(1860 - 1940)

Development of the industrial relevance of catalysis and its physiochemical basis

> **“We are gifted with the power of imagination and by this power we can enlighten the darkness which surrounds the world of the senses. Bounded and conditioned by co-operant reason, imagination becomes the mightiest instrument of the physical discoverer”.**
>
> J. Tyndall

This was the period when industrial catalysis and the formulation of the relevant physiochemical principles developed simultaneously. The excellence of chemistry in Germany was recognised through Nobel Prizes being awarded to Nernst, Haber, Bosch and Ostwald all of whom had made significant contributions to heterogeneous catalysis which had, to some extent, been stimulated by the requirements of the First World War. The synthesis and oxidation of ammonia dominated the scene but also saw the emergence of catalytic hydrogenation through the work of Sabatier and also Fischer-Tropsch catalysis. Fundamental ideas on adsorption were put forward by Polanyi in Hungary, Langmuir in the USA and Eucken in Germany with Langmuir being awarded the Nobel Prize in 1932 for ‘Discoveries and Inventions in Chemistry’. The concept of ‘activation energy’ was enunciated by Arrhenius, Nobel Prize winner in 1903.

Concern was being raised concerning the nature of ‘active centres’ and the concept of activated adsorption was introduced by Rideal and Taylor while others such as Langmuir and J.K. Roberts paid attention to the preparation of “clean” surfaces with Otto Beeck making significant contributions through the use of evaporated metal films as substrates.

The production of ammonia by the catalytic combination of hydrogen and nitrogen was considered by Rideal and Taylor in 1926 “as one of the greatest triumphs of modern physical and engineering chemistry”. These authors provide in their book “Catalysis in Theory and Practice” a detailed account of what they believe were the significant events prior to the development of the Haber-Bosch process reported at a meeting in Karlsruhe in 1910. A brief summary of these is as follows; more details can be found in the contribution by Kenzi Tamaru in the book “Catalytic Ammonia synthesis; Fundamentals and Practice” edited by Jennings (1991).

In 1865 Deville observed that ammonia decomposition, in the presence of a spark discharge was never complete indicating reversibility $2NH_3 \rightarrow N_2 + 3H_2$. Matignon at the Inaugural Session of the Societé de Chimie

Fritz Haber

Industrielle summarised the patent literature where in a patent attributed to Dufresne in 1871 for the production of oxygen he stated “that a large quantity of nitrogen is liberated in these operations. To utilise this gas I passed it over hot iron which absorbed the nitrogen but it was released as ammonia when hydrogen was passed over it.” This, Matignon suggested, was a way of lowering the price of oxygen!

In 1881 Tessié du Motay took out a patent for a continuous process of ammonia synthesis, passing hydrogen over various metal nitrides. there were other similar patents from Ramsay and Young in 1884, an Austrian patent of Hlavati in 1895, a Norwegian company Christiania Minekompanie in 1896, and Le Chatelier in 1901 (who claimed direct combination of H_2 and N_2 at high pressures, 100 atmospheres, in the presence of appropriate catalytic material).

Haber initiated his work on the thermodynamic equilibria between ammonia, hydrogen and nitrogen in 1904 which led to his first publication on this topic in 1905. Although Le Chatelier had already reported the synthesis of ammonia using high pressures he had been obliged to stop these experiments because of an accidental explosion when one of his assistants had been killed. Haber’s major contribution to achieving a commercially viable process for the synthesis of ammonia was his persistence and tenacity in establishing good experimental data with Le Rosignol and van Oordt for equilibria data. He concluded that there was the possibility of synthesising ammonia from its elements at room temperature providing a suitable catalyst could be discovered.

The next phase was a reconciliation between Nernst (Nobel Prize 1920) and Haber on what were the correct equilibrium concentrations particularly at high (30 atmosphere) pressures. The results using iron and manganese catalysts were in good agreement with those obtained at one atmosphere pressure and the data published in 1908. Whether it would be a commercially viable process still remained to be established, the equilibrium concentration of NH_3 being only 8% at 600°C and 200 atmospheres.

BASF became interested in ammonia synthesis and through two of their engineers Bosch and Mittasch initiated in 1909 collaborative work with Haber in Karlsruhe. Osmium was used as the catalyst at a pressure of 175 atmospheres and the successful demonstration of ammonia synthesis reported in 1910 at a meeting in Karlsruhe. BASF immediately initiated a programme for the industrial production of ammonia with the first objective being to obtain significantly better catalysts. There were severe problems to be overcome particularly the construction of large scale, high pressure reactors operating at high temperatures. As for catalyst preparation, iron was favoured with Mittasch realising that whereas some additives could be effective as promoters, others had little effect while others could be positively detrimental. Apparently over 2000 kinds of catalysts were tested in some 6000 experiments before the now-accepted promoted iron catalyst shown to be the most effective.

Haber was awarded his Nobel Prize in 1919 for the synthesis of ammonia and Bosch his in 1931 for his contribution to high pressure technology in industrial chemistry. However, in this context we should not overlook that Ostwald, who had also shown an interest in the fixation of nitrogen, had been awarded a Nobel Prize in 1912 for his contributions to fundamental physical chemistry. Ostwald had, however, alerted (BASF, Hoechst) to his work on ammonia synthesis but which Bosch (later) showed to be erroneous, Ostwald having used an impure iron catalyst which contained residual nitride and ammonia.

It is important to recognise how Haber, originally an organic chemist, took advantage of the rapidly developing, and new field of physical chemistry, associated with the names of van’t Hoff (Nobel Prize 1901), Arrhenius (Nobel Prize 1903) and Ostwald, the latter part of the 19th century being a period where the industrial application of organic chemistry dominated much of German science with BASF synthesizing indigo in 1897. Haber and Bosch (with Bergius, Nobel Prize 1931) opened up new and far-reaching horizons for heterogeneous catalysis. Their discoveries came also at a critical period in European history just prior to the First World War. The first ammonia plant, built at Oppau, was producing 20 tons of ammonia per day in 1915, with hydrogen being produced via the water gas shift

$$CO + H_2O = CO_2 + H_2$$

reaction over iron oxide and nitrogen, initially by the liquefaction of air but later by the reaction of air with coke to give producer gas (60%N_2 and 40%CO).

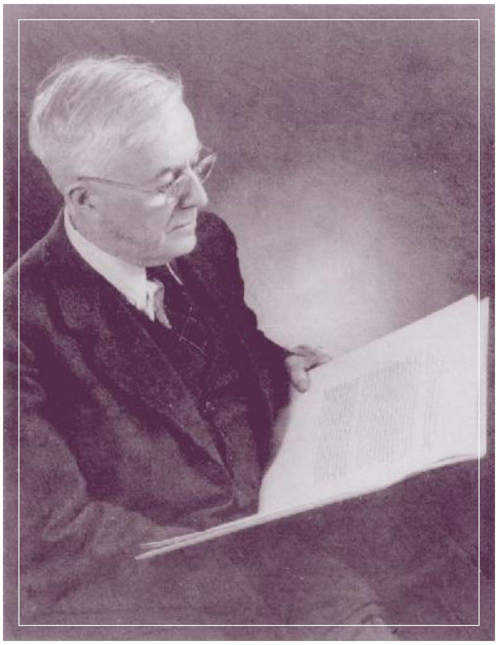
Sir William Crookes in his Presidential Address to the British Association in 1898 warned that the supply of fixed nitrogen for agricultural use was at a point where it was insufficient to support an ever increasing population. He went on to elaborate that we would not have sufficient food and highlighted "the fixation of atmospheric nitrogen as one of the great discoveries awaiting the ingenuity of chemists". Some 15 years later it had been achieved.

Although ammonia synthesis has relied heavily on iron based catalysts for much of this century, Tennison and colleagues at the B.P. Research Laboratories at Sunbury-on-Thames demonstrated some ten years ago that an alkali modified ruthenium on a carbon support can have distinct advantages over the traditional iron catalyst.

Oxidation reactions dominated much of the early developments in industrial chemistry with Humphry Davy, Henry, Döbereiner, Faraday and Grove demonstrating how specific metals could activate oxidation reactions. In 1812 Davy pointed out the function of oxides of nitrogen in the oxidation of sulphur dioxide and suggested the use of platinum sponge. Phillips in 1831 was probably the first to take up this suggestion on the industrial scale. Apparently the platinum had a short active life-time but in 1875 Squire and Messel succeeded in making the process a technical success for the production of oleum. The rapid development of what became known as the 'Contact Process' at the turn of the century was due to Kneitsch and Krauss who, influenced by the rapidly developing concepts of equilibria and kinetics, carried out a systematic investigation of conditions of equilibrium for the reaction $2SO_2 + O_2 \rightarrow 2SO_3$. Subsequently they determined the reaction rates in the presence of different catalysts. Theories were advanced to explain the mechanism of the 'Contact Process' with such intermediates as PtO and PtO_2 thought to play a role.

Although the French chemist Kuhlmann had made significant progress in facilitating the oxidation of ammonia in 1839, it was not until the experiments of Ostwald and Bauer, published in 1903, that there was a rapid development in its technical aspects. It was the development of thermodynamics and the application of the Nernst's equation that provided a firm basis of understanding and predicting the influence of temperature on experimentally observed equilibria. By 1920 all the industrial plants for ammonia oxidation were employing platinum as a catalyst - an aspect first noted by Kuhlmann in 1839. What also emerged was the sensitivity of the platinum to impurities in the ammonia, both hydrogen sulphide and acetylene being recognised as 'poisons'. During the period 1914-1920 research into the use of non-platinum catalysts was initiated, platinum becoming a scarce commodity during the war. The use of oxides, particularly mixed oxides involving binary and tertiary mixtures of oxides possessing two or more well defined oxides, led to the concept of "oxygen carriers" being considered as the *sine qua non* for ammonia oxidation. We see here clear implications of the significance of redox or variable oxidation states as effective oxidation catalysts.

The systematic investigation of hydrogenation was first reported towards the end of the 19th century by Sabatier (Nobel Prize 1912) and his co-workers, of whom Senderens played an important part, isolated observations had been made earlier. For example,



Irving Langmuir

the catalytic reduction of oxides of nitrogen to ammonia was reported by Kuhlmann in 1838 while Debus in 1863 reported that platinum black, in the presence of hydrogen, transformed ethyl nitrite into ethyl alcohol and ammonia and DeWilde showed that unsaturated hydrocarbons could be hydrogenated in 1874.

From 1897 Sabatier proceeded to establish through a series of papers published in Comptes Rendus of the Paris Academy of Science that catalytic hydrogenation was of wide applicability with an extensive range of metals being potential catalysts. The hydrogen was obtained by electrolysis and subsequently freed of water vapour, oxygen and other impurities such as hydrogen sulphide, phosphine and hydrogen chloride which were recognised as catalyst poisons.

Among the catalysts used were copper, prepared in an “active condition” by reduction of the oxide at low temperatures, nickel which was considered to be the most important and also produced by reduction of the oxide, iron and cobalt which because of the necessity to use higher temperatures for reduction sintered easily and platinum in the form of platinum sponge. Some of the reactions effected by such catalysts were as follows :

Oxides of Nitrogen

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O$$

Organic nitro compounds

$$RNO_2 + 3H_2 \rightarrow RNH_2 + 2H_2O$$

$$CH_3NO_2 + 4H_2 \rightarrow CH_4 + NH_3 + 2H_2O$$

Aniline

$$C_6H_5NO_2 + 3Fe + 6HCl \rightarrow C_6H_5NH_2 + 2H_2O + 3FeCl_3$$

Aldehydes

$$RCHO + H_2 \rightarrow RCH_2OH$$

Oxides of carbon

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

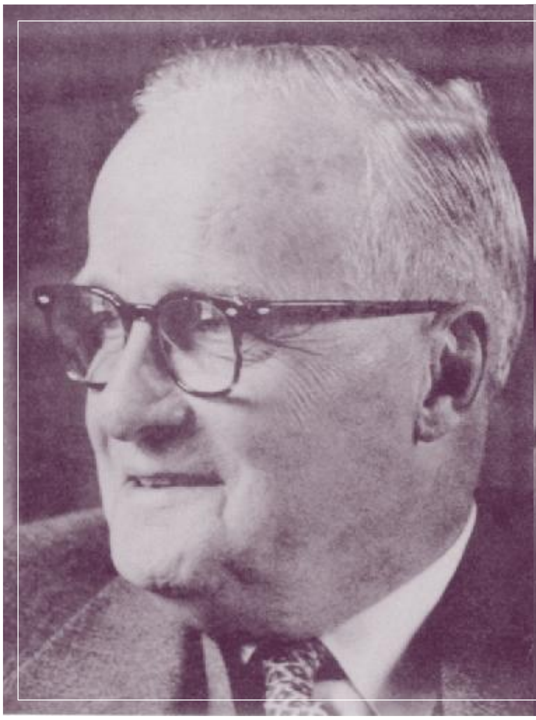
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

It was such studies as these that laid the foundation for the development of the technical processes which became operational for the hardening of oils by hydrogenation.

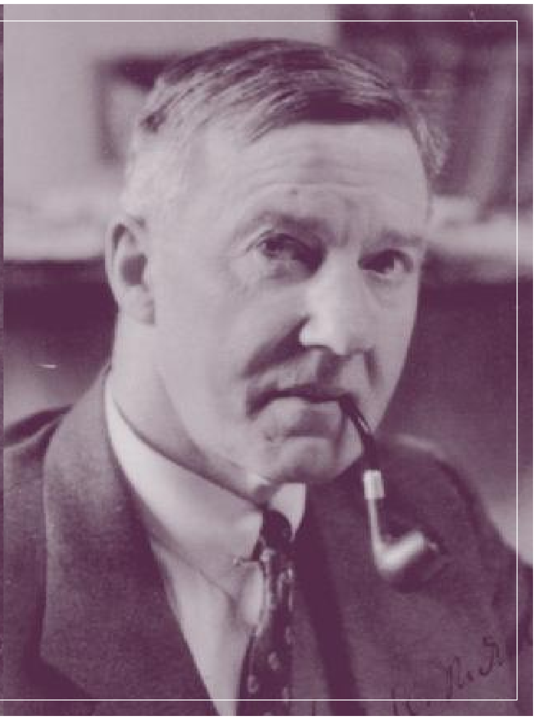
Two of the earliest patents for hydrogenation in the liquid state were by Leprince and Sieveke in 1902 and Normann in 1903. The latter was exploited by Messrs. Crosfield in Warrington but in 1913 the English courts decided that the Normann patent could not be regarded as constituting a monopoly of processes for the hydrogenation of oils and consequently many other processes became available commercially.

We have already emphasised how developments in understanding chemical thermodynamics through the evolution of the Nernst equation and chemical equilibria played a crucial role in Haber’s work on ammonia synthesis. It was realised that catalysts can not change the position of equilibrium with experimental data being in total agreement with thermodynamic calculation. A good example being the equilibrium in the Deacon chlorine process as determined by Lewis (in 1906) and von Falkenstein (in 1907) being in agreement with the thermodynamic data for the process. Clearly it followed (as a general principle) that the catalyst accelerates both the forward and reverse reactions.

Simultaneously with developments in het-



Sir Hugh S. Taylor



Sir Eric Rideal

erogeneous reactions considerable effort was being made to understand homogeneous reactions and to unravel the possible role of surfaces in what were considered to be entirely gas phase reactions. This is a problem that has persisted during much of the 20th century. The question as to how molecules became activated was addressed by Arrhenius (Nobel Prize 1903) and the concept of activation energy introduced. How interacting gaseous molecules became activated, the idea of equilibria existing between active and inactive molecules and how temperature can influence the equilibria were questions which Arrhenius extended to attempt to explain the influence of catalysts. He assumed that there was a dynamic equilibrium between active and inactive molecules, and although at that time it was not conclusive there were strong reasons for assuming that the active molecules postulated by Arrhenius were identical to the "excited" molecules of the physicist. The original experimental equation of Arrhenius could be restated in the form

$$\log_e k = \frac{-E}{RT} + C$$

so that

$$k \,\alpha\, \exp\left(\frac{-E}{RT}\right)$$

with the exponential term representing the fraction of excited or active molecules and "E the energy required to transform molecules from the inactive to the active state" i.e. the activation energy of the reaction.

Others gave more attention to the nature of the solid surface, the significance of adsorption and the existence of interfacial surface energy. There were analogies suggested to exist between adsorption at liquid and solid surfaces. Eucken in 1914 published his 'Thoughts on the theory of adsorption' (see Schwab in Vol.1 Proc. 8th International Congress on Catalysis, 1984). Polanyi drew attention to the potential theory of adsorption in 1916 while Langmuir was carrying out elegant experiments on a range of surfaces including mica and tungsten filaments.

It is worth at this stage reflecting on the impact Irving Langmuir was making to surface science as early as 1912 when he discussed the dissociation of hydrogen into atoms at hot tungsten filaments and later the same year he described 'a chemically active modification of hydrogen'. These papers emanated from Langmuir's research on the tungsten lamp at the Schenectady laboratories of the General Electric Company and were the first of a series of papers dealing with the surface chemistry of hydrogen. However, other aspects, including the study of "chemical reactions at very low pressures", were pursued by him leading in 1915 to his theory of adsorption but articulated very clearly in 1918. In this paper he states that *"Molecules take up definite positions with respect to the surface lattice and thus tend to form a new lattice above the old. A unit area of any crystal surface, therefore has a definite number of elementary spaces, each capably of holding one adsorbed molecule or atom".* He derived the "Langmuir Equation" and tested it against experimental data. In the Summary to this paper he states *"This theory requires that in typical cases of true adsorption the adsorbed film should not exceed one molecule in thickness. This is contrary to the usual viewpoint. The forces causing adsorption are typically chemical and exhibit all the great differences in intensity and quality characteristic of chemical forces".*

The "Collected Works of Irving Langmuir" published in 12 volumes (Pergamon Press, Editor G. Suits, 1960) illustrate the enormous contribution he made to surface science, emphasising the chemistry, the physics and the technology. E.K. Rideal in his Forward to Volume 1 wrote "The ramifications of Langmuir's concept of monolayers and their reactions are surprisingly great, whilst they follow one another in what now is seen to be a logical sequence. Yet each step represented a new page of a book devoted to a new and unexpected world of chemistry". In the same volume the eminent Russian scientist Roginsky paid tribute to Langmuir's "creative mind operating with definite atomic models and mechanisms" and drawing attention to his contribution to the theory of catalysis "being much more than the derivation of basic kinetic equations for catalytic reactions". As a student Langmuir had the advantage of having been exposed to one of the creators of the field of physical chemistry, Walther Nernst, and the attempts of such individuals as Bodenstein and Fink to explain experimental data obtained with platinum. He also had the advantage of the freedom given to him by the General Electric Company. But he also took advantage (according to A.W. Hull) of having listened in November 1914 to a "physicist from Leeds, England, give a colloquium on his findings on X-ray studies of crystal structures". That physicist was W.H. Bragg and probably formulated for him the concept of surface lattice sites and the checker board model used in his model of adsoprtion.

It was particularly important for the experimentalist to be able to relate surface coverage to the gas pressure, this was achieved through the development of isotherms for interpreting experimental data. Langmuir based his model on a dynamic equilibrium existing between the rate of evaporation (desorption) and condensation (adsorption). This led to the Langmuir equation which related surface coverage θ to the gas pressure P where k is a constant:

$$\theta = \frac{kp}{1+kp}$$

On the other hand Freundlich (in 1923) introduced an empirical relationship where k^1 and n are constants: $\theta = k^1 p^{1/n}$. Both isotherms became part of the armoury of surface chemists interested in heterogeneous catalysis.

Langmuir's experimental data were a water-shed in surface chemistry, they represented the first attempt to study atomically clean surfaces using tungsten filaments heated to high temperatures in vacuum to remove surface impurities. He showed that the rate of hydrogen adsorption was proportional to the square-root of the hydrogen pressure, $(P_{H_2})^{½}$, from which he deduced that adsorption resulted in the formation of two hydrogen adatoms i.e. that adsorption was dissociative.

Langmuir assumed that the adsorbing surface consisted of a uniform space lattice, each lattice space being the seat of adsorption and the surface being uniform or energetically homogeneous. It quickly became clear that this was not necessarily the case in view of the presence of edges, corners and different crystal planes. Evidence also gradually emerged that catalytic reactivity occurs on localised reaction centres - active sites - which may be relatively small in areas compared with the total surface exposed to the reactants. Experiments by Richardson on thermionic emission in 1925 showed that electron emission does not occur uniformly over the surface but occurs from localized patches. Langmuir suggested that there was a connection between these patches and those responsible for catalysis since addition of a poison prevented both electron emission and catalysis.

In 1919 Langmuir with his assistant S.P. Sweetser studied the interaction of hydrogen and oxygen over a hot tungsten filament, kinetic studies were carried out and models were developed where ‘a single layer of firmly bound oxygen atoms’ were suggested to be involved. The era of chemical kinetics and the significance of adsorption isotherms began to dominate thinking in surface chemistry and catalysis and this continued for the next twenty or thirty years. The Faraday Discussion held in Oxford in 1932 on ‘The Adsorption of Gases by Solids’ illustrates very clearly the rapid developments that had occurred over the previous decade and I draw attention to some of the topics discussed at that meeting.

Rideal discussed rates of surface migration based on the studies of metallic atoms deposited on glass from molecular beams (experimental data of Stern and Cockroft); indirect evidence of the lateral mobility of oxygen over copper oxide; energy exchange between solid and gas during adsorption and the work of J.K. Roberts on accommodation coefficients. Freundlich discussed the kinetics and energetics of gas adsorption; Frankenburger and Hodler the mechanism of the catalysis of ammonia on tungsten; Bonnhoeffer and Farkas considered the dissociative chemisorption of hydrogen at metal surfaces; H.S. Taylor and Sherman the para-hydrogen conversion over a range of oxide surfaces; M. Polanyi gave a general survey of theories of adsorption; Lennard-Jones provided a theoretical model for adsorption with an energy profile of the adsorption process involving the weakly held, van der Waals (or physisorbed) state, acting as a precursor while Evans considered deviations from the ideal translational motion of adsorbed molecules. The Lennard-Jones model, some 70 years later, still provides a useful approach to discuss chemisorption.

In the ‘General Introduction’ to the Discussion, H.S. Taylor drew attention to the Langmuir isotherm, Polanyi’s views on adsorption, the Freundlich isotherm, how to deal with non-uniform surfaces, mobility of adsorbed gases and the energetics of the adsorption process. But perhaps most significantly to the concept of ‘activated adsorption’ and the need to implicate the existence of ‘activation energy’ in discussing adsorption and surface reactions. He anticipated that much could be learnt from Polanyi and Eyring’s theoretical treatment of the kinetics of chemical reactions.

When H.S. Taylor was asked in 1946 to comment on how catalysis had progressed between the two World Wars he said “The final five year period (1935-1940) gave to heterogeneous catalysis a tool of which it had been in sore need”. He was referring to the experimental technique of deriving from experimental data for the physical adsorption of gases, the surface area of solids whether by the ‘Point B’ method or analysis of data using the Brunauer-Emmett-Teller (or BET) equation :

$$\frac{p}{VPo(1-P_{/Po})} = \frac{1}{V_m C} + \frac{(C-1)P}{PoV_m C}$$

where Po = saturation vapour pressure of the gas (eg N_2) at the adsorption temperature, V is the volume of gas adsorbed at pressure P, V_m the monolayer volume and C a constant given by:

$$C = \frac{a_1 b_2}{a_1 b_2} \exp\left(\frac{E_1 - E_L}{RT}\right)$$

E_1 is the heat of adsorption in the 1st layer, E_L the heat of liquefaction of the adsorbate and the coefficient of the exponential taken as unity. The value of V_m can be obtained from the intercept and slope of linear plots of the L.H.S. of the above equation against $P/_{Po}$. If C is large (usually!) the slope is,

$$\frac{1}{V_m}$$

which assuming a cross-sectional area for the adsorbate (15Å^2 for N_2) enables the surface area to be calculated. There is little doubt that, although Taylor made his judgement some 50 years ago, the BET equation had a dramatic influence on research in catalysis enabling researchers world-wide to compare their catalysts. It still remains a vital tool in catalytic research.

Although Faraday had recognised the need for "clean" surfaces and the phenomenon of poisoning, and Langmuir, with his access to high vacuum techniques, had in effect studied the chemistry of "clean" tungsten surfaces, one of the earliest contributions to a carefully controlled study of chemisorption at clean metal surfaces was by J.K. Roberts at Cambridge. Langmuir (in 1932) had already emphasised that the measurement of the accommodation coefficient could act as a sensitive detector of the presence of adsorbed molecules at filament surfaces. Roberts chose to study the energy exchange or accommodation coefficient of an inert gas (neon) at tungsten filaments which had chemisorbed hydrogen, oxygen and nitrogen and for which he had also determined their respective heats of adsorption. Chemisorption was rapid with approximately one hydrogen atom being adsorbed per surface tungsten atom. This behaviour contrasted with earlier studies with tungsten powders, the hydrogen isobar showing a minimum at 75°C and a maximum at 150°C while nitrogen was not adsorbed at O°C!! These results undoubtedly led to a discussion of the reason for the differences between (powder) catalysts and clean metal surfaces. It was this that prompted Otto Beeck to carry out his elegant studies with evaporated metal films a few years later at the Shell Emmeryville Laboratories in California. Beeck had obtained his doctorate in the city of Danzig, now the Polish city of Gdansk, but moved to Caltech in 1933.

Perhaps I may be allowed some personal comments here. Beeck's papers were some of the first I read as a young postgraduate student - many of them dealt with the surface chemistry of evaporated nickel films which provided me with a data base with which to compare my results obtained with reduced nickel oxide powder. Were the nickel powders atomically clean or was there an inherent difference between the reactivity of powders and evaporated (clean) films? His papers were quite exceptional; his first studies of catalysis made use of the molecular beam technique with which he, with a physics doctorate in reactions of molecular beams of alkali atoms, was familiar. He impinged beams of hydrocarbon molecules on thin strips of transition metals heated in high vacuum. Evaporated metal films (of high surface area) were used to overcome potential problems of contamination. With Wheeler and Smith he studied the hydrogenation of ethylene, using an elaborate vacuum system with a "sticking vacuum" (with a McLeod gauge) implying a pressure of 10^{-8} torr or less. In 1940 they published a landmark paper in the Proceedings of the Royal Society which was followed in 1950 by elegant calorimetric studies of the heats of adsorption of hydrogen and carbon monoxide on evaporated films of nickel.

At the Faraday Discussion Meeting in 1950 Otto Beeck presented three papers. The first, 'Hydrogenation Catalysts' described his studies of the catalytic hydrogenation of ethylene and other hydrocarbons drawing attention to how chemical properties (electronic configuration) and the resulting physical properties (crystal parameter) of the catalyst surface influence the rate of reaction. Correlations were drawn between heats of adsorption, rates of hydrogenation and the percentage d-character of the metal bond. The second with Ritchie: 'The effect of crystal parameter on hydrogenation and dehydrogenation' described studies with evaporated nickel films of different orientation while the third paper presented at the Discussion Meeting was with

Cole and Wheeler and described the experimental details of the calorimeter used and some data for the heats of adsorption of hydrogen on films of nickel and iron at 23 °C, -183°C and -196°C as a function of surface coverage. Beeck died later in 1950.

At the same meeting held in Liverpool, H.S. Taylor, who was a native of the city, gave the 5th Spiers Memorial Lecture ‘Catalysis : Retrospect and Prospect’. He emphasised the contribution Volkenstein’s theory based on the role of lattice defects had made, Schwab’s studies of alloy catalysts and the electronic theory of catalysis as perceived by Dowden and Couper and Eley.

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