

V.Y. GANKIN & Y.V. GANKIN

**NEW GENERAL THEORY
OF CHEMICAL BONDING,
KINETICS, AND CATALYSIS**

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Translated from Russian by A.P. Rogach

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FROM THE EDITORIAL BOARD

The phenomenon of chemical bonding is quite complicated, and in spite of the fact that its history is several decades old, the nature of chemical bonding is not elucidated to the end. This is why further efforts are necessary to resolve this global problem that affects the whole of natural science; we should involve more publications on various viewpoints of the existing theory. This booklet offers the problems of the general chemical bonding theory in the form of a discussion.

Firstly, we presume that all new hypotheses should be based on the proper analyses of the existing theory. The theory of chemical bonding has a strict quantum-mechanical foundation; it includes a specifically elaborated physico-mechanical apparatus; it has a grand interpretational and forecasting power, and therefore cannot be narrated superficially without consideration for all the fundamental precepts of the theory.

Secondly, new hypotheses should objectively consider parallel elaborations in the same direction, including the lodge theory, the orbital domain theory, and the atomic orbital shell conception; sorry to say, there is nothing about these in this booklet.

Thirdly, all new hypotheses should, by all means, be based on repeatedly proven and experimentally checked regulations relative to quantum-mechanical atoms and molecules. The authors' viewpoints in this booklet, relative to the theory of chemical bonding, is quite empirical and never experienced much argumentation; but, after all, let the readers be the judges.

PREFACE

Here we have an account of a new approach to the explanation of the nature of covalent chemical bonding elaborated by the authors and based on the studies of energy and entropy changes of bonding electrons during molecule formation. The *theory of elementary interactions* (TEI) is compiled on the basis of this approach — the general kinetics theory, the catalysis theory, and the alternative activated complex theory. Various types of chemical reactions are analyzed; the main regularities observed in catalysis are well explained. The shortcomings of the existing conceptions are indicated, and the illogicality of the activated complex theory is proven.

This booklet is recommended to all chemists.

FOREWORD

This booklet about the new general theory of chemical bonding and chemical kinetics is an unusual one. In the new theory, the strength of the covalent bond is explained by the fact that the main portion of heat energy, passed to the covalent molecules, which are subject to thermal breaking, there is a sort of unproductive expenditure of this energy, i.e., it is spent not on the increase of the nuclei's vibrational energy, but spent on increasing the energy and the entropy of the bonding electrons. It has been proven in the theory of chemical reactions that reaction $A + BC \rightarrow AB + C$ proceeds not via the transition state $A \dots B \dots C$ that is located on the maximum of the potential energy curve, but via the intermediate compound $A \cdot B : C$, which is situated on the minimum.

The comparatively small values of activation energy (about 40 kJ/mol) as compared with bonding energy (about 400 kJ/mol) during radical interaction with saturated molecules is explained in the new theory by the rapid electronic isomerization of compound of $A \cdot B : C$ into $A : B \cdot C$. The offered theories do not contain any suppositions that contradict modern science; all the common and individual precepts were confirmed experimentally. This new theory is based on fundamental experiments, on differentiation between atomic and molecular spectra, and that between hydrogen molecules and covalent molecules.

In the basis of the theory of chemical reactions lay the experimental data relative to the stability of molecular complexes, electron isomerization speed, the kinetics of chemically activated reactions, and the data received when studying the reactions in molecular in bunches.

Among the drawbacks in our work was the brevity of the authors in sections relative to the criticism of both quantum chemistry (including the Heitler-London model) and the transitions state theory. Here, most likely, we should have not only mentioned the works of some authors like Rutherford, Pollak, but should have included other works as well.

To conclude, I call upon the readers to discuss the theories offered in this booklet; for indeed, when introducing new conceptions, it is just as harmful to stay mum, as it is to negate them without reasoning. Examples that confirm this thesis about the harmful prejudices and inertia in science are well known. Silence and bias once impeded the introduction of the van't Hoff, Arrhenius, and Butlerov theories.

Indeed, ungrammatical were regarded the ideas about the influence of the magnetic pole on chemical reactions, which were recently awarded the Lenin Premium. Studies about vibrational and rolling waves in chemical processes were ousted from science for many years! Recall the fate of the Belousov reaction!

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INTRODUCTION

The theory of chemical bonding and chemical kinetics is the foundation of theoretical chemistry. There are many monographs and textbooks on the basics of theoretical chemistry — that is why it is necessary to write one more work on this topic in the introductory part of this booklet and explain in general terms its importance from the previous works.

In the course of the development of science, theoretical chemistry has traversed a path from a *set of recipes* on the transformation of substances via the theory of internal (atomic) structure and change of substances, electronic chemistry up to quantum chemistry — actually a mathematical description of chemical regularities.

In spite of the mentioned evolution of essence that was put into the term *theoretical chemistry*, a great number of chemists-experimentalists make use of atomic and electronic chemistry in their practical activity and in their abstract theoretical meditations. On the other hand, chemistry theorists make use of only quantum chemistry.

The main reason for such a discrepancy nowadays can be formulated thus: quantum chemical calculations, generally, help to solve digitally all the scientific and practical questions in chemistry with a precision far beyond the possibilities of chemical experiments. Nowadays the solution of problems depends mostly on the possibilities of calculators (computers) that are in the process of development. Besides this, new simplified approximate calculating methods for solving Schroedinger equation are being elaborated that will bring us closer to the time of the arrival of mathematical chemistry.

The role of traditional theoretical chemistry, in the society's scientific conscience, is gradually diminishing and today it is close to being sort of *prehistoric theoretical chemistry* that comprises the occupation and hobby of the chemists of the old school. The advantage of such occupation for theoretical chemistry is in the possibility of getting experimental data for illustrating the effect of quantum-chemical methods, for propaganda purposes and for developing qualitative and semi-quantitative conclusions about quantum chemistry (π - and σ -bonds that bond and roughen the orbitals, the exchange energy, etc.)

Most likely the following viewpoint can also have the right to exist: the birth of quantum chemistry slowed down the development of theoretical chemistry. This is explained by the fact that quantum chemistry announced and formally proved that traditionally classical theoretical chemistry is based on primitive ideas about the electron,

while all the rest of the chemical phenomena — bonding energy, structure, and the reaction capabilities of chemical compounds — is theoretically defined only by quantum chemistry. Monographs and textbooks at present are practically being written in compliance with this doctrine and according to one scheme.

To begin with, the prehistoric chemistry period is mentioned, and mainly — the history of the development of the chemical bonding and the chemical structure theories. Then comes the information about the development of quantum mechanics and a number of de-Broglie and Schroedinger equations are given, then there is a solution of some quantum problems for simple cases like an electron in a potential hole, in a box, and in a hydrogen atom. Then there is a description of the main ways of approximate solutions for the Schroedinger equation — methods of valence bonding and molecular orbitals. Then we would get a dose of the common pre-quantum (i.e., prehistoric) science, based on chemical experiments and theoretical explanations that result out of it.

The use of so-called *qualitative conclusions* in such sections, it is thought, result from quantum mechanics; however, while these are being used, a number of additional qualitative suppositions are introduced (i.e., hydrogen-like atoms, orbital hybridization), which are actually not conclusions from quantum mechanics, but rather some other, more modern description of widely known phenomena of classical chemistry.

After the chemical bonding theory and chemical structure, the theory of chemical reactions is studied in the framework of the transition state theory (TST). Historically it was the TST that first defined the borders for deepening the conscience with theoretical chemistry, and not the structure theory, since the latter postulated that the main condition that defined the reaction speed and, therefore, the chemical properties of substances, is the compound whose structure cannot be defined via chemical methods.

Thus, the different ideas of chemists relative to nucleophilia and electrophilia, as well as *marking*, used in electronic chemistry, have but a post factum explanatory character and cannot be considered as a theory in the modern sense. When dealing with the TST and the structural theory, the calculations of absolute speeds of some common reactions and the bonding energy in a hydrogen molecule are usually given as well as the final conclusions and their comparison with the experiments. The latter leave no doubt in respect to the fact that during the development of new methods of approximate solutions of equations in statistic physics and quantum mechanics relative to more complicated systems and the improvement of computing technique, a truly theoretical chemistry will come into being.

Indeed, qualitative reasoning in the form of *transition state* should be based on some kind of logic premise, but what kind of logic can there be in the explanation of transition state energy and bonding energy, if the main contribution to bonding energy is introduced by the so-called non-power contribution (exchange energy that has no vivid physical essence). Therefore, modern theoretical chemistry, given in monographs and textbooks, generally consists of two sections: theoretical chemistry with simple examples and ‘prehistoric’ theoretical chemistry, composed of a lot of experimental material, which is united via a number of rules and is awaiting its theoretical interpretation.

It is of interest to note that though 50 years ago the banner of quantum chemistry promised to produce a *truly mathematical theoretical chemistry in the near future*, and nothing came of this promise; another promise — to have the physicists compile a truly theoretical chemistry — now reminds one of Hodji Nasredgin’s worthless promises to his emir (ancient ruler in Uzbekistan). In the meantime, the division of theoretical chemistry into *modern theoretical chemistry (quantum chemistry)* and *false classical theoretical chemistry* continued to gain force in the conscience of the scientific world. And such confidence increases more readily among chemists-experimentalists than among physicists who are engaged in quantum chemistry.

Unlike the usual schemes given in modern theoretical chemistry, this booklet offers another, more logic scheme, for the construction of theoretical chemistry. It revises assurance in the elaboration of a realistic theoretical chemistry. That is, the thesis that *everything depends on the computer and the calculation methods* becomes doubtful. The revision of the possibilities of quantum chemistry logically leads to the expediency of the further development of classical chemistry. In this respect, the given work offers some new results received in the course of the further development of classical theoretical chemistry.

Indeed, we have succeeded in explaining the essence of covalent chemical bonding without any contradictions (without such terminology as ‘exchange energy’). The understanding of the essence of covalent chemical bonding allowed logical construction of a non-contradictory scheme of simple chemical reactions without the inclusion of the transition state. The main difference of this booklet, relative to theoretical chemistry, is the effort to deepen the understanding and widen the area of better understanding chemical phenomena and the rules.

As already said, the boundaries of logic traditional chemical development were installed on the level of covalent bonding theories and that of the transition state. Within these boundaries, a great number of

chemical correlations remained as empirical data that logically did not result from the existing basics. Thanks to the new approach, they have found their non-contradictory explanation, which proves their ontological and practical values.

This book, being the very first attempt at narrating the new material concerning the basics of theoretical chemistry, it is difficult to avoid mistakes, to properly express our thoughts. In this respect, the authors would be thankful to receive comments from their readers.

A Few Words about the Term ‘Theory’

The term ‘theory’ is understood in many ways. Mathematicians think that ‘theory’ is a *phenomenon described by equations*. Among the physicists and chemists there is no agreement in this respect. Some speak of a *pre-scientific theory* — a *theory of words and chemical equations*; others think a real theory is comprised of mathematical equations. Many say that *theory* involves the cause-and-effect bonds between phenomena.

The differences are still greater in respect to the essence of the *theory* when dealing with ontological values. Thus, for example, it is thought that the *theory* should foretell new phenomena — only then will it be a *true theory*. It has been confirmed that the only criterion to properly check the correctness of a *theory* is the experiment.

In the last 50 years it was fashionable for physicists to use the criterion ‘absurdity’ for checking the correctness of theories. From the viewpoint of the theory of cognition, at present the viewpoint concerning the absence of ‘things in themselves’ is prevailing, that is, regarding unlimited cognition not only in width, but also in depth.

Now let’s view some examples that stipulate the choice of mottos that should be followed in the given work. Most of this material deals with the theory of cognition, where the main questions under discussion are those concerning the limitations of cognition, criteria of the truthfulness of the theory, the adequacy of the cognition of nature.

Is the world cognizable? According to the rules of the game called ‘natural sciences’, the answer to this questions is as follows: The postulation of the fact that nature, in the process of its evolution, will produce matter capable of not only cognizing and calculating itself to the last of its own cognizant limit, but also be able to answer all the questions that this nature (brains) will ask, in the least unfounded.

One of the main questions in the theory of cognition is that of the ontological value of the theory. From the viewpoint of natural sciences, this question concerning adequacy is, in the best case, untimely, which does not correspond to the level of the development of natural sciences, and therefore, is scholastic.

In the course of the development of natural sciences, their missions and rules of the game were defined. The mission of natural sciences, which includes both experiments and abstract thinking — the finding of the cause-and-effect bonds that exist in nature, the cognition of the surrounding world. The thirst for cognition (curiosity) is the main driving force in the development of science. Satisfying curiosity is one of the physical needs of mankind (not bread alone) that is situated somewhere among the needs for something interesting, elevated that brings material gain, and that includes all the three hypostasis, which actually amounts to the practical meaning of the theory.

An analysis of the history of sciences has shown that during the period of its historic classical development, definite rules were drawn up by which we can now evaluate the advantages of this or that theory. These rules are derived from the theory itself whose aim it is to understand and explain new facts and phenomenon (the finding of cause-and-effect bonds) on the basis of known essences. Besides, unlike religion, natural sciences presuppose cause-and-effect bonds as a known factor, found experimentally, as an essence.

For example, there were gravitational and electro-dynamic interactions, serving as initial essences, on the basis of which classical physics was built.

Thus, it is no wonder that we can judge the ontological values of the theory in the classical period of its development via the criteria of *internal perfection* and *external verification (IPEV)*.

Inner perfection presupposes a minimal number of initial essences for the explanation of a maximal number of phenomena, while outer justification presupposes the possibility of direct experimental checkups of essences.

The criterion for greater understanding is the smaller digit of the initial essences in the theory. Religion ideally answers to the principle of inner perfection, it explains everything with one initial essence — the existence of God. The only drawback of religion from the viewpoint of the IPEV criterion, is the absence of outer justification — the direct experimental definition of the existence of God.

The number of essences in science indirectly speaks in favor of its level of development and its potential possibilities of development.

Besides the IPEV criterion, criteria like ‘craziness’, ‘practicality’, etc. came into being in the XX century. These took the place of ontological theories.

Some newly discovered phenomena were at once labeled as ‘new essences’. Thus, we got dependences of mass, length, and time on speed; the principle of uncertainty was regarded as a physical dependence, etc. Unlike the classical period of the development of science, when theory was regarded as important for understanding and explaining physical and chemical phenomena, and was composed of a dialectic unions of experiment and abstract understanding, in a new period of development of science, first there was a division of people, and then — a division of concepts, ideas.

New separately existing subjects appeared: theoretical and experimental physics and chemistry where mathematical equations became the theory proper, and to them were added separate criteria of ontological value (*for example, simplicity of the equations*).

Unlike the criteria of ontological values, the criterion of incorrectness was the only one to remain in science during the history of its development. It was considered that if the experiment did not correspond to the theory, then the theory is incorrect.

In the period of the classical development of science, the interrelations between the theory and experiment were of a mono-semantic nature. The history of the classical period of the development of science was not critical enough

Now let’s demonstrate this harsh conclusion with the help of several widely known examples. Thus, at the end of the XVIII century, Lavoisier calculated, on the basis of the Newton theory, relative to the attraction along the magnetic perturbation of Uranus where planet Neptune was situated. The behavior of the Uranus orbit was defined and the next confirmation of the whereabouts of Neptune contradicted the attraction theory’s calculations; this never interfered with its existence.

Having found the planet Neptune after a successful calculation, Lavoisier noticed that Mercury’s orbit had also inclined away from the calculated orbit, and on this basis he predicted the existence of a planet between Mercury and the Sun. However, this planet was not located experimentally, so several hypotheses were suggested (existence of a meteorite cloud, a non-strictly quadratic dependence) explaining the inconsistency of the calculation and the experiment.

At least for 70 years before the discovery and the discharge of atomic energy, one of the strictest laws was that of energy conservation. The French academy even stopped accepting projects of so-called ‘eternal engines’. On the other hand, everyone, including scientists,

watched the Sun every single day. This was done in the framework of the then known sources of chemical energy, for example, energy of fire, which completely contradicted the law of energy conservation. It was impossible to presuppose some kind of hypothetic chemical reactions that could explain the origin of at least a tiny part of the Sun's energy. In spite of this, the law of energy conservation has remained to be the main law of natural science.

Thus, even in the best-known cases, when considering the connections between the theory and the experiment, the scientists often did not adhere to the existing doctrines. Philosophers spend a lot of time to define the truthfulness of theories; however, it is illogic to consider even the latest of their viewpoints in this work. Besides, nowadays the philosophers themselves have been divided into those who regard philosophy not as a science, but as a scholastic argument, and those, who still regard it as a science. What finally remain from the main arguments of the defenders of philosophy as a science are the labels (*bourgeois scientists, idealistic approach, etc.*).

These lyrical deviations have nothing to do with the basing of the approach accepted in our work, they just somewhat analogously defend the approach we have chosen for our work along the principle: If the widely spread stereotypes are not proven, then the choice of criterion IPEV as the one and only criterion of ontological value mentioned by the theory, is not less based than the widely used criteria. The classical period of the development of science has proven the illogicality of pursuing this criterion.

In the process of the development of science, the new essences were actually intermediate work terms that usually found their meaning in the basis of the old essences during the further development of science. That is how it was with phlogiston and ether.

General Theory of Chemical Bonding and Chemical Kinetics

The existing theory of chemical bonding, chemical reactions, and catalysis presupposes that the main energy contribution to the energy of a covalent chemical bond is introduced by the so-called exchange energy, which is conditioned first of all, by quantum-mechanical effects (pairing electrons with various spins). Relatively, between the chemical particles that have paired electrons (for example, covalent molecules) and any other chemical particles, including radicals, according to the existing theory, we should observe repulsion within the area of the action of the

exchange force, which conditions the need for energetic expenditure. Such expenditure, according to the modern theory of chemical reactions, are actually the activation energy; and the condition (state) that the reacting particles gain after passing the repulsion exchange, is known as the transition state.

The speed of the chemical reaction in the general theory of chemical kinetics is defined by the probability (activation energy, probability factor) in gaining the transition state via reacting molecules.

The influence of the main parameters that accomplish chemical reactions (temperature, solvent, chemical nature of the initial substances) is explained, first of all, by increasing or decreasing the probability of reaching the transition state, that also includes the possible hypotheses on changing the appearance of the transition state (usually for the influence of solvent and the chemical nature of substances).

The role of the catalyst in the general theory of catalysis comes down to the change of the nature of the transition state.

The given theory is a generally accepted one. Individual (private) theories are based upon it. The latter include various quantum-mechanical means of calculating bonding energy that differ in initial mathematical or physical suppositions, which are usually introduced in order to get a digital result. The main individual theories of bonding energy are: the theory of valence bonds and the theory of molecular orbitals, which, in their turn, are detailed in various methods of quantum-chemical calculations.

Besides the development of calculations in the accepted conception, there are qualitative chemical theories that explain 1) various chemical regularities in bonding energy and in the influence of atoms on each other in a molecule, 2) the qualitative and quantitative regularities of chemical reactions (kinetics and contents of products) including the catalytic ones.

These explanations and theories most often include intermediate qualitative and semi-quantitative results of the theory of chemical bonding and chemical reactions, with the addition of new suppositions, if necessary (for example, the Hammond postulates) that allow to match the theory with the experimental results.

It is of interest to note that though the basics of each private theory were more common relative to their conceptions, the private theory usually contradicted the preceding general theory in the semi-quantitative plan. Thus, for example, the only forces that pull together the atoms in a molecule, according to the general theory of chemical bonding, are the Coulomb forces that attract the nuclei to the electrons

between them. However, the contribution of classical Coulomb interaction to bonding energy comprises only about 10% (≈ 40 kJ/mol for H_2), and >70 % of the contribution is related to the exchange interactions, which are sometimes called non-force interactions.

When we consider the Coulomb forces as the principle ones, the strength of the covalent bond correlates with the overlapping of the electronic orbitals, that is, there is an interaction of two identically charged particles.

In the equation received by Heitler and London, the exchange interactions have plus and minus signs and are identical relative to absolute values. To overcome them in case of a radical substitution, for example, $D' + H_2 \rightarrow DH + H'$ requires an energy by one order of magnitude smaller than the bonding energy; while in the general theory of chemical reactions the activation energy is connected with the need to overcome exchange repulsion.

The main driving force of chemical reactions is the kinetic energy of molecules, but at 300K (the same kinetic energy) the interaction speed of the molecules with radicals is by more than 10 orders of magnitude greater than that of saturated molecules.

The recognition of kinetic energy as the main energy, in general contradicts the use of catalysts, because after adsorption on a heterogeneous catalyst, the kinetic energy of the reacting molecules is close to zero.

Not less paradoxical was the situation in the realm of understanding the cause-and-effect bonds of the main chemical phenomena. Thus, the main questions of chemistry, as a science, involved the understanding of physical essence of such chemical phenomena as *chemical bonding* and *chemical reactions*.

However, the classical period of the development of chemistry, relative to the physical essence of chemical bonding, was unable to explain this phenomenon; only quantum chemistry explained it.

The condition of theoretical chemistry caused logic skepticism among the theorists themselves — the supporters of this chemistry. Indeed, Woodworth and Hoffman (see note [1]) wrote on this account:

“Chemistry remains an experimental science... However, the last 20 years were marked by a productive symbiosis of organic chemistry and theory of molecular orbitals. Perforce, this was a union of a bad theory with a good experiment. The initial unions appeared on the basis of theories that were such a mixture of approximations that they, obviously, had practically no right to be used. Nevertheless, in the hands

Chapter I

THE THEORY OF CHEMICAL BONDING

The classical period of the development of chemical bonding can be conditionally divided into two stages. The first stage preceded the discovery of atom structure; the second stage began after the establishment of atom structure by Rutherford and Bohr.

The main question on the first stage of the development of the theory of chemical bonding was about the theory's physical essence. Briefly, it was formulated thus: *Is there a third force that bonds atoms into molecules besides electric and gravitational forces which were known ever since the XXVII century?*

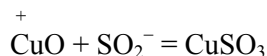
The electrostatic nature of chemical bonding was foreseen by Newton. In his discussions he believed in chemical bonding, and to explain its nature he presupposed electrostatic interaction.

Gravitational interaction is very weak as compared with chemical force. Newton didn't have enough reason to presuppose some other forces. The connection between electric and chemical forces was discovered at the beginning of the XIX century experimentally [2].

In 1800 Nicholson and Carlyle passed electric current through water and received hydrogen and oxygen. In 1807 Dewar isolated sodium out of caustic soda, and potassium out of caustic potash. He was sure that the forces, that controlled the chemical particles, were electric, and the charges on the connecting particles become obvious at contact.

Berzelius' theory of electro-chemical dualism (1812) can be regarded as the first scientific interpretation of the nature of inter-atomic forces. This theory appeared thanks to the works of Devy, as a result of the discovery of the Coulomb Law, and thanks to the invention of the galvanic elements. Berzelius distributed all the elements in a row in the order of their diminishing electrostatic properties. He supposed that each atom consisted of positive and negative electric charges, and the electro-positive atoms have a surplus of positive charges, while the electro-negative ones have a surplus of negative charges. The bonding of an element with oxygen caused the formation of the main oxide (for example, CuO) with a residual positive charge on the copper or acid oxide (SO₂) with a residual negative charge on the oxygen.

These oxides were able to bond thanks to the attraction force of the residual charges with positive and negative signs:

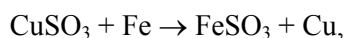


However, in spite of its merits, the electro-chemical theory was unable to explain a number of facts.

From the Avogadro hypothesis we learned that such gases as oxygen, hydrogen, chlorine, and others have molecules composed of two identical atoms. It was unclear — exactly how the two identical atoms kept together. This caused Berzelius to negate the Avogadro hypothesis. Also, great difficulties arose when interpreting the structure of organic compounds [3].

Organic chemistry began developing rapidly soon after Weller's synthesis of urea. Having utilized his knowledge about positive radicals bonded with more electronegative elements, Berzelius managed to use dual electrochemical logic in organic compounds. But he was unable to explain the substitution reactions. In inorganic chemistry these reactions could be described on the basis of the electrochemical theory.

For example, in the following reaction:



A small amount of electropositive copper was discharged by electropositive iron, which was strongly attracted by the negative residual SO_3^{2-} . However, in Dumas' experiments there was a substitution of strong electropositive hydrogen for strong electronegative chlorine. The discovery of the capability of atoms to be substituted by others, in organic chemistry, without regard to their electrochemical properties, led to the crash of the dualistic theory.

Arrhenius returned to his theory of electrolytic dissociation in an effort to explain chemical bonding via electrostatic interaction.

Helmholtz, in his lecture on Faraday in 1881 spoke to the effect that ... *"the greatest power of all the chemical forces is electric power. Atoms can accept electric charges; and charges with opposite signs are attracted to each other"* [2].

Chemical literature often featured articles about the electrostatic nature of chemical bonding. However, there were also arguments where the participants spoke in favor of the existence of specific chemical forces. The fact of the existence of inert gases in the form of atoms spoke to the effect that there are some kinds of special properties in the atoms of the rest of the elements that make the atoms attract each other.

Practically all the main chemical regulations included articles about specific forces. There were terms like: the law of brief relations, the saturation of chemical bonding, Mendeleev's periodic law (with the question: Why do chemical properties – first of all, the capacity to form

compounds – depend on the atomic weight and, besides, on the periodic law? The existence of special chemical laws was supposed to have proven the existence of special chemical forces.

The analysis of chemical regularities shifted to a new stage of its development after the elaboration of the theory of atom structure, the elucidation of the rules for the filling of the electronic shells, and the physical basing of the periodic law.

On this stage Kossel suggested a model for an ionic bond that was a logic conclusion relative to all the previous suppositions about the nature of electric forces. According to Kossel, chemical bonding was the result of the attraction of various-sized ions, which, in their turn, are formed as a result of the transition of the electron from the atom with a small ionization potential to an atom with a big potential. The Kossel theory allowed evaluating the energy of ionic bonding with the help of electrostatic classical equations. The received energy value amounted to $\approx 1,000$ kJ/mol, which explained the high stability of the molecules whose breaking into ions was practically never observed even at temperatures of about 4,000 K.

Still, the central point in the structural theory concerned the nature of covalent chemical bonding. In 1916 there was an article by Lewis entitled: The atom and the molecule where the author detailed the development the idea about homopolar (covalent) bonding.

According to Lewis, the covalent bond is formed at the expense of pairing electrons, when each of the partners builds his shell to the most stable inert gas configuration [3].

The pair of electrons, situated at identical distances from the bonding atoms, in the case of pure covalent bonding, can be moved to one of the atoms with the formation of a polar bond.

The ionic bond is but a maximal case of a polar bond — when a pair of bonding electrons can be moved to one of the atoms [3].

However, the explanation about homopolar bonding via electric attraction of the nuclei to the electrons, located between the latter, caused quantitative contradiction with the experimental data when defining the bonding energy.

Indeed, the covalent molecule, as a result of, say, thermal dissociation, breaks into two radicals, which, in the first approach, can be regarded as neutral particles.

From the viewpoint of electrostatics, with the increase of the distance, the interaction force (and therefore — the interaction energy) between them should decrease quite rapidly. Therefore, the covalent bonding energy, it might seem, should be at least by one order of

magnitude smaller than the energy in the ionic molecule that falls apart into two differently charged ions.

Experiments on defining the bonding energy in a hydrogen molecule, based on the study of the dependence of the concentration of hydrogen radicals on the temperature, offered an energy value of about 400 kJ/mol, which is only about 2 – 2.5 times smaller than ionic bonding energy, for example, in molecule CsF. The cause of the wonderful thermal stability of covalent bonding remained unclear, and also unclear were its saturation possibilities.

Indeed, if there exists a certain force that keeps two atoms together in a molecule, then why can't a third atom bond to that same molecule, then a fourth, and so on?

It is considered that the problems that stood before 'classical' chemistry had been successfully done away with the appearance of approximate methods of solving the Schroedinger equation (recall: quantum chemistry).

In 1926 a revolutionary transition in physics took place: from Bohr to the quantum description of atom structure on the basis of the Schroedinger equation. The solution of the equation relative to a hydrogen atom revealed a wonderful coincidence of the calculation and the experiment results. Also in 1926 Schroedinger offered Heitler and London the solution of a problem about homopolar chemical bonding making use of a hydrogen molecule.

Unlike the hydrogen atom, a hydrogen molecule consists of four quantum particles, that is why it was impossible to get an analytic solution of the Schroedinger equation for it. This equation, relative to a hydrogen molecule, can be solved only via approximate methods.

The Heitler – London solution, based on the supposition that in some approaches we can regard the molecular orbital as a linear combination of atomic orbitals, allowed getting a bonding energy in a hydrogen molecule equal to about 70 % of the experimental value.

The further development of the quantum-chemical approach allowed getting values for the bonding energy in a hydrogen molecule almost identical with the experimental data [2].

Only electrostatic interactions were introduced to Schroedinger's equation. That is why the coincidence in the energy results of the calculation and the experiment bear witness to the fact that there is no third force. This wonderful agreement of the calculation with the experiment was the basis for the confirmation that quantum mechanics explained how covalent bonding, remaining electrostatic, has such a

great energy. This is why it is considered that the essence of covalent chemical bonding was explained by quantum mechanics.

The approximate methods of solving Schroedinger's equation after they were successfully used in calculations with hydrogen molecules were widely used in theoretical chemistry.

Modern quantum chemistry includes qualitative ideas that are widely used to explain the observed chemical phenomena and the methods of calculating various parameters of molecules. These include the notion of reserving the number of orbitals during the formation of molecules and the anti-bonding of the orbitals, the rules of symmetry, the presence of an activation barrier in the chemical reaction, etc.

In the new qualitative reasoning we can, most likely, include efforts to compile models that explain the physical nature of bonding [4].

The experiment for defining bonding energy has shown that about 400 kJ/mol is spent on breaking a hydrogen molecule. Out of the principle for the transformation of chemical reactions we have learned that the formation of a molecule should be the result of a reverse reaction with an identical heat effect.

Under ordinary conditions, the nuclei of hydrogen molecules have energy commensurable with ckT (2.5 kJ/mol). The energy of the electrons in the atoms is equal to about 3,000 kJ/mol. Out of these simple data it was concluded that the energy of the electrons decreases during bond formation.

According to the virial theorem:

$$E = u / 2 = -T$$

where E is the complete energy of the system; u is the potential energy; T is the kinetic energy.

When used in systems where Coulomb forces are the attraction forces, this theorem confirms that the total energy of the stationary system is equal to half of its potential energy, it has an opposite sign, and its value is equal to the kinetic energy. Since there was no need to introduce 'a third force', it was supposed that such a correlation between the total, potential, and kinetic energies is guaranteed in all the stationary systems studied in chemistry — atoms, molecules [4].

Out of this theorem, it is obvious that during bond formation, only decreasing the potential energy of the electrons, during the increase of their kinetic energy, can cause the general change in energy. The general decrease of energy is defined by the fact that the increase of

kinetic energy is 2 times smaller considering absolute value, than the decrease of the potential energy.

The change of the potential energy was considered to be the result of the attraction of the electrons of one atom to the nucleus of another that occurs when the atoms approach each other.

The calculation of bonding energy made via the given simple model, offered only about 10 % of the bonding energy; while in the quantum-chemical calculations it was clear that the main contribution to bonding energy is introduced by a special kind of electrostatic energy — exchange energy, of which there is nothing of the kind in the ‘classical’ world, and therefore it is difficult to imagine.

Fok supposed that the exchange energy could not be filled with real physical contents (non-force contribution); others explained that there must be an additional increase in the concentration of electrons in the inter-nuclear field [4]. This additional increase in the electronic density cannot be calculated because of simple electrostatic reasons, and is explained by the presence of wave properties in the electron — interference of the bonding electrons.

The first explanation was a sort of refusal to explain. The second — contradicted the calculations, since the coincidence of the calculations performed by considering only the electrostatic interactions, with the results of the experiment, excluded the possibility of any significant influence of additional effects. There were also various explanations about the high energy of covalent bonding, based on the principle of indefinability. When forming a common orbital, the indefinability increases along the coordinate ΔX , and correspondingly decreases along the impulse ΔP . And the additional contribution to bonding energy is the decrease of kinetic energy during the formation of the molecule [5]. This explanation contradicted the virial theorem.

According to another hypothesis, the additional contribution is connected with the decrease of the area where the electrons are situated, because of the increase of the charge in the field between the nuclei, the corresponding increase of the kinetic energy, and the two-fold greater decrease of the potential energy.

However, there were no calculations performed on the basis of this hypothesis. And since a calculations without any accounting of the phenomena offered good coincidences with experimental results, the main explanation was as follows: *the non-force contribution is electrostatic, but its physical nature has no visual physical interpretation.*

It is of interest to analyze exactly how important it was to introduce a new essence (exchange energy) when explaining the nature of covalent bonding.

The first experiments on defining the bonding energy in a hydrogen molecule were based on studies of equilibrium: $\text{H:H} \rightleftharpoons \text{H+H}$ [6, 7]. Having measured the concentration of hydrogen radicals at several temperatures, we can define the equilibrium constant and, therefore, the change of the free energy of the dissociation reaction: ΔG°_T .

From ΔG°_T , knowing the dependence of the gas's heat capacity, on the temperature, we can go over to the enthalpy of hydrogen formation ΔH°_f at OK, which, in turn, can be compared with the calculated value of the bonding energy.

Comparing the results of the calculation with those of the experiment, a supposition was made to the effect that during the thermal dissociation of a covalent molecule, the energy that goes to heating, is absorbed by the atoms' nuclei (when the translational, rotational, and vibrational freedom stages of the dissociating molecules are defrosted) and is not absorbed by the electrons. Relatively, during the extrapolation of the results to absolute zero, the change of electronic energy during thermal dissociation was not considered. There were reasons for this.

From experimental data, it is obvious that atoms, of which molecules are received, have linear, simply interpreted spectra showing that the first level to which the electron can transit from the main state (first excitation state) in a hydrogen atom, corresponds to an energy over 10 eV. This value is much greater than the bonding energy of H_2 that comprises 4.7 eV. Besides, the quantum-chemical calculation of a hydrogen molecule, in the main state, is witness to the fact that the minimal amount of energy necessary to excite the electrons is much greater than the bonding energy.

The Illogicality of the above mentioned approach, from our viewpoint, is in the following: Unlike in the ionic molecule, the electrons that form a bond in the covalent molecule belong to both nuclei at the same time. That is why the de-freezing of the vibrational freedom stages and the change of distance between the nuclei — can greatly influence the condition of the electrons.

Unlike atomic spectra, the spectra of covalent molecules are not linear, but striped, composed of numerous lines that form into stripes. According to Hertzberg:

“The striped spectra observed in the visible and ultraviolet areas of the spectra, obviously, should not be interpreted as simple rotational or rotational-vibrational spectra, because they usually have a more

complicated structure than what could be expected according to the theory of these spectra. Besides, the frequency in the visible and ultraviolet areas is too great for rotational and vibrational frequencies. Most likely the origin of these spectra is explained by the fact that there are electronic transitions in the molecules. Such an interpretation corresponds to the interpretation of the visible and ultraviolet linear spectra, the origin of which is explained by the electronic transitions in the atoms.” [8].

Energy absorption by the bonding electrons during thermal excitation of the molecule, leads to a change of its heat capacity, and relatively, a change of its entropy. Therefore, to guarantee a correct extrapolation of the experimental results to the OK, it is necessary to define the change in the entropy of the bonding electrons during the heating of the molecules and their dissociation into radicals.

The entropy of a hydrogen mol:

$$S = S_{\text{vib}} + S_{\text{rot}} + S_{\text{tran}} + S_{\text{elec}}$$

where S_{vib} , S_{rot} , S_{tran} , and S_{elec} are, relatively, the entropy contributions of vibrational, rotational, translational, and electronic freedom stages to the general entropy of the molecule.

Each position of the nuclei $S_{\text{rot}} + S_{\text{vibr}}$ in a covalent molecule corresponds to its own position of bonding electrons S_{elec} , which finds its reflection in the experiment: the presence of so-called vibrational-rotational spectra with a stripe structure that correspond to the striped infrared spectra, connected with the energetic conditions of the nuclei. During thermal excitation of a covalent molecule, part of the energy goes to raising the entropy of the electrons and is absorbed by the electronic freedom stages.

The significance of the entropy of the electrons increases before the pre-dissociation condition and abruptly decreases during the dissociation of the covalent molecule. The increase of the electrons' entropy, which is defined by the number of energetic equations on the energy interval, is defined by comparing the atomic and molecular spectra. The atomic spectra are linear; the number of lines for the hydrogen atom is equal to about 100. Molecular spectra are striped. The number of lines already singled out for a hydrogen molecule is more than 40,000. The contribution of the entropic member into the free energy of covalent bonding is significant because of the high kinetic temperature of the electrons.

According to the offered approach, the energy of covalent chemical bonding at low temperatures is defined by the Coulomb component for nuclei attraction to the electrons, situated between them; while at high temperatures it is defined by the entropic and energetic component of the electrons. Thus, it is more proper to speak not about bonding energy, but about its free energy; and to be even more precise — about the free energy of thermal dissociation in covalent molecules.

That is, the energy of covalent chemical bonding only to a certain extent is defined by the electrostatic attraction of the nuclei that connect the electrons between them; this energy amounts to 50 kJ/mol. The main contribution to covalent bonding energy, according to the offered approach, is the change in the electronic entropy and energy during the dissociation of the covalent molecule.

One of the peculiarities of covalent chemical bonding, as already mentioned is the fact that the bonding electrons are situated in the field of both nuclei, and their energies depend on the movement of one nucleus relative to the other. In the ionic molecule where valence electrons practically all belong to a more electronegative ion, the entropic contribution to the energy, necessary to break the bond, is practically about zero. Indeed, ionic bonding is well enough described from the electrostatic viewpoint.

When going from non-polar covalent bonding to polar and ionic bonding, the entropy contribution becomes smaller relative to the change of the free energy during dissociation, which introduces absorption of energy of the bonding electrons and the change of their entropy; the Coulomb energy begins playing a greater role.

When connecting a radical to a covalent molecule (for example, a deuterium radical to a hydrogen molecule $D \cdot + H : H \rightarrow D * H : H$) the electron on the 1s-orbital goes to the 2s-orbital of molecule $H : H$, since the 1s-orbital is completely occupied. A single-electronic bond appears (*) in which the electron is much stronger bonded to the deuterium atom than to one of the H atoms of the hydrogen molecule.

The Coulomb component of this bond is very small (which is clear from elementary electrostatics). The entropic component is also small since the position and energy of the electron practically do not depend on the mutual position of atoms D and H. Since this bond is a weak one, it is practically impossible, as yet, to single out the compound $D \cdot + H : H$. This, in the framework of our approach, explains the absorption of covalent bonding.

As seen from the above material, the main difference between the new theory and the formerly accepted one is in the fact that the new

theory suggests that in the course of thermal excitation of covalent-bonded molecules, the entropy and energy of the bonding electrons changes. The correctness of this main initial condition of the new theory is confirmed by the data of the spectral analysis: The difference between molecular spectra and atomic spectra, just like the atomic spectra of hydrogen shows the minimal portion of energy that an electron in atom (>10 eV) can absorb; the molecular spectra of a hydrogen molecule shows that the minimal portion of energy that a hydrogen molecule is capable of absorbing, is much smaller than the bonding energy (4.7 eV).

However, the confirmation about energy absorption by bonding electrons in the molecule, contradicts one of the main theoretical conclusions of quantum mechanics, which has a much wider theoretical and experimental basis.

Indeed, according to quantum mechanics, the minimal portion of energy ΔE that an electron can absorb, is defined by the equation:

$$\Delta E = h\nu$$

where h — Planck constant; ν — frequency of the electron's vibration.

This equation tells us that the electron can absorb only an energy of >10 eV. Naturally, this contradiction calls for an explanation.

According to the Rutherford model, there is an electron on the atomic orbit inside the hydrogen-like atom. In accordance with the Coulomb law, this electron is attracted by the nucleus with a force equal to Ze/r^2 , [where e is the electron's charge; Z is the nuclear charge; r is the orbit's radius (distance between the electron and the nucleus)].

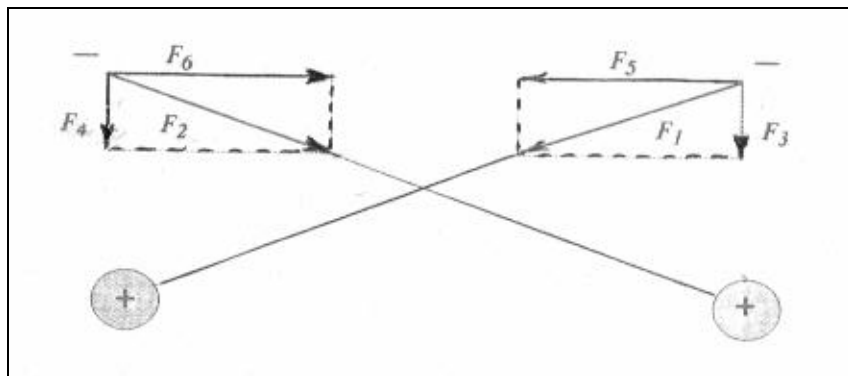
The Coulomb attraction is counteracted by the kinetic centrifugal force, equal to mv^2/r (where m is the mass of the electron; v is the speed of the electrons on the orbit). From the equation of the given forces $Ze/r^2 = mv^2/r$ we get the above-mentioned virial theorem: $Ze/r = mv^2$. Here Ze/r is the potential energy, and mv^2 is the doubled kinetic energy.

Now let's see how the system's potential energy changes with the increase of the nuclear charge Z . In this case the electron approaches the nucleus because of the decrease of r and the increase of v until a new equilibrium of the Coulomb and central forces is restored. That is, when the charge increases, the potential energy will change more abruptly than the nuclear charge.

In accordance with the experimental data, the energy of atom E_a (difference between the potential and kinetic energies) when changing the nuclear charge, it increases proportionally to the square of the charge. Thus, the ionization potential (atom's energy) H is equal to 13.6 eV, while that of He^+ is equal to 54.4 eV. We get the same kind of dependence by solving the Schroedinger equation relative to hydrogen-like atoms that have one electron on the orbital.

Now let's see how the potential energy of a system composed of two hydrogen atoms will change when the latter approach each other. According to the Coulomb law, when atoms approach each other, the potential energy of the system will increase at the expense of the increasing repulsion between the nuclei and it will decrease at the expense of the increase of the attraction of the electrons to the bonding nuclei — not only in the inter-nuclear area, but also in the area beyond the nuclei.

Schematically we can illustrate the forces in the system of a hydrogen molecule as follows:



where \mathbf{F}_1 and \mathbf{F}_2 are the additional attraction forces of the electrons striving to bond with the nuclei; \mathbf{F}_3 and \mathbf{F}_4 are the additional forces of the electrons striving to bond with the master-nuclei; \mathbf{F}_5 and \mathbf{F}_6 are the forces that pull the nuclei together.

Forces F_3 , F_4 , and F_5 are projections of forces F_1 and F_2 . Forces F_3 and F_4 are identical to the forces dealing with the increase of the nuclear charge. Thus, when the atoms approach each other, besides the appearance of the pulling forces F_5 and F_6 , additional forces F_3 and F_4 also appear that deal with the formal increase of the nuclear charges. These forces, as already mentioned, lead to the contraction of the orbitals — approach of the electrons to the master-nuclei, and therefore, to the non-proportionally big increase of the absolute value of potential energy not only at the expense of increasing the charge, but also at the expense of decreasing the radius.

Approximate calculations [9] have shown that a formal hydrogen atomic charge during hydrogen molecule formation increases by 1.19 times; that is, the energy contribution to decreasing the system's energy (electrons' energy) relative to the contraction of the electronic orbitals, can be a defining one during the general change of the electrons' energy that occurs during hydrogen-molecule formation out of atoms.

It is of interest to note that simple electrostatic calculations of schemes have shown that even when electrons were found in the anti-bonding area, the compression of the orbitals (electrons' approach to the master-nuclei at the expense of the approaching field of the nucleus) is well compensated by the repulsion between the nuclei (i.e., with an energy gain).

A qualitative study of the dependence of the system's energy on the distance between the atoms has shown that the given system has an optimum (minimal energy) because the endless approach of the nuclei leads to an endless increase of repulsion energy between the nuclei and to a final decrease of energy equal to the energy difference of a helium atom and that of two hydrogen atoms.

Now let's regard the thermal excitation of a hydrogen molecule.

After getting excitation energy that corresponds to de-freezing vibrational freedom stages, during further excitation with quanta that correspond to the vibrational energy of the hydrogen nuclei (8.4 – 16.8 kJ/mol), after the insertion of the quanta vibrational energy, the distance between the hydrogen atoms increases by leaps. Simultaneously the seeming charge on the hydrogen nuclei decreases by leaps and, relatively, the electron leaps away from the nucleus. The departure of the electron from the nucleus is connected with the absorption of energy, which it takes, relatively, from the vibrational energy of the nuclei, since the time for widening the electronic orbit is incommensurably smaller than the vibrational time of the nuclei. Thus, the electron absorbs energy in portions during molecule excitation. The portions are commensurable with the quanta of the nuclei's vibrational energy.

This explanation is relative to the great difference between the spectra of a hydrogen molecule and those of other gas molecules. The electronic hydrogen spectra are more easily dispersed (the lines are more vivid) than the spectra of other gases, those that are actually striped. The difference in spectra very well correlates with the difference in the quanta of vibrational energy, which is in reverse proportionality to the mass of the vibrating atoms. Therefore, in the case of heavy atoms, the quanta of vibrational energy that are passed to the electrons when the molecule breaks, are much smaller, and so the spectra disperse in the ultraviolet area with greater difficulty. This area corresponds to that known as the area of electron absorption.

Now, how does the molecule actually break?

The amount of energy taken by the electrons during one vibration depends on the distance between the nuclei and, relatively, gradually, with the increase of this distance, this amount decreases. That

is, not all the energy given to the nuclei goes to the excitation of the electrons. With the increase of the distance between the nuclei, the energy, taken away by the electrons, decreases. This weakens the influence of the nucleus of one atom on that of another, which finally leads to the burst of the molecule.

To explain the absorption of energy by the electrons during thermal excitation of the molecules up to the defrosting of their vibrational freedom stages, various models have been studied [10].

Earlier it was presupposed that the absorption of energy by the electrons was conditioned by bringing the electronic levels closer to each other, which was the result of moving the nuclei apart and the widening of the 'holes' where the electrons are situated during thermal excitation. According to quantum mechanics, in the process of widening the 'hole', a minimal portion of energy that an electron can absorb (ΔE) is decreased proportionally to the square width of the 'hole' (L^2). In the pre-dissociation condition, when the distance between the nuclei reaches the maximum, the value of the minimal quantum energy absorbed by the bonding electrons, can decrease by about 25 times.

Other models, besides those considered, where the electrons form a single cloud around the nuclei, the same qualitative dependence is gained and models were considered that presupposed the rotation of bonding electrons in a circle on a plane between the nuclei or their transition along the curves of figure 8 between the nuclei.

However, the first task of this section was to prove the possibility of absorbing energy via bonding electrons during thermal excitation of covalent molecules.

The above-considered detailed mechanism corresponds to this minimal requirement, which allows us to say that in accordance with the existing theoretical precepts, mainly — the proportionality of the atom's energy to the square of the nuclear charge — the bonding electrons absorb energy in portions commensurable with the vibrational quanta since the conclusion is based only on the virial theorem.

Further on, this conclusion has some independent experimental confirmation. Thus, the main conclusion about the absorption of energy by bonding electrons during thermal excitation of molecules up to the pre-dissociation condition, is based on the comparison of atomic and molecular hydrogen spectra, while the offered mechanism proves this precept theoretically, and additionally illustrates a comparison of the spectra of hydrogen rays, which are much easier to decipher on the line with molecule spectra that are composed of heavier atoms.

The given mechanism shows the change in the entropy of the electrons — the appearance of a large number of possible microstates in the course of thermal excitation.

The considered mechanism is based on the laws of elementary mechanics and electrostatics, which presupposes the possibility of a correct and comprehensible explanation of the essence of covalent chemical bonding in middle school courses.

Didactically, a good analogy of the covalent chemical bond is a model where two nuclei are pulled together with a spring. All the shortcomings in the ideology of the approach, criticized in this work, are connected with the supposition that during thermal breaking of the molecule into atoms, the electrostatic bonds between the particles of the spring break at that moment when the braking energy reaches values that exceed those of the electrostatic field.

The illustration of the offered new approach is not regarded as ideal, while the realistic bonding spring that contains the main energy that is passed to the nuclei bonded by it, is spent on the heating of the spring, which is connected with the increase of energy and entropy of the particles situated in the spring.

Chapter 2

CHEMICAL KINETICS

Theory of Active Collisions (TAC)

(The Accepted Conception)

The theory of chemical kinetics consists of two main parts. The first part explains how the concentration of reagents affects the speed of the chemical reaction; the second explains the temperature influence. The temperature influence originated from the scientific works of Arrhenius as an independent theoretical approach:

$$W = A \exp(-E/RT) \quad (1)$$

where **w** is the reaction speed; **R** is the universal gas constant; **A** and **E** are constants.

Before Arrhenius, it was supposed that chemical reactions resulted from molecular collisions. Since the number of collisions depends linearly on the temperature, the exponential dependence, found by Arrhenius, required further explanations and served as a starting point for the development of chemical kinetics.

Arrhenius supposed that not all colliding particles enter reaction, but only those, which possess enough energy. Such particles comprise an insignificant portion, and are in thermodynamic equilibrium with the rest of the molecules. The surplus energy (as compared to its average value for molecules) is necessary for molecules to enter a chemical reaction. This is known as *activation energy* and is qualitatively equal to **E** in the above given equation.

Studies of a number of gas phase reactions have allowed digital linking of such molecular parameters as diameters, transitional energies, and collision frequencies — the basis of TAC.

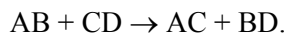
At first, only the kinetic energy of transitional motion was considered in the TAC. Therefore, the theory has brought together the achievements of the kinetic theory of gases, namely: *the Maxwell-Boltzmann Law of energy distribution in ideal gas molecules* and *the thermal dependence on the reaction rate discovered by Arrhenius*.

The Maxwell-Boltzmann Law, derived theoretically and proven experimentally, has shown that the number of molecules with energy E in the given system is proportional to $\exp(-E/RT)$. Therefore, the law of molecule distribution, relative to the energy, confirmed the Arrhenius interpretation about the discovery of the dependence of the chemical reaction rate on the temperature.

It is this wonderful coincidence and logical interpretation of one phenomenon by two independent sciences that has placed the TAC in the rank of classic expressions in scientific theory.

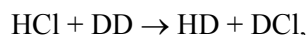
Theoretical and experimental investigations were aimed at clarifying the physical meaning of constants A and E and at searching for a model that would offer an estimation of the chemical reaction speed.

The first difficulties were encountered when determining the physical meaning of *activation energy*. It seemed that the value of this energy should be close to that of bond-breaking energy during the reaction. Indeed, this was observed in the first experiments, for example, in the reaction of hydrogen with iodine. The results served as the basis for the following scheme:



When molecules **AB** and **CD** collide, their energy **E** is sufficient for breaking the old bonds.

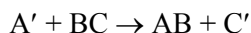
Yet, for a large number of gas-phase reactions, whose calculations only considered translational energy, gave us markedly different results as compared with the experimental data. In reaction



the speed rate, established experimentally, differed from that of the calculation by more than two orders of magnitude. In order to make the calculations agree with the experimental data, it was necessary to make use of the rotational and vibrational energies of the molecules.

Nevertheless, the calculations of almost every new reaction revealed more and more unexpected obstacles that could not be explained even in the framework of this new assumption. Thus, for example, the experimental activation energy in the reaction of a hydrogen atom with a hydrogen molecule was smaller than 40 kJ/mol. On the other hand, the bonding energy of a hydrogen molecule exceeds 400 kJ/mol. There is difference between the theory and the experiment (in reaction speed calculations) by more than 20 orders of magnitude.

Later, the progress in experimental methods provided data on the activation energy for a whole wide class of free radical reactions involving molecules, i.e., for reactions such as



whose activation energy is 5 % - 6 % of the bond-breaking energy.

Theory of Activated Complexes (TAC)

Most likely, the above-mentioned materials actually served as a *social order* that sponsored the appearance of the theory almost simultaneously by Eyring, and, independently, Polanyi and Evans in 1935. The new theory was based upon an idea that was both logical and a 'safety belt' for Arrhenius's hypothesis. It was supposed that the chemical reaction was characterized by the fact that "...*the initial concentration of atoms during the endless change of coordinates during the reaction transits to the final configuration, and simultaneously, there is always some kind of intermediate configuration that happens to be a critical one for the given process*" [12].

If the system reaches this configuration, the reaction will have a great chance to reach the end of the process. Besides, in some reactions (in those, first of all, where the observed activation energy is much smaller than the energies of the bonds being broken) the formation of new bonds can completely or partially coincide with the time of the breaking of the old ones.

Eyring regarded the intermediate configuration, which is critical for the given process — *the activated complex*, while Polanyi and Evans regarded it — *the transitional state*. Thus, the physical essence put into the term *activation energy* had changed.

The authors of the theory suggested that the molecules needed activation energy (i.e., free energy) not for breaking the old bonds, but for gaining an unstable configuration of the activated complex.

"The activated complex is regarded as an ordinary molecule with common thermodynamic properties, excluding one-way transition, namely, lengthwise along the coordinates of the reaction that leads to the breaking at a certain speed... With the help of static methods, we can find the concentration of activated complexes and their transition speed via the critical configuration of the transition state" [12].

It is impossible to observe the activated complex experimentally because of its brief lifespan; therefore, the only proof of the adequacy of the theory is the coincidence of the calculated and experimental results.

In their classical work [12] the authors of the absolute speed-rate theory offer a detailed calculation of reaction: $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$.

The experimentally received kinetic equation relative to this reaction: $w = k [\text{H}_2][\text{I}_2]$ allowed to suppose that the reaction proceeds along the molecular mechanism. Besides, the data on the activation energy value of reaction E_a and the activation energies of reactions with the participation of hydrogen radicals and iodine (which will be detailed later) spoke to the effect that the radical mechanism does not pass via energetic consideration: the total activation energy of the consecutive stages of radical formation and their interaction with saturated molecules significantly exceeded the observed energy E_a .

It is of interest that this system of proofs of molecular interaction with iodine has existed up to our times.

The presupposed calculated value of the molecular mechanism of absolute speed rates, for various temperatures, practically did not differ from those of the experiments: At 700K — 1.808 (1.808); at 575K — 0.88 (-0.85); at 781K — 3.13 (3.09).

[PS: Inside the brackets are the experimental results.]

Later it was proven experimentally that this reaction proceeds along the radical mechanism with the participation of iodine atoms [14].

The classical textbook of Melvin-Hughes [11] offers a table of calculated (via the activated complex theory) and experimentally proven values of activation energy (in kJ/mol) for some of the reactions:



Reactions with the participation of free atoms are excluded. It is now known that these reactions proceed along the radical mechanism [14, 15].

The given examples bear witness to the fact that a good agreement of the calculation with the experiment, received in the framework of modern conceptions of chemical kinetics, cannot serve as proof of their heuristic values, but rather of their matching possibilities.

Since a new essence is introduced for a better description of the chemical reaction mechanism known as the activated complex, which cannot be defined experimentally, and the calculations of which cannot be accepted as confirmed proof of its existence, most likely we should try explaining the observed chemical regularities without the introduction of some kind of additional suppositions.

In general, an unusual situation has arisen in chemistry. When citing the chemical properties of substances and their reaction possibilities, all the experimental material speaks to the effect that the possibility of preceding the reaction, and correspondingly, its speed, is defined by the chemical nature of the reacting compounds. And first of all, their reaction possibilities relative to each other, and then, when structuring the theory of chemical kinetics, it is supposed that the reaction speed is defined by the kinetic energy of the reacting molecules.

It is also important to indicate that the theory of absolute speeds in chemical reactions (TAC) has given qualitative explanations relative not only to the temperature, but also to the catalyst, the solvent, and the chemical nature of substances reacting on the chemical reaction speed.

Such explanations actually amount to the following: The catalyst decreases the activation barrier; the solvent influences the configuration and energy of the transition state, etc. Exactly how it influences, can be shown only via an approximate calculation (which, nowadays, can show anything), that is, these phenomena do not become physically understandable, while their qualitative analysis is practically impossible.

Since the majority of chemist-practitioners did not have quantum chemical and static physics apparatuses to conduct complex calculations of a computer, there occurred a breakup of chemistry into experimental chemistry (non-scientific) and theoretical chemistry. And the chemists-practitioners, as a rule, are positive that quantum chemistry has already explained everything, or almost all the chemical phenomena, and therefore there is no sense in thinking about their physical essence.

In their turn, theoreticians think that experimentalists make wide use of the achievements in their work.

The criticism of suppositions lying at the basis of the calculations relative to the theory of absolute speeds is given in work [16] and there is no need to mention them again.

In general, we can say that if Arrhenius and his followers knew about the existence of ions and radicals, they would never have explained the influence of the temperature by the increase of the number of molecules that simply had a higher kinetic energy, and therefore the development of the theory of chemical reactions, most likely, would have gone another way.

THEORY OF ELEMENTARY INTERACTIONS (TEI)

(The Offered Approach)

This new approach is an attempt at producing a common conception for chemical kinetics and chemical catalysis without the introduction of new essences such as the *activated complex*, the existence of which cannot be proven experimentally.

In the TEI the elementary interactions are the association and dissociation reactions.

The association reactions

The association reactions (AR) include such reactions where only the formation of new bonds takes place. The specter of associative reactions is extremely wide — from the transition of substances from the gaseous state to the liquid state, the solvation of ions and radicals in solvents, the formation of Van der Waals complexes, etc. up to the recombination of ions and radicals.

The interacting particles, approaching each other as a result of the chaotic heat movement within the distance of the attraction forces, enter the AR. Relatively, the stronger the attraction between the particles, the greater the reaction speed, and the smaller is the distance between them as well as the kinetic energy.

Energy serves as a measure of potential energy attraction (in the first approach) that is discharged during the associate formation, that is, the bonding energy that is formed as a result of the association. These energies have been measured for most of the cases, and they vary from 0.4 – 0.8 kJ/mol (interactions of two non-polar molecules) to 2 – 8 kJ/mol (polar molecules), 8 – 40 (hydrogen bonds), 400 kJ/mol (radical – radical), to 600 – 1,000 kJ/mol (cation – anion).

The temperature, on the one hand, accelerates the AP at the expense of increasing the number of approaches between the molecules in a unit of time, on the other hand, when the temperature increases, so does the number of particles whose kinetic energy of the heat transition exceeds the potential energy of the bond being formed. This is why they do not form an associate during their mutual approach to each other.

In the first approach the speed constant of AR is defined by the following equation:

$$K = AP[1 - \exp(-E/RT)],$$

where **A** is the number of the molecules' approaches at a unit of time, defined in accordance with the molecular-kinetic gas theory, proportional to the root of the temperature value; **P** is the steric factor; **E** is the energy of the bond being formed.

The temperature hardly influences the reaction speed of the association because the multiplier for polar molecules (in brackets) is already close to one unit even at a temperature of about 2,000 K.

The supposition to the effect that there was a non-barrier procedure of AR, to be more precise, a non-supposition of the presence of a barrier, is an empirical fact. Many experiments conducted on the studies of the influence of temperature on the AR speed speak in favor of this fact. As a matter of fact, there is no need to substantiate the absence of the activation barrier. Its existence in the AR is not confirmed by any direct experiment (at least the authors could not find any experimental data to this effect in chemical literature). The supposition of the presence of a barrier in classical kinetic theories is additional, something that helps to explain the influence of temperature on the reaction speed.

It is well known that together with the zero activation energy there is a reaction for the recombination of radicals, ions, and coordinate-non-saturated compounds (conences). Moreover, well known are the association-dissociation reactions with zero activation energy. That is, the energetic needs for the dissociation in these reactions is compensated by the energy discharged during association; thus, it is obvious that there is no use mentioning the energy needed for the association.

Examples that prove the absence of the barrier in the AR are the association-dissociation reactions with small activation energies. Since energy expenditures on the dissociation are absolutely necessary, nothing practically remains for the association. Other such reactions are those of radicals with unlimited carbon-hydrogen. The dissociation stage here is the breaking of the double carbon-carbon bond (see table) [17].

REACTION	TEMPERATURE, K	Ea, kJ/mol
$C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$	423.0	0
$CH_2Cl + CH_2Cl \rightarrow C_2H_4Cl_2$	—	0
$C_2H_4Cl + 1/2Cl_2 \rightarrow C_2H_4Cl_2$	—	0
$C_2Cl_5 + O \rightarrow C_2Cl_5O_2$	353 – 357	0
$C_2H_3 + H \rightarrow C_2H_2 + H_2$	313	0
$H + H + H_2 \rightarrow H_2 + H_2$	290 – 7,000	0
$H + F + M \rightarrow HF + M$	—	0
$H Cl + M \rightarrow HCl + M$	—	0
$H + OH + Ar \rightarrow H_2O + Ar$	—	0
$H + NO_2 + H_2 \rightarrow HNO_2 + H_2$	213 – 704	0
$H + C_2H_4 \rightarrow C_2H_5$	330 – 520	1.82
$H + C_2H_5 \rightarrow C_2H_6$	970 – 1,300	0
$H + \text{tetra-methylene} \rightarrow C_6H_{13}$	323 – 475	1.02

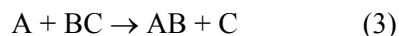
The dissociation reaction

The dissociation reaction (chemical bond breaking), for example, $\text{H}_2 \rightleftharpoons 2\text{H}$ exponentially depends on the temperature [the speed constant is proportional to $\exp(-E/RT)$, where E is the energy of the breaking bond] since it dissociates only the molecules that have energy greater or equal to bond-breaking energy. The activation energy observed in such a reaction, when studying the dependence of speed on the temperature, is equal to the bond breaking energy up to the change in the entropy.

The association-dissociation reaction

We know that the formation and breaking of the bond occurs very often in the chemical process (the association-dissociation reaction).

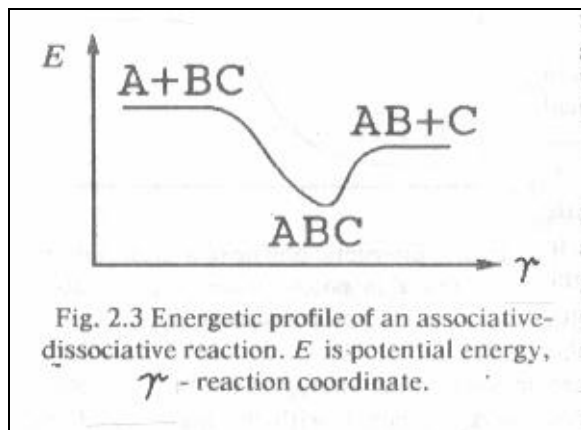
The association-dissociation reaction in the framework of the TEI is a difficult process, and it runs mainly in two stages. First comes the association and then comes the dissociation. For example, reaction



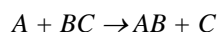
is described via the following scheme:



The energy profile of the association-dissociation reaction is illustrated in the following drawing. The intermediate compound ABC is formed as a result of the association reaction without the barrier, with a discharge of energy, one part of which can leave the associate, while another part transits to the atoms' vibrational energies. The speed of such a reaction, in a straight line, is defined by the frequency of the breaking of the associate with the formation of the final products.



The potential energy curve of the exothermic association-dissociation reaction:



The life span of the associate can be evaluated by the formula for the calculation of the speed of a monomolecular reaction [12]:

$$k = \nu \exp(-E/RT)$$

since the value $\nu \exp(-E/RT)$ 'can be regarded as a measurement of speed with which the vibrational energy accumulates in sufficient quantities to break the bond and then decompose the molecules' [12].

If dissociation is the limiting stage of the reaction, then the observed activation energy R_a has a value close to that of the bond-breaking energy in the associate. If association happens to be the limiting stage, then the reaction speed will hardly depend on the temperature, and the observed activation energy will be equal to zero.

The activation energy in TEI, necessary for breaking the bond in the associate that precedes the formation of the final products, gets a noticeable physical essence. In our example, the reaction's activation energy (3) is equal to bonding energy B—C in associate ABC.

Here two questions might arise:

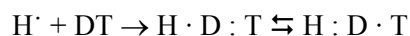
1) Why is it that if the intermediate compound has a smaller energy than that of the initial molecules and the reaction's products, all this does not 'roll down' and we get only (or almost only) associates in the mixture?

2) Why is it that the observed activation energy, in many cases, is smaller than the energy of the bond being broken? That is, why is it

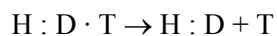
that the bond between atoms B and C in associate ABC is weaker than in molecule BC?

The answer to the first question is quite obvious [18]: The concentration of the intermediate compound is defined by the temperature and by the bonding energies in it. Since the associate is formed with an energy discharge, the increase of temperature leads to the decrease of its concentration in the mixture. At low temperatures, indeed, we observe the transition of substances into a condensed phase. If strong bonds are formed in the association reaction (in the case of a radical recombination in the liquid phase), then, under normal conditions, molecules will prevail in the mixture, which is not at all surprising.

In order to answer the second question, let's examine the reaction of a hydrogen radical with a DT molecule in detail. The deuterium and tritium are taken simply for convenience to differentiate the atoms:



When attaching a radical to a covalent molecule, the valence electrons get an energy condition equal or a close to an equal condition into which one of the bonding electrons can transit. The intermediate compound $\text{H}\cdot\text{D} : \text{T}$ is in equilibrium with bonding energy $\text{H} : \text{D} \cdot \text{T}$ which is equal to the latter. Here we have the so-called *electronic isomerization*, which can be singled out into a separate association-dissociation reaction stage. The comes the dissociation stage:



The activation energy of stage (8) is equal to the breaking energy of the single-electron bond $\text{D} \cdot \text{T}$, which can be evaluated via the heat of the hydrogen radical solvation and comprises about 40 kJ/mol, which corresponds to the experimental results.

The electronic isomerization stage at temperatures in which radical reactions are usually studied (up to 1,000 K) does not limit the reaction speed. Such temperatures practically do not influence the electron transition speed.

The electron transition speeds between various atoms have been studied in detail in works [19 and 20]. Work [19] gives the dependence of the effective exchange constants k_{exch} from the distance between the exchanging centers described by the following equation:

$$k_{\text{exch}} = 10^{17} \exp(-2R/L)$$

where \mathbf{R} can be regarded (in the first approach) as the distance between the exchanging centers (in Å): $L = 0.7$ or 6.5 .

As for non-conducting systems (saturated bonds inside molecules) the exchange fades by about 10 times per 1 Å ($L = 0.7$) for conducting systems (the centers are separated by linked bonds) the fading effect is about 9 times smaller.

Now let's evaluate the order of magnitude for the exchange constant, a value analogous to the physical essence of the speed constant reaction of the first order of magnitude for connecting $H : D \cdot T$. Accepting $R = 3\text{Å}$, $L = 6.5\text{Å}$, we get $k_{\text{exch}} \approx 10^{16} \text{sec.}^{-1}$, which is about 2 orders of magnitude greater than the speed constant reaction of the first order (usually 10^{14}sec.^{-1}) that characterizes the nuclei's vibrational frequencies at temperatures up to 1,000 K – 2,000 K. Therefore, the electrons' transition speed, according to evaluations, is greater by one order of magnitude than the transition speed of the nuclei (of course, up to a certain, very high, temperature).

Thus, the activity of the radicals is explained by the fact that during the formation of the intermediate compound with a covalent molecule, there appears the possibility of forming isomers that have either equal or close to equal energies.

Though we call them *electronic isomers*, we should understand that they differ relative to inter-nuclear distances. Besides, it is important that as a result of the interactions of a radical with a molecule, a new free radical is usually formed.

In systems of dual bonds and small inter-nuclear distances that can be regarded as conductors, the transition speed of the electrons is so great ($k_{\text{exch}} = 10^{17}$) that the isomers will uninterruptedly transit from one form to another, and the nuclei will occupy an intermediate position. The same occurs in aromatic compounds. From the viewpoint of the offered approach to explaining the nature of the covalent bond, a large number of microstates appear in the benzene nucleus, where bond electrons can be situated. Because of this, the electronic entropy increases additionally during the formation of conjugated benzene systems. This can serve as an explanation of resonance energy.

The main point relative to chemical kinetics, to which this chapter is devoted, is the explanation about how chemical systems — molecules, situated in deep energetic 'holes' 400 kJ/mol — undergo changes connected with the breaking of the old bonds and the formation of new ones at temperatures that correspond to energies of 10-20 kJ/mol.

One of the steps in the realization of this phenomenon was the proof of the fact that by considering the role of the electrons' entropy, the energy 'hole', where the system is located, is defined by values two times smaller (200 kJ/mol), but even these exceed the thermal energies of the molecules by one order of magnitude.

The next step was the realization of the fact that the energy of the system is almost completely defined by the energy of the bonding electrons, i.e., by the depth of that energy 'hole' where the electrons are situated. Concerning the question — at the expense of what forces the electrons transit from one energy 'hole' to another during electronic isomerization — at present the only accepted answer in the physics of such phenomena, is the tunnel transition conditioned by the wave properties of the electrons. The speed of the tunnel transitions of electrons to molecules, according to the experimental and energetic calculations, is proportional to $d\sqrt{E}$, where E is the additional energy, which the electron should get, and d is the thickness of the wall between the 'holes', where the tunnel transition takes place.

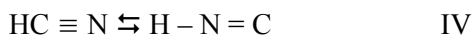
The presence of electronic isomerization has a wide chemical and experimental confirmation. Some of the examples of analogous transformation are given in work [21]. It has been shown that experimentally the following equilibrium transformations were observed:

Electronic isomerization of homotropimedene: I

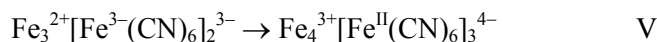
Electronic isomerization of bulvalen: II

In compounds of the acetate-acetyl-acetone type: III

In prussic acid:



For Turumbul blue isomerization into Prussian blue – see [22].

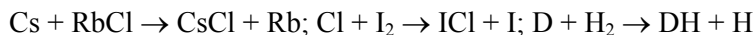


On all the researched cases, the speed of electronic (to be precise, *electron-nuclear*) isomerization proceeds at great speeds, the measurements of which became possible only with the development of complicated physical methods; for example, the nuclear-magnetic resonance and various kinds of Messbauer spectroscopy.

Thus, the speeds of the above-given processes are defined by the following values:

- 1) the life span of each isomer is less than 0.1 seconds;
- 2) each isomer lives less than 0.001 part of a second;
- 3) a thousand-fold mutual transformation takes place in 1 sec.;
- 4) reaction speed constant is measured by values 10^{17} & sec.^{-1} .

The experimental data on isomerization not only confirms the possibility of the transition of $\text{D} \cdot \text{H} : \text{H} \rightarrow \text{D} : \text{H} \cdot \text{H}$, but also supposes that the isomerization speed cannot limit the process. For some of the reactions, according to [23], on the basis of the studies of corner distribution of reaction products in the molecular pencil of rays, it was supposed that the reactions were preceded by the formation of the intermediate complex whose life span was greater than the period of its revolution ($\geq 10^{-12}$ sec.) and much greater is the length of time for the collisions of the reagents. Among these reactions are the following:



The intermediate complexes in these reactions can be regarded as Van der Waals molecules, since they can hardly have any other specific interaction besides that of Van der Waals (for example, $\text{D} \cdot \text{H}_2$ in reaction $\text{D} + \text{H}_2 \rightarrow \text{DH} + \text{H}$), and, besides, there is an opinion that “at first sight the Van der Waals complexes cannot play a significant role in chemical reactions, since the bonding energy in them is small and often smaller than kT , that is why the collision with strange molecules induces breakups of the Van der Waals molecules” [23].

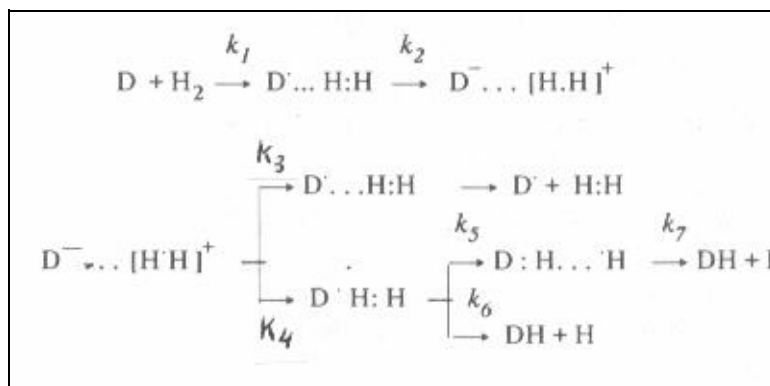
The contradictions in the interpretation of the experimental results are done away with when considering electronic isomerization, at the expense of which the Van der Waals complex can significantly strengthen. This can be expected when a great amount of electronic isomers form in the system, i.e., when the energy of the isomers hardly differ from each other. Theoretically, this can be observed when Van der Waals bonds are formed between molecules and chemically activated

particles (radicals, ions, conences); there is hardly a possibility of forming stable Van der Waals compounds between saturated molecules.

Nowadays compounds Cl_3 and ICH_3Cl have been found. As already mentioned, the time for electronic isomerization (transition of the electron) at the distance of the Van der Waals bonds, comprises 10^{-15} to 10^{-16} sec., that is, much less than the time supposed for the life span of the most unstable Van der Waals compounds.

Such consideration allows detailing the stage for the formation and the breakup of the intermediate complex. This stage can be illustrated by the following scheme:

In this scheme we can qualitatively evaluate the constants having accepted the precept that the breakup constant of a pure Van der Waals complex has a value close to that of the vibration speed. Relatively, the constants have the following values: k_1 , k_5 , and k_7 .



Stages relative to the attraction of negative and positive ions (k_4) have much greater speeds, while k_6 has a much smaller one, since k_6 presupposes the breakup of a compound where the nuclei occupy an intermediate position between two extreme Van der Waals complexes. The transition of the electrons in stages k_2 and k_3 are by more than one order of magnitude higher than the speeds relative to the nuclei vibration.

A good scheme of electronic structure includes: 1) the presence of a tri-electronic orbital where the increase of the size of the orbital is compensated by the inter-electronic repulsion and 2) a scheme that presupposes the placement of two electrons on the first, common orbital, and the third — on the next molecular orbital.

The capacities of modern physical experimentation allow defining the role (relative concentration) of compounds $\text{D} \cdots \text{H} \cdots \text{H}$ by

the difference in the proton signals. For example, in compound $\text{H}_3\text{C} \cdots \text{H} \cdot \text{CH}_3$, formed when connecting methyl to methane.

The great stability of the Van der Waals complex can be explained not only by the existence of compound $\text{D} \cdots \text{H} \cdots \text{H}$, but also by its stability at the expense of the rapid formation of $\text{D}^- \cdots [\text{H} \cdot \text{H}]^+$ and the relaxation of the translational energy and the energy discharged during its formation along the bonds in the molecule. These suppositions have been confirmed experimentally.

The first supposition is confirmed by the fact that k_2 and $k_4 \geq k_3$ and k_7 . The fact that reaction k_2 *can* proceed, is additionally confirmed by the formation of the widely known ionic compounds where the transition of electrons is accomplished with an expenditure of energy.

The comparatively high stability of the Van der Waals complex, conditioned by the relaxation time of the vibrational energy on the dissociation level (second supposition) is confirmed by examples and their interpretation.[23]. It is indicated that, for example, in the I_2He cluster, the time for the vibrational relaxation on the dissociation level is 100 p. sec. while in cluster $\text{H}_2 \cdot \text{Ar}$ it is equal to 100 n. sec., that is, by three orders more. This is explained by the weak interaction of two types of vibration in $\text{H}_2 \cdot \text{Ar}$ as compared with $\text{I}_2 \cdot \text{He}$.

Both given explanations about the increased stability of the Van der Waals complexes of the $\text{D} \cdots \text{H} : \text{H}$ type do not contradict each other and can work together.

All the given reasoning and schemes are meant for reactions where the intermediate active particles are not radicals, but ions. In the case of ions, the additional contribution to increasing the stability of intermediate compounds is provided by electrostatic attraction of the ion to the polar molecule.

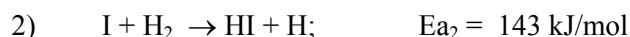
Now let's examine the use of the offered approach in respect to various types of chemical reactions.

RADICAL REACTIONS

Reactions of Hydrogen with Iodine.



When attempting to analyze reaction mechanism (10) in the framework of the activated complex theory, we encounter the following difficulties: The total observed activation energy of this reaction E_a is equal to 142 kJ/mol. When studying the reactions that could serve as elementary stages of the hydrogen-iodine interaction, we got the following results:

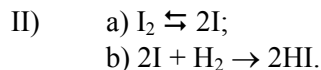
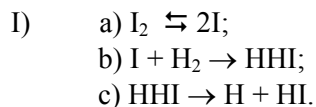


The interaction of the hydrogen molecule with an iodine radical, as supposed, proceeds via the activated complex IHH, and, according to the TAC, the observed activation energy E_{a_2} is the energy necessary for gaining the configuration of the given activated complex.

If the reaction is proceeded via the above-considered elementary stages, the total activation energy E_a will be equal $E_a \approx 0.5 E_{a_2} = 226$ kJ/mol which is much higher than that observed in the experiment of significance.

The supposition about the molecular character of the reaction was made on the basis of such logic and the analysis of the kinetic equations (see p. 28) that proved to be a mistake.

The radical mechanism for the reaction of hydrogen and iodine was discovered by Sullivan [14] in 1967. He offered two schemes:

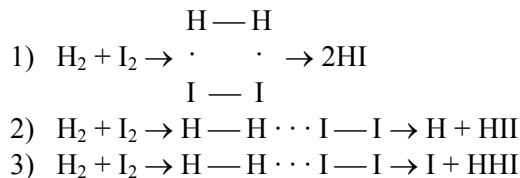


However, stage (b) in scheme I is no good as far as energy is concerned because the formation of HHI should proceed through the activated complex IHH, if we consider HHI as an intermediate compound in the framework of the activated state theory (AST).

Let's take a look at scheme II. This mechanism is hardly realistic because of the slight possibility of a simultaneous collision of three particles in stage (b). Thus, from the viewpoint of AST, it is difficult to give a positive explanation for the radical mechanism of the hydrogen-iodine reaction that was proven experimentally.

When analyzing this reaction in the framework of the offered approach, it is important to regard all the routes and choose the most appealing ones. The interaction can proceed via the following schemes:

Molecular Interactions

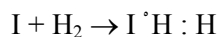


Stage (1) is hardly possible because the probability of having two reaction enters in space is extremely small. The energy for activating stage (2) is about equal to the bonding energy of a hydrogen molecule (400 kJ/mol) because molecules H_2 and I_2 are non-polar and their influence on each other in the intermediate compound (PRS) ??? is insignificant. The activation energy of stage (3) is close to the bonding energy of molecule I_2 (324 kJ/mol); this is why, from the energetic viewpoint, stage (3) is more probable than stage (2). Since the neutral covalent molecules do not influence each other in the intermediate compounds, the formation of radicals via reaction (3) requires the same amount of energy as the simple breaking of iodine into radicals.

Thus the most likely first stage of the reaction is as follows:



Let's consider the possibility of prolonging the chain:



The intermediate compound $\text{I} \cdot \text{H} : \text{H}$ can dissociate with the formation of a hydrogen radical: $\text{I} \cdot \text{H} : \text{H} \rightarrow \text{IH} + \text{H}$.

However, this variant was avoided because the energy of this reaction, as already mentioned, comprises 143 kJ/mol.

Here we see the difference between the AST and the offered approach. If, according to the AST, the activation energy is necessary to gain the configuration of the activated complex, then, according to TEI, reaction $\text{I} + \text{H}_2 \rightarrow \text{H} + \text{HI}$ proceeds via the intermediate compound HHI , the formation of which does not require any energy expenditures, while the observed activation energy in the experiment is nothing but the bond-breaking energy HH in the formed associate. As for reaction $\text{I} + \text{H}_2 \rightarrow \text{IH}_2$ this is an associative reaction and has no activation barrier.

Molecule HHI can partake in further chemical transformations. The interaction of one more I radical leads to the final products:



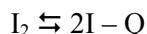
The intermediate compound (IC) dissociation does not require much energy because bond H — H is weakened at the expense of a possible polarizing influence of the radicals and the realization of different variants of electronic isomerization.

On the basis of the received dependence of the reaction speed on the temperature, we can evaluate the bonding energies in the ICs, their life spans, concentrations, and therefore we can offer methods of their discoveries with the aim of confirming the proper kind of mechanisms.

Relative to the given case, we can say that bonding energy H—H in molecule HHI comprises about 140 kJ/mol (close to the activation energy of reaction $\text{I} + \text{H}_2 \rightarrow \text{H} + \text{HI}$).

On the electronic isomerization stage in radical reactions there is a transition of only one electron into the neighboring between-nuclear area; the frequency of such a transition is great [20], that is why the radical formation stage in radical reactions usually gets to equilibrium.

Since there are hardly ever enough ‘ready’ radicals, ions or coordinate-unsaturated compounds in a realistic chemical system, the main portion of energy is usually used for their formation, i.e., on the dissociation of the covalent molecules, on the breaking of the solvate shells, on the pinching off the ligands. In this case the temperature increases the chemical reaction speed, thereby shifting the equilibrium to the side where the active particles form along the reaction:



where Q is the bonding energy in molecule I_2 .

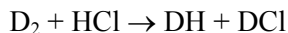
$$[\text{I}]^2 / [\text{I}_2] - [\text{I}] = k e^{-Q/RT}$$

or, if $[\text{I}] < [\text{I}_2]$, then $[\text{I}]^2 = k[\text{I}_2] \exp(-Q/RT)$. Then the reaction speed, according to the above-described mechanism, will amount to:

$$w = k[\text{I}]^2 [\text{H}_2] = k' [\text{I}_2] [\text{H}_2]$$

where k' is the speed constant.

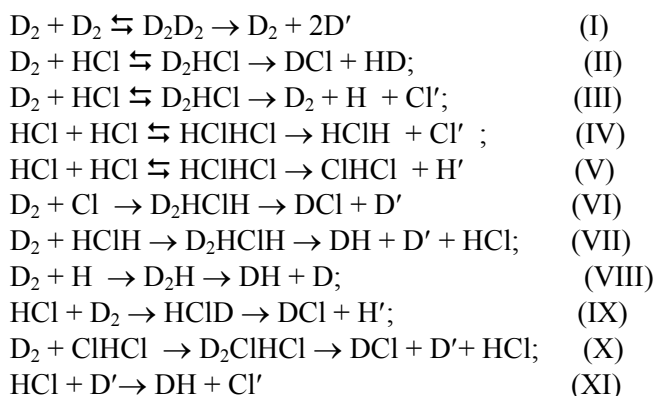
Here is another reaction:



Where we can generally expect molecular, radical, or ionic interactions. It is best to begin the analysis of a mechanism by first citing the ones that most likely will be chosen [15].

In the gas phase, where there are no catalysts, the heterolytic breaking of a covalent bond is less possible than a homolytic breaking, for this requires a great expenditure of energy. Principally, the reactions can run along either the molecular or radical mechanisms.

Let's have a look at some of the variants. The main reactions in the D_2 and HCl systems can be presented by the following scheme:



On the basis of the offered conception, let's make a first evaluation of the qualitative unit weight of each of the indicated variants. The unit weight of the route should increase when the energy increases, being discharged as a result of the association reaction, with a weakening of the bond and its breaking during dissociation; therefore we can suppose priority of (IV) and (V) over (I) to (III).

Indeed, from the viewpoint of elementary chemical reasoning, the interaction of two dipoles HCl should proceed easier and with a greater discharge of energy, than in the inter-reaction of D_2 molecules or deuterium molecules with HCl .

Even a greater priority of (IV) and (V) over (I) and (II) is observed when citing the products formed as a result of their procedure. Radicals are formed in the course of reaction (IV) and (V), which are much more reaction-capable products than valence-saturated molecules.

It is difficult to qualitatively evaluate the difference between (VI) — (XI), but it is obvious that (VII) and (X) are improbable because

of the brief lifespans of the intermediate compounds HClH and ClHCl, which break up with the formation of a hydrogen and chlorine radicals respectively. The values of the constants for reactions (I) to (XI) (in $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{c}^{-1}$) are described by the following equations [16]:

$$\begin{aligned} k_I &= 10^{17} \text{ l} / \sqrt{\text{T}} \exp (-412/\text{RT}); & k_{II} &= 10^{12} \exp (-240/\text{RT}); \\ k_{III} &= 10^{12} \text{ l} / \sqrt{\text{T}} \exp (-280/\text{RT}) \text{ for dissociation in presence of Ar);} \\ k_{IV} &\text{--- unknown; } & k_V &\text{--- unknown;} \\ k_{VI} &= 10^{14} \exp (-270/\text{RT}); & k_{VII} &\text{--- unknown;} \\ k_{VIII} &= 10^{13.5} \exp (-30/\text{RT}); \\ k_{IX} &= 10^{12} \exp (-18/\text{RT}); & k_X &\text{--- unknown;} \\ k_{XI} &= 10^{12} \exp (-18/\text{RT}). \end{aligned}$$

This data does not contradict the previous qualitative conclusions.

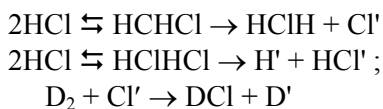
Let's compare the possibilities of chain (II) and non-chain (III, VIII, IX) routes. The data given above and in other literature on the speed of reaction $\text{HCl} + \text{Ar} \rightarrow \text{H}' + \text{Cl Ar}$ is regarded as having a lower grade among the many possible grades in the $\text{D}_2 + \text{HCl}$ reaction system for radical formation, since argon is the most inert component relative to HCl in row Ar, D_2 , and HCl. Then, at 800 K $K_{III} = 3,5 \cdot 10^9$.

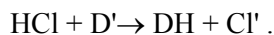
From the comparison of speeds for final product production via the chain and non-chain variants it is obvious that the time of 10^{-4} sec., during which the radical concentration in the system reaches a temperature of $10^{-15} \text{ C}^{\circ}_{\text{HCl}}$, the speed of the chain route exceeds that of the molecule by about 100 times. That is, the speed of the molecular interaction need not be considered when analyzing the reaction mechanism, all the more that in equilibrium, the concentration of chlorine and hydrogen radicals comprises 10^{-12} at 1100 K.

During the reaction, the hydrogen and chlorine radicals are in equilibrium with HCl, and the chain route is the only one working in this system. The ratio of the chain and non-chain routes is 5 : 1.

The available values of speed constants allow evaluating the relationship of various route contributions in prolong the chain.

The values of the reactions' constants in prolonging the chain at 800 K comprise: $k_{VI} = 10,012.3$; $k_{VIII} = 1,009.5$; $k_{IX} = 10,010.75$; $k_{XI} = 10,012$. From the given constant values we see that the priority belongs to routes (VI) and (XI), and therefore, the deuterium reaction with chlorine-hydrogen proceeds at 800 K mainly via the following scheme:





This reaction scheme allows evaluating the activation energy of (XI):

$$E_{a_{II}} = \Delta H / 2 + E_6$$

where $E_{a_{II}}$ is the observed activation energy of reaction (XI); ΔH is the bonding energy in molecule HCl (430 kJ/mol) [24]; E_6 is the activation energy of stage 6. Therefore $E_{a_{II}}$ is equal to about 250 kJ/mol.

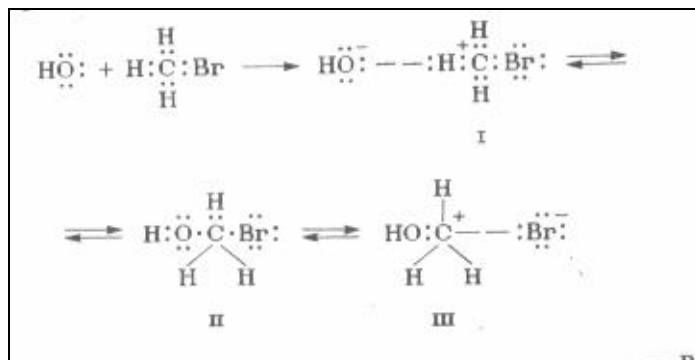
The experimental activation energy value is 239 kJ/mol. The perfection in the coincidence is more or less incidental, and can indicate the nearness of the calculation and experimental values only as a factor that confirms the adequacy of the installed reaction mechanism.

NUCLEOPHYL SUBSTITUTION REACTIONS

In the previous section it was supposed that the formation stage of the intermediate compound does not reach the equilibrium, that the process is limited by the radical formation stage. Therefore, if the system contains saturated molecules from the start, the reaction speed increases exponentially with the temp. increase. If we introduce active particles to the system (radicals, ions, conences), the influence of temperature on the reaction speed will be defined by the association-dissociation stage for the formation and breaking of the intermediate compound.

When the electronic isomerization proceeds rather slowly, the intermediated compound (IC) formation stage can reach equilibrium, simultaneously, with the increase of temperature, the equilibrium on the association stage will shift to the left where the initial substance is formed. A decrease of the reaction speed and temperatures takes place.

Now here is electronic isomerization relative to an ionic reaction offered, for example, on nucleophyl substitution of bromine in methyl-bromide on the hydroxyl group:

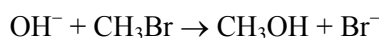


Here compounds I – III are electronic isomers. The difference between I and III is in the fact that in isomer I the bromine electron enters the electronic shell (2p) of the carbon, and one of the carbon electrons enters the bromine shell, while in isomer III the oxygen electron enters the carbon shell and one carbon electron enters the oxygen shell.

In ionic reactions, on the electronic isomerization stage, there is a transition of two electrons that have the same energy. This is why the transition frequency of one isomer form into another is much smaller than for radical reactions. A negative temperature coefficient (NTC) is observed in reactions with the participation of non-solvated ions.

The NTC phenomenon was often observed in experiments. An observation of such selected reactions is given in work [11] where they are considered as anomalies.

Let's take the nucleophilic substitution reaction based on TEI:



The hydroxyl ion in the system is solvated by water molecules; therefore the reaction can be represented as follows:

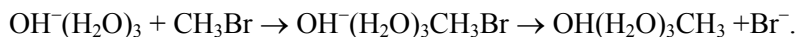


This reaction was elaborated in work [24], where it was shown that when $n = 0, 1, 2,$ or 3 , in cases where the OH^- is not completely solvated — the reaction proceeds without a barrier (with a negative activation energy). For a completely solvated OH^- ($n = 4$) the negative temperature coefficient is changed for a positive one, and in this case the authors presuppose the presence of an activation barrier, which is caused by the formation of the activated complex where the solvated shell is partly destroyed.

According to TEI, the first reaction stage is the partial desolvation of the following compound:



but further on $\text{OH}^-(\text{H}_2\text{O})_3$ takes part in the reaction (if not a less solvated hydroxyl group) which react non-barrier-like with metal-bromide.



On the basis of the offered approach, we can evaluate bonding energy OH^- in the intermediate compound $\text{OH}^-(\text{H}_2\text{O})_3\text{CH}_3\text{Br}$ by the reaction speed constants taken from the experimental data.

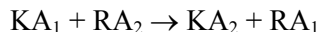
The reaction speed constants for $n = 3$ and $n = 4$ are, relatively: $k_3 = 10^{-15}$, $k_4 = 10^{-23}$ [24], while the activation energy is equal to:



(This is also the energy of the partial desolvation of fully hydrogenated OH^- that is equal to 97 kJ/mol.)

The seeming activation energy E_a of the reaction is equal to the sum of the dehydration energy E and the bonding energy E_{bond} $\text{CH}_3\text{—Br}$ in the intermediate compound, if the solvated hydroxyl group reacts completely. If $\text{OH}^-(\text{H}_2\text{O})_3$ enters the reaction, $E_a = E_{\text{bond}}$. Then $k_1 = A_1 \exp(-E_{\text{bond}}/RT)$, $k_2 = A_2 \exp(-E + E_{\text{bond}})/RT$ and if we suppose that $A_1 = A_2$ (in identical reactions) we get: $E_{\text{bond}} = 26$ kJ/mol.

In the case of ionic reactions, the solvent concentration in the solution usually does not depend much on the dissociation degree of the completely solvated ion. In this case, for the following reaction:



where K and A are the cation and the anion respectively; R is the radical; the mechanism of the reaction in water is described thus:

Since the dissolved salts are in the dissociative state, there is no need to see the scheme that considers the interaction of the non-dissociated molecules and the chain mechanism because this has no significance in diluted solutions.

The reaction speed, according to the mechanism of the given scheme, is expressed by this equation:

$$W = k_4[A_1(\beta-1)H_2O][RA_2]$$

The equilibrium constant K_e is defined by the equation:

$$K_p = k_3[A_1(\beta - 1) + H_2O] [H_2O] / k_2[A_1\beta H_2O - A_1(\beta - 1)H_2O].$$

The number of partially desolvated molecules usually comprise a small part of the solvated ones, therefore we can accept the following:

$$K_p = k_3[A_1(\beta - 1)H_2O][H_2O] / k_2[A_1\beta H_2O]$$

In this case the activation energy of the reaction of incompletely solvated ion with a molecule independent of the correlation of constants k_2 and k_3 is equal to the desolvation energy of the ion.

Thus, the main portion of the reaction's activation energy proceeding in the liquid phase is actually desolvation energy, i.e., bond breaking energy.

In work [26] are given the calculated activation energies relative to partial desolvation and observed in experiments for some nucleophil substitution in water (kJ/mol). The experimental results are given in brackets; possible error: 2 kJ/mol.

$CH_3Cl + F^-$	108.8 (113)
$CH_3Br + F^-$	108.4 (106)

$\text{CH}_3\text{I} + \text{F}^-$	107.5 (106)
$\text{CH}_3\text{I} + \text{Cl}^-$	98.7 (92)
$\text{CH}_3\text{I} + \text{Br}^-$	87.8 (81)

In the above examples we considered the partially desolvated energy of not only the attacking ion, but also that of the molecule being attacked. Thus, we can conclude that the activation energy values are about equal to the sum of the energy values of the desolvation of the ion and the dipole. The amount of ion energy desolvation is by one order of magnitude greater than the dipole energy desolvation.

Thus, the offered approach explains the observed exponential dependence of reaction speed on the temperature (Arrhenius equation) allows, in many cases, to evaluate the activation energy value on the basis of the known data relevant to bonding energy values and heat of the solvation. Correspondingly, there appears a possibility of making preliminary conclusions about the reaction mechanism on the basis of the imaginary activation energy.

CONENCE REACTIONS

Unlike the widely described ionic and radical reactions, the theory of conence reactions, to be more precise — the theory of conence chain reactions — is practically not mentioned in chemical literature. This is why we will take up these in greater detail. Undoubtedly, this is important because the elaboration of the theory of conence reaction preceded the elaboration of the new general theory of chemical bonding and chemical reactions [27].

In the framework of the theory of conence reactions we managed to realize the more general meaning of chemical activation in chemical reactions and in catalysis, as well as the role of the chain processes in the transformations of coordinate compounds and in catalysis.

On the other hand, the elaboration of the new general theory helped to better understand the physical essence of the role of the vacant orbitals in weakening the chemical bonding energy, and therefore, deepen the understanding of both conence reactions and conence catalysis.

The intermediate active particles in conence reactions are the coordinate non-saturated compounds.

A coordinate non-saturated compound is a coordinate compound where the number of electrons in the outermost layer of the metal, calculated according to the rules of valence schemes, is fewer than 18.

The name itself, *coordinate non-saturated compound*, for quite some time has been used in literature to indicate coordinate compounds with the number of ligands smaller than that in the known coordinate saturated compound. The introduction of the contraction 'conence' was not meant to introduce a new word to science, but was regarded as a convenient substitute for the combination 'chain conence reactions'. The term 'conence' also has another meaning, since with the help of this word we can single out the type of reaction that has a different character as compared with that of the intermediate particles of ions and radicals. The main mass of conences, besides the free orbitals, contains lone pair electrons, i.e., the conences are acidic and Lewis bases at the same time.

The expediency of singling out the conences into a separate class with a special name is defined not only by the specifics of the wide variety of reactions where conences take part, but also by considering the coordinate compound reactions and the catalysis of the of the complex catalysts.

CONENCE FORMATION

Conences (ψ) can be formed as a result of
dissociation reactions: $ML_n \rightarrow M^\psi L_{n-1} + L$
elimination reactions: $HNn(CN)_5 \rightarrow HCN + Mn^\psi(CN)_4$.

Conences are capable of interacting with ligands, coordinate saturated compounds, and between themselves.

The interaction of a conence with a ligand can lead to the formation of a coordinate saturated compound via the scheme:



or to the substitution of the ligand at the expense of the energy discharged when connecting the entering ligand:

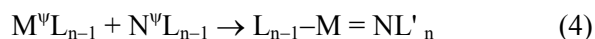


The interaction of a conence with a coordinate saturated compound can proceed with the formation of another conence via the scheme:

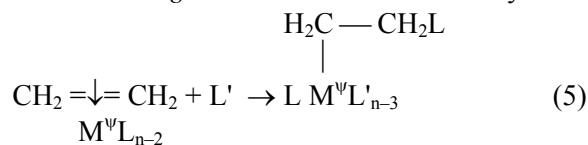


or with the formation of a cluster: $M^{\nu}L_{n-1} + NL'_n \rightarrow L_{n-1}M - NL'_n$

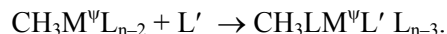
With the formation of the cluster, the interaction of two conences takes place:



The interaction *conence – ligand* leads to the introductory reaction:



or:



All the above-shown types of conence reactions are actually common coordinate compound reactions:

(1) is the second stage in the ligand substitution reaction proceeding via the dissociation mechanism;

(2) is the ligand substitution reaction that proceeds via the association mechanism; as a rule, this takes place among conences;

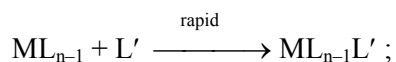
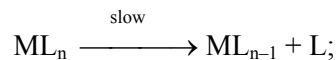
(3) is the ligand redistribution reaction; many acidic substitution reactions also proceed via this mechanism;

(4) is typical for many carbonyl complexes.

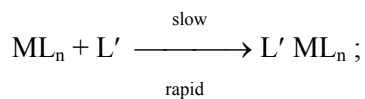
SUBSTITUTION REACTIONS AND LIGAND EXCHANGE REACTIONS

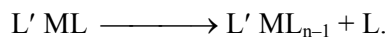
Substitution reactions (exchange of one ligand in the complex for another) and ligand exchange (change of one ligand for another identical radioactive one) are the most widely studied of the complex compound reactions. To explain their kinetic regularities, two main mechanisms are offered:

dissociative:



and associative





The dissociation mechanism described reactions that have the first order of magnitude relative to the complex and the zero order relative to the ligand, while the association mechanism describes reactions of the first order of magnitude relative to both the complex compound and the ligand.

In order to explain the often encountered significant deviation in the orders relative to the reagents, a supposition was made to the effect that both of the above given mechanisms are extreme, and that some reactions proceed via a mixed mechanism in which one of the mentioned routes is simply a prevailing one.

However, these additional suppositions failed to explain other anomalies that were observed in the process of the substitution and exchange of ligands [25].

Examples:

1. The speed constants for the exchange of CO in row: Ni(CO)₄, Fe(CO)₅, Cr(CO)₆ comprise $7.5 \cdot 10^{-4} \text{ sec}^{-1}$ at 0°C, 4 years (half-period of the exchange at 25°C) at 117°C, while bonding energy M—C in this row decreases.

2. The speed constants and parameters of the activation of the substitution and exchange reaction CO in Ni(CO)₄, carried onto P(C₆H₅)₂ and ¹⁴CO, should be close, since both reactions proceed via the dissociation mechanism. However, for the substitution reaction $k = 8 \cdot 10^{-4} \text{ sec}^{-1}$ at 0°C and $H = 85 \text{ kJ/mol}$, $\Delta S = 2$ entropic units, while for the exchange reaction — $k = 8 \cdot 10^{-4} \text{ sec}^{-1}$, $\Delta H = 49 \text{ kJ/mol}$, and $\Delta S = -26$ entropic units.

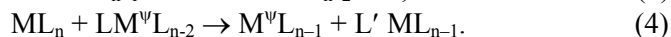
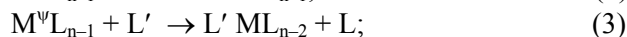
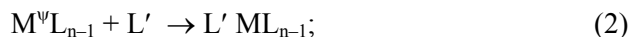
Analogous phenomena are obvious when comparing the kinetic parameters of exchange and substitution in reactions with the use of other compounds.

3. From the kinetics viewpoint of the substitution reaction, it is necessary to have a high exchange speed of CO in Co₂(CO)₈ as compared with the carbonyls of other metals.

The enumerated anomalies point to the insufficiency of the descriptions of the ligand substitution and exchange mechanisms with simple (dissociation and association) schemes.

The use of the theory of conence reactions for ligand substitution and exchange reactions in complex compounds allowed suggesting a mechanism for such reactions:





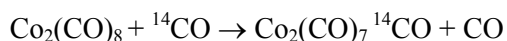
According to this mechanism, the first order of magnitude is observed via the slow dissociating coordinate saturated complex compounds of the complex, and the zero order is observed via the ligand. Indeed, as a rule, the coordinate saturated compounds react along the dissociation mechanism, while the conences — along the association mechanism.

Compared with the above-mentioned dissociation mechanism, this one has additional stages (3) and (4) whose possibilities were shown previously.

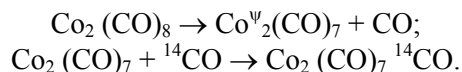
A mechanism that includes reactions (1) — (3) can be called, just like the chain radical mechanism, a *chain conence mechanism*. Reaction (1) is the embryonic chain reaction, (3) is the continuant chain reaction, (4) is the transmission reaction, and (2) is the chain breaking reaction. The common dissociation scheme [reactions (1) and (2)] are exclusive cases.

In general, any non-chain mechanism can be regarded as an exclusive case of a chain mechanism with a chain length equal to 0. From the energetic viewpoint, the chain route is more preferable than routes (1) and (2) because, in this route, one endothermic act is accompanied by acts of exchange, proceeded via reactions with exothermic heat effects — in the case of the substitution reaction, and by zero heat effects — in the case of the exchange reaction.

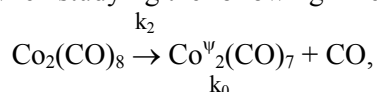
It was of interest to experimentally find some exchange chain reactions — research the chipping off of carbon oxide and then restoring it in decobaltoctacarbonyl, for which there was an anomaly high exchange speed. Thus, exchange reaction



has a speed constant of $k_1 = 1.5 \cdot 10^{-3} \text{ sec.}^{-1}$. When using a common dissociation scheme, the mechanism of this reaction includes the following stages:



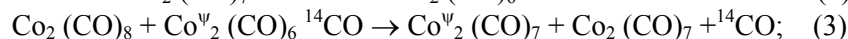
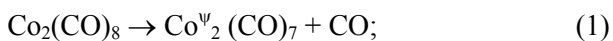
However, when studying the following kinetic reactions:





It was found that $k_2 = 2 \cdot 10^{-5} \text{ sec.}^{-1}$, while $k_3 = 1.1 \cdot 10^2 \text{ lit./ (mol} \cdot \text{ sec)}$. It is obvious that a simple comparison of the speed constants of reactions (1) – (3) allow excluding the use of the simple dissociation scheme for the description of the mechanism of the reaction.

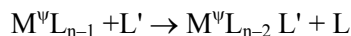
The use of the principles of the consecutive chain reactions, mainly the account of the possible interactions *conence* — *ligand* and *conence* — *coordinate non-saturated compound with the formation of new conences* brings us to the following reaction:



Because the reaction has the first order of magnitude relative to $\text{Co}_2(\text{CO})_8$, it is obvious that the speed of stage (3) does not limit the process. Considering this fact, it was found that reaction (2) has a speed constant $k = 10 \text{ lit./mol} \cdot \text{ sec.}$) at activation energy $E = 20 \text{ kJ/mol}$.

The greater speed constant of reaction (2) as compared with the speed constant of reaction (4), and the small activation energy during the inclusion of carbon oxide with a simultaneous elimination of the ligand, is well explained by the fact that this reaction proceeds more readily than a common saturation, that is, the speed of the given reaction is controlled by spatial difficulties, but not by bonding energy $M-L$.

The chain mechanism and the defining role of the continuant chain reaction:



that proceeds practically with a zero effect, well enough explains the above-mentioned anomalies.

The increase of the exchange speed CO in the carbonyl row $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$ is explained by the consecutive increase of the screening of the central atom.

Various reaction speeds for the exchange of different types of ligands (for example, CO for ${}^{14}\text{CO}$ changes faster than CO for triphenylphosphine) can be explained, in part, by the various volumes of the ligands, that is by spatial difficulties for the continual chain reaction. Besides carbonyl reactions, the chain mechanism has been proven to be of value for the photochemical ligand exchange reactions in PtCl_6^{2-} and PtBr_6^{2-} for marked Cl^- and Br^- [26], while PtCl_5^{2-} and PtBr_4^{2-} , offered as

chain carriers, were actually conences. The branched chain mechanism of the reaction well agrees with the large quantum discharge.

During the research of the ligand substitution reaction, it was found that, as a rule, the substitution reaction in octahedral halogen complexes P(IV) has the first order of magnitude relative to the complex and to the ligand, which is characteristic for an associative mechanism. Not only was the second order of magnitude observed in many complexes of the P(IV), but also observed was the dependence of the reaction speed on the type of substituting ligand.

Complexes $\text{Pt}(\text{NH}_3)\text{Cl}_3^+$ and $\text{Pt}(\text{en})(\text{NH}_3)(\text{NO}_2)\text{ClBr}$ [where (en) is the ethylene-diamine] react with pyridine via the reaction of the second order of magnitude. $\text{Pt}(\text{NH}_3)_4\text{Cl}_2^{2+}$ also reacts with ammonia via the reaction of the second order of magnitude. There are also deviations from the substitution rule for carbonyl octahedral complexes.

For most of the metal carbonyls, the ligand substitution reaction has the first order of magnitude relative to the complex and a zero one relative to the substituting ligand. However, it was observed that $\text{Co}(\text{NO})(\text{CO})_3$, $\text{Fe}(\text{NO})_2(\text{CO})_2$ and some others had a total second order of magnitude of the substitution reaction. Relatively, it was supposed that the indicated reactions proceeded along the SN_2 mechanism.

The observed deviations and seeming contradictions in these cases can be explained in the framework of the offered approach by the existence of the following stage:



Besides the qualitative explanation, one could have expected that in some cases, the transition chain reaction could limit the speed of the process, which would be observed in the kinetics of the process. Indeed, when researching the kinetics of the exchange reaction, the ligand substitution reaction in complexes Pt(IV) [in part Cl^-] in $\text{Pt}(\text{en})_2\text{Cl}$ [on radioactive Cl^-] and NO_2^- , it was found that the exchange reaction speed in darkness adheres to the equation:

$$w = k[\text{Pt(II)}] [\text{Pt(IV)}] [\text{Cl}^-]$$

while the substitution reaction speed adheres to:

$$w = k[\text{Pt(II)}] [\text{Pt(IV)}] [\text{NO}_2]$$

which coincides with the chain conence scheme of the given reactions [interaction of coordinate non-saturated complexes P(II) with coordinate saturated complexes P(IV) as the limiting stage of the process].

When introducing conences or compounds to the system that readily dissociate in the solvent, the substitution reactions proceed via the scheme analogous to the association mechanism. However, in this case, the further dissociation of the complex via the following equation is not excluded:



Thus, the conence reaction conception for the substitution is as follows:

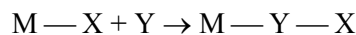
- 1) It is based upon chemical non-contradictory suppositions.
- 2) Each of the stages has serious experimental confirmation.
- 3) The total chain mechanism is completely confirmed for both carbonyl complex and non-carbonyl complex reactions.

Further, this conception explains:

- a) the anomalies in the substitution reactions when they are explained in the framework of the then existing association-dissociation schemes — various activation parameters and substitution reaction speeds that proceed via the dissociation mechanism;
- b) the influence of the various types of substitution ligands for various reactions;
- c) the second order of magnitude relative to the ligand for particular kinds of reactions.

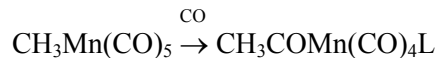
LIGAND INTRODUCTION REACTIONS

Ligand introduction reactions in complex compounds are described by the following general scheme:



where $X = H^-, R^-, OR^-, NR_2^-, NR_3, OH^-, H_2O, Cl^-, Br^-, I^-$; $Y = CO, \text{olefin, diene, acetylene, RCHO, RCN, SO}_2, O_2, \text{ or other non-saturated systems. Peculiarity details of this reaction are available in work [27].}$

A number of mechanisms were suggested for the first opened introduction reaction:



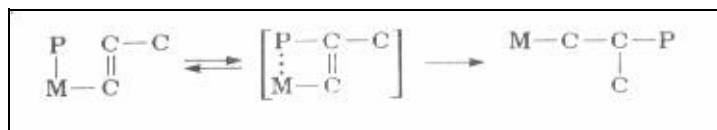
In the following mechanism:



we see a correlation with the kinetic regularities of the reaction, but the given mechanism did not explain the value of the activation energy for this reaction. For example, the activation energy comprised 62 kJ/mol, while the strength of bond M—C was equal to 125 – 380 kJ/mol.

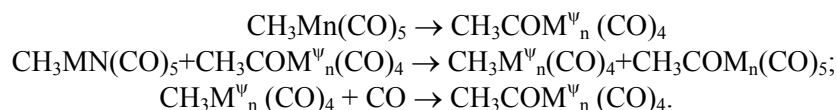
Analogous phenomena were also found when introducing ethylene via a metal – hydrogen bond in ethyl-rhodium. In this case the activation energy comprised 72 kJ/mol, the strength of the coordinate rhodium-ethylene bond was about 130 kJ/mol, while for the breaking of a carbon-carbon double bond required 264 kJ/mol.

To explain the low activation energy, it was supposed that the introduction reaction proceeds as if by some coordination, that is, via the more or less polar cyclic bonding with a simultaneous breaking and bond formation. Thus, for the ethylene introduction reaction, relative to a metal-hydrogen bond in ethyl-rhodium, the mechanism of the reaction is described by the following scheme:



Such polar complexes have never been confirmed.

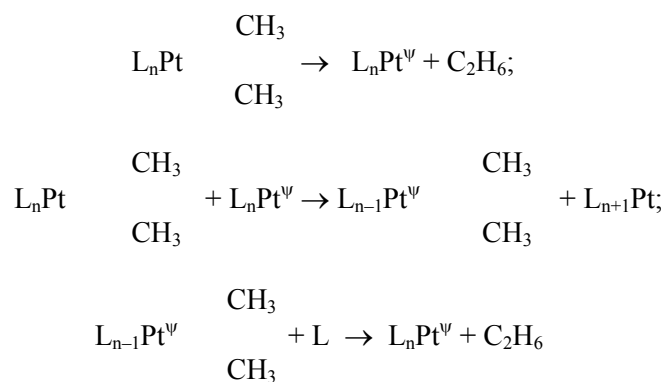
Unlike the given schemes in the framework of the conception of conence reactions, the mechanism, say, the introduction reaction of CO in carbonyl manganese, is illustrated as follows:



In this case the comparatively unlikely endothermic reactions serve only to initiate chains.

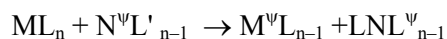
ELIMINATION RESTORATION REACTIONS

When researching the mechanism *ethane elimination restoration* out of complex $\text{PtX}(\text{CH}_3)_3(\text{L} - \text{L})$, [where $\text{X} = \text{Cl}, \text{Br}$ and $\text{L} - \text{L} = 1,2$ encore (diphenylphosphine) ethane] it was also found that the elimination activation energy comprises 69 kJ/mol (less than half the bonding energy of CH_3Pt). There is a coordinated mechanism for this reaction as well [27]. Analogously to the chain reaction, the introduction of the conence mechanism for this reaction can be presented as follows:



OXIDIZING RESTORATION REACTIONS OF CONENCE COMPOUNDS

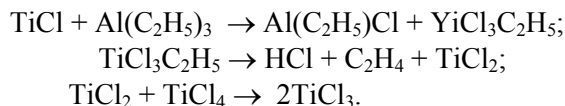
Oxidizing restoration reactions of conence compounds are often described in the following manner:



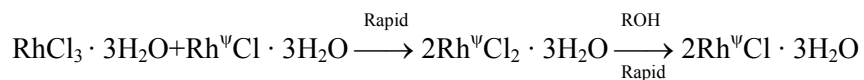
That is, these reactions are actually like reactions for the transition of the chain in the chain conence mechanism. For this kind of reactions, if we put them into a separate group, the transition of the ligand with a charge is typical. This group of reactions will border between the oxidizing restoration and conence reactions. They can be referred to either group.

The existence of reactions of both types stresses the fact that we need accounting in the reactions of interaction mechanisms that lead to the transition of the chain or its branch. The presence of chain reactions confirms the Semyonov hypothesis about the wide use of chain processes.

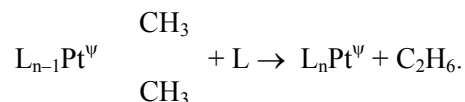
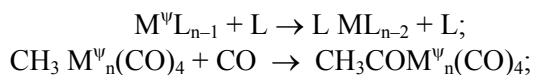
An example of a chain-branched oxidizing restoration reaction is the reaction for the formation of a catalyst for the polymerization of olefins:



Reactions of this type are meant to explain the autocatalytic character of reactions for the formation of mono-valence rhodium — isomerization catalyst and demerization of olefins:



Here the two-valence rhodium is a radical conence. The regarded mechanisms of the substitution, introduction, and chip off reactions include the following stages:



What is common for these reactions is that they proceed in the complex at the expense of the insertion of the ligand into the conence, that is, analogously to the reactions that proceed in collisions of two radicals; they can be regarded as chemically activated. The chemical activation energy, in this case, is received at the expense of the interaction between the conence and the ligand.

The main method of forming a conence in the viewed cases is via the dissociation of the initial complex, or via its interaction with other conences. It is supposed that in the general case, the interaction with another conence is a much quicker reaction, which allows having influence on the speed of the main conence reactions by introducing conences or labial coordinate non-saturated compounds.

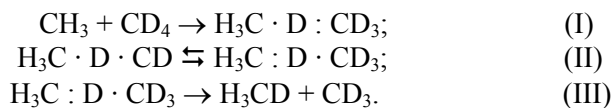
**INTERPRETATION OF KINETIC
REGULARITIES IN REACTIONS FROM THE VIEWPOINT
OF THE NEW APPROACH**

Let's go into some details about how the new approach to chemical bonding and chemical reactions explains the widely known, experimentally proven kinetic regularities of chemical reactions.

Such regularities include: the great speed in the interaction of active particles with saturated molecules, and relatively, the wide use of chain processes; the use of ionic, radical, conence, and catalytic reactions; resonance rules, the influence of solvents, the widely known rules about the linearity of free energy and their special cases (the BEP ??? rule and the Semyonov-Polanyi rule), and the exponential influence of the temperature on the reaction speed.

We know that in the process of a chemical reaction there is a breakup of the old bonds and the formation of new ones. During bond-breaking, energy is used, while during bond formation energy is discharged. Between all the chemical particles (ions, radicals, molecules) besides ions of the same name, there is *attraction*, which is conditioned by electric forces. This becomes obvious when the temperature decreases in the process of the formation of associates, solvates, and analogous compounds that have weak bonds.

As already mentioned, during associate formation there occurs a possibility of making use electronic isomerization as a result of which the newly formed bond is strengthened while the old bond abruptly weakens, that is, the reaction, in the case of radicals and ions proceeds in the following manner:



Concentration $\text{H}_3\text{C} \cdot \text{D} \cdot \text{CD}$ is referred to as **A**;

Concentration $\text{H}_3\text{C} : \text{D} \cdot \text{CD}_3$ is referred to as **B**.

Stage I proceeds with a speed close to the diffusion speed; stage II proceeds with a speed close to that of electronic isomerization, which usually does not limit the process; the speed of the whole reaction is limited by stage III. The speed of the last stage is proportional to the concentration of compound B and exponentially depends on the energy necessary for the breaking the single-electron bond in compound B.

Even when the bonding energy amounts to <20 kJ/mol, it is not the molecules with an average energy that enter reaction, it is the molecules with an energy that differs greatly from the average, the concentration of which is characterized as $\exp(E/RT)$, where E is the energy necessary for breaking a single-electron bond in compound B. T is the temperature of the reaction's media. The concentration of compound B partakes in the reaction speed equation in the pre-exponent, and relatively, the chemical reaction speed is defined by the following equation:

$$w = kc_B \exp(E/RT)$$

where c_B is the concentration of compound B.

The concentration of compound B is defined relative to the difference between the free energies — in the first, more comprehensible approach — by the relation of the potential energies of the electrons in compounds A and B. As previously indicated, the minimal potential energy corresponds to the maximal approach of the electrons to the nuclei, which, according to experimental data, in turn, corresponds to the optimal filling of the atoms' orbitals with electrons that is quantitatively defined by the Bohr equation $2n^2$, where n is the orderly number of the atom's orbital.

Compounds A and B are practically symmetric, therefore the concentration of compound B can be approximately equal to half the number of initial radicals CH_3 introduced to the system.

The same is observed during the interaction of ions with polar molecules in the widely known nucleophil substitution reaction.

Unlike the interaction of ions and radicals with saturated molecules, when forming associates out of common covalent molecules, the concentration of electronic isomers, which have weak bonds, is much lower. Firstly, this is explained, by the fact that the concentration of associates exponentially depends on the association energy (solvation), which is by one order of magnitude higher for ions and radicals than for saturated molecules. And secondly, what is more important, during electronic isomerization the weakening of the bond (decreasing the number of electrons) can be expected only of the electronic isomer whose electron distribution does not correspond to the minimal potential energy of the electrons. In one of the atoms, the electron will surely transit to a more remote orbital away from the nucleus, which defines, considering the high values of electronic energy, an extremely small concentration of the isomer.

Energy is discharged during the interaction of a radical and an ion with saturated molecules; the bond-to-be-broken abruptly weakens as

a result of electronic isomerization, and a radical and ion are formed again when the bond is broken. The procedure of chemical reactions via the radical and ionic chain mechanism are proposed, first of all, when studying non-catalytic interactions of covalent molecules.

The numerous experimental materials of organic and inorganic chemistry prove the overwhelming priority of radical and ionic routes in chemistry. It is of interest to note that all the approaches to the theory of chemical reactions and the explanations concerning its regularities, from the viewpoints of physics, quantum mechanics, and the calculations based upon the latter, at present are used only in a small number of chemical reactions, or have proven to be incorrect. Thus, the widely known Budworth-Goffman rule of orbital symmetry is relative only to molecular reactions (it does not react in ionic, radical, and catalytic reactions) and therefore, at present, it is used and illustrated almost exclusively as the Dills-Alder reaction.

The kinetic speed calculations of some of the simple reactions in the gas phase that were the basics during the origination of the theory of active collisions and the transition state theory, having become canonical and having entered practically all the textbooks on physical chemistry, and which proved to be nonsensical, incorrect.

A molecular mechanism was presupposed in all the calculations, and there was a brilliant coincidence of the calculative and experimental results [11]. However, the quantitative studies of the elementary stages, conducted in the framework of the research of the interaction of radicals with saturated molecules, have shown that the reactions proceed along the radical mechanism.

When discussing the structural theory, it was shown that the new approach to the theory of chemical bonding explains the physical essence of the existence of the resonance rules, which, in their turn, explain not only the stability of aromatic compounds, but also the direction and the correlation of the speeds in chemical reactions.

This new approach to the theory of chemical bonding, if the resonance rules are properly used relative to the chemical reactions, explains the physical essence of the resonance rules. The four main resonance rules define the concentration of electronic isomers in the system since, according to the offered approach, the energy of the system, composed of electrons and nuclei, is defined, first of all, by the minimal electronic potential energy, i.e., by the maximal approach of the electrons of the given system to the nuclei they are to bond; and the number of electrons on the atoms' orbitals does not exceed $2n^2$, where n is the ordinal number of the orbit.

The free energy linear rule (FELR) according to which the logarithms of speed constants of single-type reactions are proportional to the change of free energies via the generally-accepted quantum-chemical conception is not explained even as a functional dependence.

Conformably to the FELR correlation, even calculations with quantitative unevaluated additional suppositions were never done.

All the correlations observed when studying the kinetics of chemical reactions in the framework of the transition state theory, were empirical since, according to this theory, the reaction speed was defined only by the possibility of reaching the transition state, the conclusions which could not be made on the basis of the theory of chemical structure.

In the framework of the new approach, there is no transition state, and the bond between chemical properties of reacting systems and the chemical reaction speed is quite clear.

As indicated above, the chemical reaction speed is defined by the equilibrium of the electronic isomers that are formed after the association stage. Relatively, the concentration in the electron-isomer system is defined by the potential energy of the electrons in the given isomer.

When touching upon the theory of covalent bonding, it was indicated that the Van der Waals bond was very weak in both isomers, and therefore, the difference in the energies of the isomers is defined by the energy differences in the initial and final products or by the heat of the reactions.

The difference in the potential energies of electrons in the initial and final products is defined by the heat effect of the chemical reaction and by the change in the thermodynamic potential. The observed correlations — FELRs, the Semyonov – Polanyi rules — that were no longer empirical. Moreover, these are experimental facts that confirm the ontological value of the new approach as well as the quantitative data received by optimal methods which allows quantitative evaluation of the chemical reaction speed, that is, to transit from qualitative explanations and presumptions to quantitative ones.

According to the above-mentioned main procedure scheme for the complex association-dissociation reaction, its speed is proportional to the associate concentration that is defined by the correlation of the bond-breaking speed and the associate formation in the forward direction (towards the reaction) and in the reverse direction (breakup into the initial components).

Unlike the general explanations about the spatial correlations, — mostly coincidental with the generally accepted ones — the new approach has a principally new way of explaining the influence of the solvent and catalyst on the chemical reaction speed. As indicated, according to the new approach, when introducing saturated molecules into the system, that mechanism will undoubtedly have priority in speed, which presupposes the interaction of active particles (ions, radicals) formed out of one valent-saturated molecule with another saturated molecule. The thermal breakup of the molecules in the gas phase into ions (heterolytic breakup) from the energy viewpoint is less possible as compared with their homolytic breakup into radicals.

The energy of thermal dissociation into ions $\approx > 800$ kJ/mol, while the energy of thermal dissociation into radicals $\approx > 400$ kJ/mol.

According to the offered approach, in ionic bonds, unlike covalent bonds, during thermal breaking, the defining factor is the cation-anion attraction, since, as a rule, in the case of ionic bonds, the outermost electrons are not generalized. Relatively, the dissociation energy, in this case, is completely defined by electrostatics, for which the decrease of the attraction forces is characteristic, and which is proportional to the product of the charges and the square of the distance.

Using this scheme, it is a simple matter to explain the breakup of the ionic bond in polar solvents (like water) since, as a result of solvation, the effectiveness of the charges on the cation and anion, and the interaction of the anion and cation decreases abruptly.

Because there are two main types of reactions (radical and ionic), it is expedient to take up these reactions separately when studying the influence of the solvent on the speed of each of the reaction types

To illustrate a reaction proceeding along the ionic mechanism, let's consider the interaction of chloride sodium with methyl bromide.

During the hydration of chloride sodium and methyl chloride, as indicated above, the chloride sodium is dissociated into solvated anion and cation. The dependence of this reaction's speed on the temperature, is, first of all, be defined by the dissociation energy of the anion, which is much greater than the breaking energy that was weakened after isomerization in the associate of bond C—Cl in methyl chloride. In this respect, the quantitative correlation of activation energy, solvation, and the absence of activation energy when accomplishing the anion desolvation reaction with haloid-alkyl, is expected, as indicated above.

The limiting stage of nucleophyl substitution in a mixture is the desolvation of anion, and, of course, the reaction speed, depending on the type of incompletely solvated anion attacker, which decreases with the

increase of the anion's hydrogenation energy, that is, in row: I^- , Br^- , Cl^- , as seen in the experiment.

In the gas phase, where reactions can be observed only after introducing ready anions to the system, the dependence of the reaction speed on the type of anion, has a reverse order.

In radical reactions, after introducing ready radicals into the system, the solvation is usually the association stage; for example, in reactions of radicals with carbon-hydrogen, the activation energy is close in value to the association energy.

Association energy can be used to continue the dissociation reaction in the uncharged gas phase. Reactions of this type are widely known as *chemically activated reactions*.

When introducing saturated molecules to the system, the speed-limiting reaction, proceeding along the radical mechanism, is the dissociation of one of the reagents into radicals. The breakup reaction of the initial saturated substance into radicals under conditions of the non-branched chain process, usually manages to get to the equilibrium.

Therefore, the influence of temperature on the chemical reaction speed is actually observed on the dissociation stages and on equilibriums between active and inactive particles.

According to thermodynamics, an exponential influence of temperature is observed in cases of dissociation and equilibrium. As a rule, the observed exponential influence of temperature on the speed of both elementary and complex chemical reactions should be clear from the above given material without any introduction of additional suppositions. Also without any additional suppositions (like the *transitional state*) we have explained the low values of activation energy (20-40 kJ/mol) observed when introducing active particles to the system; during the interaction with saturated molecules whose bonding energy is equal to 400 kJ/mol.

Much greater values of activating energy (80 kJ/mol) observed in mixtures of ionic reactions, are connected with desolvation. The activation energy (200 kJ/mol), observed in radical gas-exchange reactions that proceed in accordance with to the conception of the chain mechanism, are connected with the influence of the temperature on the equilibrium: *saturated molecule* — *radical*. Higher activation energy (400 kJ/mol) corresponds to elementary reactions of dissociation into radicals. In this case the activation energy is equal to the energy needed to break the bond — the energy of thermal dissociation.

Chapter 3

GENERAL CATALYSIS THEORY

The explanation of catalysis in the framework of the generally accepted approach always had various levels of not only special, but also of common explanations. Besides, definitions like, “*a catalyst is a substance that accelerates a reaction*” were regarded as an explanation. Another ‘serious’ explanation was a definition to the effect that “*the catalytic process proceeds along a mechanism that requires a smaller activation energy*” in order to prove this, a drawing showed the phenomenological difference between a double-humped camel and a single-humped one.

In the pre-quantum chemical period, when explaining catalysis, the teacher would limit himself to primitive reasoning: “*The reaction speed is defined by an equation which contains a pre-exponent and an exponent. A catalyst greatly accelerates the reaction, which influences the exponent. The exponent has only one variable, depending on the kind of reaction. In the general case, the catalyst decreases the activation energy.*” Etc.

Such explanations may have been sufficient in the middle school. A special chemical education on university level (with general explanations of catalysis) did not differ much; but when explaining catalysis there was a systematization of various catalytic reactions, the theory of catalysis was given, which was a phenomenological, correlational dependence in the realm of catalysis. This included such ‘theories’ as: multiplet, ensemble, semiconductor, etc.

Some of the general theories were attempts at deepening the understanding of the cause of lowering the activation barrier in chemical reactions. These include the chain theory — the barrier is overcome at the expense of the energy of the previous reactions; the compensational theory — a variant of the transition state theory ideology in catalytic reactions. In this theory, the decrease of the activation barrier was explained by the simultaneous procedure of the dissociation and association reactions.

A number of explanations of the general actions of catalysts are based on interpretations offered by quantum chemistry. Thus, some scientists say that the catalyst allows accomplishing the reaction along a route that excludes the barrier along the symmetry [14], others say that the catalyst produces additional electronic levels, which ease the transition of electrons from one reagent to another in acid-restoration reactions.

General explanations also include general reasoning of the semiconductor catalyst theory where the action of the catalyst is explained by the fact that the catalyst changes the electronic structure of the reacting compounds at the expense of the surplus electrons on its surface or at the expense electronic vacancies (holes).

Variations on this theme — *the catalyst decreases the activation barrier* — with the aim of deepening knowledge, are still continuing. Thus, for example, it is thought that the decrease of the activation energy occurs at the expense of the formation of aromatic systems in the transition state in the presence of the catalyst, that is, the activation barrier is overcome at the expense of the *resonance* energy.

The general shortcoming, that defined the uselessness of the given trend to deepen the understanding of catalysis, is the fact that it was based on the wrong understanding of the procedure of a simple (non-catalytic) chemical reaction. That is, there was a lack of understanding that in the basis of all theories, meant to deepen the knowledge about how the catalyst's mechanism works, there was a theory of absolute speed rates, the procedure of reactions through the transition state, for the formation of which kinetic energy is required. The illogicality of the given ideas has been proven in this work.

It is of interest to note that in the framework of the catalysis theory, the inadequacy of the generally accepted theory of chemical reactions becomes even more obvious.

Chemical research of catalytic reactions has shown that such reactions proceed via intermediate compounds, which have a much smaller kinetic energy in a heterogeneous catalysis and whose concentration, according to thermodynamic reasoning (abrupt entropy decrease during formation), is much smaller than the initial one.

Thus, catalysis – reaction acceleration – as compared with its non-catalytic route in the framework of the generally accepted idea of chemical reactions (*the speed of the chemical reaction is proportional to the concentration and to the kinetic energy of the reacting particles*) contradicts the main accepted model for chemical reactions.

Before going over to the explanation of catalysis in the light of the new conception of chemical reactions, let's consider some details concerning the active forces in chemical reactions.

As indicated above, the speed of any chemical transformation is defined by the breaking speed of the chemical bond, by the concentration of initial and intermediate substances in the course of the complex reaction. The breaking of the bond occurs as a result of the accumulation of the necessary amount of energy on the vibrational freedom stages.

Correspondingly, the driving force of the chemical reaction is the molecule's mechanical energy; to be precise — its separate parts — that is obvious from the increase of the reaction speed with an increase of the temperature.

Besides the energy that accumulates on the vibrational freedom stages, in the case of chemically activated reactions, the energy of the previous exothermic reaction can be used for the breaking of the chemical bond.

Thus, the chemical reaction driving forces are the heat and chemical energies. The chemical reaction speed increases 1) with the increase of the driving forces (the increase of heat energy, the increase and full use of the energy of the preceding exothermic reaction) and 2) with the decrease of energy necessary for bond breaking during the reaction; that is, when increasing the degree of weakening the bond.

A significant weakening of the bonds in saturated molecules occurs as a result of connecting ions, radicals, and conences to them, and as a result of the consequent electronic isomerization in the associate. Relatively, the chemical reaction speed abruptly increases when the chemically active particles – ions, radicals and conences – appear in the system.

Since the distance between the atoms defines the electronic isomerization speed, and the shell construction changes during the isomerization, depending on the type of bond, the reaction speed increases when chemical substances are introduced into the system. These substances, in turn, increase the concentration of chemically active particles that ease the possibility of electronic isomerization and allow the use of the energy of the previous exothermic chemical reactions in order to proceed with the next.

Just as expected, substances that accelerate the reaction via the enumerated possible mechanisms are catalysts, and the essence of a catalysis, in the general approach, becomes more comprehensible, as compared with the general interpretations: *A catalyst is a substance that accelerates the reaction, it leads the reaction along another route that requires a smaller activation energy.*

The main task of the catalysts — to increase the number of chemically active particles in the system — was used in many explanations without the use of any new understanding of the essence of chemical bonding and reaction. Chemical experiments had proven that the interaction speed of ions, radicals, and conences is much greater than that of saturated molecules, the reactions proceed via chemically active particles, and the catalysis is accomplished via simple chemical reactions which are joined by either chemically active particles or by intermediate compounds with weakened, and later on, with breaking bonds.

When studying conence reactions and catalysis, we learned about the role of the catalyst in increasing the possibilities of chemically activated routes. What is new in this work?

Unlike the existing catalysis theories, and the studies of chemical routes of catalytic reactions, logically not connected with them, the above-mentioned main methods of accelerating can be regarded as a general catalysis theory, where the decrease of the activation energy reaction is simply one of many consequences drawn from the general theory of catalysis.

For ionic, radical, and conence catalytic reactions the chemical activity of particles is defined by the ease of electronic isomerization in their formed intermediate associates. The weakening in the course of isomerization and then the breaking of the bonds leads to the decrease of the heat energy necessary for their breaking. Therefore, the need for heat energy decreases. This is obvious from the experiment — the temperature has less influence on the reaction speed (decrease of the activation energy) and on the routes that continue with chemical activation increases. That is, one of the most frequent general approaches to catalysis is the result drawn from the general chemical interpretation of the work of the catalysts.

Theories in the realm of catalysis are of great importance because here they are not empirical dependencies, but experimental correlations that offer quantitative dependencies of reaction speeds from the row of measured initial catalyst parameters, which have their own non-contradictable explanations in the old general approach.

Thus, on the first stage the theory of chemical catalysis allowed explaining the main kinetic regularities of chemical reactions including the acceleration mechanism of the catalyst.

The next task was to deepen the understanding connected with answers to the next questions. *Why are the ions, radicals and conences so active? What is the mechanism for weakening the chemical bond? How does the weakening of the chemical bond influence the chemical reaction speed (in the framework of the transition state theory this was one of the questions)?* Of course, all the answers to these questions depended on the physical essence of chemical bonding, which was still incomprehensible. In order to explain kinetic and catalytic dependencies, it was not enough to have only qualitative reasoning (the nuclei are attracted to the electrons situated between them).

This is why it was decided that the next step in deepening the understanding of the essence of chemical phenomena was the structure of the atom and the molecule (essence of chemical bonding), the elementary, complex, and the catalytic chemical transformations.

It was indicated above that the correlational catalysis theories result from the general chemical catalysis theory, based on the new understanding of the essence of chemical bonding and chemical reaction.

To illustrate and concretize this with samples in practical use of the general theory, we can view the more widely used correlations that have been observed in catalytic reactions.

Thus, a correlation between the bonding energy of a substance with a catalyst and a relative geometry of a catalyst and reagents with the speed of catalytic reactions were observed in the Balandin multiple theory. These dependencies, besides those simpler reactions described by kinetic regularities (LSE and BEP rules) ??? remained empirical even in accordance with the transition state theory which required an expenditure of energy on the formation stage of the transition state. Relatively, the bonding energy, whose essence was misunderstood, was not connected functionally (logically) with the chemical reaction speed.

In general, the explanation about kinetic regularities of chemical reactions without the help of 'speed parameters', the transition state, and the elucidation of the need for energy for breaking the associate-weakened chemical bond, relative to establishing a direct logical bond between the initial strength and the weakened strength of the bond, allows understanding the principle of the energy correlation, as well as to shift the located empirical dependencies to the row of quantitative experimental data on chemical theory in correlational kinetic dependencies and resonance rules.

Analogously, in the semiconductor catalysis theory — where the speed correlation of the catalytic reaction with a forbidden zone width were observed, and where the correlation of the chemical reaction speed with the position of the elements of the Mendeleev table was also

observed. ??? That is, with their electronic structure, the received quantitative dependencies were empirical in the transition state theory. In the offered approach, we have shown the logical connection between the electronic structure of chemical substances and the speeds of their chemical transformations; and the observed correlational dependence becomes comprehensible.

The latter, just as in the case of the multiple theory, shifts the found dependencies from the category of 'correlational empirical' to the category of 'experimental'.

Now let's return to a more common case relative to explaining the homogenous and heterogeneous catalysis.

As a good example of a homogeneous catalyst, let's take a look at some catalytic possibilities of one of the more universal and well studied catalysts — cobalt hydrocarbonyl $\text{HCo}(\text{CO})_4$.

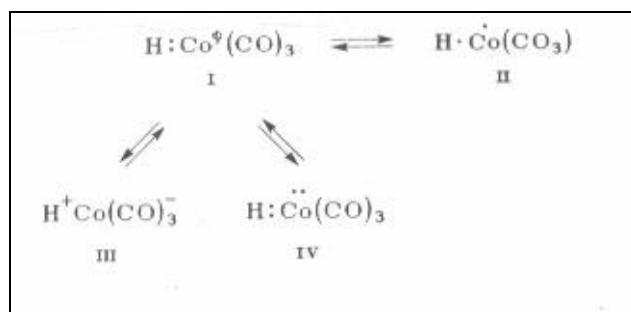
Cobalt hydrocarbonyl in water is an acid that dissociates into H^+ and $\text{Co}(\text{CO})_4^-$. Besides this, cobalt hydrocarbonyl can dissociate along the following scheme:



where Ψ is coordinate-non-saturated compound — conence-compound with a vacant orbital.

According to the principles of electronic isomerization or via the empirical rules of the resonance theory $\text{HCo}^\Psi(\text{CO})_3$, as a result of electronic isomerization, a number of electronic isomers can form, whose relative concentration is defined by the isomers' energy.

As an example, let's examine a limited number of isomers:

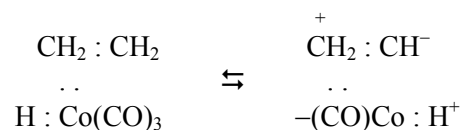


There is one electron in isomer II; there are two hydrogen – cobalt electrons in isomer III that go to the vacant orbital. In a biradical isomer, one of the non-bonding electrons leaves for the vacant orbital.

Thus, cobalt hydrocarbonyl can offer not only ions in solutions, and accomplish proton- and anion-catalyzing reactions that appear on the

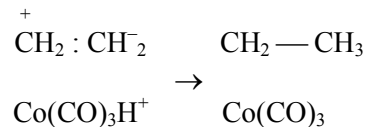
elementary stages as electrophilia and nucleophilia, but it can conduct radical reactions as well.

If we consider that $\text{HCo}^\Psi(\text{CO})_3$ contains a vacant orbital to which other ligands can connect (say, olefins) it is of interest to examine the electronic isomerization of the π complex that is formed out of $\text{HCo}(\text{CO})_3$ and an olefin. According to the main precept that defines the possibility of electronic isomers, one of the possible schemes for the isomerization of the π complex can be presented thus:



The possibility of a π complex in the system can be explained by a partial compensation in the formation energy of less possible carbons that have a charge at the expense of decreasing the interelectronic repulsion, which can be presupposed in the tri-centered quad-electronic bonds in the π complex.

Further, the value of compound II in further transformations of the following type



can be significant at the expense of the high speed of the given reaction that proceeds along the ionic mechanism.

“My God!” the disappointed reader might say, “another conception is offered, promising a lot, and foretelling nothing!”

A conception, indeed, offers unlimited opportunities for speculation. Moreover, a conception doubts the often declared efforts, in this book, to understand chemical phenomena without any wishful thinking, that is, to separate the theory from the hypothesis, thereby separating *understanding, expectation, proof, and explanation*.

The absence of a precise division of these points has historically helped to confirm incorrect phenomena (transition state theory, quantum chemistry) and physically unexplainable (unclear) theories, like the resonance theory which satisfied one of the main mobile feelings — that of self-approval.

However, the sequential development of the all-explaining hypotheses that are regarded as theories, were harmful to the hypotheses themselves. Instead of just declaring the observed correlation concerning the stability of the compounds at various electron combinations, the gradual additions to this rule with concrete chemical utilization in the absence of nuclei mobility (but no contents) led to an unnoticeable and baseless transformation into the resonance theory. Then the unlimited speculative possibilities of the resonance theory were regarded as shortcomings of this theory.

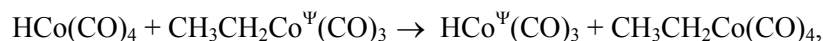
The routes considered for the transformation of the catalyst and its complexes is by no means theoretical proof of the priority or even the realistic procedure of the given routes, but is just an illustration of possibilities, i.e., phenomena that do not contradict the initial position of the general theory. The minimum of free energy connection is reached during the maximal approach of the electrons to the nuclei — theory with the experimentally installed limitation $2n^2$, where n is the ordinal number of the orbital.

The main aim of the theory is comprehension that is based on logic without the introduction of new essences. In our case it is understanding by what special properties of the catalyst — in our case – cobalt hydrocarbonyl — can be explained more thoroughly; the procedure in its presence, of the well known acid-catalyzing, radical, and conence reactions without the introduction of new essences and additional suppositions.

The choice of cobalt hydrocarbonyl is connected with the fact that during electronic structure (the presence of occupied nonbonding orbitals – analogies of anions and unoccupied orbitals) it well enough models the surface atoms of the heterogeneous catalysts, which have both electronic vacancies (holes) and nonbonding (excessive) electrons.

On the example of cobalt hydrocarbonyl we can also illustrate the mechanism for the acceleration of the reaction at the expense of the use of association reaction energy in dissociation reactions.

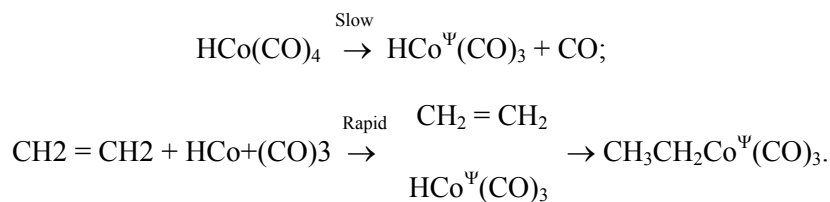
The action of catalysts was regarded as a manifestation of chemical activity. The interaction of conences, ions, and radicals with initial reagents relative to the following case:



convincingly explains the widely noted characteristic complex catalytic phenomena — more rapid procedure of the whole catalytic cycle than that of its model elementary stage.

Conences, radicals, and ions capable of active association, were known as being *statistically activated*, while the intermediate compounds that received the energy of exothermic reactions, were known as *dynamically activated*.

Statistic and dynamic activations can be shown on the example of the π -complex formation out of olefin and cobalt hydrocarbonyl and its π -complex, its transition into alkyl-carbonyl (first stages of the hydroformylation mechanism):



The presence of dynamically activated particles in catalytic reactions, and the possibility of forming statistically activated particles in the chain mechanism, relatively cannot be observed in model reactions where the possibility of chain formation, in the statistic and activated compounds, is excluded.

The given examples also illustrate the general position of the accelerated actions of the catalysts — in the catalyst the process proceeds via the intermediate products that are either statistically or dynamically activated, which, at some level of understanding actually defines the high speed of catalytic reactions.

To illustrate a catalysis mechanism, the following reaction mechanism for hydroformylation illustrates can be observed:

This detailed illustration allows to more vividly understand the role of conences in catalysis. The presence of vacant spaces in conences (with close energy values) is not for ligands, but for electrons, guarantees the possibility of passing the electronic regrouping and, therefore, the appearance of ions and radicals. The formation of ion and radical associates with saturated molecules (stage XII) and the consequent electronic isomerization leads to the formation of weak bonds the breaking of which is aided by the energy discharged during the bonding of the ligand to the conence (stage XIV).

The homogeneous conence catalysis, unlike the heterogeneous one, has a maximally available surface, which accounts for its much greater activity.

The joint possibilities of the conences in chemical and dynamic activation explain the importance of their roles in biological catalysis.

CONCLUSION

This work is an attempt at generalizing and further developing the new approach to the main chemical phenomena: chemical bonding, chemical reactions, and chemical catalysis. Therefore it is of interest to briefly generalize what we managed to realize and what we would like to convey to the readers in this respect.

The traditional classical development of chemistry ended with the introduction of the pre-quantum electronic chemistry, which qualitatively explained the possibility of chemical bonding, the chemical properties of substances, and quite a number of correlations.

In this period of pre-quantum electronic chemistry, the high thermal stability of covalent bonding and its saturation were not understood in the quantitative aspect relative to electrostatic calculations. The main correlation of the structural theory remained unexplained: the filling of the electronic shells of the atoms that enter the chemical compounds that are discharged in pure form up to the shells of the nearest inert gas. The physical essence of the correlation of the resonance theory was not understood.

Indeed, electronic chemistry did not explain why, in order to break a chemical bond, which takes place in the course of the interaction of ions and radicals with saturated molecules, energy of almost by one order of magnitude less was required than in the case of the thermal breaking of a covalent bond.

Misunderstood in the transition state theory was the physical essence of the main kinetic correlations observed in experiments and found when studying simple and complex chemical transformations including catalytic ones. These correlations include: the influence of solvents, a much greater interaction speed for ions and radicals with saturated molecules, kinetic rules (FELR, BEP, etc.) ??? and various correlational theories in the sphere of catalysis.

Thus, pre-quantum chemistry resembled something like separate fields of experimental research qualitatively explained in the atom structure theory and quantitatively explained in experimentally found and used, as a rule, in the given realm of quantitative correlations — systematized empirical experimental data.

After electronic chemistry — which happened to be one of the sequential stages in the development of the general principles of theoretical chemistry, based, first of all, on chemical and physical experiments, which strived to qualitatively, then semi-quantitatively, and

finally quantitatively understand (i.e., explain on the basis of the known essences) the newly observed phenomena — came quantum chemistry.

Quantum chemistry *broke the time line*, and practically did away with main question of classical science — “why?” Quantum chemistry appeared to try and change the patriarchal logic understanding for modern quantitative data on bonding energies and transition state, received as a result of approximate solutions of the Schroedinger equation.

In canonic cases, just as for bonding energy in a hydrogen molecule and for the transition state energy of some reactions, results were received that differed from experimental results by less than 1 %. This strengthened quantum chemistry as a topmost theoretical basis for quantitative calculations of the main chemical phenomena and solved important questions in theoretical chemistry, the basis of which had formerly been electronic chemistry.

The success of quantum chemistry in calculations that actually became canonic, gave assurance that in the process of the development of the computer, all chemical phenomena will be calculated.

The results received from quantum-chemical calculations of bonding energy and of transition state energy coincided with the results of incorrectly elaborated experiments; no good were the model presentations with the help of which experimental data was elaborated.

The main mistake, when elaborating experimental data relative to the bond-breaking energy, was the wrong supposition to the effect that the bonding electrons in covalent bonds do not absorb energy during the thermal excitation of the molecules up to the pre-dissociative condition. The mistake, during the calculation of the transition state energy, was in the wrong supposition about the need for additional energy for the formation of the transition state.

The wonderful coincidence of the results of the quantum-chemical calculations and the experimental results have shown the unlimited matching possibilities of this method, that is, this method was discredited as an incorrect method for quantitative calculations of chemical phenomena.

Thus, quantum chemistry failed to qualitatively answer the questions that stood before pre-quantum theoretical chemistry, while the quantitative calculations proved to be incorrect. The efforts to answer those questions that became next in turn in the course of the traditional pre-quantum development of chemistry, was undoubtedly regarded as being of interest for the further development of traditional theoretical chemistry.

If the critical part of this booklet was devoted to the incorrectness of the basics of quantum chemistry and its qualitative conclusions, and to the transition state theory, — the constructive part was an attempt at understanding and conveying the essence of quantum chemical bonding to explain the indicated quantitative inconsistencies, first of all, between the bonding and the activation energies.

Then what is the logical and quantitative connection between the more common (main) chemical phenomena? What did we manage to understand from this research material? How, in the light of the new approach do you understand the logic of chemical regularities?

And so, we managed to realize that the greater expenditures of heat energy, as compared with the simple electrostatic calculations, are connected with the fact that the main part of the energy, discharged to the covalent-bonded molecule, is spent sort of unproductively, for the excitation of the electrons, and only a small part of this energy is spent on prolonging the electrostatic attraction of the nuclei to the electrons bonding them, that is, on the breaking of the chemical bond.

The ‘unproductive’ expenditures of energy increase much more abruptly than the electrostatic component of covalent bonding. The latter is defined by the attraction of the bonding electrons not to their atom-masters, but to the atom-acceptors.

The potential energy of a *chemical compound* (a mixture of electronic isomers, whose statistic weight is defined by the potential energy of the isomer) is defined by the distance of the electrons from the nuclei — the smaller the distance, the closer are the electrons to the nuclei. According to the experimental results, electronic isomers are the most highly probable; they have a number of electrons in the outermost shells of the atoms that correspond to the number of electrons in the shell of the nearest inert gas in accordance with the table of elements.

Relatively, if the chemical structure of the compound, which is defined by the position of the nuclei, can have more electronic isomers, considering their statistic weights, the stability of this compounds, according to thermodynamic law (the more microstates — the higher the entropy) should be higher, which makes the resonance rules more comprehensible.

Chemical reactions between chemically activated particles (ions, radicals) and saturated molecules proceed via the following elementary stages: **association** — **electronic isomerization** (as a result of which the old bond weakens and the new one strengthens) — **dissociation**. The abrupt weakening of the old bond is conditioned by the transition of its bonding electrons onto the next orbital of the atom-acceptor.

The greatest concentrations in a mixture of electronic isomers (isomers with a very weak chemical bond) can be formed only when bonding to saturated ionic or radical molecules. Thus, it becomes obvious why their interaction speed with saturated molecules, is by many orders of magnitude greater than the interaction speed of saturated molecules among themselves. During the interaction of radicals or ions with saturated molecules, again we get radicals and ions. Thus, the defining role of ionic and radical chain routes in chemical reactions when introducing saturated molecules to the system becomes comprehensible.

Also comprehensible, in the light of the above, is the paradox that served as one of the main stimuli for writing this booklet. Much less energy is required to break a covalent bond when it is interacting with a radical, as compared with the energy necessary to break a bond thermally. This is conditioned by electronic isomerization in associate *saturated molecule — radical*.

The statistic weight of electronic isomers in the associate is defined by the electro-affinity of acceptor atoms, and the thermodynamic stability is defined likewise, therefore, the observed correlations in chemical kinetics become quite obvious.

Understanding the essence of the chemical activity of ions, radicals, and conences allows elucidating the essence of catalytic processes and the influence of temperature and solvent on the chemical reaction speed. The main influence of temperature and catalysts was conditioned by increasing the number of chemically active particles in the system.

The activity of one chemical particle (a system containing nuclei and electrons) relative to another particle is defined by the concentration of the electronic isomer with the weakest bond that is formed as a result of the association of reacting particles followed by electronic isomerization.

Correspondingly, with the increase of the temperature, the concentration increases along the exponent of radicals in the gas phase, and incompletely solvated ions in the liquid phase.

Catalysts are substances that accelerate the reaction and produce a much greater concentration of chemically active compounds under the same conditions.

The gained understanding of the main chemical phenomena with the help of experimental research on electronic structure of thermally stable compounds, the togetherness of thermal stability with the completion of the atoms' shells in these compounds up to the shells of the nearest inert gas, which differ from the generally accepted, widely used chemical phenomena considering that some phenomena were first

explained via spectral physical data (physical essence of covalent chemical bonding) while others got alternative explanations (theory of chemical reactions and catalysis), served as the reason for the pretentious title under which we are publishing this series of works: New General Theory of Chemical Bonding, Kinetics and Catalysis.

Besides the purely chemical questions, some philosophical and physical questions connected with chemistry have been studied [15].

Thus, V.Y.Gankin considered the criteria of ontological values of the theory. It was shown that the negation of quantum mechanics CTO and OTO from the previously accepted criterion of ontological value theory, the principle of internal perfection & external Verification (IPEV), its exchange for the criterion of 'beauty', 'craziness', etc. are baseless nowadays.

In the framework of the IPEV, which has been well tested for defining the further paths for fundamental research and discrimination in theories in chemistry, some physical theories have been mentioned.

Qualitative explanations are offered in the form or hypotheses for already known physical phenomena and for those now under discussion like *quantum energy*, *wave properties of particles*, *gravitational*, *inertial*, *inter-atomic forces*, and *relative effects*, which are based on the discoveries of electro-dynamic interactions, atom structure, and elementary particles. Two types of physical phenomena are described qualitatively: positive and negative charges, and three types of their charges in regard to their transition relatively to each other: uniform, accelerated, and vibrational.

Micro-bodies (common ones) and macro-bodies (including cosmic ones) are combinations of charges that are in equilibrium with free charges (electrons, positive and negative ions) in space, which surround the macro-bodies and the uniform ones. The electrons leave the bodies more readily than the protons, so the electro-neutrality of bodies, when explaining via accepted physical theories, is not at all obvious.

The presence of free charges and those bonded in macro-bodies allows forming a model of ether — the free charges (concentration of only electrons in cosmic space around the earth 10^6 cm^3), and the interaction of both the macro- and micro-objects via ether without the introduction of the additional essence — field.

Heated objects in an equilibrium system (stars) are charged positively, while the cold objects (planets) — negatively, which suggests the possibility of their electrostatic attraction analogous to that of the ion. The attraction between cold, identically charged bodies, is accomplished via the ether — analogous to covalent bonding.

To imitate gravitation, it is sufficient to have a transition of only 10^{-11} % of the electrons from one body to another.

A hypothesis of inner-atomic forces has been constructed in complete analogy relative to covalent chemical bonding. Weak and strong interactions are regarded as interactions of variously organized micro-particles (elementary charges, dipoles, quad-poles, polarized) by which the dependence of the interaction force on the distance is defined.

Quantum and wave effects are characteristic for interaction via the ether of vibrational systems (bonded charges).

In order to even make an approximate semi-quantitative evaluation of the offered hypotheses nowadays, we need to have some important experimental data (we don't know the charge of the Sun). As compared with the generally accepted theories, the offered hypotheses, to a great extent, yields to the long accepted, long elucidated comparisons of theoretical and experimental results. Indeed, all the experimental results, presupposed by the existing theories, wonderfully coincided with the calculations.

However, the effects that are accepted as principle ones in the offered hypotheses of the existing theories (presence of charges in bodies, in ether) were not discriminated, which causes doubt in regard to the correctness of the coincidence of the theoretical calculations and the experimental results.

From the viewpoint of the IPEV criteria, the offered hypotheses are more favorable than the old ones because of the exclusion of additional essences (field, gravitation, additional postulates, quantum mechanics, CTO and OTO). ???

The exclusion of additional essences makes these hypotheses more understandable than do the modern theories; which explains the interest to these hypotheses that the authors wish to convey to the readers.

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