# A STUDY OF PHYSICAL CHARACTERISATION AND ELECTRONEGATIVITY OF FEW MOLECULES

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**ABSTRACT**

A study of relation between band gaps of semiconductors with quantities like heats of formation per mole[2], electro negativities[5] is taken up. The band gap energy depends upon binding energy and effective change of atoms. The energy gap has a tendency to increase progressively in going from element to II-VI compound semiconductor. This is a tendency of increasing ionicity in the chemical bond. The bond energies are calculated by methods of Thermo chemical process, Pauling method, Matcha method and Reddy etal[24-26] method. The empirical relation proposed by Reddy et al is used to calculate bond energies of both ionic and covalent molecules. The results that are obtained by Reddy et al method fairly agreed with Pauling empirical relation[16], Matcha et al method.

**Keywords:** Chemical Bonding energy, Binding energy, Ionicity, Ionization of Potential.

## Introduction

Chemical bonding is an interpretation of the physical reality of the association of same and different kinds of atoms, among more complex units of structures. Most of the general principle of molecular structure and nature of chemical bonding were formulated long ago by chemical facts. The understanding of principles of molecular structure became easy by the advent of powerful experimental techniques. As a result structural chemistry became significant to various branches of chemistry, neology and medicine.

The concept of chemical bond and molecular structure was introduced[1]. In 1857 kekulae[2] deduced that the carbon is tetravalent and introduced the C atoms would form bonds with one another. The tetravalent of C is independently proposed by Couper[3,4], Frankland[5], Couper, Butlerov[6], formulated theory of valence and wrote structural formulae. In 1859 Kekule formulated multiple rings to C and in 1865, he formulated hexagonal flat ring of C having alternate single and double bonds. This Kekule's structure of C successfully explained the isomerism of benzene and the development of molecular structure.

Molecular orbital theory is another method of calculation of chemical bonds based on atomic orbitals. Phillips[7] suggested dispersion theory to discuss chemical bond in crystals by applying quantum mechanics. In 1857, Pasteur investigated the optical isomerism of tartaric acid and similar compounds, the results were interpreted by Van Hoff[8,9] and le Bel[10].

According to Van Hoff, in the case of four affinities of an atom of C are saturated by four different univalent groups, two and only two different tetrahedral can be obtained of which are the mirror image of the other. This development marked the beginning picture of a molecule of atoms found by bonds, which are called as ball and stick model. The theory of valence explains the number of bonds, their length and angles between them.

The electron was discovered by JJ Thomson[12]. In 1913 Bohr[13] proposed a dynamic model for electrons by applying Quantum theory

which gave a satisfactory explanation to many features of atomic spectral lines. Bohr introduced that only certain orbits of the electrons around the nucleus are allowed. Bohr's theory could not explain the stability of atom although the stable orbits were identified. Bohr suggested that an explanation for the chemical bond could be found in a dynamic model of electron.

In 1916, Lewis[14] basing on Bohr model developed the electronic theories of bonding. He formed the basis of the electronic theory of valence which not only discussed the formation of ions by completion of stable shells of electrons but also the formation of chemical bond, called as covalent bond which is formed by sharing of two electrons between atoms. The symbolism of dots is represented for electrons in the bonding.

Lewis emphasized the pairing of shared or unshared electrons and of the stability of eight electrons. According to the theory of valence, there are two main types bonds (i) Ionic bond (ii) Covalent bond.

In order to obtain stable octets between the atoms, pairing of electrons is identified as driving force for bond formation. This idea of electron pairing had successful theories of chemical bond which was a description of electron sharing in wave mechanical terms.

The theory of Quantum mechanics helps in calculation of properties of simple molecule and phenomena involved in formation of covalent bond between two atoms.

The chemical bond is defined by Pauling[15] as "There is chemical bond between two atoms or groups of atoms in case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species".

The bonds are classified into

*(i) Electrostatic or ionic bond:* Two atoms or groups of atoms having definite electronic structure essentially independent of the presence of the other atom or group and such that electrostatic interactions are set up that lead to strong attraction and the formation of a chemical bond. The most important electrostatic bond is the ionic bond. These bonds might also result from the attraction of anion for the induced dipole of a polarizable molecule or from a mutual interaction of a permanent electric dipoles of the two atoms.

*(ii) Covalent bond:* Covalent bonding arises when molecular orbitals formed by overlap of atomic orbitals, are occupied by a pair of electrons with opposed spins; direct overlap forms σ bonds and additional overlap of parallel atomic orbitals forms π bonds. Covalently bonded molecules are capable of rotational and vibrational motion on absorption of energy. Polar covalent bonds are formed from elements with different electronegativity, the resulting dissymmetry of charge gives rise to molecular dipole moments. Permanent dipoles are source of secondary forces of attraction between molecules and induced dipoles give rise to weaker inter-molecular forces.

*(iii) Metallic bond:* The bond formed between the atoms of the metal is called Metallic bond. Metals are distinguished chemically by loss of electrons to form cations, physically by properties which are characteristic of metallic bonding in Solid State. Partly filled atomic orbitals having high-lying elements requires metallic bonding, so that the electrons occupied can easily promote energy bands which are delocalized, thus permitting conduction of heat and electricity. Study of chemical properties become a major tool, the distances of separation and relative arrangement of nuclei are observed by X-ray, electron and neutron diffraction methods. Electron diffraction in molecules is studied by light polarization, dielectric constant measurement and UV spectral measurements. Rotational and vibrational spectra throws light on motions of nuclei.

## CONCEPT OF ELECTRONEGATIVITY:

There is a quantitative relation between the dipole moment of bond and its ionicity. The term ionicity can be understood by the concept of Pauling[16,17] electronegativity of the atoms. There is a well stabilized theory regarding ionicity and electronegativity of the atoms or differences in ionization potentials. Ionicity is used as a tool for studying structural analysis of crystals[18]. The concept of crystal ionicity has proved to be useful unifying concept for understanding chemical trends in diverse problems in Chemistry and Solid State Physics.

Crystallographers noted that binary compounds of atoms A & B with large differences in

electro negativity tended to form rock salt structures, while small differences in electro negativity favored more open covalent structures. When the difference in electro negativity is large the heat of transformation of A B bond is large, providing a thermo chemical use for the concept of electro negativity. The greater the difference in electro negativity the more ionic the bond is said to be and the greater is its heat of formation.

Pauling introduced the concept of electro negativity of atoms in 1932 and described its quantitative aspect as a measure of tendency of an atom in a molecule to attract electrons to itself. He was forced to introduce this idea to explain the reason why the energy of a heteropolar bond A-B is higher than both the average arithmetic and geometric mean value of the homopolar bond energies of molecule A-A and B-B. The difference in energy is equated in terms of extra ionic energy, which is denoted by $\Delta_{AB}$. For a diatomic molecule $\Delta_{AB}$ can be estimated in terms of electro negativity difference of the atoms. This concept relates the bond energy with the electro negativity. The quantitative description of the electro negativity difference gives the concept of the nature of bonding. Pauling pointed out that certain bonds are essentially covalent with only 5% or 10% of ionic character, that others are about equally ionic and covalent and that others are essentially ionic. He formulated a relation between the partial ionic characteristic of a bond and the difference in electro negativities of the two atoms between which the bond is formed. It gives an insight in understanding the nature of bond.

A systematic relationship between electronegativity and the atomic number of the elements of the periodic system given by Pauling are represented in table 1. It is clear that the electronegativity increases with the increase of atomic number, but it is not in the case of some group elements. In order to estimate the ionic character of the single bond between atoms A & B electro negativities are essential.

According to the equation proposed by Pauling the bonds between atoms with electro negativity difference 1.7 have 50% of ionic and covalent characteristic.

The heats of formation of chemical bonds play a fundamental role in Molecular and Crystal Physics. Phillips pointed out that spectroscopic approach with heats of formation involves solving the crystalline wave equation using the best one electron potential. The optical spectroscopy can supplement one electron terms and facilitate to derive Pseudo potential form of factors for each term. The determination of parameters from the optical spectrum gives a basis in quantum mechanics.

Table 1. General Properties of Various Bonds

| S NO | Properties | Ionic Bond | Covalent Bond | Metallic Bond | Vander walls Bond |
|------|-----------|-----------|--------------|---------------|-------------------|
| 1 | Bonding force | Electrostatic attraction of oppositely charged ions. | Mutual sharing of Valence electrons between atoms. | Attraction between the ion cores and conduction electron gas | Electrostatic force due to oscillating dipoles, or permanent dipoles between molecules or dipole between similar molecules. |
| 2 | Energy of bond KJ/mol. | $(500\text{-}1000)\,10^3$ | $(60\text{-}700)\,10^3$ | $(100\text{-}350)\,10^3$ | |
| 3 | Character of bond | Non-directional | Directional | Non-directional | Directional for dipole and hydrogen bonds, non-directional for dispersion ones |
| 4 | Bond formation condition | When one of the atoms has smaller | When atomic orbitals of two | For elements having small | For molecules forming dipoles. |

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| | | number of valence electrons. | atoms overlap | number of valence electrons. | |
|---|---|---|---|---|---|
| 5 | Conductivity | Low conductivity | Low electrical conductivity | Highly reflective | Low conductivity |
| 6 | Lusture | Transparent or coloured, but not highly reflective. | Transparent to highly reflective | Highly reflective. | Transparent or coloured. |
| 7 | Colour | Wide variety of good colours | White to grey | Usually grey with a few exceptions | Colour derives from molecule, not from crystal. |
| 8 | Density | Intermediate | Intermediate | High | Low |
| 9 | Clevage | Very Good | Fairly Good | Difficult except at low temperatures because of high ductility. | Easy |
| 10 | Melting Point | Intermediate | High | Intermediate | Low |
| 11 | Vapor State | Diatomic molecules or atoms | Atoms or occasionally small molecular aggregates. | Atoms or occasionally small molecular aggregates. | Molecules |
| 12 | Examples | NaCl, CsCl, etc | Diamond, Germanium, etc., | Al, Cu, Na, etc., | Argon, Calomel, ice, solidCo$_2$, etc., |

Table 2.Electro Negativity Values of Elements in a Periodic Table

| H 2.1 | | | | | | | | | | | | | | | | | He - |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Li 0.97 | Be 1.47 | | | | | | | | | | | B 2.01 | C 2.50 | N 3.07 | O 3.50 | F 4.10 | Ne - |
| Na 1.01 | Mg 1.23 | | | | | | | | | | | Al 1.47 | Si 1.74 | P 2.06 | S 2.44 | Cl 2.83 | Ar - |
| K 0.91 | Ca 1.04 | Sc 1.20 | Ti 1.32 | V 1.45 | Cr 1.55 | Mn 1.60 | Fe 1.64 | Co 1.70 | Ni 1.75 | Cu 1.75 | Zn 1.66 | Ga 1.82 | Ge 2.02 | As 2.20 | Se 2.46 | Br 2.74 | Kr - |
| Rb 0.89 | Sr 0.99 | T 1.11 | Zr 1.22 | Nb 1.23 | Mo 1.30 | Tc 1.36 | Ru 1.42 | Rh 1.45 | Pd 1.35 | Ag 1.42 | Cd 1.45 | In 1.49 | Sn 1.72 | Sb 1.82 | Te 2.01 | I 2.24 | Xe - |
| Cs 0.86 | Ba 0.97 | La 1.08 | Hf 1.23 | Ta 1.33 | W 1.40 | Re 1.46 | Os 1.52 | Ir 1.55 | Pt 1.44 | Au 1.42 | Hg 1.44 | Tl 1.44 | Pb 1.55 | Bi 1.67 | Po 1.76 | At 1.90 | Rn - |
| Fr 0.85 | Ra 0.97 | Ac 1.00 | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | |
| | | | Ce 1.08 | Pr 1.07 | Nd 1.07 | Pm 1.07 | Sm 1.07 | Eu 1.01 | Gd 1.11 | Tb 1.10 | Dy 1.10 | Ho 1.10 | Er 1.11 | Tm 1.11 | Yb 1.06 | Lu 1.11 | |
| | | | Th 1.11 | Pa 1.41 | U 1.22 | Np 1.22 | Pu 1.22 | Am 1.2 | Cm 1.2 | Bk 1.2 | Cf 1.2 | Es 1.2 | Fm 1.2 | Md 1.2 | No 1.2 | | |

## Results and discussion

The Phillips theory elucidates the specific mechanisms which play an important role in determining heats of formations, it is not only more accurate than general chemical theories of the heats of transformation of molecular bonds but it also provides insight into characteristically crystalline effects. This theory involves in a number of independent factors and independent parameters. Pauling's theory basically contains the concept of extra-ionic energy and the elemental electronegativity. Phillips suggested that the heat of formation is proportional to $f_i$, the spectroscopic

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ionicity where in covalent and ionic energy gaps are involved.

In the present study the various parameters like Bond energy, Ionization potential and Ionicity of various materials are estimated utilizing different theories. Pauling described the bond energy with electronegativity differences. The correlation between ionicity (differences in Ionization potentials) and dipole moment is already interrelated. Garbo et al[19,20]., have given a relationship between effective nuclear charge and the ionization potential. The average effective charge determines the bonding energy of the valence electrons of the matter and the ionicity describes the nature of bonding[21-26].

The brief introduction enables the correlation between bond energy, ionicity and ionization potential of the crystals. The concept of the above theories have been tested in various crystals, the estimated parameters are in good agreement with the experimental values available. The approach adopted in various theories is oversimplified and interrelate different properties of the crystals which stimulate basic research in the field of physical characterization. This work is a part of M.Phil., titled 'Bonding Characteristics of Materials' submitted by the author at S K University during 1997.

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