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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.

The general character of all the explanations of chemical phenomena in the existing textbooks — first of all, the quantum-chemical explanations — does not leave any doubt in the students that at least such phenomena as wave properties of particles and delocalized electrons actually exist, that there are atoms and molecules in the orbitals where only electrons can be situated, and that these orbitals can hybridize.

The fact that quantum-chemical explanations, given in chemistry textbooks, are actually fabrications of the authors, has been admitted in one of the main textbooks "Quantum Chemistry" that were reissued five times from 1970 to 2004 by Ira Levine. Thus, in the first edition, 1970, on page 559 we read: "There is a tendency to consider 'configuration interaction', 'hybridization', etc. as real physical phenomena. Such concepts are only artifacts of the approximations used in the calculations. Even the concept of orbitals is but an approximation, and strictly speaking, orbitals do not exist."

In the fifth edition (2004) on page 609 we read:

“The difference between the energy for the individual structure I and that found when all VB structures are included is the resonance energy of benzene. One says that benzene is “stabilized by resonance,” but, of course, resonance is not a real phenomenon.”

Such concepts as “configuration interaction,” “resonance,” “hybridization” and “exchange” are not real physical phenomena, but only artifacts of the approximations used in the calculations. Likewise, the concept of orbitals is but an approximation, and, strictly speaking, orbitals do not exist.
That is, in accordance with quantum chemistry, all the explanations based on such logic of the students as realistic physical phenomena accepted as orbitals, resonance, exchange, hybridization, etc., are related to false knowledge, which, as we all know, is worse than the lack of knowledge.

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

When making his report at the 225th meeting of the ACS at New Orleans, just to amuse of the listeners a bit, Spencer 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 lie in the fact that this problem had never been solved by science in the previous century.

J.Ogilvie wrote:

"What 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?" [JCE, 1990, 67, 280]

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

Feynman went on: “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, R.Feynman had made a prophetic prediction.

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 the paradigm related to the problem of chemical bonding (see V.&Y.Gankin’s — *How Chemical Bonds Form and Chemical Reactions Proceed, 1998*) that 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
stating 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, cause-and-effect connections between these phenomena, and relatively, the cause-and-effect links between micro-world (atoms, molecules), macro-world (solid bodies), and, what is most important for education — to make these explanations really teachable.
BRIEF HISTORY: REFOCUSING THE GENERAL CHEMISTRY CURRICULUM

In 1990 the ACS Division of Chemical Education formed the Task Force on the General Chemistry Curriculum as follows:

**Task Force Members:** Stephen Berry (University of Chicago), George Bodner (Purdue University), Orville Chapman (UCLA), William [Flick] Coleman (Wellesley College), Arthur Ellis (University of Wisconsin at Madison), John Fortman (Wright State University), Ron Gillespie (McMaster University), Stephen Hawkes (Oregon State University), Dudley Herschbach (Harvard University), Herbert Kaesz (UCLA), Joseph Lagowski (University of Texas at Austin), Ram Lamba (Inter American University of Puerto Rico), David MacInnes (Guilford College), Patricia Metz (Texas Tech University), Jerry Mohrig (Carleton College), Karen Morse (Utah State University), Lyman Rickard (Millersville University), Ethel Schultz (National Science Foundation), James Spencer, *Task Force Chair* (Franklin & Marshall College), Jeffrey Steinfield (Massachusetts Institute of Technology), Judith Strong (Moorhead State University), Tamar [University] Susskind (Oakland Community College), Hesy Taft (Educational Testing Service).

**Task Force Resource Group:** Theodore Brown (University of Illinois), Ernest Eliel (University of North Carolina), Clark Fields (University of Northern Colorado), Baird Lloyd (Emory & Henry College), Joseph Morse (Utah State University), Alan Pribula (Townson State University).

**JAMES SPENCER’S VIEWPOINT**

James Spencer (Task Force chairman) published a report in 1991 on the results of the work of the Task Force in the JCE (No. 3 p.182). According to Spencer:

“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 that has not been previously said. The pitfalls have been noted, various philosophies debated, delivery and assessment have been treated in detail. Nothing much has come from all this attention. Never before, however, has there...”
been such a consensus movement towards a reconsideration of the general chemistry curriculum.

“The college general chemistry course is crowded with respect to the number of topics it covers. This is true despite the oft-cited criticism that the curriculum of introductory college chemistry attempts to cover more topics than students can be reasonably expected to learn.

“There are no guiding principles for general chemistry. We need to ask what we should do in the classroom and laboratory and why we should do it. Why are we teaching this? What do we hope to accomplish with the students? What are the desired outcomes? Why are there no behavioral objectives for the instructor? We lack a framework.

Textbooks are too thick because we have no common core, no agreed-upon set of principles, and no teaching strategy.

“Is it possible that we try to teach some things that are unteachable at the general level? Perhaps the phrase “presently unteachable” should be used. If there are topics that need to be mastered, we need to find new ways, appropriate to the general level, to teach them. There are some presently unteachable things that could be taught if we are willing to spend more time on that subject and less on another. Some of these topics are listed in Table 1.

“Consider, for example, standard free energy. The statement, “If \( \Delta G \) is negative — the reaction is said to be spontaneous; and if \( \Delta G \) is positive — the reaction is non-spontaneous.” appears in numerous texts. Aside from the questionable usage of the terms ‘spontaneous’ and ‘non-spontaneous’ — I have seen it written that ‘the more negative is \( \Delta G \), the more spontaneous is the reaction’ — the statements are generally incorrect. Note further that \( \Delta G \) itself has a very restricted usage. The conditions must be that T, P are constant and that non-pressure volume work is not permitted.
TABLE 1

Topics Requiring Careful Consideration before Being Taught in General Chemistry (or, What is Unteachable at the General Level)

Calorimetry
\[ \Delta G^\circ \]
Phase Diagrams
Ksp
Atomic Spectra
Quantum Mechanics
Colligative Properties
Schroedinger Equation
Clausius-Clapeyron Equation
LeChatelier’s Principle

“Why do we introduce \( \Delta G \) at all? Presumably so that the equation \( \Delta G = -RT \ln K \) can be introduced. Can we teach the concepts without \( \Delta G \)? I think we can, and I think we should because principles first learned are most difficult to unlearn. If we believe standard free energy is essential, we must teach standard states, we must introduce the relation: \( \Delta G = \Delta G^\circ +RT \ln Q \) in some manner; but does this not go away from an introductory course and over into something else? We believe we must simplify ideas so they can be learned for the first time. These simplifications are remembered more easily than correct descriptions.

“We ask students to ‘fill in’ the appropriate numbers and calculate \( \Delta T \) or molecular mass. We are guilty here of wanting to do a calculation; rather than teaching the concept we calculate. I believe that one reason we do what we do is because of the ease of testing. Conceptual understanding is more difficult to test than numerical plug-ins. Content-oriented exams reward memorization; exams should reward understanding of process and concepts (2).
TABLE 2
Topics that Might Be Better Reserved for Later Courses
(or, We Should Not Answer Questions Until We Ask Them)

MO Theory
CFT/LFT
Hard/Soft Acids–Bases
Statistical Thermodynamics
Metal Carbonyls and the EAN Rule
Nomenclature for Compounds with a Bridging Ligand

P.S. Table 2 contains topics that might be better taught in a later course.

TABLE 3
Topics that Are Not Necessary for General Chemistry
(or, Why do They Need to Know That?)

Balancing Redox Equations
The Saponification Value of a Glyceride
Extended Buffer Calculations
Metal Clusters
Valence Bond Theory of Complexes
Geometrical Isomerism of Coordination Compounds
Iodination Number
Declaration and Shapes of MOs
Band Theory of Metals

“The final question I want to raise could be the guiding philosophy behind everything we teach: Why do they need to know that? In this context a careful consideration of what we are attempting to have the student take away from the course must be made. Do we teach some material because it is easy to test? How is the student supposed to be changed after encountering this material? Some suggestions are made in table 3 for topics that perhaps students do not need to know after a course in general chemistry.

“Before presenting any topic at the general level, these questions and others should be asked: Has this material been simplified to the point where it has lost all integrity? Are we answering questions before we ask them? Why do they need to know that?”
“Philosophical arguments about what is essential or desirable in general chemistry are not new, but little progress has been made in addressing new directions in this curriculum. There are always those who say “we, who want a change, are trying to make the course easier.” This is not what I advocate. Chemistry is a demanding subject — it will remain so. We must set high goals, but those goals must be attainable; and having been attained, must have been worth the effort. Removing material that is basically incomprehensible/unteachable may, in fact, make the material in the course more attainable because by doing so, we may focus more time and attention on certain topics. But the course should not be made less demanding.

'I think it is inconceivable that we, as chemists, can’t agree upon a few basis concerns that could constitute a course. One very important aspect for me, and it could be the sole aspect of certain courses, is that the students understand that science is not a collection of facts, that science is a method.

“Because chemistry is hierarchical and requires vertical development; the course should provide some preparation for higher courses. The idea, however, that there is a certain amount of material that must be covered, is not as important as covering less better. We have been constrained, in part, by what we think our advanced courses and other disciplines expect of us. I do not believe we should slavishly follow a certain content. It is better that the students understand what a saturated solution is than to be able to do calculations. No student should leave general chemistry without knowing why chemists believe in atoms.

“Students should get an understanding of the macroscopic picture of nature and the structure of matter, properties of elements, their compounds, and their reactions. Students should have a sense of the overall structure of chemistry. That is, they should have a sense of the microscopic structure and properties of matter that allow chemists to explain, predict, and control macroscopic properties of matter.

“There is no approach that is likely to meet all requirements, but a core curriculum supplemented by modular material, may meet many objections. The core approach assumes that there is a basic set of concepts/principles that every student who takes the course should know. Once this core is defined, the core is supplemented.
Ronald Gillespie's viewpoint

In May 1997, Ronald Gillespie, member of the Task Force, published the article: Commentary: Reforming the General Chemistry Textbook in which he wrote:

“Most of us who teach chemistry want students to understand what we teach them. But many students, perhaps most, do not try to understand. Even if they set out trying to understand, they usually soon conclude that it is too difficult, at least in the time they have available, and they resort, like the others, to learning the material. By learning they mean memorizing names of substances, formulas, definitions of oxidation and reduction, shapes of orbitals, recipes for assigning oxidation numbers and doing pH calculations, etc., etc.

“Most students do not particularly object to doing this because it is what they did in high school and is what it means to study. Many will object to being expected to understand, as they find it easier to memorize and most of them have little understanding of what it means to understand. Surprising, as it may seem to us, they see chemistry as very abstract, very difficult, and unrelated to real life.

“But this is perhaps not so surprising if we remember that for these students, chemistry consists of a large amount of apparently unrelated, irrelevant, and useless material that they have memorized rather than understood! Their main objective is to pass the course and get on to something they consider more interesting and more useful. They take from the course very little of value in other courses or in later life and little, if any, understanding of what chemistry is really about — merely a conviction that they will never understand it.

“Over many years I have noticed that when I meet people socially and reveal that I am a professor of chemistry, they are amazed. How could an otherwise normal-appearing sort of guy possibly understand that stuff? They often admit, somewhat apologetically, that chemistry was their worst subject at high school or university or that it was the most difficult of all the subjects they took. Why do I rarely meet anyone who tells me
chemistry was fascinating or exciting, or at least interesting? Why do most find chemistry so abstract and difficult? Why don't they understand the chemistry we try to teach them?"

**Chemistry:**
*Relation Between the Macroscopic World of Observation and the Microscopic World of Atoms and Molecules*

“Many of us have felt for a long time that there must be something wrong with what we are teaching, but there has been very little agreement about what is needed to change the course so that students will not find chemistry so difficult, irrelevant, and abstract. One problem is that students have difficulty making the connection between the *macroscopic* world of observations and the *microscopic* world of atoms and molecules. Yet it is this aspect of chemistry that sets it apart from other sciences. If students do not make this connection, they fail to see the relevance and importance of chemistry to the real world. An understanding of this connection is probably the most important thing that a student can get out of an introductory course.

**Why Were There So Few Changes in the Chemistry Courses?**

“General Chemistry has been discussed at countless conferences and symposia, in task forces and committees, and in department meetings; but little change has occurred, and General Chemistry remains much as it was 20 or even 40 years ago. Why? One reason may be that textbooks have not changed. No widespread change can occur until a new kind of text is published and widely adopted. There are many well-written and lavishly illustrated texts, but almost all of them treat the same conventional material in more or less the same conventional way. No matter how excellent these texts appear to the instructors who choose them, they have not succeeded in interesting the majority of students or in providing them with an understanding of chemistry or even with useful information that they remember and use later in life.

“Why have only few textbooks tried a new approach? Publishers are reluctant to invest in unconventional books on the chance that one might become a best seller and revolutionize
General Chemistry. Even authors who are convinced of the need for change are reluctant to write a book that is too unconventional because of the difficulty of finding a publisher and getting it adopted. Why have none of the few non-mainstream books that have been published been widely adopted, leading to widespread reform of General Chemistry? Because most instructors do not see the need for change, or do not have time to adapt to a new text and write new course notes? Because no author has yet hit upon the right formula for stimulating the much-needed change?"

Who Will Initiate and Support the Reform?

“It seems to me that discussion has gone on long enough. We will probably never get widespread agreement on how to reform General Chemistry until a truly new textbook is published, which influences enough teachers to change, so that the new way of teaching becomes the accepted way. Getting such books published and adopted will need some initiative from bodies such as the National Science Foundation, the American Chemical Society, and one or more of the large chemical manufacturers. Their support and financial assistance will be required not only to subsidize the writing and publication of such books, but also for retraining workshops for instructors. These organizations could make no more important contribution to the future of chemistry than to provide this support.

1) **Forget about the needs of chemistry majors.** Very few students in General Chemistry will become chemistry majors and only a small number will take even one more chemistry course. Although it is not the main reason for reforming the course, we hope to persuade more students to become chemistry majors. However, there is no need to include material in the text simply because it will be needed by majors. When the students' enthusiasm for chemistry has been ignited, they will easily and eagerly absorb this material in the majors' courses.

2) **Continually emphasize the relationship between the macroscopic world of observations and the microscopic world of atoms and molecules.** This relationship is the unique aspect of
chemistry, and understanding it makes chemistry alive and relevant. Demonstrations of the properties of substances and references to the role of these substances in the real world, followed by explanation of the observations in terms of the atoms and molecules of which substances are composed, is essential. Putting observations first — shows students that the theories and principles that are a great part of General Chemistry, are there not just to be learned, but to help in understanding these observations.

3) **Cut out unnecessary details and busy work; concentrate on what is needed to understand chemistry.** Why start a textbook with details about the names and formulas of substances? This is boring. Show students some real chemistry. Bring in what is essential for naming and writing formulas of substances only when they are being discussed. How many chemists ever bother to balance an equation, particularly the complicated redox equations so common in textbook exercises? A few students will enjoy the challenge, but are they learning chemistry? Although the principle is important, time spent balancing any but the simplest equation is time better employed on other topics.

Is it really important that students know how to calculate the pH of a solution when they will never have to do such a calculation again? Even if at a future time they do need to know the pH of a solution, they will use a pH meter. This will give them a more accurate (much more accurate) value than the simplified calculation they learned (and probably forgotten) how to do in General Chemistry. Do students really need to learn the shapes of orbitals? These shapes cannot be made understandable to students at this level. Is it not enough to understand that atoms are held together by the electrostatic attraction between electrons and nuclei? Details of bonding theories should be left for chemistry major courses.

4) **Show the broad scope of chemistry.** Students in General Chemistry have a broad range of interests. Why not show them that chemistry is indeed the central science, basic to understanding all materials, whether organic or inorganic, synthetic or naturally occurring; show them how chemistry is relevant to the geologist, biologist, engineer, astronomer, doctor, environmentalist — indeed, to everybody? Make General Chemistry truly general,
rather than the elementary physical chemistry course it is at present.

5) **Make the textbook shorter**, so that the material can be covered at a pace that allows time for understanding. Many students are overwhelmed by the amount of material and detail in most texts.

Perhaps these suggestions will inspire some author to write, some publisher to publish, and some organization to support the revolutionary text that we need. Perhaps such a text will follow only some (or none) of my suggestions, but I hope the questions I have raised will provoke some potential authors to propose their own solutions. The approach of the year 2000 is inspiring many to think about change. Let us hope that chemists will be able to celebrate the new millennium with a new, more inspiring approach to General Chemistry.”


In 1996 the *Preliminary Edition of Chemistry, Structure and Dynamics* was issued by James N Spencer, George M.Bodner, and Lyman H.Richard.

The authors wrote in the preface of the book: “In 1989 the Division of Chemical Education of the American Society recognized the need to foster the development of alternative chemistry curricular. The Task Force on the General Chemistry Curriculum was created to meet the need. We were members of the Task Force and our book, *Chemistry: Structure Dynamics,* is one of the products of the work of the Task Force.

“The text is written for students taking introductory chemistry for science and chemistry courses. We decided which concepts to include in the core based on two criteria. First, the concepts should be the fundamental building blocks for understanding chemistry — concepts that provide the basis for both the core and the modules. Second, these concepts should be perceived by the students as being directly applicable to their majors or careers.
“Traditional texts present concepts and principles in isolation, with little, if any, connection between each concept or principle and the rest of the material. In *Chemistry: Structure and Dynamics* unifying themes are used to integrate the core topics.

“The new models used in this text can be divided into three types: (1) data-driven models, (2) models that reflect current understanding of chemical theories, and (3) models that make it easier for students to understand traditional concepts. The development of electron configurations from experimental photoelectron spectral (PES) data is an example of a data-driven model that supports the unifying theme of the process of science by demonstrating to students how experimental data can be used to construct models. This approach gives students a more concrete, and still scientifically correct, foundation on which to base their understanding of electron configuration than does the use of the more abstract quantum numbers.

“Models that reflect current understanding of chemical theories include the replacement of the valence shell electron pair repulsion (VSEPR) theory for predicting molecular geometry with Gillespie’s more recent electron domain (ED) model.”

These textbooks took into account the above-mentioned publications. The main difference in the change was the return to the classical chemical phenomenological system of explanations known by the authors as data-driven models. Thus, the authors had gone against the generally accepted mode in science that reigned in the scientific world for the last 50 years. These books are actually milestones in the general chemistry curriculum.

In 1997 an article was published in the JCE #7, page 862 by R. Gillespie in which the author offered the idea of limiting the course of General Chemistry by the explanations of six of the greatest essences of chemistry. Gillespie says:

“To answer the question ‘What must be included in the course of general chemistry?’ we need to ask what fundamental ideas of chemistry are essential to understand and appreciate modern chemistry. We must remember that the general chemistry course is not (or should not be) designed as the first step in the training of future professional chemists. Biologists, physicists, geologists, engineers, medical practitioners, environmentalists, and indeed, every educated citizen need to understand chemistry. The course should be oriented toward the needs of these science, engineering, and medical students, so that they know how chemists
think about the material world, what chemists are doing today, and what questions chemistry can answer. We need to show them the importance of chemistry in their chosen field as well as in everyday life.

“I call these fundamental ideas the ‘great ideas of chemistry’. Here is my list of the six concepts that form the basis of modern chemistry. I believe every high school and college introductory chemistry course should include these ideas — indeed, the course should be built around them. In what depth each of these is treated depends on the level and aims of the course. I will illustrate what I think is the minimum depth to which these ideas should be treated in the college general chemistry course. Part of the problem with the present overloaded freshman course is that these concepts are often presented in greater detail than necessary for good understanding at the level appropriate for the students’ needs.”

**Atoms, Molecules, Ions**

“Modern chemistry starts with Dalton and the concepts of atoms and molecules. Elements are a kind of matter that consists of atoms of only one kind. Compounds consist of two or more kinds of atoms held together in definite ratios. To understand how atoms are held together to form molecules, we move on to Rutherford and the concept that an atom consists of a central nucleus surrounded by electrons. The arrangement of these electrons in energy levels or shells can be readily deduced from data provided by ionization energies and photoelectron spectra, leading to the concept of a positively charged core surrounded by a valence shell.

**The Chemical Bond: What Holds Atoms Together in Molecules and Crystals?**

“All chemical bonds are formed by electrostatic attractions between positively charged cores and negatively charged valence electrons. Electrostatic forces are the only important force in chemistry. Bonds are not formed by the overlap of orbitals, as we read not infrequently; this is just a model — admittedly a very useful one and essential for the chemistry major, but I don’t think it is essential for students at the introductory level. We can obtain a
very good understanding of chemistry without it; indeed, many chemists make little use of it. It distracts attention from the real reason for bond formation: the electrostatic attraction between electrons and nuclei.

“There are more important and more relevant topics to treat at the introductory level. Moreover, the orbital model gives students the incorrect impression that chemistry is a difficult, abstract, mathematical subject based on a mysterious concept that is not and cannot be satisfactorily explained at the introductory level. We can simply describe ionic bonds as resulting from the electrostatic attraction between ions and covalent bonds, as resulting from a shared pair of the electrons’ attraction to the two atomic cores. The corresponding Lewis structures tell us how many bonds an atom will form. In my opinion, these concepts are all we need to discuss relative to chemical bonding at the introductory level.”

Molecular Shape
Geometry: Three-Dimensional Chemistry

“The concept of molecular shape and geometry has been important in chemistry since the days of le Bel and van’t Hoff. It has gained increased importance since the advent of X-ray crystallography. Understanding shape is vital to understanding a wide range of topics in modern chemistry: for example, biomolecules and their functions, industrial catalysts such as zeolites and solid surfaces, and synthetic polymers. Our understanding of shape and ability to control it are now such that we can synthesize almost any shape needed for a specific purpose: cages that trap ions of a particular size; molecules that have the shape necessary to bind to only one specific type of molecule (molecules that “recognize” each other); long-chain molecules that conduct an electronic current and thus behave as molecular wires; and so on.

“The variety and complexity of molecules that chemists can now create is amazing and illustrates a very important aspect of chemistry, namely, that it is creative science in the material sense. Chemists make new structures (molecules) that never existed before. This aspect of chemistry receives too little emphasis in the introductory course, although it is one that can stimulate and excite students by showing that chemistry is practical, useful, and challenging, not dull, theoretical, mathematical, and abstract.
“We have a very simple model, the VSEPR, that provides a basis for discussing the shapes of simple molecules and most features of even very large molecules. We need go no further at the introductory level. Hybrid orbitals, often discussed in this part of the course, are just another aspect of the orbital model. Moreover, they do not explain molecular geometry but merely describe it in terms of the orbital model. Understanding the concept of hybrid orbitals is essential for chemistry majors but not for general chemistry students. Molecular modeling programs now make it even easier for students to understand and become familiar with the shapes of molecules.”

**Kinetic Theory**

“By kinetic theory I do not mean the derivation of $pV = 1/3 nmc^2 = nRT$, which is not an essential topic in the course, but rather the concept that the above absolute zero atoms and molecules are in constant random motion: the higher the temperature the faster the molecules move. Combining this concept with that of intermolecular forces — electrostatic forces between nuclei and electrons — provides an understanding of the gas, solid, and liquid states. The constant motion of atoms means not only that molecules are moving in space, but that they are not static objects — they are rotating, librating, and vibrating. We can use this concept to introduce infrared spectra and their use, for example, in the identification of organic molecules.”

**Chemical Reactions**

“This brings us to the concept of the chemical reaction. Reactions occur because molecules are moving and when they bump into each other sufficiently violently, bonds break and atoms are exchanged to give new molecules. Or a molecule that is vibrating sufficiently violently may break up into smaller molecules. These statements constitute a simple but fundamental explanation of a chemical reaction. To go further, we can introduce the concept of activation energy so that we can explain why some reactions are very fast and others are immeasurably slow at ordinary temperatures. This is the minimum that students need to
understand about how chemical reactions take place. The details commonly presented — the plots needed to establish reaction rate and reaction order, the integrated rate laws, and so on, — are secondary to these fundamental ideas. These details are essential for chemistry major but I doubt that they are necessary for students in the introductory course.

“But there is much more to the chemical reaction — perhaps the most important of the six great ideas — because reactions are the heart of chemistry. Understanding reactions has been a primary aim of chemists fro the days of the alchemists. We now recognize many different types of reactions, but two in particular: acid-base and redox, which are of fundamental importance throughout inorganic, organic, and bio-chemistry, and I believe they must be dealt with in the introductory course. But they cannot be fully understood simply in terms of their definitions as proton transfer and electron transfer. They should be introduced and discussed in terms of observations on real reactions carried out by the student in the laboratory or, as a second best, as lecture demonstrations live or on video. These two reaction types along with a few others such as precipitation reactions, and in organic chemistry – addition and substitution reactions, enable us to make sense of the many thousands of reactions that we use and study in chemistry.

“The study of reactions has been neglected in the introductory course partly because it has come to be known as descriptive chemistry and therefore to be regarded as dull. Of course, mere description is dull. But chemistry has advanced far beyond the stage of mere description: understanding reactions and using them for specific purposes – is what chemists are trying to do. Much of both industrial and academic chemistry deals with syntheses of new substances — materials, plastics, drugs — and the preparation of known substances by better methods — cheaper, environmentally friendly methods, and so on.

“What causes the most excitement in the chemical world? The preparation of new molecules, such as those of the noble gases, and buckminsterfullerne. We have to place more emphasis on the fantastic things that imaginative chemists have done and will continue to do in making new molecules, to show the students that chemistry offers endless opportunities for creative and imaginative minds.
“The periodic table is of great assistance in classifying and understanding reactions. It has been of such importance in the development of chemistry, that I might well have included it as one of the great ideas. It is important to emphasize that the periodic table was invented by Dmitry Mendeleyev (1834-1907) long before anything was known about the detailed structure of the atom, as a means for classifying and better understanding the properties of the elements and their compounds. It remains one of the chemist’s most useful tools for this purpose. In understanding reactions, we also make extensive use of concepts such as electronegativity, atomic size, and core charge or effective nuclear charge, which can be developed directly from the simple model of atomic structure described earlier.”

**Energy and Entropy**

“Finally, we need to know why some reactions occur and others do not, or more exactly, why some reactions reach equilibrium where very little product is formed, while others go essentially to completion. We understand this in terms of thermodynamics — more particularly in terms of the concepts of energy and entropy, the first and second laws of thermodynamics, which is a forbidding term for students. The equations, on which formal thermodynamics is based, are even more forbidding. If it is taught in a formal way, it can be dull and difficult. Even *entropy* can be a frightening word that can be made to seem abstract and difficult. But it need not be. Everyone can understand the concept of disorder, and that is really all there is to entropy. The students will have already met the concept of random chaotic motion in the discussion of kinetic theory.

“Reactions occur when the disorder of the universe (or, more simply, the reaction system and its surroundings) is increased. This is the case for exothermic reactions: heat transferred to the surroundings increases its entropy or disorder. The majority of reactions that occur under ordinary conditions are exothermic because the heat released to the surroundings causes an increase in the disorder or entropy of the surroundings; this is usually larger than any entropy decrease that might occur in the system. We can have endothermic reactions if the disorder increase in the system is greater than the disorder decrease of the
surroundings owing to heat transferred from the surroundings to
the system. This is, basically, all there is to understanding the role
of thermodynamics in reaction chemistry: a reaction will go if the
total entropy of the system and its surroundings increases.

“These are the important ideas that must be understood
before it is worth going on further to the concept of free energy
and equations such as \( \Delta G = \Delta H - T \Delta S \). In my view, we do not
need to go this far in the introductory course. Plugging numbers
into equations will not appreciably enhance a student’s
understanding of basic concepts, and solving numerical problems
will be a dull, uninteresting, and irrelevant exercise if students
have not understood the basic concepts.”

**Basing the Freshman Course on the Great Ideas**

“These great ideas are the concepts that I think must be in
the freshman chemistry course to give a basis understanding of
chemistry. For chemistry majors they will be expanded and applied
throughout all courses. Students in other science, engineering, and
medicine courses will also meet them again. I have indicated the
minimum treatment needed to understand these concepts at the
freshman level. I do not think they need to be taken further,
although some instructors will wish to do so. In any case, a
substantial amount of time needs to be spent in making sure that
the great ideas are truly understood. We need to use a large number
and variety of qualitative questions to really test students’
understanding of basic concepts. Qualitative problems that can so
often be answered, by plugging numbers into memorized formulas,
generally do little to test students’ understanding.

“Treating these concepts at the level indicated would give
students the needed understanding but would not take up all
available time. Such a treatment would go a long way toward
solving the major problems of present courses: too much material,
too much emphasis on abstract theory, and not enough on reaction
chemistry; no time for updating the course with new, more relevant
material such as environmental chemistry, materials science,
macromolecules and polymers, and biochemistry — some of
which also must be in general chemistry if we are to present a true
introduction to modern chemistry.
“How should we present the basic ideas? It would not be satisfactory to treat each one completely and in sequence because most of them are needed from early on. Rather we should introduce the ideas early but not develop them fully, and then show how they are used to understand the properties of substances and their reactions, developing them further as needed. In other words, we would use them to rationalize a limited number of properties and reactions of inorganic and organic substances — choosing as far as possible simple, relatively well-known or common substances and those of some relevance in everyday life. Then we can show that they also provide a basis for understanding areas where much of the current process in chemistry is occurring, such as environmental chemistry, materials science, and biochemistry. Only in the context of applications such as these can students fully appreciate the importance and usefulness of the great ideas of chemistry.”

**OUR VIEWPOINT**

In his article, Ronald J. Gillespie offered the idea of limiting Introductory Chemistry to six main topics: atom structure, the periodic law, chemical bonding, chemical reactions, chemical thermodynamics, and stereochemistry.

We presume that the introductory chemistry curriculum should be limited by an up-to-date explanation of the main chemical phenomena concerning chemical bonding, chemical reactions, the connection between these phenomena and between the physical and chemical properties and the structure of substances.

The rest of the material, including physical and mathematical aspects, should be given only if it is meant to serve as a basis for the structure of a theory of chemical phenomena.

In what cases do we give the students additional material?

1) When it is vital for structuring a theory, say, in atom structure, or to reveal its layer-like structure.

2) When the material is important, during the illustration of the general precepts of a theory, for example, various types of bonds and/or chemical reactions.
3) When systemizing the material; for example, the Mendeleyev periodic table of elements.

With this in mind we will approach our aim, which was defined as a result of the 30-year discussions mentioned above.

“A thin book — if such things exist — containing guiding principles, basic knowledge, a thematic approach to general chemistry, would be prepared.”

We can even do as the above-mentioned authors of textbooks do — consider that the given book “is one of the products of the work of the Task Force.” At least the time of its issue, the number of subjects touched upon, and most importantly — the data-driven models precede the theoretical discussions.

The types of models that we generally use are actually copies of model types given in the preface of the book *Structure and Dynamics* mentioned on the previous pages under the numerals of 1, 2, and 3.

Explanations concerning the layer-like structure of the atom and the method of defining the number of electrons in each layer on the basis of defining the ionization energy, the defining of valence on the basis of the data on the structure of stable compounds, The structure of models of chemical bonds on the basis of the comparison of the valence data and the data concerning atoms of the ionization energies, etc. are good examples of data-driven models.

Examples of models that reflect current understanding of chemical theories are well understood and therefore quite teachable as far as the theory of chemical bonding and chemical reactions are concerned.

The appearance of these models is conditioned by the fact that at the end of the twentieth century, according to Lippard (C&EN, Aug. 7, 2000), “as a result of the recent revolutionary changes in chemistry, older paradigms are giving way to new principles.”

The paradigm, to the effect that the problem of chemical bonding can be solved only in the framework of quantum mechanics, was exchanged for a paradigm to the effect that this problem could be solved in the framework of the classical phenomenological approach. What is most important in education is to make these explanations really teachable
In 1868 Lotar Mayer announced: “Chemical phenomena must be treated as if they were problems of mechanics.” This announcement serves as an epigraph to the chapter Rates and Mechanisms of Chemical Reactions issued by Chemical Principles in 1979. In textbooks there are visual aids for students illustrating drawings

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Linus Pauling General Chemistry 1970, p.563

where the interacting molecules approach each other at a great speed (A), then they collide (B) and break up(C).

Experimental facts that have been collected over the last fifty years lead to change in paradigms of chemical kinetics and catalysis. According to the new paradigm, chemical phenomena must be treated as problems relative to the change of the potential energy of the electrons in the outermost atomic shells. A comprehensible phenomenological explanation of chemical kinetics and catalysis phenomena in the framework of the new paradigms are suitable for introductory chemistry.

Gillespie not only indicated the minimal number of topics that introductory chemistry should be limited to, but he also indicated exactly what kind of material should be included in each of the six sections.

Our suggestion about the contents of the introductory chemistry course completely coincides with the main conclusions made by the Task Forces and mentioned in Spencer’s and Gillespie’s articles: 1) The exclusion of unteachable material; 2) The use of the core approach.

We support Gillespie’s suggestion on how the Introductory Chemistry Curriculum should be limited. But generally, the curriculum that we suggest, differs from that suggested by Spencer and Gillespie in as much as our suggestion considers what Lippard called, “the results of the quiet chemical revolution,” that occurred at the end of the twentieth century.
In accordance with the results of this revolution, Lippard suggested more than 10 points relative to grants among which were: “We wish to evolve new theoretical approaches to understand chemical bonding and reactions and to test these theories via real chemical systems.”

That is, in the course of the chemical revolution, the problem of chemical bonding and chemical reactions was solved, and the comprehensible methods of conveying these phenomena to the students have been found.

To compare the Gillespie suggestion with the newly offered explanation of the results of the researches carried out in 1990-2002, let’s observe in greater detail, the contents of Gillespie’s suggestions with those of the herewith-offered ones:

**Atoms, Molecules, Ions**

Researches conducted in 1990-2000 have shown that, indeed, we must limit the material suggested by Gillespie. The slight changes by which our explanations differ from those of Gillespie are relative to the fact that we use only ionization energy for defining the number of electrons in the outermost layer of the atom, and not the more modern data on photo-electronic spectroscopy. This is because the difference between electrons s, p, and d in the outermost layer, relative to the energy, is small and is obvious during photo-electronic spectroscopy, and is not obvious in the energy or in the chemical properties of bonds formed out of these electrons.

**Chemical Bonds; What Holds Atoms Together in Molecules and Crystals?**

Great progress was gained in the interpretation and explanation of the physical essence of chemical bonding in the course of the quiet chemical revolution.

We offer the interpretation of chemical bonding in our manual *Introductory Chemistry (Teaching Guide)* on two levels
that differ in depth of knowledge. Both levels of explanations, as already mentioned, are based upon the knowledge that the students received in their former period of education. The main difference between the old and the new explanations when teaching chemical bonding is that the latter answers the following questions:

1) How does the chemical bond form between the atoms?
2) What is the nature of the forces that bond atoms into molecules and molecules into substances?
3) Which interactions between the nuclei and the electrons are the most important ones?
4) Why does the thermal breaking of a bond require two times more energy than that, which is discharged during bond formation?
5) Why don’t noble gases form covalent chemical bonds between themselves?
6) Why is it that the bonds between elements of group II are by one order of magnitude weaker than those between the elements of groups I and III, etc?

The main difference in the new explanation is the fact that it is phenomenological, that is, completely structured on the basis of the analysis and comparison of the experimental data. Thus, the conclusion about the layer-like structure of the atoms and the number of electrons in the outermost shell of the atoms is made from the experimental data via the ionization energy of the atoms of elements of the 2nd and 3rd periods.

All the concepts of the theory of chemical bonding are built on the basis of the comparison of experimental data relative to the number of electrons in the outermost shell and the data on the valence of the elements.

This comparison led to the introduction of a model for chemical bonding in a hydrogen molecule. According to this model, a covalent chemical bond is formed of two electrons rotating on a plane perpendicular to the axis and connecting the nuclei. Moreover, both bonding electrons enter the outermost shells of both bonding atoms. All these precepts are not mere declarations; they are based upon the above given comparisons.

In the case of a hydrogen molecule (two protons and two electrons), when presupposing that the usual electrostatic interactions exist between these four particles, the molecule’s energy is calculated via an analytic (algebraic) solution. The
energy value of a molecule, received in the course of the calculation, differs from the experimental result by less than 3%, which proves that the defining forces in chemical bond formation are the electrostatic forces.

The attraction of the initial atoms’ nuclei to the bonding electrons, situated between them, offers about 10% of the energy gain (the hydrogen atom’s affinity to the electron is equal to 0.72 eV). The main electrostatic contribution is the increase of the nuclei’s attractions to the electrons at the expense of the increase of the effective charges of the atoms being bonded, which occurs during chemical bond formation.

Equations compiled on the basis of a model allow answering the question: What is the optimal number of electrons necessary to form a bond? Or: Why is it that two electrons take part in bond formation, and not one or three? According to calculations, if one or three electrons took part in bond formation between two neutral atoms in the gas phase, there would be no energy gain, i.e., the molecule would not form.

Then, as a result of calculations of the model for chemical bonding, it was shown that the bonding energy increases with the increase of the difference between the first ionization energies of the atoms being bonded. The calculated dependence of the bonding energy of one atom with others (dependence of the bonding energy on the first ionization energy of the second atom) coincided with the experimental results. This proved that in the course of the formation of ionic compounds of the NaCl type, there is no electron transition from Na to the halogen. A greater energy gain, in this case, is conditioned by a greater approach to the bonding electrons of the nucleus of an atom with greater first ionization energy. The distance between the nuclei of the Na and Cl atoms and the bonding electrons in the molecules is smaller than the distance between the nuclei and the electrons of the outermost shells in anions Na\(^-\) and Cl\(^-\).

Gillespie’s suggestion about limiting this section with the explanation of ionic and covalent bonding on the level of the Lewis rules, offered by the author in 1913, proved to be baseless in 1997.

These rules included such ‘facts’ as the wish of the atoms to build their shells up to the shells of the inert gases by a) transferring the electrons or b) sharing them among the atoms.
Neither supposition had any physical sense. Even worse, the general supposition about the atoms wanting to build their shells up to the shells of the inert gases had an anthropo-physical sense. Lewis introduced this supposition with the aim of uniting the ionic and covalent bonds.

The first calculations of ionic bonding energy which were initiated out of the Lewis rules and the Kossel theory, that is, they presupposed that ionic bonding (for example, in NaCl) is formed at the expense of the attraction of all kinds of ions, as a result of the transition of electrons from sodium (Na) to chlorine (Cl), and differed from the experimentally defined bonding energy by less than 10%.

However, in 1970 Pimentel proved that these calculations are incorrect, and that the discrepancy between the calculation and the experimental results equaled to more than 80%. That is, the Lewis-Kossel supposition concerning the formation of ionic bonds via their scheme, contradicted the calculation that proved the groundlessness of this supposition.

Analogously, considering a calculation as the basis of the electric nature of covalent bonding, as a result of the attraction of the nuclei to the bonding electrons, also led to results that differed from those of the experiments.

In the case of accounting for the hydrogen atoms’ affinity energy to the electrons at the expense of the attraction of the nuclei to the electrons, the additional energy comprised 1.4 eV, which amounts to 30% of the bonding energy without considering the inter-nuclear repulsion. Together with the inter-nuclear repulsion, the energy gain at the expense of the nuclei’s attraction to the bonding electrons amounts to 10% of the bonding energy. That is, the readily accepted explanation, offered by Gillespie, argumentatively contradicted the scientific viewpoints on the nature of ionic and covalent bonding of the second half of the twentieth century.

To be more precise, the problem of the physical nature of chemical bonding was not yet solved by science. Therefore, this problem could only be included in the Introductory Chemistry course only as one that was not solved as yet.

The Lewis Rules are an exception. The electron-deficit (BF$_3$) and the electron-surplus compounds SF$_4$, PF$_5$, XeF$_4$, etc., cause problems during the representation of structures such as SO$_2$,
NO₂, C₆H₆, etc., and there are also problems when explaining the structure of stable compounds of the I₃, I₅, Br₃ type, etc.

The existing textbooks, that limit the description of chemical bonding with the Lewis Rules, include exceptions to the Lewis Rules and solutions to the above-mentioned problems. Simultaneously, the structure of electron-deficit compounds is not explained, while the formation of stable electron-surplus compounds of the SF₄ type is explained by the participation of d-orbitals in the bond formation. The structure of compounds (like I₃) is explained, as a rule, only in monographs. The problem of writing such structures as SO₂ is explained in the framework of the resonance theory. In other words, all the explanations are different and they are all quantum-chemical, that is, the students should be taught quantum chemistry, which is regarded as being unteachable.

In the framework of the new explanation of bonding energy such as homo-atomic (H₂, Cl₂) and hetero-polar (NaCl) both bonding electrons enter the outermost shells of the atoms to be bonded. That is, the number of electrons in the outermost shell of both atoms to be bonded is increased by one electron. Relatively, 8 electrons in the outermost shells of the atoms of the second and third periods is not at all the aim of the atom during stable molecule formation, but rather a limitation of the possibilities of the atom to connect (bond) other atoms. Correspondingly, the anthropo-physical component of the Lewis Rule is excluded.

The electron-deficit compounds are not exceptions to the theory. The theory, besides analyses of data on the valence of stable compounds, and the number of electrons in the outermost electronic layers of atoms of the second and third periods, also includes analyses of experimental data regarding electronic isomerization. These experimental data were received in the second half of the twentieth century.

It was proven experimentally that when one atom is bonded with analogous ones with various kinds of bonds (single, double, donor-acceptor, covalent, Van der Waals), electronic isomers turn into each other with at a great speed thanks to the rapid transition of the electrons. That is, the 50-year old quarrelsome question was solved: the structure of compounds like SO₂, C₆H₆, I₃, PCl₅, SF₄, and XeF₄.

This explanation is the one and only one regarding all compounds, and it does not require the knowledge of quantum-chemical hypotheses and theories.
Moreover, it shows that confirmations of quantum chemistry about resonance hybrids, about the absence of electronic isomerization, are absolutely incorrect.

Explanations of exotic structural compounds in the framework of the Lewis Rules allowed declining the quantum-chemical explanations about the structure of these compounds.

The quantum-chemical explanations regarding compounds like $\text{SO}_2\ C_6\text{H}_6$ included such terms as \textit{resonance} while quantum-chemical explanations of the structure of surplus compounds (SF$_4$ PCl$_5$) included such terms as \textit{d-orbital}.

The introduction of the terms \textit{resonance} and \textit{orbital} was also required by the theory of valence bonds, which, in textbooks explained the valence rules. Analogously, the introduction of the term \textit{orbital} was necessary in order to formulate the theory of molecular orbitals.

In order to explain the essence of the word \textit{orbital}, today’s Introductory Level Course of the General Chemistry textbook, introduces a description of the discovery made by Plank, Einstein, De Broglie, Bohr, and Schroedinger.

The authors of the discovery could not understand the physical contents of their discoveries — that is, the given material was regarded as unteachable.

Indeed, A.Einstein wrote:

“All these fifty years of cautious brooding have brought me no nearer to the answer to the question: 'What are light quanta?' Nowadays every Tom, Dick and Harry thinks he knows it, but he is mistaken.”

N.Bohr was known to have made remarks about quantum mechanics to the effect that "If you think you understand it, that only shows that you don't know the first thing about it."

E.Schroedinger also left his message about quantum mechanics: "... it is not only practically inaccessible, but not even thinkable. Or, to be more precise, we can, of course, think it, but however we think it, it is wrong: not perhaps quite as meaningless as a \textit{triangular circle}, but much more so than a \textit{winged lion}.”

“Nobody understands quantum theory,” said R.Feynman, the greatest physicist of his generation, in 1980.

The Bohr Theory of hydrogen atom structure, given in textbooks, explains that the specter of the hydrogen atom has only a historic connection with the origin of the term \textit{to quantize energy},
and further on, no mention is made in textbooks regarding the spectroscopy of atoms.

Thus, the exclusion of quantum-chemical explanations of chemical phenomena allows to: 1) exclude the explanations that are unteachable; and 2) exclude the descriptions of physical discoveries that have no direct cause-and-effect connections with chemical phenomena.

The general character of all the explanations of chemical phenomena in the existing textbooks — first of all, the quantum-chemical explanations — does not leave any doubt in the students that at least such phenomena as wave properties of particles and delocalized electrons actually exist, that there are atoms and molecules in the orbitals where only electrons can be situated, and that these orbitals can hybridize.

The fact that quantum-chemical explanations, given in chemistry textbooks, are actually fabrications of the authors, has been admitted in one of the main textbooks "Quantum Chemistry" that were reissued five times from 1970 to 2004 by Ira Levine. Thus, in the first edition, 1970, on page 559 we read: "There is a tendency to consider 'configuration interaction', 'hybridization', etc. as real physical phenomena. Such concepts are only artifacts of the approximations used in the calculations. Even the concept of orbitals is but an approximation, and strictly speaking, orbitals do not exist."

In the fifth edition (2004) on page 609 we read:

“The difference between the energy for the individual structure I and that found when all VB structures are included is the resonance energy of benzene. One says that benzene is “stabilized by resonance,” but, of course, resonance is not a real phenomenon.”

Such concepts as “configuration interaction,” “resonance,” “hybridization” and “exchange” are not real physical phenomena, but only artifacts of the approximations used in the calculations. Likewise, the concept of orbitals is but an approximation, and, strictly speaking, orbitals do not exist.

That is, in accordance with quantum chemistry, all the explanations based on such logic of the students as realistic physical phenomena accepted as orbitals, resonance, exchange, hybridization, etc., are related to false knowledge, which, as we all know, is worse than the lack of knowledge.
Molecular-shaped Geometry: Tri-Dimensional Chemistry

This is one of the most important sections of knowledge in chemistry. However, its explanation, even in Gillespie’s simplified form, is still rather complicated as compared with the other sections of Introductory Chemistry. This is why in our Teaching Guide we have shifted the topic *Three-Dimensional Chemical Structure* to the third level of explanations and introduced our more simplified form of interpretation, instead of that of Gillespie.

Our interpretations contain cause-and-effect connections with the bonding theory that is given in each corresponding section.

Chemical Reactions

The changes in understanding and explaining chemical reactions in the course of the last chemical revolution took place on the level of changes in the paradigms. It was found that:

1) The interaction of saturated molecules proceeds, as a rule, not along the molecular mechanism, but through an intermediate formation of chemically activated particles (ions, radicals, conenees, etc.). Active particles are formed of initial molecules in the course of dissociation that occurs as a result of thermal, photochemical, and other methods of increasing the energy, or, for example, dissolving and dissociating initial molecules in a solvent.

Previously, in the times of the old paradigm, it was supposed that a direct molecular interaction is a general mechanism for chemical reactions, while reactions via intermediate active particles were regarded as special cases.

2) The active particle interaction with saturated molecules proceeds not via the transition state (TS) situated at the top of the potential barrier, but via the intermediate compound (IC) situated in the minimum.

3) In the general case that lay at the bottom of the old paradigm, it was supposed that the interaction of molecules
between themselves, and active particles with molecules, proceed in one stage. According to the new theory (i.e., new paradigm) the interaction of active particles with molecules proceeds in three stages: association, electronic isomerization, and dissociation.

4) The main driving force of chemical reactions, according to the old paradigm, was the kinetic energy of transiting initial molecules [theory of active collisions (TAC) and transition state theory (TST)], which is spent on breaking the old chemical bonds during the reaction. Here it was not clear exactly how, in the course of the chemical reactions that proceed at temperatures of $30^\circ - 200^\circ$ C, most of the chemical bonds break, though they require over $2,000^\circ$ C thermal breaking.

According to the new paradigm, during the interaction of an active particle with a saturated molecule proceeding via the above indicated three stages, as a result of the electronic isomerization reaction, the strong old covalent bond turns into a weak Van der Waals bond (VWB) without any energy expenditure or energy discharge during isomerization. Thermal energy is spent mainly on the formation of extremely small (>0.01 %) active particles. Therefore, the visual pictures of the colliding saturated molecules, as a result of mechanical transition, commonly given in textbooks, are incorrect as far as the modern viewpoint is concerned.

5) In the framework of the mechanical approach, when describing the factors that define the reaction speed, only the influence of the temperature and the initial substance concentration were described.

The question concerning the influence of nature of the reacting substances on the speed reaction was actually never raised.

In spite of this, according to experimental data, the chemical reaction speed is defined, first of all, by the chemical nature of the reacting substances. Thus, for example, radicals interact with saturated molecules by more than 10,000 times faster as compared with the interaction speed of the saturated molecules between themselves.

In the framework of the new approach, this point was not only mentioned as a main point, we managed to understand and
explain the influence of the nature of the reacting substances on the speed of the chemical reactions.

6) In the framework of the old interpretation, the general explanation of catalysis turned out to be a ‘black hole’. From 5 to 10 pages of the 800-page textbook are devoted to catalysis, though more than 90% of the chemical reactions are catalytic.

While in the framework of the new interpretation of the chemical reaction, the catalysis phenomenon becomes comprehensible and explainable in the Introductory Chemistry course relative to both general and special cases of catalytic reactions. Just as the theory of chemical bonding, the theory of chemical reactions is phenomenological.

The theory of chemical reactions is built on the basis of the analysis and comparison of experimental data via the interaction speeds of the active particles (ions, radicals, Lewis acids, Lewis bases, etc.) with saturated molecules.

The mechanism for the interaction of active particles with saturated molecules is based on experimental data relative to the electronic isomerization received from the biological, inorganic and organic chemistry.

**Energy and Entropy**

Just like Spencer, Gillespie considers the interpretation of thermodynamics unteachable. He suggests that ‘entropy’ should be explained as a degree of disorder.

Gillespie offered to include this section in the Introductory Chemistry course because the energy and entropy allow answering the questions: 1) *Why do some reactions take place and others do not?* 2) *Why do some reactions proceed to the end and others do not?*

In the course of the chemical revolution, it was found that reactions proceed when there are chemically active particles in the system, but not at all saturated molecules with a greater energy than that of the products received from the latter. That is, after answering the question *how chemical reactions proceed*, the answer to the first question in the framework of thermodynamics is incorrect.
The second question: Why do some reactions proceed to the end and others do not? The answer to this question is obvious and teachable if we study not only the direct reactions, but also the reverse ones.

In Introductory Chemistry, this question, as well as the question about chemical kinetics, is of the same rank in chemistry, but this rank greatly prevails over the main questions included in Introductory Chemistry.

That is, this question, just as the question concerning chemical kinetics (reactions of various orders of magnitude, mechanisms and kinetics of various reactions) can be included in Physical Chemistry for Majors.

The inclusion of explanations of entropy as a degree of disorder in Introductory Chemistry, we think is a contentious point because of the following:

1) Out of the two explanations about entropy being discussed in literature — thermo-dynamic and statistic (Boltzmann) — the first is unteachable, while the second is mathematical, since it has no physical contents.

2) The introduction of the notion ‘entropy’ (without the introduction of the notion ‘free energy’ and the equation $\Delta G = \Delta H - T\Delta S$) has no practical sense. According to Spencer, ‘free energy’ is unteachable in the framework of Introductory Chemistry; and according to Gillespie, ‘thermodynamics’ is a forbidding term for students, and besides, the equations on which formal thermodynamics is based, are even more forbidding.

The question concerning ‘free energy’ relative to chemistry (but not Introductory Chemistry) is a generalized (i.e., philosophical) question. After realizing the details of the formation and breaking of the chemical bond, the unproductive expenditure of energy during the thermal breaking of the bond that causes the decrease of the potential energy of the electrons (the increase of the distance between the bonding electrons and the nuclei) in the unbroken molecules, all the chemical questions can be explained without the introduction of the notions of ‘free energy’ and ‘entropy’.

What should be inserted in Introductory Chemistry besides the above mentioned by Gillespie and Spencer?
This is a question about the correlation of the macroscopic world of observations and microscopic world of atoms and molecules.

A more complete answer to this question was received in the course of the chemical revolution. We described the connections between the parameters of atoms and molecules, and the physical and chemical properties of substances formed out of these atoms and molecules in the section ‘Physical and Chemical Properties of Substances’.

In 1998 we have issued the book *How Chemical Bonds Form and Chemical Reactions Proceed*. This book contains the results of all our work conducted in the years of 1982 to 1998. In the course of our work, we managed to answer the main questions dealing with chemical bonding and chemical reactions. That is, we have managed to get to the bottom of the physical essence of these phenomena and the cause-and-effect relations between the electronic structure of the atoms, chemical bonding, and chemical reactions.

Proper comprehension of the physical essence of phenomena, and the cause-and-effect relations between them was gained in the framework of the accepted classical (pre-quantum) phenomenological approach, which presupposed the possibility of a distinct (clear), but not quantum-chemical interpretations of such phenomena to the students.

In 1998 we began work on structuring General Chemistry, which will assist the chemistry teacher. Some of the chapters, including those concerning chemical bonding and chemical reactions were reported at conferences at the ACS twice a year (1999 to 2006 - more than 25 reports). The complete reports were published at our site: [http://www.ITChem.com](http://www.ITChem.com)

The questions and discussions at the conference have shown that for 6 years our explanations concerning chemical bonding, kinetics, and catalysis had passed two of the three stages.

It is well-known that before a new concept takes the place of an old one, it must undergo three stages in the social and scientific conscience before it gets its common recognition.

The stages are as follows:
1) That is impossible!
2) M-m-m ---- I guess you've got something there!
3) Recognition of a theory by society. Such recognition usually happens under such slogans as:
   This is a very well-known concept.
   This is the well-forgotten past!

The discussions of the reports at ACS conferences, the reviews on the book and on our site have shown that our interpretations of these chemical phenomena are comprehensible to a wide range of readers. As an example, here is an e-mail to us from a reader:

“I'm a research civil engineer and left chemistry behind when I was 18. At that time [1950] catalysis was presented as something of a black art. However, recently I needed to understand the phenomena of catalysis. So having tried various phrases in Google with the hope of finding a 101 explanation, I eventually hit upon "mechanism of catalysis" which turned up on your site. Congratulations on a most interesting and clear exposition, which, even with my intermediate B.Sc. level of chemistry (and a modicum of subsequent treading), I had no difficulty in understanding and accepting as entirely logical.

Good luck in your future endeavors. Frank Grimer”

In conclusion of this introduction, we would like to thank Professors J.N.Spencer and R.J.Gillespie for their articles, which stimulated our work in the realm of chemical education, and, what is most important — their efforts have defined the direction of further action including the contents of a new chemistry textbook Introductory Chemistry.

We are thankful to all the authors who took part in the thirty-year discussion, and especially to Professor S.J. Hawkes who compiled a compendium of proposals for changes in the Introductory Chemistry Curriculum and articles devoted to relative questions.

We are also thankful to the members of the Task Force for their contribution.
1. AIM OF CHEMISTRY AS A SCIENCE
In the course of its development, *chemistry*, like any other science, has undergone a number of stages. Each stage has invariably led to a better understanding of phenomena that are studied by *chemistry*. Chemistry involves the structure of *substances*, their properties and transformation. Indeed, chemists have always been interested in the kind of particles that substances are made of, which properties of these particles define the various substances that surround us, which of them define those transformations of chemical substances that we observe in nature and in experiments.

Everything that surrounds us is made up of substances, and the properties of various substances are different. For example, things made of the substance called *wood* or *cotton* can burn, while things made of *metal* cannot. Indeed, there are ever so many different substances: wood, metals, gasoline, water, gas, etc., all of which differ by their substances.

Properties of substances are diverse as far as color, solidity, electrical conductivity, etc. are concerned. Besides, substances can enter various processes of chemical transformation as a result of which we get new substances. For example, gasoline, a fluid, turns into carbon dioxide (CO$_2$) and water (H$_2$O) when it burns inside a motor. Methane, a gas, used in gas stoves for cooking, as a result of several chemical transformations, performed at large chemical plants, is transformed into chemical fertilizer.

Chemistry answers such questions as: *How are substances constructed? Why do substances differ from each other? How does the transformation of substances take place?*

Chemistry, like physics, is a *fundamental* science. However, physics includes the study of *energy* and *force*, while chemistry mainly studies *substances* and their *transformations*.

General chemistry studies the *fundamentals* necessary for understanding organic, inorganic, physical, and biological chemistries, but for the comprehension of science as a whole.

General chemistry is among those subjects that educated people cannot do without. Indeed, a person, ignorant of chemistry, would be out of touch with modern society; he would be unable to take part in an ordinary conversation in the 21st century!

Indeed, a person without the basic knowledge of chemistry is unable to understand the notes on labels that accompany
foodstuffs. He cannot take part in conversations that occur in our modern society concerning such important matters as chemical weapons, narcotics, smoking, alcoholism, etc. Such a person cannot understand the differences in the brands of gasoline at the filling stations, he does not understand why cholesterol can be harmful, or which detergents are dangerous and why, etc., etc.

Professions directly connected with chemistry (nuclear fission chemists, pharmacists, chemists-analysts) are included in the first ten most prestigious and most well paid professions. Without the knowledge of chemistry, one cannot become a doctor, a judge, a lawyer, or a businessman. Besides, the prosecutor and the counsel for the defense call upon most every American citizen to serve his country in the capacity of a juror from time to time where he/she must understand the various proofs offered by the prosecutors or the lawyers. Indeed, the basis of many proofs lies in the knowledge of chemical analyses.

What does it mean to know chemistry? This means: to understand the physical sense of chemical phenomena. Physical sense includes the explanations of chemical phenomena arising from the knowledge of physics and mathematics, already gained in high school. Thus, in order to ease assimilation when studying chemistry, the student should get a review dose of physics and mathematics.

When studying general chemistry, the students learn about the structure of the smallest particle of a substance — the atom. They learn about the various properties of atoms, they define the substances of things surrounding us, they learn how chemical and physical transformations of substances take place, how the structure of substances defines their physical and chemical properties.

2. DEPTH OF KNOWLEDGE
Having arrived in America from Russia in 1991, the elder of the two authors of this book was accustomed to go for a walk with his nine-year-old granddaughter. The girl would converse with her granddad about her new friends and about her acquired knowledge of English, while the elder, in turn, would share his knowledge of natural sciences. Once he told the girl a bit about atom structure.

Six years passed. The granddaughter came home from school one day — extremely upset. She said that the teacher had asked the class “Who knows what an atom is?” To her surprise, almost all the kids raised their hands. So did she, for this was a chance to boast of her knowledge in chemistry. She thought she would be the only one to properly answer that question. Who else had such a smart granddad-chemist as she did?

First of all, to soothe the girl, the grandfather explained that the phrase “I know what the atom is” is illogical. On the one hand, it amounts to nothing; on the other hand, it can signify knowledge of various depths. Now what do we mean by the depth of knowledge?

Let’s answer this question relative to the atom and the molecule. This question will cause many students to raise their hands:

1) those who know that atoms are tiny particles;
2) those who know what kind of particles atoms are made of;
3) those who know how atoms are formed;
4) those who know how atoms form molecules;
5) those who know what forces bind atoms into molecules;
6) those who know how to calculate the bonding energy;
7) how the atoms’ properties define the molecules’ properties;
8) what physical laws deal with atom and molecule structure;

As we see, knowledge about the atom differs in depth.

Indeed, in the process of explaining the chemical phenomena of the atom, the molecule, chemical bonding, the structure of chemical substances, chemical reactions, the physical
and chemical properties of substances, etc., we will deepen our knowledge of chemistry. That is, we will answer the question:

Why is it that a simple description of atom and molecule structure precedes the section of the book devoted to a historic view where various experiments and theoretical proofs are given to show how atom and molecule structure were established?

3. GENERAL CHEMISTRY
Bearing in mind that, after all, the whole world and we, ourselves, are all made up of substances, here are the main questions concerning substances, that are answered by general chemistry:

1. What is the smallest particle of a substance?
2. At the expense of what forces do these particles bond with each other?
3. How do the bonds between the particles break up in the course of transformation?
4. How is the likeness and difference of substances that surround us defined?

The world-famous bongo drums player, Richard Feynman, who won the Nobel Prize for Physics, asked: “What is the shortest phrase, concerning the most important scientific knowledge we possess, would you pass on to the next generation?” Feynman, himself answered: “Everything is made of atoms.”

Then he went on to say: “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.]

It is a known fact that all the substances around us (iron, stone, salt, bread, liquids, etc.) consist of molecules, which are the smallest particle of a substance consisting of atoms. An atom consists of a positively charged nucleus around which negatively charged electrons rotate. A nucleus consists of nucleons (protons and neutrons).

Protons are always positively charged, their charges (in absolute units) being equal to those of the electrons.

Neutrons do not carry any electrical charges. Protons and neutrons consist of quarks.

There are $6.02 \cdot 10^{23}$ molecules of water in 18 grams of water. A molecule of water consists of an atom of oxygen (O) and two atoms of hydrogen (H), i.e., $\text{H}_2\text{O}$. 
An oxygen atom consists of a nucleus and 6 electrons.

A hydrogen atom consists of a nucleus and one electron.

To break up water into molecules, we must heat the water to a temperature of 100° C. To further break up a water molecule into atoms, we must heat the steam of the water to a temperature of about 5,000° C.

To tear away the electrons of the oxygen atom from its nucleus, it is necessary to raise the temperature to more than 10,000° C.

Thus, according to experimental data, the limit for breaking up particles into the smallest unit possible depends on the temperature (energy) that we use in order to break up the substance.

Now let’s see how the atom is constructed.

3.1* ATOM STRUCTURE
As already stated, the atom is made up of a positively charged nucleus around which negatively charged electrons rotate.

The nuclear charge is equal to the sum of the proton charges in the nucleus. The positive charge of a proton is equal to the negative charge of an electron (in absolute units). The number of electrons rotating around the nucleus is equal to the number of protons. That is why the sum of the atom’s charges is equal to zero.

The electrons are distributed around the nucleus in layers, like clouds around the earth. In the first layer, closest to the nucleus, there are always 2 electrons starting with elements in the second period; in each of the outer layers there are 8 electrons, or less in the second and third period. The atom’s outermost layer contains a various number of electrons, from 1 to 8. The main forces inside the atom are the electrostatic forces.

Electrons with identical negative charges repulse each other. They remain in the atom due to their attraction to the atom’s nucleus that has a positive charge. The electrons do not fall onto the nucleus because they rotate at a great speed around the nucleus. During the electrons’ rotation around the nucleus, there appears a force like that which we get if we rotate a spring with a metal ball at the end of it. Such a force is known as the centrifugal force. Likewise, centrifugal forces are directed in the opposite direction of the electrostatic forces, thereby drawing the electrons from the atom’s nucleus.

If neutral atoms have an identical number of electrons, the distribution of electrons in the layers of these atoms is also identical. That is, the structure of the electronic shells of these atoms is the same. Substances formed of identical atoms (same nuclear charges or same number of protons and electrons) are known as elements.

At present 109 elements are known to exist. All the elements are systematized into a table of elements, a copy of which usually hangs on the walls of chemistry classes. Each box in the table of elements contains the element’s symbol and name.

Above we have already used some of the symbols and names of elements when giving the formula of water (H₂O), oxygen (O), hydrogen (H), etc.
The element’s number (given in the box) coincides with the amount of protons that the atom’s nucleus of the given element contains. Each column is called a group, and is marked with Roman numerals and each row is called a period and is marked with Arabic numerals.

Elements of one and the same group all have close physical and chemical properties. The elements of main group I: Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs), and Francium (Fr), known as alkali metals, are light, soft, with low boiling and melting temperatures, have high heat conductivity and good electrical conductivity. These elements can readily take part in reactions.

Elements of main group VII (halogens): Fluorine (F), Chlorine (Cl), Bromine (Br), and Iodine (I) are also highly reactive elements, but unlike the elements of group I, they are all non-metallic. They have low heat conductivity and do not conduct electricity.

Elements of main group VIII include inert gases: Helium (He), Neon (Ne) and noble gases: Argon (Ar), Krypton (Kr), Xenon (Xe), Radon (Rn). Unlike other elements, these do not form stable molecules of the He₂ type and are mainly chemically inert elements.

All atoms, when they have plenty of energy, are capable of losing their electrons and turning into positively charged ions.

The energy, necessary to tear an electron away from the atom, is known as ionization energy. The energy necessary to tear the first electron from the atom is known as the first ionization energy (FIE). The more energy we need to tear away the electron, the more stable is the given system.

Most of the neutral atoms are capable of connecting an electron spontaneously (i.e., with energy discharge). Such a property of the atom is called the affinity of the atom to the electron. The energy discharged during this process is called the atom’s affinity energy to the electron.

The main obstacle for the electrons that strive to get into the shell of these atoms, is the inter-electronic repulsion force of the electrons already inside the atom, and which hinder additional electrons to enter the outermost shell.

Let’s take atom structure of a hydrogen atom, as an example. This atom is made up of a nucleus and only one electron. The electron has a negative electric charge, while the nucleus has a
positive one equal to that of the electron. The total value of the atom’s charges is zero.

The mass of the electron is 1,840 times smaller than that of the nucleus. That is, the atom’s mass is almost completely situated in the atom’s nucleus around which the electron constantly rotates at a distance of \(0.53 \cdot 10^{-10}\) m at a speed of \(3 \cdot 10^8\) cm/sec.

The electron is attracted to the nucleus by electric forces. The attractive force of the electron to the nucleus (bonding force \(F\)) is proportional to the charge (\(Z\)) of the nucleus and the electron; it is inversely proportional to the square of the distance (\(R\)) between them. That is:

\[
F = \frac{Ze}{R^2} \quad (3.0)
\]

As we see, the smaller the distance between the electron and the nucleus (\(R\)), and the greater the nuclear charge (\(Z\)), the greater is the attractive force of the electron to the nucleus, and therefore, we need more energy in order to tear the electron away from the nucleus.

The more energy is required to break the bonding, the more stable is the system. That is, if the breaking of the bond (the separation of the electron from the nucleus) in one system requires more energy than in another, then the first system is more stable. The energy required for the breaking of one gram of a hydrogen atom has been defined experimentally. It is equal to 13.6 eV (electron volts).

Also experimentally, was defined the energy necessary for the breaking of the electron away from the nucleus in atoms composed of one electron and having a positive nuclear charge twice that of a hydrogen atom. It was found that in this case it was necessary to spend four times more energy (54.4 eV). That is, an atom with a two times greater charge is four times more stable.

As known from electrostatics, the energy (\(T\)) that is necessary for breaking two bonds by charges with opposite signs (\(Z\) and \(e\)) situated at the distance of \(R\) from each other is defined by the equation:

\[
T = \frac{Ze}{R} \quad (3.1)
\]

That is, the energy necessary for breaking the bonds is proportional to the charge values and inversely proportional to the distance between the charges.
Such a correlation is quite comprehensible: the greater the charges, the greater their attraction to each other; therefore, more energy should be spent on breaking the charges. And the smaller is the distance between them, the more energy should be spent on breaking them. This makes it clear why an atomic system with a nuclear charge two times greater is more stable and requires more energy in order to break it up.

However, the following question requires additional explaining:

*Why is it that when the nuclear charge is doubled, the amount of energy necessary for breaking the bond between the nucleus and the electron increases four times or is equal to the square value of the doubled nuclear charge (54.4/13.6 = 4)?*

This is especially incomprehensible if we return to equation (3.1) according to which – if one of the charges is doubled, the energy necessary for breaking the bond should also be *doubled* but not *squared*.

This discrepancy is due to the following:

In systems where charges $Z$ and $e$ are at rest in reference to each other, energy $T$ is, indeed, proportional to $Z$. That is, when charge $Z$ increases, energy $T$ increases proportionally. Unlike these systems, atomic systems where the electron with charge $e$ rotates around a nucleus with charge $Z$, and charge $Z$ is increased, the radius of rotation $R$ is proportionally decreased. This is because the electron is attracted to the nucleus with a greater force.

Now let’s see how the FIE changes in regard to the change of the nuclear charge.

In figure 3.1 we see the dependence of the FIE on the nuclear charge for the first 20 elements of the table of elements.
According to experimental data, when the nuclear charge changes with a simultaneous increase in the number of electrons in the outermost electronic shell, the FIE increases in five cases and decreases in two during the period.

Thus, for example, the FIE of lithium (Li), with a nuclear charge of 3 proton units, is equal to 5.4 eV; the FIE of beryllium (Be) with a nuclear charge of 4 proton units and whose outermost shell contains 2 electrons, is equal to 9.3 eV. That is, when the nuclear charge of a Li atom increases by one proton unit with a simultaneous increase in the number of electrons in the outermost shell by one unit, the FIE increases by 3.9 eV (i.e., $9.3 - 5.4 = 3.9$) as we transit from Li to Be.

Unlike the transition from lithium (Li) to beryllium (Be), the transition from beryllium (Be) to boron (B) shows that the FIE decreases. Thus, if Be has a FIE of 9.3 eV, then B has a nuclear
charge of 4 proton units with 3 electrons in the outermost electronic layer, and the FIE is equal to 8.3 eV, i.e., by 1 eV less (9.3 – 8.3 = 1).

When transiting from boron (B) to carbon (C), from nitrogen (N) to oxygen (O), from oxygen (O) to fluorine (F), and from fluorine (F) to neon (Ne) — the FIE increases by 3.1: (11.4 – 8.3 = 3.1), (14.5 – 11.4 = 3.1); or by 3.8: (17.4 – 13.6 = 3.8); or by 5.2 (21.6 – 17.4 = 5.2) respectively. That is, here we see regularity like that seen during the transition from Li to Be.

When transiting from nitrogen (N) to oxygen (O), the FIE decreases by 0.9 eV (14.5 – 13.6 = 0.9); this is a dependence analogous to the one we had when transiting from beryllium (Be) to boron (B).

When transiting from neon (Ne) to sodium (Na) the FIE decreases by 16.46 eV (21.6 – 5.14 = 16.46). In the course of this transition, the nuclear charge also increases by 1 proton unit and 1 electron is added.

Thanks to experimental data, we know the IEs for all the electrons in the elements. In figures 3.2 – 3.5 (next two pages) we see the logarithmic dependence of the energy required for the consequent extraction of electrons from the Be, B, N, Ca. atoms.

The logarithmic scale is used so that the scheme (graphic) would not be stretched out vertically.
Figure 3.2

Figure 3.3
Figure 3.4

Figure 3.5
The electrons situated on one straight line belong to one and the same layer (shell). The electrons of one shell are situated at approximately the same distance from the nucleus. This is why during the successive breakaways of the electrons (as a result of ionization) the ionization energies of the consecutive electrons gradually increase while the repulsive forces between the electrons of one and the same layer decrease. This is in accordance with electrostatics.

During the transition to the next layer, the difference between the IEs of the consecutive electrons abruptly increases. This is clearly seen by the difference of the FIEs in the elements that have been mentioned above. The difference in the FIEs between the previous and consecutive elements, located in the same period, comprises less than 4 eV.

When forming a new shell, the comparison of the FIEs in the last element of the second period of neon (Ne) and the first element in the third period of sodium (Na), this difference increases to 16.46 eV. That is, according to the data on the FIEs, Li, Be, B, C, N, O, F, Ne, Na contain 1, 2, 3, 4, 5, 6, 7, 8, and 1 electron respectively in the outermost shell.

The study of ionization energies (necessary to tear an electron off the atom) of various atoms has shown that the electrons in the atoms are situated in layers. There are two electrons in the first shell nearest to the nucleus and there are 8 electrons in each of the other inner shells.

According to experiments, the number of electrons in the outermost layers of the atoms changes periodically when the nuclear charge increases. For elements with fewer than 20 electrons, the maximal number of electrons in the outermost shell (layer) is 8. That is, the number of electrons in the outermost shell, when the nuclear charge increases, changes periodically from 1 to 8. (See figure 3.1).

The layer-structure of the electronic cloud surrounding the nucleus and the periodic change in the amount of electrons in the outermost shell is explained by the fact that during the gradual increase of the number of electrons (when the shell is being filled) the inter-electronic repulsive forces begin to exceed the electron's attraction to the nucleus, and the joining of the electrons to the outermost shell requires additional energy.
We know that molecules are made up of atoms. As we spend energy to break a molecule into atoms, (i.e., we heat the molecule to a temperature of 2,000° to 5,000° C) we say that the atoms are bonded into molecules. The bonds with which atoms are thus connected to each other to form molecules are known as chemical bonds.

Since atoms are made up of negatively charged electrons and positively charged nuclei, it is natural to suppose that chemical bonding occurred at the expense of the attraction of the negatively charged electrons of one atom to the positively charged nuclei of another atom.

One of the questions that will undoubtedly help understand the process of chemical bonding is as follows:

*How many electrons take part in the formation of a chemical bond?* In the case of a hydrogen molecule, it is clear that in order to form a chemical bond, 2 electrons are sufficient, since each of the hydrogen atoms bonded into a H₂ molecule, have but one electron.

All the other atoms (besides those of hydrogen) contain more than one electron.

If our supposition about the formation of molecules at the expense of the attraction of one atom’s nucleus to another atom’s electrons is correct, it was not clear why the helium atom (He), having 2 electrons, does not form stable molecules of the He₂ type.

Studies on the composition of molecules, including hydrogen molecules and atoms of elements of the II period: Li, Be, B, C, N, O, F, and Ne, have shown that the number of hydrogen atoms that each of these elements can bond amounts to 1, 2, 3, 4, 3, 2, 1, 0, respectively. That is, the atoms of Li and F form stable molecules LiH and HF, while B and N form stable molecules BH₃ and NH₃. Ne does not form any stable molecules with hydrogen.

As indicated in the previous section, the amount of electrons in the outermost shells of Li, Be, B, and C atoms
comprises 1, 2, 3, and 4 respectively. That is, the number of hydrogen atoms that can bond to the given atoms is equal to the number of electrons in the outermost shells of these atoms.

In the case of molecule formation of the $\text{H}_2$ and $\text{Cl}_2$ type, both atoms entering the bonding process are equivalent. Two electrons take part in bond formation — one from each of the atoms to be bonded.

We can draw two conclusions from this data:

1) Only the electrons in the outermost shell of the given atoms take part in bond formation.
2) Only one electron of an atom is spent on bond formation in a hydrogen atom to form a single bond.

According to the second conclusion, the number of hydrogen atoms that an atom can bond to (in the case of Li, Be, B, and C) is equal to the number of electrons in the outermost shell of the central atom.

On the other hand, atoms of nitrogen (N), oxygen (O), and fluorine bond 3, 2, and 1 hydrogen atoms respectively, while the neon (Ne) atom does not bond to a hydrogen atom at all.

From the data concerning the structure of electronic shells, we know that the number of electrons in the outermost electronic shell of elements of the 2nd period (including N, O, F, and Ne) cannot exceed 8.

The previously cited FIEs indicate that after the increase of the number of electrons up to 8, the atoms of the 2nd period begin forming a new outermost shell.

A comparison of this data with that of the amount of hydrogen atoms (with only one electron) that can bond to N, O, and F atoms, allows to make the following conclusions:

1) During bond formation of the N–H, O–H, F–H type [here the dash (–) indicates chemical bonding] the electron of the hydrogen atom enters the outermost shell of the central atom.
2) The number of hydrogen atoms, which an atom of the 2nd period can bond to, is limited to the maximal amount of electrons that the outermost shell of such atoms can contain. According to the data on FIEs, this amount is equal to 8.

According to these conclusions, Ne, which already has 8 electrons in the outermost shell, cannot form stable molecules of the NeH type. In reality such molecules do not exist.
Thus, experimental data on the FIEs, reveals their comparison with the chemical contents of stable molecules, and we can draw the following conclusions:

1) Only electrons situated in the outermost electronic shell of the *atoms being bonded* take part in the formation of chemical bonds.

2) Only one electron of the outermost shell offers the possibility for one bond formation.

3) Two electrons – one from each atom – take part in chemical bond formation between two atoms. These two electrons are *bonding electrons*.

4) After bond formation, both bonding electrons enter the outermost shells of the *atoms to be bonded*. Therefore, in the course of bond formation, the number of electrons in the outermost shell of the atoms to be bonded increases by one unit.

5) The amount of bonds that an atom can form is limited at the bottom by the amount of electrons present in the outermost shell of the given atom. For atoms of the 2nd and 3rd periods this limitation is applied to atoms with fewer than 5 electrons in the outermost shell, i.e., to atoms Li, Na, Be, Mg, B, Al, C and Si.

6) The number of bonds that an atom of the 2nd and 3rd periods can form is limited at the top by the number of electrons that can be present in the outermost shells of these atoms. The maximal number of electrons that can be present in the outermost shells of atoms of the 2nd and 3rd periods is equal to 8 according to the data on the FIEs. This limitation applies to atoms with more than 4 electrons in the outermost shell, i.e., to atoms N, P; O, S; F, Cl; Ne, Ar.

The data on IEs, FIEs, and the composition of stable molecules – their true values and comparisons – in the case of free atoms and atoms bonded into molecules, have allowed us to understand how atoms bond into molecules.
Now let’s take a few examples to see how we can make use of our rules to define the number of covalent bonds that an atom can form if we know the amount of electrons in the outermost shell of the given atom and its nuclear charge.

The nuclear charge and the amount of electrons in the outermost shell are defined experimentally and are included in the table of elements which shows the nuclear charge values and the amount of electrons in the outermost electronic shells of atoms.

For example, let’s calculate the number of covalent bonds that Na, Al, P, and Cl can form. Na and Al have 1 and 3 electrons in the outermost shell respectively, and according to our first rule — one electron in the outermost shell is used to form a covalent bond — they can form: Na – 1 and Al – 3 covalent bonds. After the bond formation, the number of electrons in the outermost shells of Na and Al is equal to 2 and 6 respectively; i.e., less than the maximum (8) for these atoms.

P and Cl have 5 and 7 electrons in the outermost shell respectively, and, according to the second of the enumerated regularities, they could have formed 5 and 7 covalent bonds.

According to the 4\textsuperscript{th} regularity, during the formation of a covalent bond, the number of electrons in the outermost shell of these atoms increases by 1. According to the 6\textsuperscript{th} regularity, when the covalent bond forms, the number of electrons in the outermost shell of the atoms being bonded cannot be more than 8. That is, P can form only 3 bonds (8–5=3), while Cl can form only 1 (8–7 =1).

The described regularities for the formation of covalent bonds allow us to theoretically foretell the molecular structure of substances on the basis of an elementary analysis.

For example: on the basis of analyses, we have found that a certain substance consists of Na and Cl atoms. Knowing the regularities of covalent bond formation, we can say that Na can form only 1 covalent bond. That is, we can expect that every Na atom is bonded with a Cl atom via a covalent bond in this substance, and that the substance is composed of molecules of NaCl. The structural formula for this molecule is Na – Cl. Here the dash (−) indicates the covalent bond. The electronic formula of this molecule can be illustrated thus:
According to the electronic formula the outermost shell of a Na atom in NaCl contains 2 electrons, while that of a Cl atom contains 8.

In the given formula, the electrons (dots) between the Na and Cl atoms are bonding atoms. Since the FIE of Cl is equal to 13 eV and that of Na is equal to 5.14 eV, the bonding pair of electrons is situated much closer to the Cl atom than to the Na atom.

Let’s observe another case. On the basis of analyses, we have found that a substance is made up of Al atoms and Cl atoms. Al has 3 electrons in its outermost shell; thus, it can form 3 covalent bonds, while Cl, as in the previous case, can form only 1. This substance is represented as AlCl₃ and its electronic formula can be illustrated thus:

\[ \text{Cl} \cdots \text{Al} \cdots \text{Cl} \]

whose structural formula is:

\[ \text{Cl} - \text{Al} - \text{Cl} \]

This electronic formula shows that there are 8 electrons in the outermost shell of the Cl atoms in AlCl₃, while there are 6 in the outermost shell of the Al atom.

On the basis of the comparison of the data on the FIEs with the data on the structure of stable molecules, we have found that during bond formation, both bonding electrons (one from each atom) enter the outermost shells of the atoms to be bonded. This conclusion allows us to imagine how a dual-atomic molecule actually looks. For example, the simplest dual-atomic molecule is a hydrogen molecule.
Hydrogen atoms are all perfectly identical, that is, the bonding pair of electrons is not only in the outermost shells of both atoms to be bonded, but is also at the same distance between the nuclei. Thus, there is only one definite place for the electrons — between the nuclei at equal distances from them.

Before the bonds were formed (i.e., in divided atoms) the electrons rotated around their nuclei, that is, when the nuclei are united, the electrons continue rotating. And, as indicated above, during their rotation both electrons are at the same distance from the hydrogen nuclei being bonded by them.

During bond formation, the bonding electrons enter the outermost shells of both atoms to be bonded.

This conclusion allows us to introduce a scheme for chemical bonding. According to this scheme, say, in the case of a hydrogen molecule, the bonding pair of electrons rotates on a plane perpendicular to the axis connecting the nuclei of the hydrogen atoms. The center of the electrons' rotation is situated at equal distances from the nuclei to be bonded. It is only in this case that the electrons can simultaneously enter the outermost electronic shells of both atoms to be bonded.

Thus, the hydrogen molecule can be illustrated as follows:

![Figure 4.1](image)

A hydrogen molecule is composed of 2 hydrogen atom nuclei located at a distance of about 0.7Å from each other. Two electrons in the hydrogen molecule rotate in a circular orbit on a plane perpendicular to the axis connecting the nuclei. This
electronic pair draws the nuclei together at the expense of the electrostatic forces and the nuclei’s attraction forces to the two electrons rotating between them.

The center of the circle, around which the electrons rotate in a hydrogen molecule, is located in the middle of the axis connecting the hydrogen nuclei. That is, the electrons are at identical distances from the nuclei are bonded by the electrons.

When the same kind of atoms are bonded chemically (like atoms of Na–Na, F–F, Cl–Cl, etc.) the bonding electrons, just as in the case of a hydrogen molecule, are at the same distance from the nuclei of the atoms being bonded.

When various atoms are chemically bonded (like Na–Cl, etc.), the center of the circle of the bonding electrons is closer to the nucleus of the Cl atom. That is, the bonding electrons are shifted towards the atom that attracts the electrons more readily, i.e., towards the atom with a higher FIE.

The bonding electrons are at about the same distance from the nuclei being bonded by them, as are the non-bonding electrons. That is, when the bonding electrons form chemical bonds, they enter the outermost shells of the atoms being bonded.

The inner electrons are often called core electrons (see fig.4.2).
The dots on the circles are the electrons. The smaller circles are the cores of the atoms. The core of the atom includes, besides the nucleus, all the inner electronic shells, i.e., all the electrons in the inner layers around the nucleus. That is, in the Cl atom this core includes a nucleus with 17 protons and 10 electrons (2 electrons in the layer closest to the nucleus and 8 electrons in the next closest layer).

These inner electrons, like the atom’s nucleus, do not take part in chemical transformations; that is why, for convenience, the drawing shows them united with the nucleus. Thus, the Cl core carries a surplus positive charge equal to 17–10 = 7 proton units. Seven electrons located in the outermost shell and indicated on the drawing with dots compensate this positive charge. These are called valence electrons since only these electrons in the atom take part in chemical bond formation and chemical transformations.

When forming a Cl₂ molecule, both Cl atoms take part in bond formation and they increase the number of electrons in their outermost shells by 1 unit; that is, both outermost shells contain 8 electrons. When forming a NaCl molecule, the Na atom contains 2 electrons in the outermost shell (1 previous one and 1 acquired one) while the Cl atom contains 8 electrons.

The described manner of bonding atoms together is known as covalent bonding. The bond formed between such atoms is known as a covalent bond.

The bond used to connect identical atoms is called a homoatomic covalent bond; if the atoms are different, the bond is called a heteroatomic covalent bond. [The Greek prefixes homo and hetero mean identical and different respectively.]

When the atoms’ first ionization energies (FIEs) differ greatly (as during bond formation between Na and Cl atoms), the formed bond in the NaCl molecule is known as a polar bond.

Atoms with more than one electron in the outermost shell can form not one but several covalent bonds between themselves. Such bonds are called multiple bonds. Examples of such bonds are those of nitrogen (N≡N) and oxygen (O = O) molecules.
As a result of the studies of various chemical reactions, it has been confirmed that during such reactions the existing chemical bonds break and new ones form. Thus, for example, in the reaction of hydrogen (H₂) and chlorine (Cl₂) we get hydrogen–chlorine. The formula of this reaction can be illustrated as follows:

\[ \text{H}_2 + \text{Cl}_2 = 2\text{HCl} \]

During this reaction, the old bonds are broken between the hydrogen atoms in the hydrogen molecule (H₂) and between the chlorine atoms in the chlorine molecule (Cl₂) while new bonds are formed between the hydrogen and chlorine atoms in the hydrogen–chlorine molecule (HCl).

It was originally supposed that the initial hydrogen molecules (H₂) and chlorine molecules (Cl₂) collide with each other resulting in the breaking of the old bonds and the formation of free hydrogen and chlorine atoms which unite into molecules of hydrogen–chlorine. That is, it was supposed that the old bonds break during the reactions.

However, this explanation contradicts the experiments. According to experimental data, in order to break a bond between chlorine atoms in the chlorine molecule (Cl₂) the molecular chlorine should be heated to a temperature more than 700°C, while many reactions containing chlorine proceed at temperatures of 100°C to 200°C and even at normal room temperatures.

Numerous studies of mixtures taken from reactors have shown that besides the initial and final products, these mixtures contain atoms (H, Cl) formed of initial molecules in very small quantities, and that the interaction of these atoms with the initial molecules proceed at a great rate, thereby forming the final product and new atoms.

That is, it turned out that the interaction of hydrogen molecules with chlorine proceeds not via the presupposed scheme:
H₂ + Cl₂ → 2HCl

but in another scheme:

\[
\begin{align*}
\text{Cl}_2 & \rightarrow \text{Cl} + \text{Cl} \quad (1) \\
\text{H}_2 + \text{Cl} & \rightarrow \text{HCl} + \text{H} \quad (2) \\
\text{Cl}_2 + \text{H} & \rightarrow \text{HCl} + \text{Cl} \quad (3)
\end{align*}
\]

this interaction mechanism is known as a *chain mechanism*. Stage 1 is known as the stage of initiation. The active species – chlorine atom – is originated at this stage. Stages 2 and 3 are the chain’s propagation. However, the given scheme contains contradictions.

At stage 2 the chlorine atom interacts with a hydrogen molecule forming the final product (HCl) and a hydrogen atom. During the interaction of a chlorine atom (Cl) with hydrogen (H₂) the bond in the hydrogen molecule breaks at a temperature of 30°C; while the breaking of the bond in a hydrogen molecule requires a temperature of more than 3,000°C.

Analogously, at stage 3 a hydrogen atom reacts at a high rate of speed with the consecutive initial chlorine molecule (Cl₂) and forming the final product (HCl) with a new chlorine atom. This reaction takes place at a great speed at room temperature. In the course of this reaction, the bond in molecule Cl₂ breaks. It has been experimentally defined that in order to break such a bond – a temperature of 700°C is required.

The answers to the following questions will help to more readily understand this material:

*Why are atoms active particles? Are the atoms of other elements just as active with molecules? What other particles, besides atoms, are active? How did we get our information about atom and molecule structure and what is this information based upon? What is the physical nature of chemical bonding? What other bonds, besides covalent ones, can form molecules?*

In order to answer these questions one should know the kinetic and potential energies of the electrons in the atoms, and
correspondingly, the rates and transition trajectories of their electrons.

Molecules and atoms cannot be seen even through a microscope. The kinetic energy of electrons cannot be measured in any way. That is, from the pure experimental viewpoint, the argument concerning the amount of energy in the electrons and their transitional speeds, and therefore, the conclusions about the structure of molecules and about the electronic energy in these molecules, are actually unfounded.

In spite of all this, scientists have managed to define the size of the molecule, its structure, its speed rate, and even the kinetic energy of the electrons transiting inside the molecule.

Exactly how scientists discovered such seemingly impossible phenomena will be studied later, when you increase your knowledge with the forthcoming material.
5** ATOM STRUCTURE

5.1 Brief History;

There is a chronological story about the scientific process via which scientists (mainly chemists) came to the conclusion that chemical compounds are made up of a definite number of various atoms. Such facts are detailed in many textbooks, including the amusing book *Chemical Principles* by Richard E. Dickerson, Harry B. Gray and Gilbert P. Haight, Jr.

Relative to this book, it is worthwhile mentioning that it were namely the chemists, and first of all — Antuan Lavoisier, John Dalton, and Stanistao Kannitsaro whose works originally introduced the concept that substances are composed of atoms.

A. Lavoisier laid the foundation for the newest chemistry having proved that mass is actually the fundamental property that is retained in chemical reactions.

J. Dalton turned the philosophical notion about atoms into reality.

S. Kannitsaro offered a method of defining atomic mass based on A. Avogadro’s hypothesis.

Physicists, first of all, J.J. Thomson, Earnest Rutherford, and Nils Bohr elucidated atom structure.

In 1912 E. Rutherford discovered that the positive charge in atoms is concentrated in the nucleus. Now let us see just how Rutherford managed to investigate the sizes of the atom and the nucleus.

Rutherford's assistants (Geiger and Marsden) passed $\alpha$-particles of helium atom nuclei through thick metal foils. More than 99% of these particles penetrated the foil without changing their straight trajectory, while 1% went aside, and an insignificant part (less than 0.1%) bounced back. This demonstrates that the alpha particles must have struck something massive and positively charged.

On the basis of experiments on the penetration of $\alpha$-particles through foil, Rutherford suggested a planetary model of an atom where the atom was presented as a system analogous to our solar system: a nucleus in the center of the atom around which electrons rotate.
The electrons had a negative charge, while the nucleus – a positive one. The total negative charge of the electrons was equal to the positive charge of the nucleus, i.e., the atom was electrically neutral.

To find out how the electron’s energy in the atom is defined, one should get acquainted with the virial theorem. It can be formulated as follows:

*When there are only Coulomb forces in the charge system, the kinetic energy of the system is equal to half of its potential energy.*

Now let’s take a look at the proof of this theorem for a simple, though interesting case: a hydrogen atom.

In figure 4.1 we see the scheme of a hydrogen atom. We know that the electrons are attracted to the nucleus by electrostatic forces. The electrons cannot fall upon the nucleus because of their kinetic energy. Such stable systems are subordinated to the virial theorem. Here is a proof of this theorem for a simple system:

The electrons are at a definite distance from the nucleus because the forces, striving to move them away, are equal to the forces attracting the electrons to the nucleus. From mechanics we know that if we have a ball fixed to a string, and rotate it around a center, force $F_c$ will make the ball strive to leave its orbit. This is called a centrifugal force, and is calculated by the equation:

$$F_c = mV^2/R; \quad (5.1)$$

where $V$ is the ball's speed on the orbit, and $R$ is the distance to the center of the orbit, $m$ is the mass of the ball.

The electrostatic force ($F_{el}$) can be calculated by the equation:

$$F_{el} = Ze/R^2 \quad (5.2)$$

where $Z$ is the positive charge of the nucleus, $e$ is the negative charge of the electron, and $R$ is the distance between them. Since $F_c = F_{el}$, we get:
\[ Z e/R^2 = mV^2/R \]  \hspace{1cm} (5.3)

Cancel the \( R \), and we get:

\[ Z e/R = mV^2 \]  \hspace{1cm} (5.4)

From mechanics we know that kinetic energy, which we will indicate as \( T \), is defined by the equation:

\[ T = mV^2/2 \]  \hspace{1cm} (5.5)

From electrostatics we know that potential energy \( E \), in systems where electric forces are in action, can be defined by the equation:

\[ E = q_1 q_2 / R, \]  \hspace{1cm} (5.6)

where \( q_1 \) and \( q_2 \) are the charges of the species (in our case \( q_1 = Z; q_2 = e \)); \( R \) is the distance between them. Thus, we get:

\[ E = 2T, \]  \hspace{1cm} (5.7)

or, in other words, during equilibrium in such systems where there are electrostatic and mechanical forces, the kinetic energy of the system (in mobile species) is equal to half of its potential energy. The energy of atom \( E_a \) is equal to the sum of the kinetic (\( T \)) and potential (\( E \)) energies:

\[ E_a = -E + T \]  \hspace{1cm} (5.8)

Thus, in order to tear the electron away from the atom, the electron should get energy (\( E_{\text{ion}} \)) equal to \( E_a \):

\[ E_{\text{ion}} = E_a \]  \hspace{1cm} (5.9)

The virial theorem allows evaluation of the distance between the electron and the nucleus. For single-electron atoms this can be evaluated by considering the following: *The kinetic energy of an electron is equal to half of its potential energy, therefore it is sufficient to measure the electron's potential energy.*
As already said, the minimal energy required to tear the first electron off an atom is called the first ionization energy (FIE). From the virial theorem we know that the potential energy $U$ of an electron is equal to the double value of the ionization energy (IE). For hydrogen $U = 2 \text{IE} = 2,620 \text{kJ/mol}$, or, for one atom:

$$2,620/6.02 \cdot 10^{23} = 435 \cdot 10^{-23} \text{kJ/atom};$$

where $6.02 \cdot 10^{23}$ is the Avogadro number. Then we get:

$$435 \cdot 10^{-23} = (1.6 \cdot 10^{-19})^2 \cdot (9.48 \cdot 10^4)^2 / R$$

here $9.48 \cdot 10^4$ is the conversion factor, $R$ is the radius of the atom:

$$R = (1.6 \cdot 10^{-19})^2 (9.48 \cdot 10^4)^2 / (435 \cdot 10^{-23} \cdot 10^3) = 5.29 \cdot 10^{-11} \text{m} = 0.529 \text{Å}$$

The diameter of the atom's nucleus is $10^{-5} \text{Å}$. To better realize the difference in the sizes of the nucleus and the atom, imagine this:

*If the atom's nucleus is the size of a golf ball (about 2 inches in diameter); then the size of the atom would have to be greater than the largest sports stadium!*

The virial theorem allows us to calculate exactly how the kinetic and potential energies change when the charge increases. Both these energies are proportional to the square of the nuclear charge. Recall that the kinetic energy of a hydrogen atom is equal to $1.317 \text{kJ/mol}$, while its potential energy amounts to $2.634 \text{kJ/mol}$. The kinetic energy of a hydrogen-like atom (having only one electron) with a charge of 2 proton units is equal to $1.317 \cdot 2^2 = 5.241 \text{kJ/mol}$, while the potential energy is equal to $2.634 \cdot 2^2 = 10.482 \text{kJ/mol}$.

The stability of the system is defined by the amount of energy necessary for its breaking, for tearing the electron off the nucleus.

The potential energy is calculated by equation $E = Z e/R$. The greater the nuclear charge $Z$ and the smaller the distance
between the electron and the nucleus, the greater is the potential energy.

The increase of the electron’s attraction force to the nucleus (i.e., the increase of the system’s stability) when the nuclear charge increases and the distance decreases – is obvious without any explanation.

The electron’s kinetic energy \( (T) \) is calculated via the equation:

\[
T = \frac{mV^2}{2},
\]

where \( v \) is the electron’s transition speed in the orbit. The greater the transition speed, the easier it is to tear the electron off the nucleus. The increase of the kinetic energy causes a decrease in the system’s stability.

According to equation 5.4:

\[
mV^2/2 = Ze/R;
\]

the kinetic energy, in atomic systems, is proportional to the nuclear charge and inversely proportional to the radius of the electron’s orbit. By increasing the nuclear charge, and decreasing the radius, we increase the potential energy (which causes an increase in the system’s stability) and the kinetic energy (whose increase causes a decrease in this stability).

The increase of the system’s stability (when the charge increases and the radius decreases) is explained by the fact that the increase of the kinetic energy, according to the calculation and experimental results, is twice smaller than the simultaneous increase of the potential energy.

Thus we can realize the increase in the system’s stability by the absolute value of the change in the potential energy: the greater this value, the more stable is the system.

When the system absorbs energy, the potential energy decreases and the electron transits farther away from its nucleus. When the nuclear charge increases, the absolute value of the potential energy also increases and energy is discharged. This energy discharge is analogous to the energy discharge when a stone falls onto the earth from a great height. As a result of this fall, both the stone and the point of contact on the earth are heated.
5.2** HELIUM-LIKE ATOMS

Helium-like atoms, unlike hydrogen-like atoms (figure 5.2.1) have two electrons rotating around the nucleus:

Since energy $E$ of a hydrogen-like atom is equal to the electron’s kinetic energy, the energy of a helium-like atom is calculated as follows:

$$ E = 13.6 \cdot Z^2 $$

where $Z$ is the nuclear charge of the hydrogen-like atom in proton units.

The helium-like atom’s energy, naturally, is equal to the kinetic energy of the two electrons rotating around the nucleus.

As the electrons are situated at the same distance from the nucleus, their energies are equal. That is, in order to calculate the energy of the helium-like atom, we should define the kinetic energy of one of the electrons and multiply that by two.
According to the model (figure 5.2.1), besides the attractive force of the electron to the nucleus, there is inter-electronic repulsive force \( F_2 \) acting upon the electron in the helium-like atom, which is calculated by the following equation:

\[
F_2 = \frac{e \cdot e}{4R^2}
\]

where \( R \) is the radius of the circle around which the electrons rotate.

Before we go any further, let’s define the term effective charge:

**The effective charge is the sum of all charges acting upon the electron.**

As the electron’s charge \( e \) is equal to that of the proton, and the distance between the electrons is two times greater than that between the nucleus and the electron, the interaction of the electrons leads to the decrease of the helium-like atom's nuclear charge by 0.25 proton units.

That is, the effective charge of the nucleus in a helium-like atom is by 0.25 proton units smaller than the actual charge. Thus, the energy of an electron in a helium-like atom is calculated by the equation:

\[
E_e = 13.6 (Z - 0.25)^2
\]

where \( Z \) is the actual nuclear charge in proton units, \( (Z - 0.25) \) is the effective charge, and 13.6 is the energy of a hydrogen atom in eV.

According to the above mentioned, the energy of a helium-like atom \( L_{HeA} \) with a charge \( Z \) is calculated by the following equation:

\[
E_{LHeA} = 13.6 \cdot (Z - 0.25)^2 \cdot 2.
\]

Now let’s calculate the energy of a helium-like atom with a nuclear charge of 26 proton units:

\[
E_{LHeA} = 13.6 \cdot (26 - 0.25)^2 \cdot 2 = 18,035.3 \text{ eV}.
\]

Let’s compare this result with that of the experiment.
The experimental data amounts to the sum of the two final ionization energies of an iron atom (Fe); i.e., to the ionization energies of the two electrons closest to the nucleus. According to the experiment, we get:

\[ E'_{LHeA} = 8,828 + 9,277 = 18,105 \text{ eV} \]

where \( E'_{LHeA} \) is the energy of the helium-like atom calculated on the basis of the experiment. The discrepancy between the calculation and the experimental data comprises:

\[ \frac{(18,105 - 18,035.3) \cdot 100}{18,035} = 0.3\% \]

That is, the helium-like atom model is adequate. We calculate the radius of this atom and show it in a scaled drawing.

The radius of an atom with a nuclear charge of 26 proton units is calculated thus:

\[ 0.529 / (26 - 0.25) = 0.02 \text{ Å}; \]

where 0.529 is the radius of a hydrogen atom.

Considering the material on ionization energies, we have determined the hydrogen atom’s radius as being equal to 0.529Å, while the radius of the atomic system, with a charge twice that of a hydrogen atom’s nucleus, is two times smaller. The energies of these atoms, according to the defined ionization energies, are correspondingly — 13.529 eV and 54 eV.

As the virial theorem is applied only in systems with electric and mechanical forces, its observance in hydrogen-like atomic systems means that the energy is defined by the well-known mechanical and electrical interactions.

A comparison of the energies, the radii, and the nuclear charges of hydrogen-like atoms shows that when the nuclear charge \( Z \) increases in these systems, the radius \( R \) of the electron’s orbit decreases proportionally to the increase of the nuclear charge.

The system’s potential energy \( (E_{pot}) \) is defined by the equation:

\[ E_{pot} = eZ / R \]
which increases proportionally to the square value of the nuclear charge, increase. Because the atom’s energy is equal to half of the absolute value of the potential energy, it is proportional to the square of the nuclear charge value.

In calculations made for hydrogen-like and helium-like atoms it was supposed that there were only electrostatic forces in the atomic systems. That is why the discrepancy in the calculation and the experimental values, which is smaller than 1%, proves that the forces defining the behavior of the electrons in the atoms, are electrostatic interaction forces.

Studies of ionization energies (necessary to tear electrons off of various atoms) have shown that the electrons in the atoms are situated in layers. There are two electrons in the first layer nearest to the nucleus and there are 8 electrons in each of the rest of the inner shells.

According to experiments, the number of electrons in the outermost layers of the atoms changes periodically when the nuclear charge is increased. For elements with fewer than 20 electrons, the maximal number of electrons in the outermost shell is 8. That is, the number of electrons in the outermost shell, when the nuclear charge increases, changes periodically from 1 to 8.

The layer-structure of the electronic cloud surrounding the nucleus and the periodic change in the number of electrons in the outermost shell is explained by the fact that during the gradual increase of the number of electrons (while the shell is being filled) the inter-electronic repulsive forces begin to exceed the electron's attraction to the nucleus, and the joining of the electrons to the outermost shell requires additional energy. This is why, when the nuclear charge is increased, the electrons start forming a new outermost shell.

While studying the properties of atoms, it was found that most atoms bond to the electrons with a release of energy. This feature of the atom, if you remember, is called the atom’s affinity to the electron.

Comparing the atom’s first ionization energy (FIE) and its affinity to the electron, it was found that these parameters change periodically. (Recall figure 3.1)
CONCLUSIONS

The atom is a system in which negatively charged electrons rotate around a positively charged nucleus. The electrons stay around the nucleus thanks to the electrostatic forces. Centrifugal forces keep the electrons from falling onto the nucleus.

Because of the inter-electronic repulsive forces, the electrons are distributed in layers.

Experimental data have claimed that the number of electrons in the inner layers is the same in all atoms, while the number of electrons in the outermost shells changes periodically.

The atom’s energy is equal to the sum of the ionization energies of its electrons. The energy of a single electron atom is proportional to the square of the nuclear charge value.
6**   MOLECULE STRUCTURE

6.1   THE HYDROGEN MOLECULE

According to the model (see Fig 4.1) 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 eV · 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 Å. 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.

The hydrogen molecule is formed of two atoms of hydrogen. During molecule formation, two electrons, hitherto having belonged to two different hydrogen atoms, begin rotating on a plane perpendicular to the axis connecting the nuclei (see figure 6.1.1)
In order to well realize the correctness of this model, let’s calculate the energy of a hydrogen molecule as we did in the case of the atom. Here, also, the molecule’s energy is equal to the sum of its electronic energies.

According to the model, the electrons rotate around point E on a plane perpendicular to the axis connecting the nuclei A and B. The electrons’ attraction forces to the nuclei are directed perpendicular to the plane of the circle where the electrons rotate.
and where they are mutually counterbalanced. Their mutual action is therefore equal to zero. That is, the problem of calculating the energy of a hydrogen molecule is reduced to the problem of defining the energy of a helium-like atom (atom with 2 electrons).

Previously (see 5.2) it has been shown that for this calculation it is necessary to know the nuclear charge since the energy of a helium-like atom is defined by the equation:

$$E_{HA} = 13.595(Z - 0.25)^2 \cdot 2$$  \hspace{1cm} (6.1.1.)

It must be noted that there is no real positive charge at point E. The electrons are attracted to this point at the expense of forces $F_1^1$ that are projections of forces $F_1$ onto axis $DC$.

These forces are identical to the forces that hold the electrons on the orbit of a helium-like atom with charge $Z$. These forces prevent the breakaway of the electrons because of the mutual repulsion of $F_3$ and the centrifugal forces, that is, $2F_1^1 = F_3 + F_4$ where $F_3$ are the inter-electronic repulsion forces and $F_4$ are the centrifugal forces.

Here, as always, we use the system of calculations introduced by Bohr for the calculation of atomic systems. The system’s energy and the linear parameters in these calculations are defined via the comparison of charges and distances (radii) with the electron’s energy and the orbit’s radius in the hydrogen atom. The electron’s charge is accepted as a unit charge, while the radius of the hydrogen atom (0.529Å) serves as a unit of length. The unit force in this case is the interaction force of the proton with the electron in a hydrogen atom, equal to the distance of 0.529 Å.

Thus, the nuclear charge can be resembled as $Ze$ since the proton’s charge is equal to that of the electron. Considering all the accepted designations, let’s define the effective charge $Z$ at point $E$ of a hydrogen molecule (see figure 6.1.1)

The electrons here are situated at points C and D while the nuclei (protons) – at points A and B. Point E is situated in the center around which the electrons rotate on a plane perpendicular to that of the drawing. The attraction forces of the electrons to the nuclei are designated in the figure by $F_1$. The repulsive forces between the nuclei are designated as $F_2$. The repulsive forces between the electrons are shown as $F_3$.

The projections of $F_1$ onto axis $CD$ are indicated as $F_1^1$. The projections of $F_1$ onto axis $AB$ are indicated as $F_1^{11}$.
The properties of hydrogen molecules do not change with time, so the distances between the electrons and the nuclei are constant. That is, forces $F_1$ attracting the nuclei $F_{11}$ are equal forces of inter-nuclear repulsion. Forces $F_{11}$, acting upon the electrons, are also equal for the same reason. These forces act upon electrons C and D in contrary directions and are equal in value, i.e., their resultant force amounts to zero. The same is true of forces $2F_1$ and $F_3+F_4$.

Now let’s designate the radius of the electron’s orbit as $a$ (EC = $a$), the distance between the nucleus as $2b$ (AB = $2b$), the distance between the electron and the nucleus as $c$ (AC = $c$), and half of the force attracting the electron to point E as $F_5$. Thus we get:

$$F_5 = F_1 + F_{11} = 2F_1 \quad (6.1.2)$$

On the other hand, since the forces acting upon each electron are equal to the forces in hydrogen-like atoms with a radius of $a$ and a charge of $Ze$, we get:

$$F_5 = Ze^2/a^2 \quad (6.1.3)$$

If we substitute the value of $F_5$ in equation 6.1.2, we get:

$$Ze^2/a^2 = 2F_1 \quad (6.1.4)$$

i.e., in order to define $Z$ and the energy of a hydrogen molecule, we must solve this equation.

$F_1$ as already indicated, is the projection of $F_1$ onto axis CD. According to trigonometry, (see figure 6.1.1)

$$F_1 = F_1 \times \cos \angle ECB \quad (6.1.5)$$

Then $\cos \angle ECB = EC/CB$ or, according to the accepted designations, EC = $a$, and BC = $c$; therefore $\cos \angle ECB = a/c$. According to the Pythagorean Theorem and the accepted designations, EB = $b$:

$$\cos \angle ECB = a/(a^2+b^2)^{0.5} = a(a^2+b^2)^{0.5}$$
Substituting the value of $\cos \angle ECB$ in equation 6.1.5 we get:

$$F_1^1 = F_1 x a(a^2+b^2)^{-0.5}$$

According to the accepted designations, $BC = c$

$$F_1 = e^2/c^2 \quad (6.1.6)$$

since the positive charge at point $B$ is equal to 1.

Substituting the value of $F_1$ from this equation, we get:

$$F_1^1 = e^2/c^2 x a(a^2+b^2)^{-0.5}; \quad \text{that is, } c^2 = a^2 + b^2$$

Thus we get the Pythagorean Theorem:

$$F_1^1 = e^2 a(a^2+b^2)^{-0.5}/a^2 + b^2 = e^2 a(a^2+b^2)^{-1.5}$$

Substituting the value of $F_1^1$ from this equation to equation 6.1.4, we get:

$$Ze^2/a^2 = 2e^2 a(a^2+b^2)^{-1.5}$$

By multiplying both parts of this equation by $a^2$ and dividing them by $e^2$, we get:

$$Z = 2a^3(a^2+b^2)^{-1.5}$$

Now let’s divide and multiply the value in brackets by $a$:

$$Z = 2a^3 \cdot a^{-3}(1+b^2/a^2)^{-1.5} = 2[1+(b/a)^2]^{-1.5} \quad (6.1.7).$$

That is, in order to define the value of $b$, we must define the value of $b/a$ for which we will make use of the following equation.

According to figure 6.1, $2F_1^{11} = F_2$ or, according to trigonometry and figure 6.1, $F_1^{11} = F_1 \cos \angle CBE$ since $\cos \angle CBE = b/(a^2+b^2)^{1.5}$ according to trigonometry and the Pythagorean Theorem.
Then, making use of the Coulomb Law we get:

\[
F_{11} = \frac{e^2}{(a^2+b^2)^{0.5}} \cdot b/(a^2+b^2)^{1.5} \quad (6.1.8)
\]

On the other hand, according to fig. 6.1 and the Coulomb Law:

\[
2F_{11} = e^2/4b^2, \text{ that is, } 2e^2b/(a^2+b^2)^{1.5} = e^2/4b^2
\]

Now multiply both parts of the equation by the following:

\[
4(a^2+b^2) \cdot (a^2+b^2)^{0.5} / b \cdot e^2
\]

and we get:

\[
e^2 \cdot 4(a^2+b^2)(a^2+b^2)^{0.5} / 4 \cdot b^2 \cdot b \cdot e^2 = 2e^2 \cdot b \cdot 4(a^2+b^2)(a^2+b^2) / (a^2+b^2)^{0.5}(a^2+b^2)^{0.5} \cdot b \cdot e^2.
\]

We thus have:

\[
(a^2+b^2)(a^2+b^2)^{0.5} / b^3 = 8.
\]

The square of both parts of the equation gives us:

\[
(a^2+b^2)^2 \cdot (a^2+b^2) / b^6 = 64 \quad \text{or: } (a^2+b^2)^3 / b^6 = 64.
\]

By deriving the cubic root on both parts of the equation, we get:

\[
(a^2 + b^2)/b^2 = 4 \text{ or } a^2/b^2 + 1 = 4; \quad a^2/b^2 = 3; \quad a/b = 3^{0.5} \quad (6.1-8a)
\]

Substituting the values of \( b/a = 1/3^{0.5} \) in equation 6.1.7 we get:

\[
Z = 2(1+1/3^{0.5})^{-1.5} = 2(1,333)^{-1.5} = 1,299
\]

Substituting the value of \( Z \) in equation 6.1.1, we finally get the value of the energy of a hydrogen molecule (\( E_{H2} \)), which is equal to:

\[
1,317 \text{ kJ/mol} \cdot 2 \cdot (1,299-0.25)^2 = 1,317 \cdot 2 \cdot (1,049)^2 = 2,898 \text{ kJ/mol}.
\]

Calculating the energy of a hydrogen molecule, we get the data that helps us calculate the geometrical parameters of a molecule.

The resulting charge acting upon the electrons is equal to 1.049 proton units. Therefore the radius of the electron’s transition
is by 1.049 smaller than that of a hydrogen atom, which is equal to 0.529\ Å.

Respectively, the radius of the orbit (circle) in which the bonding electrons are rotating in a hydrogen molecule is equal to 0.504 \ Å \ (0.529/1.049 = 0.504). Since the distance between the nuclei is equal to 2b and b is equal to \( a/3^{0.5} \), the distance between the nuclei is equal to \( 0.582(0.504 \cdot 2/3^{0.5}) = 0.582 \) Å.

The distance between the nuclei and the electrons is defined by the Pythagorean Theorem and is equal to \( (0.504^2 + 0.291^2)^{0.5} = 0.582 \) Å.

The scaled up values of the distances \( a, b, \) and \( c \) allow us to imagine the actual size of a hydrogen molecule shown on figure 6.1.1.

These values allow us to define the energy of a hydrogen molecule and independently of the calculation via the virial theorem.

The potential energy of a hydrogen molecule is calculated via comparison with that of a hydrogen atom whose potential energy is equal to 2,634 kJ/mol. Hydrogen atoms (whose electrons and protons are charged with identical absolute values and have contrary signs) are attracted to each other and are located at a distance of 0.529Å. The potential energy is calculated via the equation: \( E = \frac{q_1q_2}{R} \) where \( q_1 \) and \( q_2 \) are the charges in the particles and \( R \) is the distance between them.

In atoms and molecules the positive and negative charges are equal in value just as in a hydrogen atom. That is why the energy of their Coulomb interaction is counter proportional only in reference to the distance between the charges in hydrogen molecules and atoms.

The summed up potential energy of a hydrogen molecule is equal to the difference between the electrons’ attraction energy to the nuclei and the inter-electronic, inter-nuclear repulsion energy. The attraction energy is:

\[
E_{\text{at}} = 2,634 \cdot 0.529 \cdot 4 / 0.582 = 9,577 \text{ kJ/mol}.
\]

The repulsion energy is equal to:

\[
E_{\text{rep}} = 2,634 \cdot 0.529 / 0.582 + 2,634 \cdot 0.529 / 1.008 = 3,776 \text{ kJ/mol}.
\]
The difference between the attraction energy (which defines the stability of the molecule) and the repulsion energy is 9,577 – 3,776 = 5,801 kJ/mol. The electrons’ attraction energy to the nuclei in two hydrogen atoms comprises 2,634 · 2 = 5,268 kJ/mol. That is, the gain in attraction energy (i.e., potential energy) during molecule formation comprises 5,801 – 5,268 = 533 kJ/mol. That is, the nuclei in a molecule are more firmly bonded with the electrons, and in order to break a molecule into atoms, more energy is required.

This has been proven experimentally. In order to break a hydrogen molecule into atoms, the molecule should be heated to a temperature of more than 3,000º.

The total energy of a hydrogen molecule is equal to the difference between the kinetic and potential energies of the electrons. According to the virial theorem, the kinetic energy is equal to half of the potential energy of a system where only Coulomb forces are at work. Relatively, the total energy is equal to half of the potential energy.

That is, the total energy of a hydrogen molecule is equal to 5,801/2 = 2900 kJ/mol. The total energy of two hydrogen atoms, as indicated above, is equal to 2,634 kJ/mol. That is, the energy gain, when forming a hydrogen molecule out of a hydrogen atom, comprises 2,900 – 2,634 = 266 kJ/mol.

In the course of our calculations on the basis of equalizing forces, we found that the energy of a hydrogen molecule comprised 2,898 kJ/mol and that the potential energy was equal to 5,800 kJ/mol. In accordance with the virial theorem, the total energy of a hydrogen molecule was equal to 5,800/2 = 2,900 kJ/mol. That is, the total energy, calculated by both methods, coincided, thus proving that there are only common Coulomb interactions in the molecule.

To check the correctness of the solution, let’s check the correctness of the initial equations. The equality of the $F_1$ forces is obvious from the equality of the $F_1$ forces.

Let’s check the correctness of equation: $2F_1^{11} = F_2$.

According to the Coulomb Law, $F_2 = 1 \cdot 1/(2b)^2$ since the charges at points A and B are equal to 1 proton unit.

On the other hand, $2F_1^{11} = (1 \cdot 1 \cdot 2) / c^2$.

Let’s substitute the values of $b$ and $c$ ($b = 0.291\text{Å}$; $c = 0.582\text{Å}$):
\[ F_2 = 1/0.582^2 = 2.952. \]

\[ 2F_1^{11} = 2 \cos \angle ABC/0.582^2 = 2 \cdot \frac{b}{c} \cdot 0.582^2 = 2 \cdot \frac{0.5}{0.582^2} = 2.952. \]

Thus the equation \( 2F_1 = F_1^{11} \) is correct. As we see, the forces in the described model, acting upon the nuclei and the electrons, are balanced via counteracting forces, i.e., the system is balanced.

According to the virial theorem the energy of a molecule made up of electrons and nuclei (\( E_{\text{mol}} \)) is defined by the sum:

\[ E_{\text{mol}} = E_{\text{kin}} - E_{\text{pot}} \]

where \( E_{\text{kin}} \) and \( E_{\text{pot}} \) are the electrons’ kinetic energies and the system’s potential energy (i.e., the electrons’ attraction energy to the nuclei and the interelectronic repulsion energy).

According to the virial theorem, \( 2E_{\text{kin}} = E_{\text{pot}} \) in absolute value. Thus, the value of 2,905 kJ/mol is equal to the electrons’ kinetic energy and half of the molecule’s potential energy. Then 2,640 kJ/mol corresponds to the double value of the electron’s kinetic energy and the electron’s attraction potential energy to the nuclei in a hydrogen atom. During the formation of the molecule, the kinetic energy of the electrons increases by 265 kJ/mol, while the absolute value of the potential energy increases by 2,905 \( \cdot \) 2 – 2,640 \( \cdot \) 2 = 530 kJ/mol.

That is, the electrons in the molecules move more rapidly than they do in the atoms, though in the first case, they are more readily attracted to the nuclei. The energy gain at the expense of the greater attraction of the electrons to the nuclei is twice higher than the loss of energy caused by the electrons’ kinetic energy increase. The molecules are formed with energy gain, which explains their stability at room temperature (\( \approx 20^\circ \text{C} \)).

Since the process of molecule formation proceeds with a discharge of energy, in order to break a molecule into atoms, i.e., accomplish the reverse process; the molecules should get some energy, which is calculated via the scheme in section 6.1.

In this scheme we presume that the molecule is a system in which two nuclei are bonded by two electrons rotating in a circle whose plane is perpendicular to the axis connecting the nuclei. We also presume that the defining forces in the given system are the
Coulomb and centrifugal forces. The correctness of these presumptions can be proven only by comparing the calculation data with those of the experiment.

In accordance with the experimental data, the FIE of a hydrogen molecule is equal to 1,494 kJ/mol. As a result of breaking an electron off a hydrogen molecule, a positive hydrogen ion is formed (H$_2^+$). Chemical literature does not contain any experimental data on the second ionization energy of a hydrogen molecule. This is why, in order to compare the calculated data with the experimental data, it is necessary to calculate the energy of the positive hydrogen ion along the same scheme that we used to calculate the energy of a hydrogen molecule. We will find that the energy of a positive hydrogen ion, according to the following scheme, is now equal not to the helium-like atom, but to the hydrogen-like atom with a charge of Z which is equal to the reduced charge at point E while Z can be calculated via the equation:

$$Z = \left( \frac{N^2}{2n} \right) \left[ \left( \frac{4n}{N} \right)^{2/3} - 1 \right]^{3/2} - S_n$$

where N is the nuclear charge in proton units; n is the number of bonding electrons; S_n is the term that considers the inter-electronic repulsion. In the case of one electron (H$_2^+$) S_n is equal to zero. The detailed deduction of this equation will be described later. See section 6.4, equation 6.4-13.

When calculating via this equation, we find that:

$$Z = \left( \frac{1^2}{2} \right) \left[ \left( \frac{4}{1} \right)^{2/3} - 1 \right]^{3/2} = 0.5 \left( 4^{0.666} - 1 \right)^{1.5} = 0.93$$

Respectively, energy H$_2^+$ is defined by the equation:

$$E_{H_2^+} = 1,317 \cdot 0.93^2 = 1,150 \text{ kJ/mol}$$

Molecule H$_2^+$ can be represented as a molecule formed of a hydrogen atom and a proton. The total electronic energy of the initial components is equal to the FIE of the hydrogen atom, i.e., 1,317 kJ/mol. That is, according to calculations, during the formation of the H$_2^+$ ion, there is no energy gain, but there is energy loss of 167 kJ/mol. That is, molecule H$_2^+$, according to the calculation, is extremely unstable. [The Encyclopedia of Inorganic Chemistry (1994) mentions this fact on page 1,463.] Relatively,
when breaking away one electron from a hydrogen molecule, it breaks into a hydrogen atom and a proton. The total energy is equal to 1,317 kJ/mol. Thus, the experimentally defined electronic energy of a hydrogen molecule (E_{H2}) is defined by the equation:

\[ E_{H2} = 1,317 \text{ kJ/mol} + 1,494 \text{ kJ/mol} = 2,811 \text{ kJ/mol} \]

where 1,317 kJ/mol is the energy of a hydrogen atom; 1,494 kJ/mol is the FIE_{H2}. The calculated energy of the hydrogen molecule was equal to 2,900 kJ/mol. The discrepancy between the experimental and calculated data comprised 3.06 \%.

That is, \([(2,900 \text{ kJ/mol} - 2,811 \text{ kJ/mol}) / 2,900 \text{ kJ/mol}] = 0.0306\). Thus the calculated energy value of the hydrogen molecule proved to be by 3.06 \% greater than the experimental data offered.

As previously said in this section, the energy of a hydrogen molecule is defined, according to figure 6.1.1, as the energy of a helium-like atom (a nucleus surrounded by two electrons). According to the calculation of helium-like atoms via equation (6.1-1) we get:

\[ E_{hel} = 1,317 (Z - 0.25)^2 \cdot 2. \]

The energies of helium-like atoms with nuclear charges equal to 1, 2, and 3 proton units, comprised 1,485; 8,025; and 19,825 kJ/mol respectively. In comparison, the experimentally defined energy of these atoms (the sum of the ionization energies of H\(^-\); He; and Li\(^+\)) comprised 1,395; 7,607; and 19,090 kJ/mol respectively.

In other words, the experimentally defined energy value for atoms of H\(^-\); He; and Li\(^+\) was smaller than the calculated data by 6.1 \%; 5.2 \%; and 3.7 \% respectively.

As already noted above, the experimentally defined energy value of a hydrogen molecule was by 3.06 \% smaller than the calculated one on the basis of the model, which proves quite convincingly that the model is a perfectly correct one.

Besides the above cited experimental defining of the hydrogen molecule's energy via the ionization energy, there are other experimental ways of defining the same as well. The most common method is the thermal method where we define the energy necessary for the molecule to break the bonds between the atoms.
It has been defined experimentally that in order to break up a hydrogen molecule into atoms, the hydrogen should get energy of 437 kJ/mol. Indeed, it might seem sufficient to add 437 kJ/mol to 2,640 kJ/mol (energy of two hydrogen atoms) in order to get the experimental energy value of a hydrogen molecule.

However, let’s not hurry to the conclusion, but, for the time being, let’s dwell in detail upon the experimental methods, which define the energy necessary to break the bond of a hydrogen molecule.

To begin with, let’s compare two problems.

Problem #1.
Define the energy necessary to break the bond between a magnet and a piece of iron.
This problem can be readily solved with the help of an electric device that will tear the piece of iron off the magnet. Here the energy consumption can be calculated via the amount of electric energy used by this device during the process.

Problem #2.
In the case of a hydrogen molecule, we cannot separate the atoms in a molecule with the help of a device, and therefore we cannot directly measure the energy necessary to break the bond in this molecule.

Here we must heat 100 ml of hydrogen, measure the amount of energy used in this process and the amount of broken hydrogen molecules received via reaction $\text{H}_2 \rightarrow 2\text{H}$. The hydrogen molecules must be given enough energy (heat) necessary to break the bond. In the process of heating the hydrogen, the molecules’ kinetic energies increase; the molecules start moving quicker straightforward and rotationally and the hydrogen atoms’ nuclei begin to vibrate more readily causing collisions.

In the course of these collisions between the molecules, caused by the exchange of energy between them, such molecules appear in which the average distances between the nuclei are greater than those in the initial (non-excited) hydrogen molecules. The initial charges in these molecules become smaller, $Z_{\text{H}_2}$, and the potential energies of these molecules decrease while their electronic energies become equal to those of two hydrogen atoms, causing the molecules to burst.
Thus, when we measure the energy necessary for breaking the bond in a hydrogen molecule, we cannot measure such energy in the molecule as we can in the case of a magnet and the piece of iron. In the second case we have to impart energy to the system with more than $10^5$ hydrogen molecules.

In this system, as a result of the exchange of energies between the molecules, there are molecules with sufficient energy accumulated so as to cause the burst of the molecules into atoms. That is, in order to convey sufficient energy to molecules to break them into atoms, we must excite (heat) the energy of other molecules, which do not break into atoms during the experiment. Unlike the case with the magnet and iron, we have to spend more energy than is normally necessary for the breaking of a molecule into atoms.

This is why the experimentally defined value of 437 kJ/mol (expenditure of energy necessary to break a hydrogen molecule into atoms) exceeds the value of the difference in energy between that of the molecule and of the divided hydrogen atoms.

*How can we define the expenditure of energy on the heating of the non-breaking molecules (i.e., on the non-productive, useless expenditure of energy)?*

This can be done if we know how much energy (heat) is discharged in the course of the chemical reaction. *How can we measure the heat of the reaction?* For this we impart to the system energy whose value is equal to, say, the expenditure of electricity, and then we define the energies of the final products and the non-reacting initial products.

The energy of the non-reacting products is equal to the products’ initial amount multiplied by the heat capacity and by the temperature at which the experiment was conducted. The energy of the final products is equal to their heat capacity multiplied by the temperature at which the experiment was conducted.

The energy imparted to the system, which we are to measure, is spent on heating the initial and final products up to the reaction temperature, and also on the energy increase of the hydrogen molecule’s electrons up to the energy of the atoms’ electrons. The value of this energy was determined in the course of a theoretical calculation.
To compare the calculation of the molecule’s energy with that of the experiment, we must add not 437 kJ/mol to the electronic energy, but the difference between these values plus the difference in the energies spent on the heating of the initial and final products up to the reaction temperature. To define this difference, we should find the difference between the heat capacities of the initial and final products.

The heat capacity of a substance is the relation of the amount of heat (energy) received by the substance, or discharged at cooling, to the corresponding temperature change in the substance.

If we take heat capacity in relation to one gram of substance, this is regarded as a unit of heat capacity. Relative to $z$ atom, or $g$ mol of substance, it is called either atomic or molar heat capacity. See the supplement for more details on heat capacity.

Thus, the imparted and measured amount of energy (437 kJ/mol) has been spent on the increase of electronic energy ($\Delta E_{el}$) and on the difference of the energies in the initial and final products:

$$\Delta E = E_{ini} - E_{fin}; \quad E_{ini} = C_{H2} \cdot T_p; \quad E_{fin} = C_H \cdot T_p;$$

where $C_{H2}$ and $C_H$ are the heat capacities for hydrogen ($H_2$) and hydrogen atoms. The nuclear heat capacities of hydrogen and two hydrogen atoms are practically equal.

The expenditure of energy during the heating of molecular hydrogen up to a temperature that causes the breaking of the atoms (2,500°-5,000°C) is well stipulated by the increase in the electrons’ energies. The mechanism for the increase of the electrons’ energies in a molecule have been described (See Gankins’ How Chemical Bonds Form and Chemical Reactions Proceed – 1998, p.441)

This mechanism does not work with divided atoms, for in such atoms the energy of the electrons does not depend on the distance between the atoms. Experiments proved this judgment. According to experiments, the electronic heat capacity of atoms is equal to zero.

To calculate the experimental value, which should be added to the electronic energy of two hydrogen atoms, we must subtract the value of $C_{elH2} (T_2 - T_1)$ from 437 kJ/mol. [$C_{elH2}$ is the electronic heat capacity, $T_2$ is the reaction temperature, $T_1$ is the temperature at which the electronic freedom stages defrost or becomes noticeable.]
According calculation (See Gankins’ *How Chemical Bonds Form and Chemical Reactions Proceed* – 1998, p.441) from the 437 kJ/mol, received from measuring the expenditure of energy for thermal bond breaking, we should subtract a value equal to about 200 kJ/mol.

That is, to get the experimental energy value of a hydrogen molecule (H₂), we should add not 437 kJ/mol, but a value smaller by 200 kJ/mol, i.e., 237 kJ/mol to the experimental value of the energies of two hydrogen atoms (2H). The experimentally defined energy value of a hydrogen molecule comprised 2,877 kJ/mol, while the calculated energy value of the same comprised 2,905 kJ/mol.

Thus, the experimental value differs from the calculation by less than one percent. Such a coincidence allows us to say that the real hydrogen molecule is identical to the hydrogen molecule model from which the calculated data was received.

In the calculation based on the model, only electrostatic interactions were considered. As the calculation results differed from the experimental data by less than 3%, we can say that the forces defining the formation of molecules out of atoms are electrostatic.

Let’s take the distance between the nucleus and the electron if we bond an electron to a hydrogen atom. The attraction of each electron to the nucleus decreases by 25%; the effective charge of the atom’s nucleus decrease by 25%; the distance between the nucleus and the electron in a hydrogen atom, bonding the electron, will be 0.65Å.

We have calculated the distance (C) between each of the bonding electrons and the nuclei in a hydrogen molecule, which is equal to 0.582Å. As previously indicated, a hydrogen atom with a radius of 0.529 Å, can bond (connect) an additional electron entering the unfilled outermost shell of the hydrogen atom which contains one electron.

The distance between the electrons and the nuclei in a molecule is 0.582Å greater than the distance between the electron and the nuclei in an atom (0.529Å), but smaller than that between the electron and the nucleus when an electron is bonded to an H atom (0.65 Å).

This proves that both electrons enter the outermost shell of the atoms being bonded. Thus, via simple arithmetic, on the basis of the virial theorem and the data on the electron’s and the proton’s
charges, we have managed to calculate the electronic energy of a hydrogen molecule and the energy which is gained during chemical bond formation between two hydrogen atoms.

We have also calculated the distances between the nuclei and the electrons in a hydrogen molecule and the distances between the nuclei.

According to the calculated model, the angle between the attraction forces bonding the electrons to the nuclei of the hydrogen is equal to 60° C. 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 $F_{CH}$ (Fig 6.1) 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 atom to the outermost shell of another, that is, by the attraction of the nuclei of one atom to the electrons of another.

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 inter-nuclear 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 nuclear charge of 1.5 proton units can be evaluated as an average value between the energy of a hydride ion ($\text{H}^-$) and a helium atom (He), that is, by the value of $(54.4\text{eV})$ i.e., close to the previous calculation, and therefore — greater than the repulsion energy.
CONCLUSIONS

The calculation of a hydrogen molecule has shown:

1) When chemical bonding takes place, there is energy gain. The potential energy of one molecule is greater than that of two atoms.

   It is more difficult to tear an electron off a hydrogen molecule nucleus than off two hydrogen atoms, unless we impart more energy.

2) Two electrons – one from each atom – take part in bond formation.

3) During molecule formation, both bonding electrons enter the outermost shells of the atoms being bonded.

4) A hydrogen molecule consists of two protons joined by a circle in which two electrons are constantly rotating on a plane perpendicular to the axis connecting the nuclei. This plane is situated at equal distances from the nuclei being connected.

5) 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.

   That is, the bonding of an electron to a hydrogen atom offers a much smaller energy gain than the bonding of another hydrogen atom containing a positive nucleus and an electron. This is because, in this case, there is an increase in the effective charges of both nuclei of the hydrogen atoms to be bonded. The increase of the effective charges of the atoms' nuclei and the relative increase of the potential energy of the bonding electrons, as a result of this, is the main contribution in the energy gain in chemical bond formation.

   In the case of a hydrogen molecule, the energy gain at the expense of the affinity of the hydrogen atom to the electron comprises, according to calculations: 3.4 eV, and at the expense of increasing the nuclei's effective charges: 57.8 eV. This is conditioned by the fact that the potential energy in atomic systems is proportional to the square of the effective charges of the nuclei.
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.
6.2** MOLECULES FORMED OF

MULTI-ELECTRON ATOMS

All atoms, except hydrogen ones, contain more than one electron. Since one electron takes part in bond formation, all the other atoms (besides those of hydrogen) will either form not one but several chemical bonds, or the molecules formed of these atoms will contain electrons that do not take part in bond formation.

The calculation of the electronic energy of molecules with more than one bond or with electrons that do not participate in bond formation, as we did in the case of hydrogen molecules (i.e., without additional suppositions), is impossible.

To elucidate exactly how the regularities set for hydrogen molecules are reserved for multi-electron atoms, we will make use of experimental data.

According to the 2\textsuperscript{nd} precept (see section 4) the number of bonds that an atom can form is equal to the number \( n \) of electrons that the given atom contains if \( n < 4 \).

According to the 4\textsuperscript{th} precept (see section 4) during chemical bond formation, both of the bonding electrons enter the outermost shell of the atoms being bonded. That is, the number of electrons in the outermost shells of the atoms being bonded increases by one electron.

As far as the question under study is concerned \( \text{[Are the regularities set for the hydrogen molecule common for other molecules?]} \) let's first detail the results of the studies of atomic ionization energy.
6.3** IONIZATION ENERGY OF MULTI-ELECTRON ATOMS

Since the electrons in the atom are attracted to the atom's nucleus via Coulomb (electrostatic) forces, we must use energy in order to tear the electrons away from an atom.

The data on the IE and FIE allow us to realize how much energy we should apply to an electron in order to tear it away from the atom.

Multi-electronic atoms contain active electrostatic attraction forces that attract the electrons to the nucleus and they also have inter-electronic repulsion. An increase of the attraction forces (nuclear charge increase) leads to the increase of the IEs. A decrease in the number of electrons of a multi-electron atom with an unchanged nuclear charge leads to a decrease of the inter-electronic repulsion, and therefore, to the increase of the IE.

The IEs have been defined experimentally for all the electrons of most atoms. The data given in figures 3.1 – 3.5 offer energy values necessary for extracting an electron from atoms contained in 1 gram mole of atoms, i.e., out of all the atoms contained in \( x \) grams of substance, where \( x \) is the atomic weight of the element.

For example: A hydrogen atom has an IE equal to 13.595 eV (1,317 kJ/mol.) This means that in order to extract all the electrons out of 1 gram of hydrogen (there is but one electron in a hydrogen atom) we must spend energy of 13.595 eV (1,317 kJ/mol).

The FIE (IE\(_1\)) of an aluminum atom is equal to 580 kJ/mol; the second ionization energy (IE\(_2\)) is equal to 1,815 kJ/mol; the third (IE\(_3\)) is equal to 2,740. This implies that in order to extract the first electron out of 27 grams of aluminum, we must spend 580 kJ/mol of energy; to extract the second electron – 1,815 kJ/mol of energy; to extract the third one – 2,740 kJ/mol of energy.

The increase of ionization energy during the decrease of the number of electrons is explained by the decrease of the interelectronic repulsion energy when the number of electrons in the atom is decreased. The first electron is torn away from the
atom with 13 electrons; the second and third electrons are torn away from the atoms with 12 and 11 electrons respectively.

In figure 3.5 we see the logarithm dependence of the energy required for the consequent extraction of electrons from the Ca atom. The logarithmic scale is used so that the graphic would not be stretched out vertically. Figure 3.5 shows that the electrons are sort of divided into 4 groups: there are 2 electrons in group I; 8 electrons in groups II and III; and 2 electrons in group IV.

The decrease of the IE in each group when going from one IE to the next is significantly smaller than when going from one group to some another. Thus, if for the extraction of the first electron in a Ca atom we need the energy of 610 kJ/mol; for the second – 1,180 kJ/mol, then, to tear off the third electron, we need energy of 5,000 kJ/mol. That is, if the difference between the energies of \( \text{IE}_1 \) and \( \text{IE}_2 \) is 570 kJ/mol, then the difference of energies between \( \text{IE}_2, (\text{IE}_1) \) and \( \text{IE}_3 \) is already 4,000 kJ/mol. On the other hand, the difference in tear-off energies between the 3rd and 4th electrons, the 4th and 5th, etc., etc. are very close in value.

The difficulty in tearing electrons off the atom depends on their distance from the nucleus: the closer the electrons are to the nucleus, the harder it is to tear them off the nucleus.

According to the data given graphically on the IEs in figure 3.5 the first and second electrons are situated farther away from the atom's nucleus than the electrons from #3 to #11. All this proves that the electrons in the atom are distributed in layers. That is, a Ca atom has 4 layers of electrons: there are 2 electrons in the outermost layer (shell); then there are 8 electrons in the second and third inner layers; and finally there are 2 more electrons in the layer closest to the nucleus.

The data on the IEs, elaborated identically as with the Ca atom, shows that the atom structure of practically all the atoms in the table of elements is identical. That is, the electrons surrounding the nucleus in all the atoms are distributed in layers, and the layer of electrons closest to the nucleus always contains 2 electrons. The rest of the layers, known as inner layers contain 8 electrons each.

The number of electrons in the outermost shell for elements of the 2nd and 3rd periods is given in the following table:
TABLE 6.3-2

Number of Electrons in the Outermost Shells in the Atoms of Elements of the 2nd and 3rd Periods

<table>
<thead>
<tr>
<th>ELEMENTS</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td>Ar</td>
<td></td>
</tr>
<tr>
<td>Number of Electrons</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>Valence</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Each following element in the table of elements differs from the previous one in respect to the nuclear charge by one unit, and relative to the number of electrons – by one additional electron. That is, when going from lithium (Li) to beryllium (Be) the nuclear charge increases from 3 to 4 proton units, while the number of electrons surrounding the nucleus also increases by 3 and 4 units respectively, and the increase of the amount of electrons occurs at the expense of the amount of electrons in the outermost shell (see table 6.3-2). This is what happens in almost all the elements when going from element to element – besides the transition from neon (Ne) to sodium (Na).

Though the nuclear charge of sodium (Na), as in all other cases, is by one unit greater (Ne has 10 proton units, Na has 11) and the number of electrons in Ne is 11 while Na has 12, the number of electrons in the outermost shell (table 6.3-2) Na = 1 and Ne = 8. That is, the additional electron does not get into the neon's existing outermost electronic layer, but starts the formation of a new outermost electronic layer.

According to the experimental data, given in the table 6.3-2, the maximal number of electrons that can be contained in the outermost shell of the electrons of the 2nd and 3rd periods is limited by the digit 8.

Now let's return to the question in connection with which we detailed the electronic structure of atoms of the 2nd and 3rd periods; namely, to the question of whether or not the regulations were observed in reference to the calculation of a hydrogen molecule (made up of two hydrogen atoms) for molecules formed of other multi-electron atoms.
According to the 2nd precept (section 4), one electron from the outermost shell is utilized for the formation of one bond; and relatively, the number of bonds that can be formed of a multi-electronic atom is equal to the number of electrons in the outermost shell. According to the 4th precept, both bonding electrons enter the outermost shells of the atoms being bonded; and relatively, the number of electrons in the outermost shell of the atoms being bonded increases by one unit.

Experimental data on the IEs have shown that the maximal number of electrons that can be contained in the outermost shell of elements of the 2nd and 3rd periods is equal to 8.

That is, on the one hand, the maximal number of bonds in these periods is limited by the number of electrons in the outermost shell (one electron is utilized for one bond).

On the other hand, the number of bonds the given atom can form, is limited by the number of electrons contained in the existing outermost shell of a multi-electron atom after bond formation. This is actually the 4th precept of bond formation.

The existence of stable compounds, made up of atoms of the 2nd and 3rd periods and of hydrogen atoms or halogens such as lithium hydride (LiH), boron trifluoride (BF₃), methane (CH₄), water (H₂O), ammonia (NH₃), hydrogen sulfide (H₂S), etc., is experimental proof of the fact that the above indicated 2nd and 3rd precepts relative to bond formation and based upon the calculation of a hydrogen molecule, are valid also in the case of multi-electron atoms.

In each of the above-mentioned molecules (LiH, BF₃, CH₄, H₂O, NH₃, H₂S) the number of bonds is either equal (the first three molecules) or fewer (the last three) than the number of electrons in the outermost shell of the relative atoms: lithium (Li), boron (B), carbon (C), oxygen (O), nitrogen (N), sulfur (S).

Hydrogen atoms and those of halogens (F, Cl, Br, I) can form only one chemical bond in accordance with the above-mentioned precepts. The hydrogen atom has but one electron. The halogen atoms have seven electrons in the outermost shell, and therefore, they can bond only one additional electron to the outermost shell.

That is, the existence of such stable compounds as LiH, BF₃, and CH₄ (where the number of bonds equals the number of electrons in the outermost shells of lithium, boron, and carbon
atoms) and the absence of stable compounds (where the number of bonds exceeds the number of electrons in the outermost electronic shells) indicates that the 2\textsuperscript{nd} precept, concerning bond formation with a hydrogen molecule, is valid for multi-electron atoms as well.

The number of electrons in the atoms of the outermost shells of the above mentioned molecules does not exceed 8, which proves that there is no violation of the 5th and 6th precepts (section 4) concerning multi-electron atoms introduced as a result of the hydrogen molecule calculation with a simultaneous check up of the comparison of bond formation with the ionization energy (IE) data of multi-electron atoms.

The coincidence of the regularities found during the calculations of bonding energy in a hydrogen molecule with data on the ionization potentials allows adding some new precepts to the regularities concerning the formation of a hydrogen molecule. This is characteristic of multi-electron atoms (those with more than 1 electron).

As far as the 5th precept is concerned — in the case of multi-electron atoms, it is the electrons in the outermost electronic shells of the atoms being bonded that take part in chemical bonding.
6.4*** CHEMICAL BONDING ENERGY

A comparison of the data in respect to the number of electrons in the outermost shell, with the number of chemical bonds the given atom can form, has shown that the main precepts for chemical bond formation set for hydrogen molecule bond formation, are valid for other atoms as well. That is because the bond is of electric nature and is formed at the expense of two electrons (one from each atom). Because of this precept we should expect a correlation between the FIEs of the atoms and the bonding energies of dual-atomic molecules.

At present the experimental bonding energies (those that are necessary for breaking a 1-mole bond of a dual-atomic molecule in the gas phase) have been defined.

Experimental data on bonding energy for a number of dual-atomic molecules (in the gas phase) formed of atoms of the 2nd and 3rd periods are given in table 6.4-1 and figure 6.4-1.

<table>
<thead>
<tr>
<th>Molecule $A_2$</th>
<th>FIE of $A$ (eV)</th>
<th>Bonding Energy (kJ/mol)</th>
<th>Molecule $A_2$</th>
<th>FIE of $A$ (eV)</th>
<th>Bonding Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$</td>
<td>5.4</td>
<td>110</td>
<td>Na$_2$</td>
<td>5.1</td>
<td>72</td>
</tr>
<tr>
<td>Be$_2$</td>
<td>9.3</td>
<td>30</td>
<td>Mg$_2$</td>
<td>7.6</td>
<td>8.5</td>
</tr>
<tr>
<td>B$_2$</td>
<td>8.3</td>
<td>274</td>
<td>Al$_2$</td>
<td>6.0</td>
<td>168</td>
</tr>
<tr>
<td>C$_2$</td>
<td>11.3</td>
<td>602</td>
<td>Si$_2$</td>
<td>8.1</td>
<td>314</td>
</tr>
<tr>
<td>N$_2$</td>
<td>14.5</td>
<td>941</td>
<td>P$_2$</td>
<td>10.5</td>
<td>477</td>
</tr>
<tr>
<td>O$_2$</td>
<td>13.6</td>
<td>493</td>
<td>S$_2$</td>
<td>8.1</td>
<td>421</td>
</tr>
<tr>
<td>F$_2$</td>
<td>17.4</td>
<td>140</td>
<td>Cl$_2$</td>
<td>13.0</td>
<td>240</td>
</tr>
</tbody>
</table>
Experimental data given in table 6.4-1 and fig.6.4-1, shows that the bonding energy between the atoms practically does not depend on the FIEs of the atoms to be bonded.

Thus, for example, the bonding energy of a molecule composed of two nitrogen atoms (N₂) is equal to 941 kJ/mol (the FIE of N is equal to 1,406 kJ/mol) while the bonding energy in a fluorine (F₂) molecule is equal to 140 kJ/mol, and the FIE of the F atom (FIE_F) is equal to 1,682 kJ/mol which insignificantly differs from the FIE of a nitrogen (N) atom.

Analogously, the FIE of beryllium (Be), equal to 900 kJ/mol, has a value close to that of boron (B). FIE_B = 800 kJ/mol. The same is true of the FIE_C of carbon, which is equal to 1,088 kJ/mol. While the bonding energies in molecules Be₂, B₂, and C₂ comprise 30 kJ/mol, 225 kJ/mol, and 602 kJ/mol respectively. That is, a molecule, made up of 2 beryllium atoms, does not exist in the gas phase, it is unstable, while molecule C₂ does not break up into atoms even at a temperature over 5,000°C.

On the basis of the analyses given in table.6.4-1 one might think that when switching from a hydrogen molecule bond to dual-atomic molecules with more than one electron, there is either a
principle difference (additional non-electric forces) or action of some additional factors that explain the above-mentioned inconsistencies like the absence of correlations between the FIEs of the atoms being bonded and the bonding energy – in accordance with the electric nature of bonding.

Explanations based on suppositions of new (non-electric) forces are not logic explanations. After such explanations, there is always the problem of how to explain the physical essence of these forces.

This is why we will begin by looking for additional factors that explain the absence of the expected correlations and the *independence* of experimental data relative to the FIEs of bonding energy in dual-atom molecules in the atoms being bonded.

**Table (6.4-1) can be conditionally divided into four groups:**

**Group I** includes molecules composed of identical atoms whose bonding energies are below 40 kJ/mol. These molecules fall apart into their constituent atoms when in a gas phase.

**Group II** includes dual-atomic molecules composed of identical atoms whose bonding energies vary between 400 kJ/mol and 1,000 kJ/mol. Indeed, the bonding energy in these molecules greatly differs towards the plus side as compared to the bonding energy of a hydrogen molecule whose energy is equal to 429 kJ/mol.

**Group III** includes dual-atomic molecules composed of various atoms whose bonding energies range from 340 kJ/mol to 550 kJ/mol.

**Group IV** includes dual-atomic molecules built of identical atoms whose bonding energies vary from 50 kJ/mol to 350 kJ/mol.

Before we begin the explanation, let's specify the questions that we are to cover. The gathered experimental data on bonding energies between atoms of the 2nd and 3rd periods of the table of elements allows us to formulate the first question as follows:
Why is it that the chemical bonding energy between the multielectron atoms is much smaller or much greater (table 6.4-1) than in a hydrogen molecule ($H_2$)

### TABLE 6.4-2

**MOLECULES AND THEIR BONDING ENERGIES**

Chemical Bonding Energy (kJ/mol) in a Row of Dual-Atomic Molecules

<table>
<thead>
<tr>
<th>Group I</th>
<th>Group II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule</td>
<td>Bonding Energy</td>
</tr>
<tr>
<td>Be$_2$</td>
<td>— 30</td>
</tr>
<tr>
<td>Ne$_2$</td>
<td>— 4</td>
</tr>
<tr>
<td>Mg$_2$</td>
<td>— 7.6</td>
</tr>
<tr>
<td>Ar$_2$</td>
<td>— 7</td>
</tr>
<tr>
<td>S$_2$</td>
<td>— 421</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Group III</th>
<th>Group IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule</td>
<td>Bonding Energy</td>
</tr>
<tr>
<td>LiF</td>
<td>— 572</td>
</tr>
<tr>
<td>NaF</td>
<td>— 447</td>
</tr>
<tr>
<td>LiCl</td>
<td>— 480</td>
</tr>
<tr>
<td>NaCl</td>
<td>— 439</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The data on the number of electrons in the outermost shell allows us to define the maximal number of electrons that can be situated in the outermost shells of the atoms of the 2nd and 3rd periods. The data on the FIEs of the atoms of these periods are given in table 6.4-2.

The following table will help us answer the question:

*Why does the bonding energy in dual-atomic molecules differ so much in reference to the bonding energy in a hydrogen molecule?*
This table offers data on the atoms' affinities to the electron, which is also of great use for additional confirmation of the correctness of the conclusions made on the basis of the comparison of the FIE data. The data on the affinity of atoms to the electron indicates the energy that is discharged when the electron is bonded to the atom.

**TABLE 6.4-3**

**First Ionization Energies (FIEs) and Affinity to the Electrons in Elements of Periods 1, 2, and 3 in the Table of Elements in kJ/mol**

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H</td>
<td>He</td>
<td>Li</td>
<td>Be</td>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
<td>Ne</td>
</tr>
<tr>
<td><strong>FIE</strong></td>
<td>1310</td>
<td>2372</td>
<td>519</td>
<td>900</td>
<td>799</td>
<td>1086</td>
<td>1406</td>
<td>1314</td>
<td>1682</td>
<td>208</td>
</tr>
<tr>
<td><strong>Aff.</strong></td>
<td>67.4</td>
<td>&lt;0</td>
<td>77</td>
<td>&lt;0</td>
<td>31.8</td>
<td>119.7</td>
<td>4.5</td>
<td>141.8</td>
<td>349</td>
<td>&lt;0</td>
</tr>
</tbody>
</table>

The affinity data given in the table is actually the result of studies of FIE values of atoms to which electrons were bonded. That is, for example,* the energy discharged when connecting the electron to the Na atom [(the affinity value for sodium (Na)] via the reaction

\[ \text{Na} + \text{e}^- \rightarrow \text{Na}^- \]

is measure by defining the FIE in reaction:

\[ \text{Na}^- \rightarrow \text{Na} + \text{e}^- \]
The affinity values smaller than zero, indicated in the table, show that the electron does not bond to atoms with an affinity equal to <0.

Another question might arise:

What is common between the FIE value, the affinity of the atom to the electron, and the bonding energy? Or: Why do we think that the FIE values and those of the affinity can help us answer the question about the cause of the great difference in bonding energy in a number of dual-atomic molecules.

As we indicated in section 4, in the case of multi-electronic atoms during bond formation, just as in the case of a hydrogen molecule, chemical bonding takes place via the electronic pair (one from each of the atoms being bonded) while both bonding electrons enter the outermost shell of both atoms to be bonded.

The observance of this rule for multi-electronic atoms was proven on the basis of chemical experimental data relative to the existence of stable compounds (for example, compounds of atoms of the 2nd and 3rd periods were taken) where the number of electrons surrounding each atom and entering the molecule, does not exceed eight. This value coincides with the maximal number of electrons that can exist in the outermost shells of the atoms of the 2nd and 3rd periods.

To explain the significant deviation of the bonding energies in multi-electronic atoms, as compared to that in a hydrogen molecule, it is necessary to deepen our understanding of the reason why the number of electrons in the outermost shell is limited.

It was already shown that the main forces in the atomic and molecular systems are the electric forces that attract the electrons to the nucleus and the interelectronic repulsion forces.

The increase of the attraction forces increases the absolute value of the potential energy of the system: \textit{neutral atom + free electron}. On the other hand, the increase of the interelectronic repulsion forces decreases the absolute value of the system's potential energy: \textit{neutral atom + free electron}.

The bonding of the electron to the atom occurs when there is energy gain, or, in other words, if the absolute value of the potential energy of the system \textit{atom + electron} increases as a result of the bonding of the electron to the atom. The data on the affinity of the atom to the electron shown in table 6.4-3 gives us a digital value of the energy gain during the bonding of the electron to the atom.
During the bonding of the electron to the atom, the total attraction energy of the electrons to the nucleus increases at the expense of the increase of the number of electrons attracted to the nucleus. On the other hand, the inter-electronic repulsion energy increases because of the increase of the amount of electrons. That is, the bonding of the electron to the atom takes place if, as a result of this bonding, the attraction energy gain is greater than the energy loss received at the expense of the increase of the repulsion energy.

To illustrate this, let's have a look at the inter-electronic repulsion forces, the electron-nuclear attraction, and the effective nuclear charge when the electron is attached to a hydrogen-like atom (composed of one nucleus and one electron) and a helium-like atom (composed of one nucleus and two electrons).

When an electron is bonded to a hydrogen atom, there appears an inter-electronic repulsion force, and the electrons' attraction energy to the nucleus undergoes a change.

Let's calculate the potential energy change that occurs during the bonding of an electron to a hydrogen atom. The hydrogen atom turns into a helium-like atom with a nuclear charge of 1 proton unit and with 2 electrons at equal distances on either side of the nucleus. The potential energy of this system is equal to the difference between the electrons' attraction energy to the nuclei and the repulsion energy.

In the cited case (when the nuclear charge and the electron's charge have identical absolute values), the electrons' attraction energy to the nucleus is equal to: $2e^2/R$, where $R$ is the radius of the orbit along which the electrons rotate. The inter-electronic repulsion energy is equal to: $e^2/2R$. The total potential energy is equal to the difference between the attraction energy and that of inter-electronic repulsion. That is:

$$2e^2/R - e^2/2R = 3e^2/2R \quad \text{(equation 6.4-1)}$$

In accordance with equation (6.1-1) the energy of a helium-like atom is equal to: $E = [13.6 \ (z - 0.25)^2] \cdot 2$. At $z = 1$ (cited example):

$$E = [13.6 \ (1 - 0.25)^2] \cdot 2 = 15.3 \text{ eV}.$$  
Here 13.6 eV is the hydrogen atoms' energy ($E_{\text{H}}$).

According to equation (5.6):
E_H = e^2 / 0.529

where 0.529 is the radius of a hydrogen atom. The potential energy is equal to 2E_H. Thus: 2e^2 / 0.529 = 27.2 eV and e^2 = 14.38. By substituting e^2 in equation 6.4-1, we get: 3 ∙ 14.38 / 2R = 30.6 eV, — where 30.6 eV is the double energy (15.3 ∙ 2) of the helium-like atom’s charge 1.

Thus: R = 0.705 Å

Knowing the radius of the helium-like atom, we can calculate the change of both the potential attraction energy and the potential repulsion energy, since we know that (e^2 / 0.529) ∙ 2 = 13.6 eV (energy of 1 gram of hydrogen atoms): e^2 = 14.4 eV. From this we get:

2e^2 / R = 2 ∙ 14.4 / 0.705 = 40.8 eV; e^2 / 2R = 10.2 eV.

The potential energy of the system, where the electron is separated from the hydrogen atom at an infinite distance, is equal to the potential energy of a hydrogen atom: 2 ∙ 13.6 = 27.2 eV.

That is, when the electron is bonded to a hydrogen atom, the potential energy of the electrons’ attractions to the nucleus increases by 13.6 eV. On the other hand, when bonding an additional electron to a hydrogen atom, the inter-electronic repulsion energy increases by 10.2 eV. There is no inter-electronic repulsion in the initial hydrogen atom.

Thus, when adding an electron to a hydrogen atom, the absolute potential energy value increases by 3.4 eV (13.6 – 10.2 = 3.4). The potential energy of 1 gram of hydrogen atoms is equal to 27.2 eV (double value of the hydrogen atoms’ energies).

Respectively, the energy of 1 gram of helium-like atoms, with a charge equal to that of a hydrogen atom, constitutes, according to the calculation: 30.6 eV (27.2 + 3.4 = 30.6). According to experimental data, the potential energy of such atoms comprises

28.7 eV [(13.6 + 0.74) ∙ 2 = 28.7].

where 13.6 is the energy of a hydrogen atom; 0.74 eV is the affinity of the hydrogen atom to the electron.
Processes proceeding via attraction forces (a stone falling onto the ground, an electron striving towards a nucleus, etc.) occur spontaneously with a discharge of energy. That is, in accordance with the calculation, the bonding of the electron to a hydrogen atom occurs spontaneously with a discharge of energy. In other words, the hydrogen atom should have a positive affinity to the electron. This has been confirmed via experiments.

Now let's cite the change of the potential energy when bonding an electron to a helium atom. The above-described calculations have shown that the change of the system's energy, during the bonding of the electron, is equal to the value of the potential energy change divided by 2. According to the virial theorem, half of the system's potential energy is equal to the system's energy. That is, when calculating the energy of a system consisting of electrons and nuclei, we need not calculate the kinetic energy of the electrons.

It is enough to define the potential energy of the system (i.e., the distance between the electrons and the nuclei) and divide the result by two. To compare the calculated and experimental results, we define the ionization energies of all the electrons. The sum of all these energies, according to the above mentioned, is equal to the energy of the system.

According to equation (6.1-1) the energy of 1 gr. mol of atoms with a nuclear charge of 2 proton units and with 2 electrons orbiting in a circle around the nucleus, on one plane is calculated by the equation:

\[ E_{\text{He}} = 13.6 (2 - 0.25)^2 \cdot 2 \]

where 13.6 is the energy of the hydrogen atom; 2 is the nuclear charge of the helium atom; 0.25 is the allowance for inter-electronic repulsion.

Analogously, the energy of 1 mol of atoms with a nuclear charge of 2 proton units and with 3 electrons rotating around the nucleus in one circle, can be calculated by the equation:

\[ E_3 = 13.6 (2 - 0.577)^2 \cdot 3 \]

where 0.577 is the inter-electronic repulsion allowance (relative to three electrons). See the book: "How Chemical Bonds
Form and Chemical Reactions Proceed” (p.78). The calculation concludes as follows:

$$E_2 = 83.3 \text{ eV} ; \quad E_3 = 82.6 \text{ eV}$$

That is, the bonding of the electron leads not to the increase of the potential energy, but to its decrease. Recall the fact that the absolute value of the system’s energy is equal to half of its potential energy. The bonding of one electron to a helium atom is accompanied by a decrease of the absolute value of the potential energy, and therefore, cannot take place spontaneously, i.e., without the use of energy. Indeed, stones do not reveal themselves from under the ground spontaneously.

In other words, the calculation shows that an electron cannot bond to a helium atom, which has been proven experimentally. The affinity of a helium atom is less than zero.

Therefore the bonding or nonbonding capacity of the electron to the atom is defined by the difference in the change of the absolute values of the potential attraction energies of all the electrons to the nucleus and the mutual interelectronic repulsion. If this difference is greater than zero — the electron will bond; if it is smaller than zero — it won’t.

The data on atoms' affinities to the electron given in table 6.4-3, show that for the atoms of periods 1, 2, and 3 in the table of elements, besides the atoms of helium (He), beryllium (Be), magnesium (Mg), neon (Ne), and argon (Ar), the atoms' affinities to the electron are greater than zero. During the bonding of electrons to atoms of periods 2 and 3 (besides Be, Mg, Ne, Ar) there is an energy gain. Thus, the increase of the attraction energy during the bonding of electrons to the nucleus is greater than the increase of the repulsion energy.

In the case of He, Be, Mg, Ne, and Ar atoms, the increase of the attraction energy during the bonding of the electrons to the nucleus, is smaller than the energy increase of the inter-electronic repulsion. An independent confirmation of this conclusion is the data on the FIEs for atoms of the 2nd and 3rd periods given in the table 6.4-2. Each of the numbered elements differs from the next by nuclear charge and by the amount of electrons surrounding the nucleus.
The atom of each of the following elements has a positively charged nucleus by one proton more. The number of electrons in the electronic shell of each of the following atoms is by one electron more than in the previous shell.

The transition from one element to the next, for example, from sodium (Na) to magnesium (Mg) can be represented schematically as two consecutive processes: first the nuclear charge of the Na atom increases by one proton unit and turns into a Mg nucleus, then one electron is bonded to the atom that has a nuclear charge of 12 proton units and an electronic shell that has 11 electrons [shell of a sodium (Na) atom].

With such consideration, the atoms’ FIE values correspond to the energy gain during the bonding of the electron to an atom whose nuclear charge had been increased by one proton unit.

The FIE values of table 6.4-3 increases the values of the atoms' affinities to the electrons. For example, the FIE for Na is equal to 498 kJ/mol, while the affinity is equal to 117.2 kJ/mol. Thus, the bonding of an electron to an atom with a nuclear charge of 11 proton units and surrounded by 10 electrons offers energy gain of 498 kJ/mol. The bonding of an electron to an atom with a nuclear charge of 11 proton units and surrounded by 11 electrons offers energy gain of about 4 times smaller (117.2 kJ/mol). That is, during the bonding of an electron to an atom, the increase of the nuclear charge abruptly increases the energy gain.

During chemical bond formation, the number of electrons in the atoms’ outermost electronic shells increases by one electron, and the effective charges of the atoms being bonded are changed. The effective charges of the nuclei to be bonded are changed because of the attraction of the charged nuclei and because of the increase of the number of electrons in the outermost shells of the atoms being bonded.

In order to compare the bond formation process with the processes of bonding an electron to an atom without changing the nuclear charge of the atom, and the process of bonding the electron to the atom with a simultaneous increase of its nuclear charge by one proton unit, we should evaluate the influence of the atoms being bonded on the effective nuclear charge, and the attraction of the nuclei of these atoms that occurs during bond formation.

An additional attraction force of the electron to the atom’s nucleus in a hydrogen molecule (force occurring as a result of the attraction of the atom’s nucleus) is equal to the projection of force
F₁ that attracts the electron to a nucleus that bonds the same
electron to another nucleus. (See figure 6.1.1) The value of this
projection force is equal to:

\[ F₁ \cdot \cos 60º = 0.5 F₁. \]

That is, the mutual approach of the nuclei leads to the
increase of the attraction force of the bonding electrons to the
nuclei by 50%; which is equal to the increase of the effective
charge of the nuclei to be bonded by 0.5 proton units.

Bond formation is, from the viewpoint of the energy gain, a
sort of middling process between the bonding of the electron to a
neutral atom (measured affinity to the electron) and the bonding of
the electron to the atom whose nuclear charge is increased by one
unit.

The data on the affinity of atoms to the electron and the
data on the FIEs allow us to elucidate exactly why the bonding
energy in molecules given in table 6.4-2 is much smaller than the
bonding energy in a hydrogen molecule.

Beryllium (Be) and Magnesium (Mg) having an affinity
smaller than zero, according to table.6.4-3, we can say that when
an additional electron is introduced to the outermost shells of Be
and Mg, the inter-electronic repulsion energy is increased to a
greater extent than is the attraction energy of the electrons to the
nucleus.

A comparison of the atoms' FIEs changes when going from
lithium (Li) [an atom that precedes Beryllium (Be)] to Be; and
when going from Be to boron (B) [an atom that follows Be in table
6.4-2].

According to the data in table 6.4-3, when going from
lithium (FIE - 519 kJ/mol) to beryllium (FIE – 900 kJ/mol), the
FIE increases by 400 kJ/mol; but when going from beryllium to
boron (FIE – 799 kJ/mol) the energy gain decreases to 100 kJ/mol.

According to table 6.4-3, there are 3 electrons in the
outermost electronic shell of boron, while there are 2 electrons in
the outermost shell of beryllium. That is, when the electron is
bonded to beryllium with a simultaneous increase of the nuclear
charge by one proton unit, the electron being bonded enters the
existing outermost shell of beryllium, and the energy gain will thus
be by 100 kJ/mol smaller than during the entrance of the electron
to the outermost shell of lithium (when going from lithium to beryllium).

Thus the decrease in the energy gain, when the electron enters the outermost shell of a beryllium atom, can be evaluated as greater than 100 kJ/mol and smaller than 400 kJ/mol.

During the formation of molecules $\text{Li}_2$, $\text{Be}_2$, $\text{B}_2$, two electrons enter the outermost shells of the atoms being bonded (one electron into each atom). In the case of lithium and boron, according to the data on the affinity of atoms to the electron, the energy gain amounts to 77 kJ/mol and 32 kJ/mol respectively for each of the two atoms being bonded, and therefore these atoms have 154 kJ/mol and 64 kJ/mol respectively.

In the case of beryllium, when the electron enters the outermost shell of this element, according to the atoms' affinity to the electron, energy is not gained, but even lost. According to the above – the energy loss is generally equal to 100 kJ/mol or 200 kJ/mol.

Since the energy gain, say, during hydrogen molecule formation out of hydrogen atoms with a positive (>0) affinity value to the electron, comprises 250 kJ/mol, the abrupt decrease of bonding energy for atoms with a negative atom affinity to the electron, mentioned in table 6.4-3, is quite comprehensible.

The explanation concerning the anomaly small bonding energies in elements of the II and VIII groups of the table of elements is an independent semi-quantitative proof of the fact that during covalent bond formation, both bonding electrons enter the outermost shells of the atoms to be bonded. This conclusion was made only on the basis of the comparison of the data of the number of electrons in the outermost shell with the elements' valences.

The fact that atoms of the II group form stronger bonds, as compared to the inert gases, is also proof that in the course of covalent bond formation, the effective charge of the atoms to be bonded increases.

Now let's answer the question: *Why is the bonding energy in dual-atomic molecules shown in table 6.4-1, namely, in molecules of carbon ($\text{C}_2$), nitrogen ($\text{N}_2$), oxygen ($\text{O}_2$), etc. 1.5 to 2 times greater than the bonding energy in a hydrogen molecule?*

The outermost shells of carbon (C), nitrogen (N), and oxygen (O) atoms contain 4, 5, and 6 electrons respectively. The number of bonds these atoms form, is limited by the number of additional electrons that enter their outermost shells. Thus, atoms
of C, N, and O can form 4, 3, and 2 chemical bonds respectively. And not one but several chemical bonds can be formed between any two atoms listed in table 6.4-2, which presupposes a much greater energy gain, as compared with the formation of 1 bond in the case of a dual-atomic molecule where the atoms being bonded each have 1 electron in the outermost shell.

Additional confirmation of the correctness of this explanation are the data on the bonding energy in multi-atomic molecules, where the possibilities for the formation of additional bonds between two atoms of C, N, and O come to naught at the expense of bond formation, say, with hydrogen atoms.

It was found experimentally that the bonding energy between carbon atoms in molecule $\text{H}_3\text{C} – \text{CH}_3$, nitrogen atoms in molecule $\text{H}_2\text{N} – \text{NH}_2$, and oxygen atoms in molecule HO – OH is by 1.5 to 2 times smaller and close in value to the bonding energy of a hydrogen molecule.

When atoms are bonded with one chemical bond, such a bond is known as a common chemical bond or a single chemical bond. When atoms are bonded with several common or single bonds, thereby forming double or triple ones, such bonds are known as multiple bonds.

Single bonds, when describing chemical structures, are illustrated with a dash (—). For example, the structure of methane (CH$_4$) is described by the formula:

```
H

H—C—H

H
```

Each dash represents a pair of bonding electrons. The electronic structure of methane is described by the formula:

```
H

H : C : H

H
```

Here the dots represent bonding electrons. Multiple bonds, for example, in nitrogen (N$_2$) and oxygen (O$_2$) molecules are described by structural formulas:
\[ N \equiv N \quad \text{and} \quad O = O \]

and by electronic ones:

\[ :N::N: \quad \text{and} \quad :O::O: \]

Here the electrons between the atoms are bonding ones, while those, sort of on the outside, are nonbonding ones (which do not take part in bond formation).

According to electronic formulas \( N_2 \) and \( O_2 \) in nitrogen (N), after the formation of a triple chemical bond, there remain 2 nonbonding electrons or 1 free electronic pair with each of the atoms. After the formation of a dual chemical bond in oxygen, 2 free electronic pairs remain in each of the 2 atoms bonded via a dual bond in molecule \( O_2 \).

Now let’s take the question: *Why is the bonding energy in some of the dual-atomic molecule, which are made up of various atoms, much greater than that of other molecules that are made up of identical atoms?*

According to experimental data (table 6.4-2.) the bonding energies in molecules \( Na_2 \) and \( Cl_2 \) comprise 74 kJ/mol and 242 kJ/mol respectively, while the bonding energy in molecule NaCl is equal to 439 kJ/mol. In all the three molecules (\( Na_2 \), \( Cl_2 \), and \( NaCl \)) the bonding takes place at the expense of the attraction of the atoms’ nuclei in sodium and chlorine to the electronic pair rotating in a plane perpendicular to the axis connecting the atoms’ nuclei.

From this point of view, it seems logic that the total attraction energy of the atoms’ nuclei in the Na and Cl to the bonding electronic pair should have an average value between 74 kJ/mol and 242 kJ/mol (the attraction energies of two Na atoms’ nuclei and two Cl atoms’ nuclei, respectively, to the bonding pair of electrons).

Sodium and chlorine atoms differ greatly relative to their affinity to the electron. As previously indicated, bond formation can be represented as a dual process on the first stage of which the energy gain is received at the expense of the atoms’ affinities to the electrons. That is, from this point of view, the energy gain, when forming a \( Cl_2 \) molecule, should be greater than when forming a NaCl molecule.
There is a surprisingly great difference in the bonding energies of molecules in table 6.4-2, which seems anomalous and requires some explanation, to which we are now proceeding.

As we have indicated when calculating the bonding energy in a hydrogen molecule, the bonding energy (i.e., energy which is required to break a molecule into atoms) is the sum of two components:

1) the difference between the electronic energy of a hydrogen molecule and that of two hydrogen atoms;
2) the additional energy spent on the heating of the unbroken molecules. The second component is calculated on the basis of the first. These components have close values.

Calculating the first component, we calculate the electronic energy of the molecule, which amounts to the difference between the attraction energies of the hydrogen atoms' nuclei to the bonding pair of electrons and the sum of repulsion energies of the inter-electronic and the inter-nuclear forces (between their bonding electrons).

To evaluate the nuclei's attraction energies to the bonding pairs of electrons, and to evaluate the energy of inter-electronic repulsion, we should first know the charge value of the nuclei to be bonded.

The electrons surrounding the atoms in the molecules, (table 6.4-2) are distributed not in one layer, as in the case of hydrogen (H) and helium (He) atoms, but in several layers. Besides, the outermost layers of most atoms contain more than one electron. The attraction energy, which bonds the electrons to the hydrogen atoms' nuclei in a hydrogen molecule, is defined by the nuclear charge of the hydrogen atoms.

In the case of atoms with more than two electrons (the molecules in the table include such atoms) the attraction energy of the bonding electrons (unlike hydrogen molecules) is defined by the difference between the attraction energy to the atoms' nuclei and the repulsion energy of the bonding electrons from those electrons that do not take part in bond formation.

In order to define the inter-nuclear repulsion energy, we should first define this energy without considering the presence of the electrons that do not take part in bond formation.

That is, when calculating a molecule with atoms having more than one electron, the main drawback is the impossibility of evaluating the inter-electronic and electron-nuclear interactions of
the electrons that do not partake in bond formation in dual-atomic molecules.

To evaluate the influence of the nuclear charge and the nonbonding electrons on the molecule's energy, and therefore, on the bonding energy, we can make use of the experimental data on the FIEs of the atoms being bonded and on the atoms' affinities to the electrons.

To make things easier, we can make use of only the data on the FIEs since the affinity value, on the average, is almost by one order of magnitude smaller than that of the FIE, therefore, the consideration of the affinity data will hardly have any influence on the evaluation.

We know that the data on the atoms' FIEs (table 6.4-3) indicate the energy that is necessary in order to tear one atom away from an atom. In a multi-electronic atom, the energy necessary to tear away an electron from an atom is equal to the difference between the attraction energy of this electron to the nucleus and the total repulsion energy of this electron from all the other electrons in the atom.

We also know that two electrons (one from each of the atoms) take part in chemical bond formation. When calculating the molecule's energy, we are interested in the attraction energy of the nuclei towards the bonding electrons.

As already mentioned in section 5, the ionization energy of a hydrogen-like atom (with 1 nucleus and 1 electron) is proportional to the square of the nuclear charge. The relation between the energy, the ionization, and the nuclear charge can be expressed thus:

\[ E_{ion, Z} = E_{ion, H} Z^2 , \]

where \( E_{ion, Z} \) and \( E_{ion, H} \) are the ionization energies of the hydrogen-like atom and the hydrogen atom, and \( Z \) is the nuclear charge in proton units.

Out of this equation we can calculate the value of \( Z \):

\[ Z = (E_{ion, Z} / E_{ion, H})^{0.5} \]  \hspace{1cm} (Equation 6.4-2)

Ionization energy is actually the bonding energy between the electron and the atom.
In multi-electron atoms, as previously indicated, the FIE is also equal to the bonding energy value of the electron with the atom. In this case the FIE is not equal to the electron's attraction energy to the atom's nucleus, but is equal to the difference between the electron's attraction energy to the nucleus and the total repulsion energy of one electron of all the rest (those that are in the inner and in the outermost shells).

As indicated above, in order to evaluate the energy of molecules made up of multi-electronic atoms, it is necessary to evaluate the bonding energy of the electrons bonding with the nuclei, the nuclear charge of the multi-electronic atom, and the inter-electronic repulsion energy of the bonding electrons from all the other electrons in the molecule. According to the above, it is clear that the atom's FIE is considered in both the bonding energy of the electron with the nucleus and in the energy of interelectronic repulsion.

In order to define the molecule's energy in accordance with the calculation methods for the hydrogen molecule's energy, we must evaluate the nuclear charges of the atoms bonded into molecules. In the case of multi-electronic atoms, the values of the nuclear charges used in the calculation, are not the true nuclear charges of these atoms. In such calculations we should make use of the so-called effective nuclear charges (positive charges that act upon the bonding electronic pair).

The value of these charges, as previously indicated, can be expressed by the equation 6.4-2. Likewise, the energy value of internuclear repulsion, which is necessary to evaluate the molecule's energy, can also be evaluated with the help of the effective nuclear charge of the nuclei via the equation:

\[ E_{\text{rep eff}} = E_{\text{repH}_2} \cdot Z_{\text{eff1}} \cdot Z_{\text{eff2}} \]

where \( E_{\text{rep eff}} \) is the effective inter-nuclear repulsion energy in a molecule composed of the 1\(^{\text{st}}\) and 2\(^{\text{nd}}\) atoms; \( E_{\text{repH}_2} \) is the repulsion energy in molecule \( \text{H}_2 \); \( Z_{\text{eff1}} \) and \( Z_{\text{eff2}} \) are the effective nuclear charges of the 1\(^{\text{st}}\) and 2\(^{\text{nd}}\) atoms.

Considering all the above mentioned, the energy evaluation of dual-atomic molecules composed of multi-electronic atoms, can be imagined as single-electronic or hydrogen-like atoms with a nuclear charge equal to their effective nuclear charge.

To define the change in the electronic energy during molecule formation out of atoms, just as in the case of the hydrogen molecule, we subtract the energy of two atoms from that
of the molecule, and find that this energy is equal to the FIEs of the free atoms bonded into a molecule.

It is the same as in the case of a hydrogen molecule because of the balancing of all the forces on perpendicular planes and the circles in which the electrons rotate (the resultant force of all the forces is equal to zero). The molecule’s energy is equal to that of the atom with a charge of \( Z \) at point \( D \).

Once more we mention the fact that there is actually no real charge at point \( D \). The bonding electrons are attracted to point \( D \) at the expense of forces \( F_7 \) and \( F_8 \) which we got as a result of expanding the attraction forces \( F_3 \) and \( F_4 \) which bond the electrons to the nuclei being bonded by the bonding electrons.

We know that bonding energy is energy required to break up a molecule. As we have a molecule at the beginning of the process, and atoms – at the end, energy is spent, which, at least, equals the difference between the electronic energy of the molecule and that of the atoms.

The molecule is in equilibrium (the repulsive forces between identically charged particles are balanced by the attractive forces between differently charged particles via figures 6.1-1 and 6.4-1).
Figura 6.4-1
Attraction and Repulsion Forces of an AB Molecule

In Figure 6.4-1: \( AD = x_1 \), \( BD = x_2 \), \( AB = 2b \), \( CD = a \) (radius of electron’s orbit), \( N_1 \) and \( N_2 \) are nuclear charges.

\( A \) and \( B \) are locations of the nuclei;

\( C \) and \( E \) are locations of the electrons.

Also in Figure 6.4-1 \( F_5 \) and \( F_6 \) are projections of the attractive forces \( F_1 \) and \( F_2 \) applied from the electron to nuclei onto the axis connecting the nuclei.

The repulsion force between the nuclei is given by this equation\(^1\):

\[
F_{\text{rep}} = e^2 N_1 \cdot N_2 / (x_1 + x_2)^2 \quad [6.4-1]
\]

Likewise, the electrons’ attractive force at point \( D \) is equal to the sum of forces \( F_7 \) and \( F_8 \), which are the projections of forces \( F_3 \) and \( F_4 \):

---

\(^1\) In these equations, as well as in other ones in this book, the Coulomb’s coefficient \( K_e = 8.9876 \times 10^9 \) Nm\(^2\)/C\(^2\) is omitted because it could be cancelled in the equations.
\[ F_9 = F_8 + F_7 - F_e \]

where \( F_8 \) and \( F_7 \) are projections of forces \( F_3 \) and \( F_4 \) onto axis BD, and \( F_e \) is the sum of the repulsive force projections of electron C from other electrons (or the centrifugal force in case of a single valent electron).

Figure 6.4-1 does not reveal the projections of these forces.

We will touch upon evaluation of repulsion forces between electrons later. All the following forces are calculated by these equations. See figure 6.4-1.

\[
F_7 = F_4 \cos \angle DCB = F_4 \cdot \frac{a}{(a^2 + x_2^2)^{0.5}} = e^2 N_2 a / [(a^2 + x_2^2) \cdot (a^2 + x_2^2)^{0.5}] \\
F_8 = e^2 N_1 a / [(a^2 + x_1^2) \cdot (a^2 + x_1^2)^{0.5}] \\
F_9 = e^2 N_1 a / [(a^2 + x_1^2) \cdot (a^2 + x_1^2)^{0.5}] + e^2 N_2 a / [(a^2 + x_2^2) \cdot (a^2 + x_2^2)^{0.5}] - F_e = (e/a)^2 [N_1 \{ (x_1/a)^2 + 1 \}^{-3/2} + N_2 \{ (x_2/a)^2 + 1 \}^{-3/2}] - F_e / (e/a)^2 \]  [6.4-2]

Here \( F_e \) is the sum of the projections of the repulsive forces of electron C from other electrons.

By introducing \( F_0 \) and \( S_n \) such that \( F_0 = (e/a)^2 F_0 \) and \( F_e = (e/a)^2 S_n \), we get: \( F_0 = N_1 \{ (x_1/a)^2 + 1 \}^{-3/2} + N_2 \{ (x_2/a)^2 + 1 \}^{-3/2} - S_n \).

On the one hand, according to the Coulomb law,

\[ F_9 = e^2 \cdot Z / a^2 \] (where Z is the effective charge at point D in proton units).

On the other hand, we have: \( F_9 = e^2 F_0 / a^2 \). Hence \( Z = F_0 \).

For \( F_5 \) and \( F_6 \), we have:

\[ F_5 = e^2 N_2 \cdot x_2 / [(a^2 + x_2^2) \cdot (x_1 ^2 + a^2)^{0.5}] = e^2 N_1 \cdot N_2 / (x_1 + x_2)^2 \]  [6.4-3]

\[ F_6 = e^2 N_1 \cdot x_1 / [(a^2 + x_1^2) \cdot (x_2^2 + a^2)^{0.5}] = e^2 N_1 \cdot N_2 / (x_1 + x_2)^2 \]  [6.4-4]

Equations 6.4-3 and 6.4-4 are based on the equality of the forces attracting the nuclei to point D (\( F_5 \) and \( F_6 \)) and the repulsive forces between the nuclei when in equilibrium. We have three unknowns: \( x_1 \), \( x_2 \), and \( a \). To solve this system, we should have a third equation, which is compiled on the basis of the virial theorem. From this theorem, we know that distance \( a \) is inversely proportional to charge \( Z \) or \( F_0 \).

The proportionality coefficient can be easily defined since we know the distance and charge \( Z \) of a hydrogen atom. The inter-electronic repulsive force (\( S_n \)) can be calculated from the equation, which we will demonstrate later.
Hence, we have a system of three equations with three unknowns:

\[
\begin{align*}
N_1 \frac{n x_1}{(x_1^2 + a^2) (x_1^2 + a^2)^{0.5}} &= N_1 \frac{N_2}{(x_1 + x_2)^2} \quad [6.4-5] \\
N_2 \frac{n x_2}{(x_2^2 + a^2) (x_2^2 + a^2)^{0.5}} &= N_1 \frac{N_2}{(x_1 + x_2)^2} \quad [6.4-6] \\
a &= \frac{R}{F_0} \quad [6.4-7]
\end{align*}
\]

Here: \( n \) — number of bonding electrons, 
\( R \) — Bohr’s radius equal to 1.

\[
F_0 = N_1 [(x_1/a)^2 + 1]^{3/2} + N_2 [(x_2/a)^2 + 1]^{3/2} - S_n \quad [6.4-8]
\]

According to the above, \( F_0 = Z \) (where \( Z \) is the effective charge at point \( D \) in proton units). That is, the molecule's energy is equal to the energy of the atom with a nuclear charge of \( Z - S_n \) with \( n \) electrons in the case when the electrons rotate around the nucleus in one circle.

Later, it will be shown that in the case of two bonding electrons \((n = 2)\), the molecule's energy is equal to the energy of the helium-like atom with a nuclear charge that is equal to \((Z - 0.25)\).

Now let’s calculate this energy. The energy of these systems with various nuclear charges is experimentally defined as the sum of the last two ionization energies in each of the elements listed after helium (table 6.4-1).

Helium-like atoms can be presented by a scheme with the electrons situated on both sides of the nucleus.

According to this system, three forces act in a straight line that can be readily summed up. Each electron is under the influence of a force, which is equal to that of the nucleus minus the repulsive force. Electrostatic forces are directly proportional to the square of the distance between them, as presented by the following equation:

\[
F = q_1 \cdot q_2 / R^2 \quad [6.4-9]
\]

Now let's calculate the total force acting upon each electron in the ion hydride. The repulsive force between the electrons is 0.25 of the electrons’ attractive force of the nucleus, i.e., the attractive force of each electron towards the nucleus comprises 0.75 of the force, which would exist if the
second electron were not present.

A system whose nuclear charge is known and which contains one electron, is defined by the equation:

\[ E_n = E_H \cdot Z_n^2 \] \[ 6.4-10 \]

where \( E_n \) is the atom's energy with charge \( Z \); \( E_H \) is the hydrogen atom's energy. The helium-like atom's energy can be calculated by the equation:

\[ E_n = E_H (Z_n - 0.25)^2 \cdot 2 \] \[ 6.4-11 \]

The calculated energy value is multiplied by 2 just as in the calculation of the bonding energy in a hydrogen molecule. According to calculations, the bonding energy in molecules Na\(_2\), NaCl, and Cl\(_2\) comprise 100 kJ/mol, 640 kJ/mol, and 240 kJ/mol respectively.

That is, according to the calculation based on a model like that used for the calculation of a hydrogen molecule, the bonding energy in a molecule of sodium chloride (NaCl) is much greater than that of molecules Na\(_2\) and Cl\(_2\), which corresponds to the dependence found experimentally. Recall that in accordance with the experiment, the bonding energy in molecules Na\(_2\), NaCl, and Cl\(_2\) comprises 74 kJ/mol, 439 kJ/mol, and 242 kJ/mol respectively.

The coincidence of the calculated and experimental dependencies (previously considered paradoxical) confirms that even in the case of bonds in molecules made up of atoms with considerably different FIEs (like NaCl), the bonding takes place just as in a hydrogen molecule.

In the course of such calculation, the distances between the nuclei and the planes, where the bonding pair of electrons rotate, it was found that unlike hydrogen molecules and other dual-atomic molecules, made up of atoms with similar FIEs, in the case where the FIEs are quite different, the nuclei of atoms with greater FIEs are situated closer to the center of the circle where the bonding electrons rotate, than the nuclei of the atoms with smaller FIEs.

That is, for example, the nucleus of a sodium atom (Na) in molecule NaCl is at a distance twice that of a chlorine atom (Cl).
According to electrostatics, a nucleus with a greater charge (i.e., with a greater FIE) should be attracted to the bonding pair of electrons more readily than the nucleus of an atom with a smaller FIE.

The closeness of the atom's nucleus (with a great FIE) to the bonding electrons, offers a greater energy gain, and therefore, a greater bonding energy. That is, with the FIE increase in an atom with a large FIE, the bonding energy in dual-atomic molecules, made up of very different FIEs, will increase.

In order to check this conclusion, the bonding energy dependencies for a number of dual-atomic molecules were calculated with the help of a system of equations.

For comparison, the experimental dependencies are shown on the same drawing (figures 6.4-3, 6.4-4). See the next page.

Hence, we have a system of three equations with three unknowns:

\[ N_1 \frac{n x_1}{[(x_1^2 + a^2) (x_1^2 + a^2)^{0.5}]} = N_1 N_2 / (x_1 + x_2)^2 \quad [6.4-5] \]

\[ N_2 \frac{n x_2}{[(x_2^2 + a^2) (x_2^2 + a^2)^{0.5}]} = N_1 N_2 / (x_1 + x_2)^2 \quad [6.4-6] \]

\[ a = R/F_0 \quad [6.4-7] \]

Here:
- \( n \) — number of bonding electrons,
- \( R \) — Bohr’s radius equal to 1.

\[ F_0 = N_1 [(x_1/a)^2 + 1]^{3/2} + N_2 [(x_2/a)^2 + 1]^{3/2} - S_n \quad [6.4-8] \]

According to the above, \( F_0 = Z \) (where \( Z \) is the effective charge at point \( D \) in proton units). That is, the molecule's energy is equal to the energy of the atom with a nuclear charge of \( Z - S_n \) with \( n \) electrons in the case when the electrons rotate around the nucleus in one circle.

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\[ F = \frac{q_1 \cdot q_2}{R^2} \quad [6.4-9] \]

Now let’s calculate the total force acting upon each electron in the ion hydride. The repulsive force between the
electrons is 0.25 of the electrons’ attractive force of the nucleus, i.e., the attractive force of each electron towards the nucleus comprises 0.75 of the force, which would exist if the second electron were not present.

A system whose nuclear charge is known and which contains one electron, is defined by the equation:

$$E_n = E_H \cdot Z_n^2$$  \hspace{1cm} [6.4-10]

where $E_n$ is the atom's energy with charge $Z$; $E_H$ is the hydrogen atom's energy. The helium-like atom's energy can be calculated by the equation:

$$E_n = E_H (Z_n - 0.25)^2 \cdot 2$$  \hspace{1cm} [6.4-11]

The calculated energy value is multiplied by 2 just as in the calculation of the bonding energy in a hydrogen molecule. According to calculations, the bonding energy in molecules Na$_2$, NaCl, and Cl$_2$ comprise 100 kJ/mol, 640 kJ/mol, and 240 kJ/mol respectively.

That is, according to the calculation based on a model like that used for the calculation of a hydrogen molecule, the bonding energy in a molecule of sodium chloride (NaCl) is much greater than that of molecules Na$_2$ and Cl$_2$, which corresponds to the dependence found experimentally. Recall that in accordance with the experiment, the bonding energy in molecules Na$_2$, NaCl, and Cl$_2$ comprises 74 kJ/mol, 439 kJ/mol, and 242 kJ/mol respectively.

The coincidence of the calculated and experimental dependencies (previously considered paradoxical) confirms that even in the case of bonds in molecules made up of atoms with considerably different FIEs (like NaCl), the bonding takes place just as in a hydrogen molecule.

In the course of such calculation, the distances between the nuclei and the planes, where the bonding pair of electrons rotate, it was found that unlike hydrogen molecules and other dual-atomic molecules, made up of atoms with similar FIEs, in the case where the FIEs are quite different, the nuclei of atoms with greater FIEs are situated closer to the center of the circle where the bonding electrons rotate, than the nuclei of the atoms with smaller FIEs.
That is, for example, the nucleus of a sodium atom (Na) in molecule NaCl is at a distance twice that of a chlorine atom (Cl).

According to electrostatics, a nucleus with a greater charge (i.e., with a greater FIE) should be attracted to the bonding pair of electrons more readily than the nucleus of an atom with a smaller FIE.

The closeness of the atom's nucleus (with a great FIE) to the bonding electrons, offers a greater energy gain, and therefore, a greater bonding energy. That is, with the FIE increase in an atom with a large FIE, the bonding energy in dual-atomic molecules, made up of very different FIEs, will increase.

In order to check this conclusion, the bonding energy dependencies for a number of dual-atomic molecules were calculated with the help of a system of equations.

For comparison, the experimental dependencies are shown on the same drawing (figures 6.4-3, 6.4-4). See the next page.
It was found that the bonding energy, indeed, increased linearly with the increase of the FIE of the atom with a greater FIE. Moreover, the calculated dependency
coincided with the experimental result, which also proved to be linear.

In addition, it is worth mentioning that the experimental data were close to the calculation results, which proved that the model is not only qualitatively correct, but also semi-quantitatively.

Considering the above-made approximations, let's compile an equation necessary to calculate the energies of molecules made up of atoms with more than one electron:

Now let's go over to table 6.4-2 (group IV).

As a result of the calculation of a hydrogen molecule, we have found that the formation of a molecule out of atoms is conditioned by the decrease of the system's electronic energy, or, to be precise, by the increase of the attraction energy to the electrons, which increases the inter-electronic energy and inter-nuclear repulsion that were not present in the divided hydrogen atoms and appeared during molecule formation.

In the course of calculating both atoms and molecules, only the electrostatic (Coulomb) interactions were considered. The discrepancy in the calculation and experimental results, which is smaller than 1%, proves that the electrostatic interactions are of the greatest importance in both the atoms and the molecules.

The dual-atomic molecules in table 6.4-2 (group IV) differ from each other only in respect to the effective nuclear charge. Thus, according to the calculation via equation 6.4-2, the effective nuclear charge of a sodium atom is equal to 0.61:

\[
\left \frac{5.14}{13.6} \right \^0.5 \approx 0.61
\]

where 5.14 eV and 13.6 eV are the FIEs of the sodium and hydrogen atoms respectively. Analogously, the effective nuclear charge of a chlorine atom is equal to 1

\[
\left \frac{13.01}{13.6} \right \^0.5 \approx 1
\]

One pair of electrons, rotating between the molecules, bonds the nuclei. According to the Coulomb law, when the effective nuclear charge increases, there is an increase in both
the electrons' attraction to the nuclei and in the inter-electronic repulsion.

That is, the expected dependence of bonding energy on the effective nuclear charge for molecules given in table IV is defined by the difference between the energy increase in the inter-nuclear repulsion and the attraction energy bonding the electrons to the nuclei.

If during the increase in the effective nuclear charge, the increase of the inter-nuclear repulsion energy is higher than the increase of the electron-nuclear attraction, we should expect a decrease in the bonding energy with the increase of the effective nuclear charge, or, which is the same, with the increase of the FIEs of the bonding atoms; and visa versa.

![Experimental Data on the Bonding Energy of Mol. X-X vs. the FIE of Atom X for Elements of the 2 period](image)

Figure 6.4-5

Figures 6.4-5 and 6.4-6 show the dependence of bonding energy on the FIEs of atoms comprising these molecules.

Unlike the expected, the curve is in the form of a parabola. That is, when the FIE is increased from 5 eV to 11 eV [from lithium (Li) to carbon (C)] the bonding energy
increases, while during further FIE increase from 11 eV to 20 eV, the bonding energy decreases.

That is, the experimentally defined dependence of bonding energy needs an impossible explanation. Namely, according to experimental data, it was supposed that when the FIEs of the atoms being bonded are increased from 5 eV to 11 eV, the energy increase of the nuclear attraction electrons is greater than the increase of the inter-nuclear repulsion. And during further FIE increase, the increase of the inter-nuclear repulsion begins to overtake the increase of the electron-nuclear attraction.

The experimentally defined dependence and its explanation seem paradoxical. Indeed, it is hard to realize that if the FIEs of the atoms to be bonded are changed within a small interval (from 5 eV to 16 eV) the character of the dependence of bonding energy on the FIEs of the atoms to be bonded is changed to the reverse.

The existence of sudden and doubtful dependencies lessens the assuredness of the completeness and correctness of our knowledge of the physical nature of various
phenomena, in this case the physical nature of chemical bonding.

In order to reject or confirm any doubts concerning the equations deduced to show the dependencies of bonding energies on the FIEs of atoms to be bonded, we can calculate the expected dependency on the FIEs of bonding energies between identical atoms for which we have to know the value of $F_0$.

Attraction and Repulsion Forces of an AB Molecule
AD = X_1  
BD = X_2  
AB = 2b  
CD = a

N_1 and N_2 are nuclear charges C is the location of the electron.

Since we have equations N_1 = N_2 and X_1 = X_2; in specific cases the analytical method can be used. Let’s try one of them when charges N_1 and N_2 are equal. Then x_1 = x_2 = b, and:

\[ F_0 = N_1 \left[ (x_1/a)^2 + 1 \right]^{3/2} + N_2 \left[ (x_2/a)^2 + 1 \right]^{3/2} - S_n \]

[6.4.8]
This equation turns into:

\[ F_0 = 2N_1 \left[ (b/a)^2 + 1 \right]^{1.5} - S_n \]

[6.4.12]

To solve this equation, it is necessary to know the ratio \( b/a \) and \( S_n \); \( b/a \) is defined from equation 6.4-6:

\[
e^2 N_1 \frac{n x_1}{(x_1^2 + a^2)} (x_1^2 + a^2)^{0.5} = e^2 N_1 \frac{N_2}{(x_1 + x_2)^2}
\]

If we substitute \( x_1 = x_2 = b \), we get:

\[
n N_1 x_1/(x_1^2 + a^2) (x_1^2 + a^2)^{0.5} = N_1 x_1 / (x_1 + x_1)^2 \quad \text{or:} \quad n x_1/(x_1^2 + a^2)^{1.5} = N_1 / 4 x_1^2
\]

If we substitute \( x_1 = b \) we will get:

\[
n b/(b^2 + a^2)^{1.5} = N / 4 b^2
\]

\[
4n/N = (b^2 + a^2)^{1.5} / b^3
\]

Raise both parts to the second power and we get:

\[
(4n/N)^2 = (b^2 + a^2)^3 / b^6 = (1 + a^2/b^2)^3
\]

Find the cube root of each part of the equation:

\[
(4n/N)^{2/3} = (b^2 + a^2)/b^2 = 1 + a^2/b^2; \quad a^2/b^2 = (4n/N)^{2/3} - 1
\]

or:

\[
(b/a)^2 = 1/[(4n/N)^{2/3} - 1].
\]

Add 1 to each part of the equation, then we get:

\[
(b/a)^2 + 1 = 1/[(4n/N)^{2/3} - 1] + 1 = (4n/N)^{2/3}/[(4n/N)^{2/3} - 1]
\]

After inserting \((b/a)^2 + 1\) in equation 6.4-12:

\[
F_0 = 2N \left[ ((b/a)^2 + 1)^{1.5} - S_n \right], \quad \text{we get}
F_0 = 2N \left[ (4n/N)^{2/3}/[(4n/N)^{2/3} - 1] \right]^{1.5} - S_n =
= 2N \left[ ((4n/N)^{2/3} - 1)/[(4n/N)^{2/3}]^{1.5} \right] - S_n
\]
\[
\begin{align*}
S_n &= \frac{2N}{\left(4n/N\right)^{2/3}} \cdot \left(1.5 - \frac{1}{2}\right) \\
F_0 &= \frac{N_2}{2n} \cdot \left(\frac{4n}{N}\right)^{2/3} - 1^{3/2} \cdot S_n \\
\text{That is, in this case the equation can be solved analytically, without the use of a computer.}
\end{align*}
\]

The dependence of the energy of a single bond on the FIEs of atoms to be bonded, defined by calculation, is described just like the experimentally defined dependence via the parabola. For convenience in comparing the calculated and experimentally defined dependence, figures show the dependence curve defined experimentally, besides the calculated dependence curve of bonding energy on the FIEs of the atoms being bonded.
A comparison of the two curves shows that both dependencies are presented as parabolas. The coincidence is not only in the form of curves (parabolas), but also in the maximums of both curves (maximal value of bonding energy) which corresponds to the FIEs of the atoms being bonded, i.e., 10 eV to 12 eV.

The experimentally defined and calculated minimal bonding energy (equal to zero) in both cases are achieved with close values of the FIEs of the atoms being bonded. This is one of the experimental facts that confirm the correctness of the theory.

It is of interest to note that the bonding energy, according to both curves, is equal to zero when the FIEs of the bonding atoms are greater than 17 eV. The FIE of a helium (He) atom is equal to 24.6 eV; that of a neon (Ne) atom – 21.6 eV. That is, these atoms, according to the found dependencies, do not form stable molecules of the He\(_2\) and Ne\(_2\) type.

Previously we indicated that these atoms do not form stable molecules of this type because they do not bond electrons to the outermost electronic layer (shell) even when the nuclear charge is increased by 1 proton unit. That is, these elements are sort of twice inert from the viewpoint of bond formation.
Thus, the parabolic dependence of the single bond energy (where identical atoms are bonded) on the FIEs of the atoms to be bonded, does not contradict the theory of chemical bonding, but rather is one of the convincing experimental factors that confirms the correctness of the theory.

6.5*** BOND LENGTHS

Bond lengths have been defined experimentally for a great number of molecules. In most cases – the greater is the bonding energy, the smaller is the length of the bond.

The bonding energies for molecules in table 6.4-1 NaF, NaCl, and NaBr comprise 476 kJ/mol, 412 kJ/mol, and 368 kJ/mol respectively. The bond lengths in these compounds will be respectively: 1.9 Å, 2.3 Å, and 2.5 Å. That is, the molecules in the table have an expected (non-paradoxical) regularity: the stronger the bond, the shorter it is; the closer the atoms are attracted to each other, the shorter is the distance between them.

Analogously, the bonding energies Li–Li, Na–Na, K–K comprise 110 kJ/mol, 72 kJ/mol, and 49 kJ/mol, while the bond lengths of Li–Li, Na–Na, K–K are equal to 2.7 Å, 3.08 Å, and 3.9 Å respectively. And the energy of a single C–C bond, as indicated above, comprises 347 kJ/mol while its length is equal to 1.54 Å, i.e., smaller than the bond length of Li –Li whose energy amounts to 110 kJ/mol.
However, for some of the molecules in table 6.4-1 this unquestionable (non-paradoxical) dependence changes to the opposite (paradoxical) dependence, which causes a WHY question to arise.

According to experimental data, bonding energies of C–C, Cl–Cl, and F–F, comprise 347 kJ/mol, 239 kJ/mol, and 158 kJ/mol, while the bond lengths in row C–C, Cl–Cl, F–F comprise 1.54 Å, 2 Å, and 1.4 Å, respectively, that is, first it increases, then it decreases.

To prove that this anomaly is not incidental, on figure 6.5-1 we see the experimentally defined dependencies of single-bond lengths on the FIEs for elements of periods 2 and 3.

The curves on figure 6.5-1 show that the lengths of single bonds in molecules of the Li₂-F₂ and Na₂–Cl₂ type decreases with the increase of the FIEs of the atoms to be bonded. In accordance with the previously cited dependence, the energy of a single bond between identical atoms in elements of the 2nd and 3rd periods depend on the FIEs of the atoms to be bonded and are expressed by a parabola.
During the increase of the FIEs up to the middle of the periods, the bonding energy increases with the increase of the FIEs; after which, with the further increase of the FIEs of the atoms to be bonded, the energy decreases. See figures 6.4-5 and 6.4-6.

Because of the decrease in the bond's length when the bonding energy increases, it was expected that the dependence of the bond lengths on the FIEs should also be expressed by a parabola (a curve with the maximum). However, according to experimental data, the curve of the bond length's dependence on the FIE was expressed by a hyperbola.

Indeed, the bond lengths decreased with the increase of the FIEs of the atoms to be bonded. That is, the paradoxical dependence, noted above, was not at incidental. This regularity can be considered as paradoxical on the basis
of simple, logic, qualitative, reasoning like: *the stronger the bond, the closer are the atoms to each other.*

We have seen that such simple qualitative reasoning was contradictory in respect to dependencies that were necessary in the experiment. We also thought that experimentally defined dependencies qualitatively contradict the main precepts of the theory of chemical bond formation. However, the semi quantitative evaluation of the expected dependencies, on the basis of solving the system of algebraic equations, has shown that the qualitative but seemingly paradoxical dependencies (simple, logic reasoning) in reality is well desired, not at all paradoxical, but logic.

That’s why, just as in the previous cases, by solving the system of equations 6.4-5 to 6.4-7 we can calculate the expected dependencies of the bond lengths on the FIEs of the atoms to be bonded for the given case. The results of the calculation are given in figure 6.5-2.
These calculations show that the dependence of the bond length on the FIE, just as in the experiment, is expressed by a hyperbole.

In accordance with the calculations made via the same equations, a parabola expressed the dependence of the bonding energy on the FIEs of the atoms to be bonded. Therefore, the observed dependencies of the bonding energy and bond lengths on the FIEs, (which at first sight seemed paradoxical in regard to each other and to the theory) proved to be not at all beyond one’s expectations as a result of their semi-quantitative evaluation on the basis of the solution of the system of equations (a more fundamental approach at second glance).

That is, if at first sight they seemed to contradict the theory, at second glance they become convincing proofs of the correctness of the theory of chemical bonding.

Having studied the materials given in sections 5 and 6, we have learned about the structure of atoms and that of simple molecules. We have understood why atoms are bonded into molecules, and how to define the energy necessary to impart to a dual-atomic molecule in order to break it into atoms.

The data given in figure 6.5-2 coincides, relative to the curves, since three curves are hyperbolas, though they differ greatly relative to absolute values. Thus, for example, in the case of a chlorine molecule \((\text{Cl}_2)\) \((\text{IE}_\text{Cl} = 13.0)\), the experimental value is 3.4 times greater than what was calculated.

This discrepancy has a simple explanation. As already indicated, in the course of the calculation it was supposed that the atoms X in molecule \((\text{X}–\text{X})\) are hydrogen-like; that is, they have only one electron rotating in the one and only layer. The ionization energy of this electron, according to the supposition suggested for the calculation, was equal to the ionization energy of atom X in molecule X–X.

In reality, the atoms of all the periods (besides the 1st — hydrogen and helium) contain inner electronic layers. According to the experiment, the distance between the
nucleus and the electron in a hydrogen-like chlorine atom is 3.4 times greater than in a hydrogen atom.

According to the model, all the distances defined in the course of the calculation, are proportional to the distance between the nucleus and the electron, i.e., the distances between the nuclei and the bonding electrons (c), between the nuclei (2b), and between the electrons in molecules Cl₂ – by 3.4 times greater than in molecule H₂.

When calculating dual-atomic molecules with identical atoms or with atoms having an identical number of electronic layers (atoms of an identical period) we should expect close results relative to the calculated and experimental dependencies of bonding energies on IE (ionization energy) exactly what we see in figure 6.5-2

On the other hand, it may not be clear as to how molecules of the HF, HCl type, (where hydrogen atoms bond to atoms of other periods) are formed. In these atoms, as indicated above, the distance between the electron and the nucleus (at identical ionization energies) was more than three times greater than the distance between the nucleus and the electron in a hydrogen atom. This means that, according to the model for bonding molecules of the HF, HBr, HCl type cannot be formed. It is known that these molecules are stable; therefore the question about their formation, in the framework of the given model, is regarded as paradoxical.

Indeed, the radius of circle (a) where the bonding electrons rotate in molecule HCl, should, on the one hand, be equal to the radius of the circle where the bonding electrons rotate in molecule H₂, while on the other hand, the radius of molecule Cl₂ should be three times greater.

In the first approach, in answer to this paradoxical question, it was expected that the circle where the bonding electrons rotated, and relatively, all the geometric values of the molecule (a, 2b, and c) in this case should be averaged, i.e., greater than in H and smaller than in Cl.

Thus, in molecule HCl, the bonding electrons are farther away from the hydrogen atom than is the H₂ molecule, and closer to the nucleus in the chlorine atom than in a Cl₂ molecule. We suppose that the change of distances causes the anomalous dependencies of the bonding energy on the ionization energy.
A comparison of the calculated and experimental dependencies for compounds of hydrogen with elements of the 2nd and 3rd periods (fig. 6.4-3) shows that, unlike all the former cited cases, here the calculated and experimental dependencies do not coincide. That is, as compared with the previously cited cases (where they coincided) these dependencies are actually anomalous.

In the first approach, the anomalous increase of distance between the hydrogen atom’s nucleus and the electron (when bonding the hydrogen atom to elements of the 2nd and 3rd periods) one can imagine the bonding of the hydrogen atom to a charge of 1 proton unit, but well distanced from the nucleus of the electron, i.e., to a hydrogen atom that has a smaller ionization energy (compared with that of a normal atom).

On the other hand, the bonding electrons, situated closer to the chlorine atom than to the Cl₂ molecule, cause the effective ionization energy of the chlorine atom to increase. The decrease of the hydrogen atom’s dissociation energy (increase of the distance between the hydrogen and the bonding electrons) is connected with energy expenditure, while the approach of the bonding electrons to the chlorine atom is connected with energy gain that compensates the energy loss.

The difference between the effective FIEs of atoms H and Cl and the dipole moment of molecule HCl increases when the distance between the bonding electrons and the hydrogen atom increases, and the distance between the chlorine atom and the bonding electrons decreases.
To double-check the correctness of this supposition, we calculated the energy dependence in bonds of H-X molecules (where X is an atom of the 2nd – 4th periods) on the potential energy of the first electron of atom X for two variants of ionization energy relative to the hydrogen atom: 8, and 6 eV.

The calculated dependencies are seen in figure 6.5-4.
The coincidence of the calculated and experimental curves and the closeness of the calculated and experimental data (when the hydrogen atom’s ionization energy, taken for the calculation, was equal to from 8 eV to 10 eV) that coincided qualitatively and semi-quantitatively with the experimental dependencies, allows to confirm the correctness of the explanation relative to the anomalous dependence of bonding energy in dual-atomic molecules like H–X on the ionization energy of atom X.

The anomalous properties of molecule H–X have been known in chemistry for quite some time when studying the dependence of ionic covalent bonds on the first ionization energy of atoms A and B in molecules A–B.

The main part of dual-atomic molecules was well described quantitatively by a dependence according to which
— the greater the difference in the ionization energy of atoms A and B in molecules A–B, the greater is the degree of ionization in molecules A–B.

The degree of ionization was defined as the correlation of the experimental value of the molecule’s dipole momentum to the calculated value of the dipole momentum. When defining the calculated dipole momentum, a supposition was made about the transition of one electron from atom A to atom B.

There is almost an identical ionization degree in H–X molecules that was accomplished at great differences in ionization energies of the bonding hydrogen atoms (see table 6.5-1).

Thus, for example, the ionization degrees for FCl and HBr have close values – 11 % and 12 % respectively – (table 6.5-1). At the same time, the difference between the ionization energies of the atoms in molecule FCl comprises 4.4 eV while the difference between the ionization energies of the atoms in molecule HBr comprises 1.8 eV.

The ionization degree in molecule HBr (12 %) corresponded to the ionization energy of the hydrogen atom at about 6 eV smaller, i.e., a value of about 7.5 eV.

Likewise, in molecule HI, the degree of ionization amounted to 5 when the difference in the ionization energies was about 3 eV. An almost identical degree of ionization, according to table 6.5-1, is accomplished in molecules BrCl (5) and ICl (6) where the difference in ionization energies comprises 1.2 eV and 2.5 eV relatively.

That is, the ionization energy of a hydrogen atom in HI corresponded to the ionization energy of a hydrogen atom (8 eV – 9.4 eV), i.e., values close to those that were received during the interpretation of the anomalous dependence of bonding energy on the ionization energy of the atoms to be bonded in molecule H–X.
The dependence of ionization degree on the difference of ionization energies of atoms A and B in molecules A–B was defined for two cases: 1) when A = H and 2) when A ≠ H. B is never equal to H.

The same ionization degree, observed in molecules H–B, as compared to molecules A–B, is received with a greater difference in the ionization energies. Studies of properties of compounds containing hydrogen, have shown, that the ionic character of bonds with hydrogen, is about the same as in the case if hydrogen had ionization energy equal to 10 eV, that is, a value close to what we got when explaining the causes of the anomalous dependence of the bonding energy in molecules H–B with dependence on the ionization energy of the atoms to be bonded.
One and the same supposition based on substantiated models (via calculation and experiment) and the quantitatively close results, allow to confirm the correctness of the explanations relative to the anomalous values of the degree of ionic hydrogen compounds H–B by the great discrepancy of the radiuses of the initial atoms H and B.

**Figure 6.5-5**

It is of interest to recall the fact that the anomalous degree of the value of hydrogen has been touched upon in many textbooks from the 1960s to the 1980s. However, the material was given in these textbooks without an explanation about the cause of such anomalies.
CONCLUSIONS

It has thus been proven experimentally that atoms are bonded into molecules; therefore, in order to break up a molecule into atoms, energy should be applied. For example, to break a hydrogen molecule (H₂) into two atoms, it is necessary to heat the hydrogen to a temperature over 3,000 K or spend energy of more than 400 kJ/mol.

At 3,000 K the nuclei of hydrogen atoms have energy of about 20 kJ/mol. As the atoms contain no other particles besides electrons, we can conclude that the energy spent on breaking the molecule into atoms, is actually used to change the electrons' energies.

The energy gain during bond formation is conditioned as follows: During molecule formation the electrons start moving in a field with a unified positive charge of the bonding nuclei.

The electrons' energies are proportional to the square of the nuclear charges, and the inter-nuclear repulsion energy is proportional to the charges in the first power. That is why, when the atoms approach each other at a certain point, the system's energy decreases.

When a molecule is formed out of atoms, the kinetic and potential energies of the electrons increase. The energy gain is conditioned by the fact that the increase of potential energy is twice greater than the increase of the electrons' kinetic energy.

That is, during the formation of a chemical bond, the electrons rotate around the greater positive charge and at a closer distance from the charge, which causes a greater stability of the system. This stability is defined by the energy that should be added to the system so as to break it up into constituent parts. In the case of molecules and atoms, it is the energy necessary to break up these systems into electrons and nuclei.

In a dual-atomic molecule, the positively charged nuclei are united with a circle of electrons rotating on a plane perpendicular to the axis connecting the nuclei. All the main parameters have been calculated for this system.
As a result of calculations, it was found that:

1) When the bonding atoms have identical FIEs, the electrons' rotation plane is at the same distance from the bonding atoms. If the atoms' FIEs are different, the rotation plane will be shifted towards the atom’s nucleus with a greater FIE. Two electrons partake in the formation of a chemical bond;

2) Both bonding electrons enter the outermost shells of the atoms being bonded.

3) During chemical bond formation, the number of electrons in these outermost shells is increases by one.

4) During covalent bond formation, the bonding pair of electrons is composed of electrons from the atoms being bonded: one from each atom. The number of covalent bonds that one atom can form with other atoms (atom’s valence) is limited (due to inter-electronic repulsion) by the number of electrons that the given atom can connect to its outermost shell with energy gain.

5) The maximal number of electrons that the outermost shell can contain is equal to the number of electrons in the shells of the noble gas nearest to it in the table of elements. Noble gases cannot bond electrons in the outermost shell even when increasing the nuclear charge by 1 proton unit; therefore, they cannot form covalent bonds.

Thus, the number of covalent bonds, which an atom can form (atom’s valence), is defined by the number of electrons in the outermost shell of the given atom (one outermost-shell electron is spent on the formation of one bond) and by the maximal number of electrons that can exist in the outermost shell of the given atom (amount of outermost-shell electrons is increased by 1 unit).
6.6 ** DONOR-ACCEPTOR BOND (DAB)

As indicated above, during the formation of the covalent bond, the bonding electrons enter the outermost shells of the atoms being bonded.

During covalent bond formation, both bonding electrons enter the outermost shells of both atoms being bonded. Respectively, the number of electrons in the outermost shells of the atoms to be bonded is increased by one electron.

In the case of double and triple bond formation between the atoms, the number of electrons in the outermost shells of the atoms to be bonded is increased by two and three respectively.

If one atom, say, carbon (C), forms four bonds with hydrogen and chlorine atoms, the number of electrons in the outermost shell of a carbon atom increases by four electrons.

That is, the increase of the number of electrons in the outermost layer during chemical bond formation, is not limited by the number of electrons that enter the outermost layer during bond formation, but is limited only by the maximal number of electrons that can be situated in the outermost layer.

Recall that for elements of the 2nd and 3rd periods with fewer than 4 electrons, the number of covalent bonds, which the given element can form, is equal to the number of electrons in the outermost shell of the given element. Thus, for example, lithium (Li), beryllium (Be), and boron (B) can form 1, 2, and 3 covalent bonds respectively.

On the other hand, for elements of these periods with more than 4 electrons, the maximal number of electrons that can enter the outermost shell of the given element, when forming a covalent bond, defines the number of covalent bonds that the given element can form.

The total number of electrons that can be situated in the outermost shell of the elements of the 2nd and 3rd periods is equal to 8. Therefore, nitrogen (N), oxygen (O), fluorine (F), and neon (Ne) with 5, 6, 7, and 8 electrons in the outermost shell can form 3, 2, 1, 0 covalent chemical bonds respectively.
Atoms of sodium (Na), magnesium (Mg), and aluminum (Al), after forming the maximal number of covalent bonds, for example, after the formation of molecules of the NaF, MgF$_2$, AlF$_3$ type, contain 2, 4, and 6 electrons in the outermost shell respectively. This proves that the atoms’ outermost shells contain fewer than 8 electrons, i.e., they remain non-saturated.

However, atoms of nitrogen (N), oxygen (O), and fluorine (F), after the formation of 3, 2, and 1 covalent bonds, contain 8 electrons in the outermost shell, of which the bonding ones are: nitrogen (N) – 6 electrons; oxygen (O) – 4 electrons; fluorine (F) – 2 electrons.

Atoms of nitrogen (N), oxygen (O), and fluorine (F), in compounds like ammonium (NH$_3$), water (H$_2$O), and hydrogen fluoride (HF) contain 2, 4, and 6 electrons relatively in the outermost shells and do not take part in chemical bond formation, i.e., they are regarded as being free. Since in the formed compounds of NH$_3$, H$_2$O, and HF there are 8 electrons in the outermost shell of the N, O, and F atoms, the free, nonbonding electrons cannot take part in covalent bond formation because the outermost shell of these atoms is saturated with electrons.

These free (nonbonding) electrons do play the role of the electrons’ donors in chemical bond formation.

*What can be a truly reliable helper for these electrons in the formation of such bonds?*

First of all, of course – those atoms whose shells contain fewer than 8 electrons. The atoms in molecules, formed of elements of the 2nd and 3rd periods (with fewer than 4 electrons in the outermost layer), are of this kind; for example, recall the previously sighted Na, Mg, and Al in compounds NaF, MgF$_2$, and AlF$_3$. As already said, the outermost shells of Na, Mg, and Al in these molecules are unsaturated, i.e., capable of bonding electrons. Molecules like NaF, MgF$_2$, and AlF$_3$ are good partner-acceptors for such donor-electrons as atoms of N, O, and F in molecules that include these atoms.
The following stable compounds are well known:

\[ \text{H}_3\text{B} \leftrightarrow \text{NH}_3; \quad \text{H}_3\text{B} \leftrightarrow \text{N(CH}_3)_2; \quad \text{F}_3\text{B} \leftrightarrow \text{NH}_3; \quad \text{F}_3\text{B} \leftrightarrow \text{O(CH}_3)_2; \]

\[ \text{Cl}_2\text{Be} \leftrightarrow \text{O(C}_2\text{H}_5)_2; \quad \text{Cl}_3\text{Al} \leftrightarrow \text{NH}_3; \text{ etc.} \]

The arrows (\(\leftrightarrow\)) here indicate the donor-acceptor bonds.

Donors (N and O atoms) offer two electrons in these examples. The acceptors are B, Be and Al.

When forming DABs the acceptor atoms increase the number of electrons in their outermost shells by 2.

According to DAB formation rules, inert gases can form DABs as donors of electronic pairs with the atoms having 6 electrons. Thus the synthesis of XeO, XeO\(_2\) and XeO\(_3\) is an experimental confirmation of this theoretical supposition.

It is not only neutral atoms and molecules that can play the role of electrons’ donors and acceptors, but also – the positively and negatively charged atoms and molecules, i.e., cations and anions.

Thus, for example, with the help of ammonia (\(\text{NH}_3\)) a hydrogen cation (\(\text{H}^+\)) forms the cation (\(\text{NH}_4^+\)) where one atom is bonded to the nitrogen at the expense of the nitrogen’s electrons. Anion (\(\text{Cl}^-\)) is the donor of the electron pair in such ions (\(\text{ClO}^-\)).

The bonding energy between Al and N in compound \(\text{Cl}_3\text{Al} \leftrightarrow \text{NH}_3\) comprises 165 kJ/mol; while the covalent bonding energy between Al and N is equal to about 400 kJ/mol.

A molecule of NaCl is formed of atoms of sodium and chlorine. Chlorine has 8 electrons in its outermost shell, while sodium has only 2. That is, the outermost shell of the sodium is unfilled. On the other hand, only 2 electrons from the filled chlorine shell take part in the formation of the heteropolar bond Na–Cl. Six electrons (3 pairs) in the outermost shell of Cl do not take part in bond formation. That is, in the case of molecule NaCl, the sodium can bond 6 more
electrons while the chlorine can offer 6 electrons for bonding. Thus, one NaCl molecule can connect another NaCl molecule with the formation of a dimmer Na₂Cl₂.

The Na₂Cl₂ molecule was received experimentally, so was the reaction energy 2NaCl → Na₂Cl₂. This energy is equal to 186 kJ/mol (one DAB being equal to 93 kJ/mol). The bonding energy of a NaCl monomer is equal to 410 kJ/mol, while the bonding energies of Na – Na and Cl – Cl comprise, relatively, 75 kJ/mol and 238 kJ/mol, i.e., the DAB is much weaker than the covalent bond. As a rule, the DAB is only half as strong as the covalent bond.

One of the main reasons for the comparatively weak DAB is as follows. When calculating the bonding energy, the initial atoms’ electronic energy, taking part in bond formation, is subtracted from the molecule’s calculated energy. The ionization energy of the two non-bonding chlorine electrons in NaCl exceed the sum of the FIEs of both sodium and chlorine atoms.

That is, the energy gain (difference between the electronic energies of the divided and bonded atoms via chemical bonding) in the case of the DAB is smaller at the expense of the energy increase of the divided atoms.
6.7 VAN DER WAALS BOND (VWB)

The third type of bond is the Van der Waals bond (VWB). It has been experimentally defined that molecules in which the outermost shells of all the atoms are filled, say, molecules of nitrogen (N$_2$), chlorine (Cl$_2$), ammonia (NH$_3$), and the atoms of inert gases – He, Ne, etc. – also bond among themselves. Such bonds have been named after the Dutch physicist Van der Waals. These are weak bonds.

It has been found experimentally, that, indeed, bonds between inert gas atoms do exist, but their length (the distance between the nuclei) is about two times greater than in the case of a covalent bond and a DAB; and the bonding energy differs by more than 10 times.

As indicated above, the approach of the hydrogen atoms’ nuclei in the course of the formation of molecule H$_2$, as seen from the calculation of the hydrogen molecule, leads to the increase of the effective charge (the charge of the nuclei acting upon the bonding electrons in the molecule) by 1.5 times. A ten times greater decrease in the bonding energy when increasing the distance by 2 times, is due not only to the decrease of the Coulomb interaction, but also to the decrease of the effective charge of the nuclei to be bonded, with the increase of the distance between them.
6. 8**  DYNAMIC BONDS

Studies conducted on energies and bond lengths in chemical compounds, where one atom is bonded with various types of bonds to other atoms, have shown that, as a rule, the energy of weak bonds (DABs and VWBs) increases while that of the strong bonds (homopolar and heteropolar covalent bonds) decreases.

Simultaneously the length of the weak bonds decreases, while that of the strong ones increases. This fact was realized only after the studies of the phenomenon called electron-nuclear isomerization, which will further be referred to as electronic isomerization or electron-nuclear isomerization.

It has been found experimentally (see details Appendix A 16.), that the electrons in molecules transit so rapidly, that they cause isomerization of the chemical compound. Thus, for example, if we take a cation like ammonia (NH$_4$)$^+$ the process of electronic isomerization can be demonstrated thus:

\[
\begin{array}{c}
H \\
H \Leftarrow N : H \Rightarrow H : N \Rightarrow H \\
H
\end{array}
\]

Here the two dots (:) indicate covalent bonds; the single arrows (← →) indicate DABs. Since the speed of the electronic transition by far exceeds that of the nuclei, the hydrogen atoms’ nuclei occupy an intermediate position. That is, the bond lengths between all the hydrogen atoms and the nitrogen atom are the same, but greater than the covalent bond and smaller than the DAB.

Simultaneously the energies of bonds N–H are smaller than those of covalent bonds, but greater than those of DABs.

The thermal stability of the compound (at high temperature) is defined by the energy of the weakest bond in the compound. That is why electronic isomerization leads to the increase of the thermal stability in the compound.
The greatest effects of isomerization (including the compounds’ stability increase) are evident in cases when, as a result of this isomerization, identical electronic isomers are formed. In the above cited example, the electronic isomerization of an ammonia ion (NH$_4^+$) has an identical initial and final molecule and has 3 covalent bonds of N and H and one DAB of nitrogen-hydrogen.

That is, the electronic energies of both isomers are the same, and the electronic isomerization leads to a complete equalization of both the lengths and energies of all the bonds in ionic ammonia (NH$_4$).

Cases when different bonds bond one atom to other atoms are a common phenomenon. Thus, for example, in molecule

\[
\begin{array}{c}
\text{N}==\text{O} \\
\mid \\
\text{O}
\end{array}
\]

the nitrogen atom is bonded with two oxygen atoms via double and single bonds.

Analogously, in a benzene molecule:

![Benzene molecule diagram]

The carbon atoms are bonded between themselves via single and double covalent bonds. In the anion NO$_3^-$ the oxygen and nitrogen atoms are bonded via single and double covalent bonds and DABs:
Likewise are bonded the oxygen anion (O) together with the chlorine in the anions ClO$_2^-$ (chlorite ion), ClO$_3^-$ (chlorate ion), ClO$_4^-$ ( perchlorate ion), covalent bonds, and DABs. In all the above-mentioned compounds, as a result of electronic isomerization, we see the equalizing of various bonds in respect to their lengths and energies.

Electronic isomerization allows us to realize why substances, composed of molecules, and having, according to the theory, a DAB or a VWB, are stable at temperatures much higher than those necessary for breaking these bonds. For example, isomerization explains the existence of such compounds as (I–I–I)$^-$, (Br–Br–Br)$^-$ (Cl–I–Br)$^-$. In such molecules anions of halogens (I$^-$, Br$^-$, Cl$^-$) are bonded strongly with molecules of I$_2$, Br$_2$, IBr. These have 8 electrons in the outermost shell; that is, this shell is filled. Halogen atoms in halogen molecules just like I$_2$, Br$_2$, IBr, also have filled electronic shells. That is why there can be only a VWB bond between a halogen anion and a halogen molecule, which is a very weak bond that excludes the synthesis of a substance like I$_3^-$, Br$_3^-$, Cl$_3^-$. The bonding energy value between a halogen anion and a halogen molecule is close to that of a VWB formed between the atoms of inert gases; that is, about 10 kJ/mol. The bond’s length is just over 4Å.

It has been found experimentally that compounds like I$_3^-$, Br$_3^-$, Cl$_3^-$ are stable. In these compounds the length of the bonds of the topmost atoms with a central I atom comprise 2.9Å for I–I–I, and 2.53Å for Br–Br–Br. These values are close to those of a common covalent bond in molecules I$_2$ and Br$_2$, which are equal to 2.66Å and 2.28Å respectively.

According to the structure of these compounds, there should proceed electronic isomerization along the scheme:

$$\Gamma \ldots I \ldots I \quad \Rightarrow \quad I \ldots I \ldots \Gamma$$
Dots (...) indicate VWBs; the dash (−) indicates covalent bonds.

As a result of the electronic isomerization, we get a compound where both I – I bonds become equal in energy and length.

The structure of stable compounds of inert gases with halogens such as XeF$_2$ is explained identically as that of I$_3$. The structural formula of such a compound can be demonstrated analogously to that of I$_3^−$ thus:

$$(F : Xe)^+ ... :F$$

Here (:) indicates a covalent bond formed at the expense of one electron of a fluorine (F) atom and one electron of a xenon (Xe) atom. The three dots (...) indicate a VWB which is formed between the fluorine (F) anion and the cation (F : Xe)$^+$. Therefore, this VWB should be much stronger than a common VWB, at the expense of the electrostatic attraction.

There is an additional contribution to the strengthening of this bond offered by the process of electronic isomerization, which proceeds via the following scheme:

$$(F : Xe)^+ ... F \rightleftharpoons F^- ... (Xe : F)^+$$

The outermost shells of all the atoms in molecule (F : Xe)$^+ ... F^−$ are completely filled (there are 8 electrons). In order to have such a bond formed, we should compensate the energetic expenditures connected with the transition of the electrons from the xenon (Xe) shell to the fluorine (F) shell with the formation of anion-fluorine (F$^−$).

The FIE of xenon is equal to 12.13 eV; the affinity of fluorine to the electron is equal to 3.34 eV. That is, the transition of the electron from the xenon to the fluorine requires the expenditure of a large amount of additional energy, i.e., 8.79 eV (12.13 − 3.34 = 8.79 eV). The compensation of this energy is possible at the expense of the addition of a second fluorine atom to the xenon with the formation of a covalent bond: xenon (Xe) – fluorine (F). Here the bonding pair of electrons, formed of single-fluorine and
single-xenon electrons, enter the outermost shells of both fluorine and xenon.

The formation of the covalent bond xenon-fluorine in the course of the formation where the number of electrons in the outermost shell of xenon increases by 1, compensates the energetic expenditures needed for the transition of the electron from the xenon to the fluorine. In the course of the formation of this covalent bond, the electron transits from the fluorine atom to the cation-xenon \((\text{Xe}^+)\) shell, which presupposes the discharge of energy equal to that of the xenon’s FIE \((12,13 \text{ eV})\).

Thus, according to the theory, we should get a synthesis of stable compounds of xenon and fluorine only of types \(\text{XeF}_2\), \(\text{XeF}_4\), and \(\text{XeF}_6\). The synthesis of these compounds and the lack of literature describing such compounds as \(\text{XeF}, \text{XeF}_3,\) and \(\text{XeF}_5\) serve as experimental confirmation of the correctness of our theoretical reasoning.

Now let’s take some inert gas compounds and study possibility their synthesis.

*What stable compounds can we expect on the basis of the theory of chemical bonding, and what stable compounds, according to the theory, are hardly possible?*

The union of inert gases and halogens, generally, can be seen in the formula: \(\text{In Hal}_n\) (where \(\text{In}\) is the inert gas, \(\text{Hal}\) is the halogen, and \(n\) is the even number 2, 4, or 6).

In the general electronic formula, when \(n = 2\) these compounds can be represented as \(\text{Hal} : \text{In} \ldots \text{Hal}\) (where \(\vdash\) corresponds to the covalent bond and \(\ldots\) to the VWB.

As a result of electronic isomerization, the energies and lengths of the bonds equalize. As the energy of the VWB is about ten times smaller than that of the covalent bond, we can suppose that the equalized energy of both bonds in the molecule, as a result of the isomerization, are defined by the energy of the covalent bond \(\text{Hal} : \text{In}\).

Now let’s see how the inert gas halogen depends on the type of halogen and type of inert gas according to the bonding energy theory.

Each group of halogens and inert gases has the same number of electrons in the outermost shell. The halogens have 7 electrons while the inert gases have 8. These atoms differ mainly by their FIEs.
The FIEs of the inert gases in the following row are:
He (24.58 eV), Ne (21.55 eV), Ar (15.76 eV),
Kr (14.00 eV),
Xe (12.13 eV), Rn (10.75 eV).

The FIEs of the halogens in the following row are:
F (17.42 eV), Cl (13.01 eV), Br (11.84 eV),
I (10.42 eV).

According to the general bonding theory, the energy of the homoatomic covalent bond, when the FIE is greater than 11 eV, will decrease when the FIE increases. According to experimental data, the bond in the fluorine molecule (F₂) comprises 159 kJ/mol, while that of chlorine (Cl₂) comprises 242 kJ/mol. The FIEs for F and Cl comprise 17.4 eV and 13.01 eV respectively. That is, the compound of the ArF₂ type is less stable than compound KrCl₂.

According to our theory of chemical bonding, the energy of heteroatomic covalent chemical bonds is higher than that of homoatomic chemical bonds; and the energy of the bonds increases proportionally to the FIE differences of the atoms being bonded.

Therefore, the strongest heteroatomic covalent bonds can be expected thus: F : Rn and F : Xe since the FIE of fluoride (F) is equal to 17.4 eV, that of Xe - 12.13 eV, Rn - (10.74 eV). The energy of this bond is ≈ 400 kJ/mol according to experimental data. The energies of the rest of the heteroatomic covalent bonds are much smaller.

Besides covalent bonding energy, another main condition for stable compounds of the halogen + inert gas type: Hal : In ... Hal, is that the electronic energy in these compounds should be smaller than the total of the electronic energies of the halogen molecules (Hal₂) and the inert gas atoms (In), which can form out of them as a result of electronic isomerization via reaction:

Hal : In ... Hal → Hal₂ + In
or: F : Rn ... F → F₂ + Rn
Thus, the stability of the compounds of inert gases and halogens is defined as both covalent bond energy $\text{Hal}:\text{In}$ and bonding energy $\text{Hal}:\text{Hal}$, formed via the breaking of this compound into a halogen molecule ($\text{Hal}_2$) and an inert gas atom. The smaller is the bonding energy in the halogen molecule ($\text{Hal}_2$), the greater is the stability of the compound halogen + inert gas which is described as $\text{Hal}:\text{In} \ldots \text{Hal}$.

Fluorine (F) has the smallest bonding energy ($\approx 159$ kJ/mol) in the halogen row. This element, as indicated above, offers a very strong bond with xenon (Xe) and radon (Rn) atoms. According to the above mentioned, the bonding energy between fluorine and xenon or radon is about 400 kJ/mol.

When forming a fluorine molecule out of $\text{F} : \text{Xe} \ldots \text{F}$ and a xenon atom, the bonding energy decreases to 158 kJ/mol. That is, molecule $\text{F} : \text{Xe} \ldots \text{F}$ is stable. It will not change into a fluorine molecule and a xenon atom all by itself.

During electronic isomerization, covalent bond energy ($\text{F} : \text{Xe}$) and VWB energy ($\text{Xe} \ldots \text{F}$), according to theory and experiments, the total energy value of these 2 bonds was about equal to the energy of a fluorine covalent bond with xenon ($\approx 400$ kJ/mol).

Likewise, in accordance with the bonding theory, the fluorine and xenon in molecule $\text{F} \text{Xe} \text{F}$ can be evaluated at $\approx 200$ kJ/mol. According to experimental data, the energy of this bond is equal to 130 kJ/mol. Analogous studies have shown that in the cases of $\text{Cl} : \text{Kr} \ldots \text{Cl} \text{Cl} : \text{Xe} \ldots \text{Cl}$ and $\text{Cl} : \text{Rn} \ldots \text{Cl}$, the covalent bonding energy $\text{Cl} : \text{Xe}$ amounts to $\approx 240$ kJ/mol while the bonding energy in a chlorine molecule comprises 240 kJ/mol. This presupposes both a significantly lower thermal stability of such compounds as $\text{Cl} \text{Xe} \text{Cl}$ and a lower chemical stability. That is, it presupposes their transformation into a chlorine molecule and an atom of inert gas.

Thus, according to the above, we can expect only a synthesis of stable compounds of halogens with inert gases of type $\text{F}_n \text{Xe}$ and $\text{F}_n \text{Rn}$, where $n = 2, 4, 6$. The synthesis of compound xenon-fluorine ($\text{XeF}_2$, $\text{XeF}_4$, $\text{XeF}_6$) and the unsuccessful attempts at synthesizing $\text{ArF}_2$, $\text{KrCl}_2$, and $\text{XeBr}_2$ are experimental proofs of this conclusion.
The elucidation of the comparatively exotic compound structure of inert gases with oxygen and halogens gives us to understand the structure of the widely used compounds in chemistry such as: sulfuric acid (H\textsubscript{2}SO\textsubscript{4}), phosphoric acid (H\textsubscript{3}PO\textsubscript{4}), phosphorus pentachloride (PCl\textsubscript{5}), and sulfurous hexafluoride (SF\textsubscript{6}).

In the framework of the explanations given in textbooks, it was supposed that the central atom in these compounds [sulfur (S) and phosphor (P)] contained more than 8 electrons in the outermost shell. It was also supposed that the extra electrons were located on the 3d orbitals.

This explained the cause of finding more than 8 electrons in the outermost shell, and the difference between phosphorus (P) and sulfur (S) on the one hand, and nitrogen (N) and oxygen (O) on the other, which do not form analogous compounds. Nitrogen (N) and oxygen (O), according to quantum chemistry, did not have any closely situated 3d orbitals, and correspondingly, did not have any free space for extra electrons.

This explanation was seriously contradicted both experimentally and by the quantum-chemical theory itself. According to the theory and experiment, the filling of the 3d orbitals by electrons began with scandium (Sc). Between Sc and S in the table of elements, there are four elements (Cl, Ar, K, Ca), which have no electrons on the 3d orbitals.

That is, if the 3d orbitals of the elements of the 3rd period were energetically available, then the chlorine (Cl) and argon (Ar), whose nuclear charges are greater than those of phosphorus and sulfur, would bond the extra electrons to the 3d orbitals. Relatively, these elements (Cl, Ar), seemingly, should have a valence greater than 1 (chlorine) and greater than zero (argon). This has never been proven experimentally.

How is the structure of these compounds explained in the framework of our new approach?

In complete analogy with compounds of inert gases with oxygen and halogens (compounds, phosphor and sulfur are also connected with either halogens or oxygen) the structure of sulfuric and phosphoric acids can be shown thus:
Here there is a covalent bond between the hydroxyl oxygen and the central atom (sulfur and phosphor), and there is a DAB between the sulfur and phosphor with an atom of oxygen. This is a complete analogy of the bonding in molecules of the XeO$_3$ type.

Compounds of phosphor (P) and sulfur (S) with halogens are structured analogously to XeF$_2$. That is, phosphorous pentachloride is described by the following structural formula:

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl}
\end{array}
\begin{array}{c}
\text{P} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F}
\end{array}
\]

That is, it has \textit{three} covalent bonds and \textit{two} VWBs, while the sulfurous hexafluoride, described by the following scheme,

\[
\begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F}
\end{array}
\begin{array}{c}
\text{S} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F}
\end{array}
\]

has \textit{four} covalent bonds and \textit{two} VWBs.

In all the described compounds the energies and the bond lengths between the central atom and the oxygen or halogen are equalized at the expense of electronic isomerization.

The similarity of bonds XeF$_4$ and PCl$_5$ is confirmed by the similarity of the types of formation and break-up reactions of these compounds. It is known that when heating five-chlorine phosphor, a reverse reaction takes place:

\[\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2\]
Likewise, just as in xenon bonds with fluorine, in the case of sulfur and phosphorous well known stable compounds PCl$_3$, PCl$_5$, SF$_4$, SF$_6$ and the unknown PCl$_4$, PCl$_6$, SF$_3$, SF$_5$.

Analogous to the compounds of inert gases with oxygen and halogens, we can explain why nitrogen and oxygen do not form the same kind of compounds.

Stable compounds form only when the FIEs of the halogens and oxygen are greater than that of the inert gas, which is the central atom. In our case, the FIEs for sulfur (S) and phosphorus (P) are 10.36 eV and 10.48 eV respectively. The FIEs for oxygen (O), chlorine (Cl), and fluorine (F) are 13.61eV, 13.01eV, and 17.40 eV respectively. On the other hand, the FIE of nitrogen (N) is equal to 14.53 eV.

Remember that compounds of xenon (Xe) with a FIE of 12 eV, are the only stable compounds of inert gases with oxygen and halogens. Krypton (Kr) with a FIE of 14 eV, does not form such compounds.

Analogously to the above-cited compounds, we can explain the structure of compounds where the central atom is bonded to identical atoms via double and single bonds like SO$_2$, SO$_3$, NO$_2$, C$_6$H$_6$, etc.

Experiments have proven that these compounds also reveal the tendency to equalize the lengths and energies of single and double bonds.

Up till now, school texts and scientific literature explain the equalizing of bonds, relative to their energy and length, in the framework of quantum chemistry of the resonance theory.

The resonance theory presupposes that such a structure, as SO$_2$ is a super-position of two structures, which is illustrated thus:

![Resonance Structure](image)

The possibility of electronic isomerization in the framework of the resonance theory, is not only rejected, but even ridiculed: “This is the kind of foolish propositions the chemists had before quantum chemistry was introduced.”
In the framework of the above said, between the structures $\text{SO}_2$ there is dynamic equilibrium:

![Diagram](image.png)

which, in this case, as in all other cases, leads to the equalizing of chemical bonds.

One very interesting example involves a combination of the VWB and polar bond for a hydrogen atom. In chemical literature these bonds are called hydrogen bonds. This can be shown as: $A - H \ldots B$; where $A$ most often represents oxygen or halogen, while $B$ represents oxygen, halogen, or nitrogen.

The increase of the VWB energy is conditioned by electron-nuclear isomerization that proceeds, just as in the above cited cases, along the following scheme: $A \rightleftharpoons H \ldots B \rightleftharpoons A \ldots (H \leftarrow B)^+$. In this case, the covalent bond and the VWB change into a polar VWB.

Just as in all the previously cited cases, the electronic-nuclear isomerization leads to the strengthening of the weak bonds and the weakening of the strong ones. As a matter of fact, the energy of the weak VWB ($H \ldots B$) increases, while the energy of the covalent bond $A \rightleftharpoons H$ decreases. Thus, the increase of the VWB energy is more than 5 times greater than $H \ldots B$ observed in the experiment, as compared with the common VWB, this is not paradoxical.

As a rule, the energy of a hydrogen bond (the increased VWB between $H$ and $B$) is equal to $10 - 150 \text{ kJ/mol}$. (See table 6.6-1)

When this bond is formed, the distance between $A$ and $B$, in the presence of hydrogen, is smaller (in spite of the hydrogen atom) than in analogous compounds without the hydrogen atom.
According to the theory, in compounds of the I$_3$, XeF$_2$, FHF, types, the bonding energy is defined by the energy of covalent bonds I$_2$, XeF, FH. That is, the greater the energy of these bonds, the greater the bonding energy in compounds of the I$_3$, XeF$_2$ type.

In the row of compounds HF$_2$, HCl$_2$, HBr$_2$, and HI$_2$, the bonding energy decreases when transiting from left to right. The covalent bonding energy decreases in row HF, HCl, HBr, and HI (See table 6.6-1).

Once more we mention the fact that all the atoms situated in molecules SF$_6$, PCl$_5$, XeF$_2$, HF$_2$, etc., cited above, the number of electrons in the outermost shells do not exceed 8; that is, the limitation of the number of covalent bonds that one atom can form with others is not violated. Likewise, other main precepts of the theory — the formation of chemical (covalent bonds, DABs, and VWBs — are not violated.

During the formation of one covalent bond, the number of electrons in the outermost electronic shell of the atoms being bonded increases by one unit. When DABs are formed, the number of electrons in the outermost shell of the donor atom does not change, while the number of electrons in the shell of the acceptor atom increase by 2 units. During VWB formation, the number of electrons in the outermost shells of the atoms being bonded does not change.

The main difference of the bonds, described in this section, is in the fact that the central atom in these

---

**TABLE 6.6-1**

**HYDROGEN BONDS AND BONDING ENERGIES IN COMPOUNDS A−H...B**

<table>
<thead>
<tr>
<th>ALCOHOLS</th>
<th>ENERGY (kJ/mol)</th>
<th>INORGANICS</th>
<th>ENERGY (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$O−H...O(C$_2$H$_5$)$_2$</td>
<td>10</td>
<td>(F−H−F)$^-$</td>
<td>148</td>
</tr>
<tr>
<td>CH$_3$O−H...N(C$_2$H$_5$)$_3$</td>
<td>12</td>
<td>Cl−H...Cl$^-$</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br−H...Br$^-$</td>
<td>52</td>
</tr>
<tr>
<td>PHENOLS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_5$O−H...O(C$_2$H$_5$)$_2$</td>
<td>14.8</td>
<td>H O−H...OH$_2$</td>
<td>20</td>
</tr>
<tr>
<td>C$_6$H$_5$O−H...N(C$_2$H$_5$)$_3$</td>
<td>23.2</td>
<td>F−H...F−H</td>
<td>28</td>
</tr>
</tbody>
</table>
compounds is bonded to other atoms with various types of bonds. For example — with a covalent bond and a common VWB, a covalent bond and a DAB, a single covalent bond and a double one, etc.; the weak bonds in these compounds strengthen while the strong bonds weaken. This is because in this case there is electronic isomerization, which proceeds reversibly. As a result of electronic isomerization, so-called electromers are formed, i.e., electronic isomers where the bond used to be, for example, a covalent one, but then becomes a VWB.

With the decrease of the difference in the electronic energies of the electromers, the effect of energy decrease of the strong bond and the energy increase of the weak one is increased.

If the electronic energies of the electromers are equal, which is observed when the atoms are identical and bonded to the central atom, they have equalized energies and lengths. This is because, in this case, the transition speed in the reverse direction reaches the maximum — the greatest value for the given system.

Since the atoms’ cores move 10 to 100 times slower than the electrons, they mainly occupy an intermediate position. Relatively, the number of electromers with weak bonds (like VWBs) abruptly decreases in the system, which decreases the speed of their eruption.

On the other hand, the high concentration of electromers where the nuclei occupy an intermediate position, there is an increase in nonproductive energy expenditure during thermal eruption.

Since the thermal stability of the bond (bonding energy) is defined experimentally by the total expenditure of the energy spent on the change of the electrons’ potential and kinetic energies (where the potential energy decreases via the absolute value while the kinetic energy also decreases) and by the energy expenditure on the heating of the molecules that were not broken during the reaction (unproductive energy expenditure). With the increase of the unproductive expenditures, the experimentally defined bonding energy value increases.

The above-cited chemical bonds with common electronic isomerization that condition their peculiarities
(first of all, the equalization of the length and the energy) and also their difference as compared with common bonds, allows giving these bonds the name of ‘dynamic bonds’.

In the chemical bond section, these bonds look exotic, as if they are on the outside of the usual path of explaining the main chemical phenomenon — chemical bonding. However, when explaining the second main chemical phenomenon: chemical reactions, understanding the physical essence of dynamic bonds is the key. This fact once more underlines the good logic of their being singled out into a separate group with a separate name. Previously bonds, related to dynamic bonds, were cited separately in textbooks and scientific literature.

Thus, hydrogen bonds were described as dipole bonds; bonds like SF₆ and PF₅, XeO₃, XeF₄ were explained as expanding the valence shell of the central atom that holds more than 8 electrons. The structures of compounds SO₂, NO₂, C₆H₆ were explained as resonance rules, as possible super-positioned structures written on the basis of the Lewis rules. Compounds like I⁻, FHF⁻, Cl⁻, BrCl⁻, and some others were never discussed in textbooks.

In monographs (see Chemical Bonding Clarified Through Quantum Mechanics by G.C.Pimentel & R.D.Spratley) the bonds in I⁻, Cl⁻, HF₂⁻, HCl₂⁻, and some others, were explained in the framework of the theory of molecular orbitals as 3-electronic bonds. That is, various quantum-chemical suppositions were required in all the cited cases: super-positions, hybridization, molecular orbital theory, etc., which were regarded as unteachable.

The offered explanation is phenomenological and does not violate the theory of chemical bonding, which is also phenomenological in the framework of Introductory Chemistry.

According to the theory of chemical bonding, the outermost shells of atoms of electrons of the 2nd and 3rd periods in the table of elements, cannot contain more than 8 electrons.
CONCLUSIONS

At present the process of deepening the understanding of the physical nature of chemical bonding is continuing. Results, already gained in this respect, are as follows. Bonds with which atoms are bonded into molecules can be divided into two types.

1) The first type of bond is the covalent bond. During its formation, the two outermost electrons (one from each of the atoms being bonded) rotate in a plane perpendicular to the axis connecting the bonding nuclei. These electrons will further be referred to as bonding electrons.

In the case of hydrogen, the nuclei being bonded are actually nuclei of hydrogen atoms. In all other cases, beginning with Li, when we speak of the atom’s nucleus, we mean the nucleus and all the surrounding layers of the atom excepting the outermost shell.

When we speak of the effective charge of a nucleus we mean the charge, which acts upon the bonding electron from the atom’s nucleus and from all the other (nonbonding) electrons of the given atom.

There are two types of covalent bonds:

1a) If the effective charges of nuclei N₁ and N₂ are the same, such a bond is called a covalent homoatomic bond. The circle in which the bonding electrons rotate is situated at the same distance from the nuclei as the atoms being bonded. Such bonds are situated in dual-atomic and multi-atomic molecules composed of similar atoms like F₂, Cl₂, Na₂, C₆H₁₄ etc.

1b) If the effective charges of nuclei N₁ and N₂ are different, then the circle in which the electrons rotate is closer to the atom with a greater nuclear charge. Such a bond is called a covalent heteroatomic bond. Such molecules as ClF, BrF, BrI, are bonded with this kind of bond. If the effective nuclear charge of the atoms being bonded differs greatly, we are dealing with a super-polar or ionic bond. The atoms in salt molecules (NaCl, KF, LiF, etc.) are bonded with such bonds.
Even when forming the super-polar bond, the electrons do not transit from one atom to another. Moreover, the distance between the bonding electrons and the nuclei in the formed molecule (for example LiF) is smaller than the distance between the electrons and the nuclei in anions Li\(^-\) and F\(^-\); that is, during bond formation, the number of electrons in the outermost shells of atoms such as lithium (Li) and fluorine (F) increases by one electron.

The number of covalent bonds that one atom can form with other atoms is limited by the number of electrons that are situated in the outermost shell of the central atom. The number of bonds that atoms of groups I – IV of the table of elements can form is equal to the number of electrons in the outermost shells of these atoms. The number of covalent bonds that elements of groups V – VIII can form is limited by the maximal number of electrons that can be situated in the outermost electronic shells of atoms of this group. (See the table of elements.) When forming one covalent bond, the number of electrons in the topmost shell of the atom increases by one electron.

2) The second type of bond is the donor-acceptor bond (DAB). Here both bonding electrons belong to one of the atoms being bonded. The energy of this bond is about twice smaller than that of the covalent bond.

When forming DABs the number of electrons in the outermost shell of the donor atom does not change, while the number of electrons in the acceptor atom increases by 2 units.

The number of DABs that one atom can form with other atoms is limited, relative to the acceptor atom, by the number of electrons that the outermost shell of the given atom can contain. For atoms of periods 1, 2, 3 and 4 the maximal number of electrons in the outermost shells is equal to 2, 8, 8, and 18 respectively.

The number of DABs that the electrons’ donor atoms can form is limited by the number of free electronic pairs (which do not take part in covalent bond formation).

Since the energy gain is greater during covalent bond formation (covalent bonds are stronger than DABs), first the atom forms all the possible covalent bonds.
The energy gain during chemical bond formation is conditioned by the approach of the electrons to the nuclei and by the increase of the effective charges of the nuclei of the atoms being bonded.

There is a greater energy gain in the case of a polar or super-polar bond than that in the case of a covalent homopolar bond, which is conditioned by a closer approach to the electrons of the nuclei and a greater effective charge (a greater initial FIE).

DABs, just as covalent bonds, can be polar. Just like in the case of covalent polar bonds, the strength of the polar DABs increases with the increase of the difference of the FIE of the atoms to be bonded.

That is, with the increase of the FIE difference, the possibility of DAB formation (stable compounds with DABs) increases.

3) Molecules are bonded between themselves via the third type of bond: the Van der Waals bond (VWB) which is about ten times weaker than a covalent bond. During the formation of VWBs, the number of electrons in the outermost shells of the atoms does not change.

The amount of energy that should be spent on breaking the bond (the strength of the bond) decreases according to the row thus: triple > double > heteroatomic > homoatomic covalent > DAB > VWB. The length of the bond increases in the same order.

The electrons of the outermost shells of the atoms take part in chemical bond formation. In the course of this formation, the potential and kinetic energies of the electrons change. The absolute value of the potential energies of the bonding electrons during bond formation increases and the kinetic energies of the bonding electrons increases. The energy gain (energy dispatch during bond formation) is conditioned by the kinetic energy increase (energy loss), which is two times smaller, relative to absolute value, than the potential energy increase. That is, the energy gain is equal to half of the potential energy gain.

Thus, bond formation is conditioned by the increase of the absolute value of the potential energies of the bonding electrons.
If various types of bonds bond an atom to similar atoms, such bonds become equal in respect to energy and length. The weak bonds become stronger while the strong ones become weaker. Analogously, the long bonds become shorter while the short ones become longer. The cause of this phenomenon is electronic isomerization.

In the course of isomerization, the electrons and the atoms’ nuclei shift (move) reversely, therefore, this type of bond can be singled out into a separate group of *dynamic bonds*. The strengthening of the weak bonds during isomerization explains the thermal stability of these compounds since the thermal stability of a compound is defined by the energy of the weakest bond in the compound.

The decrease of the strength of the thermal stability of the strong bond in the course of isomerization defines the key role of the dynamic bonds in chemical reactions.

The intermediate products of chemical reactions are compounds in which atoms of the reaction center are bonded with dynamic bonds. First of all, the key role of these bonds in chemical reactions is the basis for the singling out of this type of bond into a group called *dynamic bonds*.

The energy gain during molecule formation can be conditionally divided into two contributions: The first (smaller one) is connected with the attraction of the nuclei to the bonding pair of electrons. The second (bigger one) is connected with the increase of the effective charge of the nuclei to be bonded during bond formation.

The amount of energy necessary for the thermal breaking of the chemical bond is about two times greater than the energy decrease during its formation out of atoms. This is because about half of the given energy is used rather uselessly on heating the unbroken molecules.
CHEMICAL BONDS IN SOLID BODIES

In the preceding chapters we cited chemical bonds in molecules in the gas phase. Now let’s see what kind of bonds there are in substances relative to their physical state. That is, let’s cite the bonds between atoms in gas, liquid, and solid states.

So far, the bonds we have studied were bonds between atoms, i.e., bonds within the molecule to which are added bonds that connect the molecules in liquid and solid states.

Which of the cited bonds can we expect between molecules? Let’s study a few examples.

Example I

In the gas phase we have a dual-homoatomic molecule where the outermost shells of both atoms being bonded are filled. These molecules can form only VWBs between themselves, i.e., in liquid and solid states these substances have covalent bonds and VWBs. When heated, these substances transit from the solid to the liquid state and then to the gas state where the atoms of these substances are connected in pairs via covalent homoatomic bonds. That is, the transition of these substances into liquid and gas phases is connected with the breaking of the VWB whose energy is dozens of times smaller than that of the covalent bond.

Correspondingly, the bond-breaking temperature of these bonds during their transition, from the liquid to the gas phase, is much lower than the temperature needed for breaking a dual-atomic molecule into atoms. Examples of such substances are nitrogen, oxygen, halogens (Cl₂ I₂ Br₂) noble gases (He, Ne, etc.).

Example II

In the gas phase we have a dual-atomic molecule where the outermost shell of one of the atoms to be bonded is completely filled while the other is not yet filled. Examples of such substances are molecules where the atoms are connected with heteroatomic covalent bonds. Since the shell
of one atom in the molecules of these substances is completely filled, and the outermost shell of the other atom is not completely filled, such molecules can bond between themselves via donor-acceptor bonds (DAB).

Molecules of sodium chloride, as mentioned before, offer the dimmer Na\(_2\)Cl\(_2\). In this dimmer the sodium (Na) and the chloride (Cl) are bonded via two covalent heteroatomic bonds and two DABs. The structure of Na\(_2\)Cl\(_2\) can be illustrated as follows:

\[
\begin{array}{c}
\text{Na} : \text{Cl} \\
\uparrow & \downarrow \\
\text{Cl} : \text{Na}
\end{array}
\]

where the arrows (\(\uparrow & \downarrow\)) show the bonding DAB electrons and the dots (\(\cdot\)) show the bonding electrons of the covalent hetero-polar bonds. According to this scheme, the outermost shell of the sodium atom (Na) in Na\(_2\)Cl\(_2\) contains 4 electrons, while the outermost shell of chloride (Cl) - 8 electrons. That is, the outermost sodium shell is only half filled. Therefore, we can form two more DABs with sodium chloride along the scheme:

\[
\begin{array}{c}
\text{Cl} : \text{Na} \\
\downarrow & \uparrow \\
\text{Na} : \text{Cl} & \text{Na} : \text{Cl} \\
\uparrow & \downarrow & \uparrow & \downarrow \\
\text{Na} & \text{Cl} : \text{Na} & \text{Cl} : \text{Na} \\
\downarrow & \uparrow \\
\text{Na} : \text{Cl}
\end{array}
\]

According to this scheme, the sodium is connected with 4 atoms of chloride, 3 DABs, and 1 covalent hetero-polar bond. At the same time, a single unlimited molecule is formed in which the outermost sodium and chloride atomic shells are completely filled. The formation of VWBs between such molecules is possible. The structure of such associates in the solid phase are easily imagined. (See Figure 7.1)
Here each sodium atom is connected with 6 bonds of chloride atoms, and each chloride atom is connected with 6 bonds of sodium atoms. One of these bonds is a covalent hetero-polar one, 3 of them are DABs, and 2 of them are VWBs.

According to the theory of chemical bonding, if the molecular structure of a crystal can be represented in the form of isomers with close electron energy values, then the energies and the bond lengths in this molecule equalize. The electronic isomerization in the case of Na₂Cl₂ can be shown schematically thus:

\[
\begin{align*}
\text{Na} & : \text{Cl} & \rightarrow & \text{Na} \leftarrow \text{Cl} \\
\uparrow & \downarrow & \rightarrow & \ldots \ldots \\
\text{Cl} : \text{Na} & \rightarrow & \text{Cl} \rightarrow \text{Na}
\end{align*}
\]

In accordance with the theory of chemical bonding, all the bonds between the sodium and chloride in a sodium-chloride crystal should be of the same length.

That is, the bonding electrons in the crystal constantly transit between covalent bonds, DABs, and VWBs while the nuclei occupy an intermediate position.

Electronic isomerization leads to the fact that the energy of all the 6 bonds where one sodium atom is bonded to 6 chloride atoms surrounding it (and vice-versa – 1
chloride atom with 6 sodium atoms) is the same, which is proven by the identical lengths of these bonds.

According to experimental data, the distance between all the chloride and sodium atoms in crystal NaCl is identical and equal to 2.814Å while a NaCl molecule has a bond length between the sodium and chloride equal to 2.36Å. As a result of electronic isomerization, the bond lengths and energies become equal. And the lengths of the equalized bonds are greater than the length of the strongest bond (in this case – the covalent hetero-polar bond) in accordance with the theory.

Example III

When the atom has 4 electrons in the outermost shells of carbon or silicon, it can form 4 covalent homopolar bonds. For example, in diamond and graphite, each carbon atom is bonded by a covalent homo-polar bond and by 4 other carbon atoms. The melting and boiling points of these crystals depend on the breaking of the covalent homopolar bond or the carbon-carbon (C – C) bond.

All this proves the need for high temperatures and great melting and evaporation heat for these substances.

Example IV

Unlike the molecules described in examples I, II and III, the molecules formed of atoms from group I of elements in the table of elements with one electron in the outermost shell (Li2, Na2, K2, etc.), according to the theory of chemical bonding, cannot form covalent bonds, DABs, or VWBs. As a matter of fact, when cooling the substances formed of these molecules to a temperature of about 100 degrees C, they transform into a solid substance.

According to the chemical bonding theory, the number of covalent bonds that an atom of group I can form is limited by the number of electrons in the outermost electronic shell. Two electrons are utilized to form one covalent bond: one electron from each of the atoms being bonded by this bond. That is, all the possibilities of forming covalent bonds in molecules of the Li2, Na2, type are utilized when forming dual atomic atoms.
Also according to the bonding theory, DABs and VWBs form between molecules when the atoms in the molecules have electrons in the outermost shell that do not take part in bond formation. That is, bonds between molecules formed of atoms of group I cannot be formed.

Though, as a matter of fact, a comparison of the temperatures at which substances are transformed into solids, has shown that there is a bond in solids between the molecules of these substances, for the breaking of which the substance will need a temperature of more than 100° C; that is, the bonds here are much stronger than VWBs for the breaking of which, in the case of nitrogen (N$_2$) and oxygen (O) in the solid state, a temperature of minus 200°C will suffice.

The importance of the question concerning the nature of bonds between atoms in solid substances, formed of atoms of group I, has grown immensely since these substances belong to a group that has been historically known as metals.

These are known to include about 70% of the substances formed of identical atoms. Such substances are considered as a group of metals because they have a number of common properties (metallic shine, high electric and heat conductivity, plasticity, etc.).

The physical properties of metals, as noted above, speak in favor of the fact that the bonding between the atoms in metals is much stronger than in DABs. Besides the described kinds of bonds in molecules in the gaseous state (covalent, DABs, and VWBs) we should examine the covalent bonds that differ from the previously cited covalent bonds. The previously cited covalent bonds in dual atomic molecules in the gas phase, according to the above mentioned, were dual electronic.

The participation of two electrons in bond formation was based on the comparison of the experimental data in reference to the number of electrons in the outermost shells of the atoms and the number of atoms that these atoms can bond (for example, in hydrogen and chlorine).

On the other hand, the conclusion about the dual electronic covalent bond, between the atoms in dual atomic molecules, was confirmed by the coincidence of the
dependencies of the energies and bond lengths on the FIEs of the atoms being bonded.

Now let's repeat this method in regard to metals. As seen in examples I – III, the same complex of bonds, their existence and nature explains the solid substance properties of non-metals, the structure of which we had elucidated after analyzing the experimental data received when studying the substances in the gaseous state.

A comparison of the data on the number of electrons in the outermost shell of atoms of Li and Na, with the number of strong bonds they form between themselves in the solid phase, has shown that these atoms with one electron in the outermost shell, actually form eight strong bonds with identical atoms.

Strong bonds, as already mentioned, are formed when the bonding electrons enter the outermost shells of both atoms to be bonded. In the case of metals of group I, the bonding of one atom to more than one atom in the presence of one electron in the outermost shell (a single-valence electron) is possible if only 1 electron is utilized to form one bond (not 2). That is, it is logic to suppose that metal atoms in the solid state are bonded between themselves via a single-electron bond.

Bonding electrons enter the outermost shells of both atoms to be bonded which causes its rotation in the molecule on a plane perpendicular to the axis connecting the bonded nuclei.

To evaluate the bonding energy in the lithium molecule Li$_2^+$ we can use the data on the potential energy of the lithium atom and the lithium molecule Li$_2$ received experimentally.

According to the experimental data, the first ionization energy (FIE) of molecule Li$_2$ is equal to 495 kJ/mol while that of the Li atom is equal to 523 kJ/mol, which means that it is easier to tear the electron away from the lithium molecule than from a lithium atom.

When tearing two electrons from the Li$_2$ molecule, this molecule breaks into two nuclei and two electrons; that is, the sum second ionization energy (SIE) of Li$_2$ and the first ionization energy (FIE) of Li$_2^+$ is equal to the energy gain during Li$_2^+$ formation out of atoms Li and Li$^{+1}$. 
If we indicate the Li₂ molecule’s bonding energy as \( E_{\text{Li}_2} \).

Then: \( \text{FIE}_{\text{Li}_2} + \text{SIE}_{\text{Li}_2} = 2 \text{FIE}_{\text{Li}} + E_{\text{Li}_2} \)

Experimental data also offer us the following results:
\( \text{FIE}_{\text{Li}_2} = 495 \text{ kJ/mol}; \) and \( \text{FIE}_{\text{Li}} = 523 \text{ kJ/mol}. \)
Thus: \( \text{SIE}_{\text{Li}_2} = 2 \cdot 523 - 495 + E_{\text{Li}_2} = 551 + E_{\text{Li}_2} \).

As indicated above, \( \text{SIE}_{\text{Li}_2} \) is equal to the electronic energy \( \text{Li}_2^+ \). The bonding energy in molecule \( \text{Li}_2^+ \) is equal to \( \text{SIE}_{\text{Li}_2} - 523 \) where 523 kJ/mol is the ionization energy of atom Li.

Therefore: \( E_{\text{Li}_2^+} = 551 - 523 + E_{\text{Li}_2} = 28 + E_{\text{Li}_2} \). That is, the bonding energy in \( \text{Li}_2^+ \), according to the experimental data, is higher than in \( \text{Li}_2 \), or, in other words, the mono-electronic bond in molecule \( \text{Li}_2^+ \) is much stronger than that in molecule \( \text{Li}_2 \).

The same is true of the relation-ships between mono- and dual-electronic bonds in all the elements of group I. The MEB in \( \text{Na}_2^+, \text{K}_2^+, \text{Rb}_2^+, \) and \( \text{Cs}_2^+ \) is much stronger than the dual-electronic bond in molecules \( \text{Na}_2, \text{K}_2, \text{Rb}_2, \) and \( \text{Cs}_2 \).

Figure 7.2 shows the dependence of the bonding energy in dual-atomic molecules \( \text{M}_2^+ \) (where M is a hydrogen-like atom) from the FIE of atom M. This dependence is calculated via the equation given in section 6.4.

According to figure 7.2 the dependence of the bonding energy curve on the FIEs in molecules \( \text{M}_2^+ \) (where M is the hydrogen-like atom) is a parabola whose maximal bonding energy value is reached when the FIE of the atoms to be bonded are in the interval of 4 eV - 5 eV. When the FIE is equal to 13 eV, the energy of a MEB is equal to zero.

That is, the formation of a MEB in molecules \( \text{M}_2^+ \) when the \( \text{FIE}_M > 13 \text{ eV} \), according to the calculation, is hardly possible. According to the experimental data, molecule \( \text{H}_2^+ \) is an unstable molecule, which immediately breaks up into a hydrogen atom (\( \text{H}^+ \)) and a proton (\( \text{H}^+ \)). Recall that the FIE of a hydrogen atom is equal to 13.6 eV.
Experiment and Calculated Bonding Energy of Molecule X-X vs. FIE of Atom X (for 1 Bonding Electron)

Figure 7.2

In figure 7.3 are given the energy dependencies for mono- and dual-electronic bonds in molecules x-x on the FIE of x.

According to the calculated data, the MEB, relative to energy, is commensurable with the dual-electronic bond up to the FIE value of about 10 eV. Elements with the physical properties of metals have a FIE equal to less than 10 eV. On the other hand, almost all the elements with the physical properties of non-metals, have a FIE greater than 10 eV.

During the formation of MEBs between two metal atoms, the number of electrons in the outermost shell of one of the atoms being bonded (donor atom) does not change. The number of electrons in the outermost shell of the
The MEBs in metals explains the main difference between metals and non-metals. During MEB formation between atoms, one electron of the donor atom is utilized in order to form the bond. The electrons of the acceptor atom do not take part in bond formation. The number of electrons in the outermost shell of the acceptor atom increases by one unit.
during the formation of one MEB that causes the increase of the inter-electronic repulsion forces.

In the first approach, the ionization energy of the first electron in the acceptor atom that was equal to the FIE of this atom before bond formation, can be evaluated close to the energy of the affinity to the acceptor atom's electron before bond formation. For example, during MEB formation between two Na atoms, we can expect the decrease of the ionization energy of the electron that does not take part in MEB formation from 5.14 eV to 0.55 eV, where 5.14 and 0.55 are the FIEs and the affinity of the Na atom to the electron respectively.

When forming one more MEB of an acceptor atom with another donor atom, we can expect a further decrease of the ionization energy of the acceptor atom's electron, which does not partake in the formation of the MEB. That is, in the solid state of metals where, according to the analysis, each metal atom is surrounded by 8 or 12 atoms of the same metal, we can presuppose with great assurance, that a situation will arise that if we extract the electrons that do not partake in bond formation, there will not only be no expenditure of energy (when the ionization energy is < 0), but there is a discharge of energy during the dissociation of the electron that does not take part in bond formation.

Atoms from which the electron separated have the same kind of negative affinity to the electron as, say, inert gases and the elements of group II. That is, a part of the electrons in the metal is not attached in the atom with the nuclei, and is present in the metal in the form of a sort of electronic gas. From experiments with gas discharging tubes and from experience with electronic lamps, it is well known that free electrons in the electric field transit towards the positively charged pole (cathode) thereby producing electric current. That is, the presence of MEB in metals qualitatively explains their great electric conductivity (as compared to non-metals).

The great electric conductivity of metals correlates with their great heat conductivity. These correlations allow us to presuppose that the mechanism of electric and heat conductivity of metals are identical, and that heat, just as electricity, transits via electronic gas.
As indicated above, 8 or 12 identical atoms surround each atom in pure metal. During MEB formation, the bonding electron enters the two of the outermost electronic shells of the atoms to be bonded. In the case of alkali metals of group I, according to the experimental data, each metal atom is surrounded by 8 other atoms.

Respectively, the outermost shell of each atom contains 8 electrons, and 1/8 of the electrons are not bonded to the free atoms and are present in the metal in the form of electronic gas. The regularities of chemical bond formation, introduced by us when studying chemical bonding in dual-atomic molecules in the gas phase, are not violated. The number of electrons in the outermost shell of atoms does not exceed the maximum, i.e., eight.

However, 8 atoms surround one atom in metals only in 15 cases out of 41. These are metals of the 2nd — 5th periods in the table of elements. In the rest of the 26 cases, 12 other metal atoms surround each metal atom in the solid state.

Analogous to the explanations concerning the formation of stable molecules of the SF$_6$ and PF$_5$ types, in the gas phase, previously cited, we can suppose that all 12 bonds are equalized relative to energy and bond length (8 MEBs and 4 VWBs). All this occurs in the course of one electronic isomerization in solid metals very intensely.

The much greater durability of the MEB as compared to the dual electronic bond, and all the more – to the dual-electronic DAB and VWB, very well explains the much higher boiling and evaporation temperatures for metals as compared to those of non-metals. More detailed information about bonds between the FIEs of elements and their physical properties will be given in the section devoted to the physical and chemical properties of substances.

The main advantage of the cited mono-electronic bond in the solid state is that its energy, if we suppose that this bond is formed analogously to that of the H$_2^+$ and can be evaluated via the computer program, is meant for solving the system of equations compiled for molecule H$_2^+$. 
However, in the solid state, the mono-electronic bond can also be formed at the expense of the transition of one atom's electron into a non-ionized shell of another atom along this scheme: $\text{Na}^- + \text{Na}^+ \rightarrow \text{Na} \cdot \text{Na}^-$ or along the scheme:

$$\text{Na}^- + \text{Na}^+ + e^- \rightarrow \cdot \text{Na} \cdot \text{Na}^-$$

where the additional electron comes from the metal volume or from other atoms. These systems cannot be calculated with the same precision as the chemical bonding in systems like $\text{H}_2^+$ since it is difficult to evaluate the energy change of the electrons that do not partake in bond formation.

During chemical bond formation, as already mentioned, the effective charge increases as a result of the mutual approach of the nuclei to be bonded, which should lead to the increase of the potential of the electrons that do not partake in bond formation.

On the other hand, the increase of the number of electrons in the outermost shell of the atoms to be bonded decreases the potential energy of the electrons that do not partake in bond formation. This leads to the decrease of the system's potential energy, that is, to a decrease in the energy gain during bond formation — a decrease in bonding energy.

During the calculation of dual-electronic bonds, a supposition was made to the effect that both opposed electrons mutually compensate each other. The coincidence of the calculated energy dependencies of lengths in homo- and hetero-polar bonds, defined experimentally, proved that the supposition was not baseless.

The coincidence of the maximal number of electrons that can be situated in the outermost shell of an atom from groups IV — VIII of the 2nd and 3rd periods with the maximal number of electrons that can be in the shell of the central atom after the formation of the maximal number of bonds — all this qualitatively proves that the above mentioned contradictions that act upon each other, are mutually counterpoised.
The high transition rate of the electrons, close to that of the organic polymers with conjugated bonds and good conductors, allows us to presuppose an alternative explanation for the electric and heat conductivity of metals.

In the case of organic polymers, the high electric conductivity of these polymers correlates with the high speed of electronic isomerization, which contains conjugated (single and double) chemical bonds.

From the viewpoint of physics, the analogy between the high speed of the electronic transitions and the high electric conductivity is not considered as being great. That is why the supposition that the rapid electronic isomerization, which occurs in solid metals and is conditioned by low ionization energies of the electrons in metals (both bonding and non-bonding) and by a great number of possible electronic states with close energy values, can be at least a second explanation concerning the high electric and heat conductivity of metals.

It is thus supposed that the electric current in metals occurs not as a result of the transition of free electrons (when the mechanism is observed in gas-discharging tubes) but along the mechanism where electro-conductivity occurs in organic conductors and super-conductors (conjugated polymers), that is, from atom to atom.

The two given explanations about electric conductivity of metals are not alternative, and have only a slight quantitative difference. For example, an electron bonded to an atom and having an ionization energy smaller than 0.5 eV, do not differ in performance (behavior) than the so-called 'free electron' because this electron takes part in the energy exchange with the electrons that have energy greater than 5 eV, and of which there are by one order of magnitude more in the system.

Thus, the difference in the properties of metals in the solid state and nonmetals is the comparatively high temperature, the boiling and melting heat; on the other hand, the general properties of metals are conditioned by low FIE values (<10) for atom metals.

Such a low FIE value is conditioned the possibility of forming a strong single-electron bond, which, in turn,
conditions the high metal melting and boiling temperatures which are much higher than those of nonmetals.

On the other hand, the presence of a large number of possible positions for electrons with equal energies, the electron that takes part in a single-electron bond presupposes a high speed for the transiting for the bonding electrons between identical minimums of energy or a high transition speed of the bonding electrons, which, in turn, explains the high electric-conductivity of the metals.

The high speed transition of bonding electrons is also obvious among conjugated (single, double bonds) organic conductors which additionally proves that this property of a conducting system is most important for better electric conductivity and that the mechanism of electric conductivity in metals and in organic conductors are identical.

The likeness between the mechanism of conductivity in metals and organic conductors (in both cases the electro-conductivity correlates with the transition of the electrons) allows us to say that this mechanism, where the electrons move in jumps from atom to atom is more possible than a mechanism that presupposes the presence of electronic gas, and therefore a conductivity mechanism very much like the electro-conductivity mechanism in the gas-charged tubes.

Additionally, in favor of the above-mentioned mechanism, the electro-conductivity in metals speaks of the fact that at least, from the viewpoint of chemists, the supposition about the presence of free electrons (not bonded to atoms) is not at all convincing. This is because the whole volume of the conductor is filled with atoms: 1) whose outermost shells are not filled with electrons; 2) which have a positive affinity to electrons; 3) which have a positive charge. See Appendix C for details.
Three-Dimensional Structures of Chemical Compounds

The question of spatial arrangement of molecules arises when one atom is connected with 2, 3 or 4 other atoms. If the atoms, connected to the central atom, have almost identical FIEs, we should expect the placement of the axis (connecting the outermost atoms with the inner ones) to be as far apart as possible.

This is conditioned by a mutual repulsion of the bonding electrons. The spatial arrangement of molecules is not changed even if some atoms have different FIEs and are connected to the central atoms with another type of bond.

From stereometry we know that an angle between two straight lines projected from one point, and placed at a maximal distance from each other, comprises 180°. In the case of 3 straight lines (interchangeable) this angle comprises 120°; in the case of 4 – 109°. Here the experimental data quantitatively corresponds to the calculations.

According to this experiment, the angle between the atoms when connecting 2, 3 or 4 identical atoms to the central one is equal to the theoretically calculated angle. The angle is hardly changed when the connected atoms differ in their FIEs. In the above-cited cases, all the outermost electrons of the central atom take part in bond formation.

Now let’s take a case where not all of the atoms’ outermost electrons form bonds. Our theory allows calculating the spatial placement of these nonbonding electrons where one of the atoms, bonded by a covalent bond, has a very small FIE. In such a case the atom’s FIE is equal to zero (i.e., at the limit), and allows evaluation of the spatial position of the nonbonding electrons.

Using equations 6.4-5 to 6.4-7, the value of ‘a’ was calculated. [Here ‘a’ is the radius of the circle on which the connected electrons rotate.]

We have determined the changes of ‘a’ in molecule A-B when the FIE of atom ‘A’ is changed from 17 eV to 5 eV at two constant ‘B’ atoms’ FIEs (14 eV and 5 eV), which are
expressed via the following equations and shown in figures 8-1 and 8-2:

\[ a = -0.0166x + 1.16 \quad (\text{FIE}_B = 14) \]
\[ a = -0.016x + 1.7 \quad (\text{FIE}_B = 5) \]
\[ x = \text{FIE}_A \]

**Radius of Circle 'a' vs. FIE of Atom 'A'**

(FIE of Atom 'B' = 14 eV)

![Figure 8.1](image)

**Radius of Circle a vs. FIE of Atom A**

(FIE of Atom B = 5 eV)

![Figure 8.2](image)
According to these equations, when the FIE of atom A decreases, the radius of the electronic circle increases; when the FIE of atom B decreases, the radius of the orbit increases. When atom B’s FIE is 14 eV, the electronic orbits’ radii a comprise 1, 1.1, 1.16 units of the Bohr radius (0.529 Å) respectively when the FIE of atom A = 10, 5, 0.

Likewise, atom B’s FIE is equal to 5 eV, the electronic orbits’ radii a are equal to 1.54, 1.62, and 1.7 units of the Bohr radius respectively, and the FIE for atom A is equal to 10, 5, 0 respectively. Thus, according to the model, with the decrease of the FIE in atoms A and B — the radius of the bonding electronic orbit increases. When the FIE of atom A is equal to zero with the constant FIE of atom B, the radius achieves the maximal value. Then, when the FIE of atom B is decreased, we expect an increase in the radius of the electronic orbit.

If we extrapolate these results with reference to the question asked above, we can expect the following dependency for the radius of the electronic orbit a of the nonbonding pair of electrons in the atom: the radius of this orbit should increase when the FIE of atom B decreases.

Now let's see what dependencies we should expect in spatial structure (i.e., angle values between the bonds) according to this bonding model which can be represented thus:

( :) m B (A) n

where n is the number of atoms A bonded to atom B; m is the number of undivided pairs of electrons ( : ).

According to the model, the angle between atoms A (angle A B A) is defined by the repulsion between the electronic orbits and by their radii.

In all cases, independent of the FIEs of atoms A and B, the orbit’s radius of the nonbonding electron pairs is bigger than the radius of the orbit in the bonding electron pairs. Therefore, we should expect a decrease in the repulsion between the electron pairs in the following manner:

Nonbonding pair of electrons — nonbonding pair of electrons > nonbonding pair of electrons — bonding pair of electrons — bonding pair of electrons — bonding pair of electrons.
This sequence was also observed experimentally and was generalized by the Valence Shell Electron Pair Repulsion Theory (VSEPR), offered in 1940 by N.Sidgewick and H.Powell, and later modernized by R.J.Gillespie and R.S.Nyholm.

According to the model, the interelectronic repulsion should increase when the FIE of the central atom decreases. Then the value of angle ABA should increase when the FIE of atom B decreases.

Experimental data has shown that some groups of compounds in the periodic table reveal a decrease in the angle value between the bonds when the FIE of the central atom decreases. For example, in rows NH₃, PH₃, AsH₃, SbH₃ the angle between the bonds comprises respectively: 107.3°; 93°; 91.5°; and 91.3°.

The FIE of these elements decreases in the same sequence: 14.5; 10.5; 9.8; 8.6 eV. Likewise, in row H₂O, H₂S, H₂Se, H₂Te, the angle between the bonds comprises: 104.5°; 92.2°; 91°; 88°. The FIE of the central atom of these molecules comprises 13.6; 10.4; 9.75; 9.01 eV respectively.

In the framework of the VSEPR these dependencies were regarded as anomalous and required additional suppositions to the explanations.

Thus, our theory of chemical bonding can quantitatively explain the dependencies observed in experiments on the study of spatial structures of chemical compounds without any supplemental suppositions. The explanation about the spatial structure of chemical phenomena in the framework of our theory allows us to specify the model of the atom. In the first approach we have cited the atom in a single plane.

According to the spatial structure of water, for example, the bonding and nonbonding electrons rotate in circles situated at the top of the tetrahedral. If the placement of the 8 electrons in the molecule (i.e., their rotation along the circular orbits at the tops of the tetrahedral) greatly differed in energy, as compared to their placement in the atom, we would have a much smaller energy gain during bond formation.

That is, we can suppose that the placement of electrons in the atom hardly differs from that in the molecule.
More precisely, this conclusion can be formulated as follows:

Electrons in the atom can be placed as electronic isomers, among which there is a possibility of the existence of an electronic isomer where the placement of electrons is identical to that of molecules formed out of these atoms. If the atom has 2 electrons in the outermost shell, we can presuppose the existence of 2 isomers. In one of the isomers the electrons rotate in one circle, while in the other they rotate in parallel circles.

Another factor that causes an increase in the possibility of such an electron distribution can be the presence of the nuclei's magnetic moment. This phenomenon is present in our earth. Indeed, we know that electrons, coming from space, gather in circles on the magnetic poles of the Earth.

The appearance of an atomic electron isomer in a helium-like atom, where the electrons rotate in parallel planes, can be caused by the fact that in these circles the electrons rotate in opposite directions.

The first ionization energy (FIE) of the isomer mixture can be defined by the FIE of an isomer with the smallest value since (in the process of defining the FIE) electronic isomerization of the isomers can take place. The appearance of atomic electron isomers, when the electrons rotate is in opposite directions can be expected when the number of electrons in the atom’s outermost layer is more than two.

Atomic electron isomers, which differ by the direction of the rotation of their electrons in reference to the axis around which the atom’s nucleus rotates, can exist even in hydrogen-like atoms (atoms with one electron). Experimental confirmation of the existence of atomic isomers is the atomic spectra, in part, the radiation of a helium atom and the splitting of the spectral lines in alkaline metals.

The correlation of the isomers and their FIEs can even depend on the nuclear charge. Indeed, according to the experimentally defined correlation, the deviation of the calculated energy value of helium-like atoms, as compared to that of the experiment, depends on the nuclear charge. If the nuclear charge is equal to 20, the calculated energy coincides with that of the experiment with a precision of 0.1%.
Such a coincidence of calculated and experimental results confirms the fact that a common Coulomb interaction well describes the electrons' energies of both hydrogen and helium-like atoms. The quantitative evaluation of the atomic and bonding energies, and their theoretical and experimental discrepancies, are given in greater detail in our chemistry book entitled: *How Chemical Bonds Form and Chemical Reactions Proceed*, page 300.

The energy deviation between small values in experiments and helium-like atoms with small charges can be caused not only by the presence of an isomer or entropy phenomenon, but also by a change of the electronic orbit – from a circular to an elliptical one.
In the course of chemical transformation, the old bonds between atoms break and new ones form. Millions of chemical reactions take place simultaneously in live organisms at temperatures of 20°C to 40°C.

As we have seen in the previous section, we need energy of about 200 kJ/mol (i.e., about 2,000°C) to break a chemical bond. Thus, the main question concerning chemical reactions is:

How do chemical reactions proceed at temperatures of 20°C to 30°C if, in order to break a bond, a temperature of more than 2,000°C is actually required?

Before we go on to study complex reactions in organisms, let's take up some simple examples, which can be studied in any school lab. One of the best-known and most instructive experiments is as follows:

The teacher prepares a mixture of two gases: oxygen and hydrogen in a test-tube. He demonstrates that these gases will never start a reaction by themselves. Then he lets the gas mixture go into a tin can through an opening at the bottom and he passes an electric current (spark) into the gas. The current causes an explosion, which is the result of a momentary interaction of the hydrogen and oxygen via the reaction:

$$2H_2 + O_2 \rightarrow 2H_2O$$

That is, in the process of this reaction, the bonds in molecules $H_2$ and $O_2$ were broken, and new bonds were formed between the hydrogen and the oxygen. It is worth mentioning here again that in order to break the bonds in molecules of hydrogen and oxygen a temperature of more than 2,000°C is required.

Of course we can suppose that the spark had caused the momentary heating of the mixture to this temperature. However, a test made by passing a spark separately into either of the two gases has shown that the temperature of these gases practically does not change.
The motor of a car receives air (oxygen) and fumes of gasoline (mixture of hydrocarbons) but the motor will not work because the reaction takes place only when the motor is switched on (when the spark appears). The process that takes place in a motor is well described by the following reaction:

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$$

We can also observe in a similar experiment, that if we mix water solutions say, of barium chloride (BaCl$_2$) and sodium sulfate (Na$_2$SO$_4$), we will not get a transparent mixture as with other combinations; we will get some sediment of barium sulfate that is formed via the reaction:

$$BaCl_2 + Na_2SO_4 \rightarrow 2NaCl + BaSO_4$$

In this case the bonds between barium (Ba) and chloride (Cl), and between sodium (Na$^+$) and sulfate (SO$_4^{2-}$) will break, though they actually require a temperature of more than 5,000°C for their rupture.

It is of interest to note that we had dried both these salts at a temperature over 200°C and then mixed them; there was no reaction between them.

Other such phenomena are observed in interactions of chloride (Cl$_2$) and hydrogen (H$_2$). If we mix these gases in darkness, we will see that there is no reaction between them. If however, we momentarily irradiate the mixture with light, then the following reaction takes place:

$$Cl_2 + H_2 \rightarrow 2HCl$$

What conclusions can we make on the basis of these examples?

1) Reactions between molecules for which energy of 200 kJ/mol is required for bond breaking (i.e., heating to over 2,000°C) in reality do not proceed at normal temperatures — with mixed substances.

2) To proceed with the reaction, we need a momentary energetic stimulant (spark or flash) or the introduction of a third substance (water).
In order to understand the essence of these momentary energetic stimulants, scientists have studied the composition of gas after such coercions. They have found that gas (oxygen + hydrogen) contain separate atoms of oxygen and hydrogen though the initial gases did not contain separate atoms. The concentration of separate atoms amounted to nothing (less than 0.01%) of the number of molecules in the mixture.

Thus, there can be no suggestion that the momentary action of the spark or light leads to bond breaking in the molecules and to dissociation into atoms which then unite to form new molecules.

At the same time we must understand how the presence of species (separate atoms) in tiny concentrations leads to an explosive interaction of the whole mass of hitherto passive molecules.

During the development of lab experiments, scientists invariably studied the interaction of separate atoms and ions with molecules. They have found that an atom of chloride rapidly reacts with a hydrogen molecule along the following scheme:

\[ \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}, \]

and that an atom of hydrogen also rapidly reacts with a chloride molecule even at room temperature according to the following scheme:

\[ \text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl} \]

These results help us to answer the question: \textit{Why and how do reactions cause chemical transformation of molecules?}

If we take the transformation of the mixture hydrogen + chloride, the reaction can be described as follows. When this mixture is irradiated with light, a small portion of the chloride molecules dissociate into atoms along the scheme:

\[ \text{Cl}_2 + \text{hv} \rightarrow 2\text{Cl}^- \]
The cited scheme also explains why small concentrations of free atoms cause the transformation of many substances. Every atom performs a large number of cyclic transformations, i.e., this scheme shows how the chemical reaction between molecules proceeds, and the role of short-term energetic action upon reaction mixtures.

However, this scheme does not answer the main question, which arose during the studies of chemical reactions. Indeed, it has been found that the interaction of molecules is possible via the chain route where the carriers of the chain are radicals or ions. The mechanism scheme of the cited above reactions, has two more steps:

\[
\begin{align*}
\text{Cl}_2 + \text{hv} & \rightarrow 2\text{Cl} \quad \text{and} \quad \text{Cl} + \text{H}_2 & \rightarrow \text{HCl} + \text{H} \\
\text{Cl}_2 + \text{H} & \rightarrow \text{HCl} + \text{Cl}
\end{align*}
\]

In the first of these reactions, all was logical. The molecule of chlorine under the influence of a portion of light (strong, energetic action) broke up into atoms. But in the second reaction, in the presence of the chlorine atom, the bond in the hydrogen molecule dissociated at room temperature without any additional energetic influence. That is, this scheme for chemical transformations allows specifying the main question which is now formulated as follows:

\textit{Why is it that the interactions of H}_2 + \text{Cl} \rightarrow \text{HCl} + \text{H} \quad \text{and} \quad \text{Cl}_2 + \text{H} \rightarrow \text{HCl} + \text{Cl} \text{ in the course of which bonds between hydrogen atoms in molecule H}_2 \text{ break; and bonds between chlorine atoms in molecule Cl}_2 \text{ (that require heating up to over 2000° C and 700° C respectively) break during reaction with chlorine and hydrogen atoms at room temperature?}

It is of interest to note that the answer to this question was first received theoretically (via discourse) and only then was it proved experimentally. To be more precise, the basis for the theory was a more strictly limited experimental material than was the experimental material that appeared after the elaboration of the theory.

\textit{Then what is the answer to the above-mentioned question?}
The authors of this theory have suggested that the reaction of the active species (atom, ion, radical, etc.) proceeds not in one step, but in three: 1) **association**, 2) **electronic isomerization**, 3) **dissociation**.

For example, in the case of interaction between a chlorine atom (Cl) and hydrogen (H₂) the reaction mechanism is described thus:

\[
\text{Cl} + \text{H} : \text{H} \rightarrow \text{Cl}...\text{H} : \text{H} \quad (1) \\
\text{Cl}...\text{H} : \text{H} \rightleftharpoons \text{Cl} : \text{H}...\text{H} \quad (2) \\
\text{Cl} : \text{H}...\text{H} \rightarrow \text{Cl} : \text{H} + \text{H} \quad (3)
\]

Thereon, the colon (:) represents electrons on the atoms' outermost shell. Three dots (Cl...) indicate Van der Waals bonds (VWB).

*Then how does the above reaction scheme actually answer the above-mentioned question?*

Each of the three steps have been studied experimentally, and it was found that each of the reactions proceeds at room temperature, and that the reaction rate of step #3 is close to that of the interaction of a chlorine atom with hydrogen. Then it was found that steps #1 and #2 proceed with rates by two orders of magnitude higher than that of step #3. That is, the rate of the whole reaction can be defined by the rate of step #3, i.e., step #3 is the *rate-determining step*.

Now let’s make out what the *rate determining step* is, or figure out why the slow reaction stage defines the speed of the whole process that proceeds subsequently via several stages. The speed of the whole chemical process is measured by the amount of final product in the given case, by the amount of HCl molecules formed, say, in one minute.

As already indicated, the reaction speed of #1 and #2 are more than 100 times faster than that of #3. That is, reactions #1 and #2 reach equilibrium. Analogous processes, consisting of successive stages, are found in everyday life.

For example, let’s take a poorly organized car assembly line at a factory. The body of a car is moving on a conveyor. During the movement of the conveyor, the body gradually gets its wheels, its motor, its interior, etc. One man is working on each stage of this conveyor.
In order to complete each operation (of #1, #2, and #3) this would require, say, 10, 60, and 5 minutes respectively, while for all the previous and consequent operations less than 5 minutes is spent. Such a conveyor will produce only one car every 60 minutes; that is, the time required for installing a motor; that is, the time that corresponds to the slowest stage of the sequential process.

Relatively, stage 2 (the motor installation stage) is the stage that defines the speed of the whole process. Since the speed of the slowest stage defines the speed of the whole process, this stage is called the limiting stage, since the speed of the whole process (assembly of one car) cannot be less than 60 minutes. That is, this stage limits the amount of cars produced in 60 minutes — to one car.

If we want to increase the production of cars, we should increase the speed of the defining stage, increase the number of workers on the motor-installation stage. The increase of the number of workers on stages 1 and 3 will not have any effect on the production speed.

Relative to such consequential multistage reaction, the defined HCl formation speed of stage #3 (the slowest), in the process is equal to the speed of HCl formation during the process, since stage #3 is the limiting stage. The influence of parameter change (like the increase of temperature) is obvious (just as the change of the number or workers on the conveyor belt) mainly on stage #3 — the defining stage for increasing the speed of the whole process.

The increase of temperature, just as the increase of the number of workers on the conveyor belt, increases the speed of all the stages in the process. But the temperature increase will cause the speed of the whole process to be close to that of the slowest stage.

We have noted that the speed increase of the fast stages does not effect the whole process. That is, its speed is always defined by the defining stage — the speed of the slowest stage.

When we study the influence of temperature on the speed of final product formation in a process proceeding via some sequential stages, we define the influence of temperature (temperature coefficient or activation energy) as the very slowest of the sequential reactions.
Here is a well-known problem: A person has to travel from point A to point B in the shortest time possible. He is offered two possibilities: 1) he can drive half the way at 30 miles per hour and walk the second half of the way at 3 miles per hour; or 2) he can drive at 90 miles per hour half the way and walk the second half of the way at 1.5 miles per hour. Which of these two methods should the traveler choose to get to point B sooner?

Spend a while solving this problem; then try to realize the answer if all the conditions remain unchanged, but the cars travel at the rate of 120 and 150 miles per hour. Your reflection in this respect should lead you to the conclusion that the question which is the quickest way? depends on the correlation of the walking rates, but not on that of the driving rates. That is, the time of transition from point A to point B is actually defined by the rate of speed of the traveler’s transition while walking, i.e., the rate of the slower transition step.

Likewise, the speed rate of the whole multi-step reaction is defined by the rate of the slowest reaction step. It is this rate that is regarded as the rate-determining step, and in the above-mentioned scheme step #3 is the rate-determining step:

\[ \text{Cl : H...H} \rightarrow \text{Cl : H + H'}. \]

The VWB, with energy of less than 20 kJ/mol, breaks up at this step.

In the case of a thermal break-up of a hydrogen molecule, the reaction proceeds via a single step according to the following scheme:

\[ \text{H : H} \rightarrow \text{H' + H'}. \]

In this case, the covalent bond, whose energy is equal to more than 200 kJ/mol, will break up on the rate-determining step. The ten-fold difference in the energies of bonds, which break on the rate-determining steps, explains why in the presence of radicals the bond breaking reaction proceeds at room temperature while for breaking such bonds
without active species, a temperature of more than 2,000°C is required.

According to the scheme for the interaction of a chlorine atom with hydrogen, a VWB is formed between the hydrogen atoms as a result of electronic isomerization. As a result of this isomerization (transition of one electron), the covalent bond (H : H) is changed into a VWB.

Positive and negative ions react like radicals with saturated molecules do. Thus, for example, it has been experimentally confirmed that the interaction of a positively charged ion of potassium (K⁺) with sodium chloride proceeds via the mechanism as follows:

\[ K^+ + Cl:Na \rightarrow K^+ \leftrightarrow :Cl:Na \Leftrightarrow K:Cl \rightarrow Na^+ \rightarrow K:Cl + Na^+ \]

In this case, we can suppose that the formation of associate occurs via the DAB between the calcium (K⁺) cation and the sulfur chlorine (NaCl) at the expense of the lone electronic pair of the chlorine atom. During DAB formation, according to the theory of chemical bonding, the bond between the chlorine and sodium weakens. The breaking of the weakened covalent-polar bond in the gas phase is accelerated at the expense of the use of part of the energy that is discharged during DAB formation between the calcium and the chlorine.

As you see, 2 electrons transit from bond Na:Cl to bond K:Cl.

Thus, the presence of the electronic isomerization step in reaction schemes explains why and how chemical bond breaking reactions take place at room temperature.

In school textbooks the interaction of bromide anion with gaseous chlorine is demonstrated by the oxidation-reduction reaction. When we add a water solution of chlorine to the colorless solution of sodium bromide, the NaBr solution becomes orange-red because of the formation of bromine. Thus, we get the reaction:

\[ Cl_2 + 2 Br^- \rightarrow 2 Cl^- + Br_2 \]

However, the direct interaction of bromide anion (Br⁻) with chlorine (Cl₂) accompanied by the transition of the
electrons from the bromide anion (Br\textsuperscript{−}) to the chlorine molecule is impossible since the ionization energy of bromide anion (Br\textsuperscript{−}) is equal to 3.36 eV, while the affinity of the gaseous chlorine to the electrons is equal to 2.38 eV.

In the framework of the offered approach, the interaction of bromide anion with gaseous chlorine is described analogously to that of the interaction of the anion with a molecule. This process proceeds in two phases:

\[
\text{Br}^- + \text{Cl} \rightarrow \text{Br}^- \ldots \text{Cl} \leftrightharpoons \text{Br}^- + \text{Cl} \ldots \text{Cl} \rightarrow \text{Br}^+ + \text{Cl}^- \\
\text{Br}^- + \text{Br} \rightarrow \text{Br}_2 + \text{Cl}^- 
\]

The enthalpy (electrostatic component) of bonds BrCl, Cl\textsubscript{2}, and Br\textsubscript{2} are equal to 1.14, 1.18, and 0.93 eV/mol, correspondingly.

The affinities of the chlorine (Cl) and bromide (Br) atoms to the electrons are equal to 3.6 eV and 3.36 eV correspondingly.

That is, there is not loss of energy in reaction:

\[
\text{Br}^- + \text{Cl}_2 \rightarrow \text{Br} \cdot \text{Cl} + \text{Cl}^- 
\]

which is equal to the difference between the electrostatic components of bonds Cl\textsubscript{2} (1.18 eV) and BrCl (1.14 eV) equal to 0.04 eV (1.18 − 1.14) and there is an energy gain equal to the difference in the affinities to the electrons of the bromide (3.36 eV) and chlorine (3.6 eV) atoms equal to 0.24 eV. That is, the energy gain in this reaction is 0.2 eV (0.24 − 0.04).

The energy gain in the course of the second reaction is:

\[
\text{Br}^- + \text{Br} \rightarrow \text{Br}_2 + \text{Cl}^- 
\]

The electrostatic component in bonding energy Br\textsubscript{2} is equal to 0.93eV. Relatively, the energy loss at the expense of the formation of bond Br − Br instead of bond Br − Cl is equal to 0.14 eV (1.07 − 0.93). The energy gain at this stage, which is reached at the expense of the difference in the affinity of the chlorine and bromide atoms to the electron,
just as in the first stage, that is, 0.24 eV; which increases the energy loss (0.14 eV). Thus, the reaction proceeds with an energy gain.

The intermediate products offered by this reaction — BrClCl and BrBrCl — are the same as those of the well-known stable compound I$_3$. Likewise the interaction of anion bromide (Br$^-$) with halogens and other oxidation-reduction reactions are described in textbooks.

The analogy is in the fact that during the reaction, the bonding electrons (one or two) transit from one energetic minimum to another. For example, the interaction of metals of group I (Li, Na, etc.) with oxygen proceeds thus:

\[
\text{Na : Na + : O : : O} \rightarrow \text{Na : Na ... : O : : O} \rightarrow \text{Na : Na : O : : O} \rightarrow \text{Na : ... Na : O : : O}
\]

Analogous to the oxidation-reduction reactions, there are interactions between acids and bases of proton transition reactions. Just as in the case of oxidation-reduction reactions, the weakening of the old (strong) bond and the formation of a new one occurs as a result of electronic isomerization. And just as in the case of interaction of anions with molecules, electronic pairs take part in the isomerization.

The new electronic pair sort of 'squeezes out' another electronic pair from the atom's shell during the isomerization process.

Unlike the interaction of anion with molecules, in this case the associate forms not at the expense of the Van der Waals bond (VWB), but at the expense of the formation of the hydrogen bond. That is, the reaction proceeds along the following scheme:

\[
A : H + : B \rightarrow A : H ... : B \Leftrightarrow A : ... H : B \Leftrightarrow A : + HB
\]

where B is the molecule with a lone pair on one of the atoms (that does not partake in bond formation)

Since the transition speed of the proton in the liquid phase is much greater than that of the other atoms, in this case, besides the electronic isomerization, the transition of
the proton can play a role here thereby increasing the transition speed of the system from one minimum to another.

With the formation of the intermediate compound at the expense of the hydrogen bond, acid dissociation proceeds in the elementary fashion as indicated in the following scheme:

\[
\begin{align*}
H_2O : + H : Cl & \rightleftharpoons H_2O : \ldots H : Cl \rightleftharpoons H_2O : H \ldots Cl \\
& \rightleftharpoons H_3O^+ + Cl^-
\end{align*}
\]

and the neutralization of acids by the bases.

\[
\begin{align*}
HO^- + HCl & \rightleftharpoons HO^- : \ldots H : Cl \rightleftharpoons H : O : H \ldots Cl^- \\
& \rightleftharpoons H_2O + Cl^-
\end{align*}
\]

The dissociation of salts proceeds with DAB formation (O : Na) and hydrogen bond formation (Cl : H)

This example illustrates exactly how, under the influence of water, the bond in molecule NaCl, for whose eruption in the gas phase or in a carbon-hydrogen solvent requires heating up to 5,000°C, actually falls apart into ions at room temperature.

As seen from the above, the formation of the intermediate compound occurs at the expense of the formation of all the types of dynamic bonds described in the section devoted to chemical bonding.

Generally, the chemical reaction can be illustrated thus:

The molecules that enter the reaction break up into ions, radicals, etc. thereby forming intermediate compounds
with the initial molecules. These compounds differ from the initial molecules by the fact that the intermediate compound has more electronic isomers, which have practically the same potential energy, as compared to that of the initial molecules.

In the course of electronic isomerization, the electrons transit from one minimum to another. Since the transition speed of the nuclei is by more than one order of magnitude smaller than that of the electrons, the nuclei occupy an intermediate position in the molecules.

The existence of each electronic isomer is defined by the electronic energy of the given isomer. The greater is the attraction energy of the electrons to the nuclei, the greater is the isomer concentration in the mixture (and the greater is the bonding energy). Proportionally it is as follows: \( e^{E/2} \); where \( E \) is the energy of the electronic isomer. The energy of the electrons is measured in values of about 1,500 kJ/mol.

The electrostatic component of chemical bonding is equal to about half the sum of the electrostatic components of bonds in the initial (non-isomerized) associate; that is, half the sum of the electrostatic components of a covalent and hydrogen bonds, or a VWB bond; i.e., equal to about 100 kJ/mol, which comprises less than 7% of the average energy value of the electrons in the molecule. The latter presupposes the existence of electron-nuclear isomers in measurable amounts in the mixture.

As already indicated, the concentration of isomers exponentially depends on the potential electronic energy of the given isomer \( e^{E/2} \). On the other hand, the reaction speed of the isomer’s transition to the final product exponentially depends on the energy of the breaking bond:

\[
W = k e^{-EcB}
\]

The greater is the bonding energy, the smaller is the reaction speed. Or, the greater the bonding energy, the more electronic isomer there is in the mixture, and the smaller is its final product transformation speed. That is, in the first approach, the transformation speed and the activation energy can be evaluated via the breaking speed and by the energy of the weak bond in the associate (VWB or hydrogen bond).
The bonding energy in the Van der Waals complex (VWC) is equal to about 15 kJ/mol; that is, this complex is more stable from the thermodynamic viewpoint than the products formed of it.

*Why doesn’t the reaction cease on stage 2 (stage for the formation of the VWC)?*  
Indeed, the VWC is more thermodynamically stable than the equilibrium in the system

$$\text{Cl} : \text{H...H} \rightleftharpoons \text{Cl} : \text{H} + \text{H}$$

is shifted to the left with a normal temperature (300 K). The speeds of the direct and reverse reactions according to experimental data, are very large even at 300 K. The reaction reaches equilibrium in less than 1 second. The amount of HCl in the beginning of the reaction is much smaller than that of initial products in Cl₂ and H₂. Interaction of H with HCl leads to the formation of initial H₂ and Cl₂ products via the scheme:

$$\text{HCl} + \text{H} \rightarrow \text{H}_2 + \text{Cl} ; \text{That is: } \text{HCl} + \text{Cl} \rightarrow \text{Cl}_2 + \text{H}$$

This scheme is accomplished only after producing concentrations of HCl in the system that is commensurable with the concentration of initial substances (H₂ and Cl₂).

Previously, the formed hydrogen atom reacted with Cl₂ of which there was more than HCl along the scheme:

$$\text{Cl}_2 + \text{H} \rightarrow \text{HCl} + \text{Cl} ; \text{that is,}$$

together with the formation of the final product and the Cl atom.

However, the following question still remains:

*Why are radicals and ions considered as active species? Why can’t saturated molecules react between themselves?*

We have thus returned to the question given at the beginning of this chapter, only now we can answer it on a higher level.

In accordance with the following chemical reaction scheme:
Cl + H:H ⇌ Cl...H:H ⇌ Cl:H...H → Cl:H+H

the reaction rate is equal to the rate of the third step which is directly proportional to the concentration of the isomerized associate (IA) (i.e., to the concentration of compound Cl:H...H) and which exponentially depends on the energy of the VWB (H...H) of this compound.

Concentration IA depends on the concentration of the nonisomerized associate and on the rate of the isomerization step. The greater the concentration of the nonisomerized associate (in our example: Cl...H:H) and the greater the isomerization rate — the greater is the concentration of isomerized associate in the compound, and the greater is the rate of the whole reaction. The concentration of non-isomerized associates is defined by the concentration of initial products (in our case, Cl, H₂ and bonding energy Cl...H in compound Cl...H:H).

In order to answer the above offered question: Why don’t saturated molecules react among themselves along the mechanism: association → electronic isomerization → dissociation? we should compare the probable interaction mechanism for saturated molecules and its interaction along the radical mechanism.

The molecular interaction mechanism for hydrogen (H₂) and chlorine (Cl₂), according to the theory, can be shown as follows:

\[
\begin{align*}
H : H & \quad H ... H \\
1 & 2 \\
H : H + Cl : Cl & \rightarrow : : \rightarrow \ldots \rightarrow 2HCl \\
Cl : Cl & \quad Cl...Cl
\end{align*}
\]

Now let’s compare the rates of each of the steps of the radical and molecular mechanisms. We will begin with step 1.

The origin of the four-part complex, as a result of the association reaction (step 1), is not only a rare phenomenon as compared to the origin of the associate between radical and saturated molecules; it is hardly possible. The obstacle in
its formation is the mutual repulsion of the two electronic circles between the hydrogen and chlorine atoms.

There is a much greater possibility in the formation of a linear complex of the H:H...Cl:Cl type. Out of this complex, as a result of electronic isomerization via the scheme we get:

\[ H:H...Cl:Cl \quad \rightleftharpoons \quad H...H:Cl...Cl. \]

An associate is formed containing two VWBs and one covalent bond. The concentration of this associate is much smaller than the initial, non-isomerized associate. The initial associate has two covalent bonds (H:H...Cl:Cl) and one VWB (H:H...Cl:Cl). The final associate has one covalent bond (H:Cl) and two VWBs, i.e., the electronic energy in this associate is much greater than in the initial one - over 100 kJ/mol.

The concentration of a non-isomerized associate is defined by the bonding energy between the molecules. The greater the energy — the greater is the associate concentration. The VWB energy between the saturated molecules comprises less than 5 kJ/mol; to break the bond of a radical-saturated molecule, energy of more than 20 kJ/mol is required.

When studying electronic isomerization reaction, it was found that the isomerization rate depends on the distance between the atoms and on the number of electrons transiting in the course of isomerization. Thus, for example, isomerization reaction:

\[ Cl^-...H:H \rightarrow H:Cl...H^- \]

where one electron transits a distance of 1.5 Å in the course of the isomerization, the time is equal to \(10^{-13}\) sec.

The transition of two electrons in the isomerization reaction:

\[ K^+...Cl:Na \rightarrow K:Cl...Na^+ \]

is possible at a time equal to about \(10^{-12}\) and by changing two electrons in the following reaction:
The isomerization rate becomes smaller than that of the association reaction, i.e., it takes place during more than $10^{11}$ sec., that is, the isomerization rate in the case of molecular interaction is by two orders of magnitude smaller than in the case of the radical route.

And finally, what is most important, during the breaking of the VWB in an isomerized associate, according to the scheme:

$$H \cdot H:Cl...Cl \cdot \cdot \rightarrow H \cdot H:Cl + Cl \cdot$$

A radical is formed that enters reaction with hydrogen molecules along the chain mechanism described above.

The formation of radicals during the interaction of hydrogen and chlorine is not due to the interaction of hydrogen and chlorine, but it is due to the more rapid reaction along the following route:

$$Cl : Cl + Cl \cdot Cl \rightarrow Cl : Cl \cdot Cl \cdot Cl \cdot Cl \rightarrow Cl \cdot + Cl \cdot$$

As a result of this reaction, the final product is not produced. The greater radical formation rate in this route is conditioned by the fact that the bonding energy in Cl$_2$ is much smaller than in H$_2$.

When studying the interaction mechanism for chlorine with hydrogen at high temperatures, it was found that as a result of direct interaction of chlorine molecules and hydrogen, less than 0.001% of the final product is formed. That is, after the formation of about 0.05% of the radicals from Cl$_2$ the reaction proceeds along the chain radical route.

Thus the molecules can start an interaction between themselves. This interaction proceeds along the same mechanism:

\textbf{association - electronic isomerization - dissociation.}
However, this interaction proceeds much slower than does the interaction of active species (first of all — radicals and ions) with saturated molecules. This is conditioned by: a much smaller energy gain during the formation of the initial associate: *saturated molecule -- saturated molecule* as compared to the associate: *radical - saturated molecule*; a great loss of energy as a result of the isomerization reaction of the initial associate; a smaller electronic isomerization speed.

The greater activity of the radicals and ions (as compared to that of saturated molecules) is caused by: 1) a greater bonding energy of the *radical - saturated molecule*, 2) a greater associate isomerization rate, and 3) a greater energy gain during isomerization (as a result of which the number of covalent and VWBs does not change). Interactions between saturated molecules proceed along the chain mechanism; radicals or ions play the role of the active intermediate species.

There is almost no reaction between saturated molecules at normal conditions (T = 20°). The reaction speed between saturated molecules increases abruptly when there are active species like ions, radicals, etc. in the system.

In cases where the initial saturated molecules form stronger bonds with each other, than do the common VWBs, and where the formed associates turn into electromers, which have electronic energies identical to those of the initial associates, as a result of electronic isomerization, the interaction between these molecules proceeds with a great speed, usually limited only by diffusion. Examples of such reactions are the dissociation of salts in water, the neutralization of acids with alkalis, and the Lewis bases. These reactions have been described in detail above.

These reaction speeds practically do not depend on the temperature, which implies that the temperature does not have any influence on the electronic isomerization speed, which is much greater than that of the diffusion.

The paradigm, regarding the fact that reactions occur as a result of the collision of molecules with high kinetic energies, has existed for more than 150 years.

In 1868 Lotar Mayer announced: “Chemical phenomena must be treated as if they were problems of
mechanics.” This announcement serves as an epigraph to the chapter Rates and Mechanisms of Chemical Reactions by Richard E. Dickerson, Harry B. Grey, and Gilbert P. Haight, Jr. issued by Chemical Principles in 1979. In textbooks already issued at the beginning of the twenty-first century, there are visual aids for students that illustrate drawings where the interacting molecules approach each other at a great speed thus then they collide and break up:

Relative to the model for the observation of the influence of the parameters on the reaction speed, this is limited by the observance of the influence of the temperature and of the initial substance concentration on the reaction speed.

To illustrate the model, precipitation reactions are given, then there are reactions for the neutralization of acids via bases, and there are oxidation-reduction reactions proceeding in compounds.

All these reactions proceed at room temperature. The kinetic energy of molecules at room temperature is close to 2 – 4 kJ/mol, while the bonding energy of the breaking bonds during the reaction amounts to 200 – 500 kJ/mol. That is, those molecules that have enough kinetic energy to break the initial bonds are measured by the value of $e^{-100}$.

In the framework of the formerly, and still existing, paradigms, saturated molecules enter the reaction.

During the 150 years of the existence of the mechanical approach to chemical phenomena, the electron
was discovered, atom structure was elucidated, it was resolved that chemistry was actually the change of potential energy of the electrons in the outermost shells of the atoms.

During the existence of the paradigm that was confirmed only by the calculations of three or four reactions of the $H_2 + I_2 \rightleftharpoons 2HI$ type, it was found that these reactions proceed along the radical mechanism.

The mechanisms of millions of reaction had been studied — mainly in organic chemistry.

Already, more than 50 years, reactions in organic chemistry are divided into

1) nucleophyl reactions (with active anion particle),
2) electrophyl reactions (active cation particle) and
3) radical reactions.

It was found that ions and radicals enter reaction with saturated molecules. It was also found that the speed of their interaction with the molecules was by 10 orders of magnitude greater than the speed of the separate molecules’ interaction.

In 1982 we offered the theory of elementary interactions (TEI), which was a chemical theory, but not a mechanical theory of chemical reactions. This theory proved that the main role in breaking the old chemical bond is played by the transition of the bonding electrons from the old bond to the new one, formed in the course of the reaction.

As a rule, in the course of this process, the absolute value of the potential energy of the electrons increases. That is, the electrons in the products of the reaction are closer to the nuclei than they are in the initial products. The general models of chemical reactions for the interactions of ions and radicals with saturated molecules can be illustrated thus:

For cations:
$$A^+ + B : C \rightarrow A^+ \ldots B : C \rightleftharpoons A : B \ldots C^+ \rightarrow A : B + C^+$$

For radicals:
$$A^{\cdot} + B : C \rightarrow A^{\cdot} \ldots B : C \rightleftharpoons A : B \ldots C^{\cdot} \rightarrow A : B + C^{\cdot}$$

For anions:
$$A^{\cdot} - + B : C \rightarrow A^{\cdot} - \ldots B : C \rightleftharpoons A : B \ldots C^{\cdot} \rightarrow (A : B) + C^{\cdot}$$
In the case of cations and radicals, the breaking of the old bond and the scatter of the atoms formerly bonded by this bond, is conditioned by the repulsion of the nuclei of atoms B and C because of the absence or decrease of the bonding electrons that were situated between them.

In the case of anionic reactions, the scattering of the atoms is conditioned by the repulsion between the electrons of the outermost shell of atom B and anion C\(^-\).

**What is the physical nature of the phenomenon called electron-nuclear isomerization?**

Answer: The electrons in the molecules are situated in energy minimums of 1-2 eV.

But first let’s take the question which arises in this connection:

**At the expense of what energy does the electron transit from one minimum to another?**

The difficulty in answering this question was caused by one of the main principles of quantum mechanics, which presupposed that the electron could not change its energy in such small portions as 2 or 3 eV.

Traditionally, the energy exchange between electrons was never presupposed in quantum chemistry, while in the framework of our theory, the energy exchange between electrons is not only presupposed, but is even proven by the exchange mechanism via the energy exchange between the electrons.

The electronic energy in molecules is defined by the energy of the nuclei. The Maxwell-Boltzmann law describes the distribution of the vibrational, rotational, and translational energies of the nuclei. Relatively, we can suppose that this law describes the distribution of the electrons’ energies as well.

Besides this energy-transmitting mechanism, which can be regarded as a mechanism of translational movement, the atomic systems (electrons and nuclei) should also have a mechanism for changing the vibrational energy.
If, in a mechanism of translational movement, the energy transits from particles with a greater energy to particles with a smaller energy, then, in the case of vibrational energy, the energy transition is defined by the vibrational phase, and not by the energy.

Recall the energy exchange between pendulums vibrating on one axis. Both mechanisms allow us to presuppose an accumulation of sufficient energy on the minor portions of electrons, so that the latter could overcome the barrier that divides the minimums, since the average energy of only the outermost electrons in the system is equal to 12 eV.

The evaluation of the barrier energy that the electrons have to overcome, is possible judging by the following consideration:

According to the chemical bonding theory, the energy gain during chemical bond formation is conditioned by the approach of the nuclei to the bonding electrons located between them. In system D ... H : T, the transition of the electrons from covalent bonding (H : T) to VWB (D ... H) with the formation of D : H ... T, is connected with the receding of the electron from atom T and its approach to atom H. That is, the topmost barrier limit, during the transition of one electron from bond H : T onto atom H, amounts to half of the energy gain (enthalpy) during bond formation and is equal to 1 eV.

The receding from one nucleus of atom T with a simultaneous approach to the nucleus of atom (H) does not significantly change the general potential energy of the system, and therefore, the height of the barrier is much lower (close to zero) and not 1 eV.

However, if we consider that the electron recedes from atom T and approaches two D ... H atoms during the transition, then the height of the barrier is equal to 0 — 0, 2 eV; that is, a height that is greater than what the electrons with an average energy of 12 eV can overcome.

The electron in the atom has kinetic energy of about 10 eV. The following equation for kinetic energy

\[ E = \frac{mv^2}{2}, \]

helps to evaluate the speed of the electrons:
\[ v = (2E / m)^{0.5} = (2 \cdot 10 \cdot 96 \cdot 10^3 / 9.1 \cdot 10^{-31} \cdot 6.02 \cdot 10^{23})^{0.5} \]
\[ \approx 10^6 \text{ m/ sec} = 10^{16} \text{ Å/ sec}. \]

This speed can be compared with the transitional speed of an electron measured experimentally and calculated as follows:

\[ v = 10^{17} e^{-2R/L} \]

where \( R \) is the distance Å (in our case 1Å); and \( L \) is the coefficient equal to 6.5 in conjugated systems, and — 0.7 in non-conjugated ones.

According to this equation, the transitional speed of the electron for conjugated systems can be estimated at \( 10^{17} \text{ Å/sec} \), while for non-conjugated ones — \( 10^{16} \text{ Å/sec} \), i.e., values close to those already calculated. The above-mentioned explanation and the data obtained from the experiment, coincide semi-quantitatively.

As mentioned above, the vibrational system can contain another mechanism, which imitates the transition of electrons. In this case it does not really transit but simply passes its energy to another electron, which happens to be rotating, for example, in a parallel circle.

As a result of this exchange, the bond that had hitherto been covalent, for example, in the system \( \text{D} \ldots \text{H} : \text{H} \), becomes a VWB, and vice versa — the system becomes \( \text{D} : \text{H} \ldots \text{H} \). The time of these transitions can be evaluated by the electron’s rotation frequency, which is about \( 10^{16} \text{ sec} \). The simultaneous existence of both mechanisms is possible.

The mechanism, being characteristic of translational movement, should bring the system to equilibrium as far as the nuclei are concerned. The system is in dynamic equilibrium defined by thermodynamics, i.e., the speed of the mutual transitions is defined by the free energy change.

In the vibrational mechanism the system transits from one state to another with an identical speed, irrespective of the change in the free energy. Indeed, according to the experiment, there are cases of electronic transition when the transition speed depends on the free energy change, and cases when it does not.
The mechanism, which is usually given in textbooks, presupposes a tunnel transition for electrons. At present this popular mechanism offered by R. Markus (Nobel Prize winner in 1993) supposes that the tunnel transition is a rare phenomenon.
10** C A T A L Y S I S

As indicated in the previous section, the concentration of active species can be created thermally (heating the reaction system), by radiation, or by electric charges.

Another way of creating the necessary concentration of active species in the system is by introducing available active species like ions, radicals, or substances causing the dissociation of initial substances into active species, or substances that dissociate into ions and radicals much easier than the initial saturated molecules.

Examples of reaction acceleration at the expense of substances causing the dissociation of the initial substances into active species are reactions in water solutions where the initial substances (salts) dissociate into ions. In such cases the mechanism of the reactions does not change. The reaction proceeds along the chain ionic or radical mechanism.

The acceleration of a catalyst reaction by introducing active species into the system (radicals, ions, conences, etc.) is described in textbooks. The reactions most commonly offered are as follows:

1) \( \text{RCO}_2R + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{RCO}_2\text{H} + \text{ROH} \)
2) \( \text{Cl}_2 + \text{H}_2 \xrightarrow{\text{Cl}} 2\text{HCl} \)
3) \( \text{SO}_2 + \text{O}_2 \xrightarrow{\text{NO}} \text{SO}_3 \)
4) \( (\text{CH}_2 = \text{CH}_2)n \xrightarrow{\text{R}} (-\text{CH}_2 - \text{CH}_2)n \)
5) \( \text{O}_3 \xrightarrow{\text{Cl}} \text{O}_2 + \text{O}^- \)
6) \( \text{RCO}_2\text{R} \xrightarrow{\text{OH}} \text{RCO}_2 + \text{ROH} \)

The acceleration mechanism of the hydrolysis process in compound ethers in the presence of bases can be illustrated thus:
In the presence of bases, the concentration of hydroxyl ions is by many orders of magnitude greater than in water.

When the concentration of NaOH is equal to 0.01 mol/L, the concentration of hydroxyl is \(10^5\) times greater than its concentration in pure water. This means that the catalyst does not change its route but it does increase the concentration of hydroxyl anion, which directly starts interaction with compound ether.

This mechanism is analogous to the well-known nucleophyl substitution mechanism:

\[
\text{Cl}^- + \text{CH}_3\text{Br} \rightleftharpoons \text{Cl}^- \ldots \text{CH}_3\text{Br} \rightleftharpoons \text{Cl} \ldots \text{Br}^-
\]

The formation of the associate and the electronic isomerization of this associate into another associate were studied via spectral analyses.

The acidic catalysis of ether hydrolysis can be illustrated by the following scheme:
On the other hand, according to the theory of elementary interactions (TEI), the molecular interaction of substances is not a forbidden route; the above-cited examples are simply much slower than the catalyst reaction. As previously indicated, the reason for the slow molecule interaction is the low concentration of intermediate associates.

Another way of accelerating the reaction is by introducing substances in the presence of which molecules can react as if directly — without the participation of active particles of ions or radicals formed out of the latter or especially added.

As indicated above, the low mutual interaction speed of the saturated molecules is conditioned first of all by the following: a low concentration of the initially formed associate, a low concentration of an isomerized associate. Both of these reasons are conditioned by a small bonding energy between the molecules in the associate and by a small electronic isomerization speed. That is, in order to have the molecules react among themselves; we must introduce a substance, which forms stronger bonds with both molecules.
Direct interaction of saturated molecules (AB and CD) in the presence of a catalyst (K) can be shown on a scheme as follows:

\[
\begin{align*}
1 & : AB + K \rightarrow ABK \\
2 & : ABK + CD \rightarrow ABKCD \\
3 & : ABKCD \rightarrow ACKBD \rightarrow AC + BD + K
\end{align*}
\]

That is, at the end of the reaction we get the final products and the initial catalyst, i.e., the catalyst does not undergo any chemical changes as a result of this reaction. The use of substance K as a catalyst makes bonds AB–K and ABK–CD much stronger than the VWB AB–CD bond. However, the rate-determining step is step 4. Saturated molecule bonds with catalysts break in the course of this reaction. Thus, to accelerate the reaction in the presence of catalyst K it is important that bonds like catalyst – saturated molecule are not very strong.

Previously, in chapter *Chemical Bonding* we described three types of bonds: VWB, DAB, and covalent bonds (including homo-atomic and hetero-atomic covalent bonds and dynamic bonds).

That is, the catalyst should form bonds with saturated molecules, and these bonds must be stronger than VWBs and not so strong as covalent bonds. It can be supposed that if there is acceleration of the molecular interaction, the catalyst will form DABs and dynamic bonds with the reacting molecules. The capacity for forming DABs and dynamic bonds is defined by the presence of free space for electrons in the outermost shells of the atoms and/or by the presence of electrons that do not take part in chemical bond formation.

The greatest number electrons that do not partake in chemical bonding and have lots of free space in the outermost shells are found in metals situated in the centers of the 4th and 5th periods in the *table of elements*. The maximal number of electrons in the outermost shells of these elements is equal to 18, while the outermost shells of the atoms of these elements, situated on the surface of the metal, are about
half-filled with electrons that do not partake in bond formation. Thus, it seems quite natural that these metals are most often used as catalysts in chemical processes.

The role of the catalyst, in this case, is not only in bond formation with both reagents, but also in guaranteeing electronic isomerization in the intermediate complexes (associates) located in the middle of metals of the 4th and 5th periods that greatly differ from nonmetals that belong to these periods because of their electro-conductivity (the rapid transition of the electrons).

The great electro-conductivity of these metals is an additional property that helps to realize their great catalytic priority as compared with nonmetals located in the same groups of the table of elements, which are poor conductors of electric current.

In the chapter devoted to chemical bonding and chemical structure, we have elucidated the fact that DABs are mostly possible between saturated molecules that include atoms with non-bonding electron pairs and with molecules that include atoms with incompletely filled outermost electronic shells. Such shells have surface atoms of hard substances and coordinately unsaturated compounds called conences.

It is these atoms that catalyze molecular interaction, which are accomplished in industrial processes when synthesizing ammonia out of hydrogen and nitrogen, in getting aldehydes out of hydrogen (H₂), carbon oxide (CO), and olefins in the process of hydroformylation, etc. The coordinately unsaturated atoms in the ferment are catalysts of biochemical transformations.

As compared to the first method for accelerating chemical reactions, where the reaction accelerates at the expense of introducing active species (ions, radicals) to the system, the second method (acceleration of the direct molecular interaction) has priority from the point of view of selectivity; i.e., as a result of these processes, we generally get individual products.

Conence homogeneous catalysis is, from the viewpoint of both methods, a mixed type of catalysis. Here the acceleration is gained at the expense of the increase of the conence concentration (i.e., active species). The reaction
proceeds along the chain mechanism, but during this reaction the initial molecules do not disintegrate, and they do not form VWBs in the associates (which is characteristic of the first method for accelerating reactions). They form DABs.

The main driving force of chemical reactions is the potential energy of the attraction of the electrons to the nuclei, which decreases during the reaction. That is, as a rule, the electrons are closer to the nuclei in the reaction products than they are in the initial compounds.

Before we go over to details, the interpretation of catalysis in the light of the new conception, let us first have a detailed look at the driving forces in a chemical reaction. As indicated above, the rate of any chemical transformation is defined by the breaking speed of the existing chemical bonds and of those being formed, as well as by the concentration of initial and intermediate substances.

Besides the energy, accumulated on the vibrational freedom stages, we can use the energy of the preceding exothermic, chemically activated reaction to break the chemical bonds.

The driving forces of a chemical reaction are the chemical energies and thermal. The chemical reaction rate increases with the increase of the driving forces (i.e., with a thermal energy increase and with better consumption of energy in the preceding exothermic reaction), which also increases with the decrease of the energy necessary for the breaking of the bonds during the reaction when the bonds weaken. Such weakening of the bonds in saturated molecules occurs when the ions, radicals and conences join these molecules, and after isomerization in associates. Relatively, the speed of the chemical reaction increases significantly when the ions, radicals and conences (chemically active particles) appear in the system.

The electronic isomerization rate is defined 1) by the distance between atoms (whose shell structures changes during isomerization) and 2) by the type of bonding, the reaction rate increases when chemical substances are introduced into the system. These substances increase the concentration of chemically active species, thereby easing electronic isomerization and allowing the use of the energy of the
preceding exothermic chemical reactions in the forthcoming ones.

Substances accelerating the reaction along the above-mentioned mechanisms, are catalysts whose essence, in the general approach, becomes more comprehensible when compared with such common definitions as:

A catalyst is a substance that accelerates a reaction by conducting it along another route, which requires less activation energy.

In contrast to the independently existing catalysis theories and studies of routes for catalyst reactions, logically not connected with them, the above mentioned main methods of acceleration can be considered as a general catalysis theory — where the decrease of the reaction's activation energy is just one of the many consequences resulting from this theory.

For ionic, radical, and conence catalyst reactions, the chemical activity of species is defined by the ease of electronic isomerization in the intermediate associates produced by themselves. The further weakening of the bonds-to-be-broken (during isomerization) leads to the decrease of thermal energy, which is so necessary for their breakdown.

Consequently, the consumption of thermal energy decreases. This has been shown experimentally: the temperature has less influence on the reaction speed (a decrease of activation energy); and the more important become the routes that proceed with chemical activation. That is, one of the most commonly used approaches to catalysis is the general chemical explanation of the work of catalysts.

Of great importance here are also the catalysis theories that are not empirical dependencies, but experimental correlations, offering quantitative dependencies of reaction speed on measured initial catalyst parameters with their own non-contradicting explanations in the general approach.

Thus, on the first stage, the chemical catalysis theory — based on the knowledge gained in the process of studying elementary chemical reactions — both model catalyst transformations (interaction of special chemically active particles) and complex catalyst transformations (studies of elementary stages) allowed us to explain the main kinetic
regularities of chemical reactions including the acceleration mechanism.

The next problem was to deepen the understanding of questions that were not clear in the framework of the TST: *Why are ions, radicals, and conenes more active than saturated molecules? What kind of mechanism weakens the chemical bond? How does the weakening of a chemical bond influence the speed rate of the chemical reaction?*

The answers to these questions depended on the physical essence of chemical bonding that remained misunderstood. It was not enough to have only qualitative notions like: “*Nuclei are attracted by electrons that are situated between them,*” to explain kinetic and catalyst dependencies.

This is why explanations about atom structure, elementary, complex, and catalyst chemical transformations are seen as the next step in better comprehension of the essence of chemical phenomena.

It was mentioned above, that the correlated catalysis theories have come from the general catalysis theory, which was based on a new understanding of the nature of chemical bonding and chemical reactions.

Thus in Balandin's multiplet theory a correlation was noted between catalyst reaction speeds on the one hand, and the bonding energy of substances with a catalyst, and the relative geometry of a catalyst and reagents – on the other. These dependencies, along with the described kinetic regularities of simple reactions, remained empirical in accordance with the TST when energy was required for the transitional state's formation stage. Bonding energy, whose nature was incomprehensible, had no logic connections with chemical reaction rates.

The explanation about kinetic regularities in chemical reactions without introducing TST speed parameters, gives us to understand the principles of energetic correlation, and also to bring the defined empirical dependencies into the sphere of quantitative experimental data on chemical theory in correlative kinetic dependencies and in resonance rules.

The new approach to the bonding theory shows the logic connection between the electronic structure of chemical substances and the speed of their chemical transformations,
which makes the observed correlational dependence more comprehensible. The latter, as in the multiplet theory, shifts the defined dependencies from the category of empirical correlations to those of experimental.

Now let us return to the most general explanation of homogenous and heterogenous catalysis. Let’s take homogenous catalysis and the catalytic possibilities of one of the well studied universal catalysts: cobalt hydrocarbonyl HCo(CO)$_4$ that dissociates in water into H$^+$ and Co(CO)$_4^-$.

Besides, cobalt hydrocarbonyl dissociates according to this scheme:

$$\text{HCo(CO)}_4 \rightleftharpoons \text{HCo}^\psi (\text{CO})_3 + \text{CO}$$

where $^\psi$ is the coordinated unsaturated compound.

Experimental data has shown that the outermost shell of cobalt in complex compounds becomes saturated (i.e., does not bond any more electrons) if there are 18 electrons. Cobalt compounds in which there are fewer than 18 electrons are known as coordinate non-saturated compounds.

According to the electronic isomerization principles or the resonance theory's empirical rules, compound HCo$^\psi$ (CO)$_3$ can exist in a number of electronic isomers whose concentration is defined by the energy of the isomers. As an example, let's examine a concise row of isomers:

$$\text{H} : \text{Co}^\psi (\text{CO})_3 \rightleftharpoons \text{H}^+ \text{Co}^- (\text{CO})_3$$

Thus, cobalt hydrocarbonyl can form not only ions in solutions, but can produce proton- and anion-catalyst reactions, which appear on the elementary stages as electrophyl and nucleophyl, and they can also conduct radical reactions.

HCo$^\psi$ (CO)$_3$ is a conence and therefore it can join other ligands like olefins. It is of interest to cite the electronic isomerization of a $\pi$-complex formed of HCo$^\psi$ (CO)$_3$ and an olefin. According to the main thesis that defines the possibility
of having electronic isomers, one of the possible schemes for the isomerization of the $\pi$-complex, is represented as follows:

$$
\text{CH}_2 : \text{CH}_2 \quad \text{C}^+\text{H}_2 : \text{CH}^- \quad \Leftrightarrow \quad (\text{CO})_3\text{Co}^- : \text{H}^+ \quad \text{H}^+ : \text{Co} (\text{CO})_3
$$

The probability of the $\pi$-complex in the system, can be explained, in part, by the compensation of energy formation in less probable carbons, carrying a charge at the expense of decreasing the interelectronic repulsion that is supposed to be in tri-central four-electron bonds in $\pi$-complexes. The value of compound II in other possible transformations like the following

$$
\text{C}^+\text{H}_2 : \text{CH}_2 \quad \text{CH}_2 - \text{CH}_3 \quad \rightarrow \quad \text{Co} (\text{CO})_3\text{H}^+ \quad \text{Co} (\text{CO})_3
$$

can be significant at the expense of the high rate of the given reaction proceeding along the ionic mechanism.

Cobalt hydrocarbonyl is chosen as an example because of its electronic structure, which is very much like that of heterogeneous catalysts whose topmost atoms have electron vacancies (holes) and non-bonding (surplus) electrons.

This fact also illustrates a mechanism for accelerating the reaction at the expense of the association reaction energy in dissociation reactions. The action of catalysts is regarded as chemical activation.

The interaction of conences, ions, and radicals with initial reagents runs as follows:

$$
\text{HCo} (\text{CO})_4 + \text{CH}_3\text{CH}_2\text{Co}^v (\text{CO})_3 \rightarrow \text{HCo}^v (\text{CO})_3 + \text{CH}_3\text{CH}_2\text{Co} (\text{CO})_4.
$$

This explains the widely known feature of the complex catalytic phenomena — the rapid procedure of the whole catalytic cycle, as compared to its model elementary stage.

Being capable of active association, conences, radicals, and ions are considered statically activated, while the intermediate compounds that receive the energy of exothermic reactions, are dynamically activated. Schematically, static and
dynamic activation can be illustrated on the example of the formation of the \( \pi \)-complex from olefin and cobalt hydrocarbonyl and the transformation of the \( \pi \)-complex into alkylcarbonyl:

\[
\text{Slow} \\
\text{HCo}(\text{CO})_4 \rightarrow \text{HCo}^{\psi}(\text{CO})_3 + \text{CO} ;
\]

\[
\text{Rapid} \\
\text{CH}_2 = \text{CH}_2 + \text{HCo}^{\psi}(\text{CO})_3 \rightarrow \left[ \begin{array}{c} \text{CH}_2 = \text{CH}_2 \\ \text{HCo}^{\psi}(\text{CO})_3 \end{array} \right]^{*} \rightarrow \text{CH}_3\text{CH}_2\text{Co}^{\psi}(\text{CO})_3 .
\]

* Here and further the dynamically activated particles are indicated.

The presence of dynamically activated particles in catalyst reactions and the possibility of forming statically activated particles along the chain mechanism cannot be observed in model reactions with the possibility of a chain formation in statically activated compounds.

The given examples also show the actual work of catalysts: the process in a catalyst proceeds via intermediate products, which are statically or dynamically activated, defining the high speed of catalyst reactions.

To illustrate the catalyst mechanism, we might consider the hydroformylation reaction scheme that runs as follows:

\[
\begin{align*}
\text{I} & : \text{HCo} (\text{CO})_4 \rightleftharpoons \text{HCo}^{\psi} (\text{CO})_3 + \text{CO} ; \\
\text{II} & : \text{HCo}^{\psi} (\text{CO})_3 + \text{CH}_2 = \text{CH}_2 \rightarrow \text{CH}_2 \rightarrow \text{CH}_2 \left[ \begin{array}{c} \text{HCo} (\text{CO})_3 \end{array} \right] ;
\end{align*}
\]

\[
\begin{align*}
\text{III} & : \left[ \begin{array}{c} \text{CH}_2 = \text{CH}_2 \\ \text{HCo} (\text{CO})_3 \end{array} \right] + \text{HCo}^{\psi} (\text{CO})_3 \rightarrow \left[ \begin{array}{c} \text{CH}_2 = \text{CH}_2 \\ \text{HCo}^{\psi} (\text{CO})_3 \end{array} \right] + \text{HCo} (\text{CO})_4 .
\end{align*}
\]
Such detailing allows better comprehension of the conences in catalysis. The presence of vacancies in the conences (with about the same energy) makes the electronic isomerization process possible, therefore causing the appearance of ions and radicals. The formation of ion and radical associates with saturated molecules (stage XII) followed by electronic isomerization, leads to the formation of weak bonds which can be broken by the energy discharged when the ligand is bonded to the conence (stage XIV).

Homogenous conence catalyses, unlike heterogenous ones, have a maximal available surface, and thus, their higher activity is not unusual. The combination of chemical and dynamic activation possibilities in conences explains the importance of their role in biological catalysis.

Examples of mechanisms for accelerating reactions via the first and second methods are well described in the book *How Chemical Bonds Form and Chemical Reactions Proceed* (pages 167 and 272-280), to say nothing of world chemical literature.

Unlike radical and ionic chain reactions, works proving the existence of conence reactions, conence chain reactions, and conence chain catalysis have been published mainly in the Russian language. To get an idea of these publications, the translations of some of these works on conence reactions are given in the supplement.
11** PHYSICAL AND CHEMICAL PROPERTIES OF SUBSTANCES

11.1 PHYSICAL PROPERTIES OF SUBSTANCES

During the development of chemistry, new terms were introduced: *atom* – the smallest species of an element; *molecule* – the smallest species of a substance. Transformations of substances proceeding without any change of the molecule structure are called *physical transformations*, while transformations that proceed with a change of the molecule structure, are called *chemical transformations*.

It is not difficult to see the difference between the physical and chemical transformations. Physical transformations include *melting* and *evaporation* of substances; physical properties include *glitter*, *color*, and *electroconductivity*. Chemical transformations deal with chemical properties like *chemical reaction capabilities*. *Solubility* and *dissociation* occupy an intermediate position.

According to our theory of chemical bonding, bonds that break in the course of physical and chemical processes have identical electrostatic natures but they differ relative to their energies.

There are 3 main types of bonds:

1) Type I includes bonds in which the energy’s affinity to the electrons of both bonding atoms is consumed (covalent, homopolar and heteropolar bonds).

2) Type II includes bonds where the affinity energy of only one of the bonding atoms is consumed [donor-acceptor bonds (DABs)].

3) Type III includes bonds in which the affinity energy is not consumed in either of the atoms [Van der Waals bonds (VWBs)].

These three types of bonds have one and the same electrical nature. The main energy gain during bond formation is conditioned by the concentration of the positive charge (70%-90%) and the atoms’ affinity towards the electron (10%-30%). In spite of the fact that the atom’s affinity to the electron is less than 30%, the elimination of the latter can decrease the
bonding energy by ten times. This is because 30% of the attraction energy (attraction of the electrons to the molecule's nuclei) is defined by the value of 300 kJ/mol, which is commensurable with the bonding energy.

The above-mentioned correlations between contributions have to do with the attraction power between electrons and nuclei. In fact, such a distribution of energy is but conditional. Likewise, the whole energy gain is achieved at the expense of the increase in the effective charge of both nuclei during molecule formation.

Because the nature of all the three types of bonds is identical, these bonds differ only in the energy applied to break them. In order to break the bond of type I, energy of 50 to 500 kJ/mol is required; bonds of type II require 25 to 200 kJ/mol; bonds of type III – 5 to 30 kJ/mol.

According to thermodynamics, and considering the electronic heat capacity, the energy of the system can be defined by the equation: $E = 10 RT$ (where $R$ is the Boltzmann constant and $T$ is the absolute temperature). This equation defines the temperatures of three types of bond breaking: types I, II, and III; respectively: 4,000 K; 1,500 K; and 400 K.

As already indicated, an atom is usually bound to other atoms by various types of bonds. For example, in solid metals each atom is bonded with other MEB, dynamic, single, double, or triple covalent bonds, or with DABs. Historically, this type of bond has been singled out into a separate kind called metallic bond.

Among the special bonds are conjugated bonds (combinations of double and single bonds) and aromatic bonds, like those in benzene molecules (where single and double bonds alternate with each other). Each of these bonds is manifested in special physical and chemical properties of substances.

If an atom is connected to other atoms by various bonds, the breaking energy of the weak bonds increases, while that of the strong bonds decreases. For example, the bond-breaking energy in benzene comprises 520 kJ/mol, while the breaking energy of a single bond is equal to 350 kJ/mol and the same of a double bond is equal to 600 kJ/mol. As a rule, we can assume that the energies of the weak bonds increase as do many of the strong bonds and their bonding energies.
Most of the strong covalent bonds have elements in which the outermost electronic shell is half-filled. When the number of electrons in this shell changes, as compared to the half-filled layers, the bonds break more readily. When the number of electrons decreases, the quantity of DABs increases at the expense of a decrease in the number of covalent bonds. When the number of electrons increases, the covalent bonds decrease in number. Thus, instead of DABs, we get very weak VWBs.

Carbon, in the form of a diamond, (carbon forms 4 identical bonds) is the hardest substance ever. A diamond’s compression coefficient is equal to $0.16 \cdot 10^{-6}$ cm$^2$ kg$^{-1}$, its melting-point is higher than 3,550° C, and its boiling temperature is 4,827° C. Carbon crystal has the highest evaporation heat – 718 kJ/mol; and melting heat of 104 kJ/mol. Its C-C bond is the strongest covalent bond. The physical properties of carbon are in agreement with our new theory of chemical bonding.

In the case where one electron is situated on the atom’s outermost shell and the FIE of this atom is less than 500 kJ/mol, we should expect an abrupt decrease in the bonding energy of metals formed from such atoms; this is followed by an abrupt decrease in their melting, boiling heat and temperatures. The properties of alkaline metals (Li, Na, K, etc.) differ greatly from the properties of other metals.

For example: melting temperatures vary from 28° C (Cs) to 179° C (Li); their melting heat amounts to 2 kJ/mol (Cs) and 3 kJ/mol (Li); their evaporation heat is equal to 67 kJ/mol (Cs) and 148 kJ/mol (Li). These metals are extremely soft. According to our theory, the distance between the nuclei in these metals is greater than in other metals, which is noticeable in their very low density; indeed, lower than that of water.

Physical properties depend not only on the number of electrons in the outermost shell, they also depend on the kind of bond the given atom forms. Atoms can form not only single bonds, but also double and triple ones. For example, the outermost shells of nitrogen (N) and oxygen (O) atoms are filled to the limit by 8 electrons. In liquid and solid states, both
N₂ and O₂ have multiple bonds between the atoms, and VWBs – between the molecules.

The melting temperature for solid nitrogen is -209° C, the melting heat is 0.72 kJ/mol, the boiling temperature is -195° C, and the evaporation heat is 5.38 kJ/mol. Oxygen has data close to this, the boiling temperature being -218° C, and the melting temperature being -183° C.

It is known that the physical properties of elements are influenced not only by electronic structure, but also by the atoms' masses of these elements. The dependence of the atomic masses on the density of the substances is understood; the influence of the nuclei's mass on the evaporation heat and on the boiling point is evident from the kinetic gas theory, according to which — the greater the element's atomic mass, the smaller its kinetic energy at the same temperature.

Atoms and molecules with a greater mass, when their potential energies are identical, achieve their kinetic energies at a much higher temperature. Besides depending on the mass of the nuclei, the physical properties of substances also depend on spatial structure of substances, which is described in the chapter devoted to the same.

Now let us return once more to the explanation of the regularities concerning the physical properties of substances in the framework of our theory of chemical bonding.

When the number of electrons in the outermost shell is equal to 4 (half of the maximal filling quota), the substances have the highest boiling temperature and evaporation heat. Any changes in the amount of electrons leads to a decrease in these values. The expected dependence is obvious in the first 20 elements of the periodic table with a decrease in the number of electrons. This dependence is even more obvious when comparing the physical properties of alkaline and other metals, as previously indicated.

As previously shown, the decrease of the evaporation heat and boiling temperature of nitrogen and oxygen is achieved by the formation of multiple bonds. The anomalous properties of halogens are likewise explained by the complete filling of the outermost electronic shell of halogen atoms during the formation of dual atomic molecules. The dependence of dual atomic bonding energy on the FIE proceeds via the maximum. The elements in the middle of the
period have maximal energy bonds; i.e., atoms with 4 electrons in the outermost shell form not only a maximal number of covalent bonds, but also – the strongest ones.

Thus, we can expect that the dependence of the physical properties of simple substances on the elements’ FIEs have the same character as the dependence of homoatomic bonding energies in dual atomic molecules on the FIEs. A comparison of character dependencies of some elements' physical properties on the FIEs (table 11.1-1, figures 11.1-1 to 11.1-4) with dependencies of homoatomic bonding energies on the FIEs (see figures from 6.4-5 to 6.4-6) shows that these dependencies are identical. Also, table 11.1-1, figures 11.1-1 to 11.1-4 show the data received from studying normal (not anomalous) metals.

Additional confirmation comes from the anomalous behavior of zinc, cadmium, and mercury, which form weak covalent bonds. This is evident from their anomalous physical properties. For example, mercury (Hg) has a melting point of -38° C, a melting heat of 2.33 kJ/mol, a boiling point of 356° C, and a boiling heat of 58 kJ/mol. While the element gold (Au) and the following – thallium (Tl), have a melting point of 1,064° C & 302° C, a melting heat of 12.7 kJ/mol & 4.31 kJ/mol, a boiling point of 2,966° C & 1,457° C, and a boiling heat of 310 kJ/mol & 168 kJ/mol.

The physical properties of elements following calcium are well explained on the basis of our theory with the supposition that the outermost electronic shells of atoms can contain more than 8 electrons. A comparison of the elements' FIEs from #19 to #28 shows that when the nuclear charge increases from #19 to #28, the number of electrons in the outermost shell increases from #1 to #12. In the atoms of elements from #28 to #36 and from #47 to #54, 1 to 8 electrons fill the outermost shells.

The dependence of these elements' FIEs on their placement in the rows and the rules of formation relative to both covalent and donor-acceptor bonds, are analogous to the first 20 elements of the table. The physical properties of these elements are explained by the same rules.

For elements from #26 to #28, and from #44 to #46, the maximal amount of electrons in the outermost electronic shell can increase up to 18. Saturated shells appear in such cases. For
example, stable metal compounds obey the rule of the 18 electrons: V, Cr, Mn, Fe, Ni, Nb, Mo, Ru, Rh, Pd. It is no wonder that the carbonyls of these metals, under usual conditions, exist not only as liquids: Ni(CO)$_4$, Fe(CO)$_5$; but also as gases: HCo(CO)$_4$.

The physical properties of substances, besides being influenced by bonding energy and the amount of bonds that an atom can form, are also greatly influenced by the spatial structure of substances.

As already indicated in section 2.8, the angles between atoms are, as a rule, identical. The maximal distance between the bonds is conditioned by the mutual repulsion of the bonding electrons. When the distance is maximal, there is minimal repulsion energy, i.e., a minimal energy system.

However, the repulsion energy, which defines the spatial structure, slightly changes if there is a decrease in the angle between some bonds and, simultaneously, an increase in the angles between other bonds.

Thus, for example, carbon exists in the forms of diamonds and graphite. The angles between the bonds in a diamond are identical and comprise 109 degrees. In graphite the angles between three of the bonds are 120°, and there is a 90° angle between each of these three bonds and a fourth (on a perpendicular plane).

That is, the increase of the angle from 109 to 120 degrees between the three bonds, causing the decrease of the system's energy, compensates for the energy increase caused by the decrease of the angle from 109 to 90 degrees between the three bonds and the fourth. Graphite energy is smaller than diamond energy.

Interelectronic repulsion (between bonding electron pairs) leads to an abrupt decrease in the energy of the fourth bond, as compared to the bonding energy of the diamond. Graphite is a soft substance with a layer-like structure, while diamond is the hardest possible substance with an octahedron-like structure.
Table 11.1-1
Melting Point, Fusion Heat, Boiling Point,
Evaporation Heat of Simple Substances vs. FIE of Elements

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>FIE (eV)</th>
<th>MELTING POINT °C</th>
<th>FUSION HEAT (kJ/mol)</th>
<th>BOILING Point °C</th>
<th>EVAPORATION HEAT (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>5.1</td>
<td>97</td>
<td>2.6</td>
<td>882</td>
<td>90</td>
</tr>
<tr>
<td>Al</td>
<td>5.9</td>
<td>660</td>
<td>10.7</td>
<td>2467</td>
<td>291</td>
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<tr>
<td>Si</td>
<td>8.1</td>
<td>1414</td>
<td>2.4</td>
<td>2335</td>
<td>170</td>
</tr>
<tr>
<td>K</td>
<td>4.3</td>
<td>63</td>
<td>16.1</td>
<td>774</td>
<td>77</td>
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<tr>
<td>Sc</td>
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<td>1539</td>
<td>5.6</td>
<td>2727</td>
<td>305</td>
</tr>
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<td>1657</td>
<td>13.3</td>
<td>3260</td>
<td>397</td>
</tr>
<tr>
<td>V</td>
<td>6.7</td>
<td>1890</td>
<td>22.5</td>
<td>3000</td>
<td>456</td>
</tr>
<tr>
<td>Cr</td>
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<td>1890</td>
<td>23.3</td>
<td>2482</td>
<td>349</td>
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<td>25.9</td>
<td>2595</td>
<td>305</td>
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<td>30</td>
<td>3.3</td>
<td>2403</td>
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<td>2700</td>
<td>333</td>
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<td>817</td>
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<td>139</td>
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<td>65.9</td>
<td>220</td>
<td>254</td>
</tr>
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<td>In</td>
<td>5.8</td>
<td>156</td>
<td>65.9</td>
<td>2000</td>
<td>226</td>
</tr>
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<td>232</td>
<td>75.9</td>
<td>2270</td>
<td>290</td>
</tr>
<tr>
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<td>530</td>
<td>20.9</td>
<td>1635</td>
<td>190</td>
</tr>
<tr>
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<td>449</td>
<td>20.9</td>
<td>1390</td>
<td>85</td>
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<td>10.9</td>
<td>690</td>
<td>70</td>
</tr>
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<td>3027</td>
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<td>1440</td>
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</tr>
<tr>
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<td></td>
<td>1300</td>
<td>40.9</td>
<td>3000</td>
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</tr>
<tr>
<td>W</td>
<td></td>
<td>3387</td>
<td>55.9</td>
<td>5900</td>
<td>799</td>
</tr>
<tr>
<td>Re</td>
<td></td>
<td>3180</td>
<td>55.9</td>
<td>5627</td>
<td>707</td>
</tr>
</tbody>
</table>
Melting Point of Substances (in Row Na-Ga) vs. FIE of Elements

Figure 11.1-1
Figure 11.1-2
Heat of Fusion (in row Na-Ge) vs. FIE of Elements

![Heat of Fusion Graph](image)

Figure 11.1-3

Heat of Evaporation (kJ/mol) vs. FIE of Elements (in Row Na-Ge)

![Heat of Evaporation Graph](image)

Figure 11.1-4
11.2 CHEMICAL PROPERTIES OF SUBSTANCES

Until recently, the periodic law was generally formulated as follows:

"Properties of elements are in periodic dependence on the charges of their nuclei".

As experimental examples confirming this law, data were given on the FIEs, affinity, valence of elements, and identity of the chemical and physical properties of the elements from one group in the periodic table. This experimental data was not logically connected, but served as an illustration of the periodic law.

According to our theory, the chemical and physical properties of elements are defined by the FIEs of these elements and by the number of electrons in the outermost shells. Elements with close FIE values and the same number of electrons in the outermost shell should have almost identical chemical properties.

Experimental data on elements' FIEs and the number of electrons in the outermost shell change periodically, which leads to periodic changes in the chemical and physical properties of the elements. The periodic system of elements is the main experimental proof of the correctness of our theory of chemical bonding.

Our theory explains the property changes even when the number of electrons in the outermost layer is the same, while the FIEs change significantly.

For example, all the inert gases have 8 electrons in the shell while their FIEs decrease: \( \text{He} \ (24.58 \text{eV}), \ \text{Ne} \ (21.56 \text{eV}), \ \text{Ar} \ (15.76 \text{eV}), \ \text{Kr} \ (14 \text{eV}), \ \text{Xe} \ (12.1 \text{eV}), \ \text{Rn} \ (10.7 \text{eV}) \) which accounts for the differences in their chemical properties.

Now let's see, with the help of some concrete examples, just how our theory of chemical bonding together with the theory of Elementary Interactions (TEI) explain the chemical properties of substances.
The main chemical properties of substances are their capacity to react. According to TEI, substance A–B usually reacts with radicals, ions, and conences. As far as radical reactions are concerned, as already mentioned, they proceed along the following scheme:

\[
\begin{align*}
1 & \quad A:B + M' \rightarrow A:B \ldots M' \\
2 & \quad A' \ldots B: M \xrightleftharpoons{} A' \ldots B: M \\
3 & \quad A: B: M
\end{align*}
\]

The reaction rate is defined by stage 3 with a constant rate:

\[
W_3 = k C_{A\ldots B : M} e^{-E/RT}
\]

here \( C_{A\ldots B : M} \) is the concentration of \( A'\ldots B: M \); \( E \) is the energy necessary to break bond \( A\ldots B \) in compound \( A'\ldots B: M \); and \( W_3 \) is the reaction rate.

The concentration of \( A'\ldots B : M \) is defined by the radical concentration in the system (M) and by the degree of displacement of equilibrium 2 towards compound \( A'\ldots B: M \). The concentration of radicals in an M type system is defined by the bonding energy and the concentration of the substance M–M. Concentration M exponentially depends on the bonding energy, i.e., \( K = e^{-E/RT} \) where \( E \) is the bonding energy of M–M.

The equilibrium constant of isomerization stage 2 is proportional to the difference in the bonding energies of B:M and A:B, i.e., the greater the bonding energy in B:M, as compared with that of A:B, the more of compound A....B:M there will be in the reaction mixture. Here we have not considered the importance of the Van der Waals bonds (VWB) in both compounds, since these are weaker by more than one order of magnitude, as compared to covalent bonds. Thus, we have:

\[
W_3 = k_3 \exp (E_{BM} - E_{AB}) / RT
\]

here \( E_{BM} \) and \( E_{AB} \) are respectively the bonding energies in compounds BM and AB.
According to this reasoning, the most active radical reactions are molecules where the M–M bond is weak, and the B–M bond is strong.

In agreement with our theory of chemical bonding, a weaker bond is observed in diatomic molecules with the atoms' FIEs below 500 kJ/mol and over 1,400 kJ/mol (for homoatomic bonds); the energy of heteroatomic bonds increases proportionally to the difference between the FIEs of the atoms, which form these bonds. We can expect some active interaction of the molecules formed out of atoms having FIEs below 500 kJ/mol with those formed from atoms with FIEs over 1,400 kJ/mol.

In keeping with the FIE table, such groups of substances include alkaline metals (Li₂, K₂, Na₂, etc.) and halogens (F₂, Cl₂, Br₂, I₂). The interactions of these substance groups proceed, under normal conditions, with an explosion – due to the chain radical mechanism.

It is evident from our theory that radicals should form out of the molecules of alkaline metals since the covalent bonding energy in these molecules is smaller than that in the halogen molecules.

The correlation of interaction rates is defined by the bonding energy in the metals' molecules and by the difference of energies M–h and h–h where h is a halogen atom.

Bonding energy M–M in row Li-Na-K-Rb decreases, while the bonding energy of the M–h compounds increases. Thus, we can assume that the reaction rate of both the molecules and the radicals with halogens, will increase in this row.

Bonding energy h–h in row F₂-Cl₂-Br₂, according to our theory and the experiment, proceeds via the maximum: Cl₂ has the maximal bonding energy.

Bonding energy M–h decreases in the row F-Cl-Br-I because the difference in the FIEs decreases insignificantly in row Li-Na-K, while the halogens' FIEs change significantly. For instance, F₂ should react with the atoms of alkaline metals more vigorously than any other halogens; Cl₂ is much less active than F₂.

One of the TEI conclusions is that the molecules of a substance interact as active species (radicals, ions, conences).
Previously (before the elaboration of our theory of chemical bonding and the theory of elementary interactions) the reactions of alkali metals with oxides (including halogens) were regarded as oxidation-reduction reactions of the \( \text{M} + \text{h} \rightarrow \text{M} - \text{h} \) type. And it was absolutely incomprehensible how these reactions could proceed from the viewpoint of energetics, and how ionic molecules can exist in general.

A comparison of only the first and second ionization energies with the data on the affinity of the elements to the electron have shown that even the first ionization energies of the elements of the first group have a 2-fold greater affinity energy for fluorine (F) — the most electronegative element. That is, an interaction of the \( \text{Na} + \text{Cl} \rightarrow \text{Na}^+ + \text{Cl}^- \) type is endothermic to about 140 kJ/mol. The energy gain at the expense of the formation of bond \( \text{Na}^+ - \text{Cl}^- \) comprises a value smaller than 160 kJ/mol. That is, the bonding energy in molecule NaCl is, according to this calculation, about 20 kJ/mol, i.e., it breaks up at 100°C.

It is necessary to consider that in order to form radicals of sodium (Na`) and chlorine (Cl`) out of molecules, an energy of \( \frac{1}{2}(E_b\text{Cl}_2) + \frac{1}{2}(E_b\text{Na}_2) \); (where \( E_b \) is the bonding energy in molecules \( \text{Cl}_2 \) and \( \text{Na}_2 \) relatively). That is, it is necessary to use additionally 256 kJ/mol to break the bonds, and therefore, reaction: \( \text{Na}_2 + \text{Cl}_2 \rightarrow 2\text{NaCl} \) is endothermic, while reaction \( 2\text{NaCl} \rightarrow \text{Na}_2 + \text{Cl}_2 \) is exothermic, i.e., proceeding in the reverse direction. Thus, molecule NaCl is thermally unstable.

According to experimental results, reaction \( \text{Na}_2 + \text{Cl}_2 \rightarrow 2\text{NaCl} \) proceeds with an explosion thereby proving that it is exothermic. Thus, the experiment contradicts the theory qualitatively and not quantitatively, which proves the illogicality of the theory of ionic bonding, the TAC, and the TST.

In the framework of our chemical bonding theory, the calculated energy necessary to break the NaCl molecule into two radicals, is equal to 439 kJ/mol while the experimentally defined result was 455 kJ/mol. In the course of the reaction, one endothermic stage \( \text{Na}_2 \rightarrow 2\text{Na} \) which needs an energy of 36 kJ/mol in order to proceed, guarantees a possibility of a versatile procedure of two stages.
\[
\begin{align*}
\text{Na}^+ + \text{Cl}_2 &\rightarrow \text{Na}^\cdot \ldots \text{Cl} \rightarrow \text{Na} : \text{Cl} : \ldots \text{Cl}', \\
\end{align*}
\]

which are exothermic.

On stage 2 an energy is discharged that is equal to the difference between the enthalpy (1/2 of bonding energy) and the bonds in molecules Na : Cl and Cl : Cl which amount to about 90 kJ/mol. This is sufficient energy for breaking a VWB of Cl...Cl in molecule Na : Cl...Cl' which has a value of less than 20 kJ/mol. This means that reaction: Na : Cl...Cl' \rightarrow Na : Cl + Cl' is chemically active and can proceed at a great speed. The continuation of the following chain

\[
\begin{align*}
\text{Cl}' + \text{Na}_2 &\rightarrow \text{Cl}'\ldots\text{Na} \rightarrow \text{Cl} : \text{Na} : \ldots \text{Na} \rightarrow \text{Cl} : \\
\text{Na} + \text{Na}'
\end{align*}
\]

is also a highly exothermic chemically activated route.

On stage 2 bond Na : Na breaks and a new bond Na : Cl forms with a discharge of energy that is equal to the difference of the enthalpy energies of these two bonds. That is, about 160 kJ/mol — which is more than enough to break a VWB Cl...Cl in molecule Na : Cl...Cl. That is, the initiation stage of the chain is the exothermic stage:

\[
\text{Na}_2 \rightarrow \text{Na}^+ + \text{Na}'
\]

According to the conditions of the experiment, the topmost Na atoms are radicals, which are the main sources for the initiation of the chain.

Thus, unlike the previously accepted scheme, the explanations relative to ionic chemical bonding (the only logic and comprehensible explanation), just as the theory of active collisions, are understandable and can be readily taught to students though they do differ qualitatively relative to the experimental data; and then, these explanations do not answer such questions as:
Why is the ionic bond so strong? and Why are molecules ionic bonds stable at temperatures over 1,000 °C, though, according to electrostatic calculations, they should be unstable and break with a discharge of energy along the scheme: $2NaCl \rightarrow Na_2 + Cl_2$?

It is obvious from experiments that oxygen forms the greatest concentration of radicals at a temperature of about 400 °C, as compared with other widely known gases with multiple bonds (acetylene, ethylene, nitrogen).

Single-bonding energy:

- O - O   138 kJ/mol
- C - H   413 kJ/mol
- O - H   462 kJ/mol
- C - O   351 kJ/mol

Oxygen reacts actively with almost all compounds.

Anomalous elements have not only anomalous physical properties, but chemical ones, as well.

As indicated in section 6.3, the covalent bonds of these elements are weak and therefore, bonding carbon — an anomalous element — should readily break down into radicals. Experimental proof of this is the wide use of magnesium — organic syntheses.

According to our theory, elements with 8 electrons in the outermost shell form neither homo- nor heteroatomic covalent bonds. Besides, according to calculations, elements with a FIE of more than 14 eV do not form strong covalent bonds; that is, all the rare gases and mercury are sort of twice inert.

These elements can form donor-acceptor bonds (DABs) with elements having FIEs greater than those of inert gases. The DAB energy is about two times smaller than the covalent heteroatomic bonding energy. The bonding energy of fluorine (FIE = 17.4 eV), with elements having a FIE of 12 to 15 eV, are evaluated at 250 (380) — 100 (150) kJ/mol. In brackets are the experimental data.

Thus, the DAB energy can be defined by a value of 125 (190) for radon (Rn) and 5 (75) for argon (Ar). The experimentally defined value for the bonding energy of xenon-fluorine (Xe-F) comprises 130 kJ/mol, of krypton-
fluorine (Kr-F) – 50 kJ/mol. Compounds with a bonding energy smaller than 50 kJ/mol begin a thermal decomposition at room temperature. That is, compounds of noble gases with halogens (besides compounds of radon and xenon with fluorine) are thermally unstable.

In liquid and crystal forms, the molecules of these compounds are bonded with VWBs which presupposes their chemical interaction with the final formation of fluorine and xenon according to the scheme:

\[
F : Xe : F \ldots F : Xe : F \rightleftharpoons F : Xe \ldots F : F \\
Xe : F \rightarrow 2F_2 + 2Xe
\]

The degree of the equilibrium's shift to the right is defined by the energy differences of the double bond Xe–F and bond F–F. The double bonding energy Xe–F is 260 kJ/mol; the bonding energy F–F is 150 kJ/mol.

The energy difference comprises more than 100 kJ/mol; therefore, the fluoride-xenon should be stable. Unlike the fluoride-xenon, the fluoride-krypton, for which the bonding energy is evaluated at 50 kJ/mol, should most readily turn into fluoride and krypton.

In general, according to our theory, we can expect that compounds of the n–h type (noble gas–halogen) can be stable if the FIE of n is smaller than 12 eV and the FIE of h is greater than 16 eV. In reality, only compounds RnF_n and XeF_n satisfy these conditions.

The synthesis of compound xenon-fluorine (XeF_2 , XeF_4 , XeF_6) and the unsuccessful attempts at synthesizing ArF_2 , KrCl_2 , and XeBr_2 are experimental proofs of this conclusion.
APPENDIX A

12** ANOTHER VARIANT OF INTERPRETING CHEMICAL BONDING

In your former classes, when studying physical science, you learned that all substances (of which everything is made) are constructed of atoms. You have learned that the atom consists of a positively charged nucleus around which negatively charged electrons rotate.

You have also learned that the electrons surrounding the nucleus are distributed in layers; that the number of electrons in the atom's outermost layer changes periodically when the atom's nuclear charge increases; that the properties of the elements also change periodically. For example, elements made up of atoms on whose outermost electronic layer there is but one electron, are known as light elements: lithium (Li), sodium (Na), potassium (K), etc. which have something in common, as far as chemical and physical properties are concerned, and which differ greatly as compared to other elements whose atoms contain more than one electron in the outermost electronic shell.

An analogous situation is observed when comparing elements whose atoms have 7 or 8 electrons in the outermost electronic shell. Such elements are united into a group of halogens: F₂, Cl₂, Br₂, I₂ and inert gases: He, Ne, Ar, Kr, Xe, Rn. Halogen atoms are united into diatomic molecules whose chemical properties are quite identical. Noble gas atoms, as a rule, do not unite with their own kind or with other atoms.

The coincidence of properties in elements with identical numbers of electrons on the outermost electronic shell, and the difference of properties in elements with various numbers of electrons on the outermost electronic shell, has led to the conclusion that the reason for the difference in the properties lies in the difference of the number of electrons on the atom's outermost electronic shell.

Thus, in the course of studying physical science, you have learned that: matter consists of atoms, which in their turn, consist of positively charged nuclei around which negatively charged electrons rotate; the electrons in the atoms
are situated in layers; the properties of elements are defined by the number of electrons on the atom’s outermost electronic shell.

Now you know that substance is made up of atoms. Then, what properties in the atoms cause a difference in the properties of the substances? The various numbers of electrons in the outermost electronic shells cause the difference.

Two years have passed since you studied this material. You have gained more knowledge in physics and mathematics, so we can now introduce some chemical phenomena to deepen your knowledge. What do we mean by deepening your knowledge? We mean that we are to answer the following two questions that will inevitably occur during the scientific interpretation of various chemical phenomena:

Why does the number of electrons have such a great influence on the physical and chemical properties of substances?

The second question requires an introduction: The number of electrons in the atom's outermost shell is not more than 18, while the number of elements with various properties is equal to 100. This means that atoms must have some other properties that also lead to various properties of elements besides the mentioned number of electrons in the outermost electronic shell. Now here is the second question:

What other atoms’ properties, besides the number of electrons in the outermost electronic shell, influence the properties of substances?

Let's first answer question #2. Here we must not forget the logic, which we adhered to when we concluded that the number of electrons in the outermost shell defines the chemical and physical properties of common substances (formed of atoms of one kind) and complex ones (formed of various atoms). We have made this conclusion on the basis of four regularities found in the course of an experiment:
1) the similarity in the properties of substances made of atoms with the same number of electrons on the outermost electronic shell;

2) the difference in the properties of substances made of atoms with various numbers of electrons on the outermost electronic shell;

3) the changes in the physical and chemical properties during the increase of the number of electrons on the outermost electronic layer;

4) the coincidence in the periodic change of the number of electrons and properties in the elements (common substances).

But before answering the two above-given questions, let’s cite some experiments upon which were based the conclusions concerning the influence of the number of electrons in the outermost shell on the properties of substances.

The course of physical science has gotten you acquainted with experiments conducted by Rutherford as a result of which it was realized that the atom is actually a nucleus surrounded by electrons. Then you found out that the electrons are arranged in layers. Now let’s see in detail exactly how the electrons are arranged around the nucleus in layers, and how the number of electrons on each layer was defined.

The electrons that surround the nucleus are drawn to the latter due to electrostatic forces. We can evaluate the energy necessary for removing each of the atom’s electrons. The energy necessary for removing the first (easiest) electron is known as the first ionization energy (I₁) or the first ionization energy (FIE) of the element.

We can evaluate the atoms’ affinities towards the electrons, or ionization energy of negatively charged ions, received as a result of electron bonding to neutral atoms. The ionization energy of the neutral atoms and the affinity energy (ionization energy of negatively charged atoms) are measured in kilo-joules per mole (kJ/mol). The ionization energy of the electrons in most atoms has been defined experimentally.

As a result of these experiments, the dependence of ionization energy on the ordinal number of the retreating
electron was defined. An example of such dependence is given in figures 3.2—3.5.

According to electrostatics, the difference in energy between the electrons in one and the same layer should be much smaller than that between the electrons in various layers. That is, the stepped arrangement of straight lines shown in figures 3.2—3.5 reveals a layer-like arrangement of electrons in the atom, while the number of dots on each of the lines corresponds to the number of electrons in each layer.

All the FIEs have been defined experimentally as well as most of the elements’ affinity energies. It was found that if the nuclear charge increased without change, the atoms’ FIEs would change periodically. It was also found that atoms with close FIEs and affinity energies — also have close physical and chemical properties. For example, elements with FIEs of 350-500 kJ/mol are light, soft metals (Li, Na, K, etc.); elements with FIEs of 1,400-2,500 kJ/mol are inert gases (He, Ne, Ar, etc.).

The element’s affinity also changes periodically and the atoms of elements with close properties (physical and chemical) have close values for their affinities. Most characteristic of the affinity value is the fact that electrons do not bond to inert gas atoms, and the affinity of such atoms is below zero.

Thus, after processing the experimental data on the atoms’ FIEs and affinities towards the electrons, it is evident that these properties of atoms, besides the number of electrons in the outermost shell, can also be responsible for the variation of properties in common or complex substances and for the likeness of properties in some elements.

In order to go further and deepen the understanding of this material, let’s take the path that is usually taken by researchers. We’ll try to evaluate theoretically which of the three above cited parameters (number of electrons in the outermost shell, FIE, affinity) is responsible for the likeness or difference in the elements’ properties.

Among the properties of elements, by which we define their likeness or difference, we have included physical properties such as: unit weight, firmness, brightness, and physical state at normal temperature. Now we will add a property, which is known as valence of elements.
Chemical experiments have proven that atoms are bonded to each other in substances. The number of atoms that bond with one atom is an individual matter, characteristic of the atoms’ properties. Thus, for example, a hydrogen atom can bond with only one hydrogen atom while an oxygen atom can bond with two. Atoms of alkali metals bond with one hydrogen atom, while nitrogen atoms bond with three hydrogen atoms. Atoms of noble gases do not bond with hydrogen atoms. That is, the chemical properties of atoms differ in regard to the number of hydrogen atoms a given atom can bond with.

The first 20 elements of the Mendeleyev Table of Elements that have the same number of electrons on the outermost shell also have the same valence in regard to hydrogen. This fact allows us to assume that the valence of elements is connected with the number of electrons on the outermost electronic shell of the atoms.

On the other hand, the gradual change of the elements’ physical properties with the same number of electrons on the outermost electronic shell (see table of elements from top downward) is well tied to the changes of the FIEs of these elements.

Thus, the FIEs of the elements decrease as we move through the group from the top downward. Parallel with the change of the FIEs, there is also a change in the melting and boiling temperatures of the common substances in the first three groups of the elements.

Noble gases, unlike all the other elements, do not bond with hydrogen atoms, i.e., they have a zero valence in regard to hydrogen. That is, noble gas atoms have a peculiarity of their own; noble gases do not bond any electrons to the existing outermost electronic shell.

Besides noble gas atoms with 8 electrons in the outermost shell, some other elements do not bond electrons to the outermost electronic shell (Be, Mg, Ca, etc.), which have 2 electrons in the outermost shell. As far as the affinity towards the electron is concerned, the outermost shell of both the 2-electronic and 8-electronic atoms behave identically.

The difference between atoms with 2 and 8 electrons in the outermost electronic shell is obvious when comparing the
outermost shells of the elements, which follow the elements with 2 electrons in the outermost shell (II group) and those with 8 electrons (VIII group).

The nuclear charges and the number of electrons in the outermost electronic shells of group III are by one unit greater than those of group II. This is characteristic of all the elements. When increasing the nuclear charge by 1 proton unit (moving from left to right across the periods of the table of elements) the number of electrons in the atoms' outermost layers increase by one unit. Unlike all other elements, noble gas atoms do not bond with the existing 8-electronic outermost layer when the nuclear charge increases by 1 proton unit, but begin to form a new outermost electronic layer (shell).

The difference or likeness of substances are defined by three main properties of atoms:
1) the number of electrons in the outermost electronic shell;
2) the first ionization energies (FIEs) of the atoms;
3) the affinity of the atoms towards the electrons.

Now let’s summarize the knowledge you have just gained and compare this with what you had previously learned at school.

Before you started learning this part of General Chemistry, you learned that the substances surrounding us are all made of atoms, that the atom is made up of a positively charged nucleus around which negatively charged electrons rotate. You also knew how this was discovered (via Rutherford’s experiments). That is, you found out what kind of ‘bricks’ substances are made of and how these ‘bricks’ are constructed. And, of course, you know that these ‘bricks’ in science are known as atoms.

The next question was:

*By what atomic properties are the differences or similarities of the substances surrounding us defined?*

We found that substances, whose atoms have the same number of electrons, have identical physical and chemical properties. Common substances, composed of atoms whose outermost layer has various numbers of electrons have different physical and chemical properties.

The material given in this section shows that besides the
amount of electrons in the outermost electronic layer, such properties of atoms like the FIE and the affinity of atoms to the electron, also define the difference and similarity of substances that are made up of these atoms.

Now let’s go on with expanding our knowledge in the field of such a chemical phenomenon as the structure of substances and the reason for their similarity and their difference. What immediate questions arise at this point that will help deepen your understanding of chemistry? The main questions asked when learning about substance structure are:

*How do atoms form a substance?*
*What forces make the atoms attract each other?*

In order to explain the similarities and differences between substances, another question may arise:

*How do the indicated properties of atoms influence the physical and chemical properties of substances?*

To answer this question, we must first explain *how atoms unite into molecules.* Therefore, let’s begin by answering the question:

*What forces influence atoms to bond with each other?*

It has been proven experimentally that in order to separate two hydrogen (H) atoms bonded with a hydrogen (H₂) molecule, it is necessary to heat the hydrogen (gas) to a temperature of 3,000° C – 5,000° C, in order to offer it some energy. Also, via experiments, it was found that when a hydrogen molecule is formed of hydrogen atoms, energy is discharged. It was also found that if you want the atoms in the hydrogen molecules to separate, the hydrogen molecule should receive energy equal to hundreds of kJ/mol. *Now where does all this energy go?*

At a temperature of 5,000° C, the atoms’ nuclei have energy of 20 kJ/mol; besides nuclei, the atoms have only electrons.

Thus comes the conclusion: the energy given to the molecule goes to increase the electrons’ energies, or, when the molecule breaks into atoms, the electrons’ energies in the divided atoms are greater than those of the electrons in the molecule.

To proceed towards better understanding of the physical nature of bonding between atoms, we should learn
to calculate and measure the energy of the electrons in an
atom and in a molecule of hydrogen.

On the basis of our previous knowledge about the size
and structure of the atom, this problem at first sight may
seem not only difficult but also impossible.

The experiments conducted by J.J. Thomson and
R.A. Millikan are detailed in textbooks. The methods of these
experiments allow us to understand how the electron’s mass
and charge were defined.

The electron in a hydrogen atom rotates at a great
speed around the nucleus. This is why the first supposition is
that the model of the hydrogen molecule can be regarded as a
model in which 2 electrons rotate around the axis that
connects the nuclei. [Recall figure 4.1].

According to this model, the positively charged nuclei
seem attracted to the electrons between them.

When bonding occurs, there are two new attractive
and repulsive forces between the electrons and the nuclei.
[Recall figure 6.1-1]. Since the bond is formed with a release
of energy, it seemed that the new attraction force was greater
than the repulsion force.

However, the quantitative experimental data
contradicted this simple scheme. For, indeed, it is well
known that the affinity of a hydrogen atom to an electron is
equal to 72 kJ/mol, i.e., the energy received at the expense of
the attraction energy, cannot exceed 144 kJ/mol, i.e., 72 · 2.
At the same time, in order to break the bond in a hydrogen
molecule, energy of 437 kJ/mol is required.

The discrepancy between the data of the experiment
and the calculation is even greater if we consider the
repulsive forces between the nuclei. In conformity with the
experiment, the distance between the nuclei in a hydrogen
molecule is equal to 0.74Å. With such a distance between the
nuclei, the repulsive potential energy is 1,877 kJ/mol.

Judging by the virial theorem (see part 5) the energy
loss during the formation of a hydrogen molecule at the
expense of the nuclei repulsive force, amounts to half of the
potential energy, i.e., 939 kJ/mol.

That is, according to the calculations made on the
basis of experiments, considering the affinity of the atoms to
the electrons and the distance between the nuclei, the
formation of hydrogen molecules had to proceed with a loss of energy. In other words, a hydrogen molecule could not form within the above-mentioned model, i.e., this theory did not answer the question:

*What kinds of forces unite atoms into molecules?*
QUALITATIVE EVALUATION OF ELECTRON'S ENERGY DECREASE DURING CHEMICAL BOND FORMATION IN H₂ MOLECULES

Now let us see what kind of dependence there is between the nuclear charge and the energy of hydrogen-like atoms (with one electron and various nuclear charges) in experiments. Table 2.2-1 shows the experimental data on the ionization energies of such atoms.

**TABLE 13-1**

<table>
<thead>
<tr>
<th>Nuclear Charge (proton Units)</th>
<th>Calculated Energy (kJ/mol)</th>
<th>Experimental Energy (kJ/mol)</th>
<th>Difference Calc.&amp; Exp. Energies (kJ/mol)</th>
<th>Difference (in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,317</td>
<td>1,317</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>5,241</td>
<td>5,241</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>11,796</td>
<td>11,796</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>20,971</td>
<td>20,983</td>
<td>−12</td>
<td>−0.01</td>
</tr>
<tr>
<td>5</td>
<td>32,771</td>
<td>32,783</td>
<td>−12</td>
<td>−0.01</td>
</tr>
<tr>
<td>6</td>
<td>47,188</td>
<td>47,234</td>
<td>−46</td>
<td>−0.1</td>
</tr>
<tr>
<td>7</td>
<td>64,230</td>
<td>64,275</td>
<td>−45</td>
<td>−0.07</td>
</tr>
<tr>
<td>8</td>
<td>83,892</td>
<td>83,967</td>
<td>−75</td>
<td>−0.09</td>
</tr>
</tbody>
</table>

The experimental dependence of these atoms’ energies on the nuclear charge is described by equation:

\[ E_Z = E_H Z^2 \]

where \( E_Z \) and \( E_H \) are energies of the hydrogen-like atom and the hydrogen atom; and \( Z \) is the nuclear charge in proton units.
The deviations here are equal to less than 0.1% (table 2.2-1). That is, the energy of the hydrogen-like atoms is proportional to the square of the nuclear charge. From the virial theorem we know that:

\[ \frac{Ze^2}{2R} = E_{\text{ion}}. \]

i.e., the energy of the system is proportional to the nuclear charge in the first power. Therefore, when the nuclear charge increases, radius R decreases proportionally. The virial theorem was derived on the supposition that only Coulomb forces were active in the atomic systems. Correspondingly, the coincidence in the dependencies of the atom’s energy on the nuclear charge proves that Coulomb (electric) interactions are the only forces acting in single-electron atomic systems.

The square-sum dependence is observed. It is known that the attraction (potential energy) between two identical charges q is proportional to the charges and inversely proportional to the distance R between the charges. In atomic systems, when the nuclear charge increases, the distance between the nuclei decreases proportionally. This dependence leads to a non-proportionally greater increase of potential energy when the nuclear charge increases.

In accordance with the above mentioned material the energy of hydrogen-like atoms is defined by the equation:

\[ E_Z = E_H Z^2. \]

The quadratic dependence of the energy of atomic systems on the nuclear charge, as already mentioned, is conditioned by the fact that when the nuclear charge increases in such systems, the radius of the electron's orbit decreases proportionally.

Now let's imagine how the energy changes in a system with two divided hydrogen atoms once we unite the atoms' nuclei into one nucleus while the electrons rotate around the united nucleus.

Indeed, it is impossible to combine hydrogen atoms under usual conditions because, during the infinite approach of the atoms’ nuclei towards each other, the potential energy is equal to:
E = k \frac{Z_1 \cdot Z_2}{R},

here \( Z_1 \) and \( Z_2 \) are atom charges, and \( R \) is the distance between them, which can grow to infinity.

When we unite the nuclei of two hydrogen atoms, we get a helium atom whose energy is defined experimentally.

Now let's calculate the energy gain resulting from such a process. According to the experiment, the potential energy of the He atom is 15,212 kJ/mol. The potential energy of 2 hydrogen atoms is 5,242 kJ/mol. Therefore, the energy difference 15,212 – 5,242 = 9,970 kJ/mol is the energy gain when bonding two hydrogen atoms.

Table 2.4-1 offers the energy gains of an imaginary unification of 3, 4, 5, and 6 hydrogen atoms with the formation of Li, Be, B, and C respectively. The table shows the unit calculation of the energy gain addition of a hydrogen atom.

**TABLE 13-2**

**RESULTS OF ELECTRONIC POTENTIAL ENERGY CALCULATIONS AT IMAGINARY UNIFICATION OF HYDROGEN ATOMS**

<table>
<thead>
<tr>
<th>Element</th>
<th>Nuclear Charge</th>
<th>Potential Energy of Electrons ( U_{el} ) (kJ/mol)</th>
<th>Energy Gain ( \Delta U ) (kJ/mol)</th>
<th>Energy Gain per One Hydrogen Atom (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>2,621</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>He</td>
<td>2</td>
<td>15,212</td>
<td>9,870</td>
<td>4,993</td>
</tr>
<tr>
<td>Li</td>
<td>3</td>
<td>39,212</td>
<td>33,974</td>
<td>11,324</td>
</tr>
<tr>
<td>Be</td>
<td>4</td>
<td>76,936</td>
<td>66,453</td>
<td>16,613</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>129,312</td>
<td>116,212</td>
<td>23,242</td>
</tr>
<tr>
<td>C</td>
<td>6</td>
<td>198,522</td>
<td>182,802</td>
<td>30,486</td>
</tr>
</tbody>
</table>

\[ *U_{el} = 2(\sum_{i=1}^{n} P_i), \]

Energy gain = \( U_{el} - nU_H \), where \( U_H = 2,621 \) kJ/mol.
What is the physical nature of the observed phenomenon known as ‘energy gain’?

Why is it that the sum of the electrons' energies in hydrogen atoms, being united, is always smaller than the energy of a united atom?

The energy gain is conditioned by the fact that the energies of the electrons in atomic systems increase proportionally to the square of the nuclear charge. When the nuclei unite, the electrons start rotating around the charged nuclei, which has a value equal to the sum of the charges of the bonded nuclei.

The energy calculation for an atomic system with a charge of 2 and with two rotating electrons shows the energy gain when the atoms bond with each other into molecules (without considering the repulsion energy) can reach 9,970 kJ/mol. Experimentally the distance between the nuclei in a hydrogen molecule is about 0.74Å (1Å = 10⁻⁸ cm). At this distance, the repulsion energy between the nuclei amounts to 1,800 kJ/mol. Thus we see that the gain in potential energy amounts to:

\[ 9,970 - 1,800 = 8,170 \text{ kJ/mol}. \]

A hydrogen molecule can be imagined as an intermediate product formed in the process of unifying two hydrogen atoms into a one-helium atom. That is, if each of the two electrons in a hydrogen atom rotate around a nucleus with a charge of 1, while both electrons in a helium atom rotate around the nucleus with a charge of 2, then both electrons will rotate around the nucleus in the hydrogen molecule with a charge greater than 1, but smaller than 2. Thus, the energy gain will be much smaller than \( 8,170 / 2 \) kJ/mol, but can be commensurable with the bonding energy value of a hydrogen molecule (437 kJ/mol).

When molecules are formed, the bonding electrons begin to rotate in that charge field, which is greater than the nuclear charge of the initial atoms that form the molecule. The energy gain during molecule formation (enthalpy factor) is conditioned by the fact that the energy of the electrons increases proportionally to the square of the positive charge around which the electrons rotate. This contribution to
bonding energy can be conditionally called a positive charge concentration.

The qualitative explanation for the energy gain during hydrogen molecule formation, mentioned above, allows solving the second main contradiction arising from the theory of chemical bonding. As already indicated, the energy gain is received as a result of the gain in the potential energy of the electrons’ attraction to the nuclei being bonded.

During the approach of the electrons to the nuclei, the electrons’ kinetic energies increase, according to the virial Theory; that is, the electrons’ potential and kinetic energies change during bond formation.

According to experimental data, the total decrease of energy is about 437 kJ/mol. But, according to Einstein’s theory of heat capacity, the minimal portion for which the energy of the electrons in the atom can change comprises over 1,000 kJ/mol. This value for the hydrogen atom has been confirmed by spectral data received when studying the specter of the hydrogen atom. The first excitation state of the electron in a hydrogen atom is by 1,030 kJ/mol greater than the principle one.

The inert gas energy, in the temperature interval of 2,000° C – 5,000° C, is defined by the equation \( E = \frac{3}{2} KT \). From this equation we get only the nuclear energy since the electrons in the inert gases, according to experimental data, do not absorb energy in this temperature interval. Indeed, when heating molecular hydrogen up to 5,000° C, it breaks up into atoms, i.e., the electrons change their energy.

To explain this contradiction, let’s return to the first paradoxical question. Here we have seen that when a hydrogen molecule (H\(_2\)) is formed, the effective charge, around which the bonding electrons rotate, increases. Respectively, during the breaking of the H\(_2\) molecule into atoms, the effective charge decreases because the distance between the nuclei to be bonded increases.

The distance between the hydrogen nuclei increases when heating from 2,000° C to 5,000° C since the translational and rotational freedom stages are defrosted in such heat, and the vibrational freedom stages of the nuclei begin defrosting. The change of the electrons’ energies in the
molecules, unlike that in the atoms (particularly in hydrogen atoms or inert gases) is accomplished along another scheme.

During thermal heating, the nuclear energy increases (most obviously in the rotational and vibrational cases) and causes an increase in the distance between the nuclei. The vibrations in the molecules being non-harmonic, the effective positive charge, around which the electrons rotate, decreases. This causes an increase of the distance between the electrons and the positive center around which the electrons rotate.

The removal of electrons from this center causes a decrease of their potential energy. This is caused at the expense of the decrease of the nuclear energy (vibrational and rotational) since the process is conducted adiabatically (without loss of energy).

In the case of molecules, unlike atoms, the electrons utilize energy (most commonly, they change their own energy) during thermal heating in portions commensurable with the rotational and vibrational quanta. When utilizing these portions of energy, the electrons do not transit from the lower level to the next, but the energy of the main state changes to that equal to the energy of the electrons in the non-excited state.

Just as in the case of atoms, when molecules are excited by radiation, the electrons absorb only frequencies that coincide with their own rotation frequency. That is, unlike atomic electrons, molecular electrons absorb energy during thermal heating via thermal and direct light radiation with light quanta. The absorption via small (thermal) quanta is generally explained by the fact that in the case of the molecule, the energy of the electrons depends on the distances between the nuclei of the atoms to be bonded. In the case of atoms that do not bonded to each other (inert gas atoms), naturally, there is no such bonding.

Thus, the main precondition in the theory of quantum heat capacity, according to which electrons, bonded to nuclei, do not absorb energy with the help of quanta (smaller than 1,000 kJ/mol) is relevant only to atoms not bonded to molecules.

This limitation does not affect electrons in atoms bonding into molecules. That is, the breaking of the chemical bond, connected with the electronic absorption in portions
smaller than 1,000 kJ/mol, is not a phenomenon that contradicts the theory of quantum heat capacity.
14 QUANTITATIVE EVALUATION OF THE SAME

14.1 MODELS AND MATHEMATICAL EQUATIONS

Bonding energy is energy required to break down a molecule. As we have a molecule at the beginning of the process, and atoms – at the end, energy is spent, which at least equals the difference between the electronic energy of the molecule and that of the atoms.

\[
\begin{align*}
AD &= X_1 \\
BD &= X_2 \\
AB &= 2b \\
CD &= a
\end{align*}
\]

\(N_1\) and \(N_2\) are nuclear charges; \(C\) is the location of the electron.

The molecule exists in equilibrium (i.e., the repulsive forces between identically charged particles are balanced by the attractive forces between differently charged particles in accordance with figure 2.5-1). In this figure we see that \(F_5\) and \(F_6\) are projections of the nuclei’s attractive
forces $F_1$ and $F_2$ of the electrons onto the axis connecting the nuclei. The repulsion force between the nuclei is given by formula:

$$e^2 \cdot N_1 \cdot N_2 / (x_1 + x_2)^2$$

Likewise, the electron’s attractive force at point D is equal to the sum of forces $F_7$ and $F_8$, which are the projections of forces $F_3$ and $F_4$.

$$F_9 = F_8 + F_7 - F_e$$

where $F_8$ and $F_7$ are projections of forces $F_3$ and $F_4$ onto axis BD; and $F_e$ is the sum of repulsive force projections of electron C from other electrons. Figure 14-1 does not reveal the projections of these forces. We will touch upon their evaluation later.

According to Figure 14-1, all the forces can be calculated by the following equations:

$$F_7 = F_4 \cos \angle DCB = F_4 \cdot \frac{a(a^2 + x_2^2)^{0.5}}{a} = e^2 N_2 a / [(a^2 + x_2^2) \cdot (a^2 + x_2^2)^{0.5}]$$

$$F_8 = e^2 N_1 a / [(a^2 + x_1^2) \cdot (a^2 + x_1^2)^{0.5}]$$

$$F_9 = e^2 N_1 a / [(a^2 + x_1^2) \cdot (a^2 + x_1^2)^{0.5}] + e^2 N_2 a / [(a^2 + x_2^2) \cdot (a^2 + x_2^2)^{0.5}] - F_e$$

$$F_9 = (e^2 / a^2) \left[ \left( N_1 \{(x_1/a)^2 + 1\}^{3/2} + N_2 \{(x_2/a)^2 + 1\}^{3/2} \right) - F_e / (a^2/e^2) \right] \quad (14.1-1)$$

where $F_e$ is the sum of the projections of the repulsive forces of electron C from other electrons.

By introducing: $F_9 = (e^2 / a^2) F_0$ and $F_e = (e^2 / a^2) S_n$

we get: $F_0 = [N_1 \{(x_1/a)^2 + 1\}^{3/2} + N_2 \{(x_2/a)^2 + 1\}^{3/2}] - S_n$

According to the Coulomb Law, $F_9 = e^2 \cdot Z / a^2$

(Where Z is the effective charge at point D).

On the other hand, $F_9 = e^2 F_0 / a^2$. 
That is \( Z = F_0F_5 = e^2N_2 \cdot x_3/[(a^2+x_2^2) \cdot (x_2^2+a^2)^{0.5}] \)
\[ \quad = e^2N_1 \cdot N_2 / (x_1 + x_2)^2 \quad (14.1-2) \]
\( F_6 = e^2N_1 \cdot x_1 / [(a^2+x_1^2) \cdot (x_1^2+a^2)^{0.5}] = e^2N_1 \cdot N_2 / (x_1 + x_2)^2 \quad (14.1-3) \)

Equations 14.1-2 & 14.1-3 have three unknowns: \( x_1 \), \( x_2 \) and \( a \). To solve this system, we should have a third equation, which is compiled on the basis of the virial theorem. From this theorem we know that distance \( a \) is inversely proportional to charge \( Z \) or \( F_0 \).

The proportionality coefficient can be defined since we know the distance and charge \( Z \) in a hydrogen atom. The inter-electronic repulsive force \( (S_n) \) can be calculated from the equation that we will demonstrate later. Hence, we have a system of three equations with three unknowns:

Equations 14.1-4 and 14.1-5 are based upon the equality of the forces attracting the nuclei to point D \( (F_5 \& F_6) \) and the repulsive forces between the nuclei when in equilibrium.

\( N_1 \cdot n x_1 / (x_1^2 + a^2) \cdot (x_1^2+a^2)^{0.5} = N_1 \cdot N_2 / (x_1 + x_2)^2 \quad (14.1-4) \)
\( N_2 \cdot n x_2 / (x_2^2 + a^2) \cdot (x_2^2+a^2)^{0.5} = N_1 \cdot N_2 / (x_1 + x_2)^2 \quad (14.1-5) \)

\[ a = R/F_0 \quad (14.1-6) \]

\( n \) — number of bonding electrons, \( R \) — Bohr’s radius (equals 1)

\( F_0 = N_1 \cdot [(x_1/a)^2+1]^{3/2} + N_2 \cdot [(x_2/a)^2+1]^{3/2} \) \( - \) \( S_n \)
\[ \quad (14.1-7) \]

The most effective way of solving this system is with the help of a computer. In specific cases the analytical method can be used. Let’s try one of them when charges \( N_1 \) and \( N_2 \) are equal.

Then \( x_1 = x_2 = b \) and equation 2.5-1 turns into equation 14.1-8

\( F_9 = F_8 + F_7 - F_e = (e^2/a^2) \cdot [2N_1 \cdot [(b/a)^2+1]^{1.5} - S_n] \)
\[ \quad (14.18) \]

To solve this equation, we must know the ratio \( b/a \).
and $S_n$. $b/a$ is defined from equation 14.1-5. If we substitute $x_1 = x_2 = b$, we get:

$$b/a = [(4n/N)^{2/3} - 1]^{-0.5}$$

After inserting $b/a$ in equation 2.5-7, we get:

$$F_0 = (N^2 / 2n) \cdot [(4n/N)^{2/3} - 1]^{3/2}$$

According to the above $F_0 = Z$ (where $Z$ is the effective charge at point $D$). That is, the molecule's energy is equal to the energy of the atom with a nuclear charge of $Z+S_n$ and with $n$ electrons in the case when the electrons rotate around the nucleus in one circle. When the number of bonding electrons is $n = 2$, the molecule's energy is equal to the energy of the helium-like atom with a charge of $Z+S_n$.

Let's calculate this energy. This system's energy with various nuclei charges is experimentally defined as the sum of the last two ionization potentials in the elements listed after helium (table 14.1-1). Helium-like atoms can be presented by a scheme with the electrons situated on both sides of the nucleus. According to this system, three forces act on a straight line, which can be easily summed up. Each electron is under the influence of a force that is equal to that of the nucleus minus the repulsive force. Electrostatic forces are directly proportional to the charges and inversely proportional to the square of the distance between them, as represented by:

$$F = q_1 \cdot q_2 / R^2$$

(14.1-9)

Let's calculate the force acting upon each electron in the ion hydride. The repulsive force between electrons comprises 0.25 of the electron's attractive force for the nucleus, i.e., the attractive force of each electron comprises 0.75 of the acting force, which may not have existed if the second electron were not present.

We know how to define the energy of a system whose nuclear charge is known and contains one electron. The energy of such a system is defined by the equation:

$$E_n = E_{H} \cdot Z_n^2$$

(14.1-10)
where \( E_n \) is the atom’s energy with charge \( Z \); \( E_H \) is the hydrogen atom’s energy. The helium-like atom’s energy is calculated by the equation:

\[
E_n = E_H (Z_n - 0.25)^2 \cdot 2
\]

or:

\[
E_n = E_H F_0^2 \cdot 2 \quad (14.1-11)
\]

Now we can calculate the energy of a hydrogen molecule:

In a hydrogen molecule \((N_1 = N_2 = 1)\) in proton units; \( n = 2 \) (there are two electrons in the circle connecting the nuclei). According to the equation 14.1-8

\[
F_0 = (2^2/2 \cdot 2) \cdot [(4 \cdot 2/1)^{0.667} - 1]^{1.5} \cdot 0.25 = 1.049
\]

and \( E_{H2} = 1,320 \cdot 1.049^2 \cdot 2 = 2,905 \text{ kJ/mol} \).

The energy of two hydrogen atoms is equal to \( 1,320 \cdot 2 = 2,640 \text{ kJ/mol} \).

According to the virial theorem the energy of a molecule made up of electrons and nuclei \( (E_{\text{mol}}) \) is defined by the sum:

\[
E_{\text{mol}} = E_{\text{kin}} - E_{\text{pot}}
\]

where \( E_{\text{kin}} \) and \( E_{\text{pot}} \) are the kinetic energy of the electrons and the potential energy of the system (electrons’ attraction energy to the nuclei and the inter-electronic repulsion energy).

According to the virial theorem, \( 2E_{\text{kin}} = E_{\text{pot}} \) in absolute value. Thus, the received value of 2,905 kJ/mol is equal to the electrons’ kinetic energy and half of the molecule’s potential energy. Respectively, the value of 2,640 kJ/mol corresponds to the double value of the electron’s kinetic energy in a hydrogen atom and the potential energy of the electron’s attraction to the nuclei in a hydrogen atom.

During the formation of the molecule the kinetic energy of the electrons increases by 265 kJ/mol, while the absolute value of the potential energy increases by
2,905 \cdot 2 - 2,640 \cdot 2 = 530 \text{ kJ/mol}. That is, the electrons in the molecules move quicker than they do in the atoms, though in the first case, they are more readily attracted to the nuclei.

The energy gain at the expense of the greater attraction of the electrons to the nuclei is twice higher than the loss of energy connected with the electrons’ increase of kinetic energy. The formation of the molecules occurs, according to the calculation, with energy gain, which explains their stability at room temperature (≈ \(20^\circ\text{C}\)).

Since the process of molecule formation proceeds with a discharge of energy, in order to break a molecule into atoms (to accomplish the reverse process) the molecules should get some energy.

A molecule’s energy is calculated via the above-mentioned scheme in section 6.1. In this scheme we presume that the molecule is a system where two nuclei are bonded by two electrons rotating in a circle whose plane is perpendicular to the axis connecting the nuclei. We also presume that the defining forces in the given system are the Coulomb and centrifugal forces.

The correctness of our presumptions can be proven only by comparing the calculation data with those of the experiment. It has been defined experimentally that in order to break up a hydrogen molecule into atoms, the hydrogen should get energy of 437 kJ/mol. Indeed, it might seem sufficient to add 437 kJ/mol to 2,640 kJ/mol (energy of two hydrogen atoms) in order to get the experimental energy value of a hydrogen molecule.

However, let’s not hurry to the conclusion, but, for the time being, let’s dwell in detail upon the experimental methods, which defined the energy necessary to break the bond of a hydrogen molecule.

Let’s compare two problems.

**Problem 1**

*Define the energy necessary to break the bond between a magnet and a piece of iron.*

This problem can be solved with the help of an electric device that will tear the piece of iron off the magnet.
Here the energy consumption can be calculated considering the amount of electric energy used by this device during the process.

**Problem 2**

In the case of a hydrogen molecule, we cannot separate the atoms in a molecule with the help of a device, and therefore, we cannot directly measure the energy necessary to break the bonds in this molecule. Now what can we do in this case? We heat, say, 100 ml of hydrogen and measure the amount of energy used and the amount (concentration) of hydrogen atoms (the number of broken hydrogen molecules via reaction $\text{H}_2 \rightarrow 2\text{H}$). The hydrogen molecules get energy necessary to break the bond.

In the process of heating the hydrogen, the kinetic energy of the molecules increases; the molecules begin to move quicker translationally and rotationally. Besides, the hydrogen atoms’ nuclei begin to vibrate more readily. In the course of the collisions between the molecules and the exchange of energy between them, such molecules appear in which the average distances between the nuclei become greater than those in the initial (non-excited) hydrogen molecules. Respectively, the given charge in these molecules, $Z_{\text{H}_2}$, (see section 6.1) becomes smaller, and the potential energy of the molecule is decreased.

Gradually, the electronic energy of these molecules becomes equal to the electronic energy of two hydrogen atoms causing the molecule to burst. Thus, when we measure the energy necessary for breaking the bond in a hydrogen molecule, we cannot either offer or measure such energy in the molecule as we did in the case of the magnet and the piece of iron. In this case we have to impart energy to the system with more than $10^5$ hydrogen molecules.

In this system, as a result of the exchange of energies between the molecules, there will be molecules with sufficient energy accumulated so as to cause a burst of the molecules into atoms. That is, in order to convey sufficient energy to some of the molecules to break them into atoms, we must impart energy to other molecules, which do not break into atoms in the course of the experiment. In this case, unlike that of the magnet and iron, we have to spend more
energy than is actually necessary for the breaking of the molecules into atoms.

This is why the experimentally defined value of 437 kJ/mol (energy necessary to break up a hydrogen molecule into atoms) exceeds the value of the difference in energies between those of the molecule and those of the divided hydrogen atoms.

_How can we define the energy spent on the heating of non-breaking molecules (i.e., on the non-productive expenditure of energy)?_

This can be done if we know how much energy is discharged in the course of the chemical reaction (i.e., the reaction heat).

_How can we measure the reaction heat?_ For this we convey to the system energy whose value is equal to, say, the expenditure of electricity, and then we define the energies of the final products and the non-reacting initial products. The energy of the non-reacting products is equal to their initial number multiplied by the heat capacity of the products and by the temperature at which the experiment was conducted. The energy of the final products is equal to their heat capacity multiplied by the temperature at which the experiment was conducted.

The energy imparted to the system (which we are to measure) is spent on heating the initial and final products to the reaction’s temperature, and on the increase of the energy of the hydrogen molecule’s electrons up to the energy of the atom’s electrons.

The value of this energy was determined in the course of a theoretical calculation. In order to compare the calculation of the molecule’s energy with that of the experiment, we must add not 437 kJ/mol to the electronic energy, but the difference between this value plus the difference in the energies spent on the heating of the initial and final products up to the reaction temperature. To define this difference, we should find the difference between the heat capacities of the initial and final products.
Remember that the heat capacity of a substance is the relation of the amount of heat (energy) received by the substance, or discharged at cooling, to the corresponding temperature change in the substance. If we take heat capacity in relation to one gram of substance, this is regarded as a unit of heat capacity. In relation to \( z \) atom, or \( g \) mol of substance, this is called either atomic or molar heat capacity.

Thus, the imparted and measured amount of energy (437 kJ/mol) has been spent on the increase of electronic energy (\( \Delta E_{el} \)) and on the difference of the energies in the initial and final products \( \Delta E = E_{ini} - E_{fin} \).

\[
E_{ini} = C_{H_2} \cdot T_p; \quad E_{fin} = C_{H} \cdot T_p;
\]

\([C_{H_2} \text{ and } C_{H} \text{ are heat capacities of hydrogen (H}_2\text{) and hydrogen atoms}].

In the section devoted to heat capacity (see 6.1) it has been shown that the difference in the heat capacities of hydrogen (H\(_2\)) and two hydrogen atoms is about equal to the electronic heat capacity of molecular hydrogen.

The expenditure of energy during the heating of molecular hydrogen up to a temperature that causes the breaking of the atoms (2,500° — 5,000° C) is well stipulated by the increase in the electrons’ energies. The mechanism for the increase of the electrons’ energies in a molecule has been described above (see section 6.1). This mechanism does not work in the case of divided atoms, for in such atoms the energy of the electrons does not depend on the distance between the atoms. Experiments have confirmed this theoretical judgment: the electronic heat capacity of atoms is equal to zero.

Thus, in order to calculate the experimental value, which should be added to the electronic energy of two hydrogen atoms, we must subtract the value of \( C_{eH2} (T_2 - T_1) \) from 437 kJ/mol; (where \( C_{eH2} \) is the electronic heat capacity, \( T_2 \) is the reaction’s temperature, \( T_1 \) is the temperature at which the electronic freedom stages defrost). That is, \( T_1 \) is the temperature at which the electronic heat capacity becomes noticeable. To calculate the experimental value, which should be added to the electronic energy of two hydrogen atoms, we must subtract the value of \( C_{eH2} (T_2 - T_1) \)
from 437 kJ/mol. \([C_{eH2} \text{ is the electronic heat capacity, } T_2 \text{ is the reaction temperature, } T_1 \text{ is the temperature at which the electronic freedom stages defrost or becomes noticeable.}]

According calculation (See Gankins’ \textit{How Chemical Bonds Form and Chemical Reactions Proceed} – 1998, p.441) from the 437 kJ/mol, received from measuring the expenditure of energy for thermal bond breaking, we should subtract a value equal to about 200 kJ/mol.

That is, to get the experimental energy value of a hydrogen molecule (H\(_2\)), we should add not 437 kJ/mol, but a value smaller by 200 kJ/mol, i.e., 237 kJ/mol to the experimental value of the energies of two hydrogen atoms (2H). The experimentally defined energy value of a hydrogen molecule comprised 2,877 kJ/mol, while the calculated energy value of the same comprised 2,905 kJ/mol.

Thus, the experimental value differs from the calculation by less than one percent. Such a coincidence allows us to say that the real hydrogen molecule is identical to the hydrogen molecule model from which the calculated data was received.

In the calculation based on the model, only electrostatic interactions were considered. As the calculation results differed from the experimental data by less than 3%, we can say that the forces defining the formation of molecules out of atoms are electrostatic.

Such a coincidence, received in the calculation on the basis of the given model and experimental data, allows us to say that the real hydrogen molecule is identical to the results shown by the hydrogen molecule model from which the calculated data was received.

If we know the value of \(F_0\), via equation 6.4-7 we can define radius of the circle where the electrons rotate: \(a = R/F_0 = 0.95R\). That is, the radius of this circle comprises 0.95 of the Bohr radius (i.e., the radius of a hydrogen atom equal to 0.529Å).

Equation 6.1-8a offers us: \(b/a = [(4 \cdot 2/1)^{2/3} - 1]^{-1/2} = 1/3^{0.5}\);

Then: \(b = a/3^{0.5} = 0.529/1.732 = 289 \text{ Å}\)

Relatively, \(c\) – the distance from the nuclei to the electrons is equal to \(0.5^2 + 0.289^2 = 0.57 \text{ Å}\).
The electron in a hydrogen atom is situated at a distance of 0.529 Å from the nucleus; that is, the electrons of each of the atoms, bonded to a molecule, enter the outermost incompletely filled shells of each other. This can be additionally checked by the following calculation.

Let’s find the distance between the nucleus and the electrons by connecting an electron to a hydrogen atom. The attraction of each of the electrons to the nucleus will decrease by 25%, the effective charge of the atom’s nucleus will also decrease by 25%, and the distance between the nucleus and the electron in a hydrogen atom, which has connected the electron, will be equal to 0.65Å. Which proves that both electrons enter the outermost layer of the atoms being bonded.

Figure 6.1.1 allows understanding at the expense of what forces the effectiveness of both charges is increased. On figure 6.1.1 we see that CH is the projection of force CG (F₁) onto line CB. Relatively, force CG is an additional attraction force of electrons to the nuclei (F₁). That is, the increase of the effective charge of the nuclei to be bonded, as compared with the bonding of only electrons to the nuclei (affinity of the atoms to the electrons) is conditioned by the fact that in the case of bond formation an additional attraction force GH comes into being.

Thus, via simple arithmetic, the virial theorem, and the data on the electrons’ and the protons’ charges, we have managed to calculate the electronic energy of a hydrogen molecule and the energy that is gained during chemical bond formation between two hydrogen atoms. We also managed to calculate the distances between the nuclei and the electrons in a hydrogen molecule, as well as the distances between the nuclei.

The calculation of a hydrogen molecule has shown that when chemical bonding takes place, there is a gain of energy; and the potential energy of a molecule is greater than that of 2 atoms. That is, it is more difficult to tear electrons off the nuclei of 1 hydrogen molecule (more energy is needed) than off 2 hydrogen atoms.

A hydrogen molecule consists of two protons joined by a circle in which two electrons are constantly rotating on a plane perpendicular to the axis connecting the nuclei. This
plane is situated at equal distances from the nuclei being bonded. During molecule formation, both bonding electrons enter the outermost shells of the atoms being bonded.

Having studied the material given in sections 3.1-4, we have learned about the structure of atoms and that of simple molecules. We have understood why atoms are bonded into molecules, and we understood how to define the energy, which is necessary to impart to a dual-atomic molecule in order to break it into atoms.

Now we can approach the answer to the question:

How does the bonding energy in a molecule depend on the periodically changing properties of an atom? That is, on the number of electrons in the outermost layer of the atoms, on the first ionization energy (FIE), and the affinity of the atoms towards the electron.

Let’s begin with the atoms’ FIEs. The system of equations (6.4-5 – 06.4-7) allows us to calculate the energy of molecules formed of atoms in which an electron rotates around the nucleus. The nucleus can have a charge different from that of hydrogen. There are no such atoms in nature. Real atoms are multi-layered balls in the center of which is the atom’s nucleus.

However, in the first approach, we can imagine all the atoms as being hydrogen-like, that is – atoms with one electron rotating around the nucleus with a charge different from that of a hydrogen atom. We can suppose that the total action of all the electrons and the nucleus on one electron is obvious in the ionization energy of this electron.

On the basis of the virial theorem we can calculate the nuclear charge of such a hydrogen-like atom. Let’s examine a hydrogen-like atom of sodium whose FIE comprises 5.32 eV. In the hydrogen-like approach, a sodium atom can be imagined as a hydrogen-like atom with one electron rotating around the nucleus and with ionization energy of 5.32 eV. From the above we know that the energy of a hydrogen-like atom is equal to the ionization energy of this atom, and on the other hand, it can be calculated via the equation:

\[ E_{\text{HPA}} = 13.6 Z^2_{\text{HIA}}; \]
where \( Z \) is the nuclear charge of the hydrogen-like atom in proton units, and 13.6 eV is the energy of the hydrogen atom. From this equation and from equation \( E_{\text{HIA}} = E_{\text{ion}} \) we see that the nuclear charge of the hydrogen-like atom can be calculated via equation:

\[
Z_{\text{HPA}} = \left( \frac{E_{\text{ionHIA}}}{1312} \right)^{0.5}
\]

For better comprehension, we can cite this phenomenon on a concrete example. Let’s take a sodium (Na) atom. The nuclear charge of this atom is equal to 11 proton units. If this atom had only one electron, its ionization energy (IE) could be calculated via the equation:

\[
IE = E_{\text{H}} \cdot 11^2
\]

where \( 11^2 \) is the square of the nuclear charge.

The real Na atom has a first ionization energy of 500 kJ/mol. Knowing the ionization energy (IE) of this electron we can calculate the total effective nuclear charge of the other electrons:

\[
5.14 = E_{\text{H}}Z_{\text{ef}}^2 ; Z_{\text{ef}} = \left( \frac{5.14}{E_{\text{H}}} \right)^{0.5}
\]

Since \( E_{\text{H}} = 13.6 \) eV, and \( Z_{\text{ef}} = \left( \frac{5.14}{13.6} \right)^{0.5} = 0.615 \),

Equations 6.4-5--6.4-7 allow calculating the energy of a molecules formed of identical atoms and, correspondingly, the bonding energy in such molecules at various calculated charges of these atoms. The calculation of bonding energy in dual-atomic molecules formed of hydrogen-like bonds is conducted via the scheme tested by us on a hydrogen molecule. That is, we calculate the energy of the molecule from which we should subtract the energy value of two hydrogen-like atoms (twice the ionization energy value of these atoms).

In order that we might later compare the calculated and the experimental results, we should divide the result by 0.6 (just as in the case of a hydrogen molecule) so as to consider the non-productive expenditure of energy. As a result of such calculations, we can define how the bonding energy should depend on the atoms’ FIEs. The expected calculation results concerning the dependencies of the
bonding energy on the ionization energies are shown in figure 6.4-8, 6.4-9.

To compare the dependencies received via calculations and experiments, we had chosen elements from the second and third periods in the table of elements, which differ from the hydrogen atom mainly relative to the ionization energies for which, according to chemical data, and data on chemical bonding, it is known that they form a dual-electronic chemical bond. That is, just as in the case of hydrogen, two electrons take part in the bonding – one from each of the atoms.

What is common for the chosen elements is that they have, just like a hydrogen atom, a positive affinity towards the electron.

A comparison of the calculated and experimental dependencies shows that these dependencies are almost identical; both are parabolas, which is additionally confirmed by the correctness of the model and by the correctness of the hydrogen-like approach.

The calculated and experimental dependencies show that the FIE of the bonding atoms defines the bonding energy value in the molecule. The bonding energy between the atoms in a molecule is one of the main properties of the molecule.

Now let’s cite the role of the atom’s second parameter, which changes periodically; and let’s cite the role of the atom’s affinity towards the electron in bonding energy. Let’s recall how we define the atom’s affinity towards the electron and, respectively, what this value indicates.

To define the atom’s affinity towards the electron, a stream of electrons radiates the atoms. As a result, we get negatively charged atoms with one additional electron in the outermost layer, as compared to the initial atoms. The energy required to break the electron off these atoms, according to the law of energy preservation, is equal to the energy discharged during the bonding of the electron to the atom. This energy is the same as that of the atom’s affinity to the electron: the greater the value of the atom’s affinity towards the electron, the more actively does the electron enter the
outermost electronic layer of the given atom.

The dependence of the atom’s affinity towards the electron on the nuclear charge has been studied. The data are given in table 6.4-3. It was found that this value, for most of the elements, is equal to more than zero. However, it is impossible to define the affinity energy for some elements because the atoms of such elements do not bond an electron to the outermost electronic layer. That is, unlike most elements, these required additional energy to enter the outermost electronic layer.

The value of the affinity towards the electron was less than zero in elements of the group II (Be, Mg, Ca....), inert gases (He, Ne....), and a number of other elements (Zn, Cd, Hg....). The electron in the outermost electronic layer is acted upon by repulsive forces of the electrons in the given atom and of the attractive forces of the given electron to the nucleus. A negative affinity value towards the electron in these atoms indicates that the repulsive forces of the entering electrons in these atoms are greater than the attraction forces of the electron to the nucleus. We get additional confirmation of this conclusion when comparing the ionization energy data given in table 6.4-3.

Now let’s compare the FIEs, for example, of lithium (Li) & beryllium (Be), and beryllium (Be) & boron (B). The FIEs of Li, Be, and B are equal to 5.39, 9.32, and 8.30 eV respectively. That is, when transitioning from Li to Be the FIE increases by 4.07 eV, while when transitioning from Be to B it decreases by 1.02 eV. Atoms of Li, Be, and B have a nuclear charge of 3, 4, and 5 proton units with the number of electrons being 3, 4, and 5 respectively. Thus, when transitioning from Li to Be the nuclear charge increases by one proton unit and the number of electrons in the atom increases by one. The increase of the number of electrons should increase the inter-electronic repulsive forces while the increase of the nuclear charge should lead to the increase of the attraction of the outermost layer electrons to the nucleus.

A change in the differences of the FIE between Li & Be and Be & B: +4.07 eV and −1.02 eV indicates that during the transition from Li to Be when the number of electrons is increased by one unit and the nuclear charge is increased by one proton unit, the increase of the electrons’ attraction
forces to the nucleus is greater than the increase of the inter-electronic repulsive forces.

On the other hand, the decrease of the FIE by 1.8 eV during the transition from Be to B proves that during this transition the increase of the inter-electronic repulsion forces surpass the increase of the attraction forces of the outermost layer electrons to the nucleus. That is, the increase of the inter-electronic repulsive forces when one electron is added in the outermost layer, Be by far surpasses the increase of the inter-electronic forces occurring during the bonding of one electron to the outermost layer of Li. The difference in the energy gain can be regarded as follows: $4.07 - (-1.02) = 5.09$ eV.

The energy gain at the expense of the bonding of the electron to the outermost layer of the Li and B atoms (their affinity towards the electron) comprises 0.62 eV and 0.24 eV respectively, (an average of 0.43 eV), i.e., a value ten times smaller than our calculation of 5.09 eV. This shows that the forces that hinder the entrance of an electron to the outermost layer of a Be atom, surpasses by far the forces hindering the entrance of the electron to the outermost layer of a Li or B atom.

On the basis of a quantitative evaluation, we can expect that the loss of energy during the transition of the electron to the outermost layer of a Be atom comprises about 5 eV. As the average value of the affinity towards the electron for Li and B comprises 0.43 eV; the electron does not bond to Be with a discharge of energy. The Be affinity to the electron should be smaller than zero, i.e., the anion of Be should be unstable — what is observed in the experiment (see table 6.4-1)

An evaluation of the loss of energy was made via the described scheme during the connection of the electron to a number of other unstable anion elements. The results are shown in table 6.4-1.

For comparison, in the table we have included the FIE data and the affinity towards the electron (experimental and calculated) of elements with a positive affinity towards the electron. Since the number of elements with positive affinities to the electron greatly exceeds the number of elements whose affinity to the electron is below zero, we will regard those elements that do not bond an electron to the outermost layer as anomalous elements.
Anomalous elements can be divided into two groups: 1) Be, Mg, Ca, Zn, Hg, Fe; 2) inert gases. The difference between these groups is in the following: the elements of group I (not to be confused with the groups of elements in the table of elements) bond to the existing outermost electronic layer, while the elements of group II begin to form a new outermost shell when the nuclear charge is increased by one unit. That is, if the increase of the nuclear charge by one unit in the elements of the 1st group compensates for the additional expenditure of energy caused by the penetration of the atom into the outermost layer, then the increase of the nuclear charge by one unit, as far as the anomalous elements of the 2nd group are concerned, is insufficient to compensate the losses of energy connected with the penetration of the additional electron into the outermost layer of these atoms. The electron being bonded begins forming a new outermost electronic layer.

In chapter 6.1 it was shown that during bond formation in a hydrogen molecule, the electron of one atom enters the outermost shell of another atom. That is, during bond formation, there is a process very much like the two processes cited above: the formation of an anion out of an atom as a result of connecting an electron to it, and the transition from one element to the next, according to their number in the table of elements. The electron is connected to that atom whose nuclear charge is by one proton unit greater than that of the preceding atom.

Both these processes have shown that the penetration of the electron into the outermost shell of anomalous elements is connected with additional energetic expenditure, as compared with that of normal elements. That is why we should expect that the bonding energy formed between anomalous elements should be much smaller than the bonding energy between the atoms of normal elements with FIEs equal to those of anomalous elements that are taken for comparison.

Table 6.4-2 shows the data on bonding energy where 2 electrons do the bonding and both electrons simultaneously enter the outermost shells of the two atoms being bonded. According to the data in the table, the bonding energy in a dual-atomic molecule, formed of atoms of normal elements,
greatly exceeds that in molecules formed of atoms of anomalous elements with FIEs equal to those of normal elements.

The above mentioned might cause the following question:

*Why is there a covalent bond (though a rather weak one) between the atoms of the 1st group of anomalous elements?*

Indeed, if the atoms of anomalous elements do not connect electrons to the outermost layer (shell), then *why is it that this process takes place in the course of covalent bond formation?*

As indicated above (table 6.4-2.), during covalent bond formation between normal elements with FIEs close to those of practically all the anomalous elements of group I (FIE ≈ 7) the energy gain comprises about 300 kJ/mol. This energy gain actually compensates the energy expenditure connected with the penetration of additional electron into the outermost shells of the atoms of the 1st group of anomalous elements.

As already said, the anomalous elements of group I differ from those of group II by the fact that when the nuclear charge is increased by one proton unit, the anomalous elements of group I bond the electrons to the outermost electronic shell, while group II of the elements do not, but rather start forming a new electronic layer (shell).

This proves that the resistance (energy loss) of the penetration of the electron into the outermost layer for anomalous elements of group II (inert gases) is much greater than for those of group I. Besides, group II of the anomalous elements contains elements whose FIEs vary in rows: He, Ne, Ar, Kr, and Xe; or 24.6 eV, 21.56 eV, 15.76 eV, 14.0 eV, and 12.3 eV respectively.

According to the calculation and the extrapolated experimental data, the energy gain at the expense of bond formation is evaluated, in the case of Ar, Kr, Xe, at about 150 kJ/mol, while in the case of He, Ne – zero. That is, inert (noble) gases, as compared with group I of anomalous elements, the energy gain decreases at the expense of bond...
formation (because of the high FIE in these elements) while the energy loss increases because of the penetration of the electron into each of the atoms being bonded to the outermost shells of these atoms.

Thus, it is obvious, how the atom’s affinity towards the electron is expressed in the bonding energy of a molecule, why there is an anomaly low energy in the covalent bonds of group I of anomalous elements, and why the noble gases are inert. Their chemical inertness is, in part, due to the fact that they are not connected (do not form a chemical bonds) between themselves.

According to experimental data relative to ionization energies, the anomalous elements of group I contain 2 electrons in the outermost shell, while the inert gases contain 8. Thus, on the basis of experimental data on bonding energy, and on the basis of the atoms’ affinity to the electron, atoms with two electrons in the outermost shell are capable of bonding an additional electron if the nuclear charge is increased by one proton unit, while atoms with 8 electrons do not bond an electron to the outermost layer, but begin forming a new electronic layer.
15 VALENCE

Valence is the number of electrons that an atom gains, loses, or shares when bonding with one or more other atoms. The valence in atoms is seen only when they are bonded.

One of the main questions in chemistry is:
Why is it that a strictly defined and limited number of atoms is bonded via covalent chemical bonding with one atom?

Once more: In the course of a chemical experiment it was found that each atom is capable of bonding only a certain number of other atoms. Thus, for example, the atoms of group I in the table of elements are capable of connecting one hydrogen atom with the formation of compounds called metal hydrides. Atoms of the II, III, and IV groups can bond the number of hydrogen atoms that corresponds to the numbers of the group, i.e., 2, 3, and 4. The atoms of the V, VI, and VII groups bond only 3, 2, and 1 hydrogen atom respectively.

Another important question is:
How does our theory of chemical bonding explain the valence rules?

According to our theory, only the electrons in the outermost layer of the atom take part in chemical bond formation: 1) only one electron takes part in covalent bond formation. That is, the number of electrons on the outermost shell of each atom defines the possible number of bonds that the given atom can form. 2) In the course of chemical bond formation, the number of electrons in the outermost layer of each atom increases by one.

Now let’s cite an example on the basis of the second and third periods: How do our regularities explain the valence rules?

In row: Li, Be, B, C, N, O, F the number of electrons in the outermost layer of the atom increases by one unit when consecutively transiting from one member of the row to the next. Li has but one electron on the outermost shell. According to point 1) — Li can form one bond in its outermost shell; after bond
formation, there will be 2 electrons. According to point 2) — Be, B, and C can form 2, 3, and 4 bonds respectively. And in their outermost shells, after bond formation, there will be 4, 6, and 8 electrons respectively.

In the case of N, which has 5 electrons in the outermost layer, after the formation of 3 covalent dual-electronic bonds, its outermost layer will contain 8 electrons (5 initial ones and 3 additional ones).

As indicated in the previous section, atoms, with 8 electrons in the outermost shells, do not form covalent bonds; that is, out of 5 electrons of the N-atom in the outermost layer for bond formation, the N-atom is capable of utilizing only three.

A homopolar covalent bond is one whose dipole moment has a value close to zero. It can be either homoatomic (Cl₂, Na₂) or heteroatomic (LiNa). A heteropolar covalent bond is one whose dipole moment is higher than zero (NaCl, BaCl₂, etc.)

A molecule of NaCl is formed of atoms of sodium and chlorine. Chlorine has 8 electrons in its outermost shell, while sodium has only 2. That is, the outermost shell of the sodium is unfilled. On the other hand, only 2 electrons from the filled chlorine shell take part in the formation of the heteropolar bond Na – Cl. Six electrons (3 pairs) in the outermost shell of Cl do not take part in bond formation. That is, in the case of molecule NaCl, the sodium can bond 6 more electrons while the chlorine can offer 6 electrons for bonding. Thus, one NaCl molecule can connect another NaCl molecule with the formation of a dimmer Na₂Cl₂, which can be illustrated as a molecule:

\[
\text{Na : Cl} \\
**        ** \\
\text{Cl : Na}
\]

In this molecule, the electrons, indicated via two dots (:) belonged separately to sodium and chlorine atoms before the bonding. The electrons indicated with dots (●) belonged to chlorine in molecule NaCl before the bonding.
The bond between two atoms, which is formed at the expense of the electrons of one atom are called donor-acceptor bonds (DAB). Here the bonding pair of electrons also enters the outermost shells of both atoms being bonded. The energy gain, just as in covalent bonding, is attained at the expense of the concentration of the positive charge. Its difference lies in the fact that during bond formation, not one but both electrons, which belonged to one atom (a donor) before the formation, enter the shell of another atom (an acceptor).

The Na$_2$Cl$_2$ molecule was received experimentally, so was the reaction energy $2\text{NaCl} \rightarrow \text{Na}_2\text{Cl}_2$. This energy is equal to 186 kJ/mol (one DAB being equal to 93 kJ/mol). The bonding energy of a NaCl monomer is equal to 410 kJ/mol, while the bonding energies of Na – Na and Cl – Cl comprise, relatively, 75 kJ/mol and 238 kJ/mol, i.e., the DAB is much weaker than the covalent bond.

One of the main reasons for the comparatively weak DAB is as follows. When calculating the bonding energy, the initial atoms’ electronic energy, taking part in bond formation, is subtracted from the molecule’s calculated energy. The ionization energy of the two non-bonding chlorine electrons in NaCl exceed the sum of the FIEs of both sodium and chlorine atoms.

That is, the energy gain (difference between the electronic energies of the divided and bonded atoms via chemical bonding) in the case of the DAB is smaller at the expense of the energy increase of the divided atoms. The DAB is a well-known kind of chemical bonding. It is due to the DABs that saturated molecules with non-binding (lone pair) electrons are connected to atoms in molecules with unfilled outermost shells. The above-cited example with NaCl is an example of such a bond.

Historically, molecules containing electron donor atoms are called ligands and, in the capacity of acceptors, are the elements of the 4th, 5th, and 6th periods in the table of elements. The saturation of the outermost electronic shells of these elements is possible when there are more electrons than in the outermost shell of the elements of the 2nd and 3rd periods.
Thus, for example, the saturation of the outermost shells with nickel (Ni), cobalt (Co), rhodium (Rh), is possible when each of these have 18 electrons. The atoms of these metals have only 10 electrons in the outermost electronic shells, but can bond 4 molecules of carbon monoxide via the DAB when in the atomic state.

Each molecule of carbon monoxide increases the number of electrons in the outermost shell of a metal by 2. The outermost shell of the metal molecule $M(CO)_4$ contains 18 electrons.

Historically, such compounds have been called coordinate compounds. Of these compounds we single out the $M$ (coordinate metal), and molecules (in this case – CO), or ligands.

Now let’s see what kind of interaction we can expect between atoms whose outermost electronic shells are filled. In this case, no DAB is formed, however, there is a slight energy gain at the expense of the positive charge concentration around which the electrons rotate. Bonds caused by this energy gain have been called Van der Waals bonds (VWB). The energy of these bonds is about ten times smaller than that of the covalent bonds. Such bonds are most common between molecules where the outermost shells of the atoms are completely filled with electrons. For example, bonds between halogen molecules:

$$F_2 ... F_2 \quad Cl_2 ... Cl_2$$

The VWBs are connected among themselves and to the noble gas atoms:

$$Ne \quad Ne$$

The filling of the outermost shell with atoms connected with covalent bonds can occur not only at the expense of the connection of new atoms, but also at the expense of the formation of multiple bonds. Thus, for example, in the case of carbon (C), besides the existence of compound:
where the shells of both carbon atoms are filled at the expense of the hydrogen atoms’ electrons, there are also compounds of this type:

\[
\begin{array}{c}
\text{H} & \text{H} \\
\text{H} : \text{C} & \text{C} : \text{H} \\
\text{H} & \text{H}
\end{array}
\]

In these compounds the outermost electronic carbon shells are filled partially by electrons at the expense of the electrons of each of the connecting carbon atoms. In ethylene the carbons are connected between themselves with a double bond, and in acetylene – with a triple one. Unlike cases with single bonds, in this case there is repulsion between the bonding pairs of electrons; and we should expect a decrease in the energy gain at bond formation.

In other words, if we compare the energy gain of six bonds formed between carbon and hydrogen in a carbon-carbon bond in ethane, with the energy gain at the expense of the formation of four carbon-hydrogen bonds and two carbon-carbon bonds in ethylene, the latter will be greater.
CONCLUSIONS

Thus, atoms bond to each other via the following types of bonds: covalent bonds, homo-atomic and hetero-atomic bonds (single, double, and triple), donor acceptor bonds (DAB), and Van der Waals bonds (VWB). During the formation of a single covalent bond, the number of electrons in the outermost shells of the atoms being bonded increases by one. During the formation of double and triple bonds, the number of electrons in the outermost shells of the atoms being bonded, increases by two and three electrons respectively.

DABs are formed between atoms, one of which has a filled outermost shell while the other hasn’t. Correspondingly, when forming a DAB, the number of electrons in the outermost shell of a donor atom does not change while the number of electrons in the shell of the acceptor atom increases.

VWBs are formed between atoms whose outermost shells are filled. When VWBs are formed, the number of electrons in the outermost shells of the atoms to be bonded does not change. Covalent heteropolar bonds are stronger than covalent homo-polar ones. The energy of covalent heteropolar bonds increases proportionally to difference of the FIEs of the atoms being bonded. The dependence of the energy of the covalent homopolar bond on the FIE of the atoms to be bonded has the form of a parabola. The strongest bonds of this kind are formed by elements with FIEs of 9 eV to 11 eV [for example, carbon (C). Bonds between atoms of the 2nd period with FIEs of 5 eV (Li), and 17 eV (F) are much weaker.

During covalent bond formation, both bonding electrons enter the outermost shell of the atoms to be bonded. If the electron’s entrance to the atom’s shell is connected with energy expenditure, (the atom’s affinity to the electron being close to zero), then either an anomalously weak covalent homo-atomic bond is formed (group I of anomalous elements), or no bond is formed (group II of anomalous elements — noble gases).
The DAB energy is about 2 times smaller than the covalent bond energy. The VWB energy is about 10 times smaller than that of covalent bonds. The physical nature of all the above-mentioned bonds is the same.

The energy gain during chemical bond formation is due to the fact that when the positively charged nuclei approach each other, the electrons start moving in the field of the greater positive charge (as compared to the initial charge), which causes the energy gain because in organized systems, like that of the atomic system (atoms, molecules, etc.), the electron’s energy is proportional to the square of the positive charge.

According to the valence rules whose physical nature was cited above an atom can bond to other atoms in numbers that correspond to the atom’s valence. That is, for example, carbon (C) can be bonded to 4 hydrogen atoms, or to other carbon atoms with a double bond, and with two bonds of hydrogen atoms.

For example, let’s take a molecule of ethylene:

\[
\text{H} \quad \text{C} = \text{C} \quad \text{H}
\]

Here each line corresponds to a pair of bonding electrons.

In a molecule of benzene each carbon atom is bonded with another carbon atom via a double and single bond.

In the above-cited dimmer, sodium and chlorine atoms are bonded via covalent heteropolar bonds and DABs.

\[
\text{Na} \quad \text{Cl} \\
\uparrow \quad \downarrow \\
\text{Cl} \quad \text{Na}
\]

In a molecule of organic acid, one oxygen atom is bonded to carbon via a double bond, another oxygen atom – via a single one:

\[
\text{R} \quad \text{C} = \text{O} \\
\text{OH}
\]
It was found experimentally that if the compound, in the framework of the theory of chemical bonding, may be presented in the form of isomers with a value close to that of the electronic energy, then the length of the chemical bond and, consequently, its energy, changes. That is, the weak bond becomes stronger, and the strong one becomes weaker.

Thus, in dioxide sulfur, the length of the bond between the sulfur

\[
\begin{array}{c}
\text{O} \\
\uparrow \\
\text{S} \\
\mid \\
\text{O}
\end{array}
\]

and both oxygens are identical and comprise 1.432 Å, though, according to the chemical bonding theory, the double bond should be much shorter than the single one.

Analogously, in benzene, which has double bonds and single ones, the bond-length between all the carbons is identical.

The same is true of an atom bonded with atoms by coordinate bonds and with other identical atoms through covalent bonding:

\[
\begin{array}{c}
\text{H} \\
\{\text{H : N : H}\}^+ \\
\text{Cl} \\
\text{H}
\end{array}
\]

All the bonds between nitrogen and hydrogen have the same length. The same phenomenon is observed when atoms are bonded with both covalent bonds and VWBs:

\[
\begin{array}{c}
\text{I}_3 \\
\text{Br}_3 \\
\text{Cl} \\
\text{I} \\
\text{Cl} \\
\text{Br} \\
\text{Cl}
\end{array}
\]

In all these compounds the bonding length and energy between the remote atoms and those in the middle, are the same and also have an intermediate value for the covalent bond and the VWB (see table 2.7-1).
### TABLE 15.1  Well-Known Trihalide Ions

<table>
<thead>
<tr>
<th>Bond Lengths (Å) vs. Reference Bond Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X—Y—Z</td>
</tr>
<tr>
<td>(I—I—I)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>(Br—Br—Br)</td>
</tr>
<tr>
<td>(Cl—I—Cl)</td>
</tr>
<tr>
<td>(Cl—I—Br)</td>
</tr>
<tr>
<td>(Cl—Cl—Cl)</td>
</tr>
<tr>
<td>(Cl—Br—Cl)</td>
</tr>
</tbody>
</table>

One very interesting example involves a combination of the VWB and polar bond for a hydrogen atom. In chemical literature these bonds are called hydrogen bonds. This can be illustrated as: A – H ... B; where A is the oxygen or some other good acceptor for electrons (halogens, etc.), and B is an atom with undivided electronic pairs. In this case, the strengthening of the VWB between H and B and the weakening of the polar covalent bond between A and H have been proven. As a rule, the energy of a hydrogen bond (increased VWB between H and B) is equal to 2.5 - 9 kcal / mol. (See table 2.7-2).

When this bond is formed, the distance between A and B, in the presence of hydrogen, is smaller (in spite of the hydrogen atom) than in analogous compounds without the hydrogen atom (table 2.7-2).

### TABLE 2.7-2  HYDROGEN BONDS AND BONDING ENERGIES IN COMPOUND A-H ... B

<table>
<thead>
<tr>
<th>Alcohols</th>
<th>Energy (kcal/mol)</th>
<th>Chloroform</th>
<th>Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃ O-H...O (C₂H₅)₂</td>
<td>2.5</td>
<td>Cl₃ C-H...N (C₂H₅)₂</td>
<td>4.0</td>
</tr>
<tr>
<td>CH₃ O-H...N (C₂H₅)₂</td>
<td>3.0</td>
<td>Cl₃ C-H...OC (CH₃)₂</td>
<td>2.5</td>
</tr>
</tbody>
</table>
When atoms are bound together by single or multiple bonds, their total electronic energy is much lower than expected. The decrease of electronic energy was evident from the combustion reaction, and the hydrogenation reactions of the multiple bonds.

What is the nature of this phenomenon? This is explained by the electron-nuclear isomerization, which is discussed in our bonding theory. Previously all these phenomena were explained in the framework of the resonance theory, which considered that the molecule was a hybrid.

The resonance theory confirmed that the explanations of this phenomenon, supposing mutual transitions of one kind of molecule into another, are incorrect.

Electrons in molecules move not only within the energy minimum (energy hole), which is defined by the electrostatic component of chemical bonding, but they transit with a great speed around the entire molecule. This phenomenon has been proven experimentally.
Electronic transitions between substances are common in our everyday life. We have felt a slight electric shock when we closed the door of a car, or when we walked a while on an artificial floor covering and then touched something metallic.

At your school lessons devoted to the electrostatic phenomenon, you were shown experiments, which explained the existence of two kinds of charges. You learned that if you rub a glass rod on silk cloth, the electrons on the rod shift over to the silk cloth to give a negative charge, while the rod is positively charged. Then you have learned that if you rub an ebonite rod on woolen cloth, then the electrons shift from the woolen cloth to the ebonite rod. Also you have seen that if you touch a metallic sphere on an electroscope with an ebonite rod, the electrons will shift from the rod to the petals on the electroscope.

Mysterious charges also originate when you comb your dry hair, small bits of paper seemingly stick together when touched by a comb. What is common in all these cases is that we practically do not use any energy; all we do is contact various objects and the electrons shift from one object to another. The same phenomenon takes place when atoms come close together in liquid or gas phases.

This phenomenon of electronic transition is expressed as follows:

\[ *\text{Fe}^{2+} + \text{Fe}^{3+} \rightarrow *\text{Fe}^{3+} + \text{Fe}^{2+} \]

Also studied were the biochemical systems where protein molecules connect to each other by metal atoms. Influence of the main parameters on the speed process has also been studied. Temperature has a small influence on the electronic transition speed, which is great even at temperatures close to absolute zero.

The parameter that influences electronic transition speed is the distance between the atoms. The next important thing is the medium between the atoms. The transition speed
dependence on the distance is defined by the equation: $W = kd$; ($d$ is the electron's transition distance).

Depending on the type of substance between the atoms, the speed of the electron transition is defined by the equation:

$$K_{ex} = 10^{17} \exp(-2d/L)$$

(2.7-1)

where $d$ is the distance (in Å) between the centers of the interchanging species; $L$ is a coefficient, which is defined by the type of bonding.

If all the bonds inside the molecule are saturated, then $L = 0.7$. In such systems, the exchange slows down by 10 times per each 1Å. If the system has some conjugated bonds, then $L = 6.5$ and it has a slow-down effect of about 9 times smaller than in the first case.

The number of experimental proofs on transition reactions has been increasing due to discoveries and improvements in methods to identify the compounds and increase the speed of their determination and sensitivity in the analyses. The examples include the following:

**Tautomeric Transformation:**
Electronic Isomerization of Bulvalen

Electronic Isomerization of Homotropimedene:

Electron-Nuclear Isomerization of Hydrocyanic Acid:

\[ \text{HC} \equiv \text{N} \Leftrightarrow \text{H}–\text{N} = \text{C} \]

From chemical experiments we know about electron-nuclear isomerization, which proceeds in compounds of the bulvalene and homo-tropimedene type. Benzene, according to the formula, is analogous to bulvalene compounds. Therefore electron-nuclear isomerization in benzene should occur and mutual transitions of benzene forms take place.

The anomalous energies and the bond lengths in benzene (when the energy and bonding lengths are equal) are
connected with the electron-nucleus isomerization phenomenon. Mutual transition occurs at such a great speed, which cannot be determined by present-day technique.

The example with benzene shows that with an increase in the electron-nuclear isomerization speed, all the effects connected with the latter are increased. These effects include: energy decrease, shortening of weak bonds, and a general decrease in the system's energy.

The electron-nuclear isomerization speed is determined by the transition speed of the nuclei. Thus, in the case of benzene and H-bonds, these effects are most obvious. When an H-bond is formed, the proton's transition speed is much greater than that of other atoms. In the benzene case, the atoms transit shorter distances during the isomerization process.

The isomerization of acetylacetone confirms the possibility of electron-nuclear isomerization in systems where covalent bonds and VWB are formed simultaneously.

Here is an example with a three-methyl-Al dimmer:

![Diagram of three-methyl-Al dimmer]

Here we see that even a system with only single bonds is constantly regrouping. This phenomenon is characteristic of chemical compounds and is not limited to some specific atoms or bonds. In all cases this is evident in the equalizing of the length and energy of the bonds and the increase in the bonding energy (increase of stability).

The above-mentioned explanation is regarded as phenomenological, and raises a new question:

What is the physical nature of the phenomenon called electron-nuclear isomerization?

Answer: The electrons in the molecules are situated in energy minimums of 1-2 eV.
But first let’s take the question which arises in this connection:

At the expense of what energy does the electron transit from one minimum to another?

The difficulty in answering this question was caused by one of the main principles of quantum mechanics, which presupposed that the electron could not change its energy in such small portions as 2 or 3 eV.

Traditionally, the energy exchange between electrons was never presupposed in quantum chemistry, while in the framework of our theory, the energy exchange between electrons is not only presupposed, but is even proven by the exchange mechanism via the energy exchange between the electrons.

The electronic energy in molecules is defined by the energy of the nuclei. The Maxwell-Boltzmann law describes the distribution of the vibrational, rotational, and translational energies of the nuclei. Relatively, we can suppose that this law describes the distribution of the electrons’ energies as well.

Besides this energy-transmitting mechanism, which can be regarded as a mechanism of translational movement, the atomic systems (electrons and nuclei) should also have a mechanism for changing the vibrational energy.

If, in a mechanism of translational movement, the energy transits from particles with a greater energy to particles with a smaller energy, then, in the case of vibrational energy, the energy transition is defined by the vibrational phase, and not by the energy.

Recall the energy exchange between pendulums vibrating on one axis. Both mechanisms allow us to presuppose an accumulation of sufficient energy on the minor portions of electrons, so that the latter could overcome the barrier that divides the minimums, since the average energy of only the outermost electrons in the system is equal to 12 eV.

The evaluation of the barrier energy that the electrons have to overcome, is possible judging by the following consideration:

According to the chemical bonding theory, the energy gain during chemical bond formation is conditioned by the approach of the nuclei to the bonding electrons located between them. In system D … H : T, the transition of the electrons from
covalent bonding (H : T) to VWB (D ... H) with the formation of D : H ... T, is connected with the receding of the electron from atom T and its approach to atom H. That is, the topmost barrier limit, during the transition of one electron from bond H : T onto atom H, amounts to half of the energy gain (enthalpy) during bond formation and is equal to 1 eV.

The receding from one nucleus of atom T with a simultaneous approach to the nucleus of atom (H) does not significantly change the general potential energy of the system, and therefore, the height of the barrier is much lower (close to zero) and not 1 eV.

However, if we consider that the electron recedes from atom T and approaches two D ... H atoms during the transition, then the height of the barrier is equal to 0 — 0.2 eV; that is, a height that is greater than what the electrons with an average energy of 12 eV can overcome.

The electron in the atom has kinetic energy of about 10 eV. The following equation for kinetic energy

\[ E = \frac{mv^2}{2}, \]

helps to evaluate the speed of the electrons:

\[ v = (2E / m)^{0.5} = (2 \cdot 10 \cdot 96 \cdot 10^3 / 9.1 \cdot 10^{-31} \cdot 6.02 \cdot 10^{23})^{0.5} = 10^6 \text{ m/sec} = 10^{16} \text{ Å/sec}. \]

This speed can be compared with the transitional speed of an electron measured experimentally and calculated as follows:

\[ v = 10^{17} e^{-2R/L} \]

where R is the distance Å (in our case 1Å); and L is the coefficient equal to 6.5 in conjugated systems, and — 0.7 in non-conjugated ones.

According to this equation, the transitional speed of the electron for conjugated systems can be estimated at \(10^{17}\) Å/sec, while for non-conjugated ones — \(10^{16}\) Å/sec, i.e., values close to those already calculated. The above-mentioned explanation and the data obtained from the experiment, coincide semi-quantitatively.
As mentioned above, the vibrational system can contain another mechanism, which imitates the transition of electrons. In this case it does not really transit but simply passes its energy to another electron, which happens to be rotating, for example, in a parallel circle.

As a result of this exchange, the bond that had hitherto been covalent, for example, in the system D...H : H, becomes a VWB, and vice versa — the system becomes D : H ... H. The time of these transitions can be evaluated by the electron’s rotation frequency, which is about $10^{-16}$ sec. The simultaneous existence of both mechanisms is possible.

The mechanism, being characteristic of translational movement, should bring the system to equilibrium as far as the nuclei are concerned. The system is in dynamic equilibrium defined by thermodynamics, i.e., the speed of the mutual transitions is defined by the free energy change.

In the vibrational mechanism the system transits from one state to another with an identical speed, irrespective of the change in the free energy. Indeed, according to the experiment, there are cases of electronic transition when the transition speed depends on the free energy change, and cases when it does not.

The mechanism, which is usually given in textbooks, presupposes a tunnel transition for electrons. At present this popular mechanism offered by R.Markus (Nobel Prize winner in 1993) supposes that the tunnel transition is a rare phenomenon.

Time for another question:

**Why do bonds become shorter as a result of electron-nuclear isomerization?**

The electrons’ transition speeds are by about 2 orders of magnitude greater than those of the nuclei. Because of this, the nuclei occupy an intermediate position, which leads to the shortening of the bond.

The shortening and strengthening of the weak bonds as a result of the electron-nuclear isomerization allows explaining the increased thermal stability of aromatic compounds. The thermal stability of compounds is defined by the thermal stability of the weakest bonds present in the given compound. That is why the strengthening of weak bonds leads to the increase of thermal stability.
Besides, the increase of electronic entropy is caused by the increase of the aromatic compound's stability. The increase of the electronic entropy is connected with electron-nuclear isomerization as follows:

A system with aromatic compounds contains various isomers of such compounds that lead to the increase of the number of possible electronic microstates for these systems and therefore, to the increase of the electronic entropy of the system and to the increase of the system’s thermal stability.
A P P E N D I X B

COPY OF THE SUMMARY PUBLISHED IN OUR BOOK ENTITLED:

HOW CHEMICAL BONDS FORM AND CHEMICAL REACTIONS PROCEED

Here we wish to briefly summarize the results of our work conducted from 1980 to 1997 in chemistry and physics. The main points of this book, from which a greater understanding of chemistry was gained, are as follows:

1) theory of chemical bonding;
2) theory of chemical structure;
3) theory of chemical reactions;
4) elucidation of the connection between the physical and chemical properties of substances; the number of electrons in the outer electronic shells; the atoms’ FIEs; the affinity to the atoms’ electrons out of which the chemical compounds are formed.

Now let’s briefly indicate the most important of the new results received from each of the above enumerated directions.

SUMMARY: THEORY OF CHEMICAL BONDING AND CHEMICAL STRUCTURE

In the course of the work conducted during these years, answers were given to questions, which gradually arose during the development of chemistry from alchemy to electronic chemistry. As far as the latter is concerned, back in the 1930s it was realized that the structures and transformations of chemical substances are defined by the change of the electrons’ energies in the outer layer of the elements’ atoms.

On the basis of the studies and conclusions made on chemical materials accumulated by Mendeleyev, Lewis, and Pauling, rules were formulated to better explain the structure of chemical compounds and their physical and chemical...
properties. The Table of Elements, the Lewis Rules, the Resonance Rules, and the Valence Shell Electron Pair Repulsion Rules (VSEPR) allowed foretelling the chemical and spatial structure of chemical compounds.

The discovery of a great number of chemical reactions (especially in organic chemistry) has allowed suggesting the synthesis method for chemical compounds. In the beginning of the 19th century the scientific basis for chemistry was formed: the atom-molecular theory of substance structure and the theory of chemical transformation.

In the framework of the structure theory, it was found that chemical compounds (molecules) consist of atoms, which are connected to chemical bonds. As far as the theory of organic compound structure is concerned, rules were formulated (first of all the four-valence carbon rule) which allowed foretelling the structure of organic compounds. The Lewis Rules and the Resonance Rules allowed foretelling the structure of both organic and inorganic compounds.

Most urgent was the general question concerning the physical nature of chemical bonding. Also urgent were the questions concerning the elucidation of the physical nature of the above mentioned rules (Periodic Law, Lewis Rules, Resonance Rules, etc.).

The following questions, concerning the theory, were unclear: Why is it that two electrons (one from each atom) and not one or three take part in the formation of the bond? Why is it that atoms taking part in chemical bonding strive to build their shells to the level of those of the inert (noble) gas? Why is there an exception to this rule? Etc.

Such questions arose in the course of the development of traditional (classical) chemistry as a science. In the 1930s the traditional development of chemistry was exchanged for quantum chemistry, which, in the 1980s, proved to be a false path in the development of science. At the beginning of the 1980s we continued the traditional path directed at deepening the understanding of the main chemical phenomena (i.e., chemical bonding and chemical reactions).

The improvement of the knowledge of the physical nature of chemical bonding involved a shift from the conclusion that during chemical bond formation the system’s
energy decreases to the explanation why the system’s energy decreases (qualitative explanation of the enthalpy factor) and by how much the system’s energy actually decreases (quantitative evaluation of the enthalpy factor for homoatomic and heteroatomic molecules).

We have managed to realize why more energy is required for breaking a chemical bond as compared to the difference in electronic energies of atoms and molecules (qualitative evaluation of the entropy factor). We have also managed to quantitatively evaluate the influence of the entropy factor on the chemical bond-breaking energy. The evaluation of the enthalpy and entropy factors has allowed us to compile a system of three algebra equations with three unknowns (which we will further refer to as a system of equations), on the basis of a model which presupposes that covalent (homo- and heteroatomic) bonding is formed via electrons which rotate in one circle whose plane is perpendicular to the axis connecting the nuclei. Upon deducing the system’s equations, it was supposed that electrons were particles with a definite mass, a charge, and an orbit speed.

The solution of the system of equations, with regard to a hydrogen molecule, has shown that the value of a hydrogen molecule’s electronic energy differs from that received via the experiment by less than 4% which proves the correctness of the model. This system of equations has helped to deepen the understanding of the main questions raised in the course of the development of the theory of chemical substance structure.

The solution of this system of equations has allowed realizing the physical essence of chemical bonding and the main regularities observed when studying the latter, which are given in the form of the Lewis Rules and as additions to these rules, which explained the exclusions concerning the Lewis Rules (connections with surplus electrons, the resonance rules, etc.) For example, the system of equations has allowed calculating the optimal number of bonding electrons and the radius of the circle in which the bonding electrons rotate.

This system has allowed elucidating the functional dependence of bonding energy in dual-atom molecules on the
first ionization energy (FIE) of the bonding atoms and on the number of bonding electrons. It was found that when the FIEs of the bonding atoms are equal, a parabola describes the dependence of the bonding energy on the FIE. If the FIEs of the atoms differ, the bonding energy increases proportionally to the difference of the atoms’ FIEs.

The solution of the system of equations has made it possible to calculate the dependence of the following on the FIE of the bonding atoms: bond lengths, bond polarity, radius of the circle where the bonding electrons rotate, and the radius of the circle where nonbonding electrons rotate. All the calculated dependencies coincided with those received as a result of treating the available experimental data on the FIE of atoms, bonding energies, bonding lengths, and bond polarity.

According to the model whose correctness has been proven by comparing the calculated and experimental data when one atom is bonded to several atoms, covalent chemical bonds should have a definite direction. The corners between the bonds should be defined by the repulsion between the circles in which the bonding electrons rotate.

The calculation of the radius of the circle where the nonbonding electrons rotate has shown that this radius is greater than the radius of the bonding electrons’ circle. According to this model, the repulsion between the electronic pairs increases proportionally to the increase of the radius of the circle where the electrons rotate. That is, the interelectronic repulsion should, according to the calculation, increase in the row: nonbonding pairs — nonbonding pairs > nonbonding pairs — bonding pairs > bonding pairs — bonding pairs. Such a sequence is observed in the experiment summarized by the VSEPR rules.

On the background of a satisfactory coincidence in the calculated and experimental dependencies, for most of the elements there were great discrepancies between the calculated and experimental data for elements, which were called anomalous.

The reason for these discrepancies is explained as follows: The anomalously small bonding energy, as compared to the model calculation, had dual-atomic covalent bonds in a number of noble gases and elements with two
electrons on the atoms’ outer electronic shell. It was found that the anomalously small bonding energy in molecules formed out of anomalous elements is connected with the atom’s anomalous properties of these elements, which is obvious in the fact that unlike normal elements, the anomalous ones had negative values of affinity towards the electron.

As a result of solving the system of equations it was found that during the formation of a covalent bond, both bonding electrons enter the outer (previously existing) electronic shells of the bonding atoms. That is, in the process of covalent bond formation, the number of electrons in the outer shells of the bonding atoms increases by one unit. The coincidence of the rows of anomalous atoms (with a negative affinity towards the electron) and the rows of atoms with an anomalously small covalent bonding energy in dual-atomic molecules formed of these atoms, has shown that the anomalously small bonding energy is due to the additional energy expenditure connected with the entrance of the bonding electron to the outer layer of the atom being bonded.

We realized the anomalous behavior of atoms: inter-electronic repulsion in the outer electronic layers. The mutual repulsion of electrons in one layer causes their distribution in other layers. The number of electrons on the inner layers is the same in all atoms; that is why, when the nuclear charge increases, the number of electrons in the atom’s outermost layer changes periodically. According to electrostatics, the FIE of the atoms and their affinity towards electrons also change periodically. These three values thus define the physical and chemical properties of elements: valence, bonding energy, and reaction possibilities.

That is, the elucidation of the physical nature of the elements’ anomalous behavior helps to understand the following:

1) the physical nature of valence;
2) the connection between the FIE, the affinity of atoms towards electrons, the number of electrons in the outermost layer with the physical and chemical properties of elements, and the cause of their periodic change;
3) the physical nature of the Periodic Law.
We have deepened the understanding of the Lewis Rules.

Instead of phrases like: “A molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms...” and “The most important requirement for the formation of a stable compound is that the atoms achieve noble gas and electronic configuration....”, the following wording has been suggested:

“According to the solution of the system of equations, it has become clear that:

1) the minimal electronic energy (during the formation of two atomic molecules out of atoms) is achieved when two electrons (not one or three) rotate between connected nuclei;

2) during the formation of a covalent bond the number of electrons in the outermost shell of the atoms being bonded is increased by 1.”

The interelectronic repulsion (between the electrons of the outermost layer) limits the number of electrons that can enter the outermost layer of the atom when chemical bonding occurs. That is why the number of bonds that an atom can form with other atoms is limited. The number of electrons in the outermost layer, plus those added during bond formation, cannot exceed 8 — for the first 20 elements in the Mendeleyev Table of Elements.

The improvement of the Resonance Rules included the elucidation of the physical nature of the phenomena described by these rules. It became known that the effects, described by the Resonance Rules, are conditioned by electron-nuclear isomerization.

We have managed to answer many special questions like:

- Why are inert (noble) gases inert? Why is bonding energy in $F_2$ smaller than in $Cl_2$? Why is $F_2$ a more active oxidizer than $Cl_2$? Why is mercury, being a metal, always in liquid form at room temperature? Why is it that during molecule formation the atoms construct their shells up to the shells of inert (noble) gases?
THEORY OF CHEMICAL REACTIONS

The main questions that were raised in the course of the development of the theory of chemical reactions were as follows:

1) Why don't all chemical reactions proceed if they are thermo-dynamically possible?
2) Why does the reaction speed increase along the exponent with the increase of temperature?
3) Why is it that in reactions proceeding with bond breaking, the activation (additional) energy is usually much smaller than that necessary to break the bond thermally?

Indeed, why is it that reactions proceed with the breaking of the chemical bond in normal conditions, while we need a temperature of more than 4,000° C to break such bonds thermally? Examples of such reactions are interactions of radicals and ions with molecules, catalytic and photochemical reactions. This question was not even touched upon before the beginning of our work.

In the course of our studies we managed to learn that unlike the opinions accepted in 1980, the interactions between molecules take place not via the scheme:

\[ AB + CD \rightarrow AC + BD \]

but mainly along the chain reaction scheme:

\[ AB \rightleftharpoons A + B \]
\[ A + CD \rightarrow AC + D \]
\[ D + AB \rightarrow DB + A \]

where A, B, and D are active species (radicals, ions, conences).

That is, unlike the ideology accepted in 1980, the active elements in chemical reactions (species which cause chemical transformations) are not at all species or molecules with a high kinetic energy. The active elements are actually specific chemical species like radicals, ions, conences, etc.
It has been found that the interaction of these species with saturated molecules proceeds via three elementary stages (steps): association — electronic isomerization — dissociation.

Dissociation is the step that usually limits the process. The given scheme for the procedure of the chemical reactions answered the main questions, which arose during the development of chemical kinetics, mentioned above.

Active species are in thermodynamic equilibrium with the initial molecules. When the temperature decreases, the concentration of active species exponentially drops, causing an abrupt decrease in the speed of the chemical reactions. This dependence of the chemical reaction rate on the temperature explains why all the possible thermodynamic chemical reactions do not proceed at normal temperature (1st question) and why the reaction rate between the molecules exponentially depends on the temperature (2nd question).

The presence of the electronic isomerization step in the mechanism of the chemical reaction answers the 3rd question. The electronic isomerization speed is by many orders of magnitude higher than that of the dissociation step. That is why the kinetic parameters of the electronic isomerization step, and first of all — the activation energy, do not effect the activation energy of the whole reaction process which defines the energy consumption. That is, the energy necessary to break the chemical bond in the initial molecule is equal to the activation energy of the slowest step (dissociation) in the reaction of an active species with a saturated molecule.

As a result of electronic isomerization, the initial covalent bond, which requires about 400 kJ/mol in order to break, transforms into a Van der Waals bond (VWB), which requires less than 20 kJ/mol for its rupture. Thus it becomes comprehensible why, in order to break a chemical bond in a molecule in the presence of an active species, we need an energy one order smaller than for the thermal rupture of the bond in this molecule (3rd question).

In the framework of the offered scheme, the driving forces of chemical reactions have become comprehensible.
In the light of the above, such notions as *catalysis* become understandable. A *catalyst* is a chemical compound which forms (produces) a greater number of active species in the system than initial molecules do at the same temperature.

The second method for accelerating the interaction of molecules is by increasing the concentration of the associates in the system in the presence of catalysts. Thus, for example, a catalyst substance unites other substances that react with each other along the scheme:

\[
\begin{align*}
AB + K & \rightarrow ABK \\
ABK + CD & \rightarrow ABKCD \\
ABKCD & \rightarrow AC + BD + K
\end{align*}
\]

where \(AB\) and \(CD\) are reacting substances.

The acceleration of the reaction (catalytic action of the substance) is explained thus: Due to the absence of the catalyst, the intermediate compound in the reaction is: \(AB \rightarrow CD\); while in the presence of the catalyst it is: \(AB \rightarrow K \rightarrow CD\). The speed of the whole reaction in both cases is proportional to the concentration of the intermediate compound. In correlation with concentration \(AB \rightarrow CD\) (without the catalyst) and \(AB \rightarrow K \rightarrow CD\) (with the catalyst), the concentration of these compounds in the system is defined by bonding energies \(AB \rightarrow CD\) and \(AB \rightarrow K \rightarrow CD\).

The bonding energies of both molecules with catalysts are much higher than the bonding energy between themselves, so the concentration of the intermediate compounds with catalysts is much greater, and correspondingly, much greater is the reaction speed.

This mechanism for reaction acceleration is typical for biological systems in which the catalysts are actually ferments (enzymes), which unite the reacting molecules in their centers.

Besides the above-mentioned mechanism for accelerating reactions, the catalyst can accelerate the reaction by other mechanisms:
1) it can improve the role of chemically activated routes;
2) it can serve as a bridge for the transition of electrons.

As expected, the substances that accelerate reactions in the above-mentioned mechanisms are catalysts; and the essence of catalysis, in the general approach, becomes better understood if compared with such general definitions as:

“A catalyst is a substance that accelerates a reaction. A catalyst carries the reaction along the route requiring less activation energy."

As a result of elucidating the nature of chemical reactions and chemical bonding, the nature of chemical reaction capability has become comprehensible as well as the physical nature of chemical properties in substances. In the course of the studies were clarified the connections between the atoms’ FIEs, out of which are formed the given substances, and their physical and chemical properties.

In the framework of the elaborated Theory of Elementary Interactions (TEI) an explanation was found about the main correlations discovered experimentally in the course of the studies concerning chemical kinetics. Among these studies were Influence of a Solvent, Linearity Rules Relative to Free Energy, Greenberg Rules, Resonance Rules, and some others that were imperial until the TEI came into existence.

To systematize all the above we can say the following. As a result of the performed work, we managed to realize the electronic structure of the molecule. We found that four main items of the covalent molecule’s electronic structure define the properties of the molecules.

1) Bonding electrons rotate in a circle whose plane is perpendicular to the axis connecting the nuclei.

This peculiarity of the electronic structure of molecules explains:
a) the dependence of bonding energy on the number of bonding electrons and on the FIE of the atoms being bonded,
b) the dependence of the bond’s length on the FIE of the atoms being bonded,
c) the dependence of the bond’s polarity on the FIE of the atoms being bonded,
d) the physical nature of the VSEPR Rules.

2) Bonding electrons simultaneously enter the outermost layers of the atoms being bonded.
   This peculiarity of the electronic structure of molecules explains:
   a) the saturation of covalent chemical bonding,
   b) the Lewis Rules and their exceptions,
   c) the physical nature of inertia in noble gases,
   d) the small covalent bond energies in anomalous elements.

3) Electrons in the molecules and in the molecules’ associates exchange energy and change their positions among themselves.
   This peculiarity of the electronic structure of molecules explains:
   a) the physical nature of equalizing bond lengths and their bonding energies when one atom is bonded to other atoms with various types of bonds,
   b) the phenomena described by the Resonance Rules
   c) why in the presence of radicals, ions, etc. the chemical bonds, for whose thermal breakage we need a temperature of more than 4,000° C, actually break at a temperature of 400° C.
   In turn, the physical nature of the radicals’ activity explains how the reaction proceeds between saturated molecules; it explains the mechanism (in the physical sense) of catalytic and photochemical reactions.
   Generally, the elucidation of the molecules' electronic structure in our bonding theory, the cause of the
anomalous behavior of some elements, and the physical nature of various phenomena, described by the Resonance Rules, allows us to interpret the physical phenomena without the use of all the above-mentioned rules and the Periodic Law.

4) The electrons in the molecules, unlike those in the atoms, change their energy when the molecules are given heat energy during excitation of the vibrational and rotational freedom stages.

The breaking of the molecule into atoms is connected with the electrons' absorption of energy and with the increase of the distance between the atoms, which is caused by the increase of the rotational and vibrational energies of the molecules during thermal excitation. At interatomic distances greater than 5 Å, the energy of the bonding electrons is close to that of the electrons in separate atoms.

In the intermediate points (internuclear distance in the molecule - about 2 Å) the electrons' energies have intermediate values. That is, the electrons in a molecule can directly absorb energy in large (luminous) quanta and they can indirectly use energy in small (thermal) quanta at the expense of the rotational and vibrational energies of the nuclei.

This peculiarity of the electronic structure explains:

a) why the energy, necessary to break a chemical bond, is about two times greater than the difference between the energies of the electrons in the divided atoms and those in the molecule;

b) the difference in atomic and molecular electronic spectra.

Here are the main points, united by cause-and-effect ties, to which the authors focus the readers' attention:

1) The electron is a particle.

2) There is a quadratic energy dependence of atomic and molecular systems on the nuclear charge.

3) There is a difference in molecular and atomic spectra.

4) The atom has a layer-like structure.

5) Electron-nuclear isomerization takes place whenever possible.
A set of simple equations has shown that the use of the electron’s properties, such as a negatively charged particles with a definite charge, mass, kinetic and potential energies, were sufficient to semi-quantitatively explain the physical nature of chemical bonding and chemical reactions.

As far as teaching chemistry is concerned, we have managed to simplify the interpretations, and therefore, improve the comprehension of the material by high school students. To explain the physical nature of the main chemical phenomena, the student should have at least a 10th grade knowledge of mathematics (algebra, geometry), physics, and chemistry.

The authors say that one of the main practical significances of the system of explanations for chemistry teachers is in the fact that this system spares them from such fear as described in the article of W.S. Shilard (J. Chem. Educ. 1955. 72. 215) and the fear of being asked such questions as:

Why do you offer us quantum chemical explanations nowadays even though the discussions of 1990–1992 have led the scientific world to conclude that these are false explanations? Or: Why don’t you make use of the new system of explanations?

The teacher is able to use various schemes of explanation in his work, depending on the level of knowledge of the listeners. Here are some examples of schemes:

Level I

Atom structure: Nuclei surrounded by layers of electrons.
Chemical bonding: Electrons rotating in a circle perpendicular to the axis connecting the nuclei.

Level II

What questions were raised and answered in the course of the development of science?
What is the smallest particle of a substance and an element?
What forces connect (bond) the smallest particles?
What forces can break the bonds between the smallest particles?

Atom structure on the phenomenological level:

1) Rutherford's experiment (empty atom, positively charged nucleus);
2) Experiments on ionization energies; layer-like structure of the electronic cloud; number of electrons in each layer, in the outermost layer, periodic change of the FIEs;
3) Structure and properties of molecules on the phenomenological level. Periodic changes of the FIEs as a result of the layer-like structure of the atoms.

On the next level, some of the questions in the section about chemical bonding can be formulated in a paradoxical manner:

*Are there any special chemical forces?* (This involves the question about the so-called third force besides gravitational and electric forces.)

*What in atom structure, at first sight, contradicts common electric interactions?*
1) the layer-like structure of the atom;
2) the identical number of electrons in the inner layers;
3) the periodicity of chemical and physical properties of elements depending on their atomic weights;
4) molecule structure;
5) the participation of only two electrons in bond formation;
6) lack of regularity between the FIE and the bonding energy;
7) various types of bonds;
8) saturated bonds.
Such points are explained in our Theory of Chemical Bonding. The answers to these questions are given either at qualitative or quantitative levels with or without derivations from the main equations.

Approaches to chemical questions can be made in the traditional phenomenological manner: by explaining the notion valence, by experimental data on various types of bonds and their energy values.

Next comes the question of the physical nature of various bonds: Are there any special chemical forces that bond atoms?

Then comes the point concerning the nature of the main correlations found in experiments: 1) the Periodic Law, 2) the Lewis-Langmuir-Sidgewick Rules, 3) the Valence Rules, 4) the Resonance Rules, and 5) the VSEPR theory.

One can also emphasize both the logic and mathematical dependencies using equations, which can be solved analytically. For example, one of the simplest (one plane) atom models leads to the layer structure of electron shells, and then to a limited number of electrons in the outer shell, which is confirmed in experiments on electron affinity towards atoms and ionization potentials. Experiments specify the number of electrons in the layer and the various kinds of anomalous elements.

Further, we should derive the main equations involving bonds and compare the results with experiments. Then we will see that the calculated bonding energy semi-quantitatively coincides with the experimental data. Moreover, both the anomalies and correlation dependencies previously received and formulated as rules and theories also coincide.

Both chemical bonding and chemical reactions can be explained via various logical steps depending on the educational level of the audience.

The reaction speed measurements of chemically active species (radicals, ions, conences, etc.) with molecules, the discovery of chain routes and their study, the quantitative study of equilibrium molecule ⇋ active species, show that the interaction of saturated molecules proceeds, as a rule, via the formation of active species, according to the scheme:

I) A B → A + B; A + C D → A C + D; D + A B → D B +A
and not according to scheme:

II) $A \cdot B + C \cdot D \rightarrow A \cdot C + D \cdot B$;

where $A$, $B$, and $D$ are active species. This is because the reaction speed in the first scheme is by many orders higher than that in the second. For example, we can consider the radical and ionic reactions whose quantitative data are well known, including some of those that were shown in the main text of the book. The activity of chemical species is also explained on a phenomenological level with the help of electron-nuclear isomerization.

One can also explain chemical reactions as follows: within a historic analysis, or with a narration of the TEI and its illustration by simple, complex, or catalytic reactions of various types (ionic, radical, etc.), and their main rules relative to speed (the Semyonov-Polanyi and Greenberg Rules, Taft's correlation, the compensation rules, etc.) and selectivity — the direction of the reactions (Resonance Rules on reaction examples, replacements in aromatic compounds).

Thus, when explaining chemical bonding, one can say that upon evaluating all the positive energy contributions — the affinity of the atoms to the electron, i.e., the attraction of the electrons of one atom to the nucleus of another, which increases with the approach of the atoms to each other — the energy is much smaller than the bonding energy received in the experiment.

Only when the energy gain, received as a result of the mutual approach of the positively charged nuclei (charge concentration), was considered, did we get an energy value close to the experimental data. That is, it appeared that the main energy gain is received at the expense of the mutual approach of the identical nuclear charges. As a rule, such paradoxical explanations are most interesting, and therefore, are easy to remember.

When one explains chemical reactions, one should consider the following scheme of explanation: It was formerly thought that molecules reacted molecularly. Such a scheme corresponded, in many cases, to kinetics (first power along both reagents), but this disagreed with energetics, and
therefore, with the reaction speeds. Then radical reactions and chain radical processes were discovered.

The reaction rate measurements reveal a high rate of interaction between radicals and molecules when viewed energetically. For quite some time radical and chain radical processes were considered as exceptions. For many decades the term *chain process* has been used only in reference to radical reactions.

Chain conence reactions were discovered in the 1980s. Before this discovery chain schemes for ionic reactions were constructed without calling them *chain reactions*; gradually the scientific world drew the conclusion that the truly rare exceptions were molecular reactions. Indeed, in the course of this evolution, some psychological difficulties had to be overcome. Thus, for example, when chain reactions were first discovered, these were followed by chain branched reactions of Nernst, Bodenstein, Semyonov, Hernshelwoods. Then the general principles of chain radical reactions were studied.

In the course of experimental and theoretical research, it was proven that one of the characteristics of these reactions was the radical concentration in the reaction's compound, which was greater than that of the equilibrium equations. This feature was stressed as one of the main indications of the chain process. Thus, if the ionic reactions, say in the liquid phase, did not have such indications, the process was not classified as a chain reaction.

However, if we consider such factors as high-speed reaction, low energy activation, low energy consumption, the formation of new active species, as intrinsic to chain chemical reactions, then ionic reactions also become chain processes. The chain process of a chemical reaction actually answers the following question:

*How does the intermolecular reaction proceed with bond breaking at temperatures of about 400K if, in reality, bond breaking requires a temperature of more than 3,000K?*

The next question is one concerning the actual activity of the active species, which is well explained by the electronic isomerization phenomenon.
Finally, molecular reactions (their speed and energetic parameters) that are not at all an exception but rarely cited, are explained with the help of electronic isomerization.

**EXAMPLE QUESTIONS CONCERNING CHEMICAL BONDING AND CHEMICAL REACTIONS**

Why is chemistry known as a fundamental science?
How does chemistry differ from physics?
Give three examples of physical and chemical properties of substances.
Write the symbols of the first three periods from the table of elements.
Name these elements.
To which groups do the following elements belong: K, Si, Ca, S, Mg, He, Cl?
Write the structural formulas of the following compounds: SO₂, SO₃, NO₂, HClO, XeO, CH₄, NaCl.
How do dynamic chemical bonds differ from covalent bonds and DABs?
What role is played in chemistry by the electrons, the atoms’ outermost shells, and the electrons’ innermost shells?
What is the role of the atom’s nucleus in chemistry?
**At the expense of whose energy (nuclei or electrons) does the energy gain occur?**
Why is there an energy gain during bond formation?
Explain this qualitatively and quantitatively.
Compile an equation by which we can calculate the bonding energy in a hydrogen molecule.
What approximations are necessary to calculate the bonding energies of dual-atomic molecules besides H₂?
Speak on dual-atomic molecules formed of: atoms with close FIEs; atoms with various FIEs.
Why do we need much more energy than the calculation requires for the breaking of the bond in a hydrogen molecule? Find out how much more energy is required.
How is a hydrogen molecule formed?
How is a covalent homoatomic bond formed? How is a heteroatomic bond formed?
How does the energy of a covalent homoatomic and heteroatomic bond depend on the FIEs of the atoms being bonded?
How does the length of a covalent homoatomic bond depend on the FIEs of the atoms being bonded?
What other bonds (besides covalent ones) do you know?
What is the physical essence of DABs and VWBs?
What is the valence of an element?
How many chemical bonds (covalent and DABs) can an element form?
Why is it that when an atom is connected with various types of bonds to identical atoms, the bonds equalize their energy and length?
What is electronic isomerization? Give some examples. How is the speed rate of electronic nuclear isomerization defined? What phenomenon does this reaction explain?
What experimental facts speak to the effect that two (not one or three) electrons take part in the formation of a covalent bond?
What experimental facts confirm the correctness of theory of chemical bonding?
Explain the essence of ionization energy. Explain what is meant by ionization energy of an electron in an atom.
What does FIE stand for? How many electrons are there in the outermost layers of elements #5, #10, #12, and #14?
How many protons are there in the nuclei of atoms?
Explain the meaning of the term "valence".
How is the valence determined in elements of the I, II, III and IV groups?
How do we define the valence in elements of the V, VI, VII, and VIII groups?
What is valence relative to hydrogen?
What is the table of elements?
Explain the manner in which the table of elements is constructed.
Write out the table of elements for the first 20 elements.

Speak on how the number of electrons in each electronic layer?

Offer 3 proofs of the fact that only the electrons of the outermost layer are responsible for the chemical and physical properties of the elements.

Explain why the exchange period in the main properties of the first 20 elements is equal to 8, while the valence via hydrogen (the main chemical property) has an exchange period equal to 4.

On the basis of what experimental data can we define the maximal amount of electrons that can be situated by the first 20 elements of the table of elements?

What do we mean by the affinity of atoms to the electron?

Construct a chemical bonding model based on the comparison of the number of electrons in the outermost layers of the first 20 elements and the data on their valence.

Which data on the affinity of atoms towards electrons prove the correctness of this model?

On the basis of what data do we draw a conclusion to the effect that the bonding electrons rotate on a plane perpendicular to the axis that connects the bonded nuclei?

Which electrons are regarded as bonding electrons? (...as electrons to be bonded?)?

As a rule, when we transit from one element to another, from left to right in the table of elements (2nd and 3rd periods), the FIE changes.

Are there any exceptions to this rule?

What data on the affinity of the atoms to the electrons explain these exceptions?

Why are the Lewis Rules referred to as "rules"?

What is the difference between facts, rules, laws, and theories? Give some examples.

What stable compounds are exceptions of the Lewis Rules?

Where do we find the contradiction between the offered chemical bonding model in a hydrogen molecule and the data on the affinity of hydrogen atoms towards electrons?
What elements are regarded as anomalous from the point of view of the bonding theory?

What is an anomalous element in the physical and chemical sense? Why is their behavior anomalous?

Name the groups of anomalous elements. How do they differ? Give some examples.

Why, for a thermal breaking of chemical bond in the hydrogen molecule, greater energy is needed than for the ionization of the molecule?

What are the main forces when a chemical bond is creating?

What experiments and calculations prove this?

What is a one-electron approximation justified by, how does it manifest itself and for what calculations has it been used?

For the first twenty elements, what is the correlation between valence of the element and its group?

Why the removing of valence electrons from an atom is easier than that of core ones?

Back in 1960s, on what stage of its development did the classical chemistry stopped? What had been the next tasks to be resolved?

Why is it easier, for electrons inside molecule, to absorb energy by fewer portions then for ones inside atom?

What kind of experiments have resulted in refusal of traditional (classical) explanations of chemical phenomena and caused the emergence of the quantum chemistry? How were these experiments explained after returning to the classic mode of explanations?

Define the time for electronic transition if reaction \( D + H_2 \rightarrow DH + H \) proceeds in one second.

What is the limiting stage of a reaction?

Why does this stage define the speed of the reaction?

Mention some analogies from everyday life.

Explain why, to break the chemical bond in the hydrogen molecule, it should be heated up to 3000 degrees while, in a presence of Chlorine atoms, the bond breaks up at 30 degrees. Explain why the energy needed for breaking the chemical bond in hydrogen molecule by a photochemical reaction or by an electron bombardment is two times fewer than that for the thermal breaking of the bond.
Write reaction mechanisms for following reactions:
a) \( H_2 + Cl_2 = 2HCl \);
b) \( H_2 + J_2 = 2HJ \);
c) \( Cl_2 + 2KBr = 2KCl + Br_2 \);
d) Ether + \( H_2O \) = alcohol + acid;

name the main stages of these reactions,
explain why aren’t they running using a molecular mechanism;
choose some efficient way to increase the rate of these reactions from following:
  - exposure to radiation, catalyst, solvent, heating;
  - explain the role of water in the reaction c);
  - explain the role of radiation in reaction a);
  - explain the role of catalyst in the reaction d).

Why do we need a spark plug in a car?
Why the contents of exhausted gas checked up?
How is the exhaust gas of a machine (car) cleaned?
Give some examples from physics or chemistry confirming or negating the correctness of the aphorisms given below.
PROOF OF THE CORRECTNESS OF CHEMICAL BONDING THEORY

What is Our Chemical Bonding Theory Based on?

Our chemical bonding theory is based upon the model where the bonding pair of electrons rotates on a plane perpendicular to the axis connecting the nuclei. The correctness of this model is confirmed by the fact that the analytical calculation of the hydrogen molecule’s energy differs from the experimentally defined energy by less than 4%. Only the data on the ionization energies of a hydrogen atom and a hydrogen atom’s nuclear charge were used for the calculation. It was considered that the electron is a particle with a definite mass, charge, and trajectory.

The knowledge of the structure of the hydrogen molecule has allowed us to conclude that the transformation of the hydrogen molecules of the two bonding electrons (one from each atom) enter the outermost unfinished (single-electron) shells of the atoms to be bonded. That is, during covalent bond formation, the number of electrons in the shell of each atom increases by one unit.

The calculation of the hydrogen molecule has allowed defining the increase of the effective charge (acting upon the bonding electrons) of the hydrogen atoms being bonded. The coincidence in the calculation and the experimental results, in the case of the hydrogen molecule, has shown that simple electrostatic and dynamic interactions occur during the formation of a hydrogen molecule out of a hydrogen atom.

Realizing that simple electrostatic interactions are the defining ones, we have managed to calculate a model in which the nuclei has more than one electron and the molecule has various nuclear charges. The use of this model with other atoms, besides hydrogen ones, required additional suppositions because the analytical solution was possible only when forming a hydrogen molecule out of single-electron hydrogen atoms. The essence of the additional supposition was in the fact that the action of the other electrons and the atoms’ nuclei was evident in the ionization energy of the electron taking part in bond formation.
Considering this supposition, we calculated the dependencies of the bonding energies, bond lengths, and dipole moments of dual-atomic molecules on the FIEs of the atoms being bonded. These dependencies coincided with those defined experimentally for dual-atomic molecules in the gas phase.

It is important to underline the fact that the dependencies that seemed paradoxical before the calculation, actually coincided. Thus, for example, it used to be logic that with the energy increase of a simple bond, the bond length should increase as well. Then, though the question was never considered, the dependence of covalent bonding energy on the FIE of the atoms being bonded should represent, if not a linear, then at least a ‘balanced image’ (the greater the FIE, the greater the bonding energy) or an ‘unbalanced image’ (the greater the FIE, the smaller the bonding energy).

In this respect, the coincidence of the dependencies with the experimental results (where the covalent bond length depends on the FIE of the atoms being bonded and decreases with the increase of the FIE while the bonding energy passes via the maximum) is one of the great arguments in favor of the correctness of our theory.

The analytical solution of the system of equations compiled on the basis of the model has shown that for covalent bonds – the dependence of bonding energy on the FIE passes via the maximum. And the maximum, according to the calculation, is in the form of a parabola, and corresponds to the FIE of 10 eV.

The experimentally defined energy dependence of a covalent bond on the FIE also resembled a parabola. The maximum on the curve, according to the experiment, also had a FIE of 10 eV. Moreover, both the experimental and calculated parabolas crossed the ordinate axis with FIE values of 3 eV and 15 eV for dual-atomic molecules, where the atoms are bonded with various FIEs, and between which there is a heteropolar covalent bond. The dependence of the bonding energy on the FIE of one of the atoms to be bonded was calculated; it was expressed by a straight line. The calculated and experimental straight lines practically coincided.
The correctness of the program was confirmed by the coincidence of the calculations and the analytical solutions of the equation system. The analytical system is possible when \( N_1 = N_2 \). That is why the coincidence of experimental and calculated dependencies [just as in unexpected ones, where the energy of a covalent heteropolar bond is both qualitative (linear) and quantitative for many elements] is also one of the powerful arguments that proves the correctness of the offered theory.

As far as hydrogen molecules are concerned, the distances between the nuclei and the electrons have been calculated. The received values have shown that during the formation of covalent bonds, both bonding electrons enter the outermost shells of the atoms to be bonded. That is, during bond formation, the number of electrons in the outermost shell of these atoms increases by one electron.

The fact that electrons enter the outermost shell of the atoms being bonded during bond formation, was additionally confirmed by:

1) the comparison of the calculated and experimental data on bonding energy with the experimental results of the affinity of the atoms to the electron;
2) the dependencies of the atoms’ FIEs on the number of electrons in the atoms’ outermost shells.

As the affinity to the electron has a negative value in some atoms (according to the experiment: the electrons require energy in order to enter the outermost shell of the atoms), one should expect that the calculated energy values of the covalent bonds in the molecules, formed of these atoms, will be much greater than the experimentally defined ones. In reality, when comparing the experimentally defined values in dual-atomic molecules of bonding energy formed of elements with negative affinities to the electrons with calculated bonding energies and defined experimentally for elements with positive affinities to the electrons, has shown that the bonding energies for elements with negative affinities are much smaller.

That is, this experimental data confirms the correctness of the whole model and draws a separate conclusion from the calculation of the model concerning the transition of the bonding electrons into the outermost shells of the atoms to be bonded.
These examples should suffice to confirm the correctness of our theory.

Further experimental confirmation of investigative materials based on our theory will be summarized. This confirmation will include experimental data on the structure of stable compounds, the valence rules summarized as the Lewis rules, the theoretical and experimental substantiation of our theory of chemical bonding, the role of the electron’s entropy change in the increase of the energy necessary for bond breaking in a hydrogen molecule, the elucidation of the physical essence, the reasoning for the decrease of the electronic entropy during bond formation, the increase of the effective charge (concentration of the positive charge), etc.

As far as the elucidation of the dependency of the charge value on the distance between the nuclei, and the explanation of energy consumption by the electrons with small thermal quanta, this consumption occurs along the scheme of energy increase in the nuclei, with an increase of the distance between them, with the decrease of the effective charge, the removal of the electrons from the nucleus of the helium atom, which represents the energy of a hydrogen molecule when excluding all the forces.

**EXPERIMENTAL PROOFS OF DECREASE IN ELECTRONS’ ENTRPIES**

1. The difference in the electronic spectra of atoms and molecules. If we take atoms and molecules of hydrogen, the number of lines in the specter differs by 2 orders of magnitude [atomic hydrogen < 100 lines; molecular hydrogen > 30,000 lines.]

2. The inclination of the experimentally defined heat capacity as compared with the calculation. [During the calculation it was supposed that the electronic heat capacity becomes obvious only at a temperature of more than 5,000° C.]
The experimental data confirming the possibility of electron-nuclear isomerization are the data dealing with the study of isomerization speeds of numerous compounds (including tautomeric isomerization).

All the mentioned theoretical bases of the correctness of our theory are non-contradictory (do not contain contradictory conclusions), and do not contain any additional suppositions. Indeed, there are no theoretical principles and experimental results contradicting our theory.

All this undoubtedly speaks in favor of the correctness of our Theory of Chemical Bonding!
APHORISMS THAT AUTHORS USED TO FOLLOW TO STRESS THE CORRECTNESS OF THEIR EXPLANATIONS

To research means to see what everyone sees, but to think like nobody ever thought before. St. Dardyeh

It is not surprising that we don’t know much about nature; it is surprising that we do know something about it.

Only God knows what “heights” the human brain can reach in a free (non-experimental) flight.

Just as there is nothing more reliable than an experiment, there is nothing more doubtful than an experiment.

If the result of an experiment, meant to confirm a theory, coincides with the theoretical results up to the third digit, this means that the initial results of the experiment were tampered with.

If the theoretical and experimental results coincide up to the third digit, this means that the theoretical calculations contain suppositions that cannot be evaluated quantitatively.

Quantitative theoretical calculations, containing suppositions that cannot be evaluated quantitatively, do not have any scientific essence.

Mathematical equations that have no digital solutions for experimental conditions (like the Schroedinger equation, etc.) do not have any scientific essence. They are very much like “the road that doesn’t lead to the Temple.” There is no use for such a road.

Truth is the Daughter of Time, not of Authority.
F. Bacon (1561-1626).

If a scientist cannot explain the essence of the question a student of the 10th grade is working at — he is not a scientist, but a charlatan.

Make me to believe that 2 x 2 = 5, and I will prove that witches fly out of the chimney. D.Hillburt.

It was always this way: The closer man approaches Truth, the simpler and more comprehensible it becomes.
A.P.Chehov (1860-1904).

Science that was not derived from experiments — the bases of all cognition — is useless and full of delusion.
The question concerning the nature of chemical bonding is the heart of chemistry. Brike Crawford (1953).

The discovery of paradoxes in science is just as important as the explanation of these paradoxes.

You would expect that people would prefer simplicity, but complexity appears to be more attractive to them, or it simply fascinates them more.
APPENDIX C

Theory of Metallic Bonding

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According to J.N. Spencer (JCE No. 3 p.182 1991) base of
quantum-chemical interpretations are ‘unteachable’. 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
theory of metallic bonding and 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 (primarily thermo and
electrical conductivity) of metals and non-metals

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 504 Phenomenological explanation 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 nor 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**


**CHED 1773Phenomenological explanation of metallic bonding and electrical conductivity**

Yuriy Gankin, Yuriy_gankin@hotmail.com, Elsevier MDL, 30 Corporate Drive, Suite 400, Burlington, MA 01803 and Victor Gankin, victor_gankin@hotmail.com, Institute of Theoretical Chemistry (ITC), 8 Shrewsbury Green Drive, Shrewsbury, MA 01545.

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
nonmetals. 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

**Theory of Metallic Bonding**
Victor Gankin, Yuriy Gankin,

The Division of Chemical Education of the American Chemical Society and NSF recognized in 1989 the need to foster the development of alternative General Chemistry Curriculum.

The major differences of the new Curriculum had to be the exclusion from it the quantum-chemical explanations of chemical phenomenon. The widely used quantum chemical explanations include paradigms and principles whose physical bases are unclear. According to J.N. Spencer (JCE No. 3 p.182 1991) base of quantum-chemical interpretations are 'non-teachable'. In 2004 we placed on our web-site ITChem.com the draft of the General Chemistry textbook, in which we tried to explain the basic chemical phenomenon (the physical nature of the chemical bond in daltonoids and the chemical reaction, including the explanation of the physical nature of the periodic law, Lewis’ rules, and the resonance rules) without using the quantum-chemical approach. These data were reported by us and discussed on the previous conferences of ACS (see SciFinderGankin).

Currently, we managed to elucidate the physical nature of the chemical bond in bertolloids or,
speaking simpler, the nature of the metallic bond, more correctly, the chemical nature of the bond in the solid metals.

Clearing out the physical nature of the chemical bond in the solid metals allowed answering the next major questions, coming up in the process of the traditional classical development of Chemistry and Physics.

Approximately 80 of 100 known elemental substances (elements) are metals. The metallic double-atom molecular systems present more than a half of all chemical compounds. Accordingly to Pauling (L. Pauling The Nature of the Chemical Bond P.394 1959) the metals must represent a basic part of Chemistry. In reality, only 1% of the pages in the current Chemistry text books is dedicated to the metallic bonds.

The major reason of the existing situation, accordingly to Pauling, is that unlike nonmetals, no structure theory similar to nonmetals was elaborated for metals.

The existing explanations of the metal properties are the explanations ad hoc. For example, in physics the to explain the nature of the electric current, one assumes, that the part of the valent electrons is free and exist in metal as the electron gas. This assumption explains the electric current in metals forms at the extremely low voltage of \(10^{-8}\) volt.

This assumption contradicts the chemical bond theory; accordingly to which the chemical bond forms due to the increase of the absolute value of the valent electron potential energy. I.e., after the chemical bond formation, the valent electrons are connected with the atom nucleus harder, than in the separated atoms.

Accordingly to the experimental data, obtained during the study of the photo-effect, electron emission, and metal atomization, not less than 2 eV of energy should be spent to break off the electron from the atom in the solid metal. Accordingly to I.V.Saveliev (Course of general physics, b.2, p.294, 1998), the electron emission from the metals takes place in the case, when the electric field of the conductance at about \(10^8\) volt/cm is formed near the metal surface. These data completely exclude the possibility of the free electrons in the form of electron gas existence in the metal.
In the previous works, we showed that the metal atoms in the gaseous phase are connected between themselves with the covalent bond identical both by physical nature and the physical and chemical properties to the covalent bond, formed by the nonmetal atoms.

However, the properties of metals and nonmetals in the solid state are sharply different. The metal valence in the solid phase, determined by the number of the metal atoms joined to one atom, is also sharply different from the nonmetal valence. For example, the first group elements valence in the gaseous phase is constant and equal 1, but in the solid phase it is either 8 or 12. At the same time, the energies of the chemical bonds between metal atoms in the gaseous and solid phases are equal.

Carbon has the valence of 4 both in diamond and the organic substances. Similarly, iodine is connected with the firm co-valent bond with one iodine atom in the solid as well as gaseous phase.

The physical properties of metals and nonmetals in the solid state are sharply different. Metals are electric and thermo-conductive, but nonmetals are isolators.

Accordingly to Peter P. Edwards (The New Chemistry, Editor-in-chief Nina Hall Cambridge university press 2000 p 85), nobody succeeded until 2000 to answering the such basic questions, related to the metal electric conductivity, as: Why does metal conduct the electric current, and nonmetal is the isolator? What is metal? Why are the metal properties are so different from the nonmetal properties? What is the electric current? What is its physical nature? Etc.

We could solve the mentioned contradictions and answer the above listed questions in the frames of the elaborated by us theory of the chemical bond. The question, connected to the thermal stability of the compounds of halogen molecules with halogen anions, arose during the working out this theory. The middle iodine atom in the molecules, described as I-I-I, had the valence 2 (i.e., two times higher, than it is in the molecule I₂) and contained 9 electrons in the outer sphere, what contradicted the covalent bond theory. Accordingly to the chemical bond theory, the connection between iodine molecule and it could be formed
only with the thermally unstable Van der Waals’ bonds. The investigation of this compound showed, the both bonds in it are equal by the length and the strength. The investigation of compounds, with the identical atoms but the bonds, which are different by the length and the strength, showed, that in all occasions, all the bonds of the central atom are equal by the length and the strength. Phenomenological explanation of this occurrence was achieved as a result of the evaluation and generalization of the experimental works on the electron-nuclear isomerization. We proved, that in the case, when, accordingly to the chemical bond theory, the structural formula can be presented with more than one way, the fast and uninterrupted electron transfer in these compounds takes place. As a result, the dynamic equilibrium between the possible structures is established. During elaboration of the chemical bond theory, it was shown that the bond energy equals the energy difference between the energy of valent electrons in the separated atoms and the formed molecule. During the formation of molecule, the valent electron energy of it decreases, i.e., the valent electrons are getting into the energy minimum. This minimum corresponds to their rotation in the plane perpendicular to the axis, connecting the nucleus, bonded by them. During the isomerization process, the ring, in which the electrons are rotating, moves from one energy minimum into another. For example, in the case of the molecule I—I—I-I, the electron couple, rotating in the ring and belonging completely to anion, forces out, during the isomerization process, the electron couple, which bonds iodine molecule in the process of isomerization. As the result of isomerization, the molecule I—I—I is formed. Its electron energy is equal the initial molecule energy. The electrons start moving in the opposite direction. Because the rate of the nucleus transition is one – two orders slower than the speed of the electron movement, the nucleus in such molecules take the intermediate position. This leads to the length and energy smoothing of the bonds, what is observed experimentally. From the other side, when one atom connected to the same or identical others atoms with the different types of the chemical bond and the length and the strength of the bond in these atoms are the same, it is possible to say, that these experimental data are the proof, that the
bonding electrons in these compounds are moving with the rate (approximately $10^5$ m/sec) higher than the nucleus moving speed (approximately $10^3$ m/sec) along the bonds from one bond to another. In the frames of the chemical bond theory, developed by us, the bonding electrons are moving along the axis, connecting the nucleus of the bonded atoms. This electrons cross from one bond to another (from on energy minimum to another, closed by the energy level). These bonds, named dynamic, were put apart in the separate group. These bonds, in particular, are formed into multi-atom (more than 2 atoms) molecules, in which the different types of bonds connect the central atoms with the identical atoms. If the system consists of the connected atoms, having only one different by its depth energy minimum, the prevailing in quantity isomer amongst all possible isomers in the equilibrated mixture is the one having the maximum potential energy. I.e., the electrons in this isomer are the closest to the nucleus. In this case, the ring of the bonding electrons moves between the energy barriers, limiting this movement from the both sides.

**The short historical review.** The compounds in the frame of the Lewis’ theory could be presented by not one but the several structural formulas, that, accordingly to Pimentel and Spratly (How the quantum mechanic explains the chemical bond, Mir, Moscow, 1973), caused the serious complications. Pimentel and Spratly in the chapter named “There are too many structures. The situation is saved by the resonance” rote: “There are quite a few structures, which agree with not only one, but with the several accepted inert gases configurations. **In the each such case, every structure means, that the non-equivalent bonds could be formed, but by the unknown reason they are never formed.** Let’s review, for example, the sulfur dioxide (SO$_2$); One can imagine two such electron configurations, in which every atom will have the respective inert gas configuration. The single and double-electron bond will be in the each structure - one bond will be long and another – short. However, it is known, that the lengths of the two sulfur – oxygen bond in sulfur dioxide are exactly even. To solve this contradiction for chemists was not difficult. The presence of two structures made the matter somewhat mixed up. Nobody
could decide, which structure is more preferable. Both structures from the energy point of view have to be equivalent for electrons. The decision is obvious – due to the extreme mobility of electrons, two equivalent structures are realized simultaneously. Chemists introduced the new term “resonance”; it means, that electrons are moving back and forth. Now the both sulfur-oxygen bonds acquire the averaged character thanks to the impetuous electron movement between the two possible configurations. In the light of the quantum mechanic ideas, the individual structures do not take into account the electron movement along the whole molecule, i.e., do not take into account the molecular orbitals. In the reality, during the molecular bond character evaluation in each molecule, using the molecular orbital method, it is necessary to introduce the $\pi$-MO, which expand on the whole molecule. The $\pi$-orbital influence on the bond stability effects equally all bonds that correspond to the experimental results."

The quantum mechanic proclaims, that the come resonance structures do not exist in reality. The assumption that electrons are moving between two electron configurations is simply the invention. It is interesting, that more than 20 reports and 3 monographs have been published since we determined the chemical bond nature, based on the experimental data (1982) Respectively, the articles on the real physical nature of the occurrences, described by the resonance rules and the experimental data supporting the explanation, that the different structures exist and electrons are moving between two electron configuration (not paying attention to the quantum mechanic statements) were published in the 70s. Despite all of this, the attitude presented in the bald font is kept unchanged. The discussion touches only the formal sides of this problem. For example, the work, published in 2006 (JCE, v.83, #2, p.223, February 2006) suggests to replace the words “resonance”, “resonance energy”, and “resonance hybrid” with the words “delocalization”, “delocalization energy” and “hybrid structure” respectively. As a whole, we support the scientific expressions – the new is a very well forgotten old, the correct theory is the child of time, but not of authority. We have returned to the well forgotten isomerization. The new experimental data were the reason for the return.
Additionally, it should be noted that the earlier explanation by chemists about the chemical bonds leveling off was spreading on the equilibrated isomerization of the compounds, containing the single and double bonds. During the evaluation of the new information, obtained in the recent years, we applied this mechanism to the all cases when the central atom connects wit the different bond types, (Van der Waals’, donor-acceptor, etc) with the identical or close to each other by first ionization energy (FIE) of atoms. Our most closed predecessor in this case was L. Pauling. It had been assumed before him, that the resonance is when there were the single and double bonds in the compound. He already assumed the resonance between covalent and ionic bonds in metals. Our explanation is principally different. Instead of the incomprehensible from the physical point of view word “resonance”, the following mnemonic rule was introduce in science: if more than structural formula in the frames of the Lewis’ rules can be suggested, this compound will be more stable, accordingly to quantum chemical calculation. The additional energy gain was named “the resonance energy”. Before Pauling, all structures, described by the resonance rules, were the structures, containing the single and double bonds. Pauling expanded the field of this rule, by the application of the bonds in metals. Our achievement was, that we found out this phenomenon physical sense and widened the number of the bond types, in which this phenomenon is observed (more accurate, the widening of the circle of bonds in which this phenomenon is observed through the inclusion in the evaluation besides the simple and double covalent bonds, also the donor-acceptor, Van der Waals’, single and double electron bonds). Clearing out the physical sense of the resonance rules became possible after the discovery of the isomerization reaction in the analogous to benzene molecules and the study of this reaction kinetics. These experimental data were obtained in the second half of the 20th century and were not generalized before us. It was because at that time in the theoretical chemistry the theory prevailed that the theoretical chemistry is the quantum chemistry and, respectively, all chemical phenomenon’s had to find their explanations in its frames.
The investigation of the electron nucleus isomerization kinetics allowed to determine, that the rate of the electron movement from one minimum to another depends on the bond type, the distance between the minimums, the value of the energy barrier, separating the minimums, and the number of electrons in the moving electron ring.

It was found out in the process of the G-theory development, that electrons, bonding the nucleus, are rotating in the ring perpendicular to the axis, connecting the nucleus. The experimental data generalization, described above, allowed to conclude, that the ring, formed by the bonding electrons, is moving easily (i.e., with the energy expenditures less than 10 kJ/mol) along the chemical bond line with the speed, described by the following equation:

$$V = 10^{17} e^{-2R/L},$$

where R is the distance in Å L (the distance between the minimums of system energy in the described case is 1 Å) and L is a coefficient, depending on the type of the chemical bond, connecting the atoms (L=6.5 for the conjugated systems and L=0.7 for the non-conjugated systems).

Accordingly to this equation, the electron transfer rate for the conjugated systems is valued at $10^{17}$ Å/sec and for the non-conjugated systems as $10^{16}$ Å/sec.

Accordingly to the experimental data, the electron ring transfer rate, which contains one electron, is higher than for the two-electron ring.

As a result of the evaluation of the co-valent bond physical nature, it was found out, that the chemical bond forms thanks to the electric forces and the model, described by three algebraic equations with three unknowns, was suggested. Solving this system of equations allowed determining the bond energy (BE) on the first ionization energy (FIE) of the bonding by it atoms.

The calculation showed (Fig.1),
that the dependence $BE$ on FIE both for single and double electron bonds is parabolic. The bond energy maximum is being reached at 5 and 10 eV for the single and double electron bonds, respectively. The double electron bond is not formed if the bonding atoms FIE is less than 3 eV and more than 16 eV. The single electron bond is not formed if the
bonding atoms FIE is less than 1 eV and more than 11 eV. The single and double electron energies are equal, if the bonding atoms FIE is 7 eV. Accordingly to the experimental data, the single electron energy in the double atom molecules, formed by the first group metals, is higher than the energy of the two atom bond, which proves, that the calculation, using the model, was correct.

Nonmetallic simple substances (consisting of the identical atoms) accordingly to K.Saito at al (Chemistry and Periodic Table, Moscow, Mir, 1982, p.87) “are built from molecules, in which atoms group into 2, or 4-8 in one molecule and have the same valences as in gaseous phase and even are directed in the space.

In the solid state many of these substances are presented as molecular crystals, in which molecules have the structure of the elongated and other forms, form the structure with the rather loose packing”. “The typical representative of the simple substances, capable of forming the gigantic molecules, is carbon. The length of the bond C-C and the carbon valence angle for diamond is the same as in aliphatic hydrocarbons”.

“The particular peculiarities of metals are the following, specific only for them, properties: electric conductivity, thermal conductivity, specific shine, forging, and plasticity; for their structure, the isothropicity, i.e., the absence of the specific properties along the selected directions, is also typical”. In the same work on page 118: “many metals, depending on the temperature, have the different structure. The amount of the emitted or absorbed energy (the transition heat), does not exceed 1 kJ/mol, if limited by the mutual transitions between the structures A1, A2, A3 (every atom in the structures A1 and A3 is surrounded by 12 atoms and by 8 atoms in the structure A2). This value is extremely small compare to the heat of melting (10 – 40 kJ/mol). Therefore, there is a very small difference between the Energy State of the different crystalline structures”.

How, in the light of the given above, did we succeed to answer the following questions:

Why does metal conduct the electrical current?
Why is nonmetal the isolator?
Why do the metal properties so much differ from the properties of nonmetals?

Let’s compare on the molecular level the properties of the first group metals with the nonmetal – diamond.

In crystalline lithium, every atom is connected with 8 or 12 other lithium atoms (crystalline lithium consists of the 3 structures A1, A2, A3). Every lithium atom has only one valent electron. It is necessary to have 16 electrons for the formation of 8 double electron bonds. Further, after the formation of 8 double electron covalent bonds, the outer sphere of all lithium atoms will contain 16 electrons, because the both connecting during the covalent bond formation electrons are included in the outer layers of the both atoms. At the same time, the maximum possible number of electrons, which can be present in the lithium outer sphere, is 8. I.e., the formation of the 8 double electron covalent bonds is excluded. Accordingly to the experimental data and the calculations (Fig.1) the atoms of the first group can form the single electron covalent bonds. During the formation of the single electron covalent bond, and as well, the double electron bond, the connecting electron is included in the outer spheres of both atoms. I.e., the structures A1 and A3, detected during the solid lithium structural analyses, can not form with only the single electron bonds, because in this case, the atoms of lithium will contain 12 electrons in the outer layer. The only possibility for lithium to form 12 bonds, as in the case of I3, is a formation of the Van der Waals’ bonds along with covalent (single and double electron) bonds. In this case, the lithium atom will be connected to the other atoms with the different bonds - covalent (single and double electron) and Van der Waals’. Accordingly to the experimental data and the chemical bond theory, in this case, the bond leveling by the length and energy takes place, because the connecting electrons (the rings, in which the bonding electrons are rotating) transfer from one bond to another, i.e., the bonds become dynamic. The movement of the electron rings takes place along the bonds with the rate of the order of $10^6$ m/sec, which is close to the heat movement rate at the room temperature – $10^5$ m/sec. Because every atom in metal is connected, as minimum, to eight atoms, evenly separating the space, surrounding each atom and 8
sectors, the behavior of the bonding electrons is not distinguishable from their behavior in the electron gas, where electrons possess three degree of freedom. The bonding electrons in metal, which remain as bonding the nucleus, behave, at the same time, as the free electrons. This allows to coordinate the listed above experimental data, obtained as a result of the studies of the photo-effect, electron emission, and metal atomization, with the data on the electric current occurring at the voltage less than $10^{-7}$ eV. Accordingly to Soloviov (p. 272) the average rate of straitened by the field electron movement (even at the very large current density) is $10^3$ m/sec. The kinetic energy of the electron, bonded with atoms, equals the half of its potential energy and is measured in the eV values. The electron movement rate on the orbit is $10^5$ m/sec, which are $10^8$ higher. The kinetic energy of the electron is proportional to its movement speed squared. Respectively, The kinetic energy, additionally provided to electron to electron, is $10^{-14}$% of the thermal energy, which the electrons have at the room temperature and are measured by the values of the order $10^{-13}$ eV. I.e., the energy practically is not spent on the increase of the kinetic energy of the electrons. During the voltage creation in metal, electrons are moving along the bonds. At this point, the system energy changes insignificantly, because, while moving away from one atom on the certain distance, the electron is approaching another on the same distance. Because the electron movement speed is two orders higher, than the nucleus movement speed, and because the system energy is completely determined by the distance between the electrons and nucleus, the system energy does not have to change significantly during the bonding electron movement. Also, the energy provided during the imposition of the energy field, does not practically have to be expended on its compensation (its increase) and on the exit of the bonding electrons from the drop of the potential. The independent (in this case semi-quantitative) experimental confirmation of the basic distinguish of the metallic bond from the covalent and Van der Waals’ bonds is the comparison of the experimental data on these bonds lengths (Pimentel and Spratley. How the quantum mechanic explains the chemical bond, p.248, Moscow, Mir, 1973).
The ratio of the Van der Waals’ and co-valent bond lengths for the first period elements varies in the range of 1.7 – 2.2. Accordingly to Pimentel and Spratley, the ratio is 1:1 between the dynamic bonds in the compounds of the type \((I_3)^-\) and the covalent bonds in the compounds of the type \((I_2)^-\).

Accordingly to the experimental data by K. Saito (p. 110), processed by us, the ratio the bond lengths in the solid metals and double-atom molecules, consisted of the identical atoms, varies in the range of 1.03 – 1.2. For example, this ratio for the row of metals Li, Na, K, Rb, Mg, Ca, Al, Cu, Ag, Au is 1.14, 1.2, 1.16, 1.14, 1.03, 1.13, 1.2, 1.08, 1.07, 1.07 respectively. I.e., the bond length ratio in the solid metals and double-atom molecules, consisted of the identical atoms, practically numerically coincides with the 1:1 ratio between the dynamic bonds in the compounds of the type \((I_3)^-\). It sharply (one even can say qualitatively) differs from the ratio of the Van der Waals’ and co-valent bonds for the same period elements and varies in the range of 1.7 - 2.2. For the comparison, for nonmetals, the ratio the bond lengths in the solid non-metals and homogeneous double-atom molecules, consisted from the identical atoms, varies in the range of 0.7 – 1.0. For example, the ratio in the raw of non-metals N, O, C (diamond) is 0.74, 0.8, and 1.0, respectively.

The direct experimental confirmation of the dynamic bond role in the electric conductivity is the comparison of paraffin (it does not contain the dynamic bonds), which has the conductivity of \(10^{-16}\) ohm and polyethin (polyacetylene \(-(CH)_x-CH=CH=CH=CH=\) ), where the dynamic bonds are present \(10^{-12}\). At the same time in treated with iodine polyethin (see Table1, page 344), where the number of the dynamic bond is higher due to \((I_3)^-\), the conductivity is \(1x10^{-3}\).

One can see from the presented photograph (The New Chemistry, Editor-in-chief Nina Hall Cambridge university press 2000 p 85), that the polyethin film, treated with iodine, possesses the metallic shine, at the same time, the not treated film did not have it. The higher metallic shine of the film, in which the number of the dynamic bonds is larger, than in the film, having fewer metallic bonds, allows
to assume, that the dynamic bonds (their type and quantity) are the main reason of the metallic shine, typical for metals.

Accordingly to L.E.Smart E.A.Moore (Solid State Chemistry, 2005, p.245), it was shown during the further studies of the organic polymers with the conjugated bonds, treated and not treated by halogens, that the results, obtained during polyethin study, are typical for all investigated polymers with the conjugated bonds, in particular for

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The experimental data, carried out by L.E.Smart E.A.Moore were generalized in the form of the table:

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Table1

It is a solid confirmation, that the explanation of electric conductivity in the solid metals and the luck of it in nonmetals by the different bond types in metals and nonmetals are correct. The bonds in the solid metals are dynamic, and in the solid nonmetals they are static. The differences in the bond types in the solid metals and
nonmetals without any additional suggestions explain, along with the electrical conductivity, all other different chemical and physical properties of metals and nonmetals. In particular:

The valence of metal is different in the gaseous into solid phases.

The formation of the electric current in the metal when the voltage is more than two orders lower, than necessary for pulling electrons from the metal.

All general statements of the bond theory in the solid homogeneous metals, besides the analogy, have the direct experimental confirmations. For example, equality of the all twelve bonds in the majority of metals is the direct confirmation of the dynamic bond presence in solid metals. The additional independent confirmation is the measured length of all bonds, which is the intermediate between the co-valent and Van der Waals’ bond lengths. As a common case, the number of bonds in the homogeneous atom nonmetals in the solid phase is equal to their number in the gaseous phase, does not exceed four bonds, and corresponds to the G-theory of the chemical bond.

Till 2006, we did not find the experiments in the literature, which contradicted or gave the simple explanation (in the frame of offered by us theory), why there were the unusual (paradoxical in the G-theory of the static bond) properties and differences in the behavior of metals and nonmetals. There were also no experiments, in which the answers on the paradoxical questions had not been received until the working out of the chemical bond theory, presented in this report.

By our opinion, all listed above data testify not only about the applicability of the suggested chemical bond theory in the solid metals, but, also, that this theory is correct.

Theory of electrical conductivity
Yuriy Gankin, Victor Gankin,
“What is electricity?” – the professor asked.
“I knew, but I’ve forgotten.” - the student replied.
“What a loss!” – the professor exclaimed,
“The only person in the whole world who knew, but has forgotten” - old anecdote

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 $\text{I}_3$ along with the equilibrium:

$$\Gamma \ldots \text{I} - \text{I} \Leftrightarrow \text{I} - \text{I} \ldots \Gamma$$

There can also exist the equilibrium between different forms $\text{I}_6$ and $\text{I}_9$, and so on. $\Gamma \ldots \text{I} - \text{I} \ldots \text{I} - \text{I} \ldots \Gamma \ldots \Gamma \ldots \Gamma$, $\Gamma \ldots \Gamma \ldots \Gamma \ldots \Gamma \ldots \Gamma$.

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 $\text{I}_3$ ($\Gamma \ldots \text{I} - \text{I}$). It is known, that $\text{I}_2$ has the positive affinity to an electron. When an electron attaches to the $\text{I}_2$ molecule, $\Gamma_2$, which has a structural formula $\Gamma \ldots \Gamma$, is formed. Respectively, if an electron is attached to $\text{I} - \text{I} \ldots \text{I} - \text{I} \ldots \sum \ldots \sum \ldots \sum$, both these compounds have to easily attach an electron forming respectively only compound $\Gamma \ldots \Gamma \ldots \Gamma$.

In its turn, the emission of energy, stipulating the easiness of the next electron attachment, is expected because the iodine ($\text{I}_2$) 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 $\Gamma \ldots \Gamma$, assumes that this stage will proceed similarly to the all known cases.

All three atoms in the molecule $\Gamma \ldots \Gamma \ldots \Gamma$ 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 $\Gamma \ldots \text{I} - \text{I}$ due to electrons, supplied from anode, converts into $\text{I} - \text{I} \ldots \Gamma$, first from the left reversible isomerization ceases (for the electron pare, being transferred in the process of isomerization farm the foremost
In all electron spheres of three anions in the $\Gamma \ldots \Gamma \ldots \Gamma$ molecule, there is no place no only for the same energy level, which this electron pare had in the $\Gamma \ldots \Gamma \ldots \Gamma$ molecule, but not even the close level of energy. At the same time the rate of the electron pare transfer reaction from $\Gamma \ldots \Gamma \ldots \Gamma$ to $\Gamma \ldots \Gamma \ldots \Gamma$ 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 bond 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)

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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 I₂ 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 I₂ molecule accompanied with the breakage of the co-valent bond in I₂ molecule can be estimated by the value 2.34 of I₂ (3.06 – 0.72 = 2.34). Accordingly to the experimental data, the iodine molecule affinity the electron equal 2.55 eV. The analogous calculations for chlorine and bromine molecules gives the estimated values for these molecules affinity of 2.40 and 2.36 eV, 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 Na₂ and K₂ 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 ... I molecules breaks, when the outer atomic layer of the left iodine atom is filled in completely. This bond enthalpy is appraised 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 I₃ 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° respectively. Unlike diamond, the bonds in graphite have the different length (Figure 1)
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 (1.54 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),
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 $4 \times 10^{-5}$ to $7 \times 10^{-5}$ ohm.cm, and perpendicular to the layers ranges from $1 \times 10^{-1}$ to $5 \times 10^{-1}$ 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 the 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 polyethylene (polyacetylene -(CH)x-CH=CH-CH=CH-) equals $10^{-5}$ to $10^{-8}$ ohm.cm., what is closed to the value of $4 \times 10^{-5}$ to $7 \times 10^{-5}$ ohm.cm, shown above.

**Semi-quantitative modeling of electrical conductivity in metals and non-metals**

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Previously we have developed a phenomenological (non-quantum chemical) approach (www.ITChem.com) that explained the differences between bonding in solid metals and non-metals. We have shown that atoms in solid non-metals are connected via static two-electron covalent bonds while atoms in solid metals are linked by dynamic one-electron bonds. We have also presented quantitative explanations of how that bonding difference determines dissimilarity between properties (primarily thermo and electrical conductivity) of metals and non-metals and a mathematical model describing covalent bonding. Based on those findings, in this report we present a semi-quantitative model of electrical conductivity that describes electrical conductivity dependency on bonding characteristics (ionization energy).
The change of the net (total) energy ($E_{\text{net}}$) of the system with the moving ring of bonding electrons, orbiting in the plane perpendicular to the line connecting the bonded nuclei, was calculated in the process of solving the system of three algebraic equations with three unknowns. The calculation was carried out the following variants: the single-electron bond, the double-electron bond, depending on whether one or two electrons are rotating in the ring, moving along the bonds. The two extreme versions were being calculated in both cases: 1) the nuclei are moving with the speed close to the speed of electron’s ring; and 2) the nuclei are not moving at all when electrons are in the process of transition. These systems, shown on the graphs, are named the systems with the free and frozen nuclei. The demonstration of concepts of “free” and “frozen” molecules is shown at [http://lsanin.dyndns.org/alex/Molecule/gifmolec.htm](http://lsanin.dyndns.org/alex/Molecule/gifmolec.htm). Besides these extreme versions, the intermediate ones, i.e. the systems with the different degree of “nuclei freeze”, were being calculated.

The meanings of the accepted designations, for molecules with identical atoms (homoatomic molecules), are shown in slide 1 and the calculation results are presented in slides 2 - 9.

As a result of these calculations, it was found out that the system energy increases when the ring in which the bonding electrons (one or two of them) are rotating is moving to the right or to the left of the equilibrium state. Respectively, it is necessary to add the energy to the system for the ring movement along the bond. In the process of calculations, it was found out, that the needed amount of energy depends on one or two electrons are rotating in the ring and on the atom ionization potentials in the investigated system (slides 2 and 3). For example, it is necessary to provide 0.003 eV of the additional energy in the case of the single-electron bond for the 25% displacement of the ring of the electrons, connecting atoms, which ionization potential (First Ionization Energy – FIE) is 8 eV. In the case when the atom ionization potentials are equal to 4 eV, the necessary energy expenditures are 0.03 eV (slide 4). In the case of the double-electron bond, the necessary expenditures of energy
for the double-electron ring 25% displacement are 0.12, 0.18, 0.21, and 0.21 eV when the atom ionization potentials equal 6, 10, 14, and 18 eV respectively (slide 5). Thus, the resistance to double-electron ring movement along the bond was 40 to 70 times higher, than resistance to the single-electron ring movement.

Generalized dependencies $E_{net}$ on $FIE$ for homoatomic molecules are shown in slide 6.

The lower resistance to single-electron ring movement along the bond compared to the double-electron bond presents to qualitative explanation of the higher rate of single-electron isomerization and the higher electric conductivity of metals compared to doped non-metals. The atoms in metals are connected with the dynamic single-electron bond; the atoms in the polyethylene doped by $I_3$ poliacetylene, that is non-metal, are connected with double-electron dynamic bond. The electric conductivity difference in the doped non-metals varies in the range of $10^5 - 10^6$ [Ohm$^{-1}$ cm$^{-1}$] and $10^6 - 10^8$ for metals, Thus the calculated ratio is 40-70 times out of the experimentally determined one. From this point, the calculation can be viewed not only as the quantitative, but also as qualitative assessment how correct is the model chosen for calculation. It also semi-qualitatively confirms the correctness of the suggested explanation of the electric current nature.

As shown earlier, during the calculations for metals having atoms connected with the single-electron bond, it was found out that the metal conductance (if the model is correct) can depend on the ionization potentials of the metal atoms. The evaluation of the calculation data showed, the metal resistance value dependence on the atom ionization potentials is expressed by the curve, having the minimum, i.e., it has a paradoxical character. It is really difficult to expect, the raise of the ionization potentials from 4 to 8 eV, leads to the 10 times increase of the metal electric conductivity, but the further increase of the ionization potentials to 11 eV causes two times decrease of the electric conductivity. However, as presented in slides 7 and 8, the comparison of the calculated dependence with the dependence of the metal electric conductivity on the atom ionization potential (which was obtained using the experimental data) showed not only the
qualitative, but also practically quantitative coincidence of dependencies, calculated based on the model and the results, based on the experimental data evaluation. The dependence, which is obtained based on the experimental data, also is expressed with the curve having a minimum. Even more, this minimum is situated, if calculated accordingly to the model, at the ionization potential of 9 eV for the atoms with the frozen nucleus and 8 eV with the free nucleus. The minimum on the curve, obtained as a result of the experimental data evaluation for the first group elements (Li, Na, K, Rb, Cs) and silver (Ag), copper (Cu), and gold (Au) is situated at 7.5 eV. It is situated at 8 eV in the case of vanadium (V), chromium (Cr), niobium (Nb), molybdenum (Mo), rhodium (Rh), and platinum (Pt).

Above mentioned dependencies calculated for homoatomic molecules are applicable to molecules consisting of two different atoms. For example, in case of NaCl, a change of Enet with movement of two-electron ring along the bond (see slide 9) is similar to that for homoatomic non-metals (compare with slide 8) and corresponds with known data of NaCl conductance.

Obtained results were reported at the 232nd ACS National Meeting, San Francisco, CA, September 10-14, 2006.
Molecule’s geometry and energy

$E_{net} = P\,E + K\,E$

$P\,E = K_\epsilon e^2 \left( \frac{N_1 N_2}{2b} - \frac{N_1}{c_1} - \frac{N_2}{c_2} \right)$

$K\,E = K_\epsilon e^2 a^2 \left( \frac{N_1}{c_1^3} + \frac{N_2}{c_2^3} \right) / 2$

Slide 1. Molecule’s geometry and energy (a sample graph).
Definition of Enet (a sum of potential and kinetic energy) and dEnet
Slide 2. Enet as a function of electron position for free and frozen nuclei; n=1
Comparison of Enet vs $r=x_1/b$ for FIE = 6 to 18 eV

$n=2$

--- frozen b   --- free b

Slide 3. Enet as a function of electron position for free and frozen nuclei;

$n=2$
Slide 4. Detailed graphs Enet as a function of electron position for frozen nuclei; n=1

Slide 5. Detailed graphs Enet as a function of electron position for frozen nuclei; n=2
Slide 6. Generalized graphs dEnet vs FIE for molecules with free and frozen nuclei, single and two bonding electrons.

Slide 8. Single-electron bonding in metals of 5-7 groups. Comparison of dEnet and experimental data

Slide 9. Two-electron bonding in NaCl molecule for free and frozen nuclei
Dynamic Balance and Energy Distribution in Three-Nucleus Molecules with Single Valent Electron

The exploration of dynamic balance and distribution of energy in two-nucleus molecules presented in [2], [3], and [4] has found that, for molecules with one bonding electron, some zone of “flat” energy distribution around equilibrium point exists. The electron’s ring movement of about ±25% of internuclei distance results in energy change of 0.05 to about 0.15 eV depending on nuclei’s first ionization potential. However, when the ring moves closer to any nucleus, energy change increases sharply (up to about 1 eV) requiring some additional energy for electron’s displacement out of molecule’s border. But someone could have expected that, in reality, an influence of surrounding nuclei should decrease this effect i.e. increase conductivity.

Thus exploration of three- and four-nucleus molecules with one or two bonding electrons could promise some particular interest.

In this article, theoretical analysis of two-nucleus molecule’s model with one bonding electron developed in [2] and [3] is extended to three-nucleus case.

1. Model of Three-Nucleus Molecule and Main Equations

We have considered this molecular configuration:
Nuclei A, B, and C have the same positive charge of \( N \) elementary units for each. The valent electron E is rotating around ABC axis with radius \( a \).

First of all, let’s consider equation of equilibrium of electrostatic forces applied to each nucleus.

For nucleus A such an equation is:

\[
-N^2e^2/(2d)^2 -N^2e^2/(2d+2b)^2 +Ne^2(2d+x)/(a^2+(2d+x)^2)^{3/2} = 0
\]

In this equation, two first terms represent components of repulsive forces applied along the \( x \)-axis to the nucleus A from two other nuclei; third term represents such a component of force applied by electron.

After all cancellations and expressing all linear sizes in ‘a’ units \( (x=xa, b=ba, d=da, \) and 1 instead of \( x, b, d, \) and \( a, \) respectively, this equation looks this way:

\[
N(1/d^2 +1/(d+b)^2)/4 = (2d+x)/(1+(2d+x)^2)^{3/2}
\]

Equation (1)

Similarly, for nucleus B:

\[-N(1/d^2 -1/b^2)/4 = x/(1+x^2)^{3/2}
\]

Equation (2)

And for nucleus C:

\[
N(1/b^2 +1/(b+d)^2)/4 = (2b-x)/(1+(2b-x)^2)^{3/2}
\]

Equation (3)

For practical calculations, it is convenient to use, instead of variable \( x \), another variable, let’s name it \( r \), such that \( x=rb \). So, \( r=x/b \).

Thus equations (1) to (3) would be transformed to:

\[
N(1/d^2 +1/(d+b)^2)/4 = (2d+rb)/(1+(2d+rb)^2)^{3/2}
\]

Equation (1')

\[-N(1/d^2 -1/b^2)/4 = rb/(1+r^2b^2)^{3/2}
\]

Equation (2')

\[
N(1/b^2 +1/(b+d)^2)/4 = (2-r)b/(1+(2-r)^2b^2)^{3/2}
\]

Equation (3')
It is possible to consider some special configurations, such as, for example:

a. Symmetrical configuration with \( r = 0 \).

Electron rotates around the middle nucleus (B). This kind of configuration is illustrated by figure 2.

\[
N(1/b^2 + 1/(4b^3))/4 = 2b/(1 + 4b^2)^{3/2} \quad \text{Eq (1”)}
\]

or

\[
\text{Eq (3”)}
\]

For nucleus B, the equilibrium is trivial and has automatically fulfilled.

Equation (1”) or (3”) can be solved analytically yielding the formula of distance \( b = d \) between nuclei as the function of charge \( N \):

\[
b = d = ((5/32)^{2/3} N^{2/3} / (1 - 4(5/32)^{2/3} N^{2/3}))^{1/2} \quad \text{Eq (4)},
\]

or:

\[
b = d = (0.290099 N^{2/3} / (1 - 1.1604 N^{2/3}))^{1/2}, \quad \text{or,}
\]

finally, in terms of first ionization energy:

\[
b = d = (0.12155(FIE)^{1/3} / (1 - 0.4862(FIE)^{1/3}))^{1/2} \quad \text{Eq (4’)}
\]

(with \( FIE \) in EV).

The graph of this equation is shown on figure 3.
When \( N = 1/(4(5/32)^{3/3})^{3/2} = 4/5 \), we have: \( b \to \infty \), and \( d \to \infty \).

This means that such molecule cannot exist because attractive force of the electron is not enough to overcome mutual repulsion of nuclei. So, in order to create a molecule of this type, \( N \) should be less than 0.8 (exactly), or \( \text{FIE}<8.7007 \text{ eV} \).

In order to define absolute dimensions and energy parameters, of such molecule, we should use the approach similar to one described in book [1] pages 127, 128.

This gives following formula for \( a \) as a function of dimensionless parameter \( b \) (remember that \( b=d \)):

\[
\frac{a}{R_{F}} = \frac{2}{3} \frac{3/2}{2} 0 + 2 = + 1 \quad \text{Eq (5)}
\]

and \( R=1 \) in Bohr radii units (1 Bohr radius=0.5292 Å).

Dependencies of \( b \) on \( N \) (or FIE) are defined by equations (4) or (4').

With known \( a \), the electrostatic potential energy of this configuration is defined by formula:

\[
PE = k_{e}e^{2}N(1.25N / b - 1 - 2/(1 + 4b^{2})^{1/2}) / a \quad \text{Eq (6)}
\]

and kinetic energy:
\[
KE = k_e e^2 N \left( \frac{1}{1 + 4b^2} \right)^{3/2} \left( 1 + \frac{1}{2} \right) / a^2.
\]

Eq (7)

This is actually the kinetic energy of electron rotating around the A-B-C axis.

The total (net) energy:

\[
Enet = k_e e^2 N (1.25N / b - 2/((1 + 4b^2)^{1/2} + 1/(1 + 4b^2)^{3/2} - 1/2)) / a
\]

Eq (8)

here \( k_e e^2 = 27.115 \ (eV) * (R_{Bohr}) / C^2 \).

The graph of Enet as function of FIE is shown on figure 4:

Figure 4

Absolute value of Enet increases monotonously with increase of FIE.

It is interesting to check if the Virial rule could be applied to systems of this kind.

For this, we can use the criterion \( D_v = |PE|/(KE) - 2 \) showing a deviation from Virial’s rule (see article [2]). Using equations (4), (5), and (6), it could be shown that, for any value of charge \( N \), value of \( D_v \) is equal exactly 0 that is Virial rule is applicable for such systems.

b. In the context of three-nucleus configuration, the two-nucleus case with charges \( 2N \) and \( N \)

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\(^2\) As follows from this formula and equation (5), \( KE = \frac{k_e e^2}{2a^2} \), but in order to have equations in more general form, we use equation (5).
also could be considered as a limiting case with the distance $2d$ being equal 0. Equations (1’) and (2’) are not workable in this case, but they can be transformed to one equation without the $1/d^2$ term.

Better yet, such configuration can be solved by methods described, for example, in the book [1].

2. Non Symmetrical Three-nucleus Configuration

In general case, when $r \neq 1$ or 0 and $d \neq 0$, we have to solve the system of three nonlinear equations with variables in fractional degrees.

This system can be reduced to the system of two equations with two variables in the following way.

Equation (2’) can be solved for the variable $d$:

$$d = N^{1/2}b(1 + r^2b^2)^{3/4} / (N(1 + r^2b^2)^{3/2} - 4rb^3)^{1/2}$$

Eq (9)

Substitution of this expression in equation (3’) gives:

$$N(1/r^2b^2 + 1/b + N^{1/2}b(1 + r^2b^2)^{3/4} / (N(1 + r^2b^2)^{3/2} - 4rb^3)^{1/2}) / 4 - (2 - r)b / (1 + (2 - r)^2b^2)^{3/2} = 0$$

Eq(10)

As follows from this equation, $d \to \infty$ when $N(1 + r^2b^2)^{3/2} \to 4rb^3$, so this expression gives the limiting case, such that the three-nucleus system is reduced to two-nucleus one.

Equation (10) involves only two variables, $r$ and $b$, but cannot be solved analytically. Nevertheless the solution can be found either by iteration methods, or graphically.

Then the general algorithm for solution of a three-nucleus scheme can be described as follows.

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3 For iterations, it would be helpful to get a derivative $d/db$ of the equation (10). Such derivative has the following form:

$$\frac{d}{db} (\text{equation}(10)) =$$

$$-12N^{1/2}r^3b^2(r^2b^2 - b + 1) / (1 + r^2b^2)^{3/4} / ((N(1 + r^2b^2)^{3/2} - 4rb^3)^{1/2} + N^{1/2}(1 + r^2b^2)^{3/2})^3$$

Eq (11)

This formula may be used for solving equation (10) by Newton method.
Using equations (9) and (10), for considered value of nuclei’s charges \( N \), and for any value of parameter \( r \), the longitudinal dimensions of molecule (parameters \( b \) and \( d \)) can be calculated. Substitution of this set of parameters in equation (1’) (the rest one from all original equilibrium equations (1’) through (3’)) will show if this configuration is statically balanced, i.e. equilibrium of forces applied to nuclei exists. This would be the case if the left and right parts of this equation are equal (with some accuracy). Otherwise, the maximal difference between them gives the measure of misbalance (\( D_f \)) for the systems as a whole.

Next, for any given configuration, the energy parameters of molecule can be calculated using following formulas:

\[
a = 1/F_0,
\]

where

\[
F_0 = N(1/(1+(2-r)^2b^2)^{3/2} + 1/(1+r^2b^2)^{3/2} + 1/(1+(2d+rb)^2)^{3/2})
\]

Potential energy:

\[
PE = 27.115N(1/(1 + (2-r)^2b^2) + 1/(1 + r^2b^2) - 2 - 1/(1 + (2-r)^2b^2)^{1/2})
\]

\[
-1/(1 + r^2b^2)^{1/2} - 1/(1 + (2d + rb)^2)^{1/2})/a
\]

Eq (12)

Kinetic energy:

\[
KE = 27.115N(1/(1+(2-r)^2b^2)^{3/2} + 1/(1+r^2b^2)^{3/2} + 1/(1+(2d+rb)^2)^{3/2})/(2a)
\]

Eq (13)\(^4\)

Total (net) energy:

\[
E_{net} = PE + KE.
\]

Calculations have been completed for three-nucleus schemes with \( N=0.5 \), \( 0.6 \), \( 0.7 \), \( 0.7698 \), and \( N=0.79 \)

\[^4\] Again \( KE = \frac{k_e^2}{2a^2} \).
(FIE=3.399, 4.894, 6.662, 8.056\(^5\), and 8.485 eV, respectively).

Some results of the calculations are shown on following graphs.

Figure 5 shows dependencies of Enet on r for various FIE. The graphs show that limiting value of parameter r (for which the scheme turns to two-nucleus because \(d \to \infty\)) equals approximately 1 for schemes with nuclei’s charges up to about 0.77 (FIE=8.056 eV) and decreases with further increase of charge. For FIE=8.056 eV, the shape of graph of Enet as function of r shows some different patterns compared with the graphs for other values of FIE (see figure 10). Namely, the graph becomes flat at the “tails” (near \(r = -1\) and +1). This kind of behavior corresponds with results of studies of dual-atomic molecules in [2].

Also for configurations with FIE equal or greater than 8.056 eV, there is a small interval around \(r = 0\) (about \(r \leq 0.03\)) where a small, albeit “shallow”, potential well exists. This implies some increase of stability for symmetrical schemes in this interval.

\(^5\) As shown in article [2], this value of FIE corresponds to the border of splitting zone (S-zone) for two-nucleus homoatomic molecule, so this supposed to be a point of special interest when r approaches 1, i.e. three-nucleus scheme turns to two-nucleus one.
Figure 5

Figure 6 shows graphs of dimensions $2b$ and $2d$ for nuclei with charges $N=0.6$, while figures 7a and 7b show such dimensions, separately, for $N=0.79$. 

Figure 6
Figures 7a and 7b also show that, in the same narrow zone around the middle nucleus B (\( r \leq 0.03 \)), any small displacement of electron results in decreasing of both 2b and 2b distances, that means that both outer nuclei (A and C) move toward point B.

Figure 8 shows dependencies of misbalance criteria \( D_f \) and \( D_v \) on \( r \) for nuclei charge of \( N=0.79 \).

Energetic misbalance criterion \( D_v \) should have been estimated against its nominal absolute value of 2. Estimation
of the force misbalance criterion $Df$ could have been done against the computational accuracy of calculation of balance which usually is about $10^{-6}$. So, criterion $Df$ is more limiting than $Dv$.

Comparison of Enet dependencies on electron motion along the $x$-axis for two- and three-nucleus schemes is shown on figure 9, for $N=0.7698$ (FIE=8.0563 eV). For two-nucleus scheme, parameter $r$ along abscissa axis is $x_1/b$, where the distance $x_1$ measures from left nuclei toward right one (see [3]).

Unlikely two-nucleus scheme, the Enet curve for three-nucleus one is more steep, obviously because of more complex mutual interaction between nuclei.
3. Frozen Molecular Model versus Free One

In the article [2], the conception of “frozen” two-nucleus schemes was introduced. Here, we will extend this conception to three-nucleus models. Accordingly, we will distinguish model with “frozen” nuclei from models with “free” nuclei that has been considered before. In cases of “frozen” three-nucleus models, we will also refer to them as “schemes with ‘frozen $b$, $d’”.

Estimation of main dimensions and energetic parameters for “frozen” models is similar to that of free ones with the exception of internuclei distances $b$ and $d$ which remain constant.

Some results of such calculations, together with ones for “free” models, are shown on figures 10 and 11.

![Comparison of Enet vs r=x/b for frozen and free 3-nucleus schemes with N=0.6 (FIE=4.894 eV)](image)

Figure 10
As one would expect, electron’s motion in “frozen” models is related with higher level of molecule’s total energy, so these states should be less stable and less likely than for “free” models.

Real situations would occur somewhere between these two models.

In order to have some quantitative estimation, it is useful to introduce such a special criterion, let’s name it the degree of frozenness – $z$. Mathematically, frozenness of $z$ degree means that any change in distances $b$ and $d$ between nuclei occurs, for $100(1-z)\%$ as if the nuclei have moved with the same speed as electron has moved along x-axis, and for $100z\%$ as if nuclei were stationary. The change in radius of electrons orbit $a$ is also assumed to be proportional to $z$.

Graphs of $\text{Enet vs } r$ for various $z$ are shown on figure 12.
One can see, from this graph, that there could be some degree of frozenness, namely $z \approx 31\%$, such that the curve of $\text{Enet}$ is almost flat, with maximal difference less than $0.3$ eV in all range of electron’s motion. Actually, for all $z$ in the range between $30\%$ and $32\%$, such a difference is also less than $0.3$ eV. This might result in special interesting effects, for example, high electrical conductivity.

Unfortunately, we have no reliable estimation of a real degree of frozenness.

Figures 13 and 14 show dependencies of misbalance criteria $D_v$ and $D_f$ on $r$. 

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**Figure 12**

**Figure 13**
Figure 14

Misbalance of forces (Df) has a sharp increase when model approaches the state of full frozenness (z=1).

4. Conclusions

1. Introduced calculations based on equilibrium equations have showed that, with some limitations, three-nucleus molecular configurations with a single bonding electron are likely to exist, with the electron having some degree of freedom for motion between nuclei.

2. One of the limitations for three-nucleus schemes is the charges of nuclei should be less than 0.8, in other words, FIEs should be less than 8.7 eV.

3. There have existed certain relationships between two- and three-nucleus schemes with possibility of mutual transfer from one scheme to another.

4. Equilibrium criteria (Dv and Df) developed for two-nucleus schemes are applicable for three-nucleus case.

5. The concept of “frozen” molecule, developed in [3] for two-nucleus case, is applicable and useful for three-nucleus one. There might be some degree of frozenness (about 31%) for which a motion of valent electron’s ring is especially easy that would mean a maximum electric conductivity.

One of important tasks for future researches should be the calculations of real degree of frozenness in three-nucleus molecule.
References:
1. General Chemistry (Teaching Aids)  
2. Asymmetry Zone for Dual-Atomic Molecules with Single Bonding Electron  
4. Semi-quantitative modeling of electrical conductivity in metals and non-metals  