

FRIEDEL MEMORIAL LECTURE.

By J. M. CRAFTS, Professor.

THE tomb of Friedel at Montauban bears the inscription :

CHARLES FRIEDEL

né à Strasbourg le 12 Mars 1832

décédé à Montauban le 20 Avril 1899.

Membre de l'Institut.

"Le juste vivra par la foi

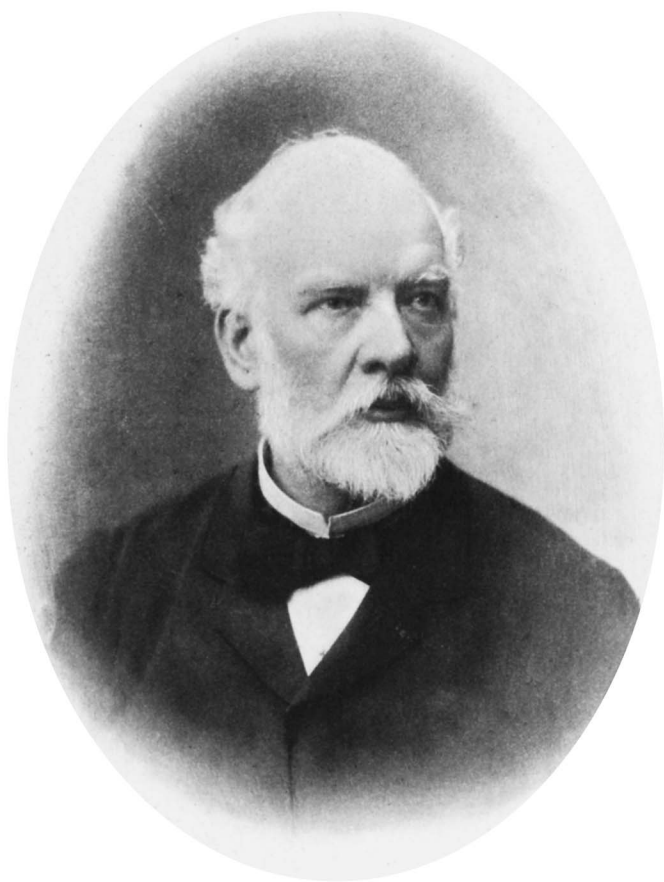
La mémoire du juste sera en bénédiction."

So far as a tombstone can bear faithful witness to a life, this short description is true of a man who chose science for his occupation, and strove to do his duty towards God and man with keen observation of things temporal and a simple faith in things eternal.

We, as members of the Chemical Society, are chiefly concerned with his contributions to science, but enumeration of these will not be complete unless it is said that high among his contributions to the advancement of science stands the influence of a very beautiful character and of a well-balanced judgment upon the men of his time, even extending beyond his own nation, and during the excited period after the French national disaster, serving as a connecting link between the scientific reasoning of his countrymen and the spread of philosophy abroad.

The influence of individuals and of schools upon the patronage of the younger men for educational positions is peculiarly important in France. The destiny of a student of science depends greatly upon the leader whom he chooses to follow, and there is sufficient cohesion among the members of a school to make it an effective body. That founded by Wurtz was continued by Friedel, who was the oldest of the French followers of Wurtz, and only fifteen years younger than his leader. His immediate associates were Gautier, Grimaux, Salet, Lebel, and, later, Hanriot and the Combes. With Friedel, as with Wurtz, charm of character, as well as scientific talent, contributed to enlarge this group of men, bound together by a common regard and by community of views, until the school became an important factor in the nation's progress.

One of the most notable channels through which scientific patronage is exercised is in the Academy of Science, whose organisation offers very effective means of exerting influence in the election of new members, in the appointment to professional places, in the annual distribu-



C. Friedrich

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tion of large numbers of prizes, and in the examination by committees of questions of scientific, and sometimes of national, interest. Friedel played an important part in this work, and his competency in chemistry, mineralogy, and mathematics, together with his evident fair-mindedness, gave great weight to his opinion among his colleagues.

There is much significance in the way in which the title, Member of the Institute, is used as the only record of occupation placed upon Friedel's gravestone, and it is quite in accord with French usage to consider this distinction one of the highest that the nation can bestow; thus Napoleon, in familiar letters, having nothing to do with science, signs himself, "Bonaparte, Général en Chef, Membre de l'Institut."

The circumstances of Friedel's family, as well as his subsequent position, favoured the development of his scientific career. His childhood, passed at Strasbourg, brought him, even during school years, in contact with men of science, and his inclination for scientific studies was favoured by his parents.

He took his Bachelor's degree in letters in 1849, and that in science in 1850. He then entered his father's counting-house, and while there had an opportunity of attending lectures by Pasteur, Daubrée, Bertin, and Lereboullet at Strasbourg University. His stay in the counting-house lasted only a year, and, as might have been expected, the attractions of science presented by such men drew him away from commerce.

In 1851, he went to Paris to live with his maternal grandfather, G. L. Duvernoy, Professor at the Collège de France and the Museum of Natural History. He took the Licentiate degree in mathematics at the Sorbonne in 1854, and that in physical science July 7th, 1855. While pursuing these studies, he commenced research work at the Museum, and a letter, dated December 21st, 1854, speaks of the discovery of two new faces in crystals of corundum, given him for examination by Dufrénoy (he had refused a place of assistant with that mineralogist), and also of a research confided to him by Wurtz.

He followed the lectures of Senarmont at the School of Mines, and formed a strong personal attachment to him while engaged in mineralogical studies under his guidance. In 1856, Friedel was appointed Curator of the mineralogical collection of the School of Mines, then under the direction of Dufrénoy, and for the remainder of his life was actively occupied with enriching that important collection. He was at first attracted by the crystallographical side of mineralogy, and then towards optics, until, at the suggestion of Senarmont, he thought of devoting himself to mathematics and becoming an astronomer; but soon the chemical side absorbed his attention, and during the remainder of his life his time was divided between pure chemistry

and chemical mineralogy, although he always took especial pleasure in the examination of crystalline forms. Somewhat later, he was advised by Pasteur to seek an entrance to the Academy of Science in the section of mineralogy, to which Pasteur himself belonged, but Friedel preferred to make chemistry his principal study.

On November 10th, 1854, Friedel entered Wurtz's laboratory, and soon became its most distinguished pupil. There were some sixteen places, of which usually one-third were occupied by foreigners, particularly Russians, Germans, Austrians, and Italians. The rooms at the School of Medicine were inconvenient, having been designed for other purposes, and the balances were placed in an anatomical lecture room; yet this school succeeded in some measure to that of Liebig, and was visited by chemists of all nations; for European science still held to the traditions of the time of Humboldt, and a sojourn, however short, at Paris was considered a desirable part of a scientific education.

Friedel's researches upon acetones and aldehydes were made at this time, 1857—1863, in the laboratory of the School of Medicine, and his views of their constitution, and his discovery of secondary propylic alcohol, were immediately recognised as important contributions to chemical science.

In 1866, the privilege of a small laboratory at the School of Mines was attached to the place of Curator of the mineralogical collection, and it was there that Friedel's work in mineralogy was done, as well as the researches upon silicon compounds and the aluminium chloride reaction. He had, between 1866 and 1880, an apartment in the buildings of the School of Mines. In 1869, he took his Doctorate degree, offering two theses, one upon acetones and aldehydes, and the other upon the pyroelectric properties of crystals. In 1871, he gave the lectures in mineralogy at the Normal School (*Ecole normale supérieure*), replacing Des Cloizeaux.

In 1876, he was appointed Professor of Mineralogy at the Sorbonne, succeeding Delafosse, and he there organised a laboratory for mineralogy. Two years later, he was chosen Member of the Academy of Science in the chemical section, filling the place left vacant by the death of Regnault.

The death of Wurtz in 1884 left Friedel the oldest representative of Wurtz's school and he succeeded to Wurtz's professorship of organic chemistry at the Sorbonne, exchanging this chair for that of mineralogy. The laboratory accommodation for chemical students was very insufficient at Paris and the old buildings at the Sorbonne were still more unsuited to such work than were those of the School of Medicine. A project for new and greatly enlarged buildings was under consideration, but with small prospect of immediate realisation, so that Friedel devoted his energy to the construction of a temporary

laboratory building beyond the Luxembourg Garden in the Rue Michelet, where also the inorganic laboratories of the Sorbonne under Troost were located. These rooms, although lacking the luxury of the modern laboratory, proved to be convenient and the places for about fourteen students were always filled.

In January, 1895, the new laboratories at the Sorbonne, built upon Friedel's plans, were opened with places for thirty students in organic chemistry, and at the same time he organised a three years' course of lectures and laboratory instruction in industrial chemistry at the provisional laboratories in the Rue Michelet. Such instruction had heretofore been wanting in Paris. It was undertaken at Friedel's instigation by the Municipal Government, and the attention required by the initial steps, and afterwards by the direction of this new course, formed an important occupation during the last four years of his life.

He took the chief part in 1899 in founding the *Revue Générale de Chimie pure et appliquée*, which is largely devoted to industrial applications. Friedel was associated with Wurtz in editing the *Dictionnaire de Chimie pure et appliquée* and after Wurtz's death in 1884 became the chief editor of the supplements, of which the second has only progressed to the letter G. During the later years of his life, editorial work, together with the work upon committees and administrative duties, engrossed more and more of his time, and he often regretfully looked back upon the hours spent upon experiments in his laboratory which he ever considered the most enjoyable.

He was one of the founders of the French Chemical Society, four times its President, and a constant attendant at its sittings. He took the initiative in founding the French Society for the advancement of Science in 1885, and presided at the meeting at Nancy in 1886. He presided at the International Congress of Chemists held in 1892 at Geneva for the reform of the nomenclature of the fatty acid series, and up to the time of his death was occupied with the arrangement of a similar meeting to attempt the construction of a common system of nomenclature for the other classes of organic compounds.

He was awarded the Davy medal by the Royal Society in 1880; received the degree D.C.L. from Oxford University in 1894.

The following societies conferred their membership or honorary membership on Friedel: Foreign member of the English Chemical Society, 1876; Industrial Society of Mulhouse, 1879; Physical Society of Geneva, 1880; Royal Society of Turin, 1882; Academy dei Lincei, 1883; Academy of Munich, 1883; Royal Academy of Lisbon, 1890; Natural History Society of Maxon, Society Antonio Alzato Mendio, 1890; Roy Society of Brussels, 1892; Society of Physics and Chemistry of Bucharest, 1892; Literary and Philosophical

Society of Manchester, 1892; honorary member of the German Chemical Society, 1894; Royal Society of Sweden, 1894; corresponding member of the British Association for the Advancement of Science, 1895; Royal Society of St. Petersburg, 1895; Physical Society of Frankfort, 1898.

He was made Chevalier of the Legion of Honour in 1869, and Officer in 1886. He was Officer of Public Instruction, and was also Commander of the Orders of St. James of Portugal and of the Crown of Roumania.

Before taking up the record of Friedel's work in science, a further description may be given of the fortunate surroundings, which not only favoured the development of a judicious and amiable character, but also gave full play to his scientific ability. His tastes found immediate and hearty appreciation and support from his parents and relations, and sufficient pecuniary resources were always at his command to allow him to do his chosen work in the best way.

His love of science was hereditary. His father, Charles Friedel, although beginning his long commercial career in a banker's office at the age of thirteen, attended scientific lectures at Strasbourg whenever he had the opportunity, and, at the age of eighty-four, expressed his regret that necessity had prevented him from following a scientific career, and his satisfaction that the choice had been offered to his son.

The mother was a woman of strong character, and came of a professorial family. Her father was George Louis Duvernoy, a physician established at Mountbéliard, and later Dean of the Strasbourg Faculty of Science, and finally Professor at the Museum of Natural History at Paris.

The gathering of a small collection of minerals by the boy was encouraged, a laboratory was tolerated in his father's house, and later, when he was staying with his grandfather Duvernoy, he was aided in his choice of studies by the veteran in science, until failing health made the older man dependant upon the younger. A letter written in 1854 describes occupations which are not generally attributed to a student in the gay capital; thus the day was devoted to arduous studies to prepare for the baccalaureate examination, long evenings were spent in watching with or reading to the grandfather, and on Sundays some hours were given to visiting the poor.

Senarmont, with whom he began mineralogical work, took a strong and friendly interest in the young student, and Friedel's friendship with Wurtz was a very important factor in his career. Both Alsacians, united by tastes, opinions, and pursuits, the elder chemist opened the way for the younger in professional and editorial work. Wurtz's high reputation, his activity in public affairs as well as in science, led to the creation of the chair of organic chemistry at the

Sorbonne, and after Wurtz's death in middle age, Friedel's studies and talents naturally marked him out as the successor. Wurtz's influence in Government circles also prevailed, after long-continued effort, in obtaining support for laboratory instruction, and, shortly before his death, the orders were given for the construction of a large modern laboratory at the Sorbonne, the plans of which were matured, and the construction superintended, by Friedel.

The two friends were very intimate, and were thoroughly in accord regarding all matters of public and scientific interest, but in later years Wurtz became much occupied with duties connected with his senatorship, whilst Friedel was never diverted from scientific pursuits. In consequence, the share of the latter in editing Wurtz's chemical dictionary became larger.

Until within a few years of his death, Friedel never had a well-equipped laboratory provided with labour-saving contrivances, nor was he disposed to have much work done by assistants, preferring to leave very ample opportunities to all those about him for doing original work and publishing it alone, whilst aiding them untiringly with his counsels. For these reasons, the volume of his contributions to chemical research is not very large, and many an idea passed into other hands for execution.

Most of the work in organic chemistry was done in a small room in the fine palace on the Luxembourg Gardens which is used for the School of Mines, whilst a dark, vaulted cellar served for the artificial production of minerals at high temperatures and pressures. Here Friedel and Edmond Sarasin heated "Jacob" to a very low red heat at whatever pressure boiling water gives at that temperature. The origin of the name is lost, but "Jacob" was the only designation of a very heavy steel tube lined with platinum, in which water and pure materials intended to make silicates were heated overnight, and the fate of "Jacob" was a matter of lively interest each morning in the laboratory. There was no serious explosion, but any attempt to economise in the weight of the thick interior platinum tube led to a disaster.

Friedel married Miss Emilie Koechlin of Mulhouse on December 29th, 1856. One son and four daughters were born of this marriage. The surrender of Paris in 1871 brought to him the sad news of the death of his charming and amiable wife, who had been obliged by failing health to pass the winter at Montreux and died on January 19th, 1871, while her husband was serving in the national guard during the siege. On April 7th, 1873, he married Miss Louise Combes, daughter of the director of the School of Mines, and a son was born of the second marriage. The character and education of his wife, who still survives, made her a most efficient aid and companion. During his last illness,

his wife and several of his children were with him at the house of his son-in-law, Professor Henri Bois at Montauban.

Friedel's life in Paris was wholly devoted to science, and was not unlike that of the professor in a university town. Weekly evening receptions kept him in touch with his scientific friends and scholars. In the discussions which took place on these occasions, his modesty led him instinctively to play the part of a listener until every one had expressed an opinion, and then all were glad to hear a new and fundamental treatment of the subject from Friedel's lips. It is a piece of good fortune for an honest man to have a face expressive of character, and his was eminently one which immediately convinced a new acquaintance that the man was incapable of guile, and thus inspired ready confidence and the ease of intercourse which goes with it.

He was a lover of music and of art, and his favourite recreation was sketching from nature. He took a strong and judicious interest in political affairs. Very happy in his family life, and in many intimate friendships, escaping unfriendly rivalries by his character and circumstances, he was permitted from the beginning to the end to carry on with a single mind the pursuits which he loved. The pursuit of science and his duties as a husband, father, friend, and citizen made up Friedel's existence. He was always disposed to work somewhat beyond his strength, and in 1885 a severe illness diminished considerably for the remaining years his capacity for experimental work, but not for editorial labours.

One of the elements contributing to a certain retirement from the disturbing interests of life in the French capital were the associations into which Friedel's Protestant faith (*Eglise réformée*) led him. Isolation is too strong a word to be applied to Protestant society at Paris, and yet in certain ways their habits of thought are different from those of their neighbours. Strong motives for these differences still survive among the Protestants of the older generation from the south of France, and the second wife of Friedel cannot forget having passed her childhood near Nismes in a house where the coffins of her relations occupied one of the drawing rooms because, as Protestants, they were refused Christian burial. No memories of persecutions haunt the immediate past of the Alsatian Protestants. Those who elected French nationality after the war, or who, like Friedel, were fortunate in having already chosen their residence in Paris, have had full recognition of their patriotism and of their value as citizens; nevertheless, a mental barrier is raised to some extent between Protestants and Catholics, and curious testimony of this attitude was lately offered when the latter joined with an army of Freethinkers and affected to confound the Protestants with the Jews. Not religious controversies, but different habits of thought, as marked as racial characteristics,

make a distinct, although faint, line of separation between general Parisian society and that in which Friedel moved. For a man of his character, it must not be supposed, however, that any distinct obstacle prevented perfect freedom of intercourse with men of all shades of opinion.

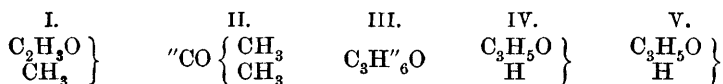
After very deliberate reflection, the writer cannot forbear adding a piece of personal testimony to this sketch of a life's work. During thirty-eight years in which a close friendship made him a witness of conduct and actions, he cannot recall a single instance in which he would have wished his friend to have thought or acted otherwise than he did.

Chemical Researches.

Friedel at the age of twenty-five chose the ketones (acetones they were called at that time) for the subject of his first research, and he was fortunate enough to establish experimentally the properties of the first of the important series of secondary alcohols, besides preparing many new ketones and their derivatives (*Ann. Chim. Phys.*, 1869, [iv], 16, 310). While preparing new substances, he held the theoretical side of the subject distinctly in view, and did much to set it on a firm basis.

At this period, Gerhardt was the authority on organic chemistry. The type theory had been well developed, and owed much of its value to the discoveries of the compound ammonias and the bivalent alcohols by Wurtz. Kekulé, in the first volume of his organic chemistry, published in 1861, used the existing ideas of types and radicles in a much more rational way than his contemporaries, but there was some confusion in the use of what he called rational and reactional formulæ, and much remained to be done in presenting schemes of structure capable of explaining the relation between the constitution and properties of a substance. With greater or less distinctness, the chemists of the day recognised the possibility of explaining functions by formulæ, and Friedel was the first to so enlarge the data as to give what were accepted as convincing proofs of the dependence of the functions of the CO group in acetones upon the form of combination.

Kekulé devotes only seven pages in his first volume to the known ketones; he does not mention them under the section "Carbonyl compounds," and he uses five formulæ for acetone:



The first two he calls rational formulæ, and probably considered II to be a developed form of I and V of IV. On page 617, he says that

the mesityl compounds point to V as the rational formula for acetone; the remaining reactions are explained by III.

It is unnecessary to give a catalogue of the new ketones obtained by Friedel, using known methods. In his first paper (*Compt. rend.*, 1857, 45, 1013), he describes phenyl methyl ketone and methyl butyl ketone. He also studied the products of the action of phosphorus pentachloride on the ketones, obtaining a new propylene dichloride and monochlorinated propylene. The chief purpose of this work was to furnish further proofs of a similarity of function between aldehydes and ketones. This had already been indicated by certain reactions common to both series. Thus Limpricht had described the additive compounds with sodium hydrogen sulphite, and Städeler those with hydrocyanic acid. Cahours had shown that an aldehyde treated with phosphorus pentachloride does not break up like an alcohol or an ether, but that two atoms of chlorine are substituted for oxygen. Friedel completed the demonstration by showing that acetone behaved in the same way.

Friedel, in a second paper (*Compt. rend.*, 1862, 55, 53), described the behaviour of aldehydes and ketones on reduction with sodium amalgam (zinc and an acid cannot be employed because the production of hydrogen is arrested by aldehydes). Wurtz had used the sodium reduction for ethylene oxide, but was prevented from applying it to aldehydes because of the resinifying action of caustic soda on common aldehyde. Friedel succeeded in reducing benzaldehyde and valeraldehyde to the corresponding alcohols, and acetone to a propylic alcohol, which was not identical with the primary one (b. p. 97.3°) discovered by Chancel in 1853 among fermentation products. He believed it to be identical with a propylic alcohol prepared by Berthelot in 1855 by the action of sulphuric acid on propylene.

No experiments had been made to prove that Chancel's alcohol gave propionic acid and Berthelot's alcohol acetone on oxidation, and Friedel considered it superfluous to ascertain whether a substance derived from acetone by reduction would give acetone on oxidation. Kolbe took advantage of this omission to bring forward his theoretical views, predicting this nearly evident fact, and at the same time giving a clear exposition of the difference between a primary and a secondary alcohol. The capital point was the discovery of the relation of a secondary alcohol to its oxidation product, and it may be considered that Friedel's reduction of acetone accomplished this task.

Berthelot (*Ann. Chim. Phys.*, 1855, [iii], 43, 399) afterwards tested the alcohol derived from propylene, and found that it also gave acetone on oxidation.

It should be stated that Kolbe recognised more clearly than the other chemists of that time the significance and the importance of the

existence of two kinds of propylic alcohol, one of them offering the first example of a secondary alcohol.

Friedel also observed the formation of pinacone, and pointed out its true constitution. It had been discovered by Fittig, and supposed to be a hydrate of $C_6H_{12}O$. Later, in 1873, Friedel and Silva (*Bull. Soc. Chim.*, [ii], 19, 289) described a process for the convenient preparation of large quantities of pinacone.

The True Formula of Lactic Acid.—Wurtz and Friedel (*Ann. Chim. Phys.*, 1861, [iii], 63, 101) showed the difference between the alcoholic and the acid functions of the two hydroxyl radicles in lactic acid, and the corresponding properties of the two esters. They explained that lactic acid is intermediate between propyl glycol and malonic acid, as glycollic acid is intermediate between glycol and oxalic acid. The alcoholic hydroxyl they call basic.

Friedel and Machuca (*Compt. rend.*, 1861, 52, 1087) described the synthesis of lactic acid from bromopropionic acid, glyceric acid from dibromopropionic acid, hydroxybutyric acid from bromobutyric acid, and butalanine by the action of ammonia on bromobutyric acid.

The Theory of Double Decompositions.—Friedel and Crafts (*Compt. rend.*, 1863, 57, 877, 986) showed that when the ester of an alcohol is heated with another alcohol, one radicle partially displaces the other as one metal displaces another in salts. Mixed esters of polybasic acids are formed by a similar process. Alkyl iodides heated with esters give rise to similar displacements, but here a little hydrogen iodide is set free, and serves to esterify a large quantity of alcohol.

Friedel subsequently made a contribution to the theory of esterification by means of halogen acids by showing that, in presence of phosphoric oxide, hydrogen chloride converts a considerable proportion of benzoic acid into benzoyl chloride, and supposes that a similar transformation contributes to esterification (*Compt. rend.*, 1869, 68, 1547).

The experimental difficulties of these early problems were not great, and chemists were rewarded for their labours by the rapid appearance of new substances; the next research led on to more difficult ground.

Silicon Compounds.—Friedel's interest in mineralogy led him to take up the important question of the atomic value of silicon. The school of Wurtz had completely accepted the authority of Avogadro's law under which $SiCl_4$ represents the molecule of the best known volatile compound of silicon; but Buff and Wöhler discovered in 1857 a compound, $Si_2Cl_3 \cdot 2HCl$ ($Si = 21$), whose formula is incompatible with the quadrivalence of silicon. They described the new substance as a liquid boiling at 42° , obtained by the action of hydrogen chloride on silicon. This support for the old trivalent formula was welcomed by all those who had been accustomed to the calculations of mineral analyses established by Berzelius. The new discovery, however, did

not convince Friedel, who considered that, beside the vapour density of silicon tetrachloride, the work of Marignac and the whole assemblage of facts pointed to the tetratomicity of silicon, and sought a confirmation of his views in the organic compounds of the element.

Friedel and Crafts (*Compt. rend.*, 1863, **56**, 324; **57**, 319) took up the work of Ebelmen (*Annalen*, 1844, **52**, 324; 1846, **57**, 319), expecting to find that the normal ester $\text{Si}(\text{OEt})_4$ would form a series of condensed esters of which the simplest, upon a quadrivalent scheme, must be $\text{Si}(\text{OEt})_3 \cdot \text{O} \cdot \text{Si}(\text{OEt})_3$. It was proved that this compound, and others more complicated, for example, $\text{Si}(\text{OEt})_3 \cdot \text{O} \cdot \text{Si}(\text{OEt})_2 \cdot \text{O} \cdot \text{Si}(\text{OEt})_3$, were produced by the action of a trace of water on the normal ester. The first of the series can be easily purified by fractional distillation; but the boiling points of the other members, even in a vacuum, are so high that a separation becomes impossible, since they boil at temperatures at which glass softens, without giving off much gas, but undergoing polymeric transformations. The quadrivalent character of silicon was also shown by allowing anhydrous alcohol to act on an excess of silicon tetrachloride, when a series of well defined chlorohydrins was obtained with the formulæ $\text{SiCl}(\text{OEt})_3$, $\text{SiCl}_2(\text{OEt})_2$, SiCl_3OEt . The composition and vapour densities of these substances agree only with the atomic weight 28 for silicon.

The polysilicic esters recall the series of polyglycols and the analogy between the quadrivalent elements, silicon and carbon, was so marked in all these organic compounds, that it seemed desirable to attempt to replace carbon by silicon in a hydrocarbon and to endeavour to make silicononane $\text{SiC}_8\text{H}_{20}$. It was thought that this domain might belong to Professor Frankland, but after consulting him Friedel and Crafts were courteously informed that the research was open to them, Professor Frankland stating that the few attempts which he had made to obtain a reaction between silicon chloride and zinc ethide had not been successful. A rather high temperature is required and some gas is produced, but large quantities of a pure substance, $\text{Si}(\text{Et})_4$, distilling at 153° were prepared. Unlike most organo-metallic compounds, this substance is very stable towards all reagents, and has completely the aspect of a hydrocarbon except that when it burns, it forms a smoke of silica. In it, chlorine can be substituted for hydrogen and then hydroxyl for chlorine, giving silicononylic alcohol, $\text{SiC}_8\text{H}_{19} \cdot \text{OH}$. In the same way that petroleum hydrocarbons are accompanied by small quantities of oxidation products, mostly ketones and alcohols, so also silicon tetrathide, both during its formation and afterward by contact with air, is liable to an oxidation more rapid than petroleum, but still very slow. On account of oxidation, some difficulty was experienced in obtaining the silico-hydrocarbon pure until the oxygenated products were separated

by solution in concentrated sulphuric acid, which does not attack the hydrocarbon. Thus an unmistakable analogy is established between the general character of carbon and silicon compounds, and Friedel afterwards made use of this resemblance in building up rational formulæ for mineral silicates.

Silicic esters of other alcohols were prepared and also silicon tetramethide, but with much more difficulty than the ethide.

It may be noticed that when the esters are slowly decomposed by penetration of moisture during many years, an opaline silica, hard enough to scratch glass, is obtained.

Friedel and Ladenburg (*Bull. Soc. Chim.*, 1867, [ii], 7, 322) took up the study of Buff and Wöhler's silicon hydrochloride, $\text{Si}_2\text{Cl}_3\cdot 2\text{HCl}$ ($\text{Si} = 21$), and showed that it could be separated by fractional distillation into silicochloroform, SiHCl_3 , boiling at 36° , and silicon tetrachloride, SiCl_4 , boiling at $55-60^\circ$. By action of alcohol, the former gives $\text{SiH}(\text{OEt})_3$, and with water an oxide, $\text{Si}_2\text{H}_2\text{O}_3$, which corresponds with formic anhydride containing silicon instead of carbon.

An impure silicon hydride was described by Buff and Wöhler; the pure compound was prepared by the action of sodium upon the ether $\text{SiH}(\text{OEt})_3$.

Friedel and Ladenburg (*Annalen*, 1868, 145, 174) found that a sulphide to which Pierre gave the formula SiCl_2S ($\text{Si} = 21$) really contained hydrogen and was a silico-trichloromercaptan, SiCl_3SH . The SH radicle can be replaced by bromine to obtain SiCl_3Br .

Friedel and Ladenburg (*Compt. rend.*, 1868, 66, 530) obtained $\text{SiCl}_3\cdot\text{O}\cdot\text{SiCl}_3$ by passing silicon tetrachloride through a red hot porcelain tube, the oxygen being taken from the porcelain. This oxychloride gives with alcohol the same ester, $\text{Si}(\text{OEt})_3\cdot\text{O}\cdot\text{Si}(\text{OEt})_3$, as that obtained by the action of water on the ortho-ester $\text{Si}(\text{OEt})_4$. With zinc ethide, it gives $\text{SiEt}_3\cdot\text{O}\cdot\text{SiEt}_3$ and this oxygenated compound seems also to be formed in the preparation of silicon ethide.

Silicon tetriodide, SiI_4 , and silico-iodoform, SiHI_3 , were prepared by the action of iodine and hydrogen iodide on heated silicon, and Buff and Wöhler's formula, $\text{Si}_2\text{I}_3\cdot 2\text{HI}$, for the product of the reaction, was shown to be erroneous (Friedel, *Bull. Soc. Chim.*, 1868, [ii], 9, 1). The compound, SiBr_3I , boiling at 200° was obtained by the action of bromine on silicon tetriodide, SiI_4 .

Silicon triiodide, Si_2I_6 , was obtained by heating the tetriodide, SiI_4 , with finely divided silver at 300° (Friedel and Ladenburg, *Compt. rend.*, 1869, 68, 920); a non-volatile substance, SiI_2 , was also obtained which yields hydrogen on treatment with potassium hydroxide. The hexaiodide reacts with water to give the compound $\text{Si}_2\text{O}_2(\text{OH})_3$, which may be regarded as oxalic acid, in which carbon is replaced by silicon.

From the triiodide, the trichloride, Si_2Cl_6 , boiling at 146° , was ob-

tained by treatment with mercuric chloride (Friedel, *Ber.*, 1869, 2, 747), and the ethide, $\text{Si}_2(\text{C}_2\text{H}_5)_6$, by the action of zinc ethide.

Silicopropionic acid, $\text{C}_2\text{H}_5\text{Si}\cdot\text{O}\cdot\text{OH}$, was prepared by the action of zinc ethide on the chlorohydrin, $\text{SiCl}(\text{OC}_2\text{H}_5)_3$, and subsequent saponification of the product.

This brilliant investigation by Friedel and Ladenburg, in which frequently great experimental difficulties were overcome, established with un hoped-for completeness the strong analogy between silicon and carbon compounds.

Titanium Compounds.—Friedel and Guérin (*Compt. rend.*, 1875, 81, 889), by the action of silver, reduced titanium tetrachloride, TiCl_4 , to the trichloride Ti_2Cl_6 , but found that when an attempt is made to purify the latter by distillation, it breaks up into the dichloride, Ti_2Cl_4 , and tetrachloride, TiCl_4 . By interaction with bromine, the dichloride gives the compound TiCl_2Br_2 . Bromine converts the trichloride, Ti_2Cl_6 , into the compound TiCl_3Br ; the oxychloride, TiOCl_2 , was also prepared.

In the description of Friedel's mineralogical work will be found an account of titanite oxides derived from these chlorides.

Friedel and Guérin (*Ann. Chim. Phys.*, 1876, [v], 8, 24) also studied the compounds of titanium with nitrogen, and isolated the nitrides, Ti_2N_2 and Ti_3N_4 .

Mixed Halogen Compounds of Hydrocarbons.—Friedel and Silva (*Jahresb.*, 1870, 419; *Compt. rend.*, 1871, 73, 955; *Bull. Soc. Chim.*, 1872, [ii], 17, 537) found that only one-half the bromine in bromopropylene is replaced by chlorine when treated with mercuric chloride; with ethylene chlorine, the action is complete at 180° , and all the chlorine is replaced. They obtained 1:2-dichloropropylene, 1:3-dichloropropylene, and 2:3-dichloropropylene by new modes of synthesis. The physical constants and chemical reactions of these bodies were determined, and so far as the methods of the day permitted, their rational formulæ were fixed.

The action of iodine monochloride on chloroform was found to give rise to carbon tetrachloride, CCl_4 (Friedel and Silva, *Bull. Soc. Chim.*, 1872, [ii], 17, 537); with ethylene or propylene, iodine monochloride formed dichlorides with separation of iodine.

Synthesis of Glycerol.—Friedel and Silva (*Compt. rend.*, 1871, 73, 1379; 1872, 74, 805) undertook the synthesis of glycerol from the elementary components. At this time, although it was recognised that the rapidly increasing number of such syntheses held out a prospect for making all natural products artificially, yet few means were at hand for supplanting the work of nature, and the synthesis of glycerol had not been accomplished. So soon as the true formula was known, $\text{CH}_2(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, the only

difficulty lay in attaching a halogen atom to each of the three carbon atoms. At first, allyl iodide was used for the preparation of trichlorohydrin, but afterwards, in answer to an objection from Berthelot that allyl derivatives came from glycerol, propylene was prepared from acetone, and by treating this with chlorine and with iodine monochloride, trichlorohydrin was obtained, which was easily transformed into glycerol.

Dimethyldiethylmethane was one of the most important substances prepared during an extended study of the products of the action of the halogens on the simpler hydrocarbons. It was the first example of the type CR_4 , and was prepared by the action of zinc ethide on dimethylmethylenedichloride, $(CH_3)_2CCl_2$ (Friedel and Ladenburg, *Compt. rend.*, 1866, 63, 1083).

A new mode of preparing allylene was discovered in the action of caustic potash on dimethylethylene chloride, $CCl_2(CH_3)_2$ (Friedel, *Compt. rend.*, 1864, 59, 294), and of phenylacetylene in the action of caustic potash on the compound $C_6H_5 \cdot CCl_2 \cdot CH_3$ (Friedel, *Compt. rend.*, 1868, 67, 1192).

Dimethyl Ether Hydrochloride.—At a time when it was imperfectly recognised that the variations from the law of Avogadro were due to dissociation, Friedel discovered a compound whose dissociation was complete at a very low temperature: namely, the combination of methyl ether and hydrogen chloride, $6C_2H_6O \cdot 5HCl$, a liquid boiling at -2° . Friedel studied the dissociation tension of this substance at various temperatures, and concluded it was a true chemical compound, although highly dissociated in the gaseous state (*Compt. rend.*, 1875, 81, 152, 236).

The Aluminium Chloride Reaction.*—The experiments which demonstrated the wide scope of the reaction were so easy of execution that those described in the first three papers were carried out in the course of five or six weeks. The discovery sprang from an accidental observation of the action of metallic aluminium on chloride of amyl. It was soon seen that the metallic halogen salt and not the metal was the active body, and a similar fact was found to give the true explanation.

* The first publications were made in 1877 (*Compt. rend.*, 84, 1392, 1450; 85, 74). A complete account of work done up to 1887 is given in the *Annales de Chimie et Physique*, 1884, [vi], 1, 449; 1887, 10, 411; 11, 263; and 1888, 14, 433). A good presentation of the literature of the aluminium chloride reaction is to be found in Elbs' *Synthetische Darstellungs Methoden* (vol. ii, pp. 140—171). He says that the Friedel-Crafts reaction is among all synthetical methods the one most commonly used, and cites a nearly complete list of its employment by its discoverers and its extension by other chemists. A curiosity in chemical literature is the book of 864 pages by Seelig upon organic reactions which makes 23 citations of 20 authors concerning the aluminium chloride reaction without mention among them of the name of Friedel.

ation of the excellent synthetical method discovered by Zincke (*Ber.*, 1873, 6, 137), in which zinc dust and benzyl chloride were used to obtain diphenylmethane. So sensitive is the reaction in some cases that benzyl chloride is decomposed by long distillation in a copper vessel if brass solder has been used, zinc chloride taken from the solder being the condensing agent.

The results obtained in the very beginning seemed to show that any number of halogen atoms in a paraffin could be replaced by phenyl; that the six hydrogen atoms in the benzene ring could each, with equal ease, be replaced successively by alkyls; and that a halogen in an aromatic side chain acted with even more readiness on the benzene ring. Halogens substituted in the aromatic ring were inactive in presence of aluminium chloride even at high temperatures. Some few exceptions were found later to these generalisations. All these reactions between chlorinated compounds and aromatic hydrocarbons took place at the ordinary temperature, or with slight warming in presence of aluminium chloride, bromide, or iodide. Zinc or ferric chloride had a similar effect, but in a less degree. Chlorides of magnesium, cobalt, copper, mercury, and antimony are without effect.

The chlorides of mono- or di-basic acids react with benzene and its homologues, giving ketones. The presence of alcohol or acids, that is, of hydroxy-compounds, prevents the aluminium chloride reaction, and it also could not at first be carried out with ethers. New compounds were obtained, like phthaloketone and pentamethylbenzene, and the way was immediately opened for preparing with great ease numerous homologues of benzene and new ketones. The preparation of such hydrocarbons as durene and hexamethylbenzene was made easy, and consequently mellitic acid could readily be obtained by a process of oxidation. Also, triphenylmethane and its homologues were prepared on a large scale, and these seemed to offer a new method of making aniline dye stuffs commercially. Unfortunately, the discoverers had at that time only a very small laboratory, with no place for students, and not even provided with the convenience of running water, whilst circumstances separated them for a time and retarded the progress of the work in clearly indicated directions.

The first publication in 1877, beside containing a record of the facts above stated, offered a theory of the reaction based upon analogies with the properties of organo-metallic bodies. It was supposed that all the observed effects might be explained by the existence, even in small proportion, of an organo-metallic chloride, $C_6H_5 \cdot Al_2Cl_5$, which, being constantly decomposed according to the equation $C_6H_5 \cdot Al_2Cl_5 + RCl = C_6H_5R + Al_2Cl_3$, and constantly renewed, would explain the contact action of aluminium chloride. This theory was kept in view

throughout subsequent work, and was strengthened by many new facts, and particularly by those relating to the readiness with which oxygen, sulphur, carbon and sulphur dioxides, and cyanogen are absorbed by the benzene compound with aluminium chloride, giving respectively phenol, phenylmercaptan and phenyl sulphides, benzoic acid, phenylsulphonic acid, and benzonitrile. The small quantity of each of these products obtained may be ascribed to the insolubility of the gases in benzene.

The action of the compound $C_6H_5AlCl_5$ should be analogous to that of aluminium triphenyl, $(C_6H_5)_3Al$. The latter was prepared by the action of aluminium on mercury diphenyl, and gives, with benzyl chloride, diphenylmethane; with oxygen, phenol; and with sulphur, phenylmercaptan, but has no action on halogens substituted in the benzene ring. Hence a well-known organo-metallic compound gives the same reactions as aluminium chloride and benzene.

Zinc ethide is known to break up by heating into ethylene and ethane. Here, again, the analogy holds good, for hydrocarbons heated with aluminium chloride break up into simpler saturated compounds which are easily isolated, and into complex non-saturated ones. The latter are probably derived from simple unsaturated substances, C_nH_{2n} or C_nH_{2n-2} , &c., which undergo condensation in presence of aluminium chloride, a reaction which can be observed in the simplest stage between benzene and ethylene, $C_6H_6 + C_2H_4 = C_6H_5 \cdot C_2H_5$. The condensation proceeds much further when halogen derivatives of the paraffins are treated with aluminium chloride, undistillable products very poor in hydrogen being formed, together with volatile paraffins.

The last investigation of Friedel in this field concerned the action of aluminium chloride on one of the simplest of the paraffins, and, in conjunction with Gorgeu (*Compt. rend.*, 1898, 127, 590), it was found that normal hexane treated with aluminium chloride at 35° gives pentane and butane together with condensed products.

The aromatic hydrocarbons are usually more stable, but they are all decomposed by heating with aluminium chloride at high temperatures. Naphthalene is very easily attacked, giving benzene and an excellent yield of hydrides of naphthalene. Triphenylmethane is also easily decomposed, giving diphenylmethane, toluene, and benzene. Benzene gives diphenyl and other products.

The alkyl groups in aromatic compounds are subject to migrations giving rise to higher and lower homologues. These changes and isomeric transformations of chloro-paraffins were found to limit the possibilities of the reaction.

The action of aluminium chloride on substances associated with petroleum, and the elimination of sulphur from them, was studied.

In consequence of the claims of various authors to have discovered the destructive action of aluminium chloride, a restatement was made of the original facts with some additions (Friedel and Crafts, *Trans.*, 1882, **41**, 115; *Compt. rend.*, 1885, **100**, 692).

Exceptions to the general rules were discovered later. In some cases, ortho-dihalogen substitution products in the benzene ring are attacked. In $\text{CH}_2\text{Cl}\cdot\text{COCl}$, only the chlorine in the carbonyl group is active, and in the case of carbon tetrachloride only three atoms of chlorine are replaced by phenyl, and diphenyl is formed as a by-product, as was shown by Fischer. The mistake in the first paper, which announced the formation of tetraphenylmethane, was due to an error in Watt's Dictionary, 2nd Suppl., p. 948, which gives 335° for the boiling point of triphenylmethane. The product isolated boiled 24° higher, namely, at 359° , and was therefore assumed to be a tetraphenyl compound, the percentage composition of the two compounds being not far different. Subsequent determinations made by Crafts with a hydrogen thermometer showed 359° to be the boiling point of pure triphenylmethane.

The synthesis of triphenylmethyl was studied anew in 1882 (*Bull. Soc. Chim.*, [ii], **37**, 6), and the conditions for obtaining a good yield were described. The proportion of diphenylmethane produced as by-product is only about one-fourth that of the triphenylmethane. Triphenylcarbinol was obtained from the product of the interaction of carbon tetrachloride and benzene by treatment with water.

These are the principal facts which characterise the reaction, and which have a bearing upon its theoretical explanation; it is only necessary to cite a few examples of its use in preparing pure products.

A class of ortho-ketonic acids is easily obtained by means of the anhydrides, such as phthalic anhydride, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}\text{O} + \text{C}_6\text{H}_6 =$
 $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{OH} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{C}_6\text{H}_5 \end{smallmatrix}.$

Phthalic chloride, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CCl}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}\text{O}$, treated with aluminium chloride and benzene, gives phthaloketone, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{C}(\text{C}_6\text{H}_5)_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}\text{O}$. It was hoped to effect the synthesis of anthraquinone by this reaction, but the yield is very poor. It suffices, however, to indicate the existence of a symmetrical phthalic chloride which gives the reaction $\text{C}_6\text{H}_4\begin{smallmatrix} \text{COCl} \\ \diagup \quad \diagdown \\ \text{COCl} \end{smallmatrix} +$
 $\text{C}_6\text{H}_6 = \text{C}_6\text{H}_4\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}\text{C}_6\text{H}_4 + 2\text{HCl}.$

Anthracene and its homologues can be obtained by a reaction which takes place according to the equation $3\text{CH}_2\text{Cl}_2 + 3\text{C}_6\text{H}_6 = \text{C}_2\text{H}_2(\text{C}_6\text{H}_5)_2 + \text{C}_6\text{H}_5\cdot\text{CH}_3$. The principal product, however, is diphenylmethane.

When toluene is substituted for benzene, dimethylantracene is formed.

The fundamental synthesis of a ketone by the action of carbonyl chloride on benzene in presence of aluminium chloride takes place with such regularity that when pure crystallised benzene is used, the crude product boils within a limit of 0.2° , and forms the best substance for standardising thermometers near 306° .

Vapour Density Determinations.—The molecular weight of aluminium chloride was found by Nilson and Pettersson to approach that required by the formula AlCl_3 , and consequently to accord with the trivalent place usually assigned to aluminium in the periodic arrangement of the elements (*Zeit. physikal. Chem.*, 1887, 1, 459).

Friedel and Crafts (*Compt. rend.*, 1888, 106, 1764; 107, 306) drew attention to the fact that the experiments of Nilson and Pettersson began at 440° , and that the method of Victor Meyer, which was used, is unsuitable for determinations near the boiling point of the substance. The physical properties of aluminium chloride were studied, and a careful series of determinations of the boiling point of aluminium chloride between the pressures of 252 and 2277 mm. of mercury were made. The chloride was liquefied under pressure, and crystallised in beautiful, white, transparent crystals melting at 186.5° , or a little above the boiling point under atmospheric pressure, namely, 183° .

Vapour density determinations by Dumas' method, modified to obtain different tensions, were made between 218° and 432° , and the vapour density was found to correspond with that required by the molecular formula Al_2Cl_6 .

Under similar conditions, vapour densities corresponding to the formulæ Fe_2Cl_6 and Ga_2Cl_6 , were found for ferric and gallium chlorides.

Camphoric Acid.—Friedel (*Compt. rend.*, 1891, 113, 825; *Bull. Soc. Chim.*, 1893, [iii], 9, 27) gave various experimental proofs that camphoric and isocamphoric acids contain, like lactic acid, two hydroxyl groups with different functions, one of them nearly alcoholic. Four esters were described, and a hypothesis regarding the constitution of camphor, with particular reference to the stereochemical formulæ of right and left rotating camphoric and isocamphoric acids, was illustrated with diagrams.

A method of analysis of isomeric xylenes and ethylbenzene was founded upon the fact that the xylenes, when treated with a large excess of bromine and a little iodine, form tetrabromo-substitution products nearly insoluble in light petroleum, and by that means separable from the dibromomethylbenzene formed under the same conditions. The tetrabromoxylenes can be oxidised quantitatively to the corresponding tetrabromophthalic acids by treatment at 160 – 170° with bromine

and water, and the acids separated by precipitation (Friedel and Crafts, *Compt. rend.*, 1885, 101, 1218).

Armstrong and Miller published a description of the now well known and convenient mode of decomposition of sulphonic acids in sulphuric acid solution by means of steam, and the priority belongs to them; but before the method was made public, Friedel and Crafts had begun its study from a somewhat different point of view, and endeavoured to utilise the different temperatures at which the reaction takes place, in order to separate hydrocarbons, and in particular the hydrides of naphthalene from naphthalene (*Bull. Soc. Chim.*, 1884, [ii], 42, 66). Phosphoric acid was afterwards used as a solvent instead of sulphuric acid, in order to avoid the destructive and oxidising action of the latter (*Compt. rend.*, 1889, 109, 95).

Thiophosphates in well crystallised forms were obtained by heating the calculated quantities of phosphorus and sulphur with iron, aluminium, copper, lead, and silver to dull redness in sealed tubes. The general formula is $M_4P_2S_8$. Thioselenium salts were also obtained (Friedel, *Bull. Soc. Chim.*, 1894, [iii], 11, 1057; Friedel and Chabrié, *Bull. Soc. Chim.*, 1895, [iii], 13, 163).

An examination of fat from an Egyptian tomb showed that the glycerol had completely disappeared, apparently through oxidation. Palmitic and stearic acids were found unchanged, and azelaic and pimelic acid had been produced by oxidation (*Compt. rend.*, 1897, 124, 648).

Mineralogical Researches.

Friedel's work in mineralogy was of capital importance and marks a transition period in the history of that branch of science. After mineralogical cabinets had been filled with natural specimens, their sources duly noted, and when each species had been analysed, measured, and arranged, the old fashioned mineralogist seemed to have accomplished his task. To a collector of an antiquarian turn of mind, only those specimens which came from veins, druses, or rocky beds were of prime interest, whilst chemical or metallurgical products of similar composition, even when well crystallised, were set apart as new comers and not considered of equal rank with those whose landed title was well established. The geologist tried to describe the rocks in terms of mineral species, as chemical compounds are identified by the proportions of their elements; but only rarely were the conditions of formation of a species known or used to give testimony concerning the modes of formation of rocky strata. It was not duly appreciated that most crystalline rocks are a mixture of crystals with mother liquor, that purer specimens can be obtained by laboratory processes,

and that the essential constituents can be best determined by synthesis with pure materials.

Then came a period of synthetical mineralogy in which Friedel played an important part. It is evident that ideas regarding the igneous origin of an eruptive rock were confirmed if it contained the same crystalline species that could be observed in the slag of an iron furnace, and that the reproduction of minerals found in veins by sublimation or by crystallisation from water gave some evidence concerning natural processes. Moreover, some ideas concerning the effect of each of the different items contributing to the formation of a crystal can be gathered by the artificial production of the same crystal, under laboratory conditions of pressure, temperature, and presence or absence of water, each element in the experiment being subject to variation at will.

Friedel's equal skill as chemist and mineralogist enabled him to attack these problems to good purpose, and he pursued the subject with unswerving patience during his whole life, seeking to grow in a few days crystals which nature had passed ages in perfecting. Mineralogical problems were never excluded from his thoughts even at times when work in organic chemistry was progressing most successfully, and the delicate operations of these researches were performed by his own hands. New views of chemical composition, as, for instance, the hypothesis of the benzene ring, were immediately brought to bear on the formulæ of minerals, and the similarity of structure between the silicon and the carbon compounds with organic radicles, shown by his researches upon the silicon ethides, suggested new formulæ for silicates.

The details of his researches will show that many branches of experimental science were brought to bear upon his mineralogical work, and that from a very elevated standpoint he kept in view the paths by which mineralogy leads to geology, chemistry, and through delicate experiments in optical and pyro-electric phenomena, to the fundamental problems of molecular physics. His last illness cut short a research intended to offer final proofs of the necessary relation between rotatory power and the asymmetrical structure of carbon compounds.

Consciously or unconsciously he followed the lead of Pasteur in grouping his theories of the natural phenomena which came before him around a distinct conception of molecular arrangement from the point of view of a crystallographer.

The transference of his professorship from mineralogy to organic chemistry interrupted his work upon a mineralogical treatise of which the first part was published in 1893. This work was of elementary character and was particularly intended for the use of chemists. It

contains an exposition of geometrical crystallography, an original view of the principle of a chemical classification of minerals together with a discussion of the classifications of other authors, and an account of isomorphism and polymorphism. A second volume was to have followed containing descriptions of mineral species.

Friedel's papers were published in the *Comptes rendus*, the *Annales de Chimie et de Physique*, and *Bulletin de la Société Chimique* until, in 1878, he took part in founding the *Bulletin de la Société de Mineralogie*, and there published all his later work. He was most assiduous in attendance upon the meetings of the French Mineralogical Society and took an active part in its councils.

He published a lecture (*Revue Scientifique*, November 23rd, 1878) upon the work of his predecessor at the Sorbonne, Delafosse. Another lecture (*Revue Scientifique*, September 11th, 1880) gives a review of the methods previously employed for the artificial preparation of minerals. An address (*Bull. Soc. Miner.*, 1881, 4, 187), before the Mineralogical Society after the death of Henri St. Claire Deville, gives an account of the brilliant work of that chemist in the same field.

Crystallography.—At the time when Friedel began his mineralogical work, the pyro-electric phenomena in crystals did not appear to be always in accord with the ideas of symmetry and homogeneity of crystalline form developed by geometrical and optical studies. He undertook to show that the apparent anomalies were due to imperfect experiments, or to false interpretations, and with true scientific instinct commenced his review of the subject by the invention of improved methods of investigation. Of the two theses offered by him for the doctor's degree, one was upon pyro-electric phenomena in crystals. He verified Marbach's discovery of two varieties of pyrites of opposite thermo-electric signs; the two often united in the same crystal. It was supposed that external hemihedral forms were an essential characteristic pointing to the pyro-electric phenomena. Such forms would be non-superposable, but Friedel showed that they do not occur in parahemihedral crystals, which, like pyrites, give thermo-electric currents, although mathematically it is possible to conceive of their existence. In natural specimens, holoaxial hemihedral crystals alone show these non-superposable forms. He concluded that some structure which does not give an external sign was responsible for the electric phenomena of opposite signs, and he attributed them in parahemihedral crystals to a molecular arrangement along axes symmetrical about a centre, like the tertiary axes of pyrites, but so placed that their extremities cannot be superposed.

In crystals which conduct electricity like pyrites, these axes should mark the directions in which pyro-electric phenomena would manifest themselves. He investigated the subject experimentally, and succeeded in demonstrating these properties with certainty and regularity, but

only after having made thin, parallel-faced sections of the crystals. With entire crystals, irregular results are obtained which are confusing and have led different experimenters to erroneous conclusions. Friedel was the first to recognise that the strong currents set up when a crystal of pyrites is cooling are due to irregular rates of cooling in the mass of the crystal, and his first care was to eliminate such phenomena by making thin sections. He then succeeded in making a model with a thermo-electric couple of bismuth and antimony which imitated the phenomena occurring when crystals of pyrites are heated, and thus confirmed his theory that the crystals contain at the same time two kinds of molecular arrangement with non-superposable axes giving rise to thermo-electric currents of opposite signs.

He found that parahemihedral crystals which do not conduct an electric current, as apatite, for instance, show no pyro-electric phenomena, and concluded that in general the pyro-electric phenomena are not due to hemihedrism, when it can be referred to a centre, and that the property does not exist in pyrites in consequence of the parahemihedrism, but is induced only by the existence of the above-mentioned molecular arrangement about non-superposable axes of which no indication is given by external form.

He then examined the rare antihemihedral crystals which are good conductors, panabase and chalcopyrites, and discovered a regular flow of a pyro-electric current, as in tourmaline.

The interesting fact was shown that currents always flow in the same direction as those which would be produced by thermo-electricity in a system of metallic tetrahedrons of the same thermo-electric sign, and arranged in the same position as the crystal, and thus the hypothesis is suggested that pyro-electric phenomena in crystals may be due to the currents set up by tetrahedral elements. This first research of the young mineralogist was distinguished by a clear conception of a hypothesis accounting for certain phenomena and excluding others. It passed through the test of controversy, for in 1871 G. Rose published statements concerning pyrites and cobaltine, and asserted that external forms distinguished the two pyro-electric varieties. Friedel (*Compt. rend.*, 1874, 78, 508) pointed out errors in these observations, and maintained his previous conclusions by new experiments. A better method of heating crystals (*Bull. Soc. Miner.*, 1879, 2, 31) was described, in which a hot metallic ball was applied to a cold surface. When this new device for heating was applied to thin sections of crystals, pyro-electric currents were shown in topaz normal to the plane of cleavage, the experiment contradicting statements by Ries and Rose, and pyro-electric currents parallel to the tertiary axes were found in blende.

Hankel had found pyro-electric phenomena in quartz: an observa-

tion which seemed to be at variance with the symmetry of this holoaxial crystal. Friedel showed that the pyro-electric direction corresponded only with binary axes, the edges of the prism being alternately of opposite sign. The fact, then, is in accord with the theory of symmetry; for there is no pyro-electricity displayed in the direction of the tertiary axis of which the two extremities are superposable, whilst it is shown where it would be expected in the direction of the binary axes, whose extremities are not superposable or symmetrical.

Subsequent investigations were made in conjunction with P. and T. Curie and with A. de Grammont, and these often took the form of a discussion with German crystallographers, because observations which appeared to contradict Friedel's views were again made by Hankel, and by Erman, Ries, and Rose.

The question required delicate handling, and the work of Friedel and his associates consisted in disengaging the phenomena which were purely pyro-electrical from others due to irregular internal tensions discovered by P. and T. Curie, and named by them piezo-electric; in other words, strains set up when a whole crystal cools irregularly are capable of producing electric currents.

In a paper published with T. Curie (*Bull. Soc. Miner.*, 1883, 6, 191), Friedel showed that, when all disturbing influences are eliminated, no pyro-electric currents can be obtained from crystals of the tertiary system, or with hexagonal crystals, like quartz, having three axes of hemimorphism in the same plane, or even in antihemidral crystals of the cubic system, in which the four axes of hemimorphism mutually compensate. Corroborative experiments were made with blende and with sodium chlorate. With reference to this theory, boracite presents a curious example in the two forms which it assumes according to the temperature. Above 265° , it is cubic and isotropic, and is not pyro-electric; at 265° , it becomes suddenly orthorhombic, and on cooling below this temperature pyro-electricity is manifested.

Later (*Bull. Soc. Miner.*, 8, 1885, 16), Friedel and T. Curie showed that a crystal of topaz, instead of being simply orthorhombic, as was held by Ries and Rose, and by other authorities, is composed of four clinorhombic individual crystals grouped about a central orthorhombic crystal. These five elements can be isolated by cutting, and a pyro-electric axis displayed parallel to the base, to which the central poles of Ries and Rose can be referred. He thus proved that the optical properties of topaz, pointing to an antihemihedral clinorhombic system grouped upon a rhombic centre, are in complete accord with the pyro-electric phenomena, namely, the central poles described above and a pyro-electric axis parallel with the axis of the prism. The twin formation of complementary crystals explains the accidental

occurrence of crystals whose two extremities have the same electric polarity.

Friedel and A. de Grammont (*Bull. Soc. Miner.*, 1895, 18, 75) studied the pyro-electric properties of scolecite, and found that a similar analysis could be made of the pyro-electric axes. They discovered in this mineral a peculiar arrangement of twin crystals, in which the two extremities show at their junction the same polarity, and consequently the macle formation cannot be explained by a rotation around an axis perpendicular to the plane of junction. This curious case of want of symmetry about the plane of junction has proved interesting with reference to a theory put forward later by Mallard.

Friedel proved that the two crystalline forms of hexachloride of benzene are in accord with the well-known theory of their "*cis*" and "*trans*" arrangement (*Bull. Soc. Chim.*, 1891, [iii], 5, 130). He developed the theory to show that tertiary symmetry is indicated for the *cis*- and binary for the *trans*-form. A calculation of the necessary ratio in which the two forms will be generated during saturation with chlorine and disruption of carbon bonds, compared with experimental results, confirmed the identification of each form.

This account would not be complete without a reference to the discussions between Friedel, Mallard, and Wyruboff (*Bull. Soc. Miner.*, 1886, 9, 121). Friedel insisted upon the capacity of crystallising together as a final test of isomorphism in opposition to views of Mallard, who was prepared to extend very widely the definition of isomorphous substances.

The *Bulletin de la Société de Mineralogie* contains a considerable number of Friedel's descriptions and measurements of mineral species.

Artificial Production of Minerals.—The synthesis of atacamite (*Compt. rend.*, 1873, 77, 211), four years later than the thesis upon pyro-electric phenomena, was effected by the action of ferric chloride upon cuprous oxide in sealed tubes at 250°.

Friedel and J. Guérin (*Ann. Chim. Phys.*, 1876, [v], 8, 24) studied various titanium compounds and obtained titanium sesquioxide in the form of rhombohedral crystals, isomorphous with oligist and ilmenite. Among the much disputed formulæ for the latter mineral, preference is given to FeTiO_3 , in which iron and titanium are mutually replaceable as silicon can replace titanium in its higher stage of oxidation. Crystallised rutile was also obtained by the action of titanium chloride on ferrous oxide at a high temperature.

The publication of the most important series of syntheses was begun in 1879 (*Bull. Soc. Miner.*, 2, 113). Most of the work done between

this date and 1887 was in collaboration with Edmund Sarasin and was published in full in the *Arch. Sci. phys. et natur. de Genève*, 1892.

The required materials, together with water, were heated in the very stout steel tube lined with platinum, already described. High pressure and a temperature of 500°, corresponding in the earth's crust to a considerable depth of rocky strata, were reached, and the results were interpreted with reference to geological theories. The use of a platinum tube guaranteed the purity of the compounds. The crystals produced within the few days devoted to an experiment were small and required care and skill in measurement to identify them with known species, but they were usually well defined and uniform in their aspect.

The first published observation of Friedel and Sarasin (*Bull. Soc. Miner.*, 1879, 2, 113) described the formation of beautiful prisms of quartz with pyramidal terminations when an excess of amorphous silica was heated with caustic potash. These crystals, which are easily measurable, appeared frequently together with other minerals in later syntheses. Quartz with a new macle was observed among the crystals (*Bull. Soc. Miner.*, 1888, 2, 29).

The formation of orthose feldspar (Friedel and Sarasin, *Bull. Soc. Miner.*, 1879, 2, 158 ; 1880, 3, 23 ; 1881, 4, 171 ; *Compt. rend.*, 1881, 92, 1374), under well defined conditions, threw new light upon the mode of formation of the so-called acid rocks. Friedel, with scrupulous care, repeated his experiments under various conditions during three years before he affirmed the absolute identity of the artificial and natural species. The materials were silicates of potassium and aluminium with a large excess of water. Quartz is usually formed as well, and when a higher temperature is employed tridymite also, showing that silica naturally crystallises in these two forms at corresponding temperatures. The bearing of these facts upon the mode of genesis of granite was pointed out.

Albite and analcime are formed by a similar process when sodium instead of potassium silicate is used. No intermediate feldspar containing the two bases could be obtained and the natural minerals having such a composition are probably mixtures (*Compt. rend.*, 1883, 97, 290).

The action of alkalis and sodium silicate on the zeolites was investigated by Friedel and Sarasin (*Bull. Soc. Chim.*, 1884, [ii], 41, 593). Friedel proposed a general formula for this mineral group and sought to verify it by transforming its different members. Sodium can be substituted for calcium in laumontite with formation of analcime. In this reaction, there is also formed a mineral nearly related to mesotype, and it was shown that the same mineral was

obtained by subjecting natural mesotype to the action of the same reagents.

Friedel, with his son, Georges Friedel, pursued a similar series of investigations upon the metamorphosis of mica. Many attempts were made to obtain white mica in presence of alkalis, but it was found that mica is not stable under these conditions, that at 400—500° it is easily decomposed by the alkalis, giving rise to other species, and when silicates or other salts are added the products of transformation resemble the well known series found at Somma.

When the micas are treated with alkalis alone, substitutions of one base for another could be obtained.

Muscovite (*Bull. Soc. Miner.*, 1890, 13, 129), at 400—500°, in presence of dilute sodium hydroxide, is transformed without residue into fine crystals of nepheline, so pure that the constitution of this mineral could be definitely established as an orthosilicate, AlNaSiO_4 . The transformation seems to consist in substituting sodium for potassium and hydrogen in muscovite without destroying the molecular arrangement. It was found impossible, however, to obtain a nepheline containing potassium without sodium. Mica is transformed into orthose by heating with potassium silicate and potassium hydroxide. Also, when a suitable proportion of silica was taken, a quadratic form of amphigene was produced without icositetrahedral grouping. This synthesis is interesting from a crystallographical point of view, because the form which appears at a temperature lower than that at which the mineral becomes cubic and isotropic shows parahemihedrism not recognised in natural specimens, and the pseudo-icositetrahedral form of the natural crystals is explained by a junction of three crystals with trirectangular axes.

Sodalite (*Bull. Soc. Miner.*, 1890, 13, 180) was formed by heating mica with sodium chloride and hydroxide. It had the same composition, $3\text{SiO}_4\text{AlNa} + \text{NaCl}$, no matter what proportion of salt was added, and was identical with Somma sodalite.

Anorthite (*Bull. Soc. Miner.*, 1890, 13, 230) can be obtained by heating mica with calcium chloride and hydroxide. The crystals are well formed, and free from potassium.

Mica is transformed by calcium hydroxide into a hydrated silicate of the cubic system not found in nature.

A mixture of sodium sulphate and hydroxide converts white mica into a new compound, $6\text{SiO}_4\text{AlNa}, \text{Na}_2\text{SO}_4, 2\text{H}_2\text{O}$. The crystals are transparent, and isomorphous with those of nepheline, cancrinite, and microsommite. A mineral like the preceding, but with one molecular proportion of water, is formed in small quantity, also a little black mica. Muscovite mica, heated with sodium carbonate and hydroxide, gives a mineral like cancrinite, $6\text{AlNaSiO}_4, \text{Na}_2\text{CO}_3, 2\text{H}_2\text{O}$.

Friedel and Sarasin (*Bull. Soc. Miner.*, 1887, 10, 737), prepared topaz by heating aluminium fluorosilicate. Quadratic crystals of aluminium fluoride are also formed. Friedel pointed out an error in the usual method of analysing topaz, arising from a loss of aluminium fluoride, as well as silicon fluoride, when the mineral is heated in a platinum crucible. The composition, instead of being variable, as was supposed, is constant, and corresponds with that required for the formula $\text{Al}_2\text{F}_2\text{SiO}_4$.

The following list comprises other syntheses of minerals achieved by Friedel and Sarasin: Libethenite (*Bull. Soc. Miner.*, 1879, 2, 157); hopeite (*ibid.*, 153); copper selenite (*ibid.*, 1881, 4, 176); phosgenite (*ibid.*, 176); leadhillite (*Bull. Soc. Chim.*, 1883, [ii], 39, 626); calcite (*Bull. Soc. Miner.*, 1885, 8, 304); mellite was synthesised by Friedel and Balsohn (*Bull. Soc. Miner.*, 1891, 14, 26); and Friedel prepared cumengeite (*Bull. Soc. Miner.*, 1892, 15, 96), bolcite (*ibid.*, 1894, 17, 6), and martite (*ibid.*, 1894, 17, 150).

From an examination of diamonds contained in native iron from Cañon Diablo (*Compt. rend.*, 1893, 116, 224), Friedel concluded that their formation had been accompanied by that of sulphide of iron at a relatively low temperature. He attempted to obtain crystallised carbon by the action of sulphur on a highly carburetted cast iron at 450–500°. A black powder was obtained hard enough to scratch corundum, but in too small quantity to be analysed. This essay is particularly interesting, as it seems to imitate a natural process.

The following new species of minerals were discovered by Friedel: Wurtzite (*Compt. rend.*, 1861, 52, 983); adamine (*Compt. rend.*, 1866, 62, 692); and delafossite (*Compt. rend.*, 1873, 77, 211); whilst carnotite was described by Friedel and Cumenge (*Bull. Soc. Miner.*, 1899, 22, 26).

The *Bulletin de la Société de Mineralogie* from 1879 to 1894 contains numerous descriptions of minerals from different localities. Many of these investigations were made by Friedel in connection with his duties as Curator of the Mineralogical Cabinet of the School of Mines, which led him constantly to examine minerals from new localities, and he was at all times actively employed in adding new specimens to that fine collection.
