

## CHEMICAL REACTIONS AT SURFACES

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The application of the term "catalysis" to a set of chemical phenomena is, in major part, a confession of ignorance. It normally indicates the existence of a series of chemical reactions of which the initial and final states are readily stated, while, of the path between, little or nothing is yet known. When known, the need for the term "catalysis" disappears for the total process becomes a succession of normal chemical reactions. This is true alike of the so-called catalytic reactions in homogeneous systems and of the heterogeneous catalytic reactions, those occurring at surfaces. The use of the term "catalysis" will steadily yield to a more penetrating analysis of the detailed steps of the gross process.

The scientific study of the heterogeneous catalytic reactions has undergone a complete revolution in the last fifteen years, a revolution which justifies the paragraph with which this discussion has been opened. Fifteen years ago these studies were hampered by an assumption that what were in reality fascinatingly interesting chemical processes might be determined in rate by purely physical processes of diffusion. This was an inheritance from some pioneering studies of Noyes and Whitney (1) on the velocity of solution of such substances as lead chloride and benzoic acid in water in which, undoubtedly, the rate of diffusion from a saturated layer next to the solid was the rate-determining factor. These studies were developed with characteristic thoroughness in the laboratories of Nernst (2) and were introduced into the realm of gas reactions by Bodenstein and Fink (3) to explain their beautiful kinetic studies of the velocity of sulfur trioxide forma-

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tion from sulfur dioxide and oxygen at the surface of platinum. The kinetics of this reaction seemed to indicate that the rate of reaction was determined by the rate at which sulfur dioxide could penetrate an adsorbed layer of sulfur trioxide to reach a platinum surface at which oxygen was already present, an instantaneous reaction of the two gases then occurring.

Langmuir initiated the revolution (4) and formulated the plan of campaign. His well-known studies of the reactions of gases with tungsten filaments led inevitably to his concept of surface forces of solids and their saturation by a unimolecular layer of adsorbed gas molecules. The x-ray analysis of crystalline solids by W. H. and W. L. Bragg had revealed both the nature of the unsaturation of the surface atoms and the geometric pattern of the atoms in the plane surface of a solid. The surface of a catalyst, therefore, from Langmuir's point of view, could be regarded "as consisting of a checkerboard in which some of the spaces are vacant while others are filled with atoms or molecules. . . . . When gas molecules condense on the solid surface in such a way that they are held on the surface by primary valence forces involving a rearrangement of their electrons, their chemical properties become completely modified. It is not surprising that in some cases such adsorbed films should be extremely reactive, while in other cases they may be very inert to outside influences. Thus, oxygen adsorbed on platinum reacts readily with hydrogen or carbon monoxide, while oxygen on tungsten, or carbon monoxide on platinum show very little tendency to react with gases brought into contact with their surfaces." Langmuir here stated explicitly what is quite frequently overlooked, namely, that the operation of surface forces might prevent reactions which in the presence of another surface might readily occur. His example of the inability of hydrogen and oxygen to react at a tungsten filament maintained below 1500°K. is, as will be shown later, a very significant illustration of newer ideas concerning surface activity. Langmuir further pointed out that "the specific nature of these various films is quite consistent with the theory that the adsorption depends on typical chemical action. In many cases, especially where we deal with adsorption of large mole-

cules, the orientation of the molecules on the surface is a factor of vital importance in determining the activity of the surface towards reacting gases.

“The reaction which takes place at the surface may occur by interaction between molecules or atoms adsorbed in adjacent spaces on the surface or it may occur between an adsorbed film and the atoms of the underlying solid, or again, it may take place directly as a result of a collision between a gas molecule and an adsorbed molecule or atom on the surface. . . . When a surface is covered by different kinds of adsorbed molecules distributed at random over the surface, we may expect in general that adsorbed molecules in adjacent spaces should be able to react with one another at a rate which is proportional to the chance that the given molecules shall lie in adjacent spaces.”

Thus, in a few swift sentences, Langmuir outlined the direction of progress in the subject, and the research of the past ten years has been abundantly rich in verification of his concepts: elementary space; surface saturation of the solid with unimolecular oriented gas layers, chemically specific in their behavior, reactive and non-reactive; interaction of adjacent molecules or of molecules by collision and at rates determined by the probability of such contact. The program had an insistent appeal, and an intensive development set in at various research centers. Among the more prominent of these may be mentioned the following: Cambridge, England, with Rideal and Constable; Oxford with Hinshelwood; Munich with Schwab; Oppau with Mittasch and Frankenburger; Ludwigshafen with Mark and his collaborators; in this country the Universities of California, Cornell, Johns Hopkins, Virginia and Princeton and also the Fixed Nitrogen Research Laboratory at Washington, D. C. It is with the progress of these studies, their contribution to our present concepts of reactions at surfaces and the new points of view which even the brilliant forecast of Langmuir did not include that the following pages deal.

In the main, two distinct types of research have contributed to the progress achieved. On the one hand, the method employed has been the study of the kinetics of suitable reactions

occurring at sufficiently simple surfaces—a study of the influence of the concentrations of reactants on the velocity with which the reaction proceeded in the reaction zone, the layer of adsorbed gas varying from a sparsely covered surface at sufficiently low reactant concentrations to a saturated unimolecular layer of gas completely covering the surface at sufficiently high concentrations. These studies have been confined practically exclusively to gaseous systems. From the influence of temperature on the velocity and the kinetics of such reactions the energies involved in the reactions have been computed, and comparisons thus facilitated between the reaction energies required when the process occurs at surfaces and when it occurs homogeneously in the gas phase. The other method of investigation has focussed attention not on the reaction but on the surface, its properties and behavior towards potential reactants, studied, in the main, singly. This phase of the work has involved studies of adsorption and heats of adsorption, the influence of extension of the surface and of the enhanced activity of surfaces secured by extension, and the deliberate admixture with the surface material of addition agents which promote or depreciate the surface activity. Conspicuous advances have been achieved also by the skillful combination of both methods of study notably by Pease (5) in the study of the poisoning action of carbon monoxide in the hydrogenation of ethylene on copper, by Russell (6) and Almquist and Black (7) in the study of the action of promoters, and quite recently by Dohse and Kälberer (8) in the elucidation of the mechanism of decomposition of alcohols at the surfaces of typical oxides by studies of reaction velocities in unimolecular adsorbed films.

#### KINETIC STUDIES OF SURFACE REACTIONS

The adsorption of a gas to form a more or less saturated unimolecular layer of adsorbate is due, according to Langmuir (4), to the time lag between condensation and reëvaporation of the molecules striking the adsorbing surface. Since, on a uniform surface, the rate of condensation  $r_1$  is proportional to the gas pressure,  $p$ , the fraction of the surface,  $1 - \sigma$ , which is bare, and to an accommodation coefficient,  $\alpha$ , characteristic of the surface

and expressing the fraction of the collisions which are inelastic (a fraction which is in many cases almost unity) we may write

$$r_1 = k\alpha p (1 - \sigma)$$

or, for a given surface under constant conditions,

$$r_1 = k_1 p (1 - \sigma)$$

Similarly the rate of evaporation,  $r_2$ , is proportional to the fraction of the uniform surface covered; hence,

$$r_2 = k_2 \sigma$$

At the steady state of constant adsorption these rates are equal, whence we derive the expression,

$$\sigma = \frac{k_1 p}{k_2 + k_1 p}$$

for the fraction of the surface covered at the pressure  $p$ . We may further simplify this to the expression

$$\sigma = \frac{bp}{1 + bp}$$

where  $b = k_1/k_2$ . From this it is evident that an adsorption isotherm at a given temperature will, in general, contain three readily distinguishable segments. At low pressures and small adsorptions  $\sigma = bp$ , or, the surface covered varies linearly with the pressure. For high adsorptions where  $bp$  is large compared to unity,  $\sigma = 1$ , and the surface covered is independent of the pressure; it has become saturated. Between these two extremes there falls a curved portion of the isotherm in which the variation with  $p$  is intermediate to those just given and which over a sufficiently restricted range of pressures may be expressed adequately by

$$\sigma \propto p^{1/n}$$

where  $n$  is greater than unity. A thermodynamic deduction of this adsorption isotherm by Volmer (9) reveals that the satura-

tion point is reached when half the surface atoms are covered with adsorbed molecules. This is attributed by Volmer to a two-dimensional mobility of adsorbed molecules, a phenomenon experimentally established by the work of Volmer and Adhikari (10), who demonstrated such motion of benzophenone molecules on glass and of adsorbed iodine on mercury surfaces.

In a similar manner the fraction of the surface covered by a gas, A, in a mixture of gases A and B, is expressible by the equation

$$\sigma_A = \frac{bp_A}{1 + bp_A + b'p_B}$$

with a corresponding expression for the gas B. A recent experimental study of such adsorption from mixtures by Markham and Benton (11) confirms in part the correctness of such an expression, though in some of the cases studied secondary factors also are operative.

(a) *Single reactant*

For reactions occurring exclusively at the surfaces in question it is assumed that the reaction velocity obtaining is proportional to the fraction of the surface covered by the adsorbed gas, which, as has been shown, is, in its turn, related to the gas concentration, or pressure  $p$ , by the adsorption isotherm. For a single reactant, the three cases already cited of slight adsorption ( $\sigma = bp$ ), complete adsorption ( $\sigma = 1$ ) and partial saturation ( $\sigma \propto p^{1/n}$ ), yield on this assumption three simple characteristic velocity equations. In the first,

$$- dp/dt = k\sigma = kbp = k'p$$

in the second,

$$- dp/dt = k\sigma = k$$

and in the third,

$$- dp/dt = kp^{1/n}$$

These constitute the simplest possible reaction kinetics at surfaces and examples of each have been studied. Each is char-

acteristic. The first expression is identical in form with that of a unimolecular homogeneous reaction. The second is unknown in homogeneous kinetics. The equation is that of a zero order reaction; the rate is independent of the concentration of reacting substance. The third case, similarly unknown in homogeneous kinetics, is intermediate to the zero and first order reactions. An expression of this form was found by Stock and Bodenstein (12) to represent the decomposition of arsine on glass surfaces covered by arsenic. The first order rate is given by the decomposition of phosphine on glass (13), of hydrogen selenide on selenium (14), of hydrogen iodide on platinum (15), and by many others. In contrast to this last case Hinshelwood and Prichard (16) found that the rate of decomposition of hydrogen iodide on gold was independent of the gas pressure and was therefore a zero order reaction. It is thus evident that the nature of the molecule undergoing change does not itself determine the type of reaction kinetics. This is determined by the reactant-surface combination and the distribution of the reactant between the surface and the surrounding medium.

With more than one gas involved in the adsorption process at the surface the kinetics become correspondingly more complex. Thus, the unimolecular decomposition of a weakly adsorbed reactant, A, might be modified by the strong adsorption of a reaction product, B. In such a case, the reaction of A can occur only on the fraction of the surface,  $1 - \sigma_B$ , which is free of B. Since  $b p_A$  in this case is negligible compared with  $b' p_B$  we find that

$$\sigma_B = \frac{b' p_B}{1 + b' p_B}$$

and

$$1 - \sigma_B = \frac{1}{1 + b' p_B}$$

Since the reaction rate is proportional to  $\sigma_A$ , and this is in turn proportional to  $p_A(1 - \sigma_B)$ , it follows that

$$- dp/dt = k \cdot p_A \cdot \frac{1}{1 + b' p_B}$$

This case is of interest for the following reasons. We may write the equation in the form

$$dx/dt = k \frac{a - x}{x}$$

where  $a$  is the initial concentration and  $x$  is the amount of product produced in time  $t$ . In its integrated form this equation yields

$$kt = a \ln a - a \ln (a - x) - x$$

For the time of half-change,  $\tau$ , we derive, by placing  $x = a/2$ , the expression

$$\tau = \frac{1}{k} (a \ln 2 - a/2)$$

from which it follows that the time of half-life is directly proportional to the initial pressure. This result is characteristic of zero order reactions. First order reactions have a half-life which is independent of the initial pressure. Nevertheless, even though the reaction kinetics yield an equation zero order in nature, the *reaction occurring is unimolecular* and the kinetic equation obtained is determined in form by the retarding effect of the product. This conclusion indicates most definitely that the order of the reaction is not alone a sufficient guide to the true nature of the process occurring at the surface. It emphasizes the need for caution in interpreting the results of kinetic studies. A well-investigated case which conforms to this type is the decomposition of isopropyl alcohol on bauxite, studied by Dohse and Kälberer (8). The reaction rate is retarded by the water vapor produced in the process. The rate as ordinarily measured is proportional to the concentration of isopropyl alcohol and inversely proportional to the water formed. By employing a new technique, studying the rate of change of small amounts of the alcohol completely adsorbed by and constituting less than a complete unimolecular layer on the bauxite surface, these authors demonstrated the correctness of this conclusion.



(b) *Two reactants*

Two interacting gases each weakly adsorbed at a surface will occupy fractions of the surface proportional each to its own gas pressure. The chance of reaction will be proportional to the product of these fractions of the surface occupied. The kinetic expression for such a case becomes therefore,

$$- dp/dt = k \cdot p_A \cdot p_B$$

which is the normal bimolecular equation for such a reaction. This behavior is shown, for example, by hydrogen and ethylene on copper surfaces of feeble activity (5, 17). Analogously to the unimolecular case just discussed, such a bimolecular process can be retarded by one of the reaction products, C, the kinetic expression becoming

$$- dp/dt = k \frac{p_A \cdot p_B}{p_C}$$

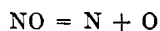
or,

$$dx/dt = k \frac{(a-x)^2}{x}$$

or, in the integrated form,

$$k = \frac{1}{t} \left( \frac{a}{a-x} - 1 - \ln \frac{a}{a-x} \right)$$

This equation gives the same unimolecular criterion as a simple unimolecular reaction; equal fractions of conversion occur in equal times. The decomposition of nitric oxide on platinum-rhodium surfaces was found by Bachmann and G. B. Taylor (18) to show this behavior, oxygen inhibiting the reaction rate. A simple unimolecular decomposition of nitric oxide would have meant that the surface reaction occurred according to the equation



to be followed by rapid combination of nitrogen atoms and of oxygen atoms. The bimolecular reaction inhibited by the prod-

uct oxygen, giving the kinetically unimolecular rate equation, leads to the much more reasonable mechanism for the reaction process



The retardation is also reasonable since the platinum metals in question are known to have strong affinity for oxygen. This example illustrates well the value of kinetic studies in determining the mechanism of surface reactions, while it emphasizes at the same time the need for care in interpretation of the experimental results.

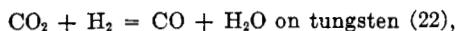
The kinetic studies cited must serve as representative of a numerous group of similar researches on the reaction kinetics of surface processes. An extended treatment of most of the good data has been given elsewhere (19, 20, 21). It is evident that examples are now known of kinetically simple unimolecular and bimolecular reactions at surfaces; indeed, they are probably more numerous and more reliable than the corresponding gaseous homogeneous reactions. The phenomenon of zero order reactions has been noted and its absence in homogeneous reactions can now be stressed. Third order surface reactions must be rare. The exemplification has been confined to gaseous reactions but the general principles are equally applicable to liquid media (21). In this latter case the conditions are not in general so simple, since the distribution of reactants between surface and medium is not so readily determined. Furthermore, the problem in such systems is complicated by the complexities of solutions in general. There is, however, no reason to anticipate that the mode of treatment found so applicable in gaseous systems cannot be extended in principle to liquid media.

The discussion thus far has been limited to reactions on a uniform surface whereas, as is now well known, the normal reaction surface is a non-uniform structure with varying degrees of surface activity. Certain kinetic studies indicate the necessity of postulating composite surfaces, but there are not many of these. As an example, one might cite the general case of two surfaces on which two reactants, A and B, are respectively moderately

adsorbed. In agreement with the foregoing principles, the rate of reaction would be given by the expression

$$dp/dt = k \cdot \frac{p_A}{1 + bp_A} \cdot \frac{p_B}{1 + bp_B}$$

where A is adsorbed by one surface and B by the other. Two reactions studied by Hinshelwood and his coworkers obey this expression. They are



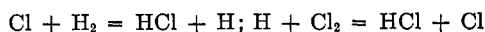
For a composite surface containing areas of progressively varying activities it is evident that the total rate would be an integration of a whole series of individual rates, each characteristic of the area on which it occurred. The resolution of the net rate into individual components is probably impossible by simple kinetic studies, though the existence of the multiplicity of rates may thus be indicated. Kinetic investigations at various pressures serve to exhibit the influence of composite surfaces. Thus, according to Schwab and Schmidt (24), the decomposition of ammonia on platinum surfaces in the pressure range up to 0.1 mm. is inhibited by both hydrogen and nitrogen. At higher pressures the influence of nitrogen is negligible. This shows a specific influence of nitrogen on the more active regions of the platinum surface which is not apparent on the more extensive regions of lower activity. Askey (25) found a similar effect of nitrogen in the decomposition of hydrazine on platinum. Donnelly and Hinshelwood (26) have also shown that the kinetics of the hydrogen-oxygen reaction in platinum at atmospheric pressure differ essentially from the results of Langmuir (27) at low pressures, a phenomenon also attributable to variations in the quality of the active surface and to variations in the extent of each type of surface. The most convincing evidence of variable surfaces comes, however, from the study of poisons and promoters of surface reactions and from the correlation of adsorption and activation energy of the reactions with the nature of the surface.

A further discussion will, therefore, be postponed until the results of such studies have been presented.

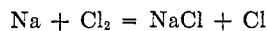
#### SURFACE EFFECTS IN CHAIN REACTIONS

The processes thus far discussed occur, under the experimental conditions chosen, only at the surface of the contact agent. The recent discovery of chains of reactions in a homogeneous medium, succeeding an initial process of activation, whether photochemical, radiochemical or even thermal, has opened up the possibility of two new types of surface action. Upon consideration, it may at once be seen that the initiation, by thermal activation, of a chain of reactions might occur at a reaction surface and that, in addition, a chain of reactions might be terminated at such a surface. Both of these possibilities have, within the last few years, been realized experimentally. Actually the termination of reaction chains by surfaces was demonstrated simultaneously and independently by Hinshelwood (28) and by Pease (29). Hinshelwood found that, in a certain temperature and pressure range, the rate of reaction between hydrogen and oxygen was suppressed by packing a silica reaction vessel with coarsely powdered silica. Pease demonstrated the same influence of packing in a variety of oxidation processes of hydrogen and hydrocarbons as well as a somewhat lesser influence of packing in certain processes of polymerization of unsaturated hydrocarbons. The surfaces in question are quite specific in their activity, especially when the chain reactions involve atoms or radicals as the propagating links in the chains. Thus, surfaces of glass coated with potassium chloride reduced the rate of the hydrogen-oxygen reaction approximately one thousandfold as compared with the clean glass surface. While, as will be seen, this effect is due in part to a varying activity of glass and potassium chloride in initiating reaction chains, a like difference in chain-breaking efficiency can be shown.

Hydrogen atoms and chlorine atoms are links in the chain of reactions involved in the hydrogen-chlorine combination:



The specific influence of surface in the rate of recombination of halogen atoms is well illustrated by the work of Senftleben and Germer (30). Platinum wire shows a marked tendency to produce recombination of chlorine atoms; the efficiency of the surface in this respect can be materially diminished by glowing the wire in chlorine, a treatment which undoubtedly covers the surface in part with metal chloride. With bromine atoms such treatment was less successful in suppressing recombination. With iodine atoms a further surface factor is of importance. The glass surface of the container causes rapid recombination. Quartz is less efficient than glass in this respect. Polanyi and Bogdandy (31) found that the nature of the surface influenced the length of the chain of reactions in the hydrogen-chlorine combination initiated by the reaction of chlorine with sodium vapor,



The chains are short at low working pressures when the glass containing surface is clean but are increased thirtyfold in length after the glass surface becomes coated with sodium chloride. A similar influence of walls on atom recombination is manifest in the chain reaction involved in the photochemical formation of phosgene and in the photosensitized oxidation of carbon monoxide in the presence of chlorine (32).

The effect of surfaces on the recombination of hydrogen atoms has been known since Wood's initial work (33) on the production of atomic hydrogen in discharge tubes. Water vapor adsorbed on the containing glass walls increases the yield of atoms as it poisons the glass walls, reducing their surface activity for recombination. H. von Wartenburg and Schultze (34) have shown that hygroscopic materials, notably sirupy phosphoric acid, are similarly efficient. Bonhoeffer (35) showed that the order of efficiency of metals in hydrogen atom recombination was that of their activity as hydrogenation catalysts. Taylor and Lavin (36) extended these observations to the recombination of hydrogen atoms and hydroxyl radicals. It was in the course of this work that it was shown that potassium chloride coated surfaces were superior to clean glass surfaces in promoting the recombina-

tion of hydrogen and hydroxyl. It was also shown that dehydration catalysts are very efficient for this latter recombination but are of negligible efficiency in hydrogen atom recombination. The specificity of surfaces for both molecular and atomic reactions is thus patently demonstrated, and the correlation of the activity of surfaces in atomic reactions with similar processes involving molecules leads to a considerable simplification of the problem involved in such cases of specific action. Once it is ascertained what factors determine the rate of recombination of hydrogen and hydroxyl at a surface, the same factors will be involved in the hydration of, and elimination of water from, molecular species. Similar considerations concerning atomic hydrogen recombination will be involved in surface reactions of hydrogenation and dehydrogenation.

The demonstration that reactions at surfaces may give rise to chemical reactions in the gas phase surrounding the catalyst has recently been supplied by the researches of Alyea and Haber (37) with hydrogen-oxygen mixtures and by Thompson (38) with carbon disulfide-oxygen mixtures. These authors, in studying the mechanism of these two chain reactions, found that no reaction occurred when two independently heated streams of the gases in question, e.g., hydrogen and oxygen, were allowed to impinge on each other away from surfaces. The introduction of certain surfaces into the crossed streams at their junction brought about the same rapid reaction that would have occurred if the two gases had been heated together to the given temperature in a single tube. That the effect of the surface was specific and not due to the additional mixing brought about by the introduction of the surface is evident from their observations that while glass, quartz, platinum, iron and copper surfaces produced the rapid change, an aluminum surface was without effect.

The initiation of chain reactions in hydrogen-oxygen systems by atomic hydrogen produced in the photochemical decomposition of ammonia has recently been demonstrated by Farkas, Haber and Harteck (39). They have shown that the chains so initiated increase in average length with temperature, the chain length being 25 at 290°, 380 at 405° and many thousands at 500°C.

The efficiency of atomic hydrogen in thus initiating chains in the hydrogen-oxygen reaction at once suggests that the chains initiated at surfaces might extend into the gas phase by liberation into the gas of atomic hydrogen as a result of such surface reactions. The evidence for such an interpretation has recently been collected by Alyea (40) and this evidence is supported by earlier data already in the literature.

Several years ago a number of publications (41, 42) dealt with the production of "active" hydrogen by various methods of activation, included in which were methods involving the use of catalytic agents, notably platinum. In many of these cases claims for the production of active hydrogen were made under circumstances which seemed to violate the laws of thermodynamics. In other cases, it was experimentally demonstrated that the production of hydrogen in an active form was associated with the occurrence of some chemical reaction. In one case in particular, the formation of active hydrogen was associated with the presence of small amounts of oxygen in the hydrogen gas which was led over a platinum catalyst, the exit gas from which was shown definitely to contain an active form of hydrogen over a stretch of 5 cm. from the catalyst material (43). In these experiments adequate experimental controls of the activity were employed. Since the reaction was carried out at low temperature ( $<120^{\circ}\text{C}.$ ), effects due to electron emission and ionization should have been entirely absent. Mitchell and Marshall finally concluded that the activity was due to the production of small amounts of triatomic hydrogen. It is now apparent that the active hydrogen was in reality atomic hydrogen and that the method employed by Mitchell and Marshall is a general method applicable at a wide variety of surfaces.

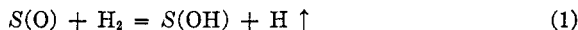
The paper by Mitchell and Marshall provides the most conclusive evidence of the liberation of atomic hydrogen into the gas stream. Low temperature activation of pure hydrogen by contact with platinized asbestos was shown not to occur. Small concentrations of oxygen, down to 0.02 per cent, were shown to promote the activation and there was combustion of hydrogen during the process. The active hydrogen produced under these

conditions was unstable and persisted for a distance of 5 cm. from the activating surface under the experimental conditions. The activity varied slightly with the time of contact. The active hydrogen reduced copper oxide at 82°C., whereas the unactivated gas did not reduce the same samples of copper oxide below 116°C. It was definitely shown that the difference in reduction temperatures was not due to the formation of copper nuclei in the oxide at which reduction might then occur at the lower temperature without platinum adjacent (44). There was also no effect due to water vapor produced on the platinized asbestos, for it was found that most of the water formed was retained on the platinized surface for considerable periods of time. In the earlier experiments of Anderson (45), which preceded this study by Mitchell and Marshall, active hydrogen from both platinum and palladium was also shown to react with sulfur, yielding hydrogen sulfide under conditions which would not yield this product with normal molecular hydrogen. Mitchell and Marshall also record the significant experiment performed by Dr. S. Judd Lewis, at the suggestion of Mr. C. Campbell, which demonstrated that the active hydrogen produced in this manner reduced the unsaturated groups in olive oil.

Recent experimental work, as well as theoretical evidence based on the Pauli exclusion principal and the new quantum mechanics, point definitely to the nonexistence of triatomic hydrogen. The reactions of the active hydrogen just recorded are all possible reactions of atomic hydrogen as demonstrated by a voluminous literature (46) in recent years. The absence of any effects when the hydrogen is pure shows definitely that the activity is not due to any such small concentration of atomic hydrogen as would be in equilibrium with molecular hydrogen after passing over a catalyst at the given temperature. The equilibrium concentration in the system  $H_2 = 2H$  at the temperature in question represents the maximum amount thus obtainable, and this is vanishingly small. It is necessary then to formulate the chemical reactions of hydrogen with oxygen which at surfaces will yield atomic hydrogen. On platinum and palladium it is known that oxygen is strongly and irreversibly adsorbed.



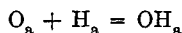
If we assume that it is present on such a surface as atomic oxygen strongly bound to the surface there are immediately suggested two possible reactions capable of yielding hydrogen atoms to the gas phase. If we represent the oxygen covered surface by  $S(O)$ , the two possible reactions are



and



Disregarding the heats of adsorption of the several species on the surface, we know, from the new experimental data on the heats of formation of hydrogen and water from the atoms (47), that both of these reactions are exothermic in the gas phase and thus provide a possible mechanism for the release of atomic hydrogen into the gas stream. It is evident that, if both of these reactions are possible, since  $O_2$  will yield  $4H$ , atomic hydrogen up to four times the oxygen concentration of the gas might be thus produced. This would represent the maximum attainable, and, in practice, concentrations well below this could be anticipated, since there is always the possibility of surface reactions of adjacently adsorbed oxygen and hydrogen atoms,



and of adjacently adsorbed hydroxyl and hydrogen atoms



For a surface initially saturated with hydrogen, the amount of atoms that could be liberated would be smaller. The reaction



is, on the best available evidence, somewhat endothermic. The collision of an oxygen molecule with two adsorbed hydrogen atoms could however yield two adsorbed hydroxyls, since the reaction

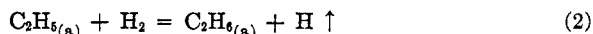
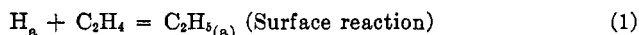


is strongly exothermic. The reaction of such adsorbed hydroxyls with molecular hydrogen to yield adsorbed water and atomic hydrogen according to reaction 2 above would thus again produce, in the gas phase, atomic hydrogen, but to only half the extent of that possible with a surface initially laden with adsorbed oxygen.

The mechanisms just cited provide an explanation not only of the active hydrogen noted by Mitchell and Marshall but also of the effect of surfaces in initiating chains of reaction in hydrogen-oxygen mixtures. It is known that atomic hydrogen produced in hydrogen-oxygen mixtures at low temperatures leads to the formation of hydrogen peroxide, often to the exclusion of water formation. It is of interest to recall in connection with the suggestions just put forward for the initiation of chains in such mixtures at higher temperatures that Pease (48) has recently demonstrated the formation of peroxide in the thermal reaction of hydrogen and oxygen under conditions which involve the chain mechanism. The reactions of such mixtures with atomic hydrogen at low temperature are thus adequately correlated with the data on reaction chains. The varying efficiencies of different surfaces noted by Alyea and Haber (37) are also in accord with the point of view here put forward. At surfaces of glass, quartz, platinum, iron and copper, the necessary activation of either hydrogen or oxygen can be secured at the operating temperatures used (49). The case of aluminium is the illuminating exception. The metal surface was undoubtedly covered with a thin film of adherent oxide. All the experimental evidence indicates that on such alumina surfaces neither hydrogen nor oxygen show any evidence of activation. As Taylor and Lavin (36) showed, alumina was quite inert in bringing about the recombination of hydrogen atoms and hence must be equally inert in activating hydrogen molecules. The absence of any evidence on the effectiveness of alumina as an oxidation catalyst is evidence against oxygen activation on this material. An oxide-coated tungsten filament constitutes a case parallel to that here presented by oxidized aluminium surfaces. As is well known from the investigations of Langmuir, neither activation of hydrogen (formation of atomic hydrogen) nor oxidation of

hydrogen (formation of water) occurs on such surfaces below 1500°K. It is very evident from experimental data, therefore, that on these surfaces there is no mechanism possible by which atomic hydrogen can escape from the surface into the gas phase; otherwise the chain reaction obtaining when other surfaces are present would also occur with the oxide-coated tungsten surface.

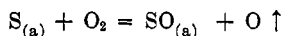
These considerations lend interest to the recent paper by Bennewitz and Neumann (50). By the use of a novel method dependent on the torque of a platinum foil only one half of which was activated, these authors were led to the conclusion that the major portion (> 99.9 per cent) of the hydrogenation of ethylene must occur as a chain reaction in the gas phase. This conclusion is not yet in accord with the results of work with atomic hydrogen produced by excited mercury atoms. Here all the most recent data (51, 52) indicate that the chains are nonexistent at room temperatures. There is, however, the possibility that, at higher temperatures, the reaction may take on the chain characteristics. By analogy with the preceding case of oxygen one might suggest the following sequence



the atomic hydrogen produced in reaction 2 being released into the gas phase. The most recent data by Mecke (47) on the energy of binding of  $\text{C}_2\text{H}_5$  and H make this reaction a definite possibility, although we have elsewhere (53) cited evidence against its frequent occurrence at room temperatures. To test this matter further, we are at present making experiments on the temperature coefficient of the hydrogen-ethylene reaction under the influence of excited mercury.

Concerning the mechanism of initiation of the carbon disulfide-oxygen chain at glass surfaces studied by Thompson (38), since the reaction is initiated by glass at as low as 140°C. and since glass shows no capacity to activate oxygen at such temperatures, one is led to the conclusion that the surface must activate the disulfide. The chain-initiating reaction on this basis

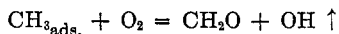
may involve the projection of an oxygen atom into the gas phase by some reaction of which



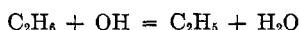
is one possible example. It is now experimentally established that oxygen atoms react quantitatively with carbon disulfide (54) to yield various oxidation products. That the presence of oxygen atoms in such carbon disulfide-oxygen mixtures may lead to a reaction chain is evident from some unpublished data obtained by Emeleus in this laboratory. Emeleus has shown that the ignition temperature of such mixtures is quite definitely lowered by introduction of ozonized oxygen into the system. With 0.5 per cent ozone an especially violent explosion was obtained with the gas mixture at as low a temperature as 55°C., markedly inferior to that noted above in the thermal reaction in glass vessels.

In the case of saturated hydrocarbon oxidation, there is definite evidence also that the chains of reaction originate at the surface of the containing vessel as well as terminate at the same. Thus, Pease (55) found that packing very considerably reduced the rate of oxidation of propane and the butanes, pointing to inhibitory action. However, in a packed tube coated with potassium chloride, the rate of reaction was materially less than in the packed tube without the coating. This definitely indicates a positive effect of the glass on the initiation of chains. In a large empty tube coating had little or no effect. This might mean one of two things; either that the reaction was almost exclusively homogeneous, or that chains once initiated at the walls were extremely long. The evidence from the packed vessels supports the latter alternative. Bone and Hill (56) in a recent paper on the oxidation of ethane at 300°C. report other data in accord with the concept of chains initiating at the wall. The slow combustion of this gas shows a definite and sometimes prolonged induction period which can, however, be eliminated by introducing a variety of substances, for example, acetaldehyde, into the reaction mixture. There is reason to believe that during the induction period a slow surface reaction occurs which liberates a chain initiator

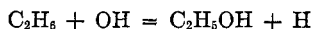
into the gas phase. By analogy with the hydrogen-oxygen case, this reaction might be between oxygen molecules and the methyl radicals formed at the surface by adsorption of ethane; thus,



the OH being liberated into the gas phase. This reaction of gaseous methyl has now been well established by the work of Bates and Spence (57). The gradual evaporation of the formaldehyde thus formed would lead to autoacceleration of reaction, since Bone and Hill showed that such was the effect of added formaldehyde. The OH would have a certain capacity as chain producer by reason of the reactions,



and



The ethane molecule might also be adsorbed on the surface as  $\text{C}_2\text{H}_5 \cdot \text{H}$ , in which case acetaldehyde would be formed on oxidation and made available by evaporation to the gas phase.

It was also shown that there was a pronounced effect of drying on the rate of ethane oxidation. This again points to the intervention of surface in the reaction, since it is difficult to account for an effect of minute traces of water vapor on a homogeneous gas reaction. The water effect may, however, mean an increased efficiency of the surface, when dry, in ending reaction chains.

There is no such definite evidence of surface efficiency in initiating reaction chains in the oxidation of the unsaturated hydrocarbons, ethylene and acetylene (58), though, in these cases, definite experimental test of such a possibility is lacking and would constitute a material contribution to our knowledge of mechanism in these reactions.

#### THE CHEMICAL COMPOSITION OF ACTIVE SURFACES

An accumulation of data relative to reactions at surfaces has revealed that certain types of elements and compounds are always associated with certain types of surface reaction. It is this speci-

ficity of surface chemical composition for particular reactions which most directly suggests the chemical nature of the surface processes preliminary to the actual reactions involved. Lacking the scientific explanation of this association of surface with reaction, the experimentalist exercises his choice of surface rather as one empirically learned in the art than as a scientist.

Reactions of hydrogenation or reduction as well as of dehydrogenation are most generally effected on one or another of a restricted series of metals or, as a result of recent researches in this field, on a similarly restricted and well-defined series of oxides or mixtures of the same. The principal metals are the platinum metals, nickel, cobalt, iron, and copper, with a few others of much less importance, such as silver, cadmium, and tin. The oxides include those of zinc, manganese, and magnesium, generally with chromium oxide in admixture as a promoter. Many more oxides have, in addition to hydrogenation-dehydrogenation activity, a marked and simultaneously manifested efficiency as dehydration catalyst; among them may be mentioned the oxides of the rare earths, cerium, praseodymium, neodymium, samarium, gadolinium, dysprosium, and oxides of earths of the ytterbium series as well as of indium, scandium, yttrium and lanthanum (59). Some recent evidence indicates that certain sulfides, notably molybdenum, cobalt, nickel, chromium and iron sulfides, may also function as hydrogenating surfaces, especially for reaction with sulfur compounds (60).

For hydration and dehydration processes a series of oxides which include alumina, silica, thoria, zirconia and tungsten oxide are especially to be recommended for their freedom from simultaneous dehydrogenation activity. The efficiency of certain of these oxides is improved by conversion to the sulfate or phosphate. Furthermore, the phosphates and pyrophosphates of oxides with pronounced dehydrogenation activity as, for example, zinc and manganese oxides, are mainly dehydrating in activity.

Of the metals at which oxidation processes are effected, platinum is the most important technically as well as in fundamental research. Rhodium, palladium, and osmium are also important members of this group. Silver and gold are used for the same

purpose. Oxides are the most important class of compounds whose surfaces accelerate oxidation processes. The most important members of this class of contact agents are oxides having several stages of oxidation. Oxides of vanadium, iron, manganese, molybdenum, tungsten, uranium, lead, copper, silver, cobalt, and nickel may be instanced. For certain purposes salts with such oxides as acidic constituents are convenient as, for example, the vanadates. The well-known case of Hopcalite illustrates the increased efficiency of mixed oxides over the constituents used singly.

The introduction of and removal of halogens from compounds may be effected at surfaces of carbon, sulfur, iodine, iodine monochloride and the halides of elements having polyvalence. Aluminium, vanadium, molybdenum, bismuth, zinc, tin, copper, and iron chlorides may be instanced. This type of catalyst may also be used for reactions involving addition or removal of the hydrogen halides.

It is a problem of the future to elucidate the reasons underlying this definite association of surface type with reaction type. A start has been made in the solution of this problem by recent studies, subsequently to be discussed, of the hydrogenation-dehydrogenation contact agents. It remains to be seen how the conclusions from such work can be generalized. Progress in this direction can best be indicated by reference to the work carried out on the physical and chemical properties of such contact surfaces.

#### THE PHYSICAL-CHEMICAL PROPERTIES OF ACTIVE SURFACES

It is obvious that, for reactions at surfaces, an extension of surface as great as practicable within the limits of the experimental conditions is desirable. Extension of surface alone is not, however, the sole criterion of successful surface action. The researches of the last decade have abundantly demonstrated, in a variety of reactions and at various surfaces, that, in addition to a quantitative extension of surface, the quality of that extended surface is of primary importance. The technique of the worker in this field is directed towards securing simultaneously with

extension of surface a high specific reactivity. The methods to be employed in the characterization of a reaction surface are, therefore, of manifest importance in this problem of surface action. It is apparent that, by processes of trial and error, suitable methods for achieving the desired reaction may be obtained. These will in general, nevertheless, be but empirical efforts, without a truly scientific basis of operation. The scientific development of method in surface chemistry must come from a deeper appreciation of the factors operative in the characterization of the surface. This really reduces the method to a study of the physical-chemical properties of surface materials upon which particular chemical processes may be achieved. The realization that adsorption at a surface is a condition precedent to reaction at such surface and that the phenomenon of adsorption becomes the more readily manifest with large extension of surface naturally provided an impetus to the correlation of adsorption and reaction at the adsorbing surfaces. A peculiarly fruitful field of study was thereby discovered. We may illustrate this development by reference to surfaces promoting hydrogenation-dehydrogenation reactions since, with these, the correlation is more complete than with any other of the typical processes and surfaces. The application of the methods of study used with hydrogen to other reacting gases would constitute an invaluable additional contribution to our knowledge of surface reactions.

An examination of the adsorptive capacity for hydrogen of a number of typical metal surfaces such as those of nickel, cobalt, iron, copper, platinum, and palladium (61) showed them to possess high specific adsorptions for hydrogen. Low adsorptive capacity was associated with low surface reactivity (62). It was shown that the extent of adsorption per unit weight of metal was determined by the method of preparation, by distribution on inert supports, by subsequent treatment of the surface with poisons, or by heating (63). In many respects, however, the adsorption was different from the adsorption of gases or vapors by inert adsorbents such as silica gel or carbon. The adsorption of hydrogen on such surfaces was definitely specific, in no way akin to a non-specific, physical condensation on inert surfaces.



The adsorption was accompanied by high heat effects, heats of adsorption of the order of 10,000 to 30,000 calories per gram-molecule of adsorbed hydrogen being common (64, 65, 66, 67, 68, 69). These contrast with the heats of adsorption of the order of magnitude of the heat of liquefaction, 450 calories in the case of hydrogen, usual with non-specific adsorbents. The adsorption isotherms were characterized (63) by saturation at low partial pressures (of the order of 100 mm. or less) of the gas, in contrast with the increased adsorptions at even high pressures with non-specific adsorptions. Of importance in the subsequent development was the observation that these apparent saturation values for hydrogen adsorption on metal surfaces decreased with increasing temperature, calculation indicating that a gas pressure of many thousands of atmospheres would be required to increase the adsorption by the small amount which differentiated the apparent saturation values at the two given temperatures.

The necessity for drawing a distinction between such different types of adsorption has become increasingly evident with progress in the study of adsorption at active surfaces. It has become customary to speak of "primary" and of "secondary" adsorptions; in other cases there has been a differentiation attempted between "reversible" and "irreversible" adsorptions; "physical" and "chemical" adsorptions have been suggested. No precise method of identification of one or the other type has been available nor has it been possible to state whether one or both types were present in a given case. In the theoretical treatment of adsorption there has been a tendency to discuss only the non-specific type and to eliminate from consideration the chemical type of adsorption. Quite recently, definite progress in such differentiation has been achieved. The study by London (70) of the nature of molecular forces from the standpoint of modern wave mechanics has recently led to a quantitative formulation of adsorption on the assumption that the gas in the adsorbed layer has the same equation of state, i.e., van der Waals' forces, as in the gas phase and that the forces of adsorption and van der Waals' forces are related. The equation obtained yielded satisfactory data for the heats of adsorption of helium, nitrogen, argon, carbon

monoxide, carbon dioxide and methane on charcoal. It is, therefore, evident that in these cases of non-specific adsorption the adsorbed gas is molecular in nature and the adsorption forces are van der Waals' molecular forces which are sharply distinguishable wave-mechanically from electrostatic and valence forces.

In the second place, it has recently been found by experimental measurements (71, 72, 73, 74) that certain gases can be adsorbed on particular surfaces in at least two different ways characterized by the extent of adsorption and its variation with temperature. The experimental evidence indicates that the low temperature adsorption is non-specific, molecular, and rapid, condensation probably occurring from a large fraction of the collisions with the adsorbing surface. On the other hand, a rapidly accumulating set of data indicate that there supervenes in a higher temperature range a slow, specific adsorption which may indeed be considerably more pronounced in the amount of gas adsorbed than the low temperature adsorption. The velocity with which this high temperature type of adsorption occurs increases exponentially with the temperature so that one can speak of the activation energy of the adsorption process in the same manner that one speaks of the activation energy of chemical reactions. The magnitude of these activation energies of adsorption varies from case to case and depends on the nature of the gas adsorbed, on the chemical composition of the adsorbent and also on the qualitative nature of the surface area (74).

The detailed theoretical analysis of the concept of adsorption with accompanying activation energy has recently been given elsewhere (73). It will suffice here to indicate some of the consequences of the concept in so far as they relate to the problem of surface reaction, and to cite some of the more conspicuous experimental data in verification of the conclusions reached. Adsorptions having activation energies of a sufficient magnitude will not be experimentally realizable at low temperatures due to inadequacy of activation energy at the temperature in question. If, as seems evident, the van der Waals' molecular adsorptions occur with little or no activation energy, this type of adsorption will occur practically exclusively in the lower temperature ranges.

At high temperatures, the adsorption with activation energies will predominate, and, if the heat of adsorption of the activated adsorption is higher than that of the van der Waals' adsorption, the extent of adsorption will be greater in the higher temperature range than in the lower. This phenomenon, which is quite contrary to any unmodified adsorption theory, will be shown to yield an important experimental criterion of activated adsorption. A second important consequence of the concept of adsorption with accompanying activation energy will also be useful. The low values of activation energy for van der Waals' adsorption imply that the velocity of adsorption will be extremely rapid. This idea concerning velocity of adsorption has been consistently held. On the other hand, with activated adsorptions having high activation energies, there will be definite ranges of temperature in which the adsorption occurs at rates either too slow or too fast to measure, but there will also be an intermediate range of temperature in which the velocity will be at a tempo convenient for experimental measurement. From such measurements, as in the kinetics of chemical change, the variation in velocity with temperature will permit a calculation of the activation energy of the adsorption process.

The best data already available in the literature indicative of increased adsorption at higher temperatures are those of Benton and White (71) for the adsorption of hydrogen on nickel, extending the earlier studies of Gauger and Taylor (63). These experiments, when combined, provide comparative data for adsorption on nickel extending from  $-209^{\circ}$  to  $305^{\circ}\text{C}$ . The data of Benton and White exhibit a minimum at about  $-190^{\circ}\text{C}$ . Between  $-190^{\circ}$  and  $-110^{\circ}\text{C}$ . there is approximately a fourfold increase in adsorption. Above this temperature range, at various pressures, there is again a decreasing adsorption with increase of temperature, the decrease being the more pronounced the lower the operating pressure. At an operating pressure of 60 cm., in the temperature range  $-110^{\circ}$  to  $0^{\circ}\text{C}$ ., the adsorption is constant. The surface is apparently saturated with the activated adsorbate. Above  $0^{\circ}\text{C}$ ., at the same pressure there is a normally decreasing adsorption with increase in temperature. The fact

that the increase in adsorption with temperature occurs in the low temperature range of  $-190^{\circ}$  to  $-110^{\circ}\text{C}$ . indicates that the activation energy of the activated adsorption of hydrogen on nickel cannot be very large. We shall discuss in subsequent paragraphs cases where the increase of adsorption occurs in higher temperature ranges and for which we have accumulated measurements of velocity at various temperatures, and hence deduced the activation energy. We can, however, note even from Benton and White's qualitative observations that the velocity of adsorptions measured by them are in accord with the concept of our assumed van der Waals' adsorption, "the pressure became constant almost immediately after admitting the gas." In the higher temperature range, equilibrium was fairly rapidly established at very low pressures, which agrees with a rapid velocity of activated adsorption on the most active portions of the surface where the activation energy is lowest. At moderate pressures, the velocity was slower, corresponding to the somewhat higher activation energy of the intermediately active areas of the surface, while, at higher pressures, when, it is obvious, the most active areas are mostly covered, the velocity of adsorption was the slowest. The existence of a slow velocity of activated adsorption is consistent with the observation of Gauger and Taylor (63) that the desorption curve of nickel always showed larger amounts of adsorbed gas at a given temperature and pressure than those obtained in the adsorption experiments. As has been pointed out elsewhere (73), the existence of high heats of adsorption and of maxima in the heat of adsorption versus amount adsorbed curves are also in accord with the concept of slow activated adsorption in the higher temperature range ( $-110^{\circ}$  to  $305^{\circ}\text{C}$ .).

Much more decisive experimental data demonstrative of the existence of two types of adsorption of hydrogen, one with low activation energy, the other with higher activation energies, have been accumulated in recent months by Mr. A. T. Williamson and the writer in Princeton. As has been pointed out in a preceding section, as a result of recent industrial developments a restricted series of oxides and mixtures of oxides now finds extended use as hydrogenation agents. These oxides are operative for certain

hydrogenation processes in a higher temperature range than the corresponding metals. These offered the possibility that they would show, in a higher temperature range, the same adsorption phenomena as noted by Benton and White for hydrogen on nickel in the region below room temperatures. Furthermore, by measurements of adsorption velocity and its variation with temperature, the actual magnitudes of the activation energies could be ascertained in place of the qualitative observations with nickel cited above. The results obtained are abundantly confirmatory of the views under consideration. We have operated with a surface of manganous oxide and, for a surface of higher specific activity, with a mixture of manganous and chromium oxides. The experimental results will be detailed elsewhere. Here, only a summary need be presented. At  $-78^{\circ}\text{C}$ ., the adsorption of hydrogen on a given sample of manganous-chromium oxide is small, rapidly attained and mostly reversible by evacuation at the same temperature. We assume this to be adsorption of the van der Waals' type. At  $0^{\circ}\text{C}$ ., the adsorption of hydrogen in this manner is less than at  $-78^{\circ}\text{C}$ ., but at this temperature there sets in an extremely slow adsorption, the rate of which makes perceptible changes in adsorption measurable only over periods of hours and days. At  $100^{\circ}\text{C}$ ., and at  $132^{\circ}\text{C}$ ., where the van der Waals' adsorption has fallen to negligible proportions, the rate of this activated adsorption has now risen to conveniently measurable velocities, and, from such measurements, activation energies have been calculated. The velocity of this activated adsorption increases rapidly with temperature as measured at  $184^{\circ}$  and  $305^{\circ}\text{C}$ ., but, and this is more striking, the amount of adsorbed hydrogen has *risen to fifteenfold that obtaining under similar pressure conditions at  $-78^{\circ}\text{C}$* . At  $440^{\circ}\text{C}$ . the extent of adsorption is still severalfold that at  $-78^{\circ}\text{C}$ ., but definitely less than at  $305^{\circ}\text{C}$ . under the same pressure conditions. The increased adsorption is a real adsorption phenomenon, completely reversible, all of the hydrogen being recoverable by evacuation, though requiring continued pumping for long intervals of time at temperatures around  $460^{\circ}\text{C}$ . We have no evidence of water formation with these adsorptions, presumably because of the well-known irreducibility of manganous oxide.

From the velocities of adsorption at 100° and 132°C., the activation energy of the adsorption process may be calculated by means of the equation

$$d \ln v/dT = E/RT^2$$

In this way we have found that, on the most active portion of the surface (10 cc. adsorbed) the velocity is relatively rapid and the activation energy small ( $E = 5900$  calories). With increasing surface covered, the velocity of adsorption sinks, whereas the activation energy rises consistently. The mean activation energy on the surface covered by the first 25 cc. of adsorbed gas amounts to 8500 calories. These data add another factor to those important in the heterogeneity of reaction surfaces. It is evident that, on the active centers, the velocity of adsorption is very much more rapid than on the less active areas of the surface. Thus, for example, on two areas of the surface at present under discussion having, let us assume, activation energies of 3000 and 5000 calories respectively (areas covered in the adsorption of the first 10 cc.) the velocities of adsorption at a temperature of 127°C. (= 400°K.) are in the ratio  $e^{-3000/2.400} : e^{-5000/2.400} = e^{2000/800} : 1 = e^{2.5} : 1 = 12.18 : 1$ . The velocity is twelvefold more rapid on the former than on the latter.

Furthermore, it is well known that the efficiency of surfaces for reactions can be enormously enhanced by the use of promotor agents, and that the promotor may produce not only an extension of the surface but also a qualitative improvement of the surface. That the promotor may also yield a material change in the velocity of adsorption is evident from a comparison of the data cited above for manganous oxide promoted with chromium oxide and data obtained with an unpromoted, though fairly active, sample of manganous oxide prepared by controlled ignition of the oxalate. With this latter preparation, while the general behavior as to adsorption was the same as with manganous-chromium oxide, temperatures at which comparable velocities of adsorption were obtained were more than one hundred degrees higher. Also, from the velocity data at 184° and 305°C. it was found that the activation energy of hydrogen adsorption on the most active

centers of the manganous oxide surface was about 10,000 calories. This means that the ratio of adsorption velocities on the promoted and unpromoted surfaces is given by the expression  $e^{-(10,000-3,000)/RT} = e^{+7,000/RT}$  or, for a temperature of 227°C. (= 500°K.), a value  $e^{7,000/1,000} = e^7$  or approximately 1,100. It is very evident, therefore, that, for any reaction in which velocity of adsorption or desorption is the rate-determining factor, the employment of a promoted surface would be of enormous assistance. It is probable that this factor of velocity of activated adsorption is the one in which the function of promoters is most significant in a large number of reactions, since evidence is accumulating that what we have here demonstrated for hydrogen adsorption can be generalized for many gaseous reactants.

One additional and most definite piece of evidence as to the fundamental distinction between the rapid low temperature adsorption of hydrogen on manganous-chromium oxide surfaces and the slower but more pronounced adsorption of hydrogen in the higher temperature range is forthcoming from the heats of adsorption of the gas on the surface in the two temperature regions. As is well known, the heat of adsorption can be calculated from any two isotherms on which the equilibrium pressures for a given amount of adsorbed gas have been determined. The equation connecting heat of adsorption, pressure and temperature is

$$\log p_1 - \log p_2 = \frac{\lambda}{4.58} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

where  $\lambda$  is the heat of adsorption,  $p_1$  and  $p_2$  are the equilibrium pressures for a given adsorption at  $T_1$  and  $T_2$ , respectively. Using this equation Williamson's data show that in the temperature region  $-78^\circ$  to  $0^\circ\text{C}$ .,  $\lambda$  has a value of about 1,900 calories per mole, whereas, from the isotherms at  $305^\circ$  and  $444^\circ\text{C}$ ., a heat of adsorption greater than 19,000 calories per mole is calculated. The distinction between the calorimetric effects of the two types of adsorption is manifest. The magnitude of the divergence serves also to account for the sharp increase in amount adsorbed in the two ranges of temperature.

*The spin isomerization of hydrogen*

There exists, fortunately, in the ortho-, para-hydrogen interconversion a surface reaction which involves only one molecular reactant and product, hydrogen. This process, which may be characterized as one of spin isomerization, undoubtedly involves some form of activation of the hydrogen molecule in the association with the surface which produces one or another form. For there is evidence in the data of Bonhoeffer and Harteck (75) dealing with this subject that the influence of surface is quite specific and that adsorption alone is not sufficient to bring about the isomerization. It is for this reason that the writer has already suggested elsewhere that, on the surface of charcoal, even at liquid hydrogen temperatures, the adsorbed hydrogen must be in part in the activated form. This spin isomerization may, therefore, serve as a convenient reaction process for an auxiliary test of the ideas concerning the nature of hydrogen adsorption discussed in the preceding paragraphs.

Bonhoeffer and Harteck found nickel to possess a negligible activity for the reconversion of para-hydrogen to the ortho-para mixture even at room temperatures. Still less, therefore, might one expect it to function as an agent for the production of para-hydrogen in the lower temperature range. In order, however, to test this further, since the data of Benton and White (71) showed activated adsorption of hydrogen at temperatures as low as  $-110^{\circ}\text{C}.$ , experiments have been carried out by Mr. A. Sherman and the writer (76) with a form of nickel (10 per cent nickel on kieselguhr) known to possess an extreme activity for hydrogenation reactions and also showing specific adsorptions for hydrogen of a much higher order of magnitude than the material employed by Benton and White. It was obvious from the data already presented for manganous oxide and manganous-chromium oxide that it might be necessary to go to such nickel preparations of high activity to secure a sufficiently rapid velocity of adsorption and desorption of hydrogen at the low temperatures required for para-hydrogen formation. Our experiments at the temperature of liquid air were completely successful and it was found



possible to produce the equilibrium concentration of 50 per cent para-hydrogen as well on such an active nickel surface as on charcoal. That the activity of the surface was the important factor was readily shown by other experiments with small fragments of nickel wire as the surface material. With such, at liquid air temperatures, there was no measurable para-hydrogen formation. Again, therefore, we conclude that, at surfaces of high activity for surface reactions, we have high velocity, or, alternatively, low activation energy of the activating adsorption.

It is thus apparent that the spin isomerization of hydrogen may be utilized as an index to the nature of the adsorption process occurring at various surfaces at different temperatures. One example must suffice to establish the concordance thus anticipated between the data derived from velocity of adsorption and the isomerization process. It is evident from our data on oxide surfaces that the activating adsorption occurs in a higher temperature range than on the metals which show hydrogenation activity. This is true also of spin isomerization on a zinc oxide of high hydrogenation activity at higher temperatures, prepared by controlled ignition of zinc oxalate. With such zinc oxide, we obtain no para-hydrogen formation at liquid air temperatures although there is undoubtedly marked adsorption of hydrogen, presumably in the molecular unactivated form. At higher temperatures, from 0°C. upwards, the efficiency of the surfaces in the isomerization process can be tested by observing the extent of reconversion of a 50 per cent ortho-para mixture prepared over charcoal at liquid air to the normal 3:1 ortho-para mixture. With the same sample of zinc oxide, it has been found that the reconversion is barely perceptible after 15 minutes contact at 20°C., is definitely measurable after the same time at 50°C., is marked at 80°C., and is 80 per cent complete with the same time of contact at the temperature of boiling water. The measured velocity of reconversion increases exponentially with temperature. It may be that this represents actually the variation of the velocity of desorption of activated hydrogen from the zinc oxide surface. The velocity of desorption is slower than the velocity of adsorption since the former is proportional to  $e^{-(E+Q)/RT}$

when the latter is a function of  $e^{-E/RT}$ ,  $E$  being the activation energy of adsorption and  $Q$  the heat of adsorption. With zinc-chromium oxide, an even more active surface than zinc oxide, there is no para-hydrogen formation at liquid air temperatures even with 14 hours of contact time, but the reconversion of para- to the ortho-para-mixture is complete after 15 minutes contact at room temperature. This utilization of the para-hydrogen conversion for the purpose of determining the activity of hydrogenating surfaces is an interesting example of the applicability of

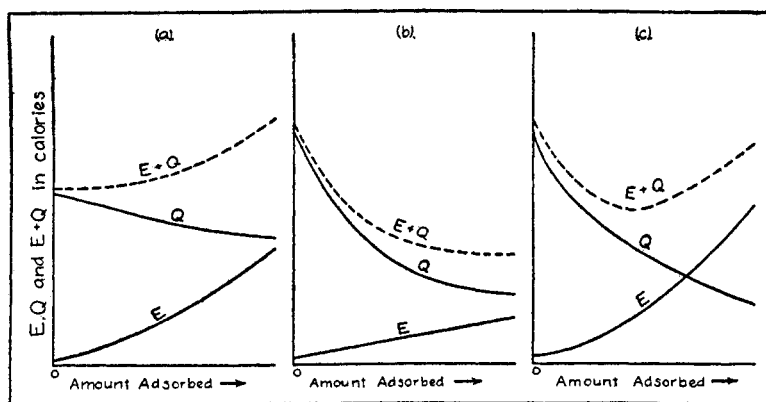


FIG. 1. DIAGRAMMATIC REPRESENTATION OF ACTIVATION ENERGY OF ADSORPTION ( $E$ ), HEATS OF ADSORPTION ( $Q$ ), AND ACTIVATION ENERGY OF DESORPTION ( $E + Q$ ), ON HETEROGENEOUS SURFACE

knowledge gained in abstract theoretical science to the practical problems of applied science. It is one more excellent illustration of the interdependence of theory and practice.

#### *Activation energy of desorption*

It is of interest to consider briefly the desorption of a molecular species which is adsorbed with energy of activation on a heterogeneous surface. On a homogeneous area, if the activation energy is  $E$  and the heat of adsorption is  $Q$ , the rate of desorption is proportional to  $e^{-(E+Q)/RT}$ . On a heterogeneous surface we have seen that, on the most active areas, the activation energy is least and that it increases steadily with increase of surface

covered. On the contrary, data on the heats of adsorption of gases on heterogeneous surfaces show high initial heats and steadily diminishing values with increased area of surface covered. Diagrammatically, the  $E$  and  $Q$  values vary as shown in figure 1. The algebraic sum of these magnitudes gives the activation energy of the desorption process for different portions of the surface area. These are indicated by the dotted lines in the diagram. It is apparent that, depending on the variations of  $E$  and  $Q$  relative to one another, various forms of the  $E + Q$  curve may be obtained. The three indicated show (a) an  $E + Q$  curve increasing with area covered, (b) one which decreases continuously, and (c) one showing a minimum. It is apparent that, from a surface corresponding to type (a), the gas would be desorbed first from the areas most active in adsorption. From a surface of type (b) the gas last adsorbed would be the first to be desorbed. In type (c), desorption would occur first from the areas of medium adsorption activity. There are at present no experimental data for  $E$  and  $Q$  for an actual surface so that nothing is known concerning the particular areas from which desorption most readily occurs. It is evident, however, that such areas would be the important areas in those surface reactions where the velocity of desorption was the controlling rate of the reaction process.

#### *Specific surface action*

Consideration will show that the possibility of adsorption at rates governed by a definite activation energy must be of fundamental importance in those cases of specific surface action which have been so puzzling a feature of the general subject of reactions at surfaces. It is well known that, by a suitable choice of surface, a given reactant may be made to undergo one or another of several alternative modes of reaction, in some cases even at comparable temperatures. There has been much discussion of the possible factors which might determine the direction of reaction along a particular path. Hitherto, however, the possibility that the rate of activating adsorption or desorption might determine the path followed has not been considered.

We can conveniently illustrate the possibilities in this respect by reference to the alternative modes of decomposition of primary alcohols at various surfaces. It is well known that, at many metal surfaces and at the oxide surfaces already discussed for their hydrogenating-dehydrogenating activity, such alcohols decompose to form aldehydes and hydrogen. At the surfaces of other oxides already discussed in a preceding section, notably alumina, silica, thoria and the blue oxide of tungsten, the decomposition of the alcohols yields, practically exclusively, the corresponding olefin and water. The direction of the change which one and the same molecule undergoes is determined in major part by the chemical nature of the reaction surface. It has already been pointed out in an earlier section that there exists a remarkable parallelism between the capacity of surfaces to induce dehydrogenation or dehydration and the efficiency of such surfaces in promoting the recombination either of hydrogen atoms or of hydrogen atoms with hydroxyl radicals. This discovery by Taylor and Lavin (36) at once focusses attention on the final steps in the dehydrogenation and dehydration of alcohols which must consist in the recombination of the respective atoms or radicals at the surface and the evaporation of hydrogen or water. These final stages are the initial stages in the activating adsorption of hydrogen or water if the activation involved in such adsorption consists in a dissociation of the molecule. On this view, activity in dehydrogenation at a given temperature should be associable with an activated adsorption of hydrogen in a somewhat lower temperature range since, in general, desorption will occur more slowly than the adsorption and hence, for a given velocity, require a higher temperature. We have seen in the preceding pages that such hydrogen activation occurs on metals and certain oxides at temperatures which would permit the dehydrogenation reactions in question to occur fairly readily at temperatures of 200°C. and upwards. With surfaces such as alumina, active almost exclusively as dehydration agents at temperatures around 200°C., it is apparent that, from the point of view here developed, there should be no activating adsorption of hydrogen gas.

Experiment has confirmed the correctness of this conclusion and has led to an extension of the temperature range over which these processes of adsorption of hydrogen with activation energy have been measured. Some recent experiments of the writer (77) have shown that an active dehydration catalyst, composed of alumina, prepared by precipitation of the hydroxide by ammonia from aluminium nitrate and ignition at 400°C., shows no measurable adsorption of hydrogen below 400°C. At 440°C. a slow adsorption of hydrogen was recorded and the velocity of adsorption was measured. The velocity of adsorption was considerably increased by raising the temperature to 525°C. From the velocity data, an activation energy of 28,000 calories was deduced. The adsorption was a reversible process, the hydrogen being evolved and removable by evacuation at a higher temperature. No water was formed by reduction of the oxide. It is, therefore, obvious from such experiments that dehydrogenation does not occur on alumina surfaces at temperatures of about 200°C., which are normal for such decomposition processes because of the inability of such surfaces at such temperatures to effect the activation of hydrogen or the reverse recombination of hydrogen atoms. It is apparent also that water vapor must undergo an activating adsorption at temperatures in the neighborhood of those at which dehydration occurs. A test of this point on the lines so fruitful in the case of hydrogen would form a useful starting point for a generalization of the subject of adsorptions with activation energies. There seems to be every reason for concluding that water vapor may be adsorbed on alumina in two different forms, at low temperatures as unactivated molecules, and at the higher temperatures in that activated form in which it is effective in promoting hydration processes and from which it changes to a normal water molecule by desorption in dehydration processes. In extension of this thesis it may also be pointed out that Alyea (40) has shown a similar increase in the adsorption of hydrogen by powdered Pyrex glass from immeasurably small values in the low temperature range to values as high as 30 cc. in the temperature range of 480° to 520°C. The adsorption was reversible and showed the now familiar increase of velocity of

adsorption with temperature. As Alyea has elsewhere shown, this adsorption of hydrogen, setting in at elevated temperatures, is an important factor in the problem of the stationary and explosive reactions of hydrogen and oxygen in glass vessels, initiated, as shown by Alyea and Haber, at the glass surfaces. In this case, also, the temperatures at which the hydrogen is activated are much superior to those at which dehydration occurs.

What has been remarked here concerning the alternative processes of dehydrogenation and dehydration of alcohols may be adapted to other types of reaction and may serve as a useful method of approach to the whole field of specific surface activity. Thus, the nature of the association between the hydrogen halides and various halide surfaces is doubtless fundamental to the problem of addition of hydrogen halides to organic unsaturated compounds. There is evidence also in the recent work of Elgin (78) on the hydrogenation of different types of organic sulfur compounds that the most resistant sulfur compounds such as thiophene are activated only on the most active portions of the surface.

#### TEMPERATURE AND THE VELOCITY OF SURFACE REACTIONS

The velocity of surface reactions increases with temperature in the same manner as the velocity of homogeneous reactions, the variation with temperature being expressible by the well-known Arrhenius equation

$$d \ln k/dT = E_o/RT^2$$

The quantity  $E_o$ , which is now identified as the observed activation energy for the process in question, is, however, not always a simple magnitude but is normally composite of several energy quantities. This arises from the nature of the surface process. The effect of temperature extends not only to the actual interaction of the reaction species, but also to the variation of the concentrations of these species in the surface area which is the reaction volume of the process. Since these concentrations in the surface area are determined by adsorption, the influence of tem-

perature on the adsorbability of both reactants and products may become an important fraction of the total effect of temperature on the reaction. In one important class of surface reactions the observed activation energy,  $E_o$ , is actually identical with the true activation energy,  $E_t$ , of the surface process. In reactions which conform to the criteria of zero order reactions already discussed, the observed activation energy is equal to the true. This is so because of the nature of reactions of zero order. These occur only when the extent of the reaction surface covered with reactants does not sensibly change with external concentration, when the surface is saturated. If, in a given temperature interval, this condition also holds, there is then no variation in adsorption with temperature and hence no effect of adsorption on the observed temperature coefficient or activation energy. It is interesting to record in two of such zero order cases studied—hydrogen iodide decomposition on gold,  $E_o = 25,000$  calories (16) and ammonia decomposition on tungsten,  $E_o = 39,000$  calories (78a)—that the observed and therefore the true activation energies of the surface processes are materially less than the possible activation energies of any process of homogeneous decomposition. The surface process therefore involves a smaller increment of energy of the reactant molecules over the average energy of the system required for reaction to occur than would be required in the homogeneous process. The surface process can, therefore, be achieved at a lower temperature. Only in such cases is a surface reaction readily noticeable. When the reverse is true, the reaction occurring on the surface with the higher necessary increment of energy is lost in comparison with the homogeneous reaction. Examples of this kind are not experimentally available. We can, however, state the existence of one such. The homogeneous reaction of hydrogen and oxygen will overwhelm the surface reaction at oxidized tungsten surfaces for reasons already dealt with in preceding sections.

When adsorption of reactants and products at the surface varies with temperature a wide variety of relations between the observed and true energies of activation are possible, too many to reproduce here. It has been shown, however, by Polanyi

(79), Hinshelwood (19) and others that certain simple relations connect the two activation energies and the heats of adsorption of the several molecular species. Thus, for a single reactant, slightly adsorbed ( $\sigma \propto p$ ), the observed and true activation energies are related by the expression,

$$E_o = E_t - \lambda_A$$

where  $\lambda_A$  is the heat of adsorption of the reactant. If, in such a process, a product of the reaction is strongly adsorbed the relation becomes more complicated,

$$E_o = E_t - \lambda_A + \lambda_B$$

where  $\lambda_B$  is now the heat of adsorption of the retarding product. This latter equation is also applicable to such a case as a bimolecular reaction in which one of the reactants, B, is so strongly adsorbed that it leads to the kinetic equation

$$- dp/dt = k \frac{p_A}{p_B}$$

This is true in the case of the combination of hydrogen (A) and ethylene (B) on copper, studied by Pease (5), and for which an activation energy at ordinary temperatures of 10 kg-cal. was found. Since actual experimental data indicate that  $\lambda_A$  is about 10 kg-cal. and  $\lambda_B$  is about 16 kg-cal., it is evident that

$$\begin{aligned} E_t &= 10 + 10 - 16 \\ &= 4 \text{ kg-cal.} \end{aligned}$$

or less than half the observed activation energy. This activation energy is also very materially less than the energy necessary for the homogeneous process, which cannot be less than 30 kg-cal. and begins to occur only around 400°C. This example must also suffice to indicate that there is no essential correlation between the observed energy of activation and observed heats of adsorption, although this has been very recently considered by Maxted (80) as a possible method of approach to the problem of specific surface action.



One aspect of this relation between true and observed activation needs emphasis. Equations of the types just discussed are applicable only when the adsorption processes involved are rapid as compared with the actual reaction process proper. They cannot hold rigorously when the adsorption processes are relatively slow. It is evident from the discussion of the preceding section dealing with the velocity of adsorptions accompanied by an activation, in which it has been shown that such adsorptions may, indeed, be very slow, that particular attention must in future be paid to this condition attaching to any relation between true and observed activation energies on the one hand and heats of adsorption on the other. This factor may account for a discrepancy existing between two measurements of the activation energy of decomposition of isopropyl alcohol on bauxite studied by Dohse and Kälberer (8). By one experimental method, these authors studied the process occurring as a zero order reaction and obtained, therefore, a true activation energy of 26,000 calories. When studied as a unimolecular decomposition inhibited by the product, water, they observed an activation energy of 39,000 calories. To derive a true activation energy from this, use must be made of the equation previously developed which, when applied to this special case, has the form

$$E_t = E_o + \lambda_{\text{C}_3\text{H}_7\text{OH}} - \lambda_{\text{H}_2\text{O}}$$

Kälberer and Dohse measured the heats of adsorption and found  $\lambda_{\text{C}_3\text{H}_7\text{OH}} = 21,000$  calories and  $\lambda_{\text{H}_2\text{O}} = 13,000$  calories. Hence, from the unimolecular inhibited reaction one derives a value,  $E_t = 39,000 + 21,000 - 13,000 = 47,000$  calories in sharp disagreement with the result, 26,000 calories, from the zero order reaction. The discrepancy is even more conspicuous when we note that water, with  $\lambda = 13,000$  calories, is inhibiting the access of isopropyl alcohol, with  $\lambda = 21,000$  calories, to the surface. It is evident that, to obtain agreement between the data for true activation energy in the zero order and unimolecular reactions, it would be necessary to employ a value of  $\lambda_{\text{H}_2\text{O}} = 34,000$  calories in the equation

$$E_t = E_o + \lambda_{\text{C}_3\text{H}_7\text{OH}} - \lambda_{\text{H}_2\text{O}}$$

Now such a value is reasonable if, instead of the measured heat of adsorption of water ( $\lambda_{\text{H}_2\text{O}} = 13,000$ ), we substitute an assumed heat of desorption of water,  $\lambda_{\text{H}_2\text{O}} = 34,000$  calories. Granting that the measured heat of adsorption is correct, this would involve an energy of activation of water at a bauxite surface equal to  $34,000 - 13,000 = 21,000$  calories. While this appears to be somewhat high, it is of the right order of magnitude. There is the distinct possibility, also, that the heat of adsorption of water actually measured by Dohse and Kälberer is too low, involving a measurement of a heat effect of adsorption only part of which was an activated adsorption. We have already seen in the case of hydrogen on manganous-chromium oxide catalyst that the data of Williamson and the writer for unactivated and activated adsorption are respectively about 2000 calories and  $>19,000$  calories. The presumption is, therefore, that the measured value for  $\lambda_{\text{H}_2\text{O}} = 13,000$  calories is in reality too small and that an energy of desorption  $\lambda = 34,000$  calories would be a closer approximation to the correct value to be employed.

What has been stated in particular for this reaction can be extended quite generally to reactions in which one of the reactants behaves as a retardant. This suggests that a degree of special importance would attach to studies of kinetics and of adsorption data for dehydrogenation reactions at oxide surfaces for which the data already presented here indicate activated adsorptions and to readily available methods of separating such activated adsorptions from the molecular adsorptions of hydrogen occurring in another temperature range. The existence, side by side, of activated and unactivated adsorption at a variety of surfaces causes a degree of doubtfulness to attach to all the measurements of heats of adsorption hitherto made in this field (8, 64, 65, 68, 69, 81). The data for hydrogen on the metals are least suspect since, apparently, the activated adsorption occurs even at quite low temperatures. The recognition of the two possible types of adsorption must, however, lead to a greater discrimination in the future in the choice of experimental procedures.

For unretarded reactions, another factor of importance in connection with the observed activation energy is the hetero-

geneity of the surface. Normally, with a heterogeneous surface, the heat of adsorption diminishes continually with increase of surface covered. In a reaction in which  $E_o = E_t - \lambda$ , we may write the velocity of reaction

$$- dp/dt = z \cdot e^{-(E_t - \lambda)/RT}$$

where  $z$  is a collision factor between the reactant and surface. On two equal surface areas on which the  $z$  factor is constant but on which the heats of adsorption are respectively  $\lambda_1$  and  $\lambda_2$ , the rates on the two areas will be, if  $E_t$  be assumed constant,

$$(1) \quad z e^{-(E - \lambda_1)/RT}$$

and

$$(2) \quad z e^{-(E - \lambda_2)/RT}$$

The ratio of these two rates is obviously  $e^{-(\lambda_2 - \lambda_1)/RT}$ . For two areas on which  $\lambda_1 - \lambda_2 = 5000$  calories this corresponds to a ratio of rates equal to  $e^{5000/RT}$  or, at  $T = 500^\circ\text{K.}$ ,  $e^5$  or 158.4. This means that the reaction on area 2 would be quite negligible as compared with that on area 1. If  $E_t$  varies from area to area the ratio of the reaction rates would be

$$r_1/r_2 = e^{-[(E_{t_1} - E_{t_2}) - (\lambda_1 - \lambda_2)]/RT}$$

Since there is evidence in available experimental material that the true activation energy increases with decreased activity of this surface, it follows that this ratio is even greater than that obtaining when  $E_t$  is constant. These ratios indicate very definitely the possibility of areas of the surface to which reaction is very largely confined and other areas on which only a negligible amount of reaction occurs. It is this effect of heterogeneity in surfaces which makes pronounced the effect of minimal amounts of poisons on surfaces. It is such heterogeneity which the use of promoters emphasizes. Conversely, it may be stated that the existence of pronounced poisoning by minimal amounts of materials or marked promotion of surface activity by small amounts of added agents is a direct index of the existence of a heteroge-

neity of surface on the most active areas of which alone is the reactions in question markedly achieved.

Such then is one record of progress in the study of reactions at surfaces. To the writer it appears as one in which there has been a steady development away from empiricism and towards a scientific analysis of phenomena which, for too long a period of time, lay hidden under the cloak of a nomenclature which served also to conceal ignorance and arrest progress. The record is not one of finality—indeed, it can be but the prelude to a more illuminating sequel in which those who read may be inspired to share, for “what I now chance to approve, may be or become to others strange and unpalatable” since “this picklock Reason is still a-fumbling at the wards.”

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