

*The Haber Memorial Lecture.*

DELIVERED BEFORE THE CHEMICAL SOCIETY ON APRIL 29TH, 1937.

By J. E. COATES.

FRITZ HABER was born on December 9th, 1868, in Breslau, the eldest son of Siegfried Haber, a prosperous chemical and dye merchant and an alderman of the town in which his family had been prominent in business and public affairs for upwards of a century. He received the normal classical education of the Gymnasium. During his later school years, however, influenced perhaps by his father's business, he developed without any help a lively interest in chemistry, which he eagerly practised at home. From his early boyhood he was always the leader and originator in the circle of his family and friends and at the same time a great favourite through his kindness of heart and the pleasure he took in helping others. With the development of his forceful enterprising nature he soon became the dominant figure in his home.

He studied first in the University of Berlin, then at Heidelberg, where under the aged Bunsen he learnt the craft of analysis but little chemistry. At last he settled down at the Technische Hochschule, Charlottenburg. Here he discovered the fascinating new world of organic chemistry and carried out under Liebermann his first research—on derivatives of piperonal and of indigo.

It was the wish of Siegfried Haber that his son should in due course carry on the family business, and accordingly on graduation he entered chemical industry in order to gain technical experience. The short periods he spent in three different factories brought him no satisfaction and after a few months he abandoned this plan and devoted a semester to the study of chemical technology under Lunge at Zürich. He then entered his father's business, but in six months both father and son had to recognise the complete failure of the experiment. The sharp difference in their temperaments made collaboration impossible. To the sedate and prudent merchant his son's lively adventurous spirit was intolerable and seemed a danger to the business. It was well that the break came so soon. Under the urge towards greater freedom, and influenced probably by the success of his friend Abegg and by the dullness of his early experiences of industry, Haber had felt a growing attraction towards academic life, and when he became free to choose his own career his first step was to resume organic chemical research under Knorr in the University of Jena, where he carried out an investigation on the constitution of diacetosuccinic ester. He had however not yet found himself. Interested as he undoubtedly was in organic chemistry, the routine operations and the working out of the constitution of compounds by more or less established methods left him unsatisfied and rather impatient. He used to delight in telling in his inimitable way a long story of how chance took him to Karlsruhe and launched him on his career. In Jena he had a friend whose suffering during a long and painful illness he helped to mitigate by every means in his power until death came. At the funeral his friend's brother, learning of his desire to leave Jena, suggested the Technische Hochschule in Karlsruhe, where, he said, he had influential relations who would, as a mark of gratitude, recommend Haber most warmly. Taking up the suggestion he found on visiting Karlsruhe that the relation was the porter of the chemistry department. However this just sufficed to gain for him an interview with the Professor, who received him coldly but in the end offered him a junior appointment. How much of this was true and how much invention no one ever knew. However that may be, Haber at the age of twenty-five became assistant to Professor Bunte in the department of Chemical and Fuel Technology. With duties to perform and ample opportunities for research, he had gained the start he desired, and moreover he counted himself fortunate to be associated with an institution that stood in such close relation with Industry. At once he threw himself into his teaching and research with tremendous zest, and was very happy in his work. At Bunte's suggestion he attacked the problem of the thermal decomposition of hydrocarbons. The subject had been investigated by others, but most extensively by Berthelot in 1863—69. On the basis of experiments with  $C_1$  and  $C_2$  hydrocarbons only, Berthelot had put forward a *general* theory of hydrocarbon pyrolysis. Haber sharply criticised Berthelot's conclusions as arbitrary,



*G<sup>r</sup> Fritz Haber*

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confused, and insufficiently supported by experiment. His criticism proved to be justified. The  $C_1$  and  $C_2$  hydrocarbons being exceptional in that they cannot decompose into other hydrocarbons, except by splitting off hydrogen, Haber adopted *n*-hexane,  $C_6H_{14}$ , for exhaustive study as a typical higher paraffin. This choice was determined not only by experimental considerations but also because of its relation to benzene (current theories of flame luminosity) and its importance in oil-gas manufacture. To Haber, the orthodox organic chemist, this type of work was quite new. In order, as far as possible, to fix the primary decomposition products, the hexane was heated for a few seconds at  $600-800^\circ$ , and the products rapidly cooled, a flow method being employed. Unlike previous investigators he determined *all* the products quantitatively. This necessitated a critical examination of analytical methods, and many improvements were devised. The most general result of this investigation may be expressed in the statement, which became known as *Haber's rule*, that, as regards thermal stability, the C-C link is stronger than the C-H link in aromatic compounds and weaker in aliphatic compounds. The great advance in our knowledge of pyrogenic change since this time has shown that Haber's rule is subject to exceptions. He regarded it however only as a broad generalisation, and as such it remains valid. Whereas benzene split off hydrogen forming diphenyl, paraffins like hexane divided at an end C-C link giving a small paraffin and a large unstable ethylenic molecule which broke down into smaller unsaturated molecules, thus:  $C_6H_{14} \rightarrow CH_4 + C_5H_{10} \rightarrow CH_4 + C_2H_4 + C_3H_6$ . With higher paraffins progressive polymerisation of unsaturated molecules and pyrolysis in this manner gave ultimately tar and coke. Although at  $600-800^\circ$  no carbon and no hydrogen were formed, yet at  $1000^\circ$ , where the gaseous product was almost entirely methane and ethylene, the C-H link weakened and hydrogen appeared. There was no evidence that acetylene played an important part in these changes, as had been claimed by Berthelot and by V. B. Lewes. Hexane gave very little benzene, and it did so, not, as had been previously supposed by splitting off hydrogen and closing the straight chain, but by a secondary reaction, probably the polymerisation of acetylene. Haber's first independent investigation stands out as a classic in the then little-known field of pyrolysis. In it we see already those qualities which distinguished all his work: thoroughness, intolerance of vagueness and superficiality, and penetration to the roots of the problem. Furthermore, this period, which included many studies on technical gas combustion, brought him into close touch with the fuel industry, a new experience which not only had a most stimulating effect upon him but also influenced the subsequent development of his interests.

Haber became privat-dozent in 1896 at the age of 27. Perhaps the most important effect of his first two years' teaching and research was to bring him to the study of physical chemistry, which had formed no part of his previous training. He taught himself. Amongst his colleagues there was only one physical chemist, Hans Luggin, a pupil of Arrhenius, and a very able man. He and Haber became the closest friends, until Luggin's early death in 1899. Their friendship had a very strong influence upon Haber's development, for it gave him what he most needed, the constant exercise and stimulus of discussion. It is significant that their main interests were in thermodynamics and electrochemistry. On Luggin's death Haber wrote a paper on the teaching of thermodynamics in memory of the friend to whom he owed so much.

On attaining the status of privat-dozent, Haber embarked upon his career as an electrochemist, and his first study, on the reduction of nitrobenzene, brought him wide recognition. The organic chemist was still strong in him and it was natural that he should first apply his physico-chemical knowledge in a familiar field. In recent studies on the electrochemical reduction of nitro-compounds by Elbs, Gattermann, and others, a great number of products corresponding to different reduction stages had been obtained, the nature and relative proportions of which were, it appeared, determined by such factors as the acidity or alkalinity of the electrolyte, the density and duration of the current, and the nature of the electrode metal (*e.g.*, zinc was more effective than platinum). Reduction was supposed to be effected by nascent hydrogen, but this conception alone could not explain the great variation in activity of the hydrogen. No general underlying principles had been discovered until 1898 when Haber threw a clear light on this confused field by establishing the fundamental importance of the electrode potential.

In conformity with Nernst's theory that the potential of a gas electrode is determined by

the effective concentration of the gas on, or in, the electrode, Haber recognised in the electrode potential a relative measure of the cathodic or anodic activity of the gas, and in his first paper (1898) on the electrochemical reduction of nitrobenzene in stages by controlled cathode potential he established for the first time the principle that this potential determines the reducing power, a higher potential being equivalent to the use of a more active reducing agent. Earlier investigators had commonly employed a more or less constant current density and hence a gradually increasing cathode potential, which, said Haber, is equivalent to using a series of chemical reducing agents of gradually increasing activity, resulting in the production of an overlapping series of primary reduction products. Haber's plan was, by varying the current during electrolysis, to hold the polarised cathode at a constant potential below the break point of the current density-potential curve, where all the discharged hydrogen is used in reducing the depolariser. In order to begin with low cathode potentials and progressively separate the primary reduction products, he used platinum (sometimes nickel) electrodes with low hydrogen overvoltage. Electrodes with high hydrogen overvoltage like zinc gave at one step far-reaching reduction (in agreement with Haber's views regarding the potential factor). Employing standard methods of measuring and controlling the cathode potential by means of an auxiliary electrode, he introduced at Luggin's suggestion, the useful device of connecting the auxiliary electrode to the cathode through a very thin-walled capillary glass tube in contact with the latter, thus eliminating the potential drop through the main electrolyte.

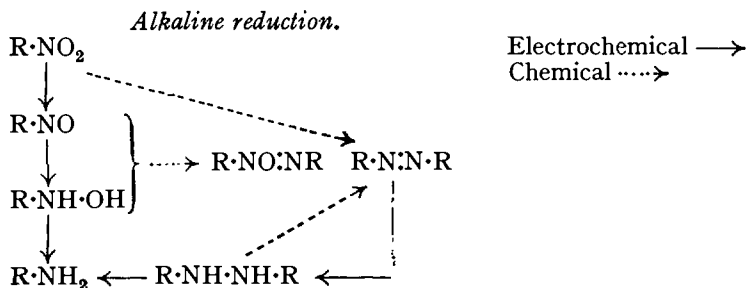
With alkaline alcoholic solutions of nitrobenzene and a platinum cathode at low potential, the main product was *azoxybenzene*,  $R\cdot NO:N\cdot R$ . This however was not, as had previously been supposed, the first reduction stage. In the light of Bamberger's studies on the reduction series nitrobenzene, nitrosobenzene,  $\beta$ -phenylhydroxylamine, Haber was able to prove that the electrochemical as well as chemical reduction followed the direct path  $R\cdot NO_2 \rightarrow R\cdot NO \rightarrow R\cdot NH\cdot OH \rightarrow R\cdot NH_2$ , and that all other products were due to chemical side reactions. Thus the appearance of azoxybenzene as the first product of reduction was due to Bamberger's reaction (very rapid in alkaline but slow in acid solutions) :



which removes  $\beta$ -phenylhydroxylamine from the direct reduction path. Haber proved the presence of the very reactive stages nitrosobenzene and  $\beta$ -phenylhydroxylamine both electrochemically and chemically. Nitrosobenzene was a far more powerful depolariser than nitrobenzene and therefore could only be present in minute concentration. Both nitrosobenzene and  $\beta$ -phenylhydroxylamine could however be detected by fixation as an azo-dye. He succeeded further in preparing  $\beta$ -phenylhydroxylamine in quantity by electrochemical reduction of nitrobenzene in a buffered, weakly alkaline solution at a potential high enough to give practically instantaneous reduction of nitrosobenzene to  $\beta$ -phenylhydroxylamine (and so to avoid formation of azoxybenzene), but not so high as to carry the reduction further. Azobenzene,  $R\cdot N:N\cdot R$ , one of the products of electrochemical reduction of nitrobenzene, had yet to be accounted for. Energetic reduction of azoxybenzene yielded only hydrazobenzene. Haber traced the formation of azobenzene to the following reaction which proceeds rapidly in alkaline alcoholic solution :

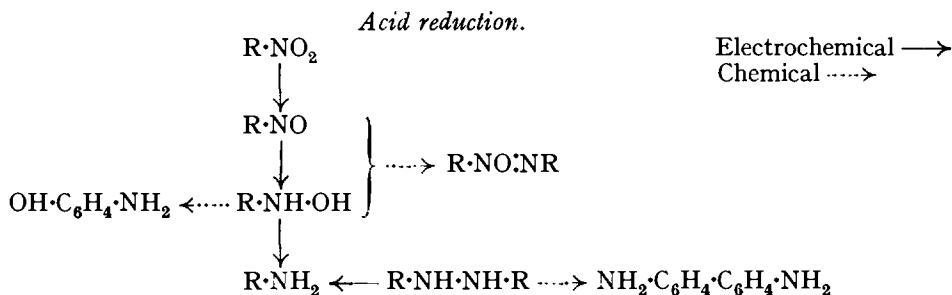


We now have Haber's scheme for the electrolytic reduction of nitrobenzene in alkaline alcoholic solution :



With cathodes of low hydrogen overvoltage the main product was azoxybenzene. More energetic reduction (favoured by the use of high overvoltage cathodes) gave hydrazobenzene and eventually aniline.

How is the scheme modified in acid solution? Reaction (1) becomes very slow, but in strong acid solution  $\beta$ -phenylhydroxylamine is rapidly transformed into *p*-aminophenol, and hydrazobenzene into benzidine  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ . The chief products were found to be *p*-aminophenol, benzidine, and aniline, in proportions depending mainly on the acid concentration. Thus in acid alcoholic solution the scheme became :



Haber's striking success, which gave a strong impetus to research in the field of electro-reduction and oxidation, earned for him promotion to the status of Professor Extraordinarius in 1898, only four years after entering Karlsruhe. In the same year he published his first book, "Grundriss der technischen Elektrochemie auf theoretischer Grundlage," which still further enhanced his reputation. Already he had established a recognised school of electrochemistry. This was a period of immense activity and effort. He worked to the very limit of his endurance and his health suffered severely. All his life he had, to a remarkable degree, the power of intense concentration on the matter in hand to the exclusion of everything else. Haber did not achieve things easily by steady even work, but rather by strenuous effort and he always overworked himself. Practically the only relaxation in those earliest years he found in a small circle of congenial spirits—teachers, writers, artists, where he enjoyed the lively discussions but got little mental rest. Over their club table hung a horn with the legend "Hier darf man etwas lügen," and no doubt it was here that he learnt to tell the long and highly entertaining stories which were always such a delight to his friends when they were fortunate enough to find him in the right mood.

A word must be said about Haber's book on electrochemistry. Technical and theoretical electrochemistry had made rapid strides, but to a large extent independently of each other. His purpose was to promote progress by discussing technical aims and methods *in the light of the modern theoretical knowledge*. This highly original and suggestive book, the first of its kind, was remarkable in that it brought out the essential problems and pointed the way for fundamental research. It provides a good illustration of his life-long urge towards the application as well as the advancement of science. His reputation at this time may be judged from the fact that the Deutsche Bunsen Gesellschaft sent him as their delegate to the annual meeting of the American Electrochemical Society in 1902, with the commission to study and report on chemical education and electrochemical industry in the United States. He impressed the Americans by his vigorous personality and by the energy and persistence he showed in pursuing his enquiries. His long and comprehensive report published in the *Zeitschrift für Elektrochemie* (1903) was acclaimed both in Europe and America as an extremely able and valuable paper, valuable not merely as an account of a vigorous young industry but because of its wealth of criticism and suggestion. It is an outstanding document of permanent value in the history of electrochemical industry.

Haber's work on nitrobenzene was followed by a study of the electrolysis of hydrochloric acid with special reference to the processes at a platinum anode. He determined the conditions of current, potential, and concentration governing the relative share of oxygen and chlorine in the anodic discharge and explained the behaviour observed in terms of concentration-polarisation and migration rates. He further discussed the complex question of anodic formation of the oxy-acids of chlorine and of hydrogen peroxide, and

analysed the conditions for anodic attack of platinum. This work was followed, a few years later, by the exhaustive studies of chloride electrolysis by Foerster and Müller. In the electrolysis of hydrochloric acid Haber noticed that, at high current density, cathodes of platinum and lead were apt to become coated with the finely divided metal. He discussed this with his friend Bredig, then at Leipzig, who had just discovered the dispersion of metals in liquids by the electric arc. Together they investigated the cathodic behaviour of various metals at high current density and at once encountered the remarkable phenomenon of "Zerstäubung." Thus with lead in aqueous sodium hydroxide, as the current density was gradually increased, thick black clouds of the metal suddenly appeared at the cathode. In acids this occurred only to a very slight extent. In explanation, they suggested the primary formation of an alloy of alkali metal with cathode metal, the alloy being decomposed by water with dispersion of the cathode metal, while in acids, alloys of hydrogen or hydrides produced a similar effect. Cathode surface disintegration occurred at lower current density and was a preliminary stage to cloud formation. Haber fully confirmed these views. The phenomenon occurred only with metals of high hydrogen overvoltage and tendency to alloy with alkali metals : lead, mercury, tin, bismuth, thallium, silver, antimony. Chemically prepared alloys of sufficient sodium content gave identical cloud-formation with water, and a correlation of cathodic polarisation studies on lead, tin, and mercury with the potentials of their sodium alloys of varying sodium content supported the theory. Later, Lorenz found the phenomenon to occur with great readiness in the case of fused electrolytes. While engaged in this work Haber made notable contributions to the theory of alloy potential.

Other studies at this period included : electrochemical aspects of autoxidation (referred to later) and an illuminating discussion of the very low concentrations that are encountered in connection with electrode equilibria and the theory of complex ions (e.m.f. measurements indicating for example that aqueous potassium silver cyanide contains 8 silver ions per litre), wherein he showed that such low concentrations should be regarded merely as calculation devices and cannot *directly* determine electrode potentials. It is noteworthy that, although potential mediators were first applied by Abegg in 1907, yet the underlying principle is contained in a footnote to a paper in 1901 on the theory of electrode potentials.

Haber's early work on electrochemical reduction was soon followed by an attack on the more physical aspects of the process. In a series of brilliant researches that have become classics, he propounded the first general theory both of irreversible reduction, such as that of nitrobenzene, and of reversible reduction, as exemplified by the quinone-quinol system. His method consisted in a close study of polarisation (current density-potential) curves in the light of the principle, which he regarded as fundamental and amply supported by experiment, that *direct* ionic discharge at an electrode is a very rapid process, but if the electrode process includes some relatively slow chemical change, then "chemical" polarisation must occur to an extent depending on the rate of the chemical process. Considering first irreversible reduction, in the stationary state the effective concentration (or solution pressure) of hydrogen on the cathode, and hence the cathode potential, is determined by the balance between the rate of consumption ( $= k_1[D][H]^n$ , where D represents the depolariser) and that of formation ( $= k_2i$ , where  $i$  represents current) of the electrode hydrogen. The electrode reaction is taken to be  $D + nH = DH_n$  solely. This leads at once to the equation for the cathode potential  $E$  :

$$E = \text{Constant} + \frac{RT}{nF} \log \frac{[D]}{i}$$

This equation was found to account reasonably well for the relations between the three variables  $E$ ,  $i$ , and  $[D]$ , but to bring it into quantitative agreement with experiment it was necessary to multiply the logarithmic term by an empirical factor  $x > 1$  which Haber found difficulty in explaining and attributed tentatively to some kind of electrode reaction resistance. The additive constant included any specific catalytic effect of the electrode metal (the history of the electrode, especially as regards previous polarisation, was shown to be an important factor). The problem of irreversible electrode reduction has not yet been fully solved. Haber's theory involves assumptions which in the light of modern knowledge

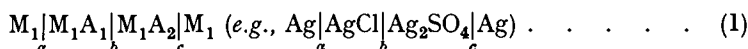
must be regarded as doubtful. Nevertheless its immense importance in the development on this subject will always be recognised. Haber completed his study of electro-chemical reduction by working out the first example of the *reversible* reduction-oxidation of an organic depolariser, namely, that of the system quinone-quinol which in later years came to acquire a special interest and practical value. He established the reversibility of the electrode process and developed the theory of the quinhydrone electrode. Being at that time mainly interested in the nature and rate of the electrode process he did not stress its application to the measurement of hydrogen-ion concentration. This was done by Biilmann many years later. Haber explained the form of the symmetrical cathodic and anodic polarisation curves on the basis of the association of a slow chemical change [ $C_6H_4O_2 + 2H = C_6H_4(OH)_2$ ] with a rapid ionic change ( $2H^+ + 2e = 2H$ ) at the electrode, the former determining the rate of the electrode process. He found support for this view by studies of the quinhydrone electrode in combination with the iodine-hydrogen iodide electrode where the process is ionic and fast.

Like many electrochemists of that period Haber was attracted to the problem of fuel cells, *i.e.*, cells in which the current-producing process is the atmospheric oxidation of carbon or carbon monoxide at relatively low temperatures. A practical cell of this kind would revolutionise power production since nearly all the free energy of oxidation would be available. Haber's study of the problem led him not to this goal but to the development of a novel method of measuring the free energy of oxidation of hydrogen, carbon monoxide, and carbon. He began by examining the "Jacques cell"  $C|NaOH (molten)|Fe (air)$ , which had attracted much attention. In it carbon dissolved as carbonate while the cell gave a steady current at about one volt, corresponding roughly to the heat of combustion of carbon. The cell reaction was supposed to be  $C + O_2 + 2OH' = CO_3'' + H_2O$ . In an elegant piece of work Haber proved this element to be not, as had been claimed, a carbon-oxidation but a hydrogen-oxidation cell. The iron in *pure* sodium hydroxide acted as a hydrogen electrode, but in practice manganese was always present, there being a constant ratio of manganate to manganite in equilibrium with atmospheric oxygen at *ca.* 400° and under these conditions the iron (passive) acted as a reversible oxygen electrode. In confirmation of this view platinum was found to give the same potential as iron. The carbon electrode potential was not determined by the process  $C \rightarrow CO_3''$  (the cell would not work with sodium carbonate as electrolyte) but owing to vigorous hydrogen evolution according to the reaction  $C + H_2O + 2NaOH = Na_2CO_3 + 2H_2$  (which Haber discovered) it acted simply as a hydrogen electrode. The e.m.f. of this oxyhydrogen cell proved to be in agreement with the thermodynamical free-energy equation for the formation of water, which had been developed independently and simultaneously in 1905 by Nernst and by Haber in his "Thermodynamics of Technical Gas Reactions." Having thus discovered for the first time an oxygen electrode that, unlike the aqueous oxygen electrode, was reversible (owing to the complete dissociation of platinum oxide at high temperatures), Haber was quick to apply it in gas cells for the study of high-temperature oxidation reactions.\* The limitations of temperature and gas concentration imposed by molten alkali were overcome by using as electrolyte a thin glass or porcelain diaphragm coated with platinum or gold as electrodes in contact with the two gases. The producer-gas cell, for example (of no practical value owing to great polarisability):  $air|Pt|hot\ glass|Pt|CO + CO_2$ , with e.m.f. *ca.* 1 volt, in which the cell reaction  $CO + \frac{1}{2}O_2 = CO_2$  is the sum of the electrode reactions  $\frac{1}{2}O_2 + SiO_2 + 2e \rightleftharpoons SiO_3''$  and  $CO + SiO_3'' - 2e \rightleftharpoons SiO_2 + CO_2$ , was essentially an oxygen-concentration cell with the smaller value of  $p_{O_2} = (K_p \cdot p_{CO_2}/p_{CO})^2$ . With this simple and highly original device, Haber was able to measure the e.m.f. and hence the free energy of oxidation of carbon, carbon monoxide, and hydrogen, over a range of temperature not readily accessible in other ways. The data obtained agreed with Haber's thermodynamic equations, but by more recent standards they were not very accurate.

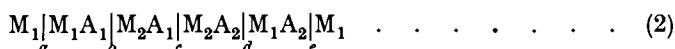
Haber now took up the question of the electrochemistry of crystalline salts and broke new ground in a field of which but little was then known. Hittorf had studied the electrolysis of solid salts, the electrolytic conductivity of mixed oxides had found application in

\* A good account of this work is given in Haber's "Thermodynamics of Technical Gas Reactions," transl. Lamb, Macmillan, 1908.

the Nernst filament, and the validity of Faraday's law had been demonstrated in the electrolysis of glass by Warburg and of porcelain by Haber; but fundamental quantitative knowledge on crystalline salts was lacking and Haber set out to fill this gap by studying their electrolysis and their galvanic action. He was attracted to the subject, not only for its intrinsic interest, but also because of the special thermodynamic importance of solid reactions. The accepted idea that in the case of solid reactions the free-energy change was practically equal to the heat of reaction (Thomson's rule), could be tested by setting up reversible solid galvanic cells; and the free-energy equation of such reactions, with no concentration terms, involved only thermal quantities and the indeterminate constant, in the problem of which he was deeply interested. Haber was the first to prove the validity of Faraday's law in the electrolysis of crystalline salts. Solid barium chloride (m. p. 1000°) at 600° gave a quantitative yield of nickel chloride at a nickel anode, and when mixed with solid barium carbonate as depolariser it gave a quantitative yield of carbon at a platinum cathode ( $\text{BaCO}_3 + 2\text{Ba} = \text{C} + 3\text{BaO}$ ). Studies of the back e.m.f. of polarisation at the solid interfaces between a metal electrode and a salt gave results of great interest and afforded verification of Thomson's rule. The most important outcome of this work on solid electrolytes was, however, the study for the first time of phase-boundary potentials between solid salts or a salt and its saturated solution by means of an entirely new type of galvanic cell, constructed of a pile of salt tablets compressed between metal electrodes. Since the cell (1)



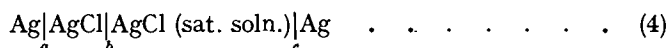
must have zero e.m.f.,  $E_b$  must just balance  $E_a - E_c$  which measures the free energy of the reaction  $\text{M}_1\text{A}_1 + \text{A}_2' = \text{M}_1\text{A}_2 + \text{A}_1'$ , so that this same reaction must proceed at  $b$ , and  $E_b$  must represent the difference in the free energy of  $\text{M}_1$  in the two states  $\text{M}_1\text{A}_1$  and  $\text{M}_1\text{A}_2$ . Incorporation of the two salts  $\text{M}_2\text{A}_1$  and  $\text{M}_2\text{A}_2$  gave the cell



involving the cell reaction  $\text{M}_1\text{A}_1 + \text{M}_2\text{A}_2 = \text{M}_1\text{A}_2 + \text{M}_2\text{A}_1$ , the free energy of which is given by the sum of the five boundary potentials (e.m.f. of the cell). These cells had the novel feature that the electrode potentials may be eliminated, for cell (3) involves the same reaction as cell (2)



the free energy of the reaction now being given by the sum of the four salt-salt potentials. It is evident that solid cells may be coupled in series without increasing the number of electrodes. Various systems were studied experimentally and gave satisfactory confirmation of the theory, the e.m.f. agreeing with the reaction heat. Haber was the first to examine systems involving the phase-boundary potential between a solid salt and its saturated solutions. In cells of the type



with zero e.m.f.,  $E_b = (RT/F) \ln[\text{Ag}^*]$ , the solid salt acting as the metal but with a different solution pressure.

Further studies in this field led to the theory of the glass electrode and its practical application. The biologist, Max Cremer, had discovered in 1906 an interface potential between glass and aqueous solutions, but Haber was the first to develop the general theory of the interface potential between an aqueous solution and a second phase permeable to water and its ions, e.g., glass or solutions of water in organic liquids like benzene, and to derive the relation characteristic of the hydrogen electrode. He obtained full confirmation of the theory by acid-alkali titrations, using not only glass but also benzene, though here the experimental difficulties were greater. Referring to the utility of the glass electrode Haber says (1909) "The electromotive forces are in such good agreement with the theory and so easy to measure if one is familiar with the quadrant



electrometer, that the method may be used for acid-alkaline titration. Böttger has titrated with the hydrogen electrode, but you can titrate quite as well with a piece of common Thuringian glass. With no hydrogen to react chemically and no platinum to exert catalytic effects on the liquid, the glass electrode, in addition to its theoretical interest, is likely to prove of much practical value." In connection with this study Haber stressed the importance of phase-boundary potentials in muscle action. Notable developments of the subject were made later by his pupil Beutner.

During the greater part of the Karlsruhe period Haber was interested in the electrochemistry of iron—his first electrochemical paper (1897) dealt with electrodeposited iron plates used for the printing of banknotes. His most important researches in this field were concerned with the anodic behaviour of iron in alkaline solutions and the phenomenon of passivity. The conditions for quantitative anodic formation of the ferrate ion and its relations with the ferrite ion were worked out. Under conditions of ferrate formation, iron was always passive, owing, as Haber maintained, to a skin of oxide. At that time (*ca.* 1905) the oxide-skin theory of passivity was out of favour, as it appeared incompatible with the continuous series of potentials that a passive metal could show, and with the fact that the passive state did not long survive the removal of the passivating influence. After much research, Haber pronounced very strongly in favour of the oxide-skin theory, with, however, the condition that the skin may be porous, thus allowing variable electromotive activity of the exposed metal. Full passivation of iron was regarded as attained with the completion of the oxide skin, composed of a higher oxide not in equilibrium with iron; on removing the passivating influence, chemical reaction between iron and the oxide caused the latter to become porous and so activity returned. In certain conditions a visible layer of oxide preceded passivation. Factors tending to dissolve the skin, *e.g.*, high concentration and high temperature of the alkali solution, caused activity to return. Haber's work played a very important part in the development of this difficult subject, and his conclusions were in substantial agreement with present-day views.

An investigation that occupied Haber's earnest attention for several years was that on the corrosion of underground water and gas mains, due to stray currents from tramway systems which in those days were commonly operated by direct current. In spite of much research, the true nature of this serious and widespread trouble remained obscure until Haber undertook its investigation in Karlsruhe and Strassbourg. With characteristic thoroughness he studied all the relevant factors such as earth composition and conductivity, the direction and magnitude of very small earth currents, and the anodic behaviour of iron in earth where chemical conditions precluded protection by passivation. In this comprehensive research, a model of its kind, he worked out the problem completely and provided standard methods for its investigation in any case that might arise. Corrosion was always found to occur where his theory predicted it. With the introduction of alternating current his work lost its practical significance, but it involved many electrochemical studies of permanent value. This is a good example of the intense interest and great satisfaction which Haber always found in working for the common good.

Haber's book "The Thermodynamics of Technical Gas Reactions" appeared in 1905.\* This remarkable book, which has been well described † as "a model of accuracy and critical insight," stands high in the history of thermodynamics for three reasons, its influence on chemical teaching, its attack on the problem which Nernst solved a year later, and its timely provision of the first systematic critical survey of all the thermodynamic data necessary for the calculation of free-energy changes in the most important gas reactions. Gaseous equilibria had been discussed mainly on the "mass-action" basis, and although as far back as 1888 Le Chatelier had pointed out the significance of specific heats in calculating equilibria over a wide temperature range, their fundamental importance and practical value had not been fully recognised by chemists generally.

\* "Thermodynamik technische Gasreaktionen: Sieben Vorträge," von Dr. F. Haber (Oldenbourg, 1905). The English translation by Arthur B. Lamb (Longmans, 1908) contains Haber's account of the Nernst heat theorem.

† Lewis and Randall, "Thermodynamics," McGraw Hill, 1923, p. 5.

By talking to them as a chemist and making constant reference to well-known and industrially important reactions, Haber succeeded brilliantly in bringing this aspect of the subject to the fore-front of physicochemical teaching and research. Writing in an easy informal style, he developed his subject with the utmost clarity and precision. His employment of entropy as a practically useful function went far to break down the shyness which chemists had felt towards this concept. Incidentally he was the first to use equations with fractional numbers of molecules (*e.g.*,  $\frac{1}{2}\text{O}_2$ ), and he it was who coined the expression "equilibrium box" for van 't Hoff's device. The greater part of Haber's book was devoted to an exhaustive thermodynamic treatment of important gas reactions in the light of existing thermal and equilibrium data, and the setting up of the best free-energy equations. It was the first time such a thing had been attempted. By his masterly handling of this difficult task and his discussion of the experimental determination of gas equilibria, he performed a great service and strongly influenced the development of research in this field.

In his book Haber discussed at some length the problem of the "thermodynamically indeterminate constant" of the free-energy equation, and it was he who gave it this name. In his first attack on this problem in 1904 he had shown that the free energy of reactions between solids (*e.m.f.* of solid galvanic cells and the back *e.m.f.* of polarisation of solid electrolytes \*) was nearly equal to the heat of reaction. The measurements were not exact enough for the determination of the temperature coefficient. This result led him to conclude that, if Kopp's law is obeyed for reactions between solids, the integration constant, *i.e.*, the entropy change at the absolute zero, must have zero value. In view, however, of the lack of knowledge about specific heats, he felt bound to leave open the possibility that the constant might perhaps have a small finite value owing to the possible deviation from additivity of atomic heat capacities at low temperature. Nernst *postulated* Kopp's law near the absolute zero. In his book Haber considered the same problem *in relation to gas reactions*. Following Planck, he explained the nature of the constant as expressible in terms of heat capacity and entropy constants characteristic of the gaseous reaction components. He showed the importance of knowing the variation of these properties with temperature in the vicinity of the absolute zero, but in the complete absence of any experimental information he proceeded very cautiously. Characteristically he could not bring himself to accept a purely speculative basis and build on ideas that were entirely unsupported by experiment. He was much influenced by T. W. Richards's discovery (1904) that the *e.m.f.* of certain galvanic cells involving reactions with zero heat-capacity change was in agreement with their reaction heat, and by van 't Hoff's discussion of it. While leaving the question open owing to insufficient knowledge about heat capacities, he concluded that in the case of gas reactions involving no change in the number of molecules the constant, if not equal to zero, was probably quite small. His examination of the experimental data for various reactions of this type supported this conclusion, and he felt justified in adopting it as a guide in setting up free-energy equations. In the case of reactions involving a change in the number of molecules a somewhat larger constant was indicated. When the heat theorem was published in the following year Haber was quick to recognise the immense importance of the bold step which, it is safe to say, could only have been taken by a man of the vision and genius of Nernst. In the history of this problem Haber must be accorded an honourable place.

Haber's researches on the ammonia equilibrium were begun in 1904. They had their origin in his collaboration as scientific adviser with the brothers Margulies of Vienna, who were interested in promoting new methods for the industrial fixation of nitrogen. To quote from the opening paragraph of Haber's first paper in 1905: "Die Herren Dr. O. und Dr. R. Margulies warfen die Frage auf, ob es aussichtsvoll sei, nach einem Metall zu suchen, dessen abwechselnde Überführung in Nitrid und Hydrür mit Stickstoff und Wasserstoff zur Ammoniakdarstellung verwendet werden könne." Continuous synthesis of ammonia might result from the simultaneous formation and reduction of nitride by the mixed gases, the solid phase thus acting as catalyst. Whatever the mechanism might be, the maximum yield must be governed by the ammonia equilibrium, and this Haber

\* See p. 1648.

decided to study first. Some preliminary experiments on the reduction and regeneration of calcium and manganese nitrides indicated little hope in the use of these metals owing to the high temperature required. Among the many early attempts at the thermal synthesis of ammonia may be mentioned that of Ramsay and Young in 1884. In the region of 800°, using iron as catalyst, they found that the decomposition of ammonia was never quite complete, but obtained no trace of ammonia on attempting to reverse the reaction.\* It was generally accepted that nitrogen was far too inert to combine with hydrogen except perhaps at a very high temperature, where however the decomposition of ammonia was practically complete.†

In his first orienting experiments by the flow method with iron as catalyst at 1020°, Haber, although fully aware of the favourable influence of high pressure, chose to employ atmospheric pressure because of the simpler apparatus required. By placing in the same furnace two reaction tubes in series, each followed by an ammonia absorber, and passing ammonia into the system, he reached equilibrium from both sides in the same experiment. Thus for the first time the ammonia equilibrium was realised, and more easily than Haber had expected. The concentrations found were however very low. They varied between 0.005% and 0.012% and it was difficult to choose the most probable value. At that time he favoured the upper limit for various reasons, but later work showed the lower limit to be in fact the true value, the high yields being traced to a special effect of the iron catalyst *when fresh*. This determination of the *order* of the ammonia equilibrium was sufficient for his original purpose, and he was now able to answer the question put at the outset in the following words: "From dull red heat upwards no catalyst can produce more than traces of ammonia under ordinary pressure; and even at greatly increased pressures the position of the equilibrium must remain very unfavourable. To attain practical success with a catalyst at ordinary pressure its temperature must not be higher than 300° C." Since the direct synthesis of ammonia appeared to be hopeless as a basis of technical nitrogen fixation Haber dropped the matter and the Margulies association came to an end. In 1906, when examining experimental data on gas equilibria, Nernst found in the single case of ammonia a large discrepancy between experiment (Haber) and calculation by the heat theorem. Nernst therefore redetermined the ammonia equilibrium using high pressures (*ca.* 50 atm.) in order to increase the concentration of ammonia and thus reduce the experimental error. Nernst was thus the first to synthesise ammonia *under pressure*. He obtained much less ammonia than Haber's original estimate and his values were in fair accord with theory: at 1000°, theory 0.0045%; found 0.0032% (Nernst); 0.012% (Haber). In the autumn of 1906 Nernst informed Haber of this in a letter, whereupon Haber and Le Rossignol redetermined the equilibrium using the original method and atmospheric pressure, but by numerous refinements, especially in the determination of small amounts of ammonia, they now obtained quite concordant results.‡ The new value at 1000° was 0.0048%, in agreement with the *lower* limit (0.005%) of the original determinations, and Haber's first estimate of 0.012% as the most probable value was proved to be much too high, as Nernst had maintained. The discrepancy with Nernst's experimental values was thus greatly reduced but by no means removed. This was clearly brought out at the 1907 meeting of the Deutsche Bunsen Gesellschaft when Nernst gave an account of his pressure experiments.§ In the discussion Haber

\* *Moist* nitrogen-hydrogen mixtures gave traces of ammonia. This effect was stressed by Perman in 1904, who also used iron as catalyst. On learning of Perman's work after the publication of his first paper on the ammonia equilibrium, Haber was quick to point out that the chemical action of water in this system has no bearing on the ammonia equilibrium.

† Le Chatelier in 1901 considered the effect of pressure and temperature on the ammonia equilibrium but his attempt to synthesise ammonia under pressure led to an explosion and he abandoned the project. His views on this subject, being stated only in a French patent (No. 313950 of 1901), did not become known to Haber until long after the ammonia synthesis had been achieved (F. Haber, "Fünf Vorträge," Springer, 1924, p. 21; C. Bosch, *Z. Elektrochem.*, 1918, **24**, 361).

‡ Haber und Le Rossignol, *Ber.*, 1907, **40**, 2144 (received April 1907 and published shortly after the meeting referred to later).

§ Nernst, *Z. Elektrochem.*, 1907, **13**, 521; Jost, *Z. anorg. Chem.*, 1908, **57**, 414.

withdrew his original estimate of 0.012% and announced his new values. As Table I shows, they were still about 50% higher than those determined by Nernst (the latter are calculated from the observed percentages in the equilibrium mixture under pressure). In

TABLE I.

*Percentage of Ammonia in the Equilibrium Mixture under a Pressure of one Atmosphere.*

Temp. ....	700°	750°	800°	850°	930°	1000°
Nernst-Jost (1907) .....	0.0174	0.0119	0.0087	0.0065	0.0043	0.0032
Haber-Le Rossignol (1907) .....	0.0221	0.0152	0.0108	0.0091	0.0065	0.0048

the course of the discussion Nernst refused to accept Haber's redetermination as accurate because of the low concentrations of ammonia in the equilibrium mixture under one atmosphere pressure, and suggested that he should work at higher pressures in order to avoid this source of error. Haber strongly maintained the accuracy of his figures. They were in fact fully confirmed by his later work. Nernst closed the discussion with the words: "Dann darf ich vielleicht nur noch eine Tatsache konstatieren, die von allgemeinem technischen Interesse ist. Es ist sehr bedauerlich, dass das Gleichgewicht nach der Seite der viel geringeren Bildung mehr verschoben ist als man nach den stark unrichtigen Zahlen\* Habers bisher angenommen hat, denn man hätte wirklich daran denken können Ammoniak synthetisch herzustellen aus Wasserstoff und Stickstoff. Aber jetzt liegen die Verhältnisse sehr viel ungünstiger, die Ausbeuten sind ungefähr dreimal kleiner als zu erwarten war." This summing up probably received general acceptance at that time. Nernst regarded the position of the equilibrium as substantially settled, Haber's figures being incorrect while his own were in sufficiently good agreement with the heat theorem.†

Haber felt this episode deeply as a personal slight and an injury to his reputation. Without delay therefore he and Le Rossignol began a new and decisive determination of the equilibrium, this time under a pressure of 30 atmospheres. In a beautiful piece of work (published 1908) they fully confirmed their earlier values at one atmosphere (Table I). Their apparatus was simple and admirably adapted to its purpose. The nitrogen-hydrogen mixture, obtained by the thermal decomposition of ammonia under pressure, was passed slowly through a thick-walled silica tube containing the catalyst (iron or manganese), whence the equilibrium mixture was rapidly removed and cooled for analysis. The outlook for industrial synthesis appeared, however, no better in 1908 than in 1905 so far as knowledge of the equilibrium was concerned. Haber's free-energy equation based on the new data indicated that yields large enough to encourage the idea of industrial development could be expected only under apparently unattainable conditions, e.g., 8% of ammonia at about 600° and 200 atmospheres (the upper limit for compressors at that time). But pressures of this order were enormously greater than had ever been used in any large-scale chemical operations, and further, the best catalysts of that time (manganese, nickel, iron) were slow in action even at 700° and higher. If, however, these formidable obstacles of catalyst and high pressure could be overcome the way lay open to the industrial synthesis of ammonia and perhaps the solution of the nitrogen question. Haber took up the challenge. In doing so he was undoubtedly influenced by the knowledge that in his friend Le Rossignol he had the ideal collaborator. The high-pressure technique then coming into general use in the Karlsruhe laboratory had been developed by Le Rossignol, whose skill and ingenuity in experiment were admired by every member of the Institute, even by the mechanic Kirchenbauer, for he was an accomplished metal worker and used to make his beautiful pressure apparatus with his own hands. Work began in 1908 when a converter enclosed in a steel bomb was constructed which worked well at 200 atmospheres. Everything now depended on finding a much more active catalyst. After a long search osmium was discovered to have high activity at a temperature as low as 550°, but osmium was much too rare. Then uranium proved to be just as efficient. Essentially the problem was now solved. With the new apparatus (uranium; 550°; 150—200 atm.) the con-

\* He is here referring to the *original* estimate of 0.012%.

† See Haber, "Fünf Vorträge," Berlin, Springer, 1924, p. 23; Nernst, "The New Heat Theorem," Methuen, 1926, p. 275.

centration of ammonia became so high (see Table II) that on moderate cooling under the working pressure it could be liquefied out as the gas mixture was circulated through the closed system of converter, condenser, and circulating pump, while fresh gas mixture equivalent to the ammonia removed was continuously fed in. Finally with the fitting of heat-interchangers the apparatus became a small technical plant producing a few hundred c.c. of liquid ammonia per hour with very low energy expenditure. The feasibility of a synthetic ammonia industry seemed assured, the more so as the laboratory plant was now in such a form that its translation to the large scale without radical modification could easily be visualised. Rarely if ever had a process been brought in an academic laboratory to such an advanced stage of technical development before being handed on to Industry. Haber's achievement becomes all the greater when one remembers that he received nothing but cold discouragement and scepticism from the industrial side. The Badische Anilin und Soda Fabrik were deeply interested in nitrogen fixation. Having launched the Schönher process in Norway they regarded Haber's work on the electrical oxidation of nitrogen as very important, but in his ammonia experiments they could see no promise whatever. It was through his old friend and colleague, Carl Engler, an influential member of the advisory council of the B.A.S.F., that the technical leaders came to take some interest in the work. Their sceptical attitude was perhaps connected with Ostwald's claim, a few years earlier, to have obtained good yields of synthetic ammonia by the use of iron as catalyst. They found that Ostwald's ammonia came from nitride in the iron.

It was an exciting day in July 1909 when the company's representatives, the engineer Dr. Carl Bosch, and the chemist Dr. A. Mittasch came to Karlsruhe to see a demonstration of the process. At first things went wrong, as they will on such an occasion, and when late in the day repairs had been made and all was well, only Mittasch was there to see the liquid ammonia flow. Deeply impressed and completely convinced, he returned to Ludwigshafen and at once Bosch and he began their great work. Three years later a synthetic ammonia factory was in regular operation. Haber had no share in the large-scale developments. The credit for this belongs to Carl Bosch. Although the "Haber process" had been brought to such an advanced stage in the Karlsruhe laboratories its translation to the industrial scale involved many new and formidable problems, and their successful solution under the leadership of Bosch stands out as perhaps the most difficult and brilliant feat of chemical engineering ever achieved. Haber was awarded the Nobel Prize in 1919. When twelve years later Bosch and Bergius received the same honour Haber in a generous appreciation of the award wrote: "It is not sufficiently recognised how little had really been done in the Karlsruhe synthetic ammonia process towards the foundation of a World Industry." In recognising Bosch and Bergius for their development of high-pressure methods in industry, we must not forget what they owe to the pioneers, Haber and Le Rossignol. As early as 1907 Haber's laboratories had become known as a centre of high-pressure research, and when Bergius conceived the idea of hydrogenating coal under pressure it was to Karlsruhe that he came in 1908 to make his first experiments.

TABLE II.

*Percentage of Ammonia in Equilibrium with a 3 : 1 Hydrogen-Nitrogen Mixture.\**

$$\log_{10} K_p = \log \frac{p_{\text{NH}_3}}{p_{\text{N}_2}^{1/2} p_{\text{H}_2}^{3/2}} = \frac{9591}{4.571T} - \frac{4.98}{1.985} \log T - \frac{0.00046}{4.571} T + \frac{0.85 \times 10^{-6}}{4.571} T^2 + 2.10.$$

$t^\circ, \text{C.}$	$K_p$	Equilibrium percentage of ammonia.			
		1 Atm.	30 Atm.	100 Atm.	200 Atm.
200	0.660	15.3	67.6	80.6	85.8
300	0.070	2.18	31.8	52.1	62.8
400	0.0138	0.44	10.7	25.1	36.3
500	0.0040	0.129	3.62	10.4	17.6
600	0.00151	0.049	1.43	4.47	8.25
700	0.00069	0.0223	0.66	2.14	4.11
800	0.00036	0.0117	0.35	1.15	2.24
900	0.000212	0.0069	0.21	0.68	1.34
1000	0.000136	0.0044	0.13	0.44	0.87

\* From Haber, *Z. Elektrochem.*, 1914, 20, 603.

The first decade of the century saw a rapid development in the study and industrial application of the oxidation of nitrogen in the electric arc, and in this field Haber's laboratory was an important centre of research. Following Nernst's determination of the thermal nitric oxide equilibrium in 1904, the purely thermal theory of arc fixation was generally accepted, but doubts soon arose, and in a critical examination of the existing experimental material Haber found much evidence for the view that the high yields on record were incompatible with the purely thermal view and that electrical factors must be operative to some extent. Impressed by the technical as well as the scientific interest of this question he made (1906—1910) a comprehensive and detailed study of fixation in the low- rather than the high-temperature arc. Owing to electrical activation of reactants, the nitric oxide content in the stationary state (electrical equilibrium) will exceed the thermal equilibrium amount at the same temperature, and on removal of the electric field the excess nitric oxide will decompose until purely thermal equilibrium is established. Since the rate of this process decreases very rapidly with fall of temperature, at sufficiently low arc temperature little decomposition will occur and conditions will be right for maximal yields of nitric oxide. High-temperature arcs must give lower, eventually thermal, yields. Haber fully confirmed this theory. The establishment of electrical equilibrium was proved. On slowly passing air along a 6-cm. length of A.C. arc burning under a pressure of 100 mm. in a narrow, cooled, silica tube, nitric oxide was obtained greatly in excess of the thermal yield for an arc at 2000°. Hotter arcs gave more oxide but also more thermal decomposition. The same general principles were confirmed with short D.C. arcs. High yields were obtained but the system was unsuitable for large-scale operation. The work as a whole was of great theoretical and technical value.

Haber's interest in problems of flame and combustion, which originated in his early association with fuel technology, was stimulated by his critical examination of technical gas reactions such as the dissociation of water and carbon dioxide, and in his "Thermodynamics" (1905) we find an account of his study of these reactions in flames. This interest remained with him to the end and led to some of his best work. His first experiments were concerned with the water-gas equilibrium, the existing data on which were unreliable above 1100°. For its study he utilised the homogeneous gas phase of a hydrocarbon flame, a high-temperature reaction space free from the disturbing effects of hot surfaces. No essentially new principles were involved. Smithells had invented the flame separator and analysed the products of primary combustion above the inner cone. Twenty years earlier Le Chatelier had calculated for the first time the dissociation of carbon dioxide and flame temperatures from the composition of the flame gases which Deville in 1865 had sucked from the interior of a carbon monoxide flame through a cold tube. Using a new form of Deville tube of high chilling efficiency to extract the interconal gases of flames, Haber showed that the water-gas equilibrium was established practically instantaneously as the gas mixture traversed an inner cone not cooler than about 1250°. Correlation of the equilibrium constant with temperature above 1250° led to an improved free-energy equation of wide range. Thus, analysis of the gases extracted at any point in the flame (not separated) gave the temperature at that point, and with this chemical flame thermometer Haber explored not only the hydrocarbon (Bunsen) flame but also the hotter flames produced by explosive mixtures of oxygen with (a) carbon monoxide, (b) hydrogen, and (c) acetylene. The method failed only at very high temperatures (over *ca.* 2500°). It had the disadvantage of requiring a knowledge of heat capacities at very high temperatures, and it was subject to analytical errors and not very sensitive. It can, however, be said that his flame temperatures were in substantial agreement with those obtained later by other observers and by different methods. During this period Haber also studied the oxidation of nitrogen in flame. The formation of oxides of nitrogen in gas explosions was well known, but (apart from some observations by Liveing and Dewar, who obtained nitric acid by the combustion of hydrogen in oxygen-nitrogen mixtures under pressure) no attention had been given to this process in flames. In a study of the carbon monoxide flame under pressure it was established that, although very little fixation occurred at one atmosphere, the yield of nitric oxide at ten atmospheres rose to nearly 5 moles (with pre-heating, 6 moles) per 100 of carbon dioxide, high enough to warrant consideration at that time from a technical point

of view. The effect of pressure was unexpectedly great and could not be accounted for on a purely thermal basis. In similar circumstances the hydrogen flame produced only half as much nitric oxide per 100 molecules of water. The abnormal behaviour of carbon monoxide was brought out again 15 years later in Bone's studies of high-pressure explosions when carbon monoxide was found to give exceptionally large yields of nitric oxide. In these early researches Haber greatly advanced our knowledge of the Bunsen flame and especially the properties of the inner cone. Its wall was estimated to be only 0.1 mm. thick; it was shown to be the coolest and not, as previously supposed, the hottest part of the flame; it was at the same time a region of extraordinarily high reaction rate, of strong chemi-luminescence, and of relatively high ionisation.\* Haber regarded these last three properties as closely inter-related but his ideas, which were before their time, could only come to full fruition when he returned to this favourite subject of his in later years.

It must suffice to mention quite briefly some other researches of the Karlsruhe period. It is of interest that as far back as 1896, in connexion with his discovery of the quantitative oxidation of ferrous hydroxide by hydroxylamine, Haber was the first to suggest its existence in the tautomeric forms  $\text{NH}_2\cdot\text{OH}$  (reducing) and  $\text{NH}_3\text{O}$  (oxidising), corresponding to the oximes and amine oxides respectively. The industrially important reaction of carbon monoxide under pressure with aqueous sodium hydroxide to give formate, due originally to Berthelot, was shown to proceed entirely in the liquid phase, and the best operating conditions were worked out. It was found that non-poisonous zirconium oxide could be used instead of the usual stannic oxide in the enamel of iron cooking utensils. The ready displacement of chlorine from the chlorides of magnesium and the alkaline earths by a mixture of air and carbon dioxide was discovered:  $2\text{MgCl}_2 + \text{O}_2 + 2\text{CO}_2 = 2\text{MgCO}_3 + 2\text{Cl}_2$ , and the related equilibrium  $2\text{MgCl}_2 + \text{O}_2 \rightleftharpoons 2\text{MgO} + 2\text{Cl}_2$  studied. Haber designed a gas interferometer, after the principle of Lord Rayleigh, for the rapid analysis of gas mixtures, and this instrument which proved very convenient in the ammonia researches came into general use. Later he devised the vibrating quartz-fibre manometer (based on the original suggestion of Langmuir) as a simple instrument for measuring gas pressures in the range of  $10^{-1}$  to  $10^{-3}$  mm. In a series of researches he made a detailed examination of the complex electrochemical reactions that occur when an electric arc discharge passes between an aqueous solution and an electrode in the low-pressure gas phase above it.

In 1911 Haber accepted an invitation to Berlin as director of a research institution that became even more famous than the school he had built up in Karlsruhe. He was then 42 years of age, and for five years had been Professor of Physical Chemistry and Electrochemistry. These years were undoubtedly the most brilliant period of his career—his "Glanzzeit," as Willstätter has called it. To have known him and worked with him at that time is an experience one does not forget. The great variety and interest of the work going on, and its dual bearing on pure science and industry so characteristic of Haber, gave his laboratory a quality of its own and exercised a most stimulating effect. Some thirty to forty men of a dozen different nationalities were united in the friendliest relations by their personal affection for Haber as well as their admiration of him as a man of science. His kindness and human sympathy endeared him to all. Discussion of progress was always most helpful and encouraging; he would devote himself wholly to the question in hand until a satisfactory position had been reached. A stupid mistake would be brought home in such a way as to give no pain, and it gave him great pleasure to find that independent work had been done. Haber was happier in Karlsruhe than at any other time. One remembers summer evenings round a punch bowl in the *Stadtgarten*, or walks through the woods to some favourite village *Gasthaus*, when his lively spirit, his stories and charming ways were a great delight. But those joys came too rarely, for he was always overworked, and took little rest and relaxation.

The research institution in Berlin which Haber directed until 1933 had its origin in the centenary celebrations of the University of Berlin in 1910, when Adolf von Harnack, a far-seeing and highly influential man, stressed the need of supplementing university research in Germany by means of richly endowed research institutes each directed by an eminent

\* The relatively high electrical conductivity of the inner cone was first reported in 1906 by Davidson and Tufts independently.

man of science with complete freedom in his work and choice of staff. This idea, which had been advocated a century earlier by Wilhelm von Humboldt, appealed strongly to the Emperor Wilhelm II, and it was through his initiative that the *Kaiser Wilhelm Gesellschaft zur Förderung der Wissenschaften* was established in 1911 as the parent body of the new Kaiser Wilhelm Institutes. The movement grew rapidly. At the outbreak of the war there were seven institutes, eight were created during the war, and in 1926 there were altogether thirty institutes covering a very wide range of research. The first to be established was that for Chemistry under Willstätter and Beckmann. In the same year (1911) Leopold Koppel, a very wealthy and influential man, undertook to build, equip and maintain the *Kaiser Wilhelm Institut für Physikalische Chemie und Elektrochemie*. His only condition was that Haber should be director. Thus arose the finest laboratory of its kind in the world at Dahlem, a spacious and pleasant suburb of Berlin. Haber's house adjoined the Institute and stood in the midst of a large natural garden where he could find quiet among the trees he loved so much. In these ideal conditions for life and work he entered upon a new phase of his career.

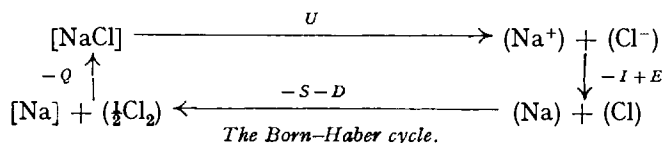
The Institute was opened in 1912 by the Emperor. At the opening Haber demonstrated the device he had invented, at the Emperor's suggestion, for detecting the presence of dangerous quantities of fire-damp in coal mines. It depended on the principle that two identical whistles which gave the same note when blown with the same air, produced beats when one was blown with normal air, and the other with air containing fire-damp. Although robust and effective the device did not come into general use.

Haber's first concern at Dahlem was finally to round off his researches on ammonia by redetermining with the greatest possible precision not only the equilibrium but all the relevant thermal data. The Le Rossignol values were fully confirmed and a final free energy equation (Table II) obtained. More recent studies have shown the need of taking into account deviations from the gas law at high pressures. At the same time he was occupied with applications of Planck's quantum theory, the significance of which in chemistry Haber was one of the first to recognise. It formed the ultimate basis of most of his Dahlem work. His study of flame reactions had suggested the idea of intermediate ionisation stages in chemical reactions, and this led him as early as 1907 to take the first step towards the study of elementary reaction processes upon which in later years at Dahlem so much light was to be thrown. In collaboration with Just he set out to answer the question whether, chemical reactivity being assumed to depend on the properties of special electrons, actual electron emission might not occur as a direct consequence of chemical reaction. To avoid thermal emission, only cold reactions could be employed. While some such reactions, *e.g.*, the oxidation of phosphorus, were known to produce gas ions, no cases of electron emission had ever been observed until Haber discovered that at low pressures reactive gases like chlorine and oxygen attacked the alkali metals with emission of slow electrons, the metal spontaneously acquiring a positive charge. The most important observation was that the intensity of the effect diminished with decrease of the chemical reaction energy. Noting the similarity of the phenomenon to the photoelectric effect, he compared the reaction heats with the few available values of the frequency  $\nu_e$  of the selective photoelectric effect, and thus, taking  $\nu_e$  to be a measure of the work of removing the electron from the metal, he found support for the view that electron emission can occur only when the heat of reaction  $Q$  per atom exceeds the work of removing the electron. Recent research\* has shown the essential correctness of this interpretation. On this basis he proposed a quantum theory of reaction heat: chemical reaction being assumed to involve only a change in the binding (frequency) of valency electrons, then for energy conservation  $Q/h = \sum \nu_e$  (resultants) -  $\sum \nu_e$  (reactants). A test was possible only for solid reactions of the simplest type, *e.g.*, the formation of alkali halides from their elements. In spite of the simplifying assumptions involved in the calculation, this first physical theory of reaction heat gave values of  $Q$  in striking agreement with experiment. A noteworthy outcome of this study arose from the fact that  $\nu_e$  was experimentally accessible (photoelectric effect) only in the case of the metals, while for the other reaction components only  $\nu_r$ , the characteristic infra-red frequency, could be observed. The difficulty was overcome

\* *Ann. Reports*, 1934, **31**, 81.



by means of a semi-empirical rule, known as "Haber's square-root relation," viz.  $v_r/v_0 = \sqrt{\text{electron mass/atom mass}}$ , which proved to be a very useful approximation. Haber's pre-occupation with the new physics and its chemical applications, broken off by the war, was eagerly taken up again in 1919, when he saw much of his friends James Franck and Max Born, and their frequent discussions were of the greatest value for the development of his ideas. Born had just worked out the theory of the ionic crystal lattice, which gave the lattice energy in terms of the ion distances and forces. The heat of a solid reaction was then given by the algebraic sum of the lattice energies of the components. Born evaluated the lattice energy as the sum of the energies involved in first discharging the free gaseous ions and then combining them to form the crystal. The energy relations were clearly demonstrated by Haber in the form that became known as the "Born-Haber" cycle (square brackets indicate solid, round brackets gas), which shows the lattice energy as the algebraic sum of the heats of formation  $Q$ , dissociation  $D$ , sublimation  $S$ , and the energies of ionisation of cations  $I$  and anions  $E$ . In a bold attempt to apply Born's



theory to gaseous hydrogen chloride instead of solid sodium chloride, Haber obtained a heat of the (gaseous) reaction  $\text{H}^+ + \text{Cl}^- = \text{HCl}$  much smaller than that calculated by the cyclic process. In order to explain this discrepancy he introduced, as early as 1919, the idea of ionic deformation which later proved so fruitful in the hands of Fajans. His further studies in this field included the calculation of the heats of hydration of ions and a new theory of metals. The metal lattice he took to resemble that of a salt with electrons in the positions of the anions, but he soon abandoned the fixed electron lattice in favour of a mobile system of electrons. His discussions of the metallic state played an important part in the development of this difficult subject.

Haber's work on solids included a study of the conditions determining the crystalline or amorphous structure of precipitated particles and sols. Their nature must depend on the relative rates of (a) aggregation from the supersaturated solution to initially amorphous particles and (b) arrangement of the unordered atoms into a crystal lattice. Slow formation brings the latter into prominence and the particles tend to be crystalline, while rapid formation (high aggregation rate) gives amorphous particles which may crystallise slowly. This view was confirmed by X-ray analysis. For instance, ordinary precipitated ferric hydroxide is amorphous, whereas the sol formed slowly by hydrolysis contains crystalline particles. Only in rare cases, *e.g.*, colloidal gold, is the rate of arrangement so fast that the most rapid precipitation gives only crystalline particles. The X-ray method was also used in a study of the hydrous oxides of aluminium and ferric iron. It may be added that as early as 1904 Haber had examined the remarkable ageing properties of beryllium hydroxide. This summary of his work on solids may be concluded by remarking that Haber appears to have been the first to suggest (in 1914) that adsorption is due to the operation of unsaturated chemical valency forces of atoms on a solid surface, the basic idea of Langmuir's adsorption theory.

The Kaiser Wilhelm Institute had been in active operation for only two years when the war broke out in 1914. Work stopped abruptly, and Haber at once placed himself and his laboratories at the service of the War Ministry. The first weeks of the war found him actively engaged upon urgent problems of the supply of essential war materials. This vital factor had not been foreseen. The army had, it appeared, tacitly assumed that industry would supply its needs in war as in peace time, and thus the mobilisation plans included no steps to ensure this. In the matter of basic materials, Germany was in fact ill prepared, even for a short war. One of the first to perceive the significance of chemical industry in war, Haber was put in charge of the department of raw materials at the War Ministry. He recognised the most urgent problem to be that of fixed nitrogen and to this he gave his special attention. The sole source of nitric acid in Germany at that time was imported

Chile saltpetre, and the stock of this material was so low that the war might have ended in a few months but for the discovery of some 50,000 tons of nitrate at the Antwerp docks. Even this could give but a short respite—until early 1915—unless industry were to come quickly to the rescue. There was only one way, the conversion of ammonia into nitric acid, and this Haber energetically promoted. A small industrial plant working the Ostwald catalytic oxidation method had been in successful operation for some years, but its output was insignificant. It was the very rapid development of a new oxidation process by the Badische Anilin und Sodafabrik that saved the situation. At the same time the supply of ammonia was enormously increased by a ten-fold expansion of the already well-established cyanamide industry. By-product and cyanamide ammonia sufficed in fact to meet the demands of the army during the first two years, with very little to spare, however, for agriculture. The output of the Haber-Bosch plant, by no means large in 1914, was steadily increased, until during the second half of the war it greatly exceeded the cyanamide output (now stationary) and kept pace with the ever-growing demand. Beginning in 1913 with an output of about 6500 metric tons (of fixed nitrogen), the production of synthetic ammonia was roughly doubled in each successive year until at the end of the war it reached the huge figure of some 200,000 tons per annum. Without synthetic ammonia it is very improbable that Germany could have carried on the war so long as she did, and in this sense it may be said that Haber saved his country from premature defeat.

During the brief early period of mobile warfare when Haber was so busy with the organisation of supply, he received his first experimental problem from the War Ministry, and solved it by proving xylene and solvent naphtha to be satisfactory substitutes for toluene which had become no longer available as an anti-freeze agent for use with benzene motor fuel. The Battle of the Marne and the wholly unexpected development of trench warfare in September 1914 shattered the belief of the German General Staff in a short fast-moving war, and they found themselves confronted with two urgent and unforeseen problems, first, that of munitions supply on a scale vastly greater than had been anticipated, and secondly, the need of rapidly devising some means of driving the Allies out of their trenches and thus resuming open warfare, when their superior numbers and tactical training would, they thought, enable them to gain a speedy victory—time they recognised was on the side of the Allies. The use of irritant substances for the purpose of rendering confined positions untenable was by no means a new idea in the history of warfare; but the Germans, not anticipating trench warfare, had made no preparation for the employment of chemical weapons. It was the check on the Marne that first suggested their use. The War Ministry consulted Nernst and the early experiments were carried out with his co-operation. Some time later, towards the end of 1914, Haber was given a share in the work. The original device was merely to include irritant substances in the filling of normal shrapnel and high explosive shell. Applied in this manner during the autumn of 1914, first dianisidine chlorosulphonate, an irritant powder suggested by Nernst, then the lachrymator  $\omega$ -xylyl bromide, proved ineffective in actual warfare because the concentrations reached were too low. Owing to the extreme shortage of steel for shells consequent upon trench warfare, shells of cast iron were tried, but on account of their thicker walls and therefore smaller bursting charge they gave bad fragmentation (the lack of good quality high explosive was also a factor), and Haber was given the problem of increasing their effectiveness. The only available way was to employ these shells as a means of scattering some new irritant in sufficient quantity to be effective without however persisting long enough to hinder the advance of troops. Experiments in Haber's laboratory had barely begun when they were brought to a tragic end in December 1914 by the detonation of a bottle of dichloromethylamine \*

\* It appears that amongst other impurities nitrogen chloride may have been present. The explosion occurred as a few drops of the dichloromethylamine were being added to a few c.c. of (impure) cacodyl chloride contained in a test-tube. The latter substance had been suggested from an industrial quarter and sent to the Institute for trial. The sample inflamed in air, and it was thought that the dichloromethylamine might perhaps inhibit the inflammation while itself exerting an irritant action. The fact that cacodyl chloride was considered at all must be regarded as indicating that, while the main purpose of the chemicals employed was undoubtedly to exert an intolerably irritant effect at low concentrations, yet the circumstances that a substance might also act as a poison when breathed in sufficient quantity was not considered as excluding its use.

which instantly killed Otto Sackur, a member of Haber's staff and one of Germany's most distinguished chemists. The problem was thereupon abandoned.

In view of the shortage and inadequacy of shell, with or without the addition of chemicals, for combating static warfare, some new method was urgently needed. To attain the necessary concentration of gas over a sufficiently wide front, the idea arose of a mass discharge of gas from cylinders. Chlorine was adopted because it was immediately available, and Haber was put in charge of the preparations. Whether he was the first to suggest the use of this gas we do not know. While it is true that the responsibility for its actual employment must lie with the War Ministry, there is no reason to doubt that he favoured a trial of the new method. This modern "Greek fire" was apparently regarded as essentially a device for enforcing the abandonment of trenches. It seems clear that when the first chlorine cloud attack was made on April 22, 1915, at Langemarck (Ypres), no one realised how effective it would be and even Haber's expectations were exceeded. What happened was that owing to unfavourable winds the attack had to be postponed from day to day for a week (the soldiers losing confidence the while), and finally it took place on a short (6 km.) front late in the afternoon when only a few hours of daylight remained. As a result relatively little military advantage was taken of a great opportunity. Impressed by its potentialities, the military authorities at once decided to adopt the gas-cloud method and at the same time, recognising the urgent need of instituting gas defence, they requested Haber to concentrate upon the latter problem. After six months' intensive work at the Institute a very neat and ingenious respirator was issued to the troops (in October 1915), the main design of which remained almost unchanged to the end of the war. The lack of rubber imposed severe restrictions. Haber had to devise a close-fitting face-piece held in position by a head harness and supporting a small drum packed with absorbent materials to remove the harmful substances from the inspired air. The success with which this was attained within the limits of weight imposed by the form of the respirator represents a great achievement. With the later development of gas warfare the effectiveness of the absorbents was continually improved to meet the growing demands on the respirator without adding to its weight.

During 1915, while Haber was mainly occupied with the design and production of the respirator, the gas-cloud method gradually lost favour owing to the danger of "blow-back," to the prevalence of unfavourable winds, and to the difficulty of combining the cloud discharge with an infantry attack, which was the primary purpose for which it was intended. The use of lachrymators in shell was continued, but on quite a small scale. The Germans had, in fact, by the end of 1915 come to regard the gas weapon as of relatively little value. In the meantime the Allies had taken up the new arm and the Germans received a great surprise when, in the spring of 1916, the French introduced a new gas shell, containing phosgene (carbonyl chloride), with a small bursting charge. So effective was this new weapon that the views of the German War Ministry as to the value of gas shell underwent a sudden change. Haber was at once put in charge of the development of gas projectiles and became technical adviser to the army on both the offensive and the defensive side of gas warfare. The introduction of the French phosgene shell marked a turning point in chemical warfare, the beginning of an accelerated development which soon (1917) raised the gas arm to the position of a serious tactical factor. The purpose of gas had changed. Originally intended to drive men out of trenches by its irritant action, the coming of gas defence had the effect of bringing its lethal aspect into prominence. This aspect, fully developed in phosgene, was also present in the monochloromethyl chloroformate, a toxic as well as an irritant substance, which the Germans had in fact used some months earlier, but without much success. Competition between offence and defence became keen and unrestricted. Gas, like other weapons, was now intended to kill.

During the first two years Haber's responsibilities for gas warfare were limited, and further he was serving two masters, the General Staff and the Medical Service. Late in 1916, however, a separate Chemical Warfare Service was formed with Haber as its Chief. The Institute, greatly enlarged, was now organised as a military establishment, and here practically the whole of chemical warfare research was carried out until the end of the war. During the last two years Haber controlled the entire chemical warfare organisation, offensive and defensive, with responsibility for research, design, supply, and even the

selection and training of all gas officers and personnel. In addition, all orders and instructions for dealing with either aspect of chemical warfare were drawn up in the first instance by the general staff officer responsible for gas in collaboration with Haber. It was an immense responsibility for one man to carry, and his success in dealing with a situation that daily became more difficult owing to the effects of the blockade and the growing intensity of chemical warfare, showed that he possessed most unusual executive ability. Speed was an essential factor in the effective use of the new weapon, and this depended largely on Haber's quickness of decision and masterly control of its every aspect. It was an entirely new experience for a University professor but Haber showed that he possessed just the right personality for this tremendous task. Though it taxed his strength to the utmost he enjoyed the experience of controlling this great organisation and of getting soldiers and chemists to work together on a common task. It is not surprising that he won the full confidence of the soldiers for they admired such executive ability in a man of his high scientific distinction.

From 1916 onwards gas warfare offensive was mainly concerned with substances which could be used in projectiles, and the effort to counter the growing efficiency of respirators. Of the hundreds of substances examined the following were used during Haber's period of control: phosgene, trichloromethyl chloroformate (diphosgene), chloropicrin, dichlorodimethyl ether, phenylcarbylaminedichloride, ethyldichloroarsine, diphenylchloroarsine, diphenylcyanoarsine, and dichlorodiethyl sulphide (mustard gas). The last substance, discovered in 1886 by Victor Meyer, who reported its remarkable action on the skin and eyes, was the most effective chemical agent of the war. It caused large numbers of casualties, only a small proportion of which were fatal, and raised new problems of defence. It was introduced in July 1917 and used by the Allies after June 1918. The Germans were well aware that their gas weapons would be turned against them and the danger of this had to be taken into account. It is related \* that when the use of this substance as a war gas was first suggested to Haber he reported its properties to General Ludendorff but advised against its adoption unless it was certain that the war would be over in a year, for he estimated that it would take the Allies a year to retaliate in kind. If they did so retaliate then, said Haber, this gas would bring about the certain defeat of Germany. Ludendorff took the risk. A year after its introduction the war was still going on and the Allies had just begun to use mustard gas. The collapse came, however, from other causes and before this substance had been employed on the scale and with the decisive results that Haber had predicted.

This is no place, nor would it serve any good purpose, to revive the controversial questions of international law and responsibility for the first introduction of gas warfare which were so much discussed during the immediate post-war years. The new chemical weapon was held in general execration and Haber was in some quarters accused of having committed an unforgivable crime against humanity. He was never himself concerned with decisions under international law, and his duty as an army officer was to advise and obey those responsible for higher policy. At the same time he did in fact find himself in general agreement with the policy of the War Ministry regarding chemical warfare, † and disputed not only its inhumanity but also the responsibility of the Germans for its first introduction. His views on every aspect of the question were fully expressed in two interesting essays ‡ to which reference may here be made.

\* General Max Hoffmann : "Der Krieg der versäumten Gelegenheiten," Verlag für Kulturpolitik, München, 1923, p. 173.

† "Mit der völkerrechtlichen Zulässigkeit der Gaswaffen bin ich niemals befasst worden. Auch habe ich in den Akten des Kriegsministeriums aus den ersten Kriegsjahren nichts darüber gefunden. Dieser Seite der Sache hat der Generalstabschef und Kriegsminister v. Falkenhayn offenbar persönlich geprüft. Aber wenn er mich auch niemals um meine Rechtsauffassung gefragt hat, so hat er mir doch keinen Zweifel darüber gelassen, dass es für ihn völkerrechtliche Grenzen gab, die er strenge innegehalten wissen wollte. Niemals würde er die Vergiftung von Nahrungsmitteln, Brunnen oder Waffen gebilligt, niemals Waffen oder Kampfweisen erlaubt haben, die nutzlose Leiden schufen. Unzweifelhaft war er überzeugt, mit dem Völkerrecht durch seine Anordnungen auf dem Gaskriegsgebiet nicht in Widerspruch zu treten. Eine entgegengesetzte eigene Meinung würde mich von der Mitarbeit zurückgeschreckt haben."—F. Haber, "Fünf Vorträge," Berlin, Julius Springer, 1924, p. 76.

‡ F. Haber, "Fünf Vorträge," Berlin, Julius Springer, 1924.



*F<sup>r</sup> Fritz Haber*

[To face p. 1661.]

The war years were for Haber the greatest period of his life. In them he lived and worked on a scale and for a purpose that satisfied his strong urge towards great dramatic vital things. For three or four generations back his family had served and fought for Germany. To be a great soldier, to obey and be obeyed—that, as his closest friends knew, was a deep-seated ideal. During his period of military service he had done exceptionally well, but the Jew did not become an officer. Early in the war he received the special and very unusual promotion directly to the rank of captain. Higher rank he did not attain though he ardently desired it. He was nevertheless a very influential military man and the consciousness of this brought him great satisfaction. It must not however be supposed that he exalted and enjoyed war *as such*—on the contrary in his heart he hated its wastage and suffering; but the coming of war brought out another side of his nature and transformed him into a Prussian officer, autocratic and ruthless in his will to victory. In normal times this latent tendency was completely suppressed, or appeared rather as great strength of purpose in a man whose true nature was kindly and benevolent. It must be remembered that at all times he put Germany first. The outcome of the war was a terrible tragedy for him. He had given all his strength, his whole being, to the struggle for victory. Unlike many of his colleagues who, in the last phase, came to see that there could be no victory, Haber maintained to the very end an invincible faith that Germany must win through unbeaten. The end was a great shock for him and he suffered deeply, so deeply that he became a changed man and never quite recovered his former self.

It was with a heavy heart that Haber turned to the reconstruction of his Institute. At this time he seemed a completely disillusioned and broken man, weighed down by the unbearable burden of failure and depressed by the unhappy personal repercussions of chemical warfare. Furthermore, his health had become permanently damaged by the constant strain and overwork of the war years; but his indomitable spirit soon rose again, and with the shaping of new plans and far-reaching aspirations he regained much of the energy and enthusiasm so characteristic of him. In re-establishing the Institute he felt strongly that the opportunity should not be missed to develop the extensive and varied scientific knowledge which had been gained under his direction during the war, and to apply it to beneficent ends. In addition therefore to the departments of Physical Chemistry, Physics (under James Franck), and Colloid Chemistry (under Freundlich), he introduced sections on Organic Chemistry, Pharmacology, Insect Pests, and Textile Chemistry, all working in close co-operation under his general control. During the first year all went well. Then came the Inflation. Money melted away and Haber's ambitious scheme had to be restricted until only Physical and Colloid Chemistry remained. However a few years later (1924—5) the position improved, Physics was reinstated under Ladenburg, and Polanyi joined the Institute about the same time. So things remained until 1933.

As on the outbreak of war, so with the coming of the Inflation, Haber strove his utmost to find a way of helping his country, this time out of her desperate economic situation. New industrial developments, to which he gave much thought, would take too long. As the immediate bar to Germany's recovery both then and in the future there loomed the demand of her former enemies for war reparations to be paid in gold—132 milliard marks or, as Haber expressed it, 50,000 tons of gold. Remembering the Arrhenius estimate of eight thousand million tons of gold in the sea, he conceived the heroic and highly dramatic idea of paying reparations from this source. Few men of his eminence would have had the courage to risk their reputation on such a quest, nor would he have done so in normal times. In 1920 then, having concluded after the most careful examination of the problem, that the prospects were not unfavourable, he decided to make the attempt with all the resources at his command, and soon a group of a dozen experienced men under the leadership of Johannes Jaenicke \* were at work on methods of analysis and processes for the economic extraction of gold. Reviewing the nine published determinations of gold in the sea, Haber was struck by the fact that, although they varied widely, yet they tended to group around the value 5—10 mg. per metric ton (micrograms per litre) of sea water, and at first (up to 1923) his own analyses gave results of the same order. For various reasons, including the difficulty of

\* An excellent review of the "Gold Episode," to which the writer is much indebted, is given by Johannes Jaenicke in *Die Naturwissenschaften*, 1935, **23**, 57.

obtaining regular and satisfactory deep-sea samples, the methods of analysis and extraction were studied not with natural but with an artificial standard sea water containing what appeared to be the most probable amount of gold, namely, 5  $\mu\text{g}$ . (as gold chloride) per litre. Several analytical methods, of which the most satisfactory was that of microcupellation of the gold carried down by a precipitate of lead sulphide, were elaborated until, when tested on the above standard, they gave about the right amount of gold, and thus when these methods were applied to actual sea water the analyses were accepted as reliable, and, although the number of samples analysed was small, the results were regarded as sufficient to confirm beyond reasonable doubt the presumed gold content of about 5 mg. per ton. Thus it came about that at quite an early stage of the work attention was directed mainly to research on methods for the economic extraction of gold *at this concentration*. The principle finally adopted was to render the minute particles of gold filterable by loading them with a minimal amount of another substance. On adding less than a gram of sodium polysulphide per ton of (artificial) sea water the carbonic acid present precipitated sulphur which reduced heavy-metal ions (it was an advantage to add a trace of copper salt), and the gold-bearing particles of sulphur could be rapidly filtered off through sulphur-coated sand. The gold was thus completely removed and the concentrate could be worked up easily. The cost of this simple operation on the large scale at sea would be covered by a few milligrams of gold per ton and with the 5 mg. believed to be present success seemed assured. Without delay, therefore, a ship was fitted with filtration plant and laboratory, and in high hopes Haber with four of his staff crossed the North and South Atlantic (coastal waters were variable and contained too much suspended matter). To their great astonishment and dismay they found only a small fraction of the expected amount of gold. It seemed incredible that the analyses should have erred in giving far *too much* gold, yet this conclusion was unavoidable in view of the undoubted efficiency of the extraction process. The basis of Haber's project was thus destroyed but even now he did not abandon all hope—there was the possibility that regions existed with constant higher gold contents—and apart from the economic aspect he determined, having gone so far, to find out the truth about gold in the sea. And so in 1924 he began the last and in many respects the most important stage of this enquiry with a scheme for the systematic collection of samples from all the seas for analysis at Dahlem, and a searching study and refinement of the analytical methods. The result was surprising. When methods that proved satisfactory for concentrations of the order of several milligrams per ton (as used in the earlier stage) were applied to water containing a tenth or a hundredth of this amount, then it became apparent that the error lay not, as had always been assumed, in the loss of gold but in its gain from outside sources, so that the earlier determinations on actual sea water came out much too high. Distributed as widely if not as plentifully as sodium and iron, gold and silver from all the reagents and vessels employed found their way into the minute bead of metal formed in the microcupellation process. With the elimination of this source of error and improvement in the separation of the silver, less and less gold was found in the samples of sea water until eventually the amount fell to a thousandth of that originally assumed. After a long period of the most exacting research a technique was evolved \* by which  $10^{-8}$  g. of gold in a litre of water could be directly determined with an error of only  $\pm 3\%$ , and  $10^{-10}$  g. with an error of  $\pm 50\%$ , the limit even then being set not so much by the method as by the demands

\* The following is an outline of the method finally adopted for sampling and analysis: On taking the samples in 2-l. glass bottles a little lead acetate was added followed by sodium sulphide, the gold being carried down in the precipitate of lead sulphide. When received for analysis a second lead sulphide precipitation was made, and after filtration the residue containing all the silver and gold was dissolved by treatment with hydrobromic acid and bromine. After addition of ammonium sulphide the heavy-metal sulphides were centrifuged into 8-c.c. V-shaped crucibles of unglazed porcelain, reduced by hydrogen or lead formate, melted with boric acid, and cupelled down to a 5 mg. bead. This was transferred for further cupellation to a small, thin-walled, unglazed, porcelain dish and the final gold-silver bead measured under the microscope. Lastly, the silver was removed by heating to  $1100^\circ$  with borax for two minutes and the minute gold bead measured microscopically. All reagents were free from gold and silver and at every stage the most meticulous care was taken to avoid adventitious gain of these metals. In practised hands this microcupellation method was capable of an extraordinary degree of accuracy.

made on the patience and dexterity of the analyst. It was not until 1926 that Haber finally abandoned all hope of economic success. The interest shifted to Oceanography and in 1927 a research ship went out to study the depth distribution of gold and its relation to plankton distribution. With the completion of this survey the gold episode came to an end in 1928.

The failure of this great purpose upon which Haber had so set himself was a bitter disappointment, which affected him more deeply than he allowed to appear. Was the Atlantic expedition of 1923 premature? Why did Haber not first discover the true gold content of the sea? Why in the early stages were so few analyses of actual sea water made? The post-war restriction of German shipping and the need for secrecy rendered the supply of reliable samples very difficult, but since the latter did in fact give results of the order indicated by earlier investigators, a relatively small number of samples were regarded as sufficient to confirm the order of the gold content. Haber undoubtedly over-rated the work of the earlier investigators and attached too much weight to the estimate which he made from their confused data. Further, the rapidly deteriorating economic situation in Germany and particularly the occupation of the Ruhr District were powerful factors urging Haber to develop the extraction process and to lose no time in putting it into practice.

It was Haber's purpose to write a monograph on the scientific yield of these years of exacting labour. Depression and ill-health delayed the project, the workers became scattered, other interests arose, and thus the monograph was never written. It was in the field of analytical method and microchemical technique that the greatest advances were made. Unfortunately they have not all been fully recorded. We are indebted to Haber for establishing at last the truth about gold in the sea, namely, that its average concentration does not exceed a thousandth of a milligram per ton, it occurs mainly as the metal (associated with suspended matter) rather than in solution, and consequently samples are very variable and may, rarely, have a misleadingly high gold content. Incidentally it is noteworthy that when in 1924 Miethe and Stammreich in Germany and Nagaoka in Japan independently reported the transformation of mercury into gold under the influence of an electric discharge, Haber performed a useful service by demonstrating with the aid of his new analytical technique that the gold was, as he suspected, all derived from the materials employed.

After the war Haber's Institute became one of the greatest centres of research in the world. Fundamental advances were made in atomic physics and spectroscopy. The collision of electrons with atoms and molecules was studied; the occurrence of resonance phenomena in the collision of atoms and molecules was for the first time experimentally demonstrated; absorption spectra of a new kind were found in the ultra-violet representing a transition stage to the X-ray absorption spectra; para-hydrogen was discovered and thoroughly investigated; pioneering work was done on the chemistry and physics of free atoms, and great advances were made in colloid chemistry. In Haber's own field, the mechanism of chemical and photochemical reactions, much new ground was broken and a wealth of fundamental knowledge gained. With every section he maintained constant and effective touch in spite of the increasingly heavy outside claims upon his time. In the 22 years 1912—1933, more than 700 original papers were published from the Institute. Of its sixty members (1929), nearly half were foreigners of a dozen nationalities. An interesting feature was the participation of foreign and German guests in the work of the Institute. They lived in the neighbouring "Harnack House," a splendidly equipped club house which the government had established to provide a centre of intercourse between German and foreign men of science.

The significance of Haber's Institute went much further than its output of research. From his earliest days at Karlsruhe, Haber always attached the greatest importance to the Colloquium. Again at Dahlem the fortnightly Colloquium formed a vital part of the life of the Institute. So valuable and stimulating were these meetings under Haber's inspiring leadership, that visitors came in increasing numbers until the "Haber Colloquium" became a widely known institution which exerted a strong influence on scientific life and work in Berlin. It was attended not only by the Berlin chemists and



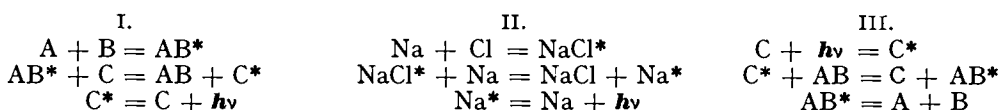
physicists, but by leaders of science from distant parts of Germany and even from abroad. Its meetings were reported in the appropriate periodicals just like those of the learned societies. In the Colloquium Haber was at his best. Here came out one of his most brilliant qualities, the capacity to grasp quickly the essentials of subjects not his own, to perceive their true bearings beyond the details, to discover errors, to indicate lines of advance. He had a genius for guiding discussion into the most profitable channels, for resolving obscurities and bringing the essential things into a clear light. He really could think aloud as he stood before his audience, in a way that aroused the wonder and admiration of all. One could never tell what would be his reaction to a new idea or to an account of new experiments and theories; it was generally unexpected and always original and stimulating.

After the war Haber's constant devotion to the national good led him to employ his great influence and talent for organisation in a wider sphere than the Dahlem Institute. When scientific research and the cultivation of science generally throughout Germany became seriously threatened by the Inflation, he not only led a vigorous campaign to uphold at all costs scientific training and research as a vital factor towards his country's recovery and future health, but in order to meet this pressing national danger in a practical way he brought into being a great scheme for the financial support of research and training throughout Germany. Established under the presidency of the Minister of Education with Haber as its effective leader, the "Notgemeinschaft der deutschen Wissenschaft" united the Government, the learned Societies, the Universities, the Kaiser Wilhelm Society, and other research interests into one national body for the purpose of allocating grants. To Haber mainly fell the burden, which he willingly shouldered, of maintaining the organisation at the high level of usefulness that he desired. Germany owes him a very great debt of gratitude for the immense service he rendered in protecting his country's science which he regarded as one of the main pillars of her strength. To Haber also was due the promotion of friendly relations between German chemists and those of other countries, a difficult task in the bitter atmosphere of the post-war years. Progress was hindered by the non-existence in Germany of an organisation competent to deal with questions of international co-operation, and it was not until 1928, after years of untiring effort, that he at length succeeded in creating the "Verband deutscher chemischer Vereine." As its President he represented his country on the Board of the Union Internationale de Chimie from 1929 to 1933, where he earned the highest regard for his statesmanship and devotion to the cause. He was particularly anxious to establish good relations with France and his efforts were greatly appreciated by the French chemists.

After the gold failure, Haber made a journey round the world and spent two months in Japan. The Japanese government conferred upon him the highest possible honour. He took an official part in a national commemoration in honour of his uncle Ludwig Haber, formerly German Consul in Japan, who had been killed fifty years earlier by a fanatical Samurai. The Japanese visit was an important incident in Haber's life. He met leading politicians, scholars, and industrialists, and studied with eager interest every aspect of Japanese life. His writings on Japan betray the sympathy of his restless striving spirit with this people which, like the Prussians, had won power by the force of its will and training. His analysis of the state of industry and education in Japan and his estimate of her economic and political significance led him to advocate close relations between Germany and Japan. So strong were his convictions that he determined himself to take immediate action, and in 1936 he established The Japan Institute, consisting of two parallel institutes, one in Berlin, the other in Tokyo, each with a German and a Japanese director. This unique twin institute for promoting mutual understanding and cultural interests between widely different peoples was recognised and financially supported by both governments. Opening the Berlin Institute Haber said: "We believe that in the long run every nation will best serve other nations as well as itself by learning to understand their thoughts and feelings." He always tried to do this.

Returning to Haber's scientific work, we find him in the early post-war years taking up again the fundamental problems arising out of his studies on flame. Of the two main

characteristics of the Bunsen flame, luminescence and ionisation, the latter had already led him to the discovery of electron emission in chemical reaction. He now attacked the familiar but little understood phenomenon of chemiluminescence. For the correlation of the thermal and radiant energies involved he employed the well-defined gaseous reaction of sodium with halogen. A jet of nitrogen containing sodium vapour was found to give, in an atmosphere of halogen, a purely chemiluminescent flame emitting the sodium lines at a temperature well below  $500^{\circ}$  (no visible thermal radiation). The simple unequivocal character of this reaction enabled him to make a fundamental advance, namely, the interpretation of chemiluminescence as a reversal of photochemical or sensitised photochemical reaction, the reaction proceeding through the intermediate formation of excited sodium atoms  $\text{Na}^*$  which may emit their excess energy by radiation. The source of their excitation energy was the heat of reaction which was transferred to a normal sodium atom in its inelastic collision with the primary high-energy product  $\text{NaCl}^*$ . The process was of the general type (I), the third energy-removing body C being in this particular case (II) a sodium atom.†



Actually only a small fraction of the reaction heat was radiated, since  $AB^*$  was mainly deactivated by collision with other molecules, its energy thus appearing as heat. Experiment showed the condition for resonance radiation to be that the heat of reaction  $Q$  shall exceed  $h\nu$  where  $\nu$  is the frequency of the sodium line and  $h$  is Planck's constant. With mercury in place of sodium no radiation occurred,  $Q$  being much less than  $h\nu$  (for mercury). Plainly, the whole process was the reversal of the sensitised photochemical reaction (III). Haber's pioneer work threw for the first time a clear light on the obscure field of chemiluminescence and provided a sure basis for its subsequent development.‡ It gave rise in the hands of Polanyi at Dahlem to a refined technique and a brilliant series of researches on low-pressure reactions of this type which led to great advances in our knowledge of reaction mechanism. Haber himself employed the Polanyi technique of the "highly dilute flame" to elucidate the mechanism of the reaction between sodium vapour and oxygen.§ Further researches on chemiluminescence, many emanating from Haber's Institute, have confirmed the principles which he laid down. Notable amongst these were the brilliant studies on atomic hydrogen by Bonhoeffer, who found that the heat of combination of hydrogen atoms to a hydrogen molecule may by inelastic collision activate a third atom such as sodium to emission of its resonance radiation. It is interesting to note that Haber's electron emission on the one hand and light emission on the other, as a direct consequence of chemical reaction, now appeared as different aspects of the same phenomenon, for the reaction heat may suffice to raise an electron to a higher quantum level (light emission) or to remove it altogether (electron emission). His later work showed, indeed, that these two processes even took place by essentially the same mechanism, for in the electron-emitting reaction between metal and halogen the primary product transfers its high energy to the metal which may then emit an electron. Heat of reaction is transferred to a third body which may either radiate or become ionised.

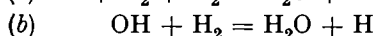
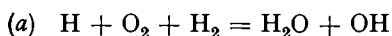
The first decade after the war was a period of rapid advance in the field of the kinetics and mechanism of chemical reaction under the stimulus of the new knowledge on atomic structure and the inter-relation of matter and energy. Haber's school became famous as

† Actually, since the primary process must involve  $\text{Cl}_2$  and not  $\text{Cl}$ , Haber tentatively suggested  $\text{Cl}_2 + \text{Na} = \text{NaCl}_2^*$  followed by  $\text{NaCl}_2^* + \text{Na} = \text{NaCl}_2 + \text{Na}^*$ , the  $\text{NaCl}_2$  becoming  $\text{NaCl}$  in subsequent processes. Polanyi later showed the mechanism to be  $\text{Cl}_2 + \text{Na} = \text{NaCl} + \text{Cl}$ , followed by  $\text{Cl} + \text{Na}_2 = \text{NaCl} + \text{Na}$ , wherein the  $\text{Na}$  atom becomes excited to radiation.

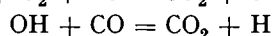
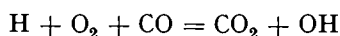
‡ Kautsky, working in Haber's Institute, made at the same time similar suggestions to explain his remarkable discovery of the chemiluminescent oxidation of certain unsaturated silicon compounds, and strongly supported Haber's theory as a general theory of chemiluminescence.

§ See p. 1669.

a centre of research in this field, where the main lines of development again had their origin in his life-long interest in problems of flame and combustion. From this source had already sprung his discovery of electron emission in chemical reaction and the principles of chemiluminescence. But the old questions relating to the flame itself, its reaction mechanism, luminosity, and conductivity still remained open, and to these problems he now addressed himself, equipped with knowledge and methods not at his disposal when he attacked them twenty years earlier. His first paper "On Band Spectroscopy and Flame Processes," written in 1928 in collaboration with Bonhoeffer, is remarkable for the wealth of ideas and fruitful suggestions which it contains. Pointing out that hitherto the mechanism of combustion of hydrogen, carbon monoxide, and hydrocarbons had been studied by means of analytical and pyrometric observations only, no attempts having been made to utilise flame spectra (apart from some early experiments by Haber's pupil A. Reis on the flames of some nitrogen compounds), these authors undertook for the first time a systematic examination of possible flame-reaction processes in the light of band-spectroscopic and thermal data. The characteristic ultra-violet band system produced by flames of hydrogen and its compounds (the "steam band" system of early spectroscopy) was now known to have its origin in the hydroxyl radical, and Bonhoeffer in Haber's laboratory had just proved its free existence as a product, with hydrogen, of the thermal dissociation of steam at 1250°. These facts together with thermal considerations led them to the firm conviction that the hydroxyl radical played an essential rôle in the flame reactions. The alternative oxidation stages,  $\text{H}_2\text{O}_2$  and  $\text{HO}_2$ , had been proposed two years earlier by Marshall and Taylor, who suggested that the mercury-sensitised photochemical union of hydrogen and oxygen at ordinary temperature yielding hydrogen peroxide proceeds by the chain mechanism (a)  $\text{O}_2 + \text{H} = \text{HO}_2$ , (b)  $\text{HO}_2 + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$ , but Haber found himself unable to accept these compounds as stages of the ordinary high-temperature reaction owing to lack of experimental evidence of their actual presence (the production of hydrogen peroxide by the ice-chilled flame was regarded as no proof of its existence in the normal flame). At this time the characteristics of chain reactions were well known and the general theory had just been developed by Semenov. Assuming flame reactions to be of this type, Haber and Bonhoeffer proposed the first chain mechanism for the combustion of hydrogen. Their scheme gained wide acceptance and held the field for many years, stimulating much research on this complex question. They were careful to employ only reaction components for the presence of which there was satisfactory experimental evidence, and reactions that were thermochemically probable. Further, their discussion of the possible elementary processes was informed by the new principle according to which those involving atoms or radicals require little or no activation energy. The "Haber chain," as it came to be called, was propagated by the hydroxyl radical and hydrogen atom in accordance with the scheme I [as modified in 1930, the original process (a) having been  $\text{H} + \text{O}_2 + \text{H} = 2\text{OH}$ ]:



Scheme I.



Scheme II.

Haber naturally considered in place of (a) the coupled binary collision processes,\* (i)  $\text{H} + \text{O}_2 = \text{HO}_2$ ; (ii)  $\text{HO}_2 + \text{H}_2 = \text{H}_2\text{O} + \text{OH}$  but preferred the ternary process because it avoided the hypothetical molecule  $\text{HO}_2$ . The most probable chain-starting process was regarded as  $\text{H}_2 + \text{O}_2 = 2\text{OH}$ , and the dissociation of hydrogen molecules by collision with high-energy primary products was not overlooked. Chain branching was provided by the reactions  $\text{H} + \text{O}_2 = \text{OH} + \text{O}$  and  $\text{O} + \text{H}_2 = \text{OH} + \text{H}$ , and breaking occurred at the walls and by the recombination of atoms or radicals. The testing of this theory led Haber to make some striking discoveries. The introduction of hydrogen atoms into a mixture of hydrogen and oxygen led, as expected, to explosion at temperatures far below the normal ignition temperature. The small but sufficient concentration

\* Compare the Marshall and Taylor scheme in which the second stage yields  $\text{H}_2\text{O}_2 + \text{H}$ .

of atomic hydrogen was produced not only directly, by passage of hydrogen gas through a tungsten arc on its way to a vessel of oxygen, but also indirectly by the photochemical decomposition of ammonia or hydrogen sulphide present in small proportion in the explosion mixture. Oxygen atoms produced by similar methods were also very effective chain starters. In the case of photosensitisation by ammonia the remarkable discovery was made that a short irradiation induced a relatively slow dark reaction culminating in explosion at the point where the rate of chain branching overtakes that of breaking. This particular case was, as Haber recognised, complicated by the probable participation of the radical  $\text{NH}_2$  as well as atomic hydrogen. In all these experiments practically the same results were obtained when *undried* carbon monoxide was substituted for hydrogen. The remarkable similarity in behaviour of the two systems led Haber to adopt the same mechanism (Scheme II) of combustion for undried carbon monoxide as for hydrogen, and this scheme gained general acceptance. The many researches of the decade following Haber's entry into this field in 1928 have, broadly speaking, upheld and developed his main ideas. Studies on the combustion of hydrogen have brought into prominence the transitory molecule  $\text{HO}_2$  as an intermediate product and favoured binary rather than ternary collision processes, but full agreement as to the details of the mechanism of this complex reaction has hardly yet been reached. It is a remarkable testimony to Haber's chemical insight and power to apply new physical concepts that his original reaction scheme should have held with so little essential modification.

At the outset of Haber's investigations in this field Hinshelwood and Thompson discovered the low-pressure explosion region for hydrogen. At temperatures well above  $500^\circ$  hydrogen-oxygen mixtures combine explosively, but in the neighbourhood of this temperature slow combination occurs almost wholly on the walls of the containing vessel. If, however, in this temperature region the pressure of the gas mixture is gradually lowered, explosion occurs at a definite critical pressure, this upper pressure limit  $p_2$  being about 100 mm. at  $550^\circ$ . As the pressure is still further reduced, a lower pressure limit  $p_1$  (a few mm. only at  $550^\circ$ ) is reached below which inflammation does not occur.\* A similar low-pressure explosion region had previously been discovered by Semenov in the case of the combustion of phosphorus, and subsequent investigations on various substances (including the case of carbon disulphide by Thompson in Haber's laboratory) have shown the phenomenon to be general. Why should explosion develop so suddenly at a sharply defined pressure? To answer this question Haber proposed first to study the effect of eliminating any influence of the surface of the containing vessel. To this end, in collaboration with Alyea, he caused a stream of oxygen to impinge at right angles upon a stream of hydrogen in an atmosphere of nitrogen under controlled conditions of temperature and pressure.† Above  $560^\circ$  and at atmospheric pressure homogeneous ignition occurred, but when conditions were such that the confluent gases were within the low-pressure region of explosion in a containing vessel, ignition did not take place. If, however, a rod of quartz, porcelain, or glass at the same temperature as the gas mixture was introduced at the crossing place the gases immediately inflamed as if lit by a match, and the flame went out again on removing the rod. By these experiments it was established for the first time that, although at high temperatures reaction chains can start in the gas phase, yet in the explosion region of low pressure and reduced temperature the chains originate mainly on the walls whence they go out into the gas as branching chains. Previously, surfaces had been supposed to have a chain-breaking effect only. On the basis of this discovery, Haber attempted to explain the two pressure limits. The lower pressure he considered to be the limit of flame propagation by the chain mechanism, very sensitive to diminishing pressure on account of its triple collision stage (according to present-day views,  $p_1$  is determined by the predominance of chain breaking on the walls). He interpreted the upper limit by supposing that with increasing pressure the number of effective reaction centres entering the gas from the surface diminishes owing, according to his first suggestion, to their back reflexion by the gas and re-adsorption, an idea which, however

\* See "The Reaction between Hydrogen and Oxygen," C. N. Hinshelwood and A. T. Williamson, Clarendon Press, Oxford, 1934.

† The method of crossed streams was first tried by von Wartenberg and Kannenberg in 1923.

he soon abandoned in consequence of his observation that  $p_2$  was appreciably influenced (in opposite senses) by pretreatment of the surface with hydrogen and oxygen. This gave rise to the idea, expressed by Aleya, that, owing to its firm adsorption at higher pressure, few chain-starting hydrogen atoms are released into the gas, but as the pressure falls to  $p_2$  the replacement of hydrogen by adsorbed oxygen liberates sufficient hydrogen atoms to initiate explosion. Haber's proof that in the low-pressure region chains start from the walls does not imply that the pressure limit  $p_2$  is determined by surface effects, and it is now generally agreed that a decreased rate of chain-branching *in the gas phase* with increasing pressure is responsible for the upper pressure limit.

Haber considered the possible rôle of other radicals present in flames. The band spectra of burning carbon monoxide (undried) and hydrocarbons were known to have as their sources not only hydroxyl but also the radicals dicarbon  $C_2$  (the green-blue Swan bands) and methine CH (blue-violet). It was shown in Haber's laboratory that these radicals could be formed at ordinary temperature by the action of atomic hydrogen or oxygen on hydrocarbons (except methane). An interesting outcome of these studies was Haber's suggestion that in the flame the hydrocarbon molecule may be stripped down to CH or  $C_2$  radicals by successive reactions of the type  $C_mH_n + H = C_mH_{n-1} + H_2$  and  $C_mH_n + OH = C_mH_{n-1} + H_2O$ . Of great interest also is his proposal of a two-stage combustion of dicarbon, (i)  $C_2 + OH = CO + CH$ ; (ii)  $CH + OH = CO + H_2$ , which might, he thought, account for the change of colour of the Bunsen inner cone from green to blue as the air supply is increased. These suggestions have not been developed and little is known of the rôle of the  $C_2$  and CH radicals. It will be recalled that Haber's earliest studies of the Bunsen flame led him to associate the relatively high electrical conductivity of the inner cone with its enormous reaction rate and its luminosity, and he was at first inclined to think that gas ions, as such, played an essential part in the reactions of the explosion zone. He was now able to establish that gas ions play no such rôle, and this conclusion is generally accepted. The nature and origin of this ionisation remains an open question.

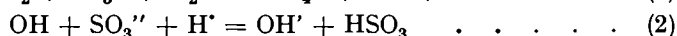
Amongst Haber's further studies in this field may be mentioned his discovery of the extremely rapid conversion of para- into ortho-hydrogen on passing through the flame front (compare the rapid establishment of the water-gas equilibrium on passing through the Bunsen inner cone); the widening of the explosion region by magnesia dust; diffusion effects in flame; the explosion of air charged with a mist of liquid fuel; and the behaviour of acetylene in internal-combustion engines.

The problem of autoxidation occupied an important place in Haber's scientific career. Attracted to this field during his early association with Carl Engler at Karlsruhe, he succeeded as far back as 1900 in throwing new light on the question by studying it from an electrochemical point of view. Various aspects of oxidation by free oxygen (*e.g.*, in flame and explosion) occupied his attention until, thirty years later, he again took up the question of wet autoxidation and found in its investigation the main interest of his last years. These researches, in spite of his serious ill-health, show all his characteristic vigour and insight and are remarkable for their wealth of new ideas and suggestions for future development. His last paper, which he completed at Cambridge a few days before his death, was connected with this theme.

Early theories of autoxidation were directed to the explanation of induced oxidation and the equal sharing of the absorbed oxygen between the "inducer" (M) and the "acceptor" (X), this equal sharing being regarded as the characteristic feature of the process. The splitting of an oxygen molecule,  $M + O-\dot{O} + X = MO + XO$  (where X was commonly  $H_2O$ ), appeared improbable at ordinary temperatures. The difficulty was met by Moritz Traube's scheme:  $M + 2HO-\dot{H} + O_2 = M(OH)_2 + H_2O_2$ , and this was later eclipsed by the "moxide" (or peroxide) theory of Engler, Wild, and Bach: (a)  $M + O_2 = MO_2$  followed by (b)  $MO_2 + X = MO + XO$ . This theory had the advantage of wide applicability and, further, the peroxide could sometimes be isolated and shown to react with water (X) giving hydrogen peroxide (XO). Haber made an illuminating contribution to the subject of wet autoxidation by the study of galvanic cells  $M|M^{++}; (H_2SO_4 \text{ aq.}); H_2O_2|Pt(O_2)$ , in which anodic oxidation of the base metal M (or an

oxidisable solute at an inert electrode) is associated with the cathodic process :  $2\text{H}^+ + \text{O}_2 + 2e \rightleftharpoons \text{H}_2\text{O}_2$ , the cell reaction being the typical wet autoxidation :  $\text{M} + 2\text{H}'\text{OH}' + \text{O}_2 = \text{M}(\text{OH})_2 + \text{H}_2\text{O}_2$ . He laid great stress on the fundamental nature of this concept. It is significant that at this early stage he recognised the connection between such oxidation reactions and electrochemical elementary processes, for this idea formed the kernel of his last researches. A generation later he again took up this problem in the light of the new principles of reaction mechanism to which he had himself so largely contributed. There was now no longer any difficulty about the participation of atoms and short-lived radicals. It is noteworthy that the first direct kinetic proof of primary "molecule" formation had in the meantime been provided by Haber in his study of the reaction between sodium vapour and oxygen gas,\* the mechanism of which was shown to be  $\text{Na} + \text{O}_2(+\text{X}) = \text{NaO}_2(+\text{X})$  (where X is a third energy-removing body), followed by rapid combination of the molecule with sodium to give the final product.

In 1928 Haber took up the study of the oxidation of sodium sulphite in aqueous solution by free oxygen. His interest in autoxidation was strongly revived by Bäckström's discovery of the chain character of this reaction. The nature of the chain was unknown. Having just worked out the chain mechanism of the gaseous oxidation of hydrogen, he set out to discover that of sulphite oxidation by the application of similar ideas. The main features of this reaction, the most thoroughly investigated of its type, were its acceleration by copper salts, by ultra-violet light, and by oxidising agents. Guided by the thought that all three agencies might produce the same chain-starting radical, Haber was led to postulate the unknown weak "monothionic acid"  $\text{HSO}_3'$ , or its anion  $\text{SO}_3'$ , as the essential radical,† since all three agencies in the absence of oxygen were found to yield sufficient dithionic acid to warrant this assumption. Every aspect of both the thermal and the photochemical reaction was worked out in great detail by a team of experienced men. It was the study of this special case which led Franck and Haber to propose an important modification of Franck's original interpretation of the absorption spectra of anions as electron-affinity spectra. The absorption of a light quantum previously associated with a single electron transfer from anion to solvent water now involved its transfer from anion to a molecule of bound (hydrate) water whereby in the one act a hydrogen atom and a hydroxyl ion were formed. This concept of the change of position of an electron in a molecule was significant for the general question of activation in chemical reaction. In the case of sulphite the photochemical primary act was thus  $\text{SO}_3'', \text{H}_2\text{O} + h\nu \rightarrow \text{SO}_3' + \text{OH}' + \text{H}$ , the chain starting from  $\text{HSO}_3'$  and not, as at first supposed, from a photo-excited molecule. The action of copper ions was similar :  $\text{Cu}'' + \text{SO}_3'' \rightarrow \text{Cu}' + \text{SO}_3' \rightarrow \text{HSO}_3'$ ; in fact, the essential chain-starting process was always  $\text{SO}_3'' - e = \text{SO}_3'$ . Haber's sulphite oxidation chain ran parallel with that which he proposed for flame reactions, the chain carriers being  $\text{HSO}_3'$  and  $\text{OH}'$  :

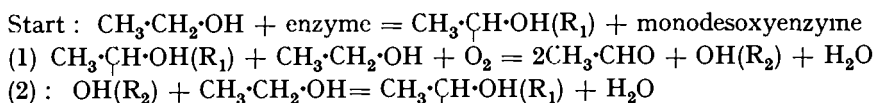


Although this special mechanism bore no implications for autoxidation processes generally, nevertheless Haber regarded it as embodying general features which served to co-ordinate oxidation-reduction reactions of apparently different character, including biologically interesting reactions with oxygen and water under the influence of enzymes. The essential primary process is the "univalent" oxidation of substrate by catalyst to an unsaturated radical  $\text{R}_1$  (e.g.,  $\text{HSO}_3'$ ) which, in link 1, undergoes its second univalent oxidation to reaction product whereby a second radical  $\text{R}_2$  (e.g.,  $\text{OH}'$ ) is formed having the properties of a univalent oxidiser; in link 2,  $\text{R}_2$  effects univalent oxidation of substrate with re-formation of  $\text{R}_1$ . The desoxy-catalyst reverts to normal by some oxidation process and starts new chains. In conjunction with his friend Willstätter he demonstrated the

\* See p. 1665.

† First suggested in 1912 by Baubigny to explain the reaction of sulphites with copper salts in the absence of oxygen.

wide applicability of this principle. The enzymatic oxidation of alcohol \* may be given as an example :



These ideas were not worked out in detail but were intended to suggest that the basic principle of univalent reaction steps might lead to a better understanding of complex oxidation-reduction reactions and especially those of biochemical interest. They aroused much discussion among biochemists. Here we see again the strong interest which Haber always maintained in organic and biochemical processes.

The discussion of these principles in relation to peroxidase and catalase reactions led Haber to take up what proved to be his last research, namely, a kinetic study of the decomposition of hydrogen peroxide catalysed by iron salts. His masterly analysis of this complex reaction brought out a point to which he attached great general significance, *viz.*, that a small alteration of conditions may change the mechanism from a chain reaction to a radical reaction or *vice versa*. Here again his idea of univalent reaction steps and single electron-transfer processes proved its importance for the mechanism of reactions in solution.

In taking a broad view of Haber's life and work one is struck by his versatility. Beginning as a typical organic chemist of his time, there is hardly any important branch of physical chemistry to which he did not make contributions of a fundamental nature, and his interests extended to border regions touching physics, biochemistry, and agriculture. All his life he was strongly imbued, as he tells us in his Nobel Prize lecture, by Fichte's idea "dass der nächste Zweck der Wissenschaft in ihrer eigenen Entwicklung, der Endzweck aber in dem gestaltenden Einflusse gelegen ist, den sie zu rechter Zeit auf das allgemeine Leben und die ganze menschliche Ordnung der Dinge übt." This dual conception of science was a determining factor in his career. Its danger to a man of his versatility was superficiality, but Haber was the very opposite of superficial. A notable feature of his scientific life is that it reflects the main developments of physical chemistry over a period of forty years. His interests were always those of his time and remained so with advancing years.

Haber was more than a great leader of science—he was a great man. His rich, full life, the institutions he made, his services to his country, even his failures—all were on the grand scale. His vigorous personality made a strong and lasting impression. He aroused great affection for himself in those who came to know him, yet some there were who could not like him. One's personal reaction to him was always strong. His forceful nature was softened by a deep humanity and kindheartedness. With large-hearted generosity he was always ready to help others, and to this end no effort was too great for him. Though by nature impulsive and temperamental, he never allowed this to affect his dealings with men. On the contrary, reason and common sense always prevailed; in fact, one of his most notable qualities was his capacity for finding a happy way out of the most difficult situations. This contributed greatly to his success in the many public activities which he undertook. Again, while his natural tendency was towards autocratic control, which he exercised with such conspicuous success during the war, yet in normal times he deliberately adopted the opposite method of giving the maximum freedom and independence to men whom he had chosen with care. Thus he could exercise a gentle but very real leadership in a way that excited the wonder and admiration of all.

Of Haber's outstanding qualities none was of greater significance than his immense capacity for work and sustained concentration. This power contributed in no small measure to his early success and rapid recognition, and it remained just as strong in his last years. Strenuous effort, often to the limit of his physical endurance, was a deeply ingrained habit. He could never relax completely. Idleness was unbearable—his mind had to be continually exercised. Even holidays brought him no true rest, for he insisted on knowing and seeing everything. Foreign travel, of which he was so fond, attracted him

\* For an experimental test of this theory see H. S. Taylor, *J. Amer. Chem. Soc.*, 1933, **55**, 859.

mainly because of the new fields of study which it afforded. Beauty in Nature made no deep impression on him. A characteristic mental relaxation from the world of science and affairs was one which exercised his mind in a different way. From his early schooldays to the end of his life he delighted in the writing of occasional verse. His verses vary in quality—one often sees in them too much striving after unusual and clever effects—but some undoubtedly reach the level of true poetry. These writings were very precious to him and he took great pains in their composition. The following verse is quoted as typical and at the same time highly characteristic of Haber. He wrote it in a gift copy of Thomas Carlyle's "French Revolution":

Wer, von den Einzelnen tief hingenommen,  
Sich schaffend wünschend leidenschaftlich regt,  
Dem wird das allgemeine bald verschwommen,  
Das uns alleine dauernd hebt und trägt.  
Dann mindert sich Gesundheit, Frohsinn, Frische,  
Zur Qual wird was uns steigert und erhebt;  
Es eckelt uns am reichbesetzten Tische,  
Weil Überreizung jeden Reiz begräbt.  
Dann muss man lesen von den grossen Dingen,  
Wie sie ein rechter Meister vor uns stellt,  
Bis wieder still harmonisch in uns klingen  
Die engen Saiten dieser Menschenwelt.

Haber was not, as these lines might suggest, a man of the contemplative type; quite the reverse, for his life was pervaded by energy, purpose, and above all, action. If he tended to be fretted by minute details, this was due only to his desire to see through them to the broad and general. His scientific work was never lacking in thoroughness and attention to detail. It is true, however, that he found no deep interest in the minutiae of experimentation as such. He liked his men to be clever experimenters and greatly appreciated good work by them, but he expected them to work out the finer details. In his writings, however, he always attached great importance to finding the exact word, the precise turn of expression, the striking phrase, and he took infinite pains to this end. His varied activities after the war involved the writing of many speeches and articles, some of which are to be found in his two volumes of collected essays.\* Perhaps his most brilliant speech was that in memory of Liebig† for it was inspired by sympathy with a spirit closely akin to his own.

Haber's sensitive nature reacted strongly to circumstances. Success moved him deeply and had a most stimulating effect, but failure he took very hardly. The outcome of the war was for him the supreme tragedy that permanently affected his life. In the years that followed he was beset with ill-health and many troubles, and apt to be depressed thereby, but his buoyant spirit and strength of purpose always prevailed and nothing was allowed to stand in the way of his work. His most deep-seated passion was love of his country and zeal to serve his Fatherland, not in war only but at all times. His great efforts to uphold the cultivation of science and the gold episode come to one's mind. On the other hand we see in his splendid work for the promotion of international good-will amongst chemists that his was no narrow patriotism. To quote from one of his speeches, "We can make progress in many parts of the world if we learn the lessons of the war we lost—that we are not the centre of the world, that we must concern ourselves about others and consider their interests." With his intense interest in other lands and peoples went a deep *Heimatsgefühl*, and he could never be permanently happy in any country but Germany.

Haber's first wife, who died in 1915, was Dr. Clara Immerwahr, an able pupil and collaborator of Abegg in Breslau. They had one son. In later life he married Charlotta Nathan and there were two children of this marriage.

Haber received many honours, not only at home but also in America and Japan as well as in European countries. He enjoyed the high title of Geheimer Regierungsrat. Medallist of a number of learned societies and honorary member of the leading chemical

\* "Fünf Vorträge," 1924; "Aus Leben und Beruf," 1927 (Berlin, Julius Springer).

† *Z. angew. Chem.*, 1928, **41**, 924.



societies of the world as well as in Germany, he greatly valued his honorary fellowship of our Society and the award of the Rumford Medal of the Royal Society. As president of the German Chemical Society he distinguished himself by his vigorous action to meet the financial difficulties of the period.

The break up of Haber's great research institution began in 1933 as a consequence of the anti-Jewish policy of the National Socialist Government. Some of the ablest members of the Institute were of Jewish race, and in the difficult and complicated situation that arose Haber felt constrained to resign, and his resignation was accepted. This great German chemist, soldier, and patriot had become—the Jew Haber. Let us read his letter of farewell to the members of his Institute: "For twenty-two years the Institute under my direction has striven to serve mankind in time of peace and the Fatherland in war. So far as I can judge it has succeeded in advancing science and defending our country. This success is due to the happy choice and creative power of my collaborators. I thank you all and hope that under new direction the Institute will find equally able men to carry on its work and maintain its standing in the world of science." Without home and country, Haber's first thoughts were for those of his colleagues who found themselves in a similar plight. He succeeded in placing many of them, and only then did he, a very sick man, retire to a sanatorium in Switzerland to consider his own future. Soon afterwards he was invited to the University of Cambridge, where he lived and worked for four months. Though weighed down by his distressing illness, his indomitable spirit would not yield. Towards the end of the year, in spite of the entreaties of his family he delayed his departure to the South for the winter in order to complete a paper on his last research. This done, he left England in January 1934, but in Basle was struck down by a severe heart attack. Even then he would not rest and eagerly discussed with his son plans for future research: but he grew rapidly worse and died two days later.

All who knew him will remember with lasting affection the man who enriched their lives. He will live as a great chemist and be honoured for his services to mankind. In his heart he wished to be remembered as, in peace and war, the servant of his country.

Grateful acknowledgement is made to the relatives and many friends of Haber for their kind assistance. I am particularly indebted to Haber's sister, Mrs. Freyhan, and his elder son, Dr. Hermann Haber, also to Sir William Pope, Sir Harold Hartley, Dr. F. Epstein, Professor H. Freundlich, Dr. E. Berl, Professor G. Bredig, Dr. A. Mittasch, Dr. H. Pick, Dr. O. H. Wansborough-Jones, and Dr. J. Weiss. Reference may be made to appreciations of Haber's life and work by Professor Max Bodenstein (*Sitzungsber. preuss. akad. Wiss.*, 1934; *Z. Elektrochem.*, 1934, **40**, 113), Prof. W. Schlenk (*Ber.*, 1934, **67**, 20), Professor Bonhoeffer (*Chem.-Ztg.*, 1934, **58**, 205), Professor H. Grossmann (*ibid.*, 1928, **62**, 953). The issue of *Die Naturwissenschaften*, 1928, **16**, 1051—1078, celebrating Haber's sixtieth birthday, contains contributions by R. Willstätter, H. Freundlich, G. von Hevesy and O. Stern, E. Terres, R. Le Rossignol, M. von Wrangell and J. Franck. A bibliography of Haber's works is appended to an appreciation by Dr. E. Berl (*Z. Elektrochem.*, 1928, **34**, 797).

The etching facing p. 1642 and the photograph facing p. 1661 are dated 1911 (age 43) and 1928 (age 60) respectively.

The following is a list of Haber's books:

- "Grundriss der technischen Elektrochemie auf theoretischer Grundlage," München, R. Oldenburg, 1898.
- "Thermodynamik technischer Gasreaktionen," München, R. Oldenburg, 1905.
- English translation of the latter by A. B. Lamb, Longmans, 1908.
- "Die elektrolytischen Prozesse der organischen Chemie" (Unter Mitwirkung von F. Haber), A. Moser, Halle, W. Knapp, 1910.
- "Aus Luft durch Kohle zum Stickstoffdünger, zu Brot und reichlicher Nahrung," E. Ramm, N. Caro, and F. Haber, R. Oldenburg, 1920.
- "Fünf Vorträge aus den Jahren 1920—1923," Berlin, J. Springer, 1924.
- "Aus Leben und Beruf, Aufsätze, Reden, Vorträge," Berlin, J. Springer, 1927.