CHED 504Phenomenological explanation of electrical conductivity

Yuriy does not change substantially Gankin, Yuriy_gankin@hotmail.com, Elsevier MDL, 30 Corporate Drive, Suite 400, Burlington, MA 01803 and **Victor Gankin**, ygankin@harcourt.com, Institute of Theoretical Chemistry, 8 Shrewsbury Green Drive, Shrewsbury, MA 01545.

The widely used quantum chemical explanations include paradigms and principles whose physical bases are unclear and 'unteachable'. We have developed system of explaining major chemical phenomena without introducing quantum chemical entities (www.ITChem.com). Based on that approach we have developed an explanation of electrical conductivity in metals. Conventionally, a solid metal is described as a 3D lattice with partially ionized atoms in the nodes. Electrons separated from the atoms move freely in all directions ("electron gas", "positive ions in a sea of electrons"). When voltage is applied, free electrons move in the direction of the field propagation. That notion contradicts the modern knowledge that electrons in metals are strongly bonded to atoms and there are neither ionized atoms no electron gas. We have shown that seemingly easy motion of strongly bonded electrons in the direction of the field propagation is determined primarily by consecutive substitution by electrons supplied by the anode.

General   Papers

8:00 AM-11:45 AM, Thursday, 14 September 2006 San Francisco Marriott -- Salon 10, Oral

Division   of   Chemical   Education

The 232nd ACS National Meeting, San Francisco, CA, September 10-14, 2006

CHED 1773Phenomenological explanation of metallic bonding and electrical conductivity

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The widely used quantum chemical explanations include paradigms and principles whose physical bases are unclear. We have developed an approach that helps explaining major chemical phenomena (covalent bonding, chemical kinetics and catalysis) without introducing quantum chemical entities. Our approach and a General Chemistry text book synopsis utilizing it are presented at www.ITChem.com. Based on that approach we have developed a phenomenological explanation of nature of metallic bonding and electrical conductivity that explained the differences between bonds in metals and non-metallic compounds. While atoms of non-metals are connected via static two-electron covalent bonds, atoms in solid metals are linked by dynamic one-electron bonds. We have built quantitative models that explain how that

bonding difference determines dissimilarity between properties of metals and non-metals. We have shown that seemingly easy motion of strongly bonded electrons in the direction of the field propagation is determined primarily by consecutive substitution of the electrons.

General   Papers

8:00 AM-11:25 AM, Thursday, 29 March 2007 McCormick Place North -- Room N230A, Level 2, Oral

Division   of   Chemical   Education

The 233rd ACS National Meeting, Chicago, IL, March 25-29, 2007

CHED 507 - Theory of electrical conductivity

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We have developed system of explaining major chemical and physical phenomena without introducing quantum chemical entities (www.ITChem.com). Based on that approach we have developed an explanation of electrical conductivity in metals. Conventionally, a solid metal is described as a 3D lattice with partially ionized atoms in the nodes. Electrons separated from the atoms move freely in all directions ("electron gas", "positive ions in a sea of electrons"). When voltage is applied, free electrons move in the direction of the field propagation. That notion contradicts the modern knowledge that electrons in metals are strongly bonded to atoms and there are neither ionized atoms no electron gas. We have shown that seemingly easy motion of strongly bonded electrons in the direction of the field propagation is determined primarily by consecutive substitution by electrons supplied by the anode.

Theory of electrical conductivity

"What is the electricity?" – the professor asked.

"I knew, but I've forgotten,"- the student replied.

"What a loss!" – the professor exclaimed, -" Only

Person in the whole world knew it, but has forgotten"

Accordingly to Peter P. Edwards (The New Chemistry, Editor-in-chief Nina Hall Cambridge university press 2000 p 85) there was no success until 2000 in the attempts to answer the following basic questions, related to electrical conductivity of metals: why does meal conduct the electrical current, but nonmetal does not (isolate)? What is metal? Why are the properties of metals so much different from the ones of non-metals? What is the electrical current and what is its physical nature? Etc.

In the Peter P. Edwards' article the major directions of the theoretical studies, in which the authors are trying to answer these questions, are described.

The evaluation of the results achieved is presented in the form of the letter to the article author (Peter R. Edwards) from Nevill Mott. Peter R. Edwards writes: "Over a period of 50 years, Professor Sir Nevill Mott pioneered the development of key concepts, models and theories for discussing the fundamental problem of metals versus insulators (nonmetal). These issues occupied the thoughts of Sir Nevill until well into his nineties. We reproduce below his letter written to present author on Thursday 6 May 1996 in which he notes "Dear Peter, I've thought a lot about "What is Metal" and I think one can only answer the question at $T = 0$ (the absolute zero of temperature). There a metal conducts and a nonmetal doesn't. Intuition at its most potent!"

In the frames of physics the explanation of the basic rules of the electrical current rests only on the explanation why the electrons in the solid matter behave as free electrons. In reality, only after settling this problem, it is necessary to find the answers to the following paradoxical questions in order to create the internally non-contradictory theory.

In physics, the free electron hypothesis is introduced for the explanation of why the electrical current in the conductor appears when the difference of potentials is less than 10^{-8} eV. The following question arises after that: the rate of the heat-induced (unbalanced) movement of free electrons at the room temperature, as mentioned earlier is 10^5 m/sec, in the frames of our explanation is 10^6 -10^7 m/sec. Accordingly to Saveliev (p.272), the average speed of the balanced (by the field) electron movement is equal to 10^{-3} m/sec. As it was already shown, the additional energy, transferred to electrons while applying the field, increases their kinetic energy only by 10^{-14}%.

It is assumed while calculating the speed increase, that the electric field increases the electron movement rate. But in reality the field increases the rate only those electrons that move in the direction of the field. It reduces at the same degree the rate of electrons moving against the direction of the field. The numbers of both electrons moving along and against the field direction are equal. If electrons present in the metal in the gaseous form, there will be exchange between them with kinetic energy. And, respectively, the creation of the field inside the conductor does not have to influence either on the speed or on the electron energy inside the conductor even at the miniscule degree (obtain by the incorrect calculation).

The properties of the conductor, conducting the current, are sharply different from the conductor without the current. The conductor with the current has the magnetic field and is warming up when the current flows.

How does this paradoxical situation can be solved in the frames of the metallic bond property explanation suggested by us?

Our new theory of electrical conductivity shows, that tightly bonded electrons in metals are moving easily (practically without the energy expenditures) along the metal bonds. Their movement in the generated by the field direction is determined not by the effect of the field but by forcing the out from one end of the conductor with the electrons entering from the opposite side of the conductor.

As it was shown earlier, every atom in the solid metal can be connected accordingly to the theory of chemical bonding (one- and two-electron, co-valent, Van-der-Waals). In this case, accordingly to the theory. The system, consisted of nucleus and the bonding electrons, has several close situated minimums. The structures described by the theory convert with the fast rate from one to another.

We indicated earlier while describing the dynamic bonding that in all cases when the one (central) atom is connected to the identical atoms with the different bond types the system, consisting of nucleus and electrons, can be described by the theory with more than one formula. The difference is only in the electron arrangement and for the same electron energy, the forms determined by the theory (accordingly to the rules of chemical bonding) convert from one to another via the electron transition. If the possible form differentiate only by their energy, the equilibrium between the forms moves in the direction of the form with the lower energy.

Accordingly to the theory of the chemical bonding in I_3 along with the equilibrium:
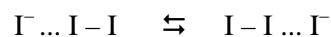
$$I^- \ldots I - I \quad \leftrightarrows \quad I - I \ldots I^-$$

There can also exist the equilibrium between different forms I_6 and I_9, and so on.
$$I^- \ldots I - I \ldots I^- \ldots I - I \ldots I^- \ldots I - I \leftrightarrows I - I \ldots I^- \ldots I - I \ldots I^- \ldots I - I \ldots I^-,$$

I.e., the possibility of the polymer molecule formation due to dynamic bonds assumes the possibility of the fast electron movement along the polymer chain.

At the beginning, let's review, how the situation will change if an electron is added to I_3 $(I^- \ldots I - I)$. It is known, that I_2 has the positive affinity to an electron. When an electron attaches to the I_2 molecule, I^-_2, which has a structural formula $I^\cdot \ldots I^-$, is formed. Respectively, if an electron is attached to $I - I \ldots I^-$

I .... $\overset{\cdot}{I}$,…I^- and I^- ... I^- …$\overset{\cdot}{I}$ can be formed. Both these compounds have to easily attach an electron forming respectively only compound I^- …I^- …I^- .

In its turn, the emission of energy, stipulating the easiness of the next electron attachment, is expected because the iodine (I_2) molecule has the positive affinity to electron. Though in this case, the attachment of the first electron takes place with the covalent bond break (i.e. with the consumption of energy). The second electron attaches to the $\overset{\cdot}{I}$, assumes that this stage will proceed similarly to the all known cases.
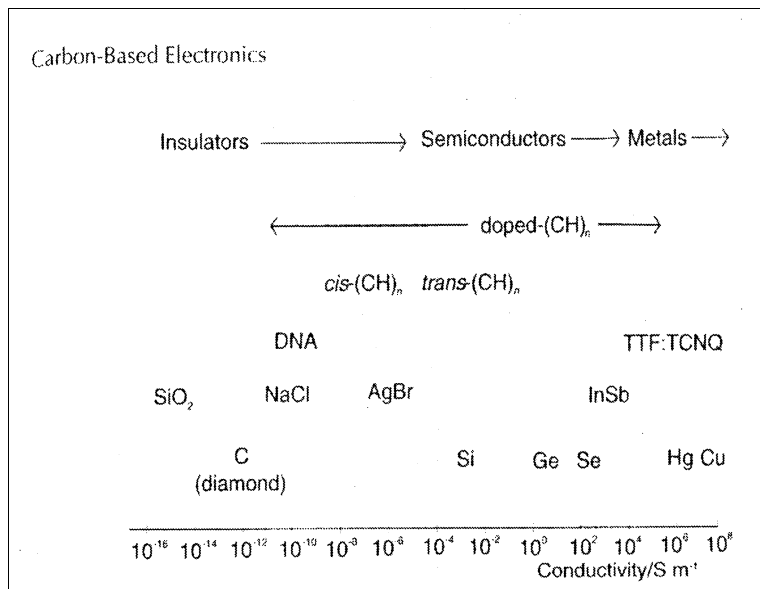
All three atoms in the molecule I^- ... I^- …$\overset{\cdot}{I}$ have three electrons in the external sphere. Accordingly to the chemical bond theory, no other bonds (including dynamical)) between atoms (except Van der Waals') can not form.

Let's review how the situation in the system changes, if the chain, consisting of iodine atoms, will be attached by one side to cathode, carrying the positive charge in the presence of electrical current. Another side of the chain will be attached to anode, carrying the negative charge. After the outer molecule I^- ... $I – I$ due to electrons, supplied from anode, converts into $I – I$ ... I^- , first from the left reversible isomerization ceases (for the electron pare, being transferred in the process of isomerization farm the foremost left anion to the foremost right one - I^- ... $I – I$ $\leftrightarrows$ $I – I$ ... I^-). In all electron spheres of three anions in the I^- ... I^- …$\overset{\cdot}{I}$ molecule, there is no place no only for the same energy level, which this electron pare had in the I^- ... $I – I$ molecule, but not even the close level of energy. At the same time the rate of the electron pare transfer reaction from I^- ... I^- …$\overset{\cdot}{I}$ to I^- ... I^- …$\overset{\cdot}{I}$ does not change substantially, because the process rate limiting stage in both cases is the stage of forcing out the bonding electrons in iodine molecule I_2 with the free iodine anion electron pare, not participation in the bond formation.

As the result, the voltage formation between cathode and anode, the anode electron concentration increase above equilibrated and its decrease on the cathode below equilibrated levels simply reduces the speed of electron movement from right to left in the polymer chain, formed by the dynamic bonds. The electron movement rate decrease is caused by the reduction of the number of places for electrons, when the total system energy does not change while these places are being occupied as a result of isomerization. At the same time, the reduction of available places for electrons is determined by their filling up by the electrons arriving from anode during the voltage appearance in the system and the electrical circuit formation. From the other hand, the decrease of the electron flow, moving from right to left increases the movement of electrons from left to right comparatively to the conductor, disconnected from the electrical current generator. All elemental stages of the suggested mechanism of the electrical current formation have the experimental confirmation in the chemical tests. The basic statutes of the suggested theory of the electric current are confirmed by physical and chemical experiments.

The basic status of this theory are as follows: the electrical current is a flow of electrons moving in conductors in one direction from anode (the negatively charged electrode) to cathode, charged positively. Physical experiments by Tolman and Stuart, carried out in 1916 and described in the text book by I.V.Soloviev (v.2, p.270) confirmed that electrons are the carriers of electrical current. Electron, bonding atoms into molecules in the presence of closely situated (0.5 – 2 Å) energy minimums are able to move from one minimum to another with the high rate of speed ($> 10^5$ m/sec). That is confirmed by the chemical experiments, as a result of which there was discovered this phenomenon and studied its kinetics.

We answered in the previous article the questions raised earlier in this article. As this article is concerned we think it is worth while to underline, that all differences between metal and nonmetal on the level of the chemical bond, even with semi quantitative correlations, are agreeable with the electrical current theory, examined in this article. As it was shown in the previous article, the two-electron statistical bond is typical for non-metals in the solid state. Single-electron dynamic pond is typical for metals. The electrical current theory, presented in this article, assumes the valent electron transfer from one bond to another. The study of the process kinetics of the electron transfer from one bond to another showed, that one electron moves from one bond to another much faster than the electron pare and that the transfer speed of electrons in the compounds with correlated bond (typical for the organic conductors) is significantly higher than in the compounds with the simple covalent bonds, typical for isolators. It is most important, that the conductance of the substances, in which atoms in the solid phase are connected with the single-electron dynamic bonds, have conductance 10^{20} higher, than the solid substances, in which atoms are connected with two-electron statistical bonds. Also, the increase of dynamic bonds in the system takes place during the polyeten, treated with halogen. As a result , the increase of the dynamic bonds quantity in polyeten its conductance raises by 8 orders – see the Table)

Carbon-Based Electronics

Insulators ——————————→ Semiconductors ——→ Metals ——→

←——————————— doped-(CH)$_n$ ——————→

cis-(CH)$_n$ trans-(CH)$_n$

DNA   TTF:TCNQ

SiO$_2$ NaCl   AgBr   InSb

C   Si   Ge Se   Hg Cu
(diamond)

10^{-16} 10^{-14} 10^{-12} 10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 10^{0} 10^{2} 10^{4} 10^{6} 10^{8}
Conductivity/S m^{-1}

 Accordingly to the electrical conductivity theory, discussed in this article, the preferable electron movement in the one direction from anode to cathode is determined by the degree of the filling in of the upper electron layers of the solid matter, which is taking place during the electron transition from anode into this solid matter until the outer electron sphere is saturated. Furthermore, one should assume the bonding type change and respectively expect the effect of the bonding type change on the scold matter conductance during the electron spheres of atom saturation (simpler speaking, it is a result of electron connecting to the atoms, bonded to the solid matters with different ore identical chemical bonds). It is supposed to expect in the semi-quantitative approximation, that the that conductance of the saturated with electrons atoms will increase with the increase of the affinity of atoms to electrons It is also expected, that the conductance decreases with the increase of enthalpy of the bond, broken during the electron attachment to one of the two atoms connected with this bond. Accordingly to the chemical bond theory, the enthalpy input in the bond energy of I_2 molecule equals approximately a half of the bond energy, i.e. 0.72 eV. Iodine atom affinity to electron equals 3.06 eV. Respectively, the heat of reaction of the electron attachment to I_2 molecule accompanied with the breakage of the co-valent bond in I_2 molecule can be estimated by the value 2.34 of I_2 (3.06 – 0.720= 2.34). Accordingly to the experimental data, the iodine molecule affinity the electron equals 2.55 eV. The analogous calculations for chlorine and bromine molecules gives the estimated values for these molecules affinity of 2.40 and 2.36eV, while the direct experimental determination gives the values of 2.38 and 2.55 eV respectively. For the additional verification of the affinity energy for the two-atom molecules, we estimated and compared with the experimental data the electron affinity to electron of Na_2 and K_2 using the identical methods. The comparison of the calculated and experimental data showed,

that the calculated and experimental (in parenthesis) values of the electron affinity for those molecules is lower, than the ones for halogens molecules and are equal 0.2 (0.43) and 0.23 (0.5) respectively.

For example, in the scheme discussed above, the dynamic bond between two left iodine atoms in the

$I - I \ldots I^-$ molecules breaks, when the outer atomic layer of the left iodine atom is filled in completely. This bond enthalpy is apprised accordingly to the bond theory by the value of the order of 0.4 – 0.7 eV. The electron affinity of iodine atom is 3.06 eV. I.e., the affinity of fairly conducting metals to electron varies in the range of 0.5 – 1.3 eV. The reaction of electron isomerization goes with the zero heat effect. All this assumes the insignificant energy expenditures for the creation of the electrical current in the substance, consisting of I_3 molecules.

Contrary to the examples, discussed earlier, the calculation of the electron affinity energy for the bonds $C - C$ and $C - H$ gave the negative energies of these electrons affinities, which are equal respectively -1.85 and -2.0 eV.

The additional independent confirmation of the negative meaning of these bonds affinity to electron is the absence of the literature data on the saturated hydrocarbon affinity to electron.

The dependence between hydrocarbons and halogens expected on the basis of the offered mechanisms is observed between halogens and hydrocarbons. The conductance of substances increases with the increase of electron affinity for the atoms connected with co-valent two-electron bonds, and the conductance of substances drops with the bonding energy between atoms increase.

In the resuming conclusion, one can say, that (while the bond type between atoms in the solid substance is identical) the higher conductance should be expected if the electron affinity to the two-atom molecule is higher.

The comparison of conductance between metals and halogens shows that in this case, the substances with the higher affinity to electron (halogens) have lower electrical conductivity.

The higher conductance of metals, where atoms connected with the single electron bonds, compare to halogens, consistent with the higher rate of the reversed single electron isomerization. It allows assuming, that the differences in the number of the bonding electrons increase the electrical conductivity more, than its drop due to the molecule affinity to electron decrease.

The appraisal of the stability of two-electron bonding effect on the electrical conductivity of the solids (which atoms are connected with two-electron co-valent bonds) allows to understand why the graphite electrical conductivity is sharply exceeds the one of diamond. Both substances consist of the identical atoms; i.e. both atoms of graphite and diamond have the same electron affinity. All bonds and valent angles

in diamond are the same as in paraffin and are equal to 1.54 Å and 109^0 respectively. Unlike diamond, the bonds in graphite have the different length (picture 1)
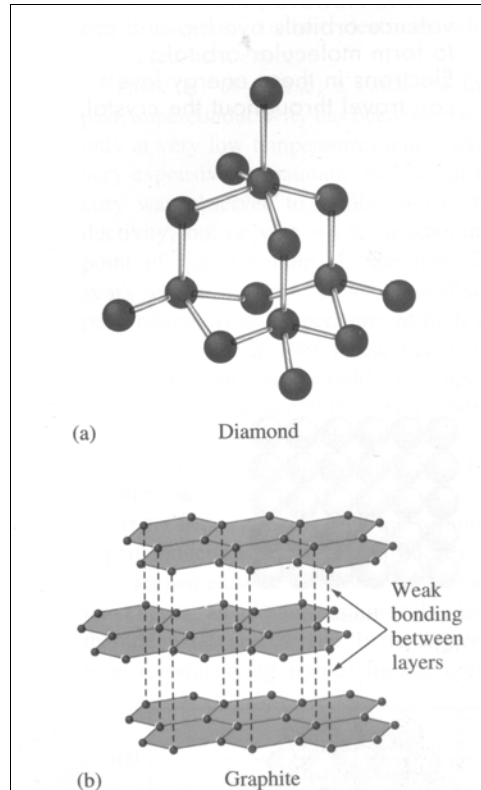

(a) Diamond

(b) Graphite

Weak bonding between layers

Fig.1

The length of the weak bonds between the layers in graphite equals 3.4 Å and between the atoms in the same layer is 1.42 Å. This distance has the intermediate value between the single covalent bond C-C length (1.5.4 Å) and the length of the double bond C=C (1.33 Å). The bond length between graphite layers is close the Van der Vaals bond length in the inert gases. The length of these bonds in the case of neon is 3.18 Å and 3.82 Å respectively. L. Pauling (L. Pauling The Nature of the Chemical Bond P.235 1959) guessed, that the carbon atoms in the graphite layers are connected with the single and double bonds (fig.2),
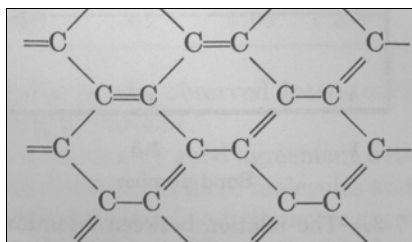
Fig.2

and between the layers with Van der Waals bonds.

The length of the central bond in butadiene equaled 1.46 Å is the independent confirmation of this explanation.

The structure of graphite, suggested by Paling, assumed, that unlike diamond, in which carbon atoms connected with identical bonds, graphite has carbon atoms connected with the other atoms by different bonds (singular, double and Van der Waals').

Accordingly to the chemical bonding theory in this case the bonds became dynamic.

The experimental data, obtained while studying the graphite electric conductivity provide another confirmation of that the graphite structure formula, suggested by L. Pauling, is correct. It was established during the electric conductivity of diamond and graphite, that electric conductivity of graphite, consisting from the same atoms as diamond, is about ten orders higher then the conductivity of diamond. Besides, it was established, that graphite, while conducting the electrical current, shows the amazing anisotropy: the specific conductivity along the layers ranges from 4×10^{-5} to 7×10^{-5} ohm.cm, and perpendicular to the layers ranges from 1×10^{-1} to 5×10^{-1} ohm.cm (K.Saito, "Chemistry and the Periodic Table", Moscow, Mir,1982, p. 104). These data were in the clear contradiction with the theory, suggesting, that substances, carrying electrical current, contain free electrons, because there could not be in this case any anisotropy.

Accordingly to the electrical current theory described in this work, the process of the establishment of the electrical current in graphite has to begin from the electron connection to the double bond. The further electron movement (its transition to another carbon atom in the equivalent energy state) can go into two directions accordingly to the graphite structure. In the graphite case, electron could move along the conjugated bonds (in the ring plane) and perpendicular to the ring plane (transfer from one ring into the parallel to it another ring). The distance between these rings is 3.4 Å . The existence of these two routes explained the amazing anisotropy, observed during electric conductivity studying of graphite, and its absence in diamond. The data, presented in literature, allows to appraise, even semiquantatively, the

expected ratio of electric conductivities along the routes possible thanks to t6he theory. The first route assumes the electron movement along the carbon chain, in which the carbon atoms are connected with the conjugated bonds. In the previous article, we   said, that determined experimentally electric conductivity of polyethine (polyacetelene $-(CH)_x$)-CH=CH-CH=CH-CH=) equals 10^{-5} -10^{-8} ohm.cm., what is closed to the value of 4×10^{-5} to 7×10^{-5} ohm.cm, shown above.