broken to the bond enthalpies of the new bonds formed.

Enthalpies of Reaction

$CH_4(g) + Cl_2(g) \longrightarrow$
$CH_3Cl(g) + HCl(g)$

In this example, one
C—H bond and one
Cl—Cl bond are broken; one C—Cl and one H—Cl bond are formed.

Enthalpies of Reaction

So,

$$\begin{aligned}\Delta H_{rxn} &= [D(\text{C—H}) + D(\text{Cl—Cl}) - [D(\text{C—Cl}) + D(\text{H—Cl}) \\ &= [(413 \text{ kJ}) + (242 \text{ kJ})] - [(328 \text{ kJ}) + (431 \text{ kJ})] \\ &= (655 \text{ kJ}) - (759 \text{ kJ}) \\ &= -104 \text{ kJ}\end{aligned}$$

Bond Enthalpy and Bond Length

- We can also measure an average bond length for different bond types.
- As the number of bonds between two atoms increases, the bond length decreases.