

The Franklin Memorial Lecture.

EDWARD CURTIS FRANKLIN.

March 1st, 1862–February 13th, 1937.

A MEMORIAL LECTURE DELIVERED ON FEBRUARY 17TH, 1938.

By ALEXANDER FINDLAY, M.A., D.Sc.

WITH the close of the Crimean War there developed in America one of those periods of crisis, due to industrial depression and financial panic, which, to use the language of the American historian, James Truslow Adams, "have been like the pulsations of a vast heart, pumping inhabitants into our unpeopled spaces." It was, we may hazard the guess, one of these pulsations which, in 1857, carried Thomas Henry Franklin, son of a Philadelphian shoe merchant, to the still undeveloped State of Kansas, where, in 1858, at the newly laid out townsite of Geary City, in Doniphan County, he erected a sawmill on the banks of the Missouri River and made lumber from the cotton-wood, sycamore, elm, oak and walnut trees which flourished abundantly along the creeks and rivers of that county. On June 12th, 1861, the young sawmill owner took to wife Cynthia Ann Curtis, a Missourian by birth, whose family had settled in Doniphan County in 1855; and it was at Geary City, on March 1st, 1862, that their first child, Edward Curtis Franklin, was born. In 1867, the Franklin home was moved to the county town of Doniphan, where Edward grew up into early manhood.

To realise the background of Franklin's life and to understand the structure of the society in which he grew up and which, I believe, exercised an important influence on his whole life and outlook, one has to bear in mind that, until 1854, Kansas was still in the hands of the Indians; and although Doniphan County, in the north-eastern corner of the State, was one of the earliest districts to be organised (in 1855), most of the State of Kansas was, in the sixties and early seventies of last century, still undeveloped, and the caravans passing westward along the California and Oregon trails were still subject to hostile attack on the part of the Indians. The life and conditions under which young Franklin spent his boyhood years were, in fact, those which were so thrillingly described by Fennimore Cooper; and it is, no doubt, to the conditions under which his boyhood was spent that one may attribute Franklin's sometimes noticeable impatience with convention and his preference for the simpler conditions which characterise a frontier society. Franklin always seemed to me, indeed, to carry about with him much of the spirit of the frontier.

Franklin received his early education in the public schools of Doniphan, but his scholastic attainments never brought him much distinction. His mind worked slowly and he preferred to learn from nature and from making things with his own hands rather than from books. And so, as he himself relates in an autobiographical sketch of his life, he "spent much time in fishing for catfish and 'sunfish'; in swimming in muddy sloughs and in the river; in roaming the hills and bluffs, picking and admiring the beautiful wild flowers, gathering and eating quantities of wild strawberries, raspberries, and blackberries. In the autumn he garnered wild grapes, plums, cherries, gooseberries, crabapples, red and black haws, and pawpaws. Also in the autumn hazelnuts, hickory nuts and black walnuts were harvested and preserved for winter consumption. With the winter came skating and snow sports, trapping and shooting cotton-tails and bobwhites, killing tree squirrels, prairie chickens, wild ducks and, occasionally, a wild goose for sport and for food, and blue jays and crows as nuisances." The keen and joyous interest which Franklin exhibited as a young boy in all outdoor pursuits and activities remained with him throughout the whole of his life.

At the age of fifteen, Franklin was sent to school at Park College, a little Methodist boarding school at Parkville, Missouri, but the dietary offered there was distasteful to him

and quite inadequate to his physical needs, and so, after two months of joyless existence, he ran away.

While the book-learning of the schools does not seem to have appealed to him, Franklin possessed a great natural interest in and curiosity about the things of nature; and, encouraged by a wise and earnest father, he found much delight in collecting fossils from the limestone rocks along the Missouri River and in examining insects and other natural objects under a microscope. Even at an early age, also, Edward Franklin and his younger brother William, who later became professor of physics at the Massachusetts Institute of Technology, employed their time in making electric batteries, Leyden jars and even a fair-sized induction coil, and they dabbled with chemicals in a corner of their father's sawmill office. Later, they erected a telegraph line and became expert in sending and receiving messages in the Morse code, and in 1877, a year after Alexander Bell invented the telephone, the brothers, with the help of their father, made a pair of Bell telephones which they used on their telegraph line. Through all these various activities, Franklin gained some knowledge of physical and chemical science, and he acquired a manual expertness and dexterity which proved of the greatest value to him and to others in later years.

Franklin developed slowly and was long in finding the real bent of his mind and in discovering his true vocation. After running away from Park College, he more or less wasted, as he confesses, the next seven years of his life. From 1880 to 1884, he worked in a drug store at Severance, carrying on at the same time a small job-printing shop, and he found expression for his emotional feelings in playing a cornet in the village band. Through all these varied activities, however, he was slowly beginning to find himself, and, under the stimulus of his brother's example, there at length awakened in him a desire for a university education. In 1884, therefore, at the age of twenty-two, Edward Franklin, with his vague ambitions and his varied but somewhat unorganised knowledge, entered the State University at Lawrence. There he studied Chemistry, Physics, and a variety of other subjects—German, French, Surveying, English, Botany, Meteorology, History of Philosophy, and Mental and Moral Philosophy—and graduated B.S. in 1888. After graduation, Franklin, who had already while an undergraduate proved his worth and value as an instructor, was appointed an assistant in chemistry, and for two years he taught elementary chemistry to students of pharmacy and carried out water and mineral analyses for the Professor of Chemistry, E. H. S. Bailey. He received the degree of M.S. in 1890.

To supplement the somewhat restricted training in chemistry which he had received at the University of Kansas, and to widen his outlook, Franklin accompanied his younger brother to Germany in 1890, and worked for a year in Tiemann's laboratory, and he attended the lectures on elementary and organic chemistry given by Hofmann for the purpose, more especially, of studying that great master's lecture technique. He attended also lectures on the calculus by Max Planck and a course on industrial chemistry, in the expectation that he would thereby have an opportunity of visiting some of the German chemical factories. In this, however, he was disappointed, for the class visited only one factory, a brewery, in the products of which there is no reason to believe Franklin had any great interest. Although there is little evidence in Franklin's own research work that his contact with German chemistry made much impression on him, his visit to Germany gave fullness and richness to his life, and he always looked back with pleasure to the evenings spent at the Opera or at concerts, and to the long tour, made largely on foot, through the Rhineland, Switzerland and South Germany which preceded the period of study in Berlin. His love of German folksongs and music remained with him through life.

On returning to America, Franklin resumed his teaching work at the University of Kansas, but the necessity of prosecuting research and of obtaining a doctor's degree, if he was to achieve success in an academic career, drove him in 1893 to Johns Hopkins University to work under Professor Remsen. The research which he carried out there on the action of *o*- and *m*-diazobenzenesulphonic acids on methyl and ethyl alcohols, gained for him in 1894 the degree of Ph.D., and appointment as associate professor at his old University. There he gave instruction in organic chemistry, mineralogy and crystallography, and assaying.

At the age of thirty-two, Franklin's scientific development was still delayed. He had



EDWARD CURTIS FRANKLIN.
(After a crayon portrait by Rem Rensen.)

had, it is true, a fairly wide experience in the teaching and practice of chemistry; he had acted for a number of years as an instructor at Kansas University; he had spent the summer of 1886 tramping among the San Juan Mountains in Colorado as an assayer and assistant mineral surveyor to a firm of prospectors; and, for a time, in 1888, he was chemist on a sugar plantation in Louisiana. He followed with interest the advances in chemical and physical science which were being made in England and in Europe, and took delight in exercising his great technical skill in constructing apparatus and in repeating some of the recent experiments. As early as 1895, for instance, he made Dewar tubes out of Liebig condensers, that being the only suitable glass then available in America, and in 1896, he blew X-ray tubes for his colleagues in physics. No sooner, moreover, was the discovery of argon announced than Franklin proceeded to prepare a quantity of the gas and to seal it up in Plücker tubes made by himself. His interest in chemistry was clearly very much alive, but he had apparently not yet felt the urge to creative work. There appears little doubt that he himself felt that something was lacking, for he recounts that in 1896, not sure that he had in him the makings of a professor, he obtained leave of absence and accepted a post as chemist and co-manager of a gold mine and mill near Los Quemados, Costa Rica. Not finding this work, however, to his taste, he resumed his teaching work at the University. In the autumn of that year, as we shall see later, the inhibitions were swept away and creative energy released, and for more than thirty years thereafter research work was prosecuted with vigour.

In 1897 Franklin married Effie June Scott, sister of the Kansas Congressman Charles F. Scott, and a student at the University of Kansas. Her affectionate devotion to her husband, her bright intellect, her interest in literature and in music, and her gifts as a pianist created a gracious, cultured and happy home life, of which music was an essential part. Franklin, it is true, laid aside his cornet, but his study door was always left open so that he might enjoy the sound of his wife's playing. There were three children of the marriage, one daughter and two sons, and of these three two are still alive. The elder son was killed in an aeroplane accident in 1928, and Mrs. Franklin died in 1931. After the death of his wife, Franklin continued to live in his home on the Stanford Campus and was there joined by his son-in-law and daughter, Dr. Anna Franklin Barnett, a medical graduate of Stanford University, who has inherited the musical ability of her mother.

In 1898, Franklin was appointed professor of physical chemistry at the University of Kansas, and five years later left that university, rather regretfully, on appointment as associate professor of organic chemistry at Stanford University, California. In 1906 he was appointed to the full professorship. Here at this great University of the west, whose widespread Campus gives a feeling of spaciousness to life and whose noble buildings with their open arches, long colonnades and red-tile roofing inspire one with memories of the ancient Spanish Missions, Franklin worked quietly, happily and persistently until his retirement in 1929; and even after his retirement he retained his office and private laboratory in the chemistry buildings and continued his research work till the end. It was, it is true, at the University of Kansas that Franklin's research activity first came to life, but it was during his long period of residence at Stanford University that he built up the great edifice of ammono-chemistry which has earned for him a foremost place among the chemists of the twentieth century. Although Stanford University was founded only in 1885, it early acquired fame through the eminence of its teachers and their contributions to knowledge; and Franklin found great happiness, mental stimulus and inspiration in the vigorous life of the young University and in the frequent intercourse which he was able to have with his colleagues at the University of California at Berkeley.

During the tenure of his professorship at Stanford University, Franklin spent two years, 1911—13, on leave of absence at Washington, where he acted as Professor of Chemistry and Chief of the Division of Chemistry in the Hygienic Laboratory of the Public Health and Marine Hospital Service. While there he not only continued the research work on which he had been engaged at Stanford, but investigated also the radioactivity of the waters of the hot springs on the Government Reservation at Hot Springs, Arkansas, for whose curative properties high claims were made. The results perhaps were regarded as disappointing, for so small was the amount of radium that, as Franklin put it, the invest-

ment on the part of the Government of twelve hundred and twenty-five dollars would supply, at the price of radium then prevailing, an amount of radium emanation equal to that given off by all the springs on the Reservation.

Franklin had a very wide and varied experience as a teacher and lecturer in general chemistry, qualitative and quantitative analysis, assaying, mineralogy and crystallography, chemistry of sugar, physical chemistry, the history of chemistry and organic chemistry. Himself an accomplished analyst, he inculcated in his students care and accuracy in their analytical work; and in the later stages of their training he stimulated their interest by making them repeat some of the preparations and experiments described in the current literature. Franklin's mechanical skill and manual dexterity, cultivated since boyhood, were a constant source of admiration, and most of the sometimes complicated and delicate glass apparatus which he used in his long series of investigations with liquid ammonia, was made by his own hands. In his practical teaching, therefore, he sought to train his pupils to become expert in the construction of apparatus, in glass-blowing and in all the laboratory arts.

As a lecturer, Franklin occupied a high place. His lectures were well prepared and were presented in a clear and orderly manner, but in language which was informal and conversational. His obvious command of his subject gained at once the respect and confidence of the students and his free and easy "western" manner and his occasional use of apt and expressive slang won their hearts. He sought, also, to give vividness to his lectures by means of numerous and striking experiments, and in the preparation and performance of these his skill as a glass-blower and his manipulative ability often played an important part. Taking Faraday as his example, also, Franklin liked to give lectures to young people, and these were largely exhibitions of glass-blowing and demonstrations of the properties of liquid air. He impressed his audience by taking liquid air in his mouth and blowing out a cloud of frozen vapour, and he sent them away happy with presents of little glass vases or coloured glass rings which he had shown them in the making. In these popular lectures, also, he used a little engine made by his father to show that the boiling liquid air in a tube, if connected with the engine, would make it go as well as the steam from boiling water.

To Franklin, literary composition of any sort, even the writing up of his research work for publication, was never an easy matter, but he laboured at it conscientiously and would sometimes spend a whole day, or more, phrasing and re-phrasing a single page of typescript. He was the author of only one book, "The Nitrogen System of Compounds," in which practically the whole research work of his life is embodied. The writing of this monograph he undertook with no feeling of pleasure, but only as a duty. The manuscript was begun about 1923—4, was rewritten at least half a dozen times and was sent in for publication in 1934. One is not surprised to learn that by that time the work had become a veritable bugbear to him.

During the Great War, Franklin served, in California, as a member of the State Council of Defence, of the Committee on Scientific Research, of the Committee on Occupational Selection, and of the Committee on Inventions. In Washington he was a member of the Advisory Board of the Bureau of Mines, of the Advisory Board of the American University Experiment Station, and of the Advisory Board of the Chemical Warfare Service. He was also physical chemist in the Bureau of Standards and consulting chemist to the Nitrate Division of the Bureau of Ordnance of the Navy, and in all these positions his knowledge, experience and judgment were of great value.

That the great services which Franklin performed to American chemistry were appreciated by the scientific and academic world is shown by the honours of which he was made the recipient. North-western University, Western Reserve University and Wittenberg University conferred honorary degrees upon him; and he was elected a member of the National Academy of Science, of the American Philosophical Society and of the American Academy of Arts and Sciences. In 1910 and in 1914 he was Chairman of the California Section of the American Chemical Society, and in 1923, American chemists conferred on him the highest honour which it was in their power to bestow by electing him President of the American Chemical Society. In 1925 the New York Section of the Society

awarded him the Nichols Medal, and a similar honour was conferred on him by the Chicago Section when they awarded him their Willard Gibbs Medal in 1931. English chemists showed their appreciation of the value of Franklin's contributions to chemistry by electing him an Honorary Fellow of the Chemical Society in 1933.

Apart from his work, Franklin's chief interests were in outdoor life. A child of Nature, he rejoiced in her beauty and her grandeur, and he would lift up his voice to heaven in shouts of joy as he gazed on the great Pacific Ocean or on the impressive beauty of the California scenery. "If you like this, stand up and yell," he would say to his companions as he drove in his car by the side of the Pacific Ocean; and for Franklin the appeal of Nature never weakened. In his younger days, he relates, he was especially fond of mountain climbing, camping, camp cooking, fishing, hunting, travelling and handling pack trains; and in his later years, of driving automobiles. His regret was that he was too old when aeroplane flying became possible; otherwise, flying would have been included in his hobbies.

For many years, a part of almost every summer was spent among the mountains of Colorado and California, and he climbed—in some cases more than once—all the best-known and highest mountains of the West, including Pike's Peak in Colorado, the beautiful Mount Shasta in California, and Mount Rainier in Washington. The certificate of the Sierra Club that he had climbed five or more mountains over 14,000 feet high, was one of his proudest possessions. One can therefore understand that it was with emotion and a feeling of wistful regret that in 1929, on his return journey from South Africa, he viewed at a distance of only thirty or forty miles the majestic Kilimanjaro with its summit rising 19,000 feet into the clear air. It may, perhaps, be mentioned here that the invitation sent to him by the Council of the British Association to visit South Africa in 1929 was one of the marks of appreciation which Franklin valued most.

Franklin's love of an active outdoor life made him hate the idea of growing old, and in his later years he fought a determined rear-guard action with age. His last defiant challenge to old age was offered in the autumn of 1936 when he made, unaccompanied, at the age of 74, a thirteen thousand mile motor car tour across the States from west to east and from north to south, lecturing before many of the local sections of the American Chemical Society. A letter, written to me on January 26th, 1937, and describing his great tour, ended with these sentences: "I left home on the first of September and got back home a few days before Christmas. A few days later I went to bed with a nasty cold from which I have not yet fully recovered. You have not lived long enough yet but some of these days you will find that this getting old is hell." From the torments of this hell he, fortunately, did not have to suffer long, for, after a brief illness due to an attack of coronary thrombosis, he passed peacefully to his rest on February 13th, 1937. Of the closing of a long life full of joyous achievement and goodwill, surely we may gratefully say:

"Nothing is here for tears, nothing to wail
Or knock the breast; no weakness, no contempt,
Dispraise, or blame; nothing but well and fair."

Chemists will remember Edward Franklin for his many valuable contributions to their science, but his friends will always think of him as a great human being. A man of simple heart and with a winning smile, he was modest even to the point of self-depreciation. Sincere and honest, warm-hearted and full of sympathetic understanding, he possessed a genius for friendship. Loving all, he was beloved by all, and converse with him was always a pleasure and frequently an inspiration. He was interested in the activities of life, and his joy was to exchange experiences and to get new impressions; but he took little part in the discussion of abstract views—political, philosophical or religious. In politics he was tolerant and non-partisan; in religion agnostic.

It has already been remarked that Franklin's scientific development was long delayed and that he did not enter on his period of active research until he was thirty-five years of age. This fact is really not to be wondered at when one recalls that in Franklin's undergraduate days chemical research was carried out at only a few of the universities of America, and not at all at the University of Kansas. There existed for Franklin, therefore, none of

that guidance in research which is available to the young graduate of the present day and none of the stimulus which comes from association with those who are engaged in the work of original investigation. Viewed in this light, the achievements of Franklin in research are all the more remarkable. The stimulus to research came from one of his students, as is related by Franklin himself. "In the autumn of 1896," wrote Franklin, "Hamilton P. Cady, then an undergraduate and now Professor of Chemistry at the University of Kansas, was working at the regulation course in quantitative analysis. Observing after a time that the young man was becoming bored with his task, the writer, at that time giving instruction in analytical chemistry, proposed to him that he prepare several of the cobaltammine salts and confirm the composition of one or two of them by analysis. Some days later, with a beautifully crystallised specimen of one of these interesting salts in his hand, Cady stated that the ammonia in these and other salts containing ammonia must function in a manner very similar to that of water in salts with water of crystallisation. He suggested furthermore that liquid ammonia would probably be found to resemble water in its physical and chemical properties. As a direct consequence of Cady's suggestion has followed all the work done in this country on liquid ammonia."

Although the greater part of Franklin's research work was of a purely chemical character, his earliest researches, as well as some of his later, were physico-chemical, and we may therefore begin with a brief survey of them.

In ignorance of the work of earlier investigators, the solubility in liquid ammonia of some five hundred different substances, elements, inorganic salts and organic compounds, was investigated, and the solvent power of liquid ammonia was shown to be second only to that of water. The alkali metals dissolve in liquid ammonia to form blue solutions from which the metals may be recovered unchanged, although, in course of time, reaction takes place with production of metal amide and hydrogen. This reaction may extend over weeks or months, but was found to be very greatly accelerated by finely divided platinum and ferric oxide. The alkaline earth metals also dissolve in liquid ammonia, and on evaporation of the solutions, solid ammoniates, such as Ca_6NH_3 , are obtained. The solvent power of liquid ammonia for salts differs, in some cases, very markedly from that of water. Most nitrites and nitrates are soluble in liquid ammonia, as are also many metal cyanides and iodides, including the iodides of mercury and silver. Fluorides and chlorides are the least soluble of the halides. Many organic compounds, also, are soluble in liquid ammonia, but sulphites, sulphates and carbonates, even of the alkali metals, are insoluble or sparingly soluble.

The differences in the solubility relations of inorganic salts in liquid ammonia and in water are well illustrated by the fact that, when a solution of silver bromide in liquid ammonia is added to a solution of barium nitrate, a precipitate of the octa-ammoniate of barium bromide, $\text{BaBr}_2 \cdot 8\text{NH}_3$, is formed. Other metathetic reactions also were found to take place in liquid ammonia just as in aqueous solutions.

Liquid ammonia, like water, was found to be an ionising medium in which not only all soluble inorganic salts but also a great variety of organic substances form conducting solutions. Determinations of the electrical conductance of solutions of a large number of substances were carried out, but only some of the more important results can be referred to here. The successful and accurate determination of the electrical conductance of such solutions, it may be emphasised, was made possible only by Franklin's ingenuity in designing and his skill in constructing the complicated apparatus which the investigation necessitated.

The equivalent conductivity of dilute and moderately dilute solutions of salts, such as potassium iodide, potassium nitrate and sodium nitrate, in liquid ammonia at -33° was found to be greater than the equivalent conductivity in water at the ordinary temperature; but the dilution at which the maximum value of the equivalent conductivity was obtained was much greater in liquid ammonia than in water. The Arrhenius coefficient, moreover, or the degree of ionisation according to the classical theory, was much less in liquid ammonia than in water, a result which was in harmony with the ebullioscopic determinations of Franklin and Kraus. This behaviour, also, was to be expected from the relatively low dielectric constant of liquid ammonia, as determined by Goodwin and Thompson; and

the conclusion was therefore drawn that the high conductivity of liquid ammonia solutions is due to the low viscosity of the solvent and the relatively great mobility of the ions. This conclusion found support in the determinations of the ion velocities which were carried out in a most masterly manner by Franklin and Cady, who, using the moving boundary method, found that the mobilities of potassium ion, silver ion, nitrate ion, etc., in liquid ammonia at -33° are from two-and-a-half to three times as great as in water at 18° . In connection with these determinations it may be noted that Franklin and Cady were probably the first to make use of a boundary which depends not on the presence of a coloured ion but on a difference of refractive index of two solutions, although in the publication of the method they were anticipated by B. D. Steele.

That the high mobility of ions in liquid ammonia is associated with a low viscosity of the solvent was proved by the experiments carried out at a later date in Franklin's laboratory at Stanford University, which showed that the viscosity coefficient of liquid ammonia at -33.4° is equal to 0.00254, while the value for water at 18° is 0.01054. It may, however, be noted that the Walden rule, according to which the product $\eta\Lambda_\infty$ is nearly constant for a salt dissolved in a number of different solvents, does not hold in the case of liquid ammonia solutions.

The analogy which had been found to exist between liquid ammonia and water as solvents and ionising media suggested to Franklin that methylamine might be analogous to methyl alcohol in its properties. On testing this suggestion, it was found that, just as methyl alcohol is a better solvent for organic compounds than water is, so methylamine is a better solvent than liquid ammonia, and may perhaps be better even than methyl alcohol. In the case of inorganic salts, however, methylamine is inferior as solvent to liquid ammonia, and therefore greatly inferior to water, and may be ranked with methyl alcohol. In its power of combining with both inorganic and organic compounds, however, it probably exceeds even the most reactive of the other solvents, ammonia.

Methylamine was found also to be a good electrolytic solvent, and on determining the change of equivalent conductivity with dilution of a methylamine solution of silver nitrate a very different behaviour was found from that met with in the case of aqueous solutions. Starting with concentrated solutions of silver nitrate in methylamine, the equivalent conductivity at first increases with dilution, reaches a maximum, then falls to a minimum and thereafter increases again. Other workers, it is true, had obtained equivalent conductivity-dilution curves which rose to a maximum and then fell, but the existence of a minimum followed by a rise in the curve had not hitherto been realised.

In their determinations of the electrical conductance of inorganic salts in liquid ammonia, Franklin and Kraus had shown that the equivalent conductivity of potassium iodide and potassium nitrate increases with dilution, at first rapidly, then more slowly and then again rapidly to its final maximum, but no decrease of equivalent conductivity with dilution was observed. The behaviour of methylamine solutions of silver nitrate, however, led Franklin to determine the equivalent conductivity of a larger range of substances in liquid ammonia, and it was found that solutions of potassium amide, copper nitrate, silver cyanide and certain other salts in liquid ammonia give equivalent conductivity-dilution curves similar to that of silver nitrate in methylamine. Similar types of curve were also found by Franklin in the case of solutions of potassium iodide in liquid sulphur dioxide at different temperatures; and in the case of these solutions Franklin was able to show that after passing through a minimum value the equivalent conductivity increases steadily towards a limiting value at infinite dilution.

The abnormal behaviour of such non-aqueous solutions compared with the behaviour of aqueous solutions depends probably on a number of factors and has been the subject of much study by a number of workers, of whom one may mention C. A. Kraus, one of Franklin's earliest collaborators.

The investigation of the solvent and ionising properties of other amines showed that the simpler primary and secondary amines at room temperature are fair solvents for many salts, but the secondary amines are poorer solvents for inorganic salts than are primary amines. They are also less effective ionising solvents.

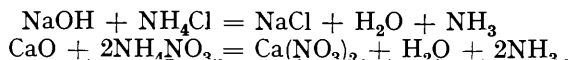
Besides a few measurements of the electromotive force of concentration cells in liquid

ammonia, from which it appeared that the E.M.F., as in the case of aqueous solutions, is approximately proportional to the logarithm of the ratio of concentrations, determinations of the specific rotation of a number of compounds in liquid ammonia were carried out under Franklin's direction. Although it was found that optical activity is shown by most of the compounds which are active in aqueous solution, the values of the specific rotation in the two solvents may be very different. This fact was most strikingly illustrated by the behaviour of fructose, which shows no measurable activity either in liquid ammonia, in methylamine or in ethylamine.

In concluding this brief survey of Franklin's physico-chemical researches one may refer to the determinations of the physical properties of liquid ammonia—the boiling point under atmospheric pressure, the heat of vaporisation, the vapour pressure of liquid ammonia at different temperatures down to the triple point of solid, liquid and vapour at -77.9° and a pressure of 45.5 mm.—and to the determination of the constants for the molecular depression of the freezing point and the molecular elevation of the boiling point, both of which were found to be abnormally low. These determinations, some of which were carried out at a time when no similar work had been done in America, are a tribute to the ingenuity and manipulative skill of Franklin and of the collaborators whom he trained. For accuracy their determinations have remained unsurpassed down to the present day.

The striking parallelism between the general physico-chemical properties of liquid ammonia and water, which had been demonstrated by the earlier investigations of Franklin and Cady and Franklin and Kraus, led to a consideration of the chemical behaviour of derivatives of water and of derivatives of ammonia.

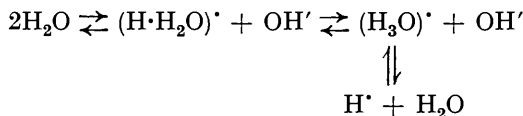
Solutions of ammonium salts in liquid ammonia were found by Franklin and his co-workers to act on sodium, lithium and other metals with formation of salts of the metals and evolution of hydrogen, and they reacted also with insoluble metal oxides and hydroxides in accordance with the equations :



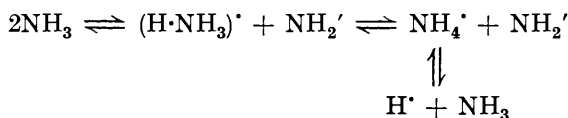
just as the aqueous solutions of hydrochloric or nitric acid act on a base insoluble in water. Solutions of ammonium salts in liquid ammonia, also, gave colour changes with phenolphthalein, carmine, safranin, etc., similar to those given by aqueous solutions of acids. It appeared, therefore, from these experiments that the ammonium salts in liquid ammonia solution act as acids.

From their early experiments, which in part confirmed and in part greatly extended the much earlier work of Divers, Franklin and his collaborators were led to an exhaustive examination of the parallelism between the chemical behaviour of derivatives of ammonia dissolved in liquid ammonia and the behaviour of derivatives of water, aquo-compounds as Franklin called them, in aqueous solution. The investigation of the behaviour of the former class of compounds, the ammonio-compounds, to use Franklin's nomenclature, constitutes the chief and most characteristic contribution of Franklin to chemistry.

Just as it is assumed that water is ionised in accordance with the equations



so liquid ammonia may be regarded as being ionised in accordance with the equations



(Parenthetically, it may be noted that the idea that the ammonium ion in liquid ammonia is an ammoniated hydrogen ion and can act, to use the language of modern theory, as a

proton donor, led Franklin to suggest, by analogy, the presence in water of the oxonium or hydrated hydrogen ion, long before the same suggestion was made by Fajans.)

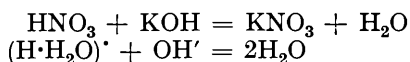
In accordance with the above schemes, the ions NH_4^+ and NH_2^- in liquid ammonia correspond with the ions H_3O^+ and OH^- in water; and substances, therefore, which dissolve in liquid ammonia to give the ammonium ion may be called ammono-acids, and those substances which give rise to the NH_2^- -ion may be called ammono-alkalis or ammono-bases. The ammono-acids, moreover, react with the ammono-bases in liquid ammonia solution in a manner analogous to the familiar reaction between oxygen acids and bases in aqueous solution.

When one regards the matter from the purely formal chemical point of view, it will be seen that a basic hydroxide may be considered as derived from water by the replacement of one atom of hydrogen by metal (*e.g.*, KOH), and a basic oxide by the replacement of both atoms of hydrogen by metal (*e.g.*, CaO). An oxygen acid, on the other hand, may be regarded as formed by the replacement of one hydrogen atom by an electronegative element or group (*e.g.*, $\text{HO}\cdot\text{NO}_2$) and an acid anhydride by the replacement of both hydrogen atoms (*e.g.*, $\text{NO}_2\cdot\text{O}\cdot\text{NO}_2$). Finally, an oxygen salt is obtained when one hydrogen atom of water is replaced by a metal and the other by an electronegative element or group (*e.g.*, $\text{K}\cdot\text{O}\cdot\text{NO}_2$). If, now, one accepts the parallelism between liquid ammonia and water, one may then say that the metallic amides and imides (*e.g.*, LiNH_2 , Li_2NH), which are related to ammonia in the same way as the metallic hydroxides are related to water, may be regarded as bases of the nitrogen system (ammono-bases), while the metallic nitrides are basic nitrides corresponding to the basic oxides of the oxygen system of compounds. On the other hand, the amides of the electronegative elements or groups and also their partly deammonated * products are acids of the nitrogen system (ammono-acids), while the final deammonated products, the acid nitrides, are the nitrogen analogues of the acid anhydrides. Thus, guanidine, $(\text{NH}_2)_2\text{C}\cdot\text{NH}$, the analogue of carbonic acid, $(\text{HO})_2\text{C}\cdot\text{O}$, and also cyanamide, $\text{NH}_2\cdot\text{C}\cdot\text{N}$, and dicyanimide, $\text{HN}(\text{CN})_2$, are ammono-acids, and carbonic nitride, C_3N_4 , is an acid anammonide, analogous to carbon dioxide or carbonic anhydride. In a like manner, potassium acetamide, $\text{CH}_3\cdot\text{C}(\cdot\text{NH})\cdot\text{NHK}$, corresponds to potassium acetate, and potassium azide, KNN_3 , to potassium nitrate.

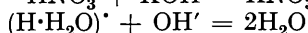
That these analogies are not merely formal but correspond to something real has, as we shall see, been amply established by the study of the chemical behaviour of the nitrogen or ammono-compounds. Moreover, the validity of the classification of the metal derivatives of the ammono-acids as true salts receives support from the fact that the alkali metal salts of an ammono-acid, in liquid ammonia solution, are much better conductors of the electric current than the acid itself, just as in aqueous solution the alkali salts of acids such as acetic acid are better conductors than the acids.

In order that we may realise the many analogies which exist between the behaviour of the aquo-compounds, or compounds of the water type, when dissolved in water, and the ammono-compounds, or compounds of the ammonia type, when dissolved in liquid ammonia, some at least of the many reactions studied by Franklin and his pupils will now be considered.

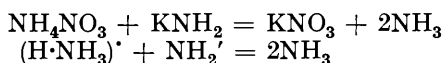
According to the Franklin classification, the metal amides and imides are ammono-bases and the analogues of the metal hydroxides. In liquid ammonia solution, therefore, they should behave analogously to metal hydroxides in aqueous solution. Moreover, ammonium salts in liquid ammonia solution are, as has been pointed out, the analogues of the strong acids in aqueous solution. Consequently, just as, in aqueous solution, the base potassium hydroxide reacts with an acid to form a salt and water, *e.g.*,



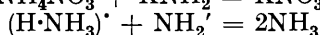
or



so, in liquid ammonia solution, potassium amide reacts with ammonium nitrate to form potassium nitrate and ammonia :



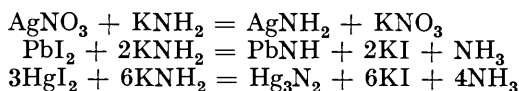
or



* The term "deammonation" is used as the analogue of "dehydration."

Other reactions of the same character are represented by the equations: $\text{NH}_4\text{NO}_3 + \text{AgNH}_2 = \text{AgNO}_3 + 2\text{NH}_3$; $2\text{NH}_4\text{I} + \text{PbNH} = \text{PbI}_2 + 3\text{NH}_3$; $3\text{NH}_4\text{I} + \text{BiN} = \text{BiI}_3 + 4\text{NH}_3$. The last reaction is, of course, analogous to the reaction between an acid and a metal oxide. The neutralisation of an ammono-acid by an ammono-base is also illustrated by the reaction, in liquid ammonia, between potassium amide and cyanamide, which is the nitrogen analogue of carbonic acid, to form potassium cyanamide and ammonia: $2\text{KNH}_2 + \text{H}_2\text{CN}_2 = \text{K}_2\text{CN}_2 + 2\text{NH}_3$. This reaction is analogous to that between potassium hydroxide and carbonic acid in aqueous solution.

Since many metallic hydroxides or oxides are precipitated from aqueous solution by the action of potassium or sodium hydroxide on salts of the metals, one was led to expect that metallic amides, imides and nitrides should be precipitated from liquid ammonia solution by the action of potassium amide. Experiment showed that this expectation was entirely justified, reaction taking place as indicated by the following typical equations,



These reactions are a very striking confirmation of the parallelism between the behaviour of the aquo- and the ammono-bases, and the parallelism extends also to the amphoteric properties of certain metal amides. Just as zinc hydroxide dissolves in an aqueous solution of potassium hydroxide to form potassium zincate, so potassium amide in liquid ammonia solution was found to act on zinc amide with the production of a crystalline compound which must be regarded as an ammonozincate of potassium, formed in accordance with the equation, $\text{Zn}(\text{NH}_2)_2 + 2\text{KNH}_2 = \text{Zn}(\text{NHK})_2 + 2\text{NH}_3$. The ammonozincate was obtained in a beautifully crystalline form containing "ammonia of crystallisation," and had the composition $\text{Zn}(\text{NHK})_2, 2\text{NH}_3$. Investigation showed that a large number of other amides, including those of such strongly positive metals as magnesium, barium, strontium, calcium and even sodium and lithium, react with potassium amide to form compounds which must be looked upon as salts in which these metals play a part closely similar to that which zinc plays in potassium zincate, or which lead and aluminium play in the compounds formed by the action of aqueous potassium hydroxide on the hydroxides of these metals.

In pursuing the investigation of the analogy between water and liquid ammonia, one is led to ask whether, in the case of liquid ammonia, reactions can take place analogous to the hydrolysis of salts by water, with production of basic salts. To this question Franklin obtained by experiment an affirmative answer. Just as aquobasic salts may be produced by the hydrolysis of salts by water, so the analogous ammonobasic salts can be formed by the ammonolysis of salts by ammonia. Thus, lead iodide is ammonolysed by liquid ammonia to form the ammonobasic lead iodide, $\text{PbN}\cdot\text{PbI}_2, 2\text{NH}_3$ or $\text{Pb}_3\text{N}_2, \text{PbI}_2, 4\text{NH}_3$; and many other salts were found to behave in a similar manner. On the strength of these investigations, Franklin discarded the view put forward by Rammelsberg and supported in more recent times by Pesci and by K. A. Hofmann, that all the mercury ammonia compounds are to be regarded as derivatives of so-called dimercuriammonium hydroxide, Hg_2NOH . According to this view, the so-called fusible and infusible white precipitates are regarded as double salts of dimercuriammonium chloride and ammonium chloride and represented by the formulæ $\text{Hg}_2\text{NCl}, 3\text{NH}_4\text{Cl}$ and $\text{Hg}_2\text{NCl}, \text{NH}_4\text{Cl}$. These views Franklin considered to be erroneous and without adequate foundation in experimental fact; and he advocated a modified and extended form of the amide theory put forward by Kane in 1839. In agreement with Kane's views, Franklin was able to show that all the mercury ammonia compounds can be regarded as (1) normal mercuric salts with "ammonia of crystallisation," (2) ammonobasic mercuric salts, (3) mixed aquo-ammono-basic salts.

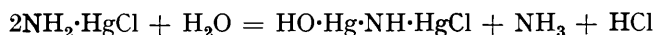
Just as water forms with salts compounds known as salt hydrates or salts with water of crystallisation, so ammonia can form analogous compounds, salt ammoniates or salts with ammonia of crystallisation, in which the combination of the ammonia with the salts is due, as in the case of water, to co-ordination. Quite a number of ammoniated mercuric salts are known, *e.g.*, $\text{HgCl}_2, 2\text{NH}_3$; $\text{HgI}_2, 2\text{NH}_3$; etc., which are formed by the action of ammonia on the mercuric salts. These salts, like the salt hydrates, show a certain vapour

pressure; and the ammoniated mercuric iodide shows the phenomenon of efflorescence when exposed to the air, the colourless ammoniated crystals passing, through loss of ammonia, into the scarlet mercuric iodide, HgI_2 .

Moreover, when mercuric chloride and liquid ammonia are brought together, part of the salt undergoes ammonolysis in accordance with the equation, $\text{HgCl}_2 + \text{NH}_3 = \text{NH}_2\text{HgCl} + \text{HCl}$, to form an ammonobasic mercuric chloride. This ammonobasic salt is identical with the long-known infusible white precipitate, the analogy between which and an ordinary basic salt was first pointed out by Kane.

Just as the hydrolysis of a salt is prevented or reduced by the addition of free acid, so the ammonolysis of mercuric chloride can be prevented by the presence of ammonium chloride, which, as we have seen, functions as an acid. Thus, when ammonia is added to an aqueous solution* of mercuric chloride, a precipitate of ammoniated mercuric chloride, $\text{HgCl}_2 \cdot 2\text{NH}_3$, identical with the compound known as fusible white precipitate, is formed, provided ammonium chloride is present in sufficient concentration to prevent ammonolysis. If, however, the concentration of ammonium chloride is reduced, ammonolysis of the mercuric salt takes place and the ammoniated mercuric chloride is converted into the ammonobasic salt, $\text{NH}_2 \cdot \text{HgCl}$.

When this sparingly soluble ammonobasic mercuric chloride is subjected to the prolonged action of water, it is converted into a substance known as the chloride of Millon's base, a substance which may be regarded as a mixed aquobasic ammonobasic salt, formed in accordance with the equation :



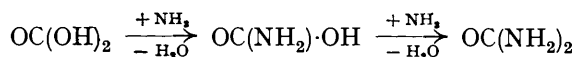
This compound is converted by digestion with ammonium chloride solution into the ammoniated mercuric chloride, just as an aquobasic salt is converted into the normal salt by digestion with acid.

The success which attended the classification of inorganic nitrogen compounds as ammono-compounds bearing the same relation to ammonia as the oxygen compounds bear to water, led Franklin to extend his classification to the nitrogen compounds of organic chemistry, and to seek experimental support for it in the preparation and properties of a number of different groups of compounds. Just as ordinary carbonic acid (or aquo-carbonic acid) and carbon dioxide may be regarded as derived from orthocarbonic acid by a process of dehydration, so, argued Franklin, guanidine, $\text{HN}=\text{C}(\text{NH}_2)_2$, biguanidine, cyanamide, dicyanimide, dicyanodiamide, melamine, melam, melon, and hydromelonic acid constitute a group of compounds which may be looked upon as ammono-carbonic acids derived by a process of de-ammonation from $\text{C}(\text{NH}_2)_4$, the hypothetical analogue of orthocarbonic acid. The last member of the group would be carbonic nitride, C_3N_2 , the analogue of carbon dioxide. Experiment showed that Franklin's surmise was correct, for although guanidine and biguanidine, in aqueous solution, show no acid properties, they and all the other compounds of the above series behave, in liquid ammonia solution, as acids—some weak, some strong—and react in liquid ammonia solution with metal amides to form salts. Thus, when guanidine nitrate in liquid ammonia solution is acted on by potassium amide, dipotassium guanidine is formed: $\text{HN}:\text{C}(\text{NH}_2)_2, \text{HNO}_3 + 3\text{KNH}_2 = \text{HN}:\text{C}(\text{NHK})_2 + \text{KNO}_3 + 3\text{NH}_3$. Moreover, if guanidine, for example, is an acid in liquid ammonia solution, then its alkyl and aryl derivatives must be regarded as esters and therefore should be capable of undergoing ammonolysis. This was, in fact, found to be the case, reaction taking place according to the equation: $\text{C}_6\text{H}_5 \cdot \text{N}:\text{C}(\text{NH} \cdot \text{C}_6\text{H}_5)_2 + 3\text{NH}_3 = \text{HN}:\text{C}(\text{NH}_2)_2 + 3\text{C}_6\text{H}_5 \cdot \text{NH}_2$. Similarly, salts and esters of cyanamide, dicyandiamide, dicyanimide and other compounds of the series of ammono-carbonic acids have been prepared.

Besides the ammono-carbonic acids derived from the hypothetical $\text{C}(\text{NH}_2)_4$, Franklin pointed out that the oxygen-nitrogen compounds, cyanic acid, carbamic acid and urea, are, on the basis of his classification, to be regarded as aquo-ammono-carbonic acids,

* Since ammonobasic mercuric chloride, unlike most ammonobasic salts, is not readily decomposed by water, it can be formed by the action of ammonia on mercuric chloride even in aqueous solution.

the last two, for example, being formed by the partial ammonolysis of aquo-carbonic acid, as indicated by the scheme :



Although urea, for example, is neutral or very slightly alkaline in aqueous solution, it reacts in liquid ammonia with the alkali metals and magnesium with the evolution of hydrogen, and with potassium amide to form mono- and di-potassium salts. Esters of urea, *e.g.*, ethylurea, diphenylurea, etc., are to be regarded as esters of an aquo-ammono-carbonic acid, which undergo ammonolysis to urea and an amine.

Further, one may regard allophanic acid ($\text{HO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$), biuret ($\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$), guanylurea [$\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$], cyanurea ($\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CN}$), etc., as aquo-ammono-dicarbonic acids; and the properties of these compounds are in harmony with this view.

The analogies which were thus, for the first time, emphasised and logically pursued by Franklin inspired a large amount of experimental investigation and enabled a large body of organic nitrogen compounds to be regarded, from one widely-embracing point of view, as the analogues of alcohols, ethers, esters, aldehydes, ketones, carboxylic acids, etc., derived from ammonia in the same way as these oxygen compounds may be regarded as being derived from water. Thus, methylamine, ethylamine, etc., are to be regarded as ammono-alcohols, and the analogues of methyl and ethyl alcohol, etc.; while trimethylamine is to be regarded as the ammonia analogue of dimethyl ether, and therefore is to be regarded as an ammono-ether. Further, it was found by Franklin and his collaborators that, when acetophenone is heated in liquid ammonia solution, ammonolysis takes place with production of an ammono-ketone, acetophenoneimine, according to the equation, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_3 + \text{NH}_3 = \text{C}_6\text{H}_5\cdot\text{C}(\text{NH})\cdot\text{CH}_3 + \text{H}_2\text{O}$; and a similar reaction takes place in the case of benzophenone. Moreover, when a liquid ammonia solution of ammonium acetate and ammonium chloride is heated, ammonolysis of aquo-acetic acid takes place with formation of ammono-acetic acid, or acetamidine, $\text{CH}_3\cdot\text{C}(\text{NH})\cdot\text{NH}_2$, the nitrogen analogue of acetic acid. From this compound one may expect formation of an ammono-ester, *e.g.*, $\text{CH}_3\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CH}_3$, by the action of methylamine on acetamidine, just as methyl alcohol yields an ester with acetic acid. Experiment fulfilled one's expectation. The formation and chemical behaviour of a large number of nitrogen analogues of organic oxygen compounds were studied by Franklin and his pupils, and the analogies between the two classes of compounds were found to be not merely formal but to extend also to the chemical behaviour of the compounds.

It will be clear that, if there is validity in the analogy between liquid ammonia and water and between the nitrogen compounds and the oxygen compounds, as experiment has, in fact, shown to be the case, then it is to be expected that corresponding to the processes of oxidation one will also find processes of nitridation; and just as oxidation may involve not merely the combining with oxygen but the loss of electrons, so nitridation also may involve loss of electrons. For the terms oxidation and nitridation used in the wider sense, Franklin suggested the term augmentation.

Nitridation or augmentation may be carried out in liquid ammonia solution by various substances, such as hydrazoic acid, iodamine and certain heavy metal amides, imides and nitrides, by reactions which closely resemble those taking place when nitric acid, hypiodous acid and the heavy metal hydroxides and oxides, the oxygen analogues of the above compounds, act as oxidising agents. Accepting the view first stated by Turrentine, that hydrazoic acid may be regarded as ammono-nitric acid, nitridation or augmentation by hydrazoic acid, *e.g.*, formation of guanidine by heating methylamine with an excess of ammonium azide in liquid ammonia solution, can be considered as analogous to the process of oxidation by nitric acid.

There is no need further to multiply examples of or to discuss in detail the numerous nitrogen compounds which Franklin and his pupils studied and which he showed could be regarded as the nitrogen analogues of the different groups of oxygen compounds met with in organic chemistry. It was an imposing edifice which he constructed under the general

idea of the analogy between liquid ammonia and water; and the classification of nitrogen compounds as belonging to the ammonia type in the same way as oxygen compounds may be considered to belong to the water type, was a stimulus and guide to investigation.

As will have been gathered from the preceding discussion, Franklin was essentially an experimentalist; and the fact that he worked in close association with only a comparatively small number of younger collaborators was due to his playing not only a directive but also a very active part in the experimental work of his research students. The scientific investigations in connection with which Franklin's name will always be remembered required great manipulative expertness, and the success of these researches was not only due in large measure to his own consummate experimental skill, but was a testimony to the careful training in experimental technique which he gave to his pupils. That his name appears at the head of only about half of the eighty-eight communications which came from his laboratory is an indication of his generous desire to detract in no way, through the prestige of his name, from the credit due to his younger collaborators.

Franklin's research work was strangely peculiar to himself and owed little or nothing to the influence of others; and the ideas on the basis of which his work was developed have given an extraordinary unity to his own investigations and a sure foundation to the work of others. He was a man whose memory we delight to honour.
