Introduction to Bonding and Properties_of Ionic and Molecular Covalent Compounds

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1. Ionic Bonding

- Ionic solids are generally stable and the bonds are relatively strong.
- electrostatic attraction between oppositely charged ions forming a 3-D crystalline lattice structure
- crystal lattice energy is the energy liberated when one mole of an ionic crystal is formed from the gaseous ions, high stability reached when energy is lost.

Properties

- do not conduct an electric current in the solid state, why?
- in the liquid phase, i.e when molten, they are relatively good conductor of an electric current, why?
- when soluble in water form good electrolytes, why?
- relatively high M.P. and B.P. (>500°C, >100°C)
- do not readily vaporize at room temperatures. These solids have relatively low volatility, low vapour pressure, this also indicates that a....
- brittle, easily broken under stress, why?

2. MOLECULAR CRYSTALS

Covalent bonding, the sharing of electrons is known as an intra molecular force.

Properties

- neither solids nor liquids conduct an electric current. This indicates ...
- many exist as gases at room temperature or as volatile solids and liquids, indicating ...
- M.P. and B.P. are relatively low, thus indicating ...
- Solids are soft and waxy
- Large amount of energy required to decompose in simple substance, indicating ...

COVALENT BONDING

How do these work?

Covalent bonding occurs between atoms that have quite high electronegativities, i.e. between two non-metals.

Example: $H + H \longrightarrow H-H$

In covalent bonding the two atoms involved share some of their valence electrons.
The attraction of the two nuclei for these shared electrons results in the atoms being bonded together.
The electrons in the bond spend enough time in the space between the two atoms to provide the "glue" that holds the atoms together.
Each nucleus is attracted toward the region of high electron density between them.
The bonded atoms come together for their electron clouds to overlap.
Only one pair of electrons with their spins paired can be shared by two overlapping orbitals.

The attraction of the two nuclei for these shared electrons results in the atoms being bonded together. The region of high electron density represented by the overlap indicates the covalent bond.

The possibility for bond formation exists when two atoms can approach each other in such a way that occupied orbitals with similar energies are able to come into contact or overlap.

The greater the amount of overlap, the stronger the bond, lower the energy of the atoms (more stable the bonds).
See: Potential Energy Curve for the formation of H_2

The Octet Rule

When forming covalent bonds, the atoms involved, other than hydrogen, tend to form bonds until they are surrounded by eight valence electrons. Therefore: # bonds = 8 - # valence electrons

Examples:
Carbon:
Oxygen:
Nitrogen:

Two covalent bonds between atoms constitutes a double bond, e.g. O_2

Three covalent bonds between atoms constitutes a triple bond, e.g. N_2
Note: bond length and type of bond, e.g. C —C, C == C, C $\equiv$ C
154 pm 134 pm 120 pm

Polar Covalent Bonds

When two atoms bonded together covalently are the same element, the sharing of those electrons is equal and the bond is said to be a pure covalent bond. Compounds made of different elements, with different electronegativities will form a polar bond. The electrons will be attracted to the atom with the higher electronegativity, more of the time.

Example: H F

Coordinate Covalent Bond (Dative Bonds)

Up until now we have always assumed that each element found in a covalent bond was responsible for providing one electron each to the bond. In a coordinate covalent bond, both electrons are contributed by one atom, e.g.

NH_4^{+1} H_3O^{+1} CO N_2O NHO_3

A coordinate bond differs from a covalent bond in only one respect. What is this?

Resonance Structures

Single bonds are longer than double bonds. Double longer than triple. (Look up the bond lengths in your Data Book)

Consider the Lewis structure for SO_3:

All of the above structures are equivalent, each has a double bond and two single bonds.

So you would expect that if the bond lengths were measured there would be some differences, right!

Well, that isn't the case. The bond lengths are all the same.

It is theorized that one pair of electrons is spread over all three bonds.

These are called **delocalized electrons**.

Covalent compounds with fewer than eight outer shell electrons per atom

When the elements with fewer than four outer-shell electrons per atom form compounds they usually lose those electrons to form ions. However, for small atoms, the relevant ionization energies may be so high that covalent bonding occurs instead. Since there are fewer than four electrons available for sharing, there will be fewer than eight outer – shell electrons per atom in the resulting compound.

Look at the ionic radii of elements with fewer than four electrons in their outer shells and select the three most likely to form covalent compounds. Explain your choice.

Be^{+2}, B^{+3}, and Al^{+3} have the smallest radii. This implies that ionisation energies are high, therefore these ions are least likely to be formed.:

Element	I. E_1 (kJ mol^{-1})	ionic radii (10^{-12} m)	
Be	900	30	(Be^{+2})
B	799	168	(B^{+3})
Al	577	45	(Al^{+3})

Draw Lewis structures for the following:

$BeCl_2$ BF_3 $AlCl_3$

How many outer-shell electrons are there around the central atom?

The above molecules exist in certain conditions, but in each case there is a tendency for the 'stable octet' to be reached by means of *coordinate bonding*.

Example: The molecule formed by the combination between NH_3 and BF_3

$H_3N: + BF_3 \longrightarrow H_3N \text{—>} BF_3$

For the *second period elements*, Li ⟶ F, which have only s and p orbitals available, *8 is the maximum number of valence electrons* that can be accommodated.

Covalent compounds with more than eight outer-shell electrons per atom

If the noble gas rule or the octet rule always applied, no atom could have more than eight electrons in its outer shell. As a result, no atom could have more than four single covalent bonds (or the equivalent) associated with it. The octet rule always applies for elements in the first two periods of the Periodic

Table (H to Ne) but many other elements show a covalency greater than four in some of their compounds.
Examples:

PF_5 BrF_5 SF_6 SiF_6^{-3} PCl_6^{-1} IF_7 XeF_3

Outermost shells of twelve electrons are quite common.

Only elements in the *third and subsequent rows* can do this because they make use of the unused d-orbitals.
Elements in Period 2 can **never** exceed an octet, because their valence shell (n = 2) can have $2n^2 = 8$ maximum of electrons .

The heavier noble gases do form a few compounds. Why?
Neil Bartlett at the University of BC prepared the first Noble gas compounds.
Paramagnetism
Compounds with unpaired electrons, example NO, exist. In these compounds one or more electrons remain unpaired, the total number of valence electrons is an odd number.
Example: ClO_2, 19 valence electrons, unstable and explosive, red-yellow gas, m.p = - 59 ^{O}C, b.p = 9.9 ^{O}C

Lewis Structures for Molecular Covalent Compounds

Lewis Structures are used to show which atoms are bonded together in a molecule. A single bond between atoms occurs when one pair of electrons (i.e. two electrons) are shared between 2 atoms. A double bond results when two electron pairs are shared and the sharing of three electron pais is a triple bond.

STEPS FOR LEWIS STRUCTURE CONSTRUCTION

STEP 1- Decide which atoms are bonded together and arrange the atoms on your page to reflect your decision, (see the "skeletal structures, p.225). It helps to first determine a "central atom", an atom to which many of the other atoms are bonded. Usually, the central atom is the atom which requires the most bonds to complete its valence octet. Another way to determine the central atom is usually the least electronegative (i.e. Si in SiF_4 or S in $SOCl_2$) Caution - this does not always work, especially where hydrogen is involved. Hydrogen in never the central atom.

STEP 2- Count all the valence electrons.

Example: BF_3
B: 1 atom x 3 valence electrons = 3 e
F: 3 atoms x 7 valence electrons = 21 e
TOTAL valence electrons = 24 e
NOTE: The charge on an ion indicates whether it contains extra electrons (negative ions) or has lost electrons (positive ions). Be sure to take these gains and losses into account where necessary.
Example: SO_4^{2-}
Add two electrons to the total number of valence electrons contributed by one atom of S and four atoms of O

Ex. NH_4^{1+}
subtract one electron from the total number of valence electrons contributed by one atom oh N and 4 atoms of H

STEP 3- Place 2 electrons (i.e. one pair of electrons) in each bond.

STEP 4- Complete the octets of the atoms attached to the central atom by adding electrons in pairs.

STEP 5- Place any remaining electrons on the central atom.

STEP 6- If the central atom does not have an octet, form double bonds. If necessary, form triple bonds.

NOTE: There are EXCEPTIONS to the Octet Rule

1. The valence shell for H is completed by 2 electrons (1 electron pair).

2. The valence shell for Li and all members of its family is completed by 2 electrons (1 electron pair).

3. The valence shell for Be is completed by 4 electrons (2 bonding pairs). NOTE: Although Be is an alkaline earth metal and therefore expected to form ionic compounds with non-metals, its ionization energy is too high for this to occur. Instead, it forms covalent bonds with a high degree of ionic character.

4. The valence shell for B is completed by 6 electrons (3 bonding pairs).
NOTE: Although the other members of its family will form ionic compounds with most non-metals, B doesn’t for the same reason sited above for Be. It, too, will form covalent bonds with a high degree of ionic character.

5. Valence electrons of elements of the third and subsequent rows of the Periodic Table may absorb enough energy during bonding so that some or all are excited into their own unfilled d-orbital (one electron per orbital).

This means that many more bonds than expected may form. (e.g. P with 5 valence electrons may form up to 5 bonds and S with 6 valence electrons may form up to 6 bonds.)

6. Some atoms, ions and molecules have orbitals containing a single unpaired electron. These are called paramagnetic because the unpaired electron(s) is/are affected by a magnetic field. Paramagnetic substances have an ODD number of valence electrons so no matter how hard you try, your Lewis structure will always show an unpaired electron. e.g. NO and NO_2

Assignment

1. Draw the Lewis electron dot structure for:
(a) CH_4 (b) CH_2Cl_2 (c) PCl_3 (d) PO_4^{-3} (e) BrO_3^{-1} (f) NO^{+1} (g) HCN (h) CH_2O
2. Draw the Lewis electron dot structure for:
(a) SO_3 (b) O_3 (c) NO_3^{-1} (d) NO_2^{-1} (e) CO_3^{-2} (f) $HCOO^{-1}$

Shapes of Molecules and Ions: Valence Shell Electron Pair Repulsion Theory (VSEPR)

Molecular geometry has become an important area of study. For instance, the effectiveness of many drugs can be attributed to their geometry being just right so they can either aid or hinder some biochemical process.
Many drugs today are first being designed theoretically on a computer. A sound knowledge of the geometry of molecules is necessary.
Once a drug has been designed in theory, it is then up to the bench chemist to design a synthesis in as few steps as possible. Some drugs are found accidentally through empirical evidence.
Finding the structure of these molecules is also necessary in order to learn what kind of action it may have on the target molecules.

The key to understanding molecular geometry is knowing what arrangement atoms or groups of atoms will take around the central atom(s) in a molecule or an ion.

A method which is surprisingly accurate called **Valence Shell Electron Pair Repulsion Theory or VSEPR** for short.

The molecular shapes are named according to the geometric shapes of the solid figures defined by the bonds between the central atom and the atoms attached to it.

The basic premise of the method is that electron pairs in the valence shell of a polyvalent ion (an atom capable of forming more than one covalent bond) are always arranged in a way so as to minimize the repulsions between them. This arrangement applies to both bonding pairs (shared) and non-bonded pairs (lone pairs) of electrons.

Main concepts of VSEPR:

1. The geometric shape of a molecule can be predicted by focussing attention on the structure's central atom(s) and the mutually repulsive valence shell electron pairs surrounding it. This approach is known as the valence shell electron pair repulsion (**VSEPR)** approach.
2. Two kinds of valence electron pairs may populate the central atom(s) of a molecule:
   -bonding pairs and non-bonding pairs (lone pairs). Repulsions between adjacent pairs of electrons vary in strength depending upon whether they are bond pair-bond pair (BP-BP), bond pair-lone pair (BP-LP), or lone pair-lone pair (LP-LP). The repulsion order is considered to be:

   BP-BP < BP- LP < LP- LP

   This concept helps explain the spatial distribution of electron pairs; lone pairs spontaneously arrange themselves to be as far apart as possible, bond pair-lone pairs are next, and bond pair-bond pairs are found to be the closest.
3. In the VSEPR approach, electron pairs on the central atom(s) are viewed as assuming positions around that atom that minimize electron pair-electron pair repulsions. The resulting electron pair geometry about the central atom determines the placement of the atoms bonded to the central atom(s). The resulting arrangement of bonded atoms determines the molecular geometry.
4. Molecular geometries may be classified according to the number of lone pairs and bonding pairs of electrons surrounding the central atom. e.g.:
   two bonding pairs = linear; three bonding pairs = trigonal planar; two bonding pairs and one lone pair = angular (bent); and so forth.
5. Molecules containing one or more polar covalent bonds may either be polar or non-polar, based on the extent of the bond polarities and molecular geometry.

6. The shape and polarity (or lack of polarity) of a given molecule helps determine the general properties of the substance composed of these molecules.

Assignment

1. Using all the Lewis structures that were drawn, predict the shape of each of the structure.

2. The molecules SiF_4, SF_4, and XeF_4 all have molecular formulas of the type XF_4, but the molecules have different molecular geometries. Predict the shape of each molecule and explain the origin of the differing shapes.

3. The three species NO_2^+, NO_2, and NO_2^{-1} all have a central nitrogen atom. The O-N-O bond angles in the three species are 180^0, 134^0, and 115^0, respectively. Explain this variation in bond angles.

4. The H — P — H bond angle in PH_3 is 93^0; in PH_4^{+1} it is 109.5^0. Account for this difference.

Predicting the Polarity of Molecules

Use the molecular structures that were derived from the VSEPR model along with electronegativities to predict whether or not molecules are polar.

Recall that polar bonds involve an unequal sharing of electrons, the presence of which, in certain compounds can make the molecule polar.

In order to determine if a molecule is polar:

1. Determine if the molecule has polar bonds.
2. Determine the shape of the molecule.

A molecule that contains polar bonds will not necessarily be a polar molecule.

If the shape of a molecule is such that the polar bonds are **symmetrically** arranged around the central atom, then their **effects may cancel, i.e. their dipoles will cancel** and there will be **no charge separation**, thus the molecule as a whole will be non-polar.

Symmetrical Molecules have the following basic geometries:

Linear, trigonal planar, tetrahedral, trigonal pyramidal, octahedral.

If a molecule is one of these shapes- **with identical atoms attached to a central atom**, the molecule is said to be **symmetrical and non-polar**.

For a molecule to be polar:

It must contain polar bonds, **and** its shape must be such that the **dipoles do not cancel** out.

The **dipole moment** is a measure of the polarity of a molecule**.**

(Dipole moment is measured in units of Debye)

Non-polar molecules have a zero dipole moment.

The more polar a molecule, the greater the dipole moment.

Assignment

1. Using all the Lewis structures that were drawn, predict the shape of each of the structure, and further predict whether each molecule is polar or non-polar.

2. The PF_3 molecule has a dipole moment of 1.03 D, but BF_3 has dipole moment of zero. How can you explain the difference.
3. Despite the larger electronegativity difference between the bonded atoms, $BeCl_{2(g)}$ has no dipole moment whereas $SCl_{2(g)}$ does possess one. Account for this difference in polarity,

Intermolecular Forces of Attractions (IMFA's)

Covalent bonding, the sharing of electrons is known as an **intramolecular** force.

Intramolecular: these forces are within the molecule.

So far we have dealt mainly with these, however we will now look at **intermolecular forces**. These are the forces that exist **between** one molecule and another.

They are often referred to as Van-der-Waals forces after Johannes Van der Waals, a Dutch scientist who studied these forces and lived between 1837 and 1923.

However, we will refer to the individual forces using separate names.

Intermolecular forces are responsible for changes of state, and all other physical properties such as melting point, boiling point, solubility and conductivity.

Solid ⟶ liquid ⟶ gas
Strong intermolecular forces Weak intermolecular forces

There are **three** principal types of intermolecular forces: dipole – dipole forces, London forces, and hydrogen bonding.

1. The Dipole-Dipole Force

These forces exist between polar molecules, i.e. those with a permanent dipole. Whether or not a molecule is a dipole depends not only on the bond polarity but also upon the molecular geometry and the presence of lone—pair electrons.

The partially negatively charged end of one molecule with dipole moment is electrostatically attracted to the partially positively charged part of another molecule. (That's why it is called dipole - dipole, there must be at least two molecules with dipoles !!!)

The dipole – dipole attraction must be overcome in melting a solid or vaporizing a liquid, it thereby influences the melting point, heat of fusion, boiling point, and heat of vaporization.

These forces are not that strong, only about 1% of the strength of your average covalent bond.

The strength will depend on: difference in electronegativity, i.e. strength of the dipole moment.

The following table illustrates the effect of dipole – dipole forces.

Silane, SiH_4, phosphine, PH_3, and hydrogen sulphide, H_2S, all have similar molecular mass, however silane, SiH_4 is non-polar and hence has the lowest melting point, boiling point and the lowest heats of fusion and vaporization.

Phosphine, PH_3, and hydrogen sulphide, H_2S, are both polar, however hydrogen sulphide has a dipole moment twice that of phosphine, PH_3, and thus has the highest melting point, boiling point and the highest heat of fusion and vaporization of the three compounds.

Property	**silane, SiH_4 non-polar**	**Phosphine, PH_3 polar**	**Hydrogen sulphide, H_2S polar**
Molecular mass (g mol^{-1})	32.09	34	34.08
Dipole moment (D)	0	0.55	1.1
Appearance	Colourless gas	colourless gas	colourless gas
Melting point (^{O}C)	– 185	– 134	– 85.6
Boiling Point (^{O}C)	– 111	– 87.8	– 60.8

2. The London Dispersion Forces (Named after Fritz London.)

London forces act on **ALL** atoms and **ALL** molecules.

London forces is the only intermolecular force present in non-polar molecules.

London forces are responsible for the condensation, at low temperatures , of even monatomic noble gases.

Sometimes London forces are referred to as “van der Waals attractions”. Sometimes also referred to as “dispersion forces”.

London forces are the result of momentary shifts in the symmetry of the electron cloud of a molecule, i.e. the electron cloud becomes polarized. In a large collection of molecules, at any given moment collisions are taking place, with resulting polarization of the molecules.

As soon as a slight positive charge is produced at one end of one molecule, it induces a slight negative charge in one end of the molecule next to it — resulting in an induced dipole.
Thus, a temporary force of attraction exists between these molecules.

London forces are the forces of attraction due to temporarily induced dipoles in atoms and molecules that are very close together.

Since London forces are the forces of attraction between fluctuating dipoles, they are extremely weak.

The strength of London forces depends on two factors:
1. The size of the molecule, they increase with number of electrons, i.e. with increasing molecular mass.

Similar molecular geometry, increasing molecular mass :

property	methane, CH_4	silane, SiH_4
polarity	non-polar	non-polar
molecular mass (g mol^{-1})		
boiling point (^{O}C)	— 161	— 111

2. The geometry of the molecule, they increase with surface area of molecule:
Linear vs. branched chain molecule: a larger region gives greater opportunity for dipole interaction than when a small amount of contact is possible, (because spheres can make contact at only one point).

Same molecular mass, decreasingly compact shape:

	Pentane, C_5H_{12}	dimethylpropane, C_5H_{12}
molecular shape	$H_3C – CH_2 – CH_2 – CH_2 –CH_3$	$H_3C – C\ (CH_3)_2 — CH_3$
boiling point (^{O}C)	36	9.5

In each series of compounds above, the increase in boiling point is due to increasing London forces.

3. The Hydrogen Bond
This is just a special case of the dipole-dipole interaction.

This is what happens when you have BIG dipoles.

When a hydrogen atom is covalently bonded to an electronegative atom that strongly attracts the shared electron pair, the small hydrogen atom is left with very little electron density around it.

Thus, the hydrogen atom carries a small positive charge and can act as a bridge to another electronegative atom.

A **hydrogen bond** is the attraction of a hydrogen atom covalently bonded to an electronegative atom for a second electronegative atom. HCl

Strong hydrogen bonds form between **hydrogen atoms** and the big three highly electronegative elements: **Fluorine, Oxygen , Nitrogen**; which are small and have their negative charges highly concentrated in a small volume.
The hydrogen is basically stripped of its electrons leaving ________________.
This means the positive end will form an attraction to just about anything negative... like ...

Hydrogen bonds are the strongest intermolecular forces.

It is the strength of the hydrogen bonds in water that is responsible for the unique properties of water.

The hydrogen bond between hydrogen and the most electronegative element, fluorine , is the strongest type of hydrogen bond:

The effect of hydrogen bonding on the properties of compounds is clearly evident when comparing the properties of the hydrogen-bonded, second period hydrides ammonia, NH_3, water, H_2O, and hydrogen fluoride, HF, with the non-hydrogen-bonded third-period hydrides phosphine, PH_3 , hydrogen sulphide, H_2S, and hydrogen chloride, HCl:

In each of the comparable pairs from the same periodic table family:

NH_3 and PH_3 H_2O and H_2S HF and HCl

the compound with the smaller molecular mass is less volatile, and has the higher boiling point.
This is due to the extra energy needed to break the intermolecular hydrogen bonds in NH_3, H_2O and HF.

See Graph of Boiling Points of Hydrides of period 2, 3, and 4 versus Molar Mass

Assignment

1. What type of IMFA are found in each of the following molecules:

a) CO_2 (b) $CH_2\ Cl_2$ (c) NH_3 (d) CH_4 (e) C_2H_5OH (f) I_2

2. The normal boiling points of N_2, O_2, and NF_3 are –196EC, -183EC, and -129EC, respectively. Explain why the boiling point of NF_3 is substantially higher than the boiling points of nitrogen and oxygen.

3. For the following substances, determine which one has a higher melting point.

(a)Xe or Ne (b) SbH_3 or AsH_3 (c) CH_4 or C_4H_{10} (d) I_2 or F_2 (e) NH_3 or PH_3

4. The following fluorides of xenon have been well characterized:

XeF_2 XeF_4 XeF_6

Draw the Lewis structure for each, state the molecular geometry for each. Determine if each is polar or non-polar, and hence state the important intermolecular forces in each.

5.The molar mass of methanol (CH_3OH) is very close to that of ethane (CH_3CH_3). Which of these substances will have the higher boiling point. Explain.

6. Describe some of the properties of water that can be attributed to hydrogen bonding.

7. Describe the intermolecular forces that exist between the following species:

a. Methanal, HCHO and H_2O b. CS_2 and CCl_4 c. BrF and BrCl

8. Place the following elements in order of increasing London dispersion forces: Xe, Ar, Kr.

9. Which substance pair should have a higher melting point: (a) I_2 or Br_2, (b) O_2 or Cl_2. Justify!

10. Would you expect to find significant hydrogen bonding between molecules of :

a) PH_3 b) CH_3F c) HBr

11. One of the following substances is a liquid at room temperature, whereas the others are gases. Which one do you think is a liquid?

a. CH_3OH b. C_3H_8 c. N_2 d. N_2O

12. Would you expect to find a significant degree of hydrogen bonding between molecules of :

d) NH_3 b. CH_3OH c. HBr

13. The following compounds all have very similar molar mass. Rank the following compounds in order of increasing:

i. Solubility in a polar solvent ii. Boiling point

C_3H_8, CH_3CHO, C_2H_5OH

14. Explain the order of the following boiling points:

Molecule	b. p. (^{O}C)		
C_6H_6	80	C_6H_5-Cl	132
C_6H_5-Br	156		
C_6H_5OH	182		