The Development of Ideas on Heterogeneous Catalysis

PROGRESS FROM DAVY TO LANGMUIR

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Since the discovery by Davy in 1817 of catalytic oxidation on the surface of platinum there has been much discussion of the underlying reasons for the occurrence of heterogeneous catalysis. Early ideas of Liebig found little favour with Berzelius, Ostwald and others. The adsorption theory of Faraday became generally accepted, although alternative views were proposed over a long period. Langmuir put the concepts of Faraday into definite form, and his formulations and developments of them have been used up to the present.

The discovery that a combustible gas can be oxidised by atmospheric oxygen on the surface of a platinum wire without the production of flame and yet with production of enough heat to keep the platinum incandescent was made by Humphry Davy during his researches which led to the miners' safety lamp, and has already been described (1,2,3,4). J. W. Döbereiner later developed a spongy platinum catalyst which caused hydrogen and atmospheric oxygen to combine at room temperature, thereby making the catalyst become red hot. This discovery was described by J. J. Berzelius in 1823 as the most important and most brilliant (5), and in that year Michael Faraday in the *Quarterly Journal of Science, Literature and the Arts* referred to the discovery as "A most extraordinary experiment ... made by M. Döbereiner" and reported that he had verified it (6). Davy had remarked somewhat dogmatically that the igniting power of platinum and of palladium, which was also an effective catalyst in his experiments, and the poisoning effect of a carbonaceous layer, must depend upon an increase in the power of the metals to radiate heat.

Dott. Ambrogio Fusinieri was one of the first to publish, in the *Giornali di Fisica* from 1823 to 1826, a hypothesis to explain the phenomena discovered by Davy and Döbereiner. He wrote:

> "The platinum in such cases is a species of wick which admits to its surface a continual renewal of solid laminae composed of the combustible substances in the gases which run, burn, evaporate and are renewed. In virtue of this their combustion on the surface increases and keeps the temperature high."

Fusinieri contended that, with the naked eye, concrete laminae of the combustible substance could be seen running over the platinum surface, but this remarkable claim seems to have been received with some scepticism, for in his 1826 paper Fusinieri remarks defensively that various of his experiments were repeated a number of times in the presence of learned persons from Vicenza, all of whom distinctly saw the things he claimed, as indeed did many others: and as he says "they saw them because they all possessed good eyesight!" Brief accounts of Fusinieri's work have been given (2,7,8).

The idea of laminae of molecular or multimolecular thickness moving over a surface is now acceptable. During crystal growth layers can advance along a crystal face by, for example, the co-operation of a pair of emerging screw dislocations; and a chemisorbed layer on a metal can advance as a lamina if it is covered

with mobile physisorbed particles which stick to the metal as soon as they reach the edge of the chemisorbed layer, when they fall over the edge and become fixed to the metal as additional chemisorbed particles.

A Weighty Paper by Faraday

Many ideas now accepted on the mechanism of the heterogeneous catalysis of gas reactions were first advanced in Faraday's long paper read to the Royal Society in 1834 (8). In this he reviewed previous work and tried to do justice to Fusinieri, but did not mention the radiant heat idea of Davy. Faraday had observed a spontaneous combination of hydrogen and oxygen on platinum electrodes at room temperature during his work on electrolysis. He proposed that the two reacting gases were condensed on the surface of the platinum, and "the approximation of the particles to those of the metals may be very great." The two reactants were brought within the action of their mutual affinities. The water formed was supposed to be less attracted by the platinum than the reacting gases, and so could evaporate. Faraday stated that there would be a continual interchange of particles between the adsorbed layer and the gas in contact with it. He emphasised the importance of forces between the particles, and wrote:

> "I am prepared myself to admit (and probably many others are of the same opinion) both with respect to the attraction of aggregation and chemical affinity, that the sphere of action of particles extends beyond those other particles with which they are immediately and evidently in union, and in many cases produces effects arising into considerable importance: and I think this kind of attraction is a determining cause of Döbereiner's effect, and of the many others of a similar nature."

The Concept of a Catalytic Force

In 1836 J. J. Berzelius referred to a new force, the catalytic force, after co-ordinating a number of observations on homogeneous and heterogeneous catalysis. But this idea of a new force was criticised. In 1851, A. W. Williamson, Professor of Practical Chemistry at University

College, said in a Royal Institution Discourse:

> "It unfortunately often occurs that names are mistaken for explanations, and people deceive themselves with the belief that, for instance, in attributing chemical decompositions to affinity, attraction, contact-force, catalysis, etc., they explain them." (9).

He remarked that various phenomena of change were attributed to occult forces. J. F. Daniell some dozen years before this Discourse had in his textbook dismissed the idea of a new catalytic force, writing:

> "...there is no occasion for the hypothesis of a new force, for all the phenomena may be explained by the action of *heterogeneous adhesion*." (10)

Justus von Liebig about this time also argued that the idea of a catalytic force was superfluous and in a long paper (11) on fermentation, putrefaction and slow decay he proposed a hypothesis of molecular vibrations communicated by contact from the catalyst to another body ("durch Berührung mit einem differenten Körper") without mentioning any relation of this idea to the Berzelius idea. Berzelius in his subsequent *Jahres-Bericht* devoted five pages to a critical review of the Liebig hypothesis of fermentation and made further observations on heterogeneous catalysis (12). He remarked that the idea of transmission of a disturbance to the atoms by contact is interesting because of its wide scope, but Liebig's application of this idea to sugar fermentation was dismissed by Berzelius as a fictitious explanation published prematurely. However, Liebig does not appear to have been impressed by the criticisms of Berzelius, for in 1851 he stated his view forcibly, writing (13):

> "All the phenomena of fermentation when taken together establish the correctness of the principle long since recognised by Laplace and Berthollet, namely, *that an atom or molecule put into motion by any power whatever may communicate its own motion to another atom in contact with it.*
>
> This is a dynamical law of the most general application, manifested everywhere, when the resistance or force opposing the motion, such as the vital principle, the force of affinity, electricity, cohesion &c., is not sufficiently powerful to arrest the motion imparted.

> This law has only recently been recognised as a cause of the alterations in forms and properties which occur in chemical combinations; and its establishment is the greatest and most enduring acquisition which chemical science has derived from the study of fermentation."

Much later, Wilhelm Ostwald remarked that the Liebig theory did not suggest new lines of investigation, and it could not be disproved since it is not susceptible to testing (14). The theory, he said, was scientifically unfruitful and had driven the whole matter into a blind alley. Later still, E. K. Rideal and H. S. Taylor gave an account of these early discussions and wrote:

> "The disadvantage of the Liebig theory lies in its unassailability since no possible test of the theory can readily be devised." (15)

By 1848, C. F. Schönbein, Professor of Physics and Chemistry in the University of Basel, was able to distinguish three hypotheses for the explanation of the catalysis of gas reactions by platinum: first, the idea of condensation of oxygen on the surface, which he attributes to Faraday and Döbereiner; secondly, the idea of an oxide of platinum formed as an intermediate compound, which he attributes to A. de la Rive and L. Gmelin; and thirdly, the catalytic force concept (16). He supported the Faraday view and remarked that catalytical actions are enigmatical. The idea of intermediates in catalysis had been proposed much earlier for the lead chamber process for sulphuric acid manufacture, and became the subject of an impressive lecture demonstration in which chamber crystals (nitrosylsulphuric acid) are made to form on the walls of a very large flask and are then decomposed by water to give sulphuric acid and oxides of nitrogen.

Development and Criticism of the Adsorption Theory

The Faraday adsorption theory of catalytic action is now generally accepted. It is interesting that even as late as 1910 a paper by Miss Ida F. Homfray, communicated to the Royal Society by Sir William Ramsay, rejected the idea of adsorption (17). This research on the uptake of gases by charcoal is remarkable for

Svante August Arrhenius
1859–1927

Arrhenius came from a Swedish farming family. The famed Arrhenius theory of electrolytic dissociation was presented to the University of Uppsala in his doctoral thesis of 1884 but was awarded only a fourth class. However with support from Ostwald, Arrhenius became lecturer in physical chemistry at Uppsala in that year. From 1886 to 1890, with a travel grant, he worked with Ostwald, Kohlrausch, Boltzmann and van't Hoff. He then became lecturer at the Technical High School in Stockholm, Professor of Physics there in 1895, and Rector from 1896 to 1905. He subsequently became Director of the Physical Chemistry Department at the Nobel Institute in Stockholm and here he developed very wide scientific interests. The Nobel Prize for Chemistry for 1903 was awarded to Arrhenius "for the services he has rendered to the advancement of chemistry by his electrolytic theory of dissociation"

the exact and quantitative approach and elegant experimentation, but the supporting theoretical arguments are very shaky. Miss Homfray obtained adsorption isosteres, a name due, she says, to Ostwald. These give the relation between pressure and temperature for points of equal adsorption, and they can be looked on as the vapour pressure curves of an adsorbed layer. She deduced heats of adsorption from these isosteres with the Clapeyron-Clausius equation and noted three classes of hypothesis to explain the uptake of gases by charcoal. The first hypothesis of chemical combination was dismissed because she did not find irreversible chemical change of the gases used. The second hypothesis of surface condensation she dismissed on three grounds: [A], a radical difference with respect to adsorption of gases was supposed to exist between amorphous bodies, which occluded gases, and crystals which did not absorb, according to work by T. W. Richards, which she quoted. But Faraday had emphasised that crystals show catalytic activity. [B], Miss Homfray argued that the thermal effect she calculated, and measured by calorimetric experiment, was too big for adsorption, and so was the temperature coefficient of adsorption which she found. [C], she could not

test the Gibbs equation, but says that it does not seem to hold. This involves the difficult problem, which she does not go into, of the definition and measurement of surface tension for an amorphous solid body like charcoal. The third hypothesis of solution to form a single homogeneous phase explains the facts, Miss Homfray contended. Adsorption isotherms are non-linear because Henry's Law fails, and there is an analogy to ionic solutions.

Miss Homfray (1869–1948) who enjoyed a private income, worked in the Chemistry Department of University College London for twenty years as an independent unpaid research worker. Her experiments on the adsorption of gases by charcoal, carried out from 1907 to 1910, were suggested by W. Ramsay. A brief biography of her has been given by S. D. Forrester and C. H. Giles in a historical survey of work on gas-solid adsorption isotherms up to 1918 (18).

In the same year as Homfray, A. Titoff also published results for adsorption of gases by charcoal and obtained non-linear isotherms which he represented by the Freundlich isotherm, which at that time was purely empirical (19). The next year the Swedish chemist Svante Arrhenius concluded that the

Freundlich isotherm did not apply well to the results of Titoff and Homfray, and he proposed another isotherm, now forgotten, which in contrast to that of Freundlich gives a limit to the quantity of adsorbed substance (20). Both Titoff and Arrhenius thought the underlying cause of adsorption should be sought in molecular attraction between the adsorbed substance and adsorbent, which is the Faraday view. Arrhenius thought that formation of a solution in the solid was negligible compared with surface action.

In 1912, H. S. Taylor, who was to become one of the leading workers on heterogeneous catalysis, instead of going to Germany which was then the foremost chemical nation for doctoral work as was then customary for so many rising chemists, as holder of an 1851 Exhibition joined Arrhenius in Stockholm. Possibly he noted the interest of Arrhenius in surface processes, which became a major theme of his research after his association with Rideal during World War I.

During the early part of this century the Faraday concept of reaction in a condensed layer was being put forward by several investigators in a more definite way. M. Bodenstein did pioneering work on the kinetics of catalytic reactions, and in 1907 with Colin G. Fink he proposed that in many catalytic reactions an adsorbed layer of the reacting substances was formed and a slow reaction in this layer determines the velocity of catalytic reaction (21). This idea in a less definite form had also been developed by Professor W. A. Bone of Imperial College who with various collaborators had carried out research on the catalytic combustion of hydrogen and carbon monoxide on a variety of surfaces. He proposed a prior occlusion of the combustible gas, and probably also of oxygen, with the rate of adsorption determining the rate of reaction (22). Bone claimed to have anticipated Irving Langmuir in a general way and he quoted a private communication from Langmuir:

"... the general viewpoint which you had in 1906 was much ahead of others of that time and is in many ways closely related to that which I have developed independently from a rather different experimental basis." (23)

Catalysis and Equilibrium in a Reversible Reaction

Both W. Ostwald and J. H. van't Hoff emphasised that a catalyst cannot alter the equilibrium point of a reversible reaction. They used the concept of thought experiments, later much used by Einstein, to show that alteration

Fritz Haber
1868–1934

Haber was awarded his doctor's degree in 1891 by the Charlottenburg Technische Hochschule and he then worked in various factories. He gained Privatdozent status at the Baden school following his book of 1896 on hydrocarbon reactions. His work on ammonia synthesis was carried out when he was Professor at the Karlsruhe Technische Hochschule. In 1912 he became Director of the Kaiser Wilhelm Institute for Physical Chemistry at Dahlem, a suburb of Berlin, and after World War I this became one of the world's greatest centres of physico-chemical research

of the equilibrium point could lead to a conceptual perpetual motion machine. Ostwald distinguished between a perpetuum mobile of the first kind in which energy would have to be created, and one of the second kind in which energy at rest would have spontaneously to set itself in motion. Rideal and Taylor in the first edition of their notable book on catalysis reach the inevitable conclusion that a catalyst cannot alter the final state of equilibrium, referring to van't Hoff but not to Ostwald (15). It is remarkable in view of this that B. Lewis and Rideal in 1926 claimed that water as a catalyst alters the position of equilibrium in the hydrogen-iodine-hydriodic acid gaseous equilibrium (24). They deduced that hydrogen and iodine do not combine when dry, and wrote:

"Under conditions of intensive desiccation or in the presence of solid phosphorus pentoxide, the equilibrium is shifted, the reversible process being rendered irreversible."

"This interpretation is given with some diffidence, as this would be the first example of a reversible system in which a catalyst does not affect the reaction velocities of each reaction to equal extents."

The powerful combination of M. Bodenstein and W. Jost showed that the experimental results on which this deduction is based were faulty because the hydrogen iodide reacted with phosphorus pentoxide to form water and iodine. They wrote with reference to Lewis and Rideal:

". . . they do not observe that in doing so they have found a *perpetuum mobile*—introduce a trace of water vapour into dry, completely decomposed hydriodic acid and we obtain 21% decomposition by a reaction performing work, then remove the trace of water and we have 99% decomposition again with the performance of work." (25)

Commenting on the work of Lewis and Rideal, C. N. Hinshelwood wrote:

"If this were correct, Bodenstein's measurements of the rate of union would lose any absolute significance, and, incidentally, the second law of thermodynamics would be untrue." (26)

In the second edition (1926) of their book on catalysis, Rideal and Taylor argue that in a homogeneous system the catalyst may have widely varying effects on the activities of the reactants so that the equilibrium constant is changed. Mole fractions are altered. This idea is not discussed in terms of Ostwald's thought experiments. A problem for a homogeneous system is how the catalyst is conceptually put into and taken out of the equilibrium system without doing any work.

Lewis and Rideal also criticise Hinshelwood's view of the hydrogen plus iodine combination as a very good example of the principle of activation by collision in a bimolecular reaction (24), and they speculate that iodine atoms may be involved—a view which has now become generally accepted and has necessitated a re-writing of textbook treatments of this reaction.

The Ammonia Synthesis and Related Technical Problems

The hydrogen-nitrogen-ammonia equilibrium at high pressures was the subject of a dispute in 1907 between W. H. Nernst and Fritz Haber concerning the values of the equilibrium constant. In 1908 Haber and R. Le Rossignol (27) published new values of the ammonia equilibrium constant which agreed fairly well with those of Nernst. Good catalysts had been found for the high pressure ammonia synthesis, and in 1908 Haber approached the Badische Anilin-und Sodafabrik A.G. In July 1909 the laboratory apparatus of Haber was demonstrated to the industrial chemist Carl Bosch, who became mainly responsible for developing the first high pressure method in the chemical industry, just before World War I. Enormous technical problems were overcome with amazing speed. In 1910 construction of the Oppau works began and in 1913 they were opened, followed in 1917 by the much larger Merseburg works. Professor W. Palmaer in presenting Bosch for the Nobel Prize for 1931, acclaimed his idea of concentric tubes as brilliant. The ammonia synthesis needed 200 atmospheres' pressure at 500°C and no substance was found that would withstand these conditions for a satisfactory length of time. The problem was solved by concentric tubes consisting of a pressure-bearing carbon steel jacket

lined with soft steel. The hydrogen diffused through the soft steel lining and escaped through holes in the outer jacket without building up its own pressure. The hydrogen did not then attack the outer steel jacket at the prevailing high temperature to form brittle iron hydride. If this reaction did occur the outer jacket eventually burst under the high pressure.

Contributions by Irving Langmuir

Langmuir is generally recognised as a towering figure in catalytic and surface research. He graduated from Columbia in 1903, and wished to do doctoral work in Germany, either in Leipzig or Göttingen, but not Heidelberg. He found on visiting Germany that Ostwald had stopped lecturing at Leipzig and had practically retired to write books. R. Luther, taking Ostwald's place, was an exceedingly poor lecturer according to Langmuir. However, he found W. H. Nernst to be a good lecturer and thought him a splendid Professor—a view he soon discarded. Langmuir at Göttingen in 1904 was assigned to Nernst who asked him to study the interaction of gases in the vicinity of a glowing electric light filament, and Langmuir produced a doctoral thesis on the dissociation of gases by hot platinum wires. This thesis has been said to be a springboard for some of Langmuir's greatest research (28). Nernst had seen that a platinum wire which by efficient catalysis established a high-temperature gaseous equilibrium would provide very valuable data for testing his ideas which led to the Heat Theorem. Langmuir found that a glowing platinum wire established an equilibrium for the dissociation of carbon dioxide and of water vapour, and he made quantitative measure-

**Irving Langmuir
1881–1957**

At Columbia University Langmuir studied in the School of Mines and graduated as a metallurgical engineer. After his German doctorate he taught chemistry at Stevens Institute in New Jersey, but he soon left to join the General Electric Company Research Laboratory in Schenectady, New York. Here he conducted many researches of great importance which showed remarkable originality and versatility. He had interests in aviation, music, the Boy Scout movement, mountaineering, conservation, atomic energy control, politics, and general philosophical issues of science. The Nobel Prize for Chemistry for 1932 was awarded to Langmuir "for his discoveries and investigations in surface chemistry"

ments which disagreed slightly with the earlier deductions of Nernst (29). The most serious difficulty Langmuir experienced was in establishing the temperature of the platinum wire from its resistance. In his 1906 paper on his doctoral work (where Nernst is not a co-author but is acknowledged) Langmuir does not discuss the bearing of his findings on the Heat Theorem (29).

Nernst did not see much promise in Langmuir, and Langmuir revised his early opinion of Nernst, seeing him as a poor instructor, not sparing attention for mere students (28). But at that time Nernst was very busy on his own research which led to the enunciation of the Heat Theorem in 1906 and to the award of the Nobel Prize for Chemistry for 1920 in recognition of his work in thermochemistry.

Langmuir later developed a kinetic rather than a thermodynamic approach to surface processes and this led him to his famed adsorption isotherm of 1916. He used a static picture of a surface as a checkerboard, and on this basis the rate of formation of an adsorbed layer was supposed proportional to $1 - \theta$ where θ is the fraction of surface already covered by adsorbed species.

We now have a more dynamic view of a surface as containing terraces, steps, and kinks in sites, and active sites as groups of possibly emerging atoms as visualised by Taylor. These imperfections cause surface mobility of atoms. Also catalytic actions can stir up surface atoms, and the roughening of a platinum catalyst used for ammonia oxidation is a good example of this. Such ideas of surface mobility were foreshadowed by Faraday in his Bakerian Lecture of 1857 to the Royal Society, when he described how thin films of gold leaf retracted to minute globular portions at temperatures much below the melting point, and silver leaf similarly retracted to separate parts.

Langmuir extended his kinetic approach to adsorption to the study of surface kinetics and he particularly deduced equations for a model of adjacent interaction between particles adsorbed on a catalytic surface, thus putting the Faraday view in a very definite form. For sub-stances A and B simultaneously adsorbed the rate of reaction can be put proportional to the product $\theta_A \theta_B$ where θ_A and θ_B are the fractions of surface covered by A and B, respectively. For strong adsorption of A, the free surface $1 - \theta_A$ is, from the Langmuir isotherm, inversely proportional to the pressure of A. Development of such ideas has led to a vast structure of kinetics.

Langmuir summarised his theories on catalytic kinetics in two important papers presented at a Discussion of the Faraday Society held in September 1921 at the Institution of Electrical Engineers in London.

On the much discussed question of physical and chemical forces in adsorption (raised earlier by Miss Homfray) and catalysis, Langmuir remarked that the distinction is

". . . not so much the nature of the forces involved as the traditional attitude of mind of physicists and chemists." (28)

After the 1921 Faraday Society Discussion, C. N. Hinshelwood and his colleagues at Oxford made many studies of kinetics of surface catalysed gas reactions, and the adjacent interaction view of Langmuir is now often referred to as the Langmuir-Hinshelwood mechanism. The writings of Hinshelwood on kinetics of catalysis on metals are notable for their lucidity and elegance, but the experiments have been criticised.

In their 1919 book Rideal and Taylor remarkably give no account of Langmuir's surface kinetic work published up to 1918, although they refer to his work on surface tension phenomena and monolayers on water, undertaken during the period 1916 to 1918 (15). However, in the second 1926 edition a very fair though brief account of Langmuir's kinetic work appears.

It is notable that Langmuir, with his profound knowledge of gaseous ionisation and surface ionisation, seems to have shown no great interest in electronic theories of catalysis. Early thoughts on ionisation and catalysis are found in a paper of 1905 by the Rev. P. J. Kirkby, Fellow of New College, Oxford, which describes experiments carried out in the

Laboratory of Professor J. S. E. Townsend, the Wykeham Professor of Physics (30). Kirkby concluded that platinum only causes hydrogen and oxygen to combine at a low pressure when its temperature exceeds a critical value of about 275°C, and he thought the reaction was connected with the corpuscular discharge emitted by hot platinum, which he supposed would produce ions. His paper, unfortunately, shows a complete lack of historical and chemical knowledge and in fact has no references to chemical work—his experiments are completely contradicted by the earlier work of Davy, Döbereiner, A. de la Rive and F. Marcet, and particularly by those of Faraday who was completely vindicated in later research from Oxford by D. L. Chapman and P. W. Reynolds (31).

The experimental results and theoretical views of Faraday have for a century and a half stood the test of time. The very definite formulation of these views by Langmuir, and his deductions of kinetic equations, have been widely used and developed over the past sixty years. But despite enormous progress in surface studies during that period many problems, both experimental and theoretical, still confront the scientist interested in heterogeneous catalysis. Modern physical techniques have gone a long way towards making the study of monolayers on metal surfaces an exact branch of science. But the relation of monolayer studies on clean metal surfaces to catalysis under practical conditions still presents great problems and there is much scope for the further development of ideas on heterogeneous catalysis.

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