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*Concepts in Catalysis.**The Contributions of Paul Sabatier and of Max Bodenstein.*

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THE ever increasing tempo of research in the natural sciences has rendered it difficult, if not impossible, to follow, far more so to digest, the contributions which are daily being made to each sector of the scientific front. It is thus important for us from time to time to survey the past, and to consider what has proved significant and to note and reject the ephemeral. In judging the importance of any experiment or theory, we must remember that ours is a growing subject. Foundations are intended to be built upon and should not need change, even if the edifice which is arising on them assumes unexpected and indeed in some aspects alarming shapes.

It is the custom in our Society to commemorate the life work of our distinguished Foreign Fellows. Owing to the exigencies of war and the pressure of subsequent events, the homage I would like to offer to two of our most distinguished European Fellows, Paul Sabatier and Max Bodenstein, is somewhat belated but none the less sincere, and it is on their contributions to our concepts in catalysis that I would like to lay special emphasis.

Those that believe in the termite world, to use the words of our former Prime Minister, or consider that distinct types of men are most useful for certain purposes as H. G. Wells's fanciful picture of the inhabitants of the moon suggests, would find it difficult to obtain evidence of any such physical or psychical similarity between these two great men; indeed this is but another example of the fact that the Divine Spirit giving us insight into the ways of Nature, like the wind, bloweth whithersoever it listeth.

Paul Sabatier was born at Carcassonne on November 5th, 1854. In 1874 he went to the École Normale Supérieure from which he graduated in 1877. In 1878 he became assistant to Berthelot at the Collège de France. For his doctorate in 1880 he submitted a thesis on the thermochemistry of sulphur and metallic sulphates. In January 1882 he entered the University of Toulouse, to which he grew greatly attached and where he spent the rest of a remarkably active life. He was released from his posts of Dean and Professor in 1930 but continued to lecture until his death on the 14th of August 1941. He married Mlle. Herail and had four daughters. He was the recipient of many honours, sharing the Nobel Prize with his countryman Grignard; he received the Davy Medal in 1915 and the Royal Medal in 1918. He was a modest and retiring man, loving his work and beloved by his students and co-workers.

Max Bodenstein was born at Magdeburg on July 15th, 1871. In 1889 he went to the University of Heidelberg, where he "promoviert" with Victor Meyer in 1893. After working a short time with Liebermann on organic chemistry and with Nernst on physical chemistry, and completing his military service, he took his degree in Heidelberg in 1899. He then went to Leipzig where he stayed until 1906. Subsequently he was two years at Nernst's Institut in Berlin. From 1908 to 1923 he occupied the chair at the Technische Hochschule in Hanover, succeeding Nernst in Berlin in 1923. In 1936 he was made Emeritus Professor but continued to work in Berlin until his death on the 3rd of September 1942.

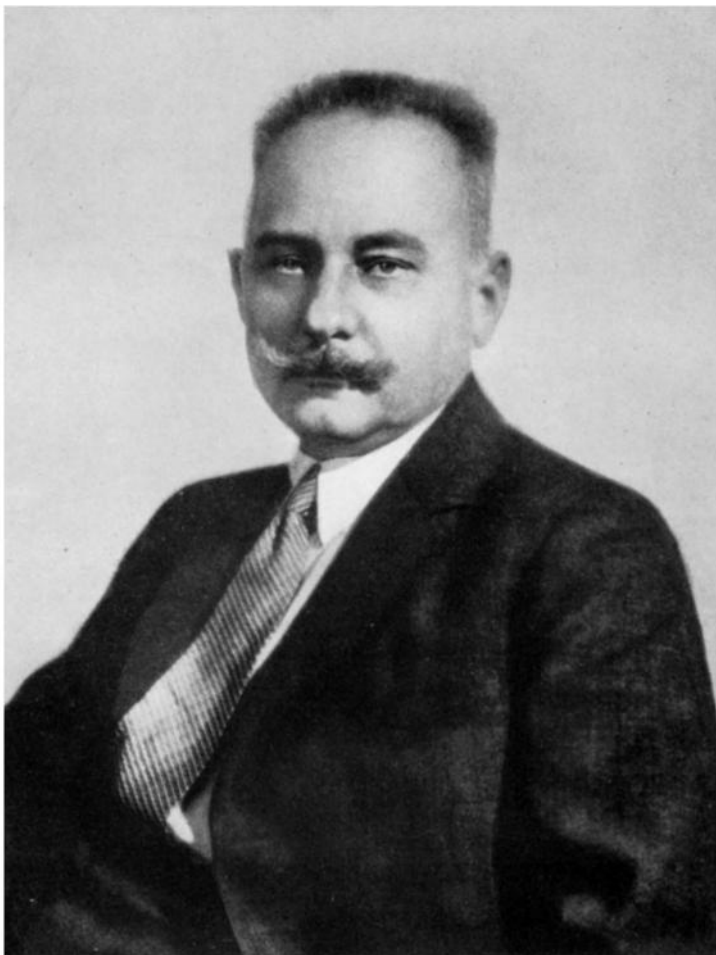
Bodenstein was a great experimentalist and, like Sir William Ramsay, uncannily skilled in the art of glass-blowing. Like many chemists he was a very keen Alpine climber, and during his lifetime gave ample proof of his capabilities as an organiser.

The method of approach to the problems of heterogeneous catalysis by these two investigators was quite different. In 1896 Moissan and Moureu had shown that acetylene reacted with reduced metals, raising them to incandescence. Sabatier decided to use the "less violent" hydrocarbon



Paul Sabatier

[Reproduced, with permission, from "Les Prix Nobel," 1912.]
[To face p. 1640.]



Bodenstein

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ethylene. On passage of this gas over reduced nickel, at 300° c. a reaction commenced, to give black carbon, and, on analysing the gas formed simultaneously, he was interested to find that it was not hydrogen as he expected but mainly ethane. Clearly the ethylene had undergone decomposition on the surface, the reaction involving a hydrogen transfer. It is interesting to note that this important observation had been ignored until attention was drawn to it quite recently by Beeck, whose untimely death we all deplore. This investigation led Sabatier to examine the catalytic reduction, by hydrogen, of ethylene to ethane and of acetylene to ethylene and ethane. He extended the scope of his enquiry to the various metals when prepared in an active form capable of bringing about hydrogenation and found cobalt, iron, and copper as well as platinum effective, but all less energetic than nickel. He likewise brought about the reduction, till then unaccomplished, of benzene to *cyclohexane*. In addition to the metals, he showed that certain oxides, *e.g.*, those of zinc and manganese, could bring about the hydrogenation–dehydrogenation reaction, whilst other oxides, *e.g.*, thoria, silica, and alumina, possessed the power of bringing about reversible dehydration–hydration reactions.

When Sabatier commenced his investigation on catalysts little was known about their mode of action, although the phenomenon of catalysis had been well established. The only consistent theory at that time had been propounded by Faraday, who wrote concerning the catalytic combination of hydrogen and oxygen on the surface of platinum: “The course of events when platinum acts upon and combines oxygen and hydrogen may be stated according to these principles as follows. From the influences of the circumstances mentioned, *i.e.*, the deficiency of elastic power and the attraction of the metal for the gases, the latter, when they are in association with the former, are so condensed as to be brought within the action of their mutual affinities at the existing temperature, the deficiency of their elastic power not only subjecting them more closely to the attractive influence of the metal, but also bringing them into more favourable states for union by abstracting a part of that power (upon which depends their elasticity) which elsewhere in the mass of gas is opposing their combination. The consequence of their combination is the production of the vapour of water and an elevation of temperature. But as the attraction of the platina for the water formed is not greater than for the gases, if so great (for the metal is scarcely hygrometric), the vapour is quickly diffused through the remaining gases. The platina is not considered as causing combination of any particles with itself but only associating them closely around it and the compressed gases are as free to move from the platina being replaced by other particles as a portion of dense air upon the surface of the globe or at the bottom of a deep mine is free to move by the slightest impulse into the upper and rarer parts of the atmosphere.” Sabatier could not accept this purely physical view of the function of the catalyst, observing that charcoal should on this view be almost a universal catalyst whereas it proved to be somewhat mediocre except for the formation of carbonyl chloride. Again, whilst metals when finely divided absorb considerable quantities of gas, these absorptions are somewhat specific being “characterised by a sort of selective affinity.” He noted that some of these reactions are remarkably specific; thus zinc oxide decomposed formic acid into hydrogen and carbon dioxide, but at the same temperature titania gave carbon monoxide and water. We see here the first suggestion that there are two kinds of adsorption, a physical one due to the action of dispersive forces and a chemical one in which an electronic switch is involved.

Sabatier thus formulated a chemical theory of catalysis in which the formation of unstable chemical compounds as intermediary stages is postulated. These determine on his view the direction and speed of the reaction. He stressed the importance of what he termed reciprocal catalysis. Thus hydrogen peroxide solutions decompose relatively slowly in the cold, and the same is true for solutions of chromic acid, but when the two solutions are mixed there is a rapid decomposition with a brisk evolution of oxygen. The decomposition takes place in a proportionate manner corresponding to $3\text{H}_2\text{O}_2 : 2\text{H}_2\text{CrO}_4$. The clue to this reciprocal action is to be found in the formation of the dark blue perchromic acid.

Sabatier showed that in several cases definite intermediate compounds could be isolated. Thus in the catalytic oxidation of organic compounds with the aid of copper, or the decomposition of carbon monoxide on nickel, the intermediaries, copper oxide and nickel carbonyl, respectively, can be isolated and identified. For the hydrogenation of ethylene, Sabatier advances arguments for the “fixation,” or in modern nomenclature the “chemisorption,” of hydrogen by the nickel as the intermediary complex. In the case of acetylene, however, he remarked that it was adsorbed more energetically than hydrogen, thus indicating the possibility of organometallic compounds playing a rôle in heterogeneous catalysis.

On the hypothesis of the existence of intermediary compounds, it is a matter of some interest

to decide whether, for those oxides which bring about the reactions both of dehydration and of dehydrogenation, the same intermediary compound is formed which can decompose in different manners, or whether two different intermediary compounds are formed each with its own particular mode of decomposition. If two different compounds are formed they should possess different properties and the ratios of the quantities of each compound might well be a function of the mode of formation of the surface. We might postulate the existence of an alkyl aluminate undergoing dehydration and a molybdenyl alkoxide undergoing dehydrogenation. This was Sabatier's view and later evidence supports it.

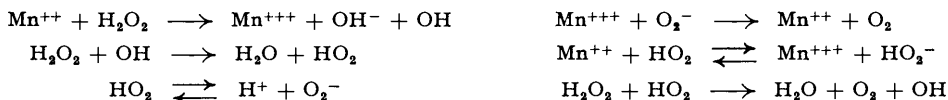
Sabatier summarises his views in respect to the mechanism of catalytic action as follows:

"As far as I am concerned, this idea of temporary unstable intermediate compounds has been the beacon light that has guided all my work on catalysis; its light may perhaps be dimmed by the glare of lights as yet unsuspected which will arise in the better explored fields of chemical knowledge. Actually, such as it is, in spite of its imperfections and gaps the theory appears to us good because it is fertile and permits us in a useful way to foresee reactions."

We must note that Sabatier was the first to demonstrate—and catalytic methods made it possible—the reversibility of the reaction, alcohol \rightleftharpoons aldehyde + hydrogen, the progenitor of the now copious thermodynamic and statistical investigations on the free energies of organic reactions. Not only did he demonstrate the selectivity of catalytic action, but also a selectiveness in their sensitivity to poisons; thus the various stages in the catalytic reduction of nitrobenzene by means of hydrogen to cyclohexylamine could be controlled by suitable selective poisons. He noted also the greatly increased activity obtained by spreading a catalyst on a support and, as early as 1897, measured the temperature coefficient of such reactions.

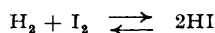
Sabatier termed the chemisorption of reactants on metals "fixation." The metal substrate can be regarded as an electron sink (the vacant *d* bands) or an electron donor (the *s* bands) depending on the nature of the reacting system; *e.g.*, we find for W_xH and Pt_xH that the dipoles are $\overset{+}{W}_x\overset{-}{H}$ and $\overset{-}{Pt}_x\overset{+}{H}$ respectively. As we fill up the surface there are an increasing mutual repulsive interaction between the surface dipoles and a progressive weakening of the interaction between substrate and chemisorbed species. The term "chemisorption" implies a constant and invariant heat of formation, but in those cases which have been examined there is a progressive fall in the heat of sorption. This fall has been attributed to heterogeneity of the surface but the actual form of the curve can be fully accounted for on the basis of an interaction energy. Similar progressive changes are to be noted in the photo-electric and thermionic work functions, and in the ratio of evaporation of atoms to ions in evaporative processes. We may observe that the peculiar effectiveness of nickel as a catalyst may be due in part to the fact that it has not only a $3d^84s^2$ ground state but two excited states $3d^94s^1$ and $3d^{10}$ respectively. It can thus act with ease both as an electron donor and as electron acceptor.

In the case of non-metallic catalysts, *e.g.*, the oxides, the concept of an electron switch is equivalent to an alteration in valency of some constituent catalyst; thus in the catalytic decomposition of hydrogen peroxide on a manganese oxide catalyst we can regard the catalytic operation as essentially a transition from $Mn^{++} Mn^{+++}$ to $Mn^{+++} Mn^{++}$. The reaction might be formulated as:



In this connection Selwood's investigations on the effect of various catalytic supports on the valency of the incorporated catalytic oxide ions seem to me to be of significance, as well as the attention being paid to semi-conducting oxides, *e.g.*, V_2O_5 , CeO_2 , CuO , and ZnO , as oxidation catalysts, and the photo-conductors such as the sulphides of lead, antimony, and cadmium.

In 1884 van't Hoff's classical work "Étude de Dynamique Chimique" had appeared and this had a great influence on Bodenstein. At that time many cases of so-called "false equilibrium" were cited in the literature, *i.e.*, systems apparently reversible in character but terminating in mixtures of different composition when approached from each end. Included in these cases was the interaction of hydrogen and iodine to give hydrogen iodide,

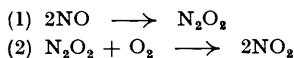


Bodenstein first demonstrated that a true equilibrium could be attained in this system from either end, and then commenced that phase of his investigations to which he devoted the rest of his

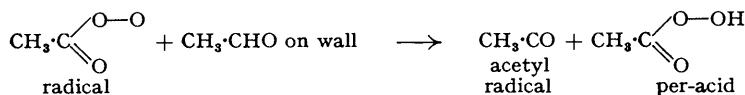
life, namely, the kinetics of gas reactions, commencing with the decomposition of hydrogen iodide and the combination of hydrogen with iodine.

The determination of the absolute rate constants and the influence of temperature permitted Bodenstein to test the applicability of the kinetic theory. As we now know, these particular reactions were eminently suitable for such an examination since the molecules involved were relatively simple. These reactions, together with the decomposition of dinitrogen tetroxide, have proved to be the corner stones of the theory of bimolecular gas reactions.

Bodenstein then investigated termolecular reactions such as $2\text{NO} + \text{O}_2$ and the reactions of nitric oxide with the halogens. Later he showed that these were really sequent reactions and he could account for a negative temperature coefficient on the assumption of the sequence :



The classical work of Bunsen and Roscoe on the hydrogen-chlorine reaction was next examined, and the concept of chain reactions in which atoms served as chain carriers permitted Bodenstein to gain an insight into the reactivities of free atoms and radicals, and the mechanism of operation of inhibitors such as oxygen, ammonia, water vapour, and the walls of the containing vessel. These experiments in turn led to the principle of detailed balancing and the concept of quasi-stationary states in which each sequent reaction could be examined for entropy or steric factors, thermal changes, and activation energies. For the combination of atoms, Bodenstein showed that a three-body collision was necessary. In the autoxidation of acetaldehyde he postulated the formation of intermediary reactive radicals

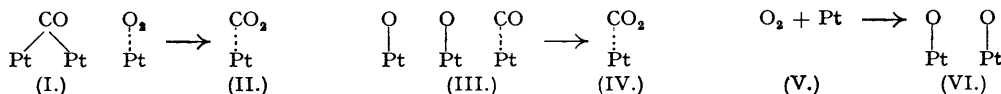


Bodenstein's approach to the problems of heterogeneous catalysis was naturally from the kinetic standpoint : under what conditions do the rate of transport or reactants to the catalyst, the rate of reaction at the catalyst surface, and, finally removal of products from the catalyst govern the overall rate of reactions ?

On investigating the combination of sulphur dioxide and oxygen at the surface of platinum, Bodenstein concluded that the rate of combination was governed by the rate of diffusion of the sulphur dioxide to the platinum, through the layer of sulphur trioxide, a view slightly reminiscent of that of Faraday. He applied similar considerations to the catalytic oxidation of carbon monoxide at the surface of crystalline quartz and quartz-glass, the reaction in the latter case being inversely proportional to the pressure of carbon monoxide.

In 1916 Langmuir published his well-known paper on the catalytic oxidation of carbon monoxide and of hydrogen at the surface of platinum. He showed that the formal reaction kinetics of the carbon monoxide oxidation at a platinum surface, even at very low pressures, obeyed the same laws as Bodenstein found for the reaction at a fused-quartz surface. Langmuir showed *inter alia* that carbon monoxide, oxygen, and hydrogen when chemisorbed on platinum occupied two elementary lattice spaces or that the surface compounds were bivalent in respect to carbon monoxide and that both hydrogen and oxygen formed elementary hydrides and oxides.

The oxidation of carbon monoxide did not take place between two neighbouring chemisorbed species and of the various alternative processes which can be depicted as :



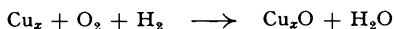
reactions (III) \longrightarrow (IV), and (V) \longrightarrow (VI), proceed much more readily than (I) \longrightarrow (II). We may regard the carbon monoxide when adsorbed as relatively inert or as a poison. It can be considered in the light of a co-ordination compound with closed (complete) electron shells, having in consequence a high ionising potential rendering electron transfer a difficult operation. The reaction competing with (I) \longrightarrow (II) is the evaporation of carbon monoxide.

It is possible that the views of Sabatier in respect to a "fixation" or formation of an intermediary compound, which received such precise formulation by Langmuir's concepts of surface atomic centres' being equivalent to free radicals in reactivity, modified Bodenstein's views. For we find that in his later investigations in respect to heterogeneous catalysis Bodenstein

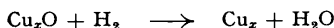
evidence for their presence on the surface; thus it is difficult to distinguish the mechanisms where the following thermal changes are involved :



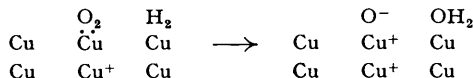
Sabatier noted the variation in catalytic activity between copper, which had been slightly oxidised, and cupric oxide which is formed above 500° c. On slightly oxidised copper the reaction between hydrogen and oxygen takes place by means of the following interesting coupled reactions :



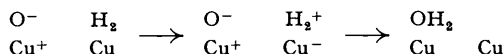
which at higher temperatures is followed by a reaction



The energy of activation of the coupled reaction is *ca.* 6500 cal./g.-mol., which is remarkably close to the work function for the elevation of electrons from the sources into the conducting bands of the semi-conducting cuprous oxide (*ca.* 0.35 volt). One might suggest that the detailed mechanism might be represented as



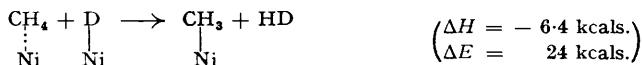
On strongly oxidised copper the combination of the hydrogen proceeds in a perfectly stoichiometric manner to water with a much higher energy of activation which is comparable to that obtained for the activated diffusion of the hydrogen in copper oxide, and the reaction scheme might be represented as :



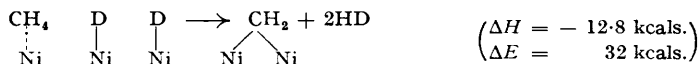
A similar reaction scheme could be proposed for the oxidation of carbon monoxide on a slightly oxidised copper surface.

It is perhaps significant in this last reaction that on copper oxide there is no exchange of isotopic oxygen between oxygen and carbon dioxide until temperatures in excess of 500° are attained, suggesting that the reaction $Cu_xO + CO_2 \longrightarrow Cu_xCO_3 \longrightarrow Cu_xO + CO_2$ requires a relatively high energy of activation, whilst the catalytic oxidation of carbon monoxide itself will proceed at 120°.

Bodenstein, as we have observed, chose as the reaction system one involving in the ultimate analysis reaction between a chemisorbed and a physically adsorbed species. Langmuir's analysis of the catalytic oxidation of carbon monoxide led him to similar conclusions. The entropy changes involved may prove to be an important factor in determining the velocity of any particular reaction system. A good example of such has recently been examined by Kemball who has shown that of the two reactions which may be written :



and



the second reaction proceeds more rapidly than the first (the former losing some 15 e.u. and the latter gaining some 20 e.u. in the process). The reaction between two chemisorbed neighbours is favoured by the entropy changes, but there are also certain basic assumptions involved : first, that the dipolar repulsive forces shall be small and identifiable with the energy of activation, and, secondly, that one or both of the chemisorbed species shall be mobile at the temperature of catalysis. Thus in the combination of hydrogen and oxygen at a platinum surface it

would appear that under certain conditions the reaction apparently involves the interaction between chemisorbed neighbours and it is possibly significant that the dipoles formed in this case from the reactants are opposite in sign, *i.e.*, $\text{Pt}_x\text{H}^+ \text{Pt}_x\text{O}^-$.

We are now reasonably confident that in many cases, if not all, of physical adsorption there is some measure of surface mobility, at any rate under the conditions of temperature and vapour or gas pressures usually involved. In the case of chemisorption, however, direct evidence is not so clear.

To identify the energy of activation of the catalytic process with the removal of the electron from the source into a migrating level, as we have seen in the case of the reduction of cupric oxide, is an over-simplification, for here we appear to demand the presence only of electron sinks in the substrate, *e.g.*, Cu^{++} or oxygen (in N-type semi-conductors). Again we note that the electron has a considerable range of motion from source to conducting level to sink, and the impurity or electron source or electron sink itself does not necessarily move. It is known, however, that these sources and sinks do begin to move at elevated temperatures (*e.g.*, movement of K^+ and Cl^- in the KCl lattice) and contribute to the conductivity.

The distinction between a mobile and an immobile film may be detected in those cases where repulsive forces exist between the chemisorbed species by the rate at which the surface fills up. If the interaction energy for the chemisorption of hydrogen be of the order $\epsilon/RT = 9.0$, this rate is given in the following Table.

θ .	Ratio of time for filling,		θ .	Ratio of time for filling,	
	mobile	immobile		mobile	immobile
0.1	1.0		0.6	2.8×10^2	
0.3	1.06		0.7	9.7×10^2	
0.4	1.20		0.8	1.9×10^3	
0.5	2.97		0.9	12.0×10^3	

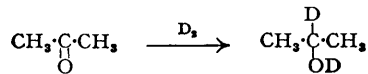
We note that at $\theta = 0.5$, when the film is mobile, the surface will, owing to the operation of the repulsive forces, tend to acquire a regular checker board arrangement. Subsequent adsorption will be dependent on fluctuations in this arrangement and thus proceed much more slowly than for an immobile film. It would appear with this criterion that chemisorbed oxygen becomes mobile on metals only at relatively high temperatures. The third factor which must play a part in such a mechanism is the surface atomic spacing. This indeed is important also in cases (2) and (3), where the act of chemisorption involves interaction with more than one atom of the substrate, *e.g.*, in chemisorption of hydrogen or of an unsaturated hydrocarbon. The hydrogenation of ethylene at various metallic surfaces is a good example of this fact, so much insisted upon by Balandin; the range of atomic spacing operative lying between 3.2 and 4.5 Å. with an optimum at *ca.* 3.75 Å. (rhodium).

It is still a much debated problem whether relatively large portions of a catalytic surface, *e.g.*, specific crystal surfaces containing appropriately spaced atomic centres, are the seat of catalytic activity or whether highly localised active patches, *e.g.*, lattice defects, are responsible. The concept of active patches has been supported on several grounds. The form of the $\Delta H-\theta$ curve has been advanced in support of the former postulate.

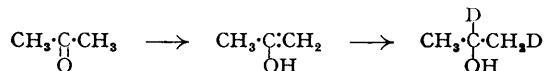
We have seen that such a falling off in ΔH values with surface coverage can be accounted for by considerations already advanced in interpreting electron, ion, and atom emission from monolayer-coated emitters. If an active-patch interpretation is to be advanced it is evident that the lifetime of the adsorbed species either on the surface or in the same spot (surface mobility) must be short compared with the duration of the experiment. This does not appear to be the case for values of $\theta < 0.5$ where ΔH attains relatively high values. The selectivity of poisons has likewise been advanced to support the concept of active patches. Here again surface mobility of the poison is a *sine qua non*. Interpretations based upon multi-point contact of a reactant lead to forms of curves which do in fact reproduce those experimentally obtained and which are frequently interpreted on the active-patch view.

If a small quantity of deuterium is admitted to a nickel catalyst and this is followed by the admission of a small quantity of hydrogen, on evacuation of the system the first samples of gas to be removed are rich in hydrogen. If we reverse the procedure, the gas is found to be rich in deuterium. This experiment has been cited in support of the view that the surface of the nickel is energetically heterogeneous. We note, however, that diffusion of the gas into the interior of the nickel would achieve the same results.

Whilst the results of the use of isotopic hydrogen in this particular experiment cannot be interpreted in a unique manner, there are, however, many cases where the use of deuterium or tritium or other radio- or mass isotopes does contribute to our proper understanding of the reaction mechanism. Thus, for example, in the catalytic hydrogenation of acetone at low temperatures the reaction proceeds as follows :



whilst at higher temperatures there is an increased intervention of the reaction,



We have noted that the formation of a chemisorbed species involves an electron transfer and that the subsequent catalytic reaction involves a similar passage of an electron. This again emphasises the necessity for the presence of electron sources and electric sinks in the catalyst itself. These, as we know especially from work on semi-conductors and binary alloys, may be increased or decreased by the inclusion of electron donors or acceptors in the catalyst or its support. In the sense that an electron switch is involved in the catalytic action, these sources or sinks may be regarded as active patches, but it is clear that if the electron can travel, as indeed it can in conductors and semi-conductors, a long distance between source and sink, the active patches need not be near the surface at all.

In this review I have attempted to show that, in the contributions of Paul Sabatier and Max Bodenstein to our knowledge of the mechanism of heterogeneous catalysis, there is much of permanent value but also there is still much to be discovered before Sabatier's beacon light suffers eclipse.

