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CHEMICAL BOND OF IONIC AND PARTIALLY COVALENT CRYSTALS

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ABSTRACT:

Rock Salt, sodium chloride is an ionic crystal and is the example of face centered cubic (fcc) lattice. The basis consists of one Na atom and one Cl atom separated by one-half the body diagonal of a unit cube.In sodiumchloride, sodium atom loses its outer electron and so acquires an excess of positive charge while the Cl atom has acquired the electron lost by the Na atom into its structure completing the M electron group and at the same time acquiring an excess of negative charge. Two such ions will attract one another because of the electrostatic forces between their excess charges .But they can not approach to within less than a certain distance owing to strong forces of repulsion which must set in when their outer electron shells come in to close proximity.When the centers of the two ions come within a certain distance of one another, attraction and repulsion balances and they can approach no closer and it is in this sense we must think of them as possessing a definite radius.

INTRODUCTION:

NaCl can be considered as two face centered cube sub lattices, one of Na ions having its origin at the points (0,0,0) the other of Cl ions having its origin mid way along a cube edge say, at point (a/2,0,0).There are four units of NaCl in each unit cube with atoms in position-

Na:	0,0,0,	½,½,½,	½,0,½,	0,½,½,
Cl	½,½,½,	0, 0, ½,	0,½,0,	½,0,0,

Each atom has a nearest neighbors six atoms of the opposite kind.The lattice is simple cubic if the difference between Na and Cl is ignored

(b) Cesium Chloride Structure:-

This is another combination of cubic structure. The lattice points of this compound are two interpenetrating simple cubic lattices, the corner of one sublattice is the body center of the other .One of the sublattice is occupied by cesium ions, the other by Cl ions.The resultant structure is termed as cesium chloride structure.There is one molecule per unit cell. Since each atom is at the center of a cube of atoms of the opposite kind, hence the coordination number is eight.

(c) Calcium Fluoride (Fluorite) structure:-

The calcium fluoride is composed of three face centered cubic lattices, one for Ca^+ and two for F^- ions.The fluoride ions form a primitive cubic cell, and the centers of alternate cells are occupied by calcium ions. The co-ordination number and the structure are closely related to the zinc-blende structure. Each F^- is tetrahedrally co-ordinatedby four Ca^{++} ions and each Ca^{++} is surrounded by two tetrahedral of F^- ions. For convenience F^- ions can be divided in to two categories F (1) and F

(2). F (1) and F (2) ions are shifted with respect to Ca^{++} ions by (1/4,1/4,1/4) and F92) by (3/4,3/4,3/4) respectively.

(d) Zinc-blende structure:-

The cubic zinc sulphide structure results from the diamond structure (Diamond structure is composed of two fcc lattices displaced from each other by one-quarter of a body diagonal) when Zn atoms are placed on one fcclattice and s atoms on the other fcc lattice . the co-ordinates of Zn atoms are 0,0,0; 0, ½, ½; ½,0, ½; ½,½,0; the co –ordinates of the S atoms are ¼,¼,¼; ¼, ¾, ¾; ¾,¼,¾; ¾, ¾,¼.There are four molecules of the of ZnS per unit cell. Each atom has about it four equally distant atoms of the opposite kind arranged at the corners of a regular tetrahedron. The diamond structure possesses a center of symmetry at the mid point of each line connecting nearest neighbour atoms; the ZnS structure does not inversion symmetry. This is particularly evident if we look at the arrangement of atoms along a body diagonal. In diamond the order is CC------CC-----CC ,Where the dots represent vacancies . In ZnS the order is ZnS --------ZnS ----ZnS , Which is not invariant under inversion . This is why atoms or ions in ZnS Type solids are not situated at these the centers of inversion. It is thought that tetrahedral bond arrangement of the ZnS structure is a sign of covalent bonding; ionic bonds would tend to favour structure is a sign of covalent bonding; ionic bonds would tend to favour structure with a higher number of nearest neighbours (co- ordination number).However, it has been found that the chemical bond of the compounds of this class under study is of mixed nature i.e. partially ionic and partially covalent. In the following section we provide a qualitative as well as quantitative account for the theories of chemical bonding.

1.2 Nature of the Chemical Bond:

Crystal ionicity is one of the very important parameter concerning semi-conducting materials. Crystal ionicity can be used in tackling problems related to various fields in solid state physics as well as chemistry such as crystal structure, band structure, elastic constants, alloys problems, effective charges, cohesive energies, heat of formation, micro hardness etc [1-5]. The ionicity of a bond compared to the fraction f_i of a covalent or homopolar character, by definition these fraction satisfy the relation $f_i + f_h=1$.In an elemental crystal like Si, one most have $f_h=1$and $f_i=0$,on the other hand, we shall find that rock salt crystals like NaCl are more than 90% ionic character i.e. $f_i=0.9$ and $f_h=0.1$,the more ionic crystals exhibit larger energy gaps between the balance band and conduction bans. Because of this the more ionic crystals are less polarizable and they correspondingly smaller dielectric constants. Various models and phenomenological theories [1,2,29-34] have been put in order to investigate crystal iconicity. In this section we shall discuss some important theories in brief as follows: -
(a) Coulson's Models. (b) Pauling's Models. (C) Phillip's Models.(d) Tubb's approach. (e) Phillips Van-Vechten Model.

(a) Coulson's Model:-

Coulson [49], used an explicit representation for ionicity, based on atomic orbital each valence wave function can be written in the form of,

$\Psi_{valence}=\Psi_A+ \lambda \Psi_B$

Where Ψ_A and Ψ_B denote a hybrid valence orbitals centered an atom as A and B respectively. The trial wave function (1.1) is inserted in the wave equation and an estimate is made of the total energy. When the latter is minimized, the best value of λ is obtained. Because the two atomic wave function in (1.1) are assumed to be orthogonal and Coulson crystal ionicity is defined by the following relation,

f_i= [(prob.on A)-(prob.on B)/(prob.on A)+(prob.on B)]   (1.2)

(prob.=probability of finding a valence electron)

Or, $f_i = (1-\lambda^2)/(1+\lambda^2)$ (1.3)

With in the framework of quantum theory based on atomic orbitals, equations (1.1) to (1.3) probably give a good definition of ionicity as can be obtained.

The trouble with this definition is that it suffers from two weaknesses.

(i) The restriction to a trial function of the form (1.1) is must to severe, because the formation of bond charges the localized orbital about each atom from what they were in free atom, making (1.1) a poor choice for defining that bond ionicity.

(ii) The energy calculated does not give the cohesive energy of the bond.

(b) Pauling's Model: -

The second objection regarding Coulson's ionicity defined by Pauling based his definition [88-89] of ionicity not on the total energy of the bond but on empirical heat of formation. Pauling criterion of ionicity is based on the electronegativity consideration [86-90]. It is observed that binary compounds of two different atoms with small differences in electronegativity favour open covalent structure, while large difference in electronegativity tend to from 'NaC1' structure. Moreover, when the difference in electronegativity is large, the heat of formation of the bond is also large, providing a thermochemical use for the concept of electronegativity, which is defined by Pauling **"The power of an atom in a molecule to attract electrons to itself"**. Thus greater is the difference in electronegativity, the more ionic bond is said to be and greater is the heat of formation. The above definition of Pauling reflects the origin of the concept of charge flow and focuses attention on the actual charge centered on each atom. However, even if the complete charge distribution of the molecule or crystal is known precisely, it is difficult to scheme out the decomposition of the total distribution into a superposition of distributions centered on component atoms. To circumvent the difficulty of calculating charge distribution, Pauling switched over to the bond energies, which may easily to be calculated from the heats of formations when two elements e.g. A & B differ in electronegativity (denoted by X_A and X_B) of the AB bond satisfies the relation.

$D_{AB} > (D_{AA} + D_{BB})/2$ (1.4)

Where D_{AA} and D_{BB} represent the bond energies of the elements A and B respectively. The 'AB' bond energy refers to a structure in which the coordination numbers of A & B are different from what they were in the pure 'A' or pure 'B' compounds, showing the orbital dependence of electronegativity. The ionization energies of free atoms are known to be quite different for different multiples and when suitable average over multiples is taken corresponding to each state of hybridization, one fined substantial variations in the ionization energies. This lead Moffit [109] to suggest the differences in hybridization influence the properties of predominantly covalent bonds to a greater extent then do differences in electro negativity. However the proton potential is much more singular than are in other atomic valence potential because in other atoms the valence electrons do not penetrate the core region because of the exclusion principle. At the same time the electron-electron interactions which are responsible for multiples formation in polyvalent atoms are less important in large molecules and crystals, where the spacing of energy level is much smaller than typical bond energy. It is therefore justified in retaining the concepts of electro negativity and iconicity. Differences in hybridization states can be taken into a account by following the usual Huckel approach and allowing the parameters of theory to vary with bond length in a smooth manner, thereby allowing quantitatively for most hybridization effects. Ideally one should study homogeneous systems in which the hybridization states vary as little as possible in order to isolate trends associated entirely with electronegativity and ionicity.Pauling resolves this problem by suing the concept of resonating bonds. In $A^{N}B^{8-N}$ crystals, the number of resonating bond 'M' per atom is equal to its classical valence i.e. M=N, when the number of bonds different from the coordination number of the atom, one has resonating bonds. Consider a molecule 'AB' in which the atoms A and B are not similar, one being more electronegative than the other; we must use a more general wave function.

$a\Psi A : B + c\ \Psi A^{+} B^{-} + d\ \Psi A$
(1.5)

To represents the bond, the best values of c/a and d/a being those that make the bond energy a maximum. The energy of an actual bond between unlike atoms is greater than the energy of a normal covalent between these atoms. This additional bond energy is due to the ionic character of the bond. Then the difference bond energy,

$\Delta_{AB} = D_{(AB)} - ½ (D_{AA} + D_{B}$ (1.6)

and relates the electronegativities X_A and X_B and the number of resonating bonds per mode by,

$\Delta_{AB} = -23M (X_A + X_B)^2$ (1.7)

The heat of formation can be obtained from equation (1.7) after allowing for extra stability of O_2 and N_2 bonds. Let n_N and n_O be the number of nitrogen and oxygen atoms per 'AB' molecule, then heat of formation ΔH_{AB} is given by

$\Delta H_{AB} = -\Delta_{AB} + 554n_N + 260n_O$ (1.8)

If one accepts Pauling prescription for 'M' the from a collection of heats of formation, one can prepare a table of values of X_A. It is should be noted that the difference between bond energy would never be negative. Many elements in their standard states are, however liquid or crystals, rather than gases, and many compounds considered by Pauling are liquid or crystals. The energy of a liquid or a crystal many be considered as involving not only the bond energies but also the energy of Van-der walls interactions of adjacent non-bonded atoms. But in facts in some cases such as alkali hydride gas molecules to have some ionic character $M^{+}H^{-}$ that the values of Δ_{AB} are negative. Then a quantum mechanical treatment of one electron bond has been carried out that leads to the conclusion that the postulate of additivity should be replaced by a similar postulate involving the geometrical mean of the bond energies D_{AA} and D_{BB} in place of arithmetic mean i.e.

$\Delta'_{AB} = D_{AB} - (D_{AA} + D_{BB})^{½}$ (1.9)

Should always be greater than or equal to zero. It has been found that the value of Δ'_{AB} do not satisfy the additivity relation. They cannot be represented as differences of terms characteristics of two atoms in the bond. However the square roots of the values of Δ' do not satisfy approximately the relation of this sort. In the original formulation of the electronegativity scale the electron volt, 23Kcal/mole was used. This procedure which was followed by Pauling leads to a convenient range of electronegative values. Some values are obtained with the postulates of the geometric mean and the unit 30Kcal/mole. If the extra ionic energy Δ'_{AB} is given accurately by the equation.

$\Delta_{AB} = 30 (X_A - X_B)^2$ (1.10)

and bond energy (in kcal / mole) by the equation,

$D_{AB} = \{D_{AA}.D_{BB}\}^{½} + 30 (X_A - X_B)^2$ (1.11)

Where X_A and X_B are the electro negativities of atom A and B. The values of the $0.18\sqrt{\Delta'}$ and $(X_A - X_B)$ would be equal but it is approximately true. The electronegativity values given in Table 1.1 refer to common oxidation state of the elements. Pauling goes on to estimate that f_i (AB) is the function of $(X_A - X_B)$ only and is independent of other quantities (e.g. bond length r_{A-B} etc.) clearly $f_i$must be even function of $(X_A - X_B)$, and it measures the fraction of ionic character it should be in the interval between zero and me. The conditions

$f_i(A, B) = f_i(B, A)$ (1.12)

And

$0 \leq f_i(A, B)$ (1.13)

and specified by all definition of ionicity including Pauling's definition,

$f_i(AB)=1-\exp[-(X_A-X_B)^2/4]$ (1.14)

The values of f_i calculated by equation (1.14) are relevant to simple bonds only. The above definition of ionicity was later modified in order to take account of the coordination number 'M'. Let the modified value of ionicity be represented by f_i, then the homopolar and covalent part is,

$f'_h=1-f'_i=(N/M)f_h=(N/M)(1-f_i)$ (1.15)

And,

$f_h=(N/M)\exp[-(X_A-X_B)^2/4]$ (1.16)

The physical interpretation of equation (1.16) is that the total covalency N, f_i is being shared amount 'M' resonating bonds (M = 4 or 6).

(C) Phillips Model:-

Phillips has recognized the difficulties encountered by both theoretical and empirical approaches to defining ionicity on band structure approach. According to Phillips the formation of covalent bond leads to the appearance of an energy gap between bonding and antibonding states of the compounds. The average energy gap sp^3 hybridized state centered on an atom in terms of free atom energy E_s and E_p as follows,

$E_A= ¼ [E_s(A)+ 3 E_p(A)]$ (1.17)

For the atoms A and B the differences between E_A leads and E_B leads to charge transfer when the atoms are bonded two atoms. The fractional ionic character of a covalent bond $f_i$shoulddepend on the magnitude of the antisymmetric potential V_{ionic} compare to the symmetric potential $V_{covalent}$. While discussing the average energy gaps it has shown that E_h and E_c are 90^0 out of phase. Where Φ is defined as ionicity phase angle ($\tan \Phi = E_c/E_h$). From the graph we may define crystal ionicity f_i and homopolarity f_h as follows,

$f_i = \sin^2\Phi = E_c^2/E_g$ (1.18)

$f_h = \cos^2 \Phi = E_h{}^2/E_g^2$ (1.19)

(d)Tubb's Approach:-

According to Tubb's the crystals ionicity of a system is defined in terms of average energy gap E_g or Penn gap E_p and plasma energy gap $\hbar\omega_p$ by the following relation,

$f_i=(E_p/\hbar\omega_p)=(E_g/\hbar\omega_p)$ (1.20)

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