

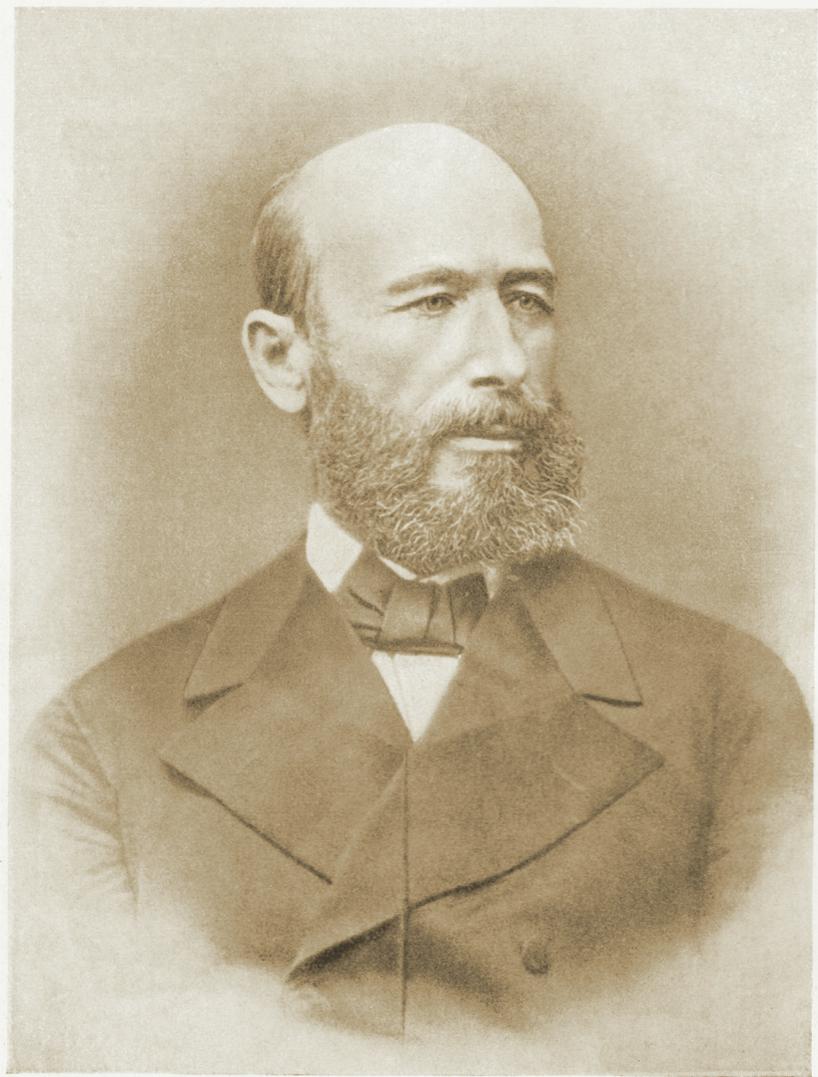
A.I.KONOVALOV

# THE BUTLEROV THEORY

OF CHEMICAL STRUCTURE OF ORGANIC COMPOUNDS

REPORT ON THE INTERNATIONAL CONGRESS ON  
ORGANIC CHEMISTRY

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*Ed. S. Myer*

# Introduction

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Almost exactly 150 years ago, on September, 19 1861 (i.e. the difference is because of difference in calendar styles) in the German city Speyer at the 36 German Naturforscherversammlung the 33-year old professor of the Kazan university A.M.Butlerov made his report “On the structure of substances”, in which for the first time he presented the initial statements of his views concerning the chemical structure of matter. I emphasize “the chemical” structure of substances. In this there is the peculiarity of his approach. The theory was being developed and improved over decades. But its initial essence is the same.

Today, celebrating the 150<sup>th</sup> anniversary of the creation of the theory of chemical structure, we honour A.M.Butlerov as the great Russian chemist, who is famous by his theoretical views, which defined the development of chemistry for the decades ahead, we honour the outstanding researcher who made the great contribution in different spheres of the chemical science: Butlerov’s synthesis of alcohols, polycondensation of formaldehyde with producing of sweetening agent (reaction of A.M.Butlerov), synthesis of isobutylene and research of its acid-catalyzed polymerization, research of pinacolic rearrangement. Yes, J.Berson recently demonstrated that exactly A.M.Butlerov *«recognized one of the first rearrangements of carbon skeleton.»*

We honour A.M.Butlerov as the creator of the greatest scientific school. Later I will call the well-known names of the outstanding representatives of this school.

We honour A.M.Butlerov as the head of the Russian chemists of the second half of the XIX century. But I will talk about this later.

Today there is the anniversary of the theory of chemical structure of the organic substances. In my report I will say exactly about it. But, let’s talk about all one after another. The order is the following:

- Summary of biography of A.M.Butlerov,
- The theory exposition of the chemical structure of the organic compounds and views of A.M.Butlerov of nature of chemicals,
- Role of A.M.Butlerov as the head of the scientific school and the leader of the Russian chemists.

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So, A.M. Butlerov was born on September, 3(15) 1828, and he spent his childhood in the family estate Butlerovka. By origin A.M. Butlerov was a nobleman. Mother of A.M. Butlerov Sofia Alexandrovna died on the eleventh day after her son's birth. At first the child's aunts brought him up. But his father Michael Vasilievich Butlerov greatly influenced the formation of his personality. He promoted him love for nature, got him used to independence, and not only in actions, but in thoughts as well. M.V. Butlerov was an artilleryman, war veteran with Napoleon. From Paris he came back with some freethinking. He resigned as a lieutenant colonel. He taught Sasha to make fireworks.

From the age of 8 A.M. Butlerov was brought up in the well-known in Kazan boarding school of Topornin. And here one very remarkable incident happened. A.M. Butlerov was making components of firework in the kitchen, and suddenly – explosion. Sasha was not harmed, but he was punished. The punishment was the following: in the dining room of the boarding school he was put in front of all pupils with the tablet on the chest with the inscription “Great Chemist”. Well, the teachers were right. A.M. Butlerov really became the great chemist.

After graduating the gymnasium in 1844 A.M. Butlerov – at the age of 16 – was enrolled to the natural department of the physico-mathematical faculty of the Kazan Imperial university. A.M. Butlerov was lucky. At that moment N. Lobachevsky, the founder of the non-Euclidean geometry, was the rector of the university. The famous chemists worked at the university, and they became his teachers: N.N. Zinin, who was the first who synthesized aniline from nitrobenzene and thus laid the foundations of the aniline-dye industry, and K.K. Klaus, discovered the element rhenium.

In 1849 A.M. Butlerov graduates from the university with the scientific degree of candidate, presented the work “Diurnals the Volga-Ural fauna”. The collection of butterflies of A.M. Butlerov has still been keeping in the zoological museum of the university. At that time A.M. Butlerov was keen on

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botany, zoology and, in particular, entomology. But chemistry as well. And the university makes the decision to prepare A.M.Butlerov for the rank of professor. Here is the decision of the faculty:

*“The faculty, from its side, is absolutely sure that Butlerov – with his knowledge, gift, love to sciences and to the chemical scientific research – will be an honour to the university and will deserve the reputation in the scientific world if circumstances favour to his scientific mission”*[1].

It happened exactly so.

In 1851 A.M.Butlerov defended the Master dissertation “On the oxidation of the organic compounds”. The conclusion of the work which is not directly relevant to the topic of it is very remarkable. But first I will remind you the words of F.Wöhler, referred to 1828– the year of birth of A.M.Butlerov.

*“Nowadays organic chemistry can drive mad anyone. For me it is like a thick wood full of fantastic things, the enormous endless depths without exit where you do not dare to enter”*[2].

But here are the words of 23-year old A.M.Butlerov. They are interesting that they characterize the mental state of mind of the young scientist, his mentality. Ten years are left before the formulation of his theory! But what an idea!

*“We cannot but wonder – having look back – what an enormous step our organic chemistry made during the short period of its existence. Although, it has ahead of it incomparably more; but the time will come when the products of the organic conversion will be examined not only qualitatively, but quantitatively as well, when – step by step – their genuine exact laws will be discovered and defined, and their bodies will take their natural places in the chemical system. This time can and must come for our science, and meanwhile, how much effort for the inquiring mind is ahead!”*[3]

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This is a program. And we lived, and live now in time when – from level to level – this program is implemented. And the theory of the chemical structure prepared this time.

1854 is the year of the defence of the dissertation for the doctor scientific degree “On the essential oils” and the confirming in the rank of the extraordinary professor of chemistry and physic of the Kazan university.

It is necessary to say that in 1847 N.N.Zinin leaves Kazan and moves to Saint-Petersburg. He was elected as a professor of the Medical-surgical academy. The year of 1852, K.K.Klaus moves to the Derpt, now Tartu, university. N.N.Zinin becomes the academician, and K.K.Klaus – the corresponding member of the Academy of Sciences of Saint-Petersburg. All burden of the teaching of chemistry falls on the shoulders A.M.Butlerov. But it is not only the burden – it is the stimulus as well: from what positions, on what theoretical basis to teach?

This time A.M.Butlerov – thanks to N.N.Zinin – holds the views of Ch.Gerhardt and A.Laurent, but he comes to the conclusion that the typical formulas are too narrow for the factual condition of chemistry of that time.

In 1857 A.M.Butlerov goes abroad to the 1-year business trip to the Western Europe. He visits all the best laboratories of Germany, France, Switzerland, Italy, England. He gets acquainted with H.Kolbe, A.Kekule, R.Bunsen, E.Erlenmeyer and other west-European scientists. But the main part of his time he spends in Paris in the laboratory of A.Wurtz, and, what is especially important becomes the member of the Paris chemical society, where at that moment all vital problems of chemistry are discussed. He was elected the member of the Society on December, 22 1857. In two weeks A.Cooper becomes the member of the Paris chemical society.

A.M.Butlerov takes an active part in the activities of the Society and on February, 17 1858 he makes the report “On the body structure”. For a very long time the protocols of the meetings of the Paris chemical society for the 1857-1858 years were considered to be lost. They were published in the

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Bulletins of the Society only in 1953, almost 100 years later. Unfortunately, the text of the report, which was referred in the protocol to, is not still found. The records in the protocol say:

“- *Sir Butlerov tells the members of the Society about the body structure in general.*

- *Sir Rosen thanks sir Butlerov for his great report on behalf of all members of the Society and says about his strong wish that this theoretical research that is of great interest should be continued”*[4].

A.Cooper attends the report of A.M.Butlerov and after some time on June, 23 1858 he presents his report to the Society, but by this time A.M.Butlerov had already left Paris. The complete updated text of the report of A.Cooper in the form of the article “On the new chemical theory” was published in French, German and English in 1858. A.Cooper was not published ever again.

I have to say that in April 1858 the article “On the constitution and transformations of the chemical compounds and the chemical nature of carbon” by A.Kekule was published.

After coming back to Kazan, in 1858 A.M.Butlerov was confirmed as ordinary professor. In that time he keeps on thinking over the situation in chemistry and he works out his own approach to the problem. Apparently, by the beginning of 1860 generally he has already defined his views, as far as, according to V.V.Markovnikov, in 1860-1861 he gave the course of lectures of organic chemistry already on the basis of the theory of the chemical structure.

A.M.Butlerov feels the necessity to bring his views to the chemical society by direct communication with west-European scientists and in 1861 he goes abroad to the second business trip. He again visits the laboratories of Germany, Belgium, France, but, the most important, on September, 19 1861 on the 36 German *Naturforscherversammlung* in Speyer he makes the report “On the chemical structure of substances” where he describes the main



### Einiges über die chemische Structur der Körper.

Von Prof. Dr. A. Butlerow.

(Vorgetragen in der chemischen Section der 36. Versammlung deutscher Naturforscher und Aerzte zu Speyer am 19. Septbr.)

Bei dem gegenwärtigen Zustande der Chemie, wo wir in den Besitz einer Masse ebenso unerwarteter als interessanter Thatsachen gekommen sind, lässt es sich ziemlich allgemein fühlen, dass die theoretische Seite unserer Wissenschaft ihrer thatsächlichen Entwicklung nicht genug entspricht.

In der That, die jetzt fast allgemein angenommene typische Betrachtungsweise, obgleich sie erst vor wenigen Jahren entstanden, und für die Entwicklung der Chemie ungemein fruchtbar gewesen ist, genügt uns doch kaum.

Es sind sogar in der neuesten Zeit einige Thatsachen entdeckt worden, welche viel mehr für die Wahrheit mancher älteren Ansichten sprechen. In der That spricht die Bildung der von Wurtz neu entdeckten Oxyäthylbasen zu Gunsten der Ansicht von Berzelius, welcher die Alkaloide als copulirte Ammoniake betrachtete, und die Aethylen-theorie der Aethylverbindungen erscheint bis zu einem gewissen Grade richtig, wenn man der Bildung des Alkohol's aus Aethylen und Wasser, der Bildung des Jodäthyl's aus Aethylen und Jodwasserstoff u. s. w. gedenkt.

Die Sache ist so, dass die Mehrzahl der älteren und, ebenso die neue Ansicht, nur einem gewissen Kreis von Thatsachen angemessen sind, und zwar denen, auf welche sie sich hauptsächlich stützen.

Dieser Kreis ist natürlicherweise viel grösser für die neue Ansicht.

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statements of the theory of the chemical structure of the organic compounds. I have already said that I will say a little bit late about its essence.

Coming back to Kazan, A.M. Butlerov starts the research in which the theory of the chemical structure is the guiding pole-star. These are the works on the explanation, proof and, what is very important, synthesis of the previously unknown but following from the theory isomers. In 1863-1864 the following articles are published:

- “On different explanations of some cases of isomerism”.
- “On tertiary pseudo butyl alcohol”.
- “On systematic application of the principle of atomism (valence) to forecast the cases of isomerism and metamerism”.

These are the landmark articles in the development of the ideas of the theory of the chemical structure.

At the same time at that moment A.M. Butlerov started to write the textbook “Introduction to the complete study of the organic chemistry”.

The first edition of the textbook in Russian was published in 1864. The publication was fully completed in 1866. And in 1867-1868 in Leipzig the textbook was published in German.

In my opinion, the publication of the Butlerov’s textbook is the historical event in chemistry. For the first time the textbook which was not only based on the theory of chemical structure but also penetrated by this theory was published. The ideas of the theory of chemical structure are consistently led through all classes of the organic compounds. The structure of the textbook is also new in a way. There was no such textbook before A.M. Butlerov. And it is no coincidence that, according to the words of the long-term employee of H. Kolbe Ernst von Meyer, the famous author of “History of chemistry”, “*Butlerov greatly influenced especially by his textbook of the organic chemistry*”[5]. The modern American historian of chemistry D. Lewis echoes him: “*It was the most influencing textbook of that time*”[6].

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In 1868 on the proposal of D.I.Mendeleev A.M.Butlerov was elected the ordinary professor of the Saint-Petersburg university. Here are the words from the recommendation of D.I.Mendeleev:

*“A.M.Butlerov is one of the outstanding Russian scientists...The student of our famous academician N.N.Zinin, he became the chemist not in other countries, but in Kazan, where he continues to develop the independent chemical school. The direction of the scientific work of A.M.Butlerov is not the continuation or development the ideas of his predecessors, but it belongs to him. In chemistry there is the Butlerov’s school, the Butlerov’s direction”*[1].

In 1868 A.M.Butlerov was 40 years old. He leaves Kazan and moves to Saint-Petersburg. Here he continues his research and pedagogical activities. From the works connected with the theory of chemical structure I would like to say about two articles: “Contemporary importance of chemical structure” (1879) and “Chemical structure and theory of substitution” (1882). A few statements of these articles will be considered later.

It is necessary to say that in 1870 A.M.Butlerov was elected as the adjunct, and then – the extraordinary academician, and in 1874 – the ordinary academician of the Saint-Petersburg Academy of Sciences.

His scientific authority increases. In connection with the successful development of the theory of chemical structure the number of his students who play the leading role at the main universities of Russia increases. N.N.Zinin was elected the first President of the Russian chemical society founded in 1868, A.M.Butlerov was the next.

In A.M.Butlerov the Russian scientists saw not only the founder of the scientific school but also the person who was the symbol of the Russian chemical science, the head of the Russian chemists.

The activities of A.M.Butlerov in the Free economical society is very great; there he was the chairman for several years. Being a beekeeper, he actively promoted the methods of the rational beekeeping and published a few manuals on beekeeping.

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A.M.Butlerov was an energetic supporter of the education of women. He was the professor of the Higher courses of women in Petersburg. By the way, one of the first woman-chemist Yu.M.Lermontova held the research work in the laboratory of A.M.Butlerov.

The fruitful scientific-pedagogical activities of A.M.Butlerov ended up very suddenly. A.M.Butlerov died on August, 5 (18) 1886, 125 years ago, at the age of 58 in his estate Butlerovka where he was buried.

Some time after the death of A.M.Butlerov the collection of public money to mount a monument to the great scientist was announced. But the following events of the Russian history did not allow this project to be implemented. The monument to A.M.Butlerov was mounted in Kazan in 1978, in the year of his 150-anniversary. The authors of the monument: the sculptor Yu.G.Orekhov, the architects V.A.Peterburzgtzev and A.V.Stepanov.

But there is monument that was not made by hands – it is the scientific legacy of A.M.Butlerov, and, first of all, his theory of structure of chemical compounds.

However, it is necessary to say that the situation here is ambiguous and questionable.

In general, between the Russian chemists there was the point of view, according to which they give the due to A.Kekule and A.Cooper in creation of structural concepts but it is considered that A.M.Butlerov takes his place in this row by right, with good reason as well. Alas, in the western educational literature the role of A.M.Butlerov is either underestimated or kept silent about. I will not analyse the reasons of this situation. There are some. I will just say that historiography – according to the estimate of role of A.Kekule and A.M.Butlerov – is very great. Some authors give preference to A.Kekule, the others – to A.M.Butlerov. In general one of the problems of many foreign authors is that they do not have enough information about all works of A.M.Butlerov. By the way, the Russian scientists would be in the same situation if not the great work of

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the Commission of the development of the scientific legacy and publishing of the works of A.M.Butlerov under the chairmanship of the academician B.A.Kazansky and the scientific secretary of the Commission G.V.Bykov. G.V.Bykov did very great work as far as he studied thousands of the original works of western European, as well as Russian chemists of the XIX century, so to study objectively the situation with the development of theoretical views in organic chemistry and experimental facts which were the basis of it. The edition is full of remarks of the editorial staff. I bow my head and admire his work.

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So, Butlerov's theory of the chemical structure of organic compounds.

Now I am going to describe my vision of the contribution of A.M.Butlerov in creation and development of the theory of chemical structure of organic compounds. I am not going to say about debatable questions, but I would like to make a few comments. As I have already said, I will tell you about wider views of A.M.Butlerov on the nature of chemical compounds so that the audience would see more vividly the figure of this thinker. A.M.Butlerov is a very deep scientist, and I dare to say only A.M.Butlerov managed to understand so deeply the essence and meaning of the ideas that were described in the theory of chemical structure. It's natural. The theory is his, exactly his, brainchild. He gained it. Gained in struggle, as far as it is impossible to say that it was accepted with enthusiasm.

The notion "Chemical structure» A.M.Butlerov introduced in his report in Speyer in 1861. But what was before the introduction of this notion?

The chemists defined the notion "molecule" (particle, body), the components of molecules – "atoms" (although here there are some details, and later I will say about it). The notion "valence" (atomicity) was introduced. In the works of the 1857-1858 years A.Kekule and A.Cooper find out that the

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atom of carbon, the basis of organic compounds, is tetravalent (four-valence). There is the conclusion that atoms of elements join in molecules according with their atomicity. Atoms of carbon in molecules of organic substances can join with each other so to provide the variety of organic compounds. What's next? Nothing special. Unfortunately, A.Cooper left the game. A.Kekule writes the textbook on organic chemistry, its first edition was published in 1859. The theory of types of Ch.Gerhardt is in its basis. And it was so until September 1861, until the report by A.M.Butlerov. In his report A.M.Butlerov first says that *"nowadays the theoretical side of chemistry does not correspond with its actual development"* and then he criticizes the theory of types of Ch.Gerhardt and makes a statement: *"now only atomicity, constituting the definite and constant characteristic of elements, can be the basis of the general theory"*, and he introduces the notion *"chemical structure"*[7]. What does A.M.Butlerov understand by chemical structure? Here is his definition:

*"Coming from the idea that every chemical atom, constituting the body, takes part in formation of the body and acts here by the definite quantity of chemical power belonging to it (affinity), I call the distribution of influence of this power, as a result of which chemical atoms - directly or indirectly influencing each other - join and constitute the chemical particle, as the chemical structure».* And then: *"I think that for now it is possible to change the well-known rule, saying that the nature of complex particle is determined by nature, quantity, and arrangement of elementary components, is possible to change in the following way: chemical nature of the complex particle is determined by nature of elementary components, their quantity and chemical structure"*[7].

It is necessary to comment the above-mentioned things.

First, I have to admit that from the above-mentioned definition it is

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not easy to understand at once what the chemical structure is. If to think it over – everything is right. However, is it possible to make it easier? Yes, it is possible. And A.M.Butlerov did it himself in his textbook where chemical structure is the order (in the Russian variant of the textbook) or the sequence (in the German edition) of the mutual chemical bonding (interaction) of different elementary atoms in the molecule.

But this corresponds to our understanding of the structure of the molecule. It's absolutely right. And the American scientist D.Lewis is right when he says that «A.M.Butlerov was the first who introduced the notion “chemical structure” that corresponds with our contemporary notion»[6].

And – nevertheless, why chemical structure – and not simply structure – and why chemical atom – and not simply atom?

Here is the essence of the approach of A.M.Butlerov. The point is that at that time atomism was just hypothesis. Later, explaining the theory of structure, A.M.Butlerov says:

*“What is atom and does it really exist? For the chemist atom is the least quantity of the element consisting the particle. In this sense atom is as real quantity as the particle. The question is if we deal with the real atom, that final, non-divisible last particle of matter, for the chemist the question is irrelevant (as for me, I rather deny such atom)”[8].*

Now I am not going away from the main topic, but later – as far as I promised to show A.M.Butlerov-thinker – I will give comments concerning of Butlerov's negation of indivisibility of atom. Now I will only say that it is not just an occasional phrase, it is the point of view of A.M.Butlerov.

For us in the given quotation it is important that A.M.Butlerov says: atom in the chemical sense, i.e. chemical atom is reality. Physical (real) atom is hypothesis, but on this stage we do not need it! A.M.Butlerov deliberately simplifies the situation.

In the article “On different ways of explanation of some cases of isomerism” A.M.Butlerov writes:

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*“The atomistic hypothesis (in the physical sense) – although it is probable – but now, at least for chemistry, it is absolutely unnecessary”*[9].

Why does A.M.Butlerov deny the necessity to consider the ideas concerning physical atoms so energetically?

Because now these ideas – are really unnecessary but not harmless – for the idea that A.M.Butlerov offers.

Because first Ch.Gerhardt, and then A.Kekule use the notion “constitution of the molecule”, understanding under constitution the arrangement of atoms (physical atoms) in space:

*“The molecular constitution of bodies is the genuine arrangement of its atoms”*[10].

But, according to Ch.Gerhardt, chemistry that deals with the matter in the condition of transformational change, cannot judge about the mechanical body structure and, according to A.Kekule, *“the rational formulas are just formulas of transformation, and in no case the constitutional formulas”*[11]. Is it a deadlock? No, - says A.M.Butlerov. On this stage we do not need to know *“the genuine arrangement of atoms”*. We just need to know the chemical relations of the elements constituting the body structure – and this is the chemical structure of body (molecule). This is the idea of simplification.

*“We do not know the connection, - says A.M.Butlerov before giving the definition “chemical structure”, - that exists inside the complex particle between the chemical interaction of atoms that constitute it and their mechanical arrangement, - we do not know, for example, if the atoms, chemically influencing each other, adjoin close to each other, but nevertheless, even when we will not talk about the notion “physical atoms”, it will be impossible to deny that chemical characteristics of the complex body are appointed mainly by chemical relationship of constituting it elements”*[7].

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The last part of the sentence is underlined by me. In this part there is the main idea of the theory of chemical structure: chemical characteristics of compounds depend on their chemical structure (but only preferably).

That is why: *“Coming from the idea... and so on”*. And it becomes very evident why A.M.Butlerov says not about the molecule structure in general, but exactly about chemical structure. We also understand changes in the definition of “well-known rule...” when the words “arrangement of elementary constituent parts (of molecule)”, presupposing the spatial arrangement of atoms, are changed to the notion “chemical structure”.

So, does A.M.Butlerov denies to consider the spatial arrangement of the molecule? No way. He says: *“now, at that moment, for the time being”*. But,

*“If atoms really exist, I do not see, why – how H.Kolbe thinks – all attempts to establish their spatial arrangement should be vain, and why it is impossible to learn to define it in the future?”*[9]

That's it.

As for the transformed rule, A.M.Butlerov says:

*“I am far from considering the rule quite true and expressing all conditions which properties of matter depend on, but having accepted it, we will deal with such problems that can be solved by a chemical experiment. It will be already a step forward ... The further development of the view expressed here will show how much chemical properties of substances depend on chemical structure”*[7].

Then A.M.Butlerov says that will be found and *“what cross influence two atoms (that do not chemically influence each other) in a molecule can have»*.

Then there is the statement: *“The possibility to say about the chemical structure is sufficiently proved by the present condition of our knowledge”*[7]. And A.M.Butlerov shows on the basis of what reactions and how it is possible to make conclusions concerning chemical structure. It's synthesis, and

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decomposition, and double decomposition (exchange reactions). And pay attention to the following words:

*“There are such transformations, at which the chemical role of some shares changes, and consequently – the structure”*[7].

But this is rearrangement!

Then the set of rules concluded from the facts that may help to recognize the chemical structure *“with the present state of knowledge”* follows.

And, finally, (listen attentively, think it over!):

*“If to try now to define the chemical structure of substances, and if we manage to express it (i.e. chemical structure) by our formulas, these formulas will be, although not absolutely, but to some extent, the real rational formulas. In this sense for every body it will be only one rational formula, and when the general regularities of chemical characteristics of bodies from their chemical structure become known, then the formula will be the expression of all these characteristics”*.

And then:

*“Time and experience will show better what the formulas of chemical structure should be”, i.e. structural formulas in our contemporary understanding. But A.M.Butlerov says: “Typical formulas in their actual understanding should... come out of use... The point is that these formulas are narrow for the present condition of science”*[7].

Here it is necessary to make some comments. A.M.Butlerov makes several important statements.

First, according to A.M.Butlerov, for every substance only one formula expressing its chemical structure, i.e. the order of connection of atoms in molecule, is possible. In this article A.M.Butlerov calls such formulas real rational formulas”. In his textbook A.M.Butlerov writes: *“It will be fair with*

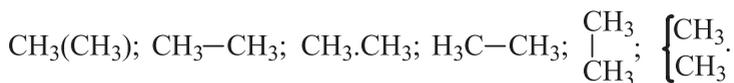
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*the actual condition of science – to give the name rational only to formulas which express chemical structure[12]*". We remember that – according to A.Kekule in accordance with the theory of types – every substance can be expressed by several formulas, but these are the formulas of transformation, and not of the atoms' arrangement

Second, it is important that A.M.Butlerov again emphasises the dependence of chemical characteristics of substances from their chemical structure.

Third, A.M.Butlerov thinks that typical formulas in their "actual" meaning should go out of use. This circumstance is important because sometimes we hear that A.M.Butlerov, in spite of all his declarations, goes on using typical formulas. I assert that it is not so. All formulas written by him are the formulas of chemical structure, but the method – alas – reminds typical formulas. A.M.Butlerov himself (I think we have to say – unfortunately) considered the way of writing the formulas as "the secondary question". According to A.M.Butlerov [13], the main is "not in the form, but in the essence, in the notion, in idea". And formulas of particles must express "some chemical relations existing in it". It's important that the method "conveniently expresses these relations". These formulas can be "detailed or short-cut" [12]. Later A.M.Butlerov showed this on the example of ethane [13].



A.M.Butlerov finished his report by the following words:

*"I only wanted to say that it is time to found our understanding concerning the chemical constitution of substance on the ideas of atomism and chemical structure, to give up typical views, and these ideas probably promise to help to the actual inconvenient position of chemistry"*[7].

Thus, A.M.Butlerov presented complete, deeply thought over, carefully

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and comprehensively worked conception which allowed to look at the chemical world of molecules in interrelation with chemical atoms forming them absolutely in a new way. The revolutionary conception, as far as the ideas of the theory of types were consciously denied and new ideas and notions were introduced in it. But fairness and efficiency of the conception demanded additional proofs. And A.M. Butlerov brilliantly finds such proofs, absolutely logically applied to the explanation and the prediction of isomerism of organic compounds.

Why do I say absolutely logically? It's evident. The basic situation of the conception of chemical structure says: *“chemical structure of the particle is defined by nature of elementary components of it, their quantity and chemical structure”*. Thus, if two or more substances have the same qualitative and quantitative composition, but different characteristics, they should have different chemical structure. And what are isomers? Isomers are substances with the same qualitative and quantitative composition, but different characteristics. It means that isomers are substances with different chemical structure of their molecules with the same qualitative and quantitative composition! And in 1863-1864 there was the series of works that I have already said about:

- On different explanations of some cases of isomerism”[9];
- “On tertiary pseudo butyl alcohol”[14];
- “On systematic application of the principle of atomism (valence) to forecast the cases of isomerism and metamerism”[15];

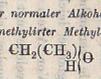
In these works A.M. Butlerov shows: yes, it is really so. The reason of isomerism is in the different chemical structure of molecules.

The work “On tertiary pseudobutyl alcohol” was of principal importance. In this work A.M. Butlerov intentionally synthesizes tertiary butyl alcohol and on this basis derives the series (rows) of all alcohols. Methyl and ethyl alcohols cannot have isomers. But, starting from propyl alcohols, isomers appear. In his consideration A.M. Butlerov stops on amyl alcohols

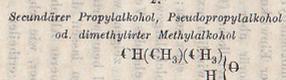
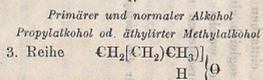
Man hat:  
1. Reihe



2. Reihe



3. Reihe



Primäre	Alkohole	3.
1. Normaler Butylalkohol od. propylirter Methylalkohol od. äthylirter Aethylalkohol	2. Dimethylirter Aethylalkohol od. primärer Pseudoämylalkohol	3. Secundärer Pseudoämylalkohol od. methyl-äthylirter Methylalkohol
4. Reihe $\text{CH}_2(\text{CH}_2)(\text{CH}_2)(\text{CH}_3)\left\{\begin{matrix} \text{O} \\ \text{H} \end{matrix}\right\}$	4. Tertiärer Pseudoämylalkohol od. trimethylirter Methylalkohol	$\text{CH}(\text{CH}_2)(\text{CH}_3)\left\{\begin{matrix} \text{O} \\ \text{H} \end{matrix}\right\}$

5. Reihe.

Primäre	Alkohole	3'
1. Normaler Amylalkohol od. butylirter Methylalkohol od. propylirter Aethylalkohol	2. Dimethylirter Propylalkohol, (ein primärer Pseudoämylalkohol)	3' Methyl-äthylirter Aethylalkohol (ein primärer Pseudoämylalkohol)
$\text{CH}_2(\text{CH}_2)\left[\text{CH}_2(\text{CH}_2)(\text{CH}_3)\right]\left\{\begin{matrix} \text{O} \\ \text{H} \end{matrix}\right\}$	$\text{CH}_2(\text{CH}_2)\left[\text{CH}(\text{CH}_3)(\text{CH}_3)\right]\left\{\begin{matrix} \text{O} \\ \text{H} \end{matrix}\right\}$	$\text{CH}_2\left[\text{CH}(\text{CH}_3)(\text{CH}_3)\left\{\begin{matrix} \text{O} \\ \text{H} \end{matrix}\right\}\right]\left\{\begin{matrix} \text{O} \\ \text{H} \end{matrix}\right\}$
4. Trimethylirter Aethylalkohol (ein primärer Pseudoämylalkohol)	5. Dimethylirter Methylalkohol (ein secundärer Pseudoämylalkohol)	6. Methylpropylirter Methylalkohol (ein secundärer Pseudoämylalkohol)
$\text{CH}_2(\text{C}(\text{CH}_3)(\text{CH}_3)(\text{CH}_3))\left\{\begin{matrix} \text{O} \\ \text{H} \end{matrix}\right\}$	$\text{CH}(\text{CH}_2)(\text{CH}_3)\left\{\begin{matrix} \text{O} \\ \text{H} \end{matrix}\right\}$	$\text{CH}(\text{CH}_2)(\text{CH}_2)(\text{CH}_3)\left\{\begin{matrix} \text{O} \\ \text{H} \end{matrix}\right\}\left\{\begin{matrix} \text{O} \\ \text{H} \end{matrix}\right\}$
	7. Tertiärer Pseudoämylalkohol oder dimethyl-äthylirter Alkohol	
	$\text{C}(\text{CH}_2)(\text{CH}_3)\left\{\begin{matrix} \text{O} \\ \text{H} \end{matrix}\right\}\left\{\begin{matrix} \text{O} \\ \text{H} \end{matrix}\right\}$	

Die Theorie geht hier also bedeutend weiter als die Versuche; diesen letzteren aber müssen wir die Entscheidung der Frage, ob alle theoretisch möglichen Alkohole wirklich existenzfähig sind, überlassen.

## Butlerov's theory

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as far as the number of isomers increases like an avalanche. We know this very well. He makes the conclusion *“that existing facts allow to assume the existence of very big quantity of isomeric alcohols... consequently, here theory goes further than experiments ...»* [14].

In the article “On systematic application of the principle of atomism (valence) to forecast the cases of isomerism and metamerism” A.M. Butlerov sets a goal – to show how – based on atomism – it is possible to derive formulas of chemical structure of all theoretically possible isomers of different organic compounds. He makes it only for two-carbon systems containing different number of atoms of oxygen and hydrogen and gets about 100 formulas. I demonstrate it on the example of the first line of all table information. So, on the basis of ethane it is possible to present the row of its hydrate-derivatives. Already on this example it is clear that some part of formulas corresponds to really non-existing compounds. A.M. Butlerov understands this and thinks that it is necessary to determine *“which molecules that are possible in accordance with the principles of atomism and chemical structure really exist”*, and to give the answer to very reasonable question, *“why some molecules are not able, and the others are able to exist”*[15].

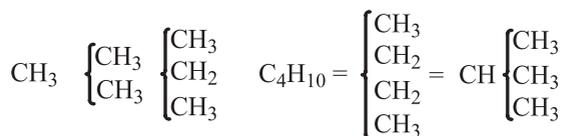
It's interesting that in the same article A.M. Butlerov makes a question concerning isomerism of the saturated hydrocarbons. The point is that at that time isomerism of the saturated hydrocarbons was not studied well enough. But A.M. Butlerov says with reason that, if for the first three members of the row of the saturated hydrocarbons – methane, ethane and propane – isomerism is principally impossible, in case of butane it can be two isomers, and in case of pentane – three, and so on. It's interesting how this section is presented in the Butlerov's textbook. First isomerism of the saturated hydrocarbons is stated *“according to theoretical ideas”* in full compliance with what has just been said, and then in the Russian edition (1864) there is the statement: *“There are almost no any facts related to isomerism of saturated hydrocarbons”*. In the German edition (1868) this phrase is given in different



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way: "Facts related to isomerism of saturated hydrocarbons became known only recently". The point is that in 1867 A.M. Butlerov got isobutane and compared its characteristics with characteristics of the known normal butane. A.M. Butlerov wrote: "It is impossible to doubt that two hydrocarbons  $C_4H_{10}$  are really not identical, but only isomeric between each other. They present the first case in which isomerism of saturated hydrocarbons is explained, chemical structure of particles is well-known and which was previously foreseen by the theory" [16]. We will add – by the theory of chemical structure of organic compounds of A.M. Butlerov. Many famous chemists of that time studied the reasons of isomerism, but this phenomenon is studied systemically and fully only in the works of A.M. Butlerov. Explanation and prediction of isomerism, synthesis of predicted by the theory isomers is the triumph of the theory of structure of organic compounds.



But A.M. Butlerov goes further. Based on the facts – how we say today – of the dual reaction of some compounds he comes to the conclusion about the possibility of simultaneous existence and interconversion of such compounds [17]. As we know, later this phenomenon got, according to C. Laar, the name "tautomerism".

D.I. Mendeleev, initially being the opponent of the views of Butlerov in 1889 gives his due to "structural theory" by the following words: "This theory led so brilliantly to understanding of many chemical relations and case of isomerism or difference of characteristics with the same composition and it is so successful in the great number of its applications and further consequences concerning carbon compounds, that it's necessary to accept it as great success of chemical knowledge" [18]. We have to say that then D.I. Mendeleev saw his task in the following: "to reconcile the structural theory with the dynamics of

# Butlerov's theory

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Newton”, as far D.I.Mendeleev was “*the follower of the universality of Newton's Principia*” and compared chemical compound with astronomical system. It was the reason of his initial non-acceptance of “structural theory”. Not only D.I.Mendeleev had such point of view.

By the way, and what were the views of A.M.Butlerov? I will give only some his statements which, among other things, were reflected in his textbook. It is important.

*“Joint stay of atoms in the particle, in some definite mutual interaction, we call chemical compound. Conventionally we say that atoms between themselves are connected or bound, but by that we do not mean either any real fixing atoms to each other, or their relative immobility”[19].*

And also:

*“Now we look at chemical compound as not at something dead, immovable; vice versa, we understand that it is capable to move constantly, and this ability is in his smallest particles”[20].*

Why A.M.Butlerov thought this way will be clear from the further information. Now I will say about my supposition (it is only supposition, nothing more) that such view was the reason why A.M.Butlerov did not use hyphens between atoms or groups of atoms in his formulas for a very long time, preferring to use the set of different brackets (from here – similarity of his formulas with the typical ones). Hyphens are the attaching of atoms to each other; it is deprivation of their mobility. But let's listen:

*“It is impossible to doubt that composition of substances and all their characteristics, chemical and physical, are in casual interconnection. According to this, the full explanation of laws controlling the activities of matter – its evidences, can be reached only by thorough study of all characteristics in their interdependence”[21].*

This idea gets its development:

## Butlerov's theory

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*Actual connection between chemism, warmth, light and other manifestations of the activity of matter is evident: "light is movement" is the hypothesis that is now developed until the level of almost indisputable truth; "warmth is movement": this statement became more than probably since the moment when the mechanical theory of warmth appeared and, maybe, (listen!) the person who will call all phenomena of chemism as "movement" will not be mistaken. If the time that will clarify the casual connection between all kinds of this movement comes, then phenomena of chemism will get their mechanical theory, - theory in the full sense of this word, - and, having taken its place in science as the definite part of the ensemble, this theory, together with other parts - theories of movements of another kind, will be submitted to the mathematical analysis"[22]. (I can only spread my arms.)*

As far as movement is the equivalent of energy, A.M. Butlerov offers "to call that huge amount of movement that is peculiar to atoms "chemical energy". I will say that he knew very well not only the mechanical theory of warmth but thermochemistry as well.

When I read the works of A.M. Butlerov, I have the feeling that with any discussion of problems of his time his thought was always aimed at future and he feels this future. That is why initially I wanted to call my report "A.M. Butlerov – our contemporary". Of course, in his ideas we can see some limitations connected with the condition of science at that time. But in general his idea is right. And it is true that A.M. Butlerov is our contemporary.

And now I want to come back to the question of indivisibility of atoms. In 1886 (the last year of his life) A.M. Butlerov published the essay "Main notions of chemistry" where it is said, in particular, the following: "At the beginning of this essay it was said that substances which cannot be divided until now are called elements; but chemical complexity (although it is complexity of special kind) of some of them is not impossible. (In connection with this I will

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say that A.M. Butlerov knew and did not reject the hypothesis of W. Prout stated in 1815, according to which atoms of all elements are arranged on the basis of atoms of hydrogen.) *It means that maybe the so-called "atoms" of some elements essentially... are not indivisible by their nature, but indivisible by means only available to us now... Such strict attitude to the idea of atom fully corresponds to the spirit of exact science real meaning of scientific theories*". By the way, about theories: *"The more fundamental the theory is, the more number of facts it is based on, explaining them with satisfaction, the more scepticism should be in the attitude to all new observation and finding which does not correspond with the theory..."*[23]. And then: *"Facts that are not explained by existing theories are the most valuable for science as far as exactly from their study we should expect its further development in the near future"*[24].

Again "future", as well as here:

*"It goes without saying that when we know better the nature of chemical energy, the very nature of atomic movement – when mechanic laws get here their application as well, then theory of chemical structure will fall down, as well as previous theories fell down. But, like the majority of these theories, it will fall down not in order to disappear, but in order to enter in the circle of new and wider views in the modified form. – The statement that the theory of chemical structure exists now legally, - that it had already served well – dozens of thousands of facts that were found thanks to exactly this theory and which this theory managed to predict beforehand are the evidence of it"*[25].

Dear colleagues! There are a lot of quotations of A.M. Butlerov in my report. Of course, I could say all of this in my own words. But it would be my words, my summary, my narration. But I would like that you would feel A.M. Butlerov himself and accept him *"as one of the main philosophers of the structural theory"*. This is the characteristic of A.M. Butlerov by Ch. Ingold in his letter to G.V. Bykov in 1961 [26].

# Cradle of Russian organic chemistry

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A.M. Butlerov had a lot of students and followers. From numerous students I will call the names only of those who are well-known.

Of course, first of all, it's V.V. Markovnikov, who picked up the ideas of A.M. Butlerov concerning the interaction of atoms in molecules and developed in the independent concept. Everyone knows "the rule of Markovnikov" in reactions of addition. V.V. Markovnikov laid the foundation of the chemical research at the Moscow university.

It's A.M. Zaitsev, actually the successor of A.M. Butlerov at the department of the organic chemistry at the Kazan university, known by "Zaitsev" synthesis of alcohol that proves the theory of chemical structure. The author of "The rule of Zaitsev" in elimination reactions.

It's E.E. Wagner, well-known by different research, especially in the sphere of chemistry of terpenes. He is the co-author of "Wagner–Meerwein rearrangement".

It's G.G. Gustafson, for many years being the employee of A.M. Butlerov at the Saint-Petersburg university, well-known by his research on catalytic effect of halogenides of aluminium in different organic compounds, including aromatic substances.

And finally, it's A.E. Favorsky, also the follower of A.M. Butlerov at the Saint-Petersburg university, well-known by his research of acetylene compounds.

Thanks to his talent, pedagogical gift and character in the Petersburg period of his activities A.M. Butlerov becomes first informal, and then formal (as the president of the Russian chemical society) leader of the Russian chemists.

These are characteristics of A.M. Butlerov by his followers – outstanding Russian scientists [27].

V.V. Markovnikov: *"...Teaching talent, art of experimentalist, independent development of the main theoretical questions of*

# Cradle of Russian organic chemistry

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*science – all of this together greatly influenced the followers of Alexander Mikhailovich, as well as the other Russian chemists. All of them confess that Butlerov created the independent school of Russian chemists which consider it its head.*

*No one of his predecessors had such great importance, and if to take into account the number of his followers, he has to be fairly considered the father of the Russian chemistry”.*

*A.E.Favorsky: “...A.M.Butlerov is – in our opinion, as well as in the opinion of the foreigners – the head of the Russian chemists. And of course, there is the question: why Butlerov – and not anyone else – takes this honourable place...*

*...Although in Butlerov we have the lucky combination of the philosophical mind of great capacity and the ability of skilful experimentalist, maybe he did not create the scientific chemical school if not his pedagogical talent and that charm of his personality on his followers”.*

*G.G.Gustafson: “We could always count on his attention – any time and in any circumstances. It was very rare character, and I do not know any other like his. We felt very easily and happily in his presence. Vivid good nature, sociability, nice simplicity in communication and very smart delicacy attracted everyone to him.*

*All working in the laboratory of Butlerov always have the most gratifying reminiscences of this time. And also people who did not work there, and only visited the laboratory, did not they go there attracted by the personality of Butlerov? It was the natural order of common practice that everyone goes there, local chemists, as well as guests. The laboratory of Butlerov got the importance of the scientific-social centre”.*

# Cradle of Russian organic chemistry

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Yes, A.M. Butlerov is great. He is great as the deep, thorough, foresighted and brave scientist. He is great as the attentive teacher who created the scientific school that embraced all chemical Russia by its influence. He is great as the recognized head of the Russian chemists. A.M. Butlerov is great as a person.

150-anniversary of the Butlerov's theory of chemical structure of organic compounds we celebrate in Kazan, the scientific motherland of A.M. Butlerov. Here, in the walls of the Kazan university he was a student, learning the basics of the chemical science. Here he became the great master, offered the ideas that became the guiding star in "the thick wood" of organic chemistry. Here, in Kazan in 1928 at the Mendeleev's congress devoted to 100-anniversary of A.M. Butlerov, A.E. Favorsky said: "*Bringing up Butlerov, the Kazan university thereby did a service to the Russian chemistry, as no other university, and it can fairly be called the cradle of Russian chemistry*"[28].

150 years passed from the moment when A.M. Butlerov stated his idea concerning the chemical structure of organic compounds. Many things happened during these one and a half centuries, and in many cases happened "according to Butlerov". Today we study the fine spatial structure of chemical compounds, we study molecules by physical methods. Yes, in fact, today "*products of chemical conversion are studied not only qualitatively but quantitatively as well*". The relations "structure-characteristics" are studied very thoroughly and in very different aspects. We better know "*the nature of chemical energy and the very nature of the atomic movement*". "*The laws of mechanics got their application*". (Of course, the quantum mechanics, but the principal idea of A.M. Butlerov was right) and so on and so forth.

But one thing is the same from the times of Butlerov till our days and, and I am sure, it will be the same in the future: the chemical structure of any chemical compound in Butlerov's understanding, i.e. actually the Butlerov's chemical structure – is its fundamental basis. And it means that the contribution of A.M. Butlerov in the development of chemistry will live forever.

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