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Catalysis—A Challenge to the Physicist

(As Exemplified by the Hydrogenation of Ethylene over Metal Catalysts)

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INTRODUCTION

CATALYTIC processes are becoming of ever-increasing importance in chemical technology. The hundreds of million gallons of aviation gasoline produced per month in the United States at the time of the writing of this article are almost without exception tailor-made by a variety of catalytic processes with catalytic cracking in the lead and catalytic alkylation, isomerization, hydrogenation, and dehydrogenation playing an important part. Styrene and butadiene, the chief constituents of Buna-S rubber, are for the most part produced by catalytic processes. The catalytic synthesis of hydrocarbons by coal hydrogenation or by the Fischer-Tropsch Synthesis has played an important role in Germany's war economy. Nor should the older catalytic processes be forgotten, such as the ammonia synthesis and oxidation, the methanol synthesis and fat hydrogenation, to name a few.

Suffice this to indicate the tremendous importance of catalysis from the technological and economic point of view and to indicate the great strides which the "art" of catalysis has made. This is admittedly in glaring contrast to our understanding of the fundamental phenomenon of catalysis, whose technological progress is still largely based on empirical methods often involving the systematic testing of thousands of materials.

The phenomenon of catalysis was first observed and recorded by J. J. Berzelius (1836) who introduced the term catalytic agent into chemistry to include those substances which, by their mere presence and without being altered themselves, accelerate the rate of reactions. In reversible systems the catalyst accelerates the establishment of the equilibrium until at the equilibrium point both forward and reverse reaction are equally accelerated as demanded by the law of microscopic reversibility. We can distinguish between homogeneous and heterogeneous catalytic reaction, the former occurring in gases and liquids where the catalyst is dissolved, the latter taking place at gas-liquid, gas-solid, or liquid-solid interfaces, the catalyst usually being the liquid or the solid. Heterogeneous catalysis is by far the most important type from the industrial standpoint.

While theoretically the life of a catalyst should be infinite, loss of activity during use generally occurs in practice. This loss may result from (a) side reactions that produce carbon or other materials, thereby covering the surface and making the catalyst inaccessible to the reactants (b) impurities in the reactants or products from side reactions that poison the catalyst either by being preferentially adsorbed or by chemically reacting with the catalyst, or (c) sintering of the catalyst causing loss of active surface from overheating.

Often, when the loss of activity is due to a reversible process such as oxidation, the catalyst may be regenerated by reduction with hydrogen. If the poisoning is a result of physical adsorption, purging with an inert gas will reactivate the catalyst. And in the case of carbon formation, burning with air or oxygen may be feasible if the heat developed by this oxidation process does not irreversibly alter the catalyst.

CATALYSIS AND CHEMICAL KINETICS

Since the beginning of practical catalysis, the industrial chemist has been struggling with poisons, declining activity, disintegration of the catalyst, and similar problems, in addition to finding the proper catalyst for a given reaction through time-consuming empirical methods. Simultaneously, the theoretical chemist has attempted to understand the phenomenon of catalysis by way of the kinetic approach. This approach has not proved altogether satisfactory, especially for the industrially important heterogeneous reactions. Although the basic method of chemical kinetics is simple, it is quite indirect and insensitive when applied to heterogeneous cata-

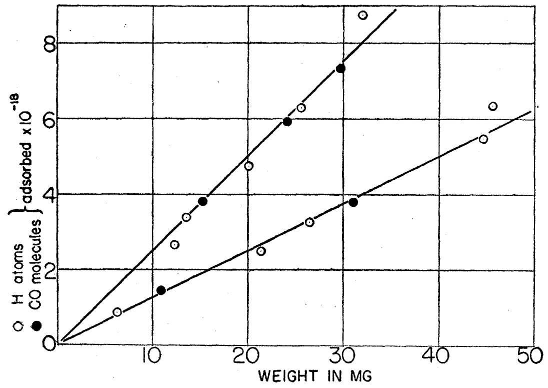

FIG. 1. Adsorption of hydrogen and carbon monoxide on films evaporated in 1 mm Hg of N_2 (upper curve) and in high vacuum (lower curve).

lytic reaction for the sake of solving the riddles of the mechanism of a given reaction. Basically, the method of chemical kinetics involves the quantitative determination of the reaction products and their dependence on time and temperature, the expression of rates in terms of concentrations and temperature, and the construction of a model or mechanism to fit the observations. Such a mechanism has to include assumptions with regard to the step or steps involved in the catalysis proper, and if agreement is obtained with one of often many imaginable mechanisms, this mechanism will then be pronounced the right mechanism until more or better measurements may prove it wrong. However, it does not seem surprising that measurements may easily be misinterpreted with regard to the mechanism of the catalytic reaction proper if one remembers that at least five steps are involved in the reaction: the diffusion of the reactants to the catalyst, the process of adsorption, the chemical change at the surface, the process of desorption, and, finally, the diffusion of the reaction products away from the catalyst. The slowest of these steps will determine the rate of the over-all reaction. In numerous cases the wrong conclusions have been drawn as to which step is actually rate-determining in a given reaction. It is no surprise, therefore, that the mechanism of the rearrangement of the molecules on the surface cannot be deduced with any certainty from kinetic measurements alone. Kinetics will have to be used, of course, but only to complement more direct physical measurements and observations.

On the other hand, the over-all kinetics may be the primary quest with the mechanism of the surface rearrangement either known or of minor interest. Here the search may be for the best catalyst particle size and for the optimum average pore diameter of the network of pores in the particle in order to produce maximum conversion to a desired product with a minimum of side reaction producing carbon or other undesirable materials. Obviously, a very fast reaction will proceed on the outer surface of the particles (no pores are necessary), and a very slow reaction will take place on the internal surface of the network of pores. The mathematical treatment of chemical kinetics in porous systems, especially when flow systems are involved, is complicated and has by no means completely been solved, although notable contributions in this field have been made by Watson,[1] Thiele,[2] D. M. Hurt,[3] and by A. Wheeler of these laboratories.

In the detailed consideration of chemical kinetics in porous systems as well as for classification and correlation purposes, measurements of the internal surface of catalysts have become of great importance. Here the van der Waals' adsorption method by Emmett, Brunauer, and Teller[4] has been most successful. The determination of a few points on the adsorption isotherm is usually sufficient for a surface measurement of high precision. Adsorption isotherms also lend themselves to the determination of pore distribution when the Kelvin equation for capillary condensation is used in conjunction with isotherms. A combination of the Emmett-Brunauer-Teller theory of adsorption and the Kelvin equation should be used in this case. Recent unpublished studies by A. Wheeler show that this treatment will lead to pore distributions that fit Gaussian distribution functions.

THE HYDROGENATION OF OLEFINS OVER EVAPORATED METAL CATALYSTS

Rather than through a general discussion, the purpose of this presentation can best be served by giving an example of the role of physical

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[1] O. A. Hougen and K. M. Watson, Ind. Eng. Chem. **35**, 529 (1943).

[2] E. W. Thiele, Ind. Eng. Chem. **31**, 916 (1939).

[3] D. M. Hurt, Ind. Eng. Chem. **35**, 522 (1943).

[4] S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. **60**, 309 (1938).

methods in the clarification of the reaction mechanism of a given reaction. While it is not claimed that the work to be discussed is complete, it does, nevertheless, touch the very root of the catalysis problem and is apparently the first instance of a nearly complete elucidation of a catalysis mechanism.

Only a small part of this work has already been published while the rest has been presented in form of progress reports at the yearly AAAS Gibson Island Research Conference on Catalysis in the years 1940 to 1944. Although this work deals with one of the simpler and well-known catalytic reactions, a great deal more information and experimental evidence had to be accumulated than was anticipated. A detailed account of the work, of which this presentation can only give the highlights, will be published later.[5]

The hydrogenation of ethylene was chosen for various reasons. The reaction has been widely studied from the kinetic standpoint and has easily measurable rates at 0°C and at room temperature. But more important, the favored catalysts for this reaction are pure metals of the eighth group of the periodic system, including the nickel, palladium, and platinum series. Such catalysts as had been prepared in the past were obtained from the oxides by reduction with hydrogen, a customary procedure which produces a large surface. These catalysts were not reproducible from the standpoint of absolute or intrinsic activity (activity per unit surface), and neglecting various then current hypotheses on the necessity of oxygen or hydrogen impurities, pure metal catalysts were prepared by evaporation from pure and carefully degassed metal wires under the most scrupulous conditions of high vacuum technique. Catalysts of extremely high intrinsic activity were produced by this method and were obtained in a glass apparatus representing a continuous circulatory flow system in which circulation was maintained by an all-glass turbine.[6] *The films thus produced in a high vacuum are highly porous*, a film with an apparent surface of 30 sq. cm and weighing 50 mg having an interior surface of about 5000 sq. cm. When evaporated in an inert gas atmosphere of, for instance, argon, at 1 mm Hg, the surface for the same weight of film is about twice as large. Figure 1 shows the adsorption of hydrogen at room temperature and carbon monoxide at −183°C on nickel films evaporated in 1 mm Hg of nitrogen (upper curve) and high vacuum (lower curve). In this figure the number of hydrogen atoms or carbon monoxide molecules adsorbed is plotted against the weight of the films.[7] Since both adsorptions are of the chemisorbed type (high heats of adsorption—see below), the figure shows at once the homogeneity with respect to surface and the atomic character of the hydrogen adsorption which was first shown by Langmuir, as well as the molecular nature of the carbon monoxide adsorption. (The carbon monoxide adsorption at room temperature is identical with that at −183°C.) Each available lattice space on the surface is occupied either by a hydrogen atom or a carbon monoxide molecule.

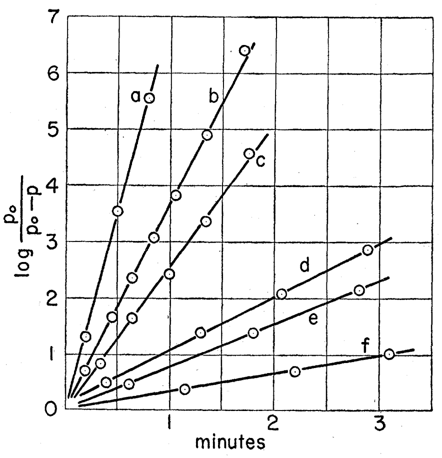

FIG. 2. Logarithmic plot showing first-order reactions on various catalysts. (p_0 is the initial pressure and p the instantaneous pressure.)

The hydrogenation of ethylene over these films is strictly first order with respect to hydrogen, i.e., proportional to the hydrogen pressure at any time. Figure 2 shows the usual logarithmic plot for first-order reactions, the curves (a) to (f) representing hydrogenation reactions of ethylene

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[5] The author is indebted to Professor H. S. Taylor for suggesting full publication of this work in the form of a monograph by the Princeton University Press. Preparation of this monograph is in progress in collaboration with A. Wheeler.

[6] O. Beeck, A. E. Smith, and A. Wheeler, Proc. Roy. Soc. **177**, 64 (1940).

[7] For the given apparent surface of about 30 sq. cm, the films contain 212 atom layers per mg (taken along the [100] axis).

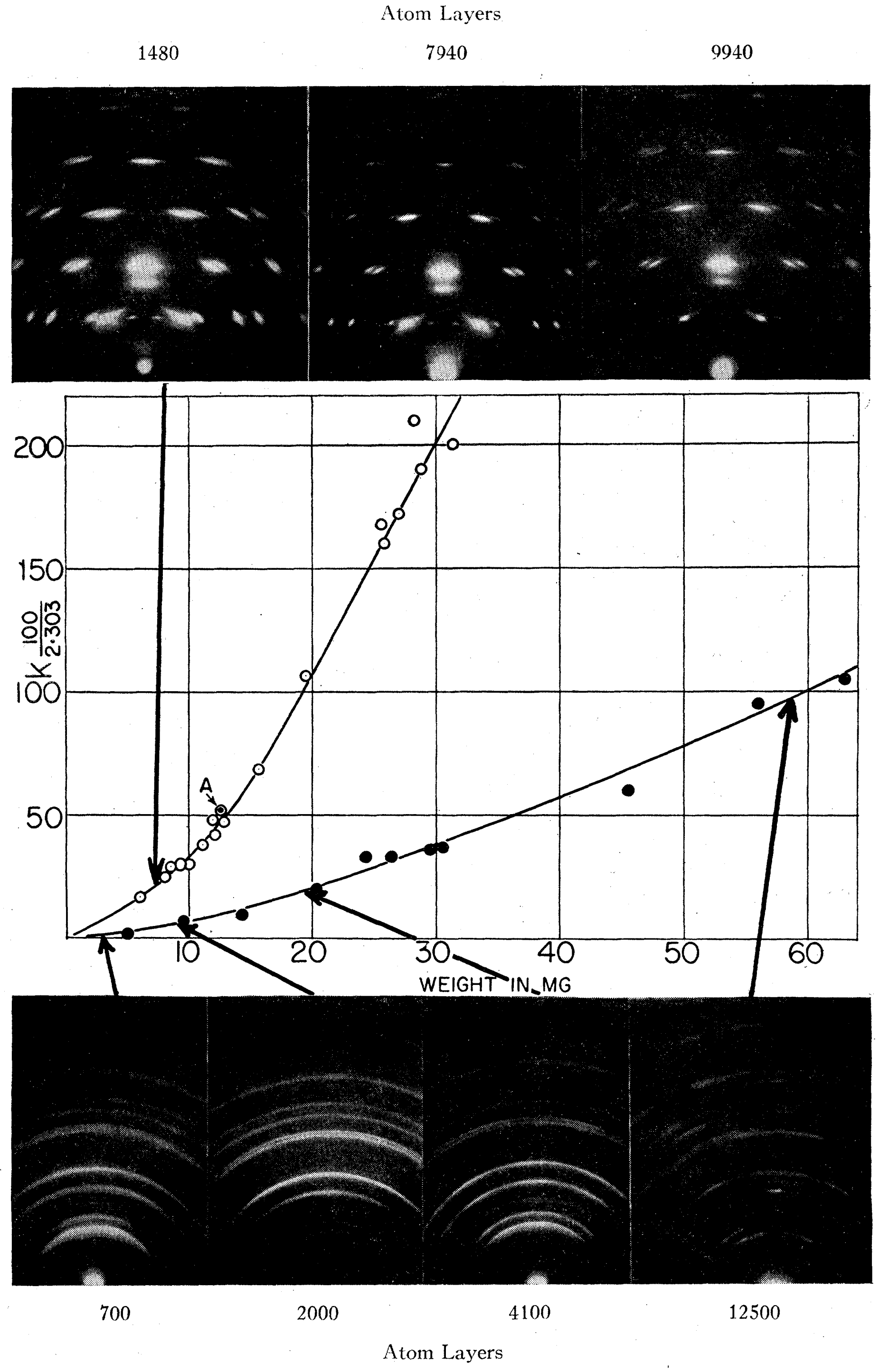

FIG. 3. Electron diffraction patterns of evaporated nickel films. (Weight and activity indicated by arrows; the patterns above the figure correspond to the upper curve giving activities of films evaporated in 1 mm of nitrogen, the lower patterns correspond to high-vacuum films. The oriented films of 7940 and 9940 atom layers are too heavy to be shown in the figure.)

over evaporated nickel films of various activities. Slopes of similar straight lines are used throughout this work for evaluation of the velocity constants.[8]

Measurements of the activity (velocity constant) of the two types of films of various thickness showed as expected, proportionality of the activity with film surface or film weight, but the gas-evaporated film having twice the surface showed about a tenfold activity. Electron diffraction measurements on both types of film showed *the gas-evaporated films completely oriented* with the (110) plane of the face-centered cubic nickel lattice parallel to the glass backing while *the high vacuum evaporated films showed the uniform Debye-Scherrer rings of a randomly oriented aggregate of crystallites.* Figure 3 shows the results for both types of films. It is seen that the very thin gas-evaporated films are somewhat less active than the heavier ones and that the heavy vacuum evaporated films are slightly oriented. The orientation of the latter could be prevented by evaporating the high vacuum films onto a glass surface cooled to liquid air temperature. Figure 4 shows the activity of such non-oriented films at 0°C in comparison with the activity of highly oriented films reduced to the same surface.

The mechanism by which orientation is produced in gas-evaporated films has not yet been studied in detail. It is significant, however, that the (110) plane in nickel is the plane of least atomic density or highest surface energy and that similar evaporation of iron in a gas atmosphere produced highly oriented iron films with their (111) plane parallel to the backing, the plane being the least dense plane, i.e., the plane of highest surface energy. If orientation is produced through the presence of the gas, it seems likely that the oriented planes obtained are also exposed to the gas. Differences in contact potential or photoelectric emission would give the most direct proof of this assumption since theoretically the work function is expected to be different for different crystal planes. Such experiments are planned. In agreement with these expectations Paul A. Anderson[9] has reported a contact potential of 0.12–0.01 v between an oriented (100) silver film (deposited on rocksalt, Brück[10]) and an unoriented film deposited on glass. The comparison of very accurate measurement of chemisorption and van der Waals' adsorption may also lead to a conclusive answer; such work is planned.

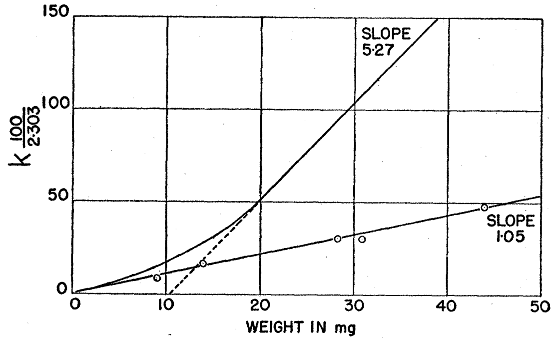

FIG. 4. Activities of oriented and non-oriented nickel films reduced to the same adsorptive surface.

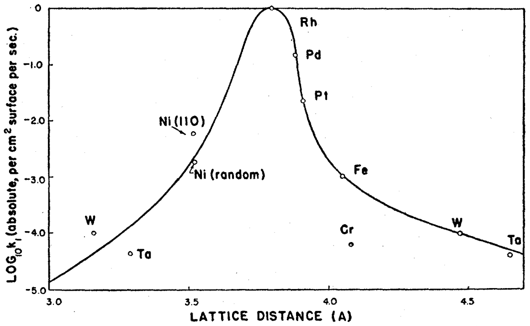

FIG. 5. Activity at 0°C *vs.* lattice distance in A.

The discovery of fivefold difference in the intrinsic catalytic activity of oriented and non-oriented films of the same metal proves conclusively the importance of the crystal parameter in catalysis, at least for the hydrogenation reaction, and lends at once much weight to a comparison of the activity of different hydrogenation catalysts on the basis of crystal parameter. This has been done for a number of pure metals, including chromium, iron, cobalt, nickel, rhodium, palladium, platinum, tantalum, and tungsten. In Fig. 5 the logarithm of the velocity constant is plotted against the crystal parameter of the various metals investigated. From this curve the

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[8] The rate of diffusion of reactants and reaction products into and out of the porous structure of the very thin films was found to be fast as compared with the reaction rate, and theoretical calculation showed the effect of diffusion to be within the experimental error.

[9] P. A. Anderson, Phys. Rev. **56**, 850 (1939).

[10] L. Brück, Ann. d. Physik **26**, 233 (1936).

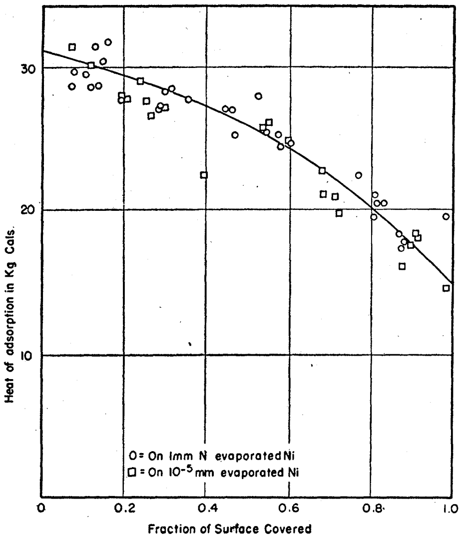

FIG. 6. Heat of adsorption of hydrogen on nickel.

high activity of rhodium was originally predicted before the actual measurements were made. The maximum occurs at about 3.75A which is approximately the distance between the hydrogen atoms in opposite methyl groups of the ethane molecule. All of the metals fulfill the prerequisite of chemisorbing hydrogen.

Since the kinetics of the hydrogenation reaction demands that the surface at all times be sparsely covered with adsorbed hydrogen, thus tying the rate determining step to the hydrogen adsorption, one would be inclined to search for an explanation which correlates the activation energy of adsorption with the crystal parameter. The activated adsorption of hydrogen on nickel has been discussed by Okamoto, Horiuti, and Hirota[11] who have calculated activation energies for pairs of adjacent metal atoms in the three main crystal planes of nickel and have come to the conclusion that the activation energy is lowest for the (110) plane. Their calculations are based on Sherman and Eyring's[12] quantum mechanical treatment of the hydrogen adsorption on a pair of carbon atoms which showed that a most favorable carbon-carbon distance exists (about 3.6A) for which the activation energy of adsorption is a minimum.

However, chemisorption of hydrogen is practically instantaneous for oriented and non-oriented nickel film and all other metals investigated, both at room temperature and at −183°C, indicating that the activation energy is very low. Differences in activation energy of the hydrogen adsorption cannot, therefore, be responsible for the observed differences in rate of hydrogenation. (In comparison, the rate of chemisorption of nitrogen on iron was found to be measurably slow at room temperature and much faster at 100°C—a typical example of activated adsorption.)[13]

In order to elucidate further the mechanism of hydrogenation, measurements of the heats of adsorption of the reaction partners were undertaken. A detailed description of the apparatus would be beyond the scope of this presentation. It is sufficient to note that the same type of metal films was used in these experiments as was used in the measurements of catalytic activity. Figure 6 shows the heat of adsorption of hydrogen on nickel and Fig. 7 that of ethylene on nickel. These measurements are of significance in several re-

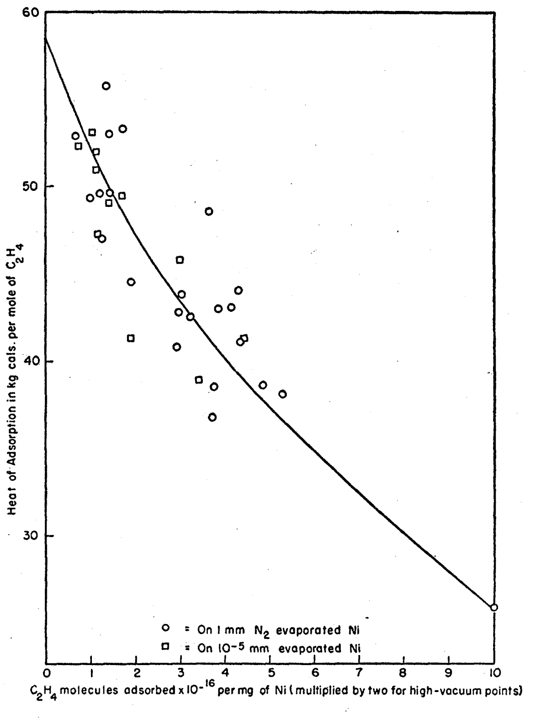

FIG. 7. Heat of adsorption of ethylene on nickel.

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[11] G. Okamoto, T. Horiuti, and K. Hirota, Sci. Pap. Inst. Phys. Chem. Res. Tokyo **29**, 223 (1936).

[12] A. Sherman, and H. Eyring, J. Am. Chem. Soc. **54**, 2661 (1932).

[13] O. Beeck and A. Wheeler, J. Chem. Phys. **7**, 631 (1939).

spects. The heats of adsorption were measured by admitting the gases in small increments to the film in order to permit observation of the changes in heat of adsorption with coverage of the films. Figure 6 shows that the heat of adsorption of hydrogen on the bare surface is 30 Cal./mole and that the heat of adsorption decreases to 18 Cal./mole when the monolayer is completed, the same values being obtained for oriented and non-oriented films at room temperature and at −183°C. Similar results were obtained by Roberts[14] who studied the adsorption of hydrogen and other gases on a tungsten filament thoroughly cleaned by heating in vacuum to high temperature, and were also obtained in this investigation on evaporated tungsten films. In both cases saturation of the monolayer occurs at the pressure of about 10^{-4} mm Hg with a hydrogen atom occupying each crystallographic site. The adsorption is very fast both at room temperature and at −183°C. The heat of adsorption decreases from 45 Cal. on the bare tungsten surface to about 18 Cal. on the nearly covered surface. The results of Roberts' and of this investigation are presented in Fig. 8, and the agreement is quite remarkable since the adsorbing surface of the porous evaporated tungsten film was 10^6 times larger than that of the single wire used by Roberts. Roberts explains his results by a relatively simple theory assuming a repulsive potential effective between neighboring hydrogen atoms adsorbed in the crystallographic sites. This seemed like an over-simplification since the hydrogen atoms are too far apart to affect each other in the manner assumed. However, Wheeler was able to show that a quantum-mechanical treatment along the lines of Eyring's adsorption theory leads to exactly the same result.

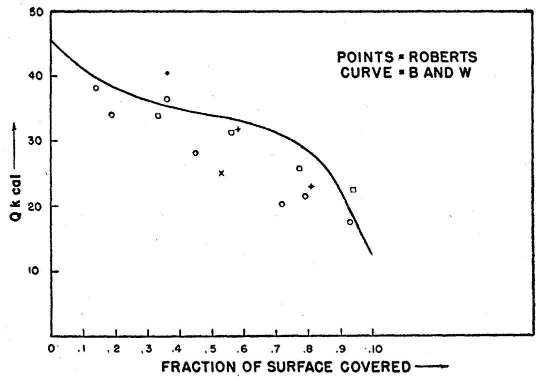

FIG. 8. Heat of adsorption of hydrogen on tungsten: comparison of data of J. K. Roberts with that of Beeck-Wheeler.

The measurements carried out with evaporated metal films reveal an additional result. Since practically the whole adsorptive surface of the films is contained in the porous structure, the molecules to be adsorbed will have to penetrate from the surface of the film into the interior, while in Roberts' experiments the molecules strike the single bare wire at random. Unless, therefore, the adsorbed molecules or atoms are mobile, each increment of gas admitted to the film would have the same heat of adsorption until the interior surface of the film is filled up. Experimental evidence for this argument is ample. The heats of adsorption of carbon monoxide and oxygen on all metals investigated are the same for each increment of gas admitted until a sudden drop occurs when the surface is saturated. The same is true for hydrogen on iron at −183°C, whereas at room temperature hydrogen on iron is mobile, showing the characteristic decrease in heat of adsorption with coverage. For further details of this thoroughly investigated field, the reader must be referred to forthcoming publications.

While the heat of adsorption of ethylene shows the same general characteristics, its adsorption process was found to be complicated by the phenomenon of self-hydrogenation, i.e., on admitting ethylene to the surface a part of the ethylene is hydrogenated to ethane. A careful study of this phenomenon leads to the conclusion that on adsorption the ethylene is dissociated into two adsorbed hydrogen atoms and an acetylenic residue. These acetylenic complexes, as they might be called, poison the surface for the hydrogenation reaction in agreement with the well-known inhibiting effect which an excess of ethylene has on this reaction.

Before discussing further the important part which is played by the adsorbed acetylenic complexes in the hydrogenation reaction, conclusions can be drawn from the quantitative measurements of the heats of adsorption of hydrogen and ethylene. The over-all heat of reaction is well

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[14] J. K. Roberts, Proc. Roy. Soc. A152, 445 (1935).

known through direct thermal measurement as well as through calculation from the bond energies. In the catalytic course of this reaction three steps are thermally important: the adsorption of the reactants, the rearrangement on the surface, and the desorption. The heats of these reactions must add up to the over-all heat of the reaction of 32.5 Cal. The heat of adsorption of hydrogen was measured to be about 30 Cal. for a sparsely covered surface. Since hydrogenation will not occur unless hydrogen is chemisorbed, it is seen that most of the heat of reaction is already expended in the hydrogenation process. This allows several important conclusions. Since the heat of desorption of ethane is zero (ethane is not adsorbed measurably), only about 2.5 Cal. remain for the heat of the surface rearrangement, i.e., the reaction between hydrogen and ethylene. It had been assumed in the past that in a bimolecular surface reaction both partners will have to be adsorbed on the surface side by side. This evidently cannot apply to the hydrogenation reaction, since the heat of adsorption of ethylene was found to be 60 Cal. for a sparsely covered surface. It must be concluded, therefore, that ethylene simultaneously picks up two hydrogen atoms from adjacent sites of the surface, and it is at once evident that in this process again the distance between the hydrogen atoms as determined by the crystal parameter plays an important role. From many careful experiments carried out at low pressures with pre-adsorbed hydrogen, it can further be concluded that the reaction between ethylene and adsorbed hydrogen is extremely fast so that this step, like the adsorption of hydrogen, cannot be the rate determining step in the reaction. The rate must, therefore, be determined by the fraction of the surface which is not covered by acetylenic complexes, i.e., the fraction that is free to adsorb hydrogen in a form available for hydrogenation. Since in the lower temperature regions, that is below approximately 150°C, the hydrogen adsorption is so strong that the fraction of the surface available for the hydrogenation reaction is always covered with hydrogen, and since it was found that ethylene is not adsorbed in the hydrogenation step proper, the rate of this hydrogenation step must be proportional to ethylene pressure. This leads to the very reasonable conclusion that the surface available for the hydrogenation step must be proportional to the hydrogen pressure and inversely proportional to the ethylene pressure because the over-all reaction was found to be proportional to the hydrogen pressure and independent of the ethylene pressure, so that:

$$\frac{dp_{C_2H_6}}{dt}=kp_{C_2H_4}\frac{p_{H_2}}{p_{C_2H_4}},$$

or

$$\frac{dp_{C_2H_6}}{dt}=kp_{H_6}.$$

This, in turn, must mean that the poisoning acetylenic complexes are removed from the surface by hydrogenation, and it is the rate of this removal which determines the rate of reaction.[15] In other words, the very fast rate of hydrogenation producing the reaction product is controlled by a second hydrogenation process of relatively slow rate. While crystal parameter considerations must enter both reactions, it is in the slow reaction that the effect becomes observable and part of the rate-determining factors.

In agreement with these general conclusions is the observation that in a given system the initial rate is retarded by an excess of ethylene; in fact, a monolayer of pre-adsorbed acetylenic complexes (produced through self-hydrogenation on admission of ethylene followed by short pumping to

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[15] Conversely, the same result can be arrived at by employing the Langmuir isotherm for a gas mixture. Let p and p' denote the pressures of hydrogen and ethylene, respectively, b and b' the respective adsorption coefficients, i.e., the ratios of rates of adsorption to desorption, and σ and σ' the fractions of surface covered by the respective gases, then:

$$\sigma=bp/1+bp+b'p', \quad \text{and} \quad \sigma'=b'p'/1+bp+b'p'.$$

If hydrogen were weakly adsorbed or, as in this case, if it is removed fast from the surface through hydrogenation of ethylene from the gas phase, hydrogen will be displaced by the strongly adsorbed ethylene so that $bp \ll b'p' \gg 1$, and

$$\sigma=bp/b'p',$$

and hence the over-all rate of hydrogenation which is proportional to the surface available for hydrogen adsorption and proportional to the ethylene pressure will be

$$dp_{C_2H_6}/dt=kp\cdot p'/p'=kp_{H_2}.$$

Obviously, these considerations are not changed by the knowledge that in the adsorption process ethylene decomposes into two hydrogen atoms and an acetylenic complex.

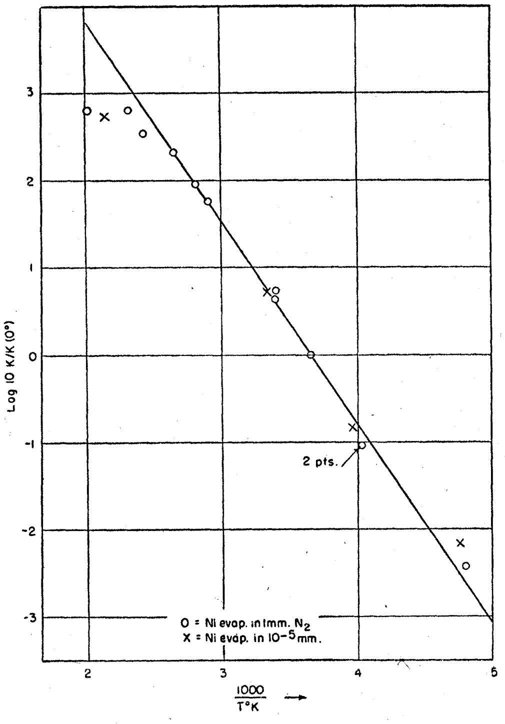

FIG. 9. Relation between over-all rate of hydrogenation and temperature.

high vacuum) will retard the over-all hydrogenation reaction by 50 percent.

It is, of course, difficult to investigate the slow rate-determining reaction independently from the fast product-producing reaction because of the small quantities of material involved. In this respect it may be of interest to state that with the observed reaction rates on nickel, and under the assumption that every gas kinetic collision of ethylene with the hydrogen covered part of the surface leads to reaction, only 10^{-6} part of the surface is available for hydrogenation. Since it is more likely that, because of steric factors, every hundredth or thousandth collision will lead to reaction, the fraction of the surface available will be 10^{-4} to 10^{-3} part of the total or in the case of rhodium 10^{-2} to 10^{-1} part.

Evidence of the removal of acetylenic complexes has been obtained by measuring the rate at which hydrogen removes a pre-adsorbed layer of these complexes. At room temperature, several hours are necessary to clean 20 percent of a nickel surface, whereas with rhodium 80 percent can be cleaned in a few minutes. In the case of rhodium, the accelerating effect of higher hydrogen pressure and higher temperature can readily be observed.

The dependence of the over-all rate of hydrogenation on the temperature is shown in Fig. 9 where the logarithm of the reaction rate is plotted against the reciprocal of the temperature. (For convenience log K/K_0 is used, where K is the velocity constant at any given temperature and K_0 the velocity constant at 0°C. $1/T$ is multiplied by 1000 for convenience.) The straight line between about -80°C and $+150$°C shows that in this temperature interval the activation energy is constant according to the Arrhenius' equation:

$$k = Ce^{-E/RT}$$

where k denotes the over-all reaction rate, E, the activation energy, and C, a constant. E is in this case the "apparent" activation energy of the over-all hydrogenation reaction since, as has been shown, the rate is controlled by the slow hydrogenation of the acetylenic complexes. This latter reaction is, of course, only one of several processes which determine the equilibrium condition with regard to the surface available for hydrogenation. Also involved are the rates of adsorption of hydrogen, the rate of removal of hydrogen by hydrogenation, and the rate of adsorption of ethylene. All these steps are very fast, the last mentioned, by virtue of dissociation, also carrying to the surface two hydrogen atoms which can hydrogenate ethylene. At the same time the slow hydrogenation of the acetylenic complexes is taking place. Neither the hydrogen adsorption nor the ethylene adsorption are temperature dependent within the temperature and pressure ranges considered,[16] and their heats of adsorption should not, therefore, affect the energies of activation measured. It is significant that under these conditions the observed activation energy of 10.7 Cal. should not only be the same for oriented and non-oriented films as shown in Fig. 9 but also for iron, platinum, palladium, and rhodium covering about a thousand-fold range in the rate constant. It must be concluded, there-

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[16] That is, the surface areas covered with these gases do not vary with temperature according to a Boltzmann exponential function $b = (k_1/k_0)e^{\lambda/RT}$ where λ is the heat of adsorption and b the adsorption coefficient (see footnote 15).

fore, that the differences in rate are governed only by the constant C in Arrhenius' equation with the same temperature coefficient for all reactions. It would be beyond the scope of the present presentation to discuss in more detail the theoretical implications of these findings, although brief mention of this will be made in the concluding remarks.

The results of this investigation have a strong bearing on the concept of active centers which have been pictured as "extra-lattice atoms" and whose existence has largely been based on kinetic considerations of the phenomenon of catalyst poisoning.[17,18] While the great service of this hypothesis in explaining a large and diverse complex of phenomena will always remain a most important step toward the understanding of catalysis, as will the concept of activated adsorption, both concepts appear here in a new light The results of this investigation would suggest that, at least for the metal catalysts under consideration, the catalyst surface is uniform and that high activity is a function of normal lattice spacing in certain crystal planes, thus supporting, at least ideologically, Balandin's "multiplet theory" and before him Burk's "multiple adsorption" hypothesis. Both postulate that catalysis arises through the geometrically determined action of various catalyst centers.

The original concept of activated adsorption, in contrast to van der Waals' adsorption at lower temperatures, stipulated that the stronger type of binding often observed at higher temperatures was a relatively slow process requiring activation energy. It was found in this work, however, in agreement with Roberts, that instantaneous adsorption with high heats of adsorption can be found over very wide temperature ranges with very low activation energies. If this process is called "chemisorption" and embraces all adsorption processes with high heats of adsorption irrespective of activation energy, then "activated adsorption" can be reserved for processes having a measureable energy of activation, i.e., showing a higher rate of adsorption with increasing temperature.

CONCLUDING REMARKS

It is the author's sincere hope that the foregoing presentation of the high-lights of recent researches in hydrogenation catalysis has given the reader a better insight into the many difficulties with which the investigator of the problems of catalysis is confronted than could be gained from a more general discussion of the phenomenon. After tracing this reaction through its winding and rather elusive path, one is, of course, still confronted with the major task of explaining the role of the C factor in Arrhenius' equation which here so largely affects the rate of removal of the acetylenic complexes from oriented and non-oriented nickel and other metal surfaces, and which appears to be solely responsible for the large differences in the resulting over-all rates of hydrogenation.

It is indeed the most important problem of chemical kinetics to derive this essentially temperature independent "frequency" factor of a chemical reaction from fundamental atomic and molecular data, a field in which relatively little progress has been made as applied to simple homogeneous systems and still less with regard to heterogeneous reactions. It has long been recognized[19] that this "frequency" factor thermodynamically corresponds to an entropy factor which also has been called the "entropy of activation." Part of this entropy arises from "steric factors" or "sensitive districts." It is most gratifying that the present experimental work which for the first time relates differences in rate quantitatively to differences in crystal parameter of the catalyst should also give the entirely independent kinetic result that the observed differences in rate must indeed be due to an "entropy of activation" (steric factors). It still remains surprising that the separation of energy of activation and entropy of activation should be as complete as the experiments appear to indicate, although the reason for this is undoubtedly the quantitatively almost identical behavior of the

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[17] H. S. Taylor, *Twelfth Report of the Committee on Catalysis* (John Wiley and Sons, Inc., New York, 1940), Nation Research Council, first edition, p. 29–41.

[18] Georg-Maria Schwab, *Catalysis from the Standpoint of Chemical Kinetics* (D. Van Nostrand Company, Inc., New York, 1937), English translation by H. S. Taylor and R. Spence, 1937.

[19] See for instance: Scheffer and Brandsma, Rec. Trav. Chim. **45**, 522 (1926).

various metals investigated with regard to the absorption of hydrogen and ethylene in spite of their differences in crystal parameter.

There seems to be no doubt that the basic problems of heterogeneous catalysis cannot be solved without the closest attention to the physics of the solid state, especially with regard to structure, energy, and entropy of the surface.

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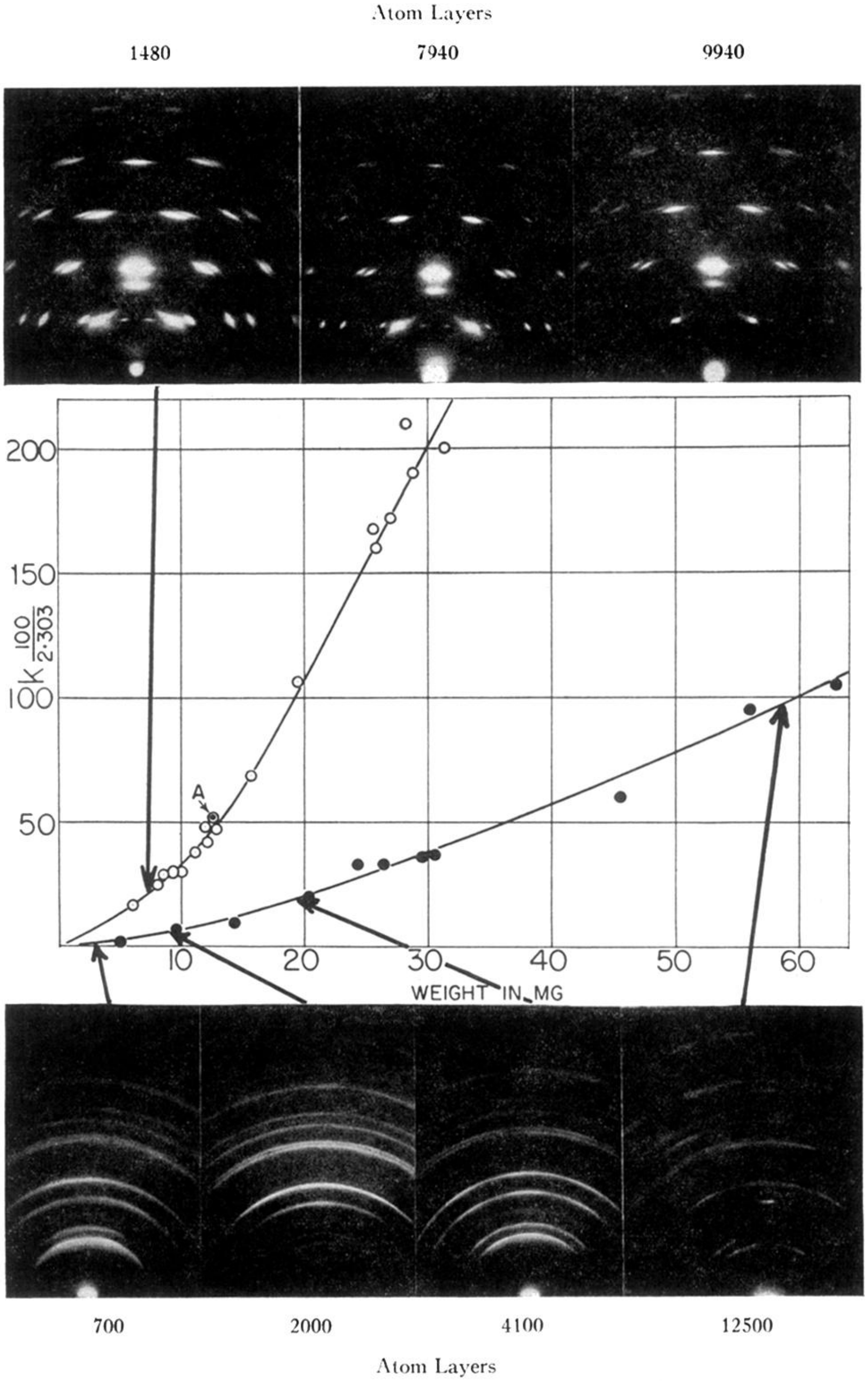

FIG. 3. Electron diffraction patterns of evaporated nickel films. (Weight and activity indicated by arrows; the patterns above the figure correspond to the upper curve giving activities of films evaporated in 1 mm of nitrogen, the lower patterns correspond to high-vacuum films. The oriented films of 7940 and 9940 atom layers are too heavy to be shown in the figure.)