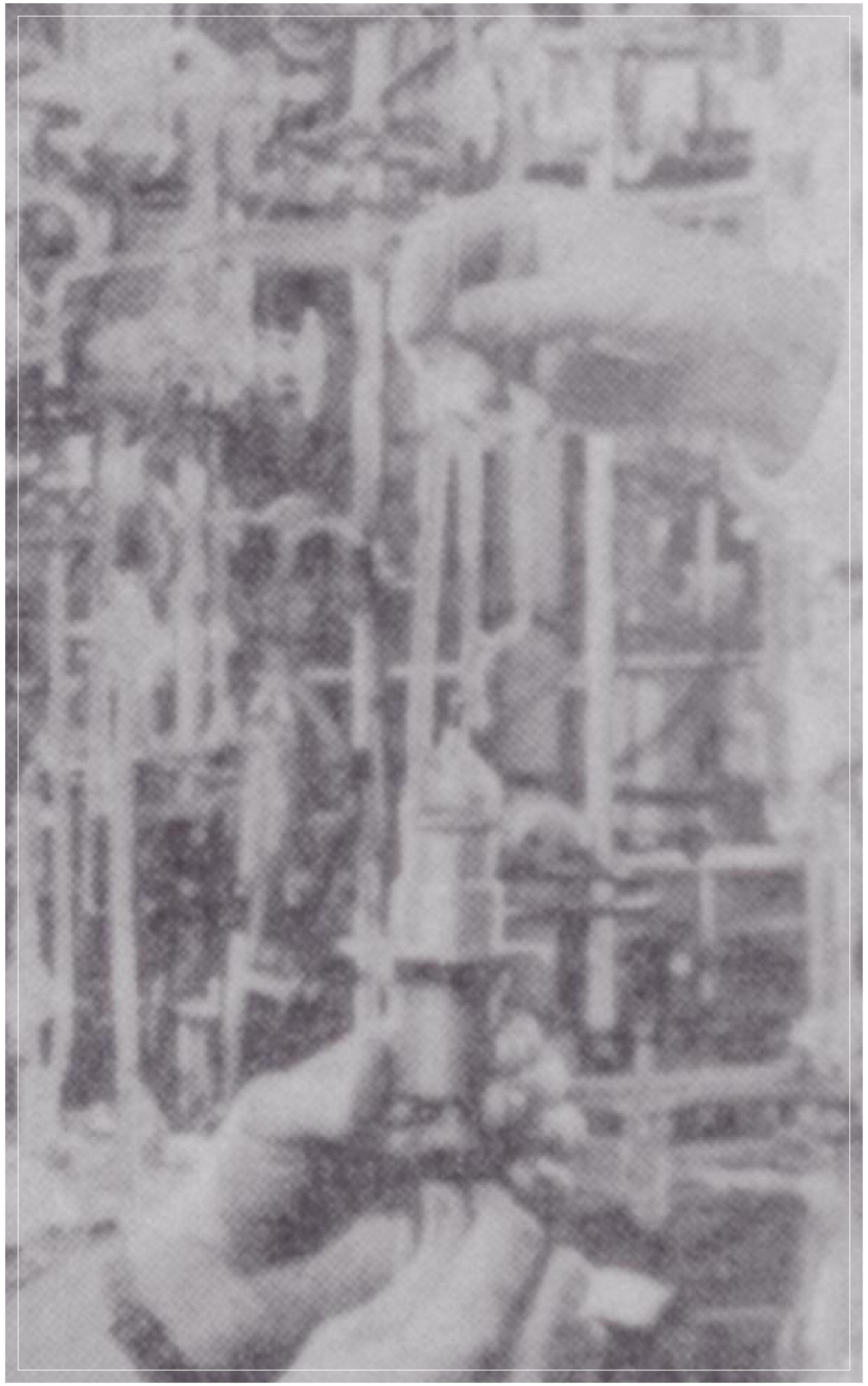

Birth of the catalytic concept

"To understand science it is necessary to know its history" Augusta Comte

The early days of the development of the concept of catalysis are described with contributions from Berzelius, Faraday, Davy, Döbereiner, Dulong, Thénard, Phillips, Ostwald, Henry, Wilhelmy and Kuhlmann. Experiments relating to heterogeneous catalysis included oxidation reactions at platinum surfaces, hydrolysis of esters, formation of ethylene from alcohol, the first patent in 1831 for the manufacture of sulphuric acid and the development by Humphry Davy of the miner's lamp.

The development of catalysis as a concept is accorded to Berzelius who in 1835 realised that a number of isolated observations made by various investigators in the early part of the nineteenth century could be rationalised in terms of what he described as "catalytic power". This he defined as the ability of substances "to awaken affinities, which are asleep at a particular temperature, by their mere presence and not by their own affinity". The catalytic concept was used to explain Kirchhof's observation of the conversion of starch to sugar by acid, Thénard's studies of hydrogen peroxide decomposition by metals and Davy's discovery that when finely divided platinum soaked in spirit of wine conversion took place of ethyl alcohol to acetic acid. Others whose experiments had contributed to the crystallisation of catalysis as a concept included Priestley, Döbereiner, Dulong, Payen and Persoz with Thénard showing as early as 1813 that ammonia decomposed when passed through a red-hot porcelain tube but only if iron, copper, silver, gold or platinum were present in the tube. Döbereiner, formulator of the law of triads, was fortunate to have available several kilos of platinum supplied by the Duke Karl August in Weimar, and oxidised alcohol to acetic acid. In an experiment in 1823 he led a stream of oxy-hydrogen gas over platinum and found that it combined and that the platinum became very hot. A few days later he passed hydrogen over platinum, in air, resulting in a reaction and a flame. This as far as we know was the first lighter - but soon to be replaced by the safety match.

However, the first clear realisation that chemical reaction between two gaseous reactants can occur at a metal surface, without the latter being chemically changed, is due to Humphry Davy and published by the Royal Society (London) in 1817. This paper described the discovery of a "new and curious series of phenomena". During his research which led to the development of the miner's safety-lamp, Davy fixed a fine platinum wire above a coal-flame in a safety lamp. When more coal-gas was introduced into the lamp, the flame was extinguished but the platinum wire remained hot. Davy deduced that the coal gas and air (oxygen) combined without

Jöns Jacob Berzelius

Humphrey Davy

Michael Faraday from the drawing (1852) by George Richmond

flame, when in contact with the hot-wire, thus sustaining it in a hot state, the reaction being exothermic. Only platinum and palladium wires were effective; copper, silver, gold and iron were ineffective. This must be the earliest recorded patterns of selectivity in catalysis.

In these experiments Davy was assisted by Michael Faraday but it is unclear as to their relative individual contributions. A cousin of Humphry Davy, Edmund Davy a Professor of chemistry at Cork in Ireland, and formerly of the Royal Institution in London, prepared in 1820 a finely divided platinum of such high activity that it was active as an oxidant even at room temperature.

H.S. Taylor in his Introduction to the General Discussion held by The Faraday Society in 1932 on the topic of 'Adsorption of Gases by Solids' emphasised Michael Faraday's contributions to the problem of adsorption and suggested that they were "as conspicuously in advance of his time as were his discoveries in other fields of work". Faraday realised from his studies of reactions of hydrogen and oxygen at the surface of platina plates that the phenomena are:

"dependent upon the natural conditions of gaseous elasticity combined with the attractive force possessed by many bodies, especially those which are solid....."

His studies of the inhibitory action of other gases on the process leading to the observation that:

"the very power which causes the combination of oxygen and hydrogen is competent under the usual casual exposure of platina, to condense extraneous matters upon its surface, which soiling it, take away for time its power of combining with oxygen and hydrogen, by preventing their contact with it".

Clearly these are pioneering efforts in the field leading to the concepts of adsorption and surface poisoning. What is also evident is that

communication between those active in this embryonic development of catalysis in various European countries was good. Dulong and Thénard in Paris were aware of Döbereiner's work through private communications from Liebig while in a letter dated September 16th 1923, J.N.P. Hachette had informed Faraday of Döbereiner's results. Within a few days Faraday repeated the experiment and confirmed its findings. In a brief note he wrote "it was communicated to me by Hachette and having verified it I think every chemist will be glad to hear its nature".

Faraday, in a very good review of early work, drew attention in 1834 to the merits of Dulong and Thénard's experiments. He wrote:

"In the two excellent papers by 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 Dö'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".

Some significant contributions to catalytic oxidation were also made by others, amongst whom was William Henry (the formulator of Henry's Law). Döbereiner however was the first to describe the use of supported platinum. Balls were made of china clay and spongy platinum and it was shown that ethylene prevented the surface combination of a mixture of hydrogen and carbon monoxide with oxygen. The concept of surface poisoning was established.

It was an Italian, Fusinieri, who first attempted to give a theoretical discussion of the observations of Döbereiner, Davy and others. He contended that the combination of ether on platinum occurs with flame, which may be obscured by light from the platinum, and that "concrete laminae" of the combustible substances could be seen with the naked eye, the laminae running over the platinum surface and disappearing by burning. Faraday in his 1834 review emphasised the idea that there had to be simultaneous adsorption of both reactants at the surface and confessed that he could not form a precise view of what Fusineri meant by 'native caloric' and acknowledged that his knowledge of the language (not modern Italian!) in which the paper was written was imperfect.

The last significant contribution prior to Berzelius' introducing the concept of catalysis was due to Mitscherlich who in 1833 summarised the reactions which had occurred by "contact" substances. They included the formation of ether, the oxidation of alcohol to acetic acid, the fermentation of sugar and the formation of ethylene from alcohol by heating. Berzelius did no research himself on catalysis - he set out to systematize this field of chemistry as he had done with the concept of isomerism - and in effect his contribution was to give the name 'catalysis' to describe the phenomena observed by others. He saw the possibility that this 'catalytic force' also plays a major part in living organisms. Liebig who had been in correspondence with Berzelius quickly took up this idea and suggested that the function of a catalyst was to overcome a kind of "inertia" which prevented an unstable substance from undergoing chemical changes

Johann Wolfgang Döbereiner

and to accelerate a process which takes place very slowly by itself. Liebig was also critical of Berzelius and indicated that the creation of a new force through a new word - catalysis - explained nothing and was harmful as it might inhibit future research!! However, it is apparent that the word 'catalysis' was already known to Berzelius, and taken to mean "decomposition", in that it is found in Andreas Libavius', Alchemia, published in 1597.

In commenting on the achievements of Berzelius Sir Harold Hartley said:

"Chemistry was indeed fortunate that in the years it was becoming an independent science, and the stream of knowledge was growing so rapidly it had the encyclopaedic mind, the judgement, the craftsmanship and the watchful eye of Berzelius to guide it".

The first report of an entrepreneurial role for catalysis is attributed to Peregrine Phillips who in 1831 took out a British Patent (No. 6069) for "Improvements in Manufacturing Sulphuric Acid commonly called Oil of Vitriol". It was, however, C.F. Kuhlmann, who reported results to the Lille Scientific Society in France in 1838, who described how nitric acid could be produced through the catalytic oxidation of ammonia over platinum.

In the development of what at the time was a controversial concept, the relationship between catalysis and reaction rates, Wilhelmy made a significant advance through his studies of the hydrolysis (by acid) of cane sugar to give dextrose and laevulose. He showed that the reaction rate was proportional to the concentration of sugar present at any given point in time.

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$

However, Ostwald (Nobel Prize 1909) claims to have introduced the concept of reaction velocity as a criterion of a catalytic process by his insistence, since 1888, that a catalyst should be regarded as an accelerator (or inhibitor) of a reaction already taking place i.e. in contrast with the view that a catalyst can initiate a reaction. He put forward the following definition of catalysis in 1895:

"Catalysts are substances which change the velocity of a reaction without modification of the energy factors of the reaction".

There was, however, not universal agreement with others (J.J. Thomson, H.E. Armstrong, Schönbein and Duhem) of the view that catalysts could initiate a reaction.

One of the earliest examples of the connection between catalysis and reversible processes is the studies by Lemoine on the decomposition of hydriodic acid (a heterogeneous reaction) $2HI \rightarrow H_2 + I_2$ and of Bertholet on the equilibria attained in esterification (homogeneous catalysis). Lemoine (1877) demonstrated that in the presence of platinum sponge the decomposition limit at 350^{o}C was 19% attained "immediately". However, without the catalyst at the same temperature, and a pressure of 2 atmospheres, a limit of 18.6% was reached only after about 300 hours. The relationship between the independence of the equilibrium state in catalysis was established and from 1880 onwards the study of catalytic reactions rapidly gained impetus. They became very much part of the development of modern physical chemistry; the catalyst was perceived as operating to produce equilibrium in a system more rapidly than could be achieved in the absence of a catalyst. However, the catalyst could not shift the position of equilibrium, it is independent of the catalyst as was clearly recognised in studies of the Deacon chlorine process by Lewis and von Falkenstein in 1906 and 1907 respectively. It followed from such discussions of equilibria and catalysis that in a reversible process the catalyst must accelerate both the forward and the reverse reactions i.e. for example a hydrogenation catalyst should be equally efficient in the reverse dehydrogenation reaction.

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