

Adolf von Baeyer

31 October 1835 - 20 August 1917

Kaloyan Manolov in "Great Chemists", Sofia, V. 1 and 2, 1972, 1974 Translated to English from Russian edition: Kaloyan Manolov "Great Chemists" 3rd ed., Volume 2, Mir, Moscow 1986, p. 167 - 187. (Калоян Манолов "Великие химики", пер. с болг., пер. К. Манолова, С. Тасева ; под ред. Н.М. Раскина . – 3-е изд., испр. и доп . – Москва : Мир, 1986, т.2, стр. 167 - 187)

It was getting darker and the spring wind was getting colder. Professor Baeyer and his assistant, Richard Willstätter, slowly walked along the empty streets of Munich. Carried away by conversation, they would often stop and gesture to explain something to each other and then move on.

Professor Baeyer was of a medium height, his grey hair neatly trimmed, and his blue eyes had a youthful sheen. Willstätter would rub his forehead with his hand from time to time - a sign that he was concerned about something. They had been talking for an hour now, but Willstätter did not get to the main subject of the conversation.

'Professor Baeyer,' Willstätter began hesitantly, 'your seventieth birthday is coming soon. We are going to have a grand celebration. Also, your students are preparing the publication of a complete collection of your works.'

Baeyer stopped and looked at Willstätter in surprise.

'Who took on this difficult task?'

'Well, several people actually: Grebe, Fischer, Liebermann ... I would also like to include a short essay about your life and work. No one can write this better than you. We would like to invite you to write the memories of your life.'

Baeyer considered the request for a moment, then in comic despair pressed his hand to his chest.

'To write memories? That will be real torture! No, this idea is not feasible.'

They moved on and crossed the square and went to Arcisstraße, where on the corner of the street stood the house of professor Baeyer. They walked closer to the house and watched as blackbirds jumped in the neglected garden overgrown with weeds. 'My friends are already hungry!' Baeyer looked at the birds affectionately. He said goodbye to Willstätter and entered the house. From the office window, he threw a handful of grains down to the blackbirds, closed the window, then leaning his elbows on the windowsill, returned his thoughts to the conversation with Willstätter.



Adolf von Baeyer's laboratory (left) and family residence (right) (Source: K. Schmorl. Adolf von Baeyer, 1835–1917. Stuttgart, 1952, p. 95.) MV

'70 years! How quickly they flew by... Well, where would I start?' Baeyer took a piece of paper, sat behind his desk, and wrote down the first few lines.

'Memories of my life. 1835-1905.

I, Johann Friedrich Wilhelm Adolf Baeyer, was born on October 31, 1835 in Berlin, Friedrichstraße 242 ... '

One after another, the memories of his childhood appeared before his eyes.

... Here is a vast country courtyard in Müggelheim, a small village southwest of Berlin, where his grandfather lived. Every summer young Adolf would come here with his sisters Emma and Klara. The children would run through the meadows, and catch butterflies and beetles. When they would find a nestling that had fallen from the nest, they would rush to show it to their mother, Eugenie. Their mother would then tell them how birds take care of their offspring, how they incubate their nestlings, and how they feed them. Adolf loved listening to these stories; they spurred his interest in nature. At his grandfather's house, he began to assemble collections of insects, plants, and minerals.

Professor Baeyer also remembered the house of his other grandfather, his mother's father. Here, in one of the rooms on the second floor, Adolf kept his herbariums and collections of insects and minerals. He was happy to be alone for long periods, examining new specimens of plants or insects. He would be in no hurry to go down to the living room where his grandfather, the writer Julius Hitzig, often hosted crowded literary evenings. The most prominent representatives of German literature and art of that time would frequently gather there.

The happy days of Adolf Baeyer's childhood were soon overshadowed by great misfortune when his mother died during childbirth. As Adolf was the eldest of the children, he felt the loss more than the others and he was inconsolable. The thought that his mother would never lead him through the flowering meadows or tell wonderful stories about plants and animals brought the eight-year-old boy to experience bouts of despair.

Adolf and his sisters were then placed under the care of governesses and teachers as their father, Johann Jacob, a geodesy specialist, would spend most of the calendar year travelling. Upon his return, he would stay home for some time and then would take Adolf to Müggelheim.

Every time they went, Johann Jacob would bring books to his father. Adolf remembered one of them in particular because it was the book that sparked his interest in chemistry. Handing the book over to his grandfather, Adolf's father said: 'It was written by some professor of chemistry named Liebig. The author claims that if the soil is fertilized with mineral salts, the yields will be much greater'

'This is interesting,' the grandfather answered, 'this, perhaps, needs to be tested.'

Adolf asked his grandfather if he could borrow the book. He read it and decided to conduct his own experiments. He planted date seeds in pots of earth and waited for the sprouts to appear. When the first shoots appeared, Adolf began experimenting. He watered one plant with a solution of sodium chloride, another plant with milk, and a third plant with plain water.

Johann Jacob noticed his son's interest in experiments, and on Adolf's birthday, he presented him with another book, called "Die Schule der Chemie" by Julius Adolph Stöckhardt.¹ Soon after that, Adolf organized a small laboratory in the tiny corridor just in front of his bedroom. It was equipped with test tubes, flasks, mortars, tripods, and chemical reagents.

After reading his new book, Adolf wanted to attempt the experiments described in the book himself, but this required 'funds.'

Every Saturday Adolf was given 15 pfennigs for sweets. He would save every pfennig and once he eventually saved up a small amount, he would buy the chemicals necessary for his experiments. When the experiments would not work out, Adolf would stubbornly repeat them, changing the conditions each time. These initial experiments led to Adolf's first successes, although they remained unknown to science. One day, while working with the solutions of sodium bicarbonate and copper sulfate, Adolf obtained a light blue precipitate. Then, after ten days, blue crystals appeared at the bottom of the flask. Adolf determined that the crystals were composed of sodium,

¹ Julius Adolph Stöckhardt (1809 –1886) was a German chemist, one of the pioneers of agricultural chemistry. His book named Die Schule der Chemie was an inspiration to many young people including those who later became renowned chemists and Nobel Prize winners, such as A. von Baeyer, E. Fisher, W. Ostwald, O. Wallach.

Source: Wienhaus, O. Julius Adolph Stöckhardt – a pioneer of applied chemistry. *Fresenius J Anal Chem* **363**, 139–144 (1999). <u>https://doi.org/10.1007/s002160051161</u>. MV

copper, carbon dioxide, and water. He did not find a description of such a composition in any reference book. Professor Eilhard Mitscherlich,² a friend of his father, was also unable to answer whether Adolf's crystal composition was already known.

'It looks like this salt was previously unknown,' said Mitscherlich, examining the blue crystals. 'Could you please describe the exact conditions under which you obtained the crystals?' Adolf provided all the details of his experiment. Mitscherlich took the data and searched through the textbooks and reference books he had access to but found no description of such a salt. The young researcher's discovery remained unknown to science until three years later when the same salt (double salt - copper and sodium carbonate) was isolated and described by Heinrich von Struve.

The high school teacher, whose name was Shelbach, was an excellent mathematician and physicist. He also taught chemistry, and actively supported Adolf's interest in physics and chemistry. Adolf studied subjects with exceptional diligence, and Shelbach made Adolf his assistant in the chemical laboratory. Adolf conducted chemical demonstrations for the audience in the class. It appeared, however, that the experiments he performed in his home laboratory had the most profound impact on his development as a chemist. After reading Wöhler's³ "Outlines of Organic Chemistry," Adolf became much more interested in an intriguing, mysterious, and at that time, littlestudied field of science - chemistry. In his home laboratory, he began conducting more complex experiments. Unpleasant smells would often carry through the house. Adolf's relatives would reprimand him, and his sisters would tease:

² Eilhard Mitscherlich (1794—1863) - a philologist (Persian language) turned chemist and crystallographer. Studying arsenates and phosphates formulated his law of isomorphism. He was appointed a professor of chemistry at the University of Berlin in 1822. Mitscherlich also synthesized and characterized selenic acid, named benzene and investigated nitration of benzene with nitric acid. Source: Eilhard Mitscherlich. Oxford Reference. <u>https://www.oxfordreference.com/view/10.1093/oi/authority.20110803100202237</u> Accessed 7 Jan. 2022 MV

³ Friedrich Wöhler (1800–1882) was a German chemist, a professor of chemistry at the University of Göttingen. He was the first to isolate aluminum, beryllium and yttrium elements in their pure metal form. Wöhler was also first to synthesize an organic compound, urea, from an inorganic reagent, ammonium cyanate, thus becoming a father of synthetic organic chemistry. Wöhler and Justus Liebig introduced a laboratory practicum for students studying chemistry. Source: Rocke, Alan J.. "Friedrich Wöhler". *Encyclopedia Britannica*, 19 Sep. 2021, https://www.britannica.com/biography/Friedrich-Wohler. Accessed 7 January 2022. MV

'It is smelly all around - this is brother's lab ground.'4

Adolf began to spend the pfennigs given to him more economically in order to save more money to buy chemicals for his experiments. On one occasion, he bought two grams of indigo for two guilders and began experiments with the substance. In India, thousands of hectares were used to grow the Indigofera plant. The dye was extracted from the plant stems and then used to dye cotton fabrics in a beautiful blue colour. Young Adolf pondered the structure of indigo.

At the high school, Adolf became fascinated with mathematics and physics and as a result, he devoted a lot of time to these subjects. After graduating from the high school, he decided to study at the Faculty of Physics and Mathematics of the University of Berlin.

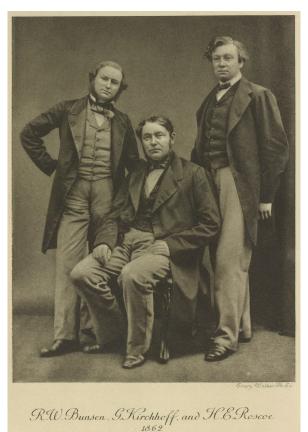
At the end of his third semester of university, Adolf was drafted into the army. The young man served for a whole year in the 8th Berlin regiment. It was a difficult time for Adolf. After all, for a year he did not even have time to read a book. Eventually, after serving the required time Adolf returned home and faced the problem of deciding what to do next.

After some deliberation, he decided to go to the University of Heidelberg and study in the laboratory of Professor Bunsen.⁵ Studying at the university was not limited to attending lectures; from the beginning of the academic year, students were being prepared for research work. Young chemists who came to Heidelberg to work under the guidance of Robert Bunsen - a famous master of experimental chemistry - would frequently find it difficult to get a placement in the laboratory.

⁴ This is my free translation of the Russian version of the verse. Unfortunately, there is no reference available in Manolov's text to obtain the German original if it existed. MV

⁵ Robert Wilhelm Bunsen (1811 - 1899) - a German chemist well-known for his studies of organoarsenic compounds, spectroscopy, gas analysis, photochemistry, electrochemistry and analytical chemistry. Bunsen was greatly admired by his students, colleagues and citizens of Heidelberg. Bunsen had a great sense of humour and was a character in many anecdotes. Here is a great example: "At one dinner party an elderly lady, on being introduced, mistook him for the famous German diplomat and scholar, Baron Christian Charles Josias von Bunsen, who had died in 1860. "Pray sir." asked the lady, "have you not yet finished your great work on God and History?" "Alas no, madam," replied Bunsen, "my untimely death prevented me from completing my task." Source: Jensen, William B. "Robert Bunsen's Sweet Tooth: Bunseniana in the Oesper Collections." (2013). MV

Bunsen's research focused primarily on physical chemistry. Aluminum was first obtained using electrolysis, and a new method of spectral analysis was also developed in his laboratory. He also discovered two alkali metals, rubidium and cesium. Bunsen demanded exceptional accuracy and diligence from his trainees. He meticulously monitored the conduct of even the simplest experiments and was intolerant of mistakes and oversights in their work.



Gustav Kirchhoff (left), Robert Bunsen (centre), and Henry Enfield Roscoe (right) (Source: Roscoe, Henry E. (Henry Enfield). "Bunsen, Kirchhoff, and Roscoe." *The Life & Experiences of Sir Henry Enfield Roscoe... Written by Himself*. London, England: Macmillan Company, 1862–1906. https://digital.sciencehistory.org/works/7m01bm800.) MV

Adolf began studying qualitative and quantitative analysis. From the very first sessions, he recognized the great benefit of the experience he gained from his home laboratory experiments. It took Adolf just one semester to accomplish the same amount of work as three semesters worth of work from a beginner student. The laboratory assistant was pleased with Adolf's work, and Bunsen himself noticed the success of his talented

student. At the end of May, Bunsen invited Adolf to his office. At the precisely appointed time, Adolf knocked on the door.

'I am glad you are so punctual,' Bunsen began, 'I am even more pleased with your successful work in the laboratory. I think you will become a great researcher. I would like to offer you an opportunity to work on an independent project.'

His mentor's words of approval made Adolf feel shy and embarrassed and he was not able to find words right away to express his gratitude to Bunsen.

'Well,' Bunsen said, 'Let's begin the work.'

'Definitely! Your praise of my work is very important to me. I have dreamed of scientific research since childhood', Adolf replied.

'Very good', Bunsen said, 'Professor Roscoe and I recently completed a study of the photochemical interaction of equal amounts of chlorine and hydrogen. It turned out that in the first minutes of the reaction the mixture did not explode. We found that the violent reaction begins only after a certain period. We called this period induction. Several questions remained, however, such as: What is the role of light? How does the intensity of the light affect the reaction? Would you like to address these issues?'

'Can I use your experimental conditions?', Adolf asked.

'No', Bunsen replied, 'I think that some changes should be made. I suggest taking bromine instead of chlorine. Bromine reacts much slower and the reaction will be easier to control.'

Bunsen then described the proposed project in detail.

A few months later, Adolf completed the research and wrote his first scientific paper for Liebig's Annalen der Chemie. He achieved excellent results but was not satisfied with the subject of his research. The main reason was that the topic was given by Bunsen. Adolf was not very interested in inorganic chemistry. He wanted to do research in organic chemistry - the chemistry of carbon-containing substances.⁶

⁶ The modern definition of organic chemistry is: "the study of the structure, properties, composition, reactions, and preparation of carbon-containing compounds. Most organic compounds contain carbon and hydrogen, but they may also include any number of other elements (e.g., nitrogen, oxygen, halogens, phosphorus, silicon, sulfur)." <u>https://www.acs.org/content/acs/en/careers/chemical-sciences/areas/organic-chemistry.html</u> MV

Adolf believed that the development of science as a whole depended on solving fundamental problems of organic chemistry. The theories of Gerhardt, the novel views of Kekulé ... No doubt, organic chemistry is the most interesting area there is. But how would one tell Bunsen about this? An accident helped with that. Once, when Adolf was dismantling a distillation apparatus, he was approached by Leopold von Pebal - a trainee, who worked in the laboratory at a nearby desk. Leopold was upset with something.

'Did the boss scold you?', Adolf asked.

'No, but he suggested a topic for research, which I just don't like', Leopold replied.

Adolf looked inquiringly at his labmate.

'Bunsen synthesized methyl bromide with a boiling point of 17 ° C', Leopold explained, 'and he used cacodylic acid as a starting material. When he used methyl alcohol instead of cacodylic acid, the resulting methyl bromide boiled at + 13 ° C. He wants me to find out what causes the difference in boiling points. It might be that the cause is isomerism.' 'This is very interesting!', Adolf exclaimed, 'I would have dreamed about such a research topic'.

'I am not interested in organic chemistry', Leopold replied, 'If the boss does not mind, I will gladly give my project to you.' Fortunately, Bunsen did not mind.

The days of hard work, the days of expectations and hopes came. Adolf used chlorine gas and obtained the corresponding chlorine derivatives. He also used cacodylic acid and methyl alcohol as starting materials. The product of the reaction turned out to be the same - methyl chloride.

There is only one methyl chloride and one methyl bromide. Adolf concluded that the compound obtained by Bunsen had a lower boiling point because it was contaminated with impurities. Adolf explained his results to his labmate, Shishkov.

'Your conclusions are completely consistent with the theory of radicals', Shishkov said.

'The same view was shared by Marcellin Berthelot. Have you read his article in the Annals?', Adolf said and opened the cabinet and took two large jars with a white crystalline substance inside.

'Is it cacodylic acid?', Shishkov asked.

'Yes, it is', Adolf replied.

'Why don't you try a reaction with phosphorus pentachloride', suggested Shishkov. 'I think this is a good idea!', Adolf perked up, 'thanks for the advice! I'll start right away.' Adolf would conduct several experiments simultaneously and check the results the next day. Once, in one of the flasks, he noticed beautiful shiny crystals, which he had not seen before. Was it a new compound? But why did it form only there? The experiment must be repeated. Adolf repeated the experiment several times, but the crystals never appeared again.

Working with organic compounds required special methods and techniques, which were not known in Bunsen's laboratory. There was no one there who could help Adolf or give him advice. He was still most interested in natural products and organic chemistry. He kept his sample of indigo at home and patiently waited for the day when armed with knowledge and experience, he would try to uncover the secret of the chemical structure of indigo. The need to find a laboratory to work with organic compounds became more and more apparent. Adolf thought constantly about it even when he spent evenings with friends over a mug of beer, told and listened to funny stories, and sang student songs. Once, after such a friendly feast, Adolf left the bar with August Kekulé⁷ to get some fresh air. It was late at night. They got into a conversation and imperceptibly their conversation moved on to a topic that occupied their thoughts constantly - organic chemistry. Kekulé said that he recently opened a small laboratory. At that time being an assistant professor and working in your laboratory was not the most reliable and profitable occupation, but out of love for science, Kekulé went for it. That evening Kekulé got his first trainee - Adolf enthusiastically accepted Kekulé's offer.

Kekulé's laboratory was cramped and poorly equipped. Adolf, however, found in Kekulé an outstanding teacher who had excellent skills in experimental organic chemistry and a vast knowledge of chemical theory. Under the mentorship of Kekulé, the research

⁷ Friedrich August Kekulé, later August Kekulé von Stradonitz (1829 - 1896) was a German chemist and one of the researchers who began the development of the modern structural theory of organic chemistry. Kekulé proposed a structural formula of benzene and synthesized and characterized several unsaturated acids and thio acids.

Source: Britannica, The Editors of Encyclopaedia. "August Kekulé von Stradonitz summary". *Encyclopedia Britannica*, 2 May. 2020, https://www.britannica.com/summary/ August-Kekulé-von-Stradonitz. Accessed 9 January 2022. MV

proceeded quickly and with great success. Using cacodylic acid as a starting substance, Adolf synthesized new, previously unknown compounds - methylated arsenic chlorides. One day working in the laboratory Adolf reduced cacodylic acid with a mixture of sulfur dioxide and hydrogen iodide and, after passing hydrogen chloride through the reaction mixture, he distilled it. A colourless liquid was collected in the receiving flask, which soon separated into two phases. Adolf disconnected the receiving flask from the apparatus and poured the mixture into a separatory funnel. A pungent, irritating odour spread through the laboratory. The vapours had a very strong effect on the mucous membranes of the airways. Adolf began to gasp, tears streaming down his face. He felt a sharp pain in his eyes and chest. Adolf tried to leave the laboratory but he staggered and fell unconscious on the floor before reaching the exit.

When Kekulé entered the laboratory, Adolf showed no signs of life. Sensing a pungent smell, Kekulé realized what was going on and quickly pulled Adolf into the next room and opened the windows. After the incident, Adolf had to remain in bed for several days. The skin on his face was severely inflamed.

Kekulé was sad to part with the talented assistant, but he recommended that Adolf finish his research in Emil Erlenmeyer's laboratory, where working conditions were much better. Although the study of alkyl chloroarsines posed a great danger due to their toxicity, Adolf was eager to continue this work. This was the first time he experienced true satisfaction, as this was his first independent research. Adolf synthesized and studied dimethylchloroarsine, methyldichloroarsine, and several other derivatives. At the beginning of 1858, he finished experiments and began to summarize the results, which were the basis of his doctoral dissertation.

When Adolf went to Berlin for spring break, the manuscript of his dissertation "De Arsenici Cum Methylo Conjunctionibus" ("On the compounds of arsenic with methyl") was ready. He submitted his work to the University of Berlin as a candidate for a doctoral degree.

Eilhard Mitscherlich, Heinrich Rose, and Heinrich Gustav Magnus were the official examiners at the dissertation defence. None of them were organic chemists, therefore their questions to Adolf about the dissertation during the defence were so abstract and so far from the subject of the dissertation that he almost failed the defence.

Nevertheless, Adolf Baeyer received his doctorate, although his disappointment was endless.

'I cannot stay in Berlin! No one here understands organic chemistry.'

'Are you going to leave again and wander from one place to another? I think you should stay at home, his brother advised him.

'I disagree, Edward. I would like to continue working with Kekulé and I am leaving immediately. I will stop at Elberfeld to see Emma on the way to Heidelberg.'

In honour of Adolf's arrival, Emma organized a small family celebration. The evening was attended by close friends, among whom was the chemist Adolf Schlieper, the owner of a small chintz factory. Baeyer immediately felt sympathy for this man and they had a lively conversation.

'Those were good times, Herr Baeyer, but many years have passed since then. I studied derivatives of benzene and synthesized several derivatives of picric and uric acids while working in Liebig's laboratory, but this is now in the past. The factory is taking up all my time.'

'Have you published the results of your research?'

'No, the research was left unfinished. The vials with the compounds I synthesized are still in my office.'

'Would you give me some of them? During my school years in Berlin, I had a home laboratory where I studied uric acid. Perhaps, among the substances you made, there will be some that are unknown.'

'I am quite sure of that. If you like I can give them all to you.'

'If I find anything new among the samples you gave we will write a paper together.' The next day Schlieper brought Baeyer a large box filled with vials containing chemical samples - a real treasure for the researcher.

When Adolf arrived in Heidelberg, he learned that Kekulé had been invited to work at the University of Ghent. Without hesitation, he went to Ghent following Kekulé.

In Ghent, Baeyer began studying picric and uric acid derivatives. Based on the new structural theory of organic substances (in the creation and development of which Kekulé actively participated) Baeyer described and systematized various, often contradictory data related to the properties of purine derivatives. This work laid the basis

for the final determination of purine alkaloid structure completed by Emil Fischer sometime later.



August Kekulé (first row, sitting in the centre), Ghent University, ~1866 (source: <u>https://commons.wikimedia.org/wiki/File:August Kekulé Gent ca1866.ipg</u>) MV

While working in Ghent Baeyer did not have any independent income and he lived on the monthly support he received from his father, Johann Jacob Baeyer. Although Johann Jacob, a well-known scientist-surveyor and General, had the means to support his son, he insisted that Adolf should think about his future career.

'It may be easier to find a job in Berlin, in industry or the academy - it's up to you. If you are attracted by the academic path, then move to Berlin and start as a private docent. You will be without a salary in the beginning, but then you will have a roof over your head, and, most importantly, a career prospect', his father wrote to the young Baeyer.

In early 1860 Baeyer arrived in Berlin. He brilliantly passed the exam for assistant professor and began preparing for the upcoming lectures. There was no laboratory in

which to conduct experimental work in Berlin and Baeyer did not have the financial means to equip his own laboratory. There was only one option left - to work on theoretical problems.

Even after the death of Adolf's grandfather, the famous scientists, writers, and art critics continued to gather in the Baeyers' house, as before. An old friend of Adolf's, Privy Councilor Bendemann, who almost always came with his daughter Adelheida, often attended these evenings. Adelheida became friends with Adolf's sisters, Clara and Jeanette. When Adolf arrived in Berlin, Adelheida - a beautiful and well-educated friend of his sisters caught his attention immediately. However, living at the expense of his father, Adolf could not even think about marriage. He needed a job with a steady income as soon as possible and fortune smiled at him. In 1860, a new discipline, organic chemistry, was introduced in Gewerbeinstitut Berlin (the future Königlich Technische Hochschule zu Berlin). Baeyer accepted a position of a lecturer of organic chemistry at Gewerbeinstitut Berlin. Although his salary was quite small, he had to give half of it to his assistant who otherwise would have been paid nothing at all.

At Baeyer's insistence, Gewerbeinstitut began the construction of the laboratory and it was completed a year later.

From the very first scientific publications, Baeyer attracted the attention of other chemists. He started to receive requests from students who wished to become trainees in his laboratory. In the laboratory in Gewerbeinstitut Adolf made his first chemical discoveries. He developed a qualitative reaction for double and triple bonds in organic compounds, as well as the zinc-dust distillation technique, which became an important experimental method.

Chemists such as Karl Grebe and Karl Liebermann worked under the supervision of Baeyer for several years. Grebe began his research with quinic acid and the product of its oxidation, quinone. Together with Liebermann, he studied the natural dye alizarin, which was structurally similar to quinones.

'Undoubtedly, alizarin is a quinone derivative,' Grebe said.

'You need to get to the original compound, the hydrocarbon,' Baeyer said. 'When we know which hydrocarbon forms the basis of alizarin's structure, then the synthesis of this substance will not present any difficulties.'

'So far we know that the initial hydrocarbon is aromatic, but it is not known which derivative it is - benzene or naphthalene, Grebe said.

'Why don't you try to heat the substance with zinc dust? I successfully applied this method to determine the approximate structure of indigo. We know now that oxidation of indigo leads to isatin, which can be reduced with zinc into indole - a compound that does not contain oxygen. I think you should try this method as well.'

Grebe thanked Baeyer for the advice and went to the laboratory where Liebermann worked.

'What did Baeyer advise you to do?' Liebermann asked.

'He suggested heating alizarin with zinc dust, but I think it would lead to nothing. What did he achieve by getting the indole? The structure of indigo remains unsolved.' 'You may be right,' Liebermann agreed.

... A month had passed. One day Baeyer, while discussing the experimental results with his assistants, drew attention to a flask in which a red liquid was boiling. 'Well, what about the distillation with the zinc dust? Did it work?

'We didn't carry this experiment out,' Grebe confessed, embarrassed.

Baeyer sharply straightened up, blushing with anger.

'Grebe, while you are my assistant you must follow my orders. My instructions were quite clear - heat alizarin with zinc dust!'

Furious Baeyer left the laboratory.

Grebe and Liebermann had to comply. Although initially, they did not take much pleasure in following Baeyer's instructions, after a few days they were admiring the scientist's ingenious intuition. As a result of the distillation, Grebe and Liebermann obtained anthracene, which, after oxidation, was converted into alizarin.

'This is fantastic!' Grebe exclaimed. 'Now alizarin will become the cheapest dye. After all, anthracene is a by-product of coal tar processing, and has been simply discarded as waste until now.'

The news about the synthesis of alizarin was received ambiguously. Scientists welcomed the outstanding discovery but among the peasants who grew Rubia tinctorum on huge plantations, from the roots of which alizarin was extracted, the news caused panic. Nevertheless, it was a great achievement that Baeyer's laboratory found a

method to obtain hundreds of tons of valuable alizarin from waste. The method discovered by Baeyer for the reduction of organic substances by heating them with zinc dust - the zinc-dust distillation method - became of great importance for both science and industry.

The prestige of Baeyer's laboratory at Gewerbeinstitut grew significantly. He attracted the attention not only of scientists but also of industrialists. Baeyer's income increased significantly and he was finally able to think of family life.

Adelheida Bendemann and Adolf Baeyer got married on August 8, 1868. The young wife not only skillfully took care of the household but also helped Adolf with his correspondence. Adolf Baeyer did not like to write. Even the scientific papers that summed up his research results were written by Baeyer with great reluctance.

The problem of indigo synthesis remained unresolved and it constantly occupied Baeyer's thoughts.

'Grebe and Liebermann were lucky. Anthracene production is very cheap, it can be easily obtained in large quantities ... Indigo can be converted into indole by oxidation and then reduction. Marcellus Nentsky, on my advice, tried to oxidize indole and isolated isatin. We need to find a way to turn isatin into indigo,' mused Baeyer. He put down the test tube and sighed. 'Well, what can we achieve by this? It turns out to be some kind of vicious circle. Perhaps we need to find a way to synthesize indigo from other starting materials, which are cheap and readily available.' He dipped a few orange-red isatin crystals into a test tube, mixed them with phosphorus pentachloride, then heated the mixture gently. The mixture melted, and he set it to cool down. After a while, crystals appeared in the test tube. With excitement, Baeyer began an analysis of the crystals. In addition to carbon, hydrogen, nitrogen, and oxygen, the new compound contained chlorine. 'This is a chlorine derivative of isatin! Let's try to heat it with zinc.' Baeyer poured acetic acid into a mixture of zinc powder and isatin dichloride. The reaction was violent and the mixture became frothy, but no other visible change was noticeable ... Baeyer poured the mixture into a glass and left it overnight. The next day brought a surprise - at the bottom of the glass, dark blue sediment was found. 'Is it really indigo?' - Baeyer mused, then he divided the dark blue substance into several tubes and began the analysis. The elemental analysis confirmed his assumption - it was

indigo! Indigo! Indigo! Finally a success. Baeyer decided to repeat the experiment several times and determine the structure of the compounds. Synthesis of indigo is, no doubt, a great success, but how to synthesize isatin? The only way to get this substance now is by oxidizing indigo.

One winter evening in 1872, Freiherr von Roggenbach came to Baeyer's house. He brought a long-awaited invitation.

'A university is opening in Strasbourg and I was asked to find out if you would agree to take the professor of chemistry position. It is true that the working conditions will not be easy at first. The city was badly damaged by the war, but we will try to help you,' von Roggenbach said.

'I need to consult with my wife,' Baeyer replied. Adelheida did not hesitate for a moment: 'An ordinary professor of chemistry is a very prestigious position. I think you should accept the offer.' Baeyer agreed and accepted the offer.

It was hard for him to part with his laboratory at Gewerbeinstitut and with his students, but he made the decision.

In the fall of 1873, classes began at the University of Strasbourg. Baeyer assigned the department of inorganic chemistry to his assistant and became the head of the department of organic chemistry. Young chemists began to come to Strasbourg to work in Baeyer's laboratory and master the art of experimental organic chemistry. Baeyer continued to study the molecular structure of indigo, barbituric acid, phthaleins, and chloral. Dozens of amazing dyes were first synthesized in Baeyer's laboratory. The small-scale synthetic experiments completed by Baeyer would then be continued by his assistants. They would optimize the conditions of the experiment, prepare compounds in large quantities, analyze them, and study their properties to establish the chemical structure.

Baeyer synthesized phenolphthalein for the first time in his laboratory at the University of Strasbourg. In an alkaline medium, the colourless solution of this white crystalline compound turned a crimson-red colour. Phenolphthalein soon became widely used in chemistry as an indicator. Baeyer determined its molecular structure and began a series of syntheses of other dyes with a similar structure. The dye fluorescein, which was synthesized from phthalic anhydride and resorcinol, became especially known. Its aqueous solution was pale green, and when illuminated, it gleamed yellow-green. There were a lot of problems in the lab with this substance. The laboratory assistants would spend hours washing test tubes and flasks, but the water from glassware would continue to fluoresce. The news of the strange properties of this substance soon spread throughout Strasbourg. It all started when drops of solution accidentally fell on Emil Fischer's hair. For several hours Fischer washed his hair in the city's public bath, but it was all in vain - greenish, strongly fluorescent water continued to flow from his hair. The water flowing from the drain pipes of the bathhouse was also yellow-green for three days. Even the waters of the deep Rhine river began to fluoresce. People crowded on the shore. People were surprised, admired the colour, but they were also worried.

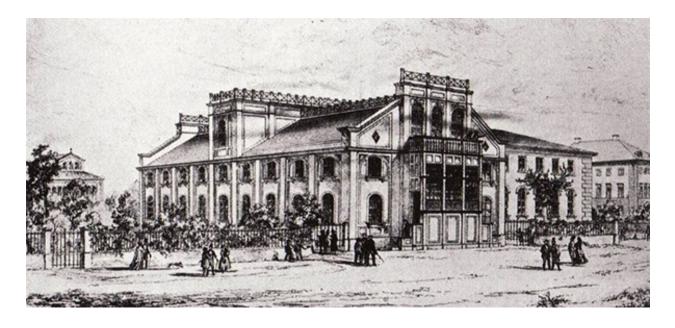
During his time in Strasbourg, Baeyer made many friends. Sometimes after work, the laboratory staff would gather at the Baeyer's apartment, which was in the building next to the laboratory. At a large and noisy table, funny stories and jokes were told, and songs were sung. Adelheida loved these cheerful companies and knew how to enliven them with her art of an excellent hostess. These young people, in love with science, rallied into one large family, in the center of which was Professor Baeyer.

Baeyer lived in Strasbourg for three years. At the beginning of 1875, he received an invitation to take the place of the deceased professor Liebig in Munich and soon moved there with his family.

Baeyer left the organization and decoration of their new house on Arcisstraße to Adelheida, and he took up (yet again!) the organization of chemical laboratories. The laboratories were located next to his house and were connected by a narrow corridor with Baeyer's office. Baeyer's private laboratory was located in the courtyard. This very modestly equipped laboratory later became the site of many outstanding discoveries. In 1878, Baeyer finally achieved his cherished goal - the synthesis of indigo. He was on the verge of this discovery in Strasbourg. Baeyer finally found a way to obtain isatin from *o*-nitrophenylacetic acid ... and then he used the method of converting isatin into indigo he developed previously.

The cousins Emil and Otto Fischer moved to Munich to complete the research they began in Strasbourg. Baeyer's laboratory soon was no longer able to accommodate all the trainees - young chemists who came to work under the guidance of Baeyer. Baeyer monitored the work of each trainee, gave lectures, and conducted his research.

On days off, he and his wife and children would roam in the outskirts of Munich. His favourite place was the Bavarian Lakes. The whole family roamed the meadows, fished, swam in the clear water on warm summer days. During the summer holidays, they would usually go to the Alps and stay in a rented house in the mountains.



The Munich Chemical Laboratory under the direction of Adolf von Baeyer (Source: History of the Faculty for Chemistry and Pharmacy, Faculty for Chemistry and Pharmacy at the Ludwig-Maximilians-University. <u>https://www.cup.uni-muenchen.de/en/faculty/history/</u>) MV

The summer of 1881 passed, as usual, merrily and carelessly, and no one suspected what tragedy it would end with. The Baeyers lived in a small Swiss village and every day they went hiking in the mountains. Hans and Otto were still too small for long walks and stayed at home, while Eugenia and Franz would usually go with the parents. One day Franz decided to stay at home. While Eugenia and her parents were away nothing much happened except some dog bit Franz. Nobody paid attention to the minor wound. Adelheida applied some cologne to it and everyone forgot about the incident. Much

later, Franz started to feel unwell. He had difficulty swallowing, he had pain at the back of his head, and his eyes shone feverishly.

'We'll return to Munich at once,' Adolf said anxiously. 'Maybe it is not too late."What do you think he has?' Adelheida asked in a trembling voice.



Muller, Friedrich. Portrait of Adolf Von Baeyer, circa 1884. (Source: Williams Haynes Portrait Collection, Box 1. Science History Institute. Philadelphia. <u>https://</u> <u>digital.sciencehistory.org/works/cc08hf749</u>) MV

'I'm afraid these are symptoms of rabies' Adolf replied.

Unfortunately, when they arrived in Munich, it was too late and physicians were not able to help Franz.⁸ The disease progressed rapidly, and Franz passed away. Adolf and Adelheida were overwhelmed with sadness and despair.

The rabies vaccine was introduced by Louis Pasteur only four years after Franz's death. Louis Pasteur has earned the eternal gratitude of humanity for the development of a vaccine against such a terrible disease.

Despite the grief, Baeyer did not stop his research and continued his attempts towards the synthesis of indigo. He developed methods for obtaining the dye and even tried to

⁸ The recollection of this tragic event by Hans von Baeyer did not quite match Manolov's description. There is no reference to the story source in Manolov's text. MV

organize industrial manufacturing; however, synthetic indigo was still very expensive. The fact that the chemical structure of indigo was determined, made it possible to search for other less expensive ways of its synthesis. Thus, Karl Hoyman developed two new methods for the synthesis of indigo, and after a few years, Indigofera cultivation was stopped as the dye could now be obtained synthetically at a low cost. In his laboratory, Baeyer synthesized and studied the properties of several compounds that were obtained by condensation of phenols with aldehydes, amines, and other compounds. He also continued his research to solve the remaining questions regarding the structure of phthalein dyes and the properties of unsaturated compounds.⁹

When Baeyer successfully carried out the condensation of compounds with double and triple bonds, he developed the idea to sequentially carry out a multi-stage synthesis to obtain the long-chain compounds with alternating triple and single carbon-carbon bonds. Such a chain, according to his assumption, would not contain other atoms except carbon, and, therefore, will be the new allotropic form of carbon. He called it "explosive diamonds". Although Baeyer did not obtain "explosive diamonds", some of the polyyne compounds that he made were explosive. In addition, the research of polyyne compounds helped to formulate his famous "theory of ring closure". According to this theory, the most stable are the five and six-membered rings. The strain theory explained the chemical properties of cyclic compounds.

While examining the data regarding the properties of aromatic compounds, Baeyer concluded that none of the structural formulas of benzene suggested so far fully and accurately reflected its chemical properties. As the result of his theoretical work, he proposed a new formula for benzene.

This period of Baeyer's scientific career was somewhat intense, and sometimes even painful. He would go back to projects which were already finished, and then switch to other research directions. All this on the background of typical university life - lectures, classes with students, exams. Baeyer's lectures were not at all similar to the exquisite lectures of his predecessor, Justus von Liebig. 'I throw people into the sea, and let them

⁹ It is important to add, that in 1885 on his fiftieth birthday Adolf Baeyer was given a hereditary knighthood by King Ludwig II of Bavaria, and became known as Adolf Ritter von Baeyer, the second-lowest rank of Bavarian nobility. This links to the surname von Baeyer that he and family members are known by thereafter. CvB

swim out as best they can,' Baeyer would say, describing his teaching style. During his lectures, he would give a detailed description of complex organic syntheses, illustrating them with many structural formulas. Baeyer knew very well that for understanding the complex process of chemical transformation visual representation is the most essential. Therefore, his lectures were accompanied by numerous chemical demonstrations. Baeyer would often use funny comparisons and comic analogies. All this helped the students to understand and retain the knowledge. For example, during his lecture on starch, touching upon the issue of starch hydrolysis by various enzymes, Baeyer said in the most serious tone:

'This enzyme is also found in saliva. If you chew rice porridge for several minutes, you can find in it a substance obtained by hydrolysis of starch - glucose. Now you can see for yourself the hydrolytic ability of the saliva enzyme. I think our laboratory assistant,

Mr. Bernard, will not refuse the courtesy and will demonstrate this to us.'

Bernard walked over to the pulpit. Baeyer took out a large porcelain dish of rice porridge from under his desk and handed it to Bernard.

'Now Mr. Bernard will chew the porridge well, and then we will find out if it contains glucose.'

It was so unusual that the students couldn't help laughing.

Baeyer's Munich laboratory attracted more and more young chemists not only from Germany but also from all over Europe, the UK and from the USA.¹⁰ In the laboratory, students and scientists synthesized previously unknown substances and classes of organic compounds, determining chemical structures, and developed synthetic methods to prepare natural products as well as new, easier, and less expensive ways to prepare a variety of organic compounds. In the evenings, as in Strasbourg, Baeyer's students and staff members gathered at his house. Adelheida would also invite artists, poets, and philosophers to attend the evening gatherings.

... The years passed quickly. The eldest daughter, Eugene, married professor Oskar Piloty. Hans and Otto also found their way in life. Baeyer became a grandfather ...

¹⁰ <u>https://academictree.org/chemistry/peopleinfo.php?pid=21401</u> MV

It was 1905. Dozens of Baeyer's students, now well-known scientists, gathered in Munich to celebrate his 70th birthday. It started with a solemn ceremony and followed with lunch in the large hall. Greetings came from all over the world. It was during the celebrations, the news came that Baeyer was awarded the Nobel Prize for his contribution to organic chemistry.



Adolf von Baeyer with his students and assistants, University of Munich (source: https://www.cup.lmu.de/en/faculty/history/) MV

Baeyer stopped teaching the following year. His deputy, Richard Willstätter, moved to the house on Arcisstraße, while Baeyer and his wife, Adelheida, moved to their home in Starnberg. In Starnberg Baeyer continued his research in his private laboratory. New syntheses, new successes!

The house was always filled with grandchildren's voices and it warmed the heart of the old scientist. Well, sometimes grandchildren went too far in their practical jokes. Once, when Baeyer was walking in the garden in anticipation of the arrival of the famous English physicist Ernest Rutherford, the mischievous grandchildren made a straw effigy and put it in a guest chair inside the house. They then told his grandfather that the guest arrived long ago and was waiting in the house. Baeyer hurried into the living room and, bowing, began to apologize long and politely for missing the guest's arrival. One of the grandchildren hid behind a chair and slightly rocked the stuffed figure. When the deception was discovered, Baeyer became very angry, specifically because

Rutherford had indeed arrived and was waiting for the host in the garden.

Baeyer communicated with many eminent European scientists. Using almost no written correspondence, he always would find time to visit his colleagues and friends, would chat with them, learn about their recent achievements, and tell them about his own. He was respected and welcomed everywhere as a dear guest. His students became professors in many European universities. They retained great affection for their teacher and, when they came to Munich, they would always visit Baeyer's house.

The last years of Baeyer's life were overshadowed by the outbreak of the world war. The people of Germany bore all the hardships of the war, and Baeyer took it hard. His health quickly deteriorated, and he would often suffer from bouts of a dry cough, and soon fell very ill. On August 20, 1917, Adolf Baeyer died. An outstanding scientist, one of the founders of the classical German school of organic chemistry passed away.

From the translator:

I am writing this note at the request of Cornelius von Baeyer to explain my interest in the subject.

I first read about Adolf von Baever in the book of Manolov in 1986. The first volume of Manolov's "Famous Chemists" I got a year earlier. I loved it so much I was hardly able to wait for the second volume to appear in our local bookstore. The second volume did not disappoint. I enjoyed reading the engaging stories about the lives and work of chemists. The list included big names such as Kekulé, von Baeyer, Fisher and Willstätter. As you already know from the translated text, the stories of them are interconnected. Although I had another year before the formal start of the chemistry subject in school, I already fell in love with the science of chemistry. I had a small chemical lab set up at home. Thanks to the "Young Chemist" kit my parents bought me when they noticed my interest in chemistry and the supplies of simple reagents available from a pharmacy I had everything I needed to perform simple and even advanced experiments. The fact that Adolf von Baever had a small lab when he was a child inspired me even more. A great source of experiments was a Russian translation of "Chemie Selbst Erlebt" written by Erich Grosse and Christian Weißmantel. The book had a chapter on preparations of phthalein dyes and details about the work of von Baeyer, Fisher and Caro. I learned more about von Baeyer's work much later while studying organic chemistry at Kharkiv Pharmaceutical Academy in Ukraine and when I took an advanced organic chemistry course during my doctoral studies at Weizmann Institute of Science in Israel. I was happy to find Richard Willstätter's "From My Life" and Vladimir Ipatieff's "The Life of a Chemist" memoirs in the Weizmann Institute library. Willstätter and Ipatieff were von Baever's students and wrote their recollections of the time they worked in his lab.

When not long ago I heard in the store the name von Baeyer I was delighted to find out that one of our customers is a great-grandson of Adolf von Baeyer. I was very happy to translate the inspirational story about Adolf von Baeyer I read way back in my childhood. I hope you enjoyed reading it.

Please feel free to reach out to me if you have any questions or comments at <u>maxymvasylyev@gmail.com</u>

Max

Max Vasylyev R.Ph., Ph.D. (organic chemistry)