

EXPLANATION OF THE CHEMICAL BONDING PHENOMENON VIA
THE TWO-YEAR COLLEGE CURRICULUM ([HTTP://WWW.ITCHEM.COM](http://www.itchem.com)).

Y.V. Gankin, MDL Information Systems, Burlington, MA 01803;
V.Y. Gankin, Institute of Theoretical Chemistry, Shrewsbury, MA 01545.

The main difficulty in teaching chemistry lies in the explanation of chemical phenomena on the basis of *quantum chemistry* — when the teachers have to explain things that they hardly understand themselves. The widely used quantum chemical explanations include paradigms and principles whose physical bases are unclear. The Lewis rules, widely employed to explain chemical bonding phenomenon at the introductory level, have unclear physical reasoning and multiple exceptions.

According to J.N. Spencer (JCE No. 3 p. 182 1991) the basics of quantum-chemical interpretations are ‘unteachable’.

J.Spencer, making his report at the 225th meeting of the ACS at New Orleans, just to amuse of the listeners a bit, offered examples of quantum-chemical interpretations taken from traditional textbooks. The listeners reacted most lively, and heartily applauded the speaker. This undoubtedly proved the truth of the well-known premise: *When mankind laughs, it parts with its misconceptions.*

The main difficulties in explaining chemical bonding and chemical reactions are connected with the fact that this problem had never been solved by science in the previous century.

J.Ogilvie writes:

"What then is the status of the chemical bond in 1990? We know what it *is not*: *a stick between two balls* -- as the organic chemists of the 19th century might have imagined. It is certainly not orbitals. If we know what the nature of a chemical bond *is not*, can we state what the nature of the chemical bond *is*?" [Journal of Chem. Educ., 1990, 67, 280]

Richard Feynman, who won a Nobel Prize for Physics, once asked the following question: “If you had only one sentence with which to pass on to the next generation the most important scientific knowledge we possess, what would that sentence be? Feynman’s own answer was: “*Everything is made of atoms.*”

“But what is their size and shape?” the next generation might ask, “and how do they stick together?”

[Colin J.Humphrey NATURE September 1999 #401 p.21.]

As we see, Feynman’s phrase turned out to be prophetic.

According to S.Lippard (C&EN, Aug. 7, 2000), as a result of the recent revolutionary changes in chemistry, older paradigms have been giving way to new principles.

In part (see V. and Y.Gankin's — *How Chemical Bonds Form and Chemical Reactions Proceed, 1998*) the paradigm to the effect that the problem of chemical bonding can be solved only in the framework of quantum mechanics (relative to the supposition that the electron is a particle-wave) was exchanged for a paradigm to the effect that this problem can be solved without the wave properties of the electron, i.e., in the framework of the classical phenomenological approach, in whose framework the problem of the atom's layer-like structure and the physical essence of the periodic law were previously solved.

In the course of the chemical revolution, answers to questions like 'How do atoms stick together?' and 'How do chemical reactions proceed?' allowed transiting to changes in the interpretation of the main chemical phenomena: atom structure, periodic law, chemical reactions, catalysis, and cause-and-effect bonds between these phenomena, and relatively, the cause-and-effect bonds between micro-world (atoms, molecules), macro-world (solid bodies), and, what is most important for education — to make these explanations really teachable.

We have developed an approach to describing chemical bonding based on experimental data, on ionization potentials, and on the valence of elements. A comprehensible explanation of chemical bonding phenomenon, suitable for a two-year college program, is presented [details provided at <http://www.itchem.com>].

In this work we have included two variants for the explanation of chemical bonding. The first variant is meant for students who are not majoring in chemistry, while the second is for those majoring in this subject.

Part I .

The data on the ionization potentials of elements in the first three periods of the Table of Elements have shown (see figure 1.)

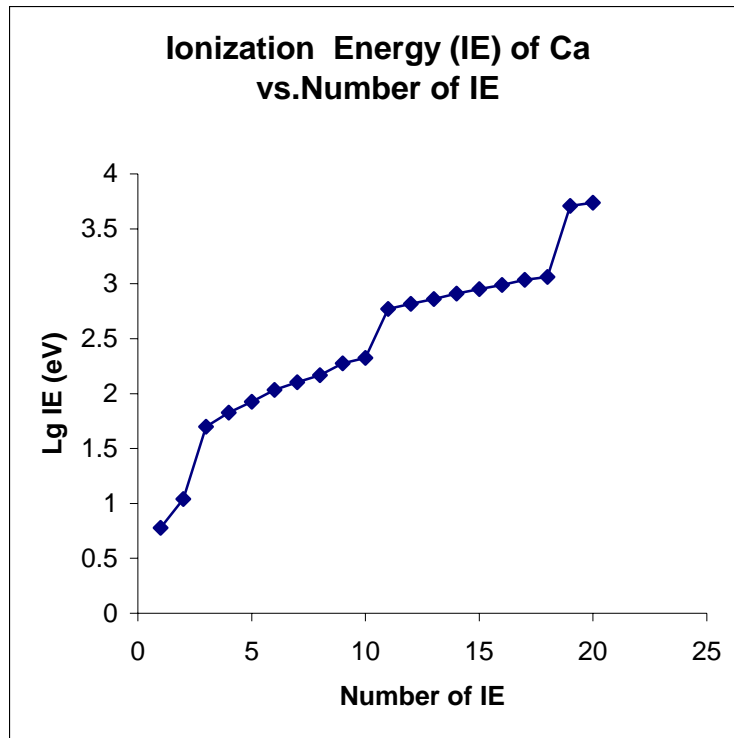


Fig.1

The electrons in the atoms are situated in layers and the number of electrons in the outermost layers of the elements of the 2nd and 3rd periods changes when transiting from the first group to the last, from 1 to 8 (Table 1)

Table 1

| Elements: | Li | Be | B | C | N | O | F | Ne |
|---------------------|----|----|----|----|---|---|----|----|
| | Na | Mg | Al | Si | P | S | Cl | Ar |
| Number of Electrons | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |

| Valence of elements according to hydrogen (H) and Chlor (Cl) | 1 | 2 | 3 | 4 | 3 | 2 | 1 | 0 |
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According to the received data, after the accumulation of eight electrons in the outermost layer, a new outermost electronic layer starts forming.

A comparison of the data on the number of electrons in the outermost layer with the valence of elements relative to hydrogen (H) and chlorine (Cl) (Table 1) has shown that the valence of elements, relative to hydrogen and chlorine, is equal to the number of electrons in the first four groups. This proves that only one electron of the central atom actually takes part in bond formation. Relatively, the number of bonds is limited, for elements of the first four groups, by the number of electrons in the outermost layers of the atoms.

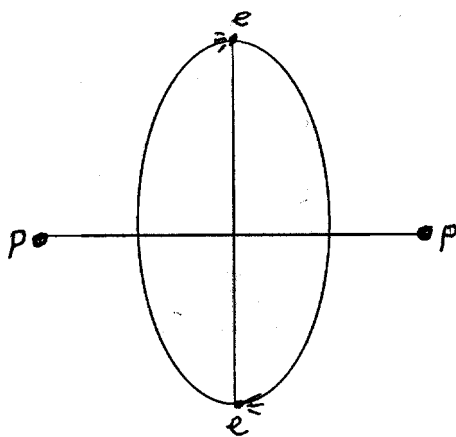
In dual molecular atoms, formed of identical atoms — both atoms are the same. That is, two electrons take part in bond formation — one from each of the atoms being bonded.

The valence in the last four groups is equal to $8 - X$, where X is the number of electrons situated in the outermost layer of the central atom.

The fact that $8 - X$, on the one hand, is equal to the valence of the element, and on the other hand, is equal to the number of additional electrons that can enter the outermost layers of the atoms in the last four groups, has shown that in the course of bond formation, both bonding electrons enter the outermost layers of the atoms to be bonded.

That is, the number of bonds that the elements of the last four groups can form is limited by the number of electrons that can enter the outermost layers of these elements.

A simultaneous presence of electrons to be bonded in the outermost shells is possible only if the bonding electrons are rotating on a plane perpendicular to the axis connecting the nuclei. (see slide #.2).



This model logically explains the physical essence of chemical bonding which is formed at the expense of the electrostatic attraction of the atoms' cores to the pair of electrons rotating between them.

According to the model and the physical essence of chemical bonding, this bonding is possible even if the bonding pair of electrons belonged to one of the atoms being bonded before the bonding took place. In order to form such a bond, it is necessary that the outermost shell of the second *atom to be bonded* should contain fewer than seven electrons. Indeed, the formation of such bonds is well known: XeO, XeO₂, XeO₃, HClO, HClO₂, HClO₃, etc. In all these compounds, oxygen (O) bonds to xenon (Xe) and to anion chlorine (Cl⁻) at the expense of its free space and the lone pairs of xenon and chlorine anions.

Langmuir called chemical bonds that were formed at the expense of electrons and belonged to different atoms — '*covalent bonds*'. Bonds formed at the expense of electrons that formerly belonged to one atom became historically known as '*donor-acceptor bonds*' (DABs).

In H₂SO₄ and H₃PO₄ the bonds between hydroxyl and sulfur are covalent ones, while the bonds between sulfur and phosphorus with oxygen are DABs.

According to the model, the attraction of the nucleus of one atom to the electrons of another is observed also when the outermost shells of both atoms are saturated. Experiments have shown that such bonds exist. Their existence is obvious during the transition of substances, like inert gases — from the gas state to the liquid state. Such bonds are known as Van der Waals bonds (VWB)

Covalent bonds can be *heteroatomic* (when atoms with various IPs are bonded); and also *double* and *triple* (when there are two or three covalent bonds between the two atoms). According to experimental data, the amount of energy that is spent on breaking the bond, decreases according to the row thus: triple > double > heteroatomic > homoatomic covalent > DAB > VWB. The bond's length increases in the same order.

It has been proven experimentally that if an atom is bonded to the same kind of atom by various types of bonds, such bonds become equal relative to energy and length. Simultaneously, the weak bonds become stronger while the strong ones become weaker; analogously, the long bonds become shorter and the short ones become longer. It is electronic isomerization that causes this phenomenon.

Experiments have proven that the transition speed of the electrons is by two orders of magnitude greater than that of the nuclei.

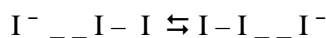
The difference between the speeds of the electrons and the nuclei leads to the fact that the distances between the atoms and the bonding energies of the atoms are equalized with those of the central atom. The thermal stability of the compound is determined by the stability of the weakest bond. That is why the equalizing of the bonds relative to the energy leads to the increase in the thermal stability of the compound.

According to experimental data, this explanation, concerning the influence of electronic isomerization on equalizing the lengths and energies of the bonds, and on the thermal stability of compounds, is more vividly observed if, as a result of the isomerization, there is an identical or close to identical energy in the initial compound.

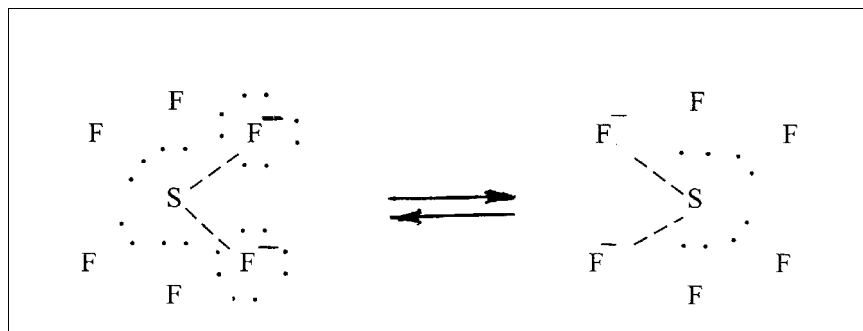
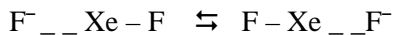
Electronic isomerization explains the equalization of the lengths, the bonding energies, and the thermal stability of the compounds (stability that was observed in the experiment) that contradicted the theory of bond formation.

Indeed, in the framework of the theory, which considers the formation of only covalent bonds, DABs, and VWBs, the thermal stability of such compounds as XeF_2 , XeF_4 , PF_5 , SF_6 , $(\text{G}_3)^-$ — where G stands for halogen — contradicts the bonding theory. In the framework of simple valence schemes, I_3^- contains one VWB and, therefore, it disintegrates at room temperature.

The existence of equilibrium [where (—) indicates VWBs]



makes this compound much more stable thermally. Analogously, the stability of XeF_2 , XeF_4 , PF_5 , and SF_6 is explained by the reverse process of electronic isomerization proceeding along the following scheme:



All these compounds are constructed analogously to $(\text{I}_3)^-$; all the atoms in the molecules contain 8 electrons; i.e., the number of electrons in the outermost shells does not exceed the maximal number of electrons — in accordance with the theory of chemical bonding. The stability, under normal conditions, when the temperature is equal to 20°C , the equalization of all the bonds is due to electronic isomerization.

The existence of the stable compounds confirms the main precepts of the bonding theory, including the fact that the maximal

number of electrons in the outermost shells in atoms of the second and third periods does not exceed 8.

On the other hand, the syntheses of compounds XeF_2 , XeF_4 , and the mishaps in the syntheses of XeF and XeF_3 are independent confirmations of the fact that two electrons actually take part in the formation of covalent bonds (one from each of the atoms) and that both bonding electrons enter the outermost shells of both atoms to be bonded.

Thus, the theory of chemical bonding, including electronic isomerization, is based on the comparison of experimental data on the ionization potentials of atoms of the second and third periods including data on the composition and structure of stable compounds, as well as experimental data received when studying electronic isomerization. All of which is very well substantiated experimentally.

The given theory does not contain any suppositions that have not been proven experimentally (like the supposition about the electrons striving to finish structuring 8 electronic shells, or the supposition about the increased stability of the outermost 2, 4, and 8 electronic shells). This theory describes the structures of known chemical compounds without any exceptions; it leads us to a visual model of chemical bonding.

Part II

However, when considering a semi-quantitative evaluation of the theory, a number of questions arise, which, at first glance, contradict the bonding theory, and therefore require a detailed investigation.

1) According to the model (see page....) during the formation of a covalent chemical bond, there is an energy gain received at the expense of the transition of the electrons of one atom to the outermost shell of another. This energy gain can be defined by the affinity of hydrogen atoms to the electron. That is, by the value of about $0.72 \text{ eV} \cdot 2$, where 0.72 eV is the affinity energy of one hydrogen atom relative to one electron.

Simultaneously, during bond formation, the electrons and the nuclei approach each other, which leads to an energy loss. According to experimental data, the distance between the nuclei in a hydrogen molecule comprises 0.74 \AA . Relatively, the energy loss, at the expense of the mutual repulsion of the nuclei, is equal to about 9 eV

That is, a hydrogen molecule, according to this calculation, cannot be stable.

2) During DAB formation we have found that the number of electrons in the outermost shell of the acceptor atom increases by two.

The data on the affinity have shown that only one electron can bond to an ordinary atom.

3) According to the model, chemical bonding occurs at the expense of the attraction of the nuclei to the electrons to be bonded. Since the FIPs and the affinity of the atoms to the electrons are different, there is an increase in both the bonding energies and the FIPs. However, experiments have shown that there is no correlation between the FIPs and the bonding energies.

4) The bonding energy in NaCl (and other analogous heteroatomic molecules) is much greater than the bonding energy in Na₂ and Cl₂, though at first glance the energy of this bond should amount to something intermediate of the bonding energies of Na₂ and Cl₂

The next section is devoted to answering these questions and some others.

The solution of these paradoxical questions was received as a result of the analysis of the model of a hydrogen molecule based on the comparison of the data on the IP of the structure of the stable molecules. As indicated above, the molecule, according to this comparison, represents two protons (in the case of H₂) between which two electrons rotate on a plane perpendicular to the axis that connects the nuclei. This model is shown in figure..... with the forces acting in the system.

The algebraic solution of this model leads to the following system of three equations with three unknowns, that is, it leads to an analytical solution.

$$e^2 N_1 n x_1 / (x_1^2 + a^2) (x_1^2 + a^2)^{0.5} = e^2 N_1 N_2 / (x_1 + x_2)^2 \quad \text{Equation 2.5-4}$$

$$e^2 N_2 n x_2 / (x_2^2 + a^2) (x_2^2 + a^2)^{0.5} = e^2 N_1 N_2 / (x_1 + x_2)^2 \quad \text{Equation 2.5-5}$$

$$a = R/F_0 \quad \text{Equation 2.5-6}$$

n is the number of bonding electrons, **R** is Bohr's radius equal to 1:

$$F_0 = N_1 [(x_1/a)^2 + 1]^{-3/2} + N_2 [(x_2/a)^2 + 1]^{-3/2}] - S_n \quad \text{Equation 2.5-7}$$

In rare cases (with homoatomic molecules) the system of equations can be solved without the use of a calculator or a computer. Generally, the most effective way of solving the system of equations with fractional powers is with the help of a calculator or a computer in accordance with special programs worked out for the given system.

In the course of solving the system of equations, we define all the distances between the particles (electrons and protons) and,

respectively, the potential energy of the molecules and the kinetic energies of the electrons. The calculated values of the energies of the hydrogen molecules differ from the experimental data by less than 3%, which proves the correctness of the model.

According to the calculated model, the angle between the attraction forces bonding the electrons to the nuclei of the hydrogen, is equal to 60° . Respectively, the projection of the attraction force bonding an electron of one of the nuclei to the attraction force of the same electron to another nucleus, force (), is equal to half of the electronic force attraction to the nuclei. Relatively, the attraction force of the electrons to the atoms increases by 1.5 times, as compared to the variant when only one atom is bonded to one electron and not to another atom. The increase of the attraction force of the entering electron and its own electron to the nucleus by 1.5 times is equal to the increase of the effective charge of the nuclei by 1.5 times, which, in turn, leads to an abrupt increase in the energy gain.

Thus the electronic energy of a helium-like atom with a nuclear charge of 1 and 1.5 proton units comprises, according to the calculation: 15.3 eV and 42.5 eV respectively. That is, when bonding only an electron to a hydrogen atom, the energy gain, according to the calculation, comprises 1.7 eV i.e., $(15.3 - 13.6 = 1.7 \text{ eV})$. When an atom is bonded (electron + nucleus) during the formation of a hydrogen molecule, the energy gain is equal to 28.9 eV $(42.5 - 13.6 = 28.9 \text{ eV})$ for each of the atoms being bonded, which fully compensates the internuclear repulsion energy. That is, the total energy gain during chemical bond formation, is conditioned, paradoxical as it may seem, to a greater extent by the mutual approach of the atoms' nuclei, than by the transition of the electrons of one atom to the outermost shell of another, that is, by the attraction of the nuclei of one atom to the electrons of another.

Experimentally, the energy of an atom with two electrons and a charge of 1.5 eV can be evaluated as an average value between the energy of a hydride ion (H) and a helium atom (He), that is, by the value of (54.4eV) i.e., close to the previous calculation, and therefore — greater than the repulsion energy. The main role in energy gain and the increase of the charge allows us to solve the rest of the above mentioned paradoxes, namely, the possibility of bonding two electrons when forming DABs, a greater energy of a polar bond, as compared with a covalent bond. A detailed solution of these paradoxes on the basis of the model is well described in other sources???

The description of chemical bonding viewed in our work *The Theory of Chemical Bonding and Chemical Reactions* differs from that of previous works ideologically. For example, in polar molecules, the electrons do not transit from one atom to another, and the cores of the

atoms are closer to the bonding electrons than they are in divided atoms, and the effective positive charge that acts upon the bonding electrons is much greater than in the case of divided atoms (in the case of molecule H_2 — by 1.5 times). That is, the role of the atom's positive charge in the energy gain is much greater than the role of the attraction of the nuclei of one atom to the electrons of another.

August 26, 2003

The introduction of quantum-mechanical interpretations in the 1960s of the XX century was accomplished due to the euphoria caused by the revolution in physics connected with the discoveries of light quantumizing, the wave properties of electrons

Slide 1 The Lewis Rule:

- Atoms form chemical bonds as a result of the loss, connection, or unification of such a number of electrons, which leads to the completion of the electronic configuration of inert gas atoms.

- “The corresponding Lewis structures tell us how many bonds an atom can form. In my opinion, these concepts are all we need to discuss chemical bonding at the introductory level.”

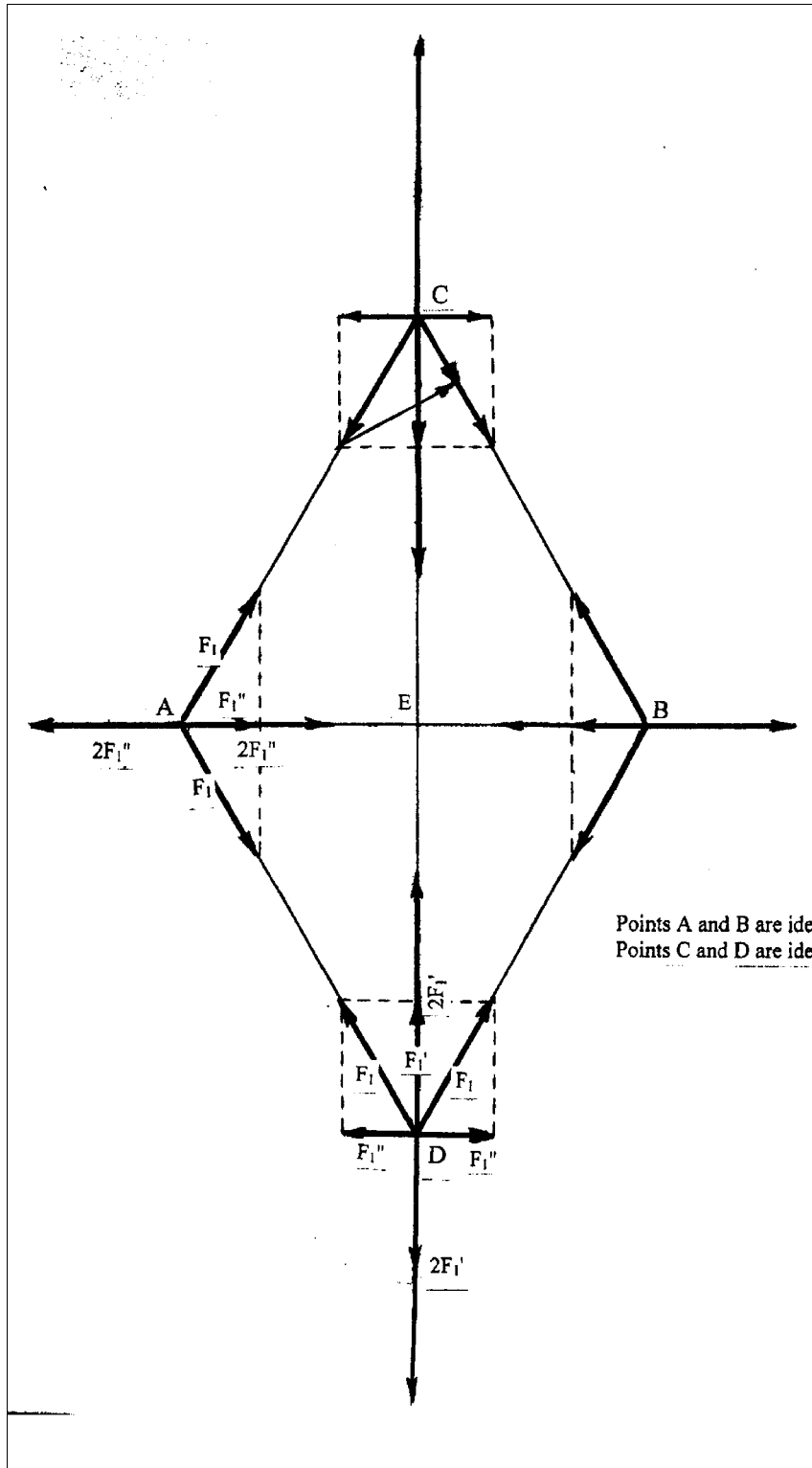
R. Gillespie [Journal of Chem. Educ., 1997, 74, 862] •

(In 1990 the ACS Division of Chemical Education formed the Task Force on the General Chemistry Curriculum Task Force Chairman was ???James N. Spencer.

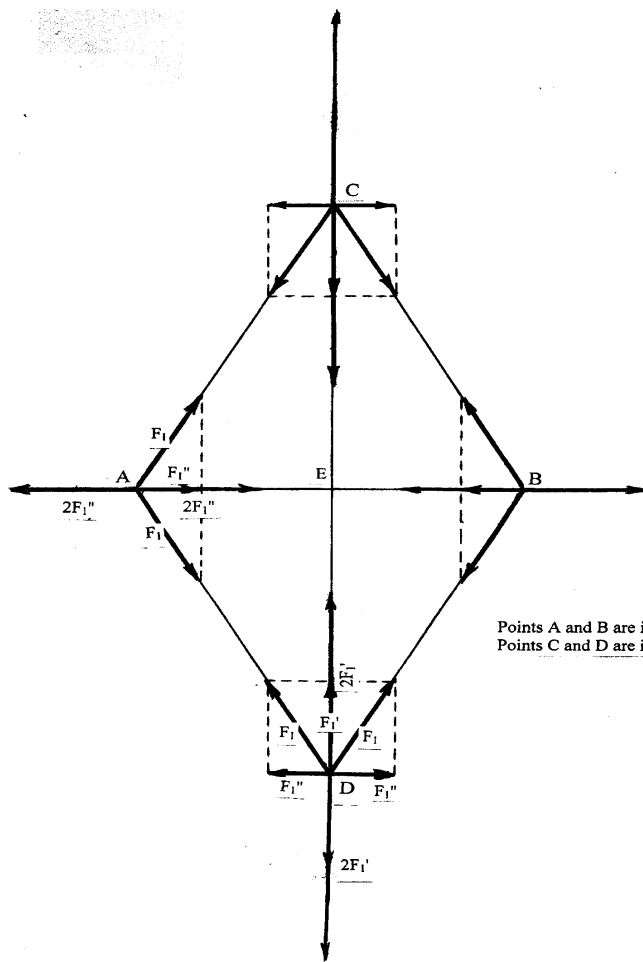
In 1991J Spencer published his report in the JCE (No. 3 p. 182 1991) that was offered by him at the two hundred and first (201st) American Chemical Society meeting. According to Spencer, “General Chemistry has been the subject of countless symposia meetings and conferences over the past 30 yearsJ.N.Spencer

Franklin & Marshall College, Lancaster, PA 17604

General chemistry has been the subject of countless symposia, meetings, and conferences over the past 30 years. There is little left to be said about the course, which has not been previously said.¹⁾



Points A and B are identical
 Points C and D are identical



Points A and B are identical
 Points C and D are identical