

OBITUARY NOTICE.

PERCY FARADAY FRANKLAND.*

1858—1946.

PERCY FARADAY FRANKLAND was born in London on October 3rd, 1858. He was the second son of Sir Edward Frankland, whose contributions to chemical thought in the nineteenth century, and whose researches on the purification of water, have established his reputation as one of the most outstanding scientists of the period.

Edward Frankland, who was resident in London, succeeded Hofmann as Professor of Chemistry at the Royal School of Mines in 1865, and his son thus had the opportunity of becoming acquainted with many of the famous scientific personalities of the day, including, when he was very young, Faraday, who was his godfather. When a boy he was taken by his father to the Scottish Highlands (in 1867 and 1870), as well as to the English Lake District. He also stayed frequently with his grandparents at Leyland in Lancashire. Perhaps in this way he developed a great liking for the North, and more especially for its wilder scenery.

Percy Frankland was a pupil at University College School from 1869 to 1874, and in 1875 proceeded to the Royal School of Mines. He was a student under Edward Frankland, Guthrie, Huxley, Judd, and Warrington Smyth, at a period when the science establishments of the Royal School of Mines were being transferred to South Kensington. Until 1881, there was no Associateship course in subjects other than mining, metallurgy, and geology in the Royal School of Mines, and Frankland took the Associateship (A.R.S.M.) in geology, which included, however, a considerable amount of chemistry, as well as biology, physics, and applied mechanics. It appears that students taking the Associateship course used to oscillate between Jermyn Street and South Kensington in attendance at the science laboratories. Frankland gained the A.R.S.M. diploma in geology and the Forbes Prize. He was awarded a Brackenbury entrance scholarship at St. Bartholomew's Hospital in 1878, and graduated B.Sc. of the University of London in 1881. As a young man he was keenly desirous of entering the medical profession, but parental persuasion induced him to take up chemistry, although his interest in biology persisted throughout his life.

He spent two years at the University of Würzburg, where he came under the influence of Wislicenus, under whom he graduated Ph.D. with the distinction *summa cum laude*. The scientific interests which he acquired at Würzburg were to influence his choice of a field for research. There is, in fact, a line of continuity from the researches of Sir Edward Frankland, through Wislicenus, to those of Percy Faraday Frankland. At Würzburg he had astonished the Germans by riding a "penny farthing" high bicycle, and his affection for cycling continued throughout a good deal of his life. He was a good linguist and spoke German like a native, his French was a dramatic *tour de force*, and he would enjoy declaiming a few appropriate phrases from Dante. He saw the Germans in occupation of France in 1871, and on that occasion saw Bismarck, Moltke, and von Roon. He was strongly impressed by the glamour of military operations, and, familiar with conscription in Germany, he advocated it in this country. On his return from Germany, he enlisted enthusiastically in the Artists' Rifles, commanded by Sir Frederick Leighton, who appeared on field days on a white charger.

On his return to London in 1880 from Würzburg, Frankland became a demonstrator of practical chemistry in charge of the north chemical laboratory at the Normal School of Science, South Kensington, under his father, Edward Frankland. He occupied a private room at the west end of the building, from which he supervised the laboratory training of the students. The courses at that time included no organic chemistry, but consisted of qualitative inorganic analysis during the first term, and gravimetric analysis, including a complete analysis of minerals and ores, during the second term of the course. Frankland, who was very interested in consulting practice, spent much time, in conjunction with his father, on the chemical analysis of water supplies, and himself developed their bacteriological investigation.

He married in 1882 Grace, youngest daughter of Joseph Toynbee, F.R.S., the celebrated aurist. He lived at Grove House, Pembridge Square, an old house, now demolished, which had formerly stood in a large garden in the open country. Here he set up the laboratory in which he conducted water analysis in conjunction with his father. His interest in biology was instrumental in enabling him to become a pioneer in bacteriology and in striking out from the purely chemical side of water analysis practised by his father. He contributed to the British

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PERCY FARADAY FRANKLAND,
PRESIDENT, 1911—1913.

[To face p. 1996.]

and foreign scientific journals on bacteriology and on the techniques for the analysis and the purification of water, and his discoveries proved to be of considerable value to the water companies in this country. In 1885 he was responsible for the inauguration of a monthly systematic bacteriological examination of London's water supplies.

On one occasion, a leaking bottle of ether led to an explosion which blew out the windows of his laboratory and even demolished the banisters of the staircase. His wife rushed upstairs and was relieved to find that he and his assistant were somewhat dazed, but unhurt. A crowd gathered outside, suspecting that the house was occupied by anarchists. It was probably this experience which led to his taking meticulous precautions against fire and explosions in his laboratories.

On his wedding tour he visited Westmorland and Yorkshire, and became much attached to Ravenstonedale, which was visited afterwards on several occasions. He and his wife returned in 1909 and purchased some farms, and from 1910 to 1914 they carried out farming during the university vacations, with a considerable measure of success. His country house and farm was Needlehouse, and it was mainly a sheep farm on the Fells. In the earlier days he and his wife did a good deal of cycling, and on one occasion they rode a "sociable" bicycle from London to Norwich, accompanied by a collie dog.

Frankland and his wife travelled extensively in Germany, Austria, Italy, Switzerland, Norway, and Sweden, and also visited Finland, Russia, Athens, Constantinople, and Ragusa. They paid long visits both in summer and winter to Norway and Sweden, where they made many friends and enjoyed the type of life and setting which they were afterwards able to reproduce to some extent in Westmorland among kindred people. He was a competent skater and took up ski-ing.

Frankland was keenly interested in history, both British and European, and had a considerable bias towards chemical history: he deplored the fact that the history of science was taught so inadequately. Although not a performer, he was keenly interested in music, his favourite composers being Mozart, Wagner, and Tchaikowsky, but he was not attracted by modern music or modern art. He was ahead of his time in his enjoyment of the rural scene and lonely places, as is obvious from his decision to settle in one of the most remote corners of Westmorland and his later retirement to Loch Awe.

After leaving London in 1888 to become Professor of Chemistry at Dundee, he lived at 2 Norwood Crescent, in that town, and took much pleasure in the romantic view from his windows across the Tay to the hills of Fife. He was a great friend of the late Professor Purdie of St. Andrews, and of Sir D'Arcy W. Thompson, then his colleague at Dundee. Purdie and Frankland were students together under Wislicenus, and they were the pioneers of stereochemistry in this country. Sir D'Arcy Thompson says of him in a letter to his son: "Your father was my colleague for a few years only, but he and your mother, too, made a far deeper impression on my life than many others with whom I worked for a much longer time. To tell you all that that impression meant is not possible to me, but the main thing is that I soon learned to look upon him as a man of singularly high principle, of unusual integrity and of simple goodness."

In a presidential address which Sir D'Arcy Thompson gave on the fiftieth anniversary of the foundation of the Dundee Social Union (in 1938), he spoke of the dreadful poverty of Dundee fifty years before: "Of all those young professors who had just come to the town, I doubt if there was one who was not shocked and saddened by the poverty which Dundee openly displayed. A certain professor came for a few years, and then left Dundee on promotion. He was a little better off than the rest of us, but far from a rich man; but he left a large sum of money to be spent quietly and without advertisement to help the poorest children of Dundee." The professor was, of course, Percy Frankland.

In the early history of University College, Dundee, the number of professors was small, and they were all men of exceptional gifts. Carnelley, the first Professor of Chemistry, came to Dundee at the foundation of the College in 1882, and was succeeded by Frankland in 1888. Frankland was liked as a good teacher who took pains to illustrate his lectures by experiments which always succeeded. Although his lectures were experimental, there was insistence on the necessity for a full understanding of the philosophic background of chemistry. He was considered by those who knew him to be one of the great teachers of the time. The subject of textile chemistry being of great importance at Dundee, he and his wife paid visits to various German technical institutes in a search for information of use to the industry.

At Dundee, his main scientific interest was in stereochemistry and in the preparation of pure cultures of bacilli, which were allowed to grow in solutions of sugars. In these latter researches he was much helped by his wife, and jointly with her, he published a volume on "Micro-

organisms in Water" (1894) and a life of Pasteur (1897). He also published in 1892 a popular book entitled "Our Secret Friends and Foes," which he dedicated "to the companion whose sympathy and invaluable assistance have so greatly enhanced the enjoyment of scientific work." Probably in few cases have husband and wife collaborated so effectively and enthusiastically in both research and professional work. On one occasion it was said, "Many women in the past have helped their husbands, but Percy Frankland is the first man who had the chivalry to admit it." The researches on the chemical reactions occurring during fermentation and his results on the chemistry of optically active compounds, which were recognized by the award of the Fellowship of the Royal Society in 1891, are referred to later.

On going to Birmingham in 1894 as Professor of what was then Mason College, where he succeeded Professor W. A. Tilden, he lived first in Edgbaston, where he took with great enthusiasm to the safety bicycle, and later at The Dell, Northfield, where he devoted much of his time to walking, riding, and driving in the attractive rural surroundings. His interest in cycling did not extend to motor-cycling or to the motor-car. He regarded high speeds on the road as criminal, and was very indignant at the high death-rate due to this cause.

He was an impetuous, generous, warm-hearted man, ever eager to combat injustice of any kind. This sometimes led to his frequent intervention in situations to which most people would have preferred to turn a blind eye. On one occasion he attempted to prevent the arrest of a small boy by a police officer for picking up apples under a hedge. Shortly after this exploit, which led to his appearance in the police court, he was made a J.P. on the Birmingham Bench, in which capacity he was greatly respected, devoting much thought and energy to his duties.

It was often assumed that Frankland would keep himself apart from the life of the students when he moved to Birmingham, but nothing was further from the truth. Under a superficial irascibility there lay a kindly disposition and a deep interest in his students, and his irascibility was invariably found to be occasioned by good reasons. He visited the teaching laboratories daily, and his manner was dignified and somewhat unbending. His experience in chemical analysis and gas analysis led him to take a deep interest in quantitative analysis. He was very insistent on scrupulous cleanliness and was very critical of any untidiness. He was very stimulating when the work was done well. Carelessness of experiment, speech, or thought made him very angry, sometimes violently so. He could not tolerate anything bogus or insincere.

Once his outer skin had been penetrated, the student realized that he had found a true friend who was always ready to give help to enable him to overcome difficulties. The penetration was frequently brought about by tennis or croquet parties at The Dell during week-ends. Soon after his appointment, the tempo of the work done in the department began to quicken. Students were not encouraged to continue a placid existence. They were encouraged to develop their talent for lecturing and participating in debate at the University of Birmingham Chemical Society, which society Frankland conducted with enthusiasm and success.

His lectures at Birmingham were very fully illustrated by experiments prepared with great care. He regarded them as very important, and his standard was very high. His lectures were not conversational or colloquial, but given in the somewhat old-fashioned correct lecture style. The lecture assistant was by far the most important member of the laboratory staff, and Frankland said on one occasion, "Always remember you can get a professor by sending a telegram or two, but not a lecture assistant."

By 1900 the number of students was large and the staff inadequate in numbers, so that the teaching duties were very heavy. Very thorough in his methods himself, he did not tolerate anything that looked like slackness on the part of his staff. Once seriously offended in this respect, he did not forget, and it was not easy afterwards to repair the mischief. As a chief, though outwardly severe in his demeanour, he was extremely helpful in discussing research problems with them and obtaining financial assistance for their researches.

He had an agreement with the University by which he could run a private water analysis laboratory in the department and employ staff for the purpose. He acted as consultant to many of the largest water companies in the kingdom.

The University of Birmingham owes much to Frankland's strong personality and his organizing ability as Dean of the Faculty of Science. He believed strongly in the value of research as part of the student's training for the first degree in science, and his influence was felt in the establishment in this country of science degrees for postgraduate research. He took a keen interest in chemistry as a profession and as a part of the national life. He was President of the Institute of Chemistry from 1906 to 1909, and was the first president to hold that office who had entered by the "iron gates of examination." This was particularly appropriate since

his father was the first President of the Institute. As President, he contributed very largely to the solution of the problems which confronted the chemical profession at that time. He was keenly interested in the code of ethics of professional men, and from his position as a university professor and also as a consultant he was able to legislate wisely on points of divergence between the two branches of the profession. He served as censor of the Institute from 1906 to 1921. At his suggestion, Council established its examination in biological chemistry, and he provided the funds for the special apparatus needed in the examination.

Frankland was President of the Chemical Society in 1912 and 1913, and his two presidential addresses review, amongst other topics, the definition of an asymmetric carbon atom, the quantitative connexion between the degree of molecular rotation and constitution, the question of *cis-trans* addition to unsaturated compounds, and the Walden inversion. His major writings were distinguished by their completeness and thoroughness. The length of the paper was a minor consideration. His lectures to the Chemical Society were models of clarity, and still have their value for their suggestiveness regarding stereochemical problems. He was always sure of a "full house," although his lectures were liable to extend over two hours rather than one. His Memorial Address to Pasteur (*J.*, 1897, 71, 683) is an example of his literary powers and gift of fine writing. This lecture forms one of the classics of the series of memorial lectures of the Chemical Society and shows his deep insight into the problems of bacteriology and into the personality of one of the most striking figures of all time.

He introduced many students and members of his staff to an appreciation of the problems of chemical industry. In 1915 he addressed the Society of Chemical Industry in Birmingham on "the chemical industries of Germany," and stirred the imagination of the industry. He realized very early the importance of the part which would be played by science in the development of this country. At the end of his lecture he referred scathingly to the popular slogan of the time, "business as usual, that *vulgar* phrase."

As Professor of Chemistry in the University of Birmingham, he was largely responsible in 1909 for the internal arrangements of the chemistry laboratories at Edgbaston, designed by Aston Webb. The students entered the building before the contractors had left, and it is recollected by some students that chemical analysis was carried out for a time in one laboratory before the floor-boards were complete. Five years later he was to vacate these laboratories and return to the Mason College laboratories in Edmund Street, to make room for an emergency military hospital which took over all the buildings at Edgbaston until the end of the first world war. The laboratory buildings were mainly used as a store and a mortuary. In very cramped laboratory accommodation at Edmund Street, Frankland carried out much research from 1914 to 1918, for the Chemical Warfare Committee, on synthetic drugs, on high-explosives intermediates, and on river effluents from explosives factories. He was a member of the Admiralty Inventions Board, and the Anti-Gas and Chemical Warfare Committees. He was Deputy Inspector of High Explosives (Birmingham Area) and took entire charge of tar-testing in the Midlands. He was very much involved in researches on mustard gas, and, in conjunction with Sir William Pope, was responsible for the adoption by Churchill, then Minister of Munitions, of Guthrie's method—by which this substance was prepared from ethylene and sulphur chloride, a vastly easier process than that employed by the enemy. Investigators had been misled by the references to Guthrie's method being incorrect, owing to the change in the atomic weight of carbon from 6 to 12. In 1916, he paid an extended visit to the Western Front, and in 1917 was a member of a special mission sent to Italy to report on chemical technology in that country. For his war activities he was awarded the C.B.E. and by the Italian Government he was made an Officer of the Order of St. Maurice and St. Lazarus. He received honorary doctorates from the Universities of Birmingham, Dublin, St. Andrews, and Sheffield. He was awarded the Davy Medal of the Royal Society in 1919.

At the end of the first world war, he retired at the age of sixty. His laboratory required rehabilitation after being used as a hospital, his academic researches had been seriously interrupted, and he felt that the problems of post-war were those for a younger man. He lived after his retirement at the House of Letterawe, Loch Awe, Argyllshire, among surroundings that had always appealed to him, and entertained his friends who visited him there. His house lay under the shadow of Ben Cruachan, with Ben Lui in the distance, in a beautiful and romantic setting. Close by, on a small promontory, stood the ruins of Kilchurn Castle, formerly a stronghold of the red MacGregors against their hated foes, the black Campbells, in those grim days when the clansmen settled their disputes by resorting to the claymore and the *sgian dubh*. Farther to the south was the conspicuous memorial of the Gaelic poet, Duncan Ban MacIntyre.

Frankland was very fond of small boats and he learned to sail single-handed with the

assistance of books. He also had a motor-boat with an internally fixed motor, the *Circe*. This was like a life-boat, which would stand the sudden squalls and changes of wind very frequent on Loch Awe. He also had a small outboard motor-boat which he regarded as a fair-weather, light-load craft. He was delighted to take his friends by boat to see the beauty spots of Loch Awe, or by road to Inverary, Glencoe, or Ballachulish. In his retirement, even up to a few days before his death, he was always alive to the latest news from the political, scientific, and philosophical worlds, and followed the careers of his old students with great interest. Although the Franklands did not "have the Gaelic," they were very well liked by the Highlanders of the district for their easy friendliness, generosity and kindness. He survived the death of his wife only a few weeks, and they were buried together in the churchyard of Glenorchy. He leaves one son, Dr. Edward Frankland.

Research.

Frankland's research is characterised by its accuracy, and although most of his work was done in collaboration he was very careful to satisfy himself that the results were accurate, as far as he could tell. If anything was doubtful, it was checked again and again before it was accepted as a fact. He mistrusted the use of four-figure logarithms and the slide-rule by his students, and checked their work by arithmetical methods. He wrote to Professor McKenzie in 1939, "It has seemed to me for some time past that chemists are much less concerned about the accuracy of their results than they formerly were. In the old days, the publication of a result which proved to be erroneous was almost enough to shipwreck his career, and would, in any case, render all his subsequent work suspect. Indeed, a few errors of this kind would be sufficient to cast doubt upon a man's character for common honesty."

There was one occasion when Frankland described the optically active methyl and ethyl lactates prepared by the direct action of acid on alcohol, but his values for the rotatory powers were considerably lower than those of Purdie, who had prepared his esters by the interaction of alkyl halide and optically active silver lactate. Purdie suggested that Frankland's method led to optically impure products, owing to partial racemisation. As a matter of fact, Purdie found later that it was his esters which were impure; they were contaminated with a small quantity of alkylated product. The mistake was fortunate, for it led to the method of alkylation by silver oxide and methyl iodide, which proved of such great value in the study of carbohydrates.

On another occasion Frankland resolved inactive glyceric acid by the action of *Bacillus ethaceticus*, obtaining for barium L-glycerate a rotation $[\alpha]_D - 10.01^\circ$ in aqueous solution. Neuberg prepared the barium salt from D-glucuronic acid, obtaining $+ 17.1^\circ$ and resolved DL-glyceric acid with brucine to get barium salt with $- 17.38^\circ$. Neuberg suggested that the biological method of resolving acids is rather unsatisfactory. Accordingly, Frankland and Done (*J.*, 1905, **87**, 618) made a careful revision of the whole question and repeated the earlier results. Finally, Neuberg corrected his error, which was due to faulty polarimetric readings.

Frankland's earliest research was carried out in Wislicenus's laboratory in Würzburg on the interaction of diazonaphthalene with salicylic acid (*J.*, 1880, **37**, 746). The object of the investigation was to determine the place of entry of the diazo-group into salicylic acid, the group being introduced in the form of diazonaphthalene. The diazo-group was found to be attached in the *para*-position to the hydroxyl group, as is the case for most other substitutions into salicylic acid.

On his return to London, he became very much interested in consulting practice, in the methods of analysis of inorganic substances, and in the bacteriological examination of water. Frankland's interest in analysis is shown by the publication of a book on agricultural chemical analysis in 1883. He was also interested in gas analysis, and made a systematic investigation in 1884 of the coal gas supplied to consumers in the large towns in Great Britain and compared the analyses with those obtained by his father in 1851 (*J.*, 1884, **45**, 189). He noted that there had been a striking increase in the nitrogen content of coal gas due to the replacement of iron retorts in the manufacturing process by the more porous fireclay retorts.

His father, Edward Frankland, as a climber in Switzerland, had made the pioneer investigation of the diminution of the illuminating power of a flame with increasing altitude. In 1878 with Thorne (*J.*, **33**, 89) he had studied the luminosity of benzol when burnt with non-luminous combustible gases. In 1884—1885, the son published a series of papers on the illuminating power of gases which extended the work of his father (*J.*, 1884, **45**, 30, 227; *J. Soc. Chem. Ind.*, 1884, **3**, 271; *J.*, 1885, **47**, 235; *J. Soc. Chem. Ind.*, 1885, **4**, 387). He found that benzene was three times as effective as ethylene in increasing the illuminating power of coal gas, and that for ethane and propane the illuminating power is directly proportional to the number of carbon atoms in the molecule.

In 1885 he commenced an extensive series of investigations into the bacteriology of air and water (*Proc. Roy. Soc.*, 1885, **38**, 379; 1886, **40**, 509, 526; 1887, **42**, 267; 1889, **45**, 292; *J. Soc. Chem. Ind.*, 1885, **4**, 698; 1887, **6**, 316). These included the study of the methods of filtration of bacteria from water by greensand, coke, animal charcoal, and spongy iron, and the duration of the efficiency of such materials when employed as filters. He also modified the existing methods for extracting bacteria from the air (*Phil. Trans.*, 1887, *B*, **178**, 113). Instead of aspirating air slowly through wide glass tubes coated inside with nutrient gelatine, as was the current practice, Frankland aspirated air rapidly through a plug of glass wool which was afterwards shaken up and disintegrated in a flask containing melted gelatine. The flask was rotated until the medium solidified in a film, and was then incubated till the bacterial colonies developed and could be counted. This method was employed for the investigation of the numbers of bacteria in the air of towns, in the open, and inside buildings. A study was also made of the effect of common gases on the rate of growth of organisms (*Proc. Roy. Soc.*, 1889, **45**, 292).

In conjunction with his wife, in 1887 he determined the characteristics of a large number of bacteria obtained from the air, water, and soil, which had not been previously described, and studied their behaviour in dilute nitrate solutions (*Phil. Trans.*, 1887, *B*, **178**, 257; *Proc. Roy. Soc.*, 1888, **43**, 414; *J.*, 1888, **53**, 373). In 1890 they isolated nitrifying bacteria from the soil (*Phil. Trans.*, 1890, *B*, **181**, 107), and showed that they could be cultivated in ammoniacal solutions, the growth being accompanied by the gradual transformation of ammoniacal into nitrous nitrogen. He was invited to address many scientific societies, both at home and abroad, on the bacteriology of water. He also gave many popular lectures, and these and his books were important in bringing home to the general public the importance of this knowledge in the life of the community.

In association with Professor Marshall Ward, he was responsible for four reports to the Research Committee of the Royal Society on "The vitality of pathogenic organisms in water" (*Proc. Roy. Soc.*, 1892, **51**, 183; 1893, **53**, 164, 177; 1894, **56**, 315, 395, 549; 1896, **59**, 265). The persistence of anthrax bacillus, typhoid bacillus, and *B. coli communis* was studied under a wide variety of conditions in Thames water and Loch Katrine water. It was shown that the waters, after infection, were potentially dangerous over a long period of time.

Frankland was one of the first after Pasteur to study the chemical reactions in fermentation processes and to apply these to the isolation of pure substances. In this work he owed much to the assistance of his wife. His investigations on fermentation were mostly accomplished while at University College, Dundee, from 1888 to 1894.

He succeeded in obtaining optically active glyceric acid and sarcosolactic acids by Pasteur's biochemical method of resolution. At that time glyceric acid was only known as a substance devoid of action on polarized light. In the fermentation of inactive calcium glycerate by *B. ethaceticus* he showed that approximately one half of the glycerate was not attacked by the bacillus (*J.*, 1891, **59**, 81, 96), and he was able to isolate the calcium salt of pure levorotatory glyceric acid from this residue. The crystallographic and optical properties of crystals of the calcium salt were investigated by Tutton (*J.*, 1891, **59**, 233), and the crystal faces were found to show hemihedrism, which is usually associated with crystals of optically active substances. This investigation is similar to that on racemic tartaric acid by Pasteur, who was of the opinion that in the resolution of this acid accomplished by biochemical agency, the dextrorotatory acid was destroyed, leaving the levorotatory acid unchanged. Following the preparation of this active glyceric acid, Frankland commenced an extended and very accurate investigation of the properties of esters of glyceric acid and its derivatives, which was of very great value in elucidating relationships between optical rotatory power and chemical constitution.

Frankland drew attention to changes in the activity of bacteria caused by their employment on unaccustomed tasks. A decrease in activity occurred if they were employed to ferment substances which were attacked with difficulty, but the activity was restored if they were allowed to act on easily fermented substances. He used mainly *B. ethaceticus*, *B. ethacetsuccinicus*, and *Pneumococcus friedlander* in his investigations on the chemical changes occurring during fermentation, and their action was shown to be highly specific (*Proc. Roy. Soc.*, 1890, **46**, 345; *J.*, 1891, **59**, 253; 1892, **61**, 254, 432, 737; 1893, **63**, 1028). The first two bacilli were first isolated by him. *B. ethaceticus* attacks glucose, cane sugar, milk sugar, and calcium glycerate, but there is no action on dulcitol, erythritol, glycol, calcium lactate, tartrate, citrate, and glycollate.

By the then available methods he carried out very detailed and accurate analyses of the chemical products from the fermentations. This followed on earlier investigations (*J.*, 1883, **43**, 294) in which he had studied the gases evolved from dry and moist grass and had shown that

the processes involved were probably those due to lactic fermentation. He concluded that the products were ethyl alcohol, acetic acid, some formic and succinic acids, carbon dioxide, and hydrogen. The formic acid was produced to the greatest extent when the fermentation was carried out in the absence of air. In the presence of air there was more carbon dioxide and hydrogen. From the carbon, oxygen, and hydrogen balance sheets of the reactions, it was concluded that some of the carbon dioxide and the whole of the hydrogen were derived from formic acid. After deducting the carbon dioxide liberated by acids from the calcium carbonate present in the medium, it was found that carbon dioxide and hydrogen were produced in equimolecular proportions in the gaseous products.

There were differences in degree between the products obtained from the fermentation of different pure substances. Thus, mannitol and dulcitol, fermented with *B. ethacetsuccinicus*, did not yield the final products in the same proportions (*J.*, 1892, 61, 254). The same decomposition products were obtained with six, five, and three carbon-atom carbohydrates and polyhydric alcohols, but the proportions of acetic acid to ethyl alcohol varied.

His chemical researches on fermentation ceased in 1893, although he retained a considerable interest in bacteriology, as was shown by his papers on this subject and by his address to the Society of Chemical Industry in 1911, when he lectured on the bacteriological purity of water (*J. Soc. Chem. Ind.*, 1911, 30, 319). He had, however, found another line of research that offered greater prospects of getting to grips with the problems of stereochemistry in which he became interested while under the teaching of Wislicenus.

A research on the optical rotations of the salts of glyceric acid in aqueous solution (*J.*, 1893, 63, 296) was important in that it demonstrated that the relationships between optical activity and chemical constitution could not be interpreted in terms of existing theories. The results did not conform with Ostwald's dictum that the molecular rotation of salts in dilute solution should be independent of the inactive part of the molecule, nor were they in accord with the suggestion made by Crum Brown and Guye independently that the molecular dissymmetry was determined by the product of asymmetry.

In his stereochemical studies Frankland employed mainly derivatives of the optically active glyceric, tartaric, lactic, and malic acids. One series of derivatives was prepared by substitution of acetyl, benzoyl, toluoyl, chloroacetyl, pyromucyl, nitrobenzoyl, and methoxypropionyl groups in place of the hydrogen atom in the hydroxyl groups of the acids. Both mono- and di-substituted acids were employed, although mainly the latter. In another series, similar groups were introduced into the amido-group, starting with tartramide. These compounds gave a very wide variety of groups around the asymmetric carbon atom, with very different masses and very different chemically.

The study of the quantitative connexion between the degree of molecular rotation and constitution received its initial impulse from the theory proposed by Crum Brown and Guye that the *product of asymmetry* is a measure of the dissymmetry of the molecule as a whole. In this theory, P is the product of asymmetry which can be calculated, assuming that the four different masses (a, b, c, d) attached to the asymmetric carbon atom are concentrated at the apices of the tetrahedron, by the formula :

$$P = \frac{(a-b)(a-c)(a-d)(b-c)(b-d)(c-d)}{(a+b+c+d)^3} (l \sin \alpha)^6.$$

From an examination of the existing data it was concluded by Guye and Crum Brown that P was proportional to the molecular rotatory power. This theory was found by Frankland to be quite incapable of accounting even qualitatively for the facts of optical activity.

Frankland used the conception of the product of asymmetry as a basis for his earlier investigations, and he devised tests of its applicability. These tests consisted in modifying the masses of the groups around the asymmetric carbon atom and observing the effect on the molecular rotation and molecular volume. Also, by the use of isomeric substituents, such as the *ortho*-, *para*-, and *meta*-benzene derivatives, he examined the effect of altering the centre of gravity and moment of mass of the substituent group. He studied also the introduction of double and triple bonds and conjugated double bonds and cyclic groups into constituents placed around the asymmetric atom. Measurements of molecular volume were made at the same time as those on molecular rotatory power, and these were compared with those calculated by Traube's method, in order to be able to assess what degree of abnormality in the rotation was caused by association of the molecules. Also, the rotation was measured over a wide range of temperature, and the temperature coefficients were sometimes anomalous and had to be taken into account in the interpretation of the results.

He says about the stereochemical researches based on optical activity, "Although the researches have not led to any comprehensive generalization, they have revealed a number of interesting regularities, which form in some measure a compensation for the enormous amount of labour which has been bestowed on the subject, which is admittedly of great complexity."

Optical Activity in Homologous Series.—The esters of glyceric and acetylglyceric acid, ranging from methyl to octyl, were prepared from levorotatory glyceric acid, obtained by the fermentation method (*J.*, 1893, **63**, 511, 1410, 1419; 1894, **65**, 750, 760; 1897, **71**, 253). The curves for the rotatory power of the glycerides and acetylglycerates showed a flat maximum in the position of the 4th to 6th members of the homologous series, and they ran parallel to one another. The positions of the maxima were approximately what would be expected from the Crum Brown-Guye hypothesis, but the breakdown of this hypothesis was very clearly evident in the case of the methyl and ethyl diacetylglycerates (*J.*, 1894, **65**, 750). For these substances, two groups around the asymmetric carbon atom are of equal mass and therefore the product of asymmetry is zero, whereas both are powerfully optically active. He concludes that since the maximum occurs at the same place in the glycerates and acetylglycerates, it is very likely that the position of maximum rotation is determined by some property of the hydrocarbon chain rather than by the product of asymmetry.

Frankland studied two further homologous series in some detail, the dibenzoylglycerates (*J.*, 1896, **69**, 104) and the dimethoxypropionates (*J.*, 1905, **87**, 864). In the former, the maximum occurred very early in the series at the second member, and in the latter at the seventh member. In his presidential address to the Chemical Society in 1912 he summarises his own work and that of Tschugaeff, Guye and Chavanne, Pickard, Kenyon, and others on the optical rotatory power of homologous systems. "In some series there is a progressive change in the molecular rotation until a maximum is reached and this is followed by a much less marked decline in the rotation, which tends towards a limiting value. In other series, the rotation progressively changes, a limiting value being reached without the appearance of any definite maximum or minimum. In either case the maximum or limiting value is generally reached at a surprisingly early term in the series." After a very careful critical examination of all the experimental results (*J.*, 1899, **75**, 347), he came to the conclusion that the position of the maximum could not be linked with association phenomena, nor could it be accounted for by the changes in masses of the groups around the asymmetric carbon chain. He made the suggestion that "according to the commonly accepted view of stereochemistry, a continuous chain of five carbon atoms will all but return on itself, and beyond this, further addition to the chain will lead to such interference as must necessitate a readjustment of the exact position occupied by the carbon atoms in the shorter chain. It is surely highly probable that the stereochemical change should be betrayed by some irregularity in the rotation manifestations, for example, by the exhibition of a rotation maximum."

Position Isomerism in Aromatic Compounds on Molecular Rotation.—The introduction of a cyclic group such as benzoyl, toluoyl, pyromucyl, or phenacetyl in near proximity to an asymmetric carbon atom always produced a marked change in the optical rotatory power. The deviation was sensitive to small changes in the constitution of the cyclic group and thus afforded a means of studying the stereochemical changes occurring on substitution. Frankland suggested (*J.*, 1896, **69**, 1309, 1583; 1898, **73**, 307; 1901, **79**, 266) that for reasons based on the relative position of the centre of gravity of the aromatic nucleus, the effect on the optical rotatory power of the *o*-, *m*-, and *p*-substituted benzoyl groups should be in the order ortho < phenyl < meta < para. This was found to be generally true, although some anomalous effects due to variable temperature coefficients of the rotatory power or possibly to association to double molecules were responsible for minor irregularities. It was almost invariably found that the *o*-toluoyl group had a rotatory effect of a different order from those of the phenyl and *m*- and *p*-toluoyl groups, which were always close together, but the relative order of the last three groups was in a few cases not in line with the above sequence. The validity of the rule was confirmed by Cohen (*J.*, 1910, **97**, 1732) for a large number of substituted methyl benzoates, and in all of the nine cases studied, the rule, ortho < phenyl < meta was found to hold.

A number of series were found for which the reverse order held, the dextrorotatory effect of the substitutions being in the order, para < phenyl < meta < ortho for the methyl and ethyl toluoylmalates (*J.*, 1899, **75**, 337) and ditoluoylglycerates (*ibid.*, p. 493).

Series in which the methyl group was replaced by the nitro-group and the halogens followed. The esters of the di-*o*-, *m*-, and *p*-nitrobenzoyltartrates were compared with the toluoyl derivative (*J.*, 1904, **85**, 1571). The order for the methyl esters was para < meta < ortho, and for the ethyl esters the same relationship held at high temperatures, but the ethyl di-*o*-nitrobenzoyl-

tartrate had an anomalously high temperature coefficient, which led to departures from the rule at the lower temperatures. In the final paper on the series on benzoyltartrates (*J.*, 1912, 101, 2470), the chloro-, bromo-, and iodo-derivatives gave very convincing support for Frankland's rule, supplementing it by some very interesting conclusions which showed the sensitiveness of this method of approach to stereochemistry. The halogens exert an influence on the rotatory power which is of the same kind as that of the methyl group in the toluoyl radical, but in a greater degree. The order para < meta < ortho is maintained, but the rotatory effect increases with the atomic weight of the halogen.

The same general relationships were found when the cyclic group was attached to the amido-groups of tartramide (*J.*, 1903, 83, 1349). The order of exaltation was para > meta > anilide > ortho, the substitution behaving similarly to that of the same aromatic groups into the hydroxyl groups of tartaric acid. A close parallelism was found between the effects of the acetyl, phenacetyl, benzoyl, and toluoyl groups replacing the hydrogen atom of the hydroxyl groups of the optically active hydroxy-acids and those due to ethylamine, benzylamine, aniline, and toluidine replacing the hydroxyl of the carboxyl group. Although the halogens replacing methyl in the aromatic groups (*J.*, 1910, 97, 154) increase the exaltation they, however, appear to have an effect by virtue of their electronegative character, which Frankland suggests is possibly due to the intramolecular attraction forces between the negative group and the hydrogen of the tartaric nucleus, which changes the asymmetry.

Rotatory Effects of Specific Groups.—A very large amount of data was accumulated by Frankland and his pupils on the specific effects of particular groups, notably on the effects of double bonds, cyclic groups, and nitro-groups as compared with methyl groups, halogen groups, etc. The work is difficult to summarise, since the effect of the substitution depended on the asymmetry of the molecule as a whole, and also on the solvent used. Certain regularities were, however, found, some of which are summarised in his presidential address in 1912 (*J.*, 1912, 101, 654).

Unsaturation. "There is a general consensus of opinion that of two similar groupings, the one saturated and the other unsaturated, the latter will have the greater rotatory effect. It would, however, in my opinion, be more correct to say that the presence of unsaturation leads to an irregularity in the rotatory effect, and not necessarily to an increase in rotation." The relations are not so simple and harmonious as at first supposed; in some cases, the double linking has a smaller effect on the rotatory power than the saturated grouping. Conjugated double bonds, however, exercise a very powerful exaltation, as pointed out by Rupe and Hilditch.

In the case of some *n*-propyl and allyl derivatives of menthol (*J.*, 1911, 99, 2325) the differences were small, and this is ascribed to the great distance of the double bond from the asymmetric carbon atom. The constitutional change is made at such a great distance from the asymmetric carbon atom that it has little effect on the rotation.

It was shown that, in the substitution of both tartramide (*J.*, 1906, 89, 1852) and malamide (*ibid.*, p. 1899) by *n*-propyl and allyl alcohol respectively, the *n*-propyl derivative had the higher rotation, which is contrary to the accepted rule. Here again the active group is 3 or 4 carbon atoms removed from the asymmetric atom. The behaviour in these substances is also very much affected by the solvent in which the rotation is measured.

However, in certain derivatives of tartramide, $\text{NHR}\cdot\text{CO}\cdot[\text{CH}\cdot\text{OH}]_2\cdot\text{CO}\cdot\text{NHR}$, in which R is varied, the influence of unsaturation is brought out very clearly (*J.*, 1903, 83, 1349).

$M_D^{20^\circ}$.		$M_D^{20^\circ}$.	
$\begin{array}{c} \\ -\text{C}-\text{CO}\cdot\text{NH}_2 \\ \end{array}$	+ 158°	$\begin{array}{c} \\ -\text{C}-\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_5 \\ \end{array}$	+ 554°
$\begin{array}{c} \\ -\text{C}-\text{CO}\cdot\text{NH}\cdot\text{NH}_2 \\ \end{array}$	+ 170°	$\begin{array}{c} \\ -\text{C}-\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_4\text{H}_9\text{O} \\ \end{array}$	+ 736°

Cyclic groups. Frankland investigated the changes in rotatory power due to the introduction of conjugated and saturated cyclic groups into the optically active molecule. The rotation was not appreciably affected by saturated rings, but with conjugated rings there was a marked exaltation when they were introduced into tartrates and tartramides (*J.*, 1896, 69, 1309, 1583; 1901, 79, 511; 1903, 83, 1342, 1349; 1906, 89, 1852). The furan ring was similar to benzene in giving a considerable exaltation of the rotation, and the tetrahydrobenzene ring in *ac*-tetrahydro- β -naphthyl groups, being a saturated ring, exerted a very small rotatory effect.

The α -naphthyl group was found to resemble the *o*-toluoyl group and the β -naphthyl group the *p*-toluoyl group in their general effects. The effect of isomerism in the cyclic group has been dealt with on page 2003.

Nitro-groups. Frankland devoted much attention to the rotatory influence of the nitro-group relative to that of the methyl group. The dinitrotartaric acids and the methyl esters of mononitro- and dinitro-tartaric acids were investigated (*J.*, 1903, **83**, 154, 168). Also, the diethyl monobenzoyl- and mono-*p*-toluoyl-tartrates were nitrated. From these experiments and those quoted earlier, it is concluded that NO_2 has a higher rotatory effect than CH_3 and $\text{O}\cdot\text{CH}_3$ when attached to a ring, but when present as $\text{O}\cdot\text{NO}_2$ it has a less effect than $\text{O}\cdot\text{CH}_3$. These differences he ascribes to modifications in the chemical constitution of NO_2 when attached directly to carbon or through oxygen. The summary of a very complex situation as regards the relative effects of NO_2 and CH_3 groups is given by Frankland in the paper in 1903 (p. 168).

In the years preceding the first world war, Frankland was extending his range of interests in the stereochemical field. This is shown by his two presidential addresses to the Chemical Society in 1912 and 1913. He commenced researches on the Walden inversion (*J.*, 1914, **105**, 456, 1101) and on rotation dispersion (*J.*, 1919, **115**, 636). With the onset of the war his activities were entirely absorbed in Government work, and, since he retired immediately after the war, these lines were not further pursued by him.

W. E. GARNER.
