



iJRASET

International Journal For Research in
Applied Science and Engineering Technology



INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 7 Issue: III Month of publication: March 2019

DOI: <http://doi.org/10.22214/ijraset.2019.3451>

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Correlation between Bond Energy and Electronegativity Differences in a Few Semiconductors

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Abstract: Studies of bond energies of diatomic molecules are of great importance in thermochemistry, astrophysics and combustion physics. The bond energies of diatomic molecules and various semiconductors are evaluated. The bond energies are experimentally verified by thermal mass and spectroscopic techniques. The present method is an improvement over Pauling's relation. The bond energies evaluated by this present method are in excellent agreement with that evaluated by other methods. For e.g., in the case of BN (Boron Nitride) the bond energy, D_{AB} obtained by present study is 86.88 and that obtained by Pauling equation is 86.62. In the case of GaSb, it is 43.66 by the present equation is 43.66 by the Pauling equation it is 43.66. Also the average percentage deviation by the present study is 15.00, by the Pauling equation it is 14.20 and by Match et al it is 14.66. the studies of bond energies of various semiconductors taken up by the author are in good agreement with the evaluated equations proposed by literature, Pauling and Matcha.

Keywords: Electronegativity, ionicity, energy gap, bond energy

I. INTRODUCTION

In the chemical approaches taken for the approximate prediction of band gaps of semiconductors, correlations have been proposed between band gaps and various other quantities like single bond energies¹, heats of formation per mole², heats of formation per equivalent³, atomic numbers⁴, electronegativities⁵ etc. Some of these approaches especially those seeking relationships between bond energy and band gaps have also been presented in the form of reviews either detailed⁶ or synoptic¹.

According to Welker's postulate⁷ the energy gap depends on binding energy and the effective charges of atoms, the energy gap being related to a great number of parameters⁸⁻¹⁰ that are directly or indirectly connected with the binding energy or the lattice energy - of these the bond length taken by Goodman¹¹ leads to a linear relation between ' E_g ' and ' d ', where ' E_g ' is the energy gap and ' d ' is the bond length in diamond structures. According to Pauling¹², the covalent bond energy between two atoms sharing equal number of electrons at a minimum bond distance, is proportional to the reciprocal of bond length. So, the energy gap of a pure covalent semiconductor of diamond type structure will exhibit a similar relationship as a function of bond strength or an inverse function of bond length. Suchet¹³ after a study of the importance of the covalent coordination and of the structure type in the prediction of the semiconductivity of inorganic compounds, relates the atomic and structural results to the value of the energy gap by means of empirical formulae allowing the computation of homopolar and heteropolar contributions to this value. The energy gap has a tendency to be progressively increasing in going from element of II-IV compound semiconductor. This tendency is a result of increasing degree of ionicity in the chemical bond. The difference between covalent and ionic bonding is the charge transfer that is involved in forming an ionic bond. Ge and Si are considered to be covalent semiconductors while lead salts are considered as polar semiconductors. Information concerning charge transfer and hence the degree of ionicity can be obtained by computing the static and optical dielectric constants. Pauling's¹² procedure gives fairly accurate estimate of bond energy between two uni-valent atoms held together by a single bond. However, this approach emphasizes the correlation between ionicity and type of bonding through electronegativities. Degree of ionicity in a chemical bond can be understood through bond energy. It was well emphasized by Pauling¹⁴ in a graph between electronegativity difference and amount of ionic character. Recently Manca^{1,15} has attempted to calculate the energy of a single bond for different semiconductors crystalizing in the diamond and blende structures by means of Pauling relation¹⁶. In this equation he utilised the work on electronegativities of elements by Gordy and Thomas¹⁷.

In the absence of reasonably complete quantum mechanical calculations, empirical and semi-empirical approaches are employed in the construction of potential energy terms and to understand the nature of molecular binding and bond energies. Bond energies of diatomic molecules have a great importance in thermochemistry, combustion physics and astrophysics. In quantitative problems of

valency, statistical calculations of equilibria at high temperatures, chemical bonding and in other problems, bond energies play a fundamental role. Astrophysicists, chemists and spectroscopists are therefore concerned with the determination of reliable values for bond energies of the diatomic molecules. Thermal and mass spectroscopies are the most important experimental methods used to evaluate bond energy values¹⁸⁻²⁰.

In view of the above importance a study of investigation of bond energies of various semiconductors is taken up.

II. METHODOLOGY

For calculations of bond energies some of the methods available are

A. Thermochemical Process

In this process the bond energy of NaCl is obtained by the equation

$$D(\text{Na-Cl}) = \Delta H_s + \Delta H_{\text{diss}} + \Delta H_f \text{ ----- (1)}$$

Where $D(\text{Na-Cl})$ is the required bond energy, ΔH_s is the heat of sublimation of Na metal per mole, ΔH_{diss} is the heat of dissociation of Cl_2 molecule into Cl atoms per mole, ΔH_f is the heat of formation of NaCl per mole in its standard state. The bond energy in eq.(1) is the heat of atomization of NaCl. In the case of NaCl, only one shared electron pair is involved in the bonding. In the case of complex compounds like Ta_2O_5 more than one bond (i.e., shared electron pair) is involved and hence a suitable normalizing factor must be used to obtain from eq.(1). The heat of atomization per mole is normalized with respect to the participating valencies to obtain heat of atomization per equivalent, which is the bond energy. For example heat of atomization per equivalent (i.e., the bond energy) for Ta_2O_5 is of the heat of atomization per mole as calculated from eq.(1).

The bond energies thus obtained after second order corrections (e.g., spin correlation stabilization energies and coordinate valence) as discussed by Howald²¹ are the actual values of the average bond energies as obtained from experimental and theoretical data. The accuracy of these energies is limited only by the accuracy of the thermodynamic data used in computing them. Vijh²² concluded that this procedure is strictly valid for alkali halides only, because alkali halides do not involve in any coordinate bonds.

B. Pauling Process

Pauling¹⁴ stated that the energy of an actual bond between unlike atoms is greater than the energy of a normal covalent bond between the same atoms. This additional energy is due to ionic resonance or ionic character i.e.,

$$D(\text{A-B}) \geq [D(\text{A-A}) + D(\text{B-B})] \text{ ----- (2)}$$

If the additional ionic resonance energy is indicated by Δ then eq.(2) can be written as

$$\Delta = D(\text{A-B}) - [D(\text{A-A}) + D(\text{B-B})] \text{ ----- (3)}$$

This postulate of additive law is not valid for alkali hydrides. When quantum mechanics is applied to study electron bonds, arithmetic mean can be replaced by geometric mean. The values of energies for normal covalent bonds obtained using geometric mean is involved is more satisfactory than that obtained using arithmetic mean.

$$\Delta(\text{A-B}) = D(\text{A-B}) - [D(\text{A-A}) + D(\text{B-B})]^{1/2} \text{ ----- (4)}$$

$\Delta(\text{A-B})$ is obtained directly from heats of reaction using the relation

$$\Delta(\text{A-B}) = 30 (\text{X}_\text{A} - \text{X}_\text{B})^2 \text{ ----- (5)}$$

Where X_A and X_B are the Pauling electronegativities of the atoms. The bond energy (K cal/mole) is evaluated through Pauling's¹⁴ relation.

$$D(\text{A-B}) = [(D(\text{A-A}) \cdot D(\text{B-B}))]^{1/2} + 30 [\Delta \text{X}]^2 \text{ ----- (6)}$$

C. Matcha Process

Matcha²³ used simple quantum mechanical theory to study the interaction of potential between two atoms and obtained an appropriate form of bond energy, electronegativity relationship which is valid for both ionic as well as covalent bond. The final equation obtained is

$$D_{\text{AB}} = (1-f) D_{\text{AB}} + \frac{f}{R_e} [R D_{\text{ion}} - \frac{R_e E_{\text{ct}}}{f}] \text{ ----- (7)}$$

E_{ct} is the energy associated with partial charge transfer, D_{AB} is the average covalent bond energy, f is the effective charge transferred in the curve crossing region during bond formation and R_e is the inter nuclear distance of the molecule.

Substituting the constants E_{ct} , R_e and D_{ion}

$$D_{AB} = (1-f) D_{AB} + 252 \frac{f}{R_e} \text{ ----- (8)}$$

A comparison between $\frac{f}{R_e}$ and i (ionic character defined by Pauling) suggests a strong correlation between these quantities. This suggests such that D_{AB} can be related to ΔX by replacing $\frac{f}{R_e}$ by $\frac{2i}{3}$

$$\text{Where } I = 1 - e^{-\frac{\Delta X^2}{4}}$$

Matcha gave a relation for the construction electronegativity scale as

$$D_{AB} = D_{AB} + \frac{f}{R_e} [252 - R_e D_{AB}] \text{ ----- (9)}$$

The term in the square brackets is approximately constant (169) for a series of bonds. Thus the above equation can be written as

$$D_{AB} \approx D_{AB} + 169 \left(\frac{f}{R_e}\right) \text{ ----- (10)}$$

$$\text{Replacing } \frac{f}{R_e} \text{ by } \frac{2i}{3}$$

$$D_{AB} \approx D_{AB} + 113 i \text{ ----- (11)}$$

To increase the accuracy of this equation, Matcha added two adjustable parameters k & i ,

$$\text{Thus } D_{AB} = D_{AB} + ki \text{ ----- (12)}$$

For smaller values of ΔX , ki becomes

$$K \left[1 - e^{-\frac{\alpha X^2}{1}} \right]$$

Matcha found that $k=103$ and $\alpha=0.29$

$$\text{Finally } D_{AB} = D_{AB} + K \left[1 - e^{-\frac{\alpha X^2}{1}} \right] \text{ ----- (13)}$$

D. Reddy et al., process:

The Pauling's empirical relation¹⁶ fares badly when applied to ionic bonds. The error in estimated ionic bond energies is as much as 190%. So Reddy et al.,²⁴⁻²⁶ worked out a relation, using which they calculated bond energies of both ionic and covalent molecules. The relation developed by them²⁴⁻²⁶ is simple and straight forward, which is deduced as follows.

The empirical relation for bond energies proposed by Pauling is

$$D_{AB} = D_{AB} + 30 [\Delta X]^2 \text{ ----- (14)}$$

Where $D_{AB} = [(D_{AA} \cdot D_{BB})]^{1/2}$ and $\Delta X = X_A - X_B$ (Pauling electro negativity difference).

Equation (14) gives a reasonable accurate estimates of covalent bond energies. Matcha²³ derived an equation

$$D_{AB} = D_{AB} (1-f) + 252 \left(\frac{f}{R_e}\right) \text{ ----- (15)}$$

It was later transformed to the following form with adjustable parameters k and i as,

$$D_{AB} = D_{AB} + k i \text{ ----- (16) (where } k=103)$$

For ionic cases Reddy et.al., derived an empirical relation

$$D_{AB} = D_{AB} (1 - 0.2075 \Delta X r_e) + 52.29 \Delta X \text{ ----- (17)}$$

On comparison of equations (15) and (17) we get

$$\frac{f}{R_e} = 0.2075 \Delta X \text{ ----- (18)}$$

$$\text{But Matcha}^{23} \text{ gave } \frac{f}{R_e} = \frac{2i}{3} \text{ ----- (19)}$$

From equations (18) and (19)

$$i = 0.31125 \Delta X \text{ ----- (20)}$$

substituting the value of I from equation (20) and $k=103$ in Matcha's relation (16), Reddy et al., obtained

$$D_{AB} = D_{AB} + 32.058 \Delta X$$

----- (21)

Table 1.
Single Bond Energies (K CAL / MOLE)

S. No.	Molecule	Single bond energy(K cal / mole)
1	B-B	70.00
2	Al-Al	45.00
3	Ga-Ga	27.00
4	In-In	24.00
5	Si-Si	53.00
6	Zn-Zn	164.30*
7	Cd-Cd	90.13*
8	N-N	40.00
9	P-P	48.00
10	As-As	35.00
11	Sb-Sb	70.60
12	S-S	64.00
13	Se-Se	41.00
14	Te-Te	30.00
15	C-C	83.00

Table 2.
BOND ENERGY, D_{AB} OF SEMICONDUCTORS

S.No	Semiconductor	ΔX	Bond energy, D_{AB} (K cal / mole)			
			Literature [Ref.1,22&27]	Pauling Equ. (6)	Matcha Equ.(13)	Present study Equ.(21)
1	BN	1.06	95.69	86.62	81.55	86.88
2	BP	0.05	84.76	58.04	58.04	59.56
3	BAs	0.19	69.41	50.58	50.57	55.58
4	BSb	0.19	64.56	71.38	71.37	76.38
5	AlN	1.60	106.76	119.20	96.40	93.70
6	AlP	0.59	71.71	56.91	56.36	65.38
7	AlAs	0.73	58.11	55.67	54.43	63.08
8	AlSb	0.35	50.73	60.03	59.95	67.58
9	GaN	1.25	96.85	79.73	70.39	72.92
10	GaP	0.24	60.41	37.72	37.70	43.69
11	GaAs	0.38	48.88	35.07	34.96	42.91
12	GaSb	0.00	42.19	43.66	43.66	43.66
13	InN	1.58	85.78	105.87	84.04	81.62
14	InP	0.57	47.27	43.68	43.20	52.20
15	SiC	0.76	71.94	83.69	82.25	90.72
16	ZnS	0.78	127.54	120.70	119.20	101.23
17	ZnSe	0.18	87.84	83.04	83.03	88.31
18	ZnTe	0.35	81.42	73.81	73.80	81.63
19	CdS	0.98	107.35	104.76	100.98	84.86
20	CdSe	1.02	93.48	92.00	87.61	73.79
21	CdTe	0.55	69.62	61.07	60.64	67.56
Average percentage deviation				14.20	14.66	15.00

III. RESULTS AND DISCUSSION

In order to evaluate the bond energies of different semiconductors, we use the experimental homo nuclear bond energies of constituent atoms of the semiconductor and Pauling electronegativity reported in Lide²⁷, Pauling¹⁴ Manca¹ and Sandersen²⁸. The estimated bond energies from equations (6), (13) and (21) are presented in table 2. Bond energies obtained with the above formulae are in excellent agreement with the literature values^{1,22,27}. The average percentage deviation in table 2 indicates that the calculated values obtained with the above formulae are in good agreement with the literature values. The magnitude of the electronegativity difference between two atoms indicates the degree of ionicity. It has been observed from the tables that the magnitude of ΔX of the semiconductor is below 1 in most of the cases. It indicates the nature of the bonding is covalent. It is noted that when different species of atoms are involved in covalent bonding, their electronegativities may influence their bonding. Electronegativity describes the pre-disposition of an atom to absorb electrons, its units are the square root of bond strength. Thus an atom with higher electronegativity will be more reactive chemically than one with a lower electronegativity. When the electronegativities with an atom engaged with covalent bonding are similar, this factor has little influence on bonding. However, when the difference in electronegativities of the two compounds is equal to or more than about 0.2 units, small amounts of ionic bonding may take place along with the covalent bonding. Larger electronegativity differences involve higher degree of ionicity in the bonding. It is probable that perfectly pre covalent bonding normally does not exist in compounds because no two atoms have identical electronegativities, small degrees of ionicity are present. BP, BAs, BSb, GaSb and ZnSe are some semiconductors will fall in this category. A careful observation of the table 2 reveals that their bond energies are below 90 K cal/mole.

According to Pauling¹⁴, the percentage of ionic bonding in a compound increases from ionicity 0.2 to 0.63 to 0.89 as difference between the electronegativity values of its elements increases from 1 to 2 to 3, where the values of electronegativity is not sufficiently accurate in comparing the relative degree of ionicity in different compounds. The percentage of ionic bonding based on Pauling's criterion, is estimated to be 22 % in CdS and ZnS. The value of ionicity quoted by Phillips²⁹ are accurate in comparing the Pauling's¹⁴ values. The above study is extended to understand the relation between ionization potentials, energy gaps and optical electronegativity of few semiconductors.

The above work is a part of M.Phil., submitted by the author at S.K University in 1996.

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