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Celebration of inorganic lives: Interview with A.E. Shilov☆

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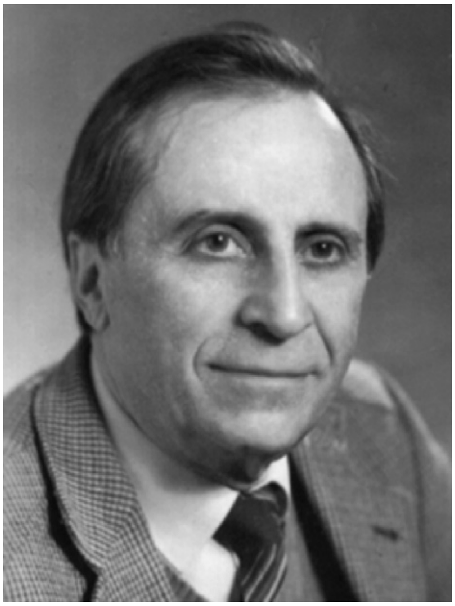

A.E. Shilov was born in 1930 in the city of Ivanovo. In 1947 he finished secondary school No. 30 in Ivanovo, receiving a silver medal. His father, Evgenii Alekseevich Shilov, was a Professor at the Ivanovo Institute of Chemistry and Technology. He was elected as a corresponding member of the Ukrainian Academy of Sciences, and in 1947 he moved to Kiev with his family. A.E. Shilov, in 1947, was admitted to the Chemistry Department of Kiev University, from which he graduated in 1952, obtaining a degree with distinction in Organic Chemistry. In 1952, after an invitation from N.N. Semenov (Nobel Prize winner for Chemistry, 1956) he was admitted to a post-graduate course in the Institute of Chemical Physics (ICP) of the USSR Academy of Sciences in Moscow, from which he graduated in 1955, having defended a thesis "Experimental research of the mechanism of the elementary act of break-down of some organic halide derivatives". After post-graduate study he started working as a research associate in the ICP. During 1958–1959 A.E. Shilov was chosen to go to Oxford (England) as a visiting researcher, where he worked for 9 months under the supervision of Nobel Prize winner Prof. C.N. Hinshelwood. In 1958 he was elected a senior research associate in the ICP, in 1962 – the Head of the Laboratory of Metallocomplex Catalysts. In the same year, he moved to Chernogolovka, where he soon became the Head of the Department of Kinetics and Catalysis, and the Deputy Head of the ICP. In 1966 he defended a doctor of science's thesis "Investigating the mechanism of initiation and branching in chain reactions". In 1972, after the reorganisation of the ICP, he became the Head of the Kinetics and Catalysis sector of the ICP, becoming the Deputy Director of the United Institute. In 1981 he was elected a corresponding member, in 1990 – a member of the USSR Academy of Sciences. In 1991 he was elected into the Academia Europaea. In 2000 he became a member of the Russian Academy of Natural Sciences. In 1994 the Institute of Biochemical Physics of the Russian Academy of Sciences was formed in Moscow, and A.E. Shilov was appointed the Director of the Institute, and in 2004 he became the Head of Research of the Institute. During his work A.E. Shilov was awarded the Order of the October Revolution, two Orders of the Red Banner of Labour, and medals. Overall, A.E. Shilov has 370 publications. He is an author and co-author of eight monographs.

Where and when were you born? Who were your parents?

I was born on the 6th of January 1930 in the city of Ivanovo, and I lived there until I was 17, when I went to university. My father, Evgenii Alexeevich Shilov, was a Professor of Chemistry at Ivanovo Institute of Chemistry and Technology, and my mother – Alexandra Gavrilovna Shilova – for a short time was a primary school teacher (Photo 1). But at one point in life my father said that it would be difficult for both to work, so someone has to sacrifice their professional career in favour of the other. My mother understood who was to make this sacrifice, agreed and became a housewife. I also have an older sister (7 years older

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Photo 1. Prof. A.E. Shilov with his mother and father in 1960. In the left corner is a photograph of Alexandra G. Shilova with her son Sasha (Alex Shilov) and daughter Nata, 1932.

than me), and also had a brother from my father's first marriage. My brother was a Professor of Mathematics at Moscow State University, he died in 1975.

Did your father influence your choice of profession?

My father was an organic chemist and studied reaction mechanisms. As a father he was not strict, he never urged me to follow in his footsteps in deciding on a profession and did not impose chemistry on me. If it were otherwise, I would never have – out of contradiction – engaged in chemistry. Even to this day I cannot manage to do anything that is forced on me as a duty.

In a broader sense, no special upbringing from my father was noticeable . . . I suppose that he was occupied with his work too much and was simply busy. But at one stage I understood that my father could answer practically any of my questions, and after that he became a teacher to me. And in life my father let me have complete freedom and did not impose his opinion and did not over-protect me; in day-to-day life, at least at first, I was closer to my mother.

Which subjects interested you in school?

In general, I noticed that during my study at school I was most interested in the things that I studied on my own. And I was not particularly attracted by any of the school subjects. Nevertheless, I studied well.

My father knew English, French and German very well, and I followed his example in this field also. In school I studied German as a compulsory language. At 22 I started to learn French on my own. I started to learn English at school, also on my own, with a teaching manual. I liked this language very much, unaccountably . . . I would read English books during German lessons, and this extremely surprised my teacher, when she used to catch me doing it. Sometimes I even got confused and answered in English, when I had to answer in German. The love for this language has lasted to this day, and even now I listen to BBC radio news every morning.

As for chemistry, I did not like it very much in school. It was "paper" chemistry and it did not seem interesting to me. Overall, because I received the best grades and was the son of a Chemistry Professor, the teachers often called me up to answer in lessons when the school was inspected. Once I was called up in Chemistry when the representative of the Gorono (the organisation which controlled the schools in the city), but, contrary to the expectations, I answered terribly and everything turned out quite stupid.

What attracted you outside of school?

In my childhood, I collected stamps, and that was my biggest passion. Also I read a lot. Books were the main entertainment of that time. At one time I read, or rather, *swallowed* a book a day. Most of all I liked detective stories and adventure literature. My father told me that I was doing “nonsense”. Although once I woke up in the night and saw him avidly reading Conan Doyle. Later I started to like Tolstoy, and then read and properly appreciated Dostoevsky.

At one point I started to collect coins and gathered a considerable collection of ancient Russian coins. My next passion was minerals. My father approved of this passion, although he used to say that mineralogy is what is created independently from man, but chemistry is what man can create himself. In my home city of Ivanovo there are not even traces of mountains, but I walked around the city and searched for minerals. At that time the roads were paved with cobbles, and I broke bits off them with a pick. Generally speaking, it was damage of state property. But for some reason nobody paid any attention to that, and luckily for me, this small-scale sabotage was left without legal consequences.

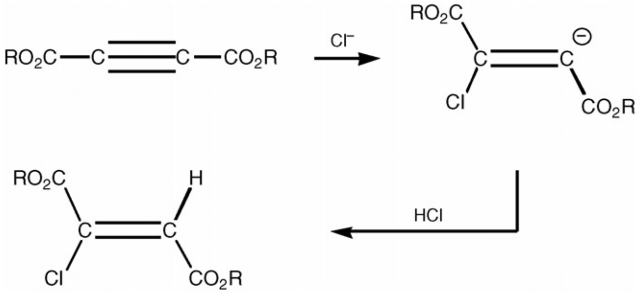
Where did you continue your education after school?

In 1945, my father was elected a corresponding member of the Ukrainian Academy of Sciences, and we moved to Kiev, where I was admitted to the Department of Chemistry of Kiev University (Photo 2). Already in the second year I and my friend Volodya Spivakovsky, under the supervision of Prof. Y.A. Fialkov, started studying peroxides and peroxy acids. Probably at that particular time chemistry started to really interest me. Later we made a report on that subject together. First one of us was explaining and the other was showing demonstrative experiments, then we changed roles. For this report we were highly praised by Prof. Izbekov, who was the Head of the Department of Inorganic Chemistry and was the chairman of the seminar. What is more, we were asked to make a presentation for higher-year students, and here, it has to be admitted, we failed. Firstly, we decided to show experiments that were too complicated, which we did not manage to do well. Secondly, we referred to some foreign publications, and at that time there was a battle against cosmopolitism.[1] After the presentation, the secretary of the Department's Communist Party bureau spoke, blaming our referencing of the publications of foreigners. We hung our heads as we listened. We were very upset.

Photo 2. A.E. Shilov in 1951.

During the first 3 years at the University, all students studied the same courses, but at the end of the third year we were to choose a specialisation, and I chose Organic Chemistry. There I did a coursework, and based on the results my first article was written, about the regrouping of aminosulphoacids [1]. It was written and published with my father as a co-author.

I did my final-year project also in my father's laboratory. At that time he worked in the Institute of Organic Chemistry, but he combined work in the Institute with work in the University, where he gave a small course “Mechanisms of organic reactions”. I remember very well my final-year project and my success. My father was in hospital, I was left on my own, and I managed to discover nucleophilic addition of a chloride ion to a triple bond. As it turned out, the rate of the reaction is determined by the addition of the halide ion to acetylene dicarbonic ester, and does not depend on the proton concentration [2] (Scheme 1).



Scheme 1. Nucleophilic addition to the CC triple bond.

My father offered to publish a paper with just me as an author, but I told him that in any case the readers would decide that it is just an error, as A.E. Shilov would appear in the article instead of E.A. Shilov.

After some time (in 1958) in London I spoke with Professor Ingold and I told him about this work. He said that he knew it, and that it was very interesting. I was very flattered.

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[1] Though the meaning of the *word* “cosmopolitism” is the same in English and in Russian, the *label* “cosmopolitism” by communist functioners in the Soviet Union implied a scornful attitude to national culture and traditions, to the extent of their full denial. This was the extreme display of nationalism (*Interviewer*).

After finishing University, how did you get your post-graduate course with Semenov?

I graduated from university in 1952 with “distinction” and was offered a post-graduate position, but at that time there was a battle against nepotism, and I could no longer stay in my father’s laboratory. At that time there was a conference in Kiev on organic chemistry, in which Nikolai Nikolayevich Semenov took part. He was not a Nobel Prize winner yet – he received the Prize in 1956. Semenov was invited to our house, he talked to me and invited me to do a post-graduate course in the Institute of Chemical Physics in Moscow, which he himself headed. He said that organic chemists are exactly what they needed in the Institute. What is more, he reassured me, saying that I should not worry about entry exams, and that they will give me an exam intermediate between physical and organic chemistry (obviously, I knew the latter much better than the former). This moment became decisive for me in choosing a place for my post-graduate study. Although in the exam, from which Semenov was absent, everything turned out not as I expected. The commission asked me a lot of questions, and the idea that the exam would be intermediate between organic and physical chemistry . . . no one knew what that meant. I answered some questions better than others, but, somehow or other, I received the highest grade and was accepted into the post-graduate course. There were seven candidates, but only two were admitted, and I was one of them.

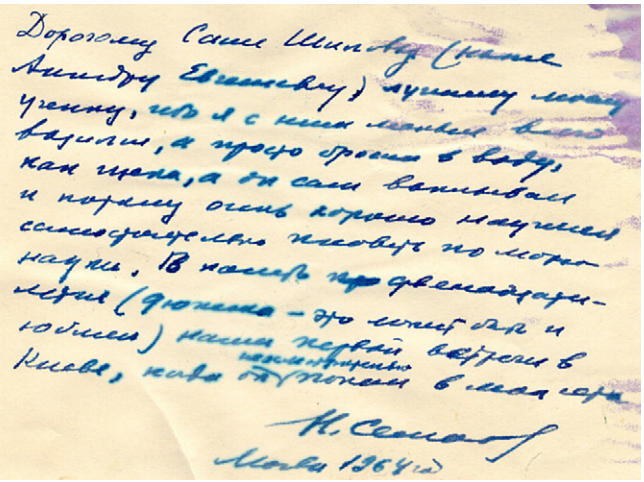
Where in Moscow did you live during your post-graduate study?

At first I lived with my cousin, then I rented a room in a wooden house from a cleaner in our Institute. A very small room with a huge bed – no one could understand how the bed got into the room through the small doorway. They said that first they put the bed, and then built the house around it. I remember that the landlady also had a malevolent cockerel, and I had to slip inside very quickly so that he did not peck me on the leg. He served as a guard dog! I lived there for 2 years or so, and then moved into a post-graduate resident hall.

Who was your post-graduate supervisor?

The study lasted from 1952 to 1955. N.N. Semenov himself became my supervisor. His style of supervision was the most suitable for me. I went to him when I needed (without limitations) for discussion. I talked with him quite rarely, but I did not have any need for more frequent discussions. Overall, Semenov always proceeded from the so-called “puppy” theory: the young scientist needs to be thrown into the “water”, and if he swims out, then it is good. If he sinks, then so be it. Although his students usually “swam out” (Photo 3).

Semenov liked me and always said that I was his last post-graduate, and, as a last child, he likes me most of all. At least that is what he wrote – best and favourite pupil. I am proud of this.



Дорогому Саше Шилову (ныне
Александру Евгеньевичу) лучшему моему
ученику, ибо я с ним меньше всех
возился, а просто бросил в воду,
как щенка, а он сам выплывал
и поэтому очень хорошо научился
самостоятельно плавать по морю
науки. В память двенадцати-
летия (дюжина – это может быть и
юбилеем) нашей первой встречи в
Киеве, когда он неосмотрительно попался в мои сети

Н. Семенов
Москва 1964 г.

Photo 3. Autograph of Prof. N.N. Semenov on the reverse of the photograph. *Text*: To dear Sasha Shilov (now Alexander Evgenyevich), my best pupil, for I spent the least time on him, but just threw him in the water like a puppy, and he swam out by himself, and because of this learned to swim independently in the seas of science very well. In memory of the 12-year jubilee (a dozen might be a jubilee) of our first meeting in Kiev, when he indiscreetly got caught in my nets. N. Semenov, Moscow, 1964.

What impression did Semenov make on you at first meeting and after the passing of many years?

At first I did not really appreciate Semenov, but in the end I got very attached to him and grew fond of him. In his personality I was attracted to the way he worked with his students and stimulated their independence.

Generally he was a charming, pleasant, smiling person (Photo 4). The main thing was that he never put himself above the person with whom he was having a conversation – even with post-graduates and under-graduates. He was able to separate the wheat from the chaff very well. As a result he formed a strong school, from which came, for example, Zeldovich, Khariton, Emanuel, Voevodsky, Kondrat’ev, Nalbandyan, Goldanskii and others.

Where did you discuss your current work with Semenov?

Semenov and his family lived right in the Institute in a two-story flat given to him by the government. His home study was located right next to the Director’s office, and the door from this study lead straight into it. However, I have never seen him going into the Director’s office from his own study, and often Semenov gave even official receptions in his home (Photo 5).

He usually invited various scientists and talked with them in order to formulate ideas for writing his book “Some Problems in Chemical Kinetics and Reactivity”, published in 1954 (the second edition of the book was published in 1958). I was also invited, about once a month, to participate in these discussions.

I remember how once one of the guests said that it is possible to distinguish a free radical mechanism from an ionic mechanism by the rule that is satisfied – Polanyi’s or Hammett’s rule. I doubted that, and after some thought came to the conclusion

Photo 4. Prof. N.N. Semenov with Alla Shilova and Shilov's dog Blanka (Chrnogolovka, 1980).

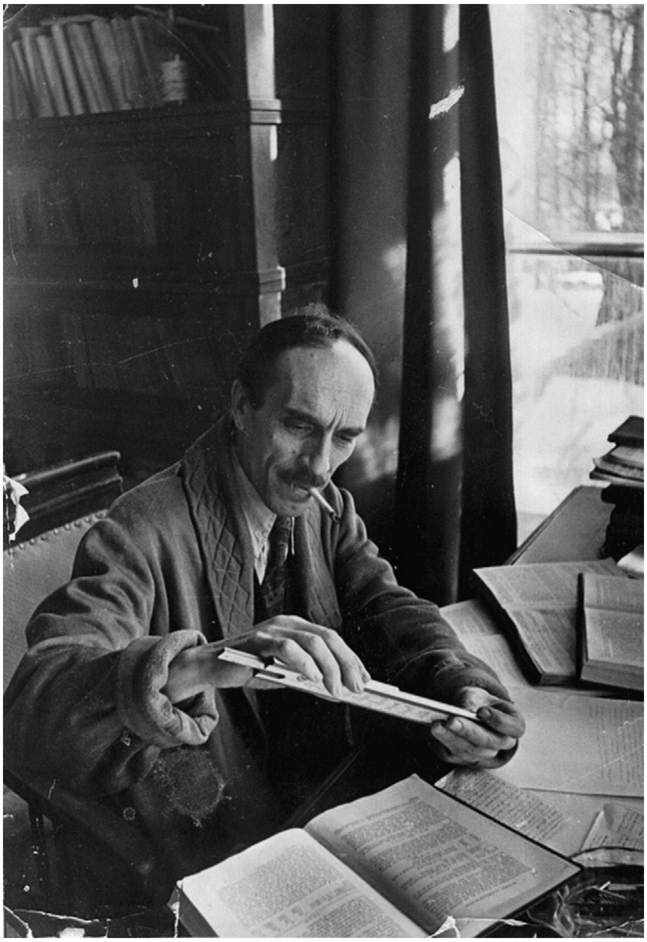


Photo 5. Prof. N.N. Semenov in his home study.

that these rules are closely linked. Semenov took that into consideration.

How did your work develop in post-graduate study? What was your main achievement in post-graduate years?

During the first conversaton N.N. Semenov suggested that I should study the decomposition of some molecules in the gaseous phase and determine the mechanism by which they decompose – molecular or free radical. Which molecules to study and which methods to use – I had to choose that myself. And that was all! What is more, he demanded that I discuss my ideas with him and present a plan of my work before he gave me a workplace. I objected and said that ideas would come after I got something. We squabbled in this way, but in the end I worked out what I should do. Semenov agreed with the plan and after this gave me a place for experimental work. It was a small workroom near the lavatory. Semenov never went in there during the whole time of my Ph.D. work. Once he commented on how well and for how long I worked, often into the night. However, malicious gossips claimed that, coming home late in the evening, and since Semenov lived in the Institute, he mistook the constantly lit up window of the neighbouring lavatory for my window.

During the Ph.D. years I did not have a single joint work with Semenov. I decided that I did everything myself, wrote everything myself and should be the only author of the article. It seemed to me that this was completely natural and that Semenov would not want to be one of the authors. Semenov himself sent this work to "*Doklady Akademii Nauk*." [3], and this, in my opinion, characterises him very well. The fact that I published an article on my own favoured my fast development as a scientist. At the age of 25, I was already completely independent.

My main achievement as post-graduate was that I found that, along with a molecular mechanism (for example, ethyl bromide breaks up into ethylene and hydrogen bromide) and free radical mechanism (for example, allyl chloride breaks up into an allyl free radical and a chlorine atom) there is a mechanism with the formation of carbene. For example, chloroform initially breaks up into CCl_2 and HCl [4].

Did you meet your future wife before moving to England?

Yes, that is right. After finishing the post-graduate study in 1955, I continued to work in the Institute as a research associate,

Photo 6. Prof. A.E. Shilov with his wife Alla in 2001.

and there were five people in my group. I met my future wife Alla (Photo 6) in 1958, when she joined our laboratory as my co-worker. She is a chemist – she graduated from the Department of Chemistry of Moscow State University. When she started work, I suggested that she should carry out a particular research programme, and said, that if you do not do this, I am going to fire you. She, however strange it may be, took this seriously. After my return from England it turned out that her work was going really well, and she stayed in our laboratory.

How did you come to work in England? Where and with whom did you work there?

N.N. Semenov nominated me to work in England, and the nomination was approved. I was one of the first scientists from the USSR to come to work abroad for a very long time. The attention paid to my visit from the Soviet side was big. For example, I was purposely introduced to two Englishmen, whom I had to, on one hand, accompany on a trip around the USSR, and on the other hand to learn the language from them. Later on, twice in shops in England I was taken for an Englishman, and this was my biggest linguistic success.

Coming back to my visit, I would like to note that initially it was planned for me to go to Oxford to Hinshelwood, who simultaneously with Semenov received a Nobel Prize. At the time he was the President of the Royal Society, and, obviously, was a very important person.

I called Hinshelwood Sir Cyril, close friends called him Hinsh. He was a very nice person. He treated me marvellously – here is a little proof of that: Hinshelwood gave an order for all my requests to be carried out very quickly. Colleagues grumbled that in order for their requests to be carried out, the most sensible thing to do is to ask for it through me.

Which English customs seemed unusual to you?

There were many differences between our style and behaviour, and there was a lot that I did not understand. I will give you one episode as an example, which I remembered for the rest of my life. Hinshelwood invited all colleagues to a reception. Everyone came in black suits and white shirts with bow ties, I alone came in casual dress. When I saw that I made an unacceptable blunder, I said to one of the people present (in the hope that he would reassure me): I was not told that I should be in full dress. He did not reassure me, quite the opposite, he lamented, how can it be, you were not informed, that is so bad! After this occasion I bought a black suit and a bow tie, and always, wherever I was invited, I wore this suit, a white shirt, and carried the bow tie in my pocket: I attached it when it was necessary. Another amusing incident. I lived in a private house in Oxford. My landlady, Mrs. Fitzgerald, showing me around the house, in particular showed me the bathroom where I could wash. The landlady said to me that before I get in the bath, I should insert a coin into a slit in a particular place. But I noticed that there was hot water without the coin, and one time, when I did not have the necessary coin, decided to wash without it. Of course, when I soaped myself, the hot water stopped, and I had to wash the soap off with cold water.

As you were one of the first Soviet visiting researchers in the West, you probably attracted a lot of attention?

Yes, even too much! Everybody was interested in me, because then I was one of the very few representatives of the Soviet Union in Oxford. I was from a completely unknown world, which intrigued them, and practically every evening somebody invited me to have dinner, and people asked questions about life in the USSR. Although I tried speaking objectively, I stressed the advantages of our life in the Soviet Union. But once one of our Soviet visiting researchers, who worked in London, came here and spoiled the whole picture for me. He behaved very uncompromisingly, did not shake hands with former Russian emigrants who worked in Oxford, saying that he would not even talk to betrayers of the Motherland. The English friends said to me, now we understand that you are not a true communist, but this guy is! He behaves exactly the way it is described in the papers! All my "propaganda work" was wasted.

These dinners were rather similar. The questions were the same . . . Everyone asked about Boris Pasternak's refusal of the Nobel Prize, which he was awarded after publication of the novel "Doctor Zhivago". The sharpest questions were from the left-wing socialists – "Why did everyone unanimously vote for the banishment of Pasternak from the Writers' Union? Why was there no one against it?" I was in a difficult position there. "I do not know, I am not a member of the Writers' Union", I replied.

What were your scientific achievements during the time of your visit?

In our Institute, one of the first in the World, was developed the method of EPR in application to chemistry. In collaboration with V.V. Voevodsky's laboratory, where this method was developed, we, in our group, actively used it in the gaseous phase and in solutions. In particular, we used the EPR method to confirm the formation of atoms and free radicals in reactions between fluorine and olefins and other molecules, and reactions of ethyl lithium and triphenylchloromethane.

Photo 7. A.E. Shilov with the Randall's family. Photo by Edward Randall.

I also started working with Ziegler catalysts and discovered (together with N.N. Bubnov) that $AlEt_3$ yields paramagnetic particles with $TiCl_4$ and (homogenously) with Cp_2TiCl_2.

In my work in Oxford I measured the enthalpies of reactions (or rather, the change in enthalpies), for which Hinshelwood before demonstrated the fulfilment of Hammett's rule, in order to test my idea that Hammett's rule and Polanyi's rule are very similar (now we call the latter the Polanyi–Semenov rule). That did really turn out to be true. I obtained the relationship $E = 20.8 - 0.32q$ for heterolytic reactions (reactions of anilins with benzoylchloride).

But, being introduced to other laboratory members, I got to know, and then became friends with Edward Randall (Photo 7), who worked on homogenous Ziegler catalysts. He studied spectra, measured electroconductivity and dipole moments. It turned out that, during the interaction between aluminium alkyls and Cp_2TiCl_2, the dipole moment and electroconductivity sharply increase. I, naturally, told him about EPR spectra, which were sent to me from Moscow. Having returned to Moscow, I started to work on electroconductivity.

Soon we left EPR (for studying Ziegler catalysts), as we became convinced that the EPR signal appears when titanium becomes trivalent, and the system loses its activity.

But Edward Randall took our EPR method and published a paper on this method (in the system of Cp_2TiCl_2–$AlRCl_2$). After that he started working on NMR spectra. It seems that we exchanged methods. I do not regret that.

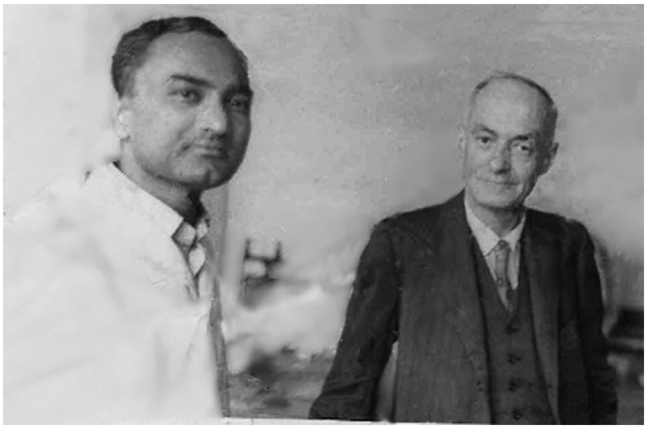


Photo 8. Vencataraman and Hinshelwood. Photo by A.E. Shilov.

Using the data from my visit I wrote an article, including Vencataraman and Hinshelwood as co-authors (Photo 8). Vencataraman was an Indian student, who worked in the same room as me. At one moment Hinshelwood decided that he should join my work. But Hinshelwood wrote to me that he himself refuses co-authorship because, even though he followed the work, he did not take part in it. This paper was then published in *J. Chem. Soc*. [5].

But my main achievement during my work in England was the switch to ionic concepts in Ziegler catalysis. . .

Did you remember England often after your return (Photo 9)?

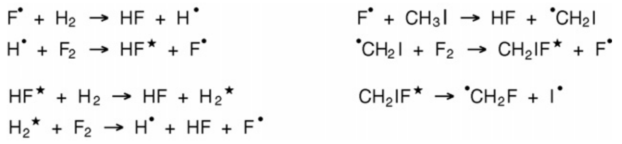
Yes, of course – it was a marvellous time. What is more, I remembered that country so often, that I even annoyed all my friends when I was saying “we in England”. Although there truly were a lot of positive things, what especially caught my eye was that in the USSR there was an incommensurable number of officials. When I said this to the Head of the Provision Department of the Institute, his reaction was curious – he said to me “*We* seized power in 1917 not to have anything like in England!”. It seemed funny to me, because in 1917 he was not even a year old.

What did you start to do after your return from England?

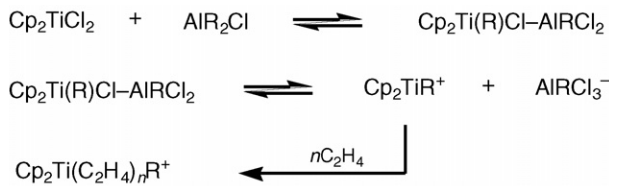
One of the subjects was energy branching. Studying reactions of molecular fluorine in a gaseous phase with hydrogen, and, with a group of organic compounds (CH_3I, CH_2Cl_2, etc.) we determined that these are branching-chain reactions, the branching being given rise to by vibrationly excited particles, products of exothermic reactions of molecular fluorine (Scheme 2).

In the 1920s of the 20th century, a similar mechanism was suggested by N.N. Semenov, but due to a lack of experimental confirmation this idea was abandoned. After the discovery of the mechanism of energy branching, it was possible to extend it to other cases of branching in chain reactions.

Photo 9. A.E. Shilov in 1960.



Scheme 2. Energy chain-branching.



Scheme 3. Ionic mechanism of catalytic polymerization.

These works were registered in 1976 as discovery. At that time in the USSR there was a practice of registering some works as discoveries. Now this procedure no longer exists.

Another subject was studying the catalysis in the Ziegler–Natta system. I discovered that it is the ions that are catalytically active and are responsible for polymerisation (Scheme 3). I was constantly criticised for this ionic theory in the Institute. What is more, at that time nobody in the West was interested in the ionic theory of the Ziegler–Natta catalysis. These ionic reactions were recognised only after 20 years or so.

Were you worried that nobody paid attention to the direction of research that captivated you?

Yes, and in the late 1950s I constantly thought what I could do that nobody has done before, and so that it would be a significant topic. At the time a conference was held in Leningrad, which I took part in. After the sessions I walked around the city, and accidentally an article caught my eye in the "*Literature Newspaper*" which I read. This article was called "Azote? No, Zote" [6]. This was how the author decided to present the results by Volsky from the city of Gorky. He made a "discovery" that nitrogen can be assimilated during breathing. That is where the name came from – Azote (nitrogen), which does not support breathing, and "Zote", the antonym thought up by the journalist, does support it. Straight away I had a feeling that this work is most probably nonsense, but at the same time I remembered from the school programme that nitrogen, although it is relatively chemically inert, can be fixed by bacteria. Volsky's false idea stimulated me, and I decided to work on the problem of nitrogen fixation. This was the beginning of the 1960s, and in 1962 I moved to Chernogolovka, and there was easy for me to find young and enthusiastic researchers for the new work.

What was the reason for moving to Chernogolovka?

I was directed to Chernogolovka – a small town near Moscow – by N.N. Semenov, and was welcomed by F.I. Dubovitskii, who was the Director of the Branch of the Institute of Chemical Physics, which then transformed into the Institute of Problems of Chemical Physics. In 1960 I got married (my son was born a year later), and we moved to Chernogolovka. I was very attracted by the closeness to nature. Housing conditions did not concern me then, and the most important thing was that I received one of the Institute buildings for my work. Soon I became the Deputy Director of the Branch. Having moved to Chernogolovka, I started working on nitrogen fixation and continued working on Ziegler polymerisation. The 1960s and 1970s were the most productive years of my scientific life.

Tell us, please, how you started working in the field of nitrogen fixation

If I were asked "What was the most significant thing you did during your scientific career?" I would have answered, without hesitation: "Nitrogen fixation". At first it all seemed quite easy to us. The main problem is to obtain a complex of a metal with nitrogen, and this small molecule would already be activated enough for further reactions, and, in essence, everything would be done. Allen and Senoff obtained such a complex [7]. They synthesised a complex of ruthenium with nitrogen $[Ru(N_2)(NH_3)_5]I_2$ using hydrazine, which as a result of oxidation gave an N_2 ligand. They also discovered that an N_2 molecule in the complex is easily reduced by sodium borohydride to ammonia and hydrazine. But we obtained the same and similar complexes (for example, $[RuCl_2(N_2)(THF)_3]$), using nitrogen and not hydrazine, and showed that the ligand is not reduced by any means, including the method described by Allen and Senoff. They did an excellent work, but in this aspect they made a mistake. We wrote about this in an article with Borod'ko [8]. The reason was that in Allen and Senoff's system there was always some initial hydrazine left, and it were these impurities that they reduced to ammonia, thinking that reduction of dinitrogen was taking place.

Semenov insisted that we do something constructive in nitrogen fixation. I even started avoiding him, because when we met, every time he asked "Well, have you finally reduced it?". He thought that we simply did not work well enough! One of our first articles on this subject was published in 1966 [9], but we got the first, in my opinion, really significant results later. In 1969 my wife Alla, Lena Kvashina and I found an intermediate complex, which is reduced to derivatives of hydrazine and ammonia [10] in Vol'pin's system ($Cp_2TiCl_2 + RMgCl$). In the same month, but in different journals, van Tamelen and we showed that, on reducing N_2, hydrazine is formed [11]. Then in 1970 we made our main discovery – we discovered several compounds, which reduced nitrogen in a protic solution – water or methanol [12].

To make a long story short, from an energy point of view, the easiest way is to reduce nitrogen straight to ammonia. But for this you need to transfer six electrons and add six protons to an N_2 molecule, and that is very difficult from the point of entropy. The best way to do this is using a cluster containing, for example, eight atoms of a transition metal. We obtained such a cluster made of eight Mo atoms. If an electron donor is situated nearby, for example, the amalgam of Na, the cluster can become a catalyst for the reduction of nitrogen. Nature went by the same path: nitrogen is reduced by a cofactor which contains seven iron atoms and one atom of Mo; at a small distance there is P-cluster, acting as electron donor.

When was the first acknowledgement of your contribution to the problem of nitrogen fixation?

I remember one incident in this context, which stuck in my memory. Around 1972, when I had already obtained really significant results in nitrogen fixation, I presented my data at a conference, at which two Nobel Prize winners were present – Fischer and Semenov. After my presentation we had a group talk, Fischer congratulated me on the interesting data, but asked Semenov why the problem of nitrogen fixation is worked on in the Institute of Chemical Physics and not in any other Institute for example in the Institute of Inorganic Chemistry. Semenov was very pleased when he heard the question translated by me, and answered that as soon as a person understands chemical physics, all the other problems for him would be solvable.

In the USSR, formally, acknowledgement came at the end of the 1970s, when work on nitrogen fixation was registered in 1979 as a discovery, and for this work my colleagues and I received a State Award of the USSR (1982).

Did you know about Vol'pin's work on nitrogen fixation?

As it turned out later, Vol'pin independently from me started working on nitrogen fixation. He published his first paper in *Doklady AN SSSR* [13] in 1964, and then in *Nature* [14]. It has to be said that before them, nobody worked on nitrogen fixation. At the time it was considered that nitrogen reacts only with lithium. And now it is a huge field – low-temperature nitrogen fixation.

In his paper, Vol'pin proceeded from the analogy between carbon monoxide and nitrogen, and employed reducing systems, uncluding some of the Ziegler catalysts, which we actively worked with at the time. We had everything in our hands. Semenov later reproached me for the rest of my life that we were not the first to do what Vol'pin did.

Photo 10. Portugal, 1979. A.E. Shilov and M.E. Vol'pin at the house of Prof. A.J.L. Pombeiro.

Photo 11. Portugal, Sintra, 1979. Symposium on *New Trends in the Chemistry of Nitrogen Fixation*. Left group: A.E. Shilov (right) speaking to J.H. Teuben. Right group: J. Chatt and his wife, K. Tamaru, and R.L. Richards taking a picture.

I, of course, had a rivalry with Vol'pin, but there was collaboration too (Photos 10 and 11). For example, at one time Vol'pin could not carry out experiments because of a fire in his laboratory in the Institute of Organoelement Compounds (INEOS), and we invited his colleagues to work in our Institute. At the conference in Leningrad (International Symposium on Nitrogen Fixation, 1995), I spoke on mine and his behalf, presenting his data.

You knew M.E. Vol'pin well, when he was the Director of INEOS, and what about his predecessor on the Director's post – President of the Academy A.N. Nesmeyanov – did you know him personally?

No, I did not know him personally, that is, I knew him, of course, but not very well. Once I was present at some important meeting, which A.N. Nesmeyanov also attended. Nesmeyanov was walking past and accidentally tripped on my legs – "I beg your pardon!" said Alexander Nikolayevich. I was telling everyone after that – "I saw the President of the Academy of Sciences the other day. He was begging my pardon!".

When and where were the first results of another project – activation of the C–H bond – published?

We published the first results on this subject in the "*Russian Journal of Physical Chemistry*" [15] and nobody paid any attention to them. Later we wrote an article in *Nouv. J. Chim.* (now *New J. Chem.*) [16], and it was these papers that produced a resonance in the chemical community. The fact that the first results were published in a journal of limited circulation was not just our luck – we could work peacefully. All in all, it is my general principle to publish in Russian journals, which are read by fewer people, to work peacefully and only then, at a later stage, to make my results available to a wide scientific community.

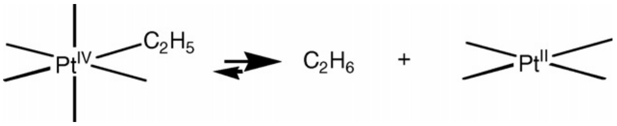
How did you start working on the C–H bond activation?

We worked on the process of ethylene hydrogenation on homogenous platinum catalysts and discovered that if the reaction is carried out in D_2O, then C_2H_5D is obtained. Ethane is formed in the reaction (Scheme 4).

Formation of C_2H_5D in the case of D_2O means that if there is a reaction of C_2H_6 with Pt^{II} then we shall have the exchange C_2H_6 with D_2O in the presence of Pt^{II}.

It helped us a lot that right before the start of these experiments, articles by Garnett and Hodges [17] came out, in which it was shown that aromatic compounds in the presence of a platinum(II) compound $[PtCl_4]^{2-}$ undergo H–D exchange. The authors suggested that the exchange happens due to the formation of a π-complex of Pt^{II} with a benzene ring. But the most curious thing for us was that when they used PhC_2H_5 as a substrate, it was revealed that hydrogen is substituted in the ethyl group. For us it was a brilliant hint. We tried using methane and ethane, and it turned out that they undergo H–D exchange in the presence of $[PtCl_4]^{2-}$. Our next step was introducing a platinum(IV) complex $K_2[PtCl_6]$ into the system. We discovered that in this case (Pt^{IV} as oxidizing agent and Pt^{II} as catalyst) in the case of ethane and methane, ethyl chloride and ethanol and methyl chrolide and methanol, correspondingly, are formed. Therefore, it is a completely general reaction with the simplest platinum compounds!

Another aspect of our work should be highlighted – we discovered a series of reactions of alkanes on iron complexes, which model biological oxidation. Contrary to the general opinion about the radical character of these reactions, we suggested a mechanism of the reaction via five-coordinated carbon. Work on metal complexes, reacting with alkanes with the formation of metal alkyls was registered in 1983 as a discovery. For the work on the biological oxidation mechanism and its modelling in 1998 we were awarded a State Award of the Russian Federation.



Scheme 4. Last stage of the hydration reaction; the reverse reaction is an alkane activation.

In the world, akane activation is called "Shilov chemistry". When did this term appear?

I think that this term appeared at the time, when many still did not believe that the C–H bond is so easy to functionalise even in methane. But, in any case, in 2002 in Orlando (Florida), at the 223rd meeting of the American Chemical Society, the term "Shilov Chemistry" officially appeared as a heading for one of the sessions. This term seems unfair to me, at least because I worked on the subject with Shteinman, Goldshleger, and also Khrush, Shul'pin, Lavrushko, Moravsky and others. But it was not I who had suggested this term, and somehow or other, it stuck.

Which other directions of your work would you like to highlight?

In about 1975 Semenov was very interested in photosynthesis and wanted to use the photosynthesis models for the decomposition of water into hydrogen and oxygen by sunlight, and to store energy in this way. Peter Kapitsa, the Nobel Prize winner in Physics, thought of it sceptically. Although, it seems to me, Semenov turned out to be right. In this way Graetzel later obtained quite efficient systems with an efficiency of up to 10%, and it seems to me that the systems for obtaining hydrogen using the Sun's energy are quite promising.

Semenov suggested this project to me, and I started working on it with interest. We were the first to produce hydrogen under the influence of visible light in a so-called sacrificial system [18]. We made a reaction vessel in the shape of a leaf, with a yellow solution. When brought into sunlight, the solution turned green, like a living leaf, and hydrogen bubbles were evolved. We demonstrated this vessel with the solution to the "big bosses" who visited us. One of them said: this is all that we need! Hydrogen is evolved, that means the problem is solved. I said that we also need to simultaneously produce oxygen. Why do we need oxygen, there is a lot of it anyway, he insisted. It was very difficult to convince him . . .

Then we managed to generate oxygen from water in the presence of polynuclear metal compounds. We showed that in a neutral solution, manganese compounds (which form an oxygen-evolving centre in natural photosynthesis) produce oxygen much more easily than other metals. So it is clear why nature chose manganese for an oxygen-evolving centre. In vesicular systems it is possible to obtain hydrogen and oxygen simultaneously. Recently we also showed that, along with oxygen, ozone is also emitted via six-electron oxidation [19]. For the work on metal complexes in biomimetic chemical reactions, in 2001, I was awarded a Semenov Gold Medal, by the Russian Academy of Sciences.

Can it be said that you often changed your directions in chemistry? Did you follow the fashion in chemistry?

It is believed that one should work on a particular field for 10 years. One is unlikely to do something significant in a short space of time, and after 10 years many things get tiresome. Although

. . . I have been working on nitrogen fixation since the early 1960s, and it still fascinates me to this day.

As for fashion . . . In general I tried and still try to stay out of “booms” in science. All this creates unnecessary tension, and it is best to work when nothing interferes. I was generally lucky: I started working in science, when there was government financing in the USSR and I did not need to think about any grants and the fuss caused by writing and presenting them.

What is science for a teacher and what is teaching for a scientist?

I think that it is very useful for a scientist to teach. At a young age, teaching gives variety and widens your horizon, and at a senile age it disciplines. Now I, being disciplined by a teaching load, prepare lectures on photosynthesis.

And talking to students is pleasant and sometimes amusing. Once in a lecture I was saying that, of course, it is not necessary to learn the Periodic Table, but to understand the system – that is what is important. Then one student asked me, what would happen if they still learn it for the oral exam? I took it as a joke and said that, of course, I would not ask anything else and will give the highest grade. To my surprise, two students really did learn the whole Periodic Table off by heart, and I had to give them the best grades. After that I did not give the students such advantages, but the memory of this amusing incident remained.

Photo 12. Prof. A.E. Shilov on the eve of his 75th jubilee in his office. Behind is a portrait of N.N. Semenov.

Now several short questions. Are you a lucky person in chemistry and in life?

In Chemistry – yes, and probably in life too.

How did you celebrate your 75th jubilee (Photo 12)?

I celebrated as usual, with my family. In general I thought that it is not a jubilee, and only after receiving numerous birthday wishes and a greeting telegram from President Putin, was I taken by this event.

What does a scientist need for happiness?

To live long and be needed! The freedom of creative work, luck and success are necessary.

What qualities must a scientist have?

There should be ambition, self-affirmation is also very important. But simple ambition is not enough. It should be added to a thirst for knowledge.

What is the final aim of science?

Final? There is not one – science does not have an end . . .

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