The Early History of Catalysis

By Professor A. J. B. Robertson
Department of Chemistry, King's College, London

One hundred and forty years ago it was possible for one man to prepare an annual report on the progress of the whole of chemistry, and for many years this task was undertaken by the noted Swedish chemist J. J. Berzelius for the Stockholm Academy of Sciences. In his report submitted in 1835 and published in 1836 Berzelius reviewed a number of earlier findings on chemical change in both homogeneous and heterogeneous systems, and showed that these findings could be rationally co-ordinated by the introduction of the concept of catalysis. In a short paper summarising his ideas on catalysis as a new force, he wrote (1):

> "It is, then, proved that several simple or compound bodies, soluble and insoluble, have the property of exercising on other bodies an action very different from chemical affinity. By means of this action they produce, in these bodies, decompositions of their elements and different recombinations of these same elements to which they remain indifferent."

Berzelius proceeded to propose the existence of a new force which he called the "catalytic force" and he called "catalysis" the decomposition of bodies by this force. This is probably the first recognition of catalysis as a wide-ranging natural phenomenon.

Metallic catalysts had in fact been used in the laboratory before 1800 by Joseph Priestley, the discoverer of oxygen, and by the Dutch chemist Martinus van Marum, both of whom made observations on the dehydrogenation of alcohol on metal catalysts. However, it seems likely that these investigators regarded the metal merely as a source of heat. In 1813, Louis Jacques Thénard discovered that ammonia is decomposed into nitrogen and hydrogen when passed over various red-hot metals, and ten years later, with Pierre Dulong, he found that the activity of iron,

Louis Jacques Thénard
1777–1857

Born at Nogent-sur-Seine, Thénard came to Paris at the age of 17 during the Reign of Terror to study pharmacy. His keenness brought him to the notice of Vauquelin and Fourcroy, both of whom advanced his career. In 1804 he replaced Vauquelin in the chair of chemistry at the Collège de France while in 1810 he was appointed Professor at the École Polytechnique and succeeded Fourcroy in the Academie des Sciences. In 1825 Charles X created him Baron.

From the portrait in the Wellcome Institute of the History of Medicine

Humphry Davy
1778–1829

Davy taught himself by reading Lavoisier's "Traite Elementaire de Chimie" and began his career at the newly formed Pneumatic Institute at Bristol. In 1801 he was offered a post at the Royal Institution by Count Rumford, and it was here that he carried out most of his brilliant experimental work and gave his famous lectures. In 1812 he was knighted by the Prince Regent and he was elected President of the Royal Society in 1820.

From the portrait by Sir Thomas Lawrence in the possession of the Royal Society

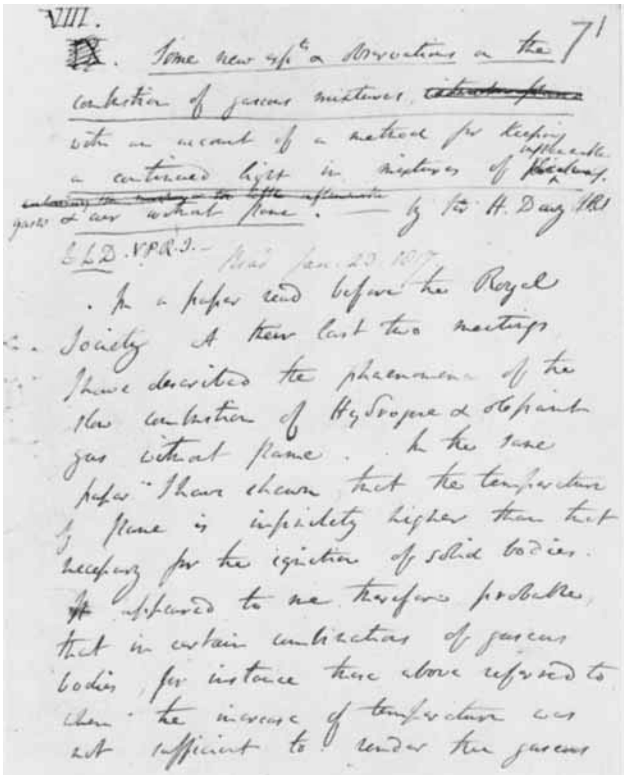
copper, silver, gold, and platinum for decomposing ammonia decreased in the order given. This is one of the earliest recorded examples of a pattern of catalytic activity.

Thénard, the son of a peasant, after experience with Vauquelin in Paris as a laboratory boy, became assistant and later Professor at the École Polytechnique. In 1857, then a peer, he became Chancellor of the University of Paris. His collaborator Dulong was Professor of Physics in the École Polytechnique, later becoming Director. He is, of course, famed for the law of Dulong and Petit. He also proposed a hydrogen theory of acids independently of Davy.

Homogeneous catalytic processes have been used by mankind for some thousands of years, for example in fermentation. Perhaps the first attempt at a rational theory of catalysis is the intermediate compound theory proposed by Charles Bernard Désormes and Nicolas Clément (2) for the homogeneous catalytic effect of nitrogen oxides in the lead chamber process for the manufacture of sulphuric acid. This particular process was later discussed more fully by Humphry Davy, and has received a huge amount of attention and discussion since these early times.

Clément studied science in Paris and became assistant at the École Polytechnique. Later he became Professor at the Conservatoire des Arts et Métiers, and after winning a lottery, married the daughter of Désormes.

That a chemical substance can speed up a chemical reaction without itself being chemically changed became clear in a research on the decomposition of hydrogen peroxide, carried out by L. J. Thénard, who announced his discovery of this substance in 1818. Thénard had become interested in barium peroxide, probably because of the notable discovery by Davy in 1807 of sodium and potassium, which he prepared by the electrolysis of their moist hydroxides. Davy's first Bakerian lecture in 1806 "On some Chemical Agencies of Electricity" described work of such importance that the 3000 francs prize given by Napoleon I was awarded to him. Napoleon seems to have been somewhat peeved that the prize went to an Englishman when a state of war existed between England and France, and, noting the vital part the large Royal Institution voltaic pile had played in the research, he ordered two large voltaic piles to be built. Perhaps he adopted the type of argument we note even now from some political circles, that two voltaic piles will do twice as much useful work as one, irrespective of who originates the ideas to be tried out with the piles. Thénard probably investigated the alkaline earth



The opening page of the manuscript of Sir Humphry Davy's paper read to the Royal Society on January 23rd, 1817, "Some new experiments and observations on the combination of gaseous mixtures, with an account of a method for keeping a continued light in mixtures of inflammable gases and air without flame". The paper goes on: "I had intended to expose fine platinum wires to oxygen and olefiant gas and to oxygen and hydrogen during their slow combination under different circumstances, when I was accidentally led to the knowledge of the fact, and at the same time to the discovery of a new and curious series of phenomena." Davy had discovered heterogeneous catalytic oxidation

oxides with the initial aim of electrolysing them. The work he did on the reaction of barium peroxide with nitric or hydrochloric acid led to the discovery of hydrogen peroxide. This he found to decompose when in contact with many solids, some of which were not chemically changed. He also found that the action of metals in bringing about decomposition became more vigorous as the metal was reduced to a finer state of subdivision.

Humphry Davy's Classic Paper

The first clear realisation that chemical reaction between two gaseous reactants can occur on a metal surface without the metal being chemically changed is found in a paper by Humphry Davy (3) published by the Royal Society in 1817. This describes "the discovery of a new and curious series of phenomena". During the researches which led to the miners' safety-lamp, Davy fixed a fine platinum wire above a coal-gas flame in a safety-lamp. When additional coal gas was introduced into the lamp, the flame went out but the platinum wire remained hot for many minutes. Davy immediately deduced that the oxygen and coal gas combined without flame when in contact with the hot wire, thereby producing enough heat to keep the wire incandescent. A hot platinum wire introduced into a mixture of coal gas and air immediately became incandescent. Furthermore many combustible vapours mixed with air were found by Davy to produce the same effect. Davy had discovered the phenomenon of heterogeneous catalytic oxidation.

Only platinum and palladium wires were effective; wires of copper, silver, gold and iron were ineffective. This is one of the earliest recorded patterns of catalytic activity. In these researches Davy was assisted by Faraday but it is unclear whether Faraday contributed to the development of the ideas or acted mainly by carrying out Davy's instructions. The two-man team which made these discoveries about heterogeneous catalysis must have been one of the strongest in the whole history of chemistry.

In order to initiate catalytic oxidation the wires used by Davy needed to be hot, but in 1820 Edmund Davy (4), Professor of Chemistry at Cork in Ireland, formerly Assistant at the Royal Institution, and cousin of Humphry Davy, prepared a finely-divided platinum catalyst of such high activity that it acted at room temperature. When this catalyst was dropped on to any porous substance moistened with alcohol, oxidation occurred so rapidly that the catalyst became red hot.

Döbereiner's Experiment

J. W. Döbereiner (5), Professor of Chemistry at Jena and formulator of the law of triads, reduced a catalyst prepared by the procedure Edmund Davy had described and obtained a spongy platinum which brought about the combination of hydrogen and oxygen at room temperature and quickly became red hot as a result. This remarkable discovery was rapidly followed up by Dulong and Thénard (6) in Paris, who discovered that palladium and iridium could also act at ordinary temperatures whereas cobalt, nickel, rhodium, silver and gold acted catalytically only at higher temperatures. Their note actually appeared in the *Annales de Chimie et de Physique* before Döbereiner's paper because his discovery was communicated privately by Liebig to Dulong and Thénard.

Döbereiner's work had, however, been communicated from Paris to Faraday in a letter of September 16th, 1823, from J. N. P. Hachette and within a few days Faraday had proceeded to repeat the experiment and confirm the findings. In a brief note (7) signed merely "M. F." he wrote "it was communicated to me by M. Hachette and having verified it I think every chemist will be glad to hear its nature".

Faraday's Review

Dulong and Thénard in a later paper (8) reported that the ability to bring about gaseous combination is a general property of sufficiently-heated solids, while Faraday (9), in a very good review of early work on heterogeneous catalysis, drew attention to the merits

Johann Wolfgang Döbereiner
1780–1849

Born the son of a Bavarian coachman, Döbereiner was apprenticed to a pharmacist and practised as an assistant in Karlsruhe, Bayreuth and Strasbourg. He attended lectures on chemistry, mineralogy and philosophy and in 1810 was proposed for an Extraordinary Professorship in chemistry at the University of Jena. Here he also became a chemical assistant to Goethe. He interested himself in the refining of some South American native platinum, and after learning of Edmund Davy's experiments on the power of platinum black to promote the oxidation of alcohol he showed that platinum sponge would ignite a stream of hydrogen

of their experiments. He wrote (paragraph 611):

> "In the two excellent papers by MM. DULONG and THÉNARD, these philosophers show that elevation of temperature favours the action, but does not alter its character, Sir HUMPHRY DAVY's incandescent platina wire being the same phenomenon with DÖBEREINER's spongy platina. They show that *all* metals have this power in a greater or smaller degree, and that it is even possessed by such bodies as charcoal, pumice, porcelain, glass, rock crystal, etc., when their temperatures are raised; and that another of DAVY's effects, in which oxygen and hydrogen had combined slowly together at a heat below ignition, was really dependent upon the property of the heated glass, which it has in common with the bodies named above."

Later in the paper Faraday wrote (paragraph 618):

> "The effect is evidently produced by most, if not all, solid bodies, weakly perhaps by many of them, but rising to a high degree in platina. DULONG and THÉNARD have very philosophically extended our knowledge of the property to its possession by all the metals, and by earths, glass, stones, etc. (611.); and every idea of its being a known and recognised electric action is in this way removed."

This last sentence in effect rejects a somewhat vague suggestion made by Dulong and Thénard that the power of solids to bring about reactions of gases is electrical in origin, although, as Faraday noted, Dulong and Thénard expressed themselves with great caution on the theory of the effect.

Additional significant experimental discoveries concerning heterogeneous catalytic oxidation were made by William Henry (10), who used as a catalyst either platinum sponge or moulded balls made of china clay and spongy platinum. These catalytic balls were first described by Döbereiner, to whom Henry refers. The two papers by Döbereiner and Henry were the first to describe the use of a supported platinum catalyst. Döbereiner's contributions to catalysis have been reviewed in more detail by McDonald (11). Henry found that ethylene prevented the surface combination of a mixture of hydrogen and carbon monoxide with oxygen, and carbon monoxide slightly slowed down the surface reaction between hydrogen and oxygen. He also found, when working with mixtures of hydrogen, carbon monoxide and methane, that selective catalytic oxidation on platinum is possible.

Henry had studied under Joseph Black in Edinburgh and had also worked with the noted Scottish chemist Thomas Thomson. Later he directed his father's chemical works. He is famed for Henry's law concerning gaseous solubilities.

Fusinieri's Theory

The first attempt to give a detailed theoretical discussion of heterogeneous catalytic oxidation on platinum was made by the Italian physician Ambrogio Fusinieri (12) in a paper published in 1824. He discussed the effects discovered by Döbereiner and others. He also explained in more detail his own experimental observations (first expounded in a note) and remarked that these would dispel all confusion and doubt, writing:

> "Ora espongo in più dettaglio le mie osservazione che dissipano ogni confusione ed ogni dubbio; ed altre ancora ve ne soggiungo di più recenti."

Fusinieri contended, in opposition to Davy, that in fact the combustion of ether on platinum occurs with flame, which may be obscured by light from the platinum, or may be invisible. He further contended that during the oxidation of ether "concrete laminae" of the combustible substance could be seen with the naked eye, the laminae running over the platinum surface and then disappearing by burning. Fusinieri thought that the ether forming the laminae was solidified, although he noted a relation between the appearance and disappearance of the laminae and capillary action of liquids. According to Fusinieri, the platinum catalyst acted like a candle wick with the laminae burning like candle wax. As an explanation of the formation and burning of the concrete laminae, which Fusinieri thought he saw, he proposed the concept of "native caloric" (Faraday's translation).

Faraday in his momentous paper of 1834 (9), which proposed the idea (increasingly supported since the researches of Langmuir) of simultaneous adsorption of both reactants on a platinum surface, reviewed Fusinieri's views at some length, but he confessed that he could not form a distinct idea of the concept of native caloric, and remarked that his knowledge of the language in which the Fusinieri memoir is written was imperfect. Faraday during his European tour with Davy and Lady Davy, in which he acted as scientific assistant and unofficial valet, had learnt Italian, but the Fusinieri paper of 1824 uses Italian which is as out-dated as Chaucerian English, and sentences in which "calorico nativo" appears have been said to be totally incomprehensible (13). It is not surprising that Faraday was unable to form a distinct idea of what Fusinieri meant by "calorico nativo."

The Beginnings of Industrial Catalysis

The industrial possibilities of heterogeneous catalytic oxidation were appreciated as early as 1831 by Peregrine Phillips, Junior, who in that year took out a British Patent (No. 6096) for "Certain Improvements in Manufacturing Sulphuric Acid commonly called Oil of Vitriol." The specification states:

> "The first improvement then, namely, the instantaneous union of sulphurous acid with the oxygen of the atmosphere, I effect by drawing them in proper proportions by the action of an air pump or other mechanical means thro' an ignited tube or tubes of platina, porcelain, or any other material not acted on when heated by the sulphurous acid gas. In the said tube or tubes I place fine platina wire or platina in any finely-divided state, and I heat them to a strong yellow heat, and by preference in the chamber of a reverberatory furnace; and I do affirm that sulphurous acid gas being made to pass with a sufficient supply of atmospheric air through tubes as described, properly heated and managed, will be instantly converted into sulphuric acid gas, which will be rapidly absorbed as soon as it comes into contact with water."

This far-sighted patent has made Phillips one of the inventors who have devised a really new process of manufacture of an important chemical substance. The process was first worked to make fuming sulphuric acid by Messel in 1875. Very little is known about the inventor, despite a search of local records made by E. Cook (14), except that he was the son of a tailor and was born in Milk Street, Bristol.

The first to use platinum as a catalyst for ammonia oxidation was C. F. Kuhlmann who reported his results to the Scientific Society of Lille, France, in 1838. An account of early developments with platinum catalysts for the ammonia oxidation process for nitric acid manufacture has been given by L. B. Hunt (15).

From these small beginnings vast industries based on catalysis have arisen and a huge quantity of scientific information has been accumulated. Despite numerous theoretical discussions catalytic action is still to some extent a mystery—indeed it is notable that large-scale processes are based on catalysts which from a theoretical point of view can hardly be described. Catalysis a century and a half after Davy's discovery still remains a challenge to the chemist.

References

1 (J. J.)* Berzelius, *Annls. Chim. Phys.*, 1836, **61**, 146
2 (C. B.)* Désormes and (N.)* Clément, *Annls. Chim.*, 1806, **59**, 329
3 H. Davy, *Phil. Trans. Roy. Soc.*, 1817, **107**, 77
4 E. Davy, *Phil. Trans. Roy. Soc.*, 1820, **110**, 108
5 (J. W.)* Döbereiner, *Annls. Chim. Phys.*, 1823, **24**, 91
6 (P. L.)* Dulong and (L. J.)* Thénard, *Annls. Chim. Phys.*, 1823, **23**, 440
7 M. F(araday), *Quart. J. Science.* 1823, **16**, 179
8 (P. L.)* Dulong and (L. J.)* Thénard, *Annls. Chim. Phys.*, 1823, **24**, 380
9 M. Faraday, *Phil. Trans. Roy. Soc.*, 1834, **124**, 55
10 W. Henry, *Phil. Mag.*, 1825, **65**, 269; *Phil. Trans. Roy. Soc.*, 1824, **114**, 266
11 D. McDonald, *Platinum Metals Rev.*, 1965, **9**, 136
12 A. Fusinieri, *Giornali di Fisica*, 1824, **7**, 371
13 M. Farinelli, A. L. B. Gale and A. J. B. Robertson, *Annals Sci.*, 1974, **31**, 19
14 (Sir) E. Cook, *Nature*, 1926, **117**, 419
15 L. B. Hunt, *Platinum Metals Rev.*, 1958, **2**, 129

* Initials are not given in the original paper